Stellingen
behorende bij het proefschrift

Instrumental and Organizational Aspects
of
a Neutron Activation Analysis Laboratory

1. Koolstof-koolstofcomposiet heeft aantrekkelijke mogelijkheden als constructiemateriaal voor experimenteerfaciliteiten in onderzoeks-kernreactoren.
(Dit proefschrift)

2. De toegevoegde waarde van het analyseren van grote monsters, in vergelijking met het analyseren van daarvan afgeleide, na homogenisatie verkregen kleine monsters, is wel degelijk aanmerkelijk; vooropgesteld dat de mate van homogenisatie feitelijk geverifieerd dient te worden.
(Dit proefschrift, en stelling no.IV proefschrift J. Keijzer, TU Delft 1996)

3. Gamma-spectrometers met grote Ge-detectoren en Ge-putdetectoren zijn op een INAA laboratorium te prefereren boven de gebruikelijke Anti-Compton spectrometers.
(Dit proefschrift)

4. De 'z-score' zoals berekend volgens het AOAC/ISO/IUPAC 'International Harmonized Protocol for Proficiency Testing of (Chemical) Analytical Laboratories' levert, in tegenstelling tot wat wordt beoogd, juist geen mogelijkheid tot het trekken van conclusies omtrent de analytische kwaliteit van laboratoria omdat de onzekerheid in de gerapporteerde analyseresultaten niet in acht wordt genomen.
(M. Thompson, R. Wood, J. AOAC Internl. 76 (1993) 926 - 940)

5. In de Nederlandse voornorm NVN 5623 (1991) 'Bepaling van de activiteit van gammastraling uitzendende nucliden in een telmonster met behulp van halfgeleider-gammaspectrometrie' is de geringe aandacht die besteed wordt aan coïncidentie-verliezen, een norm onwaardig.

6. Het tijdschrift 'Analytical Chemistry' heeft met ingang van 1996 beëindigd de reeks tweejaarlijkse 'Fundamental Reviews' op het gebied van 'Nuclear and Radiochemical Analysis'. Dit zou als indicatief kunnen worden beschouwd voor de omvang en belangrijkheid van nieuwe ontwikkelingen in dit vakgebied, in relatie tot die in andere gebieden van de analytische chemie.

7. Het trekken van conclusies omtrent de chemische structuur op basis van tijdsgeïntegreerde richtingscorrelatiemetingen is riskant.
(M. de Bruin, R.W. Hollander, J. van der Plicht, J.Inorg.Nucl.Chem. 38 (1976) 2149 - 2152; P. Bode, M. de Bruin, R.W. Hollander, Polyhedron 5 (1986) 1645 - 1646)

8. Door voorkeur uit te spreken voor het hanteren van specifieke analyseprotocollen voor element-bepalingen ter ondersteuning van het overheidsbeleid, wekt het ministerie voor VROM de indruk dat zij onvoldoende vertrouwen heeft in de mede door haarzelf ondertekende raamovereenkomst ten behoeve de kwaliteit van milieuonderzoek, en de doelstellingen en voordelen van laboratorium accreditatie.

9. Het promotiereglement van de Technische Universiteit Delft, uitgegeven door het College van Dekanen in December 1993 combineert in zich een kwaliteitsprocedure en een kwaliteitsinstructie hetgeen een goede aanzet is tot eenduidigheid. De nagestreefde eenduidigheid wordt evenwel weer in gevaar gebracht doordat deel III, Volgorde van Handelingen, niet in detail overeenstemt met de voorgaande delen.

10. Kwaliteitszorg in experimenteel wetenschappelijk onderzoek moet en kan.

11. De rasstandaard van de West Highland White Terrier vermeldt als kenmerken onder meer: '....small, active, game, hardy, possessed of no small amount of self-esteem....' ('...klein, actief, met de wil om allerlei roofwild aan te pakken, gehard, met een niet geringe hoeveelheid gevoel van eigenwaarde...'). Bij exterieurkeuringen en daarop gerichte fokselectie wordt vaak aan deze kenmerken op onthutsende wijze voorbij gegaan.
(Rasstandaard no. 85b van de Fédération Cynologique Internationale, 1987)

12. Wetenschappelijke presentaties kunnen aan waarde winnen indien een kwantitatieve beperking wordt gesteld aan het aantal dia's en transparanten dat in een lezing vertoond mag worden; verbanning van deze visuele hulpmiddelen zou voor menigeen wellicht nog beter zijn.

Peter Bode, 10 December 1996

INSTRUMENTAL AND ORGANIZATIONAL ASPECTS OF A NEUTRON ACTIVATION ANALYSIS LABORATORY

Peter Bode

Interfacultair Reactor Instituut
Technische Universiteit Delft / Delft University of Technology
10 december 1996

The research described in this thesis was performed within the Department of Radiochemistry of the Interfacultair Reactor Instituut, Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands

INSTRUMENTAL AND ORGANIZATIONAL ASPECTS OF A NEUTRON ACTIVATION ANALYSIS LABORATORY

PROEFSCHRIFT

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft,
op gezag van de Rector Magnificus Prof.ir. K.F.Wakker,
in het openbaar te verdedigen ten overstaan van een commissie,
door het College van Dekanen aangewezen,
op dinsdag 10 december 1996 te 16.00 uur
door

Peter BODE

scheikundig ingenieur

geboren te Vlissingen

Dit proefschrift is goedgekeurd door de promotoren:

Prof.dr.ir. J.J.M. de Goeij
Prof.dr.ir. M. de Bruin

Samenstelling promotiecommissie:

Rector Magnificus,	voorzitter
Prof.dr.ir. J.J.M. de Goeij,	Technische Universiteit Delft, promotor
Prof.dr.ir. M. de Bruin,	Technische Universiteit Delft, promotor
Prof.dr.ir. C.W.E. van Eijk,	Technische Universiteit Delft
Prof.dr. R. Dams,	Rijks Universiteit Gent
Prof.dr.ir. H. van Dam,	Technische Universiteit Delft
Prof.dr. L.M.C. Buydens,	Katholieke Universiteit Nijmegen
Dr.ing. M.L. Verheijke,	gepensioneerd, voorheen Philips' Natuurkundig Laboratorium, Eindhoven

CIP-DATA KONINKLIJKE BIBLIOTHEEK, DEN HAAG

Bode, Peter

Instrumental and organizational aspects of a neutron activation analysis laboratory / Peter Bode. - Delft : Interfacultair Reactor Instituut,
Delft University of Technology. - Thesis Technische Universiteit Delft. - Ill.
With ref. - With summary in Dutch.
ISBN 90 - 73861 - 42 - X
NUGI 813
Subject headings: instrumental neutron activation analysis / irradiation facilities / detection limits / quality assurance / quality management

Ter nagedachtenis aan mijn vader

TABLE OF CONTENTS

CHAPTER 1 INTRODUCTION

1 INTRODUCTION

1.1 NEUTRON ACTIVATION ANALYSIS

Activation analysis is a method for the determination of elements based upon the conversion of stable nuclei to other, mostly radioactive nuclei via nuclear reactions, and measurement of the reaction products. In neutron activation analysis (NAA) the nuclear reactions occur via bombardment of the material to be analyzed with neutrons. The reaction products to be measured are either the radiation, released almost promptly upon neutron capture; or, if the resulting new nuclei are radioactive, the induced radioactivity. Only the latter mode will here be discussed since it is the most common way to perform NAA.

All of the stable elements have properties suitable for production of radioactive isotopes albeit at different reaction rates. Each radionuclide is uniquely characterized by its decay constant -the probability for the nuclear decay in unit time- and the type and energy of the emitted radiation. Amongst the several types of radiation that can be emitted, gamma-radiation offers the best characteristics for the selective and simultaneous detection of radionuclides and thus of elements.

The activation will result in a mixture of radioactivities, which can be analyzed for individual contributions by two approaches:

(i) The resulting radioactive sample is decomposed, and through chemical separations it is divided into fractions with a few elements each: Destructive or Radiochemical Neutron Activation Analysis.

(ii) The resulting radioactive sample is kept intact, and the elements are determined by taking advantage of the differences in decay rates via measurements at different decay intervals utilizing equipment with a high energy resolution: Non-destructive or Instrumental Neutron Activation Analysis (INAA).

A procedure in INAA is characterized by (i) activation via irradiation with reactor neutrons, (ii) measurement of the gamma-radiation after one or more decay times and (iii) interpretation of the resulting gamma-ray spectra in terms of radionuclides, associated elements and their concentrations.

Results of experiments on the action of neutrons on the rare earth elements by Hevesy and Levi in 1936 marked the onset of neutron activation analysis. These pioneers stated [1]:

> ".... The usual chemical methods of analysis fail, as is well known, for most of the rare earth elements and have to be replaced by spectroscopic, X-ray, and magnetic methods. *The latter methods can now be supplemented by the application*

of neutrons to analytical problems by making use of the artificial radioactivity and of the great absorbing power of some of the rare earth elements for slow neutrons....".

In 1949 Boyd [2] suggested to term the procedure ".... the method of radioactivation analysis ....", or, more succinctly, ".... *activation analysis*...." and he discussed the use of the ".... chain-reacting pile ...." as a source of neutrons and an example of an analysis was given. In the same year Brown and Goldberg [3] gave a new impulse to this method by demonstrating that with the ".... neutron pile (nuclear reactor).... very high specific activities ...." could be obtained -as compared with isotopic neutron sources used so far- thereby extending the capabilities of NAA.

The potentials of NAA method were explored in the 1950s and 1960s, initially by the analysis of the decay and characteristic absorption of the radiation emitted, and/or radiochemical separations. To make the most of the high characteristic activities it became necessary to improve on the counting efficiency of radiation detectors. Gamma-ray spectrometry with scintillation detectors gave a great impulse to the improvement of the radionuclide -and thus element- selectivity of the technique. For many applications chemical separations were still a necessity to resolve the mixture of radioactivities. The introduction of the semi-conductor detector in the midst 1960s increased selectivity in gamma-ray spectrometry to such an extent that for many applications chemical separations became superfluous. It marks the onset of INAA as principal form of neutron activation analysis which development was further stimulated by the availability of multi-channel pulse height analyzers and laboratory computers.

INAA has found its usage in many fields of science. Particularly advantage is taken of the fact that the samples do not have to undergo any chemical treatment, neither prior, nor after the activation: INAA is 'non-destructive'[1]. In addition, light elements such as H, C, N, O, Si which in many materials belong to the major matrix components, do not produce radioactive products upon neutron activation which would interfere with the determination of the other activities. It enables the observation of trace elements, often at detection limits in the $mg.kg^{-1}$ to $\mu g.kg^{-1}$ level in matrices composed of the light elements. The high selectivity of gamma-ray spectrometry allows for simultaneous determination of many radionuclides to be interpreted as multi-element determinations.

---

1 *The description 'non-destructive' is commonly used to emphasize that the analytical portion does not have to be dissolved prior to the analysis. As will be further described in paragraph 2.1, under certain conditions also in INAA the analytical portion may be damaged.*

The non-destructive character makes the technique attractive for application in geochemistry and related sciences. Because of the limited sample handling operations, there is also a lower risk to contaminations compared to element analysis methods in which the sample has to be dissolved. This advantage has been exploited in many biological applications of INAA and for the analysis of minute quantities of material such as atmospheric and cosmic dust.

Since the signals in INAA are related to the properties of the atomic nucleus, the results in INAA are not affected by the chemical and physical state of the elements[2]. The method is well described by physical law and selectivity is unambiguous for all elements since the combination of the nuclear properties (i) decay constant (often converted to half-life, i.e. -for a single radioactive decay process- the time required for the activity to decrease to half its value) and (ii) energies and intensities of the gamma-radiation is uniquely characteristic for each radionuclide. It all contributes to a high degree of accuracy which makes INAA well acknowledged for analyses related to e.g. certification of reference materials.

An introduction to the principles and characteristics of INAA is given in *Chapter 2* of this thesis.

1.2 INAA AT THE INTERFACULTY REACTOR INSTITUTE

With some exceptions[3], INAA has remained a technique typically reserved to be developed and applied in research establishments, most of them affiliated to a nuclear research reactor. At the Interfaculty Reactor Institute (IRI) in Delft, development and application of NAA belongs to the scientific mission of the department of Radiochemistry. The activities in the first twenty years of its operation (1963 - 1983) are characterized by several technical originalities within the field of INAA such as the use of computer integrated data acquisition, well-type semiconductor detectors and a high

---

2 *When a radionuclide decays by emission of gamma-radiation in cascade and fulfills certain constraints, in principle the intensity of sum-peaks in the gamma-ray spectrum can be affected by the chemical form of the element due to perturbation of the directional correlation between the gamma-rays involved. The extent of this effect can be neglected in INAA considering the way the measurements are carried-out and the relative unimportance of sum-peaks.*

3 *Typical alternatives are INAA using 14 MeV neutrons, supplied by a neutron generator, or using neutrons from isotopic neutron sources such as ^{252}Cf or ^{238}Pu-Be. These forms of INAA each have their own methodological aspects and fields of applications, and do not form part of the work, described in this thesis.*

degree of automation in gamma-ray spectrum analysis and interpretation. Simultaneously the capabilities of INAA were advocated -amongst others- at the universities. Efforts were made to reduce the thresholds for its use by laymen in order to enable e.g. students from other universities to include INAA as a method of choice in their own research programs.

The thesis 'Instrumental Neutron Activation Analysis: a Routine Method' by M. de Bruin [4] more-or-less marks the point of time at the IRI at which the first wave on developments was rolled-out, and applications started to get most of the attention of the research group. Feedback from the users of the facilities for INAA, challenging opportunities raised by the technique itself and a sense of responsibility to secure the position of INAA were the incentives to continue research in the development of facilities for, and methodology of INAA.

1.3 SCOPE OF THE THESIS

Different types of scientific research and development activities can be distinguished at a university laboratory for methods in chemical analysis:

(i) *FUNDAMENTAL OR BASIC RESEARCH* to increase insight, to test hypotheses e.g. with respect to the physical and chemical principles of the technique; all without directly aiming at practical implementation or any spin-offs in applications. Fundamental research has an unpredictable nature, it may result in new possibilities but it generally has a long term response with respect to the value of its contribution.

(ii) *STRATEGIC RESEARCH AND DEVELOPMENT* directed to make the existing knowledge on the technique available for utilization in the applied fields. The term 'strategic' emphasizes the importance of the long-term vision and policy of the laboratory with respect to future opportunities and applications which may secure and improve the position of the technique. In an early stage of the scenarios to be developed the specific demands set by the applied fields forecasted have to be taken into account. Strategic research is innovative, particularly when carried out in direct interaction with fundamental research. The response can be short to medium term.

(iii) *APPLIED RESEARCH* to demonstrate the full potentials of the analytical technique by using it as a supporting tool in an applied field of science. Applied research includes further optimization, tailoring to the specific problem at hand, of facilities and existing operations resulting from the strategic research effort. The response can be very short term.

The strategic and applied research and development of the chemical analysis result in analytical data that may be used in either fundamental or strategic and applied research programs of the applied fields.

Performing these research tasks requires and/or involves *OPERATIONAL ACTIVITIES* of the laboratory. Operational activities is a collective term to denote operational research, supporting investigations and management activities all aiming to improve the performance and traceability and recoverability of the laboratory's operations. The quality assurance program is an example of operational activities. The response of control programs may vary from short to medium term. Situations of non-conformance may be observed. These mark often the onset of research-by-research. Whereas unexpected problems are characteristic for fundamental research and form the basis for ongoing activities, in strategic and applied research the consequences of such problems may be to abandon the forecasted pathway. Trouble shooting and results of operational research may result in the need for research and development not anticipated on to achieve a -practical or pragmatic- solution to proceed, or at the definition of the need to start new fundamental, strategic or applied research. Their response thus may vary from very short to long term.

The operational activities also include the operational management of the laboratory.

The research and development activities have been summarized in *Table 1-1* closely following the classification of decision problems in the analytical laboratory [5].

Table 1-1. Classification of research and development activities of the laboratory for INAA

	Objectives	Time horizon	Nature of information	Degree of uncertainty
fundamental research	resource definition	unpredictable, often long (> 5 years)	indicative	very high
strategic research and development	resource implementation	long, 2 - 5 years	contour	high
applied research	resource utilization	medium, 0.5 - 2 years	interactions	moderate
operational activities	optimal laboratory performance	hour ... month	detailed	low

The scientific research and development program of the laboratory for INAA at IRI is a consequence of the mission of the related research group in the department of Radiochemistry: the development, implementation and use of physical and mathematical methods in nuclear analytical chemistry. Part of the laboratory's activities forms the basis of this thesis. In the following paragraphs these contributions are described in short using the classification defined above, together with the developments at IRI as such and with some important developments in the field of INAA worldwide.

1.3.1 Fundamental research

DEVELOPMENTS IN GENERAL

Fundamental research in INAA has been limited for a long time. As stated often in the past decade by reviewers: ".... the technique is mature..." [e.g. 6]. Some activities in the framework of the so-called k_0-method for standardization in INAA may be considered to be fundamental, particularly where they deal with the theoretical description of the neutron energy dependence of the activation cross section for epithermal neutrons and the considerations on the effect of neutron temperature [7]. Another study to be considered as fundamental is related to activation self-enhancement due to microscopic neutron scattering inside the sample [8].

DEVELOPMENTS AT IRI

At IRI fundamental research in INAA has not got priority in the research programs. The policy of the institute was to concentrate on strategic and applied research. Once established by strategic research, routine operations and applied research complied with the mission of the institute to serve other universities. Fundamental research programs were carried out as a research-by-research spin-off. Examples of contributions to fundamental research in INAA are the approach to gamma-ray spectrum interpretation using multiple gamma-ray lines, multiple radionuclides and multiple gamma-ray spectra of the same sample [9] and the approach to subtract information on the gamma-ray self-attenuation from the changing intensity ratios between peaks in the spectrum [10].

1.3.2 Strategic research and development

DEVELOPMENTS IN GENERAL

Several impulses have been given to broaden the possibilities of NAA as a nuclear analysis technique taking advantage of the characteristics of the method. The availability of 'clean' neutron beams (in which the ratio of neutrons over reactor gamma's was considerably improved) enlarged the capabilities of the prompt gamma NAA technique [11]. Further improvement was obtained via the combination with cold neutrons and neutron focusing devices, offering certain prospects for micro-beam INAA [12, 13]. A demonstration combining INAA with mass spectrometry showed unique capabilities for studies involving Li and B [14]. Position sensitive INAA based on simultaneous position sensitive determination of via β^- decaying radionuclides and gamma-ray spectroscopy of these same radionuclides offered μm resolution possibilities in thin specimen, e.g. aerosols [15].

Supporting research related to routine operations can be focused on improving the detection limits of INAA. Examples are epithermal neutron activation procedures by which the production of -often interfering- ^{24}Na and ^{82}Br activities is relatively stronger suppressed than the production of other trace metal activities; the use of Compton suppression spectrometers to reduce the signal-background level caused by Compton scattering of the photons in the detector [16], gamma-gamma coincidence measurements for very selective determination of radionuclides [17]; and other varieties in gamma-ray spectrometry including high count rate spectrometry and loss-free counting [18, 19].

The nuisance and difficulties in preparing adequate standards, the repetition of calibration procedures in various laboratories have largely been overcome by the development of a versatile method for quantification in INAA, the k_0-method [20]. It is a example of problem-solving research which originates from observed problems in methodology.

DEVELOPMENTS AT IRI

Evaluating the characteristics of the various methods for element analysis it was observed [21] that on fundamental considerations, only with NAA there are no fundamental restrictions regarding the size of the analytical portion. Development of a method for direct (i.e. non-destructive) trace-element determinations in samples with sizes of several kilograms was considered to be a challenge for chemical analysis. Some applications could be forecasted like (i) the analysis of materials in which the inhomogeneity requires that a sample size reduction step is necessary, with care for

homogenization, to obtain a representative analytical portion for traditional analysis; this all might be avoided when analyzing the sample as a whole, and (ii) the analysis of materials which are easy to contaminate during sub-sampling. In large sample INAA effects of neutron self-shielding and self-thermalization, gamma-ray self-attenuation and deviations from the point-source geometry whilst counting require adequate correction methods. Such methods have been developed and validated indicating that results may be obtained which are of almost comparable quality with respect to accuracy as can be obtained in routine INAA on small samples [22].

At IRI the supporting research program in the period 1984 - 1996 comprised, except for the regular assessment of detector types, renewal of the gamma-ray spectrum analysis software which was aimed to improve the quality and quantity of the results [23]. Simultaneously the computer configuration and the interface structure of the gamma-ray spectrometers was modernized [24].

An example of research-by-strategic research at IRI comprised the quantification of sources of variation which lead to better insight in sample preparation techniques and corrections for flux gradients [25]; the ever lasting efforts in the determination of element standardization parameters requiring thorough insight in decay schemes and gamma-ray coincidence occurrences; the development of a method making possible to determine efficiency curves for highly efficient detectors with enhanced problems related to coincidence summing effects [26]. The development of an irradiation system which facilitates automation of INAA via short half-life radionuclides is also an example of a strategic research-by research spin-off.

DEVELOPMENTS RELATED TO THIS THESIS

The existing irradiation facilities at the Hoger Onderwijs Reactor were not suitable for irradiation of samples of (multi) kilogram size. Moreover, to limit neutron self-thermalization effects when irradiating such large samples, a well-thermalized neutron flux would be desirable. Therefore, an irradiation facility for large samples was designed in the reactor's thermal column for neutron activation of samples with sizes up to 15 cm diameter and 100 cm length. Since study of inhomogeneities was one of the objectives of large sample INAA, a device was required which allowed for segmented counting scans by gamma-ray spectroscopy of the activated sample. The design and realisation of the irradiation facility in the framework of the Big Samples Neutron Irradiation System project (acronym BISNIS) are described in *Chapter 3* of this thesis.

Applicability of short half-life radionuclides in INAA was limited at IRI because of the contamination of the irradiation container ('rabbit') during transfer with activated wear particles from the transfer tube, and because of the substantial time for unloading

the sample capsule. These problems also hampered automation of the procedures. Between 1984 and 1989 a new automated, autonomous facility was developed for short half-life INAA. Starting point in the design was to avoid contamination of the irradiation container by using appropriate construction materials which would allow to count the sample while still in the rabbit, without unloading it. This was accomplished by making use of carbon-carbon composite material for the irradiation end of the facility, and plastic for all other components the rabbit might come in contact with. The facility was equipped with a sample changer. The design, realisation and use of the Carbonfiber Autonomous Facility for Irradiation and Analysis (acronym: CAFIA) is described in *Chapter 4* of this thesis.

1.3.3 Applied research

DEVELOPMENTS IN GENERAL

The list of studies in which INAA has been applied as a method for (multi) element determinations is large. Many fields of science are covered such as: archaeology, biology and life sciences, environmental sciences, nutritional sciences, forensics, geology, mineralogy, materials sciences, metallurgy, pharmaceutical science, agriculture, medicine. Not all of these applications can be characterized as applied research by its definition in paragraph 1.3 since some of the analyses might have equally well done with other methods of elemental analysis. However, it can be derived from the selected representative applications in the 1994 Analytical Chemistry Fundamental Review on Nuclear and Radiochemical Analysis [27] that in many cases advantage is taken of the non-destructive character (e.g. with ceramics [28], plastics [29], diamond-ore [30], archaeological artifacts [31]), the ability to analyze very small samples (aerosols [32], cosmic dust [33], forensic samples [34], activatable microspheres [35]) and the relatively small influence of the analytical blank (diets [36], human tissue [37], ultrapure materials [38]).

DEVELOPMENTS AT IRI

The applied research between 1984 and 1996 comprised large scale biomonitoring program for air pollution studies resulting in several hundreds of samples to be analyzed. The multi-element character of INAA was employed at its full strength in this work since it enabled the use of factor analysis methods to assist in the interpretation in terms of sources of air pollution [39].

The possibility to determine selenium with adequate detection limit in short turn-around times via the measurement of the short-lived ^{77m}Se radionuclide (half life 17.5 s) resulted in the analysis of thousands of samples for which alternative analysis methods were less advantageous [40, 41, 42].

When compared to other methods for elemental analysis -in which often the material has to be dissolved- the non-destructive character of INAA is well exploited for the determination of trace element in plastics. This research program has had an important spin-off via third party contracts resulting in additional funding and an improvement of the reputation of the laboratory.

DEVELOPMENTS RELATED TO THIS THESIS

Applied research is not a major subject to be presented in this thesis. *Chapters 3* and *4* include paragraphs with suggestions and examples how the result of the strategic research may be employed in applied research.

1.3.4 Operational activities

DEVELOPMENTS IN GENERAL

Operational research and development in INAA comprise e.g. the development of e.g. high count-rate electronics [18] (although to be considered as strategic research in the counting equipment market segment). Typical supporting operational activities are e.g. investigations to improve the detection limits by examination of alternative analysis protocols or use of different counting equipment [e.g. 19, 16]; the determination of flux gradients in irradiation facilities [43]; investigations to describe mathematically the detection efficiency [44], and methods for internal quality control. Recently harmonised guidelines have been suggested [45] for internal quality control. The introduction of commercial laboratory information management system software (LIMS) in INAA laboratories has not (yet) been described.

Economic considerations (like the need to improve the efficiency and quality of operations) and external reasons (e.g. legislative in view of the unified European Market structure) have contributed in industry and related laboratories to the acceptance and implementation of quality (management) principles in accordance to internationally accepted standards. Though there may be different motivations to change the organisation of work at laboratories in university organizations accordingly, it is not (yet) observable that laboratories in university organizations follow the example of industry

for compliance with a new order, set by society. In a few NAA laboratories the necessity has been anticipated upon to make this step to quality management [46]. The International Atomic Energy Agency (IAEA) has recognised the need for laboratories to implement an appropriate program of quality assurance measures [47].

DEVELOPMENTS AT IRI

In epithermal NAA the low neutron flux and small activation cross sections often require long irradiation times. Because of the relatively high temperatures in the irradiation facility due to thermal neutron capture in cadmium or boron, an irradiation time longer than 15 minutes causes degradation of plastic capsules, and sealed quartz ampoules have to be applied which limits the ease-of-operation. However, the low induced radioactivity at irradiation times up to 15 minutes can be compensated for by the high efficiency of well-type germanium detectors. As such, ease-of-operation in epithermal NAA is maintained [48].

A germanium detector signals simulating pulse generator has been developed at IRI for use as dead-time and pile-up correction in gamma-ray spectrometry [49]. Unlike many commercially available pulse generators, the IRI pulse generator does not lead to distortion of the detector spectrum.

The software developed at IRI for gamma-ray spectrum analysis has been integrated with software to manage all other information related to the samples. The users of INAA participated in defining the various steps and information streams that had to be assured. Criteria have been defined to which analysis results have to comply; the software now generates alarms when these criteria are not met. Also for the management of γ-ray spectrometers levels of acceptance have been defined. Control charts can be generated allowing for visual inspection of various parameters varying from data related to the setting of the spectrometers [50] to concentrations in quality control materials [51]. The laboratory regularly participates in proficiency testing for an independent assessment of the quality of its performance.

The absence of a manageable system for documentation and documenting self-designed equipment and facilities 'as build' hampered progress at the institute and resulted often in unnecessary duplication and repetition of work. In 1989 a quality assurance manager was appointed at IRI to improve this situation by introducing quality management principles in the various branches of the institute. A system for the management of documentation was developed, and quality principles were firstly applied with reactor operations and lateron with the purchasing and financial departments and the workshops.

The institute's policy on quality management resulted further in the approval and stimulation to develop a quality system at the laboratory for INAA to increase the efficiency of operations and the analytical quality.

DEVELOPMENTS RELATED TO THIS THESIS

Improvement of detection limits in INAA may be pursued because of (i) the need of better detection limits in view of the related (trace) element studies, (ii) the need to reduce the turn-around time of the technique by achieving equal or better detection limits at shorter decay times and (iii) to shorten the counting time for a given detection limit and thus to increase the throughput of a laboratory. The latter two considerations are of importance for a laboratory in which research programs are carried out involving many hundreds of samples; a shorter counting time, and particularly a shorter turn-around time can lead to a reduction in the order of weeks or more in total project counting and analysis time. Obviously, such an improvement is also of importance for students who implemented INAA in their -often tight- research programs.

In 1976 the first well-type Ge-detector was introduced at the laboratory for INAA, followed by two other well-type detectors in the 1984 and 1988. The development of semi-conductor detectors with very large volumes at the end of the 1980's has made necessary to evaluate the characteristics of the different types of detectors (coaxials, well-types, planars) for use in INAA; also the use of a Compton suppression shield is considered as an option to improve detection limits. A relation has been derived which describes the influence of the detector characteristics on the detection limits in INAA. Only those characteristics are needed which are specified by the vendors. It allows for an evaluation of the potentials of detectors of different type, size and configuration for improvement of the detection limits in INAA. The derivation of this relation, its use and the evaluation of detector types is described in *Chapter 5*.

To keep an automated system with a full capacity of over 10,000 multi-element analysis per year operational and in a continuous improvement, the system for quality assurance must have an integrated system for response and feedback. Thus systematic preventive and corrective actions become possible. Starting point in the design of this system was that the analyst should be able to perform his own checks on basis of criteria to evaluate them, but also that the analyst should have the mentality and opportunities to improve on the quality of his work. The system for quality assurance and associated tools are described in *Chapter 6*, together with an evaluation of the performance over the period 1992 - 1995 and a cost-benefit consideration.

The facilities for INAA have been used in third party contracts and services. By 1989 there were indications that governmental organizations and industry were increasing the demands to the supporting laboratories on compliance of the programs for quality assurance with internationally -and mutual accepted- standards. Simultaneously, in the various -INAA using- research programs at IRI often repetition of work was observed because of e.g. improper starting conditions or badly defined requirements for the analysis. Also results and the conditions under which they had been obtained were not traceable which hampered interpretation in case of abnormalities and the analytical quality could not always be assured and demonstrated. It all affected the analysis' costs and the reputation of the laboratory.

It was decided in 1990 to apply quality management principles to the INAA facilities and operations in order (i) to increase the efficiency of the laboratory's operations, (ii) to assure the quality of the analytical data including their traceability and (iii) to strengthen the laboratory's position in the competition for third party research contracts and service. A quality system has been implemented complying with the Euronorm EN45001 which closely follows the ISO/IEC[4] guide 25. Early 1993 this quality system was officially accredited by STERLAB[5] which made the laboratory for INAA the first university laboratory in The Netherlands with such an accreditation, and at that time probably the only accredited laboratory for INAA in the world. The objections for this development, the route to accreditation and a cost-benefit evaluation are among the subjects treated in *Chapter 7.*

1.4 FINAL INTRODUCTORY CONSIDERATIONS

Innovations, modernization and change in attitude have been characteristic for the research and operational activities of the laboratory in the period 1984 - 1996. The strategic research has led to new facilities for INAA the importance of which has to be reflected to the developments of the technique in general, and in view of the developments of other methods and facilities for elemental analysis.

The developments described in *Chapters 3 - 7* of this thesis are discussed in *Chapter 8* effectuating in a prospect for the future position of INAA. The thesis is concluded with *Summaries* both in English and Dutch.

---

4 *ISO : International Organization for Standardization; IEC : International Electrotechnical Committee*

5 *STERLAB : acronym for the Dutch Accreditation Board for Calibration Laboratories, Test Laboratories and Inspection Bodies, in 1995 merged in the Dutch Council for Accreditation*

1.5 REFERENCES

[1] G. Hevesy, H. Levi, 'The Action of Neutrons on the Rare Earth Elements',
Det.Kgl.Danske Videnskabernes Selskab, Mathematisk-fysiske Meddelelser XIV, 5 (1936) 3 - 34

[2] G.E. Boyd, 'Method of Activation Analysis',
Anal.Chem. 21 (1949) 335 - 347

[3] H. Brown, E. Goldberg, 'The Neutron Pile as a Tool in Quantitative Analysis; The Gallium and Palladium Content of Iron Meteorites',
Science 109 (1949) 347 - 353

[4] M. de Bruin, 'Instrumental Neutron Activation Analysis: A Routine Method', Thesis, Delft University of Technology (1983)

[5] G. Kateman, L. Buydens, 'Quality Control in Analytical Chemistry', J.Wiley & Sons, New York (1993)

[6] W.D. Ehmann, J.D. Robertson, S.W. Yates, 'Nuclear and Radiochemical Analysis',
Anal.Chem. 64 (1992) 1R - 22R

[7] E.M. Gryntakis, J.I. Kim, 'Absorption, Activation and Fission $g(T_n)$-functions for non 1/v-nuclides',
Radiochim.Acta 22 (1975) 128 - 147

[8] E.A. Mackey, G.E. Gordon, R.M. Lindstrom, D.L. Anderson, 'Effects of Target Shape and Neutron Scattering for Neutron Capture Prompt γ-ray Activation Analysis',
Anal.Chem. 63 (1991) 288 - 292

[9] P.J.M. Korthoven, M. de Bruin, 'Automated Interpretation of γ-Ray Data obtained in Non-Destructive Activation Analysis',
J.Radioanal.Chem. 35 (1977) 127 - 137

[10] P. Bode, M. de Bruin, P.J.M. Korthoven, 'A Method for the Correction of Self-absorption of Low Energy Photons for Use in Routine INAA',
J.Radioanal.Chem. 64 (1981) 153 - 166

[11] R. Henkelmann, H.J. Born, 'Analytical Use of Neutron-Capture Gamma Rays',
J.Radioanal.Chem. 16 (1973) 473 - 481

[12] R.M. Lindstrom, R. Zeisler, M. Rossbach, 'Activation Analysis Opportunities using Cold Neutron Beams',
J.Radioanal.Chem. 112 (1987) 321 - 330

[13] H. Chen, R.G. Downing, D.F.R. Mildner, W.M. Gibson, M.A. Kumakhov, I.Y. Ponomarev, M.V. Gubarev, 'Guiding and Focusing Neutron Beams using Capillary Optics',
Nature, 357 (1992) 391

[14] G.V. Iyengar. W.B. Clarke, R.G. Downing, 'Determination of Boron and Lithium in diverse Biological Matrices using Neutron Activation - Mass Spectrometry',
Fres.J.Anal.Chem. 338 (1990) 562 - 566

[15] R.H. Fleming, R.F. Fleming, Y. Dewaraja, 'Imaging Neutron Activation Analysis',
Book of Abstracts, 8th.Int.Conf.on Modern Trends in Activation Analysis, Vienna. Austria, September 16 - 20 (1991)

[16] S. Landsberger, 'The Instrumental Determination of Cadmium in Biological Samples at Nanogram Levels with the Aid of a Compton Suppression System and Epithermal Neutron Activation Analysis',
J.Radioanal.Nucl.Chem. 161 (1992) 5 - 10

[17] J.B. Cumming, P.P. Parekh, A.V. Murali, 'A Novel Approach to the Determination of Iridium via Ge-Coincidence/NaI(Tl)-Anticoincidence Gamma-Ray Spectroscopy',
Nucl.Instr.Meth. A265 (1988) 468 - 474

[18] G.P. Westphal, 'Gamma-Spectrometry shatters the 100 kc/s Throughput Barrier',
J.Radioanal.Nucl.Chem. 168 (1993) 513 - 517

[19] G.P. Westphal, 'On the Performance of Loss-Free Counting - a Method for Real-time Compensation of Dead-Time and Pileup Losses in Nuclear Pulse Spectroscopy',
Nucl.Instr.Meth. 163 (1979) 189 - 196

[20] A. Simonits, F. de Corte, J. Hoste, 'Single Comparator Methods in Reactor Neutron Activation Analysis',
J.Radioanal.Chem. 24 (1975) 31 - 46

[21] M. de Bruin 'Present and Future Position of Instrumental Neutron Activation Analysis', (Proceed.VII Polish Spectroanalytical Conference, Orun, Poland (1988)
Chemia Analityczna 35 (1990) 99 - 107

[22] R.M.W. Overwater, P. Bode, J.J.M. de Goeij, J.E. Hoogenboom, 'Feasibility of Elemental Analysis of Kilogram-Size Samples by Instrumental Neutron Activation Analysis',
Anal.Chem. 68 (1996) 341 - 348

[23] M. Blaauw, 'The Holistic Interpretation of Gamma-Ray Spectra in Instrumental Neutron Activation Analysis', Thesis, Delft University of Technology (1993)

[24] M. Blaauw, R.M. Lindstrom, 'Local Area Networks in NAA: Advantages and Pitfalls',
J.Radioanal.Nucl.Chem. 169 (1993) 443 - 452

[25] R.M.W. Overwater, J.E. Hoogenboom, 'Accounting for the Thermal Neutron Flux Depression in Voluminous Sources for Instrumental Neutron Activation Analysis',
Nucl.Sci.Eng. 117 (1994) 141 - 157

[26] M. Blaauw, 'The Use of Sources emitting Coincident Gamma-Rays for Determination of Absolute Efficiency Curves of Highly Efficient Ge detectors',
Nucl.Instr.Meth. A332 (1993) 493 - 500

[27] W.D. Ehmann, J.D. Robertson, S.W. Yates, 'Nuclear and Radiochemical Analysis',
Anal.Chem. 66 (1994) 229R - 251R

[28] C. Dardenne, N. Deschamps, G. Revel, G. Riglet, C. Herviou, 'Application of the k_0-Standardization Method in Neutron Activation Analysis of Ceramic Materials',
J.Radioanal.Nucl.Chem. 168 (1993) 417 - 427

[29] P. Bode, 'The use of INAA for the Determination of Trace Elements, in particular Cadmium, in Plastics in Relation to the Enforcement of Pollution Standards',
J.Radioanal.Nucl.Chem. 167 (1993) 361 - 367

[30] J.J. Fardy, Y.J. Farrar, 'Trace Element Analysis of Argyle Diamonds using Instrumental Neutron Activation Analysis',
J.Radioanal.Nucl.Chem. 164 (1992) 337 - 345

[31] R.G.V. Hancock, W.A. Fox, T. Conway, L.A. Pavlish, 'Chemical analysis of archaeological copper and brass from Northeastern Ontario',

J.Radioanal.Nucl.Chem. 168 (1993) 307 - 315

[32] W. Maenhaut, E.I. Kauppinen, T.M. Lind, 'Study of Size-fractionated Coal-combustion Aerosol using INAA',
J.Radioanal.Nucl.Chem. 167 (1993) 259 - 269

[33] C. Koeberl, 'INAA of Geochemical and Cosmochemical Samples: a Fast and Reliable Method for Small Sample Analysis',
J.Radioanal.Nucl.Chem. 168 (1993) 47 - 60

[34] T.J. Kishi, 'Instrumental Neutron Activation Analysis of Graphite Electrode of a Dry Battery',
J.Radioanal.Nucl.Chem. 168 (1993) 413 - 415

[35] R.J. Mumper, M. Jay, 'Poly(L-lactic Acid) Microspheres Containing Neutron-Activatable Holmium-165: a Study of the Physical Characteristics of Microspheres Before and After Irradiation in a Nuclear Reactor',
Pharm.Res. 9 (1992) 149 - 154

[36] J.J. Fardy, I.M. Warner, 'A Comparison of Neutron Activation Analysis and Inductively Coupled Plasma-Mass Spectrometry for Trace Element Analysis of Biological Materials',
J.Radioanal.Nucl.Chem. 157 (1992) 239 - 244

[37] K.H. Ng, D.A. Bradley, L.M. Looi, C.S. Mahmood, A.K. Wood, 'Differentiation of Elemental Composition of Normal and Malignant Breast Tissue by INAA',
Int.J.Appl.Radiat.Isotop. 44 (1993) 511 - 516

[38] M.L. Verheijke, H.J.J. Jaspers, J.M.G. Hanssen, M.J.J. Theunissen, 'Application of Neutron Activation Analysis in the Field of Silicon Technology for the Modern Electronic Industry',
J.Radioanal.Nucl.Chem. 113 (1987) 397 - 403

[39] P. Kuik, J.E. Sloof, H.Th. Wolterbeek, 'Application of Monte Carlo Assisted Factor Analysis to Large Sets of Environmental Pollution Data',
Atmosph.Environm. 27A (1993) 1975 - 1983

[40] P.A.H. van Noord, 'Selenium and Human Cancer Risk: Nail Keratin as a Tool in Metabolic Epidemiology', Thesis, State University of Utrecht (1992)

[41] P. van den Brandt, S. Bausch-Goldbohm, 'A Prospective Cohort Study on Diet and Cancer in The Netherlands', Thesis, State University of Limburg (1993)

[42] A.A. Goede, 'Selenium in Marine Waders', Thesis, State University of Utrecht (1993)

[43] P. Bode, M. Blaauw, I. Obrusník, 'Variation of Neutron Flux and Related Parameters in an Irradiation Container in Use with k_0-Based Neutron Activation Analysis',
J.Radioanal.Nucl.Chem. 157 (1992) 301 - 312

[44] L. Moens, J. de Donder, Lin Xi-Lei, F.de Corte, A.de Wispelaere, A.Simonits, J.Hoste, 'Calculation of the Absolute Peak Efficiency of Gamma-Ray Detectors for Different Counting Geometries',
Nucl.Instr.Meth. 187 (1981) 451 - 472

[45] M. Thompson, R. Wood, 'IUPAC/ISO/AOAC - 1995 Harmonised Guidelines for Internal Quality Control in Analytical Chemistry Laboratories',
Pure and Appl.Chem. 67 (1995) 649 - 666

[46] e.g. Malaysian Institute for Nuclear Technology (MINT), Kajang, Malaysia;
Centre for Analytical Research in the Environmentm, Ascot, United Kingdom;
Institute of Nuclear Chemistry and Technology, Warszawa, Poland;
Nuclear Physics Institute, Řež near Prague, Czech Republic

[47] UNDP/RCA/IAEA Regional Training Workshop on Application of ISO-25 and other International QA/QC Standards in Laboratories employing Nuclear and Complementary Techniques for Environmental Analysis',
Taejon, Republic of Korea, June 24 - July 5, 1996

[48] I. Obrusník, P. Bode, 'Improved Ease-of-operation in Epithermal NAA by Irradiation in Plastic Capsules and Use of Well-type Ge-spectrometry: a Feasibility Study',
J.Radioanal.Nucl.Chem. 158 (1992) 343 - 351

[49] S.S. Then, F.D.P. Geurink, P. Bode, R.M. Lindstrom, 'A Pulse Generator simulating Ge-detector Signals for Dead-time and Pile-up Correction in Gamma-Ray Spectroscopy in INAA without distortion of the Detector Spectrum',
accepted for publ.in J.Radioanal.Nucl.Chem.

[50] M.J.J. Ammerlaan, P. Bode, 'Modern Spectrometer Performance Control of Gamma-Ray Spectrometers for INAA',
accepted for publ. in J.Radioanal.Nucl.Chem.

[51] P. Bode, C.P. van Dijk, 'Operational Management of Results in INAA utilizing a Versatile System of Control Charts',
accepted for publ. in J. Radioanal.Nucl.Chem.

CHAPTER 2 PRINCIPLES AND CHARACTERISTICS OF INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

2 *PRINCIPLES AND CHARACTERISTICS OF INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS*

2.1 INTRODUCTION

Neutron activation analysis (NAA) allows for the qualitative and quantitative determination of elements. The method is based upon the conversion of stable atomic nuclei into radioactive nuclei by irradiation with neutrons and the subsequent measurement of the radiation released by these radioactive nuclei. Amongst the several types of radiation that can be emitted, gamma-radiation offers the best characteristics for the selective and simultaneous determination of elements.

By neutron activation, radionuclides may be produced from all elements present in the sample, albeit at sometimes strongly different production rates. This mixture of radioactivities can be analyzed in two different ways:

(i) The resulting radioactive sample is chemically decomposed, and by chemical separations the total number of radionuclides is split-up into many fractions with a few radionuclides each: Destructive or Radiochemical Neutron Activation Analysis. This form of NAA will not be discussed in this thesis.

(ii) The resulting radioactive sample is kept intact, and the radionuclides are determined by taking advantage of the differences in decay rates via measurements at different decay intervals utilizing equipment with a high energy resolution for gamma-radiation: Non-destructive or Instrumental Neutron Activation Analysis (INAA).

A procedure in INAA is characterized by (i) activation via irradiation with reactor neutrons, (ii) measurement of the gamma-radiation after one or more decay times and (iii) interpretation of the resulting gamma-ray spectra in terms of elements and concentrations.

2.2 ACTIVATION

The activation with neutrons is the first stage in a INAA procedure. Its purpose is to convert some of the stable nuclei in radioactive nuclei emitting radiation that can be used for analytical purposes. Insight into the reactions that may take place during activation facilitates the identification of the relation between the observed radioactive nucleus, its target nucleus and associated element. Insight into the reaction rates is of importance for the quantitative analysis and for a priori estimates of the feasibility of an analysis.

Each atomic nucleus can capture a neutron during irradiation. A nuclear reaction results, in which often the nuclear mass changes; immediately after the capture ('promptly')

excess energy in the form of photons and/or particles will be emitted[1]. The newly formed nucleus may be unstable. When unstable, already during activation it starts to decay to a stable state by the emission of radiation through one or more of the following processes: α-decay, β^--decay, electron capture, β^+-decay, or internal transition decay. In most cases γ and X-radiation will be emitted too.

The capture of a neutron by a atomic nucleus and the resulting reaction may be illustrated, in the case of a cobalt target nucleus, by

$$^{59}Co + {}^{1}n \rightarrow {}^{60}Co + \text{(prompt) } \gamma\text{-radiation}$$

The resulting ^{60}Co nucleus is radioactive and decays by emission of β^- and γ-radiation. Commonly, the reaction is written in the shorthand notation as

$$^{59}Co\ (n,\gamma)\ ^{60}Co$$

The most common reaction occurring in NAA is the (n,γ) reaction, but also reactions such as (n,p), (n,α), (n,n') and (n,2n) are important. Some nuclei, like ^{235}U are fissionable by neutron capture and the reaction is denoted as (n,f) yielding fission products and fast neutrons.

The reaction rate R per nucleus capturing a neutron is given by

$$R = \int_0^\infty n(v)v\sigma(v)\ dv \qquad 2\text{-}1$$

where

v = the neutron velocity (ms^{-1})

$\sigma(v)$ = the neutron cross section (in m^2 ; 1 barn = 10^{-28} m^2) for neutrons with velocity v;

$n(v)dv$ = the neutron density (m^{-3}) of neutrons with velocities between v and $v+dv$, considered to be constant in time

The production of radioactive nuclei is described by

$$\frac{dN}{dt} = RN_0 - \lambda N \qquad 2\text{-}2$$

in which

N_0 = number of target nuclei

N = number of radioactive nuclei

λ = the decay constant, s^{-1}; $\lambda = \ln 2/t_{1/2}$ with

$t_{1/2}$ = the half-life of the radionuclide, s.

---

[1] *This prompt radiation can also be used for analytical purposes. It requires measurement during activation. This method is not applied at IRI and therefore not considered further.*

The disintegration rate of the produced radionuclide at the end of the irradiation time follows from

$$D(t_{ir}) = N(t_{ir})\lambda = N_0 R(1 - e^{-\lambda t_{ir}}) \qquad 2\text{-}3$$

with

D = disintegration rate, Bq, of the produced radionuclide, assuming that $N = 0$ at $t = 0$ and N_0 = constant

The cross section and the neutron flux are neutron energy dependent. In nuclear research reactors -which are intense sources of neutrons- three types of neutrons can be distinguished (see *Figure 2-1*):

(i) Fission or fast neutrons released in the fission of ^{235}U. Their energy distribution ranges from 100 keV to 25 MeV with a maximum fraction at 2 MeV. These neutrons are slowed down by interaction with a moderator, e.g. H_2O, to enhance the probability of them causing a fission -chain- reaction in the ^{235}U.

(ii) Epithermal neutrons. These are neutrons in the process of slowing down by collisions with the nuclei of the moderator. Epithermal neutrons have energies between approximately 0.5 eV and 100 keV.

(iii) Thermal neutrons, i.e. neutrons in thermal equilibrium with the atoms of the moderator. The energy distribution of these thermal neutrons is Maxwellian, with a most probable velocity v_0 of 2200 ms^{-1} at 20 °C, corresponding to an energy of 0.025 eV.

Typically thermal neutron fluxes in a nuclear research reactor are in the order of 10^{16} - 10^{18} $m^{-2}s^{-1}$. As can be seen from *Figure 2-1*, the thermal neutrons have the highest flux. The epithermal and fast neutron fluxes strongly depend on the configuration of the reactor, particularly on the choice of moderator. In the irradiation facilities of a light water moderated reactor such as with the Hoger Onderwijs Reactor (HOR) at IRI, the epithermal neutron flux is typically a factor 40-50 lower than the thermal neutron flux.

Reactions of the (n,γ) and (n,f) type have the highest cross section (typically in the order of 0.1 - 100 barn) for thermal neutrons whereas the other reactions ((n,p), (n,α), (n,n'), (n,2n)) mainly occur with fast neutrons at cross sections 2 or 3 orders of magnitude lower. In several cases nuclear reactions result into the conversion of a stable nucleus into another stable nucleus.

The cross section for thermal neutrons is often inversely proportional to the neutron velocity; in the epithermal region the neutron cross section can be very high for neutrons of a discrete energy and the neutron cross section vs. neutron energy relationship shows 'resonance peaks' (see *Figure 2-2*).

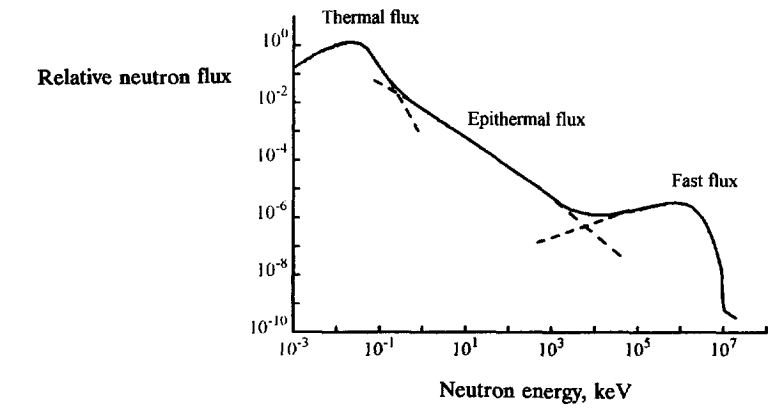


Figure 2-1. Schematic representation of the neutron flux spectrum in a nuclear reactor

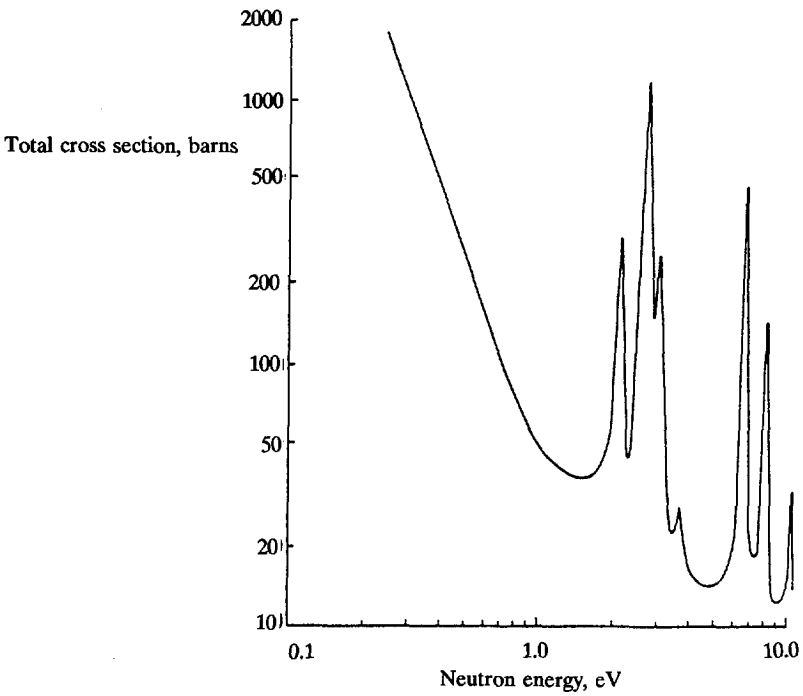


Figure 2-2. Relation between neutron cross section and neutron energy

The dependence of the activation cross section and neutron flux to the neutron energy can be taken into account in *Equation 2-1* by dividing the neutron spectrum into a thermal and an epithermal region; the division is made at E_n = 0.55 eV (the so-called cadmium cut-off energy). This approach is commonly known as the Høgdahl convention [1]. The integral in *Equation 2-1* can then be rewritten as

$$R = \int_0^{v_{Cd}} n(v)v\sigma(v)\ dv + \int_{v_{Cd}}^{\infty} n(v)v\sigma(v)\ dv \qquad 2\text{-}4$$

The first term can be integrated straightforward:

$$\int_0^{v_{Cd}} n(v)v\ dv = v_0\sigma_0\int_0^{\infty} n(v)\ dv = nv_0\sigma_0 \qquad 2\text{-}5$$

in which

$$n = \int_0^{\infty} n(v)\ dv \qquad 2\text{-}6$$

is called the thermal neutron density, and when $\Phi_{th} = nv_0$,

Φ_{th} = the 'conventional' thermal neutron flux, $m^{-2}s^{-1}$, for energies up to the Cd cut-off energy of 0.55 eV

σ_0 = the thermal neutron activation cross section, m^2, at 0.025 eV

v_0 = the most probable neutron velocity at 20 °C: 2200 ms^{-1}

The second term is re-formulated in terms of neutron energy rather than neutron velocity and the infinite dilution resonance integral I_0 -which effectively is also a cross section (m^2)- is introduced:

$$\int_{v_{Cd}}^{\infty} n(v)v\ dv = \Phi_{epi}\int_{E_{Cd}}^{E_{max}} \frac{\sigma\ (E_n)\ dE_n}{E_n} = \Phi_{epi}\ I_0 \qquad 2\text{-}7$$

with

$$I_0 = \int_{E_{Cd}}^{E_{max}} \frac{\sigma(E_n)\ dE_n}{E_n} \qquad 2\text{-}8$$

in which

Φ_{epi} = the 'conventional' epithermal neutron flux per unit energy interval, at 1 eV

From this definition of I_0 it can be seen that the energy dependency of the epithermal neutron flux is proportional to $1/E_n$.

In the practice of nuclear reactor facilities the epithermal neutron flux Φ_{epi} is not precisely following the inverse proportionality to the neutron energy; the small deviation can be accounted for by introducing a epithermal flux distribution parameter α:

$$I_0(\alpha) = \int_{E_{Cd}}^{E_{max}} \frac{\sigma(E_n)\, dE_n}{E_n^{(1+\alpha)}} \qquad 2\text{-}9$$

The expression for the reaction rate can thus be re-written as

$$R = \Phi_{th}\sigma_0 + \Phi_{epi} I_0(\alpha) \qquad 2\text{-}10$$

Expressing the ratio of the thermal neutron flux and the epithermal neutron flux as $f = \Phi_{th}/\Phi_{epi}$ and the ratio of the resonance integral and the thermal activation cross section as $Q_0(\alpha) = I_0(\alpha)/\sigma_0$, an effective cross section can be defined:

$$\sigma_{eff} = \sigma_0(1 + \frac{Q_0(\alpha)}{f}) \qquad 2\text{-}11$$

It simplifies the *Equation 2-7* for the reaction rate to

$$R = \Phi_{th}\sigma_{eff} \qquad 2\text{-}12$$

In the majority of INAA procedures thermal neutrons are used for the activation. Sometimes activation with epithermal reactor neutrons is preferred to enhance the activation of elements with a high ratio of resonance neutron cross section over thermal neutron cross section relatively to the activation of elements with a lower such a ratio.

The neutron activation of a number of low Z elements (H, He, Be, Li, B, C, N, O - which belong often to the most abundant in many materials-) and of a few high Z elements (Bi, Tl, Pb) is characterised by either one, or a combination of (i) very low activation cross sections, (ii) activation products with very short half-lives (in the order of seconds) and (iii) the emission of radiation which does not interfere with the measurement of the radiation emitted by the other activation products.

In principle materials can be activated in any physical state, viz. solid, liquid or gaseous. There is no fundamental necessity to convert solid material into a solution prior to activation; INAA is essentially considered to be a non-destructive method although under certain conditions some damage may occur due to thermal heating, radiolysis and radiation tracks by e.g. fission fragments and α-radiation emitting nuclei.

During activation the material is heated by primarily the absorption of both reactor and prompt gamma-rays. The gamma-rays already present in the reactor because of the uranium fission, the fission and activation products are denoted as reactor gamma-rays, to distinguish from the prompt gamma-rays released upon neutron capture.

Radiolysis is another effect caused by the reactor gamma-rays and prompt gamma-rays. In water H_2, O_2 and H_2O_2 are formed. The gasses cause pressure build-up in the

sample container. Because of explosion hazard samples are preferentially dried prior to activation. Radiolysis may also lead to decomposition of proteins into gaseous compounds.

Fission fragments and α-particles may produce small holes in dedicated plastic foils; these holes can be made visible under a microscope after chemical treatment of the foil.

2.3 MEASUREMENT

The nuclear transformations are established by measurement of the number of nuclear decays. The number of activated nuclei $N(t_{ir}, t_d)$ present at the start of the measurement is given by[2]

$$N(t_{ir}, t_d) = \frac{RN_0}{\lambda}(1 - e^{-\lambda t_{ir}})e^{-\lambda t_d} \qquad 2\text{-}13$$

and the number of nuclei ΔN disintegrating during the measurement is given by

$$\Delta N(t_{ir}, t_d, t_m) = \frac{RN_0}{\lambda}(1 - e^{-\lambda t_{ir}})e^{-\lambda t_d}(1 - e^{-\lambda t_m}) \qquad 2\text{-}14$$

in which

t_d = the decay or waiting time, i.e. the time between the end of the irradiation and the start of the measurement

t_m = the duration of the measurement

Since the spectrum of emitted gamma-radiation in combination with the half-life of the radionuclide makes radionuclide identification unambiguous, the measurement in INAA is performed using gamma-ray spectrometry. In this, the demand for a high selectivity surpasses the demand for a high counting efficiency. It requires an optimal separation of the peaks in the gamma-ray spectrum. Germanium semiconductor radiation detectors have the best energy resolution of the detectors available for practical application varying typically from approximately 1 keV for photons of approximately 100 keV to approximately 2 keV for photons of approximately 1.5 MeV. In *Chapter 5* a more detailed description is given of the principles and characteristics of semiconductor detectors.

