**Direct Elemental Analysis of Solid Materials by Inductively Coupled
Plasma Emission and Mass Spectrometry (ICP-ES/MS) using Slurry
Nebulization and Direct Powder Introduction**

By

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of the requirements for the degree of Master of Science

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Abstract

Inductively Coupled Plasma Emission (ICP-ES) and Mass (ICP-MS) Spectrometry are among the most powerful analytical techniques used for elemental analysis down to parts per trillion concentrations for wide variety of applications. In spite of their popularity, traditional method of sample introduction into the ICP is solution nebulization. This requires conversion of solid samples into solution by tedious digestion procedures. There has been a growing interest in developing sample introduction techniques to analyze solids directly. This thesis deals with some new developments in direct solid analysis based on Slurry Nebulization (SN) and Direct Powder Introduction (DPI).

The presence of big particles causes major difficulties in implementing SN as a viable approach. A new method based on sedimentation was developed to effectively eliminate particles bigger than a well-defined cut-off and to meet challenging analytical demands. A theoretical model was developed to study the effect of various experimental parameters on extraction efficiency during the sedimentation process. A spreadsheet program was developed to perform the calculations interactively. An air segmented flow system was developed to minimize commonly encountered problems associated with particle stagnation and blockage of transfer lines during slurry sample introduction. The technique was applied successfully to analyze a series of glass reference materials with precision in the order of 1-2%.

Several versatile approaches possible for signal normalization in Direct Powder Introduction were demonstrated. Preliminary data using mass normalized measurements provided good accuracy and excellent precision (1-2% RSD) for series of sediments and soil reference materials. Volume based signal normalization without weighing of the samples also can be used as a viable approach, particularly useful for field applications, which provided excellent reproducibility in packing density (<1% RSD). Capability of DPI-ICP for signal measurement from single particles was demonstrated using chalcopyrite particles.

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CHAPTER 1 - INTRODUCTION:

1.1 ICP-ES and ICP-MS as analytical tools

Inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectroscopy (ICP-MS) are among the most popular and powerful techniques used for the analysis of a wide range of matrices for trace, minor, and major elements ^{1,2}. They provide rapid, sensitive and convenient ways of measuring the elemental concentrations of solutions with superior analytical figures of merits for many elements, with respect to other elemental analysis techniques such as atomic absorption spectrometry (AAS) and X-ray fluorescence (XRF). ICP-ES and ICP-MS techniques have the ability to measure a large number of elements simultaneously with a linear dynamic range of typically over 6 orders of magnitude and have detection limits typically down to ultra trace levels such as parts per trillion with good analytical precision. Such a high dynamic range often allows simultaneous measurement of major, minor and trace elements during the same analytical run without having to go through serial dilutions. ICP techniques can be used to identify and quantify almost all elements in the periodic table with the exception of argon which is the most commonly used plasma gas.

1.2 The Inductively Coupled Plasma (ICP)

The heart of an ICP based spectrometer system is the gaseous plasma. Argon is the choice of plasma gas primarily due to its thermal conductivity, high temperature characteristics, and its availability as a result of high relative abundance in the atmosphere compared to other inert gases. The high temperature plasma is generated

inside a torch which typically consists of three concentric quartz or ceramic tubes as shown in Figure 1. The tip of the torch where the plasma is formed is surrounded by the so called load coil which is water cooled and carries a radio frequency (RF) current typically at 27 or 40 MHz.

The main *Plasma gas flow* (10-15 L/min) which is introduced into the torch tangentially into the outer most annular space also acts as the coolant gas to isolate the high temperature plasma from the quartz wall. *Auxiliary gas* (0-4 L/min) which is introduced in the same tangential direction is normally used for minor adjustments of the vertical position of the plasma relative to the torch and to optimize the stability. The central gas flow of typically 1 L/min, named as *sample injector flow* or the *nebulizer gas*, carries the sample aerosols into the center of the plasma through an orifice of typically 1-3 mm id. Generally, the linear velocity of the injector flow is maintained higher than the average velocity of the plasma gas to maintain the analyte in the central channel.

Plasma is ignited by applying RF electrical energy of about 1-1.5 kW and seeding the argon gas with some electrons using a device such as a Tesla coil or piezo-electric igniter. Seeded electrons acquire sufficient kinetic energy from the oscillating electromagnetic field to collide with neutral argon atoms to generate more argon ions and free electrons. The process continues as a chain reaction until the gas becomes a self sustained highly ionized and energetic medium) within a fraction of a second. As shown in Figure 2, certain regions of the plasma can reach temperatures as high as 10,000K.

Figure 1 – The Inductively Coupled Plasma Torch

Figure 2 – Temperature regions in the ICP

The sample is introduced into the plasma most commonly as a fine aerosol of liquid droplets, typically of less than 20 microns, generated by aspiration of the sample solution using a pneumatic or ultrasonic nebulizer. The droplets entering the plasma undergo a series of events within a short time period of few milliseconds as schematically shown in Figure 3. These serial events; desolvation, solute evaporation, molecular decomposition, atomization, ionization, and electronic excitation, occur at different regions of the plasma as shown in Figure 4. During the excitation and de-excitation process of the atoms and ions, *photons* are emitted at wavelengths characteristic to the particular analyte element. Temperature of the plasma is also high enough to efficiently ionize and generate a high population of *analyte ions* for most of the elements in the periodic table.

Figure 3 - Fate of Solution Droplets Entering the Plasma

Figure 4 – Different regions of analytical interest

1.3 Detection Modes

In ICP spectrometry two primary detection modes are employed, either by measuring the intensity of emitted *photons* (optical spectrometry) or by measuring the *ions* (mass spectrometry).

1.3.1. ICP emission spectrometry (ICP-ES)

In emission spectrometry (ICP-ES), intensity of the emitted light is measured at characteristic wavelengths to generate atomic/ionic spectra. Measurement of the wavelength of emitted radiation allows the identification of a particular analyte element, whereas the corresponding intensity of the emitted radiation with appropriate calibration can be used as a measure of the concentration of that particular analyte element.

The emission spectra obtained using plasmas can also be quite rich in spectral lines and structure, thereby increasing the probability of spectral overlaps, which would demand an optical spectrometer with a high resolving power. The emission lines can be in the vacuum-ultraviolet region (VUV, 120-190 nm), ultraviolet (UV, 190-400 nm), visible (VIS, 400-700 nm) and near infrared (NIR, 700-850nm). Due to the fact that it is an optically thin source, ICP has an exceptional linearity over a wide range of concentrations without being affected by self-absorption. This large dynamic range, typically over six orders of magnitude, permits the determination of trace, minor and major elements in the same sample simultaneously, without the need for serial dilution. Availability of multiple wavelengths with a different degree of sensitivity can also be exploited to increase the dynamic range of the technique, for verification of the accuracy

of the measurement, and to diagnose interferences. The detection limits of ICP-ES technique are generally low for most elements typically at the parts per billion (ppb) levels.

Early ICP optical spectrometer designs used photomultiplier tubes (PMTs) to detect light emitted from the plasma. There are two basic types of PMT based spectrometers. *Simultaneous polychromater systems*, also known as direct readers, occupy a number of sets of optical slits and PMTs that are placed at fixed locations of the focal plane of the spectrometer to simultaneously monitor several analytical wavelengths. Although they provide high analytical throughput, changing the analytical wavelength by the user is somewhat impractical. On the other hand, *sequential monochromater systems* offer the user the flexibility for selecting wavelengths as desired by scanning across the spectrum. However, in spite of their flexibility, they allow measurement of only one wavelength at a given time, which makes them relatively inefficient in terms of the analytical throughput. Modern spectrometers utilize *semiconductor array detectors* in place of PMTs to achieve the best of both worlds; high throughput simultaneous measurement capability, as well as the flexibility of wavelength (analyte) selection. These solid-state semiconductor detection systems are based on either Charged Coupled Devices (CCD) or Charge Injection Devices (CID) of a relatively small detector surface area of a few cm^2 , which differ in the way how they measure the electronic charge created by photons on the surface of the detector. These detectors are generally used in conjunction with an echelle polychromator which creates a 2 dimensional high resolution spectrum with wide wavelength coverage.

