

CHAPTER 7: CONCLUSION

Increasingly large numbers of environmental, industrial 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 sample or analysis, speed, sample consumption, convenience and freedom from reagent contamination. In this study, a modified slurry nebulization ICP-OES procedure has been successfully developed for quick, accurate and precise quantitative determination of Pt, Pd, Rh, Ru and Au as well as base metals, Ni, Cu, Fe and Co in varied matrices (mineral and organic).

In this method reduced sample grinding time has been accomplished from 960 minutes [16 hours] to 30 minutes thus reducing sample preparation time by 97% to obtain particles size distribution to less than 5 μm (> 60%) and 10 μm (> 80%) by grinding of a dry sample mass. This is a significant improvement because sample grinding or milling constitutes the biggest percentage of sample preparation time in slurry analysis and a substantial reduction in sample preparation time was achieved. It also allowed for aqueous solution to be used successfully for calibration. This was important to guarantee a uniform suspension of fine particles of low viscosity (similar to that of water) to ensure similar behavior in the spray

chamber, torch and plasma by both the calibration standards and the slurry solution.

An optimal slurry concentration of 0.2% m/v^{-1} was used in this method and was established on the basis of the mean analyte content in the samples, the need to ensure representative sampling and the detection limit of ICP-OES instrument. An overly high slurry concentration results in clogging of the sample introduction system and also in a more difficult dissociation of large number of particles in the excitation source. On the other hand, an excessively dilute slurry concentration may compromise the detection of analytes of low concentration in the sample.

Reagent-dispersant media contribute considerably to accuracy and precision of a method. In this method, good results were obtained using aqua regia-Triton X-100 reagent-dispersant media. The optimum concentration of the dispersant used was 0.1% v/v for a 0.2% m/v slurry solution. The use of a second reagent-dispersant medium, thiocyanate, was also studied. This is the first documented study that involves the use of cyanide and thiocyanate as reagent-dispersant medium in preparing slurry solutions. It produced good results with slightly better precisions than aqua regia reagent-dispersant medium. However, aqua regia yielded better accuracy as well as good precisions especially for platinum and palladium. Aqua regia was therefore the best dispersant-reagent medium for the method and was matched in samples, standards and blank solutions during metal determinations.

A novel extension elbow introduced between the spray chamber and the torch has been designed and successfully used in this method. This extension required very minimal adjustments in the ICP-OES sample introduction system. An increase in residence time of the sample in the plasma was achieved by the introduction of this elbow due to the increase in cross-sectional area or path length resulting into a decrease in linear velocity of the sample for better atomization efficiency. In addition, gravitational sieving out of the large particles was attained. This has been applied in the new ICP-OES model, Spectro Genesis, Vision 1.0.

A higher ICP-OES plasma power input, in this case 1600W for PGMs and gold and 1450W for base metals, was optimized for use in this method to ensure higher plasma temperature for excitation of solid particles. Other important parameter that were optimized to account for this adjustments for good results by this method included coolant gas flow (13.0 mL min^{-1}), nebulizer gas flow (0.8 mL min^{-1}), sample uptake rate (2.0 mm min^{-1}) and torch position (table 6.14).

One serious limitation of slurry sampling is the lack of suitable slurry standards. In this method, aqueous standards have been successfully used for method calibration. Standard addition calibration technique was used to validate the use of aqueous standards and no significant deviation between the two calibration modes was noted. This certified the use of aqueous standards in this method as valid and

good regression coefficients were obtained by this method for all the metals (table 6.18).

Assessing it against analytical figures of merit that include accuracy, precision, limit of detection/quantitation, robustness and percentage recoveries validated this method. The limits of detection that can confidently be quantified by this method range between 0.035 - 0.237 $\mu\text{g g}^{-1}$ for precious metals and 0.15 - 0.5 $\mu\text{g g}^{-1}$ for base metals. Good precisions (< 11% RSD) and accuracy were realized with this method for PGMs, gold and base metals. Good percentage recoveries of a range of 75% - 100% were obtained by this method for most metals. The method was applied across samples of different matrices from minerals (concentrates) to organics (grass, lichens, leaves and tree trunk) and metal concentrations determined successfully proving its robustness.

One limitation of this method is background concentrations due to accumulation of sample particles in the sample delivery system especially when aspirating a large number of samples. Proper rinsing of the delivery system using dilute acid after each sample with a blank solution was used to minimize this effect. Internal standards can also be used for this purpose.

In conclusion, this slurry nebulization ICP-OES method provides an exciting tool for quick analysis and monitoring of metal concentrations. Rapid quantification of

precious metals and base metals in mineral concentrates or separates in a variety of industrial materials as well as in environmental or biological materials was achieved. The method displays significant advantages over other analytical procedures available for the precious metals, particularly where lengthy sample preparation procedures are required like wet acid digestion and nickel sulfide fire assay technique. The absence of a dissolution step in this method helps circumvent the problems of incomplete digestion of refractory minerals and/or the loss of volatile metals like osmium and ruthenium. The small sample sizes of 0.2 g necessitate a high degree of homogenization during the initial stages of sample preparation. Adequate homogeneity might be difficult to achieve for some samples like geological materials. However, the analysis of multiple slurry preparations would readily circumvent this.

The simplicity and low cost of sample preparation used in this method enables it to be easily adopted in any ICP-OES laboratory. A single analyst may achieve more sample through-puts than before per day (including re-grinding and analysis), resulting in a highly economical and rapid method for precious metals and base metals determination for controlling production of materials like concentrates, for monitoring of pollution using organic samples as bioindicators and environmental risk assessment of wastes and dust.