CHAPTER 5

THE QUANTITATIVE DETERMINATION OF THE PLATINUM GROUP ELEMENTS AND GOLD IN A CERTIFIED REFERENCE MATERIAL

5.1 Introduction

In order to assess the validity of the ICP-MS methods developed in chapter 3 it was decided to analyse a certified reference material for its content of the platinum group elements and gold. It was decided to analyse the certified reference material SARM 7 because it has certified values for all the platinum group elements and gold. The platinum group elements and gold will be extracted by means of the lead fire assay technique and the resulting prills will be dissolved and analysed by means of the ICP-MS methods as developed in chapter 3. The results obtained will also be discussed and compared to those of other researchers who employed similar techniques in the analysis of the material, SARM 7.

Certified reference materials are normally used to assess the accuracy, precision and detection limits of analytical methods. In this study the author unfortunately had very limited access to a fire assay laboratory, i.e. only four samples and a blank could be sent for analysis. Three more samples were sent to a commercial fire assay laboratory for analysis. Furthermore, the fire assay analysis was performed by laboratory assistants and not by the author herself. Due to the small number of results it was not possible to perform statistical analysis in order to assess the precision and determine detection limits. The five prills from the first laboratory and the three from the commercial fire assay laboratory were dissolved and analysed for their platinum group elements and gold content. The results reported here could therefore only be considered as preliminary.

In this text "% Recovery" refers to results obtained in terms of the certified value of the analyte in the reference material, e.g. if the reference material has a certified value of 0.31 mg kg^{-1} for Au and after analysis a value of 0.25 mg kg^{-1} was obtained for Au, this will be reported as a "% Recovery" of (0.25 / 0.31 x 100), i.e. 80.6%.

5.2 Certified reference material *[95]*

The source of the certified reference material, Platinum Ore SARM 7, is described as a composite of samples from the Merensky Reef taken from five localities in the Bushveld Complex in the Transvaal, South Africa. The material consists mainly of a felsphathic pyroxenite. Major constituents are pyroxene, olivine, serpentine and plagioclase. Minor constituents are chromite, pentlandite, chalcopyrite and pyrrhotite. The platinum minerals are mainly ferroplatinum, cooperite, sperrylite, braggite and moncheite. Silica and magnesia account for about 70% of the sample and oxides of iron, aluminium and calcium for a further 24%.

Table 5.1: Certified property values and confidence / uncertainty limits of selected elements in SARM 7.

Element	Certified value in mg kg^{-1}	Limits at 95% confidence level
Platinum	3.74	± 0.045
Palladium	1.53	± 0.032
Gold	0.31	± 0.015
Rhodium	0.24	± 0.013
Ruthenium	0.43	± 0.057
Iridium	0.074	± 0.012

5.3 Lead fire assay *[96]*

The technique consists of two consecutive pyrochemical separations. The finely ground sample is fused with a suitable flux, under reducing conditions which promote the separation of the platinum group elements and gold from the gangue, with simultaneous collection, as a lead alloy. Subsequently, the lead is removed by oxidising fusion (cupellation) and the platinum group elements and gold, thus isolated, are available for measurement.

Silver is normally employed to collect gold and the platinum group elements and added to the flux as a powder or in solution to give a ratio of Ag to total platinum group elements and gold of 20:1 *[97]*. The flux combines with the gangue to a form fluid slag and the litharge in the flux is reduced to minute globules of lead. The rain of lead globules, falling through the molten mass, collects the particles of some of the platinum group elements and gold and coalesces into a button at the bottom of the crucible. For effective collection, the composition of the flux, the

temperature and its rate of increase must be optimised. On cooling the slag solidifies and is separated from the lead button containing the platinum group elements and gold. Lead is removed by oxidation, vaporised and absorbed into the cupel thus leaving the silver prill containing the extracted platinum group elements and gold *[97]*.