Viewing direction of the plasma relative to the spectrometer can be done in two

basic orientations; “radial” and “axial” (Figures 5). In the so called “radial” configuration (Figure 5a), the center of the plasma is viewed radially in a direction perpendicular to the axis of the torch. In this orientation the observation zone in the plasma can be easily adjusted to a desired position by moving the torch along the axis. However, the light emitted from the thin central channel enters the spectrometer through the fireball, which adds high-intensity continuum background radiation to the analyte spectrum.

More recently the axial, also called “end-on” viewing orientation (Figure 5b) has also gained popularity in commercial systems. In this orientation, emitted light is collected from a deeper region along the central channel of the plasma resulting in a bigger volume of the analytical region being sampled. As a result, the signals produced can be much stronger than in the case of radial viewing. Secondly, the optical path lies along the central channel of the plasma, avoiding intense background radiation originating from the fireball region surrounding the central channel. Thus in the axial mode, a more intense signal can be collected with smaller background intensity than in the radial mode providing as much as an order of magnitude lower detection limits depending on the analyte element, wavelength and the optical system. However, due to the longer path length of the measured volume of the plasma, some compromise may have to be made in terms of the dynamic range and the robustness of the measurement for matrix interferences.

5a - The radial view

5b - The axial view

Figure 5 - Viewing modes in ICP-ES

1.3.2 ICP mass spectrometry (ICP-MS)

In ICP-MS, a part of the central region of the plasma containing the analyte ions is sampled through a vacuum interface into a mass spectrometer. The extracted ions then pass through a water cooled sampling cone with an orifice of approximately 1 mm in diameter. A typical configuration of an ICP-MS system with a quadrupole-based mass spectrometer is shown in Figure 6. It illustrates a two-three-stage differentially pumped interface used to extract ions from the atmospheric pressure plasma into the low pressure mass spectrometer. Behind the first orifice the gas expands, and a portion passes through a second orifice in the skimmer cone. A series of ions lenses are used to direct the ions into the quadrupole mass analyzer. The ions are transmitted through the quadrupole on the basis of their mass to charge (m/e) ratio and then detected by an electron multiplier. ICP-MS instruments typically use an electron multiplier detector with a dynamic range of eight orders of magnitude (6 orders in high-gain or pulse-counting mode and 2 additional orders in low gain or analog mode).

Various configurations of ICP-MS systems with high resolution mass spectrometers of varying degree of sophistication are commercially available. In addition to providing orders of magnitude better sensitivity with parts per trillion detection limits compared to ICP-ES, another main advantage of ICP-MS technique is its ability to provide isotopic information about the analyte. Its sensitivity coupled with isotopic information has made ICP-MS an extremely powerful tool for geological, environmental, biological and many other scientific applications. ICP-MS allows additional analytical calibration strategies such as isotope dilution. In isotope dilution, the change in isotope ratio for two selected isotopes of an element of interest is measured in solution before and

after the addition of a known quantity of a spike solution containing different enrichment of the two isotopes, which permits calculation of the concentration of the element. For certain applications, isotope dilution can be the most reliable method of accurate determination of elemental concentration which avoids certain analytical errors.

In spite of its high sensitivity and other advantages, ICP-MS technique involves physical extraction of the plasma gas into the vacuum system of the mass spectrometer, which makes the technique less robust compared to ICP-ES in terms of matrix effects, particularly for samples with high dissolved solids. Thus, ICP-ES and ICP-MS act as complementary rather than competing techniques for most applications.

Figure 6 – Schematic of an ICP-MS System

1.4. Sample Introduction

In spite of the high level of sophistication of the commercially available spectrometer systems and software, the versatility and the power of ICP-ES and ICP-MS can significantly be augmented by the choice of the sample introduction technique, depending on a particular application. On the other hand, irrespective of the sophistication and quality of the instrument, a poor performance of the sample introduction system can significantly deteriorate the performance of the overall analytical system. As a result, improvement or development of new sample introduction techniques to meet the new and old analytical challenges has been the most active area of research (just as the focus of the research presented in this thesis) in ICP-ES and ICP-MS. Sample introduction step is generally regarded as the Achilles heel of atomic spectroscopy.

Liquid sample introduction is the most common way of introducing samples into the plasmas. Among the three physical states of matter, liquids (solutions) are the most convenient and practical analytical medium to deal with in terms of ease of handling, sample dilution, and calibration for quantification with excellent measurement accuracy and precision. Solutions are converted into a fine aerosol using a nebulizer as the first step of bringing the analyte into the gaseous phase. There are two basic types of nebulizers. Pneumatic nebulizers (Figure 7a, 7b) are the simplest and most commonly used. Ultrasonic nebulizers, similar to those used in domestic humidifiers are also commercially available which are relatively more complex and costly. In ultrasonic nebulization, the sample solution is introduced onto the surface of a piezoelectric transducer driven by an ultrasonic generator at a frequency of 200 kHz to 10 MHz. In contrast to the pneumatic nebulizer, the aspiration process of an ultrasonic nebulizer is

independent of the carrier gas flow, and generally provides a finer droplet size distribution than its pneumatic counterparts.

The actual performance of the analytical measurement is directly affected by the quality of the aerosol generated. The generated aerosol can have a range of droplet size distribution from sub microns to tens of microns. Introduction of larger droplets can result in perturbation and instabilities in the plasma leading to poor analytical performance. In order to remove larger droplets, the nebulizer is normally attached to a spray chamber which acts as cut-off filter to remove the larger fraction of the droplets by momentum impact and allows passage of only the fine aerosol droplets into the plasma as shown in Figure 8. However, this process result in wastage of a significant amount of the sample (typically > 95% going into the drain) with a poor analyte transport efficiency of typically less than 5%, which is considered to be one of the main disadvantages of solution nebulization. A typical set up of an ICP sample introduction system is shown in Figure 9.

Figure 7a – Concentric Glass Nebulizer

Figure 7b – Cross-flow Nebulizer

Figure 7 - Commonly used Pneumatic Nebulizers

Figure 8 – Fractionation of aerosols in the spray chamber

Figure 9 –
A typical set up with a conventional sample introduction system

1.5. Direct Analysis of Solids

Although the most common approach of sample introduction in plasma spectrometry is solution nebulization, a vast majority of samples subjected to elemental analysis exists as solids. Analysis of solid materials such as rocks, minerals, sediments, biological and pharmaceutical materials need first the conversion of the solid material into solution by an appropriate chemical digestion/dissolution procedure. Such sample preparation procedures can have several drawbacks: (1) usage of hazardous chemicals such as HF, HClO₄, and peroxides (2) long sample preparation time (3) high cost of pure reagents and labour (4) potential for contamination or loss of analytes due to incomplete dissolution or volatility leading to poor accuracy and precision, etc. Having realized these difficulties, and potential of the ICP as a powerful analytical source, researchers have long been trying to develop viable sample introduction techniques to analyze solid samples using ICPs, directly without chemical digestion, but with minimal or no sample preparation.

There are several approaches that have been proposed for the direct analysis of solid materials with varying degrees of success depending on the application. Some of the common methods include swirl cup ³ fluidized bed chamber ^{4, (5, 6)}, direct powder introduction US patent 5,286,451 (DeSilva and Guevremont) , direct sample insertion ^{7,8,9}, electrothermal vapourization ¹⁰, spark ablation ^{11,12,13} , and laser ablation, ^{14,15}. In recent years, laser ablation (LA) has become a popular direct solid analytical technique, in spite of relatively high cost of hardware. An alternate approach to these techniques is the slurry nebulization, conceptually a somewhat intermediate approach between dry solid analysis and solution nebulization.

The research described in this thesis was focused on two approaches of direct solid analysis; namely, slurry nebulization and direct powder introduction. Chapter 2 of the thesis deals with some new developments in slurry nebulization (SN-ICP) and Chapter 3 deals with the evaluation, improvement and various feasibility studies of the direct powder introduction technique (DPI-ICP) which was pioneered in our laboratory.

