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Quality control in large sample analysis

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Quality control, as applied in normal activation analysis by the simultaneous analysis of well-characterized quality control samples, blanks and sometimes duplicates, cannot fully be applied in large sample analysis. Well characterized control samples are, e.g., not available at the size of large samples. Different approaches have to be developed to monitor and to control sources of errors in this new type of chemical analysis. Some of the measured sample parameters dealing with gamma-ray and neutron attenuation can only vary between well known values of elemental constants. These parameters can much easier be determined in large sample analysis than with samples in the milligram range, thus offering an outlook for direct verification of the quality of the related correction algorithms. Some examples are given here from experience with the kg-scale neutron activation analysis at the facilities in Delft.

Introduction

There is a trend in many analytical techniques towards smaller sizes of the test portion, and sometimes sub-milligram amounts are being used. An opposite trend has been introduced in the 1990s by the development of large sample neutron activation analysis,[1–5] later followed by large sample photon activation analysis.[6] The analysis of samples with quantities larger than a few grams is a unique feature of activation analysis. It opens opportunities for a wide array of applications, varying from studies with heterogeneous materials to samples in which integrity should not get lost, like cultural or archaeological artifacts. 'Normal' activation analysis is known for its high degree of accuracy. It is obvious this tradition should be extended towards large sample activation analysis to receive respect for this new trend in chemical analysis.

The high degree of accuracy in normal activation analysis results from decades of experiencing in the development of certified reference materials. Many sources of error and the quantification of their impact are known.[7–9] Methods commonly denoted as quality control practices have been developed to inspect for the occurrence of errors during the analysis, whereas implementation of quality assurance contributes to minimizing and even avoiding the occurrence of errors. The known sources of error in normal activation analysis may occur in large sample analysis too. Some of them – like gamma-ray self attenuation and neutron/photon fluence rate or, e.g., neutron spectrum gradients – have much larger effects. Extreme inhomogeneities are an additional phenomenon in large sample analysis[10] with an impact on the degree of accuracy.

Quality control in normal activation analysis includes the simultaneous analysis of well characterized quality control samples, blanks and sometimes duplicates. In addition, inspection of the intensity ratios of gamma-ray peaks of a given nuclide and/or the quantified results on the basis of different radionuclides formed from a given element also provides a unique opportunity to inspect for errors. The applicability of these quality control approaches for samples of increasing mass is given in Table 1. It is clear that basic problems emerge when extending the traditional approaches to samples with sizes of more than a few grams. First, well characterized control samples available of the size of large sample (several grams to kilograms) are either very expensive in consumption or not available at all. Secondly, large sample analysis may be required because of the heterogeneity of the object, which cannot be simulated by a control sample even if it would be available. Thirdly, duplicates – assuming identical composition in mass fraction and in degree of homogeneity – may probably not be available when larger sample masses are needed. The problem related to the blank – impurities in the sample container and/or contamination – has, on the contrary, a smaller impact on the final result since the increase in the ratio of sample mass to container mass may result in negligible contribution of the blank (Table 2).

New strategies have to be developed to control the analytical quality in large sample analysis. One of the opportunities is to continue with the use of performance indicators, derived from the actual sample analyzed. In fact, this is not different from most quality control in, e.g., manufacturing and production, in which the quality of a final product depends on pre-defined specifications being met, like dimensions, tolerances, mass, color or operation. The inspection of gamma-ray intensity ratios and the use of different radionuclides of one element are already examples of such a form of quality control in activation analysis. This approach can further be extended to other sample/material characteristics based

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on physical sample properties such as gamma-ray self attenuation and neutron attenuation parameters, but also via the degree of inhomogeneity (Table 3).

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Some materials may be difficult to be processed to such homogeneity that representative sub-samples can be taken at the <1 g level. For such materials it may be advantageous to analyze much larger quantities without homogenization and to assume that the inhomogeneities are thus randomly distributed throughout the sample that the entire quantity can be considered as homogeneous. However, this assumption has some limitations. OVERWATER and BODE[10] demonstrated the impact of extreme inhomogeneities on the correction mechanisms for the attenuation of gamma-ray attenuation and neutron self-shielding. Inhomogeneities with strong gamma-ray absorbing properties have stronger effects on the degree of accuracy than inhomogeneities with strong neutron absorbing properties. Therefore, it is relevant to inspect for the presence of such extreme inhomogeneities in order to decide on the value of the finally calculated mass fractions. Two opportunities to inspect for such inhomogeneities are given here.

