Fundamental Studies on Direct Injection Nebulisers for Sample Introduction in ICP Spectrometry

Aerosol Properties, ICP Characteristics and Analytical Performance

by

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Title: **Fundamental Studies on Direct Injection Nebulisers for Sample Introduction in ICP Spectrometry**

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Abstract: The performance of different types of nebulisers: Vulkan direct injection nebuliser (Vulkan DIN), direct injection high efficiency nebuliser (DIHEN), microconcentric nebuliser coupled to cyclonic or double pass spray chamber (MCN-C or MCN-DP, respectively) was investigated and compared when used for sample introduction to ICP-MS or ICP-OES. With ICP-OES, in axial viewing mode, intensity distributions across the radius of the plasma (radial intensity profiles) were determined for different spectral lines with $E_{\text{exc}}$ 1.85-15.41 eV to determine fundamental plasma properties for various matrices using Vulkan DIN and MCN-C. The results showed that with the MCN-C the ionisation temperature ($T_{\text{ion}}$) was about the same across the measured region of the plasma ($\pm$3.0 mm) whereas with the Vulkan DIN the $T_{\text{ion}}$ was significantly lower in the centre of the plasma. A large deviation from local thermodynamic equilibrium, as well as deteriorated stability, was observed for the plasma when using the Vulkan DIN.

With ICP-MS noise power spectra (NPS) were generated to identify sources of noise. NPS showed that the magnitude of white noise for the tested sample introduction systems decreased in the following order: Vulkan DIN > DIHEN > MCN-C > MCN-DP. This order follows the decrease of mean droplet size and span of the size distribution, indicating that the white noise is caused by spatial and temporal non-uniform desolvation and ionisation. Another source of noise arose from the peristaltic pump and the magnitude of pump interference noise decreased in the following order: DIHEN > MCN-C/DP > Vulkan DIN. Mains power interference noise and 1/f noise were lower for the direct injection nebulisers compared to the spray chamber systems. The contribution or effects of these noise components on relative standard deviations of steady-state ion-count rate and isotope ratio measurements is discussed in this thesis.

Aerosols generated by the Vulkan DIN and the DIHEN were also directly characterised using Particle Dynamic Analysis. The Vulkan DIN produced particles with a mean diameter of ~30 µm and a size distribution between 2-80 µm. With the DIHEN the corresponding values were ~11 µm and 1-40 µm, respectively, with a few particles at 55-78 µm. The mean velocity of particles from the Vulkan DIN was ~10 m s$^{-1}$ and from the DIHEN ~18 m s$^{-1}$. The lower velocity allows longer residence time counteracting the effects of the larger droplet size.

Keywords: ICP, ICP-MS, ICP-OES, sample introduction, DIHEN, Vulkan DIN, non-spectral interferences, noise power spectra, analytical precision, plasma diagnostic parameters, particle dynamic analysis (PDA)

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In the memory of my father . . . .
This thesis includes the following five papers, which are referred to in the text by Roman numerals.

I  D. Goitom, E. Björn, W. Frech and M.T.C. de Loos-Vollebregt
Radial ICP characteristics for ICP-AES using direct injection or microconcentric nebulisation

II  D. Goitom and E. Björn
Comparison of aerosol characteristics and ICP-MS analytical performance with different direct injection nebulisers
Manuscript, 2005

III  E. Björn, T. Jonsson and D. Goitom
Noise characteristics and analytical precision of a direct injection high efficiency and micro concentric nebuliser for sample introduction in inductively coupled plasma mass spectrometry

IV  E. Björn, T. Jonsson and D. Goitom
The origin of peristaltic pump interference noise harmonics in inductively coupled plasma mass spectrometry

V  D. Goitom and E. Björn
Noise characteristics and analytical precision of inductively coupled plasma mass spectrometry using a Vulkan direct injection nebuliser for sample introduction

LIST OF ABBREVIATIONS
AC.................. Alternating Current
CCD.................. Charge Coupled Device
D$_{3,2}$................. Sauter mean diameter
DIN®.................. Direct Injection Nebuliser (trade name)
DC..................... Direct Current
DIHEN................. Direct Injection High Efficiency Nebuliser
$E_{\text{sum}}$............ Energy sum of excitation energy and ionization energy
EIE.................. Easily Ionisable Element
FT..................... Fourier Transformation
IP..................... Ionisation Potential
ICP................... Inductively Coupled Plasma
ICP-AES............. Inductively Coupled Plasma Atomic Emission Spectrometry
ICP-OES............. Inductively Coupled Plasma Optical Emission Spectrometry
ICP-MS.............. Inductively Coupled Plasma Mass Spectrometry
LTE .................. Local Thermodynamic Equilibrium
MCN-C.............. Microconcentric Nebuliser-Cyclone spray chamber
MCN-DP............ Microconcentric Nebuliser-Double Pass spray chamber
MCN.................. Microconcentric Nebuliser
MS.................... Mass Spectrometry
m/z.................. Mass to charge ratio
$n_e$.................. Electron number density
NPS.................. Noise Power Spectra
PDA.................. Particle Dynamic Analysis
PN................... Pneumatic Nebuliser
RSD.................. Relative Standard Deviation
SCD.................. Segmented array Charge Coupled device Detector
$T_{\text{scn}}$........... Ionisation Temperature
Vulkan DIN......... Vulkan Direct Injection Nebuliser
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1. Introduction

Among the various analytical techniques for trace element determinations inductively coupled optical emission (ICP-OES) and inductively coupled plasma mass spectrometry (ICP–MS) are powerful and the most widely used.\textsuperscript{1,2} Multielement capability, wide linear dynamic ranges up to 8 order of magnitude, high sample throughput, excellent precision and high power of detection, especially with ICP-MS, are among the attractive features of ICP based techniques. In addition, non-spectral interferences are less severe with ICPs compared to other atomisation sources such as flames.\textsuperscript{3}