CHAPTER 2

SLURRY NEBULIZATION

2.1. Introduction

Slurry nebulization (Figure 10) is the process where an aerosol of droplets and particles is generated by nebulizing a suspension of fine particles in a liquid (slurry). In the past, DCP emission spectrometry was used for earlier studies into slurry sample introduction ^{16,17,18}. The latest trend now uses ICP-AES and ICP-MS instrumentation. Similar to other direct solid analysis techniques, slurry nebulization has many advantages over traditional solution nebulization, such as elimination of complex dissolution procedures and the avoidance of hazardous chemicals. It combines the advantages of both solid and liquid sampling since the sample can be transported conveniently to the plasma using a conventional pumping system (Figure 10). Perhaps, the most attractive feature of slurry nebulization over the other direct solid analysis techniques is its simplicity. The only additional hardware requirement relative to the conventional ICP for analysis of solutions is the use of a high solid nebulizer. Another potential advantage of slurry nebulization is that it can, at least in principle, be calibrated using aqueous solutions in an analogous way to solution nebulization. It has been applied to both ICP-ES and ICP-MS ^{19,20}. Slurry nebulization have been reported for a variety of materials such as tissues, vegetation, and geological materials ^{21,22,23}, ores ²⁰, clay minerals ²⁴ and coal ²⁵.

Figure 10 - Solution Nebulization vs Slurry Nebulization

In spite of the above advantages, there are several serious practical difficulties associated with the technique. Although, the calibration procedures using aqueous standard solutions have been attempted, the value of the approach appeared to be questionable depending on the elements and the preparation method of the slurry. Direct calibration with simple aqueous solutions requires the satisfaction of two criteria if accurate analyses are to be obtained: (a) that both the analyte transport efficiency of the slurry particle and (b) the subsequent atomization efficiency of that particle must be identical to that of a simple aqueous solution. If either or both of these conditions are not met, then the analytical accuracy of slurry nebulization is degraded ^{26,27}. Accurate determinations require small particle sizes, typically less than 2-3 microns. Inability to control the particle size during sample preparation is considered to be one of the main reasons for poor performance. Thus, in spite of its apparent convenience, the viability of slurry nebulization relies heavily on the ability to prepare samples of a fine particle size in a reproducible and uniform manner.

Slurries with such fine particle sizes are prepared by wet-grinding of a known composition of the slurry using ball mills, which could be a long process and negates the main benefits of direct solid analysis. Grinding with ball mills can also lead to contamination. Tyson and co-workers ²⁸ applied both laser ablation and slurry nebulization for the analysis of rock SRMs and achieved relatively poor agreement with the certified values, even though a milling time of as long as 16 hours was used for wet grinding of the slurries during sample preparation. It was confirmed that a significant fraction of slurry particles ranged from 7-10 microns, resulting in a significant negative

bias of the measured concentrations due to decreased relative transport efficiency through the spray chamber and incomplete volatilization. It has been reported that slurries (1% m/v) could be nebulized up to 4 hours without cone blockage with proper control of the particle size ²⁹. It should be noted that, although the grinding process brings the average distribution towards a size smaller it doesn't eliminate problematic big particles (Figure 11). Lack of control of the particle size can also aggravate nebulizer blockage, cone blockage and deposition of solid on the delicate components of the spectrometer.

Figure 11 - Effect of wet-grinding on particle size distribution

A practical approach to eliminate the presence of big particles, and being able to aspirate slurries containing only the fine particles of a certain cut-off would minimize or eliminate most of the above analytical difficulties currently associated with slurry nebulization – ICP-ES/MS. How can we come up with such a technique?

Desirable features:

- Eliminates the need for excessive grinding time, which negates the advantages expected from direct solid analysis.
- Minimizes/eliminates contamination due to wet grinding (e.g. from ceramic balls, zirconia balls, etc.)
- Minimizes the use of dispersants, which may be necessary for keeping bigger particles in suspension to stabilize slurries.
- Removes particles bigger than a desired cut-off diameter, thereby minimizing incomplete volatilization of particles leading to poor analyte recoveries.
- Totally eliminates (not just minimizes!) big particles that can lead to problems due to blockage of cones, nebulizers, and contamination of the mass spectrometer.
- Minimizes deposition of bigger particles along the transfer line (pump tubing) leading to blockage.
- Minimizes segregation effects in the spray chamber and poor analyte recoveries.
- Enhances volatilization efficiency by reducing average particle size.
- Be suitable and practical for routine analytical applications.

2.2. Hypotheses:

1. Proper design of a method for the size separation of particles in slurries according to their sedimentation velocity should provide a practical method to have a good control of the particle size to avoid most of the existing practical difficulties encountered in elemental analysis by SN-ICP-ES/MS.
2. Disruption of laminar flow characteristics of slurry by air segmentation should prevent the clogging of slurries along the transfer line during slurry nebulization.

2.3. Experimental:

2.3.1. Samples and Standards:

Most of the materials studied were NIST (National Institute of Standards and Technology, USA) standard reference materials (Glass, Dried Liver, and Plant Materials) and CANMET (Canada Centre for Mining and Energy Technology) reference materials (Sediments, Coal) which were already available in powder form (typically -200 mesh or 74 μm). The samples were prepared from a grinder (PICA Blender Mill, from Pinchford Scientific Instruments Corporation, Pittsburgh-Pennsylvania Type 3800 Serial #307) to obtain the fine powders. Smaller samples, typically less than 5g were prepared by grinding solid glass using a ceramic mortar and a pestle.

Unless otherwise specified, the composition of the slurries used for sedimentation was 4% m/V in water. The solutions were diluted to about 1% m/V prior to introduction into the ICP.

The solid content of the slurry solution used for aspiration into the plasma was determined by withdrawing 1ml of the slurry using an Ependorf pipette into a small pre-weighed glass vial and drying in the oven followed by weighing the residue.

2.3.2. ICP-ES Spectrometer and Operating Parameters:

IRIS - ICP Spectrometer (Thermo Instruments) was used for all the slurry nebulization experiments. It is equipped with Charge Injection Device (CID) detector that allows simultaneous measurement of multiple wavelengths (multiple analytes) and their backgrounds. A cross-flow nebulizer used for traditional solution aspiration was used with a standard spray chamber and the torch. ICP operating parameters are shown in Table 1. Analytical wavelengths used are shown in Table 2. Data were collected using the instrument software and imported to EXCEL spreadsheets for further processing.

Table 1. ICP Operating Parameters

ICP:

RF Power :	1.25 kW
Plasma Gas Flow:	fixed, as preset at the factory (15 L/min)
Auxiliary Gas:	1.5 L/min
Nebulizer Gas:	1.0 L/min (32 psi)
Observation Height:	15 mm above the load coil (radial)
Injector orifice:	1.5 mm id
Nebulizer:	Cross-flow (Thermo Instruments)
Pump:	Gilson Miniplus -2 peristaltic, with standard tygon tubings.

Slurry up take rate: 1.0 ml/min

Table 2 - Elements and their analytical wavelengths

Element	Wavelength (nm)
Al	396.1
B	249.6, 249.7
Ca	393.3, 396.8
Cr	283.5
Fe	238.2, 259.9
Mg	280.2, 285.2
Si	212.4, 251.6, 288.1
Ti	323.4, 334.9
Zn	202.5, 213.8
Zr	339.8

2.3.3. Mathematical Simulations:

Theoretical calculations to estimate the extraction efficiencies as a function of different parameters such as number of extractions, slurry concentration, particle size distribution, and particle density were done by using an in house developed EXCEL spread sheet.

2.4. Results and Discussion:

Irrespective of the extent of grinding and a considerable reduction in the average particle size, there is always a finite distribution of big particles that can clog the nebulizer and the transfer lines, where the presence of only a single such particle can be catastrophic, particularly in automated analysis. Instead of extensive grinding, removal of big particles can be done by sedimentation more effectively and the method developed in this study is discussed below.