5.3.1 *Flux reagents*

The selection and proportions of flux components are the most important factors in effecting a successful fusion. Hereby a summary of some of the chemical properties of the flux reagents used in this study:

Sodium carbonate: Na_2CO_3

Sodium carbonate is a powerful basic flux and readily forms alkali silicates. In the presence of air some sulphates are also formed and thus sodium carbonate may be considered an oxidising and desulphurising reagent. Sulphates are produced more readily in the presence of an oxidising reagent such as litharge:

$$FeS_2 + 7PbO + 2Na_2CO_3 \rightarrow FeO + 7Pb + 2Na_2SO_4 + 2CO_2$$

Sodium carbonate melts at 850 °C and dissociates partially at 950 °C evolving carbon dioxide and liberating some free alkali:

$$Na_2CO_3 + Na_2SiO_3 \rightleftharpoons Na_4SiO_4 + CO_2$$

Silica: SiO_2

Silica is a strongly acidic flux reagent. It combines with metallic oxides to form silicates that are fundamental to most slags. Silica slags are classified according to the ratio of oxygen in the base (metallic oxide) to the oxygen in the acid (silica). A metasilicate slag with a ratio of 1:2 is desirable because of its stability:

$$PbO + SiO_2 \rightarrow PbSiO_3$$

Borax (anhydrous sodium tetraborate): $Na_2B_4O_7$

Anhydrous borate melts at 741 °C to form a viscous slag but becomes fluid at elevated temperatures. It is a strongly acidic reagent and readily dissolves almost all metallic oxides. During fusion the dissolution by borax of metal oxides progresses through two stages: 1) the borax melts to form a colourless transparent glass consisting of sodium metaborate and boric anhydride:

$$Na_2B_4O_7 \rightarrow Na_2B_2O_4 + B_2O_3$$

and 2) the boric anhydride then reacts with the metal oxide to form metal borate:

$$MO + B_2O_3 \rightarrow MB_2O_4$$

Borax also lowers the fusion temperatures of all slags appreciably. Excess borax is detrimental to the fusion; preventing the formation of a homogenous slag and subsequent separation of the lead button.

Litharge: PbO

Litharge is a readily fusible basic flux reagent. In addition, it acts as an oxidising and desulphurising agent. It melts at 883 °C and together with the required addition of reductant (maize meal), provides the metallic lead that collects the platinum group elements and gold.

Maize meal

Maize meal acts as a reducing agent. Maize meal, which is a source of carbon, reduces litharge to metallic lead with the evolution of carbon monoxide or carbon dioxide:

At higher temperatures: $PbO + C \rightarrow Pb + CO$

At lower temperatures: $2PbO + C \rightarrow 2Pb + CO_2$

5.4 Literature survey of the analysis of SARM 7

Juvonen, Kallio and Lakomaa *[52]* determined precious metals in rocks by ICP-MS using nickel sulphide concentration with Te co-precipitation. They compared the results obtained with those obtained with other pre-treatment methods, i.e. lead fire assay (with added $AgNO_3$ as carrier for the platinum group elements and gold) and aqua regia leaching procedures. The instrument was optimised with a solution that was 10 μg dm^{-3} with respect to Mg, Rh, Pb in order to give a compromise between high sensitivity and low oxide levels. Double charged ions and oxide interferences were monitored with $^{140}Ce^{2+}$ and $^{140}CeO^{+}$. The final solutions (standards and samples) to be analysed by means of ICP-MS all contained approximately 3.6% (v/v) HNO_3 and 5.0% (v/v) HCl, as well as 50 μg dm^{-3} Tl as internal standard. They reported systematically low results for gold, which is in accordance with other workers *[98]* who also extracted gold by means of the nickel sulphide fire assay procedure. They also reported that the recoveries of Au, Pd and Pt did not differ significantly for the lead and nickel sulphide fire assay procedures. They concluded that 1) the best recoveries of Ir, Os, Rh and Ru may be obtained by means of nickel sulphide fire assay, 2) the best recoveries of Au, Pt and Pd may be achieved with lead fire assay and 3) Rh is best recovered by means of nickel sulphide fire assay with gold as collector. Aqua regia leach procedures were only recommended for preliminary studies. Their results are given in Table 5.2.

