

CHAPTER 2: LITERATURE REVIEW

2.1 INTRODUCTION

In this section, a review of platinum group metals and gold chemistry, base metals chemistry, solid sample introduction techniques, slurry technique, slurry sampling applications and slurry rheology is given. Areas such as sample handling, analytical frame work, developed methods limitations and analytical figures of merits are examined on published literature. Briefly, the chapter provides the backbone of the study by highlighting other studies done in the past relevant to this field.

2.2 PLATINUM GROUP METALS

South Africa is the world's leading producer of precious metals. The members of the platinum group metals (PGM); ruthenium, rhodium, palladium, osmium, iridium, and platinum and gold are called 'precious' or 'noble' metals. These names have roots in the unique physical and chemical properties of the metals, table 2.1, owing to their low abundance and high economic value.

Nobility and catalytic activity are unique properties of precious metals that result in their wide applications, for example, as catalysts in various chemical processes, in electrical and electronic industries, and in jewelry. Growing demand for rhodium, palladium and platinum has resulted from autocatalysts production. Since 1978, platinum complexes, cis-platinum and second-generation compounds, have

been applied in chemotherapy as effective anticancer drugs (Keppler, 1993). The investigation of ruthenium complexes as an alternative to platinum cancer inhibitors has recently become a subject of extensive studies.

Table 2.1 Physical properties of platinum group metals

	Platinum	Palladium	Rhodium	Iridium	Ruthenium	Osmium
Chemical symbol	Pt	Pd	Rh	Ir	Ru	Os
Density (g cm ⁻³)	21.45	12.02	12.41	22.65	12.45	22.61
Melting point (°C)	1,769	1,552	1,960	2,443	2,310	3,050
Vickers hardness no.	41	41	101	220	240	350
Electrical resistivity (microhm.cm at 0°C)	9.85	9.93	4.33	4.71	6.80	8.12
Thermal conductivity (watts/metre/°C)	73	76	150	148	105	87
Tensile strength (kg mm ⁻¹)	14	17	71	112	165	-
Best solvents	Alkaline oxidizing fusion	Alkaline oxidizing fusion	Hot conc.H ₂ SO ₄ ; conc. HCl + NaClO ₃ at 125 - 150°C	Conc. HCl + NaClO ₃ at 125 - 150°C	Conc. HNO ₃ , HCl + Cl ₂	Aqua regia

Source: Cotton and Wilkinson, 2001.

The six platinum metals are chemically very similar. Precious metals are colored and lustrous, exceptionally stable, hard, malleable, electrically resistant and inert to chemical attacks. Platinum, iridium and rhodium are the densest known metals, platinum being 11 per cent denser than gold and twice the weight of the same

volume of silver or lead. Palladium, rhodium and ruthenium are lighter, palladium having about the same density as silver.

2.2.1 Common features of platinum group metals chemistry

The chemistry of PGMs has some common features, but there are nevertheless wide variations depending on differing stabilities of oxidation states and stereochemistry among other things. The principle areas of general similarity include:

- Binary compounds – there are a large number of oxides, sulfides and phosphides besides others, but the most important are the halides.
- Aqueous chemistry – this chemistry is almost exclusively that of complex compounds. Aqua ions of Ru^{II} , Ru^{III} , Rh^{III} , Ir^{III} , Pd^{II} and Pt^{II} exist, but complex ions are formed in the presence of anions other than ClO_4^- , BF_4^- or p-toluenesulfonate. The precise nature of many supposedly simple solutions like rhodium sulfate is complicated and often unknown. Vast arrays of complex ions, predominantly with halides or nitrogen donor ligands, are water soluble.
- Compounds with π -Acid Ligands

Binary carbonyls are formed by all PGMs but Pd and Pt, the majority of them polynuclear. Substituted polynuclear carbonyls are known for Pd and Pt, and all six elements give carbonyl halides and a wide variety of carbonyl complexes containing other ligands and carbonyl anions.

- Nitric oxide complexes are a feature of the chemistry of ruthenium.
- The formation of complexes with trialkyl- and triarylphosphines and related phosphates, and to a lesser extent with R_3As and R_2S is a widely studied area. The most important are those with triphenylphosphine and methyl-substituted phosphines. The later are more soluble in organic solvents than PPh_3 complexes, and have proved particularly useful for the determination of configuration by NMR.
- Mixed complexes of PR_3 with CO, alkenes, halides, and hydride ligands in at least one oxidation state are common for all of the elements.
- All these elements have a strong tendency to form bonds to carbon, especially with alkenes and alkynes; Pt^{II} and Pt^{IV} , and to a lesser extent Pd^{II} have a strong tendency to form sigma bonds, and Pd^{II} very readily forms π -allyl species.

- A highly characteristic feature is the formation of hydrido complexes, and M-H bonds may be formed when the metal halides in higher oxidation states are reduced, especially in the presence of tertiary phosphines or other ligands. Hydrogen abstraction from reaction media such as alcohols and DMF is common.
- For the d^8 ions Rh^I , Ir^I , Pd^{II} and Pt^{II} , the normal coordination is square (though five-coordinate species are fairly common) and oxidative addition reactions are of great importance (Cotton and Wilkinson, 2001).

Almost all complex and binary compounds of the elements give the metal when heated above 200°C in air or oxygen. Apart from $Pd(NO_3)_2(OH)_2$ formed on dissolution of Pd in concentrated nitric acid, the complexes are mainly the octahedral halide anions.

Platinum group metal chemistry is an exceedingly active area of research, and even omitting patents, which are very numerous, the research papers number in the many hundreds per year.

Nobility and catalytic activity are unique properties of precious metals that result in their wide applications, for example, as catalysts in various chemical processes, in electrical and electronic industries, and in jewelry (Hartley, 1991). As observed

before, growing demand for rhodium, palladium and platinum has resulted from auto-catalysts production. Since 1978, platinum complexes, cisplatin and second-generation compounds, have been applied in chemotherapy as effective anticancer drugs (Keppler, 1993). The investigation of ruthenium complexes as an alternative to platinum cancer inhibitors has recently become a subject of extensive studies.

The large variety and complexity of examined materials, wide concentration ranges to be determined (from ng g^{-1} and sub-ng g^{-1} in geological, environmental and clinical samples to percentage levels in some industrial products), high inertness of noble metals towards many chemical reagents and high chemical similarities of numerous chemicals formed make the choice of the analytical methodology for their determination in the sample of interest a challenge. Extensive studies on the methods for the determination of the metals in various matrices with satisfactory sensitivity, selectivity and reliability have been carried out. Spectrometric techniques, ultra-violet visible (UV-VIS) spectrometry, atomic absorption spectrometry (both flame (FAAS) and graphite furnace (GFAAS) techniques), inductively coupled plasma combined with atomic emission spectrometry (ICP-AES) or mass spectrometry (ICP-MS), are widely applied in the analysis of a variety of samples containing noble metals over a large range of concentrations (Balcerzak, 2002).

2.2.2 Sample preparation and analytical methods for PGMs and gold

The PGMs can occur as discrete mineral phases or in solid solution in mineral phases (Juvenen *et al.*, 1994, Talkington and Watkinson, 1986, Scoats and Eckstrand, 1986, Hulbert, 2001). The distribution of PGMs can be erratic within samples, particularly if they are present as discrete platinum group minerals. This ‘nugget’ effect for Platinum Group Metals is similar to that known to occur commonly for gold, but perhaps not quite as extreme as the Platinum Group metals minerals are usually not completely PGMs where as native gold particles would be almost entirely gold. The required sub-sample size that should be chosen for analysis will depend on PGMs particle size and the mineralogy of the sample (Hoffman and Dunn, 1999).

There are many methods for determination of PGMs. The most common method is the standard lead fire assay using silver as a collector for the platinum and palladium followed by inductively coupled plasma-optical emission spectrometry (ICP-OES), or direct current plasma spectroscopy (DCP) for final analytical finish. A variation on the lead fire assay using gold as a collector is required to determine rhodium quantitatively, as rhodium forms insoluble alloys in the silver collector matrix that cannot be dissolved quantitatively (Hoffman and Dunn, 1999). These techniques are rapid and accurate. For the ultimate in sensitivity, ICP-MS is used for the analytical finish. The ICP-MS method has great application for large scale lake bottom sediment surveys and litho-geochemical surveys looking for depletion

and enrichment in magmatic stratigraphy (Hulbert, 2001). The least used analytical method for PGMs in modern laboratories are atomic absorption spectroscopy (AAS) and graphite furnace atomic absorption spectrometry (GFAAS). ICP methods are faster, cheaper and have less elemental interference (Hoffman and Dunn, 1999).

The nickel sulfide fire assay technique is effective for the determination of all PGMs and gold. After collection in the nickel sulfide matrix, the button produced is dissolved in concentrated hydrochloric acid and the residue analyzed by instrumental neutron activation analysis (INAA), or it can be further digested in aqua regia and analyzed by ICP-MS. Tellurium co-precipitation may be required to ensure that the PGMs are not partially dissolved. These procedures are usually slower and more costly than the standard lead fire procedure, but they are the only practical methods for quantitative determination of all PGMs and gold (Hoffman and Dunn, 1999).

Therefore it is evident that for many years, a number of analytical techniques have existed for elemental analysis of PGMs. Conventionally; this is done by nebulization of dissolved samples. For many samples, however, the sample preparation is protracted, and may be hazardous to the samples, depending on the preparation procedure. More importantly, however, is the extended analysis time. The direct introduction of solids would eliminate these problems, as well as

reducing the preparation time, and thus allowing quick monitoring. In Addition the sample preparation cost is much cheaper than that of solid preparation.

2.3 GOLD

Gold is a soft, shiny, yellow, dense, malleable, ductile (trivalent and univalent) transition metal. It does not react with most chemicals but is attacked by chlorine, fluorine and aqua regia. Heat, moisture, oxygen, and most corrosive agents have very little chemical effect on gold, making it well-suited for use in coins and jewelry; conversely, halogens will chemically alter gold, and aqua regia dissolves it. Common oxidation states of gold include +1 (gold (I) or aurous compounds) and +3 (gold (III) or auric compounds). Gold ions in solution are readily reduced and precipitated out as gold metal by the addition of virtually any other metal as the reducing agent. The added metal is oxidized and dissolves allowing the gold to be displaced from solution and be recovered as a solid precipitate. Gold is a good conductor of heat and electricity, and is not affected by air and most reagents.

Pure gold is too soft for ordinary use and is hardened by alloying with silver, copper, and other metals. Gold and its many alloys are most often used in jewelry, coinage and as a standard for monetary exchange. Because of its high electrical conductivity and resistance to corrosion and other desirable combinations of physical and chemical properties, gold also emerged as an essential industrial metal, table 2.2.