The effective linear gamma-ray attenuation coefficient is usually determined by measuring the transmission of gamma-rays of different energies emitted by an external source with known emission rate.[11,12] The values of the effective linear attenuation coefficients may be estimated using the tabulated values of the elements. Typically, for, e.g., biological and geological materials values can be found of $\sim 0.15\ cm^{-1} < \mu < \sim 0.60\ cm^{-1}$ at ~100 keV, $\sim 0.12\ cm^{-1} < \mu < \sim 0.25\ cm^{-1}$ at ~300 keV and $\sim 0.05\ cm^{-1} < \mu < \sim 0.15\ cm^{-1}$ at ~1000 keV. A 'band-width' of the linear attenuation coefficient can thus be determined at different gamma-ray energies for different types of materials (e.g., environmental, geological) (Fig. 1). This can assist to inspect if the experimentally determined attenuation coefficients have realistic values. Moreover, if scanned measurements are carried out, an indication of local (layer-type) inhomogeneities with strong gamma-ray absorbing properties may already be obtained. An example of this approach is given in Fig. 2. The transmission of the gamma-rays of a ^{152}Eu source was measured at different heights along a ~1 m long, ~15 cm diameter soil drill core sample prior to neutron activation. The effective linear attenuation coefficients for each of the gamma-ray energies were fitted with a polynomial so as to estimate the effective linear gamma-ray attenuation at other gamma-ray energies. The attenuation coefficients at 100 keV, 300 keV and 1000 keV all fall within the expected bandwidths. There are no indications in this example for layer inhomogeneities with strongly different gamma-ray absorbing properties.

Table 1. Opportunities of quality control measures, traditionally applied in normal activation analysis, for samples of larger sizes

Size, g	Quality control of the samples	Blanks	Duplicates	Gamma-ray intensity ratios and multiple radionuclides
1	Y	Y	Y	Y
10	N	Y/l.r.	Y/n.r.	Y
100	N	l.r.	n.r.	Y
1000	N	l.r.	n.r.	Y

Y = yes, application possible; N = no, not possible; l.r. = less relevant (see text); n.r. = not relevant.

Table 2. Typical masses of large samples and their packaging vials/bottles, demonstrating the reduction of the impact of impurities in bottles to the amounts, determined in the samples

Bottle volume, ml	Bottle mass, g	Sample mass, g	Bottle mass/sample mass
0.5	0.2	0.2–0.4	0.5–1
50	11	30–60	0.15–0.3
100	15	60–120	0.12–0.25
250	25	150–300	0.08–0.16
500	37	300–500	0.06–0.09
1000	100	1000–1500	0.06–0.1

Table 3. Opportunities of sample characteristics based on elemental constants for use in quality control in large sample analysis

Size, g	Gamma-ray attenuation coefficient	Gamma-ray intensity ratios and multiple radionuclides	n-Attenuation parameters
1	N	Y	N
10	Y/N	Y	N
100	Y	Y	Y/N
1000	Y	Y	Y

Y = yes, possible; N = no, not possible.

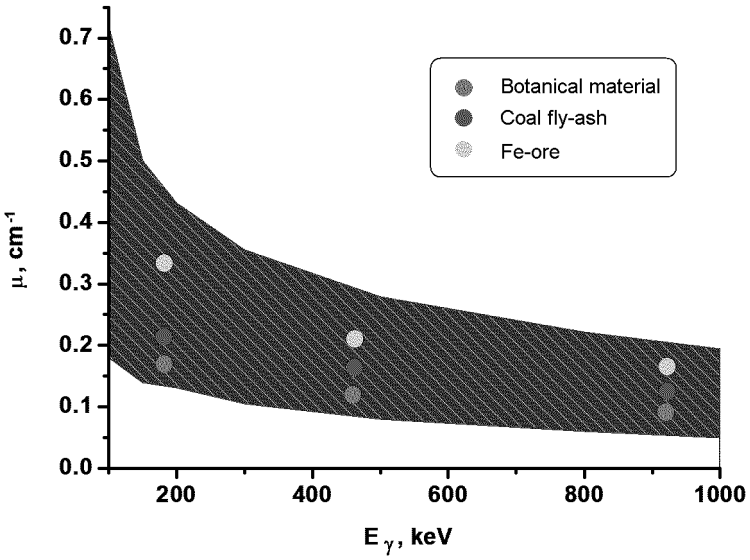

Fig. 1. Typical bandwidth of effective linear gamma-ray attenuation coefficients for samples of environmental and geological origin