ICP-OES\textsuperscript{4} was commercially introduced in 1974 and ICP-MS\textsuperscript{5,6} in 1980s. These techniques have attracted the interest of many researchers in the field of spectroscopy and analytical chemistry and at present they are well established for research and routine trace element determinations in many fields. For example, isotope dilution ICP-MS is indispensable for the study of the formation of methyl mercury in the environment and its accumulation in organisms.\textsuperscript{7}

Despite a considerable advancement in ICP instrumentation, introduction of sample into the plasma remains a major limitation for ICP techniques.\textsuperscript{1} For example, the best analytical precision that can be achieved with a modern ICP instrument is often limited by the sample introduction system used. Therefore, this calls for improvements of the existing systems or development of new types with improved performance.
The aims of this thesis are:

I To explain some processes leading to non-spectral matrix effects by comparing and characterising analyte signal intensities and fundamental plasma parameters in ICP-OES using direct injection or conventional nebulisation.

II To characterise and compare aerosol properties of the Vulkan DIN and the DIHEN to explain the observed analytical performance with these systems and to rationalise data from the fundamental studies on ICP spectrometry.

III To investigate and compare the contribution from different noise components in ICP-MS using a direct injection high efficiency nebuliser (DIHEN), a Vulkan DIN or spray chamber systems for sample introduction.
2. ICP-OES and ICP-MS Systems

2.1 Inductively Coupled Plasma

Inductively coupled plasma (ICP) is an electrical discharge usually sustained at atmospheric pressure in a noble gas in which high thermal energy is supplied by electrical current, which is induced by fluctuating magnetic fields. The unique potentials of the ICP as a high temperature atomisation/excitation source for spectrochemical analysis were first recognised by Fassel et al. and Greenfield et al. in the 1960s.

A typical setup for generation of an ICP is shown in Figure 1. Usually ICPs are generated in a torch which consists of three concentric tubes with a maximum outer diameter of 30 mm. A part of the torch is surrounded by an induction coil transmitting a 40 or 27 MHz RF power to induce a fluctuating magnetic field inside the end of the torch. Three different gas flows of a noble gas, usually argon, are directed through different compartments of the torch (see Figure 1). During ignition, electrons are ‘seeded’ inside the torch from an external spark/discharge such as a Tesla coil. The fluctuating magnetic field induces an electrical current, known as eddy current, by accelerating ions and electrons in a closed annular path. The eddy region (induction zone) is thereby heated to a high temperature, up to 10,000 K, because of ohmic resistance. Once the ionising temperature of the noble gas is reached, the ICP is self-sustained by maintaining a partially ionised support gas. To prevent the outer tube of the torch from overheating, it is cooled by a tangentially introduced high gas flow. A sample in the form of a gas, fine droplets or solid particles is transported by a nebuliser gas via a narrow injector tube to a central channel surrounded by the annular shaped induction region. There the sample undergoes desolvation, vaporisation, atomisation and ionisation. Normally, the energy is transferred from the induction zone to the central channel by conduction, convection, and radiation. Because the
sample is normally confined within the central channel through the skin effect, interference effects of aerosols or sample constituents in the energy coupling between the load coil and the induction region are minimised. Thus, the fundamental plasma properties are only slightly altered when the sample composition introduced is changed within defined limits.

2.2 Instrumentation for ICP-OES

In ICP-OES the sample is converted to an aerosol which is desolvated, particles are vaporised and molecules are dissociated into free atoms and ions in the central channel of the plasma. Energy is transferred to free atoms and ions mainly by collisions with other particles, which results in excitation and subsequent de-excitation accompanied by emission spectra. Each element has its own characteristic atomic and ionic spectral lines by which it can be identified and which can be used to determine the elemental composition of samples; whereas the intensity of the emitted radiation can be used for quantification. In addition, the emission lines are always accompanied by band spectra from ion-electron and atom-atom interactions as well as thermal emission from particles. To use the
composite emission radiation from the plasma source for analytical purposes, the radiation must pass through a spectrometer which disperses the light according to wavelength and directs the photons of specific wavelengths to detectors to quantify emission intensities at selected wavelength.

As an example a schematic view of a typical state of the art ICP-OES instrument is shown in (Figure 2).\textsuperscript{16} Emitted light from the plasma is directed to the entrance slit of the spectrometer by two toroidal mirrors. The light from the slit is directed to an echelle grating by the parabolic collimator. The echelle produces multiple, partly overlapping diffraction orders. In the UV channel, the overlapping orders from the echelle grating are sent to a second grating or Schmidt cross disperser, and subsequently the cross dispersed separated orders are imaged to form a two-dimensional echellogram at the UV detector. For the visible channel, the overlapping orders from the echelle grating are passed through the opening in the Schmidt cross disperser to the prism to form an echellogram in the visible region at the second detector. A two-dimensional segmented array charged coupled device detector (SCD) is often used with echelle polychromator to simultaneously measure emission lines of many elements.
2.3 Instrumentation for ICP-MS

A schematic diagram of a typical quadrupole ICP-MS is shown in Figure 3. Here the ICP generates singly charged atomic ions for most elements with a low level of double charged ions and molecular ions. The ICP is aligned horizontally in front of the sampler cone orifice (0.5-1.5 mm. id.). A fraction of the plasma from the central channel is probed through the sampler orifice into the first stage of the vacuum chamber where the plasma expands to form a supersonic jet. A fraction of this plasma enters via the orifice of the skimmer cone to a second vacuum chamber, held at lower pressure, and provided with ion lenses. The ion lenses consist of a series of cylinders with selected electrical potentials. A disc or photon-stop is placed at the centre of the cylinders to prevent photons from the plasma reaching...
the detector. The positive ions are focused to the central axis of the quadrupole mass analyser by the ion lenses. The quadrupole mass analyser consists of four parallel rods placed longitudinally between the ion lenses and the detector. Pairs of the diagonal positioned rods are electrically connected and RF and DC voltages are applied to each pair. For a given set of RF and DC voltages, only ions of a given mass to charge ratio, \( m/z \), will follow a stable path in the space between the rods and reach the detector, other ions will be deflected to collide with the rods. Hence, the quadrupole acts as \( m/z \) filter. The entire elemental mass spectrum can be quickly scanned by varying the voltages but keeping the DC:RF ratio constant.