Table 2.2 Properties of gold

Properties	Gold	Properties	Gold
Chemical symbol	Au	Number	79
Metal series	Transition	Density (g cm ⁻³)	19.3
Group, Period, Block	11, 6, d	Melting point (°C)	1064.18
Appearance-metallic	Yellow	Boiling point (°C)	2856
Atomic mass g mol ⁻¹	196.966569(2)	Heat of fusion (Kj mol ⁻¹)	12.55
Electron configuration	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ¹	Heat of vapourization (kJ mol ⁻¹)	324
Electrons per shell	2, 8, 18, 32, 18, 1	Heat capacity (25°C) (kJ mol ⁻¹)	25.418

Although gold is a noble metal, it can form many compounds, auric chloride (AuCl₃) and chlorauric acid (HAuCl₄) being the most common. Gold compounds can be aurous (univalent, +1) or auric (trivalent, +3). Gold also can under extreme conditions form a +5 state with fluorine (gold pentafluoride, AuF₅), as well as (unusually for a metal), a -1 state. Such compounds containing the Au⁻ anion are called aurides and include caesium auride, CsAu, rubidium auride, RbAu, and tetramethylammonium auride, (CH₃)₄N⁺ Au⁻.

Due to its relative chemical inertness gold is usually found as the native metal or alloy. Occasionally large accumulations of native gold (also known as nuggets) occur but usually gold occurs as minute grains. These grains occur between mineral grain boundaries or as inclusions within minerals. Common gold associations are quartz often as veins and sulfide minerals. The most common sulfide associations are pyrite, chalcopyrite, galena, sphalerite, arsenopyrite,

stibnite and pyrrhotite. Rarer mineral associations are petzite, calaverite, sylvanite, muthmannite, nagyagite and krennerite.

The primary source of gold is usually igneous rocks or surface concentrations. A deposit usually needs some form of secondary enrichment to form an economically viable ore deposit: either chemical or physical processes like erosion or solution or more generally metamorphism, which concentrates the gold in sulfide minerals or quartz. There are several primary deposit types, common ones are termed reef or vein. Primary deposits can be weathered and eroded, with most of the gold being transported into stream beds where it congregates with other heavy minerals to form placer deposits. In all these deposits the gold is in its native form. Another important ore type is in sedimentary black shale and limestone deposits containing finely disseminated gold and other platinum group metals.

2.4 BASE METALS

Base metals are common or at least inexpensive metals. Frequently, the term is used to refer to those metals that oxidize or corrode relatively easily, and react variably with dilute hydrochloric acid to form hydrogen. Examples include iron, nickel, lead, copper and zinc. Copper is considered a base metal as it oxidizes relatively easily, although it does not react with hydrochloric acid. These metals form part of the ore body that include the Bushveld Igneous Complex (BIG), the

Merensky reef, Upper Group 2 (UG2) and Plat Reef. They occur in close association with the PGMs and gold minerals, for example, Pyrrhotite (Fe_{1-x}S), Pentlandite $(\text{Fe,Ni})_9\text{S}_8$ and Chalcopyrite (CuFeS_2).

Table 2.3 Properties of base metals

	Nickel	Copper	Iron	Cobalt
Number	28	29	26	27
metal series	Transition	Transition	Transition	Transition
Group, Period, Block	10, 4, d	11, 4, d	8, 4, d	9, 4, d
Appearance-metallic	Lustrous	Brown	Lustrous	Gray tinge
Atomic mass g mol^{-1}	58.6934(2)	63.545(3)	55.845(2)	58.933195(5)
Electron configuration	$[\text{Ar}] 3d^8 4s^2$	$[\text{Ar}] 3d^{10} 4s^1$	$[\text{Ar}] 3d^6 4s^2$	$[\text{Ar}] 3d^7 4s^2$
Electrons per shell	2, 8, 16, 2	2, 8, 18, 1	2, 8, 14, 2	2, 8, 15, 2

Table 2.4 Physical properties of base metals

	Nickel	Copper	Iron	Cobalt
Chemical symbol	Ni	Cu	Fe	Co
Density (g cm^{-3})	8.908	8.96	7.86	8.90
Melting point ($^{\circ}\text{C}$)	1455	1084.62	1538	1495
Boiling point ($^{\circ}\text{C}$)	2913	2562	2861	2927
Heat of fusion (kJ mol^{-1})	17.48	13.26	13.81	16.06
Heat of vapourization (kJ mol^{-1})	377.5	300.4	340	377
Heat capacity (25°C) (kJ mol^{-1})	26.07	24.44	25.10	24.81

Nickel is a silvery white metal that takes on a high polish. It belongs to the iron group, and is hard, malleable, and ductile. The most common oxidation state of nickel is +2, though 0, +1 and +3 Ni complexes are observed. It occurs combined

with sulfur in millerite, with arsenic in the mineral niccolite, and with arsenic and sulfur in nickel glance. It is inert to oxidation and is permanently in air. The bulk of nickel mined comes from two types of ore deposits. The first are laterites where the principal ore minerals are nickeliferous limonite: $(\text{Fe,Ni})\text{O}(\text{OH})$ and garnierite (a hydrous nickel silicate): $(\text{Ni,Mg})_3\text{Si}_2\text{O}_5(\text{OH})$. The second are magmatic sulfide deposits where the principal ore mineral is pentlandite: $(\text{Ni,Fe})_9\text{S}_8$.

Copper is a reddish-colored metal, with a high electrical and thermal conductivity (among pure metals at room temperature, only silver has a higher electrical conductivity). Copper has its characteristic color because it reflects red and orange light and absorbs other frequencies in the visible spectrum, due to its band structure. Common oxidation states of copper include the less stable copper (I) state, Cu^{+1} ; and the more stable copper (II) state, Cu^{+2} , which forms lovely blue or blue-green salts. Under unusual conditions, a +3 state can be obtained. Copper can be found as native copper in mineral form. Minerals such as the carbonates azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$) and malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$) are sources of copper, as are sulfides such as chalcopyrite (CuFeS_2), bornite (Cu_5FeS_4), covellite (CuS), chalcocite (Cu_2S) and oxides like cuprite (Cu_2O).

Iron is notable for being the final element produced by stellar nucleosynthesis, and thus the heaviest element which does not require a supernova or similarly cataclysmic event for its formation. It is therefore the most abundant heavy metal

in the universe. It is believed to be the tenth most abundant element in the universe. It is also the most abundant (by mass, 34.6%) element making up the earth; the concentration of iron in the various layers of the earth ranges from high at the inner core to about 5% in the outer crust, contributing to the earth's magnetic field. Iron is a metal extracted from iron ore, and is hardly ever found in the free (elemental) state. In order to obtain elemental iron, the impurities must be removed by chemical reduction.

Most of iron is found in various iron oxides, such as the minerals hematite, magnetite and taconite. The earth's core is believed to consist largely of metallic iron –nickel alloy. About 5% of the meteorites similarly consist of iron-nickel alloy. Although rare, these are the major form of natural metallic iron on the earth's surface. Iron is also one of the least reactive metals, and therefore, is sometimes found pure in nature.

Cobalt is a hard ferromagnetic silver-white element. Common oxidation states of cobalt include +2, and +3, though +1 is also seen. Due to the various oxidation states, there are an abundant number of compounds. Oxides are anti-ferromagnetic at low temperature CoO (Neel temperature: 291 K) and Co_3O_4 (Neel temperature: 40 K). It is frequently associated with nickel, and both are characteristic ingredients of meteoric iron. Cobalt is not found as a free metal and is generally found in the form of ores. Cobalt is usually not mined alone, and tends to be

produced as a by-product of nickel and copper mining activities. The main ores of cobalt are cobaltite, erythrite, glaucodot, and skutterudite.

2.5 SOLID SAMPLES INTRODUCTION TECHNIQUES

A variety of techniques have been developed for the introduction of solid samples into ICP-OES. Techniques in combination with ICP-OES/MS and AAS such as direct sample insertion, electrothermal vapourization, arc and spark ablation, laser ablation and slurry nebulization bring new opportunities for trace/ultratrace analysis relative to the nebulization of aqueous samples.

Direct sample insertion (DSI) and electro thermal vaporization (ETV) share many common attributes. A few milligrams of samples is pre-weighed into a graphite or metal support and then heated electrically or by the plasma, such that the entire sample is used up. The solid sample may be in any form. The signal behavior is time dependent and ETV provides limits of detection in the $\mu\text{g g}^{-1}$ to pg g^{-1} range. Precision is typically 5 to 10% RSD, with linear dynamic ranges of three to four orders of magnitude (Montaser, 1992).

The ablation techniques, arc, spark and laser, differ from DSI and ETV in that material is removed from the sample surface without pre-weighing. While the arcs and sparks require the sample to be conductive, lasers do not. Laser ablation offers an additional advantage over the other techniques in that very small surface area

may be ablated, providing spatial information about sample heterogeneity. For the ablation techniques, the mass sampled is approximately 1 μg , with less than 1 μg necessary for laser ablation. Detection limits are in the $\mu\text{g g}^{-1}$ to ng range, and precisions are typically 1 to 5% RSD if the sampled surface area is homogeneous. Linear dynamic ranges are three to four orders of magnitude, similar to the DSI and ETV methods.

A common attribute for all the techniques is the relative independence of calibration on the matrix, provided by the Argon ICP-OES/MS. Consequently, calibration curves may be constructed with good linearity using a variety of solid materials having different elemental composition. In spark and laser ablation, solution standards may be substituted in some circumstances, greatly simplifying the calibration procedure. Solution standards may be used in slurry nebulization, but optimum particle size is different for various samples. Ultrasonic deposition of slurry on the ETV devices has certainly reduced the particle size effect based on the studies reported thus far as reviewed by Montaser (1992).

Aside from solid sampling approaches already discussed, a number of other techniques have potential for solid and slurry sampling, or have been explored with varying degrees of success in ICP spectrometry. These approaches include mechanical agitation/vibration followed by entrainment of particles in a carrier gas stream (Meyer and Barnes, 1985), collection of atmospheric particles by

electrostatic precipitation in a graphite tube followed by analysis with ETV-ICP/MS (Bitterli *et al.*,1997), fractionation of car exhaust particles by a cascade impactor and subsequent analysis by ETV-ICP/MS (Ludke *et al.*, 1996), use of powder injector device (Zerezghi and Caruso, 1984), use of an acoustically driven device (Starn and Hieftje, 1992) and fluidized-bed sampling (De Silva and Guevremont, 1990).

The greatest challenge to be met is that of finding new methods to introduce liquids and solids into inductively coupled plasmas. There is still a considerable scope for devising better and more general methods for introducing materials into plasma without the need for tedious chemical procedures (Montaser, 1992).

Slurry nebulization ICP-OES provides an exciting tool especially for the exploration geochemists. The small minimum sample size required allows for rapid quantification of metals like PGMs and gold in heavy mineral concentrates or separates and in a variety of industrial materials. Such data would usefully augment existing bulk-sample assays.