Table 5.2: Results for the analysis of SARM 7 by means of aqua regia leach, lead fire assay and nickel sulphide fire assay followed by ICP-MS.

Element	% Recovery by aqua regia leach	% Recovery by lead fire assay	% Recovery by nickel sulphide fire assay
Au	72	85	84
Ir	33	4	106
Pd	89	97	100
Pt	42	97	102
Rh	89	18	100
Ru	29	3	108

Sun, Jain, Zhou and Kerrich *[99]* analysed SARM 7 by means of nickel sulphide fire assay and Te co-precipitation. Instead of crushing the nickel sulphide button followed by open beaker dissolutions of the nickel sulphide button and the Te precipitate, they employed Teflon bombs for the mentioned dissolutions. The ion lenses of the ICP-MS were optimised so that maximum signals for Rh, Cs, Tm and Bi were obtained by using a solution that was 100 μg dm^{-3} with respect to these elements. The nebuliser gas flow rate was adjusted for maximum sensitivity while keeping the ThO^+/Th^+ ratio to 5%. The final sample solutions to be analysed by ICP-MS contained approximately 5.0% (v/v) HNO_3 and 5.0% (v/v) HCl. The acid wash that was used to rinse the system between samples contained approximately 7.1% (v/v) HNO_3 and 10% (v/v) HCl. Their results are shown in Table 5.3.

Table 5.3: Results for the analysis of SARM 7 by means of open beaker and Teflon bomb digestions of the nickel sulphide button followed by ICP-MS.

Element	% Recovery by open beaker digestion	% Recovery by Teflon bomb digestion
Au	-	88
Ir	85	108
Pd	97	100
Pt	94	104
Rh	94	106
Ru	79	104

Perry, Van Loon and Speller *[100]* used a dry-chlorination ICP-MS method to determine the platinum group elements and gold in SARM 7. They performed two point linear calibrations and the method of standard additions was used for the ICP-MS work. The prepared standards were carried in 1% (v/v) HNO_3. They reported higher recoveries, better accuracy, better precision and sensitivity for dry-chlorination than for nickel sulphide fire assay ICP-MS or lead fire assay ETAAS. Their results may be seen in Table 5.4.

Table 5.4: Results for the analysis of SARM 7 by means of chlorination and nickel sulphide fire assay followed by ICP-MS and lead fire assay followed by ETAAS. The last two methods were performed by commercial laboratories.

Element	**% Recovery by chlorination ICP-MS**	**% Recovery by nickel sulphide fire assay ICP-MS**	**% Recovery by lead fire assay ETAAS**
Au	66	not available	<65
Ir	105	43	not available
Pd	57	50	33
Pt	80	18	25
Rh	122	<79	not available
Ru	155	<44	not available

Chen, Fryer, Longerich and Jackson *[101]* analysed SARM 7 for the platinum group elements and gold using ICP-MS after ion-exchange preconcentration. They employed ion-exchange in order to separate the platinum group elements and gold from the transition elements since serious interferences from transition element argide polyatomic ions together with matrix effects from high total dissolved solids hamper the accurate determination of low concentrations of the platinum group elements and gold by ICP-MS. The nebuliser gas flow was adjusted for maximum sensitivity using a solution containing Rh, Bi and U so that $UO^+:U^+ < 0.25$, sensitivity for Rh was > 10^6 counts per second μg^{-1} and sensitivity for Bi was > 0.5×10^6 counts per second μg^{-1}. At maximum sensitivity polyatomic ion formation was higher than is normally used for trace element analysis. The internal standard solution comprised of 4031 ng g^{-1} Cd (for Ru, Rh and Pd) and 2045 ng g^{-1} Tl (for Ir, Pt and Au). The acid calibration blank solution consisted of approximately 2% (v/v) HCl and the flush solution consisted of approximately 3% (v/v) HCl and 2.8% (v/v) HNO_3. Matrix effects and drift were corrected with the internal

standards. They reported poor accuracy and precision for gold analysis. Table 5.5 shows the results they obtained with analysis of 2 mg and 20 mg fragments of nickel sulphide beads using cation exchange ICP-MS.