Figure 3  Schematic diagram of a quadrupole ICP-MS (Elan 6000).
(Source: PerkinElmerSCIEX)
3 Sample Introduction Systems

To introduce a sample into the central channel of the plasma, the sample should be converted into a gas, an aerosol of fine droplets or into solid particles with small diameter.\textsuperscript{18,19} Introduction of aerosol is by far the most common method of sample introduction in ICP spectrometry\textsuperscript{1,20-22}. The reasons for this are easy-handling of the sample, speed and simplicity as well as good reproducibility. For aerosol generation a number of devices, based on different principles, have been used: pneumatic-\textsuperscript{21-25}, ultrasonic-\textsuperscript{26,27}, thermospray-\textsuperscript{28,29}, Monodisperse Dried Microparticulate Injector (MDMI)\textsuperscript{30,31} and Oscillating Capillary Nebulisation (OCN)\textsuperscript{32,33}. Among these, pneumatic nebulisers coupled to spray chambers are the most widely employed due to their simplicity, stability, and relatively low cost.

In general, the mode of introduction of samples into an ICP plays a vital role for the overall analytical performance. Of importance are the physical properties of the aerosol, which affect thermal characteristics of the plasma, interference effects, sensitivity and precision of measurements. Despite considerable research and development, sample introduction still remains a weak area in ICP spectrometry.\textsuperscript{34}

3.1 Pneumatic Nebuliser-Spray Chamber Systems

ICP-OES and ICP–MS, in their standard configurations, are equipped with a pneumatic nebuliser combined with a spray chamber, known as conventional sample introduction systems.\textsuperscript{18,21} Today various types of pneumatic nebulisers are available, among them; cross-flow\textsuperscript{35-38} and concentric nebulisers\textsuperscript{39} are in widespread use. In normal operation, sample liquid emerging from the nebuliser at a capillary tip is converted into small droplets by interaction with a high-speed gas stream (nebuliser gas) emerging from a narrow orifice.\textsuperscript{19} The nebuliser gas transports droplets with a defined cut off diameter to the central channel of the plasma \textit{via} the
spray chamber and injector tube (see Figure 1). Among the various spray chamber designs, the two most widely employed are the double pass and the cyclonic type. The main role of a spray chamber is to remove the coarse droplet fraction from the aerosol thereby avoiding overloading or cooling of the plasma, and generation of noise associated with the nebulisation process. However, conventional sample introduction systems suffer from low analyte transport efficiency (usually 1-5%) and large sample consumption (usually 1-2 mL min\(^{-1}\)). A large volume of nebulised solution is thus wasted by using a spray chamber. Moreover, a spray chamber often possesses a large inner active surface thus causing loss of analytes, memory- and transient effects. Therefore, a large part of the total instrumental running time is needed for conditioning the spray chamber and for removing memory effects.

Over the last few years, several types of micronebulisers have been introduced. These include: i) the High efficiency nebuliser, HEN (MEINHARD) ii) the MicroMist nebuliser, MM (Glass Expansion) iii) the Microconcentric Nebuliser, MCN (CETAC). These nebulisers operate efficiently at liquid flow rates less than 100 µL min\(^{-1}\) because the inner diameter of the solution capillary is reduced. The droplets generated are finer and with a narrower droplet size distribution compared to those of conventional nebulisers. Normally spray chambers of small dead volume are employed with these nebulisers to minimise memory effects and washout times. Moreover, sensitivities and detection limits obtained with the micronebuliser systems operated at a liquid flow rates of 10-100 µL min\(^{-1}\) are similar to those of conventional nebulisers operated at 1-2 mL min\(^{-1}\). This improvement is achieved because the analyte transport efficiency with micronebulisers is as high as 20-50%. One major drawback of the micronebulisers is that they are prone to clogging, because of small inner diameter of the nebuliser sample capillary, thus
their application is limited to solutions with low concentration of dissolved salts. Recently, enhanced parallel path nebuliser types such as the MiraMist\textsuperscript{55,56} and the AriMist\textsuperscript{57} have been introduced by Burgener Research inc. With these nebulisers the risk of clogging is reduced.

### 3.2 Direct Injection Nebulisers

The micronebulisers mentioned above generate small droplets which could be introduced directly into the plasma without using a spray chamber. For some nebulisers, this is done by swapping the injector tube of a standard torch with a prolonged micronebuliser (See Figure 4). Direct injection nebulisers effectively eliminate the drawbacks of a spray chamber and provide nearly 100\% aerosol transport efficiency to the plasma.\textsuperscript{58} In general, sensitivities and detection limits achieved with direct injection nebulisers are similar to, or better than those obtained using conventional nebulisers operated at optimum conditions.\textsuperscript{59} Memory effects\textsuperscript{60,61} and response times\textsuperscript{62} are minimised because of smaller internal dead volume compared to spray chambers. For this reason direct injection nebulisers have been successfully utilized in hyphenated systems, to interface ICP-MS with microbore high-performance liquid chromatography (µ-HPLC)\textsuperscript{63,64}, capillary electrophoresis (CE)\textsuperscript{65} and flow injection analysis (FIA)\textsuperscript{66}, as a means to minimise post-column band broadening.\textsuperscript{67}