2.6 SLURRY TECHNIQUE

A number of studies have been undertaken on slurry nebulization of certain geological materials (coal and Kaolin) into ICP-AES (Ebdon and Collier, 1988a,

1988b, Ebdon and Wilkinson, 1987b). Many of the factors affecting the efficiency of slurry nebulization (for example, particle size, slurry viscosity, sample uptake) are similar for ICP-AES and ICP-MS because of their common sample introduction systems. Ebdon and Wilkinson (1987a) discussed the optimization of whole coal analysis by ICP-OES which was then used to analyze five coal samples for Cu, Fe, Mn, Ni and V (Ebdon and Wilkinson, 1987b). The quality of the results was assessed by comparison with certified values and results obtained by ashing and acid digestion followed by AAS analysis. The accuracy of the slurry nebulization results varied considerably between samples and could only be considered to be semi-quantitative at best.

Ebdon and Collier (1988a) investigated the effect of a range of dispersing agent concentrations on the emission signal of Mg by slurry nebulization ICP-OES, and concluded that the dispersing agent concentration must be matched in the samples, standards and blanks to minimize differences in transport efficiencies. Later, based on a study of five elements in a kaolin sample, Ebdon and Collier (1988b) demonstrated that the analysis of a slurry containing particles $< 8 \mu\text{m}$ could be calibrated successfully against aqueous standards.

A simple method for preparing slurries for ICP-MS was first described by Williams *et al.* (1987) for the analysis of reference soil. This study showed that aqueous slurries were valid for instrumental calibration. The application of this

method to the analysis of geological samples was explored by Jarvis and Williams (1989), Jarvis I (1992) and Jarvis I and Jarvis K.E. (1992), who demonstrated that, provided a maximum particle size of $< 5 - 10 \mu\text{m}$ and a total suspended and dissolved solids content of $< 2000 \mu\text{g mL}^{-1}$ were achieved, slurry nebulization ICP-MS is a viable method for the determination of trace elements in geological samples. Jarvis, I and Jarvis, K. (1992) analyzed 13 geochemical standard reference materials (SRMs) for 18 elements with acceptable accuracy and precision.

Ebdon *et al.* (1988) applied ICP-MS for semi-quantitative analysis of coal SRMs as slurries using a rhodium internal standard. Quantitative determinations were based on internal standardization with calibration curves prepared using aqueous multi-element standards. It was reported that slurries of 1% m/v could be nebulized for up to 4 hours without cone blockage. Mochizuki *et al.*, (1989) determined rare earth metals in silicate samples ground to fine particle sizes of $< 3 \mu\text{m}$. Method development studies examined the effect of grinding time, slurry concentration, and argon injector gas flow rate. Differences in sensitivity between the slurry and aqueous solutions were noted, but the use of aluminium as an internal standard permitted valid calibration based on aqueous standards. Results for the determination of lanthanide elements in several SRMs were in good agreement with certified values (Montaser, 1997). The method was concluded to be promising particularly for the determination of volatile elements and/or the

analysis of refractory minerals that commonly yield unsatisfactory results by conventional solution-based techniques. However, one of the most serious limitations of direct solid sampling is the lack of suitable solid standards. This is a serious limitation for all of the plasma-based techniques.

The total solid contents of sample solutions must also be controlled. Concentrations of solids above 0.2% have resulted in excessive deposition of salts on sample and skimmer orifices of the instrument and blockage of sample delivery systems in analytical instruments. Dilution of sample solutions and the use of internal standards have been recommended as means of alleviating this problem. Also, flow injection analysis (FIA) procedures have been used effectively (Jarvis, 1992).

2.7 SLURRY SAMPLING APPLICATIONS

The analysis of samples in the slurry form has been applied in a number of studies with varying degrees of success. A number of examples employing the use of different spectroscopic techniques have been documented and include applications in atomic absorption spectroscopy (AAS), electrothermal atomic absorption spectroscopy (ETAAS), atomic fluorescence spectroscopy (AFS), inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectroscopy (ICP-MS). Most of the methods developed involved the

use of hyphenated techniques. Slurry rheology has also been investigated extensively by a number of studies (Ploetgaerts *et al.*, 1997, Ebdon *et al.*, 1995, Saba *et al.*, 1981).

2.7.1 Applications in Atomic Fluorescence Spectroscopy (AFS)

Atomic fluorescence spectroscopy is reported as the least commonly used method of all slurry analysis methods. This is confirmed by the few publications available on slurry Atomic Fluorescence Spectroscopy.

Cava-Montesinos *et al.* (2004) developed an analytical procedure for the determination of As, Sb, Se, Te and Bi in milk samples by hydride generation atomic fluorescence spectrometry (HG-AFS). Samples were treated with aqua regia for 10 minutes in an ultrasonic water bath and pre-reduced with KBr for total Se and Te determination or with KI and ascorbic acid for total As and Sb. The determination of Bi was possible in all with or without pre-reduction. Slurries of samples, in the presence of antifoam A, were treated with NaBH₄ in HCl medium to obtain the corresponding hydrides, and AFS measurements were processed using external calibrations prepared and measured in the same way as samples. Results obtained by the developed procedure compared well with those found after microwave-assisted complete digestion of samples. The proposed method was found to be simple, fast and only 1 mL of milk was needed. The values obtained for detection limit were 2.5, 1.6, 3, 6 and 7 ng L⁻¹ for As, Sb, Se, Te and Bi

respectively in the diluted samples, with average relative standard deviation values of 3.8, 3.1, 1.9, 6.4 and 1.2% for three independent analysis of a series of commercially available samples of different origin.

2.7.2 Applications in Atomic Absorption Spectrometry (AAS)

AAS has been widely employed in slurry sampling studies. Several procedures involving its use have been published, majority of which are interfaced with various sample introduction techniques.

Ultrasonic slurry sampling graphite furnace Atomic Absorption Spectroscopy (GFAAS) analytical consideration for analysis of high density glass was studied by Miller-Ihli (1997). On average results were found to be 20% low as compared with mean reference concentrations. In consequence the glass sample was evaluated and its physical properties characterised, including particle size distribution and density. A systematic evaluation of analysis parameters was conducted, including slurry preparation, sample volume, pipetting accuracy and sample depth. The data suggested that the low analytical values are likely due to sedimentation resulting especially from high density of 2.6 mg cm^{-3} of the materials. The study suggested that the optimum depth for sampling for these high density materials should be approximately 10 mm below the surface. The feasibility of reducing particle size to $< 38 \text{ }\mu\text{m}$ to allow sampling at a range of depths was also demonstrated.

Lopez-Garcia *et al.* (1997) developed a slurry procedure for determination of mercury in soils and sediments by GFAAS. The detection limit for Hg in 125 $\mu\text{L mL}^{-1}$ suspension was obtained as 0.1 $\mu\text{g g}^{-1}$. Calibration was performed using aqueous standards. The reliability of the procedure was proved by analysing certified reference materials.

Dobrowolski and Mierzwa (1997) studied the slurry sampling hydride generation atomic absorption spectrometry (HGAAS) for determination of extractable or soluble arsenic in sediment samples. The accuracy and precision of slurry sampling HGAAS method was studied using certified reference materials. The relative standard deviation of the full (overall) analytical procedure was 8.5% and an absolute limit of detection of 2.75 ng was achieved. Factors which influence the reliability of this method were identified as the choice of slurry liquid phase (extraction medium), sample homogeneity and, in particular, very effective mixing of the slurry.

Lopez-Garcia (1997) further applied slurry sampling in the determination of arsenic and antimony in soils and sediments by graphite furnace Atomic absorption spectroscopy (GFAAS). The detection limit for Sb for 100 mg mL^{-1} suspension was found to be 0.03 $\mu\text{g g}^{-1}$. The results obtained for five certified

reference materials using both direct calibration against aqueous standards and standard addition method demonstrate the reliability of the procedures.

A flow injection procedure was developed by Güryelük *et al.* (2002) for determination of acid-extractable arsenic in soils by HGAAS. Several parameters, including acid and borohydride concentrations, exposure time to microwave energy, and the microwave power applied, were optimized. The on-line microwave extraction increased the recovery of the adsorbed arsenic significantly; whereas, preparation of the slurry in 10% hydrochloric acid instead of water increased the recovery only when the microwave oven was off. Low recoveries, which were investigated by removing the hydride generation manifold and connecting the system via an on-line filter to an inductively coupled plasma mass spectrometer, were due to the irreversible adsorption of arsenic on the soil. This irreversible adsorption does not allow standard additions calibration. The solution detection limit was $0.2 \mu\text{g L}^{-1}$ for a 212- μL injection loop, corresponding to 7 ng g^{-1} solid, for 2.5% m/v slurry prepared in 25 mL.

Marco *et al.* (2003) developed a simple procedure for the determination of manganese in different sections of human brain samples by graphite furnace atomic absorption spectrometry (GFAAS). Brain sections included cerebellum, hypothalamus, frontal cortex, vermix and encephalic trunk. Two sample preparation procedures were evaluated, namely, slurry sampling and microwave-assisted acid digestion. Brain slurries (2% w/v) were prepared in de-ionized water,

with good stability for up to 30 minutes. Brain samples were also digested in a domestic microwave oven using 5 mL of concentrated HNO₃. A mixed palladium and magnesium nitrate chemical modifier was used for thermal stabilization of the analyte in the electro-thermal atomizer up to pyrolysis temperatures of 1300°C, irrespective of the matrix. Quantitation of manganese was conducted in both cases by means of aqueous standards calibration. The detection limits were 0.3 and 0.4 ng mL⁻¹, for the slurry and the digested samples, respectively. The accuracy of the procedure was checked by comparing the results obtained in the analysis of slurries and digested brain samples, and by analysis of the NIST Bovine Liver standard reference material (SRM 1577a). It was concluded that the ease of slurry preparation, together with the conventional set of analytical and instrumental conditions selected for the determination of manganese ensured that the method used was suitable for routine clinical applications.

Dobrowolski (1996) demonstrated the determination of two base metals, nickel and chromium, in soil by slurry GFAAS. Later, Kamogawa *et al.* (2001) investigated trace metal content in hair as an index for exposure to potentially toxic elements. Direct determination of three base metals, cadmium, copper and lead, in slurries of hair samples was investigated using AAS with Zeeman-effect background correction. The analyte addition technique was used for quantification of Cd, Cu and Pb in hair slurry samples. A reference material (GBW076901) was analyzed and a paired t-test showed that the results for all elements obtained with

the slurry sampling procedure were in agreement at 95% confidence level with the certified values. The cryogenic grinding was established as an effective method for grinding the samples.

2.7.3 Applications in Electro-Thermal Atomic Absorption Spectrometry (ETAAS)

Slurry sampling technique is today a well established methodology for direct determination of trace metals in solid samples using electrothermal atomic absorption spectrometry (SS-ETAAS). ETAAS is reported as the most commonly used method of all the slurry analysis methods. This is confirmed by the extensive literature published on metal content in varied matrices some of which are outlined below. The direct introduction of solid into ETAAS atomiser offers many advantages over the conventional techniques in terms of shortening sample preparation time, simplicity, small reagent consumption, reduced risk of sample contamination and improved detection limits (Baralkiewicz *et al.*, 2005). A very important advantage of SS ETAAS method is the fact that it may employ aqueous solution for quantitative calibration. These advantages have popularized the slurry atomization technique, and have been highlighted in a number of publications.

