Applications of Electrohydrodynamic Atomization

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Summary

Electrohydrodynamic atomisation (EHDA) is a technique, which solely uses an electric force to atomise liquids. With EHDA, charged droplets in the order of micrometers are produced. Depending of the process conditions, droplets with a very narrow size distribution can be obtained. The charge of the droplets avoids droplet agglomeration and results in self-dispersal of the spray. These qualities make EHDA an interesting technique for many applications. To find out which for which applications EHDA has been used, a literature search was performed. The results of this search are presented in this thesis.

The majority of the articles found in the literature were dealing with mass spectrometry. In this application EHDA is used to charge large molecules, without breaking the molecules before detection. Production of powders is another application, to which EHDA has been applied. The powders are produced from a solution that is sprayed and evaporated. Using EHDA, particles in the order of nanometers to micrometers with a narrow size distribution can be obtained. This quality makes the technique very interesting for the production of drugs. For the production of powders, the charge on the droplets is a disadvantage as this results in Rayleigh explosion and deposition of the droplets and particles in the set-up. The droplets can be discharged using bipolar mixing, radioactive sources or corona ions.
The charge of the droplets is an advantage if the droplets have to be deposited on a surface, as the deposition efficiency will be increased. This quality is used in the production of thin films and in the spraying of pesticides in agriculture. Thin films of ceramics have been prepared from inorganic solutions, which were sprayed on a heated surface (electrostatic pyrolysis). The films produced were used in batteries, solid oxide fuel cells and gas sensors. Thin films of nuclear materials also have been prepared. The high deposition efficiency is the main advantage in this application as no material is lost. A few devices using the EHDA technique for spraying pesticides were developed in the past. One of them, the Electrodyn, was available on the market for a few years. This apparatus showed a much higher deposition and distribution efficiency of the pesticides on the leaves compared to other spraying techniques.
If a highly viscous liquid, such as a polymer solution, is sprayed using EHDA, charged fibres can be produced. These fibres can be used in electret filters, separation membranes or wound dressing materials.
EHDA is also an interesting technique for the use in fuel injection, because combustion improves with better atomisation of the fuel and with a smaller droplet size. In the past, the low conductivity of the fuel made the use of EHDA impossible for this purpose. Nowadays, it is possible, as special nozzles have been developed using charging techniques.
The momentum of the droplets, which exit an EHDA spraying nozzle, is high enough for the use in propulsion systems in satellites. This application was developed in the late sixties, but has never been applied in space.
The last application found in the literature, is the use of EHDA for the production of emulsions and dispersions. Instead of spraying in air, the liquid to be dispersed is sprayed in another liquid. This process uses much less energy compared to conventional processes and much smaller droplets are produced. The technique has been applied in reactors for desulphurisation of oil.

Table of Contents

1. Introduction

Many devices can be used to generate sprays from a bulk liquid. These devices, commonly called atomisers, can be found in many industrial, agricultural and propulsion systems. The transportation of the bulk liquid to sprays can be achieved with different sources of energy, from which an overview can be found in the book of Bayvel and Orzechowski (1993).

Electrohydrodynamic atomisation (EHDA) uses an electric field as the source of energy to generate a spray. An electric field is applied between a nozzle, to which a liquid is supplied, and a counter electrode. The liquid at the tip of the nozzle is atomised through the Coulomb interaction of charges on the liquid and the applied electric field. The result of this interaction includes both the acceleration of the liquid and subsequent disruption into droplets as well as the build-up of charge and subsequent disruption into droplets.

With EHDA a spray of charged droplets in the order of micrometers is generated. Depending on the spray conditions, monodisperse droplets can be produced. The charge on the droplets prevents agglomeration of the droplets and promotes self-disruption of the spray. These qualities makes the technique of EHDA interesting for many applications. A literature search was performed to find out for which applications EHDA has been used. This thesis shows the result of this search.

In the literature, the terms electrospraying or electrostatic spraying are often used to describe the process of EHDA. However, these terms also refer to processes where atomisation takes place by other sources of energy, with simultaneous or subsequent electrical charging. The electric field is primarily used to charge the liquid and to transport the charged droplets. These processes are not included in this thesis.
EHDA has also been applied to spray liquid metals. As these liquids contain a much higher conductivity compared to normal liquids, the break-up mechanism is different. Therefore this application is not described in this thesis.

First the basic principles of EHDA will be discussed in chapter 2. Chapter 3 gives an overview of the different applications of EHDA until September 1999.

2. Electrohydrodynamic Atomisation (EHDA)

2.1 Basic Principles of EHDA

In EHDA an electric field is applied between a capillary, to which a liquid is supplied, and a counter electrode. The counter electrode may be a plate, a plate with an orifice or a ring. Figure 2.1 gives a schematic picture of a set-up that uses the capillary-ring configuration.

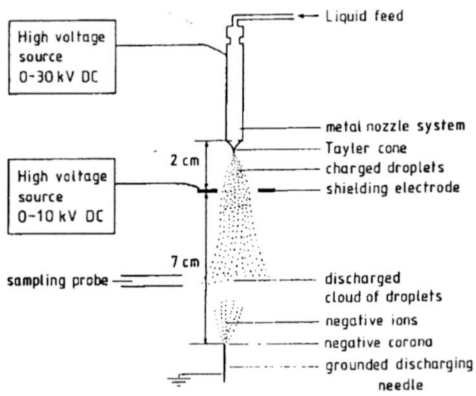


Figure 2.1. *Typical configuration for EHDA.*

In EHDA a liquid is fed to a capillary at such a flow rate that without applying an electric field droplets are formed at a low frequency. When an electric field is applied between the capillary and the counter electrode, charges in the liquid move in the direction of the droplet surface, which results in a force. Due to this force the droplets are disrupted at a higher frequency. At a certain strength of the electric field the shape of the droplet changes into a conical shape. At the end of the cone a jet is formed which breaks up into a spray of very small droplets. At even higher electric fields multiple jets are formed. These are a few examples of the different modes that occur in EHDA, which will be discussed in more detail in section 2.3

The process of EHDA can take place in various atmospheres (air, inert gas, vacuum, liquids, etc) using various fluids and experimental conditions. The process includes the production of charged droplets on different scales (nm-μm) and monodisperse and polydisperse droplet populations in high and low production.

The atomisation of a liquid is a function of both external (experimental configuration, flow rate and atmosphere) and internal (fluid) properties of the used set-up. The fluid properties which are important for EHDA are the electrical conductivity (K), the surface tension (γ), the viscosity (μ), the density (ρ).

2.2 History of EHDA

The phenomenon of an electric effect on menisci is known since the sixteenth century. William Gilbert reported the interaction between a water droplet and a piece of amber, leading to a conical shaped droplet. In the beginning of this century, Zeleny (1915, 1917) showed that liquid menisci subjected to a high enough electric field change to a conical shape and emit a mist of very small droplets. In the fifties, Vonnegut and Neubauer (1952) tried to relate the properties of a liquid to their ability of being sprayed. Taylor (1964) made the first mathematical description of the cone by balancing the forces that are present. At the beginning of the nineties, scaling laws for electrospraying of liquids were developed, to predict the characteristics of the produced droplets on forehand. A physical model that describes the shape of the cone and the droplet size of the droplets in the spray was derived by Hartman (1998).

2.3 Modes of EHDA

So electrohydrodynamic atomisation, also called electrospraying, refers to a process where a liquid jet breaks up into droplets under influence of electrical forces. However, a liquid jet will also break up into droplets without any electric force present.

Depending on the strength of the electric stresses in the liquid surface relative to the surface tension stress and the kinetic energy of the liquid jet leaving the nozzle, different spraying modes will be obtained. Several spray modes have been defined by Cloupeau and Prunet-Foch (1994). A brief summary of these spray modes is given in the following. Note that each mode has multiple characteristics and the transition between modes is not always well defined; consequently, the simple descriptions to follow cannot fully encompass the subtleties of each mode. Figure 2.2 presents a flow chart describing the modes as a function of the applied potential. In this figure the influence of other parameters on the spray mode also can be seen. Here it is not meant to imply that all liquids under all conditions will follow identically the mode progression through potential space. However, this figure, in general, locates the modes described below in the potential space of the spray.

The modes are separated into two general categories: those that exhibit a continuous flow of liquid through the meniscus and those that do not. The former consists of the simple-jet, the cone-jet and the ramified-jet, while the latter consists of the dripping, the microdripping, the spindle and the intermittent cone-jet modes. The latter are often referred to as pulsating modes.

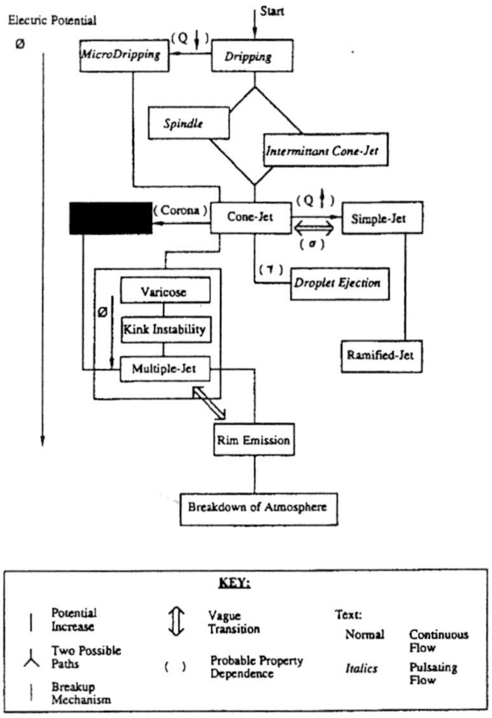


Figure 2.2: *Different modes of EHDA as function of the applied potential (Grace and Marijnissen (1994))*

The dripping mode is characterised by the production of large droplets (usually larger than the capillary diameter) at low frequency (< about 500 Hz). The production frequency and the droplet diameter vary directly and inversely, respectively, with the applied potential. The primary droplets are sometimes accompanied by satellite droplets. The microdripping mode occurs at low flow rates and produces droplets smaller than the capillary diameter at a frequency about two orders higher than the dripping mode. Figure 2.3 shows both modes. The grey areas represent the nozzle.