Today, a number of direct injection nebulisers have been commercialised by different manufacturers. These include: i) the Direct Injection Nebuliser \textsuperscript{61,68-71} (DIN\textsuperscript{®}, CETAC, ii) the Direct Injection High Efficiency Nebuliser\textsuperscript{59} (DIHEN) and the large bore DIHEN\textsuperscript{76} (LB-DIHEN), MEINHARD, iii) the Vulkan DIN\textsuperscript{72}, Glass Expansion. The DIN\textsuperscript{®} is an integral part of a torch and requires more elaborated experimental setup including a high-pressure pump for sample delivery, and it is relatively expensive. In contrast, the DIHEN, LB-DIHEN and the Vulkan DIN are simplified, less
expensive and easily mountable into a standard torch. The DIN® and the DIHEN have been well utilised for special ICP applications\textsuperscript{73,74} and fundamental studies on interference effects\textsuperscript{62,75} and aerosol characteristics\textsuperscript{76-82} are well documented. In general, it has been shown that droplets generated by the DIHEN are smaller in sizes and slower in velocities compared to that of the DIN®. Moreover, the DIHEN offers better sensitivity and precision than the DIN®. The Vulkan DIN is a relatively new system which has not yet been well characterised. Compared to the DIHEN, the Vulkan DIN has a sample capillary with a wider internal diameter and thicker wall that terminates 0.7–0.8 mm inside the end of the surrounding glass support tubing.

![Schematic diagram of the DIHEN](image)

Figure 4  Schematic diagram of the DIHEN. Reprinted from reference 59 with permission, copyright 1999 American Chemical Society.
4. Non-Spectral Interference Effects

Interference effects are normally classified into spectral interferences and non-spectral interferences. This thesis deals only with non-spectral interferences although spectral interferences are also recognised as a major limitation in ICP spectrometry. Comprehensive summaries on these subjects can be found elsewhere in books and review articles.

During the early development of ICPs, it was claimed that atomisation with these systems was essentially complete and determinations were free from non-spectral interferences because of the high temperatures in the plasma. However, lately it has been recognised that non-spectral interference effects are still present.

Non-spectral interferences in ICP-MS and ICP-OES arise from changes in analytical signals induced by a matrix. Three main types of these interference effects have been identified: i) matrix induced changes in the nebulisation process and aerosol transport efficiency ii) matrix induced changes in excitation/ionisation conditions of the plasma, iii) for ICP-MS, matrix induced changes in extraction efficiency and focusing of the ions to the mass-analyser.

The matrix effects can be caused by a wide range of substances, including inorganic acids, excess of easily ionisable elements and organic solvents. In general, matrix effects are complex and not often fully understood. The theories and arguments proposed to explain mechanisms of the matrix effects are to some extent inconsistent. Nevertheless, there are some general observations on common matrix effects which have frequently been reported in the literature. The presence of high concentration of inorganic acids is known to suppress the analytical signal whereas low concentration of acids (below 1% ) lead to signal enhancement. In ICP-OES, matrices containing excess of easily ionisable elements enhance or depress analyte signals and the magnitude
of the matrix effect is strongly related to the excitation and ionisation energy of the elements ($E_{\text{sum}}$) and the viewing height in the plasma (for side-on viewing mode). Spectral lines with high $E_{\text{sum}}$ are often strongly suppressed.

In ICP-MS, analyte signals are often suppressed in the presence of excess concomitant elements. The magnitude of matrix effect depends on the isotope mass and ionisation energy of the analyte and matrix element. Heavy matrix elements with low ionisation energy cause the most severe signal suppressions, and light analyte elements with high ionisation potentials are affected most severely. Finally, the magnitudes of matrix effects are strongly dependent on the operating conditions of the instrument.

A number of methods have been suggested to overcome or correct for matrix effects. \textsuperscript{71,100-103} These include sample dilution, matrix matching, matrix separation, the use of internal standards or other calibration strategies such as standard addition and isotope dilutions (for ICP-MS). Moreover, optimisation of instrument parameters can also minimise interferences.

4.1 Matrix Effects Related to Aerosol Generation and Transport
The physical properties of a matrix including viscosity, surface tension, density and volatility are important for aerosol generation and transport. For example a primary aerosol generated from a solution of a relatively high viscosity, such as an inorganic acid, has normally a larger mean droplet size compared to that of water. Because the inertial, gravitational, turbulence and centrifugal losses of larger and denser droplets within a spray chamber are higher, the aerosol transport efficiency of the solution containing inorganic acid will be lower compared to that of water. The effect of concomitant matrix elements on aerosol generation and transport
is similar to that of inorganic acids. In contrast, the nebulisation of organic solvents results in finer droplets compared with water aerosols mainly due to lower surface tension and viscosity (in most cases), as well as higher volatility. Consequently, the analyte transport efficiency and the solvent load in the form of droplets and vapour reaching the plasma is higher compared to water.

Nukiyama and Tanasawa\textsuperscript{104,105} empirical equation has been widely used despite some limitations to relate surface tension, viscosity, density, gas and liquid velocity to the Sauter mean diameter $D_{3,2}$ of pneumatically generated aerosol.

### 4.2 Matrix Effects Related to Excitation/Ionisation and Other Processes

Within the plasma, atomisation/ionisation of the analytes is affected by temperature changes induced by matrix components. Usually when a matrix (inorganic acids and organic solvents) is present the energy consumption (deterioration of plasma temperature) in the plasma is increased by breaking down the matrix molecules. This plasma temperature deterioration is exacerbated if the solvent load in the plasma is too high as this also consumes extra energy during desolvation and atomisation steps. Normally the solvent load from volatile solvents is higher than from less volatile solvents when conventional nebuliser spray chamber systems are used unless effective desolvation systems are employed.\textsuperscript{106} Organic solvents, having high vapour content, alter the physical and chemical characteristics of the plasma in a complex way.\textsuperscript{107-110} The excess molecular species of the vapour in the central plasma channel can easily diffuse into the induction region which can cause the plasma to shrink. This phenomenon is commonly known as the thermal pinch effect. The fragmented molecules in the induction zone can change the thermal
conductivity and the electron number density distribution of the plasma affecting the energy transfer process to the central channel of the plasma. Therefore, depending on these effects enhancement or depression of the analytical signal is observed with organic solvents.\textsuperscript{111-115}

A large number of processes within the plasma have been described to explain the effects of easily ionisable matrix elements on analyte signal intensity. These include shift of ionisation equilibrium,\textsuperscript{2,116} changes in thermal conductivity and ambipolar diffusion.\textsuperscript{94,116} The net effect of matrix is thus dependent on many variables and also on the location of the viewing/sampling position in the plasma.