Table 5.5: Results for the analysis of SARM 7 by means of nickel sulphide fire assay followed by ion exchange preconcentration of fragments of the nickel sulphide beads followed by analysis by ICP-MS.

Element	**% Recovery for 2 mg fragments of a nickel sulphide bead**	**% Recovery for 20 mg fragments of a nickel sulphide bead**
Au	77	58
Ir	124	114
Pd	82	96
Pt	116	88
Rh	120	102
Ru	99	100

Enzweiler, Potts and Jarvis *[102]* determined Pt, Pd, Ru and Ir in SARM 7 by isotope dilution ICP-MS using a sodium peroxide fusion and Te co-precipitation. The final sample solutions for ICP-MS analysis contained between 10% (v/v) and 12% (v/v) aqua regia. Their results are summarised in table 5.6.

Table 5.6: Results for the analysis of SARM 7 by means of isotope dilution ICP-MS using a sodium peroxide fusion and Te co-precipitation.

Element	**% Recovery by sodium peroxide fusion and Te co-precipitation followed by isotope dilution ICP-MS**
Ir	95
Pd	98
Pt	101
Ru	96

Gowing and Potts *[51]* evaluated a rapid technique for the determination of the platinum group elements and gold based on a selective aqua regia leach. The sample solutions for analysis by

ICP-MS contained 20% (v/v) aqua regia. The ion lens settings were optimised by maximising the $^{115}In^{+}$ signal and minimising the Ce^{2+} and CeO^{+} signals. The standard solutions were also prepared in 20% (v/v) aqua regia. The data used to apply a correction for drift in instrument sensitivity was by interpolation of count data from adjacent standard solutions. They used 100 μg dm^{-3} of Re as an internal standard for Os, Ir and Pt and 100 μg dm^{-3} of In as an internal standard for Rh, Ru and Pd. A 20% (v/v) aqua regia solution was used to flush the ICP-MS system between samples. Their results are shown in Table 5.7.

Table 5.7: Results for the analysis of SARM 7 by means of an aqua regia leach followed by ICP-MS.

Element	**% Recovery by an aqua regia leach followed by ICP-MS**
Au	97
Ir	26
Pd	77
Pt	37
Rh	73
Ru	27

Jackson, Fryer, Gosse, Healy, Longerich and Strong *[98]* determined the platinum group elements and gold in SARM 7 by nickel sulphide fire assay collection followed by Te co-precipitation and ICP-MS. A solution containing approximately 8% (v/v) HCl and 7% (v/v) HNO_3 was used in the wash station of the autosampler. The ion lenses of the ICP-MS were optimised as follows: 1) lens S2 was set to 0, 2) lens P was set for minimum background readings (usually < 5 counts s^{-1}) and 3) lenses B and E were optimised for maximum signal on Rh, Cs, Tm and Bi in a solution containing 100 μg dm^{-3} of Li, Co, Rh, Cs, Tm, Bi and Th. The nebuliser gas flow was adjusted for the optimum operating conditions by monitoring Rh, Hf (background), Th and ThO. The acid calibration blank solution consisted of approximately 5% (v/v) HCl and 6% (v/v) HNO_3. Cd was employed as internal standard for Ru, Rh and Pd and Tl as internal standard for Os, Ir, Pt and Au. Drift and matrix effects were compensated for with the internal standards. Table 5.8 shows their results.

Table 5.8: Results for the analysis of SARM 7 by means of nickel sulphide fire assay and Te co-precipitation followed by ICP-MS.

Element	**% Recovery by nickel sulphide fire assay and Te co-precipitation followed by ICP-MS**
Au	82
Ir	96
Pd	88
Pt	91
Rh	88
Ru	92

Godfrey and McCurdy *[103]* analysed SARM 7 by means of flow injection ICP-MS after a sodium peroxide fusion procedure. All standard and sample solutions were prepared in 2% (v/v) HCl. 20 μg dm^{-3} of each of Cs and Bi was used as internal standards. They also made use of synthetic standards prepared by spiking the fusion blank solution at various concentrations of the platinum group elements and gold. The ion lens settings were optimised with maximum signal on In at mass 115. Table 5.9 shows their results.