2.4.1. Theoretical Developments of Sedimentation and Simulations

Concept of the fractionation procedure:

If a column of a dilute slurry is stirred and left to settle, the heavy/bigger fraction of particles settles down faster than the smaller particles. After allowing a certain settling time, the top portion of the column can be withdrawn which contains only the small particles as shown in Figure 12. The same clean liquid that is used to dilute the slurry before nebulization, can be added to bring the level back to the top. If the slurry is stirred again, the remaining particles, which is now enriched with bigger particles, but still containing a significant portion small particles, will be dispersed uniformly in the new liquid column. The same process can be repeated and the new extracted portion of the liquid containing the small particles can be added to the previously extracted portion. Analytically, it would be desirable to extract as many useful particles as possible. The process can be repeated a number of times so that almost only the big particles will remain in the liquid column and combined extracted liquid portions contains almost all, but ONLY the small particles which can be used for the nebulization.

Figure 12 - A cycle of the slurry extraction process

Theoretical aspects:

A mathematical model and a spreadsheet were developed to calculate the sedimentation-extraction efficiency for a certain particle size cut-off. The basic dimensional parameters of the sedimentation process are shown in Figure 13.

X - Distance traveled by the top most particles after time t

E - Height of the liquid volume being extracted

H – Total height of the liquid column

X - Distance traveled by the top most particles after time t

E - Height of the liquid volume being extracted

H – Total height of the liquid column

Figure 13 -
Dimensional parameters of the slurry extraction tube

If, a slurry containing a uniform size of particles are stirred and let settle, the top most layer of the particles will drop to a height (H-X). There will be a clear demarcation above which the liquid is clear. If the level of extraction (height of portion that is withdrawn) is E, assuming that the diameter of the column is uniform, the fraction of the particles extracted will be:

$$F_e = (E - X) / H \quad \text{-----} \quad (1)$$

Any particular size for which $X > E$, none of the particles will be extracted, which would be the cut-off size.

The theory behind sedimentation is based on Stoke's Law. It is assumed that the particles are spheres of different diameters. Even though, in reality particles can have irregular shapes, it can be considered as a valid approximation for the purpose of this study as accurate dimensions of the particles are not critical, yet valuable inferences can be made. Sedimentation rate of a particle (spherical) is determined by the physical parameters and the viscosity of the liquid.

According to Stoke's Law, the viscous force acting on a sphere traveling in a viscous medium is given by³⁰.

$$\text{Force}_v = 6\pi R\eta V \quad \text{-----} \quad (2)$$

Where,

Force_v - viscous drag force acting on the particle.

V - sedimentation velocity of the particle

η - viscosity of the liquid

R - radius of the particle

The gravitational force acting on the particle, corrected for the buoyancy is given by:

$$\text{Force}_g = \frac{4}{3} \pi R^3 (\rho - \sigma) g \quad \text{-----} \quad (3)$$

Where, ρ and σ are the densities of the particle and liquid, respectively.

During sedimentation, when the particle reaches the terminal velocity, V, the viscous force, Force_v is counter-balanced by the gravitational force, Force_g . Then, from equations (2) and (3),

$$\begin{aligned} 6\pi R\eta V &= \frac{4}{3} \pi R^3 (\rho - \sigma) g \\ V &= \frac{2}{9} \frac{R^2 (\rho - \sigma) g}{\eta} \end{aligned}$$

If t is the sedimentation time, the above equation can be written as

$$V = X / t = K R^2$$

$$\text{Where, } K = \frac{2}{9} (\rho - \sigma) g / \eta \quad \text{-----} \quad (4)$$

$$X = K R^2 t \quad \text{-----} \quad (5)$$

The value of K remains constant for a given material and a liquid. The above relationship shows that the distance traveled by the particle at a given time has a square

dependence of its size (the radius). For example a 10 micron particle will fall four times as much as the distance traveled by a 5 micron particle. It can be expected that any unusually large particle present in the slurry would settle to the bottom almost instantaneously compared to the fine particles, making the separation very effective.

The fraction of particles extracted, F_e can be estimated by substituting equation (5) in equation (1) as follows:

$$F_e = (E - K R^2 t) / H \quad \text{-----} \quad (6)$$

Then the remaining fraction will be,

$$F_r = 1 - F_e$$

If the process is repeated, the fraction of the particles remaining after the second cycle would be a fraction of $(1 - F_e)$ from the fraction remained during the previous cycle, which would be equal to $(1 - F_e) \times (1 - F_e)$. If we continue the extraction process for N number of cycles, then the total fraction remaining after N extractions, $F_r(N)$ is given by

$$F_r(N) = (1 - F_e)^N \quad \text{-----} \quad (7)$$

However, more important than calculating the remaining fraction, our focus is to know the total fraction extracted after N cycles, $F_e(N)$, which can be derived as:

$$F_e(N) = 1 - (1 - F_e)^N \quad \text{-----} \quad (8)$$

A spreadsheet was developed to calculate the extraction efficiency for different variables such as: densities, particle size, sedimentation time, column dimensions, number of cycles, etc. A sample calculation is shown in Figure 14. It was extended also to calculate the extraction efficiency as a function of particle size for desired variables

which allows observation of the effect of different variables interactively. Figure 15 shows such a set of “extraction efficiency- particle size” curves for different number of cycles at three different heights (E) of the extraction volume. It is apparent that, as the extraction height E increases, the particle cut-off diameter increases, along with an increase in the extraction efficiency. Figure 16 shows similar curves for three different settling times (t). Increasing the settling time from 100 s to 1000 s reduces the cut-off diameter from about 15 to 4.5 microns. Basically, the cut-off diameters for a given set-up, can be reduced either by reducing the extraction volume or increasing the settling time at the expense of extraction efficiency. However, the extraction efficiency can be improved by increasing the number extraction cycles, N. In reality, a slurry of a ground natural material does not have a single uniform particle size. By doing similar calculations as above for a series of particle sizes, the mathematical model and the spreadsheet can be used to calculate the size distribution of both extracted and remaining fractions, for a given set of experimental parameters as the number of cycles progresses.

Input Variables:	
h - total height of the column	10 cm
e - extraction column height	8 cm
t - settling time	110 sec
Variables fed by the Table:	
N - Number of extractions	3
a - particle radius	10 micron
Variables for calculation of k	
σ - Liquid density g/cm ³	1 g/cm ³
ρ - Particle density g/cm ³	3 g/cm ³
η - Liquid viscosity cgs	0.05 cgs
k - constant, depends on visc, g, etc..	8720

Output (Efficiency of Extraction)	
fe	0.70408
Fr(N)	0.025913
Fe(N)	0.974087

Figure 14 - Sample Calculation using the Spreadsheet

(a).
 $E = 2$ cm

(b).
 $E = 5$ cm

(c).
 $E = 8$ cm

H – Total height of the column
 E - Height of the extracted volume
 t - Allowed settling time

Figure 15
 Extraction efficiency as a function of particle size
 For different number of cycles ($H=10$ cm, $t = 300$ s)

(a).
 $t = 100 \text{ s}$

(a).
 $t = 200 \text{ s}$

(a).
 $t = 800 \text{ s}$

H – Total height of the column
E - Height of the extracted volume
t - Allowed settling time

Figure 16

Extraction efficiency as a function of particle size
For different number of cycles (H=10cm, E= 2cm)

2.4.2. Implementation of sedimentation – design of the apparatus

Although the above discussed theory, mathematical model and calculations show the potential of sedimentation as an effective approach in controlling the particle size in a slurry, its implementation for the purpose of trace elemental analysis has to tackle a number of practical challenges to make it a viable approach, which are not trivial.

Basically, the method should be: quantitative, reproducible, well controlled, rapid, have minimal contact surfaces to minimize contamination, should involve minimal transfers and handling, be amenable to automation, able to be miniaturized to handle small samples, etc.