In the literature,\textsuperscript{117-120} the plasma robustness criteria have been used to describe tolerance of the plasma to small changes in matrix composition without changing the plasma characteristics ($T_{\text{ion}}$, $n_e$, and spatial distribution of analyte signal intensity profile). Normally, robust plasma conditions can be achieved by using a high RF power, low nebuliser gas flow rate and a wide injector tube. Under these conditions, matrix effects that originate within the plasma are minimised. Plasma robustness is often evaluated from measurements of matrix induced changes in plasma characteristics including temperatures and $n_e$, as described in \textit{paper I}. In ICP-OES the Mg ion-atom intensity ratio has also been used as simple diagnostic test for plasma robustness or LTE conditions. If the magnitude of Mg II (280.270 nm)/Mg I (285.213 nm) intensity ratio is higher than 8, it indicates that the plasma is robust, but a ratio of less than 4, indicates the presence of non-robust conditions. Normally, ionic lines are more sensitive to changes in the plasma conditions than atomic lines.

For ICP-MS, there is a significant contribution to the matrix effect (in the presence of concomitant elements) that occurs during transmission of ions from the ICP to the mass spectrometer. When the extracted ion beam
passes through ion-lenses, electrons escape from the beam leaving a high cation density in the beam. The coulombic repulsion force acts on the cations which results in a decrease of analyte in the beam. This is known as the space-charge effect,\textsuperscript{83,121} and it is dependent on the atomic mass of the analyte and matrix isotopes, and the concentration of the matrix. Heavy matrix ions suppress analyte signals more extensively than light matrix ions, and heavy analyte ions are suppressed less severely than light ones.\textsuperscript{122}

4.3 Non-spectral interferences with direct injection nebulisers
Matrix effects induced by 0.9 M nitric acid or 5\% (v/v) methanol in ICP-OES, operating at RF power of 1500 W and 90 \( \mu \)L min\(^{-1}\) liquid flow rate, were compared for the Vulkan DIN and the MCN coupled to a cyclonic spray chamber (\textit{paper I}). The magnitude of matrix effect induced by 0.9 M nitric acid was higher with the Vulkan DIN than the MCN system (see Table 2 in \textit{paper I}). This is explained by the non-robust plasma conditions obtained when using the Vulkan DIN providing a higher solvent load and a larger mean droplet size (\textit{paper II and V}) compared to the MCN system. The larger matrix effects observed with the Vulkan DIN were line specific but not correlated with the \( E_{\text{sum}} \) of the element lines. The reason for this behaviour is still unclear. In related investigations\textsuperscript{62} using ICP-MS and a DIHEN, it is shown that the magnitude of matrix effects induced by 0.9 M nitric acid was negatively correlated with the ionisation potential, IP, of the isotopes. Signal intensities for isotopes with IP > 9.32 eV were depressed while for isotopes with IP < 6.11 eV signal intensities were enhanced. Suggested explanations for the observed effects were changes in plasma temperature gradients combined with spatial redistribution of the aerosol.
When introducing solutions containing 5% (v/v) methanol with the Vulkan DIN, signal suppressions were observed because of deterioration of the plasma. Compared to the MCN, the magnitude of the matrix effects caused by methanol was smaller when using the Vulkan DIN. The observed signal suppressions qualitatively agree with the previous results for the DIHEN-ICP-MS in which analyte signal intensities for most isotopes were suppressed by 20-35% in the presence of 5% (v/v) methanol.

With the MCN analyte signal enhancements were observed for all lines in the presence of methanol. As discussed in section 4.2, the aerosol transport efficiency and the solvent load are normally high when organic solvents including methanol are introduced into the plasma. Moreover, the use of a spray chamber results in a large solvent load when introducing volatile solvents because it acts as an evaporation chamber increasing the amount of the solvent reaching the plasma. As the solvent vapour spreads radially outward to the induction region of the plasma, the plasma shrinks or changes its geometry thereby altering the temperature and electron number density, \( n_e \) profile of the plasma as well as its thermal conductivity. For the MCN, this effect was indicated by an increase of \( T_{\text{ion}} \) and \( n_e \) in the presence of methanol compared with that of water.

For the Vulkan DIN, the effect of increased liquid flow rate on matrix effects caused by the nitric acid or methanol was also investigated (in paper I) for liquid flow rates ranging between 20 and 90 µL min\(^{-1}\). As discussed in paper I (Table 1) the magnitude of matrix effect was not significantly affected by the increase of liquid flow rate. Moreover, as liquid flow rate increased the plasma was visually observed to diminish in size or shrink while the plasma parameters \( T_{\text{ion}} \) and electron number density, \( n_e \), were sharply increased. The changes in the geometry of the ICP and changes in plasma parameters might be counter balancing the cooling effects of the plasma that is caused by increased solvent load. The
fact that matrix effects were not affected by changes in liquid flow rate apparently disagrees with the finding of Todoli et al.\textsuperscript{77} in which the matrix effects observed with the DIHEN-ICP-OES were largely minimised by reducing the liquid flow rate to less than 40 µL min\textsuperscript{-1}. The disparities of these results could be attributed to the differences in the design of nebulisers and ICP-OES instrument as well as experimental setup and conditions.
5. Aerosol Characteristics and Analytical Performance

