

CHAPTER 5: EXPERIMENTAL

5.1 INTRODUCTION

This chapter outlines the various chemical reagents, the stock solutions and standards, instrumentation and experimental procedures that were used in this study.

5.2 REAGENTS

All reagents used were prepared from analytical grade chemicals. For wet digestion of samples, nitric acid (HNO_3), hydrochloric acid (HCl) and hydrofluoric acid (HF) supplied by German company Merck were used. Triton X-100 (Merck, Germany), tetrasodium pyrophosphate (Saarchem, South Africa), dodecylbenzenesulfonic acid sodium salt (Saarchem, South Africa), potassium cyanide (Saarchem, South Africa) and potassium thiocyanate (Sigma-aldrich, Germany) used for dispersion of particles in slurry solution were of suprapure grade. Potassium thiocyanate is less toxic than potassium cyanide and is produced from cyanide by the addition reaction of sulfur. All solutions were prepared in deionized water, distilled and passed through a Milli-Q water purification system from Millipore, Milford, MA, USA.

5.3 STOCK SOLUTIONS AND STANDARDS

Standard solutions were prepared from Specpure chemicals (Johnson Matthey) stock solutions of 10 ug L^{-1} . The spectrometer was calibrated for Au, Pt, Pd, Ru, Rh and Ir using six standard solutions diluted from the stock solutions in a concentration range selected to cover the full range of the metals in the PGMs and gold concentrates. Similarly, for base metals, stock solutions (specpure, Johnson Matthey) were prepared to cover the full range of Ni, Cu, Fe and Co for the concentrates and the samples. All solutions were prepared in deionized water; distilled and purified through a Milli-Q water purification system from Millipore, Milford, MA, USA. Standard solutions were prepared on a weekly basis. Both stock solutions and standards were kept in the refrigerator at 4°C and were stable for several months at this temperature.

5.4 INSTRUMENTATION

Fritsch GmbH Planetary mono mill “pulverisette 6” from Fritsch GmbH, Germany, was used for grinding, mixing and homogenizing materials. Zirconium dioxide (95% ZrO) bowls and balls of density 5.7 g cm^{-3} bowls were used. The grinding bowls and grinding balls of Zirconium dioxide were used because they are resistant to acids with the exception of hydrofluoric acid.

The particle size distributions were measured using Malvern Mastersizer S (long bench) instrument from Malvern Instruments GmbH, Harrenberg, Germany, with

a particulates quantification range of 0.05 μm to 900 μm . Measurements of particle size distribution were done at Anglo Platinum Research Laboratories, Johannesburg, South Africa.

Multiwave 3000 digestion instrument (Anton Paar GmbH, Vienna, Australia) with a 1400 W microwave power output via two magnetrons that ensures fast and direct heating, non-pulsed microwave power over the whole range for precise control of critical reactions and a Rotor 6MF100 was used. This system was equipped with a reliable pressure and temperature sensor for enhanced reaction control and safety. The reaction vessels used were made of quartz or fluoropolymers that can accommodate a temperature working range from 0°C to 300°C.

Spectro Ciros Inductively Coupled Plasma–Optical Emission spectrometer (ICP-OES) with a radial mode of viewing and a coupled charge detector (CCD) was used to determine the total metal concentrations. This system was equipped with a 40 MHz free running solid-state generator. A Fassel-type demountable quartz torch (Spectro, Kleve, Germany) was used with a 2.0 mm in diameter injector tube. A Babington nebulizer with a water cooled single pass spray chamber maintained at 4°C was used. The carrier gas used was UHP grade argon gas from Afrox, South Africa.

5.5 EXPERIMENTAL PROCEDURES

The experimental procedure used in solid sample introduction by slurry nebulization ICP-OES was divided into two broad sections, namely, slurry sample preparation and optimization of instrumental parameters. Slurry sample preparation involved grinding of the sample, identification of the best reagent and dispersant and agitation of the slurry solution before aspiration into ICP-OES. Optimization of instrumental parameters included the modification of the spray chamber-torch design, calibration of the instrument and adjustment of the instrumental operating parameters to obtain the best signal to background ratios for detection of the analytes.

5.5.1 Wet acid digestion procedure

0.25 g of each dried sample was weighed and placed into the reaction vessels with 5 mL HNO₃, 5 mL HF and 0.5 mL HCl and decomposition carried out for 45 minutes. The mineralized samples were placed in a 100 mL volumetric flask and topped up to the mark with deionized water. A pressure rate of 0.5 bars/second at a pressure of 20 bars and infra red radiation of 180° C was used for digestion.

5.5.1 Nickel sulfide fire assay technique (NiS-FA)

The samples were fused with nickel, sulfur, Na₂B₄O₇, Na₂CO₃ and SiO₂ in a clay crucible at 1000°C. 2.5 g buttons (20 g samples) were used for full recovery of the metals. The nickel sulfide (NiS) bead formed was separated from the slag, crushed

and then dissolved in hydrochloric acid. The matrix elements were removed under an HCl treatment. The insoluble precious metal sulfides were filtered and dissolved in HNO₃ and HCl. Losses of the metals, especially of platinum and palladium, during the NiS button dissolution step were minimized by the application of co-precipitation with tellurium.

5.5.3 Slurry sample preparation procedure

0.2 g of the ground mass of each sample was weighed into a grinding bowl; 5 ml of freshly prepared aqua regia was added and mixed well for 15 minutes in the grinder (Fritsch GmbH Mono Mill ‘Pulverisette 6’). The slurry was quantitatively transferred into a 100 ml volumetric flask and topped up to the mark with 0.1% v/v Triton-X 100 dispersant. The prepared slurry was shaken and put into a water bath for agitation ready for aspiration into ICP-OES.

For slurry preparation using thiocyanate (SCN⁻) reagent-dispersant, 2.0 g of the ground mass of each sample was weighed and quantitatively transferred into a 100 ml volumetric flask. 0.3% m/v potassium thiocyanate was added to the flask and made up to the mark with deionized water. The prepared slurry was shaken and put into ultrasonic water bath for agitation before aspiration into ICP-OES. Acids should not be used with cyanide to avoid the generation of toxic hydrogen cyanide gas.