In order to meet the above desirable features, a sedimentation apparatus was developed in this study. The basic device used for manual operation is shown in Figure 17. The slurry is placed inside a vial which is stirred using a magnetic stirrer. After stirring for a brief period, stirring is stopped and the slurry is allowed to settle for a predetermined period. Then a volume of air greater than the extraction volume of the slurry is withdrawn using the air syringe. The uptake capillary is placed inside the slurry and the syringe is connected to the collector vial which collects the fine fraction through an air-tight cap. When air is withdrawn by the syringe, the suction action withdraws the top portion of the slurry down to the level where the tip of the uptake capillary has been placed. Even if there is a variable and irreproducible amount of air is withdrawn by the operator, a precise volume of the slurry, determined by the exact location of the tip of the uptake capillary is transferred into the collector vial allowing a reproducible withdrawal.

The volume that is withdrawn can be adjusted by relocating the position of the capillary tip as desired. There is no turning or tilting of the vial to pour off the liquid which allows a symmetrical and reproducible withdrawal, without having practical problems such as having the slurry dripping over the mouth of the container. Apart from the container vials, the only contact area is the fine Teflon tubing connection between the two vials. The same collector vial can be used to store the slurry or for the analysis step. The withdrawal syringe that is used to apply suction does not come into contact with the sample, thereby eliminating potential contamination from the components or the cross-contamination between samples. A new extraction cycle can be simply executed by adding more of the pure liquid into the vial and repeating the syringe action after stirring and settling.

Figure 17 –
Basic apparatus for slurry fractionation by sedimentation

The improved device that was developed in study which can be adopted for full-automation is shown in Figure 18. As the first step, a vial containing the un-separated slurry is placed as shown and the 3-way valves are diverted in such a way that the liquid syringe is connected to the solvent reservoir and the air syringe is connected to the collector vial meant for the finer fraction. Movement of the syringe head as shown (to the right) results in filling the liquid syringe with fresh solvent and withdrawing of the top portion of the slurry into the collector vial. As it was described in the manual operation, withdrawal of the slurry takes place only to the level where the tip of the uptake capillary is located. Then the directions of the three way valves are switched as shown in Figure 18b. This results in the vial containing the un-fractionated slurry being connected to the liquid filled syringe, and the air syringe being connected to the out side for purging. With the combination of the above process, and stirring and settling (sedimentation) with a proper timing sequence, the system allows reproducible automation, with a desired number of sedimentation cycles for each sample to be processed.

(a) Withdrawal of the fine fraction and refilling of the liquid syringe

(b) Adding pure liquid and purging the air syringe

Figure 18 – Flow paths during automated slurry sedimentation

The above sedimentation procedure was used for a variety of materials such as sediments and glass. The effectiveness of the method can be seen from the SEM pictures shown in Figure 19a and 19b, before and after sedimentation, respectively, at two different magnifications. The pictures clearly show the effective removal of large particles from the slurry.

Glass Powder - Before Sedimentation

Glass Powder - After Sedimentation

Figure 19 - Glass powder before and after sedimentation

2.4.3. Analytical Results

Performance of an analytical technique depends on its robustness for the working concentration range. The reproducibility of the sedimentation process and the linearity of the signal during different amounts of sample loading were tested using different percentage (% m/v) of the slurry. Signal response as a function of slurry concentration is shown in Figure 20 for a series of element. A good linearity and agreement between the analytical duplicates can be seen from the figures, indicating that analysis can be performed with slurry concentrations as high as 4% if it can be transported properly to the nebulizer.

Figure 20- Signal Intensity versus Slurry Concentration

2.4.4. Development of a segmented flow system

Even when the maximum particle size of the slurry is significantly smaller than the internal diameter of the transport tubing, it was observed that gradual build up of particles, particularly at sharp bends and tubing joints occasionally resulted in eventual clogging of the systems. The problem gets particularly aggravated at high concentration of slurries. This phenomenon can be explained by taking laminar flow patterns of the liquid into consideration as shown in Figure 21a. At flow regimes of few mL/min through few 100 micron id tubing, the liquid flow takes a laminar flow pattern, where the liquid streams move parallel to the direction of the bulk flow. The flow velocities take a parabolic shape with a zero velocity at the surface and reaching a maximum at the centre. A relatively heavy particle that settles near the surface does not feel much momentum from the liquid due to its low velocity, and may not get swept away as much as those near the centre. Then the particles can start building up near the wall and resist the flow. A reduced flow makes the situation gradually worse to the point where the flow is stopped resulting in a complete blockage.

It was believed that a possible solution to the problem could be the disruption of laminar flow and promoting the mixing of the liquid continuously along the flow path. This was done by segmenting the liquid flow with air bubbles as shown in Figure 21b, which eliminated the problem. However, as in sedimentation, segmentation has to be done in a controlled, reproducible and reliable manner to meet our analytical challenges without compromising the performance of the system. A trivial solution seems to be

Parabolic flow has zero velocity near the tube wall

Figure 21a

Segmented flow continuously mixes the slurry

Figure 21b

Figure 21 - Effect of air segmentation on the liquid flow patterns

addition of a T- connector and use another channel of the same peristaltic pump to insert air bubbles as shown in Figure 22a. However, this does not cover the flow path from the tip of the uptake capillary to the T-joint that passes through the pump, which is a significant length of the transfer line consisting of a number of joints (Teflon to Tygon, etc...). Ideally, segmentation should be done at the earliest possible point along the flow path. The improved version of the flow system that was used to alleviate the above problem is shown in Figure 22b, which was successfully used for the analytical measurements.

Fig 22. Flow system for air segmentation

Fig. 22a

Fig. 22b

2.4.5. Analytical Results

A series of glass samples were analyzed for several elements using the developed slurry nebulization technique. Figure 23a shows the relationship between two Zn wavelengths (206.2nm versus 213.8nm) measured for the series. It shows an excellent agreement with a correlation coefficient of 0.999549 indicating that signal measured can be successfully used for quantitative measurement purposes. The certified values for Zn were available only for two of the materials. The concentrations were calculated using NIST 91 Glass as the standard, and the values are shown in Table 3. The measured values (method duplicates) for the two standards for which certified values available are plotted in Figure 23b, showing a good linearity and reproducibility. Table 4 and Table 5 show the determined concentrations of minor and trace elements by SN-ICP-ES with good agreement with the certified values and acceptable precision.

Figure 23a

Figure 23b

Figure 23- Determination of Zn in Glass by SSN-ICP-ES

Table3

Glass Standard	Zn Certified (ppm)	Measured (ppm)
NIST 81		120
NIST 81a		129
NIST 91	537	Standard
NIST 93		143
NIST 128		125
NIST 165		116
Pipette#2		116
B&M #2	140	123
NIST 664		131
ANAVS1		108

% RSD < 1-2%

Determination of Calcium by Slurry Nebulization ICP-ES			
Sample	Certified (%)	Measured (%)	%RSD
Peach	1.56	2.04	2.15
		2.07	1.88
Tomato	5.05	5.08	0.92
		5.02	1.92
Spinach	1.527	1.42	2.67
		1.57	9.32

Table 4a

Determination of Phosphorous by Slurry Nebulization ICP-ES			
Sample	Certified (%)	Measured (%)	%RSD
Peach	0.137	0.209	0.67
		0.207	0.60
Tomato	0.216	0.405	1.38
		0.376	9.05
Spinach	0.518	0.498	1.78
		0.538	5.54

Table 4b

Table 4 - Determination of Minor Elements in
NIST - Plant Reference Materials by Slurry ICP-ES

Determination of Iron by Slurry Nebulization ICP-ES			
Sample	Certified (ppm)	Measured (ppm)	%RSD
Peach	218	205	0.90
		206	0.77
Tomato	368	360	1.49
		360	1.03
Spinach		201	1.20
		218	1.17

Table 5a

Determination of Manganese by Slurry Nebulization ICP-ES			
Sample	Certified (PPM)	Measured (PPM)	%RSD
Peach	98	83.4	2.27
		84.7	1.27
Tomato	246	251.9	2.24
		240.1	13.95
Spinach	75.9	75.3	2.23
		79.2	2.18

Table 5b

Table 5 - Determination of Trace Elements in
NIST - Plant Reference Materials by Slurry ICP-ES

CHAPTER 3

DIRECT POWDER INTRODUCTION INDUCTIVELY COUPLED PLASMA SPECTROMETRY (DPI-ICP).