Replacing the number of target nuclei N_0 by $(N_{Av}\theta w)/M$ and using the *Equation 2-9* for the reaction rate, the resulting net area A of a peak in the spectrum corresponding with a given photon energy is approximated by the 'activation formula':

---

[2] *The representation given here is correct only for the simplest of cases. Complications may arise when the activated nucleus decays to another unstable nucleus of which the activity is measured, e.g.* $^{46}Ca(n,\gamma)^{47}Ca(\beta^-)^{47}Sc$; *here* ^{47}Ca *is the activation product, but* ^{47}Sc *is the radionuclide assessed.*

$$A = \Delta N \gamma \varepsilon = \Phi_{th} \sigma_{eff} \frac{N_{Av} \theta w}{M} (1 - e^{-\lambda t_{ir}}) e^{-\lambda t_d} \frac{(1 - e^{-\lambda t_m})}{\lambda} \gamma \varepsilon \qquad 2\text{-}15$$

with

A = net peak area

N_{Av} = Avogadro's number, mol^{-1}

θ = isotopic abundance of the target isotope N_0

w = mass of the irradiated element, g

M = atomic mass, $g.mol^{-1}$

γ = the gamma-ray abundance, i.e. the probability of the disintegrating nucleus emitting a photon of this energy (photons.disintegration^{-1})

ε = the photopeak efficiency of the detector, i.e. the probability that an emitted photon of given energy will be detected and contribute to the photopeak in the spectrum

Although the photons emitted have energies ranging from tens of keV's to MeV's and have high penetrating powers, they still can be absorbed or scattered in the sample itself depending on the sample size, composition and photon energy. This effect is called gamma-ray self-attenuation. Also, two or more photons may be detected simultaneously; this effect is called summation. The approximation *2-12* is valid when self-attenuation and summation effects can be neglected.

2.4 STANDARDIZATION

Standardization is the determination of the proportionality factors F that relate the net peak areas in the gamma-ray spectrum to the amounts of the elements present in the sample under given experimental conditions:

$$F = \frac{A}{w} \qquad 2\text{-}16$$

The terms standardization and calibration are used indifferently to denote the determination of F. Both absolute and relative methods of standardization exist.

ABSOLUTE STANDARDIZATION

The values of the physical parameters determining the proportionality factor θ, N_{Av}, M, σ_{eff}, γ, λ, are taken from literature. For many (n,γ) reactions and radionuclides the parameters σ_{eff} respectively γ, λ are not precisely known, whilst in some cases also θ is not known accurately. Since the various parameters were often achieved via independent

methods, their individual imprecisions will add up in the calculation of the elemental amounts, leading to large systematic errors. The other parameters A, w, Φ, ε, t_{ir} , t_d , t_m are determined, calculated or measured for the given circumstances and uncertainties can be established.

RELATIVE STANDARDIZATION

The unknown sample is irradiated together with a calibration sample containing a known amount of the element(s) of interest. The calibration sample is measured under the same conditions as the sample (sample-to-detector distance, sample size and if possible composition). From comparison of the net peak areas in the two measured spectra the concentration(s) of the element(s) of interest can be calculated:

$$\rho = \frac{(\frac{A}{t_m DCw})_{sample}}{(\frac{A}{t_m DCw})_{standard}} \qquad 2\text{-}17$$

in which

ρ = concentration, $g.g^{-1}$

D = $e^{-\lambda.td}$

C = $(1 - e^{-\lambda.tm})$

w = mass, g

In this procedure many of the parameters cancel out at the calculation of the concentration and the remaining parameters are all known. This standardization is being used in cases where the highest accuracy is required e.g. for the certification of reference materials.

The relative standardization on basis of element standards is not immediately suitable for laboratories aiming at the full multi-element powers of INAA. It is virtually impossible to produce a multi-element standard containing known amounts of all 70 detectable elements with sufficient accuracy in a volume closely matching the size and the shape of the samples. Some laboratories therefore prefer to use (certified) reference materials as a multi-element standard.

Multi-element INAA on basis of the relative standardization method is feasible when performed according to the principles of the single-comparator method. Assuming stability in time of all relevant experimental conditions, standards for all elements are co-irradiated each in turn with the chosen single comparator element. Once the sensitivity for all elements relative to the comparator element has been determined (expressed as the so-called k-factor,

see *paragraph 2.4.1*), only the comparator element has to be used in routine measurements instead of individual standards for each element.

2.4.1 Single comparator method

Originally, the single comparator method for multi-element INAA was based on the ratio of proportionality factors of the element of interest and of the comparator element after correction for saturation, decay, counting and sample weights. Girardi et al [2] defined the *k*-factor as

$$k = \frac{M_a \gamma_c \varepsilon_c \theta_c \sigma_{eff,c}}{M_c \gamma_a \varepsilon_a \theta_a \sigma_{eff,a}} \qquad 2\text{-}18$$

in which the subscripts *a* and *c* refer to element of interest in the sample and comparator, respectively. Concentrations then can be calculated from these *k*-factors; for an element determined via a directly produced radionuclide the concentration ρ follows from

$$\rho = \frac{(\frac{A}{SDCw})_a}{(\frac{A}{SDCw})_c} k \qquad 2\text{-}19$$

where
$S = (1 - e^{-\lambda t_{ir}})$

These experimentally determined *k*-factors are often more accurate than when calculated on basis of literature data as in the absolute standardization method. However, the *k*-factors are only valid for a specific detector, a specific counting geometry and irradiation facility, and remain valid only as long as the neutron flux parameters of the irradiation facility remain stable.

At IRI, Girardi's single comparator *k*-factor has been slightly modified to a more versatile factor to be used with different detectors and counting geometries. To this end, the photopeak efficiency was 'removed' from the factor, and derived separately in the calculations from the experimentally determined efficiency curves for each detector and each counting geometry [3]:

$$k_{IRI} = \frac{M_c \theta_a \sigma_{eff,a} \sum_i \gamma_{a,i}}{M_a \theta_c \sigma_{eff,c} \gamma_c} \qquad 2\text{-}20$$

in which

$\sum_i \gamma_{a,i}$ = the sum of the absolute intensities of the most important γ-ray lines of the radionuclide

The concentration now follows from

$$\rho = \frac{(\frac{A}{SDCw})_a}{(\frac{A}{SDCw})_c} \frac{\sum_i \gamma_{a,i}}{\gamma_a} \frac{\varepsilon_a}{\varepsilon_c} \frac{1}{k_{IRI}} \qquad 2\text{-}21$$

Analyses at the laboratory for INAA at IRI are still being carried out using these k_{IRI}-factors.

2.4.2 The k_0-method for standardization

At the Institute for Nuclear Sciences in Ghent, Belgium, an attempt has been made to define k-factors which should be independent of neutron flux parameters as well as of spectrometer characteristics. In this approach, which has led to the so-called k_0 method for standardization [4] the irradiation parameter $(1 + Q_0(\alpha)/f)$ and the detection parameter $\sum_i \gamma_{a,i}$ are removed respectively altered in the expression of the k-factor, which resulted at the definition of the k_0-factor:

$$k_0 = \frac{1}{k} \frac{1+\frac{Q_{0,c}(\alpha)}{f}}{1+\frac{Q_{0,a}(\alpha)}{f}} \frac{\varepsilon_c}{\varepsilon_a} = \frac{M_c \theta_a \sigma_{0,a} \gamma_a}{M_a \theta_c \sigma_{0,c} \gamma_c} \qquad 2\text{-}22$$

and the concentration, again for an element determined via a directly produced radionuclide, is found from

$$\rho = \frac{1 + \frac{Q_{0,c}(\alpha)}{f}}{1 + \frac{Q_{0,a}(\alpha)}{f}} \frac{\varepsilon_c}{\varepsilon_a} \frac{(\frac{A}{SDCw})_a}{(\frac{A}{SDCw})_c} \frac{1}{k_0} \qquad 2\text{-}23$$

The k_0-factor thus has become a purely nuclear parameter for the thermal neutron spectrum. In the k_0-convention, Au is proposed as comparator element. The neutron flux parameters f and α no longer cancel out in concentration calculations and must be measured in each irradiation facility, preferably even for each irradiation and sample [5]. At least three isotopes must be activated and measured to determine these parameters. A composed flux monitor containing adequate quantities of Au and Zr is very suitable for this purpose; in a single measurement the induced activities of ^{198}Au, ^{95}Zr and ^{97}Zr can be assessed. As such, the k_0-method is not a single comparator but a triple comparator method.

The k_0-factors and the k_{IRI}-factors can be compared to each other, which thus is a form of independent assessment of the experimentally determined k_{IRI}-factors [6]. The k_0-factors are used at IRI for the analysis of very large samples (see *Chapter 3*).

2.5 ANALYSIS OF GAMMA-RAY SPECTRA

The gamma-spectrum is analyzed to identify the radionuclides produced, and to derive the target elements and their concentrations in the activated sample. The analysis can be divided into spectrum reduction, standardization and interpretation. The spectrum reduction consists firstly of the location of the peaks. Secondly, the peaks are fitted to obtain their energies and net areas. The energies reflect the energy of the radiation emitted and are used to identify the radioactive nuclei. On basis of insight into possible nuclear reactions upon neutron activation, the (stable) element composition are derived. As explained in *paragraphs 2.3* and *2.4* the amounts of the elements are derived from the peak areas.

2.6 LIMITS OF DETECTION IN INAA

The term 'sensitivity' is often used as an erroneous synonym for the detection limit[3] of an analytical method. In INAA the detection limit relates to the ability of detecting a gamma-ray peak in the presence of interference from natural radioactivity and other radioactivities, induced by neutron activation [10]. A peak is detected when it is distinguishable from the uncertainty in this noise level. This signal-to-noise situation makes that the detection limit is related to the square root of the noise or background level.

There are several parameters which have effect to this signal-to-noise ratio. As can be derived from the activation formula (*Equation 2-12*) large photopeak areas are attained at a high thermal neutron flux Φ_{th} and a large sample mass w; the signal-to-noise ratio depends on differences between the nuclear constants θ, σ_{eff} (and thus σ_0 and I_0), γ, λ of the target element and matrix components, and on differences in the experimental parameters ϵ respectively t_{ir} , t_d , t_m and E_γ.

Increases in neutron flux Φ_{th} and sample mass w result in an improvement in detection limit by a net factor corresponding with the square root of the underlying increases

---

[3] *Currie and others [7,8] have described the confusion on nomenclature of the detection limit, the variety of which can lead to nearly 3 orders of magnitude in difference in detection limits. The detection limit in the INAA at IRI is calculated in accordance to Currie's [7] definition in which the probability of a peak to be overlooked in the spectrum analysis has been set to 2.5 % [9].*

since both the signal and noise are equally affected. However, when increasing the sample mass to pursue improvement of detection limits, increasing effects of neutron self-shielding, neutron self-thermalisation and gamma-ray self-attenuation should be anticipated on since they also may have a negative effect to the detection limit.

The consequences for detection limits by improvement of the photopeak-efficiency ε is elaborated upon in detail in *Chapter 5*. A higher photopeak efficiency not only improves -again, by the square root- the signal-to-noise ratio but often more efficient detectors have better peak-to-Compton ratios which result in an additional decrease of the noise level.

The effect of differences in λ, t_{ir} , t_d , t_m and E_γ can be illustrated by considering a radionuclide with half-life shorter than the half-lifes of the interfering nuclides which should be counted as shortly after irradiation as possible; for the determination of a radionuclide with a half life longer than the half-lifes of the interfering radionuclides it may be advantageous to extend the decay time prior to measurement. If only one element has to be determined, the optimum decay time can be chosen to attain the best signal-to-noise ratio for gamma-ray(s) of the related radionuclide. If several elements have to be determined simultaneously, either a compromise is required or results from measurements at different decay times are combined. Often in the practice in INAA, a protocol is followed in which firstly the sample is irradiated shortly and counted for the very short half-life radionuclides; then, the sample is irradiated for a longer period and counted at different decay times, typically in the order of 1 and 3 weeks respectively. The results of the three measurements are combined to the final analysis' report.

Prolongation of measurement time affects the signal-to-noise ratio by the inverse of the square root of that alteration.

Not included in the activation formula but affecting the signal-to-noise ratio is the detector's resolution: the ability to distinguish narrowly spaced peaks in the gamma-ray spectrum.

In the practice of INAA limitations are set with respect to:

(i) The amount of material to be irradiated and to be counted: often set by availability, sample encapsulation aspects and safety limits both related to irradiation (irradiation containers) and counting (e.g. with Ge well-type detectors), and possibly because of neutron self-shielding and gamma-ray self-absorption effects. For these reasons in the practice of INAA at IRI the sample mass is limited to approximately 250 mg.

(ii) The neutron fluxes: set by available irradiation facilities. At the HOR available thermal neutron fluxes range from 0.3 - 1.5 * 10^{17} $m^{-2}s^{-1}$. In epithermal irradiation facilities the ratio of the thermal over non-thermal neutron flux has been lowered e.g. from a factor 50 to a factor 10. It may allow for better detection limits for certain elements with high I_0 values in the presence of interfering elements with low I_0 values.

*Table 2-1. Detection limits in mg.kg^{-1} as observed in a plant material and in a soil material. Experimental conditions: plant: t_{ir} = 4 h @ 5 * 10^{16} m^{-2}s^{-1}, t_d = 5 days, t_m = 0.5 h at coaxial detector followed at t_d = 3 weeks and t_m = 2 h at well-type detector; sample size = 200 mg; soil: t_{ir} = 1.5 h @ 5 * 10^{16} m^{-2}s^{-1}, t_d = 5 days, t_m = 1 h at coaxial detector followed at t_d = 3 weeks and t_m = 1 h at well-type detector; sample size = 200 mg*

	Plant	Soil		Plant	Soil
Na	2	10	K	200	1500
Ca	700	4000	Sc	0.001	0.02
Cr	1	1	Fe	8	100
Co	0.02	0.3	Ni	2	30
Zn	0.4	6	Ga	2	10
As	0.2	0.8	Se	0.1	1
Br	0.3	0.8	Rb	0.4	6
Sr	5	60	Zr	5	80
Mo	4	10	Ag	0.2	2
Cd	3	8	Sn	10	20
Sb	0.02	0.2	Te	0.3	3
Cs	0.02	0.3	Ba	10	40
La	0.1	0.3	Ce	0.2	1
Nd	0.7	8	Sm	0.01	0.03
Eu	0.006	0.05	Tb	0.008	0.1
Yb	0.03	0.2	Lu	0.004	0.02
Hf	0.01	0.1	Ta	0.01	0.2
W	0.3	1	Re	0.08	0.2
Os	0.1	0.6	Ir	0.0006	0.004
Au	0.003	0.01	Hg	0.05	0.4
Th	0.01	0.1	U	0.2	2

(iii) The duration of the irradiation time: set by practical aspects, such as the limitations in total irradiation dose of the plastic containers because of radiation damage. As an example, at IRI the maximum irradiation time for polyethylene capsules varies between 5 minutes in the fast irradiation facilities to 5 hours in the standard irradiation facilities because of differences in cooling during irradiation.

(iv) The total induced radioactivity that can be measured is set by the state-of-the-art of counting and signal processing equipment, with additional radiation dose and shielding considerations. For this reason, at IRI the maximum activity at the moment of counting is typically less than 250 kBq.

(v) The duration of the counting time: a very long counting time may set limits to the number of samples processed simultaneously in case the radioactivity decays considerably during this counting time. Moreover, it reduces sample throughput. At IRI counting times are usually limited to 1 hour.

(vi) The total turn-around time: though sometimes better detection limits may be obtained at long decay times, the demands regarding the turn-around time often imply that a compromise has to be found between longest permissible decay time and customer satisfaction.

(vii) The detector size, counting geometry and background shielding. The detector's characteristics are sometimes set in advance by availability but several options exist. As mentioned before, this is further discussed in *Chapter 5*.

It all emphasizes that a limit of detection for a given element by INAA may be different for each individual type of material, and analysis conditions. In *Table 2-1* are given, as an indication, typical detection limits as derived from the analysis of a plant and a soil material at IRI. The data demonstrate the strong dependency of sample type and element involved on the detection limits.

2.7 ACCURACY IN INAA

Accuracy is defined as the closeness of the agreement between the result of a measurement and a true value of a measurand [11].

(i) The accuracy of the QUALITATIVE analysis, viz. the identification of the target elements is governed by the quality of the catalogues of radionuclide related gamma-ray energies and intensity ratios, and the knowledge of nuclear transformations involved in production routes. The qualitative accuracy may be affected by peak assignments to erroneous radionuclides due to instrumental drifts of the spectrometer from the calibration conditions, gamma-ray spectrum interferences (including narrowly spaced peaks, sum-peaks and self-absorption phenomena) and underestimated interfering nuclear reactions.

By using multiple peaks instead of single peaks for nuclide identification, multiple radionuclides for element identification and the inclusion of the energies of escape and

coincidence sum-peaks in the gamma-ray catalogues many of these effects -including the instrumental drift problem- can be accounted for or timely be observed. In principle errors may be made by assigning a single gamma-ray peak to one or more, the wrong nuclides or the wrong element. However, the number of nuclides for which such a situation may occur is very small and is reduced to zero when also differences in half-life are taken into consideration. Additionally, errors in element assignment may occur due to interfering production reactions.

The assignment of gamma-ray lines to radionuclides can be considered to be executable with a very high degree of accuracy. The accuracy of the final identification of the target elements depends on the knowledge of the production mechanisms and interfering reactions, and the ability to discriminate between potential target elements.

(ii) The degree of accuracy in the QUANTITATIVE analysis has to be assessed by the way the obtained concentrations approximate the true concentration values. Since the obtained results are in fact estimates of the true values, the results have to be accompanied by a statement of uncertainty. The sources of error contributing to this uncertainty, can be rather completely assessed in INAA since many aspects of the procedure (activation, decay, measurement) are described by physical laws. Traditionally [4], three types of errors can still be distinguished to affect the final concentrations:

(ii-1) Random errors, which vary in sign and magnitude and are unpredictable. Since they have a statistical character, they affect the precision of the analysis. Examples are differences in neutron flux between sample and standard caused by badly defined positions during irradiation, sample inhomogeneities and counting statistics.

(ii-2) Systematic errors are always of the same sign and magnitude, and produce bias between the obtained result and the true value. Systematic errors thus affect the accuracy of the analysis. Examples of sources of systematic error are contamination, moisture content, erroneous standardization, dead-time and pile-up losses, differences in geometry between sample and standard, errors in the photopeak efficiency of the detector, blank and natural background corrections, neutron self-shielding, neutron self-moderation and gamma-ray self-absorption, errors in half-lives.

---

[4] *In 1995 the International Organization for Standardization (ISO) issued new concepts describing the uncertainty, distinguishing uncertainty consisting of type A and type B components [12]. These concepts have not yet fully been incorporated in INAA as performed at IRI, reason why in this thesis still the old concepts are described.*

(ii-3) Additional errors. They may include choice of wrong method for drying with consequently loss by volatilization, erroneously entered sample weights, contaminations, errors made during spectrum analysis. These errors may either have a random or systematic character.

The type of errors related to the sample preparation (contamination, element loss due to volatilization, incomplete drying) are not unique for INAA but applicable to any method of chemical analysis. In this respect INAA has the additional advantage that the samples do not require any pre-treatment such as dissolution or mixing with an inert material for pelletizing, thus largely eliminating errors due to the blank, contamination and losses. Errors due to neutron- and gamma-ray self absorption and neutron self-thermalization can largely be accommodated for and often neglected by processing small samples. Since the principles of INAA are based on effects taking place in the atomic nucleus, the results are not affected by the chemical or physical state of the elements. Errors made in standardization have often the largest effect on the accuracy of INAA. This source of errors includes errors due to unknown purity and stoichiometry of chemical compounds, standard preparation errors (e.g. inaccuracy in pipetting and similar errors as mentioned with sample preparation). The use of the k_0-method for standardization (see *paragraph 2.4.2*) makes for many elements and radionuclides the preparation of standards superfluous, but now the inaccuracy in the experimentally determined nuclear constants becomes important.

An estimate of the accuracy of INAA can be obtained by comparison of the results of analysis of certified reference materials with the data in the certificates. However, for quit a few elements there are no reference materials available with certified concentrations. Then an indication for the degree of accuracy may be obtained by participation in laboratory intercomparison rounds or proficiency testing. In *Table 2-2* the results are given of multiple analyses of a NIST [5] Standard Reference Material 2711 'Montana Soil'. The accuracy is expressed as a standardized difference z thereby taking into account the uncertainties of the obtained result and the uncertainty in the certified value:

$$z_i = \frac{C_i - C_{ref,i}}{\sqrt{\sigma_i^2 + \sigma^2_{ref,i}}} \qquad 2\text{-}24$$

in which

C_i , σ_i = the observed concentration respectively its uncertainty

$C_{ref,i}$, $\sigma_{ref,i}$ = the concentration respectively its uncertainty in the reference material

[5] *NIST, acronym for National Institute of Standards and Technology (USA)*

Table 2-2. Observed concentration of a selection of elements as obtained by INAA, and comparison with certified (bold) and consensus values in NIST SRM 2711 'Montana Soil'

	C_i , mg.kg^{-1}	σ_i , %	$C_{ref,i}$, mg.kg^{-1}	$\sigma_{ref,i}$, %	z
Na	12,020	1.9	**11,400**	**2.6**	1.6
Al	66,880	3.2	**65,300**	**1.4**	0.68
V	82.2	3.0	**81.60**	**3.5**	0.16
Mn	659.6	1.7	**638.0**	**4.4**	0.72
Co	10.0	2.0	10	25	0.0069
Zn	336.5	4.0	**350.4**	**1.4**	−0.97
As	105.6	3.0	**105.0**	**7.6**	0.068
Rb	123.5	4.4	110	25	0.48
Cd	393.4	8.0	**417.0**	**0.60**	−0.75
Ba	738.0	4.7	**726.0**	**5.2**	0.23
Eu	1.16	2.8	1.1	25	0.22
Hg	6.17	4.9	**6.25**	**3.0**	−0.22
Th	13.9	2.2	14	25	−0.027
U	2.42	9.6	2.6	25	−0.27

2.8 CHARACTERISTICS OF INAA

The most attractive analytical characteristics of INAA are:

(i) The method is non-destructive. There is no need to convert the sample into a solution prior to analysis.

(ii) There are many adjustable experimental parameters that can be exploited so that the best detection limit for the desired element is achieved. The energy, and flux of the neutrons may be varied which allows for selective activation. The irradiation time can be varied resulting in enhanced activation of elements with short half-live radionuclides. The differences in half-life between the various radionuclides is a tool to discriminate between them. Spectral interferences can be overcome by using multiple gamma-ray lines and multiple radionuclides to identify the elements.

(iii) The method provides simultaneous multi-element data.

(iv) For many elements detection limits can be obtained at the mg.kg^{-1} to μg.kg^{-1} level.

(v) NAA is a method based upon processes that take place in the nuclei of the elements. The chemical and physical state of the elements does not influence the final result.

(vi) The absence of sample pre-treatment steps but above all the physical nature of the technique, by which each individual step can be described in a parametric form, leads to a basis for accurate results independently of the concentration over a large dynamic range.

(vii) The absence of any sample pre-treatment steps (with the possible risk to introduce contaminants) makes the technique very suitable for measurement of low concentrations in e.g. ultra-pure materials and for the handling of very small quantities of materials such as cosmic dust and air particulates.

(viii) Of the major components present in many samples, the elements C, H, N and O are almost insensitive to neutron activation whilst from other major elements only short half-life radionuclides are formed. As such, they are virtually absent making the sample by the (long) lived radionuclides transparent for its trace elements.

The following disadvantages can be noted, particularly when compared to other analytical techniques:

(i) Several elements cannot be determined or at least not at a low level. For instance activation of lead (Pb) results only at milligram quantities to measurable activities for applications related to environmental research such a detection limit is inadequate.

(ii) INAA is not suitable for sensitive analyzing water samples without extensive pre-treatment.

(iii) The method, like other methods of elemental analysis, only yields information on total element concentrations, not specified to their chemical and/or physical state.

(iv) For elements involving radionuclides with long half-lives, the turn-around time of an analysis may be in the order of 2 - 4 weeks.

(v) INAA is not available as a push-button apparatus with a complete software package to be operated 'on-the-spot' at just any analytical laboratory.

(vi) The INAA laboratory has to meet the legal requirements for radiological safety. This may imply high investment costs when a laboratory has to be adapted. A radiological health officer may be required and provisions have to exist for storage and disposal of radioactive waste. Employees have to be trained in the radiological safety and practical aspects of handling radioactivity.

(vii) The merge of a physical method and chemical analysis requires simultaneous expertise from both disciplines for an effective operation. Not all NAA laboratories have such an interdisciplinary composition.

(viii) The need for availability of, or access to a nuclear research reactor.

The fundamentals of (I)NAA are described in detail in e.g. references [13], [14] and [15].

2.9 REFERENCES

[1] O.T. Høgdahl, 'Neutron Absorption in Pile Neutron Activation Analysis', Michigan Memorial Phoenix Project, Univ. of Michigan, Ann Arbor, USA, Report MMPP-226-1 (1962)

[2] F. Girardi, G. Guzzi, J. Pauly, 'Reactor Neutron Activation Analysis by the Single Comparator Method', Anal.Chem 37 (1965) 1085 - 1092

[3] M. de Bruin, P.J.M. Korthoven, 'Computer Oriented System for Non-destructive Neutron Activation Analysis', Anal.Chem. 44 (1972) 2382 - 2385

[4] A. Simonits, F. de Corte, J. Hoste, 'Single Comparator Methods in Reactor Neutron Activation Analysis', J.Radioanal.Chem. 24 (1975) 31 - 46

[5] P. Bode, M. Blaauw, I. Obrusník, 'Variation of Neutron Flux and related Parameters in an Irradiation Container, in Use with k_0-Based Neutron Activation Analysis', J.Radioanal.Nucl.Chem. 157 (1992) 301 - 312

[6] M. Blaauw, 'Comparison of the Catalogues of the k_0- and the k_{Zn} Single Comparator methods for Standardization in INAA', J.Radioanal.Nucl.Chem. 191 (1995) 387 - 401

[7] L.A. Currie, 'Limits for Qualitative Detection and Quantitative Determination - Application to Radiochemistry', Anal.Chem. 40 (1968) 586 - 593

[8] 'Detection in Analytical Chemistry: Importance, Theory and Practice' (L.A.Currie, ed.), ACS Symposium Series, American Chemical Society, Washington DC (1988)

[9] M. Blaauw, 'The Holistic Analysis of Gamma-Ray Spectra in Instrumental Neutron Activation Analysis', Thesis, Delft University of Technology (1993)

[10] J.A. Cooper, 'Factors Determining the Ultimate Detection Sensitivity of Ge(Li) Gamma-Ray Spectrometers', Nucl.Instr.Meth. 82 (1970) 273 - 277

[11] 'International Vocabulary for Basic and General Terms in Metrology', ISO (1993)

[12] ISO Guide to the Expression of Uncertainty in Measurement (1995)

[13] D. de Soete, R. Gijbels, J. Hoste, 'Neutron Activation Analysis', John Wiley, New York (1972)

[14] S.J. Parry, 'Activation Spectrometry in Chemical Analysis', John Wiley and Sons, New York (1991)

[15] W.D. Ehmann, D. Vance, 'Radiochemistry and Nuclear Methods of Analysis', John Wiley and Sons, New York (1991)

2.10 LIST OF SYMBOLS

A	peak area
a	as subscript denoting element of interest in sample
C	$(1 - e^{-\lambda m})$
C_i	concentration of element i in sample
$C_{ref,i}$	concentration of element i in reference material

c	as subscript denoting element of interest in comparator
D	$e^{-\lambda td}$
D_{tir}	Disintegration rate (Bq) at the end of the irradtion time t_{ir}
d	as subscript denoting decay
E_γ	gamma-ray energy, keV
E_{Cd}	neutron energy at the cadmium cut-off point, 0.55 eV
E_{max}	maximum energy of epithermal neutrons, eV
E_n	neutron energy, eV
F	A/w
f	Φ_{th}/Φ_{epi}
I_0	resonance integral, m^2
$I_0(\alpha)$	resonance integral, m^2, taking into account the not perfect inverse proportionality of Φ_{epi} to the neutron energy
ir	as subscript denoting irradiation
k	Girardi's proportionality factor for standardization in NAA
k_{IRI}	IRI's proportionality factor for standardization in NAA
k_0	proportionality factor for the k_0-method of standardization in NAA
M	atomic mass, $g.mol^{-1}$
m	as subscript denoting measurement
N	number of radioactive nuclei produced
N_{Av}	Avogadro's number, mol^{-1}
N_0	number of target nuclei
n	neutron density, m^{-3}
$n(v)dv$	neutron density, m^{-3}, of neutrons with velocities between v and $v+dv$, considered to be constant in time
$Q_0(\alpha)$	$I_0(\alpha)/\sigma_0$
R	reaction rate per nucleus capturing a neutron, s^{-1}
S	$(1 - e^{-\lambda ir})$
t	time, s
$t_{1/2}$	half-life, s
v	neutron velocity $m.s^{-1}$
v_0	most probable neutron velocity at 20 °C: 2200 ms^{-1}
v_{Cd}	neutron velocity, $m.s^{-1}$ at the cadmium cut-off point, E_{Cd} = 0.55 eV
w	mass of the irradiated element, g
z	standardized or weighted difference between experimental observed concentrations in reference material and certificate data of reference material
α	epithermal flux distribution parameter
γ	gamma-ray abundance
ε	photopeak efficiency
λ	decay constant, s^{-1}
$\sigma(v)$	neutron cross section, m^2, for neutrons with velocity v
σ_0	thermal neutron activation cross section, m^2, at 0.025 eV
σ_{eff}	$\sigma_0(1 + Q_0(\alpha)/f)$
σ_i	standard deviation of experimentally obtained concentration data in reference material
$\sigma_{ref,i}$	listed standard deviation of concentrations in certificate of reference material, or assumed uncertainty for non-certified values
θ	isotopic abundance

ρ	concentration, $g.g^{-1}$
Φ_{th}	'conventional' thermal neutron flux, $m^{-2}s^{-1}$, for energies up to the Cd cut-off energy of 0.55 eV
Φ_{epi}	'conventional' epithermal neutron flux, $m^{-2}s^{-1}$, equivalent to the epithermal neutron flux density per unit energy interval at 1 eV

CHAPTER 3 BIG SAMPLES NEUTRON IRRADIATION SYSTEM

The subjects dealt with in this chapter, have been described also in the following papers:

* P. Bode, 'Analysis of Very Large Samples -up to 5 kg- after Activation with Reactor Neutrons: Aspects of Facility Design and Shielding Considerations',
  Abstract, 1989 International Chemical Congress of Pacific Basin Societies 'Pacifichem', Honolulu, Hawaii, USA, December 17 - 23, 1989
* P. Bode, R.M.W. Overwater, 'Trace Element Determinations in Very Large Samples: a New Challenge for Neutron Activation Analysis',
  J.Radioanal.Nucl.Chem. 167 (1993) 169 - 176
* J.J.M. de Goeij, P. Bode 'Neutron Activation Analysis: Trends in Developments and Applications',
  Soc.Photo-Optical Istrument.Engin. 2339 (1995) 436 - 447
* R.M.W. Overwater, P. Bode, J.J.M. de Goeij, J.E. Hoogenboom, 'Feasibility of Elemental Analysis of Kilogram-size Samples by Instrumental Neutron Activation Analysis,
  Anal.Chem. 68 (1996) 341 - 348
* P. Bode, 'Trace Element Determination in Very Large Samples - with Sizes up to 50 kg- by Neutron Activation Analysis: New Opportunities for Inhomogeneous Materials',
  Proceed. 3rd Eurolab Symposium, Berlin, June 5 - 7 1996, pp. 267 - 277
* P. Bode, 'Status and Prospects of Neutron Activation Analysis of Kilogram-size Samples',
  Abstract, American Chemical Society Spring Meeting, Symposium: Research and Education in Radioanalytical Chemistry', New Orleans, USA, 24 - 26 March 1996
* P. Bode, R.M.W. Overwater, J.J.M. de Goeij, 'Large Sample Neutron Activation Analysis: Status and Prospects',
  Accept. for publ. J.Radioanal.Nucl.Chem.

3 *BIG SAMPLES NEUTRON IRRADIATION SYSTEM*

3.1 INTRODUCTION TO LARGE SAMPLE NEUTRON ACTIVATION ANALYSIS

3.1.1 Motives for use of large analytical portions

All routine multi-element analysis techniques employ rather small amounts of material varying from microliters and milligrams to a few grams (see *Table 3-1*). For technical and fundamental reasons, larger quantities are not being handled. In AAS and ICP only small portions can be introduced; since in XRF information is derived from the surface layers, the usage of quantities larger than required to prepare the target is meaningless. In INAA the situation is somewhat ambivalent: in many (university) research institutes the size of the analytical portion is kept limited -often not larger than 1 gram- to limit effects of neutron and gamma-ray self-shielding and deviations from the

Table 3-1. Survey of sizes of the samples and analytical portions handled in several multi-element analysis techniques

Analysis technique		Solid material mass used or prepared to analytical portion	Liquid material volume used as analytical portion
Atomic Absorption Spectroscopy (AAS)	Gas-furnace	typically 1 - 2 g dissolved; maximum approximately 10 g	10 - 20 µl
	Flame		1 - 2 ml
Inductively Coupled Plasma Spectroscopy (ICP)		typically 1 - 2 g dissolved; maximum approximately 10 g	approximately 500 µl
X-ray Fluorescence Spectroscopy (XRF)		max. approximately 10 g	
Instrumental Neutron Activation Analysis (INAA)		typically approximately up to 500 mg; in some cases up to 30 g	

point-source geometry in counting. In some commercial service laboratories much larger sample masses are handled -up to 10 - 30 grams- to facilitate automated sample

weighing, to reduce effects of contamination and, because of the proportional shorter irradiation time, to limit reactor costs. In these laboratories a high degree of accuracy is not always the prime objective in the analysis.

The limitation to the size of the analytical portion can face the analyst with problems when the amount of material collected is larger. Which is often the case since e.g. soils, rocks and plant material can easier and more representative be sampled at quantities in the order of hundreds of grams to kilograms than at quantities less than 1 gram. A sample is denoted to be 'representative' when *'it can be expected to exhibit the average properties of the material, environment or population it was taken from'* [1]. Representativeness is a priori preserved when (i) the sampling is performed according to specific certified norms or when (ii) a truly homogeneous material is sampled. Homogeneity is defined as *'the degree to which a property or substance is randomly distributed throughout the material'*[1]. Homogeneity depends on the size of the units under consideration. A mixture of minerals may be inhomogeneous at the molecular or atomic level but homogenous at the particle level. In chemical analysis this unit is obviously correlated with its effect to the execution of the analysis (e.g. differences in solubility) or to its interpretation. Thus, both for practical and sampling considerations often more material is collected and presented for analysis than can be handled.

Irrespective of the analysis technique selected, attention has to be paid to representative sub-sampling to obtain a relevant final analytical portion from the originally collected material. When restricting the discussion to the analysis of solid materials this sub-sampling may imply sample size reduction techniques and other processing such as sieving, crushing, milling or blending. Problems arise when:

(i) Homogenization is impossible, or extremely expensive due to material properties. Examples are electronic circuits on printed boards, household waste, scrap from recycled electronics, automobiles, plastics. A solution to this problem is to sort the material and to perform individual homogenizations and, subsequently, analyses, thereby increasing the total project costs.

(ii) The homogenization step results at contamination of the sample. Often the contamination due to crushing or milling is not controlled on every sample type. When processing large series of samples careful interim cleaning may get the less attention since it is time-consuming and thus expensive.

Testing the degree of homogeneity is a common practice in the preparation of reference materials, but for routine operations such a procedure, requiring the analysis and statistical evaluation of at least 5 test-portions of each sample also would raise the cost of an analysis considerably.

The considerations from the above indicate that for some applications, direct analysis of the voluminous solid sample as it has been collected might have advantages, both analytical and economical.

3.1.2 Means for analyzing large analytical portions

Instrumental neutron activation analysis has all the potentials to analyze, even with adequate accuracy, large samples in the kilogram range [2,3]. Both the incoming radiation for activation (neutrons) and the outgoing radiation to be measured (gamma-rays) have sufficiently high penetrating power to facilitate NAA of samples of kilogram weights. However, differently from small samples, self-shielding by neutron absorption and scattering and neutron self-thermalization may cause substantial changes in the neutron spectrum and in the thermal neutron flux throughout the sample that have to be accounted for.

The gamma-radiation of the activation products deep inside in the sample will be stronger absorbed and scattered before leaving the sample to be measured than the radiation resulting from e.g. the surface of the sample; moreover the absorption and scattering is stronger the lower the energy of the gamma-radiation. This effect is denoted as gamma-ray self-attenuation. In addition, a sample of e.g. 1 kg cannot be considered anymore as a more-or-less point source during counting at normal sample-detector distances of e.g. 10 - 30 cm resulting in a corresponding different response of the detector for the gamma-radiation.

Differently from conventional INAA with small samples, analysis of large samples requires correction for neutron self-shielding and gamma-ray self-absorption effects, either via calibration or modelling. For selected cases such as coal and ore analysis, special bulk analysis have been applied in industrial applications and mineral exploration using 14 MeV neutrons and isotopic neutron sources [4, 5, 6]. The analyses are mainly focused at raw material analysis and for product control for one or a few major constituents. These procedures are by their calibration customized for the problems they have been developed for and cannot be translated into a routinely applicable method for the analysis of a large variety of sample types.

The advantage of reactor based INAA in the analysis of large samples lies with the higher available neutron fluxes and activation cross sections, all leading to better sensitivities for trace elements than can be obtained with 14 MeV neutron generators and isotopic neutron sources.

3.1.3 Large sample INAA at IRI

At IRI, in 1989 a project was started aimed at the development of a method for reactor based INAA of very large samples. The development of a method and facilities for large sample INAA has been partly integrated in the Delft University of Technology priority program 'Integrated Water Management' which started in 1989 by grants from the Universities' special research funds. The tools and methods to be developed were

(i) an irradiation facility
(ii) an adapted gamma-ray spectrometer
(iii) methods to correct for neutron- and gamma-ray self-attenuation phenomena. These correction methods have been developed by Overwater [7, 8, 9].

The project has been denoted with the acronym BISNIS (Big Samples Neutron Irradiation System).

3.2 DESIGN CRITERIA FOR LARGE SAMPLE INAA

3.2.1 General criteria

Several design criteria resulted from the research program on development of methods to correct for the neutron- and gamma-ray self-attenuation phenomena. One of the reflections was that a description, prediction, calculation or experimental verification of the neutron self-shielding would greatly be facilitated when any self-thermalization effects might be neglected. Such a condition would require a high ratio of thermal neutrons over non-thermal neutrons in the facility. This design demand has strongly influenced the choice to use the reactor's thermal column to locate the irradiation facility.

Another basic design consideration for the facilities and correction methods for large sample INAA has been the self-imposed obligation that the information needed to correct for the neutron self-shielding and gamma-ray self-absorption effects should be gathered without disturbing the sample by e.g. an invasive mounting of flux monitors. At first, the use of flux monitors at the surface and in the centre of a cylindrical sample may seem a logical approach for determining the average neutron flux by extrapolation. However, such an extrapolation might be a source of errors in case of local inhomogeneities; moreover it would hamper the ease of operation of the method.

For the neutron self-shielding correction, use has been made of the phenomenon of neutron flux depression which occurs outside a large -absorbing- body when placed

in a neutron field. The need for neutron flux monitors outside the sample have determined strongly the design of the irradiation container.

It was assessed that the necessary information on the gamma-ray self-absorption behaviour of the large sample could be obtained by experimental determination of the effective mass attenuation coefficient via a transmission measurement employing an external gamma-ray source.

For both aspects of the analysis (irradiation and measurement) it was considered to be important to rotate the sample during the action, to reduce the effects of small inhomogeneities to the overall inaccuracy. Since a spin-off of the analysis of large samples might be the assessment of inhomogeneities, a design criterion was to monitor the neutron flux depression at different heights around the sample, and to perform gamma-ray spectrometry (transmission measurement and measurement of the induced radioactivity) in a segmented mode.

3.2.2 Criterion for induced radioactivity and required neutron flux

The induced radioactivity in the samples should in principle be of the same order of magnitude as in conventional INAA, independent of the mass and size of the sample. It should particularly be avoided that the induced activity of the large samples would be thus high that radioactive waste disposal problems would occur. Typically, activities of less than 50 kBq of long half-life radionuclides are induced in a 200 mg sample. When upgraded to e.g. 2 kg, such an activity translates to a specific activity of 25 $Bq.g^{-1}$ which is well below the 100 $Bq.g^{-1}$ norm set for material to be considered as radioactive waste. At a given irradiation time, the increase in sample mass of 200 mg to 2 kg by a factor of 10^4 can then be translated into a proportionally lower neutron flux to induce the same radioactivity. However, a higher neutron flux might be preferred to induce a higher radioactivity, and to compensate for neutron self-attenuation, gamma-ray self-absorption, and larger sample-to-detector distances as with conventional INAA. Thus, the design criterion for the required thermal neutron flux in the new facility was 0.5 - 5 * 10^{13} $m^{-2}s^{-1}$ instead of 5 * 10^{16} $m^{-2}s^{-1}$, the typical flux in irradiation facilities employed in routine small sample INAA.

3.2.3 Criterion for sample size

Anticipating on possible applications, the typical sizes of drill cores in use in e.g. soil mechanics, geological research and in mining industry have served as a model for the

maximum sample dimensions: a diameter of 15 cm and a length of 100 cm. Such samples might involve sample weights up to 50 kg.

3.3 IRRADIATION FACILITY FOR LARGE SAMPLES

3.3.1 Location of the irradiation facility

The facility for irradiation of large samples is located in the reactor's thermal column. This is a 'J' shaped void space inside the concrete wall at the east side of the reactor core, schematically shown in *Figure 3-1.*

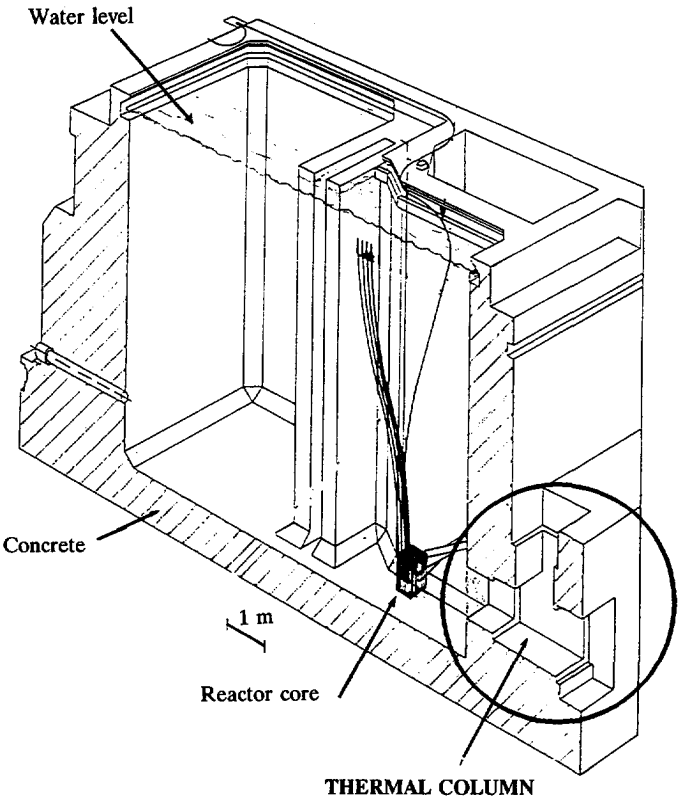


Figure 3-1. *Schematical vertical cut-away view of the reactor pool of the Hoger Onderwijs Reactor, showing the location of the thermal column*

The thermal column has been selected since it combines a few characteristic features which are beneficial for a facility for large sample activation:

(i) The thermal column was not being used for experiments nor other experiments were foreseen.

(ii) There is ample space available for installation of a dedicated facility. The space is easy accessible by two access holes at the top, at the first platform level, and via a vertical door on the floor level.

(iii) An irradiation facility located in the thermal column does not directly affect the regular operation performance of the reactor. In the design-, development- and realization stage less severe safety aspects have to be taken into account when compared to facilities installed in the reactorpool in the vicinity of the fuel elements. This enables more flexibility with respect to fulfilment of the design-demands as set by the potential users, the choice of materials and the ease of stationing the final facility.

(iv) It is not necessary to occupy or sacrifice one or more of the reactor's experimental positions with a high neutron flux.

(v) The neutron spectrum in the thermal column can be conditioned in two ways:

- the total number of neutrons entering the thermal column can be varied using the tanks in the reactor-pool which connect the thermal column to the reactor core. These tanks (widths 3 cm, 6.5 cm and 55 cm) can be filled independently of each other with water or nitrogen gas, in the latter case increasing the neutron flux in the thermal column. In 1978 it was experimentally verified that emptying the tanks had an effect of 0.1 % to the reactor core's reactivity [10].
- the neutron spectrum in the thermal column can be modified. The entrance of the thermal column at the pool side is an aluminium window of 40 mm thickness. At the pool side, this window is cladded by the pool's stainless-steel lining. To prevent exorbitant activation of the lining when the nitrogen tanks are emptied, a cadmium sheet (thickness 3 mm) is positioned between the nitrogen tanks and the lining. The sheet removes all thermal neutrons from the impinging flux. By loading the void space in the thermal column with (nuclear grade) graphite, the remaining non-thermal neutrons can be thermalized.

Neutron flux calculations[1] indicated (*Table 3-2* from [12]) that at approximately 1.4 m behind the entrance window of the thermal column the ratio of the thermal neutron flux (energy group 5) to the flux of non-thermal neutrons (energy groups 1 - 4) is approximately 235. The maximum attainable thermal neutron flux of $1.2 * 10^{14}$ $m^{-2}s^{-1}$ would amply meet the design criterion as described in *paragraph 3.2.2.* Only approximately 0.4 % of the total number of neutrons would be non-thermal and might eventually all be thermalized inside the sample. The maximum contribution of 0.4 % to the uncertainty in the final concentrations by neglection of this effect was considered to be acceptable.

Table 3-2. Calculated neutron fluxes in five energy groups at the thermal column axis at a distance of 140 cm behind the thermal column's entrance window

Neutron energy groups Group	Neutron flux per eV, $m^{-2}s^{-1}$	Neutron flux per lethargy, Φ_u, $m^{-2}s^{-1}$
1 : 14.9 - 0.82 MeV	$4.15 * 10^{9}$	
2 : 820.0 - 5.53 keV	$1.24 * 10^{11}$	$2.48 * 10^{10}$
3 : 5530 - 1.86 eV	$3.01 * 10^{11}$	$3.76 * 10^{10}$
4 : 1.86 - 0.65 eV	$9.83 * 10^{10}$	$9.35 * 10^{10}$
5 : 0.65 - 10^{-5} eV	$1.24 * 10^{14}$	$1.0 * 10^{13}$

It should be noted that the ratio of the group 5 ('thermal' neutrons) to the groups 2-4 ('non-thermal' neutrons) is not the same as the ratio *f* of the thermal neutron flux, Φ_{th}, over the epithermal neutron flux Φ_{epi}, used

1 *For the neutron transport calculations the diffusion code CITATION [11] with five broad energy groups was used. In the calculations the core had to be represented by a simplified array of thirty fuel elements, creating a box with dimensions (length * width * height) 38.5 * 48.6 * 60 cm. This model has been further simplified to a usable configuration related to the two-dimensional r-Z calculation - as applied in CITATION-code : the core is finally represented as a cylinder with a radius of 31.5 cm and a height (Z-axis) of 37 cm. The total neutron and prompt gamma production has been normalized to the reactor power level of 2 MW. With the CITATION code a total neutron production of $1.5 * 10^{17}$ s^{-1} was found. This value agrees well with the value of $1.51 * 10^{17}$ s^{-1} which can be derived on basis of the energy, released in one ^{235}U fission (200 MeV) and the average number of 2.41 prompt neutrons per fission.*

in *Chapter 2*. By definition, the epithermal neutron flux refers to the flux density of neutrons, per unit of energy interval, at 1 eV. When the calculated neutron fluxes from groups 2-4, Φ_i (i = 2,3,4), (*column 2* of *Table 3-2*) are converted to neutron fluxes per lethargy, $\Phi_{i,u}$, (see *column 3* of *Table 3-2*) it can be seen that the calculated neutron fluxes Φ_i do not show a $1/E_n$ dependency, since otherwise $\Phi_{i,u}$ should have been constant for these energy groups. Still, to obtain an indication for the ratio *f*, a $1/E_n$ dependency is assumed; the sum of the group 2 - 4 neutrons can now be expressed as

$$\sum_{i=1}^{4} \phi_i = \phi_{epi} \int_{0.55\ eV}^{0.82\ MeV} \frac{1}{E}\, dE \qquad 3\text{-}1$$

from which it follows that

$$\sum_{i=1}^{4} \Phi_i \approx 14\ \Phi_{epi} \qquad 3\text{-}2$$

The NAA-conventional ratio of thermal neutron flux over epithermal neutron flux thus would be approximately 3300. In *paragraph 3.4* the observed neutron flux is further discussed.

(vi) The walls of the thermal column are cladded with Boral (boron loaded -18% by weight- aluminium) which shields against thermal neutrons; the relatively low intensity of non-thermal neutrons requires corresponding less elaborate provisions for shielding of this fraction.

A disadvantage of the thermal column for a large sample irradiation facility is the rigidity of the concept. Once installed there is limited possibility to change the location of the facility when needing a higher thermal neutron flux.

3.3.2 Design of the irradiation facility

Inserting a voluminous sample into the thermal column requires adequate shielding against the radiation in the thermal column, viz. neutrons, reactor-gamma-rays and gamma-rays originating from absorption of neutrons in the construction materials in the thermal column. In reactor pool facilities often use is made of 'S'-shaped tubes in which the 'S' acts as a labyrinth within the surrounding water as shielding. An 'S' shaped tube for the thermal column facility was not feasible for the large samples since the curvature would be too large to be shielded within the space of the thermal column.

An alternative approach derived from fuel-element exchanging devices has been abandoned after weighing the complexity of its design and construction against the final design in which water is used as penetrable shielding against neutron and gamma-radiation.

The irradiation facility consists of (*Figure 3-2*) an interconnected aluminium tube system, connected to a stainless steel water tank on top of the plug in the horizontal access hole. The tube, closest to the reactor core, is used as irradiation channel and the other tube serves for water displacement. Irradiation containers, placed in the irradiation position are surrounded by only a 3 mm of water.

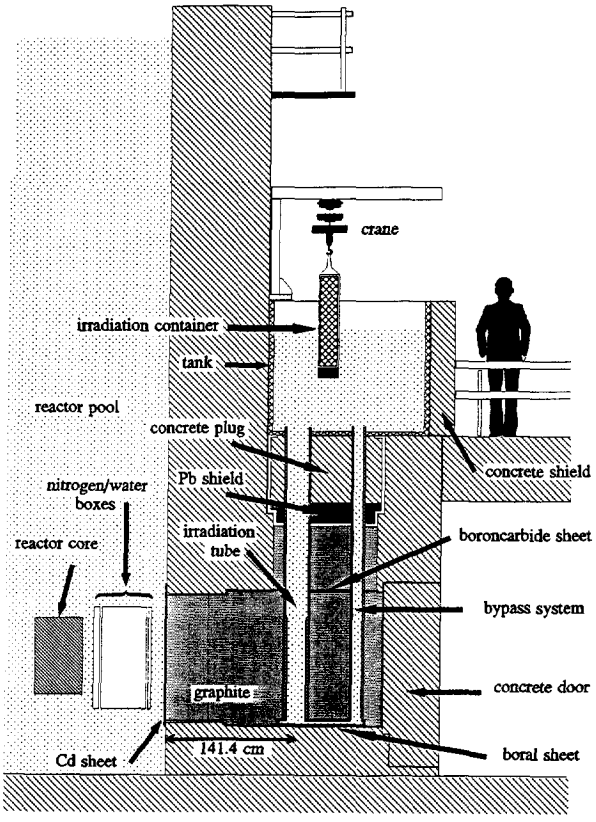


Figure 3-2. *Schematic vertical cross section of the thermal column with the large sample irradiation facility*

3.3.3 Constructive aspects

The tube system has been made from aluminium alloys. The irradiation tube has an inner diameter of 220 mm at the connection with the tank, and the diameter reduces to 206 mm at the irradiation position. The length of the tubes is approximately 3.25 m. The tube system rests on the floor of the thermal column. It is connected to the water tank by a gasket sealing which allows for thermal expansions.

Around the irradiation tube and by-pass tube aluminium plates have been mounted resulting in square tubes to facilitate the stacking of graphite. The remaining space between the circular tubes and the aluminium plates has been filled with purified carbon granules of a grain size < 1 mm.

The water tank has a height of 1.50 m and rests on a plug consisting of 'heavy' concrete (a mixture of Portland cement and barite, with a final density of approximately 3.2 $g.cm^{-3}$) in the horizontal access hole. The tank is surrounded by 30 cm thick, 125 cm high segmented shielding of the same 'heavy' concrete to shield against activated samples stored in the tank.

The remaining space in the thermal column has been filled with nuclear grade graphite blocks (Union Carbide, mostly 40 cm * 10 cm * 10 cm.). In the vertical shaft, at the 1.40 m level, a layer of aluminium boxes filled boroncarbide powder (total boroncarbide layer thickness 6mm) prevents the production of gamma-radiation due to thermal neutron capture in this vertical part of the column and the facility. Above this layer, the vertical shaft was filled with graphite blocks (for approximately 1.5 m) to thermalize any remaining non-thermal neutrons; moreover, the graphite also contributes to the gamma-ray shielding.

3.3.4 Design of irradiation container

The irradiation container (*Figure 3-3*) has been made of polyethylene. The container allows for rotation of the sample during irradiation whilst the neutron flux monitors do not rotate and remain at fixed positions.

A strip has been mounted on the outside of the container to fit into a slit on the inner side of the lower end of the irradiation tube. Thus reproducible positioning of the container in the irradiation position is accomplished.

The samples are placed in a polyethylene basket leaving for the sample(s) a space of 100 cm in length and 15 cm in diameter. This rotation device is connected at the top to a motor and on the bottom to a ceramic ball bearing. The neutron flux

monitor holder is fixed around this sample holder. The neutron flux monitors are packed in small polyethylene capsules.

In the irradiation position the lid -and inside it the metal parts- is located above the level of the boral and boroncarbide-layers. The thermal neutron flux is approximately a factor 5 lower as in the sample position.

When samples have to be counted shortly after activation, the ^{41}Ar ($t_{1/2}$ = 1.85 h, maximum activity to be produced approximately 750 kBq) produced in the air inside the container may be a radiation safety hazard. For such a use, the container can be flushed with nitrogen gas prior to activation.

The bottom of the container contains a lead (99.99 %) weight. Important impurities are Sb (4 $mg.kg^{-1}$), Zn (5 $mg.kg^{-1}$), Cu (4 $mg.kg^{-1}$), Br (1.5 $mg.kg^{-1}$) and K (15 $mg.kg^{-1}$), resulting in a saturation activity of approximately 3 MBq after 5000 h exposure. The bottom part can be removed and is re-usable.

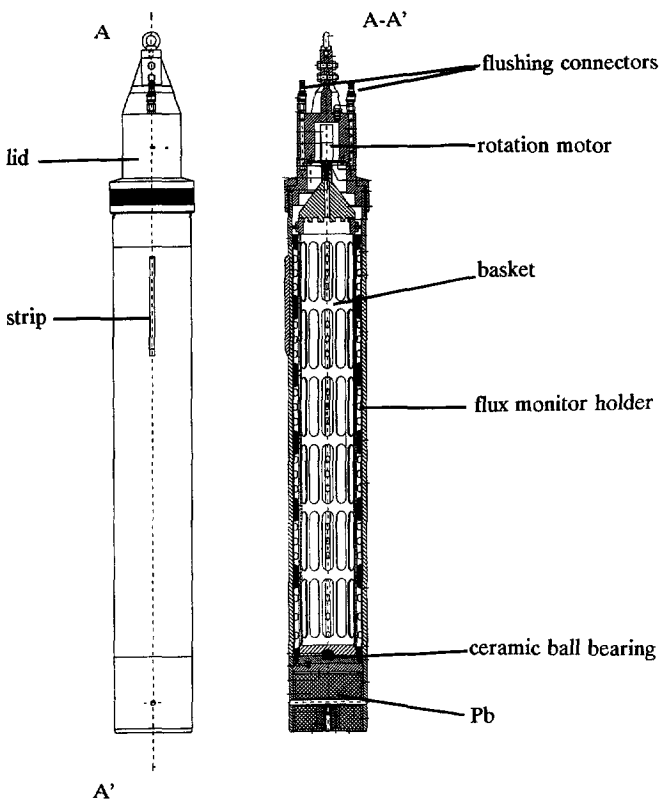


Figure 3-3. Irradiation container for large samples; exterior and interior by cross-section A-A'

3.4 NEUTRON FLUX AND -GRADIENT

The thermal neutron flux in the facility has been determined via activation of zinc-foils [9]. The zinc-foils have been positioned throughout the irradiation container, thus allowing for information on the neutron flux and -gradient in three directions. In the x-direction, i.e. horizontally directing away from the reactor core, the neutron flux decreases from 3.8 - 2.0 * 10^{12} $m^{-2}s^{-1}$; in the vertical direction the neutron flux gradient has its top in the centre of the thermal column at 3.8 * 10^{12} $m^{-2}s^{-1}$ and decreases to 1.4 * 10^{12} $m^{-2}s^{-1}$ at the bottom and at the top of the container[2]. In the horizontal direction perpendicular to the direction pointing away from the core, the gradient is less than 2 %.