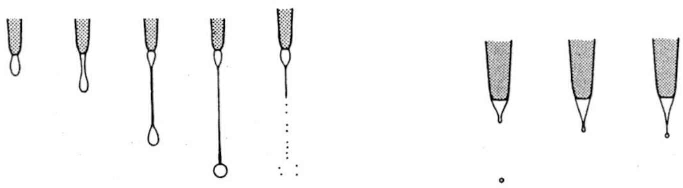


Figure 2.3: *Dripping mode (left) and microdripping mode (right). (adapted from Cloupeau et al. (1994))*

The spindle mode generates two distinct droplet sizes, a large primary droplet and several small satellites. In this mode, a jet extends from the meniscus and collapses into the primary and satellite droplets. The meniscus collapses to the capillary tip and the process is repeated with a regularity depending on the conditions. Figure 2.4 shows the spindle mode. The intermittent cone-jet mode, as the name suggest, produces an unstable cone-jet. Between the cone-jet occurrences the meniscus collapses to the capillary and several large droplets may be emitted. Previous nomenclature has grouped the spindle and the intermittent cone-jet modes into one mode, the pulsating-jet mode. The droplet diameter differentiates the two modes. The spindle mode produces two diameter classes where the intermittent cone-jet mode produces a multitude of fine droplets with a superimposed, semi-periodic large droplet population.

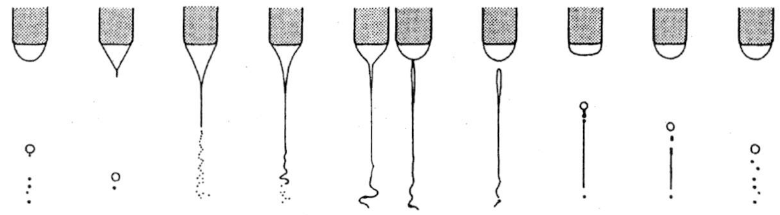


Figure 2.4: *The different stages of the spindle mode. (adapted from Cloupeau et al. (1994))*

The continuous modes are described in the following. The simple jet and cone-jet exhibit similar structures. The transition between the two is sharp for high conductivity liquids and vague for low conductivity liquids. Both consist of a single jet drawn from the meniscus by the electrical forces. In the cone-jet mode, often referred to as the Taylor cone mode, the meniscus forms a conical shape with a half angle near the 49.3° Taylor angle (as calculated from an ideal, no-flow equilibrium condition).
The jet drawn from the apex of this meniscus breaks up into droplets by three mechanisms as a function of increasing potential: varicose instabilities where the break-up proceeds as in a natural jet, kink instabilities where the break-up is more disordered due to the large lateral instabilities caused by the high electric forces and lastly, the multi-jet instability where multiple jets appear on the meniscus and the cone length is shorter. Figure 2.5 shows the three break-up mechanisms of the cone jet mode.

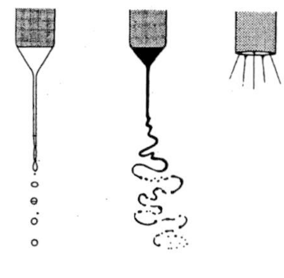


Figure 2.5: *from left to right: varicose instabilities; kink instabilities; multiple jets. (adapted from Cloupeau et el.(1994))*

The simple-jet differs from the cone-jet mode in the sharpness of the conical meniscus and in this mode break-up usually occurs via varicose instabilities. This difference is caused by the fact that the kinetic energy of the jet in the cone-jet mode is mainly generated by the electric forces, where in the simple-jet mode the kinetic energy of the jet is mainly generated by the syringe pump. For the cone-jet mode the diameter of the cone base is determined by the outer diameter of the capillary and the jet diameter mainly depends on the liquid flow rate. For the simple-jet mode, the diameter of the cone base is determined by the inner diameter of the capillary. The jet diameter depends on the extra acceleration caused by the electric field. When the electric field is increased over a simple-jet, then the surface charge on the jet becomes larger than a certain threshold value. In that case, the radial electric forces cause the occurrence of several, temporal secondary jets issuing from the surface of the primary jet, not just from the apex. This is called the ramified-jet mode, which is shown in the next figure.

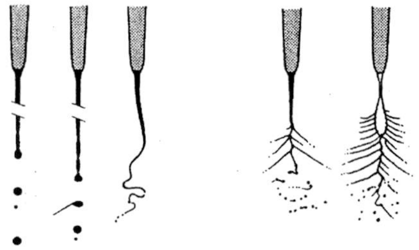


Figure 2.6: *Simple jet (left) and ramified jet (right) mode. (adapted from Cloupeau et al. (1994))*

The most reported spray mode is the already mentioned cone-jet mode, from which figure 2.7 shows a picture. There are actually three reasons for the importance of this mode. First it allows the production of aerosols within a very large range of droplet sizes, including the submicron range. Secondly, this mode is achievable for a very wide range of liquid properties in terms of conductivity, viscosity and surface tension. Thirdly, the size distribution of the particles produced can be, depending on the experimental conditions: monodisperse, bimodal or polydisperse.

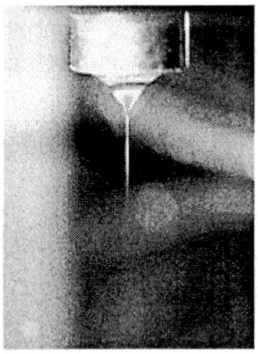


Figure 2.7: *Photograph of EHDA in the cone-jet mode.*

Electrical interaction between these highly charged droplets and differences in inertia are the main cause for a size segregation effect. Small droplets are found at the edge of the spray, while large droplets are found in the spray centre. This makes separation of the main droplets from the smaller secondary droplets possible and a monodisperse spray can be obtained. If the highly charged droplets evaporate, then the Rayleigh limit for droplet charge can be reached. In that case droplet fission can take place. This effect changes the droplet size distribution.

In the cone-jet mode, a liquid is pumped through a nozzle at a low flow rate. An electric field is applied over the nozzle and some counter electrode. This electric field induces a surface charge in the growing droplet at the nozzle. Due to this surface charge, and due to the electric field, an electric stress is created in the liquid surface. If the electric field, and the liquid flow rate are in the appropriate range, then this electric stress will overcome the surface tension stress. In that case, the electric stresses transform the droplet into a conical shape. The tangential electric field accelerates the charge carriers at the liquid surface toward the cone apex. In a liquid, the charge carriers are mainly ions. These ions collide with the surrounding liquid molecules. This results in an acceleration of the surrounding liquid. As a result, a thin liquid jet emerges at the cone apex. This jet can break up into a number of main droplets with a narrow size distribution, and a number of smaller secondary droplets and satellites. The number of secondary droplets can be of the same order of magnitude as the number of main droplets. However, the total volume of these secondary droplets is much smaller than the volume of the main droplets. Due to the excess of surface charge in the liquid cone and jet, the droplets are highly charged.

Depending on the liquid properties, the main droplet size produced ranges from nanometers with production frequencies in the order of 10^9 Hz to hundreds of micrometers with production frequencies of about 10^4 Hz.

3. Applications of EHDA

3.1 Mass Spectrometry

The last 30 years, the application of electrospraying in the field of mass spectrometry has expanded enormously. In its simplest form, a mass spectrometer is an instrument that measures the mass-to-charge ratios m/z of ions formed when a sample is ionised by one of a number of different ionisation methods. If some of the sample molecules are singly ionised and reach the ion detector without fragmenting, then the m/z ratio of these ions gives a direct measurement of the molecular weight. Ideally, a mass spectrum contains a molecular ion, corresponding to the molecular mass of the analyte, as well as structurally significant fragment ions which allow either the direct determination of structure or a comparison to libraries of spectra of known compounds.

Attempts to extend the sensitivity and accuracy of mass spectrometric methods to the analysis of large polar organic molecules of interest in biology and medicine have long been frustrated by the difficulties of transforming such molecules into gas-phase ions. The molecules are insufficiently volatile or thermally stable to permit volatilisation prior to ionisation. Consequently, it was impossible to ionise the molecules with the classic methods of ionisation such as electron-, photo- and chemical ionisation. Since, the late 1960s a number of ionisation techniques have been developed with varying degrees of success to produce intact ions from molecular species of ever increasing size and decreasing vaporisability. In these new techniques the desorption of sample ions is achieved by the impact of particles (secondary ion (SI) MS, fast atom bombardment (FAB) MS, plasma desorption (PD) MS, laser desorption (LD) MS and matrix-assisted laser desorption/ionisation MS) or by dispersion of a sample containing liquid by pneumatic (atmospheric pressure ionization (API) MS), thermal (thermospray (TS) MS) or electric field forces (electrospray (ES) MS).

Electrospraying as a method for generating gas-phase ions was introduced in 1968 by Dole and co-workers. Their intention was to determine the mass of polystyrene macromolecules measuring the ion retardation and ion mobility. The idea of coupling the electrospray technique to a conventional mass analyser was put forward as early as 1973 (Dole et al. 1973), and realised in 1984 (Yamashita and Fenn (1984), Alexandrov et. al. (1984)). Its potential for the analysis of large biomolecules was realised in 1988 (Meng et al. (1988)). Today, ES MS is used to analyse large biomolecules, such as proteins, nucleic acids, carbohydrates, lipids, and compounds composed of two or more of these components. Nowadays, the amount of research activities and publications in the field of ES MS can hardly be overlooked. Excellent reviews and books dealing with ES MS were written by Cole (1997), Kebarle and Tang (1993), Smith et al. (1997) and Dülcks and Juraschek (1999).