Direct cold vapour generation from aqueous slurries of environmental (marine sediment, soil, coal) and biological (human hair, seafood) samples have been developed using a batch mode generation system coupled with electro-thermal

atomic absorption spectroscopy by Moreda-Pineiro *et al.* (2002). The effects of several variables affecting the cold vapour generation efficiency from solid particles (hydrochloric acid and sodium tetrahydroborate concentrations, argon flow rate, acid solution volume and mean particle size) was evaluated using a Plackett-Burman experimental design. In addition, variables affecting cold vapour trapping and atomization efficiency on Ir-treated graphite tubes (trapping and atomization temperatures and trapping time) were also investigated. Atomization and trapping temperatures, trapping time and hydrochloric acid concentration were the significant variables. The 2^{2+} star and 2^{3+} star central composite designs have been used to obtain optimum values of the variables selected. The accuracy of methods was verified by using several certified reference materials (PACS-1, GBW-07410, NIST-1632c, CRM-397 and DORM-2). A characteristic mass of 390 pg was achieved. The detection limits of methods were in the range of 40 - 600 ng g⁻¹. A particle size of less than 50 mm was adequate to obtain total cold vapour generation of Hg content in the aqueous slurry particles.

Bermejo-Barrera *et al.* (1999) applied slurry sampling technique to the determination of total mercury in human hair by electro-thermal atomic absorption spectrometry (ETAAS). In addition, an acid leaching procedure with hydrochloric acid was developed in order to determine Me-Hg⁺ in human hair with ETAAS. Palladium reduced by ascorbic acid was found to be adequate as a chemical modifier for both total mercury determination in hair slurries and methyl-mercury

determination in hydrochloric acid solutions, at concentrations of 20 and 50 mg L⁻¹ for palladium and ascorbic acid, respectively. The acid leaching procedure was carried out by mechanical stirring with hydrochloric acid at 4%, and a leaching time of 2 minutes was selected. The limits of detection were 0.04 and 0.10 mg g⁻¹ for methyl-mercury and total mercury determination, respectively. The within-batch precision was between 1.8 and 8.8% for total mercury determination, and between 1.5 and 6.5% for methyl-mercury. The method was applied to 20 human hair samples from healthy people, and it was also applied to the CRM 397 human hair reference material, and the results agreed well with the certified ones.

More recently, Baralkiewicz *et al.* (2005) determined mercury in sewage sludge by direct sampling graphite furnace atomic absorption spectrometry. KMnO₄ + Pd were used as a modifier. The minimum sample amount required for slurry preparation with respect to sample homogeneity was evaluated by weighing masses between 3 and 30 mg directly into the auto-sampler cups. The method was validated using CRM 007-040 and CRM 144R certified reference materials of sewage sludge. Two sewage sludge samples from Poznań (Poland) were analysed using acid digestion and direct sampling GFAAS. Similar results were obtained for both methods within limits of statistical error. The results obtained in this work showed that slurry sampling is a rapid and economical alternative to the conventional acid digestion procedures for sewage sludge analysis.

Vieira *et al.* (2002), developed a method for the determination of arsenic in sediment and in coal without sample digestion, based on hydride generation from slurry samples. After grinding the samples to a particle size of $< 50 \mu\text{m}$, the sample powder was mixed with aqua regia and hydrofluoric acid in an ultrasonic bath for 30 minutes. After diluting the mixture with hydrochloric acid, the slurry was allowed to stand for 48 hours, and an aliquot was used for hydride generation with sodium borohydride. More than 80% of the arsenic was leached to the aqueous phase under these conditions, except for one sediment sample with very high silica content. The generated arsine was collected in a graphite tube, treated with 0.5 mg of iridium as a permanent modifier, and the arsenic determination was carried out by ETAAS. The same tube could be used for at least 160 cycles without any re-treatment. The greatest advantage of the method was that minimum of reagents was used and minimal sample handling was required, reducing the risks of contamination and/or analyte loss. However, the addition calibration technique had to be used in order to obtain results within the 95% confidence level for 11 certified reference materials, 5 sediments, 5 coals and one coal fly ash. One certified sediment slurry was spiked with the analyte and the resulting addition calibration curve was used for the analysis of the certified sediments. Similarly, one certified coal was used to obtain the addition calibration curve for the coal and coal fly ash samples. The recoveries of the certified values were between 91 and 115%. The limits of detection in the samples were 0.54 and 0.7 mg g^{-1} for the coal

and sediment samples, respectively, obtained for 1 mL of slurry containing 1 mg of sample.

The determination of selenium in serum by ETAAS using longitudinal Zeeman-effect background correction combined with automated slurry sampling was studied by Wen-Kang *et al.*, (1997). The standard reference material bovine serum (NIST, SRM, 1598) and second generation biological-freeze dried human serum were analysed to verify the accuracy and precision of this technique. The average accuracy values for certified reference serum samples and the recovery values of spiked samples indicated this method to be an efficient and rapid technique for determining selenium in biological samples.

ETAAS determination of selenium, cadmium and lead in different types of baby food using slurry sampling was also studied by Vinas *et al.* (2000). Calibration with aqueous standard solution was used for selenium and lead determination while standard addition method was used for cadmium determination. The detection limits were 5.2, 3.4 and 0.4 ng g⁻¹ for selenium, lead and cadmium, respectively. The reliability of the procedure was established by comparing the results obtained with those obtained for five fish-based baby foods using a previous microwave oven mineralization stage and by analysing six biological certified reference materials. The lead concentration was below the detection limit of all the baby food tested.

A method for determination of tin in slurry samples of sediments and coal by hydride generation graphite furnace electro-thermal atomic absorption spectrometry (HGGF-ETAAS) was studied by Vieira *et al.* (2004). The accuracy of the method was verified by analysing five certified sediments and three coal samples. By using external calibration against aqueous solutions, the results obtained were in agreement with certified values only for the sediment samples. For the coal samples, an additional calibration curve, obtained for one certified coal, was necessary to achieve accurate results. The obtained limits of detection were $0.03 \mu\text{g g}^{-1}$ for sediments and $0.09 \mu\text{g g}^{-1}$ for coal. Thorium was used as a permanent modifier. The relative standard deviations were less than 15%, demonstrating an adequate precision for slurry analysis.

A method for the determination of lead in human hair slurries by ETVAAS was optimized by Bermejo-Barrera *et al.* (1999). Particle size reduction was achieved with a vibration mill ball equipped with zirconia cups, 20 minutes being sufficient grinding time to achieve an adequate particle diameter ($< 1 \mu\text{m}$). The use of different thickening agents, namely glycerol, Triton X-100 and Viscalex HV30, was studied and glycerol was found to be the best. The use of Pd and $\text{Mg}(\text{NO}_3)_2$ at optimum concentrations of 20 and 25 mg L^{-1} respectively was found to be satisfactory for stabilizing lead at 1100°C . A limit of detection of 0.21 mg kg^{-1} was obtained. The limit of detection can be reduced to 0.05 mg kg^{-1} without loss of analytical performance by increasing four-fold the amount of hair sample.

Accuracy was studied by analysis of a CRM 397 human hair reference material with a certified lead content of $33.0 \pm 1.2 \text{ mg kg}^{-1}$. Standard addition method was used for the determination of lead in hair samples from healthy people, the levels being between 2.3 and 35.5 mg kg^{-1} .

Later, Baralkiewicz and Stepak (2001) determined lead concentrations in lake sediment samples by means of ultrasonic slurry sampling electrothermal atomic absorption spectrometry (USSS-ETAAS). Soil samples were suspended (0.025 – 0.15% w/v slurry) in three different liquid media containing 0.5% v/v nitric acid, 0.5% v/v nitric acid + Triton X-100 and 5% v/v nitric acid + Triton X-100. Effects of instrumental operating conditions and slurry preparation on the signal were examined. Palladium and magnesium were used as modifiers to improve the signal quality. The procedure was validated by analysis of the certified reference lake sediments materials. All analytical recoveries for lead were concluded to be satisfactory and varied from 95% to 104%. Relative standard deviation values were reported as 4.8, 4.7, 4.5 and 5.5. The detection limits (LOD) of lead were obtained as 0.52, 0.45, 0.35 and $0.22 \mu\text{g g}^{-1}$ for sample masses of 0.025, 0.050, 0.10 and 0.15 g respectively.

Felipe-Sotelo *et al.* (2004) developed a new method for cobalt determination in coal fly ash by slurry extraction – electrothermal atomic absorption spectrometry.

Quantitative extraction was obtained from their study with good accuracy (coal fly ash SRM 1633a and SRM 1633b) and precision (RSD < 11.5%). The limit of detection of the method was $0.02 \mu\text{g g}^{-1}$ (100 mg ml⁻¹ slurry), and the characteristic mass was $15 \pm 1.0 \text{ pg}$. The slurry extraction procedure was validated for soil and sediments analysis.

Baralkiewicz and Gramowska (2004) studied the parameters associated with the determination of cadmium in lake sediments by SS-ETAAS. In their study, cadmium concentration in the lake sediments was determined by suspending the solid samples in a solution containing 5% v/v concentrated nitric acid and 0.1% v/v Triton X-100. Three modifiers were tested for direct determination. The furnace temperature programmes and appropriate amount for each modifier were optimized and the highest signal and best separation between the atomic and background signals obtained. Drying was performed by programming 400° C temperature using a ramp time of 25 seconds and hold time of 10 seconds. Ashing was avoided and platform atomization was performed at 2200°C. The best chemical modifier for cadmium determination was W-Rh permanent modifier combined with conventional modifier using 10 μL of 0.05% w/v $\text{NH}_4\text{H}_2\text{PO}_4$ solution. The modifier also acted as liquid medium for slurry and therefore simplified the procedure further. Calibration was performed using aqueous standards ranging from 1 – 5 $\mu\text{g L}^{-1}$. The optimized method gave a detection limit of 0.56 ng mL^{-1} , characteristic mass of $10.1 \pm 0.8 \text{ pg}$ for aqueous standards, $9.6 \pm$

0.7 pg for slurry samples containing different Cd concentrations and good precision (7.6 – 5.2%). The method was validated using four certified reference lake sediment materials: LKSD-1, LKSD-2, LKSD-3 and LKSD-4. Satisfactory recoveries were obtained of between 90.0 – 96.3%. No statistical differences were reported between the experimental and the certified cadmium concentration. The developed method was used to determine cadmium in three sediment samples from lakes in Wielkopolski National Park area in Poland.

Detcheva *et al.* (2002) successfully applied slurry sampling ETAAS to the determination of sodium impurities in single crystals of potassium titanyl phosphate (KTP) and potassium gadolinium tungstate (KGW). Platform atomizers coated with titanium carbide or tungsten carbide, respectively, were used in order to avoid sensitivity drift due to the changes in the composition and the structure of the platform surface. They indicated that calibration curves with aqueous standards could be used for the KGW slurry (no matrix effects); analysis of KTP slurry required the standard additions method. The precision of the proposed method was better than 3% RSD. The results obtained by the method showed a good agreement with those obtained by an independent method-flame atomic absorption spectrometry (AAS) after sample digestion.