The measured thermal neutron flux is a factor 30 lower than the flux calculated for this situation using the CITATION code [11] (3.8 * 10^{12} $m^{-2}s^{-1}$ vs. 1.2 * 10^{14} $m^{-2}s^{-1}$). The hypothesis for this discrepancy is that, in retrospect, computing codes based on the neutron diffusion theory (such as CITATION) appear not to be applicable in calculations with geometries in which large void spaces occur as with the nitrogen tanks between the core and the thermal column. The programs do not adequately describe the behaviour of the neutron fluxes at the boundaries of these void spaces.

Table 3-3. Calculated and measured neutron fluxes at different fillings of the coupling boxes between reactor and thermal column

Thickness water layer in Nitrogen boxes, cm	Calculated flux $m^{-2}s^{-1}$ [13]	Measured flux $m^{-2}s^{-1}$
0	5.5 * 10^{12}	4.8 * 10^{12}
3	2.1 * 10^{12}	3.0 * 10^{12}
6.5	1.5 * 10^{12}	1.4 * 10^{12}
9.5	6.1 * 10^{11}	9.0 * 10^{11}
66.5	9.2 * 10^{6}	2.4 * 10^{8}

In a separate study the distribution of the neutron flux has been calculated, and partly experimentally verified [13]. The TORT discrete ordinates transport code [14] is expected to be a better approach for such calculations. From the results of these

[2] *These measurements have been carried out with the 3 cm nitrogen box filled with water.*

calculations and using *Equation 3-1* it could be derived, as has been described in *paragraph 3.3.1*, that $\Phi_{th}/\Phi_{epi} > 10^4$ at the irradiation position of the sample. The calculated thermal neutron flux has been experimentally verified via activation of zinc metal foils, and good agreement was found when little or no water is present in the coupling boxes (see *Table 3-3*). The discrepancy when all boxes are filled with water is still subject of research.

The maximum attainable thermal neutron flux of approximately $5 * 10^{12}$ $m^{-2}s^{-1}$ just meets the lower design criterion, and thus is adequate for large sample INAA.

3.5 SAFETY ASPECTS

3.5.1 Shielding and dose rate calculations[3]

The dose rate calculations have extensively been described elsewhere [12, 15] and the approach and the results are therefore only briefly summarized here. Only the shielding against gamma-rays has been subject of study, since the fraction of thermal neutrons are considered to be fully absorbed by the B_4C layer in the vertical shaft and in the boral plates along the walls at the inside of the thermal column. The fraction of non-thermal neutrons is also partly absorbed in this B_4C layer and boral plates, and diminishes by further thermalization and absorption in the vertical stacked graphite layers and in the concrete of the plug and in the walls of the thermal column.

The following calculations have been performed:

(i) Calculation of the neutron density distribution for neutrons of different energy groups, at positions between reactor core and thermal column, and in the thermal column

(ii) Calculation of the contribution of primary gamma-rays (reactor core gamma-rays, both from fission and from decay and activation products) to the dose-rate

(iii) Calculation of the contribution of secondary gamma-rays (prompt gamma-rays from the Cd-sheet after neutron capture) to the dose-rate

(iv) Calculation of the contribution of secondary gamma-rays to the dose rate. Secondary gamma-rays are prompt gamma-rays as a result of neutron capture in

---

[3] *The shielding calculations have been made by V.Havránek, on leave in 1991 from the Nuclear Physics Institute, Czechoslovak Academey of Sciences in Řež, Czechoslovakia (nowadays : Czech Republic)*

materials (aluminium, carbon, water) in the irradiation position of the facility, and in the graphite inside the thermal column.

The scattering of the primary gamma's under 90° has been neglected in the shielding calculations mainly because of the relatively low energy of the scattered gammas. The main source of gamma radiation in vertical direction relates to neutron capture gamma production. The contribution of the capture gamma-rays produced in the water of the by-pass tube has not been calculated since the neutron flux in the by-pass is about one order of magnitude lower, the water quantity is less and the viewing angle to the tank is smaller.

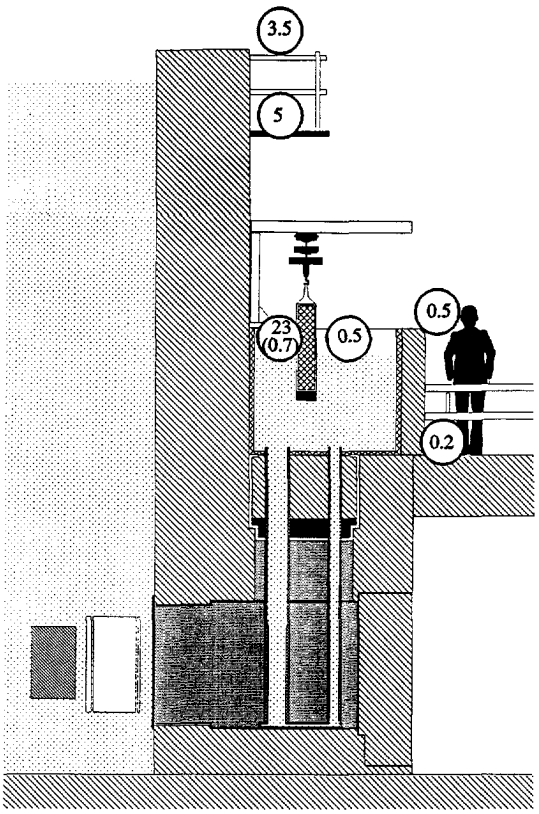


Figure 3-4. *Schematic representation of the irradiation facility (side view) with calculated and, within parentheses, observed contributions to the dose rate in $\mu Sv.h^{-1}$. Calculated contributions assuming a water level of 120 cm; observation made at water level of 125 cm*

This secondary (capture) gamma-ray source terms has been used as input information for the MARMER [16] point-kernel gamma-ray shielding code to estimate the dose rates outside the thermal column on 'man-accessible' places: aside the thermal column on the reactor hall's ground floor level, aside of facilities' water tank on the reactor's first platform, and on the second platform in a position straight above irradiation tube.

In *Figure 3-4* the calculated contributions to the dose rate are given at different positions in the vicinity of the thermal column and water tank in the finally selected shielding configuration. A water level of 120 cm is already adequate to meet the demands with respect to the maximum allowable dose rate at 'man-accessible' locations, so the finally selected level of 125 cm is an extra safety.

The calculations have been carried out prior to realisation of the project; as has been discussed in *paragraph 3.4* the measured thermal neutron flux after realization was a factor approximately 30 lower than calculated. Obviously, this lower neutron flux resulted in a proportional lower contribution to the dose rate. In *Figure 3-4* also the measured contribution to the dose-rates are depicted. The discrepancy between the estimated contribution to the dose rate of 23 $\mu Sv.h^{-1}$ and the observed contribution to the dose rate of 0.7 $\mu Sv.h^{-1}$ reflects the difference in estimated and measured thermal neutron flux in the facility.

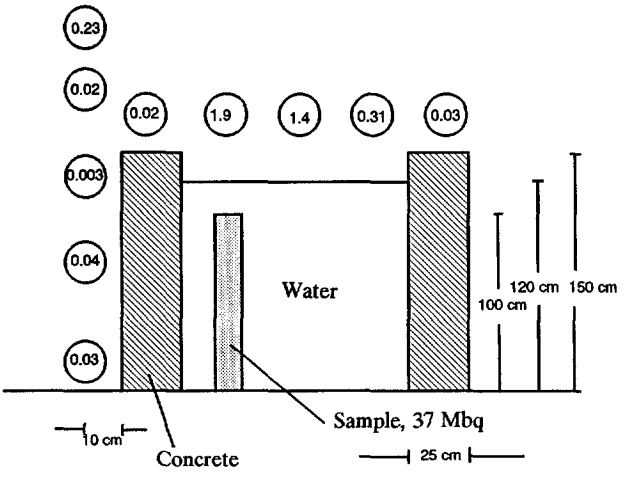


Figure 3-5. *Schematic representation of the water tank of the BISNIS facility, and dose rate estimates (in $\mu Sv.h^{-1}$) due to samples, stored in the water tank*

Also the contribution to the radiation dose by the activated samples stored in the tank has been estimated. In these calculations the sources were modelled to a strength of 37 MBq with an average gamma-ray energy of 1.2 MeV and a size of 100 cm length, and 15 cm diameter. Water was taken as the source matrix. Dose rates for the final shielding configuration are summarized in *Figure 3-5*.

3.5.2 Temperature

In the horizontal section of the thermal column also a thermal couple has been installed which continuously monitors the temperature in the graphite. When the temperature exceeds 55°C the control rods will automatically be forced into the reactor core.

3.5.3 ^{41}Ar Production

Small openings between the graphite blocks have been filled with small pieces of graphite so that the integral remaining space was reduced as much as possible; thus also limiting the ^{41}Ar production rate when using the facility. A first-order estimate has been made of this production rate on basis of the estimated remaining air volume of approximately 0.15 m^3 in the thermal column, based on a conservative estimate of the space between the graphite blocks. Assuming an -over the entire thermal column averaged- thermal neutron flux of approximately $2 * 10^{13}$ $m^{-2}s^{-1}$, a saturation activity of approximately 35 MBq ^{41}Ar is produced, assuming no ventilation of the thermal column.

In practice the thermal column is ventilated continuously. The flow through the thermal column is not precisely known; the ventilator which also serves the beam tubes has a total capacity of 0.034 m^3s^{-1}, and is connected to the main ventilation of the reactor-hall operating at 4.16 m^3s^{-1}. The total release of ^{41}Ar during reactor operation - without the thermal column 'active'- is approximately 1 $kBq.m^{-3}$ corresponding to appr 4 $kBq.s^{-1}$. The production rate of ^{41}Ar in the thermal column is 4 $kBq.s^{-1}$. As such it can be expected that usage of the thermal column facility would lead to a doubling of the ^{41}Ar release from the reactor hall. The expected final figure is below the maximum allowed release of 40 $kBq.m^{-3}$ which is the average release for a period of 1 h. This estimate should be compared with the actual observed increase with approximately 25 - 30 % in the total ^{41}Ar release from the reactor hall during operation of the thermal column facility. The difference with the estimate may be attributed to a combination of

factors such as a less effective ventilation of the thermal column, smaller volume of air inside the thermal column and lower production rate of ^{41}Ar.

^{41}Ar is also produced by activation of the argon, dissolved in the water. Even when assuming equal volumes of water exposed to neutrons, the production rate in the thermal column facility is a factor approximately 10^5 lower than the production rate in the reactor pool. The contribution of ^{41}Ar, diffusing from the facility towards the reactorhall atmosphere can be neglected to the ^{41}Ar diffusion from the water in the reactor pool.

3.5.4 Leak detection and water management

A leak detection system has been mounted under each connection of tube with tank. Upon leakage, water droplets cause a conducting contact between the leak detector and the tube system. The resulting drop in potential difference is being observed, and an alarm status is generated.

The tank is equipped with a water-purification and water-condition and level monitoring system. The water is continuously being purified on a mixed-bed ion exchanger, and the water condition is being guarded by measuring the conductivity. Typical conductivity observed is 7 $\mu S.m^{-1}$; this may be compared to the conductivity of approximately 100 $\mu S.m^{-1}$ of the water in the reactor pool. The water level is monitored by a low-high level float. There is no automatic supply of water; the facility can be emptied with an immersion pump and the water is drained off to the institute's water purification system. Filling takes approximately 1.5 h; emptying approximately 2.5 h.

Except for activation of impurities in the water, the activation of hydrogen and oxygen leads to saturation activities of 0.2 MBq ^{19}O ($t_{1/2}$ = 27 s), 250 Bq ^{16}N ($t_{1/2}$ = 7.1 s) and to a production of 0.6 $Bq.h^{-1}$ ^3H in a volume of 81 l in the irradiation tube, the by-pass tube and the connecting part. In this calculations it is assumed that there is no natural convection in the water. With the irradiation container lowered for irradiations, these figures reduce to 0.04 MBq ^{19}O, 25 Bq ^{16}N and 0.12 $Bq.h^{-1}$ ^3H.

3.6 WASTE ASPECTS

In the discussion in *paragraph 3.2.2* on the design criteria for maximum induced radioactivity the importance of restricting the induced activity to less than 100 Bq.g-1 has been mentioned shortly. The INAA software at IRI allows to calculate the remaining radioactivity after a given decay time. The experience with soil-, sediment-, and rock

material is that the activity after 3 months days decay is mainly due to the radionuclides ^{46}Sc, ^{51}Cr, ^{59}Fe, ^{60}Co and ^{152}Eu, and amounts approximately 1 $kBq.g^{-1}$. In plant material this final specific activity typically is a factor 10 lower. Though the radioactivity induced in large -e.g. 2 kg- samples of comparable composition may be higher (see *paragraph 3.2.2*) to compensate for the larger source-to-detector distance and the self-shielding losses, the specific radioactivity of such samples can expected to be well below the 100 $Bq.g^{-1}$ norm.

Disposal of materials with specific activities exceeding 100 $Bq.g^{-1}$ implies costs, the extent of which depending on the mass, activity and suppressibility of the material. Since 75 kg of solid material is processed as a unit batch, a maximum sample of 50 kg as processed in the large sample facilities would rapidly fill the available capacity of such a batch.

It can be estimated if a problem should be anticipated upon when processing different materials, e.g. composites with macroscopical inhomogeneities (waste or recyclable materials). The long-lived activation products taken into account are ^{110m}Ag ($t_{1/2}$ = 255 d), ^{133}Ba ($t_{1/2}$ = 10.5 y), ^{60}Co ($t_{1/2}$ = 5.3 y), ^{134}Cs ($t_{1/2}$ = 2.1 y) ^{152}Eu ($t_{1/2}$ = 12.4 y), ^{153}Gd ($t_{1/2}$ = 242 d) and ^{65}Zn ($t_{1/2}$ = 245 d). Assuming a sample weight of 2 kg, and an irradiation during 20 h at a thermal neutron flux of 3 * 10^{12} $m^{-2}s^{-1}$, the maximum of 100 $Bq.g^{-1}$ would be surpassed when the concentrations of these elements would exceed approximately 1 % (Ag), 50 % (Ba), 5000 $mg.kg^{-1}$ (Co), 2500 $mg.kg^{-1}$ (Cs), 200 $mg.kg^{-1}$ (Eu), 1.5 % (Gd), 5 % (Zn), respectively. Particularly the maximum concentration for Ag should be considered when e.g. analyzing scrap from electronic components.

3.7 COUNTING FACILITY FOR LARGE SAMPLES

The technical design criteria of the counting facility resulted from an interaction with the research program on methods to correct for self-attenuation phenomena:

(i) The sample should be faced side looking by the detector.

(ii) The facility should allow for displacement of the sample in vertical direction, towards and from the detector and in horizontal direction, parallel to the detector; criteria have been specified for the precisions of these displacements.

(iii) The sample should rotate around its vertical axis during counting.

(iv) Provisions should be included to mount a transmission gamma-ray emitting source of approximately 370 MBq with adequate shielding; the source's aperture

facing the sample and detector should be opened by remote control. Also collimation of the transmission source should be possible.

(v) It should be possible to mount a collimator between sample and detector.

(vi) The gamma-ray spectrometer does not have to be equipped for handling very high count rates, i.e. count rates exceeding 50,000 s^{-1}.

(vii) The detector-cryostat configuration should allow for easy surrounding with lead-shielding.

(viii) The costs of the facility should be within the project budget.

Commercial available radioactive waste barrel scanners meet these criteria but their price could not be accounted for by the available budget. Therefore a counting facility was designed with the concept derived from a waste barrel scanner. The counting facility for large samples consists of a detector-stand, a sample-displacer with turntable and a transmission source stand (see *Figure 3-6*). The entire device has the following features:

(i) Vertical displacement of the sample during counting, eventually simultaneous with rotation of the sample around its vertical symmetry axis. The vertical displacement may be continuous or step-wise, the latter allowing for segmented scans of the sample (assuming the detector has been collimated).

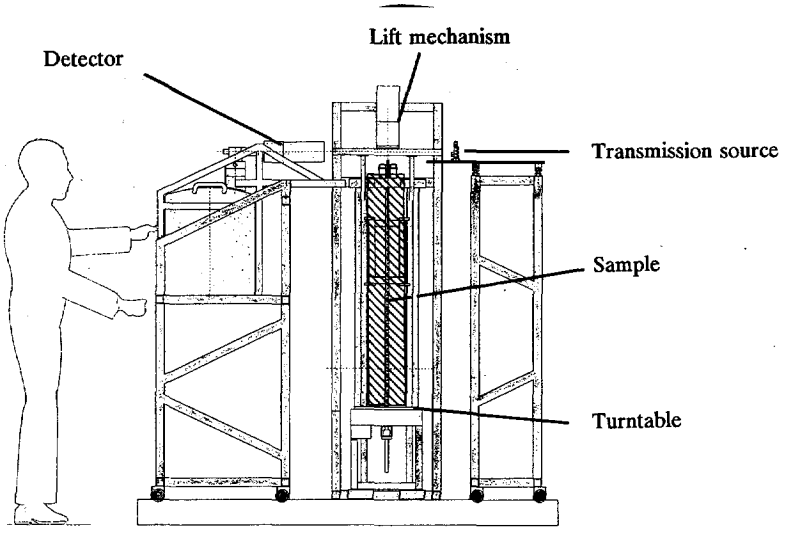


Figure 3-6. Counting facility for very large samples

(ii) Horizontal displacement of the part containing turntable and vertical displacer, in a plane parallel to the detector crystal length symmetry axis. Also this displacement may be continuous or stepwise, and eventually simultaneous with the other displacements.

(iii) Rotation of the sample around its vertical symmetry axis during gamma-ray transmission measurement and during measurement of induced radioactivity. Rotation may be continuous or step-wise, allowing for measurements of the sample under different orientation with respect to the detector. Rotational speed is typically to be chosen 1 rpm.

(iv) (Segmented) gamma-ray transmission measurement for linear absorption coefficient determination. A calibration source can be positioned, by remote control, for a pinhole collimator.

All displacements (rotation, vertical and horizontal) are achieved with precision stepping motors; the coordinates of the sample during each measurement can be derived from the stepping motor orientations. The control unit is connected to local area computer network of the laboratory for INAA.

The gamma-ray spectrometer with Ge detector (relative efficiency 96 %, as compared to the efficiency of a 3" * 3" NaI(Tl) detector, for the 1332 keV photons of ^{60}Co) is connected via an at IRI developed NIM 4k buffered memory interface to the network. The high efficiency of the Ge-detector allows for larger sample-detector distances than in conventional INAA with minor losses in counting efficiency. The detector has been surrounded with 10 cm of lead-shielding; for measurements of an entire sample at a time, the viewing window is left unshielded. A collimator may later be placed in front of the detector's viewing window, dimensions dependent on the required spatial resolution. Also here the large Ge crystal is advantageous.

For practical reasons, the counting facility has been installed in the gamma-ray spectrometry counting room of the laboratory for INAA. Initial installation in the reactor-hall on the first platform was abandoned because of the high background radiation, caused by scattered radiation of ^{41}Ar, present in the reactor hall's atmosphere during operation of the reactor and manipulations and storage of radioactive material at the second platform, straight above the spectrometer. Transfer of the activated sample to the counting facility takes approximately 10 min, which restricts to some extent large sample INAA on basis of radionuclides with half-lives of 3 m or longer.

3.8 ANALYSIS PROCEDURE

Large-sample INAA requires additional steps in the analysis procedure compared to conventional INAA as was elaborated upon in *Chapter 2*. Though actually not belonging to the scope of this chapter, a concise description of the analysis procedure is given for sake of clarity. The entire protocol has the following sequence:

(i) Background correction.
The natural background of the spectrometer is determined, followed by measurement of the spectrum of the sample's natural radioactivity. When processing samples with sizes ca 10^4 larger than in conventional NAA using neutron fluxes ca 10^4 lower than in conventional NAA, the natural activity is very well measurable and has to be corrected for later on in the procedure. When the spectrum of the activated sample is processed, the gamma-ray lines of the natural radioactivity are processed differently from the gamma-rays of the induced radioactivity since only corrections for gamma-ray self-attenuation have to be applied.

(ii) Transmission measurement.
Measurement of the spectrum of a ^{152}Eu calibration source, with and without the sample between source and detector. The results of this measurement are processed to calculate the effective linear attenuation coefficient $\mu(E_\gamma)$ as function of gamma-ray energy.

(iii) Irradiation and measurement of the activated sample.
These steps are carried out according to the traditional INAA protocols as in use for the given type of material and radionuclides to be measured. The facilities also allow for a short activation with irradiation times in the order of several minutes, and a first measurement after about 10 min decay. During the measurement normally the sample rotates around its vertical axis.

(iv) Measurement of the flux monitors.
This step is also according the traditional INAA protocols, however, now more zinc metal foils as flux monitor are involved.

(v) Data processing.
Detailed descriptions of the algorithms for correction of neutron self-attenuation, gamma-ray self-attenuation and voluminous source photopeak efficiency are given elsewhere [7, 8, 9]. Correction of the gamma-ray self-attenuation is done using the determined effective linear attenuation coefficients. Correction for neutron self-attenuation is based on the neutron flux depression just outside the sample as measured with the neutron flux monitors.
The various steps are done in the following sequence:

(v-1) The spectra from the ^{152}Eu transmission measurement are corrected for background contribution using the recorded spectrum of the not-activated sample. From the transmission measurements, the linear attenuation coefficients $\mu(E_\gamma)$ are derived which are used to calculate the gamma-ray correction factor C_γ , incorporating the "voluminous" efficiency of the detector.

(v-2) Together with the information on the neutron flux under reference conditions, the neutron fluxes derived from the zinc metal flux monitors are processed to yield the mean neutron flux Φ_m , and the effective neutron diffusion length L and neutron diffusion coefficient D of the sample.

(v-3) The overall correction factor C_t is calculated from the gamma-ray correction factor C_γ and the values for Φ_m , L and D. This overall correction factor indicate the difference in actual detector response if the sample would have been a massless point-source located in the large sample's centre, without any neutron and gamma attenuation.

(v-4) The gamma-ray spectrum of the not-activated sample is corrected for the spectrometer's background and further processed with C_γ (which includes correction for the voluminous photopeak efficiency), interpreted using a gamma-ray catalogue resulting in the natural radioactivity in $Bq.g^{-1}$.

(v-5) The spectrum of the activated sample is firstly corrected for the background contribution using the spectra of the not-activated sample and the spectrum of the spectrometer's background. Then, the spectrum is processed using the overall correction factor C_t, and the corrected peak-areas can be further interpreted for element assignment and calculation of the concentrations; the latter is done on basis of the k_0-approach.

3.9 ANALYSIS' COSTS

A comparison has been made of the costs of large sample INAA with the costs of conventional INAA. The following assumptions have been made for simplification and to emphasize the main differences between the two approaches:

(i) This comparison has been made for the running costs only, i.e. the costs made when the method is entirely routinely available and when element calibrations have been completed.

(ii) The development costs are not taken into account.

(iii) An analysis is assumed consisting of one irradiation and one measurement, e.g. approximately 5 days after irradiation.

(iv) Starting sample size is 10 kg; the analytical portion depends on the method of analysis.

(v) Sample-size reduction is carried out by methods such as crushing, milling and cryogenic homogenization. The related costs have been derived from brochures of commercial service laboratories in The Netherlands (e.g. [17]).

(vi) Sample types considered are rock (granite), soil, plastic for recycling and scrap from electronics.

(vii) The costs have been estimated for a routine analysis of 1 sample at a time, and when processed in batches of respectively 14 small (200 mg) samples and 5 large (2 kg) samples.

In the calculation of the analysis costs, the following components have been taken into account:

(i) Materials: sample containers, neutron flux monitors, rabbit costs, reference materials and other expenses for trivial utensils. In conventional INAA, a sample is irradiated together with two neutron flux monitors; in large sample NAA 4 layers with 4 flux monitors each are surrounding the sample.

(ii) Use of equipment.

(iii) Labour costs (sample handling, typical preparations, irradiation and measurement, spectrum analysis and calculation of the correction factors). In large sample INAA less time has to be spend to sample preparation but more time is needed for extra measurements, analyses and calculations:
   (a) for the determination of the mass attenuation coefficient by a transmission measurement
   (b) for the determination of the sample's natural radioactivity
   (c) more flux monitors are involved
   (d) for the calculation of the overall correction factors [9] for neutron self-shielding, gamma-ray self-attenuation and voluminous detector efficiency.

(iv) Irradiation costs.
   The irradiation costs have been estimated following the approach suggested by Marth [18]. The reactor costs per hour are estimated on estimated total annual running costs (mainly salaries and fuel consumption) and an average of approximately 3500 operational hours per annum. The costs for a facility using the reactor depend on the size of the facility (neutron consumption) and on its effect to the reactors' reactivity.

The estimates of the individual contributions to the total costs are given in *Table 3-4*. When processing one sample at a time, the estimated costs for analyzing one large sample at a time is about 20 % times higher than for analysis of one small sample, obtained after sample size reduction. When processing more samples simultaneously - which is a more realistic approach- , and comparing with routine conventional INAA in which batches comprise 14 samples, the costs of large sample analysis become comparable to the costs of routine INAA. It should be noted here that a cost analysis is carried out rather than an estimation of the price to be charged to -eventually third party- customers.

Table 3-4. *Overview of typical (rounded off) costs, encountered in conventional INAA and in large sample INAA consisting of one irradiation and one measurement. All prices in Dutch guilders reduction*

	Conventional INAA		Large Sample INAA	
	1 sample	batchwise 14 samples	1 sample	batchwise 5 samples
Sample size reduction	350	350	-	-
Materials	10	10	30	30
Use of equipment and computer	20	20	150	150
Labour costs	70	35	255	190
Preparation	*25*	*25*	*20*	*20*
Transmission experiment and natural background measurement	*-*	*-*	*15*	*15*
Irradiation and measurement	*25*	*5*	*85*	*20*
Analysis and interpretation	*20*	*5*	*90*	*90*
Correction factor calculations	*-*	*-*	*45*	*45*
Reactor costs	20	2	165	35
Total costs per sample	470	417	600	405

As can be seen from *Table 3-4,* large sample INAA still has some higher cost components than conventional INAA mainly because of two main reasons:

(i) in large sample INAA more measurements and spectrum analysis are involved than in conventional INAA:
  (i-1) Instead of 2 flux monitors, now 16 flux monitors have to be analysed.
  (i-2) The measurement of the sample's natural radioactivity.

(i-3) The gamma-ray transmission measurement.
(i-4) Additional calculations are necessary to achieve the correction factor.

(ii) Since there is no sample changer (yet) available for large sample INAA, less samples can be processed as in conventional INAA, and the contribution of the equipment to the total costs is much higher too.

However, in this comparison it should also be taken into account that large sample INAA results at information additional to conventional INAA, viz. on the natural and anthropogenic radioactivity. If this information should have been assessed via the small samples too by a measurement during e.g. 16 hours ('overnight' measurement), the total analysis costs of the small sample would increase to fl. 590 respectively fl. 515.

In this comparison it has also been assumed that in conventional INAA the final analytical portion represents the bulk material and no tests are necessary to verify the homogeneity. When for control of representativity duplicates have to be analysed, the difference in costs between small sample INAA and large sample INAA vanishes; taking also into account the extra information on natural and anthropogenic radioactivity, large sample INAA becomes more cost effective than conventional INAA.

In the present situation the absence of sample size reduction in large sample INAA compensates for the higher costs of instrumentation, absence of automation and more steps in the analytical procedure. It should be noted that in this comparison extensive, and thus relatively expensive sample size reduction procedures have been taken into account, but it reflects the type of analytical questions large sample INAA has been intended for.

3.10 APPLICATIONS AND OUTLOOK

As described in the introduction of this chapter, large sample INAA offers the possibility to analyze materials of which the sample size reduction step, sub-sampling and/or preparation of the analytical portion raise difficulties. In addition to information on the total element concentrations, information is obtained on the natural and anthropogenic radioactivity whilst the segmented scan option may give information on the longitudinal distribution of the concentrations. In a later stage, research for more precise localization of inhomogeneities can be forecasted.

Large sample INAA is also an attractive alternative for the analysis of very pure materials since the pre-analysis procedures are superfluous and the ratio of the sample mass to the mass of the sample-vials is increased.

Since the neutron and gamma-ray doses in the irradiation position are a factor of 10^4 lower than in the irradiation facilities for conventional INAA, the radiolysis of water can be neglected and pressure build-up is not a matter of concern. This makes possible the direct analysis of materials which contain water and in which the drying raises difficulties with respect to volatile components to be determined, like mercury in soil.

Large sample analysis can support research projects in which the representativity of the sampling is subject of study. As an example, Markert [19] experimentally verified that difficulties with taking a representative sub-sample in plant analysis may lead to errors almost as large as 1000 %. The analysis of large samples, in combination with conventional -small sample- INAA allows for experimental verification of the theoretical considerations of sampling and sampling constants [1].

The BISNIS facilities can be used -with some restrictions- for trace element determinations by measurement of the short-lived radionuclides like ^{28}Al, ^{27}Mg, ^{52}V, ^{51}Ti. Measurements can be started approximately 10 minutes after completion of the irradiation. Conventional INAA using the fast rabbit systems has shown that such a decay time still allows for the measurement of short-lived nuclides like ^{28}Al, ^{27}Mg, ^{51}Ti, ^{52}V, ^{38}Cl, ^{56}Mn, and ^{49}Ca in sediments, rocks and waste.

Large sample INAA via short half-life radionuclides sets restrictions to segmented scans. The individual countings may then have to be very short -with consequences for the statistics- to make possible observation of all radionuclides in each scan.

The costs of large sample INAA will reduce when automated sample changing can be implemented and the use of the spectrometer can be brought closer to its capacity.

The method of large sample INAA has been validated by analyzing different 1 - 2 kg samples and comparing the results with those obtained from conventional small sample INAA of the same materials [9, 20]. This approach may also be applied for the method of quality control to be implemented. Since no use can be made of (certified) reference materials, an in-house control material has to be selected, which can be tested for its suitability (homogeneity, stability) and characterized in trace element concentrations using conventional INAA. A candidate control material may be coal fly-ash, which can be obtained at large batches and which is known to be suitable for such purpose. Since conventional INAA has been standardized on traceable standards, and validated with certified reference materials, a chain of custody is maintained. Obviously, simultaneous processing of such a control material (and a blank) would indicate systematic errors like wrongly entered data (e.g. weights, irradiation date and time), contaminations and errors in the determination of the correction factors. The incentive

of internal quality control is to ensure that the data produced are fit for their intended purpose, which means that the accuracy achieved is compared with the level of accuracy required. Accuracy is a qualitative concept to describe how a measured value compares to the 'true' value of the measurand. In the quality control sample such an estimate for the true value can be obtained since the material may be considered as close to 'ideal for the purpose'. There is too little experience with the analysis of real large samples, particularly with respect to the consequences of local inhomogeneities, to assume that the level of accuracy indicated by the analysis of the control sample also represent the closeness of agreement of the results of such a sample to the 'true' concentrations.

3.11 REFERENCES

[1] B. Kratochvil, J.K. Taylor, 'Sampling for Chemical Analysis', Anal.Chem. 54 (1981) 924A - 938A

[2] M. de Bruin, 'Present and Future Position of Instrumental Neutron Activation Analysis', Chemia Analityczna 35 (1990) 99 - 107

[3] M. De Bruin, 'Present and future position of Neutron Activation Analysis', J.Radioanal.Nucl.Chem. 160 (1992) 31 - 40

[4] T.C. Martin, J.D. Hall, I.L. Morgan, 'An On-line Nuclear Analysis System', in: Radioisotope Instruments in Industry and Geophysics, IAEA proceedings series volume I, Vienna, 1966, 411-424

[5] M. Borsaru, R.J. Holmes, P.J. Mathew, 'Bulk Analysis using Nuclear Techniques', Int.J.Appl.Radiat.Isotop. 34 (1983) 397 - 405

[6] D.J.R. Evans, T.I. Herage, 'Neutron Activation Analysis of Intact Drill Core', in: 'Activation Analysis in Geochemistry and Cosmochemistry', (A.O.Brunfelt, E.Steinnes, eds), Universitetsforlaget, Oslo, 1971 129 - 134

[7] R.M.W. Overwater, P. Bode, J.J.M. de Goeij, 'Gamma-ray Spectroscopy of Voluminous Sources: Corrections for Source Geometry and Self-Attenuation', Nucl. Instr. Meth. A324 (1993) 209 - 218

[8] R.M.W. Overwater, J.E. Hoogenboom, 'Accounting for the Thermal Neutron Flux depression in Voluminous Samples for Instrumental Neutron Activation Analysis' Nucl.Sci Engineering 117 (1994) 141 - 157

[9] R.M.W. Overwater, 'The Physics of Big Sample Instrumental Neutron Activation Analysis', Thesis, Delft University of Technology (1994)

[10] Safety report on the Hoger Onderwijs Reactor (in Dutch), IRI internal report no. 130-78-01 (1978), p.4/21

[11] T.B. Fowler, D.R. Vondy, G.W. Cunningham, 'Nuclear Reactor Core Analysis Code: CITATION', ORNL-TM-2496, Revision 2 (July 1971)

[12] V. Havranek, J.E. Hoogenboom, J.L. Kloosterman, P. Bode, 'Shielding Calculations for BISNIS', IRI internal report RC-133-91-001 (1991)

[13] A.J.J. Bos, J.E. Hoogenboom, "Calculations and Measurements of Neutron Fields in a Facility for Big Sample Neutron Activation Analysis at the Research Reactor at Delft", Proc. 1996 Radiation Protection & Shielding Topical Meeting 'Advances and applications in radiation protection and shielding', No.Falmouth, Mass., USA, April 21-25, 1996

[14] W.A. Rhoades, R.L. Childs, 'TORT A THree-Dimensional Discrete Ordinates Neutron/Photon Transport Code',
Nucl. Sci. Eng. 107 (1991) 397 - 398

[15] V. Havranek, P. Bode, 'Shielding Calculations for Bisnis Tank and Samples',
IRI internal report RC-133-91-002 (1991)

[16] J.L. Kloosterman, 'MARMER, a flexible Point-Kernel Shielding Code User Manual,
IRI internal report IRI-131-89-03/2 (1989)

[17] Price list 1994 Tauw Infra consult, Deventer, The Netherlands

[18] W. Marth, 'Bestrahlungstechnik an Forschungsreaktoren', Thiemig Taschenbücher -(Band 13) Karl Thiemig Verlag, München (1969)

[19] B. Markert, 'Instrumental Analysis of Plants', in: 'Plants as Biomonitors', (B.Markert, ed.), VCH, Weinheim (1993)

[20] R.M.W. Overwater, P. Bode, J.J.M. de Goeij, J.E. Hoogenboom, 'Feasibility of Elemental Analysis of Kilogram-Size Samples by Instrumental Neutron Activation Analysis',
Anal.Chem. 68 (1996) 341 - 348

3.12 LIST OF SYMBOLS

C_γ	correction factor for combined effect of gamma-ray self-attenuation and detector efficiency for voluminous sources
C_T	overall correction factor
D	neutron diffusion coefficient, m
E_γ	gamma-ray energy, keV
f	Φ_{th}/Φ_{epi}
k_0	standardization factor in the k_0-method
L	neutron diffusion length, m
$t_{1/2}$	half-life, s
u	subscript to denote lethargy
Φ_m	mean neutron flux, $m^{-2}s^{-1}$
Φ_{th}	thermal neutron flux, $m^{-2}s^{-1}$
Φ_{epi}	epithermal neutron flux at 1 eV, $m^{-2}s^{-1}$
$\mu(E_\gamma)$	linear attenuation coefficient, m^{-1}

CHAPTER 4 CARBONFIBER AUTONOMOUS FACILITY FOR IRRADIATION AND ANALYSIS

The subjects dealt with in this chapter, have been described also in the following papers:

* P. Bode, M. de Bruin, 'The Use of Carbon Fiber for the Irradiation Position of a Fast Rabbit System',
  J.Radioanal.Nucl.Chem. 112 (1987) 375 - 381
* P. Bode, P.J.M. Korthoven, M. de Bruin, 'Microprocessor Controlled Facility for INAA using Short Half-life Nuclides',
  J.Radioanal.Nucl.Chem. 113 (1987) 371 - 378
* P. Bode, M. de Bruin, 'An Automated System for Activation Analysis with Short Half-life Radionuclides using a Carbonfiber Irradiation Facility',
  J.Radioanal.Nucl.Chem. 123 (1988) 365 - 375

4 *CARBONFIBER AUTONOMOUS FACILITY FOR IRRADIATION AND ANALYSIS*[1]

4.1 SHORT HALF-LIFE RADIONUCLIDES IN INAA

4.1.1 Introduction

There is no formal convention for the classification of radionuclides on basis of the length of their half-lives. To serve as a guide, radionuclides with half-lives varying from approximately 1 second to approximately 2 hour are, in INAA, considered to be the 'short half-life' radionuclides (radionuclides with half-lifes shorter than 1 second are sometimes classified as 'ultra shorts'). The group of radionuclides with half-lives up to approximately 2 days are often denoted with the 'intermediairs', whereas radionuclides with longer half-lives are all considered to be the 'long-lived'.

Short half-life radionuclides are of importance for INAA since:

(i) For certain elements, such as Li, F, Al, Mg, Cl, Ti, V, Nb, Tc, Rh, Pd, I, Pb, they are the only usable activation products.

(ii) For certain elements turn-around time can be short since the time needed for the individual steps in the analysis (irradiation, decay, counting) is in the order of seconds and minutes rather than in hours and days. For the determination of selenium, as an example, on basis of the ^{77m}Se nuclide ($t_{1/2}$ = 17.5 s) approximately 1 minute is needed (e.g. t_{ir} = 17 s, t_d = 17 s, t_m = 17 s) whereas a determination on basis of the ^{75}Se nuclide ($t_{1/2}$ = 120 d) requires a turnaround time of a few days up to a few weeks (e.g. t_{ir} = 1 - 4 h, t_d = 5 - 30 d, t_m = 1 h). The halt-time between successive samples can be kept short by overlap of e.g. irradiation and decay time with counting time. Thus, the number of samples 'waiting' to be measured can be kept short and automation is facilitated.

(iii) For certain elements and under practical irradiation and counting times, a higher sensitivity can be attained via short half-life radionuclides than via measurement of the long-lived radioactivity. Consider *Equation 2-11* representing the number of radioactive nuclei disintegrating during the measurement time t_m and the values affecting the number of nuclei disintegrating during the measurement:
If both a short-lived radionuclide and a long-lived radionuclide can be produced from neutron irradiation of an element, the ratio of the number of disintegrating

---

1 *Throughout this chapter, the facility will be denoted with the acronym 'CAFIA'.*

$$\Delta N(t_{ir}\ ,\ t_d\ ,\ t_m) = \frac{RN_0}{\lambda}\ (1 - e^{-\lambda t_{ir}})\ e^{-\lambda t_d}\ (1 - e^{-\lambda t_m}) \qquad 4\text{-}1$$

nuclei during measurement is -since $R = \Phi_{th}\sigma_{eff}$ (*Equation 2-9*), and $N_0 = (N_{Av}w\theta)/M$ -

$$f_{S/L} = \frac{\Delta N_{(t_{ir}\ ,\ t_d\ ,\ t_m)S}}{\Delta N_{(t_{ir}\ ,\ t_d\ ,\ t_m)L}} \quad \frac{(\sigma_{eff})_S\ \theta_S}{(\sigma_{eff})_L\ \theta_L}\ \frac{(1 - e^{-\lambda t_{ir}})_S\ (e^{-\lambda t_d})_S\ (1 - e^{-\lambda t_m})_S\ \lambda_L}{(1 - e^{-\lambda t_{ir}})_L\ (e^{-\lambda t_d})_L\ (1 - e^{-\lambda t_m})_L\ \lambda_S} \qquad 4\text{-}2$$

in which the subscripts *S* and *L* denote short-lived and long-lived, respectively.

The relationship in *Equation 4-2* shows that:

(a) $f_{S/L}$ is linearly proportional to the effective cross sections σ_{eff} and isotopic abundances θ of the target nuclide(s).

(b) The relationship between $f_{S/L}$ and the half-lives of the radionuclides is less easy to derive from *Equation 4-2.* However, the λ-containing term in *Equation 4-2* can be somewhat simplified when taking into account practical irradiation and counting times in INAA:

(i) With short-lived radionuclides often the irradiation time is chosen to be equal to the half-life: $(t_{ir})_S = (t_{1/2})_S$ and $(1 - e^{-\lambda ir})_S = 0.5$. This is less easier to fulfil with long-lived radionuclides; in the practice of INAA the irradiation time is limited due to the limited radiation resistance of the plastics used for encapsulation which is typically in the order of maximum 5 hours. Therefore, since $\lambda(t_{ir})_L << 1$, and, as a first approximation $(1 - e^{-\lambda ir})_L \approx (\lambda t_{ir})_L$.

(ii) In a first approximation it is assumed that $(t_d)_S = (t_{1/2})_S$ and $(t_d)_L = (t_{1/2})_L$ which makes $(e^{-\lambda td})_S = (e^{-\lambda td})_L = 0.5$.

(iii)Almost all short-lived radionuclei may be registered during the measurement and $(1 - e^{-\lambda tm})_S \approx 1$. For the long-lived radionuclides, again usually counting times are limited to 4 - 10 hours. Assuming that $(t_m)_L << (t_{1/2})_L$ and thus only a fraction of the produced radionuclei is registered; again, as a first approximation $(1 - e^{-\lambda tm})_L \approx (\lambda t_m)_L$.

With these assumptions and approximations, *Equation 4-2* can be re-written as

$$f_{S/L} = \frac{(\sigma_{eff})_S\ \theta_S}{(\sigma_{eff})_L\ \theta_L}\ \frac{0.5}{\lambda_S \lambda_L (t_{ir})_L\ (t_m)_L} \approx \frac{(\sigma_{eff})_S\ \theta_S}{(\sigma_{eff})_L\ \theta_L}\ \frac{(t_{1/2})_S\ (t_{1/2})_L}{(t_{ir})_L\ (t_m)_L} \qquad 4\text{-}3$$

This expression can be used as a quick reference how differences in half-lives may contribute to the $f_{S/L}$-ratio. It can be seen that the $f_{S/L}$ value also strongly depends on the choice of $(t_{ir})_L$ and $(t_m)_L$, and a straightforward prediction cannot be given.

Table 4-1. Number of nuclei ΔN during measurement for elements with short-lived and long-lived activation products. A_0 in Bq.µg^{-1}, after [1], with t_{ir} = 1 s; ΔN with $(t_{ir})_S = (t_d)_S = (t_{1/2})_S$ $(t_m)_S = 3.(t_{1/2})_S$ and $(t_{ir})_L = (t_m)_L$ = 1 h; $(t_d)_L = (t_{1/2})_L$

Target nuclide	θ, %	σ_0 10^{-28} m^2	I_0 m^2	Radio nuclide	$t_{1/2}$	ΔN	$f_{S/L}$
^{48}Ca	0.2	1.1	0.3	^{49}Ca	8.8 m	5.0 * 10^4	2.5 * 10^7
^{46}Ca	0.003	0.7	0.9	^{47}Ca	4.7 d	2.0 * 10^{-3}	
^{76}Se	9.0	21	16	^{77m}Se	17.5 s	0.8 * 10^3	1.7 * 10^2
74Se	0.9	52	424	^{75}Se	120 d	4.8	
^{115}In	95.7	92		^{116m2}In	2.2 s	3.2 * 10^6	3.2 * 10^5
^{115}In	95.7	160	2114	^{116}In	54 m	1.9 * 10^6	1.9 * 10^5
^{113}In	4.3	9.5	258	^{114m}In	50 d	10	
^{164}Dy	28.2	1700	440	^{165m}Dy	1.3 m	4.4 * 10^8	3.7 * 10^2
^{164}Dy	28.2	1000	340	^{165}Dy	2.3 h	1.2 * 10^6	
^{166}Er	33.4	15		^{167m}Er	2.3 s	1.3 * 10^5	1.1
^{170}Er	14.9	5	22	^{171}Er	7.5 h	1.2 * 10^5	

Obviously, if $f_{S/L} > 1$ measurements via the short-lived radionuclides might be the onset for a better detection limit -which also depends (see *paragraph 2.6)* on the radioactivity of the other radionuclides produced-. However, a value of $f_{S/L} \approx 1$ would imply that measurement of the short-lived radionuclide might result in equal sensitivity

as measurement via the long-lived radionuclide, albeit with the possible advantage of a much shorter turn-around time.

In *Table 4-1* examples are given of ΔN and $f_{S/L}$ values of selected elements from which both short-lived and long-lived radionuclides are formed by neutron activation.

The determination of short half-life radionuclides in the presence of other longer half-life activation products can be improved via cyclic activation procedures -in which a sample is irradiated several times and counted repetitive with certain constraints -[2].

An INAA procedure on basis of short half-life radionuclides requires dedicated facilities for irradiation and counting. The irradiation facility should allow for rapid transfer of the irradiation container to the counting position to limit the loss of sensitivity for the radionuclide of interest by the decay between irradiation and counting. Integration of the receiving end of the facility with the counting equipment facilitates cyclic activation procedures. High demands are set to the precise timing of the beginning and the end of irradiation, decay and counting time. Corrections have to be applied for the decreasing spectrometer's dead-time during counting, either by hardware [3] or software approach [4].

At IRI, a fast irradiation system for studies with short half-life radionuclides became available in 1970.

4.1.2 Fast pneumatic irradiation system

The fast rabbit system is located in the reactor hall. The irradiation containers or 'rabbits' (see *Figure 4-1*) are transferred through an aluminium tube using pressurized nitrogen gas. Transfer time of the rabbit from irradiation position towards receiving end is 1.1 s. Measurement of the induced radioactivity may take place immediately upon receipt of the rabbit. This enables in principle experiments and INAA with nuclides with half-lifes as short as 0.3 s [5].

During transfer the rabbit abrases material from the aluminium transfer tube resulting in radioactive contamination of the rabbit with ^{28}Al, ^{56}Mn, ^{24}Na, ^{110}Ag, ^{27}Mg and ^{65}Zn, and an accumulating contamination of the loading-and receiving station. The resulting enhanced background radiation interferes with the detection of the activity induced in the sample. The rabbits are therefore unloaded and approximately 15 - 20 s after irradiation, the measurement of the sample container can be started. It hampers

the use of very short half-life radionuclides ($t_{1/2}$ < 10 s), cyclic activation procedures and automatization.

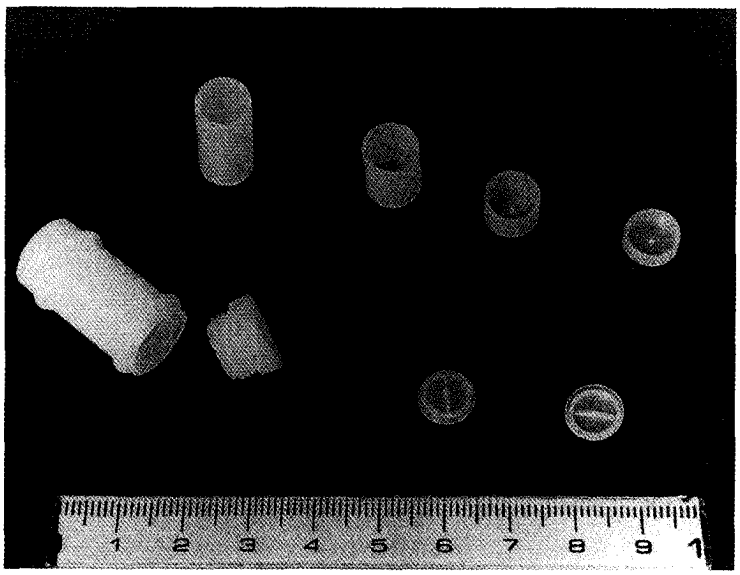


Figure 4-1. Irradiation container ('rabbit') and insert capsules in use with fast rabbit system and CAFIA

Automatic separation devices have been reported in literature [6,7] and tested at IRI. The receiving end of the fast rabbit system has been modified to use rabbits with an 'open' end; the sample container is secured in the rabbit by minute rills and notches. Upon return and blocking of the rabbit, the sample container because of its momentum can leave the rabbit to the counting position. However, it was observed that now the sample containers became contaminated probably due to turbulence of dust.

Substantial reduction of the relative contribution of the contamination problem by analyzing larger sample masses could not be achieved since only a factor of 2 - 3 larger samples could be handled in the capsules where a factor of at least 10 would be required.

In the early 1980s annually approximately 3000 samples were analysed for short half-life radionuclides, and a further increase was expected. The rabbit contamination resulted at the following operational limitations:

(i) Considerable man-power involved in the analyses with no prospect for automation which was reflected by the analysis' costs.

(ii) No options for cyclic activation analysis which would enhance detection limits for certain applications.

(iii) Inefficient working conditions; often less than 10 samples could be analyzed per hour, in which most of the time the user of the facility could do no more than watching the counting.

These operational limitations were the motives for the development of a new fast rabbit system with as starting design demand that the rabbit would not be contaminated during transfer. The rabbit to be used in the new facility would be the same as in the old facility (see above and *Figure 4-1*).

4.2 CONSTRUCTION MATERIALS FOR THE IRRADIATION FACILITY

Materials had to be selected in which only very little or no interfering radioactivity is induced upon neutron irradiation, and which also have a very high resistance against abrasion. Radioactive contamination of the rabbit would thus remain low enough to measure the activity induced in the sample without unloading the rabbit. This would facilitate automation of the system and the use of a sample changer.

4.2.1 Choice of materials

Smooth polyethylene tubing was chosen for the part of the transfer tube not subject to high radiation levels. The good stiffness of this tube makes the inner cross section of the tube to be close to circular. The tube's inner diameter (16.0 mm) matches closely the outer diameter of the rabbit (15.1 mm) enabling a high speed and little loss of pressure of the propelling gas. The polyethylene tube fits tightly inside an aluminium support tube to limit sagging. In the bends still a ellipsoidal deformation occurs which makes necessary to reduce the rabbit's outer diameter from 15.1 mm to 14.1 mm.

Trace element levels in the polyethylene tube material are given in *Table 4-2* together with impurities in the rabbit itself. Induced radioactivities, as given in *Table 4-3*, show that any contamination by abrased polyethylene particles is neglectable to the radioactivity induced in the rabbit's material itself.

For the part closer to the reactor-core a construction material had to be selected which fulfilled the following demands:

(i) Good mechanical resistance in mixed fields of high neutron and gamma-ray dose rates.
(ii) Good abrasion resistance.
(iii) High purity, implying very low induced radioactivity (both short and long half-life radionuclides).

These demands excluded all plastics and metals, their alloys and many of the modern so called 'high-tech' materials like ceramics. Carbon has many attractive sites, but in its form as graphite the abrasion would be unpractical and result in additional problems. Carbonfiber-composite is more abrasion resistant but consists of a carbonfiber substrate densified by impregnation with epoxy, phenolic or polyester resin. There is too much uncertainty with the long-term resistance of these materials in mixed fields of high radiation.

Carbon-carbon composite consists of a carbonfibrous substrate used as a reinforcement and a carbon matrix ensuring the binding of the fibres. This material appeared to have the desired properties for application as irradiation end of a rabbit facility.

4.2.2 Characteristics of carbon-carbon composite

The carbon-carbon composite selected was developed by S.N.I. Aerospatiale and Le Carbone Lorraine in France, and is being denominated 'Aerolor'. Densification of the substrate is obtained by the carbon vapour densification process, resulting in a deposition of pyrocarbon around the fibres. The duration of the densification depends on the size of the substrate to be consolidated, and was for the type of Aerolor selected about 7 months. For this application the manufacturer recommended the use of Aerolor 03 -in which the fibres are randomly dispersed- because of the best prospects with respect to purity, and to machining a smooth surface of the inner side of the transport tube.

The advantages of carbon-carbon composite with respect to application with nuclear research reactors are:

(i) Radiation resistance. It has been observed that 'normal' nuclear reactor grade graphite can be subject to dimensional changes since interactions with fast neutrons cause carbon atoms to leave their lattice positions resulting in a larger spacing of the hexagonal crystal layers. However, no experience existed on the behaviour of carbon-carbon composite in this respect.

Dimensional changes up to 1 % start to occur after exposure to fast (E_n > 0.18 MeV) neutron doses of at least 2 * 10^{24} m^{-2} [8]. Therefore, two pieces

of Aerolor 03 have been irradiated for 14 days in the rotating irradiation facility (RIF) of the High Flux Reactor in Petten, The Netherlands. The estimated integrated fast (E_n > 0.18 MeV) neutron flux was 2.5 * 10^{24} m^{-2}. The corresponding fast neutron flux in the irradiation position at HOR was estimated to be in the order of approximately 1 * 10^{16} $m^{-2}s^{-1}$. Assuming an operation of HOR of approximately 3700 hours per annum, the fluence in the test irradiation thus corresponds with an exposure time at HOR during approximately 18 years. No alterations in the dimensions (length 20.02 ± 0.02 mm, diameter 8.49 ± 0.02 mm) were observed. It was concluded that the Aerolor was acceptable with respect to radiation resistance.

(ii) Good abrasion resistance. Results from application of carbon-carbon composite applied in military and civil aircraft brakes indicate that the materials' resistance to wear-off is all the better than of other materials.

(iii) Very high purity. Trace element concentrations were determined using INAA. Differences were observed for the different types of Aerolor tested. The selected Aerolor 03 was further purified by an extra surface treatment. The trace element concentrations in Aerolor 03 are given in *Table 4-2*.

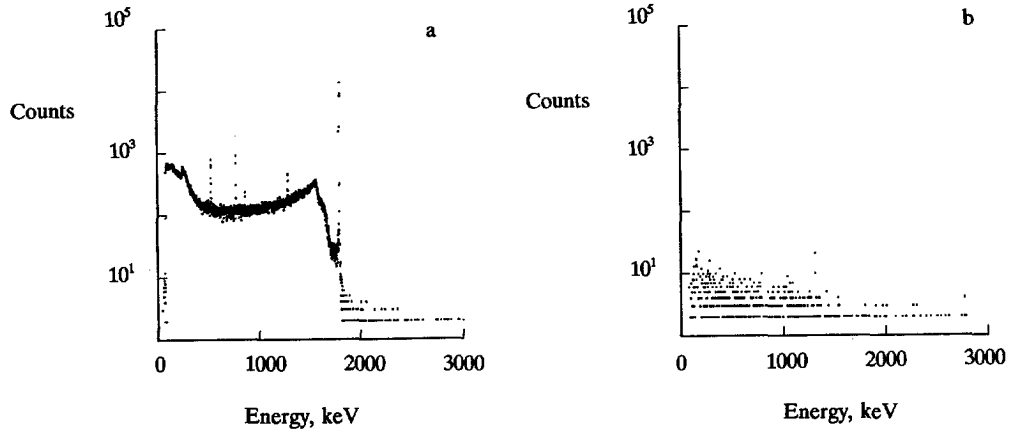


Figure 4-2. *Gamma-ray spectra of (a) 2 mg aluminium and (b) 2 mg carbon-carbon composite. Conditions: t_{ir} = 10 s, t_d = 270 s, t_c = 300 s*

Table 4-2. Trace element concentrations in rabbit polyethylene, Aerolor and transfer tube polyethylene

Element	Concentration in rabbit-polyethylene, $mg.kg^{-1}$	Concentration in Aerolor, $mg.kg^{-1}$	Concentration in transfer tube polyethylene, $mg.kg^{-1}$
Na	0.1	0.7	< 7
Al	0.6	< 3	< 9
Cl	0.5	< 15	< 30
K	0.1	0.07	< 35
Sc	< 0.0005	< 0.02	< 0.001
Ti	0.1	< 11	< 18
V	0.002	< 2	< 0.2
Cr	5	< 0.2	< 0.4
Mn	0.06	< 0.2	0.1
Fe	< 5	< 50	3
Co	< 0.1	< 0.1	< 0.03
Ni	< 10	< 3	< 3
Cu	< 0.2	0.04	< 15
Zn	< 0.03	< 0.25	< 1
Se	< 0.008	< 0.2	< 0.008
As	< 0.003	< 0.002	< 0.01
Br	0.005	0.09	0.5
Sb	< 0.002	0.02	0.04
Cs	< 0.05	< 0.06	< 0.02
La	< 0.002	0.0045	< 0.06
Sm	< 0.0005	< 0.0001	< 0.002
W	0.001	0.01	0.007
Au	0.00002	0.001	< 0.0005

Table 4-3. *Calculated induced radioactivities (Bq) of short-lived radionuclides in rabbit, construction materials of CAFLA and typical sample types (n.r.: no certified or indication concentration reported in certificate)*
*Simulated conditions: Thermal neutron flux 4 * 10^{16} $m^{-2}s^{-1}$; t_d = 0 s. Rabbit polyethylene: 3 g, t_{ir} = 30 s Aerolor: 1 mg, saturation activities; Transfer tube polyethylene: 1 mg, t_{ir} = 30 s; Apple leaves, Buffalo River Sediment, Bovine Liver: 200 mg, t_{ir} = 30 s*

	Rabbit polyethylene	Aerolor	Transfertube polyethylene	Apple Leaves, NBS SRM 1515	Buffalo River Sediment, NBS SRM 2704	Bovine Liver, NBS SRM 1577B
Na	10	50	< 0.2	135	900	13
Al	7,500	< 75	< 35	234,000	50,000,000	1,650
Cl	125	< 135	< 2.5	9,600	< 1,700	46,000
K	1	0.5	< 0.12	11,500	14,340	7,180
Ti	15	< 10	< 1	n.r.	49,000	n.r.
V	160	< 60	< 5	1,400	510,150	538
Mn	300	< 150	0.2	18,000	185,000	3,330
Cu	< 1,300	6	< 30	2,500	44,000	70,000
Se	< 1,400	< 10	< 0.5	450	10,000	6,500
Br	115	42	4	2,900	11,000	14,000

When comparing the impurity level in Aerolor-03 with the situation in the old fast rabbit system it is obvious that, assuming equal quantities of abrased material, a system constructed from Aerolor would result in a reduction of the ^{28}Al contamination by more than 10^5. This is illustrated in *Figure 4-2*. In *Table 4-3* induced activities of short-lived radionuclides in rabbit-polyethylene, and estimated quantities of abrased tube-polyethylene and abrased Aerolor are compared. The induced activities in a typical biological and sediment sample are also given in *Table 4-3*, allowing for comparison with the background (rabbit) contamination activities. It can be seen that impurities in the rabbit's polyethylene will cause some limitations to the sensitivity for Al and Se.