Table 5.9: Results for the analysis of SARM 7 by means of a sodium peroxide fusion followed by flow injection ICP-MS.

Isotope	**% Recovery for (1g SARM 7 + 5g Na_2O_2)**	**% Recovery for (0.5g SARM 7 + 4g Na_2O_2) (with matrix matched standards)**
^{197}Au	166	103
^{193}Ir	236	215
^{105}Pd	96	118
^{194}Pt	94	97
^{195}Pt	90	-
^{103}Rh	389	85
^{101}Ru	101	87

5.5 Experimental

5.5.1 Lead fire assay procedure

Samples with a high As and/or S content require roasting at 600-800°C to volatilise these elements to prevent formation of a matte during fusion which would otherwise retain the platinum group elements and gold *[97]*. Roasting of SARM 7 samples are not necessary before the lead fire assay *[52]*. A flux similar to the one used by Hall and Pelchat *[97]* was used to extract the platinum group elements and gold from SARM 7. The flux used in the lead fire assay procedure (first assay laboratory) was composed of 105 g litharge, 45 g sodium carbonate, 5 g borax, 10 g silica and 2.5 g maize meal. Silver was used as carrier for the platinum group elements and gold in the form of approximately 1.0 ml of a 5 g dm^{-3} $AgNO_3$ solution that was added to each crucible before fusion. The fusion time for the well-mixed (25 g sample and flux) mixture was set at 60 minutes at approximately 1100°C. The lead buttons were cupelled for 30 minutes at approximately 1000°C. The prills were weighed and prepared for analysis by ICP-MS.

SARM 7 was also supplied to a commercial laboratory for lead fire assay analysis and three prills were received from the commercial laboratory. The commercial laboratory also employed a procedure whereby 25 g of sample is used as well as silver nitrate as carrier solution.

Some fire assay laboratories consider a blank to be represented by carrying reagents only through the procedures, i.e. flux only, while others would substitute "clean" silica for a sample and estimate its variation in results in order to determine the method detection limit *[97]*. In this investigation the blank comprised of reagents only, i.e. flux only. A blank was produced by the first assay laboratory but no blank was received from the commercial laboratory.

Table 5.10 shows some of the masses recorded during the procedure.

Table 5.10: The masses of SARM 7 weighed for analysis as well as the masses of the prills that were obtained. The prills from the commercial laboratory are given as p1, p2 and p3.

Sample name	Mass of SARM 7 weighed in g	Mass of prill obtained after cupellation in g
1	25.02015	0.00385
2	25.06146	0.00346
3	25.05006	0.00336
4	25.03992	0.00310
5 (Blank)	-	0.00317
p1	25	0.00669
p2	25	0.00614
p3	25	0.00561

5.5.2 *ICP-MS procedure*

Preparation of sample and standard solutions for analysis by ICP-MS

The method used to dissolve the prills is similar to that of Hall and Pelchat *[97]*. The prills produced after cupellation were prepared for ICP-MS analysis as follows: 1) The prill was heated with 2.5 ml concentrated HNO_3 in a 100 ml beaker, after which 7.5 ml concentrated HCl was added and the solution was further heated. 2) The solution was cooled and transferred quantitatively to a 50 ml volumetric flask and made to the mark with distilled water. 3) The solution was diluted 20x by transferring 5 ml of the solution to a 100 ml volumetric flask and making it up to the mark with distilled water. Internal standards, Y (Pd, Rh and Ru) and La (Au, Ir, Pt), were also added before making it up to the mark. The acid content of the solution to be analysed by ICP-MS was approximately 1% (v/v) aqua regia. The standards were prepared as set out in chapter 3. Y and La were added as internal standards.