In the development of nebulisers for ICP instruments, fundamental understanding on aerosol generation mechanisms and transport processes is vital. Characteristics of the aerosol entering the ICP have a significant impact on analytical performance of ICP instrumentation. Ideally, aerosols should consist of droplets with small and uniform size, low and uniform velocity, to assist the generation of a high population of elemental ions in the central channel of the plasma. However, the commonly used nebulisers generate droplets with a broad size- (up to 80 µm) and broad velocity distribution. In ICP only droplets with diameter less than $D_{\text{max}}$ 8-10 µm are completely atomised to produce analyte signals.\textsuperscript{81,123} Incompletely desolvated droplets act as a local heat sink deteriorating atomisation efficiency and signal-to-noise ratio (S/N) which is discussed in section 6. With direct injection nebulisers, a ‘high quality’ primary aerosol (close to ideal aerosol) is needed since a relatively large volume of aerosol is introduced directly into the plasma. Therefore, the nebuliser design is more crucial for direct injection nebuliser compared to a conventional nebuliser. Aerosol characteristics of the DIN\textsuperscript{®} and DIHEN have been established by other workers.\textsuperscript{76,80,82,124-128} The Vulkan DIN is the most recently commercialised direct injection nebuliser and it has a rather different design compared to the DIN\textsuperscript{®} and the DIHEN, (see Figure 5).\textit{Paper II and V} deal with evaluation of aerosol characteristics of the Vulkan DIN and the DIHEN. The difference in sensitivity, limit of detection (LOD), precision and noise characteristics of the two nebulisers were explained based on aerosol characteristics and nebuliser design.
Figure 5  Schematic diagram illustrating the design of the DIHEN (from reference 59 by permission) (a) and the Vulkan DIN (b) tips.

Results in *paper II* and *V* have shown that droplets generated by the Vulkan DIN were coarser and had a broader size distribution than that of the DIHEN. The axial mean velocity of droplets was lower and the distribution was narrower with Vulkan DIN aerosols compared with that of the DIHEN. The lower velocity allows longer residence time counteracting the effects of the larger droplet size.

5.1 **Spatial Distribution of Aerosols with the Vulkan DIN and DIHEN**

The spatial distribution of aerosols generated from direct injection nebulisers also influences the thermal properties of the plasma which is critical for the efficiency of processes involved in the transformation of a sample into atom/ion cloud.81 Ideally aerosols should be confined to the central channel of the plasma for two main reasons. First, an aerosol which is not focused to the central axis presents less population of analyte atoms/ions in the central channel of the plasma thereby deteriorating of analytical sensitivity. Second, droplets in the fringes of the aerosol cone and interacting with the induction region of the plasma can potentially destabilise the eddy-current, or the energy coupling with the load coil. This can increase noise as well as matrix effects.
During aerosol generation and transport several processes occurs which can modify the size and velocity distributions of droplets. To gain an insight into these processes spatially resolved aerosol measurements are helpful.

For describing aerosol generation processes in nebulisers, various models have been proposed in the literature for different relative velocities of the gas and the liquid. For typical ICP nebulisers (normally higher relative velocity than 50 m s\(^{-1}\)) two mechanistic models are used to describe droplet formation. One is based on a string-wise break-up (or stripping mechanism) and the other on film-wise break-up (or bursting bag).\(^\text{129}\) The string-wise occurs “when a liquid stream, emerging from a jet in a nebulizer, interacts with a very-high-velocity gas stream, the process of liquid stream fracture takes place via formation of ligaments.\(^\text{130}\) The ligaments then become unstable and move back and forward very rapidly, causing a fragmentation process.” \(^\text{18}\) Whereas in bursting bag model “a thin film is formed from the primary droplet due to unequal pressure on the surface of the droplet\(^\text{131}\). The thin film, or hollow bag, then bursts to form a string of fine droplets”.\(^\text{19}\)

These models may be used to explain the results for axially resolved measurements of aerosols at two axial positions in Figure 4 of paper II. As aerosols move from 5 to 15 mm along the horizontal axis, the size- and velocity distributions of droplets shifted to smaller size and gained higher velocity for the DIHEN, whereas the opposite was observed for the Vulkan DIN. For the DIN\(^\text{\textsuperscript{8}}\) it has been reported that the D\(_{3,2}\) (14 µm) decreased by 40% as the aerosol moves from 2.5 mm to 10 mm along the central axis.\(^\text{124}\)

5.2 Aerosol Diagnostics  
Several aerosol measurement techniques have been utilised to investigate aerosols produced by nebulisers.\(^\text{81}\) These include Lorenz-Mie Scattering,
Laser Fraunhofer Diffraction, Optical Patternation,\textsuperscript{79} High-speed photography, Particle Image Velocimetry (PIV),\textsuperscript{78} Phase-Doppler Particle Analysis (PDPA)\textsuperscript{125} or Particle Dynamic Analysis (PDA). For our studies, in \textit{paper II and V}, a PDA (Dantec Dynamics) which is based on the principle of light-scattering interferometry was used. This system can perform non-intrusive simultaneous measurements of the size and the velocity of individual droplets at a single point in space.