An additional advantage of the low induced radioactivity in Aerolor is that much larger masses of this material can be used for construction than e.g. with aluminium

when the total induced radioactivity is taken into account. This is of importance when the facility has to be removed from the beam-tube.

4.3 DESIGN OF THE FACILITY

4.3.1 Irradiation end

The irradiation end of the facility was designed for installation in the radial beam tube L-3 of the Hoger Onderwijs Reactor. Preference was given to a beam tube above a pool-side end because of the ease of installation, thereby accepting a lower thermal neutron flux. A new pool-side facility would either require the mounting of a new positioner close to the reactor support-grid, or the sacrificing of one of the standard pneumatic facilities.

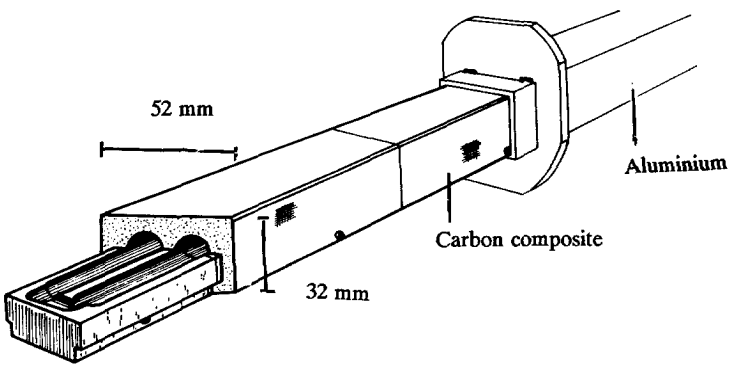


Figure 4-3. Irradiation end of the CAFIA, showing interlocking Aerolor bricks, aluminium support tube and, in partly cutaway section, the irradiation position with transfer and exhaust channels

Most of the wear-off in the 'old' fast irradiation system leading to contamination of the rabbits most likely occurred in the bends of the transfer tube. The new irradiation end therefore was designed without any bends. In 1984, the production process of Aerolor allowed only pieces with a maximum length of approximately 60 cm. The irradiation end has a length of 180 cm. It is composed of parts segmented at the length axis of the flight path (*Figure 4-3*) and interlocking to oneanother. The segmentation allows for fine machinery and inner surface treatment (e.g. polishing). Stacked together two channels result for the transfer of the rabbit and for the exhaust respectively supply of propellant gas.

The resulting rectangular shaped Aerolor is loaded in a closed-end aluminium support tube. The flange at the other end couples the aluminium support tube with the beam tube; it also connects the polyethylene tubing to the Aerolor. With the entire device mounted in the beam tube, the remaining space in the beam tube is filled with water as a primary shielding. The polyethylene transfer tube is guided outwards in a smooth bend through the stacked shielding in the shutter space (*Figure 4-4*). The irradiation end was installed in the beam tube in January 1986.

4.3.2 Transfer section

Optical sensors are inserted to monitor the passage of the rabbit in the transfer section. The arrival of the rabbit in the irradiation position is not monitored directly, but derived from the rabbit's passage just before it enters the beam tube, the last 2.3 m travelling at a speed of approximately 40 $m.s^{-1}$. Since the signal of this sensor is used as start moment of the irradiation time an extra uncertainty is introduced in the duration of the irradiation time of approximately 0.05 s. For nuclides with half lives in the order of 1 - 2 s, and an irradiation time as short as 0.5 s, such an uncertainty affects the final result by approximately 2 %. For nuclides with longer half-lives, or at longer irradiation times, the timing uncertainty is much smaller and neglectable. Eventually, the propagation of the timing uncertainty towards the correction for decay during irradiation can be accounted for by the simultaneously irradiated neutron flux monitor producing a radionuclide with the same half-life as the target radionuclide.

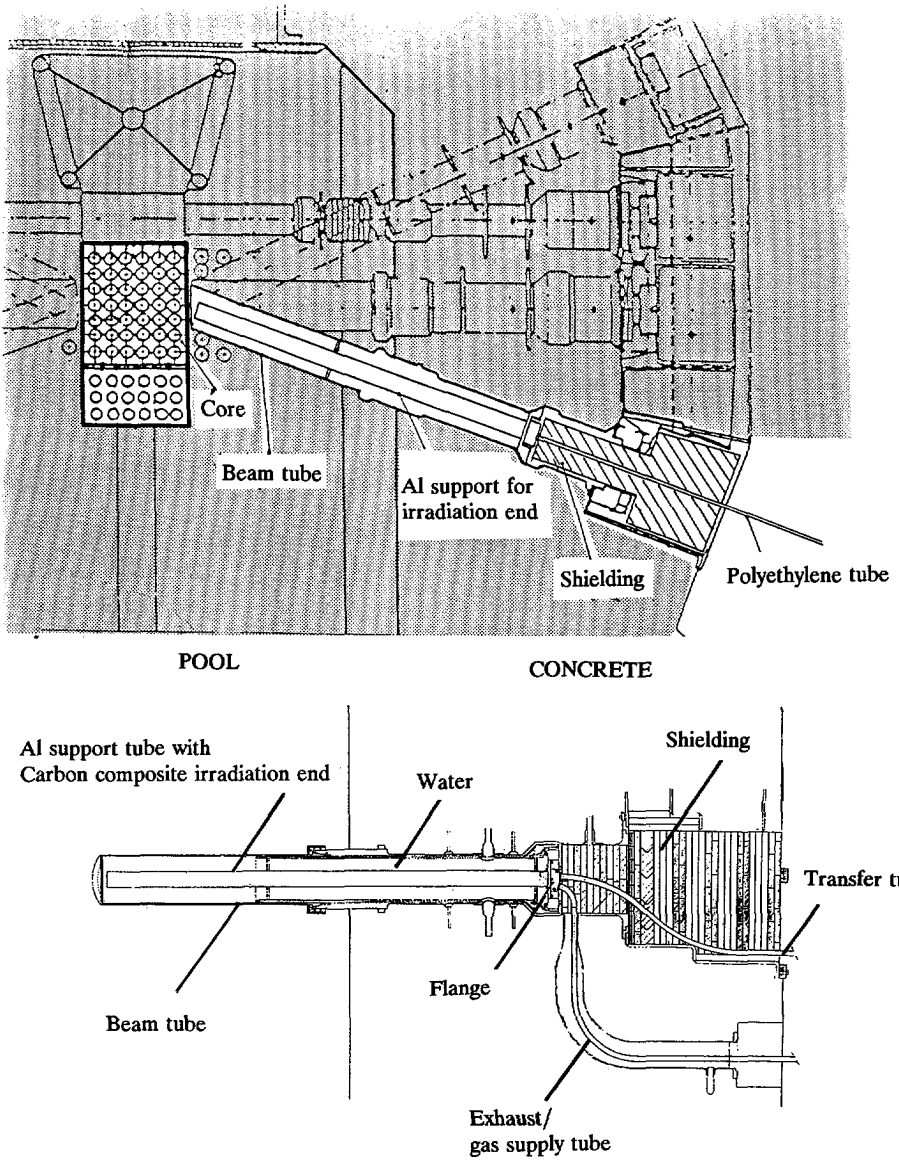


Figure 4-4. Schematic view of the location of the irradiation end in the radial beam tube, top view and longitudinal cross section along A-A', showing polyethylene transfer tube, stacked shielding, consisting of lead, polyethylene, steel and borated (30 weight % boron) polyethylene, polyethylene exhaust tube, water shielding in beam tube, aluminium support tube and radial beam tube

4.4 EVALUATION OF RABBIT CONTAMINATION AND NEUTRON FLUX GRADIENT

4.4.1 Contamination of the rabbit

Gamma-ray spectra have been recorded of rabbits irradiated in both the old fast rabbit system and the CAFIA. The two measurements were carried out with the same semiconductor detector and under almost equal counting geometries. The resulting spectra were corrected for differences in background contribution and differences in thermal neutron flux; the corrected spectra are depicted in *Figure 4-5*. The results are

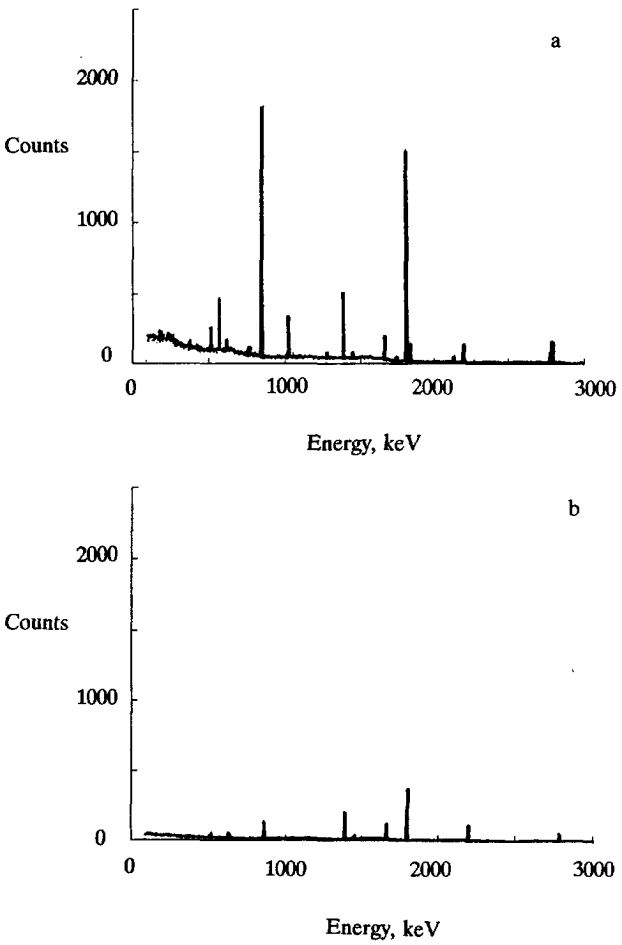


Figure 4-5. Background corrected gamma-ray spectra of the induced radioactivity in a polyethylene rabbit and its contaminants, after irradiation in (a) fast rabbit system and (b) CAFIA

as expected in *paragraph 4.2.2.*: the continuum in the spectrum is reduced by a factor of 10^2 to 10^3; the remaining peaks in the spectrum of the rabbit irradiated in the CAFIA are due to impurities in the rabbit's polyethylene, primarily Al (see also *Table 4-3*).

4.4.2 Neutron flux gradient

In the irradiation position the rabbit is facing the reactor core from aside, with the rabbit's length axis perpendicular to the vertical plane formed by the fuel elements. Since the axis of beam-tube L-3 directs well below the horizontal centre-plane of the reactor-core the irradiation position of the CAFIA is not in the highest neutron flux density of the reactor-core. Different from the 'old' fast irradiation system a flux gradient over the length axis can be expected. In normal operations, sample and flux monitor may be irradiated simultaneously in two capsules packed together into one rabbit. Therefore insight in any gradient is important to determine its contribution to the uncertainty budget of the analysis.

A rabbit was irradiated containing 6 small polyethylene capsules containing each a circular Zr foil and a circular foil of Al, containing 0.1 % Au (certified reference material IRMM 530). The foils fitted tightly in the capsules. After irradiation for approximately 900 s (by cyclic activation, 30 cycles of 30 s each with minimum decay between the cycles), the induced radioactivity of ^{95}Zr, ^{97}Zr and ^{198}Au was measured with a Ge(Li) detector. From the measurements the thermal neutron flux, and the ratio f of the thermal over non-thermal (epithermal and fast) neutron flux could be derived following the procedure suggested by De Corte [9].

The thermal neutron flux distribution over the diameter of the rabbit was also determined. A circular strip of the Al-0.1 % Au foil was positioned around the inner circumference of the rabbit, and irradiated for 2 m at a time; after the irradiation the foil was cut in 6 pieces -which were individually weighted afterwards- and the induced ^{198}Au activity was measured.

The resulting gradients are depicted in *Figures 4-6a,b,c*. The thermal neutron flux decreases approximately 25 % over 16.5 mm in the length axis of the rabbit (from approximately 3.8 * 10^{16} $m^{-2}s^{-1}$ to approximately 3.0 * 10^{16} $m^{-2}s^{-1}$). The relatively large difference in neutron flux at the position of the sample and of the flux monitor to some extent can be accounted for
by careful calibration and standardized rabbit packing procedures. Extrapolations can be applied to correct for the difference in neutron flux when dealing with 'extended' samples with a fixed geometry. More complicated are the consequences of the uncertain geometry

of samples consisting of 'loose' material. Sample capsules have to be thus small that the sample is tightly packed.

The beam tube -and thus the rabbit- directs under an angle of approximately 79° to the side plane of the reactor core which also contributes to the circumferential flux gradient of 7 %.

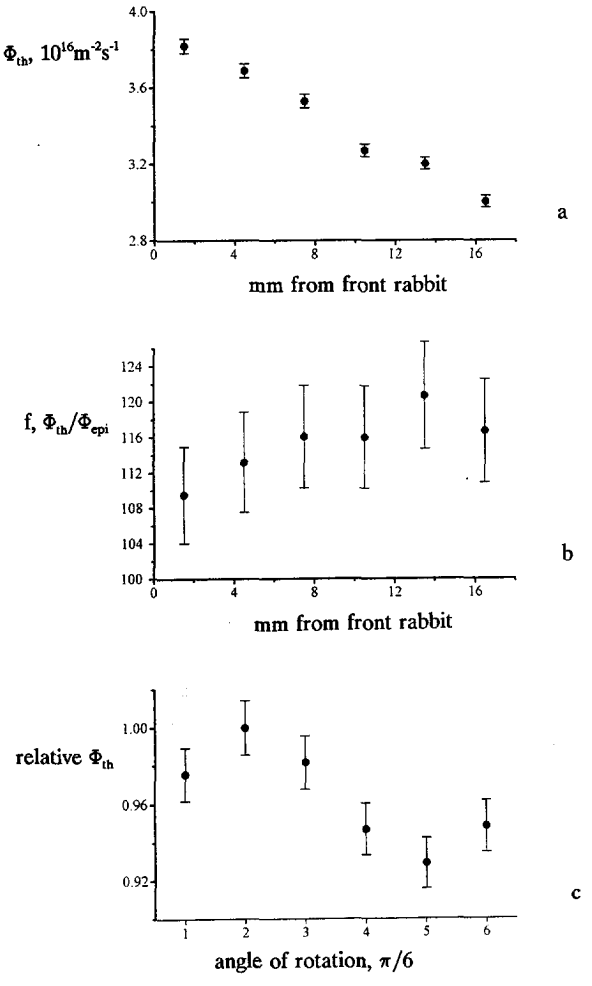


Figure 4-6. (a). Thermal neutron flux gradient, (b). variation of ratio f (Φ_{th}/Φ_{epi}) over the length axis of the rabbit in the carbonfiber fast rabbit system and (c). thermal neutron flux gradient over the circumference of the rabbit

4.5 AUTOMATION OF THE CAFIA

A sample changer has been connected to the transfer system to facilitate automation of the facility. Commercially available automated rabbit systems are equipped with automatic stack loaders and sometimes with stacked unloaders or waste barrel unloaders. Such 'front-end' designs have not been followed with the CAFIA since these systems offer little or no possibilities for e.g. cyclic activation or repetitive activation. In the latter, the decay period between cycles is long enough to allow the interfering background decay away [10]. Flexibility in operations with the CAFIA was pursued by placing the sample changer in the 'centre' of the facility (*Figure 4-7*) and incorporating two tube-dividers.

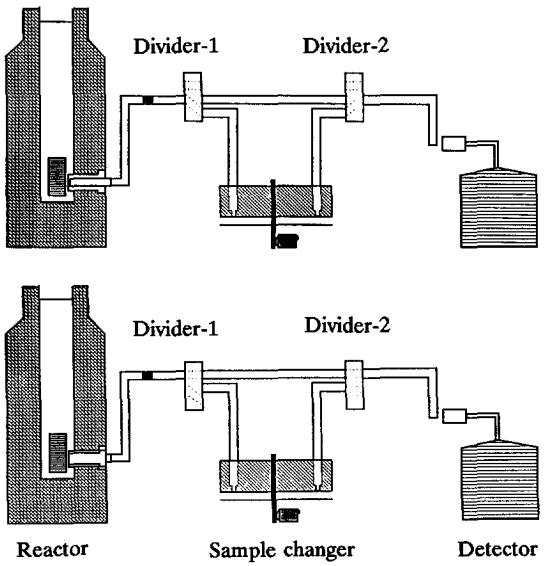


Figure 4-7. Schematic representation of the CAFIA facility with sample changer

Rabbits can be sent from the sample changer to the reactor or (eventually simultaneously) to the detector. After irradiation, the rabbit can be transferred to the detector for immediate counting, or firstly towards the sample changer for cooling. A new irradiation may be executed already during cooling of the previous rabbit(s). This system also allows for several measurements to one sample at different decay times, whilst other actions may be performed in between the counting periods.

The samples are stored in the sample changer in a circular disc holding 64 positions. Underneath this carousel a aluminium disc is mounted with drilled (through) holes containing the binary code of the sample positions. These codes are read-out optically. Pneumatically operating devices provide the coupling of the transfer tubes and the gas-supply/exhaust tubes at the carousel.

4.6 OPERATION, CONTROL AND COUNTING FACILITY

4.6.1 Operation and control

Flexibility and versatility in the operation of the CAFIA was attained by a combination of software and hardware control [11]. The irradiation, decay and measuring times of both sample and standard and the number of irradiations per sample can be chosen freely. Different sets of samples with different experimental conditions can be handled simultaneously. All desired experimental conditions are fed into a computer program which runs at IRI's central computer facility. The program calculates, on basis of optimization of time required, a sequence of individual steps to be executed. These steps include e.g. all actions (opening and closing of valves) for transfer of rabbit from sample changer towards detector. The sequence of actions with relevant information on timing is loaded into an Apple IIe microcomputer which acts as a stand-alone control system. The execution of the actions on the list occurs by routing commands to hardware control units.

The user may select from the following procedures:

(i) one irradiation and one measurement, sample and flux monitor irradiated and measured simultaneously

(ii) one irradiation and one measurement, sample and flux monitor irradiated and measured separately

(iii) one irradiation followed by more measurements at different decay times, sample and flux monitor irradiated and measured simultaneously

(iv) cyclic procedure of one irradiation and one measurement, sample and flux monitor irradiated and measured simultaneously

(v) cyclic procedure of one irradiation and one measurement, sample and flux monitor irradiated and measured simultaneously; followed by a measurement after completion of the cyclic procedure.

As the Apple-IIe acts as a stand-alone system, the facility operates without the need for continuous and direct supervision. The use of a separate front-end computer

prevents interruptions of the analysis procedure due to a long response time or break-down of the multi-user workstation. A parallel analogue control system exists for testing procedures and for manual operation of the facility, independently of the computerized control.

Though the Apple IIe microcomputer is outdated, it has been necessary to keep it as a control system since part of hardware control units has been integrated with the computer. Priority has been given to use of the facility above modernization of the hardware and software control because it would imply a long shut-down period. Recently, a new approach for autonomous control on basis of programmable logic circuits (PLC) has been realized and is being tested.

4.6.2 Safety precautions

Situations may occur in which the rabbit does not leave the irradiation position at the desired moment. Since the facility works without supervision, some time may pass before manual intervention is possible; the resulting excessive irradiation may eventually lead to melting of the rabbit and irrecoverable damage of the irradiation end. Therefore, a safety system has been included for automatic retrieval of the rabbit from the irradiation position in case of loss of propellant gas supply, and at main power interruptions. At the start of (normal) operations automatically a spare buffer tank is filled with nitrogen gas. In one of the aforementioned emergency situations normal operations are interrupted; the spare tank empties itself by a valve, closed when under power, via the irradiation end. Any rabbits left in the irradiation end are thus blown-out.

The operations and status of the facility is being displayed continuously in the reactor control room.

4.6.3 Counting facility of the CAFIA

Measurement of the induced radioactivity is done by gamma-ray spectrometry. The spectrometer consists of a shielded high purity Ge-detector with associated preamplifier and spectroscopy amplifier, high voltage power supply and analogue to digital converter (ADC). The ADC is connected to an at IRI developed NIM 4k buffered memory interface which is linked by RS232C connection to the Apollo workstation, on which also the data analysis takes place [12]. Dead-time stabilizing is achieved via an at IRI developed device [3].

The detector is shielded by 10 cm lead, cladded on the inside with the conventional Cd-Cu sandwich. The contribution of the -for reactor halls characteristic- atmospheric ^{41}Ar activity is strongly reduced by filling the remaining inner space in the lead castle with sealed plastic bags containing polystyrene pellets in a radioactivity free atmosphere.

4.7 APPLICATIONS AND OUTLOOK

Since counting can start approximately 1 s. after irradiation, the system can handle the measurements of very short half-life radionuclides such as ^{8}Li ($t_{1/2}$ = 0.84 s, via Čerenkov counting), ^{167m}Er ($t_{1/2}$ = 2.2 s), ^{183m}W ($t_{1/2}$ = 5.3 s), ^{16}N ($t_{1/2}$ = 7.1 s), ^{20}F ($t_{1/2}$ = 10 s). In the old fast rabbit system, these radionuclides were considerably or almost completely decayed before measurement could be done after unloading the rabbit. And also, albeit with poor detection limits, ^{207m}Pb ($t_{1/2}$ = 0.80 s).

Cyclic activation and measurement offers the possibility to improve detection limits. However, the method is only appropriate for radionuclides with very short half-lives (typically less than 1 m) and not too strongly activating matrices, like certain biological material. Cyclic activation has been applied with the carbonfiber facility for the determination of selenium in human toe-nail clippings via measurement of ^{77m}Se ($t_{1/2}$ = 17.5 s). When comparing a normal activation analysis procedure consisting of t_{ir} = 17 s, t_d = 3 s, t_m = 30 s with a cyclic procedure consisting of 7 consecutive cycles of t_{ir} = 17 s, t_d = 3 s, t_m = 10 s an improvement in detection limits by a factor of 3 was observed [13] towards a limit of detection of approximately 10 ng Se corresponding with approximately 0.25 mg.kg^{-1} in a typical clipping. Except for the adequate detection limits and relatively short turn-around time when processing several thousands of samples [14], INAA had been selected for these analyses because of the non-destructive aspect. Upon completion and sufficient cooling time the samples were still available and fit for additional analyses.

Another typical application is the assessment of technetium via measurement of ^{100}Tc ($t_{1/2}$ = 15.8 s, E_γ = 539.5 keV and 590.8 keV). Determination of ^{99}Tc via ^{100}Tc is highly selective and thus may be preferred in given cases above liquid scintillation counting of ^{99}Tc, in which the selectivity is rather poor. Moreover, this method of INAA is attractive when compared to assessment via Inductively Coupled Plasma Emission/Mass spectrometry, ICP-MS, or Liquid Scintillation Counting by the ease of operation and the absence of sample digestion steps. A cyclic activation procedure was followed with 6 cycles with t_{ir} = 16 s, t_d = 3.5 s, t_m = 30 s and t_d = 3.5 s (second

decay); counting with a 38 % Ge detector at a source-to-detector separation of 3 cm resulted at an interference free detection limit of 4 ng ^{99}Tc.

The analysis procedure with the old fast rabbit system consisted of one irradiation and one measurement after a given decay time. With the CAFIA it will be much less laborious to measure the activated sample more than once. As an example, in the routine procedure geological material is counted after a 15 - 20 m decay time to get rid of most of the extremely high ^{28}Al activity, but still with the possibility to establish the Al-content. It might be interesting to establish the benefits of e.g. a second measurement after e.g. 1 h decay time when ^{28}Al is completely absent and, with it, the high Compton background in the spectrum. Other possibilities are combinations of cyclic activation and a final count of the integrated activity.

The CAFIA facility is designed in a way that its location is flexible with respect to the reactor. Counting position, sample changers and dividers may be located anywhere, eventually outside the reactor hall; it only would involve longer polyethylene transfer tubes and longer transfer times. Unfortunately, the thermal neutron flux in the CAFIA facility is lower than in the old aluminium fast rabbit system , respectively 0.4 * 10^{17} $m^{-2}s^{-1}$ and 1.2 * 10^{17} $m^{-2}s^{-1}$. Part of this difference can be accounted for by cyclic activation procedures, as has been illustrated above, and the use of a more efficient gamma-ray detector.

4.8 REFERENCES

[1] G. Erdtmann, 'Neutron Activation Tables', Verlag Chemie, Weinheim, 1976

[2] N.M. Spyrou, 'Cyclic Activation Analysis - A Review', J.Radioanal.Chem. 61 (1981) 211 - 242

[3] M. de Bruin, S.S. Then, P. Bode, P.J.M. Korthoven, 'A Simple Dead-Time Stabilizer for Gamma-Ray Spectrometers', Nucl.Instr.Meth. 121 (1974) 611 - 613

[4] J.R.W. Woittiez, J. Zonderhuis, A. Faanhof, H.A. Das, 'A Correction for Dead-time Losses in γ-Ray Spectrometry for a Mixture of Short-lived Radionuclides', J.Radioanal.Chem. 53 (1979) 191 - 201

[5] P. Bode, M. de Bruin, P.J.M. Korthoven, 'A Study of Short-Lived Isotopes for Use in Non-Destructive Activation Analysis', J.Radioanal.Chem. 26 (1975) 209 - 213

[6] H.D. Schüssler, W. Grimm, U. Tharun, H.O. Denschlag, G. Herrmann, 'A System for Rapid Radiochemical Separations from Aqueous Solutions', Nucl.Instr.Meth. 73 (1969) 125 - 131

[7] J.R.W. Woittiez, H.A. Das, B.J.T. Nieuwendijk, 'Reactor-Based INAA with a Fast Rabbit System, a Summary of 15 Years Experience',
J.Trace and Microprobe Techn. 6 (1988) 181 - 196

[8] H.H. Yoshikawa, E.M. Woodruff, J.M. Davidson, J.W. Helm, R.E. Nightingale, 'Radiation Effects in Carbons and Graphites',
'Radiation Damage in Reactor Materials', IAEA Symposium proceedings series, Vienna, Austria, 1963, 581 - 592

[9] F. de Corte, 'The k_0-Standardization Method - a Move to the Optimization of Neutron Activation Analysis', Agrégé Thesis, University of Ghent (1987)

[10] K.N. DeSilva, A. Chatt, 'A Method to improve Precision and Detection Limits for Measuring Trace Elements through Short-lived Nuclides',
J.Trace Micropr.Techn. 1 (1983) 307 - 337

[11] P. Bode, P.J.M. Korthoven, M. de Bruin, 'Microprocessor-controlled Facility for INAA Using Short Half-Life Nuclides',
J.Radioanal.Nucl.Chem. 113 (1987) 371 - 378

[12] M. Blaauw, 'The Holistic Interpretation of Gamma-Ray Spectra in Instrumental Neutron Activation Analysis', Thesis, Delft University of Technology (1993)

[13] M.J.J. Ammerlaan, 'Bepaling van Selenium d.m.v. Cyclische Neutronen Aktiverings Analyse m.b.v. een Geautomatiseerd Systeem',
Graduate thesis, HLO Delft, (1990) 40 pp (in Dutch)

[14] P. van den Brandt, S. Bausch-Goldbohm, 'A Prospective Cohort Study on Diet and Cancer in the Netherlands',
Thesis, State University of Limburg, Maastricht (1993)

4.9 LIST OF SYMBOLS

A_0	induced radioactivity, $Bq.\mu g^{-1}$
E_γ	gamma-ray energy, keV
f	Φ_{th}/Φ_{epi}
$f_{S/L}$	$(\Delta N)_S/(\Delta N)_L$
I_0	resonance integral, m^2
L	as subscript denoting long-lived radionuclides
N_0	number of target nuclei being irradiated
ΔN	number of disintegrating radioactive nuclei
$Q_0(\alpha)$	$I_0(\alpha)/\sigma_0$
S	as subscript denoting short-lived radionuclides
$t_{1/2}$	half-life, s
t_d	decay time, s
t_{ir}	irradiation time, s
t_m	measurement time, s
λ	decay constant, s^{-1}
Φ_{th}	thermal neutron flux, $m^{-2}s^{-1}$

σ_{eff}	$\sigma_0(1 + Q_0(\alpha)/f)$
Φ_{epi}	epithermal neutron flux, $m^{-2}s^{-1}$
σ_0	thermal neutron activation cross section, m^2

CHAPTER 5 DETECTORS FOR INAA

The subjects dealt with in this chapter, have been also described in the following papers:

* P. Bode, 'Small Computers and Big Detectors: Powerful Tools in Activation Analysis',
  Trans.Am.Nucl.Soc. 60 (1989) 6 - 7
* P. Bode, R.M. Lindstrom, 'Advanced Detector Systems: What do they have to offer for Activation Analysis ?',
  J.Radioanal.Nucl.Chem. 167 (1993) 187 - 195

5 *DETECTORS FOR INAA*

5.1 INTRODUCTION

A laboratory for INAA may wish to pursue the improvement of performance for two reasons: (i) there may be a need for better detection limits forthcoming from demands from a particular field of application, or (ii) to achieve equal detection limits at shorter decay and/or counting times or with smaller sample masses. Within the traditional fields of application, the geological market segment may ask for better detection limits of the rare earth elements for geogenetic studies and for improvement in turn-around time for samples related to mineral exploration and mining. The market segment related to environmental studies may set higher demands to detection limits in elemental analysis due to the shifting norms, and incorporation of botanical, human and animal studies in which often very low trace element concentrations are encountered. Ultra pure materials is an important market segment in INAA since other methods of elemental analysis deal with serious problems regarding the analytical blank [1], and the demands from the proceeding technology regarding improvement in detection limits have to be accommodated.

The factors which determine the detection limits in INAA for a given element, in a given matrix and at a given counting time follow from the detailed treatment in *paragraph 2.6*, and are in summary:

- the induced radioactivity of the radionuclide(s) of interest
- the counting efficiency
- the spectral signal-to-noise ratio.

The activation analysis laboratory thus has several options to improve its performance with respect to the detection limits at a given (or fixed) counting time. However, it may not always be desirable or possible to increase the induced radioactivity. The remaining options viz. increasing the counting efficiency and/or improving the signal-to-noise ratio are detector related. With respect to the latter option, the noise or background under a peak comprises the spectral background resulting from other induced activities and the natural background. The signal-to-noise ratio may be improved by a different decay time -applicable when the radionuclide of interest has a longer half-life than the radionuclide(s) causing the spectral background and/or by improvement of the shielding. If it is assumed that the shielding is already adequate and alteration of decay time is no option, improvement of the signal-to-noise ratio is entirely related to the characteristics of the detector: the signal depends on the counting efficiency and the

noise on the spectral background. Both depend on the type, size and configuration of the detector as will be illustrated in the next paragraphs.

It has already been indicated in *Chapter 2, paragraph 2.3*, that Ge-semiconductor detectors are the common type of detectors applied in INAA; the principles of their operation, and the characteristics will be described in the following *paragraphs 5.2* and *5.3*. Ge-detectors are made in various configurations and in a range of sizes. An INAA laboratory thus has to determine what the opportunities of these detectors are for either versatile improvement, and/or for specific improvement (for a given type of samples e.g. geological, environmental or medical, or for specific elements to be determined). An experimental assessment, though desirable, is not always feasible for every laboratory before the purchase of a new detector. Some indication on detection limits attainable with different detector types can be derived from literature [2, 3, 4, 5, 6] but comparisons are hampered by differences in experimental conditions, sample types or because situations have been investigated which do not reflect common INAA conditions [7]. Besides, a laboratory may desire to understand which critical detector parameters are decisive for detection limits in INAA taking into account the various spectral shapes that may occur; rather than to decide on experimental data from others only. Once insight has been obtained, an attempt can be made to a cost-benefit evaluation of the options to improve sensitivity to support the ultimate choice.

An approach to a global but objective conclusion on the merits of Ge-detectors is presented in this chapter. It has been assumed that the specifications given by the vendors -relative efficiency, resolution, peak-to-Compton ratio- comprise the only information available to the laboratory to make the selection. A relation has been derived between these specifications and the detection limit, resulting in a "sensitivity improvement factor". This factor indicates the improvement of the detection limit -and thus in sensitivity- that may be expected when using e.g. a detector, larger in volume than the existing detector. This gain in sensitivity can also simply be translated to a gain in counting time for a given sensitivity by the inverse quadratic relationship. The sensitivity improvement factors have been estimated for small and very large coaxial detectors, well-type detectors, planar detectors, use of Compton suppression shields and different shapes of the gamma-ray spectrum.

5.2 SEMICONDUCTOR DETECTORS FOR GAMMA-RAY SPECTROSCOPY

5.2.1 Introduction

Gamma radiation detectors are based on the principle that, upon interaction with matter, the energy quantum of a photon is converted into a product which can be detected by physical or electronic means. When the relation of the interaction product with the energy of the incident photon can be determined, energy-resolved gamma-ray spectroscopy is possible. Since in INAA, Ge-semiconductor detectors are commonly used, the following paragraphs will focus on these detectors only.

The shape of the response function or gamma-ray spectrum reflects the three different interaction processes: photoelectric effect, Compton scattering and pair production [8]. An illustrative gamma-ray spectrum is depicted in *Figure 5-1* showing the photopeak as the result of photoelectric absorption, the 'Compton continuum'

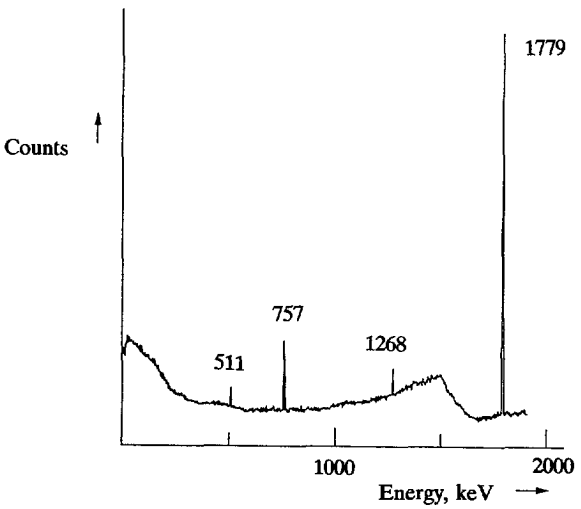


Figure 5-1. *Gamma-ray spectrum of ^{28}Al recorded with a Ge-detector showing the full-energy photopeak at 1778.9 keV, the single and double escape peaks at 1267.9 keV and 756.9 keV, respectively, and the Compton continuum. The peak at 511 keV originates from pair production processes in the shielding and construction materials upon interaction of the high energetic highly-rays.*

reflecting the distribution of the energies deposited in the crystal after photons resulting from Compton interaction have escaped from the crystal and the single and double escape peaks which reflect the energy deposited in the crystal due to escape of one, or both 511 keV quanta after pair production.

The shape of the photopeaks can be approximated by a Gaussian distribution. The width of the peak at half maximum peak height (Full Width on Half Maximum, FWHM) is used as a measure for the energy resolving power of the detector.

5.2.2 *Operation principle and construction*

The Ge semiconductor-crystal has a p-i-n structure [1]: one side of the crystal is characterised by excess positive charge carriers (p), one side by excess negative charge carriers (n). When a reverse bias is applied across the crystal, an intrinsic (or 'compensated', or 'depleted') region is formed between these contacts. Electron-hole pairs are formed upon interaction of photons in this intrinsic layer. When a reverse bias is applied across the crystal it will behave as an insulator but the electric field will drive the electron-hole pairs to the respective contacts. The charge released is proportional to the energy deposited in the intrinsic layer; this charge is integrated by a charge sensitive pre-amplifier and converted into a voltage pulse with an amplitude proportional to the energy deposited. The gamma-ray spectrum is obtained by pulse height analysis of these voltage pulses.

Originally the starting Ge-material was not pure enough to create a compensated region as such. This had to be accomplished by the lithium drifting process; the detectors are denoted Ge(Li) detectors. By the early 1980s the Ge-crystal manufacturing technology had thus developed that crystals of much higher purity could be obtained in which the intrinsic region develops itself when the bias is applied. The intrinsic or high purity (HP)Ge-detector manufacturing has pushed aside the Ge(Li) detectors almost completely because of operational convenience and economical considerations.

Ge-semiconductor detectors are operated at liquid nitrogen temperature (77°K) to reduce the thermally induced leakage current. *Figure 5-2* shows schematically the construction of such a detector.

---

1 *Surface barrier detectors, which are essentially also Si or Ge-semiconductor detectors, are not considered here since their applicability lies mainly with the detection of charged particles.*

5.2.3 Energy resolution

The actual width of the peaks in the spectrum is determined by the intrinsic resolution of the detector -which is determined by the number and statistical distribution of the charge carriers, created in the crystal upon interaction of the gamma-radiation-, and the extrinsic resolution i.e. the leakage current through or around the active volume and the broadening effects of all electronic components following the detector. The intrinsic resolution is also related to the size and type of the detector crystal, and its temperature.

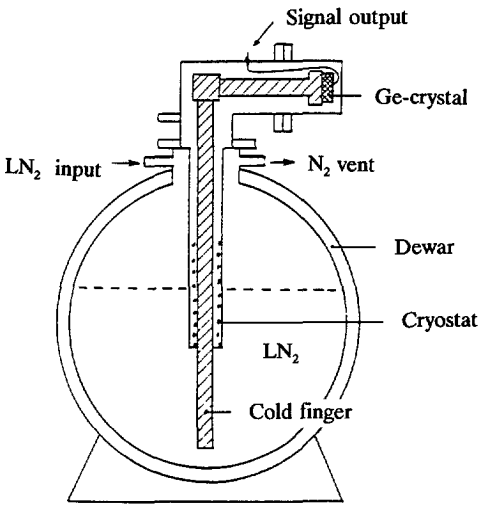


Figure 5-2. Simplified representation of a semiconductor detector

Generally, the resolution becomes worse with increasing detector size. The overall energy resolution of a Ge-detector is often quoted for the 1332 keV line of ^{60}Co and measured [9] as the FWHM for a ^{60}Co source positioned at 25 cm from the end-cap of the detector; it may vary from 1.6 to 2.2 keV. Sometimes also the resolution at lower energies is specified for the 122 keV line of ^{57}Co which may vary from 0.8 to 1.4 keV.

5.2.4 *Photopeak efficiency*

Since the probabilities of all three interacting processes are dependent on the photon energy, the detection efficiency is also energy dependent. The detection efficiency η is the fraction of all the radiations emitted from a source which produce some recorded interaction in the sensitive volume of the detector. The detection efficiency is composed of the following principal[2] factors:

(i) The interaction efficiency, ε_i, which is the fraction of all the radiations striking the sensitive volume of the detector and producing a recorded event.

(ii) The geometrical factor, G, which is the fraction of all emitted radiation which are emitted in the direction of the detector. The geometrical factor is related to the solid angle Ω:

$$G = \Omega/(4\pi)$$

(iii) The peak-to-total ratio, p_t ,which is the fraction of recorded events which result in the photopeak corresponding with the energy of the emitted radiation.

The product of interaction efficiency and geometrical factor is denoted as total efficiency ε_t:

$$\varepsilon_i G = \varepsilon_t$$

whilst the product of total efficiency and peak-to-total ratio results at the photopeak efficiency ε_p:

$$\varepsilon_t p_t = \varepsilon_p$$

The total efficiency is not specified by the vendors of Ge-detectors; it is a function of photon energy and source-to-detector distance, and can be determined experimentally. There are, however, no definitions which part of the gamma-ray spectrum should be included at the low-energy region, i.e. the region where the registration starts. The total efficiency has to be known to calculate the corrections for coincidence losses which occur when gamma-rays emitted in cascade, are detected simultaneously.

The photopeak efficiency -also dependent on source-to-detector distance- may be quoted in absolute terms, but the more common convention [9] is to express the efficiency in relative terms (percentage): the efficiency of the Ge-detector is then compared to the efficiency of a 3" * 3" NaI(Tl) scintillation detector for the 1332 keV photons emitted from a ^{60}Co point source placed at a distance of 25 cm from this detector; this efficiency is defined in absolute terms to be 1.2 * 10^{-3}. Whereas Ge(Li)

---

[2] *In calculations of the detection efficiency also has to be included a term for the attenuation of the radiation in the source itself, and in the materials between source and sensitive volume of the detector.*

detectors had relative efficiencies which often varied between 10% and 30 %, developments in intrinsic Ge-crystal manufacturing resulted at the common availability of detectors with relative efficiencies of 80 - 150 %. In 1994 a record size detector of 176 % relative efficiency was announced [10].

5.2.5 Peak-to-Compton ratio

The peak-to-Compton ratio is the ratio between the height of the photopeak and that of the Compton continuum[3]. This ratio depends on the volume of the crystal and of its shape, and, since the peak heights are compared, also to the detector's energy resolution: detector's with the same volume but different energy resolution will have different peak-to-Compton ratios though the height of the Compton continuum will be roughly equal. Peak-to-Compton ratios of Ge-detectors vary typically from 45 to 100 for detectors with relative efficiencies between 10 % and 100 %, respectively.

5.3 SEMICONDUCTOR DETECTORS FOR INAA

5.3.1 Detector crystal types

Three types of Ge-detectors are of importance for gamma-ray spectroscopy in INAA, viz. (see *Figure 5-3*) (i) the planar detector, (ii) the coaxial detector and (iii) the well-type Ge detector.

(i) A planar detector is disk shaped, with the contacts on the two flat surfaces of the disk with the thin p-contact facing the cryostat's window. The detector has a good ability for detecting photons with energies below 100 keV and a rapidly declining detection efficiency for photons of higher energies. Vendors distinguish between 'real' planar detectors and low energy detectors which are much thicker (up to 30 mm) crystals of a coaxial configuration (see below).

---

[3] *The peak-to-Compton ratio is defined [8] for a gamma-ray spectrum of ^{60}Co as the ratio between the height of the 1332 keV photopeak, and the average height of the continuum between 1040 keV and 1096 keV; and for a gamma-ray spectrum of ^{137}Cs as the ratio of the height of the 662 keV photopeak to the average height of the continuum between 358 keV and 382 keV.*

(ii) Coaxial detectors have a cylindrical shape. The lower part of the central cylinder may be removed to improve the ratio of the active volume vs the dead volume, and contacts are applied on the thus obtained surface and on the outer cylindrical surface of the crystal. The much higher depletion depth -up to 10 cm- results in the ability to detect photons with energies up to a few MeV with still reasonable efficiency.

Coaxial detectors are made from either n-type or from p-type germanium. The n-type detectors have a very thin outer contact, and they can be used to measure, with high efficiency, photons with energies as low as 10 - 30 keV. They are also less sensitive to neutron damage which is advantageous for prompt gamma NAA.

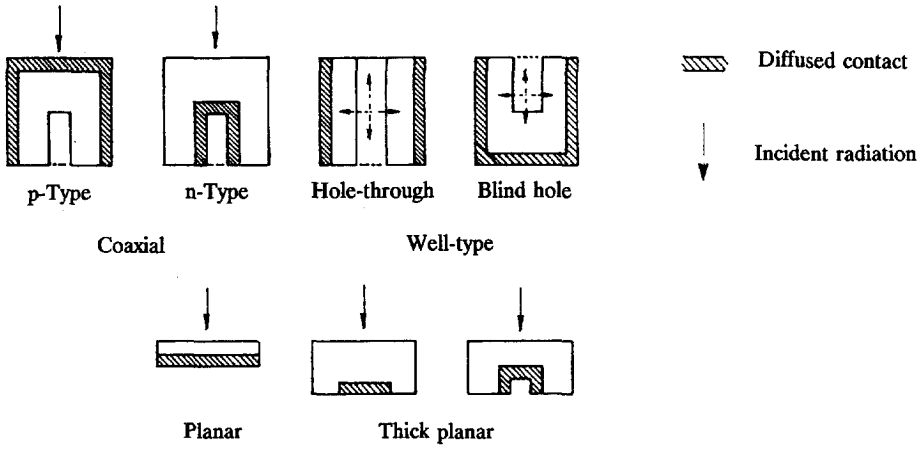


Figure 5-3. Basic detector crystal types and some characteristics

(iii) Well-type detectors are commonly made from p-type germanium. There are two approaches: crystals with a 'blind' well and crystals with a hole through. By placing the source inside the hole or 'well' in the crystal, an almost 4π surrounding with active detector material is accomplished, which has favourable consequences for the effectiveness of detection. Moreover, it also reduces the geometrical errors that occur with imprecise positioning and differences between sources and standards when counting close to the end-cap of a common coaxial detector [11]. The energy resolution of well-type detectors is worse than for comparable coaxial detectors by approximately 10 % at 1332 keV and by approximately 30 % at 122 keV. This is caused by the combination of a higher

crystal capacitance due to the construction of a hole in the crystal, more troublesome cooling of the crystal and enhanced microphonic noises.

5.3.2 The Compton suppression spectrometer

The photons which escape from the Ge-detector after scattering can be detected with a second detector which surrounds the Ge-detector. When the two detectors are operated in anti-coincidence with oneanother, a rejection of the coincident pulses from the Ge-detector leads to a reduction of the Compton continuum. Obviously, not only pulses originating from coincident Compton events and scattered photons are rejected; also pulses from gamma-rays emitted in prompt cascades and pulses related to the pair production process are rejected which leads to a reduction of the corresponding peaks. For this reason the electronics is often thus configurated that both the suppressed and the unsuppressed spectrum can be recorded, the latter one to derive the optimal information from unsuppressed coincident photopeaks and pair-peaks.

Scintillation detectors like NaI(Tl) and BGO (acronym for bismuthgermanate, $BiGeO_4$) are commonly used in Compton suppression shields because of their high detection efficiency. Many configurations have been proposed in literature; an illustrative example is given in *Figure 5-4.*

The suppression of the Compton continuum is usually quoted for the spectrum of ^{137}Cs, and may typically amount a factor of 5 - 8. Compton suppression spectrometers (CSS) have found their application in INAA [e.g. 12].

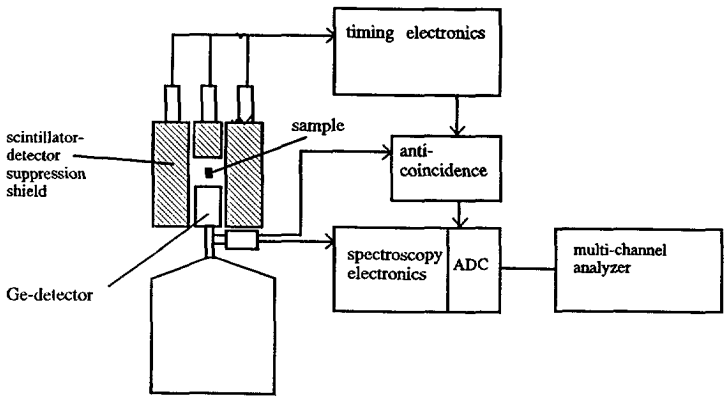


Figure 5-4. Schematic configuration of a gamma-ray detector with Compton suppression shield

An additional advantage of the suppression shield is that it works both as a passive, i.e. radiation 'stopping' material, and active shield against background radiation: both cosmic and laboratory background radiation trigger the anti-coincidence mode when detected simultaneously by the scintillation and Ge-detectors. It was shown by Landsberger [12] that this 'passive' shielding alone reduces the contribution of the background radiation by a factor of approximately 10 for gamma-ray energies at approximately 100 - 200 keV, and a factor of approximately 4 for $E_\gamma > 250$ keV. When the Compton-shield was made active, the remaining background was further reduced with approximately the same factors, so an overall background reduction by a factor of 100 - 16 was observed for the energy region 100 keV - 1 MeV.

5.4 DETECTION LIMITS IN INAA IN RELATION TO Ge-DETECTOR SPECIFICATIONS

5.4.1 Introduction

In *paragraph 5.1* it has already been elaborated upon that, with certain assumptions, detection limits in INAA are determined by the counting efficiency and the spectral background, which both are related to the characteristics of the detector. The relation between detection limits and detector specifications may be assessed through
(i) a numerical approach, in which the photopeak efficiencies and spectrum shape are estimated using Monte Carlo calculations;
(ii) an analytical approach on basis of the analytical description for the detection of a peak on a background and several simplifying assumptions.

One of the aims of this assessment is the development of a simple method to get an indication of the potentials of a certain detector. For this reason, the numerical approach was abandoned.

The analytical approach offers an outlook to link the detection limit to the detector parameters which are specified by the vendors, viz. relative efficiency for the 1332 keV line of ^{60}Co, peak-to-Compton ratio, energy resolution and, eventually, crystal dimensions. Preference is given to global assumptions rather than to -perhaps more accurate- parameterized assumptions. Global assumptions allow to keep the role of the detector parameters 'visible' which contributes to better insight into the interaction of the various parameters. Since the improvement in detection limits is of importance, i.e. the ratio of detection limits as to be obtained with a potential detector and a given detector, proportionality constants in the global assumptions may disappear when making such a ratio.

Currie's definitions [13] for the minimum amount to be detected and the minimum amount to be determined with a given standard deviation are frequently applied by the gamma-ray spectroscopy and activation analysis community to which radioactivity measurements as in gamma-ray spectroscopy and INAA should comply. Cooper [14] elaborated on the factors determining the 'sensitivity' in semiconductor gamma-ray spectroscopy. In the next section, it will be shown that Cooper's final expression for the minimum detectable disintegration rate is in accordance with Currie's definitions. In the further discussion Cooper's expression will be the starting point for the link between detection limits and detector specifications in the evaluation of detector types for improvement of the detection limits in INAA.

5.4.2 *Comparison of Cooper's minimum detectable disintegration rate and Currie's definition*

Consider the general situation of a gamma-ray peak superimposed on a background, composed of a contribution by natural background and a contribution by Compton scattering of higher energy photons (*Figure 5-5*). It is assumed that the source does not decay substantially during the counting period, viz. the count rate is constant. Traditionally, the net peak area is determined by summing the contents of the n channels included in the peak and subtraction of the background counts. The background under the peak is estimated as follows: close to the peak base, at both the lower energy side as the higher energy side.

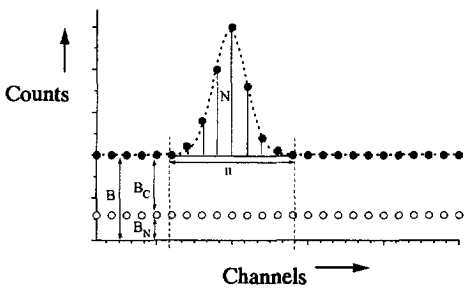


Figure 5-5. Schematic representation of a gamma-ray peak on a smooth background

of the peak a region of e.g. $n/2$ channels is selected. From the average number of counts in each of these regions, the average number of background counts per channels under the peak is estimated. If T is the total number of counts under the peak, B the average

number of background counts per channel and n the number of channels included in the peak, the net peak area is

$$N = T - nB$$

with a standard deviation

$$\sigma_N = \sqrt{T + nB}$$

Cooper defined the minimum number of detectable counts N_m after background subtraction as

$$N_m = A_m \, \sigma_{Nm}$$

with A_m the reciprocal of the fractional error and σ_{Nm} the standard deviation in N_m. The value of A_m depends on the demands to the results: if a precision of 10 % is required, $A_m = 10$; if a precision of 50 % is sufficient, $A_m = 2$.

Elaborating these principles, Cooper derives the following expression for the minimum detectable peak area after background subtraction:

$$N_m = A_m\{[2bR_1\{B_{C_{2,1}} + B_{N,1}\} + \frac{A^2{}_m}{4}]^{0.5} + \frac{A_m}{2}\} \qquad 5\text{-}1$$

in which

$B_{C2,1}$ = the number of counts per channel due to the Compton continuum of the interfering gamma-ray 2 at the location of the gamma-ray 1 of interest

$B_{N,1}$ = the natural background in counts per channel at the location of the gamma-ray 1 of interest

R_1 = the resolution at the peak of the gamma ray 1, the gamma ray of interest

b = the factor which when multiplied by the resolution gives the number n channels included in the peak: $b.R_i = n$

The expression can be rewritten as

$$N_m = \frac{A^2{}_m}{2}\{1 + [1 + \frac{4(2nB_{t,1})}{A^2{}_m}]^{0.5}\} \qquad 5\text{-}2$$

with $B_{t,1} = B_{C2,1} + B_{N,1}$

Currie's definition of the determination limit is

$$L_Q = k_Q \, \sigma_Q \qquad 5\text{-}3$$

with

k_Q = the reciprocal of the requisite standard deviation and
σ_Q = the standard deviation of the net signal

According to Currie, this general expression definition can be further elaborated for the case of determining a peak on a background levels, as with radioactivity measurements:

$$L_Q = \frac{k_Q^2}{2}\{1 + [1 + \frac{4\sigma_0^2}{k_Q^2}]^{0.5}\} \qquad 5\text{-}4$$

with

σ_0 = the standard deviation of the total background on the location of the peak.

In Cooper's approach, the average number of background counts under the peak, B, is derived from averaging the sum of $n/2$ independent terms on each side of the peak. Therefore $2nB_{t,1} = \sigma_0^2$ and since $A_m = k_Q$, Cooper's and Currie's expressions are in agreement.

5.4.3 Factors determining the detection limits in INAA

If it is assumed that there is no appreciable decay of the activity during the counting time, the minimum detectable disintegration rate $D_{m,1}$ is derived from *Equation 5-1:*

$$D_{m,1} = \frac{A_m}{\varepsilon_{p,1}\, a_{\gamma_1}\, t}\{[2bR_1\{B_{C_{2,1}} + B_{N,1}\} + \frac{A^2{}_m}{4}]^{0.5} + \frac{A_m}{2}\} \qquad 5\text{-}5$$

in which

$\varepsilon_{p,1}$ = the photopeak efficiency for the gamma-ray 1 at a given source-detector distance
$a_{\gamma 1}$ = the abundance of gamma-ray 1 in the decay
t = the counting time, s

Cooper did not make assumptions on the shape of the gamma-ray spectrum, and the location of the peak of interest in the spectrum. The following basic cases may be distinguished (see *Figure 5-6):*

a. The count-rate of the source is high and/or the required error is not so low, and thus $2bR_1\{B_{C2,1} + B_N\} >> A_m^2/4$:

(i) The peak is located on a dominant Compton continuum but the contribution of the natural background may be neglected; this case is denoted here with 'C'.

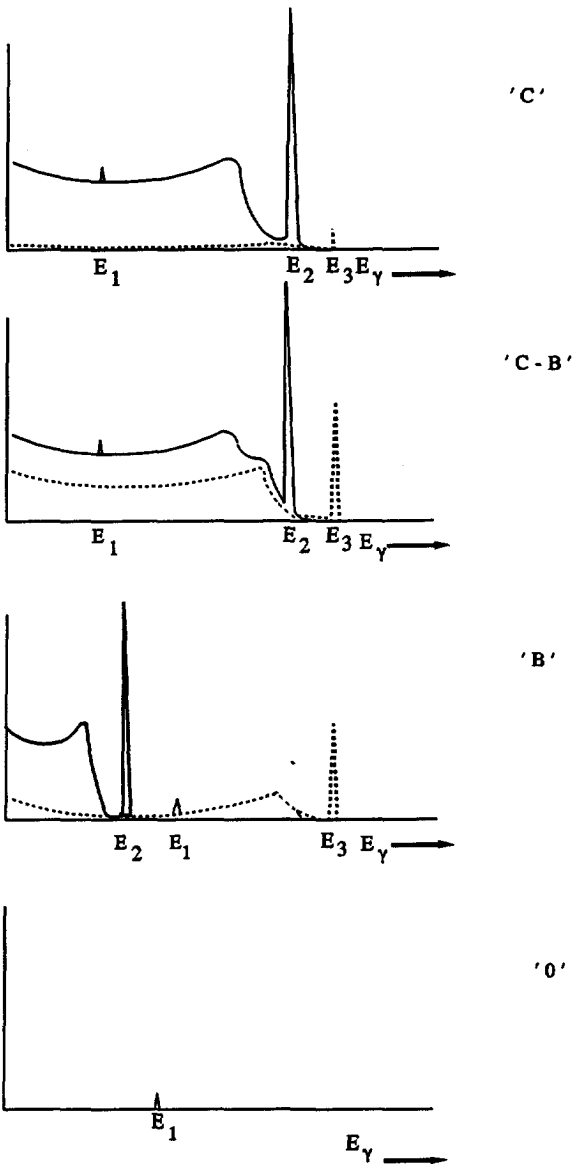


Figure 5-6. *Schematic representation of the four distinguished cases for detection of a peak in a gamma-ray spectrum. Dotted: simplified shape of background spectrum*

(ii) The peak is located on a Compton continuum and the natural background may not be neglected; this case is denoted with 'C-B'.

(iii) The peak is located at the high-energy side of the dominant photopeak in the spectrum, on natural background. Now the contribution of the Compton background is not relevant; this case is denoted with 'B'.

Table 5-1. *Overview of the relation between detection limits in INAA and detector specifications (see also Figure 5-6, and Appendix*

	Basic equation	*Linked to detector specifications*
f_C	$\frac{\varepsilon_{p,1}}{\sqrt{R_1 B_{C_{2,1}}}}$	$\varepsilon_{p,1}\sqrt{\frac{p_C}{\varepsilon_{p,2}}}$
$f_{C\text{-}B}$	$\frac{\varepsilon_{p,1}}{\sqrt{R_1 (B_{C_{2,1}} + B_{N,1})}}$	$\frac{\varepsilon_{p,1}}{\sqrt{S_S \varepsilon_{p,2} + S_B[\frac{\varepsilon_{p,2}}{p_C} + \frac{2}{E_2}\varepsilon_{p,1}]}}$
f_B	$\frac{\varepsilon_{p,1}}{\sqrt{R_1 (B_{C_{2,1}} + B_{N,1})}}$	$\frac{\frac{\varepsilon_{p,1}}{\varepsilon_{p,2}} p_C}{E_2 + 2\frac{\varepsilon_{p,1}}{\varepsilon_{p,2}} p_C}$
f_0	$\varepsilon_{p,1}$	$\varepsilon_{p,1}$

b. The count-rate of the source in the region of interest is very low and the required fractional error is low; thus $2bR_1\{B_{C2,1} + B_N\} \leq A_m^2/4$; this case is denoted with '0'[4].