Simple and rapid slurry sampling ETAAS method was also developed by Gentscheva *et al.*, (2003) for determination of sodium and iron in single crystals of

rubidium titanyl phosphate (RTP). The finely ground crystal material was dispersed in 5 mL of 0.2% (v/v) HNO₃ containing 0.005% (v/v) Triton X-100. No matrix interference was registered for either of the analytes in slurries containing 4 – 10 mg mL⁻¹ of RTP, which permitted simple calibration against aqueous standards. The precision was about 2% RSD. The results for Na and Fe in RTP were in good agreement with those obtained by flame atomic absorption spectroscopy (AAS) after sample digestion.

SS-ETAAS determination of aluminium and chromium in vegetables using hydrogen peroxide as a matrix modifier was developed by Vinas *et al.* (1995). For suspensions containing 0.1% m/v of ground vegetables, the relative standard deviation (RSD) was about 0.5% for aluminium. For chromium determination, the use of 0.5 – 1.0% suspensions lead to relative standard deviations close to 0.4%. Calibration was done using aqueous standards. The aluminium and chromium contents of a number of vegetable samples obtained by using the slurry approach agreed with those obtained by means of conventional procedure based on the total dissolution of the samples. The reliability of the procedure was also confirmed by analyzing two certified reference materials.

Gonzales *et al.* (1998) applied slurry technique to the determination of Cr, Ni and Co in wheat flour by ETAAS. They concluded that direct slurry sampling is suitable for determination of Cr and Ni in wheat flour samples at levels of 30 – 70

and 150 – 450 ng g⁻¹, respectively, as it provides results similar to those obtained by ashing the sample. However, the typically low levels of Co in these samples precluded its determination by this method (the study was made in a SRM spiked whole meal flour), at least in those samples that were contaminated with elevated levels of metals (> 90 ng of Co g⁻¹ of flour). The method provided a relative standard deviation of 6, 8 and 4% for Ni, Cr and Co respectively.

Slurry sampling with rapid atomization and an open focussed microwave digestion using conventional atomization were compared for determination of Cu, Mn and Ni in an algae matrix by Noorbasha and Sunil (1999). Transverse heated ETAAS with a longitudinal magnetic field was used for the analysis. No significant difference between results obtained by both methods was observed, when the students t-test was applied at 95% confidence level. The limits of detection by rapid slurry atomization were obtained as 1.4, 1.5, 1.3 ng mL⁻¹ while those of microwave digestion were 8.0, 3.6 and 6.5 ng mL⁻¹ for Cu, Mn and Ni, respectively. The process blank in slurry rapid atomization was found to be twice lower for Mn and six times lower for Cu and Ni as compared to open microwave digestion.

Kamogawa *et al.* (2001) applied slurry sampling to direct determination of Cd, Cu and Pb in hair samples using an atomic absorption spectrometer with Zeeman-effect background correction. The samples were pulverized in a freezer/mill for 13

minutes, and hair slurries with 1.0 g L^{-1} for the determination of Cu and Pb, and 5.0 g L^{-1} for the determination of Cd, respectively, were prepared in three different media: 0.1% v/v Triton X-100, $0.14 \text{ mol L}^{-1} \text{ HNO}_3$, and 0.1% v/v of CFA-C, a mixture of tertiary amines. The easiest way to manipulate the hair samples was in CFA-C medium. The optimum pyrolysis and atomization temperatures were established with hair sample slurries spiked with $10 \text{ mg L}^{-1} \text{ Cd}^{2+}$, $30 \text{ mg L}^{-1} \text{ Pb}^{2+}$, and $10 \text{ mg L}^{-1} \text{ Cu}^{2+}$. For Cd and Pb, Pd was used as a chemical modifier, and for Cu no modifier was needed. The analyte addition technique was used for quantification of Cd, Cu, and Pb in hair sample slurries. A reference material (GBW076901) was analyzed, and a paired t-test showed that the results for all elements obtained with the proposed slurry sampling procedure were in agreement at a 95% confidence level with the certified values. The cryogenic grinding was established as an effective strategy to efficiently pulverize hair samples.

Baralkiewicz and Siepak, (2001) applied slurry sampling for determination of Cr, Ni, Pb and Cd in sewage sludge by ETAAS. They optimized graphite furnace temperature program, prepared suspensions in a medium containing 0.5 and 5.0% (v/v) HNO_3 and 0.5 and 5.0 HNO_3 with 0.5% (m/v) glycerol. The prepared suspensions were introduced directly into the furnace. The reliability of the procedure was assessed by analyzing certified reference material, CRM 144R, sewage sludge. The contents of Cr, Ni, Pb and Cd in two sludge samples from Poland (Poznan area) ranged between 1.2 and 7.2 mg kg^{-1} for Cr; 4.5 and 44.9 mg

kg^{-1} for Ni; 0.93 and 103.1 mg kg^{-1} for Pb and 0.28 and 1.65 mg kg^{-1} for Cd. The detection limits were calculated and obtained as 0.087, 0.054, 0.068 and 0.005 mg kg^{-1} for Cr, Ni, Pb and Cd, respectively. The relative standard deviation (RSD) measurements for the slurry sampling method was 2.7 - 4.5% for CRM 144R and 7.1 - 9.4% for sewage sludge from Poland. They concluded that slurry sampling ETAAS provides adequate accuracy and precision for the determination of Cr, Ni, Pb and Cd in sewage sludge, provides a simpler and faster method for trace elements determination than wet digestion and is therefore attractive for routine determination of elements in sewage sludge.

Bermejo-Barrera *et al.* (1997) developed a slurry method for determination of the five metals, As, Cd, Pb, Hg and Sn, by ETAAS in marine sediment slurry. A mixture of Palladium and Magnesium nitrate was used as chemical modifier. Precision and accuracy of the method were investigated using the marine sediment reference material PACS-1 (National Research Council Canada). The detection limits were 44, 0.08, 60, 70 and 57 $\mu\text{g kg}^{-1}$ for As, Cd, Pb, Hg and Sn respectively. Slurry sampling technique was also used effectively for determination of Ni in human scalp hair by the same author (Barmejo-Barrera, et al., 1997). Nickel was determined by ETAAS using D_2 arc background correction combined with chemical modification (magnesium nitrate at 10 mg L^{-1}). Matrix effects were not observed. Aqueous calibration that covered the range 0.8 - 30 $\mu\text{g L}^{-1}$ Ni was found

to be suitable to develop the measurements. A characteristic mass of 22.5 pg was obtained.

A comparative determination of Ba, Cu, Fe, Pd and Zn in tea leaf samples by two atomic spectrometric techniques was studied by Mierzwa *et al.* (1998). At first, ETAAS was applied. The results of Ba and Pb determination were calculated using the method of standard additions, and results of Cu, Fe and Zn from the calibration graphs based on aqueous standards. These results were compared with the results obtained after microwave-assisted wet acid (nitric-hydrochloric-hydrofluoric acids) digestion in closed vessels followed by ICP-OES determinations calibrated using aqueous standards. The accuracy of the studied methods was checked by the use of the certified reference material tea leaves, GBW-07605. The recoveries of the analytes varied in range from 91 to 99% for slurry sampling ETAAS, and from 92.5 to 102% for liquid sampling ICP-OES. The advantages of the SS-ETAAS method used included the simplicity of sample preparation procedure and the very good sensitivity displayed. Slurry sampling ETAAS method was found to be relatively fast. However, for determination of several elements in one sample, microwave-assisted digestion procedure with ICP-OES determination was found to be a shorter method. Amin *et al.* (2003), applied slurry sampling ETAAS for the determination of copper in herbal medicine samples with molybdenum tube atomizer successfully.

SS-ETAAS method for the determination of base metals, Al, Cr, Cu, Fe, K, Li, Mg, Mn and Na, at trace and ultra-trace level in high purity quartz samples was developed by Hauptkorn and Krivian (1996). For their technique, the achievable limits of detection was in the range of 2 (Mg) to 500 (Fe) ng g^{-1} . Thus the method was concluded to be suited for ultra-trace analysis of high purity quartz for microelectronic applications.

Schäffer and Krivan (1996) applied SS-ETAAS to the analysis of graphite powder. A direct method for determination of a number of base metals, Al, Ca, Cr, Cu, Fe, K, Mg, Na, Ni, Pb, Si, Sn and Zn, in graphite powder was developed. The influence of refractory matrix on the atomization behaviour of analyte elements was examined. The method was optimised in respect of slurry preparation, pyrolysis and atomization parameters. Except for Mg and Si, no chemical modification was required. The limits of detection were in the range of 8 – 30 ng g^{-1} for Ca, Mg, Cr, Cu, Na and Zn, between 50 – 200 ng g^{-1} for Al, Fe, Ni, Pb and Sn. For Si, a detection limit of 800 ng g^{-1} was achieved.

Fast heating programs for determination of titanium and tin in soil, sediments and sludge using ETAAS with slurry sampling was developed by Lopez-Garcia *et al.* (2004). The tin and titanium content of a number of samples obtained by using slurry sampling agreed with those obtained by digesting the samples. The reliability of the procedure was also confirmed by the analysis of several certified

reference materials. The same authors also used slurry sampling for determination of silver and gold in soil samples using ETAAS.

A procedure for determining silver and gold in soil and sediment samples using ETAAS was developed by Lopez-Garcia *et al.* (2003). Slurries were prepared from the samples and fast-program methodology was used for the heating cycle. To determine silver, suspensions were prepared by weighing 5 - 200 mg of sample and adding 25 ml of a solution containing 3% v/v concentrated nitric acid, 50% v/v concentrated hydrogen peroxide and 25% v/v concentrated hydrofluoric acid. For gold determination, slurries are prepared by weighing up to 200 mg of sample and then adding 1 mL of concentrated hydrofluoric acid. For both cases, the slurries were submitted to a 10 minutes mild heating stage. After cooling to ambient temperature, the suspensions were introduced directly into the atomizer. No modifier other than hydrofluoric acid and hydrogen peroxide (for silver determination) were required and calibration was carried out using aqueous standards. The detection limits were 0.02 and 0.01 mg kg⁻¹ for silver and gold, respectively.

Cal-Prieto *et al.* (2000) reviewed literature from 1990 to 2000 on slurry sampling for direct analysis of solid materials by ETAAS. They concluded that the determination of trace metals in solid samples has traditionally been performed by acid digestion and subsequent measurement by a suitable instrumental technique.

This dissolution step is time-consuming and it shows important drawbacks. For these reasons, in the past years many efforts have been focused on the direct analysis of solid samples. Among the developed methodologies, slurry sampling-electrothermal atomic absorption spectrometry combines the significant advantages of the solid and liquid sampling methods, and it can be already considered as a mature technique, that is widely utilized for metal determination in both organic and inorganic matrices, even for routine analysis.

2.7.4 Applications in Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES)

Analytical plasma emission spectroscopy has dramatically grown in recent years as a multi-element analysis technique. The analytical advantage of ICP-OES is now widely acknowledged. The excellent performance of the ICP-OES as a multi-element source allows the rapid acquisition of data on samples introduction into the plasma and therefore significantly saves on analysis time. Several procedures have been published for determination of metals by slurry technique using ICP-OES.