The PDA (shown in Figure 6) consists of a laser source (not shown in the Figure) connected to a transmitting optics \textit{via} a fibre optic cable, a receiving optics containing multiple photo detectors and a Burst Spectrum Analyser to process the signals from the detectors. Two pairs (only one pair shown in the Figure) of laser beams (a) from the transmitting optics are focused to intersect forming a sampling volume (b). The beams generate an interference fringe pattern of alternating light and dark planes at the sampling volume (c). As droplets transverse the sampling volume, the laser light scatters, which is eventually detected by the multiple photo detectors of the receiving optics (d) positioned off-axis. Signals from each detector are converted into a Doppler burst (e). The frequency of the burst is linearly related to the velocity of the droplet whereas the phase difference between the Doppler signals of different detectors provides a measure of particle diameter. These results are processed and presented as size and velocity distributions.\textsuperscript{132}
Figure 6  Schematic diagram for a Particle Dynamic Analysis (PDA) instrument (Courtesy of Dantec Dynamics A/S).
6. Noise and Analytical Precision

The text in chapter 6 is partly taken from my Licentiate thesis\textsuperscript{152}

Precision and detection limits, LOD, of analytical measurements are ultimately limited by noise.\textsuperscript{133} To improve the precision of any measurement, sources of noise should be identified in order to reduce or avoid their effects. A Noise Power Spectra (NPS)\textsuperscript{133} allows identification of different types of noise components by converting the raw signal from the time domain to the frequency domain by Fourier transformation, FT. Three types of noises can be identified in NPS; white noise, which contains components at all frequency values; 1/f noise, which is a slow drift in signal, dominant at low frequencies and; interference noise, which appears at discrete frequencies.

In ICP spectrometry the aforementioned different noise types have been recorded by NPS and have been associated to different parts of the instrument. Different sample introduction systems are known to contribute to noise to different degrees.\textsuperscript{134-140} It has been shown that the magnitude of white noise and 1/f noise are generally dependent on the characteristics of aerosols introduced in the ICP.\textsuperscript{139} Direct injection nebulisers producing relatively large droplets with a wider droplet size distribution are known to give rise to higher white noise levels compared to spray chamber systems. Droplets that are too large to be completely desolvated act as local heat sinks, affecting plasma temperatures, and thereby atom and ion number densities within 1-2 mm of the droplet. This leads to signal fluctuations in ICP-OES and ICP–MS on the tens of microsecond time scale and gives rise to increased white noise.\textsuperscript{141-142} Different instrument components such as the RF mains power supply,\textsuperscript{144-147} sample introduction pumps\textsuperscript{145,148,147}, and the plasma itself\textsuperscript{148,149} have been reported to generate noises at discrete frequencies. The following sections discuss the different noise components and their effect on precision when
using an ICP-MS instrument with a DIHEN, Vulkan DIN or MCN coupled with different spray chambers.

6.1 White- and 1/f-noise
NPS were generated for ICP-MS when using a DIHEN (paper III and IV), Vulcan DIN (paper IV) or an MCN (paper III) coupled to a double pass or cyclone spray chamber. The magnitude of white noise for these nebuliser systems decreased in the following order: Vulkan DIN (-40.3 dB) > DIHEN (-45.8 dB) > MCN-C (-49.8 dB) > MCN-DP (-54.0 dB). This trend is correlated with the decrease of mean droplet size and size distribution obtained with these systems. In addition, a spray chamber plays a vital role in minimising random signal variations which originate from the nebulisation process, thereby lowering the white noise. In ICP-MS the precision of isotope ratio measurements is ultimately limited by the white noise level. During the last years the use of ICP-MS in applications demanding isotope ratio measurements with high precision has rapidly increased. Due to the high white noise, presently available direct injection nebulisers should be unsuitable for such applications. The 1/f noise was shown to be slightly lower for the Vulkan DIN and the DIHEN, indicating a relatively small signal drift compared to the spray chamber systems. The precision of steady state measurements of ion (in ICP-MS) and photon (in ICP-OES) count rates are ultimately limited by the 1/f noise. In line with this, precision of such measurements are normally improved when using a direct injection nebuliser compared to a spray chamber systems.

6.2 Peristaltic Pump Interference Noise
When using a peristaltic pump to inject sample and/or drain the spray chamber (if used) an intense 4 Hz interference noise and its harmonics
were observed \textit{(paper III and IV)} for both the DIHEN and the MCN system. With the Vulkan DIN \textit{(paper V)} the magnitude of this noise was very small. The pump interference noise peak was previously suggested\textsuperscript{148} to originate from the variations in the amount of analyte and solvent fed to the nebuliser and/or variations in the atomisation and ionisation effects of the plasma due to variations in aerosol loading. This explanation was valid for the DIHEN, but for the spray chamber systems other factors were dominating. It has been demonstrated \textit{(paper IV)} that the magnitude of the 4 Hz noise, for spray chamber systems, was almost the same regardless of using a syringe or peristaltic pump for sample delivery if the spray chamber was drained with the peristaltic pump. Hence, the major source of noise was the pulsations created by the drain tubing. The magnitude of this interference noise was dependent on the frequency of the drainage pump. In our case, operating at lower pump frequency $1/3$ Hz for draining the spray chamber had significantly reduced or eliminated the 4 Hz noise.

Figure 7 shows NPS for the DIHEN at different liquid flow rates. A series of intense peaks were observed in the frequency range of 8 to 30 Hz along with the 4 Hz interference noise peak. These were harmonics of the 4 Hz pump interference noise. Fourier transformation of a non-sine waveform, such as the intensity $vs.$ time signals observed for the DIHEN, in Figure 7, results in harmonics (peaks of multiple frequencies) of the fundamental frequency. This happens if the fluctuations of the noise source (peristaltic pump) are not a sine waveform and/or if there is a non-linear relation between the fluctuations of the noise source and the measured signal intensity. As shown, in Figure 8, a non-linear relation was obtained between the sample flow rate and the relative signal intensity for liquid flow rates above 60 $\mu$L min$^{-1}$. With the Vulkan DIN, the changes in signal intensity with liquid flow rate in the range 40-90 $\mu$L min$^{-1}$ was smaller compared to the DIHEN, which means it is less sensitive to
fluctuations in the liquid flow rate compared to the DIHEN. However, this also indicates there is a larger cooling of the plasma when using the Vulkan DIN.