For these four cases, *Equation 5-5* can be further simplified as is demonstrated in *paragraph A.1* of the *Appendix*. In each of the resulting equations a group of parameters can be selected which determine the minimum detectable amount. The inverse of this group of parameters is denoted as the 'sensitivity determining factor', f_S , since this factor increases when the minimum detectable amount decreases, i.e. when the sensitivity increases. The subscript 'S' denotes the cases of spectral shape as distinguished in the above, viz. C, C-B, B, 0. The expressions for f_S are given in column 2 of *Table 5-1.*

However, in this form the factor can not be used to compare the potentials of Ge-detectors to improve detection limits in INAA, because of the background terms B_C and B_N. In *paragraph A.2* of the *Appendix* it is further described how these background terms may be linked to parameters given in the detector specifications, viz. the photopeak efficiency ε_p, the peak-to-Compton ratio p_C , and the energy resolution R. The resulting converted expressions are given column 3 of *Table 5-1.*

It should be noted that in this elaboration the peak of interest is considered to be 'interference free', i.e. the peak does not form part of a multiplet (when the difference between peak positions is less than 3 times the width of the Gaussian peak [15]) and its determination is not affected by partial overlapping neighbouring peaks.

These expressions can now be used to compare the potentials of different detector types. The attainable improvement in detection limits in INAA when using a selected detector, 's' instead of a given detector 'g', can be estimated from the ratio of the respective sensitivity determining factors: $(f_S)_s / (f_S)_g = (F_S)_{s,g}$ (see *Table 5-2*), denoted here as the 'sensitivity improvement factor'. Calculation of $(F_S)_{s,g}$ requires:

(i) The ratios of the photopeak efficiencies of the two detectors at two gamma-ray energies; these ratios can be derived from the relations between photopeak efficiency and photon energy, i.e. the photopeak efficiency curves of the two detectors.

(ii) The ratio of the peak-to-Compton ratios of the two detectors.

---

[4] *It should be noted that detection of a peak on an almost zero background is an exceptional case in INAA. As an example may serve the detection of ^{49}Ca via the 3084 keV, or ^{37}S via the 3103 keV. The gamma-ray spectrum in this region does not show an appreciable natural background, whilst the Compton continuum of the ^{49}Ca peaks at higher energies also is very small.*

In *paragraph A.3* of the *Appendix* it is described how the photopeak efficiency, and the peak-to-Compton ratio of two detectors, a *'given'* and a *'selected'* detector can be linked to oneanother on basis of only the respective relative ^{60}Co efficiencies $\varepsilon_{Co\text{-}60}$.

$(F_S)_{s,g}$ has been calculated to establish the improvement in detection limits in INAA when using instead of a 20 % coaxial detector either (i) a 100 % coaxial detector, (ii) a well-type detector, (iii) a planar detector or (iv) a 20 % coaxial detector with Compton suppression shield.

The following hypothetical cases have been considered :

(i) 'C' and 'C-B' : peaks corresponding to photon energies at 250, 500 and 750 keV on a background due to a high energy peak of gamma-rays in the region between 1300 and 1400 keV, with a contributing natural background due to a source emitting gamma-rays of 1460 keV, positioned outside the lead-shielding.

(ii) 'B' : peaks corresponding to gamma-rays at 250, 500 and 750 keV at a natural background due to a source emitting gamma-rays of 1460 keV, positioned outside the lead-shielding.

(iii) 'O': peaks corresponding to gamma-rays at 250, 500, and 750 keV at a neglectable or zero background.

The results are given in *Table 5-3*. So far, it has been assumed that the gamma-ray of interest originates from a transition in a decay which does not give raise to coincidence losses. If such a case occurs, a reduction factor has to be added to the photopeak efficiency. In *paragraph A.3.2* of the *Appendix* the reduction factor has been calculated for a very simple case of coincidence losses. The effect of coincidence losses to the sensitivity improvement factor can be derived from all data in *Table 5-3* .

Table 5-2. Sensitivity improvement factors $(F_S)_{s,g}$

S	$(F_S)_{s,g}$
C	$\dfrac{(\varepsilon_{p,1})_s}{(\varepsilon_{p,1})_g}\sqrt{\dfrac{(p_C)_s}{(p_C)_g}}\sqrt{\dfrac{(\varepsilon_{p,2})_g}{(\varepsilon_{p,2})_s}}$
$C\text{-}B$	$\dfrac{(\varepsilon_{p,1})_s}{(\varepsilon_{p,1})_g}\sqrt{\dfrac{(\varepsilon_{p,2})_g}{(\varepsilon_{p,2})_s}}\sqrt{\dfrac{(p_C)_s}{(p_C)_g}}\sqrt{\dfrac{2}{1+\dfrac{(E_2+2\frac{\varepsilon_{p,1}}{\varepsilon_{p,2}}p_C)_s}{(E_2+2\frac{\varepsilon_{p,1}}{\varepsilon_{p,2}}p_C)_g}}}$
$C\text{-}B(CSS)$	$\dfrac{(\varepsilon_{p,1})_s}{(\varepsilon_{p,1})_g}\sqrt{\dfrac{(\varepsilon_{p,2})_g}{(\varepsilon_{p,2})_s}}\sqrt{\dfrac{(p_C)_s}{(p_C)_g}}\sqrt{\dfrac{2}{1+0.25\dfrac{(E_2+2\frac{\varepsilon_{p,1}}{\varepsilon_{p,2}}p_C)_s}{(E_2+2\frac{\varepsilon_{p,1}}{\varepsilon_{p,2}}p_C)_g}}}$

S	$(F_S)_{s,g}$
B	$\frac{(\varepsilon_{p,1})_s}{(\varepsilon_{p,1})_g} \sqrt{\frac{(p_C)_s}{(p_C)_g}} \sqrt{\frac{(\varepsilon_{p,2})_g}{(\varepsilon_{p,2})_s}} \sqrt{\frac{(E_2 + 2\frac{\varepsilon_{p,1}}{\varepsilon_{p,2}} p_C)_g}{(E_2 + 2\frac{\varepsilon_{p,1}}{\varepsilon_{p,2}} p_C)_s}}$
B(CSS)	$\frac{(\varepsilon_{p,1})_s}{(\varepsilon_{p,1})_g} \sqrt{\frac{(p_C)_s}{(p_C)_g}} \sqrt{\frac{(\varepsilon_{p,2})_g}{(\varepsilon_{p,2})_s}} \sqrt{\frac{(E_2 + 2\frac{\varepsilon_{p,1}}{\varepsilon_{p,2}} p_C)_g}{0.25\ (E_2 + 2\frac{\varepsilon_{p,1}}{\varepsilon_{p,2}} p_C)_s}}$
0	$\frac{(\varepsilon_{p,1})_s}{(\varepsilon_{p,1})_g}$

Table 5-3. *Sensitivity improvement factors F_S, with and without accounting for coincidence losses (see text) for (I) a 100 % coaxial detector vs. a 20 % coaxial detector, (IIa) a well-type detector vs. a 20 % coaxial detector with source placed on the endcap; (IIb) a well-type detector vs. a 20 % coaxial detector with the source placed on 5 cm from the endcap; (III) a 20 % coaxial detector with and without Compton suppression shield and (IV) a planar detector vs. a 20 % coaxial detector*

	E_γ	F_S without coincidence losses					F_S with coincidence losses				
		I	IIa	IIb	III	IV	I	IIa	IIb	III	IV
	250	1.4	2.3	6.2	2.4	0.8	0.9	0.8	1.7	0.02	0.9
C	500	1.9	2.3	6.2	2.4	0.7	1.1	1.2	2.9	0.2	0.8
	750	2.2	2.3	6.2	2.4	0.7	1.3	1.4	3.5	0.9	0.7
	250	1.4	2.1	5.6	2.7	0.9	0.9	0.7	1.6	0.03	0.9
C-B	500	1.9	2.1	5.6	2.9	0.7	1.2	1.1	2.6	0.3	0.8
	750	2.2	2.1	5.6	2.9	0.7	1.3	1.3	3.1	1.1	0.7
	250	1.4	2.0	5.3	3.2	0.8	0.9	0.7	1.7	0.06	0.9
B	500	1.9	2.0	5.3	3.6	0.7	1.2	1.2	2.7	0.5	0.8
	750	2.2	2.0	5.3	3.9	0.7	1.3	1.3	3.2	1.7	0.8
	250	2.4	3.5	25	1.0	0.6	1.5	1.2	6.7	0.01	0.7
0	500	3.2	3.5	25	1.0	0.6	1.9	1.9	12	0.1	0.6
	750	3.9	3.5	25	1.0	0.5	2.2	2.2	14	0.4	0.6

5.5 DISCUSSION

5.5.1 Comparison of detector types

From the data in *column IV* in *Table 5-3* it can be seen that, when compared to a standard 20 % coaxial detector the planar detector offers no outlook for improvement of detection limits in INAA in the region of gamma-ray energies here considered ($E_\gamma \geq$ 250 keV).

Except for the detection of a peak on an almost zero background (case '0'), the F_S values in *Table 5-3* for a 100 % detector (source on the endcap, *column I*) and well-type detector (*column IIa*) do not differ very much. The $(F_C)_{100,20}$ values in this table show that the improvement in detection limits when using a detector with an efficiency 5 times as high and a peak-to-Compton ratio twice as good is less than intuitively would be expected. It illustrates the often not anticipated limited gain in photopeak efficiency

for gamma-rays < 1332 keV; in the region 250 - 500 keV the photopeak efficiency of a 100 % detector is only a factor 2 - 3 better than of a 20 % detector.

Surrounding the 20 % detector with a Compton suppression shield (*column III* in *Table 5-3*) results at 1.5 - 2.5 times better detection limits than can be attained with a 100 % detector (*column I*) and to comparable or, at the maximum, twice as good detection limits than can be attained with a well-type detector (*column IIa*), provided the source is placed on the endcap of the coaxial detector and non-coincident gamma-rays are considered.

In practice, often sources have to be positioned further away from the endcap, sometime for practical reasons (dimensions of source holders) or e.g. to reduce geometrical errors. In these situations, the improvement factors of the CSS system and the large coaxial detector over the small coaxial detector remain the same, but the improvement factor of the well-type over a standard detector increases rapidly with the distance. At a 5 cm source-to-detector spacing, the detection limits attainable with a well-type detector are a factor approximately 1.5-2.5 better than with a CSS system.

It can also be seen from *Table 5-3* that, as could be expected, the CSS system offers no improvement for detection limits when dealing with the case '0'; the well-type detector has the best prospects for attaining better detection limits.

Whereas it is well-known that cascade-losses occur with well-type detectors, the extent of the losses when using 100 % detectors is little advocated. From *Table A-4* in the *Appendix* it can be seen that, for sources counted on the endcap, the coincidence losses result in almost equal detection limits for 100 % detector and well-type detector. The gain in improvement for coincident gamma-rays when using the 100 % detectors in such a counting geometry is much less than intuitively would be deducted from its relative efficiency: only max. a factor of 1.5. The same is the case for the well-type detector.

The coincidence losses when using a CSS system are much larger due to the very high absolute efficiency of the suppression shield. However, differently from the 100 % detector and the well-type detector, the disadvantage of the CSS system can be accommodated for by analyzing and interpreting both the simultaneously recorded suppressed and unsuppressed spectra.

In the comparison there has been no differentiation between n-type and p-type coaxial detectors. The more expensive n-type detectors are for INAA only advantageous for radionuclides emitting gamma-rays below 100 keV like ^{170}Tm, ^{166}Ho and ^{182}Ta. When radionuclides have also to be determined in the entire gamma-ray energy range between e.g. 50 keV and 3000 keV -which is commonly the case in INAA operations-,

an n-type detector of equal or larger relative efficiency than the 20 % p-type detector should be preferred above the planar detector and large p-type detectors.

The $(F_S)s,g$ values allow for instance for comparison of two specified detectors with relative ^{60}Co efficiencies which differ not much, but with differences in e.g. p_C ratio (and, thus, resolution) and possibly price: for instance a 60 % detector with p_C = 80 and R_1 = 1.8 keV resolution and a 63 % detector with p_C = 75 and R_1 = 1.95 keV. Now only the relationship between the photopeak efficiencies has to be calculated using *Equation A-24* from the *Appendix*, resulting in

$$(\varepsilon_{p,E\gamma})_{63\%} = 0.95\, E_\gamma^{0.014}\, (\varepsilon_{p,E\gamma})_{60\%}$$

and the specified characteristics can be used. It results at a $(F_C)_{63\%,60\%}$ values of approximately 0.98 at 250, 500 and 750 keV (non coincident gamma-rays). Apparently, the lower p_C ratio of the 63 % detector takes away the advantage of the higher efficiency.

5.5.2 *Comparison with experimental observations*

COAXIAL DETECTORS AND WELL-TYPE DETECTORS

The potentials of the different detector types have also been studied by the results obtained by analyzing neutron activated reference materials using a 17 % Ge(Li) detector, a 96 % Ge-detector, and a (blind hole) well-type Ge detector (see *Table 5-4*).

Table 5-4. *Characteristics of detectors used in this comparison. #: ratio specified for the ^{60}Co source placed outside the well*

	17 % Detector	96 % Detector	Well-type detector
crystal volume	101 cm^3	435 cm^3	105 cm^3
relative efficiency	17 %	96.3 %	not specified
FWHM at 1332 keV	1.77 keV	1.82 keV	2.08 keV
peak-to-Compton ratio	50.2 : 1	97.1 : 1	34.8 : 1#
crystal well diameter	-	-	23 mm
cryostat well diameter	-	-	18 mm

Samples were taken of the following reference materials: USGS-DTS-1 Dunite, USGS-W-2 Diabase, NBS-2704 Buffalo River Sediment, NBS-1633A Coal Fly Ash (all subsequently referred to as 'siliceous material'), and NBS-1577A Bovine Liver, NBS-1572 Citrus Leaves, IAEA-H-5 Animal Bone (referred to as 'biological material'). Sample weights were typically approximately 200 mg. The siliceous samples were irradiated for 1 h, and the biological samples for 4 h at a thermal neutron flux of approximately 5 * 10^{16} $m^{-2}s^{-1}$. The samples were counted approximately 5 d and 1 month after irradiation during 1 h at the three detectors. The counting conditions are given in *Table 5-5.*

Table 5-5. Counting conditions applied

	Counting after 5 d	Counting after 1 month
siliceous material	5 cm @ 17 % and 96%	5 cm @ 96 % and in well-type
biological material	5 cm @ 96 % and in well-type	1 cm and 5 cm @ 96 % and in well-type

The number of elements identified, peak intensities and the precision of the determination have been compared, together with the limits of detection [5]. Some of the detection limits observed are presented in *Table 5-6*, whilst a summary of all results is given in *Table 5-7.* The observations -agree well with the calculated values for $(F_C)_{96\%,17\%}$ and $(F_C)_{well,17,5cm}$ (no coincidence losses[5], whereas it should be noted that the conclusions on the experimental detection limit represent a gross average, including peaks subject to coincidence losses.

[5] *It should be noted that far-going assumptions have been made on the coincidence losses underlying the related $F_{s,g}$ values which were merely meant to demonstrate the effect of coincidence losses to the sensitivity improvement factors.*

Table 5-6. Detection limits as derived when counting a siliceous (W-2) and biological reference material (NBS SRM 1572) 3 weeks after irradiation on different detectors. All detection limits in mg.kg^{-1}

W-2	17 % @ 5 cm	96 % @ 5 cm	Well-type	SRM 1572	96 % @ 5 cm	96 % @ 1 cm	Well-type
Cr	64	27	12	Cr	2.7	1.1	0.86
Zn	170	95	57	Zn	3.3	1.3	1.1
Se	42	16	9.4	Se	2	0.8	0.6
Sn	2,100	1,100	400	Ag	0.64	0.27	0.7
Sb	4	2.4	2.9	Sb	0.16	0.06	0.07
Cs	8.6	2.7	2.4	Cs	0.15	0.027	0.009
Ba	3,000	1,500	930	Ba	88	40	37
Nd	630	320	190	Nd	17	7.8	5.3
Eu	1.1	0.5	0.28	Eu	0.03	0.02	0.01
Ta	3.1	1	1.6	Ta	0.074	0.024	0.024
Yb	7.7	3.3	1.7	Yb	0.5	0.2	0.2
Hg	18	7.4	3.1	Hg	0.84	0.35	0.28
Th	5.6	2.4	1.1	Th	0.25	0.1	0.08

Table 5-7. Comparison of results of measurements at different detectors; #: values derived from dividing respectively $(F_C)_{well,17,5cm}/(F_C)_{96,17}$ and $(F_C)_{well,17,0cm}/(F_C)_{96,17}$

	96% vs 17 % @ 5 cm	Well-type vs. 17 % @ 5 cm	Well-type vs. 96 % @ 5 cm	Well-type vs. 96 % @ 1 cm
measured detection limits	2 - 3 x better	4 - 6 x better	2 - 3 x better	max. 1.5 x better
calculated F_C	1.5 - 2.5	4.8 - 5.1	2.0 - 3.2#	max. 1.3#

COAXIAL DETECTOR WITH COMPTON SUPPRESSION SHIELD

Neutron activated samples of various reference materials (siliceous and biological material) have been measured with the gamma-ray spectrometer with a Compton suppression shield at the University of Illinois at Urbana-Champaign, Il., U.S.A.. The p-type Ge-detector in this system has a relative efficiency of 19 % and is surrounded with a cylindrical 12" * 12" NaI(Tl) annular detector. The opening facing the Ge-detector holds a 3" * 3" NaI(Tl) detector as a plug. The entire assembly is not surrounded with a lead shield; as a result the degree of passive shielding by the NaI(Tl) shield is higher than assumed in the calculations in the preceding paragraph, and varies from a factor of 25 at energies below 300 keV to a factor of 5 at > 500 keV. The ratio of active to passive shielding is here about 10 since still the ^{40}K contribution and its Compton continuum are not as effectively taken away by the passive shielding as with a lead shielding. The suppressed and unsuppressed spectra can be recorded simultaneously.

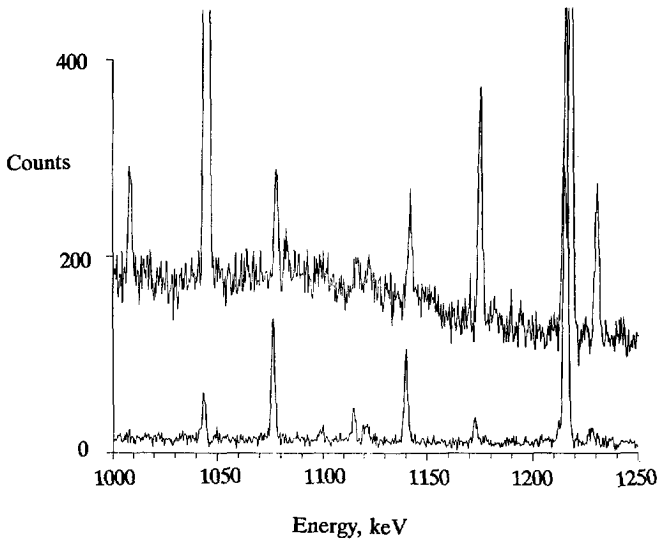


Figure 5-7. Gamma-ray spectrum as recorded with a spectrometer with Compton suppression. Unsuppressed (top) and suppressed (lower) gamma-ray spectrum of NBS 1571 'Orchard Leaves' showing the Compton continuum reduction and altered and unaltered peaks

The Compton continuum in the various measurements was caused by either 889 keV and 1120 keV lines of ^{46}Sc, the 1368 keV and 2754 keV lines of ^{24}Na or the 1778 keV line of ^{28}Al. The recorded spectra confirm the expectations in *Table 5-3*, with

respect to the improvement in detection limits due to reduction of the Compton continuum. The reduction in peaks due to coincidence summing-out effects was compared to the observations by Das and Zonderhuis [2] and agreed well. These reductions varied from a factor of 2 to 20 or more. To illustrate the Compton continuum reduction, unaltered and strongly reduced peaks, a part of a the gamma-ray spectrum of a neutron activated sample of NBS 1571 'Orchard Leaves' is depicted in *Figure 5-7.*

5.5.3 Comparison with literature data

An assessment of detection limits, attainable with various detector types was made for a study on the determination of nickel in biological materials after radiochemical separation [6]. In this work, nickel is determined via the 811 keV of ^{58}Co, and the photopeak is located on the Compton continuum of ^{60}Co. The detection limits attainable with a large volume Ge-detector, a well-type Ge-detector and two spectrometers with Compton suppression shields were compared with the detection limit as found with a standard 21 % relative efficiency Ge-detector. Radioactive sources were send to the participating laboratories and measurements were done according to a well prescribed protocol; the raw data were all analyzed in the organizing laboratory.

Though not all detector characteristics are specified, the missing parameters to calculate the F_C values can be derived according to the relationships given in the *Appendix.* In *Table 5-8* the observed ratio of detection limits is compared with the F_C values. Generally the calculated improvement factors agree well with the observations, except for one of the systems with Compton suppression shield.

Table 5-8. Observed [6] and calculated ratios of detection limits for Ni via the 811 keV of ^{58}Co in the presence of ^{60}Co. Detector types denoted by their relative efficiency or active volume (well-type)

	96 % vs. 21 %	120 cm^3 well-type vs. 21 %	CSS with 27 % vs. 21 %	CSS with 18 % vs. 21 %
observed ratio of detection limits	2.6	2	3.5	3.7
F_C values	2.3	2.3	3.5	2.8

It cannot be excluded that errors have been made in one of these assessments since it is unlikely that equal detection limits are obtained though there is a substantial difference in efficiency of the Ge-detectors since the Compton suppression factors of these two systems are almost equal [15,16].

5.5.4 Opportunities for further improvement

Even better detection limits can be achieved when combining a well-type detector with a Compton suppression shield. Such systems have been reported for use in measurements of natural radioactivity [17, 18, 19], and for a specific application in INAA [20]. The combined powers of Compton suppression, 4π counting geometry and large crystal size can be expected to result in a further improvement in detection limits when compared to the well-type used as an example in *Table 5-3*, denoted in the following by the subscript 'wg'. For a 400 cm^3 well type, denoted with the subscript 'ws', $(\varepsilon_p)_{ws} \approx 4(\varepsilon_p)_{wg}$ and $(p_C)_{ws,CSS} \approx 6(p_C)_{wg}$. Therefore $(F_C)_{ws,wg} \approx \sqrt{4}\sqrt{6} \approx 5$ (for non-coincident gamma-rays and counting on the endcap). It implies that, when compared to the standard 20 % coaxial detector, such a system might result in an improvement in detection limits of a factor of 12 for sources counted on the end-cap, and a factor of almost 70 when the source needs to be positioned at 5 cm from the end-cap. The associated total reduction in counting time for equal detection limits would be a factor of approximately 150 and 5000, respectively. Obviously the coincidence losses for a well-type detector of these dimensions would be larger too, thus reducing the improvement factor for coincident gamma-rays when counting in the unsuppressed mode.

It should be noted that the absolute photopeak efficiency of well-type detectors for low energy gamma-rays approaches 100 % (e.g. 80 % for 100 keV), whilst for the 1332 keV gamma-ray line of ^{60}Co absolute efficiencies of 10 % can be reached [18]. A further increase in crystal size of well-types does not imply a considerable increase in detection limits at the lower photon energies (e.g. < 500 keV), and eventually may worsen the detection limits because of a relatively higher contribution of the Compton background, poorer energy resolution and higher cascade summing losses.

5.5.5 *Additional considerations in selecting a detector*

FLEXIBILITY IN OPERATIONS

Coaxial detectors have the highest flexibility in operational use in an INAA laboratory. Sources can be placed on any distance from the endcap. The closest source-to-endcap geometry depends on the dimensions of the sample holders or sample changing devices. This high flexibility makes possible (automated) adjustment of counting geometry pending the observed total count-rate. An additional advantage of coaxial detectors is that there are also no restrictions with respect to sample size and orientation. As a disadvantage of the latter option it might be mentioned that more is asked of proper corrections for differences in geometry between sample and standard.

In a well-type detector the almost 4π-geometry also effectuates a smaller dependence to the sample-size and geometry than e.g. when counting on the endcap of a coaxial detector [11]. The well-type is less flexible for operations in an INAA laboratory since the allotted maximum count-rate has to be inspected, and too active samples either have to decay further or re-analyzed in smaller quantities or at a lower induced radioactivity. When there is no alternative, sources may be placed outside the well, but the advantages over the normal standard detector then vanish. Sample changing is more complicated than with coaxial detectors, and of course limitations exist with respect to the maximum size of the sample to be counted. However, for many routine applications in which samples of less than one gram are processed, the available space may be sufficient.

Spectrometers equipped with a Compton suppression shield deal with the problems of the restrictions to count rate [22]: the higher the count rate the less effective the suppression of the Compton background due to pulse separation difficulties in the scintillation detector pulse processing (random coincidence counting). This effect is a serious potential source of inaccuracy in Compton suppression counting, for instance when the difference in dead-time between standard and sample is different than anticipated upon. There are also restrictions to sample size (large sample sizes have to be avoided to keep intra-source scattering limited), and automated sample changing. Tuning and maintaining a CSS system requires additional skills of the employees. For full multi-element analyses often both the suppressed and unsuppressed spectra will have to be recorded and processed.

ECONOMICAL ASPECTS

A laboratory may wish to balance the beneficial aspects of the various options to improve detection limits in INAA against the required investments. The latter depend on the motivation for improvement.

The starting point of the elaboration in this chapter has been that an INAA laboratory wishes to pursue a better detection limits either because of specific requests, or for attaining equal detection limits in shorter counting times or with smaller sample masses. In this case, the laboratory may just wish to replace only the detector and link it to the other parts of the existing spectrometer. In addition, it is possible that the laboratory needs to increase its capacity and to balance the economics of equal performance by simply installing a new spectrometer with an equivalent detector as the existing one(s) against installing a spectrometer with a detector which equal detection limits can be attained in shorter counting time.

For both cases, the $(F_S)_{s,g}$ value can be indexed to establish the cost-effectiveness of the investment, and in order to be able to link this to the reduction in counting time at equal detection limits via $\{(F_S)_{s,g}\}^2$. Prices of detectors are partly related to the physical characteristics of the Ge-crystal, and partly to considerations known to the vendors only. The same is applicable to the signal processing electronics which is assumed to consist of high voltage supply, spectroscopy amplifier, (low voltage) power supply, PC plug-in card with analogue to digital converter and sample changer. Since the price structure may be different in different countries, the use of a parameterized relationship between detector size and price has only limited applicability.

Table 5-9. Indicative prices in US $ (assuming conversion rate of 1 US $ = Dfl. 1.60

	Detector only	Detector and spectrometer	Detector, spectrometer and sample changer
20 % detector	17,000	35,000	85,000
100 % detector	79,000	95,000	145,000
well-type detector	33,000	51,000	101,000
Compton suppression spectrometer	100,000	135,000	185,000

The price-indexing of the $\{(F_S)_{s,g}\}^2$ values is therefore only demonstrated for the detectors here considered, and based on prices as applicable in The Netherlands. The estimates of prices of detectors and electronics are given in *Table 5-9*.

The price of the respectively selected and given detector or spectrometer is denoted by P_s respectively P_g. Now a price-indexed indication for the reduction factor of counting time at equal detection limits $\{(F^*_S)_{s,g}\}^2$ follows from $\{(F^*_S)_{s,g}\}^2 = \{(F_S)_{s,g}\}^2/(P_s/P_g)$.

This has been worked-out for the spectral situation 'C' and no coincidence losses, using the data from *Table 5-3*. Results are given in *Table 5-10*.

Table 5-10. Price indexed reduction factor for counting time at equal detection limits

	Detector only	Detector and spectrometer	Detector, spectrometer and sample changer
$\{(F^*C)_{100\%,20\%}\}^2$	0.4 - 1.0	0.7 - 1.8	1.1 - 2.7
$\{(F^*C)_{well,20\%\ 0\ cm}\}^2$	2.7	3.6	4.4
$\{(F^*C)_{well,20\%\ 5\ cm}\}^2$	20	26	33
$\{(F^*C)_{CSS,20\%}\}^2$	1.0	1.5	2.7

The data in *Table 5-10* show that, though the improvement in detection limits for sources on the end-cap with a 100 % detector and the CSS system is better than can be attained with a well-type detector (*Table 5-3*), the cost-effectiveness of the achieved improvement in counting time is much better when using the well-type. When sources have to be placed at a certain distance from the endcap of the coaxial detector to reduce counting geometry errors, the cost-effectiveness of the well-type detector rapidly exceeds that of the other detectors. The cost-effectiveness of very large detector and the CSS system are almost equal when weighted by the investments.

However, the costs per analysis when using the CSS system will be higher because of the time needed to process the two spectra. The data in *Table 5-10* also show that the cost effectiveness of the four alternatives increases when an extra spectrometer is installed, but also that the mutual ratios of these priced indexed reduction factor do not differ much from the situation in which only the detector is replaced. These ratios are only slightly influenced by the extra running costs such as the costs of extra liquid nitrogen (typically in The Netherlands, approximately Dfl 1000 or US $ 600 per annum per spectrometer) and the costs of an extra spectrometer performance control (e.g. one

extra man-hour per week, equivalent with approximately Dfl. 5000 or US $ 3000 per annum).

Ease of operation could not be included in these economical considerations. For every individual case the investments, and cost effectiveness have to be balanced against aspects like flexibility to be usable in a large range of count-rates, with a broad variety of sample shapes and holders, the number and complexity of the spectra to be processed. A qualitative impression of the operational characteristics of the detector types is given in *Table 5-11.*

Table 5-11. Operational characteristics of detector types for use in INAA.
--: poor; -: limited; +: fair; + +: good; + + +: excellent

	Detection limits	Sample size	Automated sample changing	Count rate effects	Spectrum processing	Cost effectiveness
100 % coaxial	+/++	++	++	++	++	+
well-type	++/+++	-	+/++	+	+	++/+++
20 % coaxial with CSS	+/++	+/-	+	-/--	+/-	+

5.6 CONCLUSIONS

The expressions for the factors determining the detection limit in INAA using Ge-detectors serve the same use as Cooper's original figure-of-merit [14] and correspond with experimental observations and reportings in literature. The factors derived can be applied under different experimental conditions with respect to the background conditions, whilst the parameters included, viz. photopeak efficiency, peak-to-Compton ratio and resolution all can be derived from the detector's specifications. As such, these factors are easier to apply than Cooper's figure-of-merit.

The elaborations show that energy resolution has a small effect to the detection limit via interference free peaks. The situation becomes considerably more complex when peaks have to be considered which may form part of a multiplet, since not only the photon energy spacing is then of importance in relation to the resolution, but also the

ratio of the heights of the contributing peaks. When improvement in detection limit for such cases is of concern, preservation of selectivity by energy resolution may be of even higher importance than absolute improvement in detection limit. From case to case it has to be decided if the gain in detection limits counterbalances the loss of selectivity. The latter can be circumpassed by a great extent by analyzing the gamma-ray spectra via a holistic approach [17] in which the gamma-ray spectra -using all gamma-ray lines of all nuclides of every element- are fitted to the measured spectrum rather than line by line assignment and use of the most prominent gamma-ray peaks only.

When a 20 % detector has to be replaced, present day's (1996) large coaxial detectors, well-type detectors and use of Compton suppression spectrometer can attribute to an improvement in detection limits in INAA by, at the maximum, a factor of approximately 4 when sources can be counted on the detector's endcap. When larger distances have to applied with the coaxial detectors for geometrical reasons, counting the sources on the well-type detector instead may result in a further improvement by a factor of 1.5, provided that the activity of the sample is not prohibitively high. It should be noted here that these factors are derived from assumptions with respect to the size of the detectors, particularly the size of the well-type detector might be considered as conservative.

A laboratory's final choice is affected by many considerations amongst which ease-of-operation and price play an important role. Ease-of-operation is greatest with the very large detector, followed by the well-type detector which is less flexible with respect to be used with samples of different sizes, and sample changer design. The use of a CSS system introduces additional problems: limitations to the maximum activity, to sample size, complicated sample changing and sophisticated tuning of the electronics. If it is assumed that all sources to be counted can physically fit inside the well, the well-type detector shares a high improvement in detection limits with the best cost effectiveness. However, for an INAA laboratory processing samples of a great variety in compositions - and thus in induced radioactivities- the very large detector offers the greatest flexibility in operations. The higher investment may pay itself back taking into account this flexibility and the reduction of cases in which, because in case of an unexpected too high activity, analyses have to be repeated if a well-type detector had been used. With such a detector, the measurements simply can be repeated after positioning the source at a larger distance.

The conclusion of this all is that there is not one particular detector type that can be denoted as a panacea to improve the detection limits in INAA. The result of the calculation of the sensitivity improvement factor, as proposed in this chapter, should be used together with all operational considerations, and expectations with respect to the type of spectra to be analyzed and the need for a high energy resolution. When sample

sizes can be adjusted to fit inside the well dimensions, the well-type detector remains the most profitable choice for improvement of detection limits at low counting rates. It marks the correctness of the choice of the laboratory for INAA for well-type detectors in 1976, 1984 and 1988 above the contemporary alternative of a Compton suppression spectrometer.

5.7 REFERENCES

[1] M.L. Verheijke, 'Instrumental Neutron Activation Analysis developed for Silicon Integrated Circuit Technology', Thesis, Eindhoven University of Technology (1992)

[2] H.A. Das, J. Zonderhuis, 'Application of Anti-Compton Counting in Instrumental Neutron Activation Analysis',
J.Radioanal.Nucl.Chem. 114 (1987) 207 - 213

[3] P. Bode, 'Small Computers and Big Detectors: Powerful Tools in Activation Analysis',
Trans.Am.Nucl.Soc. 60 (1989) 6 - 7

[4] R.M. Keyser, T.R. Twomey, S.E. Wagner, 'The Benefits of using Super-large Germanium Gamma-Ray Detectors for the Quantitative Determination of Environmental Radionuclides',
Radioact.Radiochem. 1 (1990) 47 - 56

[5] P. Bode, R.M. Lindstrom, 'Advanced Detector Systems: what do they have to offer for Activation Analysis?',
J.Radioanal.Nucl.Chem. 167 (1993) 187 - 195

[6] J. Kučera, A.R. Byrne, 'Nickel Determination in Biological Materials at Ultratrace level by Fast neuron Radiochemical Activation Analysis',
J.Radioanal.Nucl.Chem. 168 (1993) 201 - 213

[7] G. Bellia, A. Del Zoppo, C. Agodi, R. Alba, R. Coniglione, E. Migneco, G. Russon, P. Sapienza, 'Performances of Large-volume p-Type HPGe Detectors',
Nucl.Instr.Meth. A284 (1989) 399 - 404

[8] C.M. Davisson, 'Interaction of γ-Radiation with Matter', in: 'Alpha-, Beta- and Gamma-Ray Spectroscopy, volume I (K.Siegbahn, ed.), North Holland, Amsterdam, 1968, 37 - 78

[9] IEEE Standard Test Procedure for Germanium Detectors for Ionising Radiation,
ANSI/IEEE 325 - 1986

[10] E.G.&G Nuclear Instruments Sales Engineers publication 'The Advantage' no. 177, March 1994

[11] M. de Bruin, P.J.M. Korthoven, 'The Well-Type Ge(Li)-Detector as a Tool in Radiochemistry',
Radiochem.Radioanal.Lett.44 (1980) 139 - 150

[12] S. Landsberger, 'Compton Suppression Neutron Activation Methods in Environmental Analysis',
J.Radioanal.Nucl.Chem. 179 (1994) 67 - 79

[13] L.A. Currie, 'Limits for Qualitative Detection and Quantitative Determination; Applications to Radiochemistry',
Anal.Chem. 40 (1968) 586 - 593

[14] J.A. Cooper, 'Factors determining the Ultimate Detection Sensitivity of Ge(Li) Gamma-Ray Spectrometers',

Nucl.Instr.Meth. 82 (1970) 273 - 277

[15] M. Rossbach, R. Zeisler, J.R.W. Woittiez, 'The Use of Compton Suppression Spectrometers for Trace Element Studies in Biological Materials', Biol.Trace Element Res. 26 (1990) 63 - 73

[16] S. Landsberger, G. Shift, J. Neuhoff, 'Nondestructive Determination of Arsenic in Urine by Epithermal Neutron Activation Analysis and Compton Suppression', Biol.Trace Element Res. 26 (1990) 27 - 32

[17] M. Blaauw, 'The Holistic Analysis of Gamma-Ray Spectra in Instrumental Neutron Activation Analysis', Thesis, Delft University of Technology, Delft (1993)

[18] J.-L. Reijss, S. Schmidt, F. Legelux, P. Bouté, 'Large, Low-Background Well-Type Detector for Measurement of Environmental Radioactivity', Nucl.Instr.Meth. A357 (1995) 391 - 397

[19] G. Harbottle, J.B. Cumming, 'Performance and Promise of a Compton Suppression Well Counter', Nucl.Instr.Meth. A353 (1994) 503 - 507

[20] F. El-Daoushy, R. Garcia-Tenorio, 'Well-type and Semi-planar Ge(HP) Detectors for Low-level Gamma-Ray Spectrometry', Nucl.Instr.Meth. A356 (1995) 376 - 384

[21] J.B. Cumming, P.P. Parekh, A.V. Murali, 'A Novel Approach to the Determination of Iridium via Ge-Coincidence/NaI(Tl)-Anticoincidence Gamma-Ray Spectrometry', Nucl.Instr.Meth. A265 (1988) 468 - 474

[22] S. Landsberger, S. Peshev, 'Compton Suppression Neutron Activation Analysis: Past, Present and Future', J.Radioanal.Nucl.Chem. 202 (1996) 201 - 224

5.8 LIST OF SYMBOLS

$a_{\gamma 1}$	abundance of gamma-ray 1 in the decay, photons/disintegration
A_m	reciprocal of fractional error
b	factor relating the energy resolution with the total number of channels included in the photopeak
B	average number of background counts per channel
$B_{C2,1}$	number of counts per channel due to the Compton continuum of the interfering gamma-ray 2 at the location of gamma-ray 1 of interest
$B_{N,1}$	natural background in counts per channel at the location of the gamma-ray 1 of interest
$B_{t,1}$	total number of background counts per channel at the location of gamma-ray 1
CSS	as subscript: to denote the presence of a Compton suppression spectrometer
$D_{m,1}$	minimum detectable disintegration rate for gamma-ray 1, s^{-1}
E_γ	gamma-ray energy, keV
$(f_S)_s$	sensitivity determining factor for the spectral shape S and a selected detector
$(f_S)_g$	sensitivity determining factor for the spectral shape S and a given detector
$(F_S)_{s,g}$	sensitivity improvement factor, for the spectral shape denoted with subscript S when comparing a selected detector with a given detector

$\{(F^*_S)_{s,g}\}^2$	price-indexed indication for the reduction factor of the counting time at equal sensitivities for the spectral shape S and when comparing a selected detector with a given detector
g	as subscript: to denote a given (or existing) detector
G	geometrical factor
k_Q	reciprocal of the requisite standard deviation
L_Q	determination limit, as defined by Currie
n	number of channels
N	net peak area, counts
N_m	minimum number of detectable counts
p_C	peak-to-Compton ratio
p_t	peak-to-total ratio
P_s	price of a selected detector/spectrometer
P_g	price of a given detector/spectrometer
R_1	detector resolution at the location of gamma-ray 1, keV
s	as subscript: to denote a selected detector
S	as subscript: to denote a spectrum shape
t	counting time, s
T	total number of counts under the photopeak
wg	as subscript: to denote a given well-type detector
ws	as subscript: to denote a selected well-type detector
$\varepsilon_{Co\text{-}60}$	the efficiency of the detector for the 1332 keV gamma-ray line of ^{60}Co, relative to the efficiency of a 3" * 3" NaI(Tl) scintillation detector
ε_i	interaction efficiency
ε_p	photopeak efficiency
$\varepsilon_{p,1}$	photopeak efficiency of gamma-ray 1
ε_t	total efficiency
σ_0	standard deviation of the total background at the location of the peak
σ_{Nm}	standard deviation of the net peak area (Cooper's notation)
σ_Q	standard deviation of the net signal (Currie's notation)
Ω	solid angle

CHAPTER 6 OPERATIONAL QUALITY ASSURANCE

The subjects dealt with in this chapter, have been also described in the following papers:

* I. Obrusník, M. Blaauw, P. Bode, 'Comparison of Routine INAA Procedures based on k_0 and k_{Zn}-Standardization',
  J.Radioanal.Nucl.Chem. 152 (1991) 507-518
* P. Bode, M. Blaauw, I. Obrusník, 'Variation of Neutron Flux and Related Parameters in an Irradiation Container, in use with k_0-based NAA',
  J.Radioanal.Nucl.Chem. 157 (1992) 301-312
* P. Bode, M.J.J. Ammerlaan, M. Koese, 'The Half-lives of Na-24 and Ba-131',
  Int.J.Appl.Rad.Isotop. 42 (1991) 692 - 693
* M. Blaauw, M.J.J. Ammerlaan, P. Bode, 'Quantification of Sources of Variation in Neutron Activation Analysis',
  Int.J.Appl.Rad.Isotop. 44 (1993) 547 - 551
* P. Bode, 'The role of Primary Standards, Reference Materials and Laboratory Intercomparisons in an Accredited INAA Laboratory',
  Trans.Am.Nucl.Soc. 17 (1994) 46 - 47
* P. Bode, C.P. van Dijk, 'Operational Management of Results in INAA Utilizing a Versatile System of Control Charts',
  Accept. for publ. in J.Radioanal.Nucl.Chem.
* M.J.J. Ammerlaan, P. Bode, 'Modern Performance Control of Gamma-Ray Spectrometers for INAA',
  Accept. for publ. in J.Radioanal.Nucl.Chem.

6 *PROCESS IMPROVEMENT BY QUALITY ASSURANCE*

6.1 QUALITY ASSURANCE OBJECTIVES

"*... Until a measurement operation has attained a state of statistical control, it cannot be regarded in any logical sense as measuring anything at all...*" [1]. In analogy to Eisenhart's statement from 1952 it can be stated that the quality and uncertainty of data must be known before it can be used in a logical way. The quality of data may be defined as the degree of excellence to fulfil customer's demands[1]. In INAA -as in many other methods of elemental analysis- the quality of the data is affected by the given fact that it is impossible to analyze sample and standard under identical conditions. Quality control[2] procedures were traditionally applied at the laboratory for INAA, and comprised the analysis of blanks, the analysis of (certified) reference materials and software for evaluation of reference material results in accordance to control chart principles.

Until 1991 the quality control was not embedded in a program for quality assurance[3] to ensure the quality of the analyses. The consequences of this all became clear upon evaluation of the results produced between 1986 and 1990:

(i) Sometimes, for alleged higher effectiveness and speeding-up, no reference materials and blanks were included in the batch processed.

(ii) Analysts decided themselves on the quality of their results. However, there were no unambiguous criteria specified for such an approval. As a rule-of-thumb a 10 % difference between observed value and certified/consensus value of the reference material was considered acceptable. However, the software did not print these certified/consensus values with the reported data. Whether the analyst indeed checked the data with the certificates, or used the available additional software for this (see below, (iii)) was not verified, nor registered. Additionally, the analysts were apparently not hindered by a possible conflict of interest with the purpose of the analysis. It could no be excluded that objective interpretation was sometimes less careful when dead-lines were approaching or already exceeded.

---

1 *With 'customer' the person or body is denoted who supplies the samples, regardless whether this is an employee of the laboratory itself, a scientist from one of the applied fields or a third party.*

2 *Quality control is defined [2] as " The operational techniques and activities that are used to fulfil requirements for quality".*

3 *Quality assurance is defined [2] as " All those planned and systematic actions undertaken by the organization necessary to provide adequate confidence that a product or service will satisfy given requirements for quality".*

(iii) Software was available for statistical analysis of results of reference materials, so that the analysts were alarmed if the difference between the observed concentration and certified or consensus value is larger than 2 or larger than 3 times the combined standard deviation. However, the data-bases were not maintained and could also contain false data, thus giving erroneous indications on the quality of the new results.

(iv) Single element standards were prepared from stock solutions, the quantities were determined on volumetric considerations though no records were held of the calibration of pipet and volumetric flask. Evaluation of the standards of a Cd stock solution used in 1989 show that the ratio between observed and nominal concentration was 1.14 ± 0.11 ($N = 12$, 1 σ with σ = estimate of the standard deviation); in 1988 standards were prepared resulting in 1.02 ± 0.03 (1 σ, $N = 15$). For Hg element standards this was 1.06 ± 0.07 (1 σ, $N = 7$). The high standard deviation indicate problems with reproducible pipetting. This should be compared to a standard deviation of 1 to 2 % which is considered to be technically feasible.

(v) On basis of the results of the control samples prepared from primary standards, the users adapted correspondingly the element concentrations in the results of the samples overlooking e.g. the possibility of errors in pipetting. Sometimes the concentration were modified by 20 %. No evaluation took place of the cause of such a deviating result.

As a result disputes arised between laboratory and customers on the reliability and comparability of data, a systematic approach to assess and eliminate sources of errors was not possible and any assessment occurred on an ad-hoc basis. The need to implement the quality control activities in a system for quality assurance was anticipated on by 1990 by both the users (i) to accomplish reliable and comparable data for large scale research programs, and (ii) uniformity in the decision process- ; and by the management of the laboratory on basis of its responsibility for the laboratory's outputs. The latter was emphasized by the importance of the increasing third party services.

The objectives of the quality assurance are

(i) To upgrade the overall quality of laboratory performance.

(ii) To maintain a continuing assessment of the quality of data generated.

(iii) To demonstrate that the quality control operations have been carried out.

(iv) To assure traceability of reported data.

(v) To accomplish customer satisfaction.

6.2 QUALITY ASSURANCE IN THE LABORATORY FOR INAA

The quality assurance[4] at the laboratory for INAA has been designed to fit in the quality system, described in *Chapter 7*. This quality system has been implemented to improve the internal managerial need of the laboratory and the overall effectiviness of all operations. As such, the quality assurance is composed of, and interacts with various related activities such as

(i) Internal training and qualification to assure the competence of the analysts.
(ii) Management of equipment and materials, to assure their fitness for the purpose.
(iii) Calibration, standardization and statistical evaluation.
(iv) Documentation and harmonized, validated operations by standard operation procedures to assure traceability and accountability of the data.
(v) Quality control.
(vi) Checking and reporting procedures.
(vii) Participation in laboratory intercomparisons and proficiency testing.
(ix) Inspection, supervision and audits for independent performance assessment.

The quality assurance is further characterized by the definition of quantified criteria for approval in the standard operating procedures (SOP's), and by the preventive and correction actions related to identified sources of error. Without pretending to be complete, errors in the results may occur due to differences between the analysis of sample and standard in

(i) Operating procedures:
- selection of (routine) analysis protocol, equipment and facilities; selection of optimal conditions.

(ii) Operational activities:
- sample preparation (e.g. contamination, element loss, moisture, weighing, geometry).
- standard preparation (e.g. purity, stoichiometry, isotopic abundance in chemicals, pipetting, weighing, geometry).
- irradiation (irradiation time, neutron flux gradients, neutron spectrum).
- measurement (e.g. measurement time, dead-time/pile-up, geometry, background, logistics).

---

[4] *Textbooks and recommendations exist on methods of quality assurance [3, 4, 5], statistical manipulation of data and acceptance tests [6, 7, 8], and methods for independent quality assessment such as proficiency testing [9, 10]. In addition IUPAC, in cooperation with ISO and AOAC, has issued harmonised guidelines for internal quality control [11] and proficiency testing [12].*

Table 6-1. Overview of principal sources of errors, the possibility to quantify them in the overall estimate of precision, the possible preventive and corrective actions and the impact of differences which only affect the samples, not the controls.

** abbreviations used: QA: quality assurance program, RM: reference material analysis, B: blank analysis, SOP: Standard Operating Procedure, C.S.: Common Sense, SPC: Spectrometer Performance Control; -: not quantifiable respectively no actions possible respectively not protected against incidental errors*

Abbreviations between brackets indicate that the assurance is only partly.

	Quantifiable ?	Preventive actions*	Corrective actions*	Protected against incidental errors ?*
Sample preparation				
contamination	only in blank	lab. management	QA (RM + B)	-, perhaps B
element loss	-	C.S.	QA (RM)	-
moisture	yes, measurement	SOP's, C.S.	-	-
weighing	yes, calibration	SOP's	via software	-
geometry	yes, filling height	SOP	-	-
Standard preparation				
purity chemicals	yes, certificates	SOP	re-analysis	analysis
stoichiometry chemicals	-	SOP	re-analysis	analysis
pipetting	yes, calibration	SOP's		multiple samples
weighing	yes, calibration	SOP's		-
geometry	yes, filling height	SOP		analysis
Analysis Protocol				
selection of (routine) protocol	-	SOP, C.S.	re-analysis	SOP
selection of optimal conditions	-	-	re-analysis	-
Irradiation				
irradiation time	-	(SOP)	QA (RM)	QA
flux gradients	yes, via flux monitors	software	QA	QA
neutron spectrum difference from reference conditions	-	-	via software	(analysis)
Measurement				
measurement time	yes, via pulser peak	pulser		in-line
dead-time/pile-up	yes, via pulser peak	pulser		in-line
geometry	yes, via fill height	mechanical	(SPC)	analysis
background	yes, via measurement	SPC	QA (B)	-
logistics	-	SOP	(QA) C.S.	-
Data interpretation				
analysis	yes, via software	software	software	in-line
neutron self-shielding	yes, indicative	C.S.	flux monitors	partly via QA
gamma-ray self-absorption	yes	C.S.	software	yes, via software
standardization parameters	-	calibrations	re-calculation	yes, and via QA
human eye	-	training	software (QA)	C.S., QA
Human performance				
exchange of samples	-	SOP	(QA), C.S.	-
errors and blunders	-	-	QA	-

- data interpretation (e.g. analysis, neutron self-shielding, gamma-ray self-absorption, catalogue).

(iii) Human performance:

- interchange of samples, mistakes, transposing errors etc.

In *Table 6-1* it is shown how these sources of error may be accounted for by preventive and/or corrective actions. The preventive actions are based on a priori expectations with respect to the probability of errors from professional experience. The corrective actions are based upon the assumption that the errors have a systematic character, and that these systematics are reflected in the quality control (like by the results of the reference material analysis and blank analysis).

Incidental and random errors are difficult to cope with, but this is irrespective of the analysis technique. The SOP's call, wherever possible for the analyst's attention to possible pitfalls; the system for non-conformance management contributes to corrective actions also on incidental and random errors prior to release of the report. In *paragraph 6.3.1* is described how the second-line quality control and third-line quality control also contribute to some assessment of incidental errors.

The following paragraphs focus on the quality control activities.

6.3 QUALITY CONTROL IN THE PROGRAM FOR QUALITY ASSURANCE

6.3.1 Introduction

A procedure is in statistical control when results consistently fall within established control limits. The laboratory for INAA processes a great variety of samples types (rock, sediment, biological, plastics) with also sometimes strongly varying composition; moreover the samples may be related to a variety of studies ranging from scientific research programs to industrial activities. In many of these cases, consistency of the absolute value of the results is more important than the degree of uncertainty. Therefore, the quality control at the laboratory for INAA is directed to the assessment of the accuracy of the results. The accuracy is defined as the closeness of the agreement between the result of a measurement and a true value of the measurand [13]. Accuracy thus is a qualitative concept, and may be expressed in terms varying from e.g. 'poor' to 'excellent'. Best estimates of 'true' element concentrations are obtained from the information available on primary standards, or from certified element concentrations of reference materials.

concentrations are obtained from the information available on primary standards, or from certified element concentrations of reference materials.

An objective assessment of the 'closeness of agreement' is obtained by statistical techniques. Preferentially this assessment should be thus informative that possible sources of non-conformance can be identified quickly and the laboratory can organize effective corrective or preventive actions.

The calculation of the standardized difference or z-value of a result by

$$z_i = \frac{C_i - C_{ref,i}}{\sqrt{\sigma^2_i + \sigma^2_{ref,i}}} \qquad 6\text{-}1$$

is an accepted approach to establish if the result meets the control limits as defined by the laboratory. In this,

C_i = concentration of element i in the reference material analysis
$C_{ref,i}$ = concentration of the certified or consensus value for element i
σ_i = uncertainty of the concentration of element i in the reference material analysis
$\sigma_{ref,i}$ = uncertainty of the certified respectively consensus value for element i

The definition of the standardized difference complies with the use of the z-score in proficiency testing [9, 12].

Heydorn [14] elaborated further on this in his approach of the 'analysis of precision' of results in NAA. In the analysis of precision a factor 'T' is calculated from the results of duplicate analysis of M different materials:

$$T = \sum_{i=1}^{M} \frac{(C_i - C_{ref})^2}{\sigma_i^2 + \sigma^2_{ref}} = \sum_{i=1}^{M} z^2_i \qquad 6\text{-}2$$

and it is determined if the value of T can be described by a χ^2-squared distribution. Analysis of precision allows for the detection of systematic errors and the method is applicable for continuous quality control. However, no indication is obtained on the cause of the error and the method is not suitable for detecting a bias of constant nature.

At the laboratory for INAA use is made of the z-value which is tested against the quantified criterion for approval of the results: $|z| < 3$; which means that the individual result of the control sample should be in the 99 % confidence interval of the target value. This criterion is applicable for all measures used for internal quality control, viz. (certified) reference materials, working standards, blanks, neutron flux monitors. Identification of the

sources of problems is facilitated by the use of control charts and extensive options to manipulate and sort the data and variables.

6.3.2 Means of quality control[5]

Two basic assumptions have been made:

(i) The analyst should be able to perform his own controls, and should have tools, i.e. criteria, to evaluate them.

(ii) The analyst should have the mentality and opportunities to improve the quality of his work.

INAA is not a fully automated 'black-box' technique but a labour intensive method with many human interactions. Human errors affecting the results should be anticipated on. One such an error may result from the conflict of interest an analyst deals with when controlling his own results. Therefore the quality assurance program includes at several levels a separate control by an independent body or person.

The quality control in the laboratory for INAA is performed at three levels:

'FIRST-LINE' QUALITY CONTROL

This control refers to the direct assessment of any systematic errors during the analysis of the samples, possible trends, and human errors. Several tools have been implemented:

(i) Either a sample of a (certified) reference material or a primary control standard is added together with a blank capsule to each batch of samples processed. Both quality control samples are processed simultaneously and physical closely following the unknown samples i.e. they follow the same route as all other capsules from weighing-in to counting.
The results of the analysis of these quality control samples are compared with respectively tabulated certified and uncertified values, and with experimentally determined concentrations representing a 'standard' blank. Standardized differences

---

5 *It has been assumed that prior to the analysis, all conditions are fulfilled for a proper execution of the analysis, such a spectrometer performance, including energy and efficiency calibration and element calibrations.*

are calculated for each of the concentrations reported in the analysis of the two quality control samples.The software prints alarm flags in the report when $|z| > 2$ respectively > 3.

A databank is created from these analysis results with which each individual new result is compared. This comparison occurs in the same way via the determination of a standardized difference. The control follows the conventions also in use with control charts of the format firstly pioneered by Shewhart [15] Alarms are generated and printed in the report when the 'alarm' level ($|z| > 2$) or the 'out-of-control' level ($|z| > 3$) is exceeded, and when trends occur (over 3 successive deviations of $1 < |z| < 3$). Each of these cases is identifiable from the print format.

(ii) During irradiation the sample is paired with one neutron flux monitor, or enclosed by two neutron flux monitors when the accuracy of the determinations has to be better than 10 %. A polynomial, representing the neutron flux gradient, is fitted through the calculated neutron fluxes. Similarly as in the above, z can be calculated as the weighted difference between measured flux and flux derived from the polynomial fit. Identifiable alarm flags are printed in the report when $|z| > 2$ or > 3.

(iii) The analyst inspects the data entered by himself in the computer system with his observations on the hard-copy forms: irradiation facility, - date, - time and duration, sample- and flux monitor weights, and sample codes.

(iv) The analyst inspects if the results comply with the customer's demands in terms of the number of elements reported, concentrations, precision and detection limits. This seems to be a straightforward comparison, but also some common sense is required to decide whether a result reflects a realistic situation. In case of doubt the analyst consults his superior.

'SECOND-LINE' QUALITY CONTROL

Since the composition of reference materials is a priori known, it cannot be excluded that an analyst applies different care to the processing of the reference material and the real samples. Using blind duplicate samples, the second line quality control aims to assess the performance of the analytical procedure and the analyst with respect to sample preparation, sub-sampling, interchange of samples and other human errors which are difficult to cover via the first line quality control.

The frequency of these analyses depends on the availability of suitable duplicates. To ensure true 'blindness' by preference such samples have to be provided by the customer. The success of the analysis of blind duplicates as a tool for performance assessment depends on the quality of the two samples in terms of homogeneity. As an example some results of

blind duplicate analyses are given in *Table 6-2*. The samples '*a*' in pairs of duplicates 1-4 were analyzed in 1990 before the introduction of the quality assurance; the samples '*b*' in 1992, after the introduction. Differences in the duplicates are also related to a change in gamma-ray spectrum software and standardization parameters.

Table 6-2. Examples of results of blind duplicate analyses. Pairs of duplicates 1-4 analysed in 1990 (a) and in 1992(b). Pairs of duplicates 5 and 6 all analysed in 1993 (a) and 1994 (b). All concentrations and uncertainties in mg.kg^{-1}; uncertainties reported as 2σ

sample no.		Cd	Br	Sb	Ba	Cr	Hg
1	*a*	2400 ± 50		0.028 ± 0.002	193 ± 8		
	b	2760 ± 60		0.034 ± 0.008	214 ± 10		
2	*a*	5560 ± 100		38.9 ± 0.8		288 ± 6	
	b	6090 ± 100		38.9 ± 0.8		306 ± 12	
3	*a*	33100 ± 700					11700 ± 200
	b	3500 ± 70					1220 ± 20
4	*a*	1980 ± 40					415 ± 30
	b	1960 ± 40					445 ± 10
5	*a*		9.53 ± 0.4	0.365 ± 0.088			
	b		9.35 ± 0.4	0.282 ± 0.079			
6	*a*	1.45 ± 0.20	1.10 ± 0.08	0.231 ± 0.02			
	b	1.70 ± 0.20	1.22 ± 0.09	0.249 ± 0.02			

The need for quality assurance is clearly demonstrated by the third pair of samples. Because of the absence of sufficient records and raw data on the analysis in 1990 the real reason of the large difference could not be traced anymore but most likely a sample or flux monitor weight has been introduced erroneously (decimal point).

