

CHAPTER 1: INTRODUCTION

1.1 GENERAL INTRODUCTION

Analytical methods development and its application for study of elements form the basis for determination and understanding of metals. Accurate determination of metals, especially PGMs and gold, has always been a difficult task. The metals are often present at trace levels in sample of complex matrix. 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, industrial and biological 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 determination of the metals in various matrices with satisfactory sensitivity, selectivity and reliability have resulted in the development of a number of methods. Spectrometric techniques, ultra-violet visible spectrometry (UV-VIS), atomic absorption spectrometry (both flame (FAAS) and graphite furnace (GFAAS) techniques, inductively coupled plasma combined with optical emission spectrometry (ICP-OES) or mass spectrometry (ICP-MS), are widely applied in the determination of noble metals and base metals over a large range of concentrations (Balcerzak, 2002).

Of all the techniques, inductively coupled plasma-optical emission spectrometry is a sensitive, multi-element technique which is particularly well suited to the determination of platinum group metals (Pt, Pd, Rh, Ru, Ir and Os), gold and base metals. The excellent performance of the ICP-OES in determining multiple element concentrations simultaneously allows the rapid acquisition of data from samples. This has focused attention on sample preparation as the most time consuming step in the analytical procedure. In particular, bringing solid samples into solution (acid digestion and alkali fusions) may not only be tedious and time consuming but may also involve the use of hazardous chemicals, and possibly introduce errors from contamination or incomplete dissolution.

Solid sample introduction into the plasma would clearly circumvent many of these problems. A number of studies have investigated different approaches to solid sample introduction. A comprehensive review by Langmyhr (1978) described various approaches to the direct analysis of solid samples using spectrometric techniques. In recent years, slurry sampling has surpassed other solid sampling techniques like arc nebulization and laser ablation: it combines the advantages of both liquid and solid sampling and offers many advantages over the conventional techniques in terms of shortening sample preparation time, simplicity and small reagent consumption, reduced risk of sample contamination and reduced risk of loss of volatile samples like ruthenium and osmium in the case of PGMs determination. A very important advantage is the possibility of using aqueous

solutions for quantitative calibration. Recently, it has been demonstrated that torches (Ebdon *et al.*, 1980) and nebulizers (Ebdon and Cave, 1982) for ICP-OES can be designed and optimized for improved accuracy and precision in slurry analysis.

In addition, increasingly large numbers of industrial, environmental and biological samples analyzed in laboratories for simultaneous determination of major, minor and trace elements constituents make the development of ‘preparation free’ methods of analysis extremely important from the stand point of cost per analysis, speed, sample consumption, convenience and freedom from reagent contamination. This study therefore focuses on the development of slurry nebulization ICP-OES method for determination of PGMs, gold and base metals in different matrices for quick monitoring of their concentrations.

1.2 BACKGROUND OF THE STUDY

1.2.1 Definition of Slurry

Slurry may be defined as a uniform suspension of fine particles, which is sufficiently fluid to flow viscously (Totland *et al.*, 1993). If the viscosity of the slurry is low, its behavior in the spray chamber, torch and plasma will be similar to that of an aqueous solution. This similarity should allow synthetic aqueous standards to be used, thereby overcoming calibration problems experienced in solid sample analysis (Totland *et al.*, 1992). The validity of using aqueous calibration therefore depends critically on particle size, nature of the sample, nebulizer - spray chamber design, and ICP-OES operating conditions. The viability of slurry nebulization therefore relies heavily on the ability to prepare samples of fine particle size in a reproducible manner. Clearly, a highly efficient grinding method is essential if particle size reduction is to be accomplished within a reasonable amount of time.

1.2.2 Slurry method and conventional analytical procedures

Conventional analytical procedures for determination of PGMs, gold and base metals by ICP-OES involve preparation and analysis of sample solutions. However, the requirement for a dissolution step has a number of disadvantages. Acid digestions are known to result in incomplete dissolution of some metals like PGMs especially if they are present in the sample as native metal (Beamish, 1966)

and acid attacks may also not totally dissolve other refractory phases (Totland *et al.*, 1992), including many PGM minerals (Jackson *et al.*, 1990).