3.1. Introduction

Chapter 2 of this thesis was devoted to Slurry Nebulization – Inductively Coupled Plasma Spectrometry (SN-ICP-ES/MS). As pointed out earlier in Chapter 1, SN can be considered as a hybrid between direct solid analysis and solution nebulization. However, a number of analytical and practical advantages can be realized if solid samples can be introduced directly into the ICP also in *dry powder form*, without pretreatment: the sample is analyzed in its natural state, contamination from reagents are minimized, dilution errors are eliminated, the losses during transfer of sample during sample handling steps are avoided, the time delay between sample collection and analysis is diminished, reagent and labor costs are reduced, and the increased efficiency of sample transport into the plasma has potential for providing improved detection limits. Problems associated with the formation of molecular ions originating from solvent molecules (in ICPMS) can be eliminated. Although the potential application areas are numerous (environmental, pharmaceutical, biological, etc.), with the availability of suitable techniques for direct analysis of solids, perhaps it is the geoanalyst who would be benefited the most. This chapter describes some of the studies undertaken during the present research in the analysis of *solid materials in dry form*, namely, by Direct Powder Introduction (DPI).

Several sample introduction techniques for direct solid analysis have evolved to

different levels of maturity, some of which are even commercially available. Laser ablation LA-ICP is the most popular among the techniques proposed for ICP analysis of samples in dry solid form. In laser ablation, a solid sample is placed inside an enclosed chamber typically made of quartz and a desired location of the solid surface is bombarded with a high powered laser beam. A micro volume of the solid material is ablated off the surface as a mixture of atoms, vapors and particles which is swept away into the plasma using argon carrier gas. LA-ICP has become a powerful tool, particularly in geochemical applications such as analysis of fluid inclusions and mineral grains on rock surfaces, providing information on localized concentrations and corresponding isotope ratios. However, LA-ICP is not free from analytical difficulties. For example, finding a suitable calibration strategy can be difficult due to lack of control of material introduced and lack of knowledge of the amount of sample entering the plasma. Selective volatilization may result in non-representative distribution of analytes in the plasma. If the original sample is available in powder form, the sample preparation for LA-ICP can still be an elaborate process.

Electrothermal Vaporization (ETV) and Direct Sample Insertion (DSI) can also be used to vaporize microgram quantities of solid samples directly into the plasma without prior digestion. In ETV-ICP-ES/MS, the sample is placed typically on a graphite platform which is electrically heated to a high temperature to vaporize the sample. Sample vapor is carried from the furnace into the plasma using argon carrier gas. Although calibration can be somewhat simpler than in LA-ICP, the sample size used for a given analysis generally has to be limited to microgram quantities. Selective vaporization of analyte elements depending on the matrix can lead to poor results. Unknown amounts of analyte can

deposit and be lost along the transfer lines leading to poor recoveries. Vaporized carbon off the furnace can deposit on the spectrometer components and cause molecular ion interferences in the mass spectrum.

Direct Sample Insertion (DSI) is somewhat similar to ETV in that the sample is placed on a refractory surface and vaporized off the support surface. In contrast to ETV, the sample support in DSI is a probe made of graphite or a refractory metal filament which is mechanically inserted to the base or the center of the ICP to be heated directly by the plasma energy. DSI-ICP has similar advantages and disadvantages as ETV. They both provide transient signal which may require special data acquisition hardware and software.

Spark Ablation (SA) has been used for direct analysis of solid samples, where the sample is made to be an electrode for high current spark. As the sample has to be electrically conducting, geological powder materials generally have to be mixed with conducting graphite or a metallic powder at a high proportion, which may pose problems, related to contamination and poor detection limits.

Ideally, what we require is a method to introduce only the analyte (just the dry powder) without any physical support, additives, solvents, etc., in a well controlled and quantitative manner. The concept of Direct Powder Introduction (DPI-ICP) where a well controlled continuous flow of dry powders is uniformly introduced into the plasma was pioneered by De Silva and Guevremont US patent 5,286,451 and further developments are being continued in De Silva's laboratory. Although quantitative delivery of dry

powders into the ICP with many desirable features has been demonstrated, a significant knowledge is yet to be gained in terms of possible novel developments of this technique and its numerous potential applications. What are its limitations and potential for quantitative analysis? What are the possible novel applications? What are the options for calibration strategies? Can this technique be used to generate signals from individual particles?

3.2. Hypothesis

Direct powder introduction should be a viable and versatile approach of sample introduction for plasma spectrometry to obtain quantitative analytical information of samples from individual particles to bulk powders.

3.3. Experimental

3.3.1. Powder Sampler - Direct Powder Injector (DPI)

Direct Powder Introduction system used in this study was the same device developed by De Silva and further improved at Carleton University (partly during this study). A simplified version of the device is shown in Figure 24. During operation, a pre-weighed quantity of the dry powder sample is placed inside a glass capillary of 1mm id and 4 mm od, and inserted to the sampler through the O-ring seal. Argon sampler gas is introduced into the lower chamber typically at 50- 100 mL/min. A second flow of argon carrier gas is added as a make up gas upstream to optimize the conditions in the plasma through an especially designed flow merger to keep the make-up gas as a sheath gas. The flow merger and the bottom chamber containing the sample capillary are connected with a 0.75 mm od metal tubing. The upper chamber (flow merger) is connected to a

conventional ICP-torch using a flexible 0.5mm fused silica capillary (about 30 cm) commonly used in gas chromatography. The sample tube is attached to a computer controlled linear drive that can be programmed to raise the sample vial continuously or in steps at a desired speed and with timing parameters. The mechanical attachment to the vial also has the provision for rotating the vial during the vertical linear motion.

During sample introduction, vial containing the powder is slowly raised at a uniform speed. Sampler gas entering the lower chamber passes through the metal capillary into the upper chamber. Due to high linear velocity of the sampler gas at the tip of the capillary, particles at the top surface of the powder column is entrained into the gas stream similar to the action of a vacuum cleaner. The flow of the powder is determined by the computer control feeding rate of the vial, but not by the magnitude of the gas flow rate allowing full computer control. As the tip of the uptake capillary reaches the bottom of the vial, sample is completely consumed (quantitatively). Rotation of the vial facilitates removal of the powder from the surface, makes the powder flow uniform and allow the use of hard packed materials.

Direct Powder Injector (DPI)

Figure 24 – Direct Powder Injector (DPI)

3.3.2. Samples and standards:

A series of CANMET sediment reference materials; four stream sediments (STSD1, STSD2, STSD3, STSD4) and four lake sediments (LKSD1, LKSD2, LKSD3, LKSD4) were primarily used for developmental work, along with other standards such as CANMET Soil, NIST fly ash.

3.3.3. ICP and Sampler Operational Conditions:

Spectrometer operational parameters are given Table 6, which are almost the same as those typically used for conventional solution nebulization, except the total injector gas flow.

Table 6 - Operational Parameters used of DPI-ICP measurements

ICP - Spectrometer System: LECO Plasmarray Diode Array System
RF Frequency: 27 MHz

Plasma Gas: 14 L/min
Auxiliary Gas: 4 L/min
Injector Gas: 200 mL/min

RF Power: 1.5 kW
Torch: Standard 20 mm, Quartz
Injector orifice: 1.0 mm id

DPI Powder Sampler:

Sampler Gas: 50 mL/min
Carrier (makeup) Gas: 150 mL/min
Linear feeding rate: 3 cm/6000 sec
Sample Vial id: 1 mm
Sample column height: Variable, 3 cm max.