The results of pairs 5 and 6 were obtained in 1993 and 1994, after the quality assurance became operational. The results did not give any ground to preventive or corrective actions.

'THIRD-LINE' QUALITY CONTROL

This control comprises also the proficiency testing of the laboratory. When the report of the proficiency test is issued it can be assessed whether the choice of the analysis protocol has been the most optimal on basis of the scarce information available.

The Analytical Methods Committee of the Royal Society of Chemistry recommends to conduct proficiency tests not less than quarterly [12]; in the harmonized protocol from IUPAC/ISO/AOAC any frequency between once every 2 weeks and once every 4 months is considered to be appropriate. The laboratory for INAA participates in several intercomparison programs, some of them at a bimonthly schedule. The following aspects are taken into consideration before participating:

(i) The fitness of INAA for the analysis of the relevant materials, the elements to be determined and the concentration levels.
(ii) The expected or described quality of the material in terms of homogeneity and stability.
(iii) Dead-line for reporting.
(iv) The availability of the final results of the intercomparison, and insight in the way the results have been processed.
(v) Costs.

6.3.3 Preventive and corrective actions

Preventive and corrective actions are undertaken as quick as required to ensure improvement of the performance of the laboratory and to avoid repetition of work, irritations and quality costs. Prompt feedback is given by the first-line quality control. Typical systematic errors revealed in the first line quality control are, (in arbitrary order):

(i) Errors in data, entered in the computer by the analyst himself (weights, irradiation date, time and duration, sequence of samples and flux-monitors etc.).
(ii) Errors due to gamma-ray self-attenuation, geometrical errors during irradiation and counting.
(iii) Errors in spectrometer performance (energy calibration, peak-shapes etc.).
(iv) Interchanged samples and flux monitors.
(v) Errors in preparation of neutron flux monitors.
(vi) Contaminations.
(vii) Trends in the type of deviation of a concentration (reference materials).
(viii) Conflicts in software.

The respective manager (spectrometers, computer, laboratory or general) may decide on basis of the non-conformance in the first-line quality control to postpone all further activities until the source of the error has been found, or corrected for. The manager's powers allow for such immediate decisions, irrespective of other work planned for. Often non-conformance has led to alteration of the standard operating procedures (SOP's).

Complying with this are the preventive actions undertaken to assure that the analyses are carried-out with tools fit for their purpose. In the period 1992 - 1995 at only 4 occasions the measurement of a batch of samples had to be repeated because of a malfunction of counting equipment in between performance tests. Unfortunately, no records have been kept of the repetition of analyses in the preceding period.

A preventive/corrective action is the authorization control the reports have to pass after the first-line quality control. Now the first-line quality control is repeated by a person not having any conflict of interest with the analyses, preferentially and if possible by a person of longer experience with INAA than the performing analyst. In this control also insight in trace element concentration patterns is entered to spur any erroneous conclusions by the analysis' software.

The professional skills of the analyst, his experience with the materials analyzed and element concentrations to be expected and his ability to 'translate' a sample's description to expected element concentration levels also are a form of preventive/corrective actions prior to release of a report. As an example, a geologist may decide how realistic the presence or absence of certain elements -like the rare-earth elements and their pattern- is in view of a given rock or mineral type and its known major element composition; and decide on the acceptance of the results or the need for a corrective action.

The results of the reference material analyses are evaluated via the control charts (see *paragraph 6.4*) possibly resulting in preventive/corrective actions. The results of the second-line quality control (blind duplicates) and third-line quality control (intercomparisons and proficiency testing) become available after a certain time has elapsed which may vary from weeks (duplicates) to many months (intercomparisons and proficiency testing). As such, these controls can not be used for immediate process control. The results from blind duplicate analysis haven't hitherto revealed unknown sources of error. As a result of a case of non-conformance in a laboratory intercomparison, an additional SOP was developed for a check by an independent person on data, transposed to the intercomparison reporting form. Also reports from laboratory intercomparisons initiated renewed standardizations, e.g. for Hg.

Corrective actions requiring corrections on previously reported data have not been necessary in the period 1992 - 1995 in which the quality assurance system has been active. In one case the evaluation of a deviating result between blind duplicates revealed a systematic error within the customer's organization rather than within the laboratory for INAA.

Corrective actions may result in operational research for e.g.:

(i) Systematic long-term trends in observed concentrations of reference materials.

(ii) Correlations between differences in observed and expected concentrations, and reference material type.
(iii) Correlations between differences in observed and expected concentration, and concentration level.
(iv) Systematic variations in the results of neutron-flux determinations.
(v) Correlations between observed and expected concentrations, and analysis protocol.
(vi) Need for improved prediction of optimal analysis protocol.
(vii) Interferences by nuclear reactions not accounted for, incomplete or incorrect gamma-ray catalogues and nuclear data tabulations.
(viii) A systematic bias due to errors during element standardization.
(ix) Suspected errors during sub-sampling, sample preparation.
(x) Correlations between performance and analyst.

As an example, systematic biases of results measured at different spectrometers have led to enhanced attention for the determination of standardization parameters the quantitative analysis. In this work, also such fundamental parameters as radionuclide half-life have been re-established [16]. It has been observed that many gamma-ray energy tables [e.g. 17, 18] are incomplete, thus hampering spectrum interpretation. Lacking data are typically sum-peaks, single and double escape peaks and even minor photopeaks. The IRI gamma-ray catalogue for INAA [19] is derived by conversion of the decay schemes given by Browne and Firestone [20] and include not only the full-energy photopeaks, but also the single and double escape peaks and sum-peaks.

6.4 CONTROL CHARTS FOR QUALITY ASSURANCE

One of the associated techniques in quality control is the representation of observed variables in control charts according to the type developed by Shewhart [15]. Usually, the variable is plotted in time order. The usefulness of control charts in nuclear analytical measurements has further been demonstrated by Seymour et al. [21].

In multi-element INAA more information is required to identify the source(s) of variation and to apply appropriate actions, than just the variation of e.g. the concentration with time. Deviations from certified or consensus values may be caused by e.g. (i) improper standardisation, (ii) spectral interferences, including the signal-to-noise ratio for the gamma-ray related to the analyte, (iv) the performance of the analyst, (vi) the performance of the equipment, and (vi) the fitness of the reference materials and/or the quality of the certified/consensus concentrations.

The results and underlying data (sample code, date of measurement, name of analyst)on the two quality control samples (reference material and blank) are stored in a databank. In 1995, the databank contained compiled analysis results on 20 geological reference materials (issued e.g. by USGS, Geostandards Newsletter etc.), 16 Standard Reference Materials issued by NIST, 3 Certified Reference Materials issued by BCR, 10 Certified Reference Materials issued by various organizations including the IAEA, and 7 in-house single-element laboratory control samples. Some of these reference materials have been analyzed over 100 times. Each reference material or in-house control sample -such as a laboratory working standard[6]- is specified by its certified and/or consensus values respectively the calculated concentration, and the associated uncertainties. The estimated uncertainty for laboratory working standards is based by assessment of the 'uncertainty budget' viz. the combination of individual uncertainties such as standardization parameter, neutron flux, counting statistics in sample and flux monitor.

It has been recommended [3] to have at least 20 individual samples of a reference material preferably on separate dates by different analysts before a new control chart operational can be used as a tool for active process-feedback. As a compromise -to keep things workable for a small group of analysts- new reference materials are firstly analyzed in a batch of 14 samples at a time, sometimes in the framework of the training program of new users.

The control charts can be generated by selecting the entity to be displayed, the X-axis variable and its order of sorting and the Y-axis variable. The charts can be made to inspect the results from a single analysis, or from a group of analyses. In each control chart not only the selected comparison is made, but, more importantly, in a separate graph the standardized differences are given. *Table 6-3* gives an overview of the various options for display and selection of parameters. An option exists to get direct access from any of the plotted data-points to the underlying information on the spectrum-code, date of measurement and name of analyst. It should be emphasized that at the laboratory for INAA the control charts are visually inspected for identifying sources of non-conformance, and not for statistical evaluation. Some of the control charts will be discussed below to illustrate the power of these presentations.

---

[6] *A laboratory working standard is a standard prepared from or referenced to a primary standard.*

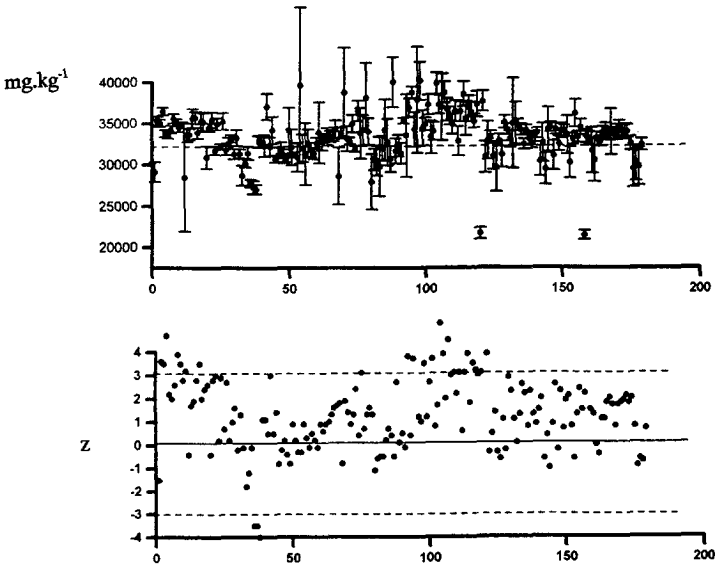
Table 6-3. Overview of control charts for evaluation of quality control sample data. The selectable parameters listed in the third column may be sorted either one of the functions given in the fourth column

Y-axis	X-axis	Selectable parameter	Sort function for selectable parameter
concentration	measurement sequence number	reference material and element	a. concentration b. date c. sample code
concentration	type of reference material	1. element 2. spectral interference	a. concentration b. concentration ratio with interfering element c. standardized difference
normalized concentration	all elements	1. reference material 2. measurement	a. atomic number b. relative uncertainty c. standardized difference

6.4.1 Control charts for comparison of concentration with measurement date

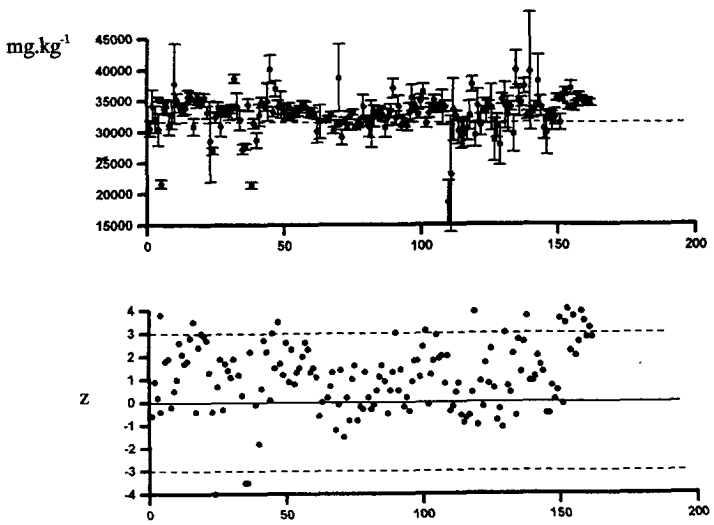
This control chart reveals incidental deviations and trends in the concentration of a selected element in a selected reference material. It helps with the identification of analyst, spectrometer, or date-dependent results. An example of such a control chart is given in *Figure 6-1a-e*. The chart in *Figure 6-1a* reveals between measurements 90 and 140 poorer reproducibility in results for Ca due to a faulty operation of a loss-free counting unit. When sorted with sample-code (*Figure 6-1b*) also analyst-dependent results were observed, e.g. in the data now sorted as measurements 150-160, 60-95, 35-50, which could be attributed to systematic differences in manual fitting of the 3084 keV peak in the spectrum. Here the *z*-score chart reveals the information more clearer than the concentration control chart.

The results with time for As in NBS 1572 'Citrus Leaves' show slighter lower values in the measurements 20 - 50 (*Figure 6-1c*). The underlying data list does not indicate any analyst dependency; also other elements determined in this R.M. in the same period are slighter lower, indication a systematic bias probably related to the sample handling (drying).



a

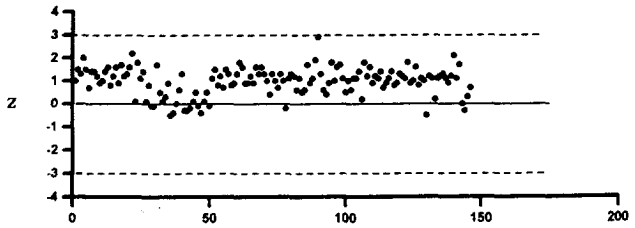
Measurements of Ca in NBS 1572, Citrus Leaves, sorted with time



b

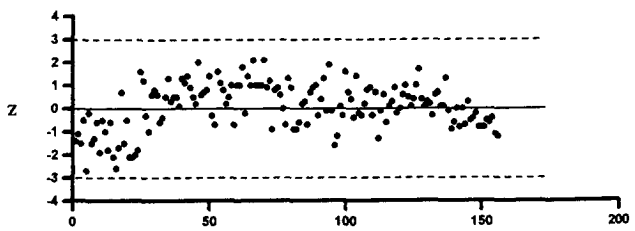
Measurements of Ca in NBS 1572, Citrus Leaves, sorted with sample code

Figure 6-1. Control charts (concentrations and z-values) for comparison of the concentration of an element with measurement date; fig.6-1a: results sorted with measurement date; fig.6-1b: results sorted with sample code



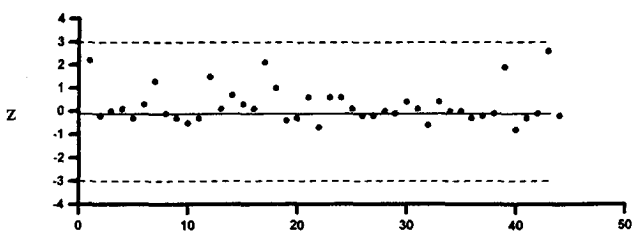
c

Measurements of As in NBS 1572, Citrus Leaves, sorted with time



d

Measurements of Fe in NBS 1632b, Bitumous Coal, sorted with time



e

Measurements of Sr in NBS 1632b, Bitumous Coal, sorted with sample code

Figure 6-1. (continued). Control charts (z-values) for comparison of the concentration of an element with measurement date; figs. 6-1c, 1d: results sorted with measurement date, fig.6-1e.: results sorted with sample code

The effect of renewed standardization is visualized by the chart in *Figure 6-1d* for Fe in NBS-1632b; the standardization constant was adjusted in the period of time approximately corresponding to measurement 30-35. Slightly lower Fe-concentration can be noticed in the most recent datapoints (measurements 140-155). These measurements correspond with samples from a new bottle of this reference material. No systematic trends

have been observed for the other element concentrations. More analyses are needed to identify the source of this small difference.

Another example how the control chart can be used to establish the competence of analyst is illustrated by *Figure 6-1e*, in which the results for Sr in NBS-1632b are sorted by sample code in which one of the alphanumerics identifies the analyst. There appears to be no significant analyst dependent difficulty with the fitting of the 511 - 514 keV doublet.

6.4.2 *Control charts for comparison of the mean concentration of a group of analyses versus the type of quality control sample*

Together with the previous control chart, this chart can give an answer to the question if an element re-standardization is necessary and/or if there is a systematic, concentration dependent, deviation possibly related to the type of material e.g. due to characteristic spectral interferences. Also the results from intercomparisons and proficiency testing are included in this presentation, thereby allowing for a judgment on the laboratory's performance in view of the by itself established capabilities. This chart is depicted in *Figure 6-2*.

The chart *6-2a* makes clear that, on basis of all reference materials in which Ca has been determined, there is no urgent need for renewed standardization. The number of measurements of the various reference materials varied from 5 to 180. For only two out of 38 reference materials $|z| > 2$; none of the results is beyond 3 standard deviations of the certified/consensus value. The sorting of the same values as a function of concentration (*Figure 6-2b*) illustrates the large dynamic range of INAA: over more than three orders of magnitude (157.5 $mg.kg^{-1}$ for NBS 1577a to 36 % for NIST-1c) the Ca-results are not biased by the concentration-level.

Via sorting on the ratio of the concentration of an element of interest to e.g. the concentration of an interfering element, this control chart can be used to monitor any errors due to spectral interferences by e.g. narrowly spaced peaks, or due to interfering nuclear reactions. With respect to the first application this control chart assists in obtaining insight in the performance of the technique for the determination of the respective element, at a certain concentration level, in a given matrix. Systematic concentration dependent errors may be revealed which may be due to signal-to-noise problems. Examples are the spectral interferences of narrowly spaced peaks and the location of small peaks on a background with a sharp gradient at the position of the peak; the presence of small interfering peaks not yet included in the gamma-ray catalogue, and contaminations not revealed by the blanks.

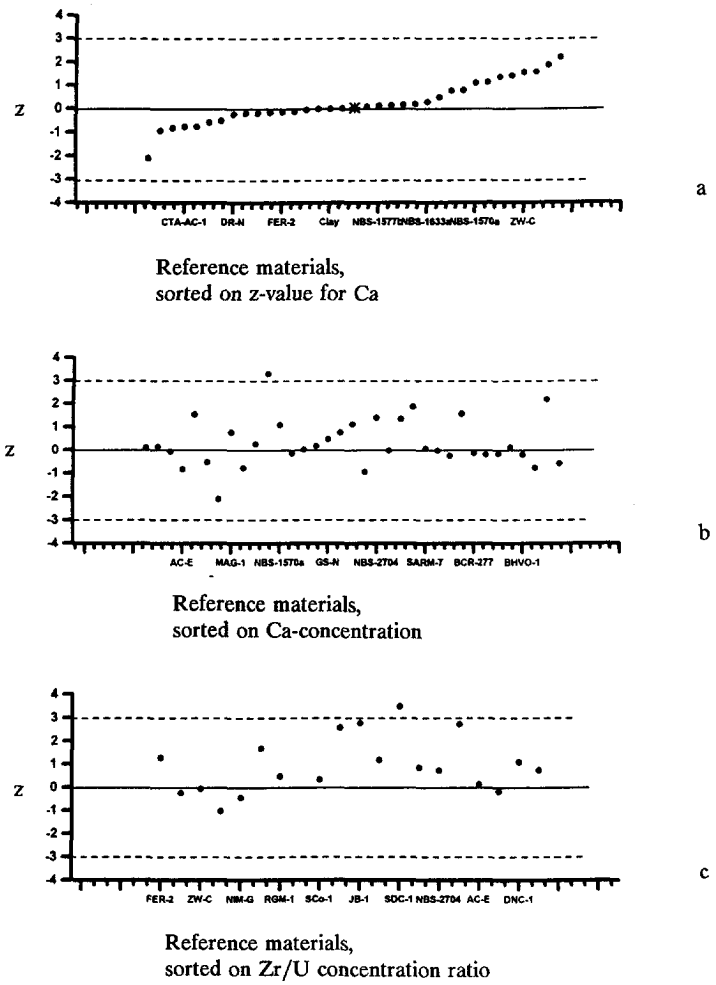


Figure 6-2. Control charts (z-values) for comparison of mean concentration of a group of analyses versus the type of control sample; Fig.6-2a: results sorted on z-value (marks a sample from proficiency testing, see text), fig. 6-2b: results sorted on concentration in control sample, fig.6-2c: results sorted on ratio of concentration of element of interest with interfering element. Note that for sake of clarity only few names of reference materials have been depicted on the X-axes*

With respect to the second application -potential errors due to interfering nuclear reactions- such a control chart is depicted in *Figure 6-2c* for the Zr-concentration and the effect of the correction for fission product contribution due to the presence of U. Even though the ratio of Zr to U ranges from 4.1 to 430, no systematic trends occur.

6.4.3 Control charts for inspection of the normalized concentrations of all elements

These charts give an impression on the way reference materials are handled as such by the analyst. The option to sort the elements of the X-axis allows for rapid inspection and 'retrieval' of elements. A systematic bias for all elements in only one reference material may be related to an erroneous way of e.g. moisture content correction, drying or storage. This is illustrated by the charts in *Figures 6-3a,3b* in which the results of individual measurements are plotted. Though in both cases the results would technically be acceptable since none of the values is outside the $| z | > 3$ range, the measurement underlying the data depicted in *Figure 6-3a* is clearly affected by a systematic error, later identified as an incorrect estimate of the neutron flux. As such, the systematic higher values in the reference material do not reflect any systematic problem with the samples simultaneously processed. The plot of the group mean against the certified value shows the for more than 100 analysis by 8 different analysts, the results are meeting the laboratory's own norms.

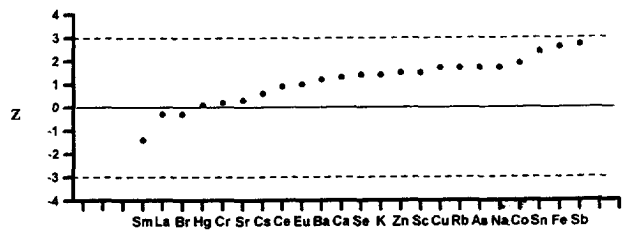
It has also been observed with these control charts that groups of elements, typically determined in one of the various measurements (like the elements Al, Mn, Ti, Mg, V, Cl; or As, Br, Na, K, La) show a bias. This may indicate a timing problem, a wrong geometry- or efficiency correction, wrong neutron flux or wrong dead-time correction.

Another remarkable outcome of this type of control charts is the difference in performance for reference materials like the NIST-2711, and the geological reference material ZW-C zinnwaldite (*Figures 6-3c, 6-3d*), issued by the International Working Group associated with Geostandards Newsletter. Baring in mind that all analyses have been carried out with the same calibration parameters, the differences in results seem to be related with the quality of the certified respectively consensus values.

The third option in sorting -by the relative uncertainty of the measured value- can reveal the influence of proximity of the detection limit: close to the detection limit uncertainties are high. Still, as depicted in *Figure 6-3e*, this should not imply that such results tend to drift away from the certified values.

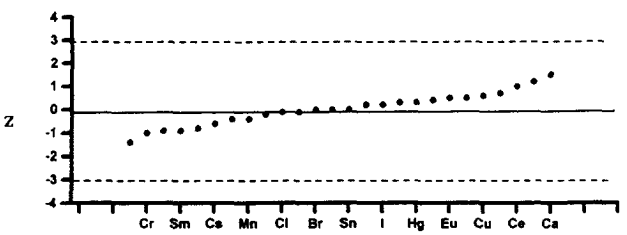
The analyst inspects the control charts immediately following the analysis and particularly when the analysis' report shows alarm-flags which cannot easily be accounted for. An option exist to 'zoom-in' on specific points in the control charts. The information list is displayed on the history of the sample analysis -such as irradiation date and -time, measurement date and -time, and spectrometer(s) used- allows for further investigation on possible correlations between outliers and e.g. the performance of the analyst or equipment which performance history has also been made recoverable in the quality system.

The control charts are also inspected randomly as part of the periodic verification of the quality system, in its turn a part of the internal quality audit program (see *Chapter 7*). To serve the annual quality audits, control charts can be generated related to only the analysis of a given book-year. Thus, the laboratory's performance from year-to-year can be evaluated.



a

Elements in NBS 1572, Citrus Leaves,
sorted on z

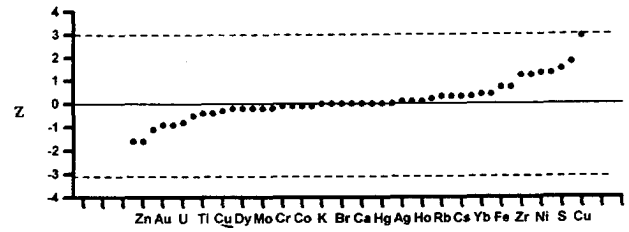


b

Elements in NBS 1572, Citrus Leaves,
sorted on z

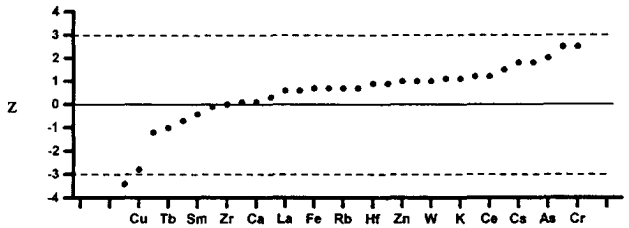
Figure 6-3. Control charts (z-values) for inspection of the normalized concentrations of all elements in one control sample; fig.6-3a,3b: results of a selected measurement, sorted on z-values. Note that for sake of clarity not all elements have been depicted on the X-axes

The control charts also permit further-in-house evaluation of the results of proficiency testing and interlaboratory studies. Upon availability of the final report of such a test, a new quality control material is specified in the databank using the consensus values, and the raw data are analyzed again. Now the performance on this special sample can be compared with the laboratory's general performance on other reference materials. In the control chart depicted in *Figure 6-2a* such a sample related to proficiency testing has been marked.



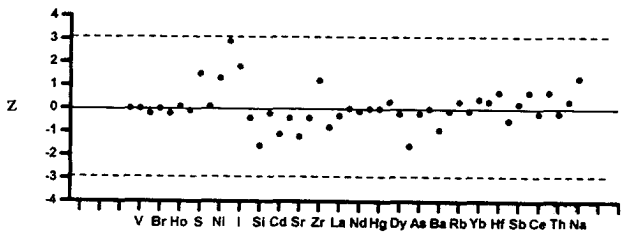
c

Elements in NIST 2711, Montana Soil,
sorted on z



d

Elements in ZW-C, Zinnwaldite,
sorted on z



e

Elements in NIST 2711, Montana Soil
sorted on relative uncertainty

Figure 6-3. (continued). Fig. 6-3c,3d: results of a series of measurements (respectively N = 48 and N = 5), fig.6-3e: results, sorted on relative uncertainty of the concentration determined. Note that for sake of clarity not all elements have been depicted on the X-axes

6.5 EVALUATION OF THE EFFECT OF QUALITY ASSURANCE TO THE ANALYTICAL PERFORMANCE

6.5.1 Analytical quality

The effect of the program for quality assurance introduced since 1992 on the analytical quality and the performance of the laboratory can be established by comparison of results obtained before and after implementing. Unfortunately, such a comparison is difficult to make since only few reports have been saved and raw data cannot be used anymore for re-analysis because of a change in computer system and associated software. When comparing results from reference material analysis, another difficulty arises from the fact that reference materials used for quality control in the period before 1992, have been exhausted. A direct comparison of analysis results of the same reference material is impossible. Still, some impression may be obtained by comparison the laboratory's performance on reference materials which grossly have similar composition, like the cumulative results of NBS SRM 1571 'Orchard Leaves', reported by Sloof and Wolterbeek [22] as part of work in the period 1986 - 1988, and the cumulative results of NBS SRM 1572 'Citrus Leaves' in the period 1992 - 1995. This comparison is presented in *Table 6-4*. The results of NBS and IRI are significantly different when $| z | > 2$ (95 % confidence level).

Many of the standardized differences obtained in the analyses of NBS SRM 1572 are smaller than for NBS SRM 1571, analyzed in the period preceding the structerizing of the quality assurance system. Except for the quality assurance several other differences related to the analysis may have, or has contributed to these improvements:

(i) The intrinsic quality of the reference material in terms of homogeneity and stability.
(ii) The quality of the certified and uncertified concentrations.
(iii) The performance of new gamma-ray spectrum analysis software [23].

Improvements in element standardization parameters, neutron flux monitoring technique, sample handling prior to analysis are all considered to be direct spin-offs of the quality assurance as preventive actions.

6.5.2 Operational quality

In *paragraph 6.3.2* it has been described how the results are checked before authorization is given for the release of the report. In these checks sometimes non-conformances are observed, and corrective actions have to applied to ensure that the results

*Table 6-4. Comparison of the mean element concentrations ($mg.kg^{-1}$) obtained at IRI of the NBS SRM 1571 'Orchard Leaves' [22] and NBS SRM 1572 'Citrus Leaves' with the certified and indicative concentrations; *: c = certified concentration; + N = the number of determinations at IRI; ++: | z | NBS-IRI = The standardized difference between the NBS values and mean IRI concentrations, calculated according to Equation 6-1*

	1986 - 1988				1992 - 1995			
	NBS 1571 'Orchard Leaves' (*)	IRI	N (+)	| z | NBS-IRI (++)	NBS 1572 'Citrus Leaves' (*)	IRI	N (+)	| z | NBS-IRI (++)
As	10.0 c	11.5	55	0.89	3.1 c	3.4	99	0.94
Ba	44.0	52.9	52	0.67	21	22.1	79	0.34
Br	10.0	9.44	55	0.19	8.2	7.6	100	0.28
Ca	20900. c	19500	55	3.2	31500. c	33020	99	1.5
Cl	690	680	35	0.05	414	374	28	0.39
Cr	2.60 c	2.89	54	0.89	0.8	0.6	94	0.04
Co	0.20	0.17	51	0.56	0.02	0.021	86	0.08
Cs	0.04	0.06	12	1.3	0.098	0.099	64	0.05
Cu	12.0 c	14.3	39	1.5	16.5 c	20.2	98	0.20
Fe	300. c	319	55	1.0	90. c	91	71	0.085
Hg	0.155 c	0.152	52	0.17	0.08	0.084	57	0.0048
K	14700. c	14200	55	1.7	18200. c	18110	99	0.10
La	-	1.12	49	-	0.19	0.17	98	0.44
Mn	91.0 c	91.8	35	0.21	23. c	22.4	28	0.28
Na	82.0 c	86.7	44	0.78	160. c	171	41	0.54
Sb	2.90 c	3.28	55	1.3	0.04	0.042	87	0.19
Sc	0.08 c	0.151	7	1.8	0.1	0.12	77	0.59
Sr	37.0 c	33.6	50	2.3	100. c	96	76	0.033
Th	0.06 c	0.11	41	5.2				
V	-	0.658	33	-				
Zn	25.0 c	26.0	55	0.34	29. c	29.7	97	0.28

comply with the laboratory's requirements and or the customers' demands. The corrective actions prevent possible re-analysis -which e.g. might occur if the customer would complain-, prevent irritation and prevent that the laboratory's reputation would be harmed. The number of samples involved in these corrective actions were taken as a basis for the cost-savings, assuming that these samples might all have to be analyzed again after the customer has observed that the results are wrong.

The mostly occurring sources of non-conformance are:

(i) unacceptable neutron flux monitor analysis results (see *paragraph 6.3.2,(i)*).

(ii) unacceptable high element quantities in the blank (see *paragraph 6.3.2, (i)*).

(iii) unacceptable accuracy in the results of reference material or control sample (see *paragraph 6.3.2, (i)*).

(iv) human errors. The latter category includes errors due to poor readability of handwriting, swapping of samples, wrong codes, wrongly entered data in the computer on weights, irradiation conditions etc.

The number of non-conformance reports, corrective actions and number of samples involved with these corrective actions are given in *Table 6-5*. It can be seen that the number of cases of non-conformance is decreasing over the three years of the operationality of the quality assurance considered in this thesis; both in absolute number of cases and in fraction. The major factors related to this reduction are:

(i) The neutron flux monitors are prepared by pipetting from a zinc stock solution on filter paper. These flux monitors are prepared in batches of typically 800 - 1000 items. The non-conformance in the neutron flux monitors was identified to result from deviations in uniformity larger than the assumed precision with which the batch was made. Further evaluation of this problems has given insight in the role of pipettes with the preparation of these flux monitors [24], and the performance of these pipettes as such [25]. The strong reduction in problems with the unacceptable neutron fluxes has been accomplished with the purchase of an automated pipet station. With this new apparatus, large batches of flux monitors can be prepared with a standard deviation of better than 0.5 % which compares to approximately 1 - 2 % when done by hand.

(ii) Evaluation of the problematic blank analyses has resulted in a procedure for regular cleaning of the sample preparation laboratory to limit a dust problem which is related to the construction of the laboratory.

Table 6-5. Overview of cases on non-conformance, corrective actions and the number of samples involved. (: including 1 series of 151 samples, corrected for an unacceptable standardization). The percentages in brackets give the number of non-conformance cases as a fraction of the total number of flux monitors analyzed, respectively the total number of element concentrations reported in all analyses of blanks respectively standards*

			1992	1993	1994	1995
		no. of reports	178	218	279	240
neutron flux	$2 < \|z\| < 3$	no. of cases	20 (0.79 %)	46 (1.32 %)	27 (0.90 %)	5 (0.21 %)
	$\|z\| > 3$	no. of cases	23 (0.91 %)	8 (0.23 %)	4 (0.12 %)	none
		no. of corrective actions	23	8	4	none
		no. of samples involved in corrective actions	44	100	4	none
blank	$2 < \|z\| < 3$	cases	14 (0.56 %)	25 (0.87 %)	17 (0.59 %)	25 (1.4 %)
	$\|z\| > 3$	cases	30 (1.20 %)	22 (0.38 %)	11 (0.25 %)	4 (0.23 %)
		corrective actions	2	11	8	3
		samples involved in corrective actions	13	100	44	22
standards	$2 < \|z\| < 3$	cases	68 (2.72 %)	79 (2.74 %)	47 (1.54 %)	58 (3.3 %)
	$\|z\| > 3$	cases	18 (0.72 %)	14 (0.49 %)	9 (0.28 %)	6 (0.34 %)
		corrective actions	-	2	5	2
		samples involved in corrective actions	-	22	168*	16
human errors		corrective actions	-	7	8	1
		samples involved in corrective actions	-	39	7	12

(iii) Element standardizations are being carried out with considerably more emphasis to the quality, preservation and usage of (old and new) chemicals (purity,

stoichiometry, hydrate water), sample preparation (geometry, pipetted quantities). Laboratory tools have been renewed: freeze drier, oven, balance, pipettes, and the latter are now also calibrated before use.

The reduction in cases of non-conformance related to the standardization -as reflected by the analysis of the reference materials and/or single element standards- is a consequence of the ongoing determination of the standardization constants, improvement of intensity ratios of gamma-ray peaks and completing the gamma-ray catalogue with weak gamma-ray peaks, sum-peaks and pair peaks. Standard operating procedures have been introduced for the final calculation of the standardization parameter, for evaluation of these constants as found with the various spectrometers, and for comparison with literature data.

Several of the $2 < |z| < 3$ cases of non-conformance occur with geological reference materials, in which the (not-certified) concentrations are derived from laboratory intercomparisons rather than from careful activities of a official certification body.

(iv) The human factor remains the most difficult to reduce. Even with documented procedures and assurance of the analytical process, human errors occur. Sample interchanging is related to the repacking with the irradiations and the loading and unloading of the sample changers. The quality of these actions depends largely on the mood, working pressure and intrinsic carefulness of the person involved.

6.6 COST-BENEFIT EVALUATION

In *paragraph 6.2* it has already been described that the quality assurance has been designed-in in the laboratory's quality system. The development costs of the quality assurance activities can therefore not be separated from the development costs of the quality system, which will be elaborated upon in *Chapter 7*. In this paragraph only the running costs are considered.

The running costs of quality assurance have been established using

(i) The average annual number of quality control samples analyzed (reference materials, blanks, laboratory intercomparisons and proficiency testing, blind duplicates) -taking into account an average cost of the analysis.

(ii) The time, estimated for performance of the first line control and report release control.

(iii) The time, estimated for periodic evaluation of the results of the first line control.

(iv) The time, estimated for evaluation of the blind-duplicates.

(v) The time, estimated for evaluation of the proficiency testing.

The final result of this estimate has been divided over the total number of the real samples analyzed, and is compared with the average costs[7] of the analysis and given in *Table 6-6*. As has been indicated in the introduction of this chapter, quality control -via the use of reference materials and blanks- was already carried out before quality assurance was implemented. The respective items are marked in in *italic* in *Table 6-6*.

In order to estimate the net costs of the program for quality assurance a correction has to be applied for the fact that in the past not always quality control samples were processed (see *paragraph 6.1*). Here, it is assumed that in every 20 series of samples, one such a series was processed without quality control samples; the net contribution of the quality assurance activities introduced after 1992 thus amounts (see *Table 6-6*):

*Dfl. 525,150 - (Dfl. 151,800 + Dfl. 82,200 + Dfl. 229,200) * 0.95 = Dfl. 85,110*

or, rounded off, *Dfl. 7.50* per sample.

In the absence of a system for quality assurance also other, less tangible, quality costs can be distinguished:

(i) One of the consequences of reporting wrong results is the re-analysis, which translates to quality costs (from a commercial point-of-view: these analyses have to be done for 'free').

(ii) Re-analysis also can imply that other scheduled analyses have to be postponed because of capacity limitations. As a result dead-lines for reporting on these other analysis may be exceeded, progress in other research projects will suffer from this postponement and eventually (in third party analyses) claims may result for non-fulfilment. All of them are quality costs.

(iii) (Third party) customers can consider to put claims with the laboratory for these bad results. The financial consequences of such a case are hard to predict and to materialize in this cost-benefit evaluation. To accommodate any such claims with third party services, the laboratory has effected an insurance covering Dfl. 2,000,000.

---

7 *The analysis' costs is composed of components related to use of facilities, labour, materials and overhead costs. The costs are differentiated to analysis protocol. The average costs of the analysis have been estimated on basis of the total number of samples processed for third party activities and the related gross income.*

Table 6-6. Overview of costs, in Dfl, of the quality assurance program in the laboratory for INAA, averaged over the period 1992 - 1995, with the resulting quality assurance costs per sample and comparison with an estimate of the quality control costs before 1992. Man-hour costs assumed to be Dfl. 85; average costs per sample analysis to be Dfl. 200

	Number of samples, respectively evaluation time	Costs, Dfl.	
reference materials	759 items	151,800	
element standards	411 items	82,200	
blanks	1146 items	229,200	
fee for participation in intercomparisons		4,800	
laboratory intercomparisons and proficiency testing	133 items	26,600	
blind duplicates	36 items	7,200	
Sub-total			501,800
time for 1st line control and time for report release control	2 * 7 m ; 873 series		17,300
time for periodic evaluation of 1st line control	10 m per audit; 3 audits a year		200
time for blind duplicate evaluation	10 m per set of duplicates		250
time for evaluation laboratory intercomparisons and proficiency testing	30 m per sample; 133 samples		5,600
total costs			525,150
total number of samples	11,377		2,275,400
TOTAL QUALITY ASSURANCE COSTS, PER SAMPLE			46
quality control costs (equivalent to situation before 1992)			*38.50*
Net contribution of quality assurance introduced after 1992, per sample:			**7.50**

(iv) The loss in respect and credibility is not to estimate financially at all.

From *Table 6-6* it can be seen that the analysis of the quality control samples is the principal contribution to the quality assurance costs. A routine INAA procedure consists in principle of the simultaneous processing of 14 samples, 1 reference material and 1 blank

sample. Thus, the analysis costs per sample would be increased by approximately 15 % by the analysis of the quality control samples. Since also smaller series of samples are processed -sometimes just one sample, but always in the presence of the control samples- the analysis costs per sample are in practice increased with 19.5 % by the quality control samples (reference materials, element standards and blanks) and with 2.5 % by the costs of the program for quality assurance (proficiency testing, blind duplicates and time for controls and evaluations).

Table 6-7. Overview of cost-savings between 1992 and 1995 by the implementation of the quality assurance system after 1992

	Number of cases, respectively number of samples involved	Corresponding costs, Dfl
corrective actions prior to release of report; average time involved in an action: 30 min	84 cases	3,570
number of samples involved	591	118,200
total costs savings		114,360
net costs quality assurance	11,377	85,110

The benefits of the quality assurance introduced after 1992 have been estimated on basis of the possible cost-savings. Only when $|z| > 3$ the results are not acceptable and analysis may have to be repeated when no corrective actions would be applied. Before 1992 such analyses reports could have been released since there was no system for controlling the reports, though quality control measures were in principle available. From *Table 6-5* it can be derived that in 84 cases between 1992 and 1995 corrective actions were required to prevent the release of bad data. An average time needed of 30 min. is assumed to carry-out such an action. If these reports still had been released and if the customers had observed the bad data, it cannot be excluded that in the worst possible case all 591 samples involved would have to be re-analyzed again. So, an investment of 84 * 30 m may have prevented the costs of re-analysis of 591 samples. These savings are compared in *Table 6-7* with the net costs of the quality assurance, implemented after 1992.

6.7 DISCUSSION

Documented and quantified criteria for approval of the results, and a harmonized rigid structure for the release of analysis reports are the measures which have made possible that the quality of the results meet the norm, set by the laboratory itself, and comply with the agreed requests of the customer in terms of reliability and comparability. Many sources of error in INAA have been identified, and related to this, preventive assurance and/or options for corrective actions have been implemented. Still situations may occur in which there is no assurance against incidental errors with the samples only which can not be derived from the results of the quality control samples e.g. contamination of the samples and not of the blank, element loss during irradiation (e.g. Hg), interchange of samples. An approach to account these errors is to analyze all, or part of the samples in duplicate or in triplicate. There are drawbacks related such an approach, viz. (i) the availability, and the quality of the duplicates or triplicates in terms of homogeneity (ii) an almost proportional increase in analysis costs and (iii) an increase in turn-around time unless the counting capacity is increased. The laboratory has decided that the analysis in duplicate or in triplicate cannot be justified considering the expectations of occurrence of the aforementioned incidental errors. When analyzing the cause of the registered cases of interchange of samples it turned out that often an entire series of samples was placed in the sample changer in a reverse order. A preventive actions have been taken to make such an occurrence less likely and easy detectable, e.g. by positioning the quality control samples ad odd positions in between the samples rather than add the end of the series.

The control charts are a valuable aid in the assessment of the accuracy of data of non-certified elements, and in trouble shooting. Further extension of the charts is considered e.g. differentiation in the charts to certified and non-certified reference data, and in-line determination of outliers and elimination from the datasets.

The registered cases of non-conformance between 1992 and 1995 show that the preventive actions have resulted in an improved quality of the performance. Particularly for the cases in which $| z | > 3$ the performance has improved considerably and appears to be close to what can be expected from statistical considerations. The registration of corrective actions prior to release of the reports indicate that the quality assurance prevented that 6 % of all analyses would have been reported with wrong results or with results of insufficient accuracy. The costs of the quality assurance -additional to the costs of the existing quality control- are lower than the estimated value corresponding to re-analysis of this 6 % part.

All measures have contributed to an improvement of the accuracy of INAA as it is performed at IRI, and at a more realistic estimate of the overall uncertainty of the results.

6.8 REFERENCES

[1] C. Eisenhart, 'Realistic Evaluation of the Precision and Accuracy of Instrument Calibration Systems', reprinted in:
'Precision Measurement and Calibration: Statistical Concepts and Procedures' NBS SP 300, vol. 1 (H.H.Ku, ed.), National Bureau of Standards, Gaithersburg, USA (1969)

[2] ISO 8402 'Quality Vocabulary' (1994)

[3] J.K. Taylor, 'Quality Assurance of Chemical Measurements', Lewis Publishers, Chelsea USA 1987

[4] J.P. Dux, 'Handbook of Quality Assurance for the Analytical Chemistry Laboratory', Van Nostrand Reinhold, New York (1986)

[5] R. Sutarno, H.F. Steger, 'The Use of Certified Reference Materials in the Verification of Analytical Data and Methods',
Talanta 32 (1985) 439 - 445

[6] F.M. Garfield, 'Quality Assurance Principles for Analytical Laboratories', publication by Association of Official Analytical Chemists (AOAC), Arlington, USA, 1991

[7] G. Kateman, L. Buydens, 'Quality Control in Analytical Chemistry', J.Wiley and Sons, New York (1993)

[8] ASTM E178 'Standard Recommended Practice for Dealing with Outlying Observations', ASTM, Philadelphia, USA

[9] 'Proficiency Testing of Analytical Laboratories: Organisation and Statistical Assessment',
Analyst 117 (1992) 97 - 104

[10] ASTM E691 'Practice for Conducting an Interlaboratory Test Program to Determine the Precision of Test Methods', ASTM, Philadelphia (1987)

[11] M. Thompson, R. Wood, 'Harmonised Guidelines for Internal Quality Control in Analytical Chemistry Laboratories',
Pure and Appl.Chem 67 (1995) 649 - 666

[12] M. Thompson, R. Wood, 'International Harmonized Protocol for Proficiency Testing of (Chemical) Analytical Laboratories',
J.AOAC Intnl. 76 (1993) 926 - 940

[13] ISO 1995 Guide to the expression of uncertainty in measurement

[14] K. Heydorn, 'Detecting errors in micro and trace analysis by using statistics',
Anal.Chim.Acta 283 (1993) 494 - 499

[15] W.A. Shewhart, 'Economic Control of Manufactured Products', Van Nostrand co., New York, USA (1931)

[16] P. Bode, M.J.J. Ammerlaan, M. Koese, 'The Half-lives of Na-24 and Ba-131',
Int.J.Appl.Rad.Isotop. 42 (1991) 692 - 693

[17] G. Erdtmann, W. Soyka, 'The Gamma-Rays of the Radionuclides: Tables for Applied Gamma-Ray Spectrometry', Verlag Chemie, Weinheim (1979)

[18] M.D. Glascock, 'Tables for Neutron Activation', Univ. of Missouri, Columbia, USA (1988)

[19] M. Blaauw, 'The k_0-consistent IRI Gamma-Ray Catalogue for INAA',
Interfaculty Reactor Institute, Delft (1996), ISBN 90-73861-32-2

[20] E. Browne, R.B. Firestone, 'Table of Radioactive Isotopes', J. Wiley & Sons, New York (1986)

[21] R.Seymour, 'Quality control and statistical process control for nuclear analytical measurements',
Radioact.Radiochem. 4 (1993) 24 - 44

[22] J.E.Sloof, H.Th.Wolterbeek, 'National Trace-Element Air Pollution Monitoring Survey using Epiphytic Lichens',
Lichenologist 23 (1991) 139 - 165

[23] M.Blaauw, 'The Holistic Interpretation of Gamma-Ray Spectra in Instrumental Neutron Activation Analysis', Thesis, Delft University of Technology (1993)

[24] M.Blaauw, M.J.J.Ammerlaan, P.Bode, 'Quantification of Sources of Variation in Neutron Activation Analysis',
Int. J.Appl.Radiat.Isotop. 44 (1993) 547 - 551

[25] M.J.J.Ammerlaan, 'A Critical Note concerning Manufacturer's Specifications of Pipettes', IRI internal report 94-001 (1994)

6.9 LIST OF SYMBOLS

C	concentration, $mg.kg^{-1}$
c	to denote certified values
i	as *subscript* to denote individual result of reference material analysis
M	number of materials analyzed in Heydorn's analysis of precision
N	number of determinations
ref	as subscript to denote certified or consensus value of concentration in reference material
T	factor for analysis of precision
z	standardized difference between observed and expected values of a parameter (e.g. concentration, neutron flux)
σ	estimate of standard deviation

CHAPTER 7 TOTAL QUALITY MANAGEMENT

The subjects dealt with in this chapter, have been also described in the following papers:

* P. Bode, Th.G. van Meerten, 'Quality Assessment and Organizational Aspects of Multi-element Analysis of Geological Material with the IRI- system for Routine INAA',
  Geologie en Mijnbouw, 67 (1988) 459 - 466
* P. Bode, R.J. Rosenberg, J.J.M. de Goeij, 'Opportunities for Neutron Activation Analysis in Environmental Research',
  Proceedings of the IAEA Intern.Symp. on Applications of Isotopes and Radiation in Conservation of the Environment, Karlsruhe, Germany, 9 - 13 March 1992
  IAEA-publication Symposium series IAEA-SM-325/192 pp. 351-361
* P. Bode, 'Aspects of Quality Practice and Accreditation for a Neutron Activation Analysis Laboratory in a University Environment',
  Book of Abstracts Conf. on Instrumental Activation Analysis, IAA 92 (Eds. J. Frána, I. Obrusník), Čs. Spectroscopic Society, May 18-22 1992, Klučenice, Czechoslovakia, 3 - 4
* P. Bode, 'Organization of Commercial Neutron Activation Analysis at the Interfaculty Reactor Institute',
  Trans.Amer.Nucl.Soc. 68 part A (1993) 14
* P. Bode, J.P. van Dalen, 'Accreditation: a Prerequisite, also for Neutron Activation Analysis Laboratories ?!',
  J.Radioanal.Nucl.Chem. 179 (1994) 141 - 148
* P. Bode, 'Experience with an Accredited INAA Service Laboratory at a University; will Research be next ?',
  Trans.Amer.Nucl.Soc. 68 part A (1993) 10
* P. Bode, 'Quality Management and Laboratory Accreditation at a University: What can be learned from Experience ?',
  Analyst 120 (1995) 1527 - 1533
* P. Bode, 'From Misconception to a Must: the Measured Merits of TQM and Accreditation in INAA',
  Accept. for publ. in J.Radioanal.Nucl.Chem.
* P. Bode, 'Quality management at the Analytical Laboratory, an Inevitable Compliance with a new Order',
  Accept. for publ. in Zhurnal Analiticheskoj Khimii (Russian J.Anal.Chem).

7 *TOTAL QUALITY MANAGEMENT*

7.1 THE NEED FOR TOTAL QUALITY MANAGEMENT AT THE LABORATORY FOR INAA

7.1.1 Internal factors

Self-evaluation in 1989 - 1990 learned that the INAA-operations and the organization of the laboratory had to be changed for three major reasons:

(i) Analyses sometimes failed and had to be repeated. This could be justified for those cases where the composition of the sample and concentration levels appeared to be entirely different from the expectations. However, analyses failed due to bad planning, and insufficient performance -like not well functioning equipment, improper calibrations, wrong choice of analysis protocol, poor arrangements between people on facilities commonly used- and/or improper conduct. In a 1985-1986 project Se, Sb, Hg, Cd, As and Zn were determined in 600 toe-nail samples. All results had to be corrected and reported again in 1987 because of incorrect blank corrections. A consequence of the repetition of work was that deadlines of collaborative projects were exceeded. A project in 1989 - 1990 involving 3900 analyses of toe-nail clippings for Se planned was completed 9 months too late because of misjudgment of the time needed for sample preparation. In the same project also in 1989 the coding of a group of 50 unique samples of toe-nail clippings got lost. In 1991 third-party analyses of different products of household goods for potential toxic elements (like Se, Hg, Sb, Ba, Cd) were delayed for 4 months because of not well-functioning of newly developed software.

Likewise, supporting activities sometimes failed due to bad planning and insufficient preparation. Examples are the shortage of zinc foil to prepare flux monitors from -which could have been foreseen well in advance and poor reproducibility of pipetted neutron flux monitors due to improper functioning pipettes -of which the need for calibration was not anticipated on at all.

(ii) The laboratory dealt with poor and incomplete documentation, absence of schemes for regular calibration, maintenance etc. Note-books were not kept in a systematic manner by every employee; arrangements on analyses to be done -elements to be determined, dead-lines for reporting- were not well documented either. The pathway of the sample through the laboratory was

also not or only poorly documented and it was difficult to retrieve the relevant conditions when afterwards results were suspected to be wrong.

Another aspect of the absence of documented guidelines was that operations (e.g. weighing, preparing for irradiation, computerized data-administration, keeping record of results of reference materials) were not carried out in an uniform manner. Each user had his own style of preparing samples for irradiation, drying samples and even use of reference materials. The many ways of working made often difficult the traceability -or better: trackability [1]- , location and interpretation of sources of errors. New users were confused by this variety in practical performance when in their training stage minor aspects of an operation were explained differently by different experienced users.

Due to poor documenting the professionals became 'single points of failure': they were the ones who knew most of the details of the analysis but who 'documented them in their head'. When such a professional left the organization -as in the case with the scientist who developed the gamma-ray software, the technician who developed the factor analysis software and technicians performing standardizations- also vital practical experience was lost from the laboratory. Key parts in the INAA-facilities were not documented either: the mechanics and control of the automated sample changers and most of the self-made auxiliary electronics; the trouble-shooting with of gamma-ray spectrometers; the conditions to be set to element standards for standardization.

(iii) As already mentioned in *paragraph 6.1* there was no rigid discipline on quality assurance, the control on the accuracy of the results was difficult to demonstrate to outsiders. By 1989 the computer software was thus organized that users could alter the raw data -not only weights, but spectral data, irradiation and counting conditions, relations to neutron flux monitors- the calibration and standardization parameters. It could not be excluded that this flexibility might lead to situations in which the raw data were 'tuned' to meet analysts' demands. Errors occurred when energy-calibrations were changed; accuracies were affected e.g. by tampering with the neutron-flux monitor data.

---

1 *Recently [1] the term 'trackability' has been suggested to avoid the confusion with the term 'traceability'. A suggestion for the definition of trackability is 'the property of a result of a measurement whereby the result can be uniquely related to the sample', whereas the ISO definition of traceability is 'the property of a result of a measurement whereby it can be related to appropriate standards, generally international or national standards through an unbroken chain of comparisons' [2].*

Moreover, the users had access to eachothers data; situations occurred in which accidentally raw and processed data were deleted.

As a result of the situation sketched in the above, the laboratory had to spend much effort to corrective actions whilst a structurized approach of preventive actions failed to come. It affected in a negative way the effectiveness of the research efforts. It was conceived that it was unacceptable in view of the research programs in which data collected over several years had to be processed and results should be of known quality to make comparison meaningful. Examples are the biomonitoring program [3] and the study of selenium in marine waders [4].

7.1.2 External factors

Since approximately 1985 the potentials of INAA gained interest of non-university organizations, initially governmental institutes from the ministry of Housing, Planning and the Environment but later on also trade and industry. The conditions under which these analyses had to be performed, were actually new to the research group: strict dead-lines, demands to demonstrable sensitivities, number of elements and quality assurance. The need for a different organization of the work process was emphasized when a governmental contract for analyses could only be acquired after the laboratory had declared that it would pursue the implementation of a quality system.

Table 7-1. Internal and external motives for introducing total quality management at the laboratory for INAA

Internal: To reduce failure of experiments due to improper planning and performance, and to reduce, consequently, repetition of experiments
Internal: To enhance trackability of procedures and errors during experiments
Internal: To prevent professionals to become a 'single-point-of-failure'
Internal/external: To assure and to demonstrate the analytical quality of the data
Internal: To curb unwanted liberties
External: To ensure eligibility for research contracts and commercial INAA services

The internal and external reasons to improve the effectiveness of operations at the laboratory for INAA are summarized in *Table 7-1*.

7.2 THE DEVELOPMENT OF A QUALITY SYSTEM

7.2.1 Objectives for quality system accreditation

The quality of analytical data and of the performance of the laboratory depends on many operational variables such as the type and condition of equipment, their calibration or standardization, the validation of methods, the training and experience of analysts and supervisors and on environmental conditions like e.g. temperature, humidity, dust or electronic interferences. The laboratory's organizational structure, procedures and resources to control these operational variables in order to produce results of consistent quality meeting defined specifications is denoted with the term 'quality system'.

Progressively, a set of international reference documents - the ISO/IEC [2] guide 25 and the derived European EN45000 series of standards- have been developed to harmonize the ways of implementing quality systems and evaluating quality assurance practices in laboratories, in connection with laboratory accreditation *(where accreditation is defined as: Procedure by which an independent authoritative body gives formal recognition that a body or person is competent to carry out specific tasks)* and, more generally, to facilitate the acceptance of test results.

In 1990 it was decided to improve the organizational structure of the laboratory for INAA, the performance and effectiveness of its operations and the assurance of the analytical quality of the results. The quality system to be implemented should be fit for formal accreditation following EN45001 for two reasons:

(i) INAA is being used for third party services, both for economical considerations as well as to demonstrate the position of the institute in the technical, scientific and social community. The laboratory for INAA has to compete with other service laboratories on a commercial basis employing alternative techniques. To maintain and to improve the position of the INAA laboratory in this competition, accreditation was considered to play an important and probably vital role in the acquisition of contracts and to retain existing clients.

(ii) INAA is used by reference materials issuing organizations as one of the supporting techniques in the certification of reference materials. Traceability of INAA-results contribute to a further enhancement of the quality of

---

2 *ISO: International Organisation for Standardisation; IEC: International Electrotechnical Commission*

certification processes. It was considered that the INAA facilities might be invited in the future for such purposes. The peer review by the accreditation body, the demonstration of technical competence, the regular participation and evaluation of laboratory intercomparisons altogether ensure the capability and quality of the participating laboratory to the reference materials issuing organization .

The quality system has been developed between 1990 and 1992 [5, 6, 7] and is in accordance to the criteria set by the organization that performs accreditation in The Netherlands (in 1992: STERLAB) [3]. These criteria contain all of the criteria from EN45001 and the relevant criteria from ISO 9001 and ISO 9002. The quality system is documented by a quality manual, which identifies the policies, organizational objectives, functional activities and specific quality activities designed to achieve the quality goals desired for operation of the system.

The quality system has been developed during a three years' period, from 1990 to 1992. This development, and the pathway towards accreditation is described in *paragraph 7.2.2.*

7.2.2 The development of the quality system

A quality system cannot be purchased nor can it be tailor-made by only one person in the organization. It has to be created by the persons directly involved in the workprocess since they need to have consensus on their future lifestyle of work and on the interpretation of the demands to be fulfilled. Realization of the quality system was possible because the scientific director of the institute justified the investment in time and money to develop the quality system and to accomplish accreditation.

The realization of the quality system included several stages:

ORGANIZATION

The activities have been managed by the head of the laboratory, supported by a consultant, viz. an analytical chemist who advised and coordinated during the awareness building and orientation and definition stages. The realisation itself has

---

[3] *In 1995 STERLAB, together with the Dutch Council for Certification -RvC-, the Dutch Calibration Organisation -NKO- and the Dutch Accreditation Board for Inspecting Bodies -STERIN- merged into the Dutch Council for Accreditation, RvA.*

been the task of all employees of the laboratory for INAA. One of the employees was selected to officiate as quality coordinator of the laboratory.