Figure 7  NPS for $^{115}$In$^+$ obtained with DIHEN using a peristaltic pump at different liquid flow rates 100 (A, E), 80 (B, F), 60 (C, G) and 40 (D, H) $\mu$L·min$^{-1}$. (from paper IV)
Figure 8  Relative intensity vs. liquid flow rate for $^{115}$In$^+$ using the DIHEN and the Vulkan DIN for sample introduction. (from paper V)

6.3  The Mains Power Supply Interference Noise

Interference noise is often observed at 50 Hz and 100 Hz in instrumental measurements. The 50 Hz is assigned to the mains electrical supply, whereas, the 100 Hz could originate from the ripple component (AC superimposed to DC) of a rectified dc voltage or the harmonics of the 50 Hz. These interference noise peaks were identified for spray chamber systems but not for the DIHEN or the Vulkan DIN at the normal sampling position in the centre of the plasma. However, they were visible with the DIHEN when measurements were carried out at 1 mm off-axis. These noise peaks could be correlated to the energy transfer efficiency from the load coil to the central channel. The presence of intense 50 or 100 Hz noise could imply that there is an efficient energy coupling to the central channel because the electrical mains frequency noise can propagate inductively with the RF source. Therefore, this indicates that energy transfer and plasma aerosol interaction is more efficient with spray chamber system than with the DIHEN or Vulcan DIN.
6.4. Analytical Precision with the Vulkan DIN and the DIHEN

Analytical precisions of steady-state signal measurements of $^{115}$In$^+$ was evaluated and compared (paper V) for the Vulkan DIN and the DIHEN at measurement frequencies of 0.1-500 Hz (see Figure 6 in paper V). When using a syringe pump, the precision values were better with the Vulkan DIN than the DIHEN at measurement frequencies 0.1 - 10 Hz. At higher frequencies the opposite was observed. This is expected from the lower 1/f and interference noise at low frequency, but higher white noise level for the Vulkan DIN. In general, when analytical precision is limited by white noise, the logarithm of RSD will linearly increase with the logarithm of the measurement frequency. The analytical precision for the Vulkan DIN was limited by white noise at least in the range 0.4 - 500 Hz, whereas for the DIHEN the corresponding graph deviated from linearity at frequencies $\leq$ 50 Hz indicating large contributions from non-white noise components.

The difference in % RSD when using a peristaltic pump instead of syringe pump, was small for Vulkan DIN because of very small pump interference noise, as mentioned above. In contrast, the effect for the DIHEN was a substantial increase of % RSD in the frequency range 3-100 Hz when using a peristaltic instead of a syringe pump mainly due to large interference noise from the peristaltic pump. Thus, the analytical precision of the Vulkan DIN was superior in this measurement frequency range.
7. Conclusions

When using the Vulkan DIN, non-spectral interference effects were not correlated with plasma diagnostics parameters such as Mg ion-atom line intensity ratio, $T_{\text{ion}}$ or $n_e$. This is partly because the plasma is too far from LTE for these spectroscopic plasma diagnostics tools to be applied. Thus it is complex to characterise the ICP and difficult to predict analytical performance when using direct injection nebulisers for sample introduction. For example the non-spectral interference effects with the Vulkan DIN were element and line specific, making the selection of appropriate internal standards complex. (paper I) The large deviation from the LTE of the plasma, when using the Vulkan DIN, resulted in a significant bias in temperature determinations. Therefore, the conclusions derived from temperature determination should be interpreted cautiously. For reliable plasma temperature and electron number density measurements other techniques such as the Thomson and Rayleigh scattering techniques are more suitable.

Studies on noise characteristics (paper III and V) have shown that the white noise level is higher with direct injection nebulisers compared with spray chamber systems. The reason for this is mainly the large droplet size and droplet size distribution. Moreover, the pump interference noise is higher for the DIHEN compared to the Vulkan DIN and spray chamber systems. As a consequence, compared to the MCN-DP the DIHEN gave 2-9 times higher relative standard deviation (RSD) for steady-state ion count rate measurements when using measurement frequencies above 1 Hz. Similarly, the precision obtained for isotope ratio measurement was also deteriorated.

Results in paper II and V show that the Vulkan DIN generates aerosols with larger mean droplet size but lower velocity than that of the DIHEN. For an optimal use of direct injection nebulisers, the aerosol
generated should consist of smaller and more uniform droplets with lower and more uniform velocity than provided by commercially available systems. It appears that there is a limitation to achieve these requirements with pneumatic direct injection nebulisers, as converting the bulk liquid into fine droplets always requires a gas with high kinetic energy. The use of energetic gas has negative effects since it deteriorates thermal characteristics of the central channel of the plasma and increases the droplets velocities thereby shorten particles residence time. To solve this problem, new direct injection nebuliser designs are needed where both the liquid and the nebuliser gas flow rates can be minimised. This would require a miniaturised, high precision nebuliser tip as well as highly stabilised flows of the liquid and the gas. Another alternative could be to modify the droplet size and velocity distributions prior to introduction into the plasma, although in a different way than using a conventional spray chamber. Recently, Todoli et al. introduced the so called torch integrated sample introduction system (TISIS). With this system a small cavity, at the base of the torch, is provided between a micronebuliser and the injector tube. This cavity acts as an evaporation chamber thus reducing the sizes and velocities of the droplets prior to introduction into the plasma. In this way the negative effects of large and fast droplets can be minimised. However, the cavity can increase the risk of memory effects.

Most studies on aerosol characteristics presented in the literature have been carried out in absence of the plasma. Such studies don’t take into account the actual high temperature gradients and gas flows within the plasma. All these factors complicate the studies related to the processes within the plasma. Therefore, there is a need for in situ aerosol measurements to investigate the distribution of aerosols and to
characterise processes within the plasma. Recently, one paper has been published describing in-situ aerosol measurements in an ICP.
8. References

72 Datasheet Supplied With The Vulkan DIN, From Analysentechnik, Tübingen, Germany


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