Ebdon and Collier, 1988b, developed a simple and rapid method for analysis of whole kaolin samples based on nebulization of slurries into ICP-OES. They discussed the importance of nebulizer design and particle size on transport efficiency. Silicon was used as an internal standard in their study and effectively

corrected for variable atomization efficiencies associated with different particle sizes. The value of dispersants in improving atomization efficiency was demonstrated. Lanthanum was used to correct for the effects of viscosity arising from different slurry concentrations of above 10% m/v.

Varga *et al.* (1996) investigated the colloidal stability of silicon nitride, silicon carbide and boron carbide aqueous slurries used for slurry nebulization ICP-OES in the pH range 2 – 10 by electrophoretic mobility and particle size measurements and sedimentation tests. They concluded that the mean particle size of silicon carbide and silicon nitride suspensions changed with increase of pH showing a maximum at isoelectric points (pH 5.5 and 7.5 respectively).

Ploetgaerts *et al.* (1997) studied the introduction of solid environmental samples as slurry into ICP-OES as an alternative to other techniques. They investigated a number of approaches to improve efficiency of slurry analysis: various preparation modes, study of optimal slurry concentration, optimization of instrumental parameters, modification of spray chamber geometry and introduction of a molecular gas into the plasma. They concluded that easy and efficient routine slurry–ICP-OES analysis could not be reasonably considered for most elements studied.

Merten *et al.* (1997) discussed the purpose, the design principle and the usage of computer software for modelling the evaporation behaviour of particles in ICP-OES. Computer software was developed in FORTRAN 77 language to simulate the evaporation behaviour of particles of refractory materials such as encountered in the analysis of advanced ceramic powders by slurry nebulization ICP-OES. Applications for the evaporation of Al_2O_3 and SiC document the usefulness of the model (for the case of 1.5 kW argon ICP of which the temperature above the load coil has been determined to be 1600 K). The model predicts the maximum particle size of Al_2O_3 and SiC that can be transported to be between 10 – 15 μm and evaporated for a given efficiency under given experimental conditions. For both Al_2O_3 and SiC, two ceramic powders of different grain sizes were investigated. The median particle covered the range typical of ceramic powders.

The use of a low-power ICP (0.65 kW) and a mini-torch (outer tube: 12.6 mm i.d.) for slurry sampling of Al_2O_3 powders was studied by Hyun *et al.*, (1997). In order to find the optimum conditions for mini-torch ICP-OES, the influence of particle size and aerosol gas flow on the signal intensities was studied. The emission intensities obtained with slurries increased as the particle size decreased and maximized in aqueous solution. The intensities obtained with slurries also increased with aerosol flow rate, but were still smaller than those from solution. The intensity difference between particles of size 0.2 - 30 μm and solutions increased with increased aerosol flow rate up to a maximum at 0.8 L min^{-1} .

Dependence of the emission intensity and its relative standard deviation on the pH of the slurries in the mini-torch ICP-OES was also studied. The best signal-to-noise ratio was obtained at pH 3, when the pH of the suspension was varied in the range 1 - 5. The analysis of Japan Ceramic Reference Materials (JCRM 032) Al_2O_3 powders for trace impurities using slurry nebulization under the optimized conditions provided a recovery of > 85% for MgO and Fe_2O_3 and 67% for Na_2O and SiO_2 , with precision of < 4.3% RSD. The analytical results were also compared with those estimated for the same material, using decomposition method in sealed PTFE vessels at high pressure.

Renfrow *et al.* (1997) discussed the direct injection of solids-water slurries into the torch of ICP-OES as a method that offers a quick and easy method for the analysis of major and minor elements in various solids. In their project, aqueous slurries of solids were prepared by wet milling with a stirred-ball slurry attractor's mill and analyzed. Slurries of standard reference materials, prepared in the same way, were used as calibration standards. The best results were obtained with solids having a small particle size (2 - 5 μm) and a close distribution of particle sizes. The average percent relative error for slurry-ICP analysis of most major and minor elements was found to be generally less than 5% for the solids studied.

Marjanovic *et al.* (2004) investigated a simplified generalized standard additions method (GSAM) as an alternative method for the ICP-OES analysis of solid materials, introduced into the plasma in the form of slurries. The method was an

expansion of the conventional standard additions method. It was based on the principle of varying both the sample mass and the amount of standard solution added. The relationship between the sample mass, standard solution added and signal intensity was assumed to be linear. Concentration of the analyte was found either geometrically from the slope of the two-dimensional response plane in a three-dimensional space or mathematically from the ratio of the parameters estimated by multiple linear regressions. The analysis of a series of certified reference materials (cement CRM-BCS No 353, gypsum CRM-GypA and basic slag CRM No 382/I) introduced into the plasma in the form of slurry was described. The slurries contained glycerol and hydrochloric acid and were placed in an ultrasonic bath to ensure good dispersion. “Table curve 3D” software was used to fit the data. Results obtained showed that the method could be successfully applied to the analysis of cement, gypsum and slag samples, without the need to dissolve them. In this way, the use of hazardous chemicals (concentrated acids) could be avoided, incomplete dissolution and loss of some volatiles. The application of the simplified GSAM for the analysis did not require a certified reference material with similar chemical and mineralogical properties for the calibration of the instrument.

Galbacs *et al.* (2000) developed a quick, novel method for tin determination in organotin chemicals by slurry nebulization inductively coupled plasma optical emission spectrometry (ICP-OES). The method was tested by the measurement of

five organotin carboxylate complexes of known composition for obtaining simple stoichiometric data. The slurries were prepared by first dissolving the organotins in an adequate solvent (methanol, pyridine or acetone) well miscible with water and then adding this solution drop-by-drop to a 0.005% TX-100 tenside solution while maintaining intensive mixing. Dynamic laser light scattering experiments showed that the average equivalent particle size in the resulting slurry was ~ 0.3 µm for all samples and solvents. Under suitable ICP-OES measuring conditions, the signal recoveries were found to be between 101.8 and 106.6%, which allowed direct nebulization and calibration against aqueous solutions. Typically, 70 mg L⁻¹ detection limit and 1 - 5% relative standard deviation (RSD) on five replicates was achieved by the method.

Ebdon and Wilkinson, 1987b, applied slurry atomisation to the analysis of aqueous suspensions (10% m/v) of whole powdered coal dispersed in Triton X-100 (1% v/v) using ICP-OES. Coals were powdered to a particle size of less than 30 µm and sprayed into a conventional torch using a high-solids type nebulizer. Slurry atomization results for Cu, Fe, Mn, Ni and V in a range of reference materials and other coal samples were obtained and compared with results obtained by ashing and digestion. Acceptable precision and percentage recoveries were obtained.

A method for the analysis of Ca, Cu, Fe, K, Mg, Mn, Na, P and Zn in infant formulas, milk powders and liquid milk was developed using ICP-OES by McKinstry *et al.*, (1999). Samples were prepared as slurries and determined against aqueous standards following La internal standard compensation for potential matrix effects. The instrument used was radially configured and incorporated a charge-transfer device detector allowing simultaneous acquisition of multi-element and multi-line measurements. Instrument and method performance parameters were estimated for precision, linearity, background equivalent concentrations, detection limits and accuracy. The method was found to be suitable for routine quality control monitoring of infant formulas and milk powders, thereby improving sample throughput and analytical confidence.

Cintia *et al.* (2001) evaluated the feasibility of Portland cement analysis by introduction of slurries in ICP-OES with axial viewing. After a fast manual grinding of the cement samples, owing to the pulverized state of this material, 0.1% m/v slurries were prepared in 1% v/v HCl. Calibration was performed in two ways: based on slurries prepared from different masses (50, 75, 100 and 125 mg) of a Portland certified reference material (NIST SRM 1881) and the other based on aqueous standard solutions. A complete analysis of cement for major (Al, Ca, Mg, Fe and Si), minor and trace elements (Mn, S, P, Sr and Ti) was accomplished. Both strategies led to accurate results except for Si and Ti, for which the

calibration using aqueous solutions produced low recovery values. Paired t-test showed that most results were within a 95% confidence level.

Tianyou *et al.* (2001) developed Fluorination-assisted electro-thermal vaporization-inductively coupled plasma-atomic emission spectrometry (FETV-ICP-OES) for the direct determination of trace amounts of refractory impurity elements in silicon carbide ceramic powders using slurry sampling. Investigations indicated that a poly-tetra-fluoro-ethylene (PTFE) emulsion is a useful fluorinating reagent for the destruction of silicon carbide and simultaneous vaporization of the refractory impurities like B, Mo, Ti, and Zr. The vaporization behaviors of the analytes in slurry and solution were comparatively investigated in the presence of PTFE. The fluorinating vaporization processes and the influence factors for this method were also studied in detail. The experimental results indicated that 80 mg silicon carbide (10 mL of 0.8% (m/v) slurry) could be destroyed and vaporized completely with 600 mg of PTFE under the selected conditions. Calibration was performed using the standard addition method with aqueous standard solutions. The accuracy was checked by comparison of the results with those obtained by solution fluorination-assisted ETV-ICP-AES and pneumatic nebulization (PN)-ICP-AES involving a wet-chemical decomposition of the sample. Detection limits between 0.5 mg g⁻¹ (B) and 0.2 mg g⁻¹ (Mo) were achieved. In most cases, the precision expressed as relative standard deviation (RSD) was better than 8%.

Matusiewicz and Golich (2004) used slurry sampling technique for simultaneous multi-element analysis by micro-wave induced ICP-OES. Slurry samples from a spray chamber were fed directly into the microwave cavity-torch assembly (power 300W) with no desolvation apparatus. The performance of SST-MIP-OES was demonstrated by determination of macro (Na, K, Ca, Mg, P) and trace (Cd, Cu, Mn, Sr, Zn) elements in three biological certified reference materials using V-groove, clog-free Barbington-type nebulizer. The method offered relatively good precision (RSD ranged from 7% to 11%) with measured concentrations being in satisfactory agreement with certified values. The concentrations of Na, K, Ca, Mg, P and Cd, Cu, Mn, Sr, Zn were determined in the range 90 – 22000 $\mu\text{g g}^{-1}$ and 1 – 420 $\mu\text{g g}^{-1}$, respectively.

Mokgalaka *et al.* (2001) evaluated the efficiency of internal standardization by varying the operating conditions of ICP-OES. A method for the determination of Au, Pt, Pd, Ru and Rh in a converter matte sample using ICP-OES with Y or Sc as internal standard was developed. They found that changes in the emission signals of the PGMs due to power variations could be effectively compensated for, using Sc, Y or Ar lines as internal standards. For variations in aerosol gas flow rate, both Sc and Y could only compensate for Pd and Au between flow rates of 0.60 and 0.80 L min^{-1} and for Pt, Ru and Rh at 0.80 L min^{-1} . They also studied the effect of sodium on the determination of Au and PGMs, and the use of Sc and Y as internal standards to compensate for Na matrix effect on accuracy. They concluded that

emission intensities of the analytes decreased with increasing Na concentration and that Sc could compensate for Pt, Ru and Rh up to 5 g L^{-1} Na as an internal standard whereas Y could only compensate for the same elements up to 1 g L^{-1} .