Figure 3.1, illustrates how an electrospray is integrated into a mass spectrometer. In ES MS, a liquid containing a sample at concentrations of about 10^{-6} mol l^{-1} is supplied to a capillary at typical flow rates of 1-20 μl/min. The capillary (typical dimensions: 0.1-0.2 mm ID, 0.2-0.5 mm OD) is raised to a potential difference of 2-5 kV (positive or negative) relative to a counter electrode located 1-5 cm away, which results in an

electric field strength in the order of 10^6 V m^{-1}. The currents flowing from the capillary are in the order of 0.1-0.5 µA.
The evaporation of the solvent from the produced droplets is enhanced by heat transfer. This is accomplished either by a counterflow of a heated dry inert gas (usually N_2 at 80 °C) as shown in figure 3.1a or by leading the droplets through a long heated capillary (typically 0.5 mm in diameter, 5-30 cm in length and heated to 150-250 °C) as shown in figure 3.1b.
After the entrance into the mass spectrometer housing the ion-containing gas beam is led trough a differential pumping system into the mass analyser. Of importance is the potential difference between the nozzle (or transfer capillary) and the entrance to the skimmer. Increasing the potential difference increases the ion energy and thus the amount of collision of the ions with the background gas. Increasing potential difference, increases the fragmentation of the sample ions, by which structural information can be obtained.

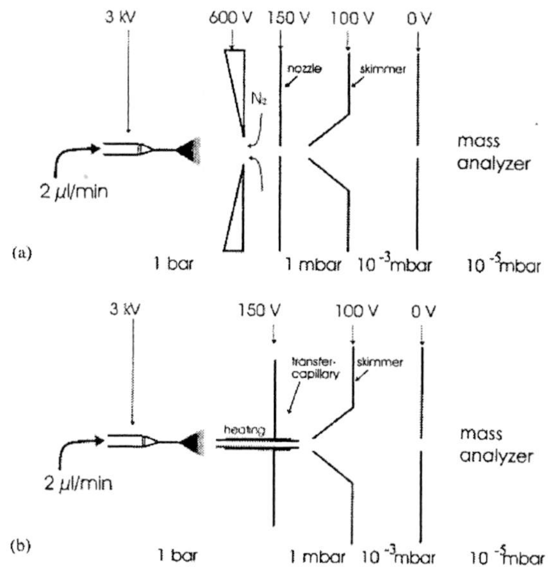


Figure 3.1: *Vacuum interfaces for the transfer of gas-phase ions from atmospheric pressure to vacuum, employing different devices for heat transfer to the aerosol droplets: (a) countercurrent of heated dry nitrogen, (b) heated transfer capillary (Dulcks and Jaraschek (1999)*

An unique feature of ES MS compared to other mass spectrometers, is the fact that molecules with a higher masses often appear as multiple charged ions. This feature offers two advantages. First the charge stage distribution allows the accurate determination of the molecular mass. Second, since most analyte ions signals fall in the mass range below m/z =2000, inexpensive mass analysers can be used. The major drawback of ES MS are the limitations of the liquids that can be sprayed.

Several variants of the original ES MS technique have been developed in order to meet requirements of practical analytical work. A sheath flow capillary was by Smith et. al. (1988) to spray highly conductive or aqueous solutions. The Ionspray® was developed by Bruins et. al. (1987) to use higher flow rates, which are needed to couple the ES MS with conventional liquid chromatography. The Nanospray was developed by Wilm and Mann (1994) to analyse very small sample quantities.

3.2 Production of Powders

Spray processes for powder production have been known for centuries. In these processes powders are produced by spraying a solution into droplets. During the drying, the solvent evaporates and particles are left over. In the conventional spray processes such as spray drying, the droplet size is seldom smaller than 100 μm. Thus a very low solute concentration must be used for the production of particles below 10 μm. This means the use of very pure solvents and thus high costs.

With EHDA in the cone jet mode it is possible to produce much smaller droplets with a narrow size distribution. The droplets produced can vary from a few tens of nanometers to a few tens of microns, depending on the liquid properties. Furthermore, from an energetic point of view the EHDA of liquid is more efficient.

The charges produced on the droplets by the EHDA of liquids in the cone-jet mode make their collection easier. However, when such a level of charge is not needed, the particles can be neutralised by different methods such as corona ions, radioactive sources or bipolar coagulation. The problem of the small quantities produced by one electrospray has often be a reason to disregard its use in an industrial environment. The answer to this problem is the scaling up of the EHDA of liquids in the cone-jet mode. This scale-up can be realised by the use of a large number of electrosprays. The feasibility of such a process has already been demonstrated. Processes that use EHDA for the production of powders are electrostatic pyrolyses and bipolar mixing. EHDA is also used for the production of drug particles, this application will be discussed in the next chapter.

3.2.1 Electrostatic pyrolysis (ESP)

In electrostatic pyrolysis, electrospraying is combined with pyrolysis. The liquid that is used to spray, contains the inorganic components that form the powder. Vercoulen *et al.* (1993) used the technique to produce a powder of SnO_2, which is used as a semi-conductor material or as an additive to alter the electric properties of powders. A precursor solution of $Sn(Ac)_4$ was sprayed into droplets which were dispersed into air and carried through an oven where the droplets were evaporated and the particles pyrolysed to SnO_2. The equipment they used was based on the Delft Aerosol Generator (DAG), which was developed by Meesters *et al.* (1992). The DAG, which is shown in figure 2.1, uses a corona needle to discharge the droplets. The droplets are discharged to avoid deposition of the particles on the counter electrode and nearby surfaces and to avoid Rayleigh explosion of the droplets. The latter takes place when, during evaporation the forces due to surface charge on the droplets becomes higher than the surface tension forces. Figure 3.2 shows the particles that were produced by Vercoulen *et al.*.

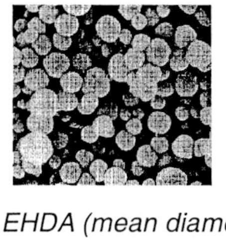


Figure 3.2: *SnO_2 powder produced by EHDA (mean diameter is 1.61 μm)(Vercoulen (1995)).*

The principle of the DAG in combination with pyrolysis was also used for the production of yttria powders. Rulison and Flagan (1994) synthesised high quality yttria powders, composed of dense submicrometer, nanocrystalline oxide particles. Concentrating solutions of hydrated yttrium nitrate in *n*-propyl alcohol were atomised using EHDA and the resulting aerosol droplets were then thermally decomposed at 500 °C in a flow tube reactor with air as the carrier gas. The choice of the chemical precursor strongly affected the structure of the synthesised particles. The yttrium oxide particles made from n-propyl alcohol solutions of 5-hydrated yttrium nitrate salts appeared to have dense structures. Those made of 6-hydrated yttrium nitrate salts were shells. According to Rulison and Flagan, the explanation for this was that the 5-hydrated yttrium nitrate formed an alcohol-vapour-permeable particle surface during decomposition while the 6-hydrated yttrium nitrate did not.

3.2.2 Bipolar Coagulation

The process of bipolar coagulation (Borra *et al.* (1998)) is based on the controlled coagulation of oppositely charged droplets through electrical forces. Thus, two sprays of oppositely charged droplets are directed towards each other and the coagulation between the droplets takes place through the electrical attraction between them. The two sprays are created using EHDA in the cone-jet mode, because of the monodispersity of this mode. After coagulation, a chemical reaction can take place in the newly formed droplet obtaining the desired product. This process is visualised in figure 3.3. Bipolar mixing can also be used for coating particles and mixing of liquids.

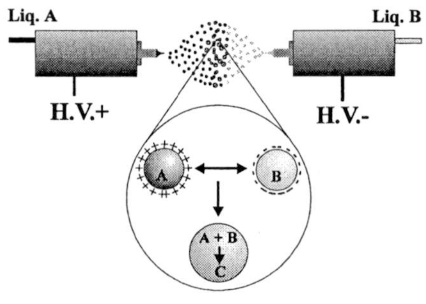


Figure 3.3: *Bipolar coagulation*

3.3 Production of Drug Particles

3.3.1 Inhalation Drugs

In the treatment of acute and chronic respiratory diseases, like asthma, bronchitis and emphysema, inhalers are used to deposit the drugs directly to the specific areas of the respiratory tract where the infection lodges. The drugs are inhaled in the form of sprays or powder capsules. With the inhalation route less drugs have to be administered compared the oral and parenteral administration route. Despite this advantage, still only 10-30% of the inhaled drug is deposited in lower airways were it has its therapeutic effect. The rest of the drug is deposited in the mouth, throat and upper airways. The low deposition efficiency is strongly related to the size of the inhaled medicine particles. Due to deposition mechanisms impaction, sedimentation and diffusion only particles in the size range of 1-5 μm are deposited in the lower airways of adults with a high efficiency. Larger particles are mainly deposited in the mouth, throat and upper airways and smaller particles are exhaled. The conventional inhalers produce polydisperse drug aerosols with a mean particle size >5 μm, which explains the low therapeutic efficiency of the inhaled drugs.
The electrospray technique has the ability of producing monodisperse aerosols with a small droplet size, therefore it is a perfect technique to produce aerosols for drug inhalation. Using this technique would result in a decrease of the drug administered and so in a decrease of adverse effects the inhalation drug have on the body. The first inhaler known using the electrospray technique was patented by Noakes *et al.* (1989). A schematic picture of their apparatus is shown in figure 3.4. The spray produced is discharged by a corona produced by a sharp discharge electrode, which is charged to a polarity opposite of the spray. Changing the potential difference between the porous disk and the discharge needle can control the intensity of the discharge. The spray has to be discharged to prevent Rayleigh explosion of the droplets, which would result in the loss of monodispersity of the spray. The shield electrode protects the part where the spray is formed from corona discharge. The hole in the shield electrode is small enough to prevent corona going through and sufficiently large enough to allow the spray through. An air stream produced by the users inhaling or by a fan moves the discharged spray to the mouthpiece. Noakes *et. al.* were not able to discharge all the droplets of the spray without influencing the formation of the spray.