Calculations for the platinum group elements and gold content of SARM 7

The mathematical formula used to calculate the platinum group elements and gold content of SARM 7 are derived as follows for e.g. Au:

$$P_{prill} = [(ICP\text{-}MS_{prill} \times df) / (m_{prill} / V_{prill})] \quad ...(1)$$

where P_{prill} is the purity of the prill with respect to the Au content,

$ICP\text{-}MS_{prill}$ is the result of the ICP-MS analysis of the prill with respect to the Au content in $\mu g\ dm^{-3}$,

df is the dilution factor of the solution of the dissolved prill,

m_{prill} is the mass of the prill in μg and

V_{prill} is the volume of the volumetric flask in which the solution was made up to in dm^3.

$$\text{Au content in } \mu g\ kg^{-1} = [(P_{prill} \times M_{prill}) / M_{CRM}] \times 10^9 \quad ...(2)$$

where M_{prill} is the mass of the prill in g and

M_{CRM} is the mass of SARM 7 weighed for analysis in g.

Substituting (1) into (2):

$$\text{Au content in } \mu g\ kg^{-1} = [([(ICP\text{-}MS_{prill} \times df) / (m_{prill} / V_{prill})] \times M_{prill}) / M_{CRM}] \times 10^9$$
$$= [([(ICP\text{-}MS_{prill} \times df) / (m_{prill} / V_{prill})] \times m_{prill} / 10^6) / M_{CRM}] \times 10^9$$
$$= [([(ICP\text{-}MS_{prill} \times df) / (m_{prill} / V_{prill})] \times m_{prill} / 10^6) / M_{CRM}] \times 10^9$$
$$= [(ICP\text{-}MS_{prill} \times df \times V_{prill}) / M_{CRM}] \times 10^3$$

ICP-MS: Instrument optimisation and method used

The instrument was optimised as set out in chapter 2. After the instrument was calibrated with the prepared standards, the prepared samples were analysed and the 5.0 $\mu g\ dm^{-3}$ standard was to monitor the drift of the instrument. The method used for analysis was as developed in chapter 3. The most abundant isotopes of each element were measured: ^{197}Au, ^{193}Ir, ^{106}Pd, ^{108}Pd, ^{194}Pt, ^{195}Pt, ^{103}Rh, ^{99}Ru, ^{100}Ru and ^{101}Ru.

5.6 Results and discussion

5.6.1 Results of the analysis of SARM 7

The number of samples analysed by ICP-MS was small, i.e. the drift control standard was only analysed three times because of the short time period that was necessary to analyse the samples. In order to assess whether it is necessary to apply drift correction to the results obtained, i.e. whether instrument drift affected any of the isotopes analysed, the values obtained for the drift control standards are analysed as shown in table 5.11. From table 5.11 it can be seen that drift

correction must be applied to the following isotopes: ^{197}Au, ^{106}Pd and ^{108}Pd. The results of the quantitative determination of the platinum group elements and gold in SARM 7 for the samples. 1, 2, 3, 4, p1, p2 and p3 by means of lead fire assay followed by ICP-MS are shown in tables 5.12 and 5.13.

Table 5.11: Data on the 5 μg dm^{-3} drift control standard. Standard deviation is in brackets. In the cases where the values of the drift control standard deviated significantly from a value of approximately 5.0 it was decided to apply drift correction in the form of the use of internal standards.

Isotope	**Average of the measurements of the drift control standard in μg dm^{-3}**
^{197}Au	6.15 (0.17)
^{193}Ir	5.10 (0.09)
^{106}Pd	6.98 (0.42)
^{108}Pd	6.97 (0.51)
^{194}Pt	5.38 (0.33)
^{195}Pt	5.40 (0.28)
^{103}Rh	5.45 (0.21)
^{99}Ru	5.25 (0.09)
^{100}Ru	5.35 (0.16)
^{101}Ru	5.27 (0.28)

5.6.2 *Recovery of Au*

Higher recoveries are reported for samples 1, 2, 3 and 4 than for p1, p2 and p3. The use of internal standards to correct for drift proved to be detrimental in both cases, i.e. weaker recoveries were then calculated.

The % recoveries for gold do not compare well to those obtained by some researchers who also applied lead fire assay to the analysis of SARM 7 *[52]*, but are similar to the recoveries of a commercial laboratory also using a lead fire assay procedure as reported by *[100]*.