3.4. Results and Discussion

3.4.1. Modes for signal normalization.

One of the unique advantages of DPI over other solid sample introduction technique is that it can introduce a continuous stream of particles at a predetermined flexible flow rate for a duration that is only limited by the physical length of the powder column and the uptake capillary inserted into the sample vial. It allows the use of normal signal measurement strategies used for steady state signals generated during traditional continuous flow solution nebulization, providing us several options in terms of signal normalization strategies.

Four basic signal normalization strategies in DPI-ICP can be used for quantitative measurement purposes.

(a) Mass normalized measurements:

By weighing the sample vial before and after the sample packing, an accurately known mass of material can be placed inside the vial. As the DPI has the unsurpassed capability of nearly 100% transport efficiency of a known mass, the signal can be integrated over the whole sample and directly normalized to the mass. Since the powder feeding rate can be set constant irrespective of the actual sample mass (powder column height) sample mass can be varied over a wide range while keeping the same material loading rate into the plasma. Figure 25 shows the integrated signal at two wavelengths of Cu as a function of sample mass measured using RTS-3 CANMET Sulphide Rock Reference Material. It shows excellent linearity up to the maximum of 12 mg of sample mass that was measured. As mentioned previously, the upper limit of the mass is only limited by the amount of sample that can be physically loaded into the vial. Table 7

shows the reproducibility of measurements as a function of mass. One interesting feature of the DPI-ICP technique is that a number of samples can be serially weighed and stacked on top of each other inside the same vial as shown in Figure 26, where each sample is spaced with a clean powder material such as silica or a polymer. It should be noted that the “spacer” material does not have to be very clean as long as it can be distinguished from the sample using a marker emission line such as Si. This way, the sample vial virtually acts as an auto-sampler.

A comparison of different solid analysis techniques in terms of the effect of increasing the sample mass on material loading in the plasma is shown in Figure 27. Most of the other solid sampling techniques such as ETV and DSI produce transient signals as shown. However, the amount of material being analyzed in DPI can be extended along the time axis without increasing the effective flow rate and thus without overloading the plasma, which can happen in ETV or DSI.

Figure 25 -
Linearity of Integrated Signal versus Sample Mass

Measurement Uncertainty (%RSD) versus Sample Size (STSD-2)									
Mass (mg)	Replicates (N)	Cr1	Zn	Cr2	Ca	Al	Fe	V	Cr1/Cr2
0.5	8	9.17	9.92	8.65	9.55	9.19	8.78	11.43	1.02
1	9	6.44	6.64	6.53	8.76	6.75	5.81	7.52	0.41
2	6	2.7	2.81	2.78	3.96	3.93	3.12	3.53	0.24
4	5	2.14	2.51	2.07	3.36	3.15	2.34	3.37	0.13
7.5	5	1.19	1.43	1.24	1.99	1.48	0.97	3.31	0.51
22	4	2.25	1.49	2.31	1.93	1.96	1.94	1.55	0.18

**Table 7 -
Measurement uncertainty (%RSD) for a series of elements as
a function of sample size (CANMET Stream Sediment STSD2)**

Figure – 26 Sample stacking inside a single vial

Figure – 27
Effect of increasing sample mass In DPI versus ETV/DSI

(b) Column height normalized measurements:

For certain exploratory work, such as geochemical exploration it may sometimes be desirable to make semi-quantitative measurements for screening purposes. Particularly in the field, it may be quite advantageous to eliminate certain steps in the analytical process. It is conceivable that the DPI technique can be used to measure signals from the vials filled to the same height, as opposed to cumbersome weighing of each sample and knowing its accurate mass. In order to investigate the feasibility of such an approach, a series of capillary vials were filled with SO-1 soil reference material to the same height of approximately 1.4 cm, which corresponds to about 12 mg of sample for the dimensions of the vials used. Measured sample mass and the corresponding length of the sample column are tabulated in Table 8, along with the calculated packing density (mass/unit length) for eight such individual measurements. Calculated %RSD of the packing density is 1.17% which is well within the same order of the estimated uncertainty (%RSD) of the measurement of the length of the column, indicating that extremely good reproducibility of sample packing for height normalized DPI can be obtained. For similar type of samples, height-normalized measurements (simply vial-full) in DPI-ICP can be as precise and accurate as mass-normalized measurements.

Reproducibility of Packing Density (PD) CANMET SO-1 Soil Reference Material			
	Mass (mg)	Length (cm)	PD (mg/cm)
	12.74	1.45	8.79
	12.65	1.40	9.04
	12.07	1.35	8.94
	12.73	1.40	9.09
	11.90	1.35	8.81
	12.11	1.37	8.84
	12.02	1.35	8.90
	12.43	1.38	9.01
Average	12.33	1.381	8.928
Standard Deviation			0.104
% RSD			1.17
Estimated Meas. Uncertainty			
of the length (cm)			0.02
% Relative Uncertainty of length			1.45

Table 8
Height normalized signal measurement in DPI –
Reproducibility of packing density

(c) Time normalized signal measurement:

A major convenience of conventional solution nebulization is the availability of continuous steady state signals which allows us to extend signal measurement as desired depending on the desired analytical data quality such as precision, etc. Almost none of the other solid sampling techniques produce such steady state signals. On the other hand, DPI can be used to generate steady state signals and therefore, time-based signal measurements can be done in DPI, similar to solution nebulization (Figure 28)

(d) Internal standard normalized measurements:

DPI can be used to conveniently introduce a wide range of sample masses from a single particle (ng) to tens of mg quantities of powders. However, a major difficulty in quantification is the measurement of the mass of such small particles and handling transient signals of short durations. As an alternative approach, a single particle can be introduced by DPI and a matrix element can be used as an internal standard to compare one particle against the other without knowing the actual mass of material (Figure 29). However, an obvious question that may come up is whether an individual particle can produce intense enough signals to be measured with a conventional spectrometer. To investigate the feasibility of multi-element measurements of single particles, DPI was used to introduce approximately 100 micron size individual particles. The clear peak profiles observed for Cu, Fe and S in chalcopyrite particles as shown in Figure 30 is a clear indication of the potential of DPI to perform such analyses. Similarly, if coupled with ICP-MS, DPI should be able to provide isotopic information on single particles, such as Pb isotope ratios in Zircon particles.

Figure 28 - Time normalized signal measurement

Figure 29 –
Internal standard normalized signal measurement

Figure 30 – Analysis of Single Particles by DPI-ICP-ES Chalcopyrite - CuFeS₂ Single Particles (~100 mciron)

Cu 224.700

Subarray Plot 12/18/01 19:21:56 page 1
Method: CF_CPPYR Element: Cu 224.700 (116)

Subarray Width : 15 Left Bkg pos: 4 Used Right Bkg pos: 11 Used Rep#: 1
Subarray Height: 3
Center Width: 3

SampleName	Raw Intens	Background	Corrected
* PF_CP_SINGL6	82.95	12.69	70.25
* PF_CP_SINGL5	236.35	20.13	216.22
* PF_CP_SINGL4	93.28	13.22	80.05
* PF_CP_SINGL3	93.94	13.41	80.54
* CF_CP_SINGL5	671.76	53.36	618.40
* CF_CP_SINGL3	494.97	43.92	451.05
* CF_CP_SINGL2	308.25	33.11	275.15
* CF_CP_SINGL1	233.37	28.95	204.42

Fe 238.204

Subarray Plot 12/18/01 19:22:14 page 1
Method: CF_CPPYR Element: Fe 238.204 (109)

Subarray Width : 15 Left Bkg pos: 3 Used Right Bkg pos: 12 Used Rep#: 1
Subarray Height: 3
Center Width: 3

SampleName	Raw Intens	Background	Corrected
* PF_CP_SINGL6	147.77	16.96	130.80
* PF_CP_SINGL5	337.21	21.99	315.22
* PF_CP_SINGL4	149.92	17.28	132.64
* PF_CP_SINGL3	172.56	17.76	154.80
* CF_CP_SINGL5	420.78	42.24	378.54
* CF_CP_SINGL3	326.21	39.80	286.42
* CF_CP_SINGL2	239.07	36.00	203.07
* CF_CP_SINGL1	219.88	34.78	185.09