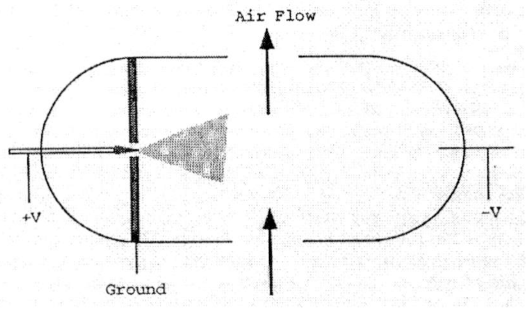


Figure 3.4: *Apparatus described by Noakes and colleagues (copied from Hickey (1996))*

Tang and Gomez (1994) developed a prototype delivery system for the use in an inhaler, quite similar to the apparatus of Noakes *et al.* A schematic picture of it is given in figure 3.5. The main difference with the system of Noakes is the flow of CO_2

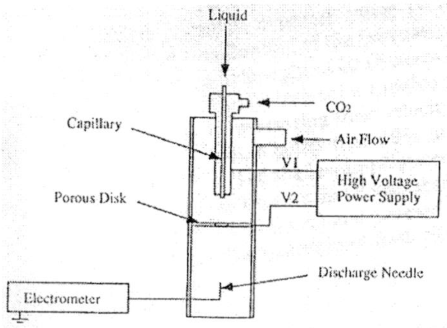


Figure 3.5: *drug delivery system described by Tang and Gomez (1994)*

that is used to isolate the capillary tip from the air. In this way the onset of corona discharge is suppressed, which makes it possible to spray water. Under typical conditions for drug inhalation, makes it possible to spray water. Under typical conditions for drug inhalation, Tang and Gomez obtained monodisperse droplets of aqueous solutions in the diameter range 2-11μm, by varying the liquid flow rate in the range of 5.8-42.4 $\mu l \cdot min^{-1}$. The liquid flow rate was found to be the dominant parameter controlling the droplet size. An increase in electric conductivity of the liquid also provided a way to decrease the droplet size. It was found that the droplet size distribution broadens at smaller droplet sizes because of the size-dependence evaporation effects.
Cannon and colleagues (1987) described the aerosol tetrode. This system is capable of producing large quantities of monodisperse particles with a moderate degree of control of their net charge. Such a system might be configured to replace air jet nebulizers.

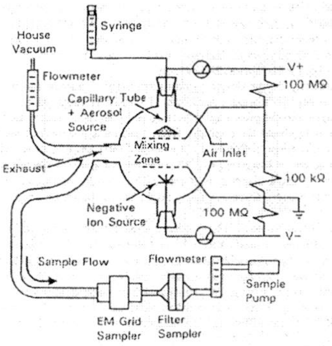


Figure 3.6: *aerosol tetrode of Cannon et al.*

Greenspan and Moss (1992) described a hand-held apparatus for the delivery of metered amounts of medication for inhalation. Their device employs a piezoelectric crystal to produce the necessary potentials to achieve atomisation.

3.3.2 Ocular Drugs

Booth and Rowe (1990) have described an apparatus for the delivery of small volumes of medication to the eyes. Their patent presents an apparatus that uses the EHDA technique to produce a spray of medicine solution. Data are presented on the administration of ephedrine and pilocarpine to the eyes of rabbits. Typical volumes of solution sprayed were 5 to 20 μL.

3.3.3 Drug formulations for injection

Reyderman and Stavchansky (1995) have sprayed cholesterol from their melts using EHDA. They produced a mixture of spherical particles of 150-250 μm and amorphous particles of 10-30 μm size. About 65% of the particles produced were in the range of 13.5±3.76 μm. Cholesterol was used as a model compound for diverse steroids that have an analogous structure. They suggested the use of EHDA for the production of microspheres of water insoluble steroids, which may act as a sustained release formulations upon intramuscular or intradermal administration.

3.4 Production of Thin Films

Another application of EHDA is its use in thin film production. The droplets produced with EHDA are deposited on a surface where they evaporate. If the liquid sprayed is a solution containing solid material a thin film is produced. In comparison with other thin film deposition techniques, such as chemical vapour deposition (CVD) and physical vapour deposition (PVD), EHDA offers a lot of advantages. These advantages are a high deposition rate and efficiency, a relatively cheap and simple system, an easy coverage of large areas and an easy process to control. The EHDA technique for the production of thin films has been applied in electrostatic pyrolysis, gas-aerosol reactive electrostatic deposition and for the production of nuclear targets. The first two will be discussed here. The deposition of nuclear targets will be discussed in the next section.

3.4.1 Electrostatic Pyrolysis

A lot of research has been performed on the production of thin films by electrostatic pyrolysis (ESP). This technique was used by Vercoulen et al. (1993) to produce powders as described in chapter 3.7. For the production of thin films the droplets containing the inorganic components are deposited on a heated substrate where the droplets evaporate and the pyrolysis occurs. By controlling the liquid content of the particles reaching the substrate and the substrate temperature, the porosity of the layer can be set. The next figure shows a typical set-up used for ESP.

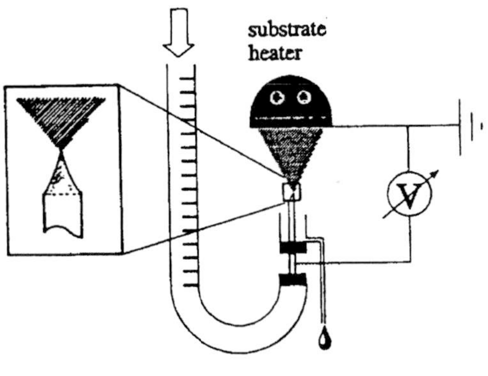


Figure 3.7: *Set-up for thin film deposition (van Zomeren et al. (1994))*

The ESP technique was first described by Karakis and coworkers in 1987. They prepared thin films of CdS by electrospraying a water-alcohol solution with the reagents cadmiumchloride and thiocarbamide. When the solutions aerosol was deposited on a heated surface (680-750 K), a polycrystalline CdS film was formed as a result of a pyrolytic reaction. Van Zomeren et al. (1994) used the ESP technique for the depositing a thin films of $LiMn_2O_4$ which is used as cathode material in rechargeable lithium batteries. The deposition of anode and cathode materials as thin films can decrease the total size of the battery. The last years the, ESP has been further developed and very extensively applied to deposit a wide range of ceramic thin films for energy conversion and storage systems and gas sensors. Examples of the thin films that were prepared are:

- yttrium stabilised zirconia (YSZ) and $BaCeO_3$ for solid oxide fuel cells (SOFC) (E.M. Kelder et al. (1994))
- $LiCoO_2$ for cathode material in rechargeable lithium batteries (Chen *et al.* (1995, 1996a, 1996b, 1996c))
- yttrium stabilised zirconia (YSZ) on Gadollinia-Doped Ceria (Chen *et al.* (1996d))
- terbia-doped yttria stabilized zirconia for SOFC (Stelzer and Schoonman (1996))
- $Li_{1.2}Mn_2O_4$ and BPO_4:$0.035Li_2O$ for secondary lithium-ion batteries (Chen *et al.* (1997))
- SnO_2-Mn_2O_3 for gas sensors (Gourari (1998))
- CdS for gas sensors (Golovanov (1995))

3.4.2 Gas-Aerosol Reactive Electrostatic Deposition

Salata *et al.* developed a technique called gas-aerosol reactive electrostatic deposition (GARED). It is capable of producing uniformly nano- and microparticles of a wide range of compound semiconductors embedded in different polymer films. In this form they can be directly applied to make devices. In GARED an aerosol of charged droplets of the spraying solution containing metal ions and polymer molecules is created by EHDA. During the drift of the droplets to the grounded substrate, a reaction takes place between the metal ions inside the droplets and a gas phase compound to form a colloidal semiconductor particle within the aerosol. The polymer surrounds the semiconductor as the solvent evaporates. By using this method Salata *et al.* (1994a,b) have produced quantum dots of CdS and GaAs in polymer, by reacting a dilute aerosol of metal nitrate with a dilute mixture of hydrogen sulphide and arsine, respectively. A schematic diagram of the set-up they used is given in figure 3.8.

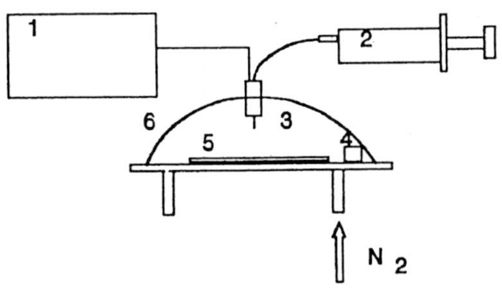


Figure 3.8: *Set-up used by Salata et al. (1994). 1. high voltage supply, 2. syringe pump, 3. stainless steel capillary, 4. source of hydrogen sulfide, 5. substrate and 6. reaction chamber*

The same set up was used for the production nano-PbS/PVA films (Salata *et al.* (1994c)). In the reactor chamber the Pb-ions in the aerosol droplets react with the H_2S from the gas phase forming PbS nanoparticles surrounded by polymer molecules. These PbS polymer particles were deposited on the substrate forming a film.

3.5 Production of Nuclear Sources

One of the earliest applications of EHDA was in the production of thin sources for radioactivity measurements. These were either thin sources of active material, such as that required for α- or β-decay studies or as thin films for the use of targets for activation in an accelerator or nuclear reactor.