Better extraction of gold was reported by researchers employing techniques other than lead fire assay *[51, 52, 98 - 101, 103]* in the analysis of SARM 7.

Table 5.12: Results for the analysis of SARM 7 by lead fire assay followed by ICP-MS. The results are the averages for samples 1, 2, 3 and 4. Blank values have been subtracted.

Isotope	% Recovery without the use of an internal standard	% Recovery with La as internal standard for Au and Y as internal standard for Pd
^{197}Au	58.9	42.0
^{193}Ir	0.8	no correction applied
^{106}Pd	95.7	89.1
^{108}Pd	94.4	87.9
^{194}Pt	90.6	no correction applied
^{195}Pt	90.3	no correction applied
^{103}Rh	2.6	no correction applied
^{99}Ru	0.3	no correction applied
^{100}Ru	0.1	no correction applied
^{101}Ru	0.2	no correction applied

Table 5.13: Results for the analysis of SARM 7 by lead fire assay followed by ICP-MS. The results are the averages for samples p1, p2 and p3.

Isotope	% Recovery without the use of an internal standard	% Recovery with La as internal standard for Au and Y as internal standard for Pd
^{197}Au	33.8	23.6
^{193}Ir	0.1	no correction applied
^{106}Pd	88.2	77.7
^{108}Pd	87.2	76.9
^{194}Pt	89.3	no correction applied
^{195}Pt	89.5	no correction applied
^{103}Rh	3.3	no correction applied
^{99}Ru	0.1	no correction applied
^{100}Ru	0.2	no correction applied
^{101}Ru	0.2	no correction applied

5.6.3 *Recovery of Ir*

The recovery of Ir from SARM 7 was negligible. Juvonen, Kallio and Lakomaa *[52]* also reported poor extraction of Ir by means of the lead fire assay as pre-concentration technique.

Other pre-concentration techniques are more effective than lead fire assay for the extraction of Ir from SARM 7 *[51, 52, 98 - 102]*.

5.6.4 *Recovery of Pd*

The recoveries obtained for samples 1, 2, 3 and 4 were better than those obtained for p1, p2 and p3. In both cases the use of internal standards caused lower recoveries to be reported.

The values obtained (before the application of internal standards) compare well to those obtained by other researchers *[52]* and better than those obtained by a commercial laboratory used by Perry, Van Loon and Speller *[100]* also using lead fire assay.

In some cases workers employing other pre-concentration techniques reported slightly better recoveries *[52, 99, 102]* and in some cases poorer results were obtained *[51, 52, 98, 100]*.

5.6.5 *Recovery of Pt*

Similar yields for Pt were obtained for all the samples analysed.

In some cases the values obtained compare well to those obtained by other researchers *[52]* and even better than those obtained by a commercial laboratory *[100]*.

Lead fire assay proved to be better for the pre-concentration of Pt from the matrix than other techniques *[51, 52, 100]* and in other cases other techniques proved to be superior *[52, 98, 99, 102, 103]*.

5.6.6 *Recovery of Rh*

Rh was extracted poorly, i.e. 2.6 % and 3.3 % for the samples analysed. These values do not compare well to those of other workers, i.e. Juvonen, Kallio and Lakomaa *[52]* reported a recovery of 18% for Rh by means of the lead fire assay procedure.

In general, other techniques proved to be superior to lead fire assay for the separation of Rh from the SARM 7 matrix *[51, 52, 98, 99, 103]*.

5.6.7 *Recovery of Ru*

The recovery of Ru from SARM 7 was negligible. Poor extraction was also reported by Juvonen, Kallio and Lakomaa *[52]*.

Ru is better extracted from SARM 7 by techniques other than lead fire assay *[52, 98, 99, 101 - 103]*.