Alkali fusions may be employed to ensure complete digestion of samples but relatively large amounts of flux are required, which increases the possibility of contamination from reagents and also necessitates further dilution of samples before analysis. Such dilutions raise considerably the lower concentration limit that can be quantified by the entire procedure (Totland *et al.*, 1993). Subsequent chemical separation of the PGMs and gold from their matrix using tellurium co-precipitation or ion exchange procedures (Sen Gupta and Gregoire, 1992) may overcome this limitation, but add sufficiently to preparation times and lead to the partial loss of some analytes. In both acid digestion and fusion methods, particular care must be taken to ensure that osmium, and to a lesser extent ruthenium, are not lost from the sample as volatile tetroxides (OsO_4 , RuO_4) (Totland *et al.*, 1993). A separate preparation procedure involving distillation is typically recommended (Van Loon and Barefoot, 1991) for accurate determination of osmium.

Fire assay, the method most commonly used to concentrate the PGMs (Van Loon and Barefoot, 1991), is a complex procedure requiring experienced staff and specialized equipment. The large amount of flux added to samples during fire assay introduces contamination and necessitates the use of subsequent wet chemical techniques to further separate and pre-concentrate the PGMs prior to

analysis. Such procedures may also lead to analyte losses. Nonetheless, fire assay remains the industry-standard method for precious-metal determination, favored for its ability to deal with large sample masses (25 – 60 g), which reduce mineral heterogeneity ('nugget') effects. The method is also amenable to a range of analytical finishes, including Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES), Inductively Coupled Plasma – Mass Spectrometer (ICP-MS), Atomic Absorption Spectroscopy (AAS) and Instrumental Neutron Activation Analysis (INAA), which provide ng g^{-1} limits of determination (Totland *et al.*, 1993).

Sample digestion and fusion methods are time-consuming, labour intensive and require stringent safety precautions, and generally represent a bottleneck in quick metal determination. An analytical method that permits direct analysis of solids would clearly have many advantages. Minimal sample handling, reduced sources of contamination, lower reagent blank levels, the retention of volatile species and fewer requirements for special equipment would contribute to significant analytical gains. Sample dilution may also be reduced compared to fusion methods, thus taking better advantage of the inherent sensitivity of ICP-OES.

The methods for direct analysis of solids are by solid sampling. A number of different methods of solid sample introduction exist. These include laser ablation, slurry nebulization, electrothermal vapourization, direct sample insertion,

powdered solids introduction and arc nebulization. A detailed review of these procedures is given in Jarvis, K.E. (1992).

However, there are a number of potential difficulties when undertaking the direct analysis of solids. Obtaining a homogeneous sample from an originally heterogeneous material may be difficult, even when the sample is reduced to a very small particle size. Rock samples are particularly problematic since they are composed of a variety of minerals that generally have widely different grain size, hardness and friability. Fractionation can easily occur during transport of the dispersed solid sample into ICP-OES (Ebdon and Collier, 1988a), resulting in poor analytical data for samples in which composition varies with particle size. Calibration in solid analysis may be a problem; in most cases, a standard with a similar matrix and chemical form to the sample is necessary to obtain fully quantitative data.

Low masses need to be weighed for replicates in direct solid sampling and this increases the dilution, in addition to the high cost required especially for laser ablation technique. On the other hand, for slurry sampling, the replicates can be performed from one slurry sample. The slurry method is also better suited to analysis of concentrated analytes as it is easier to dilute the slurry than it is to dilute the solid (to dilute the solid, graphite is added, but this increases the blank value, and modifies the thermal behavior of the sample). Besides, aqueous solution

calibration and standard addition calibration have successfully been used for slurries (Silva *et al.*, 2002, Renfrow *et al.*, 1997 and Ramsey and Coles, 1992).

The slurry method is not without its own difficulties, however. The stability of the slurry needs to be maintained until injection of the sample; it is sometimes difficult to obtain reproducible samples; there is a lack of precision if the slurry is highly diluted and some analytes may remain trapped in the solid part of the sample, allowing only a partial release.

From these limitations of slurry analysis it is evident that 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 by controlling several variables to establish the appropriate experimental conditions to obtain better precision and accuracy.