Carlswell and Milsted (1957) prepared thin films of uranyl nitrate, americium-241 nitrate and curium-242 nitrate with the set-up shown the next figure.

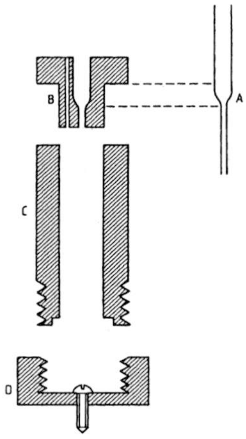


Figure 3.9: *The cell used by Carswell and Milsted (1957) for preparing thin sources for nuclear studies. A: capillary tube, B: lid to the cell, C: central section of the cell and D: base of cell with screws to C.*

A solution of the radioactive material in acetone was kept in a capillary tube A. The inner diameter of the tube was so small that no liquid left the tube before applying an electric field. The sections B, C, and D in the figure were made of perspex and fit together to form a cell. The capillary tube fits into the lid of the cell. The lid also contained a vent to prevent the atmosphere in the cell from being saturated. When an electric field was applied between the capillary and a metal disk (substrate) placed into section D, the liquid was sprayed onto the disk until the liquid was expelled from the tube. The droplets evaporated before the metal disk was reached. With this technique, the collection efficiency on the disk is very high and after repeated use the inside of the cell was still free of contamination by radioactive material.

The density distribution of nuclear films produced with EHDA was studied by Miyahara (1969) who produced thin films of ^{204}Tl from solutions in ethanol. The density distribution of the films showed very flat. Lauer and Verdingh (1963) constructed a machine to prepare thin deposits or films of uranium, plutonium and borun up to 5 cm in diameter. This was possible by moving a table on which the substrate was placed. The homogeneity of the samples was in the order of 1%.

Van der Eijk et al. (1973) give an overview of the various methods of preparing radioactive sources, including EHDA. They remarked that nuclear films deposited with EHDA have a somewhat lower quality compared to other techniques such as vacuum evaporation and electrodeposition due to impurities present in the solvent which will also be deposited on the substrate.

3.6 Agriculture

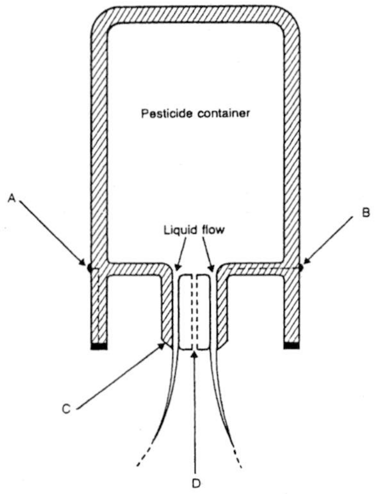
In agriculture pesticides are essential for the protection of food and fibre crops against insects, disease and weed pests. These pesticides are normally applied as sprays which usually are aqueous-based suspensions, solutions or emulsions of toxic materials.

In conventional spraying a large fraction of the spray does not reach the target because of drifting of the spray droplets in the air-stream or because of gravitational settling of droplets to the soil beneath. The small deposition efficiency causes economic losses and environmental harm. Beside, drifting of the toxic material can also endanger other nearby crops. The deposition efficiency increases a lot if the droplets in the spray are charged. Beside, in contrast to uncharged droplets, the charged droplets also move into the crevices and on the undersides of the leaves, which improves the distribution of the droplets over the target. It is of great importance that the pesticides are also deposited on the undersides of the leaves as a number of pests, such as the glasshouse white fly and the red spider, are predominantly found here.

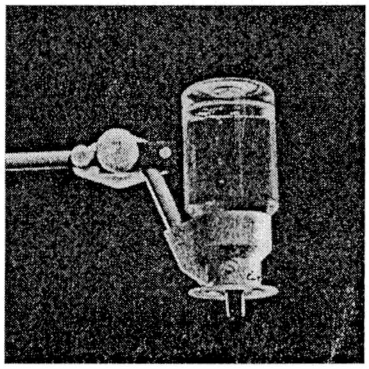
The last decades many spraying systems have been developed for agricultural proposes that produce charged droplets. In most of these systems charging takes place after the droplets are produced with conventional atomisation techniques. The most practical and reliable charging methods are the use of an ionised field corona or electrostatic induction. A few systems have been developed that solely rely on the EHDA technique to both atomise and charge pesticide droplets. These systems are the Electrodyn, the Microdyne, and the multiple jet EHD atomiser. Compared to the other charging systems, the systems using the EHDA technique produce much smaller droplets, which makes the effectiveness of many pesticides greater. The effect of the insecticide increases with decrease in the droplet size, due to the better distribution of the droplets over the plant.

3.6.1 The Electrodyn

The Electrodyn, which is a hand-held unit, was developed at ICI by Coffee (1978). In the Electrodyn system, the pesticide, formulated as an oil-based liquid, is fed by hydrostatic pressure to an annular-slit nozzle, which is at a potential of 15-25 kV with respect to a coaxial ring encounter electrode. Liquid emerging from the annular slit is charged by the applied field and pulled out by Coulomb forces into a regular of jets, which disrupt into droplets due to axisymmetric instabilities. The system operates at flow rates of 360 ml/hr. Until a few years ago, the Electrodyn, which is shown in the figure 3.10 was available on the market. Field trials with the Electrodyn have been carried out in several countries (Morton (1981, 1982), Kabissa (1991), Taneja (1993)). The use of the Electrodyn system in the control of shoot fly in grain fields showed superior results over other spraying systems. Tests with cotton cultivation showed a spray deposition 2.5 times greater with charged spray than with uncharged spray. When the crops were sprayed from the top, the drop deposition was heavily biased towards the upper regions of the crop. To achieve improved deposition lower down the crop air-blast assistance was required. For effective pest management



(a)



(b)

Figure 3.10a: *Schematic diagram of the electrodyn with (A) connection to the earth (B) connection to the voltage source (C) high voltage nozzle and (D) air inlet for constant head of gravity pressure.* **Figure 3.10b**: *Picture of the electrodyn sprayhead.*

it was desirable to spray over or between every row of crops. This because the spray plume of the Electrodyn is quite narrow, especially compared to the spray from rotary sprayers.

3.6.2 The Microdyne

The Microdyne (Bailey, 1988) is based on the same principles as the Electrodyn, but is designed to operate in any orientation and has an adjustable feed rate enabling drop size to be controlled. Tests of a hand-held Microdyne with fan-air assistance are reported by Adams and Palmer (1986). The tests demonstrated that air-assistance is necessary to obtain good penetration of the pesticide spray into the foliage of the plants. They also demonstrated that using charged droplets improves the deposition onto the undersides of the leaves significantly, especially for the top leaves where an equal amount of droplets was deposited on the upside and the underside of the leaves.

3.6.3 Multiple jet EHD atomiser

As the liquid throughput of a single nozzle is very small, it is limited in its practical use. Combining several single-jet EHD atomisers is operationally and technically complex To meet high liquid throughput requirements atomisers, Escallon and Tyner (1988) designed and patented a nozzle apparatus that uses the EHDA technique and which is able to produce numerous sprays at the same time. This nozzle apparatus was further developed by Almekinders (1992). Figure 3.11 shows a schematic of such an atomiser. The liquid enters the atomiser through a liquid feed line. The charging electrode is embedded in the atomiser. Internal distribution channels deliver a constant liquid flow to serrations at the 15 cm wide atomiser tip. The local electrostatic field between the nozzle and target results in the formation of stable Taylor cone jets, one from every serration. Typical operation variables for standard 15 cm wide atomiser are 35 kV charging electrode voltage and liquid throughput ranging

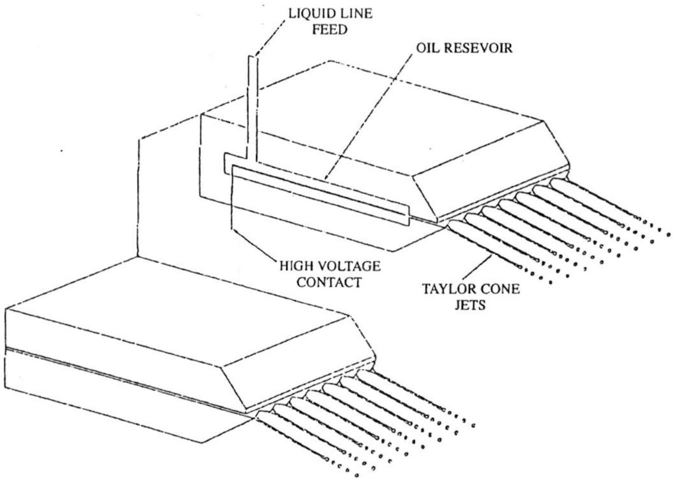


Figure 3.11: *Schematic of a multiple-jet EHDA apparatus (Almekinders (1999)).*

from 60 ml/hr up to 2000 ml/hr. Depending on the flow rate and liquid uniform droplet size distribution can be produced. Non-uniform droplet size distribution sizes can be produced by allowing different liquid feed rates to the individual serrations in one atomiser. Different spray liquids can be mixed at the latest possible stage, just prior to atomisation, i.e. the Taylor cone itself. Beside spraying of pesticides, the nozzle has been applied for uniform droplet deposition (e.g. nutrients on food products) and the production of thin films (e.g. protective coating on steel) (Almekinders, 1999).

3.7 Production of Emulsions and Dispersions

In conventional processes, emulsions and dispersions are produced by simply mixing two immiscible liquids violently, e.g. by using stirred reactors. In this way a high shear is achieved on the liquid-liquid surface, which results in the formation of droplets. Another way of producing emulsions and dispersions is directly spraying droplets of the dispersed phase into the continuous phase, using the EHDA technique. The last process is a more energy-efficient process and smaller size distributions can be obtained. Beside the droplets produced are much smaller, which is an advantage in extraction processes as the liquid-liquid surface increases.