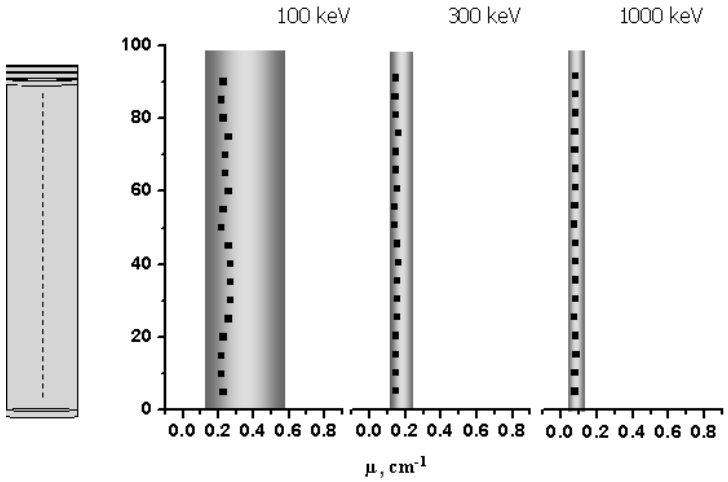

Fig. 2. Experimentally determined effective linear gamma-ray attenuation coefficients for a 0.9 m long, 11 cm diameter soil sample plotted within the expected bandwidths

BAAS et al.[13,14] developed a more sophisticated method for detection of local inhomogeneities. Segmented scanning may be considered as repetitive measurement of the same object if the sample is homogeneous at the scanned volume (or 'voxel') level. Therefore, the count rate in each channel of each segmented measurement can be compared with the average count rate in each channel after summing all individual measurements. Such a comparison, taking into account uncertainties, is made analogous to the *z*'-score principle.[15] Values of $|z'|>2$ or >3 (depending on the analyst's fitness-for purpose criterion) indicate a local inhomogeneity at the respective gamma-ray energy in a particular voxel. This approach is visualized in Fig. 3. A bottle of approximately 25 cm length, 8 cm diameter filled with soil was irradiated in the large sample facility[1] in Delft. The induced radioactivity was measured with a 96% Ge detector, collimated with a 10 cm thick Pb collimator with a 2 cm split opening. The figure shows the *z*'-scores for each channel number (gamma-ray energy) along the height of the sample. From the zoomed details it can clearly be seen that strongly deviating *z*'-scores occur at, e.g., 439 keV and 1115 keV, indicating an inhomogeneity for zinc. In addition, the histogram of all *z*'-scores in this figure provides also insight in the presence of this inhomogeneity.[14] Case-by-case it can now be decided if such inhomogeneities have an unwanted impact on the final analysis result.

The correction for neutron self-shielding in large sample neutron activation analysis may be made using information derived from neutron fluence rate depression at positions in the irradiation facility just outside the sample. OVERWATER and HOOGENBOOM[16] developed this approach to estimate the thermal neutron diffusion length L_s and the thermal neutron diffusion coefficient D_s, which subsequently can be used to reconstruct the neutron fluence rate profile inside the large sample. Both L_s and D_s are physical element properties and, similarly to the effective linear gamma-ray attenuation coefficient, boundaries can be estimated for the values of these two parameters in real materials. Though strongly correlated ($L_s^2 = D_s/\Sigma_a$ with Σ_a the macroscopic absorption cross section (cm^{-1})), typical values are ~1 cm<L_s<~20 cm and ~0.2 cm<D_s<~3 cm.