Recently, a new method that involves slurry nebulization ICP-OES analysis and permits accurate estimation of platinum group metals (PGMs) and gold in converter matte was developed by Mokgalaka *et al.* (2004). The method involves reduction of the PGMs and gold with SnCl_2 in concentrated HCl medium by heating on a laboratory hotplate and subsequent filtration of the hot mixture through a $0.45 \text{ }\mu\text{m}$ membrane filter to separate the accompanying base metals. The resulting metallic precipitate of Au and PGMs was quantitatively transferred into a micronizing mill, ground for 30 minutes, diluted to 1000 mL with distilled-de-ionized water, and placed in an ultrasonic bath for 15 minutes to ensure homogeneity. An aliquot of this concentrated slurry was diluted to give a slurry of 0.005% m/v concentration prepared in 5.0% v/v hydrochloric acid and 1.0% m/v Triton X-100 as a dispersant and was directly nebulized into the ICP-OES for the determination of Au, Ir, Pd, Pt, Rh and Ru. The concentrations of Au and PGMs determined using ICP-OES were validated employing the standard additions method and by comparing with literature values that were obtained utilizing reductive separation and conventional dissolution procedure. The method, which allows separation of the PGMs and gold from a complex matrix, offers the advantage of reduced analysis time by approximately 60% and minimized

contamination from additional sample preparation steps involved in the traditional procedure.

2.7.5 Applications in Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)

Inductively coupled plasma-mass spectrometry (ICP-MS) is one of the most sensitive, multi element technique, which is particularly well suited to the determination of metals in trace quantities. An increasingly large number of publications have demonstrated the application of slurry ICP-MS to the determination of metals in a wide range of materials.

Ultrasonic slurry sampling electrothermal vaporization inductively coupled plasma mass spectrometry (USS-ETV-ICP-MS) was applied to the determination of mercury in several fish samples by Ming-Jyh *et al.*, (1997). The effects of instrument operating conditions and slurry preparation on the ion signals were reported. Palladium was used as modifier to delay the vaporization of mercury in this study. As the vaporization behavior of mercury in fish slurry and aqueous solution is quite different, the standard addition method was used for the determination of mercury in reference materials. The detection limit of mercury estimated from the standard addition curve was in the range 0.002 - 0.004 $\mu\text{g g}^{-1}$ for different samples. This method has been applied to the determination of

mercury in dogfish muscle reference material (DORM-1 and DORM-2) and dogfish liver reference material (DOLT-1). Accuracy was better than 4% and precision was better than 7% with the USS-ETV-ICP-MS.

Liao and Jiangu (1999) applied USS-ETV-ID-ICP-MS to the determination of Cd, Hg and Pb in coal fly ash samples. Thioacetamide (TAC) was used as the modifier. Since the sensitivities of the elements studied in coal fly ash slurry and aqueous solution were quite different, isotope dilution method was used for the determination of Cd, Hg and Pb in these coal fly ash samples. The isotope ratios of each element were calculated from the peak areas of each injection peak. This method was applied to the determination of Cd, Hg and Pb in NIST SRM 1633a coal fly ash reference material and a coal fly ash sample collected from Kaohsiung area. Analysis results of reference sample NIST SRM 1633a coal fly ash agreed satisfactorily with the certified values. Precision was better than 6% for most of the determinations and accuracy was better than 4% with the USS-ETV-ID-ICP-MS method. Detection limits estimated from standard addition curves were in the range of 24 - 58, 6 - 28 and 108 - 110 ng g⁻¹ for Cd, Hg and Pb, respectively.

USS-ETV-ICP-MS was also applied by Yi-Ching *et al.* (1998) to the determination of trace metals, Ge, As, Se, Cd and Pb, in plant samples. The influences of instrument operating conditions and slurry preparation on the signals were studied. Since the sensitivities of the elements in various plant slurries were

quite different, standard addition was used. Detection limits of Ge, As, Se, Cd and Pb estimated in different samples from the standard addition curve were in the range 2.1 ± 14 , 3.8 ± 6.5 , 14 ± 18 , 1.8 ± 12 , and $7.8 \pm 18 \text{ ng g}^{-1}$, respectively. This method was applied to the determination of Ge, As, Se, Cd and Pb in tomato leaves reference material (NIST SRM 1573) and a ganoderma sample obtained from the local market. The analysis results of the tomato leaves reference sample agreed with the certified values. Precision was better than 24% for all determinations with the USS-ETV-ICP-MS method.

Coedo *et al.* (1999) used a commercial atomic absorption graphite furnace (AAGF), with a self-made adapter and valve system, as a slurry sampling cell for electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS). The system was applied to the determination of As, Sn, Sb, Se, Te, Bi, Cd, V, Ti and Mo in steelmaking flue dusts. Experimental conditions with respect to ETV and ICP-MS operating parameters were optimized. Compared to aqueous solutions, slurry samples were found to present better analyte transport. Microgram amounts of Rh were used to reduce the difference in analyte response in sensitivity for aqueous solutions of the tested analytes. No such increasing effect was observed for slurry samples and aqueous standards. An added quantity of Rh acting as modifier/carrier resulted in an increase for the same analytes in matrix-slurry solutions, even the addition of an extra Rh quantity resulted in a decrease in the signals. The effect of Triton X-100 used as a dispersant agent on

analyte intensity and precision was also studied. External calibration from aqueous standards spiked with $100 \mu\text{g ml}^{-1}$ Rh was performed to quantify 0.010 g/100 ml slurry samples. Results were presented for a certified reference electrical arc furnace flue dust (EAF): CRM-876-1 (Bureau of Analysis Samples Ltd., Cleveland, UK), a reference sample of coke ashes X-3705 (from AG der Dillinger Huttenwerke, Germany), and a representative sample of EAF flue dust from a Spanish steelmaking company (CENIM-1). For the two reference materials, an acceptable agreement with certificate values was achieved, and the results for the CENIM sample matched those obtained from conventional nebulization solution.

A procedure for the determination of As, Pb, Se and Sn in sediment slurries by electrothermal vaporization inductively coupled plasma mass spectrometry was developed by Dias *et al.*, (2002). The slurry, 1 mg mL^{-1} , was prepared by mixing the sample ground to a particle size $< 50 \mu\text{m}$ with 5% v/v nitric and 1% v/v hydrofluoric acids in an ultrasonic bath. The slurry was homogenized with a constant flow of argon in the auto sampler cup, just before transferring an aliquot to the graphite furnace. The tube was treated with Ru as a permanent modifier, and an optimized mass of 1 mg of NaCl was added as a physical carrier. The pyrolysis temperature was optimized through pyrolysis curves, and a compromised temperature of $800 \text{ }^\circ\text{C}$ was used; the vaporization temperature was $2300 \text{ }^\circ\text{C}$. The effect of different acid concentrations in the slurry on the analyte signal intensities was also evaluated. The accuracy of the method was assured by the analysis of

certified reference sediments MESS-2, PACS-2 and HISS-1 from the National Research Council Canada, SRM 2704 and SRM 1646a from the National Institute of Standards and Technology and RS-4 from a round robin test, using external calibration with aqueous standards prepared in the same medium as the slurries. The obtained concentrations were in agreement with the certified values according to the Student's t-test for a confidence level of 95%. The detection limits in the samples were: 0.17 mg g⁻¹ for As; 0.3 mg g⁻¹ for Pb; 0.05 mg g⁻¹ for Se and 0.28 mg g⁻¹ for Sn. The precision found for the different sediment samples, expressed as RSD was 1 - 8% for As, 2 - 9% for Pb, 6 - 12% for Se and 3 - 8% for Sn (n = 5).

Later, Ribeiro *et al.* (2004) developed a method for determination of trace metals, As, Hg, Sb, Se and Sn, in environmental and in geological reference materials, as acidified slurries, by flow injection (FI) coupled to a hydride generation system (HG) and detection by inductively coupled plasma mass spectrometry (ICP-MS). The HG unit had a gas liquid separator and a drying unit for the generated vapor. The slurries were prepared by two procedures. Approximately 50 mg of the reference material, ground to a particle size < 50 µm, was mixed with acid solutions in an ultrasonic bath. In Procedure A, the medium was a hydrochloric acid solution while in Procedure B; the medium was aqua regia plus a hydrochloric acid solution. The conditions for the slurry formation and the instrumental parameters were optimized. Harsh conditions were used in the slurry

preparation in order to reduce the hydride forming analytes to their lower oxidation states, As (III), Se (IV), Sb (III) and Sn (II), before reacting with sodium tetrahydroborate. To test the accuracy, 10 certified reference materials were analyzed (four sediments, three coals, one coal fly ash and two sewage sludges), with the analyte concentrations mostly in the $\mu\text{g g}^{-1}$ level. Good agreements with the certified values were obtained for Hg, Sb and Sn in the sediments using Procedure A and calibration against aqueous standard solutions. Using Procedure B, good results were obtained for Hg, Se and Sn in the sediment samples, for Se in the coal and coal fly ash samples and for Hg in the sewage sludge samples, also using external calibration with aqueous standard solutions. For As in sediments, coals and coal fly ash, Procedure B and the analyte addition calibration was required, indicating matrix effects. The relative standard deviations were found to be lower than 5%, demonstrating a good precision for slurry analysis. The limits of quantification (10 x the standard deviation; $n = 10$), in the samples, in ng g^{-1} , were: 20 for As, 60 for Hg, 80 for Sb, 200 for Se and 90 for Sn. The method required small amounts of reagents and reduced contamination and losses.

Lu and Jiang (2001) applied USS-ETV-ICP-MS to the determination of Zn, Cd, Tl and Pb in several soil samples. A mixture of 1% m/v EDTA and 1.5% m/v of ascorbic acid was used as the modifier to enhance the ion signals. The influences of instrument operating conditions and slurry preparation on the ion signals were reported. In this study, a relatively low vaporization temperature was used which

separated the analyte from the major matrix components and improved the ion signals significantly. With ETV sample introduction device, spectroscopic and non-spectroscopic interferences were alleviated significantly. Since the sensitivities of Zn, Cd, Tl and Pb in various soil slurries and aqueous solution were different, standard addition method and isotope dilution method were used for the determination of Zn, Cd, Tl and Pb in soil samples. The method was applied to the determination of Zn, Cd, Tl and Pb in NIST SRM 2711 Montana soil reference material and several soil samples collected from Kaohsiung area. The analysis results were found to be in good agreement with the certified values. The precision between sample replicates was found to be better than 9% with USS-ETV-ICP-MS method. Detection limits estimated from standard addition curves were about 260 - 620, 3 - 5, 0.3 - 1 and 9 - 20 ng g⁻¹ for Zn, Cd, Tl and Pb, respectively, in different samples.