The first attempt to use the EHDA technique to disperse one liquid into another is reported by Nawab and Mason (1958). They produced an emulsion with a droplet size of about 3 μm. Watchal and La Mer (1962) tried to improve the process, but their results were disappointing. It was until the late seventies and early eighties that the first satisfactory attempts were reported by Watanabe *et al.* (1978). They reported on a system that is shown the following figure.

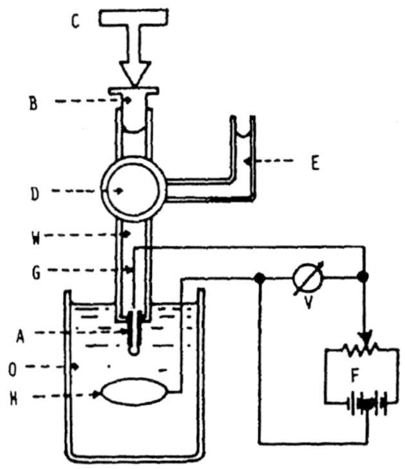


Figure 3.12: *Schematic picture of the system used by Watanabe et al. (1978). A. Teflon tube, B. syringe, C. driving motor, D three way cock, E. water phase reservoir, F. power supply, G and H. Pt electrodes, O. oil phase, V. voltmeter, W. water phase.*

The system consisted of a needle, from which the liquid to be dispersed flows, that is immersed into another liquid, the continuous phase. They applied a potential to the needle, relative to an earth counter electrode, placed a few centimetres below the needle. Watanabe and coworkers produced fine emulsions of water-in-oil with a sharp size distribution. A small amount of surfactant was added to stabilise the emulsion formed. The process they described is similar to the spraying of a liquid in the air. At a certain onset potential the process abruptly changes from a field-enhanced drop formation mode into a continuous mode were droplets are produced in the micrometer range at high frequencies. They also observed a change in shape of the droplet curvature hanging from the needle submerged into another liquid. Wannabe et al. (1978) concluded that the condition necessary to produce the emulsion is that the electrical conductivity of the continuous phase liquid must be less than that of the dispersed-phase liquid. With a set-up similar as described by Watanabe, Meesters (1992) produced stable emulsions of ethylene glycol dispersed into paraffin. He also made emulsions of water dispersed into paraffin and 40:60 w% ethylene glycol/water dispersed into paraffin, but these were less stable in time. The liquid flowing from the nozzle showed a cone like shape, like in spraying in air. However, the cone was much smaller compared to spraying in liquid-air systems. He concluded this was due to the less wettability of the nozzle as in liquid-liquid systems the cone only covers the inner opening of the nozzle, while in liquid-air systems the base of the cone also covers the outer diameter. Compared to liquid-air systems, the potential difference necessary for a continuous mode was much lower and the droplet sizes produced were much larger, using the same configuration. In contrast to liquid-air systems the conductivity showed no influence on the droplet size produced.

Mixing of two immiscible liquids is used in solvent extraction processes. Scott and coworkers (1994) developed a system, which uses the EHDA technique to achieve high-surface-areas between the two liquids. Their emulsion phase contactor (EPC) consists of two regions as shown in figure 3.13.

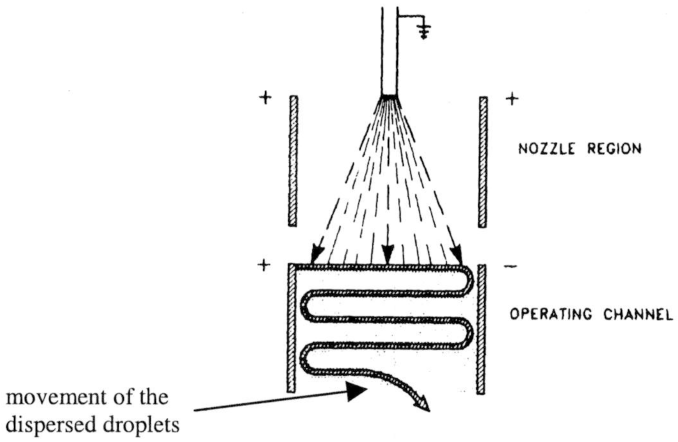


Figure 3.13: the emulsion phase contactor (Scott et al. (1994))

In the nozzle region a grounded nozzle, through which the dispersed phase enters, is immersed in the continuous phase and surrounded by two parallel electrodes. In this region the dispersed phase is electrosprayed into the continuous phase by applying a strong positive potential on the electrodes. In the second region, the operating channel, an alternating electric field is applied between the two parallel electrodes in this region. This is done to increase the residence time of the droplets in the EPC. During their way down the droplets continually coalesce and redisperse. Kaufman and co-workers (1997) used this system to remove organic sulphur from petroleum feedstocks. In their system an emulsion of aqueous biocatalyst in oil was created. At the contact area the sulphur compound was oxidised. The EPC was capable of producing aqueous droplets of about 5 μm in diameter using 3W/l. With the same power consumption, an impeller-based reactor only formed droplets between 100-200 μm.

With a set up, based on the same principles as the set-up of Watanabe, Sato *et al.* (1997) obtained emulsions by spraying a non-conductive fluid (kerosene) into a conductive fluid (water). They produced droplets over a wide range, from several millimetres to several micrometers by varying the applied voltage. Sato *et al.* (1997)

studied the atomisation mechanism of the oil in distilled water and concluded that another break-up mechanism compared to liquid-in-air and water-in-oil systems took place. In the latter systems, the electrical force acting on the liquid due to surface charge is the main factor affecting the atomisation. However, using distilled water as a continuous phase liquid, the amount of electric charge on the dispersed-phase liquid kerosene will not be kept on for a long time, because the high conductivity of distilled water. The main factor affecting the atomisation of oil-in-water systems was considered to be the electrohydrodynamic flow of the continuous-phase liquid around the capillary nozzle tip.

It is also possible to produce an emulsion with a system in which the dispersed phase particles are produced before coming into contact with the continuous phase. Hughes *et al.* (1981,1984) reported on a system where electrosprayed droplets are transported to a second liquid were they are collected and mixed. The droplets are transported to the continuous phase due to gravity and the electrostatic force. Hughes *et al.* sprayed molten wax, which solidified in the air soon after being sprayed, from a heated sprayerhead consisting of several coaxial annular slits raised to a potential of about –25 kV. The continuous phase in this case was de-ionised water. The emulsion is produced by mixing the two phases together and is stabilised by a surfactant. The counter electrode was chosen to be the continuous phase, the water in which an earth metal plate was The emulsions produced this way had the majority of the droplets in the range between one and three microns.

3.8 Polymer Fibres

When a liquid is sprayed in the cone jet mode, a charged jet is produced at the tip of the cone. If instead of a low viscous fluid a high viscous fluid is used, the normally occurring break-up of the jet does not take place. Due to the high viscosity, any disturbance on the jet is damped out. This will lead to the production of a fibre with a certain diameter, which depends of the liquid flow rate and surface charge on the jet.

Already in the beginning of the eighties, Larrondo et al (1981) made polyethylene fibres using the EHDA technique. They used the polymer melt as liquid to be sprayed, which led to a solid fibre after the polymer was crystallised. Zachariades and Porter (1995) produced polyethylene-oxide (PEO) fibres using the set-up shown in the next figure.

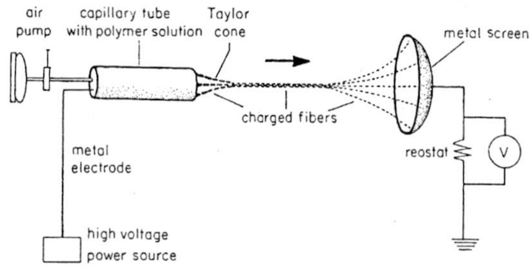


Figure 3.14: *Set-up used by Zachariades and Porter (1995)*

The fibres were produced by spraying an aqueous solution of PEO into a jet using EHDA. As the jet of solution travelled through air, the solvent evaporated, leaving behind a charged polymer fibre. They produced fibres with a diameter down to 10 μm. The large ratio of surface area to volume of the fibres may be useful for separation membranes, wound dressing materials, and as a non-woven fabric. As the fibres are charged they can also be used in electret filters. Due to the charge on the fibres these filters have a higher efficiency, especially for small particles.

3.9 Fuel injection

Fuel injection technology is employed in combustion systems as for example internal combustion engines or package oil burners. One way of improving the burning efficiency of the fuel in these systems is to improve the atomisation of the fuel and to reduce the droplet size. For this reason, since the fifties, many attempts have been made in the electrospraying of fuels. However, applications of this technology in combustion systems were limited due to low throughput, poor conductivity and high viscosity.

Using a glass capillary tube at high potential, Drozin (1955) was unable to spray benzene, toluene, kerosene and other non-conductive liquids. The low conductivity is the most significant factor why the fuels cannot be sprayed electrostatic. Non-conductive (insulating) liquids are difficult to disperse in the normal way due to their long charge relaxation time. The injected charge moves too slowly to the liquid surface, and cannot aid to the atomisation of the liquid jet.