S 182.034

Subarray Plot 12/18/01 19:22:45 page 1
Method: CF_CPPYR Element: S 182.034 (143)

Subarray Width : 15 Left Bkg pos: 3 Used Right Bkg pos: 10 Used Rep#: 1
Subarray Height: 3
Center Width: 4

SampleName	Raw Intens	Background	Corrected
* PF_CP_SINGL6	0.19	2.66	5.53
* PF_CP_SINGL5	6.89	2.44	4.45
* PF_CP_SINGL4	5.43	2.19	3.24
* PF_CP_SINGL3	2.64	1.98	0.66
* CF_CP_SINGL5	46.53	9.36	37.17
* CF_CP_SINGL3	34.22	7.87	26.36
* CF_CP_SINGL2	44.71	6.51	38.20
* CF_CP_SINGL1	37.66	6.31	29.35

3.4.2. Quantitative Analytical Measurements

Table 9 shows some analytical data obtained by DPI-ICP-ES performed on a series of reference standards for Zn. The sample size used was about 12 mg (accurately known) with 6 replicate measurements. Including any uncertainty due to heterogeneity effects that can be anticipated in small sample portions of natural materials, the observed precision is excellent (typically less than 3%). There is a good agreement between the certified and the measured concentration, except for few cases such as SO-1 demonstrating the potential of the technique for quantitative measurements. It should be noted that no extra attempt was made, other than using the experimental conditions used for solution analysis, to enhance the volatilization efficiency in generating this preliminary data. Furthermore, the standard reference materials were used as they were obtained without any effort to match or reduce the particle size by grinding. Such steps should further improve the quality of the results.

CHAPTER - 4

CONCLUSIONS AND FUTURE DIRECTIONS

4.1. Direct Solid Analysis

Quality of analytical results can be only as good as the quality of the sample presented into the analytical instrument. As a result, sample introduction has played and will continue to play an important role in instrumental analysis, particularly in elemental and isotopic analysis by using ICP-ES and ICP-MS. In spite of its popularity and certain advantages, traditional approach of solution nebulization has many draw backs. Furthermore, it does not fully exploit the capabilities of state of the art instruments and available computing power. On the other hand, direct analysis techniques can allow unique opportunities for extraction of traditional and new types of analytical information in addition to being able to eliminate tedious sample preparation procedures in many applications.

This thesis presented some research and developments that were done in the ICP laboratory at Carleton University in the directions of two of the main approaches that have been proposed for direct solid analysis, namely Slurry Nebulization (SN) and Direct Powder Introduction (DPI).

4.2. Slurry Nebulization:

Although, SN is generally categorized as a direct solid analysis technique, it can be considered as a hybrid between solution nebulization and direct solid analysis, which combines both the advantages and disadvantages of solution nebulization as well as other direct solid analysis techniques. Primary advantage of SN is that it does not require virtually any new hardware modifications of a conventional ICP system, or special operator training. In spite of the simplicity, there are certain drawbacks. The transport efficiency is only few percent, similar to solution nebulization, which can result in segregation of material in the spray chamber leading to questionable analytical results. Although, it has the potential applicability for many analytical problems, the main reason for the lack of popularity of SN as a universally used technique, is the practical difficulties encountered in preparation of slurry samples containing only fine particles, primarily the lack of control of large particle sizes which can have deleterious effects in two directions. The presence of large particles can result in poor analytical recoveries of the signals due to incomplete volatilization of the big particles, and secondly, they can originate practical problems such as clogging of the components and transfer lines.

A practical and convenient method based on sedimentation was developed to prepare slurries with well controlled particle size and a clearly defined and reproducible cut-off, in contrast to the commonly used wet grinding. The developed sedimentation method can be easily automated and meets many stringent requirements of an analytical system meant for trace analytical purposes. In spite of successfully eliminating particles bigger than a certain cut-off diameter, which can be much smaller than the tubing diameter, laminar flow characteristics of the liquid flow can result in accumulation of

particles along the transfer tubings, resulting in eventual clogging of the introduction system. Air segmentation of the flow of slurry alleviated such stagnation of particles along the transfer lines allowing un-interrupted operation. A flow system was developed in this study for automated and reproducible introduction of air segments into the stream of the slurry.

A Mathematical model was developed based on Stokes Law to predict the behaviour of different experimental parameters of sedimentation process. An EXCEL spreadsheet was developed to interactively calculate extraction efficiency of the sedimentation process.

There can be certain limitations of the sedimentation process for preparation of slurries. If the sample contains different types of particles with different densities and particle size, there is a potential for preferential enrichment of certain types of particles. For example, the particles of the same size but made of different matrices with different densities can settle at different settling rates thereby enriching low density material in the finer fraction. However, such drawbacks are not limited to sedimentation. One can encounter preferential enrichment of certain matrices even with the slurries that are subjected to wet grinding when it is aspirated, as there can be preferential segregation inside the spray chamber. Ideally, SN is most suitable for powders of uniform materials such as glass, coal, ceramics, etc. Preparation of slurries of biological material can be somewhat difficult as they tend to swell when they are soaked with water and sedimentation may not be very effective.

Due to high sensitivity of ICP-MS, it may sometimes be necessary to dilute the slurry to a very low concentration in order to match the analytical working range with the sensitivity of the detector. Such dilutions can lead to a point where the number of particles becomes small enough to make particle statistics play a significant role in the analytical uncertainties. In a different study done in De Silva's lab (Sarah Anderson, B.Sc. 2005, 4th year Chemistry Honours Thesis) theoretical models were developed using Poisson Statistics to predict such uncertainties and statistical limitations in aerosol introduction including slurry nebulization, droplets and dry particles.

4.3. Direct Powder Introduction

A number of studies were described in this thesis to demonstrate the versatility and power of Direct Powder Introduction (DPI) for quantitative analytical purposes. Although, DPI is still in its infancy, it has the potential to mature as a powerful analytical technique in the future capable of meeting many analytical challenges, while providing additional versatile features that are not available with most of the other approaches. By exploiting state of the art powerful computers, information can be processed almost on individual particle basis. As described in Chapter 3, it provides a number of different approaches of signal normalization, ability to extract heterogeneity and mineralogical information which are destroyed during sample digestion. Although data was not presented in this thesis, we have studied the feasibility of using DPI for solution analysis where the analytes are preconcentrated onto a resin such as Chelex-100 and subsequently analyzed in dry powder form. This can potentially allow very high pre-concentration factors with improved detection limits compared to traditional pre-concentration

schemes.

There are several fundamental and practical issues that have to be addressed in DPI. Efficiency of particle volatilization is of major concern. Several approaches are being investigated as a part of ICP research at Carleton University and the University of Ottawa. New design of torches where powders are introduced against the flow of the plasma gas, so called “Counter Flow ICP” which was developed at Carleton University, can significantly increase the residence time of the particles by dramatically enhancing the particle volatilization efficiency. Improvement of sampler hardware for handling smaller particles such as atmospheric particulate matter is also under development. In-situ preheating of the particles using tube furnaces, tandem plasmas, and electrical discharges are some other possibilities to enhance the capabilities of the DPI-ICP technique.

4.4. Comparison with other Solid Analysis Techniques

One sample introduction technique should not be viewed as a panacea for all challenging analytical problems and applications. The method of choice would depend on several factors, such as: the spectrometer system (ES or MS), concentration range, desired type of information (absolute concentration versus isotopic ratio), particular application, sample matrix, and the nature of the sample (e.g. powders versus metal coins).

In certain situations, one solid sampling technique can potentially enhance the capability of another. For example, as briefly mentioned in Chapter 3, in spite of its

popularity, one major difficulty faced in Laser Ablation is the calibration, as there is no easy way of introducing known quantities of analytes into the plasma in dry form. However, since DPI has such capabilities to introduce a known quantity of a dry powder of virtually any physical characteristics, DPI can be used for calibration purposes for powerful laser ablation measurements. Due to these various factors and possibilities that need to be considered most of the sample introduction techniques can be considered to be complimentary rather than being competitors.

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