Wagner *et al.* (1999) studied the analytical strategy for the evaluation of base metals, iron and copper; distribution in ancient manuscript by slurry sampling graphite furnace atomic absorption spectrometry GFAAS and laser ablation inductively coupled plasma mass spectrometry (LA ICP-MS). The aim of the study was the investigation of ink corrosion in the written area of the ancient manuscript. GFAAS was used to determine the amount of both metals in micro-samples of paper. Determination was based on aqueous standards and the precision using slurry sampling varied in range from 0.8 to 10.0% RSD for iron

and from 0.3 to 7.6% RSD for copper. The content of iron and copper varied significantly between written (32.8 +/- 0.9 mg g⁻¹ of iron, 15.2 +/- 0.5 mg g⁻¹ of copper) and non-written (3.3 +/- 1.3 mg g⁻¹ of iron, 1.6 +/- 0.8 mg g⁻¹ of copper) areas of the investigated manuscript. LA ICP-MS was used to define the distribution patterns of iron and copper on the surface of the manuscript.

Ultrasonic slurry sampling electrothermal vaporization isotope dilution inductively coupled plasma mass spectrometry (USS-ETV-ID-ICP-MS) was applied to the determination of base metals, Cu, Zn, Cd and Pb, in several fish reference samples by Yi-Ching and Shiu-Jen (1998). NH₄NO₃ was added to the sample solution to work as a modifier. Since the sensitivity of the elements studied in fish slurry and aqueous solution was quite different, isotope dilution was used for the determination of Cu, Zn, Cd and Pb in reference samples. The influences of instrument operating conditions, slurry preparation, non-spectroscopic and spectroscopic interferences on the ion signals and accuracy and precision of isotope ratio determination were reported. The isotope ratios of each element were calculated from the peak areas of each injection peak. Precision of isotope ratio determination was better than 6%. This method was applied to the determination of Cu, Zn, Cd and Pb in dogfish muscle reference material (DORM-2), dogfish liver reference material (DOLT-1) and oyster tissue (NIST SRM 1566a). Accuracy was better than 19% and precision was better than 14% with ultrasonic slurry sampling and electrothermal vaporization isotope dilution inductively coupled

plasma mass spectrometry. Detection limits estimated from standard addition curves were in the range of 5 – 50, 200 – 500, 8 – 20 and 20 – 50 ng g⁻¹ for Cu, Zn, Cd and Pb, respectively, in different samples.

Totland *et al.* (1992), determined slurry PGMs and gold in solid samples by slurry nebulization ICP-MS. Samples were ground to < 5 µg using Zr beads in polypropylene bottles. Tetrasodium pyrophosphate was used as the dispersant. Modified instrumental conditions included increased forward power and nebulizer flow rate and the use of a 3 mm torch injector tube. Calibration was done using a blank and tetrasodium pyrophosphate spiked with appropriate amounts of standards. The limits of detection for the method were obtained as 0.04–0.2 µg g⁻¹ in samples. Reproducibility was obtained as 2 - 30% relative standard deviation for most materials. Analytical accuracy was assessed by comparing the slurry results with reference concentration. The method was concluded to offer a means for rapid determination of the precious metals in mineral concentrates, PGMs ores and allied industrial materials.

2.8 SLURRY RHEOLOGY

A number of investigations have been done on the dependency of analytical accuracy upon the particle size distribution (PDS) of slurry and attempts have been made to deconvolute atomization interferences from transport effects. McCurdy and Fry (1986) examined the determination of sulphur in coal using slurry

nebulization direct current plasma optical emission spectroscopy (DCP-OES) and ICP-OES (1985). Their treatment of comparative slurry/aerosol transport assumed that the aerosol size distribution (ASD) exiting a spray chamber was indicative of the aerodynamic properties of that spray chamber. For slurry to be transported as effectively as a solution, its particle size distribution must lie within the ASD of the aerosol exiting the spray chamber. This PSD was modified according to Stokes' law to account for density differences between slurry and the calibration solution. Transport efficiencies through a horn-type spray chamber were estimated with the impact bead in place (89%) and removed (94%) for coal slurry with a particle size distribution of $d_{50} = 6.9 \mu\text{m}$ and $d_{90} = 15.8 \mu\text{m}$. Analytical recoveries were obtained as 56% and 65%, respectively, yielding atomization efficiencies of 66% and 69%, respectively. This was with the assumption that the slurry was homogeneous. The model's applicability to heterogeneous materials like coal may not be viable because analytes may be concentrated in phases with PSD and densities very different to those assumed for the bulk slurry and therefore transportable fractions cannot be estimated for these specific analytes.

Saba *et al.* (1981) studied transport efficiencies of iron particles through a number of spray chambers commonly used for either DCP or ICP spectrometry. This was the first in-depth study to distinguish quantitatively between the ability of a sample introduction system to transfer large particles and the ability to transfer as efficiently as a calibrant solution (Goodall *et al.*, 1993). Iron particles were

classified into broad size bands by centrifugation and sedimentation before suspension in base ester oil. The maximum size of an iron particle that could pass through a standard DCP spray chamber was obtained as 17 μm . 14 μm particle was obtained for a single pass, cylindrical spray chamber with baffle (ICP spectroscopy). Transport efficiency decreased as particle size increased, a $<10 \mu\text{m}$ fraction was transported only 59% as efficiently as a $< 1 \mu\text{m}$ fraction.

Fractionation of analyte-rich phases was demonstrated convincingly by Ebdon *et al.* (1988). Determination of iron in sulphide ores was investigated and low recoveries were observed. From the analysis done on the aerosol leaving the sample introduction system, the low recovery of iron from the sulphide ore could be attributed to preferential rejection of an iron-rich phase. Transport properties of alumina and silica slurries were also examined. A sample introduction system consisting of a high solids V-groove nebulizer, Scott-type double pass spray chamber and a 3 mm in diameter injector rejected all alumina particles of $> 5 \mu\text{m}$. Recoveries versus aqueous calibration showed a clear particle size distribution (PSD) dependency.

An integration of these studies suggests that accurate analyses by slurry nebulization ICP-OES requires a slurry whose PSD is 100% (by volume) $< 5 \mu\text{m}$ and possibly the bulk $< 3 \mu\text{m}$.

Atomization and transportation effects were further investigated. Silica-based SCX ion exchange materials of known particle size (10 μm and 5 μm), which had been completely converted to the magnesium form were used. It was assumed that the recovery of silica would be indicative of atomization whilst that of magnesium would be mainly dependent upon transport effects. Atomization and transport efficiencies of 20 - 25% and 3 - 4%, respectively, were estimated for a 10 μm particle, whilst values of 60 - 70% and 14 - 15%, respectively, estimated for a 5 μm particle.

Raeymaekers *et al.* (1988) studied the transport properties of slurries of refractory oxide powders. A GMK Babington Nebulizer with impact bead/single pass spray chamber was used. The droplet size distributions of slurries of alumina (1% m/v Al_2O_3) and solution (0.8% m/v Zr) exiting from this sample introduction system were measured using a cascade impactor. A 10 mL bore injector was employed to direct the aerosol droplets to the impactor. Droplet volume fraction distribution showed peak values in the 5 μm diameter size range for argon carrier gas flow rates of 0.6 – 1.0 L min^{-1} . Nebulizer efficiencies were found to be dependent on the carrier gas flow rate and the presence or absence of an impact bead. Values for the transport efficiency between 0.13 and 0.66% were obtained for solutions and slurries.

Van Borm *et al.* (1991) studied droplet size distributions, analyte transport efficiencies and analyte mass transfer rates of slurries and solutions with high dissolved solids content at different sample aspiration rates using a GMK nebulizer with impact bead, spray chamber and cascade impactor assembly as previously described. Differences between high dissolved solids solutions and slurry aerosols were observed under certain measurement conditions, such as variations of liquid flow rate, slurry standard addition and the presence of an impact bead. It was concluded that the use of simple aqueous standard solutions to obtain calibration in slurry nebulization ICP spectrometry was limited by fundamental differences in aerosol production processes for pure solution droplets and droplets containing particulate matter.

Goodall *et al.* (1999) examined how the particle size distribution of the slurry affects analytical accuracy and precision in slurry nebulization ICP-OES. An empirical upper diameter for the particle size distribution of slurry of 2.0 - 2.5 μm was derived from the analysis of a range of slurries possessing different size distributions. A model for slurry particle transport was suggested that gives good agreement with experimental data. The model assumes that for arbitrarily defined but realistic standard slurry, the maximum allowable particle size is that which allows the occupation of every aerosol droplet by one solid particle – the single occupancy diameter. Theoretical considerations and empirical data suggest that for accurate analyses by slurry nebulization, the particle size distribution of the slurry

should not exceed a value determined by density, of 2.9 μm for a material of density 1g cm^{-3} falling to 1.5 μm for a material of density 7 g cm^{-3} . Certain carbonaceous materials were shown to be susceptible to micro-flocculation, resulting in 5 - 10 member assemblies formed from primary particles.

This constraint on particle size may be seen as the fundamental limitation upon slurry nebulization with direct calibration with simple aqueous solutions. The advent of new approaches to sample grinding may allow more rapid preparation of samples. The use of desolvation devices to provide additional aerosol processing is still under investigation.

An often ignored property of slurry, the degree of dispersion of the solid within the liquid, was shown to be an important limiting factor in slurry nebulization ICP spectrometry, with micro-flocculation of very fine primary solid particles leading to reduced analytical accuracy. This can be overcome by increasing the concentration of surfactant in the aqueous dispersant allowing the successful determination of a number of analytes in a variety of environmental certified reference materials.

It is evident that sample preparation steps are of paramount importance to ensure a good quality of analytical results. The introduction of slurry samples by pneumatic nebulization devices has revealed some critical aspects. Problems associated with

sample introduction into ICP are completely different from those observed using GF-AAS techniques where the whole sample introduced is volatilized during the atomization step. In the ICP-OES analysis, only a little part of the sample reaches the plasma due to low nebulization efficiency. Slurry transport may be considered to be most efficient where every aerosol droplet is occupied by a solid particle representative of the bulk, determined by the solid's density and aerosol size distribution (Ebdon *et al.*, 1995). If this condition is achieved, then aqueous standards may be used for calibration.

Aerosols formed from solutions and slurries do not have the same behaviour in plasma where the sample is only present for a limited residence time of several milliseconds. Consequently, the time necessary for the energy transfer between the plasma and the sample is reduced. Direct analysis of slurries using ICP-OES may then be influenced by errors if the efficiency of volatilization, emission and ionization processes depends on the particle size. It is also expected that the transport efficiency of small particles in a gas or liquid stream will be better than for larger particles. With such size discrimination, the fraction transported to the plasma may be insufficiently representative of the actual sample composition. Measurement errors may also be expected if the emission intensity resulting from a constant mass of the analyte depends on the size, form and density of transported particles. These errors may result from incomplete evaporation and excitation of large particles (Ploetgaerts *et al.*, 1997).

The poor characteristics of pneumatic nebulization devices in slurry analysis and short residence time of species in the plasma are responsible for size segregation of particles and their incomplete dissociation. This results in a suppression of emission signals and consequently in poor recoveries when a simple calibration against aqueous standards is applied.