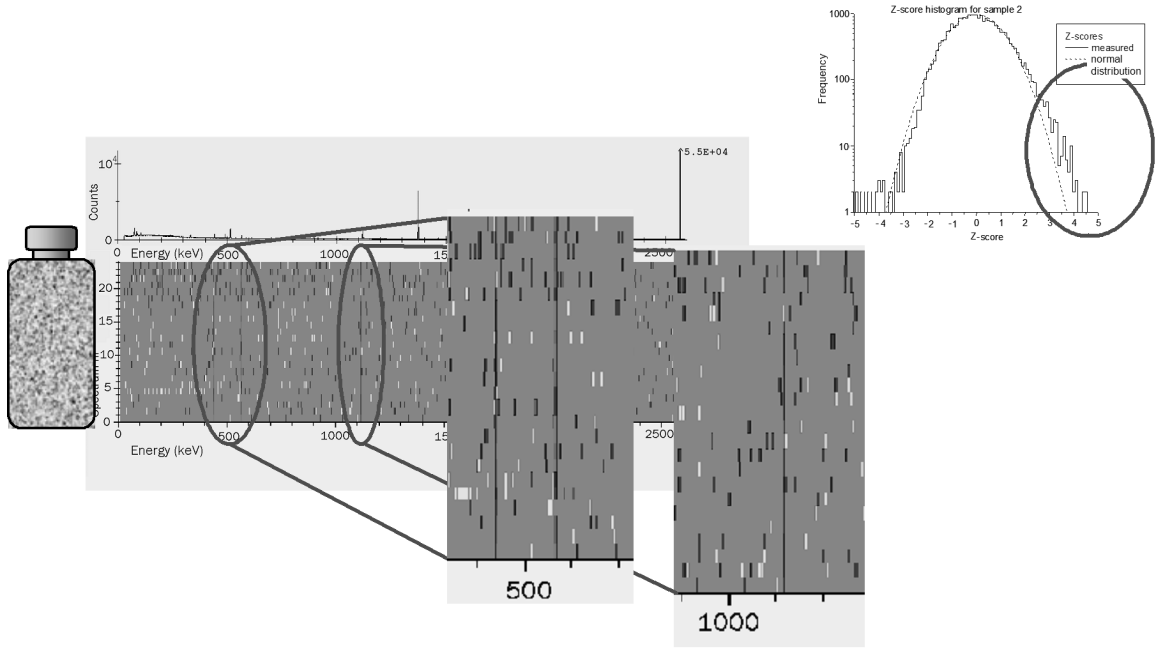

Fig. 3. z'-scores as observed in a segmented scan of a neutron activated sediment of approximately 25 cm long, 8 cm diameter. The zoomed parts show the deviating *z*'-scores at, amongst others, 439 and 1115 keV, indicating a zinc inhomogeneity. The insert[14] shows a histogram of all measured *z*'-scores (see text)

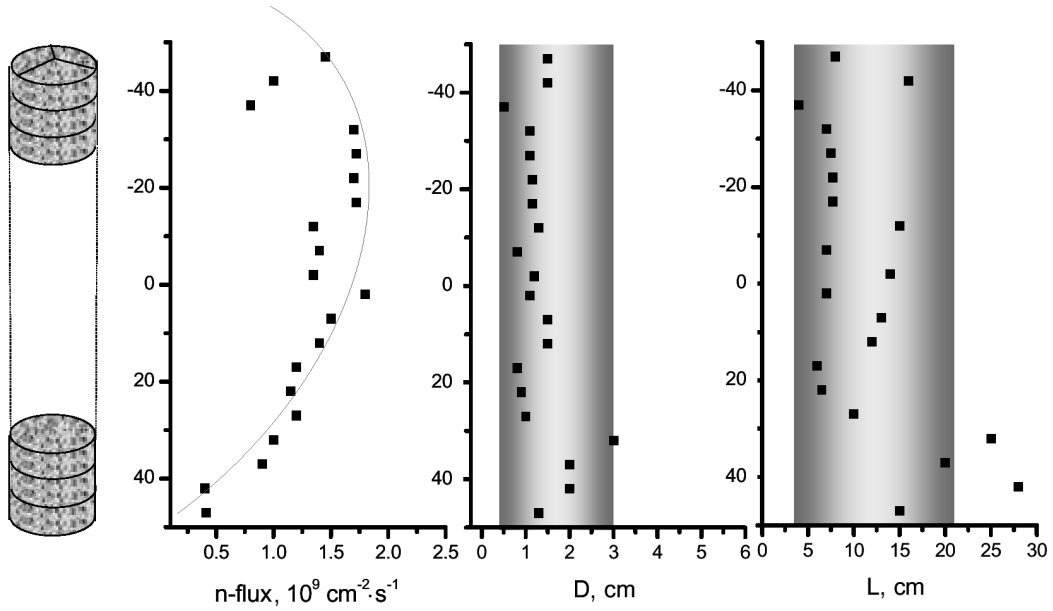

Fig. 4. Neutron fluence rate, neutron diffusion coefficient and neutron diffusion length as calculated from the neutron flux depression outside a 1 m long, 11 cm diameter soil sample

An example is given in Fig. 4. A ~1 m long, ~15 cm diameter water basin sediment drill core was analyzed in the frame of a pollution research project. Zinc foils were used as neutron flux monitors. The monitors were positioned just outside the sample container to monitor neutron fluence rate depression by comparison with the neutron fluence rates as monitored in a separate irradiation with a solid graphite sample, thus simulating an unperturbed neutron flux.[16] The calculated values of L_s and D_s at different heights are plotted within the bandwidths for these values. Also the average neutron fluence rates as a function of sample height is given. The fluence rates can be fitted with a cosine function, reflecting the flux distribution within the reactor's thermal column.

Conclusions

Large sample analysis is a new type of chemical analysis which may offer unique niches for (neutron, photon) activation analysis. Assuring the quality of the results requires insight, monitoring and control of sources of error. Quality control procedures as traditionally applied in chemical analysis are not fully applicable in large sample analysis. One of the advantages of activation analysis is that some of the measured sample parameters dealing with gamma-ray and neutron attenuation can only vary in ranges set by well known values of elemental constants. These parameters can much easier be determined in large sample analysis than with samples in the milligram range, thus offering an outlook for direct verification of the quality of the related correction algorithms.

The approaches presented in this paper merely illustrate that opportunities for quality control in large sample analysis exist to inspect for possible errors in the analysis. More research and development is needed, and dedicated quality control approaches may be needed depending on the different quantification methods to be developed in large sample activation analysis.

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