The atomisation can be improved using additives to increase the conductivity or by injecting high levels of charge. Jones and Thong (1971) successfully sprayed kerosene by using carbon tetrachloride as an additive. Tang and Gomez (1991,1994) used an 0.3 %w antistatic additive to spray heptane. However, it is generally impractical to alter fuel supplies on a large scale. Kim and Turnbull (1976) developed a technique to inject high levels of charge into insulating liquids. Most commercial liquid hydrocarbons have an electric breakdown strength of $\sim 15 \cdot 10^6$ V/m. This is to be contrasted with the $65 \cdot 10^8$ V/m needed to extract levels of charge.
Kim and Turnbull proposed and investigated a new approach for electrons from metallic surfaces. In order to bridge the difference that exists between what the liquid can sustain and what is needed to free charge from the emitter, it is necessary to have very small radii of curvature areas on the emitter surface, which can provide geometrical magnification of the surface electrical field. Kim and Turnbull were able to form electrostatically a jet of the insulating liquid, Freon 113, by immersing a sharp tungsten needle at high potential into the flow near the capillary tube outlet. Figure 3.15 shows a schematic diagram of the equipment they used.

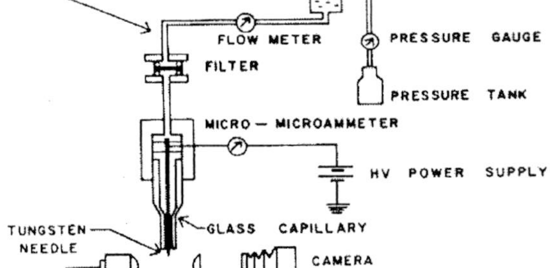


Figure 3.15: *Schematic diagram of the system used by Kim and Turnbull (1976).*

Robinson (1980) and Woosly (1980) used this technique to successfully charge and spray silicon oil and liquid hydrogen, respectively. Jido (1986) used the method for spraying two kinds of blended liquids for the application of multi-fuel combustion applications. The combined droplets were supplied to a continuous combustion burner (kerosene/water) and Otto cycle engine applications (gasoline/methanol). The flow rates used in these investigations (~2 ml/s) were very low compared to what is required for the real combustion applications.

In 1987, Jido described an alternative method for spraying fuel oil. With a spray nozzle, consisting of two co-axial electrodes, he was able to spray with a flow rate up to 60 ml/min. The system of Jido was optimised by Yule in 1995. Another nozzle for spraying insulating liquids at high flow rates was developed by Kelly (1984). He developed the 'triode' nozzle from which a schematic is given in figure 3.16. The triode contains an emitter electrode in the nozzle, which is sharply pointed or has sharp edges, and is immersed in the liquid which flows past it to the outlet spray orifice. A blunt counter electrode, which may be co-axial with the emitter or arranged in proximity to the orifice, enables a high potential gradient to be set up within the liquid, especially in the immediate neighbourhood of the emitter where charge injection occurs. Charge is returned to the circuit by a collector electrode, which in combustion systems is the flame front and combustion chamber wall. An important feature of the spray triode is a special emitter electrode made of oxide-metal eutectic composites formed into a bristly surface which consists of uranium oxide substrate from which protrude 0.5 μm diameter tungsten fibres. Typically, 1 mm diameter emitter tip insert will contain 80,000 fibres, anyone of which is capable of supplying the current necessary for a vigorous spraying. Lehr and Hiller (1993) investigated the potentialities and the limits of the spray triode. The major limiting factor seemed to be the corona discharge effect, which leads to limits for the charge density and the droplet size that can be achieved in practice. In the case of pulsed charging (instationary operation) the corona discharge was less critical as limiting factor. Hetrick and Parsons (1997) developed a modified version of the triode to port fuel injectors for spark ignition engines.

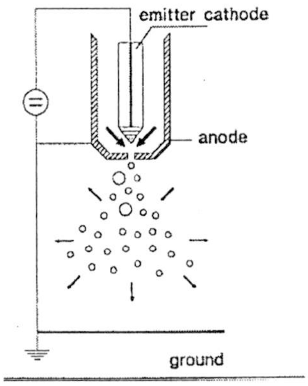


Figure 3.16: *Schematic diagram of the spray triode [Lehr and Hiller (1993)]*

3.10 Propulsion

During the late sixties and early seventies intensive research and development took place on the use of EHDA in colloid thrusters. The droplets emitted in EHDA or rather the momentum with which the charged droplets are emitted can generate the thrust in secondary propulsion systems which are used in space-crafts for station keeping (satellites) and attitude control (satellites and deep space probes).
Huberman *et al.* (1968) showed that droplets emitted from a single capillary tube or a single needle can produce a thrust of more than 0.02 mN. In their set-up, the propellant was supplied to the capillary needle, which was at high positive voltage with respect to an annular extraction electrode. The charged droplets produced were neutralised, using an electron emitter, to prevent charge built-up.
For propulsion, the most successful propellant was found to be a 19.3 %w solution of NaI in glycerol. The thrust level depends on the ratio of charge to mass of the droplet. A systematic study of a single capillary and the ratio of charge to mass, i.e. the specific charge of the droplets of the propellant NaI in glycerol was carried out by Bailey (1973a). The specific charge was found to be only slightly dependent on temperature.
Using a number of needles, the thrust can easily increased. Huberman *et al.* (1968) tried assemblies of up to 60 needles. Such an assembly gave a thrust of 1.2 mN over a testing of 108 hours. Zafran *et al.* (1975) developed a system consisting of 432 needles that gave a thrust up to 4.5 mN. Instead of using an array of needles to produce satisfactory thrust levels, linear or annular-slit emitters can also be used as described by Bailey (1973b). The three colloid thruster configurations are shown in the following figure.

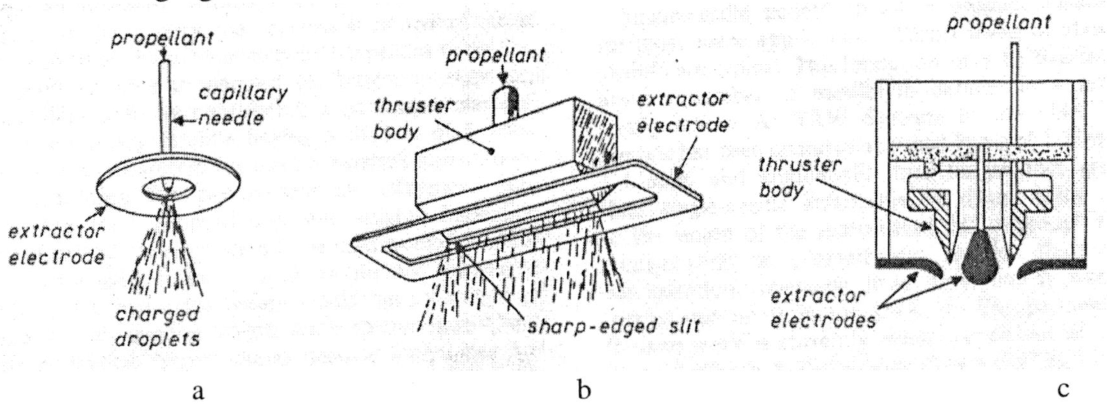


Figure 3.17: *Common colloid-thrusters configurations: (a) needle, (b) linear slit and (c) annular slit (Bailey (1973b))*

4. Conclusion

In this thesis, the different applications of EHDA were described. These applications were found, performing an extensive literature study.

The application of EHDA in mass spectrometry was already well known. Almost all articles on EHDA are dealing with this application. In mass spectrometry EHDA is used to charge large molecules, without breaking the molecules before detection.
With EHDA, it is possible to produce particles in the order of nanometers to micrometers, with a narrow size distribution. Electrostatic pyrolisis and bipolar mixing systems used the EHDA technique to produce powders. The use of EHDA for the production of drug particles has also been applied. Especially, its use in the drug inhalation therapy is promising.
As the droplets produced with EHDA are very small and charged, they can be deposited on surfaces with a very high deposition and distribution efficiency. EHDA has been used for the production of thin films and nuclear sources, and for the spraying of pesticides. Thin films of ceramics have been produced by electrostatic pyrolysis. The films produced were used in batteries, solid oxide fuel cells and gas sensors. The nuclear sources were used for α- and β-studies or as targets for activation in an accelerator or nuclear reactor. In agriculture, several systems have been developed to spray pesticides. One of them, the Electrodyn, was available on the market for a few years.
Emulsions and dispersions have been produced with EHDA by spraying a liquid directly into another liquid. Much less energy was needed, compared to conventional processes and much smaller droplets were produced. The technique has been applied in reactors for desulphurisation of oil.
Charged fibres were produced spraying a viscous polymer solution. These fibres can be applied in electret filters, separation membranes or as wound dressing materials.
The application of EHDA in fuel injection has also been studied as EHDA produces very small droplets. The large liquid-air surface improves combustion. In the past, the low conductivity of the fuel made the use of EHDA impossible. Nowadays, it is possible, as special nozzles have been developed using charging techniques.
The momentum of the droplets, which exit an EHDA spraying nozzle, is high enough for the use in propulsion systems in satellites. This application was developed in the late sixties, but has never been applied in space.

This thesis shows, EHDA can be used for many purposes. It has several important advantages compared to other spray techniques and it can be easily applied for many liquids, at a low flow rate. If a higher flow rate is needed, multiple nozzles can be applied.

5. Literature

The books of Bailey (1988) and Michelson (1990) were used as a starting point for this thesis. Both books contain a chapter on applications of electrospraying. These books had to be used carefully as they did not make a clear difference between EHDA and the other techniques called electrospraying.

The articles not mentioned in these books were found using the search engines: current contents, compendex and inspec. These engines contained scientific articles published between respectively January 1998-October 1999, January 1987-October 1999 and January 1969-October 1999.

The key words used in the search were:

- electrohydrodynamic atomisation/atomization/spraying/sprays/spray/sprayed/cone jet
- electrohydrodynamical spraying
- EHD atomisation/atomization/spraying/spray
- EHDA
- electrospray/electrosprays/electrospraying/electrosprayed/electro-spray/electro-spraying
- Taylor cone/cones

Using these keywords the search engine found a few thousand articles. Almost all articles were related to mass spectrometry. Therefore, the articles containing the following keywords were excluded:

- mass spectrometry/spectrometric/spectroscopy
- ms

This search resulted in about 475 references. When the articles that were cited double, because of the use of different search engines, were skipped, about 350 articles were left. When the articles dealing with liquid metal ionisation and the articles dealing with the theory behind EHDA were skipped about 200 articles were left. These articles had to be studied to see if they were dealing with an application of EHDA. Other articles used in this thesis were found using the references of these articles.