The scope of the quality system was defined to include all routine operations in INAA aimed at multi-element determinations in sediment, soil, rock, minerals, plastics, waste, plant- and other biological material and air particulate matter. Interference-free detection limits were also defined. Employee compliance with the quality system was defined to be applicable for all employees utilizing the facilities for INAA, irrespective whether INAA is applied for research or routine service analyses.

ORIENTATION AND TRAINING

The head of the laboratory, the quality-coordinator and several technicians attended courses on quality practice and on the interpretation of the requirements of a quality system.

AWARENESS BUILDING

Though the need for improvement was admitted, numerous objections were raised against the necessity of documentation, operating according to documented standard operating procedures and internal mutual control and assurance point. These objections were not much different from what has been observed in non-university laboratories. The academics involved were amongst the first to comply with the requirements, without proclaiming loss of 'academic freedom'.

The awareness building stage for the 10 employees (staff, technicians, students) of the laboratory for INAA stretched over a period of about 1.5 years, from 1990 till the midst of 1991. By 1991 the philosophy of quality management and laboratory accreditation was generally understood and accepted both emotionally and rationally.

SYSTEM EVALUATION

The analytical process has been evaluated in details. Not only the technical aspects like sample handling or calibration, but also organizational aspects like persons in charge, unambiguous coding, authorization of reports to be released, training and (re)qualification of personnel etc. Much time was required for the quantification of criteria for decisions in the analytical process, to harmonize the interpretations on the quality of operations and results. It all formed part of the process to harmonize operations for better effectiveness, reduction of misunderstandings and reduction of

sources of error. Critical points in INAA demanding quality assurance were identified and designed-in in the new, documented procedures; forms were developed for registration of important parameters. Though for routine operations some rigidity was needed, a 'paper' bureaucracy could be avoided by including paragraphs how to handle in cases of non-conformance.

The acceptance of far-going documentation was facilitated by the negative experiences in the laboratory with missing documents as described in *paragraph 7.1.1.*

IMPLEMENTATION

The operations in the laboratory are structurized via (i) procedures which describe how an operation is organized and which arrangements have been made in the operation and between which employees and (ii) instructions which describe the operation step-by-step via binding requirements (or recommendations -when the quality and safety of the step will not be affected when the requirement is not addressed). Most of them have been drafted by the employees of the laboratory, and verified by them on clarity, correctness and operationality.

The analysis protocol - i.e. the choice of sample mass, choice of reference material, irradiation-, decay-, counting time and type of spectrometer- is not rigidly prescribed. The variety of samples and requests for elements to be determined is so large that it is almost impossible task to anticipate in detail on each possible combination. The solution has been found by giving (i) general recommendations on the choice of irradiation, decay and counting conditions for groups of elements, (ii) file keeping of protocols collected and posted up at the laboratory on sample types and elements determined, and (iii) the requirement that new protocols have to be authorized by the head of the laboratory.

Since the laboratory is incorporated in a larger institute, certain operations interact with institute's operations such as purchasing, stock control, personnel management. The related parts of the institute are not (yet) entirely tuned to the principles of quality management, but alteration is difficult to justify just to suit one organizational unit within the institute. As a contrast, quality management is being introduced in the reactor operations which have an important interaction with INAA.

NON-CONFORMANCE MANAGEMENT

The quality system includes procedures which anticipate on the assumption that mistakes take place and can never be avoided. A corrective or preventive action is taken within a 2 weeks period, but preferably as quick as possible.

QUALITY AND PERFORMANCE ASSESSMENT

The system for quality assurance described in *Chapter 6* has been designed-in in the quality system. A procedure on internal audits is included, which is further discussed in *paragraph 7.3.2.*

QUALITY MANUAL

Upon completion and verification the documents describing the procedures and instructions are compiled in a quality manual. This manual consists of (i) a handbook, which is a comprehensive text (approximately 100 pages) describing the quality policy and (ii) annexes containing the procedures and instructions in approximately 650 pages. Particularly the annexes are subject to regular alteration and additions. The documents in the annexes are the ones used or most consulted. The contents and lay-out of the manual are brought in accordance to the criteria of the Dutch Council for Accreditation (Raad voor Accreditatie, RvA).

The quality manual is ordered by the following chapters and objectives:

Chapter 1. The table of contents. In the annex of chapter 1, a table shows the relation between the RvA criteria and the documents in the manual.

Chapter 2. In this chapter the scientific director of the institute declares his policy with regard to quality, his compliance with the objectives of the quality system and a description of the means with which the policy is being implemented. The policy is described of the laboratory's management to prevent improper influence and to protect personnel from pressure which may have a detrimental influence on the quality of work.

Chapter 3. The organization of the institute is given in organization charts. The duties, responsibilities and authorities which go with the jobs are described. The general arrangements for appointing substitutes are given. In this chapter also the procedures for in-house training are described.

Chapter 4. The scope and technical capability of the INAA laboratory are described.

Chapter 5. The procedures are given for the internal quality control, and for the internal audit of the quality system. Attention is paid to developments and changes, or possible improvements in the quality system. Procedures are given for the management of non-conformance, complaints and ideas for system improvement. Procedures for corrective and preventive actions are given.

Chapter 6. The premises of the laboratory and their environmental requirements are described. Rules for good housekeeping are given.

Chapter 7. The laboratory's policy is described for the procurement of goods, including guidelines for suppliers and guidelines for inspection of purchased goods. Also the policy on subcontracting is given, with a description on the method used to establish the competence of the other institution or the suitability of its facilities.

Chapter 8. A summary is given of the policies applicable to the administration and use of testing and reference objects. Procedures are included on maintenance and on stock control of means of testing or equipment to be regarded as consumable goods. This chapter also contains the procedures related to calibration, and it deals with calibration or adjustment of equipment but also of element calibration for quantitative analysis. The management of the computer system is described, with attention for accessibility, back-ups, a control assessment of newly developed or altered software, etc.

Chapter 9. This chapter is a compilation of all work-instructions for use of equipment, preparation of standards and samples.

Chapter 10. Procedures are given for the preparation of analyses, including coding, drawing-up an analysis protocol, appointment of the personnel to perform the analysis and for the (computerized) administration of data.

Chapter 11. This chapter contains instructions on the drafting, the contents, and the authorization of the release of reports.

Chapter 12. The policy and principal regulations on putting documents in the archives is described. It is stated how long documents are archived, where they are located and how they can be retrieved.

Chapter 13. The management of the quality manual and the related documents is described.

The quality manual is available in every office of the laboratory for INAA, in the counting room and at the sample preparation laboratory. Separate procedures and instructions are present at working places or with equipment wherever there presence is required.

After an audit in November 1992, the laboratory achieved on February 26, 1993 the formal accreditation for compliance of the quality system with the STERLAB-criteria (*Figure 7-1*). The accreditation covers the quality system of the laboratory as well as the specified INAA activities. Accreditation has made the laboratory for INAA in 1993 the first accredited university trace element analysis laboratory in The Netherlands and by that time probably also the first accredited laboratory for INAA in the world.

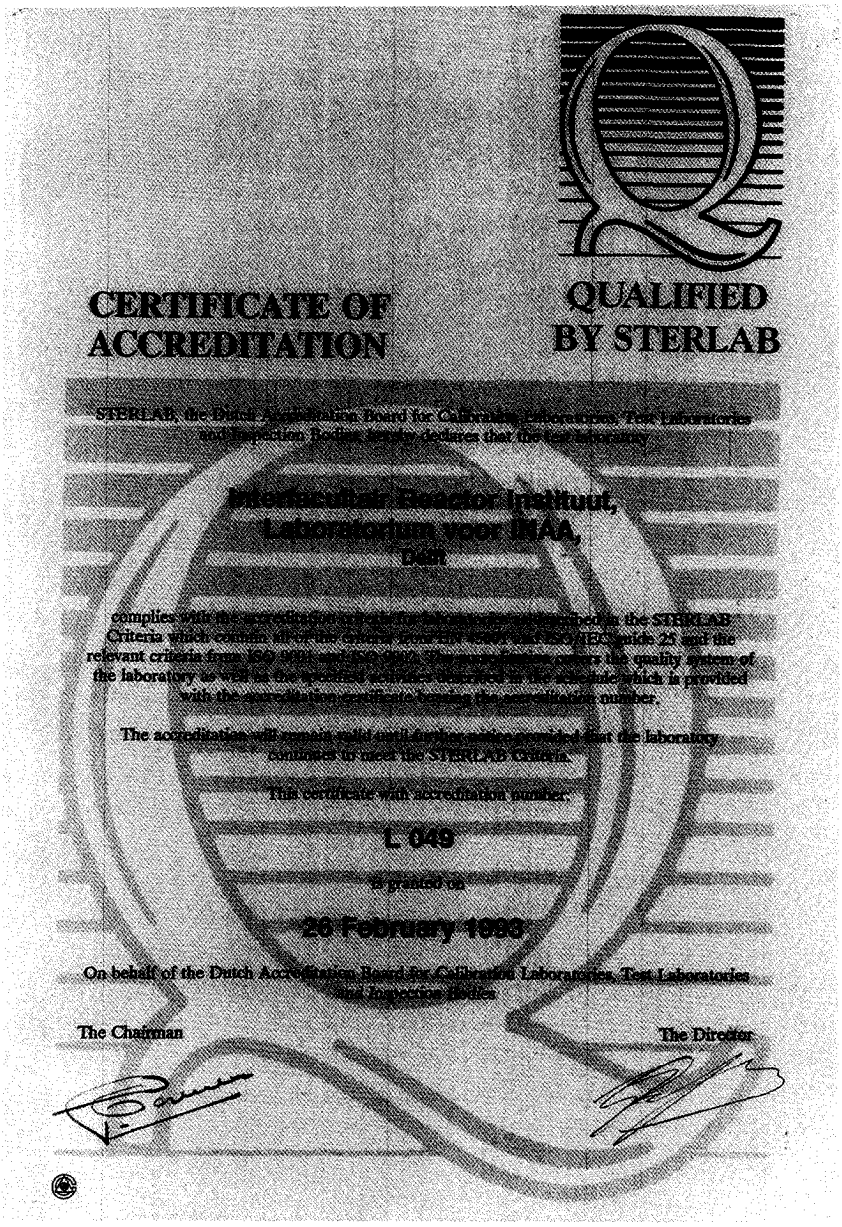


Figure 7-1. Certificate of accreditation of the Laboratory for INAA

7.3 THE EXPERIENCED EFFECTS OF TOTAL QUALITY MANAGEMENT

In *paragraph 7.1* several circumstances have been pointed-out which made necessary to improve the performance of the laboratory. In the following paragraphs it is discussed to what extent the introduction of a quality system and its management have contributed to reduce these problems, and to the desired improvement.

7.3.1 Motives for improvements and accomplishments

INTERNAL MOTIVE: TO REDUCE REPETITION OF WORK

The combination of harmonized standard operating procedures and necessity for employees to obtain -after a dedicated training and subsequent test of understanding and correct execution- authorization to perform a given task has been a first step to reduce the repetition rate of analyses. Authorization is given for a limited period of time: re-qualification is required even for routine operations to ensure that given and initial skills do not fade away when operations have not been carried out for some time.

Other measures are the filing of applied analysis' protocols, the authorization of new protocols, and the ensuring of the fitness-for-the-purpose of flux monitors, reference materials, chemicals for standardization, consumables (like capsules), equipment (balances, pipettes, spectrometers) and software. The stock control of consumables, varying from pipet-tips to forms also facilitates that the analysis is carried-out as scheduled and not delayed by shortages. After an alteration of the software a test is run on a 'standard' gamma-ray spectrum to verify the results.

As a result, repetition of work reduced drastically compared to the situation before introduction of quality management. In the period 1992 - 1995 in 6 cases (50 samples involved, whilst in total 11,377 samples have been analyzed in that period) analyses had to be repeated because of interchange of samples in the sample changer, noticed only after reporting.

INTERNAL MOTIVE: TO ENHANCE TRACKABILITY

Trackability of the laboratory's operations, including the execution of the analysis, is accomplished by the documentation and registration introduced. The personized training forms make possible to demonstrate the competence of the employees to carry out a given task. The fitness-for-the-purpose of the equipment is

traceable via the management of equipment, the registration of maintenance and calibration, and the registration of dates and reasons for being taken out-of-function. The registration of settings and particularly the reason to change a setting have come to use in the evaluation of control charts as described in *Chapter 6*. The administration of chemical compounds for standardization and reference materials (origin, including date of purchase, quality indicators such as purity, stoichiometry and usage) have facilitated the traceability of standardization and internal quality control. Lists with date and name of users link the trained and authorized employees with the equipment, facilities and execution of the analysis. The analysis' request is registered on a sample registration form which also holds the sample code. This code is unambiguous and links the samples to the analyst. Sample registration form code and sample code are also printed on the analysis' report together with detailed information on the irradiation, decay, counting conditions and spectrometer used.

The system for non-conformance makes possible to trace and to demonstrate the cause of a non-conformance and the actions taken.

The system for documentation and registration is a form of 'efficient' bureaucracy. Registration of observations takes more time than before -when it sometimes was not done at all- but much more time and certainty is gained when afterwards a reconstruction is needed or when observations have to be linked to oneanother. It was chosen to use hard-copy forms rather than entering data on forms on personal computers in some type of Laboratory Information Management System ('LIMS'). It is anticipated upon that this makes employees more aware of their actions and on the meaning of their recorded information: moreover, it forces them to formulate their thoughts. Hard-copy forms are also quicker filled-in than entering, saving and backing-up the information on a personal computer.

INTERNAL MOTIVE: TO PREVENT SINGLE-POINTS-OF-FAILURE

Each employee of the laboratory has his own specific educational level and specialism in the laboratory. It is impossible to double precisely each person's expertise with another employee. As such, there will remain single-points-of-failure. But in the quality system their interweaving with the laboratory's operations has been tackled. Deputies have been appointed and trained to ensure continuation of the routine operations in case of absence of such a specialist. The training focuses on the experience with most likely cases of non-conformance with the given operation. By documenting the laboratory's operations also part of the practical expertise has been registered. Also the keeping of notebooks, the filing of self-made electronic or

mechanical designs, software-descriptions contribute to reduce the effect of single-points-of-failure to the continuation of the routine operations.

INTERNAL/EXTERNAL MOTIVE: TO ASSURE ANALYTICAL QUALITY

The assurance of the analytical quality is effectuated on several levels. It starts with the assurance of the technical competence of the employees, the assurance of the fitness-for-the-purpose of materials, equipment and facilities and the control on the analysis protocol selected. (Re)determination of standardization parameters is carried-out with new chemical compounds of known quality with registration of usage. These compounds have got the same status as the certified reference materials.

Calculations, made by the employees to decide on further progress of work - e.g. as with the comparison of a result with approval criteria- require an independent check.

Particularly the first-line quality control of the results (see *paragraph 6.3.2*), and the subsequent procedure for authorization before release have contributed to ensure that the results comply with the level of excellence the laboratory has been accredited for.

The EN45001 norm mandatory prescribes regular participation in proficiency testing (see also *paragraph 6.3.2*). The laboratory bimonthly participates in the samples issued in the framework of the International Plant Analytical Exchange Program and the International Soil Analytical Exchange Program [8]. The laboratory offers its capacity for participation in intercomparisons organized by NIST, BCR, IAEA and others.

INTERNAL MOTIVE: TO CURB UNWANTED LIBERTIES

The most important improvement has been realized via the INAA software of which the development coincided with the awareness building for quality management. Original (raw) spectral data are inaccessible for users; user accounts have been protected; all crucial manually entered data required for the quantitative analysis is printed on the hard-copy report and is checked with the original observations of forms in the first line control and in the authorization control.

Maybe equally important as the measures to protect against potential tampering with the data is that the quality system allows to deviate from the standard operating procedures as long as it does not jeopardize the quality of the analyses and performance of the laboratory, and as long all these deviations are documented. In the standard operating procedures it has been identified where it is allowed to deviate and

where it is not. It contributes to the awareness of the employees of the necessity to comply with the standard operating procedures but with some options to deviate when operationality requires.

EXTERNAL MOTIVE: TO IMPROVE COMMERCIAL POSITION

The ministry for Housing, Planning and the Environment and the ministry for Transportation on one side, and the environmental testing laboratories, the organization of STERLAB accredited laboratories, and NKO/STERIN/STERLAB agreed in 1994 upon the necessity of reliable and uniform analyses and tests for the formulation, execution and enforcement of the environmental policy. Laboratories participating in these tests should by preference be accredited according to EN45001. The laboratory for INAA co-signed the agreement. Obviously, IRI's laboratory accreditation in principle makes possible to be invited for appropriate tests and research in this field, an invitation which otherwise would have been less likely. The laboratory's quality policy includes confidentiality of requests for analyses and customers.

7.3.2 Performance evaluation via audits

The quality system and the underlying documents in the manual are continuously being improved and extended. Forthcoming from interpretation of the EN45001 norm and from the experience with regular audits of accredited quality systems, the Dutch Council for Accreditation, RvA, may extend existing- or add new criteria to which a quality system has to comply, or may change the interpretation of the EN45001 norm from 'recommendations' into 'demands' for a quality system.

The criteria demand a system for an independent assessment of the performance of the laboratory in view of its quality objectives. Three types of internal audits have been introduced:

(i) The quality coordinator checks bimonthly the employees' compliance with the procedures and instructions. These checks may reveal e.g. the need for changes or more clarity in the written text or e.g. an update of the lay-out of forms. 'Horizontal' and/or 'vertical' audits are carried out. A horizontal audit consists for instance of the selection of a selected sample, measurement or analysis and an assessment whether all conditions were properly fulfilled to carry out the respective task: demonstration of well functioning equipment, administration of specifications, authorization and training of personnel, non-

compliance management etc. In a vertical audit, the route a selected sample followed through the laboratory is followed, from the first contact with the customer on the feasibility of the analysis to reporting an filing.

An evaluation of these internal audits over 1993 - 1995 (*Table 7-2*) learned that periodically discipline tends to decline, and sloppiness tends to affect the administration of samples, although no systematic errors have been established. Comments from customers were rapidly and satisfactorily dealt with. In these years in nine cases the comments had the character of a complaint related to insufficient customer satisfaction, often due to sloppiness in the administrative part of the analysis and human errors such as interchange of samples. Only once a complaint was registered on the analytical quality of the results and dealt with a contamination of an individual sample, not reflected by the blank analysis (see also *Table 6-1, 'Protected against incidental errors'*). Improvements were introduced in analysis' logistics (e.g. at the sample preparation laboratory) and by new laboratory tools such as an automated station for pipetting the neutron flux monitors.

Table 7-2. *Overview of registered cases of non-conformance in 1993, 1994 and 1995*
**: in 1993 not every complaints ventilated by telephone was registered, in contradiction to the prescriptions in the quality manual*

	1993	1994	1995
Customers	> 6*	16	11
Sample registration, reporting	75	101	57
General aspects	23	5	6
Infrastructure	24	-	5
Sample preparation laboratory	8	8	6
Quality manual	5	2	1
Software to calculate induced radioactivity upon irradiation	3	3	5
TOTAL	**>144**	**135**	**91**

(ii) The institute's quality manager audits at least twice a year the general performance of the laboratory. As an outsider with respect to the conduct of

analysis but acquainted with the situation in the institute as such, the quality manager investigates the documentation and the operationality of the system. He reports to the scientific director of IRI. His conclusions may be attended with recommendations for a program to further improvement of the quality system.

(iii) Once a year, the director of the institute carries out a management review in which the results of the internal and external audits are reflected at the quality goals and the quality policy of the institute, and the principal research and educational objectives of the institute. In this management review the director may consult e.g. the institute's quality manager, the laboratory's quality coordinator, the head of the department of Radiochemistry and the head of the laboratory for INAA. Also external experts may be consulted. The reflections may result in recommendations to the quality system and its interaction with routine analysis, scientific research and service activities.

Additionally, there is an external audit:

(iv) The RvA annually audits the laboratory for INAA, and assesses to what extent the performance of the laboratory complies with the STERLAB criteria and the underlying documents in the quality manual. This audit includes a review by a peer on INAA. The findings in this annual audit are decisive on continuation of the accreditation. The audit report may contain comments on the observed operationality of the quality system in view of the criteria, eventually demands for corrective actions as soon as possible and further recommendations for improvement.

7.3.3 Internal improvement management

One of the characteristics of a quality system is that it should include procedures for continuous improvement. The motives for improvement are partly derived from

(i) Day-to-day observations with the various activities.
(ii) Registered cases of non-conformance.
(iii) Suggestions from the employees.
(iv) Observations from the internal audits.
(v) External developments.

ad (i) - (iii). During the awareness building stage the employees learn the importance of recognizing and reporting situations of non-conformance and mistakes, but also to

include their own vision on the causes, opportunities for improvement and prevention of repetition. Similarly, new ideas and suggestions for minor changes of the quality system are reported. The quality system provides procedures to process the entries as soon as possible, but anyhow within two weeks, and to give feedback to the employees. In this way the quality system is in a state of continuous and (inter)active improvement and further prevention of repetition of work can be accomplished. The quality coordinator collects all entries and evaluates preventive and corrective actions and their effects. Thus, at a central point in the organization eventual correlations between cases of non-conformance may be observed.

The systematic approach to non-conformance and the rapid response contributes to maintain the discipline of the employees to comply with the prescripted procedures, even when it is observed that it is not functioning optimally; or to record precisely where different approached have been followed preceding the implementation of modified (or new) standard operating procedures.

The changing attitude and style of working of the users led to less easier satisfaction with results when these, in their professional opinion, 'wriggled'. Some of the underlying problems have been tackled by the harmonisation of operations and design of assurance steps as for the production of pipetted neutron flux monitors. But it also initiated renewed attention to those sources of error in INAA which hitherto were considered to be neglectable. Examples are geometry effects with well-type detectors [9] and the use of sum-peaks in the interpretation of gamma-ray spectra [10]. Also addendums to tabulations of nuclear reaction parameters have been published [11, 12].

The (re)determination of standardization parameters has been fully documented now, and it is understood why in the past discrepancies were observed between results obtained when counting a sample at different spectrometers. Now such discrepancies are used as a tool in a method for quickly assessing sources of variation in INAA [13].

The effects of preventive actions have already been illustrated in *paragraph 6.5.2, Table 6-5.*

ad (iv). In the internal audits attention is partly directed on the operationality of the standard operating procedures. It occurs that employees sometimes unintendly systematically deviate little from the prescripted path; such deviations also are not registered as non-conformance. Still it is important to assess the reason of it, and eventually to modify the respective part of the quality system. Modifications with consequences for the quality system as a whole are presented by the quality coordinator and discussed at the weekly work-meeting of the laboratory's employees.

ad (v). Amongst the external developments belong the suggestions from RvA's audit team during the annual audit. These professionals not only observe many different quality systems -and thus different approaches for comparable situations- also the interpretation of the criteria sometimes may alter slightly, aiming at improvement of the performance of the respective part of the quality system.

7.4 COST-BENEFIT CONSIDERATIONS

Quality management and quality assurance increase the cost of operation, but the increased costs must be fairly judged against the benefits derived. In the development stage between January 1990 and November 1992, no time keeping has been done; however a résumé learned that the effort invested by the 7 employees (staff, and some of the technicians and analysts) of the INAA actively involved in the development of the quality system summed up to about 2 man-years. The assistance and consultancy of the senior analytical chemist integrated to about 0.7 manyears. Miscellaneous costs came from small investments in the laboratory and stationery for the manual and forms. The RvA decides annually on the tariff for the process of accreditation. In *Table 7-3* these costs are summarized. An estimated overall total of about Dfl. 300,000 results.

Table 7-3. Estimation of costs (in Dfl) for realisation of the quality system of the laboratory for INAA

2 manyears (integrated) from INAA research group	200,000
0,7 manyears (integrated) from consultant	70,000
miscellaneous utensils and stationery	25,000
accreditation audit	15,000
TOTAL	**310,000**

Once accredited, returning annual costs[4] should be taken into account with respect to prevention, appraisal and correction. The most important contributions to these categories can be estimated:

(i) PREVENTION COSTS are costs required to keep unacceptable data from being generated in the first place. They include costs associated with training of personnel, the necessary system calibrations and performance checks.
Time for calibrations (equipment, elements, pipettes, balances) and performance checks integrate up to about 1 manyear. In addition to this, costs should be added for stationery for the manual and forms.

(ii) APPRAISAL COSTS are costs required to sustain the system. These include the internal audits, alterations in the quality manual, and of course the quality assurance assessment (see *Chapter 6*) including the reporting and evaluation of these activities.
The audits require much attention of the quality coordinator (0.3 manyear) and the Institute's quality manager for his internal audits (0.05 manyear). Also the costs of the audit by RvA should be accounted for, since it decides on the continuation of the accreditation. Moreover, accredited laboratories pay an annual fee to the RvA and EUROLAB. Also the (mandatory) participation in laboratory intercomparisons imply appraisal costs.
The net costs of the quality assurance activities required in the frame of the accreditation follow from *Chapter 6, Table 6-6*, and amount approximately Dfl. 7.50 per sample. Here, the appraisal costs are derived from an estimate of, on the average, 3000 samples per year.

(iii) CORRECTION COSTS are those required to correct conditions that have been found to be out-of-control, or less than satisfactory. These include the costs for problem investigation to determine the cause of poor quality data; the implementation of corrective and new preventive measures and reanalysis of samples. These aspects have been discussed in *paragraph 6.6*. From the data given in *Table 6-7* an average estimate of 20 corrective actions can be derived, each requiring approximately 30 minutes of work.

An estimate of these costs is given in *Table 7-4*. The cost increase amounts about 15 % of the operational costs of the laboratory. Most of this increase is assignable to calibrations, performance checks and quality assurance assessment.

---

4 *The realization of the quality system has, in the respective years, been justified in the annual research and development program of the institute. Therefore, the cost-benefit evaluation does not include a proportional part of these costs of realization. It is in analogy with the cost analysis of INAA which also does not include the costs related to the development of the technique, but only the running costs.*

Table 7-4. Estimate of costs (in Dfl), required for maintenance of the accredited quality system

Prevention costs:	
1 manyear (integrated)	125,100
stationery for manual and forms	5,000
Appraisal costs:	
time by quality coordinator (0,3 manyear) and quality manager (0,05 manyear)	45,800
annual accreditation renewal audit	8,000
net costs quality assurance (3000 samples at Dfl.7.50, see *Table 6-6*)	22,500
annual fee to RvA	8,000
Correction costs:	
see *Table 6-7*, assuming 20 cases per year	850
TOTAL	**215,250**

As has been demonstrated, these costs for sustaining an accredited quality system can be quantified since they are out-of-pocket costs. As a contrast, the benefits are much more difficult or impossible to quantify, and to turn into money:

(i) Less repetition of analyses and less corrections because of last moment discoveries of small mistakes and miscalculations are time savers. A conservative estimate is that approximately 10 % of the time might been saved of the 6 analysts; it corresponds to annual savings of approximately Dfl. 50,000.

(ii) The trackability of analyses by the system for coding, and the extensive documentation and registration of relevant parameters is also a time saver when applicable. The harmonisation and documentation of operations resulted at savings in time for training of new personnel.
When estimating the time save by documentation and trackability to approximately 5 %, it corresponds for all 12 employees (staff, technicians, analysts, students) in the laboratory to approximately Dfl. 70,000.

(iii) The documentation and assignment of deputies both contribute to safeguard the laboratory against 'single points of failure'. The benefit is with the continuation of operations.

(iv) The system for assurance of the analytical quality is a safeguard against the release of bad results and the possible forthcoming claims and other costs. In *Table 6-8* it has been shown that between 1992 and 1995 timely corrective actions prior the release of the report prevented that on 591 samples (out of

11,377 samples processed in total) inaccurate results would have been reported.
This implies that by the corrective actions it may be prevented that approximately 150 samples have to be re-analyzed when the errors would otherwise be detected after reporting; this represents a value of approximately Dfl. 30,000.
But the system for quality assurance also is a time-saver when it comes to discussions on the verification of results; this verification is implicitly covered by the accreditation.

Table 7-5. Estimate of annual benefits (Dfl) resulting from the accreditation of the laboratory for INAA

less repetition and less corrections	50,000
documentation and trackability	70,000
safeguard against single points-of-failure	not quantifiable, p.m.
prevention of release of bad results	30,000
prevention of claims because of bad results	
prevention of discussion on verification	not quantifiable, p.m.
	not quantifiable, p.m.
third party contracts	60,000
image building	not quantifiable, p.m.
TOTAL	**210,000**
	+ p.m.

(v) Laboratory accreditation has become indispensable to be eligible for third party contracts. At least two of the commercial INAA contracts wouldn't have been possible without the accreditation, corresponding to a turnover of approximately Dfl. 150,000 corresponding to additional funding for the laboratory of approximately Dfl. 60,000.

In addition to this considerations it should be noticed that:

(vi) The quality system and accreditation serves the image of the Interfaculty Reactor Institute and the Delft University of Technology. The Institute -and by it the University- now may demonstrate that it is possible to educate students in a culture of quality management, thus complying with needs set by

society. It may serve as an example to other university groups inside and outside the country who may have their first tangible acquaintance with quality management via the laboratory for INAA.

The estimates are summarized in *Table 7-5*, and indicate that at least Dfl. 210,000 can be accounted for as benefits of the accreditation.

7.5 DISCUSSION

7.5.1 General

From *Table 7-6* an impression can be obtained how the employees of the laboratory experienced the introduction of quality management. The employees are aware of the importance of the quality system, they realize the importance of compliance and the benefits are taken as granted (whereas the objections are sometimes disseminated). As such they do not observe directly anymore that the organized way of training and qualification, the more careful working, the care for correct preconditions altogether has led to more a far more reliable way of carrying out analyses; and thus that indeed far less analyses go wrong and have to repeated. Since repetition of work has become rather exceptional, results are now reported on time, as agreed upon, which makes the laboratory in this respect a reliable partner both in related (cooperative) research projects -often with a tight timeframe e.g. because of PhD programs- as in commercial services. This reliability is shared with the absence of doubt on the quality of the analysis' results, as described in more detail in *Chapter 6*.

The quality system at the laboratory for INAA focuses on routine analyses as typically encountered in applied research; however, since the equipment and laboratory facilities involved may be used for both routine analyses as well as strategic (and fundamental) research the management regime for equipment and facilities is applicable without compromises to both disciplines. The approach to documentation and registration as followed in routine operations is recommended but not rigidly prescribed as long as the research operations have an ad-hoc character (see below, *paragraph 7.5.3*).

Table 7-6. Summary of advantages and objections of the quality system from personal experience of the laboratory's personnel

POSITIVE EXPERIENCES	NEGATIVE EXPERIENCES
+ trackability of work, equipment, performance, etc.	- many forms and administrations
+ analysis process well structured	- difficult to cope with required approvals
+ quality coordinator	- need to check the discipline
+ management of non-conformance; beneficial in problems	- updating the quality manual is time consuming
+ attitude to work and care for work environment	- sometimes interference with scientific progress

Some consequences of quality management -particularly when related to the formal accreditation- are not always understood and accepted by outsiders, interacting with the laboratory, particularly outsiders from other units within the IRI. For instance, much higher demands than before are set to e.g.

(i) Training and the necessity to acquire formal approval to carry-out laboratory tasks: tasks which they perhaps already carry-out for many years in other laboratories.

(ii) Documentation and registration of observations.

(iii) The fitness for the purpose of equipment: it is not always understood that work may have to be postponed a while until it can be demonstrated that the performance of equipment (or laboratory tools) is meeting the requirements as defined by the quality system.

7.5.2 Cost-benefit aspects

The cost-benefit evaluation in *paragraph 7.4* indicates that the costs of sustaining accreditation of the quality system are more-or-less counterbalanced by the advantages. The evaluation also makes clear that part of the tangible benefits is the net income from commercial contracts. This evokes the question if formal accreditation of the quality system is economically justifiable if the number of commercial analyses would decrease or, eventually, if commercial activities would end. It has been experienced that the annual audit by the RvA has, unintentionally, a 'guard-dog' function: it supports staff and the quality coordinator to improve again awareness for quality, and to improve together the sometimes declining discipline. If

continuation of the accredited status would not be justifiable anymore, it is very questionable if the same quality of performance will sustain on outside pressure, changing priorities and changing motivation of the employees and in-house customers: a 'why bother' attitude may result. Moreover, as can be seen from *Table 7-5*, there are still several not-quantifiable benefits that should be included in such a decision.

7.5.3 Quality management in a university setting

Total quality management is characterised, amongst others, by the wariness with which conditions are checked before operations are carried-out and the attention spend to proper documentation, registration and keeping-up of notebooks. When quality management is applied to scientific research this way of working is often considered to be cumbersome, time-consuming and limitizing progress. One of the reasons is that scientific research is often characterised by operations and deviating pathways which are defined ad-hoc during the work, rather than following pre-defined harmonised procedures. Also the type of information to be recorded can not (always) be decided upon in advance, and equipment settings may need to be changed several times before the appropriate setting is found, or eventually return to the original setting. The necessity to record all these intermediate changes is sometimes indeed not applicable.

In *paragraph 7.3.2* it has already been mentioned that quality assurance sometimes evokes operational research when (small) systematic errors are discovered which cause conflicts with e.g. (self defined !)approval criteria for e.g. calibration, fitness-for-the-purpose or results of internal quality control. At the onset of a quality system such operational research is almost inevitable since many sources of errors may suddenly be perceptible. But when the prime sources of errors have been dealt with, the remaining problems may easily invite to invest a considerable operational research effort which is consumed of the capacity for e.g. strategic and applied research. The type of insight in the methodology that is gained from such operational research effort to solve systematic errors of e.g. 1 % -'last decimal improvement'- should be balanced to the type of insight that might be gained when the same effort would be invested in innovative research.

7.6 REFERENCES

[1] J.W. Fleming, B. Neidhart, W. Wegscheider, 'A Proposal for a New Term to describe Traceability to a Sample',
Accred.Qual.Assur.1 (1996) 35

[2] 'International Vocabulary for Basic and General Terms in Metrology', 2nd. Edition, (1993) ISO, Geneva, Switzerland

[3] J.E. Sloof, 'Environmental Lichenology: Biomonitoring Trace-element Air Pollution', Thesis, Delft University of Technology, Delft (1993)

[4] A.A. Goede, 'Selenium in Marine Waders', Thesis, State University of Utrecht, Utrecht (1993)

[5] P. Bode, J.P. van Dalen, 'Accreditation: a Prerequisite, also for Neutron Activation Analysis Laboratories ?!',
J.Radioanal.Nucl.Chem. 179 (1994) 141 - 148

[6] P. Bode, 'Quality Management and Laboratory Accreditation at a University: What can be learned from Experience ?',
Analyst 120 (1995) 1527 - 1533

[7] P. Bode, 'From Misconception to a Must: the Measured Merits of TQM and Accreditation in INAA',
Accept. for publ. in J.Radioanal.Nucl.Chem.

[8] Organizer: Wageningen Agricultural University, dept. of Soil Science and Plant Nutrition, P.O.Box 8005, 6700EC Wageningen, The Netherlands

[9] S.J. Gelsema, M. Blaauw, 'Geometry Effects in Well-type Ge-detectors due to the Introduction of High-Z Linings',
Nucl.Instr.Methods A368 (1996) 410 - 415

[10] M. Blaauw, P. Bode, 'The Interpretation of Artificial Peaks in k_0-Based NAA',
J.Radioanal.Nucl.Chem.169 (1993) 201 - 208

[11] M. Blaauw, 'Comparison of the Catalogues of the k_0 and the k_{Zn} Single Comparator Methods for Standardization in INAA'
J.Radioanal.Nucl.Chem. 191 (1995) 387 - 401

[12] M. Blaauw, C.P. van Dijk, M. Sarilar, M. Koese, 'The IRI Reaction Cross-section for Short-time Neutron Activation Analysis',
Trace and Microprob.Techn. 14 (1996) 45 - 56

[13] M. Blaauw, M.J.J. Ammerlaan, P. Bode, 'Quantification of Sources of Variation in Neutron Activation Analysis',
Int.J.Appl.Rad.Isotop. 44 (1993) 547 - 551

CHAPTER 8 DISCUSSION

8 DISCUSSION

8.1 INTRODUCTION

If it is assumed that the need for more information on distribution, transport, behaviour and interactions of elements will last, the need for elemental analysis will be prolonged in order to get information on concentration, distribution and/or chemical species of elements in a large range of samples from various origins. Instrumental neutron activation analysis (INAA) is one of the methods to be selected. Its non-destructive character makes INAA complementary to other methods of elemental analysis, whilst the nuclear physical basis of INAA may be benefitted for an independently check of results obtained via other analytical techniques. These considerations justify studies of, and with INAA.

At IRI, research into the methodology and in the applications of INAA is favoured by:

(i) The scientific basis, creativity and spirit of the scientists and technical support employees with strongly different disciplines of education.
(ii) A nuclear research reactor with a highly reliable operating performance.
(iii) State-of-the-art counting facilities and facilities for data handling.
(iv) Unique newly developed techniques, methods and organization of work including total quality management.
(v) The available expertise at the institute on related sciences, such as neutron physics, nuclear physics and radiation chemistry.

Aspirations for innovation, automation and expansion, and effectiveness of operation rather than consolidation and application have been the incentives for the laboratory for INAA in the period 1984 - 1996; part of the resulting activities have been described in this thesis. These aspirations were fed by

(i) The regular feedback from the users of the facilities; their demands for better sensitivities, shorter turn-around times and reliable results have, amongst others, been accommodated for by the automated fast irradiation system CAFIA, the prominent position of the well-type detectors, the implementation of quality control into a program for quality assurance and ultimately into a quality system.
(ii) Insight in INAA and gamma-ray spectrometry, built-up over a period of more than 25 years and the opportunity to set-up an interdisciplinary program which resulted in a facility and methods for large sample INAA.

(iii) A good portion of open-mindedness and sense of reality that organization of work in a university environment should abandon the traditions of non-commitment to improve effectiveness of operations, to reduce needless repetition of work and to improve quality and reliability of the results: the introduction of quality management which is in accordance with developments and requirements in society and industry.

The accomplishments of the laboratory described in this thesis will be discussed against the objectives of the respective research efforts.

8.2 STRATEGIC RESEARCH AND DEVELOPMENT

8.2.1 Big Samples Neutron Irradiation System

Future will tell if large sample INAA can be marked as a high-light in chemical analysis, particularly in INAA. The exploration of the opportunities of large sample INAA is a challenge for the laboratory. Further development and application will be done in close cooperation with possible customers, formulating the analytical questions, supplying the samples and using the results. Attention will be paid to aspects of inhomogeneity; not only as a nuisance for the analysis, but the determination and identification of an inhomogeneity may be considered as a goal in itself. Large sample analysis also enables experimental verification of the theory on the representativeness of sampling, and the sampling factor. The ability to analyze large samples is a unique addendum to the characteristics of INAA allowing for new niches such as waste recycling. In addition it offers an outlook for direct determination of the distribution of elements in large samples, in the most simple way by longitudinal scanning.

With routine -small sample- INAA it is generally assumed that inhomogeneities do not affect the accuracy of the final result; the degree of accuracy is derived from the analysis of the quality control sample. The situation is different for large sample INAA. The quality -in terms of degree of accuracy- of the analysis of a large, and possibly inhomogeneous, sample may have to be redefined; moreover quality control samples would have to match the real samples with respect to inhomogeneity to establish systematic errors. Finally, it will be interesting to investigate for which size and type of samples the omittance of corrections for neutron self-shielding and, possibly, neutron self-thermalization in hydrogen-rich materials, interfere with the pursued degree of accuracy of the analysis.

8.2.2 Carbonfiber Autonomous Facility for Irradiation and Analysis

Carbon-carbon composite as construction material for the irradiation end of a fast rabbit irradiation facility proved to be a close-to-ideal solution to prevent interfering radioactivity by contaminants on the irradiation container (or: 'rabbit'), abrased during transport. In the present situation the aluminium impurity in the rabbit's polyethylene, and the ^{41}Ar-activity produced in the remaining air inside the rabbit are the remaining induced activities which interfere with the measurement of the activated sample.

The concept of carbon-carbon composite has also been proposed in new irradiation facilities at Missouri University Research Reactor Columbia, Mo, USA, at the ASTRA reactor of the Österreichisches Forschungszentrum Seibersdorf, Austria, and at the newly to be developed FRM-II reactor in Garching, Germany. One of the drawbacks of the carbon-carbon composite is that the material is not water-tight, and always have to be contained in an e.g. Al casing. Progress in diamond-film coating technology indicate more general applicability of this material, and possibly it may be considered in the future as an alternative for carbon-carbon composite, or as a coating for this material.

Automated cyclic activation analysis procedures to enhance the sensitivity for certain elements are now practically feasible. The automation of the facility has resulted in lower analysis costs for the determination of short-lived radionuclides, compared to the determination using the old fast rabbit system. As an example, the cost of a selenium determination via the radionuclide ^{77m}Se in toe-nail clippings could be reduced by approximately 40 %. It contributes to an improvement of the economics of INAA, which is often percepted to be more expensive than alternative techniques.

The sensitivity of the analyses with this facility may be further improved when a higher neutron flux would be available. This may be accomplished by positioning the irradiation end in a position closer to the reactor core, i.e. in the water-reflector, in one of the Be-reflector elements or at an in-core position. As an alternative -or even as an addendum-, the receiving end for counting could be redesigned to fit inside a well-type Ge-detector.

8.3 OPERATIONAL ACTIVITIES

8.3.1 Detectors for INAA

The sensitivity improvement factor -whether or not cost indexed- is an objective tool to assess the opportunities of various detector types for improvement of sensitivity

in INAA. Well-type detectors - which offer better versatile prospects for use in INAA than Compton suppression systems- were introduced at the laboratory for INAA in 1976, 1984 and 1988. Even with the availability nowadays of very large Ge-detectors, preference would remain for a well-type detector because of smaller counting geometry effects and economical considerations.

An interesting further improvement in sensitivity may be accomplished when a well-type detector would be surrounded by a Compton suppression shield. Such a system has been reported [1], albeit not for use in INAA. The peak-to-Compton ratio of this system is 300 : 1. A very large well-type (430 cm^3) has been reported too for measurements of natural radioactivity [2]. When using such a large well-type detector together with a Compton suppression shield, the improvement in sensitivity when compared to measurements on a not Compton shielded, standard 20 % detector would be approximately 10 for samples counted on the end-cap (gamma-rays not subject to cascade losses), and a factor of 20 and more when geometrical considerations require a distance of e.g. 5 cm or more to be applied between sample and detector.

Further improvement of detectors will not contribute dramatically to an improvement of the sensitivity in INAA. The absolute counting efficiency of large well-type detectors varies already from approximately 85 % to 20 % in the region 100 keV - 1000 keV. Even when crystals could be grown of a size twice as big, e.g. 800 cm^3, the maximum extra improvement in INAA would be approximately 1.5.

8.3.2 Operational quality assurance

In the past ten years the analytical quality of the INAA results has improved partly by embedding the quality control in a system for quality assurance. By several technicalities (e.g. longer irradiation and counting times, larger sample-to-detector distances, rotation during irradiation and counting, use of more flux monitors) the contributions to final uncertainty may be further reduced, whilst better quality in terms of accuracy may be accomplished via more attention to the aspects of standardization (choice of chemical compounds, use of commercially available solutions of primary standards, further improvement of pipetting). Greenberg et al. [3] estimated that the ultimate accuracy that might be achieved in NAA would be approximately 0.06 %, relative at the 95 % confidence level.

However, the more is asked of accuracy and precision with sample analysis, also the more is also asked of the intrinsic quality -and number of element concentrations certified- of the certified reference materials to verify this better quality. In addition, it is questionable if attempts to improve further on better precision and accuracy are worth

the effort in view of (i) the ratio between the sampling variance and the analytical variance for the type of analysis the laboratory is involved: biomonitoring studies [4] have shown that the local variance when taking samples at a selected sampling site can be a factor 50 higher than the analytical variance; and (ii) the technical abilities of the laboratory and its employees: the quality of an analysis is as good as the analysts' performance. It is therefore equally necessary to pay also more attention to the analysts' attitude and ability to perform analysis with a better quality than was asked before. The quality of the analyst performance is linked to the quality of the in-house education and training, working conditions and pressure, state of the laboratory tools and equipment, environmental conditions of the laboratories, and even details like the frequency of displacements between office, counting room and laboratory.

8.3.3 Total Quality Management

Implementation of quality management in analytical laboratories, even at universities and at research facilities is possible, desirable and sometimes even inevitable. This does not implies that every laboratory should per sé pursue accreditation, since for this step other motives play an role. But specifically for NAA laboratories there are four strategical reasons that plea for the introduction of quality management and, if possible, formal accreditation:

(i) *To facilitate the validation of other methods of elemental analysis.*
As a physically independent method NAA has much to offer for the validation of other methods of elemental analysis. Particularly when this has to be done in the framework of another quality system under development, the counterpart will probably demand that the method of validation -like NAA- is under control by a quality system according to internationally accepted standards.

(ii) *To participate in the certification of reference materials.*
NAA has an acknowledged position as one of the preferred methods for the certification of reference materials. Certified reference materials play a very important role in the assessment of the technical competence of accredited laboratories. It is an understatement to say that it is remarkable that many of the laboratories which participate in establishing certified values -and there are quit a few NAA laboratories- do not have an accredited quality system themselves. It is not so strange to expect that in the future demands will be set that also the way the underlying data are acquired, is described in a quality system and assured by accreditation. If the necessary changes are postponed too long, or not

accepted, the opportunities to participate in reference material certification for these NAA laboratories may be endangered in the future.

(iii) *To ensure that in the future authorities and other laboratories will respect NAA as a full-bodied technique, and not as an academic curiosity.*
Many nuclear research facilities need some form of commercial NAA to acquire extra funds; here it improves the commercial position and acceptability by authorities and industry. In The Netherlands, the Ministry for Health, Public Environment and Environmental Affairs decided in 1994 to have all their environmental analysis and research be carried out by certified and accredited laboratories only. The European Union considers to establish 'notified bodies', i.e. accredited laboratories with a communitive mission in the enforcement of European Norms.

(iv) *To preserve the hitherto undocumented knowledge of the laboratory's staff for future generations.*
Several NAA and radiochemistry laboratories deal with the aging of their staff; it would be a waste if a new generation would have to start all over again, to a certain extent.

Without making accreditation to be a precondition, some of the principles of quality management should be mandatory and demonstrably operational in laboratories participating in (international) interlaboratory research programs to ensure or at least to enhance comparability and traceability of data and experimental conditions. The advantage of accreditation of a quality system is not only related to the thus achieved status of the laboratory: the regular audits -as a sort of 'watchdog'- imply that the laboratory should take care of the periodically fading discipline to maintain compliance with the accreditation criteria.

8.4 PROSPECTS

As has been explained in the *Chapter 1*, the period 1984 - 1996 was characterized by innovations, modernization and change in attitude. Several of these activities are forthcoming from analytical, instrumental and organizational deficiencies, observed during application of INAA. The importance of the various improvements and innovations can be demonstrated by shifting the emphasis in the research program towards applied research, albeit with an eye for strategic developments. The operational

activities that will follow are hard to predict since they are often an offspring of the strategic and applied research activities.

Some prospects for the types of research related to the scope of this thesis, are discussed here.

8.4.1 Strategic research and development

As has been described in *paragraph 1.3*, this type of research has a strong affiliation with the laboratory's vision how to secure and improve the position of INAA. This can be supported by an analysis of the strong and weak aspects of the technique, opportunities and applications which all may be different from one INAA laboratory to another.

Whereas the relatively long turnaround time of INAA is considered as a drawback inherent to the method (see below, *paragraph 8.4.4*), a weakness in the performance of the analysis at the laboratory for INAA at the IRI is the effort, required for training new analysts, particularly for the interactive interpretation of the spectrum analysis' results.

Automation of counting procedures has made progress at IRI, quality assurance has been introduced, quality management has led to a higher effectiveness and traceability of operations but complete automation of spectrum analysis has to some extent stagnated. Consequently, use of the facilities for short-term (stretched over e.g. 3 months) applied research programs by new analysts, students or (foreign) guests require a repetitive effort of the laboratory for training, thereby reducing the opportunities for real innovative research. Improvement in quality also should include improvement in the utilization of human resources. Re-design of the spectrum analysis software and the use of intelligent routines are required to reduce this substantially without reducing the responsibility of the analyst to inspect the quality control. It thus will contribute to better economics of INAA services.

Some other prospects for further strategic research and development have already been mentioned in the *paragraph 8.2.1.*: (i) large sample INAA offers, in principle, opportunities for determining the spatial distribution of the elements and of natural and anthropogenic radioactivity, e.g. in segregated and/or inhomogeneous samples and (ii) large sample INAA may contribute to studies on sampling, sub-sampling and representativeness of the analytical portion.

It has been noticed in the above that the relatively long turnaround time of INAA is often precepted as a drawback of the method, giving the customer a motive to prefer an other method of analysis. In this respect it is important to mention that

improvement of turnaround time on INAA may, except by the use of short half-life radionuclides, attained by implementing the method of prompt-gamma NAA (PGNAA). PGNAA itself is a well established technique, often exclusively used for determination of a few elements like H, B, Cd and/or Gd. But with PGNAA the results are available immediately after counting, which implies for some elements much shorter turnaround times than in conventional INAA, albeit with poorer detection limits.

8.4.2 Operational activities

In *paragraph 8.3.1.* it has already been discussed that the combination of a well-type Ge-detector with a Compton suppression shield is one of the remaining instrumental opportunities to improve detection limits in INAA.

The necessity to alter the software for gamma-ray spectrum analysis and -interpretation has been mentioned already in *paragraph 8.4.2.* Additionally to the development of the required 'intelligent' software, the programs may be further optimized with respect to the number of human interactions related to routine operations, like the related administrative aspects.

With respect to the quality assurance it will become interesting to establish how the performance and operationality of the laboratory will change, and hopefully improve once the interpretation of control charts is brought into accordance with the 'Westgard' rules, specified in the IUPAC international harmonized protocol for internal quality control [5].

8.4.3 Applied research

Applied research hasn't been directly covered by the scope of this thesis but in the interaction of the strategic research and development, and of the operational activities with the applied fields have been regularly mentioned in the various chapters. Therefore, it is unavoidable to extent the discussion on prospects for INAA to this type of research. The list of possible applications of INAA is very large, as has been described in *paragraph 1.3.3.* However, it is generally accepted that particularly due to the availability of the microwave digestion method many of the traditional 'indestructible' sample types, like rocks and/or sediments, can nowadays be processed by alternative techniques. Moreover, the alternative non-destructive method, X-Ray fluorescence analysis, has got new better prospects with respect to sensitivity by the development of

the total reflection approach. It can therefore be concluded that INAA is loosing some of its traditional niches.

However, the method still has several characteristics that make it in some respect unique, or attractive as complementary method:

(i) The nuclear principles and the well-known physics allow for a high degree of accuracy; this remains particularly important for the analysis of candidate certified reference materials, and for the inter-validation of other methods of chemical analysis, including the verification of dissolution steps.

(ii) The almost freedom from analytical blank makes the method very suitable for analysis of highly pure materials (e.g. foodstuffs, or to support certificates of purity for suppliers of chemical compounds) and very low quantities (such as air particulate matter).

(iii) The ability to analyze large quantities in those applications where sample-size reduction is difficult or too expensive (e.g. materials from waste-streams).

(iv) The ability to analyze large series of solid samples which are individually so different that it is not economical to develop tailored destruction methods for each sample (e.g. materials from waste streams, or samples from large-scale ecological studies).

(v) The ability to analyze samples with very resistant matrices such as glass and composites.

In the selection of applied research it has to be realized that the employees of the laboratory have only limited professional capabilities to cover the scientific aspects of applied fields of science: a serious cooperation is needed with professionals from these fields, though with preservation of the identity of the laboratory's efforts, rather than just supplying analytical services.

8.5 REFERENCES

[1] G. Harbottle, J.B. Cumming, 'Performance and Promise of the Compton Suppression Well Counter',
Nucl.Instr.Meth. A353 (1994) 503 - 507

[2] J.-L. Reyss, S. Schmidt, F. Legeleux, P. Bonté, 'Large, Low Background Well-type Detectors for Measurements of Environmental Radioactivity',
Nucl.Instr.Meth. A357 (1995) 391 - 397

[3] R.R. Greenberg, R.M. Lindstrom, D.A. Becker 'Accuracy in Neutron Activation Analysis -what can we ultimately achieve ?',
Invited lecture, presented at the 9th Int.Conf.on Modern Trends in Activation Analysis, Seoul, Korea, September 24 - 30 (1995)

[4] H.Th. Wolterbeek, P. Bode, T.G. Verburg, 'Assessing the Quality of Biomonitoring Surveys via Signal-to-Noise ratio analysis',
Sci.Tot.Environ. 180 (1996) 107 - 116

[5] M. Thompson, R. Wood, 'Harmonised Guidelines for Internal Quality Control in Analytical Chemistry',
Pure and Appl.Chem. 67 (1995) 649 - 666

APPENDIX DETECTION LIMITS IN INAA AND Ge-DETECTOR SPECIFICATIONS

APPENDIX DETECTION LIMITS IN INAA AND Ge-DETECTOR SPECIFICATIONS

A.1 FACTORS DETERMINING THE DETECTION LIMITS IN INAA

In *paragraph 5.4.3* of this thesis the derivation of an expression for the minimum detectable disintegration rate $D_{m,1}$ has been given (*Equation 5-4*):

$$D_{m,1} = \frac{A_m}{\varepsilon_{p,1}\, a_{\gamma_1}\, t}\{[2bR_1\{B_{C_{2,1}} + B_{N,1}\} + \frac{A^2{}_m}{4}]^{0.5} + \frac{A_m}{2}\} \qquad \text{A-1}$$

in which

A_m = the reciprocal of the fractional error

$\varepsilon_{p,1}$ = the photopeak efficiency for the gamma-ray 1, the gamma-ray of interest, at a given source-detector distance

$a_{E\gamma 1}$ = the abundance of gamma-ray 1 in the decay

t = the counting time

R_1 = the resolution at the peak of gamma-ray 1

b = the factor which when multiplied by the resolution gives the number n of channels included in the peak

$B_{C2,1}$ = the number of counts per channel due to the Compton continuum of the interfering gamma-ray 2 at the location of the gamma-ray 1

$B_{N,1}$ = the natural background in counts per channel at the location of the gamma-ray 1

In the same paragraph also the following assumptions on the shape of the gamma-ray spectrum and the location of the peak of interest in that spectrum have been distinguished (see *Figure A-1*):

a. The count-rate of the source is high, and/or the required fractional error is not so low, and thus $2bR_1\{B_{C2,1} + B_{N,1}\} >> A_m{}^2/4$

(1) the peak is located on a dominant Compton continuum but the contribution of the natural background may be neglected: this case is denoted here with 'C'

(2) the peak is located on a Compton continuum and the natural background may not be neglected: it is denoted with 'C-B'

(3) the peak is located at the high-energy side of the dominant photopeak in the spectrum, on natural background. Now the contribution of the Compton background is not relevant: it is denoted with 'B'.

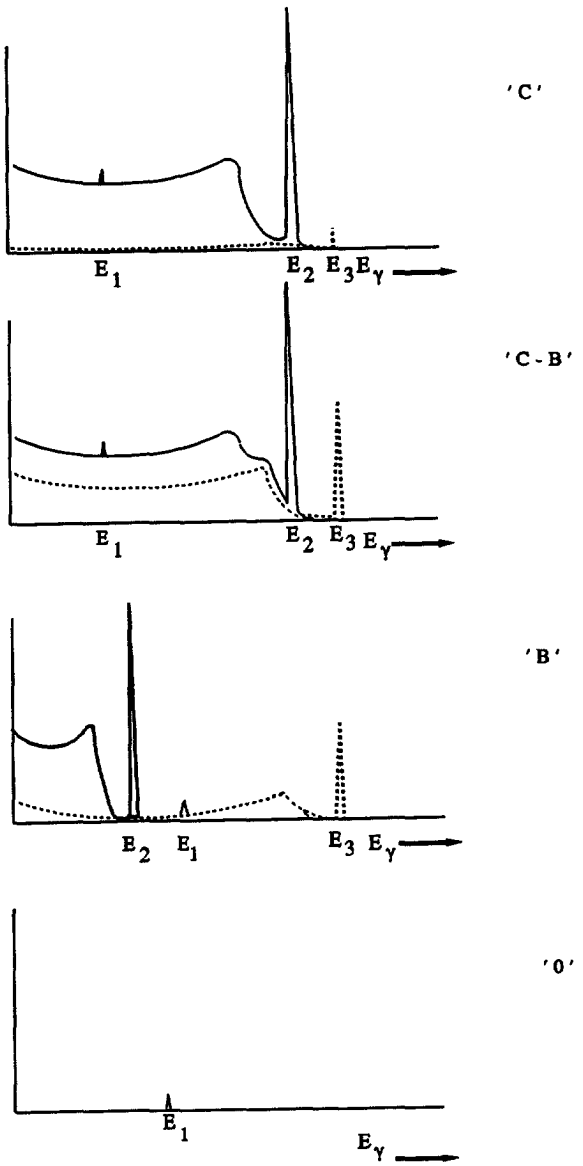


Figure A-1. *Schematic representation of the four distinguished cases for detection of a peak in a gamma-ray spectrum. Dotted: assumed shape of the background spectrum*

b. The count-rate of the source in the region of interest is very low and the required fractional error is low; thus $2bR_1\{B_{C2,1} + B_{N,1}\} \leq A_m^2/4$; this case is denoted here with '0' [1].

It should be noted that it also has been assumed that the peak of interest is considered to be 'interference free', i.e. the peak does not form part of a multiplet (when the difference between peak positions is less than 3 times the width of the Gaussian peak [1]) and its determination is not affected by partial overlapping neighbouring peaks.