1.3 OBJECTIVES OF THE STUDY

The key aim of this study is to develop a slurry nebulization ICP-OES method for determination of PGMs, gold and base metals in different matrices with a focus on quick monitoring of metal concentrations, reducing analysis time and minimizing analytical costs.

The objectives of this study were:

1. To develop a method for sample introduction in the form of slurry.
2. To optimize the method for application for quick monitoring of metals in varied matrices.
3. To apply the method in the practical analysis of mineral and biological samples.

1.4 SCOPE OF THE STUDY

The scope of this study was defined as outlined below based on the background and the objectives of the study (figure 1.1):

1. Particle size distribution - the form in which the samples have to be analyzed to obtain rapid and satisfactory results using direct calibration procedures against

aqueous standards. Emphasis has to be put on efficient grinding of the particles within the shortest time possible to minimize sample preparation time and to obtain the required particles sizes and distribution.

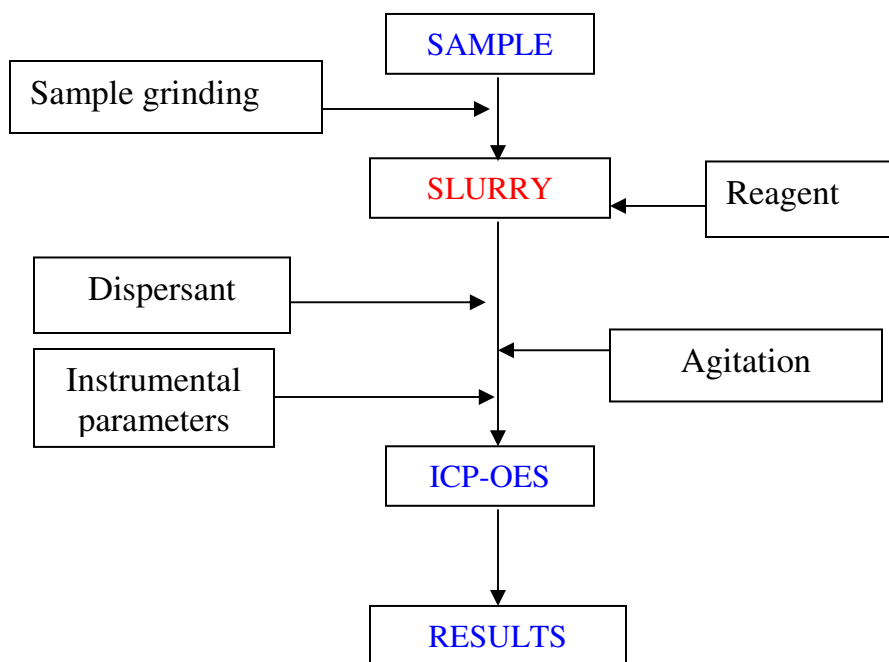


Figure 1.1 Experimental scheme of slurry nebulization ICP-OES

2. Slurry reagent and homogenization system - possible chemical interventions on the sample to improve analyte partitioning, accuracy and precision of measurements. The slurry procedure used for sample preparation should be simple and rapid to realize. A dispersant to keep especially the high density PGMs and gold particles as well as the base metals homogeneously distributed in solution coupled with a homogenization system for continuous agitation of the slurry to

prevent sedimentation after sample preparation and during sample aspiration into ICP-OES are necessary.

3. Spray chamber–torch design - modification of the spray chamber design to improve the volatilization and dissociation efficiency of solid particles by increasing the particles residence time in the plasma as well as improving the elimination of larger particles and sample droplets by gravitational sieving.

4. Optimization of essential ICP-OES parameters based on the analytical response on introduction of slurry sample (RF-power, nebulization pressure, coolant gas flow, auxiliary gas flow, sample intake rate and spray chamber geometry) is necessary for good analytical results assessed by analytical figures of merit (accuracy, precision, sensitivity, robustness and percentage recovery).

5. Application of the method to the analyses of samples.

These conditions provides an efficient guide towards realizing a reduction in sample preparation time, lowering reagent blank levels, reducing sources of contamination, retaining volatile species, limiting the requirement for specialized equipments and thus ensuring a simple, cheap and quick method for monitoring of metal concentrations with good analytical results.