A lot of old articles use the term electrostatic spraying to describe the EHDA technique. This term was not used in the search as it referred to more than thousand articles, from which most had nothing to do with EHDA. Therefore, it has to be noted that it is possible important articles are missing in this thesis. It is also possible that articles, which referred to the use of EHDA in mass spectrometry, but which were dealing with other applications, are missing.

6. References

Adams A.J. and Palmer A. (1986) Crop protection 5(5), pp. 358-364
Alexandrov M.L. et al. (1984) Dokl. Nauk SSSR 277, pp. 379
Almekinders, J.C. (1992) PhD thesis, The Ohio State University.
Almekinders, J.C. (1999) J. Aerosol Sci. 30(7), pp. 969-971.
Bailey (1988) Electrostatic Spraying of Liquids, research studies press LTD, Taunton, England
Bailey A.G. (1973a) J. Phys. D.: Appl. Phys. 11, pp.276-288
Bailey A.G. (1973b) Electronics & Power 12 july
Bayvel L. and Orzechowski Z. (1993) *Liquid Atomisation*, Taylor & Francis Ltd, London
Booth C.G. and Rowe R.C. (1990) European Patent No. 0224352
Borra J.P. et al. (1998) J. Aerosol Sci. 30(7), pp. 945-958
Bruins A.P. et al. (1987) Anal. Chem. 59, pp. 2642
Cannon W.C. et al. (1987) Pacific Northwest Laboratory Annual Report for 1986, PNL-6100 Pt. 1, UC-48, 1987:46
Carlswell D.J. and Milsted J. (1957) J. Nucl. Energy 4, pp. 51-54
Chen C.H., Kelder E.M. and Schoonman J. (1997) J. Electrochem. Soc. 144(11), pp. L289-L291
Chen C.H., Kelder E.M. and Schoonman J. (1997) Journal of Power Sources 68, pp. 377-380.
Chen C.H., Kelder E.M, van der Put P.J.J.M. and Schoonman J. (1996a) J. Mater. Chem. 6(5), pp. 765-771
Chen C.H., Kelder E.M. and Schoonman J.(1996b) J. Mater. Sci. 31, pp. 5437-5442
Chen C.H., Kelder E.M., Jak M.J.G. and Schoonman J. (1996c) Solid State Ionics 86-88, pp. 1301-1306
Chen C.H., Nord-Varhaug K. and Schoonman J. (1996d) J. Mater. Synthesis and Processing 4(3), pp.189-194
Chen C.H., Buysman A.A.J., Kelder E.M. and Schoonman J. (1995) Solid State Ionics 80, pp.1-4
Cloupeau M. and Prunet-Foch B. (1994) J. Aersol Sci. 25(6), pp. 1021-1036.
Coffee R.A. (1978) Patentschrift DE 2731712C2
Cole R.B. (1997) Electrospray Ionisation Mass Spectrometry, Wiley, New York.
Dole M. et al. (1968) J. Chem. Phys. 49, pp. 2240
Dole M. et al. (1973) Adv. Chem. Ser. 125, pp.73
Drozin V.G. (1955) J Colloid Sci. 10, p. 158-164
Dülcks Th. and Juraschek R (1999) J. Aerosol Sci. 30(7), pp. 927-943
Escallon, E.C. and Tyner, A.E. (1988), US Patent 4749125
Golovanov, V. et al. (1995) Mat. Res. Soc. Symp. Proc. 355, pp. 507-512
Gourari H., Lumbreras M., Van Lanschoot R. and Schoonman J. (1998) Sensors and Actuators B 47, pp. 189-193
Grace J.M. and Marijnissen J.C.M. (1994 J. Aerosol Sci. 25(6), pp. 1005-1019.
Greenspan B.J. and Moss O.R. (1992) US Patent No. 5115971
Hartman R. (1998) PhD-thesis, TUDelft.
Hetrick R.E. and Parsons M.H. (1997) Preparing Mixtures for Diesel and SI engines 1305, pp.171-177
Hickey A.J. (1996) Inhalation Aerosols: physical and biological basis for therapy 96
Huberman M.N. et.al. (1968) J. Spacecraft 5, pp. 1319-1324
Hughes J.F. and Pavey I.D. (1981) Journal of Electrostatics 10, pp. 45-55
Hughes J.F. and Roberts J.M.C. (1984) International Journal of Cosmetic Science 6, pp.103-113
Jido M. (1986), J. Mechanical Engineering Laboratory 40(5), pp. 224-233 (Japanese)
Jido M. (1987), J. Mechanical Engineering Laboratory 41(5), pp. 136-145 (Japanese)
Jones A.R. and Tong K.C. J. (1971) Appl Phys. 4, pp. 1159-1166
Kabissa (1991) Crop protection 10(5), pp. 354-356
Kaufman et al. (1997) Fuel Processing Technology 52, pp. 127-144
Kebarle P. and Tang L. (1993), Anal. Chem. 65, pp. 972A
Kelder E.M., Nijs O.C.J. and Schoonman J.(1994) Solid State Ionics 68, pp.5-7
Kelly, A. (1984), IEEE Trans IA-20, No 2, pp. 267-274
Kim K. and Turnbull R.J. (1976) J. Appl. Phys. 47(5), pp.1964-1996
Larrondo L. et al. (1981), Journal of Polymer Science 19, pp. 909-940
Lauer K.F. and Verdingh V. (1963) Nucl. Instrum. Methods 21, pp. 161-166
Lehr and Hiller (1993), Journal of Electrostatics 30, pp.433-440
Meesters G. et al. (1992) PhD Thesis, TU Delft
Meng C.K. et al. (1988) Z. Phys. D 10, pp.361

Michelson D. (1990) Electrostatic atomization, IOP Publishing Ltd, Bristol, England
Miyahara H. (1969) J. Phys. Soc. Japan 27, pp. 1062-1068
Morton (1981) Proc. Brit. Crop. Protec. Conf. pp. 891-901
Morton (1982) Crop protection 1, pp. 27-54
Nawab M.A. and Mason S.G. (1958) Journal of Colloid Science 13, pp. 179-187
Noakes et. al. (1989) US Patent No. 4829996
Reyderman L. and Stavchansky S. (1995) International Journal of Pharmaceutics 124 pp.75-85
Robinson K.S. et. al. (1980) IEEE Trans IA-16, No 2, pp. 308-317
Rulison A.J. and Flagan R.C. (1994) J. Am. Ceram. Soc. 77(12), pp. 3244-3250
Salata O.V., Dobson P.J., Hull P.J. and Hutchison J.L. (1994a) Appl. Phys. Lett. 65(2), pp. 189-191.
Salata O.V., Dobson P.J., Hull P.J. and Hutchison J.L. (1994b) Thin solid Films 251, pp.1-3.
Salata O.V., Dobson P.J., Hull P.J. and Hutchison J.L. (1994c) Adv. Mater. 6(10), pp.772-775.
Sato et al. (1997) IEEE Transactions on industry applications 33(6), pp. 1527
Scott et al. (1994) Ind. Eng. Chem. Res. 33, pp. 1237-1244
Smith R.D. et al. (1988) Anal. Chem. 60, pp. 1948
Smith R.D. et al. (1997) Chem. Soc. Rev. 26, pp. 191
Stelzer N.H.J. and Schoonman J. (1996) J. Mater. Synthesis and Processing 4(6), pp. 429-439
Taneja (1993) Crop protection 12(1), pp. 74-78
Tang K. and Gomez A. (1994) J. Aerosol Sci. 25(6), pp. 1237-1249
Tang K. and Gomez T. (1991) Proceeding of the 5th International Conference on Liquid Atomization and Spray systems ICLASS-91, pp. 805-812
Tang K. and Gomez T. (1994) Phys. Fluids 6(1), pp. 404-414
Taylor G. I. (1964) Proc. Roy. Soc. A 280, pp. 383-397
Van der Eijk W., Oldenhof W. and Zehner W. (1973) Nucl. Instrum. Methods 112 pp. 343-351
Van Zomeren A.A., Kelder E.M., Marijnissen J.C.M. and Schoonman J. (1994), J. Aerosol Sci. 25, pp.1229-1235
Vercoulen P. (1995), PhD thesis, TU Delft
Vercoulen P. et al. (1993) Proc. Int. Workshop on the Synthesis and Measurement of Ultrafine Paticles, Delft University Press, Delft.
Vonnegut B. and Neubauer L. (1952) J Colloid Sci. 7, pp. 616-622
Watanabe A., Higashitsuji K. and Nishizawa K. (1978) Journal of Colloid and Interface Science 64(2), pp. 278-289
Watchal A. and La Mer (1962) J. Colloid Sci. 17, pp. 531
Wilm M. and Mann M. (1994) Int. J. Mass Spectrom. Ion Proc. 136, pp.167
Woosly J.P. et. al. (1980) IEEE Trans IA-18, No 3
Yamashita M. and Fenn J.B. (1984) J. Phys. Chem. 88, pp. 4451
Yule A.J. et. al. (1995) Fuel 74, pp.1094-1103
Zachariades A.E. and Porter R.S. (1995) Polymer news 20, pp. 206-207
Zafran S., Beyon J.C. and Kidd P.W. (1975) AIAA 11th Electric Propulsion Conf., Paper No. 75-392
Zeleny J. (1915) Proc. Camb. Phil. Soc. 18, pp. 71-83
Zeleny J. (1917) Phys. Rev. 10, pp. 1-6