For each of these cases *A-1* can be further simplified:

a. The count rate of the sample is high. Since $2bR_1\{B_{C2,1} + B_{N,1}\} >> A_m^2/4$, equation *A-1* firstly simplifies to

$$D_{m,1} = \frac{A_m \sqrt{2bR_1 \{B_{C_{2,1}} + B_{N,1}\}}}{\varepsilon_{p,1}\, a_{\gamma_1}\, t} \qquad \text{A-2}$$

From this *Equation* it can be seen that the detection limits that can be attained with a given detector is determined by the ratio

$$\frac{\varepsilon_{p,1}}{\sqrt{R_1\,(B_{C_{2,1}} + B_{N,1})}} \qquad \text{A-3}$$

Cooper [2] denoted this expression as *'figure-of-merit'* for comparison of detectors. Here, this ratio is used as 'sensitivity determining factor', and denoted here as f_S , in which the subscript *S* is used to distinguish the cases *C, C-B, B* and *0*. The factor can be further worked-out for the three cases:

(1). case 'C': the peak is located on a Compton background and the natural background can be neglected: $B_{C2,1} >> B_{N,1}$, and

$$f_C = \frac{\varepsilon_{p,1}}{\sqrt{R_1\, B_{C_{2,1}}}} \qquad \text{A-4}$$

(2). case 'C-B': If the peak of interest is located on a continuum in which nor

---

[1] *It should be noted that this is an exceptional case in INAA; as an example may serve the detection of ^{49}Ca via the 3084 keV, or ^{37}S via the 3103 keV. The gamma-ray spectrum in this region does not show an appreciable natural background, whilst the Compton continuum of the higher energy gamma-ray peaks of ^{49}Ca is very small.*

the Compton background, nor the natural background can be neglected it follows that

$$f_{C-B} = \frac{\varepsilon_{p,1}}{\sqrt{R_1 \, (B_{C_{2,1}} + B_{N,1})}} \qquad \text{A-5}$$

It should be noted that with a spectrometer with a Compton suppression shield (CSS) the passive shielding reduces the background for $E_\gamma > 250$ keV by a factor of approximately 4 extra [3], and $(B_{N,1})_{CSS} \div 0.25 \, B_{N,1}$, thus:

$$(f_{C-B})_{CSS} = \frac{\varepsilon_{p_1}}{\sqrt{R_1(B_{C_{2,1}} + 0.25 \, B_{N_1})}} \qquad \text{A-6}$$

(3) case 'B': the peak is located at the high energy site of the peak(s) causing the induced radioactivity. Still, the peak is at Compton continuum of the natural background, and then, comparable to case 'C' :

$$f_B = \frac{\varepsilon_{p,1}}{\sqrt{R_1 \, B_{N_1}}} \qquad \text{A-7}$$

and for a CSS-system :

$$(f_B)_{CSS} = \frac{\varepsilon_{p,1}}{\sqrt{R_1 \; 0.25 \; B_{N,1}}} \qquad \text{A-8}$$

b. In the second situation, denoted with case '0', a peak has to be detected in a spectrum of a source with a very low induced radioactivity,
and $2bR_1\{B_{C2,1} + B_{N,1}\} \leq A_m{}^2/4$
Now *A-1* can be rewritten as

$$D_{m,1} = \frac{A_m}{\varepsilon_{p,1} \, a_{\gamma_1} \, t}\{[\frac{A^2{}_m}{4}]^{0.5} + \frac{A_m}{2}\} = \frac{A^2{}_m}{\varepsilon_{p,1} \, a_{\gamma_1} \, t} \qquad \text{A-9}$$

The attainable detection limits will now be determined by the factor

$$f_0 = \varepsilon_{p,1} \qquad \text{A-10}$$

A.2 DETECTION LIMITS AND DETECTOR SPECIFICATIONS

A.2.1 Sensitivity determining factors

Since only a global comparison is aimed at, a simplified representation of the shape of the gamma-ray spectrum is used (see *Figure A-2*).

To link the sensitivity determining factors to detector parameters, the terms $B_{C,2,1}$ and $B_{N,1}$ have to be converted. The Compton background term $B_{C,2,1}$ can be estimated from the ratio of the photopeak efficiency ε_p of the interfering peak and the peak-to-Compton ratio, p_C, which is with most detector types specified for the 1332 keV line of ^{60}Co. In the simplified representation, the p_C-ratio is independent of the photon energy.

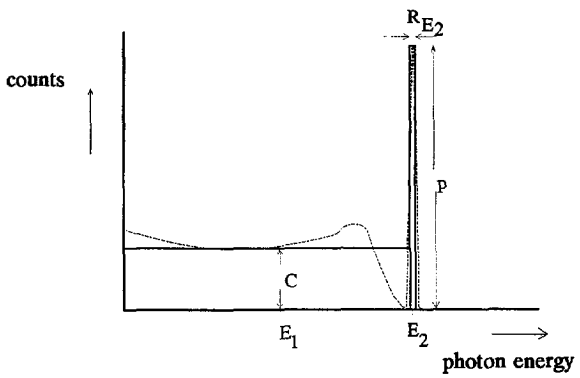


Figure A-2. Realistic (dotted line) and simplified (solid line) representation of a gamma-ray spectrum, no background assumed.

When S_S is the emission rate of photons of energy E_2 by the source, and since $N_{E,2} \approx R_{E2} P$, $\varepsilon_{p,2} = (R_{E2} P)/S_s$ and $p_C = P/B_{C2,1}$, it follows that

$$B_{C_{2,1}} = S_S \frac{\varepsilon_{p,2}}{R_{E,2}\, p_C} \qquad \text{A-11}$$

With respect to the natural background the situation is more complicated. Assume that the detector is well shielded, e.g. with a 10 cm thick Pb-layer, and that the background radiation may be represented as a monoenergetic source of photons of gamma-ray energy E_3. These photons firstly interact with this lead-layer, which alters the gamma-ray spectrum from monoenergetic to a distribution which can be schematically resembled as in *Figure A-2*; this spectrum of photons subsequently interacts with the detector crystal. Background events detected at e.g. gamma-ray energy E_1 thus are a combination of both photoelectric absorption of photons with gamma-ray energy E_1 resulting from the Compton interaction in the lead, and from Compton interaction of the high energy photons with energy E_3. Both groups of photons can be assigned with a emission rate S_B for the photons of energy E_3 and S_C for the photons with energies between 0 and E_3 keV. An estimate for the relation between S_B and S_C can be obtained as follows :

In calculations of the dose rate equivalent for shielding of photons with $E_3 \approx$ 1.5 MeV with a 10 cm lead layer, a build-up factor of ≈ 3 is taken into account [4]. This indicates that $S_C/S_B \approx 2$. The number of photons, N_{E1} with energy E_1 follows thus from:
$S_C = N_{E1}E_3 = 2S_B$, and:

$$N_{E_1} = \frac{2}{E_2} N_B \qquad \text{A-12}$$

This leads to the following general expression for the background term:

$$B_{C,2,1} + B_{N,1} = S_S \frac{\varepsilon_{p,2}}{R_{E_2} p_C} + S_B \frac{\varepsilon_{p,3}}{R_{E_3} p_C} + \frac{2}{E_2} S_B \frac{\varepsilon_{p,1}}{R_{E_1}} \qquad \text{A-13}$$

These expresssions *A-12* and *A-13* can now be substituted in the *Equations A-4 - A-10* to describe sensitivity determing factors in terms of photopeak efficiency, p_C-ratio and resolution only; in the new expressions only the parameters have been taken into account which are detector dependent:
case 'C':

$$f_C = \varepsilon_{p,1} \sqrt{\frac{p_C}{\varepsilon_{p,2}}} \qquad \text{A-14}$$

case 'C-B':

There are many cases in INAA in which the shape of the gamma-ray spectrum is determined by a high activity of a radionuclide with a prominent gamma-ray in the energy region between 1100 keV and 1500 keV, like ^{65}Zn, ^{46}Sc, ^{24}Na and ^{42}K. Moreover, quite often the natural background is primarily due to the natural occuring ^{40}K, e.g. in concrete construction materials, emitting gamma-rays of 1460 keV. These two considerations justify the simplifying assumption that $E_3 \approx E_2$ in the further calculations. Now also
$R_3 = R_2 = R_1$, which leads to:

$$f_{C\text{-}B} = \frac{\varepsilon_{p,1}}{\sqrt{S_S \varepsilon_{p,2} + S_B[\frac{\varepsilon_{p,2}}{p_C} + \frac{2}{E_2}\varepsilon_{p,1}]}} \qquad \text{A-15}$$

case 'B':

Here the same assumption has been made as in case 'C-B', resulting at

$$f_B = \frac{\frac{\varepsilon_{p,1}}{\varepsilon_{p,2}} p_C}{E_2 + 2\frac{\varepsilon_{p,1}}{\varepsilon_{p,2}} p_C} \qquad \text{A-16}$$

case '0':

$$f_0 = \varepsilon_{p,1} \qquad \text{A-17}$$

The sensitivity determining factors are summarized in *Table A-1.*

A.2.2 Sensitivity improvement factors

The attainable improvement in detection limits in INAA when using a selected detector, '*s* ' instead of a given detector '*g*', can be estimated from the ratio of the respective sensitivity determining factors: $f_s/f_g = (F_S)_{s,g}$, denoted here as the 'sensitivity improvement factor'. The subscript '*S*' is used to distinguish the cases 'C', 'C-B', 'B' and '0'. When in such a case the performance of the Compton suppression shield has to be evaluated, the passive shielding by the shield should be taken into account in the derivation of f_{CSS} for the cases 'C-B' and 'B'. The resulting expressions

are given in *Table A-2.*

Table A-1. Overview of the relation between detection limits in INAA and detector specifications

	Basic equation	*Linked to detector specifications*
f_C	$\frac{\varepsilon_{p,1}}{\sqrt{R_1 B_{C_{2,1}}}}$	$\varepsilon_{p,1}\sqrt{\frac{p_C}{\varepsilon_{p,2}}}$
$f_{C\text{-}B}$	$\frac{\varepsilon_{p,1}}{\sqrt{R_1 (B_{C_{2,1}} + B_{N,1})}}$	$\frac{\varepsilon_{p,1}}{\sqrt{S_S \varepsilon_{p,2} + S_B[\frac{\varepsilon_{p,2}}{p_C} + \frac{2}{E_2}\varepsilon_{p,1}]}}$
f_B	$\frac{\varepsilon_{p,1}}{\sqrt{R_1 (B_{C_{2,1}} + B_{N,1})}}$	$\frac{\frac{\varepsilon_{p,1}}{\varepsilon_{p,2}} p_C}{E_2 + 2\frac{\varepsilon_{p,1}}{\varepsilon_{p,2}} p_C}$
f_0	$\varepsilon_{p,1}$	$\varepsilon_{p,1}$

Table A-2. Sensitivity improvement factors $(F_S)_{s,g}$

S	$(F_S)_{s,g}$
C	$\frac{(\varepsilon_{p,1})_s}{(\varepsilon_{p,1})_g}\sqrt{\frac{(p_C)_s}{(p_C)_g}}\sqrt{\frac{(\varepsilon_{p,2})_g}{(\varepsilon_{p,2})_s}}$
C-B	$\frac{(\varepsilon_{p,1})_s}{(\varepsilon_{p,1})_g}\sqrt{\frac{(\varepsilon_{p,2})_g}{(\varepsilon_{p,2})_s}}\sqrt{\frac{(p_C)_s}{(p_C)_g}}\sqrt{\frac{2}{1+\frac{(E_2+2\frac{\varepsilon_{p,1}}{\varepsilon_{p,2}}p_C)_s}{(E_2+2\frac{\varepsilon_{p,1}}{\varepsilon_{p,2}}p_C)_g}}}$
C-B(CSS)	$\frac{(\varepsilon_{p,1})_s}{(\varepsilon_{p,1})_g}\sqrt{\frac{(\varepsilon_{p,2})_g}{(\varepsilon_{p,2})_s}}\sqrt{\frac{(p_C)_s}{(p_C)_g}}\sqrt{\frac{2}{1+0.25\frac{(E_2+2\frac{\varepsilon_{p,1}}{\varepsilon_{p,2}}p_C)_s}{(E_2+2\frac{\varepsilon_{p,1}}{\varepsilon_{p,2}}p_C)_g}}}$

S	$(F_S)_{s,g}$
B	$\frac{(\varepsilon_{p,1})_s}{(\varepsilon_{p,1})_g}\sqrt{\frac{(p_C)_s}{(p_C)_g}}\sqrt{\frac{(\varepsilon_{p,2})_g}{(\varepsilon_{p,2})_s}}\sqrt{\frac{(E_2 + 2\frac{\varepsilon_{p,1}}{\varepsilon_{p,2}}p_C)_g}{(E_2 + 2\frac{\varepsilon_{p,1}}{\varepsilon_{p,2}}p_C)_s}}$
B(CSS)	$\frac{(\varepsilon_{p,1})_s}{(\varepsilon_{p,1})_g}\sqrt{\frac{(p_C)_s}{(p_C)_g}}\sqrt{\frac{(\varepsilon_{p,2})_g}{(\varepsilon_{p,2})_s}}\sqrt{\frac{(E_2 + 2\frac{\varepsilon_{p,1}}{\varepsilon_{p,2}}p_C)_g}{0.25\ (E_2 + 2\frac{\varepsilon_{p,1}}{\varepsilon_{p,2}}p_C)_s}}$
0	$\frac{(\varepsilon_{p,1})_s}{(\varepsilon_{p,1})_g}$

A.3 DETECTION LIMITS IN INAA AND DETECTOR-TYPES AND -SYSTEMS

A.3.1 Introduction

To use the $(F_S)_{s,g}$ factors, the photopeak efficiency at the energy of interest has to be known and also the efficiency at the energy of the prime photopeak of the radionuclide causing the dominant Compton background. Vendors usually only specify the relative efficiency of the Ge detector for the 1332 keV line of ^{60}Co, the peak-to-Compton ratio and the energy resolution. As such, these specifications do not give an

indication on the efficiency of the detector at lower photon energies. Sometimes it may be desired to estimate a possible improvement in detection limits without precise knowledge of the latter two parameters, and the 'selected' detector of choice is only denoted via its assumed relative ^{60}Co efficiency (e.g. 40 %, 80 %, 100 %). Both the efficiency of the detector and the peak-to-Compton ratio depend on the detector's sensitive volume. In the following paragraphs it is shown how the efficiency at other energies and the peak-to-Compton ratio can be estimated from the relative ^{60}Co efficiency.

With the derived relations, $(F_S)_{s,g}$ values have been calculated for comparison of the following detectors to a 20 % detector (g = 20 %):

(i) a coaxial detector with relative ^{60}Co efficiency of 100 %
(ii) a well-type detector
(iii) a planar detector

or a 20 % detector, compared with

(iv) a 20 % detector equipped with Compton suppression system

The following hypothetical cases have been considered :

(i) 'C' and 'C-B' : peaks corresponding to photon energies at 250, 500 and 750 keV on a background due to a high energy peak of gamma-rays in the region between 1300 and 1400 keV, with a contributing natural background due to a source emitting gamma-rays of 1460 keV, positioned outside the lead-shielding.
(ii) 'B' : peaks corresponding to gamma-rays at 250, 500 and 750 keV at a natural background due to a source emitting gamma-rays of 1460 keV, positioned outside the lead-shielding.
(iii) 'O' : peaks corresponding to gamma-rays at 250, 500, and 750 keV at a neglectable or zero background.

A.3.2 Photopeak efficiency

COAXIAL DETECTORS

In the comparison of the coaxial detectors it is assumed -unless otherwise stated- that the source-to-detector distance is equal.

For gamma-ray energies E_γ > 200 keV the photopeak efficiency curve of a semiconductor detector can be represented by the relation $\varepsilon_\gamma = p\ E_\gamma^{\ q}$, with p,q constants. Vaño [5] described for E_γ > 200 keV a relation between absolute

photopeak efficiency, photon energy E_γ (keV) and active volume of the detector, V (cm^3):

$$\log(\varepsilon_p) = c + (0.629\ \log(V) - 2.14)\ \log(E_\gamma) \qquad \text{A-18}$$

with c being a constant.

A -dimensionally not correct- relation exists [6] between the active volume of the detector and the detector's relative ^{60}Co efficiency, $\varepsilon_{Co\text{-}60}$ (in %), viz.:

$$\log(V) = \log(\varepsilon_{Co\text{-}60}) + 0.636 \qquad \text{A-19}$$

Substituting *A-19* into *A-18* results at:

$$\log(\varepsilon_p) = c + (0.629\ \log(\varepsilon_{Co\text{-}60}) - 1.74)\ \log(E_\gamma) \qquad \text{A-20}$$

and for the exponent q:

$$q = 0.629\ \log(\varepsilon_{Co\text{-}60}) - 1.74 \qquad \text{A-21}$$

Using *A-21* it follows that for detectors of 20 % relative efficiency the exponent is approximately -1:

$$(\varepsilon_p)_{20\%} \div E^{-0.92} \qquad \text{A-22}$$

With increasing crystal volume, the contribution of multiple Compton scattering to the photopeak increases stronger for high energy photons than for low energy photons. This is reflected by the exponent for the 100% detector:

$$(\varepsilon_p)_{100\%} \div E^{-0.48} \qquad \text{A-23}$$

If two detectors with respective volumes V_s and V_g have photopeak efficiency curves which can be described for $E_\gamma > 150$ keV by $\varepsilon_{p,s} = p_s E^{q,s}$ and $\varepsilon_{p,g} = p_g E^{q,g}$ it easily follows that

$$\varepsilon_{p,s} = \frac{V_s}{V_g} \frac{(\frac{E_\gamma}{1332})^{q,s}}{(\frac{E_\gamma}{1332})^{q,g}} \varepsilon_{p,g} \qquad \text{A-24}$$

At $E_\gamma = 1332$ keV $(\varepsilon_p)_{100\%} = 5(\varepsilon_p)_{20\%}$, however only at a 25 cm source-to-endcap distance. For the here pursued global assessment it is assumed that this

relationship can also be used at other source-to-detector distances, and changes in the effect of the difference in solid angle with different coaxial detectors is omitted. Using *Equation A-24* it follows that $(\varepsilon_p)_{100\ \%} = 0.21\ E_\gamma^{0.44}\ (\varepsilon_p)_{20\ \%}$

WELL-TYPE DETECTORS

In this comparison a well-type detector of a commercially common size has been assumed with a crystal volume of approximately 100 cm^3 -corresponding roughly in size to a 25 % coaxial crystal- with an approximately 12 mm crystal 'blind' well.

The photopeak efficiency of well-type detectors is favourably affected by the almost 4π geometry of the source. The solid angle of a source placed at the endcap of a 20 % coaxial detector, at approximately 1 cm from the detector's surface, is 1.2π. [2] Thus, when compared to such a coaxial detector the geometrical component of the efficiency of the well-type detector is approximately a factor 3.3 better.

Comparison of the interaction efficiencies of the well-type detector and the 20 % coaxial detector on basis of the ratio of the active volumes is misleading since in the well-type detector the gamma-rays have a shorter available distance for interaction than in the coaxial detector. In a first approximation the photopeak efficiency of the well-type is assumed to be 3.5 * the photopeak efficiency of a 20 % coaxial detector with the source on the end-cap for all photon energies; the exponent in the efficiency vs. photon energy relation is assumed to be also the same as for the 20 % detector.

When counting sources at larger source-to-endcap distances in order to keep the geometrical difference between sample and source limited or because of irregular sample dimensions, the ratio of the well-type detector's efficiency with the coaxial's efficiencies increases in a first approximation with the square of the distance between source and detector; more precisely with the distance d between the source and the virtual interaction depth of the detector. A first approximation to the distance between source end-cap and point of virtual interaction depth is 3 cm; the efficiency thus decreases with approximately $3^2/(d + 3)^2$ (all dimensions in cm).

The photopeak efficiencies of the well-type and coaxial detectors, normalized to unity for the 1332 keV line for the 20 % detector with the source on the end-cap are included in *Table A-3*.

---

[2] *For a point source located on the detector's axis of rotation at a distance d from the crystal with diameter D= 2R, the solid angle* $\Omega = 2\pi(1-\cos\alpha)$ *[7] with* $\cos\alpha = d/(\sqrt{(d^2+R^2)}$. *The crystal volume of a 20 % detector is approximately 4.3 * 20 = 86* cm^3. *In coaxial detectors, the crystal diameter D is approximately 0.84 * the crystal length which results in* $R \approx 2.25$ *cm.*

PLANAR DETECTORS

The dimensions of planar detectors are conventionally quoted in terms of active surface area and crystal thickness. Here a crystal of 2000 mm^2 area and 2 cm thickness has been chosen, representing one of the largest types presently available. The detectors relative ^{60}Co efficiency and peak-to-Compton ratio are never specified since for the purpose of the detector, viz. measurement of low-energy photons, these parameters are irrelevant. For the here applied comparison, the relative ^{60}Co efficiency and the peak-to-Compton ratio have been estimated from the crystal's volume.

The crystal volume of such a planar detector corresponds with the volume of a coaxial detector of 9.3 % relative efficiency. The proportionality constant in the efficiency-photon energy relationship is determined via *A-20*, which is allowed since Vaño took planar detectors into account when determining his relationship. Therefore $(\epsilon_p)_{planar} \div E^{-1.13}$ and using *A-24*: $(\varepsilon_p)_{planar} = 2.11\, E_\gamma^{-0.21}\, (\varepsilon_p)_{20\ \%}$

Table A-3. *Approximate photopeak efficiencies, normalized to unity (**bold**) for the 1332 keV gamma-rays of a source on the end-cap of a 20 % detector, for coaxial, well-type and planar detectors at different photon energies and two source-to-end-cap distances.*

	1332 keV	750 keV	500 keV	250 keV
100 %, 0 cm	5.0	6.6	8.0	11
5 cm	0.70	0.93	1.1	1.6
20 %, 0 cm	**1**	1.7	2.5	4.7
5 cm	0.15	0.24	0.35	0.66
planar, 0 cm	0.47	0.89	1.4	3.1
5 cm	0.07	0.12	0.20	0.44
well-type	3.5	6.0	8.8	17

REDUCTION FOR COINCIDENCE LOSSES

The estimates for the photopeak efficiencies can be used only directly when

gamma-rays are considered from a coincidence free transition. In other cases, an estimate for the reduction of the photopeak efficiency by coincidence losses has to be taken into account. Since these coincidence losses may be rather complex because of the complexity of the decay, here a simple case will be considered as a first estimate: the gamma-ray of interest with energy E_1 is considered to be in cascade with another gamma-ray of almost equal energy E_3. The coincidence losses reduction factor c_{CL} reduce the photopeak efficiency $\varepsilon_{p,1}$ by the factor

$$c_{CL} = (1 - a_{\gamma 3}\varepsilon_{t,3})$$

in which

$a_{\gamma 3}$ = the abundance of gamma-ray 3 in the decay;

$\varepsilon_{t,3}$ = the total efficiency of the detector for photons of the energy of gamma-ray 3.

To compare the potentials of the different detectors in a global way, a hypothetical case is considered in which the losses amount 50 % for a gamma-ray line of a source, positioned on the end-cap of the 100 % coaxial detector. Thus, $a_{\gamma 3}\varepsilon_{t,3,100\%} = 0.5$, and, since $\varepsilon_t = \varepsilon_p/p_t$:

$$(a_{\gamma 3}/p_{t,100\%})\ \varepsilon_{p,3,100\%} = 0.5$$

For simplicity it is assumed that the p_t values are the same for different detectors, which allows for the substitution $a_{\gamma 3}/p_t = 0.5/\varepsilon_{p,3,100\%}$ in the expression for c_{CL} for any given detector:

$$(c_{CL})_g = [1 - \frac{0.5}{(\varepsilon_p)_{100\%}} (\varepsilon_p)_{g\%}] \qquad \text{A-25}$$

With the relations between the peak-efficiencies of the coaxial detectors and the well-type detectors now estimates can be determined for the corresponding losses with the other detectors, and the effect of larger source-to-detector distances can be examined.

When a Compton suppression shield is used, coincidence losses occur due to both simultaneous detection of the related events in the Ge-detector itself, and , simultaneously in the Ge-detector and in the suppression shield. To simplify the estimation coincidence losses between -in the Ge-detector- Compton scattered events of gamma-ray 1 and events from gamma-ray 3 detected directly in the suppression shield are not taken into account. Now only the losses by coincidence have to be accounted for in the detection of firstly gamma-ray 1 and gamma-ray 3 simultaneously in the Ge-detector, and between the resulting signal of gamma-ray 1 and the detection of gamma-ray 3 related events in the suppression shield. Thus, a first estimate of the coincidence losses results via

$(1 - a_{\gamma 3}\varepsilon_{t,3})_{20\ \%}$ * $(1 - a_{\gamma 3}\varepsilon_{t,3})_{CSS}$. The total efficiency of a typical Compton suppression shield has been estimated from vendors' catalogues, and assumed to be 0.99, 0.90 and 0.65 at 250, 500 and 750 keV respectively; for these calculations it is assumed that

$a_{\gamma 3} = 1$.

The approximated corresponding c_{CL} -factors for all detectors are summarized in *Table A-4.*

Table A-4. *Coincidence losses reduction factor c_{CL} for different detectors. Factor relates to the losses on the photon energy listed above each column when in coincidence with a photon of equal energy.*

		750 keV	500 keV	250 keV
100 %,	0 cm	0.5	0.5	0.5
	5 cm	0.93	0.93	0.93
20 %,	0 cm	0.87	0.84	0.79
	5 cm	0.98	0.98	0.97
planar,	0 cm	0.93	0.91	0.86
	5 cm	0.99	0.99	0.98
well-type		0.55	0.45	0.26
CSS,	0 cm	0.31	0.08	0.008
	5 cm	0.34	0.10	0.01

A.3.3 Peak-to-Compton ratio

COAXIAL DETECTORS

The probability that interaction events in the detector will result in a photopeak increases with the active volume, and the probability of escape of events from the crystal increases with the detector's surface area. The extend of these effects depend on photon energy which dependency however will be ignored in view of the global approach. The peak-to-Compton ratio, p_C, therefore varies in a first assumption with $V^{1/3}$. For the determination of the $(F_S)_{s,g}$ values the ratio $(p_C)_s$ $/(p_C)_g$ can therefore be replaced by the ratio $(V_s/V_g)^{1/3}$, and thus by the ratio $(\varepsilon_{Co\text{-}60})_s$ $/(\varepsilon_{(Co\text{-}60)})_g$. Ratios determined in this way agree well with ratios that follow from p_C values calculated using a parameterized expression of p_C as function of $\varepsilon_{Co\text{-}60}$ on

basis of real coaxial detectors and published data with $\varepsilon_{Co\text{-}60}$ between 10 % and 100 % [3]. Taking into account that V and $\varepsilon_{Co\text{-}60}$ are assumed to be linearly proportional (*A-19*), the general expression becomes

$$(p_C)_s = \left[\frac{(\varepsilon_{Co\text{-}60})_s}{(\varepsilon_{Co\text{-}60})_g}\right]^{\frac{1}{3}} (p_C)_g \qquad \text{A-26}$$

Thus for a gamma-ray energy of 1332 keV: $(p_C)_{100\ \%} = 1.7\ (p_C)_{20\ \%}$

WELL-TYPE DETECTORS

In a first approximation, the p_C ratio of the well-type detector is assumed to be equal to the p_C ratio of the 20 % detector. The p_C ratio when counting the source inside the well is better than as specified for a source on 25 cm distance from the endcap because of the enhanced probability that 180^0 scattered photons will be re-captured in the crystal again. It has been observed [9] that by this effect the p_C ratio increases by at least approximately 25 %. Therefore, using *A-26*:

$$(p_C)_{well} = 1.25\ (p_C)_{20\ \%} \text{ and } (p_C)_{well} = 0.73\ (p_C)_{100\ \%}$$

PLANAR DETECTORS

For simplicity reasons, the p_C ratio of the planar detector is also derived from its active volume using *A-18* and *A-26*, and

$$(p_C)_{planar} = 0.75\ (p_C)_{20\ \%}$$

EFFECT OF A COMPTON SUPPRESSION SHIELD

Situations are compared of the net effect of a suppression shield when applied to a given detector and at a given source-to-endcap distance. The photopeak-efficiency therefore is not affected by the shield; the p_C ratio typically increases by a factor of 6.

A.3.4 Summary

The calculation of the $(F_S)_{s,g}$ for comparison of two coaxial detectors, e.g. a

[3] $p_C = 34.75 + 1.068\ (\varepsilon_{Co\text{-}60}) - 4.96.10^{-3}\ (\varepsilon_{Co\text{-}60})^2$ [8]

40 % and a 20 % detector, is done via the following steps:

1. Calculate the proportionality exponent using *A-18*; it leads in this example to

$$(\varepsilon_{p,E\gamma})_{40\%} \div E^{-0.73}$$
$$(\varepsilon_{p,E\gamma})_{20\%} \div E^{-0.92}$$

using *A-24* it follows that

$$(\varepsilon_{p,E\gamma})_{40\%} = 0.52\, E_{\gamma}^{0.19} (\varepsilon_{p,E\gamma})_{20\%}$$

2. Estimate on basis of $\varepsilon_{Co\text{-}60}$ the p_C ratio from *A-26*:

$$(p_C)_{40\%} = 1.25\, (p_C)_{20\%}$$

3. All $(F_S)_{s,g}$ and related factors can now be calculated

Values for $(F_S)_{s,20\%}$ have been calculated for the cases specified in *paragraph A.3.1* and are given in *Table A-5*.

Table A-5. *Sensitivity improvement factors F_S, with and without accounting for coincidence losses (see text) for (I) a 100 % coaxial detector vs. a 20 % coaxial detector, (IIa) a well-type detector vs. a 20 % coaxial detector with source placed on the endcap; (IIb) a well-type detector vs. a 20 % coaxial detector with the source placed on 5 cm from the endcap; (III) a 20 % coaxial detector with and without Compton suppression shield and (IV) a planar detector vs. a 20 % coaxial detector*

	E_γ	F_S without coincidence losses					F_S with coincidence losses				
		I	IIa	IIb	III	IV	I	IIa	IIb	III	IV
	250	1.4	2.3	6.2	2.4	0.8	0.9	0.8	1.7	0.02	0.9
C	500	1.9	2.3	6.2	2.4	0.7	1.1	1.2	2.9	0.2	0.8
	750	2.2	2.3	6.2	2.4	0.7	1.3	1.4	3.5	0.9	0.7
	250	1.4	2.1	5.6	2.7	0.9	0.9	0.7	1.6	0.03	0.9
C-B	500	1.9	2.1	5.6	2.9	0.7	1.2	1.1	2.6	0.3	0.8
	750	2.2	2.1	5.6	2.9	0.7	1.3	1.3	3.1	1.1	0.7
	250	1.4	2.0	5.3	3.2	0.8	0.9	0.7	1.7	0.06	0.9
B	500	1.9	2.0	5.3	3.6	0.7	1.2	1.2	2.7	0.5	0.8
	750	2.2	2.0	5.3	3.9	0.7	1.3	1.3	3.2	1.7	0.8
	250	2.4	3.5	25	1.0	0.6	1.5	1.2	6.7	0.01	0.7
0	500	3.2	3.5	25	1.0	0.6	1.9	1.9	12	0.1	0.6
	750	3.9	3.5	25	1.0	0.5	2.2	2.2	14	0.4	0.6

A.4 REFERENCES

[1] M. Blaauw, 'The Holistic Interpretation of Gamma-Ray Spectra in Instrumental Neutron Activation Analysis', Thesis, Delft University of Technology, Delft (1993)

[2] J.A. Cooper, 'Factors determining the Ultimate Detection Sensitivity of Ge(Li) Gamma-Ray Spectrometers',
Nucl.Instr.Meth. 82 (1970) 273 - 277

[3] S. Landsberger, 'Compton Suppression Neutron Activation Methods in Environmental research', J.Radioanal.Nucl.Chem. 179 (1994) 67 - 79

[4] J. Weber, C.E. Rasmussen, 'Stralingsbescherming', Delftse Uitgevers Maatschappij (1985)

[5] E. Vaño, L. Gonzalez, R. Gaete, J.A. Gonzalez, 'An Empirical Function which relates the Slope of the Ge(Li) Efficiency Curve and the Active Volume',
Nucl.Instr.Meth. 123 (1975) 573 - 574

[6] EG&G ORTEC 1993/94 Catalog Instruments & Systems for Nuclear Spectroscopy; 1995 Addendum 'Modular Pulse-Processing Electronics and Semiconductor Radiation Detectors, p. 475

[7] L. Moens, J. de Donder, Lin Xi-Lei, F. de Corte, A. de Wispelaere, A. Simonits, J. Hoste, 'Calculation of the Absolute Peak Efficiency of Gamma-Ray Detectors for Different Counting Geometries', Nucl.Instr.Meth. 187 (1981) 451 - 472

[8] R.M. Lindstrom, pers.comm. (1995)

[9] F.P. Brauer, W.A. Mitzlaff, 'Evaluation of Well-Type Ge(Li) Detectors for Low-Level Radiochemical Analysis',
IEEE Transact. NS-25 (1978) 398 - 403

A.5 LIST OF SYMBOLS

$a_{\gamma 1}$	abundance of gamma-ray 1 in the decay, photons/disintegration
$a_{\gamma 3}$	abundance of gamma-ray 3 in the decay, photons/disintegration
A_m	reciprocal of fractional error
B	average number of background counts per channel
$B_{C2,1}$	number of counts per channel due to the Compton continuum of the interfering gamma-ray 2 at the location of gamma-ray 1 of interest
$B_{N,1}$	natural background in counts per channel at the location of the gamma-ray 1 of interest
$(B_N)_{CSS}$	natural background in counts per channel at the location of the gamma-ray 1 of interest for a Compton suppression system
$B_{t,1}$	total number of background counts per channel at the location of gamma-ray 1
c	constant in Vaño's relation
c_{CL}	coincidence losses reduction factor
$(c_{CL})_s$	coincidence losses reduction factor for a selected detector
CSS	as subscript: to denote the presence of a Compton suppression system
d	distance between source and detector surface, cm
D	detector diameter, cm

$D_{m,1}$	minimum detectable disintegration rate for gamma-ray 1, s^{-1}
E_γ	gamma-ray energy, keV
$(f_S)_s$	sensitivity determining factor for the spectral shape S and a selected detector
$(f_S)_g$	sensitivity determining factor for the spectral shape S and a given detector
$(F_S)_{s,g}$	sensitivity improvement factor, for the spectral shape S when comparing a selected detector with a given detector
g	as subscript: to denote a given (or existing) detector
N	net peak area, counts
N_{E1}	number of counts in photopeak at energy E_1
N_{E2}	number of counts in photopeak at energy E_2
N_{tot}	total number of counts registered in the gamma-ray spectrum
p_C	peak-to-Compton ratio
$(p_C)_s$	peak-to-Compton ratio of a selected detector (denoted with the subscript s)
$(p_C)_g$	peak-to-Compton ratio of a given detector (denoted with the subscript g)
p	proportionality constant in efficiency-photon energy relation
p_t	peak-to-total ratio
P	height of the peak in the simplified representation of the gamma-ray spectrum, counts
q	exponent in efficiency-photon energy relation
R	radius of the detector crystal, cm
R_1	detector resolution at the location of gamma-ray 1, keV
R_{E1}	detector resolution at the location of gamma-ray with energy E_1 in the simplified representation of the gamma-ray spectrum
R_{E2}	detector resolution at the location of gamma-ray with energy E_2 in the simplified representation of the gamma-ray spectrum
R_{E3}	detector resolution at the location of gamma-ray with energy E_3 in the simplified representation of the gamma-ray spectrum
s	as subscript: to denote a selected detector
S	as subscript: to denote a spectral shape
S_S	emission rate of source with photons of energy E_2, s^{-1}
S_B	emission rate of background for photons of energy E_3, s^{-1}
S_C	emission rate of background for photons of energy E_1, s^{-1}
t	counting time, s
V	detector crystal volume, cm^3
V_s	detector crystal volume of a selected detector
V_g	detector crystal volume of a given detector
α	viewing angle of detector to source
$\varepsilon_{Co\text{-}60}$	the efficiency of the detector for the 1332 keV gamma-ray line of ^{60}Co, relative to the efficiency of a 3" * 3" NaI(Tl) scintillation detector
ε_p	photopeak efficiency
$\varepsilon_{p,1}$	photopeak efficiency of gamma-ray 1
ε_t	total efficiency
$\varepsilon_{t,3}$	total efficiency of gamma-ray 3

SUMMARY

SUMMARY

Instrumental neutron activation analysis (INAA) is a method for multi-element analysis studied, developed and applied at the Interfaculty Reactor Institute (IRI) of the Delft University of Technology. General developments with respect to INAA in the period 1984 - 1996 and the achievements of the laboratory for INAA at the Interfaculty Reactor Institute are described in *Chapter 1*. Specific attention is given to those contributions underlying the scope of this thesis which are further treated in *Chapters 3* through *7*. These chapters are preceded by *Chapter 2* in which an introduction is given on the principles and analytical characteristics of INAA.

Analysis of very large samples, of kilogram size, may be advantageous e.g. in the case of materials which are difficult to homogenize or when sub-sampling causes difficulties with respect to representativeness of the analytical portion. A method for large sample INAA has been developed at IRI. In *Chapter 3* the associated irradiation facility ('Big Samples Neutron Irradiation System', BISNIS) and counting facility are described. The irradiation facility is located in the thermal column of the nuclear reactor and consists of an interconnected system of tubes, placed vertically and connected on top of the vertical shaft to a storage tank. Tank and tube system are filled with water which acts as a penetrable shielding against neutrons and gamma-rays. The polyethylene irradiation container with the samples is lowered from the tank into the irradiation tube. The gamma-ray spectrometer for the large samples is equipped with a specially designed counting facility with scanning options. The facility also offers the opportunity to perform, prior the activation, a measurement of the gamma-ray transmission of a reference source.

The chapter is completed with a comparison of the costs of large sample INAA and conventional INAA, and an outlook is given for applications of large sample analysis.

Automation of INAA with radionuclides with short half-lifes (seconds to minutes) was hampered at IRI because the irradiation container in the dedicated fast irradiation system became contaminated during transfer with weared-off radioactive scrap from the aluminium tubes, and unpacking prior to measurement was inevitable.

A new irradiation facility has been designed in which the irradiation end of the transfer tube is made of a carbon-composite. In *Chapter 4* is presented the 'Carbonfiber Autonomous Facility for Irradiation and Analysis, CAFIA'. The other transfer tubes have been made of polyethylene. Any remaining contamination of the rabbit during transfer is so low that it can be neglected with respect to the radioactivity of the blank, i.e. the radioactivity induced from impurities in the polyethylene of the rabbit. The radioactivity

of the sample can now be measured with the sample still in the rabbit. A sample changer and computer control complete the facility which can operate without continuous supervision. The system allows also for cyclic activation analysis procedures.

Examples are given of typical applications of short half-life radionuclides in INAA in which this facility is used.

Improvement of detection limits in INAA is sometimes required to determine lower concentrations for a given study, or to attain equal detection limits in shorter measuring times. Detection limits depend, under certain conditions, on the peak-to-background ratio in the gamma-ray spectrum. This ratio depends partly on the detector characteristics. The relation between peak-to-background ratio and detector specifications has been studied to get an objective view on the opportunities of different detectors for improving the detection limits in INAA. This evaluation, described in *Chapter 5*, was done using only the typical specifications of detectors as supplied by the vendors, like relative efficiency, energy resolution and peak-to-Compton ratio.

In the associated *Appendix* it is described how sensitivity improvement factors can be derived from the basic expression for the peak-to-background ratio; these factors reflect the difference in attainable detection limits when comparing two detectors.

The calculated sensitivity improvement factors have been compared with experimental observations and generally there is good agreement. In general it is found that detection limits will be comparable if determined with well-type detectors or with the presently largest, commercially available, coaxial detetctors. The well-type detector is the most economical choice, but the very large coaxial detector offers the highest flexibility in operations.

Though use of reference materials and blanks was an established approach to quality control at the laboratory for INAA, the quality of the results could not always be demonstrated. By 1991 it was decided to implement the existing procedures for quality control in a system for quality assurance. The applied methods for quality assurance and an evaluation of the effects are described in *Chapter 6.*

The quality assurance is based on the assumption that the analyst should be able to control his own work and to evaluate the results on basis of quantified and documented criteria. Control charts have been introduced for inspection of trends and search for systematic sources of error. Non-conformance with the quantified criteria is registered and systematically preventive and corrective actions are taken.

The improvement of the analytical quality could be demonstrated via comparison of results obtained before and after introduction of quality assurance. The improvement of the operational quality follows from the non-conformance registration and indicates that the number of cases of non-conformance has decreased to a level that can be justified on statistical considerations. The costs of the quality assurance measures,

additional to the existing -but not functional- quality control appear to be less than the savings by preventing the release of poor results.

Self-assessment of the performance of the laboratory for INAA in 1990 learned that, amongst others, regularly (parts of the) analyses had to be repeated and, consequently, deadlines for reporting were exceeded; trackability of operations was poor due to lacking documentation. Moreover, commercial activities were growing and customers were setting demands to demonstration of the quality of the analyses.

In 1990 it was decided to bring the operations in the laboratory in accordance to the international criteria for quality systems, and to pursue formal accreditation for this. The quality system was developed in a three years period, and by the end of 1992 fit for the accreditation audit. Formal accreditation was accomplished making the laboratory for INAA the first accredited university laboratory in The Netherlands and the first accredited INAA laboratory in the world. The development of the quality system, and the experiences with it have been described in *Chapter 7*. In this chapter also a cost-benefit evaluation is given. The estimate indicates that the running costs of the quality system, i.e. the costs to sustain the formal accreditation are almost equal to the estimated benefits, not taking into account the non-quantifiable benefits.

This chapter concludes with a discussion on, amongst others, the consequences of quality management in a university setting.

The work, described in the *Chapters 3* through *7*, reflect achievements of the laboratory for INAA in the period 1984 - 1996. In the discussion in *Chapter 8* the final results are compared with the original incentives, and further improvements and/or applications are discussed. Finally, prospects are given for future research activities in the field of INAA, which concludes this thesis.

SAMENVATTING

SAMENVATTING

Instrumentele neutronen-activeringsanalyse (INAA) is een methode voor multi-elementanalyse die bestudeerd, ontwikkeld en gebruikt wordt bij het Interfacultair Reactor Instituut (IRI) van de Technische Universiteit Delft. Algemene ontwikkelingen op het gebied van INAA in de periode 1984 - 1996 en een overzicht van de onderzoeksverrichtingen van het laboratorium voor INAA op het IRI worden gegeven in *Hoofdstuk 1*. Daarbij gaat de aandacht vooral uit naar het gedeelte dat de basis vormt van dit proefschrift en dat verder wordt behandeld in de *Hoofdstukken 3 tot en met 7.* Hieraan voorafgaand worden in *Hoofdstuk 2* de beginselen en de analytische kenmerken van INAA behandeld.

Er zijn een aantal redenen waarom de analyse van zeer grote monsters, met massa's in de orde van kilogrammen, aantrekkelijk is, bijvoorbeeld wanneer de monsters moeilijk te homogeniseren zijn of wanneer bij het nemen van een deelmonster de representativiteit in gevaar komt. Op het IRI is een methode van INAA ontwikkeld voor grote monsters. In *Hoofdstuk 3* worden de bestralingsfaciliteit ('Big Samples Neutron Irradiation System', BISNIS) en de meetfaciliteit beschreven. De bestralingsfaciliteit is gebouwd in de thermische kolom van de kernreactor en bestaat uit een verticaal geplaatst buizenstelsel dat aan de bovenzijde uitmondt in een klein bassin. Bassin en buizen zijn gevuld met water dat gebruikt wordt als afscherming voor neutronen en gamma-straling. De monsters bevinden zich in een polyethyleen bestralingshuls die vanuit de tank in een van de buizen naar de bestralingspositie wordt neergelaten.

De gamma-spectrometer is uitgerust met een speciale faciliteit waarmee het grote monster 'gescand' kan worden. Bovendien biedt de faciliteit de mogelijkheid om, voorafgaand aan de bestraling, de gamma-zelfverzwakking van het monster te bepalen door meting van de transmissie van gamma-straling van een referentiebron.

Dit hoofdstuk bevat verder een globaal vergelijk van de kosten van INAA aan grote monsters en de gebruikelijke INAA aan kleine monsters; verder worden verwachtingen geuit ten aanzien van de toepassingen van analyse van grote monsters.

Het automatiseren van INAA waarbij kortlevende radionucliden worden bepaald, was moeilijk uitvoerbaar op het IRI doordat de buitenzijde van de bestralingshuls tijdens het transport in de snelle buizenpost in de aluminium buizen langs de wand schuurde en daardoor radioactief besmet raakte. De bestralingshuls moest na bestraling worden geopend om de radioactiviteit van de monsters storingvrij te kunnen meten.

Een nieuwe bestralingsfaciliteit is ontwikkeld waarbij een koolstof-composiet is gebruikt voor het bestralingsuiteinde, en polyethyleen voor de overige transportleidingen.

In *Hoofdstuk 4* wordt deze 'Carbonfiber Autonomous Facility for Irradiation and Analysis', CAFIA, beschreven. Voor zover er nog besmetting van de bestralingshuls optreedt blijkt deze verwaarloosbaar te zijn ten opzichte van de geïnduceerde radioactiviteit in het polyethyleen van de bestralingshuls zelf. Daardoor behoeft de huls niet meer te worden geopend om de activiteit van het monster te kunnen meten. De faciliteit is verder uitgerust met een computer-gestuurde monsterwisselaar, en er is geen permanent toezicht nodig bij gebruik. Ook kan nu INAA via cyclische activering worden uitgevoerd.

Voorbeelden worden gegeven van INAA waarbij deze faciliteit kan worden ingezet.

Soms vereist het toegepast onderzoek lagere detectiegrenzen in INAA, terwijl een voordeel van verbetering van de detectiegrens is dat een zelfde (oude) detectiegrens bereikt kan worden in kortere tijd. De detectiegrens wordt deels bepaald door de piek-ondergrond verhouding in het spectrum; deze verhouding hangt weer deels af van de kenmerken van de detector. Het verband tussen de piek-ondergrond verhouding en detectorkenmerken is bestudeerd teneinde een objectief beeld te krijgen van de mogelijkheden van verschillende detector-typen om betere detectiegrenzen te bereiken. Dit onderzoek wordt beschreven in *Hoofdstuk 5*; een van de uitgangspunten was dat alleen die kenmerken worden beschouwd die worden opgegeven door de leverancier van de detector, zoals relatieve gevoeligheid, piek-Compton verhouding en energie-scheidend vermogen.

In de verwante *Appendix* wordt beschreven hoe een kwaliteitsfactor voor de verbetering van de detectiegrens kan worden afgeleid uit de vergelijking die de piek-ondergrond relatie beschrijft. Deze kwaliteitsfactor geeft weer hoe detectiegrenzen zich verhouden als twee detectoren worden vergeleken.

De berekende kwaliteitsfactoren stemmen goed overeen met gemeten verbeteringen van de detectiegrens. In het algemeen blijkt dat vergelijkbare detectiegrenzen kunnen worden bereikt met put-detectoren en met de momenteel grootste, commercieel verkrijgbare coaxiale detectoren. De put-detector is economisch het aantrekkelijkst; de grote coaxiale detector biedt het laboratorium de grootste flexibiliteit.

Referentiematerialen en blanco's werden al geruime tijd op het IRI gebruikt ten behoeve van kwaliteitscontrole, maar toch kon de kwaliteit van de analyses niet altijd worden aangetoond. In 1991 is besloten om rond deze kwalititeitscontrole een systeem van kwaliteitsborging te ontwikkelen. Deze kwaliteitsborging, en een evaluatie van de gevolgen zijn beschreven in *Hoofdstuk 6.*

De kwaliteitsborging is gebaseerd op de veronderstelling dat de analist in staat moet zijn zijn eigen werk te controleren, en daartoe kwantitatieve en vastgelegde criteria

moet hebben. Verder is het gebruik van controlekaarten ingevoerd voor de inspectie van trendmatige veranderingen en voor het onderzoek naar bronnen van systematische fouten. Een registratie wordt bijgehouden van situaties waarin de criteria worden overschreden en preventieve en correctieve acties worden aangewend.

De verbetering van de analytische kwaliteit kon worden aangetoond door vergelijking van analyseresultaten bereikt voor en na de invoering van de kwaliteitsborging. De verbetering van de kwaliteit van de werkzaamheden kon worden afgeleid via de registratie van de afwijkingen; hieruit is gebleken dat dit aantal is afgenomen tot een niveau dat statistisch in overeenstemming is met het aantal verrichtingen. De kosten van de kwaliteitsborging bleken minder te zijn dan de besparingen die het gevolg zijn van het voorkomen van de rapportage van verkeerde resultaten.

Het laboratorium voor INAA besefte in 1990 dat er regelmatig (delen van de) analyses moesten worden herhaald en dat mede daardoor regelmatig te laat gerapporteerd werd; verder dat het werk nauwelijks naspeurbaar was door de gebrekkige verslaglegging of het ontbreken ervan. Bovendien nam de commerciële dienstverlening toe en opdrachtgevers gingen eisen stellen aan de aantoonbaarheid van de kwaliteit.

In 1990 is besloten om alle werkzaamheden in overeenstemming te brengen met de internationale criteria waaraan kwaliteitssystemen behoren te voldoen en erkenning (accreditatie) van dit kwaliteitssysteem na te streven. De ontwikkeling van het kwaliteitssysteem heeft drie jaar geduurd en eind 1992 vond de beoordeling plaats. Het laboratorium voor INAA was het eerste universitaire laboratorium in Nederland met een officiële accreditatie, en het eerste geaccrediteerde laboratorium voor INAA in de wereld. De ontwikkeling van het kwaliteitssysteem en de ervaringen ermee worden beschreven in *Hoofdstuk 7*. Tevens wordt een kosten-baten schatting gegeven. Het blijkt dat de kosten voor instandhouding van de accreditatie ongeveer gelijk zijn aan de baten ervan, waarbij opgemerkt moet worden dat er ook een aantal niet-meetbare voordelen zijn.

Dit hoofdstuk besluit met een bespreking van onder meer de aspecten van kwaliteitszorg in universitaire instellingen.

De werkzaamheden die in *Hoofdstuk 3* tot en met *7* worden beschreven hebben plaatsgevonden in het laboratorium voor INAA tussen 1984 en 1996. In de discussie in *Hoofdstuk 8* worden de eindresultaten vergeleken met de uitgangspunten en verdere verbeteringen en toepassingen komen aan de orde. Tenslotte wordt vooruit gekeken naar mogelijke nieuwe onderzoekslijnen op het gebied der INAA, waarmee dit proefschrift wordt besloten.

DANKWOORD

Dit proefschrift beschrijft ontwikkelingen in de INAA in de laatste 10 jaar op het IRI. Ontwikkelingen die voor het merendeel waren aangevangen om uiteindelijk beschreven te worden in een proefschrift. Ontwikkelingen die grotendeels niet het werk van één enkele persoon zijn geweest, maar waarbij de werkeenheid Fysisch-Mathematische Radioanalyse, en veel medewerkers van diverse afdelingen van het IRI betrokken zijn geweest. Ik zou hen allen graag hier willen bedanken en met name zij die wel heel sterk hum stempel op de voorbije periode hebben gedrukt.

Twee collega's hebben mij begin 1994 overtuigd van de noodzaak om dit proefschrift te realiseren: Jeroen de Goeij en Marcel de Bruin. Als promotoren hebben zij mij de ruimte en tijd geboden om zelf de inhoud te bepalen. Jeroen, het was altijd weer een plezier om met jou de stukken tekst door te nemen, en te leren hoe jij met jouw nauwgezetheid telkens weer onbegrijpelijke of te snelle formuleringen ontdekte. Vaak klaagde je over de 'hoofdpijn' die ik je daarmee bezorgde, hetgeen mij spijt, en ik ben je dan ook dank verschuldigd voor je geduld, en de prettige discussies die wij gehad hebben. Marcel, met jou begon ik op het IRI, en ik vond het fijn om jou als promotor te hebben. Ik heb erg veel van je geleerd, en je maakte me wegwijs in de INAA en gamma-spectrometrie. Ten aanzien van dit proefschrift denk ik met plezier terug aan de wijze waarop je me voortdurend hielp het 'evenwicht' in de behandelingen te houden, en het geheel van een hoger abstractie-niveau te bezien. Jeroen en Marcel: geweldig bedankt !.

De medewerkers van mijn werkeenheid zijn dank verschuldigd niet alleen voor hun individuele bijdragen tot de onderwerpen in het proefschrift, maar ook voor de wijze waarop zij in de afgelopen twee jaar het onderzoek hebben voortgetrokken waar mijn directe betrokkenheid minder moest zijn. Menno, zelf net klaar met zijn promotie, moest een jaar de groep gaan leiden en ik ben hem, en Anneke, Folkert, Karen, Rob en Theo veel dank verschuldigd voor de wijze waarop ze hun schouders eronder hebben gezet, en voor hun immer goede humeur en belangstelling. Gelukkig was er over en weer ook steun van Mehmet, René, Ronald, Sjoerd, Thea en later ook Erwin en Frank. Verder hebben ook een aantal oud-medewerkers van de werkeenheid hun sporen nagelaten in dit proefschrift, zoals Piet Korthoven, Peter Kuik, Astrid van der Meer, Bert Wolterbeek, Lucie van Westing en Jaap Wüst, Henk van Zeijl. Allen: dank, dank, dank.

In het proefschrift worden faciliteiten voor INAA behandeld die voor een belangrijk deel, of in zijn geheel zijn gerealiseerd door de Technische Dienst en werkplaatsen van het IRI. Veel dank gaat uit naar Piet Gerz, die mijn steun was bij de realisatie van de BISNIS bestralingsfaciliteit, Zeger Boerendonk die de meetfaciliteit ontwierp, en alle medewerkers van de instrumentmakerij, allereerst onder leiding van

de heer Bok en later onder Koos Kolfers. Jullie hebben door je deskundigheid het IRI aan twee internationaal unieke faciliteiten geholpen, BISNIS en CAFIA, waar je trots op kunt zijn. Dank, dank, dank.

I am indebted to Dick Lindstrom from the NIST, Gaithersburg, USA, and Sheldon Landsberger from the University of Illinois te Urbana-Champaign, USA for their support in the comparison of the different detectors for INAA. Dick, working with you on the comparison of the large coaxial and the well-type detector for our paper for the Modern Trends in Vienna was the onset of what now has become a prominent part of this thesis. Sheldon, your hospitality was great, you gave me all opportunities to learn the Compton suppression spectrometer system. Both of you are great collegues and friends. Thanks a lot for all your support and good discussions we had.

Verhandelingen over kwaliteit nemen een belangrijke plaats in dit proefschrift. Het is mede dankzij Hans van Dalen dat wij inzicht kregen hoe aan de kwaliteitsgedachte in de praktijk inhoud moest worden gegeven. Dit heeft uiteindelijk heeft geleid tot de accreditatie voor een universitair laboratorium, en voor INAA hetgeen aanvankelijk in Nederland en internationaal uniek was. Hans, samenwerken met jou was een ontzettend leuke ervaring waar ik en de anderen veel van geleerd hebben. Nog steeds meen ik af en toe jouw "..hoe zit dat, jongens.." te horen. Dank, dank, dank.

Voorts dank aan alle medewerkers van HOR-B en HOR-O, aan Vladimir Havránek, aan de kwaliteitsborgings manager Jan van Tricht, aan de medewerkers van de Centrale Werkplaats van de TU Delft, en ... en natuurlijk aan de secretaresses Martina en Hermien, die mij zo voortreffelijk hielpen bij alle papierwerk rondom de promotie, en de uiteindelijke lay-out. Een rustpunt op het moment dat de grillen van WordPerfect mij zo nu en dan tot wanhoop dreven. Martina en Hermien: geweldig bedankt, zonder jullie was het nooit op tijd gelukt.

Ik heb maar niet het aantal uren bijgehouden dat thuis aan het proefschrift besteed is. Zeker in de laatste maanden heeft Joke veel avonden en delen van het weekend 'alleen' gezeten, terwijl het beeldscherm van de PC langzaam op mijn netvliezen inbrandde. Ook Vincent en Camiel kregen in de afgelopen periode minder aandacht dan waar zij recht op hadden. 'Begrip' voor deze situatie, en geduld is nogal op de proef gesteld, en tot hun verademing is het nu allemaal achter de rug. Maar het 'begrip' was de steun die ik nodig had op al die avonden. En waarvoor ik hen hier bedank.

Gelukkig zijn er nog altijd Wolvey, Fay, Mordred, Terry, Merlijn, Grace en Ginny die mij elke dag weer duidelijk maakten dat er nog andere dingen op de wereld zijn dan een proefschrift, en dat 'begrip' slechts een menselijk trekje is... En zoals Edmund Hillary zei tegen Tenzing Norgay bij het bereiken van de top van de Mount Everest: "...nou, dat was het dan. Laten we naar beneden gaan en iets fatsoenlijks drinken..."

CURRICULUM VITAE

Peter Bode werd geboren te Vlissingen, op 19 februari 1948. Na de lagere school doorliep hij van 1960 tot 1965 de HBS in diezelfde plaats waarbij het diploma HBS-B behaald werd. Vervolgens werd in 1965 een aanvang gemaakt de studierichting 'Scheikundige Technologie' aan de Technische Hogeschool te Delft. In 1971 studeerde hij af in de richting Chemische Technologie bij prof.ir. J.P.W. Houtman op het onderwerp 'Een onderzoek naar de toepassingsmogelijkheden van kortlevende isotopen in de niet-destructieve activeringsanalyse'. Aan dit onderzoek werd de jaarlijkse prijs van het Delfts Hogeschool Fonds toegekend. Nadat hij al in 1970 in dienst was getreden van het Interuniversitair Reactor Instituut als student-assistent werd hij na zijn afstuderen in 1971 aangesteld als wetenschappelijk medewerker in de onderzoekgroep Stralingsmeting en Dataverwerking van de vakgroep Radiochemie. Voornaamste aandachtsgebieden waren en zijn nog steeds de gamma-spectrometrie, neutronen-activeringsanalyse, verstoorde richtingscorrelaties en kwaliteitszorg. In 1988 volgde hij prof.dr.ir. M. de Bruin op als leider van de werkeenheid Stralingsmeting en dataverwerking. Deze werkeenheid, die het laboratorium voor instrumentele neutronen-activeringsanalyse beheert, ging verder onder de benaming 'Fysisch-Mathematische Radioanalyse'.
Peter Bode is getrouwd met Joke van de Meeberg; samen hebben zij twee zonen, zes West Highland White Terriers en één Parson Jack Russell Terrier.