5.6.8 *Lead fire assay as pre-concentration technique for the platinum group elements and gold*

According to Perry, Van Loon and Speller *[100]* the exploration industry is in general disappointed with fire assay procedures because of inaccurate results generated. However, the platinum group elements and gold must be separated from the sample matrix and concentrated before analysis *[104 - 106]* and fire assay procedures remain the most important way of doing this. Lead fire assay remains the most reliable and cost effective means of preparation for analysis of rocks, soils and sediments for Au, Pd and Pt provided certain modifications are carried out to suit the sample type *[97]*. The elements Au, Pd and Pt are effectively and quantitatively collected in a silver bead by means of the fire assay procedure *[51, 97, 104, 107]*. For the collection of Ir and Rh a gold bead is recommended *[106]*. Flux composition and assay conditions are very important if Ir and Rh are to be collected by means of the lead fire assay procedure *[51, 106]*.

Precision at low levels of the analytes is dominated by homogeneity of the elements in a particular sample rather than by the invariability inherent in the method itself *[97]*, i.e. the determination of the natural concentrations of precious metals must take into consideration their occurrence in small, rare, discrete and inhomogeneously distributed minerals *[101, 102, 107]*.

For accurate results the assay conditions and skills are very important, especially at the cupellation stage *[107]*. This may in part explain the different recoveries of the platinum group elements and gold obtained by the two fire assay laboratories employed in this study.

5.6.9 *ICP-MS procedure*

There are several potential polyatomic interferences that may influence the isotopes measured in this study: ^{197}Au ($^{181}Ta^{16}O$), ^{193}Ir ($^{177}Hf^{16}O$), ^{106}Pd ($^{90}Zr^{16}O$, $^{89}Y^{16}O^{1}H$), ^{108}Pd ($^{92}Zr^{16}O$), ^{194}Pt ($^{178}Hf^{16}O$), ^{195}Pt ($^{179}Hf^{16}O$), ^{103}Rh ($^{86}Sr^{16}O^{1}H$, $^{87}Sr^{16}O$, $^{63}Cu^{40}Ar$), ^{99}Ru (-), ^{100}Ru ($^{84}Sr^{16}O$) and ^{101}Ru ($^{84}Sr^{16}O^{1}H$, $^{61}Ni^{40}Ar$, $^{64}Ni^{37}Cl$) *[106]*. According to Hall and Pelchat *[97]* the oxides of Y and Sr were not in evidence in SARM 7 samples processed through the lead fire assay procedure. Godfrey and McCurdy *[103]* reported the oxides of Zr, Hf and Ta to be present in the system if zirconium crucibles were used during sodium peroxide fusion procedures in the analysis of SARM 7 samples. They also reported ArCu to be present due to the copper content of the SARM 7 samples. However, due to the lead fire assay procedure (separation of the platinum group elements and gold from the matrix containing base metals such as copper and nickel) none of the interferences $^{63}Cu^{40}Ar$, $^{61}Ni^{40}Ar$ or $^{64}Ni^{37}Cl$ was present in the samples that were analysed by ICP-MS.

During this study care was taken not prepare the samples in such a way that it contained a high contents of dissolved salts or high acid contents. Perry, Van Loon and Speller *[100]* reported that the signal intensity in the mass spectrometer was continuously diminished because of the gradual build-up of salts on the skimmer and sampler cones. As the salts form, the effective diameter of the sampler orifice is reduced, the amount of plasma sampled decreases and the signal diminishes. Gowing and Potts *[51]* also reported interference effects occurring due to the suppression of signals in sample solutions containing particular high contents of dissolved salt. Their samples were prepared in a 20% aqua regia matrix with > 0.1% TDS.

Some workers *[98, 101]* reported memory effects for Pd and Au when determined by ICP-MS. Due to adequate rinsing times between samples and adequate preflush times during analysis none of these memory effects were encountered in this study.

5.6.10 *Comparison of ICP-MS procedure with those of other workers*

The main differences between the ICP-MS procedures followed by other workers and that of the author may be summarised as follows:

Other workers (5.4) have a very simplistic approach to the optimisation of the ICP-MS, usually monitoring only a few isotopes. The author optimised the various parts of the instrument

(chapter 2) and not only the ion lenses. Care was also taken to keep the levels of the doubly charged ions and oxide interferences to a minimum.

Other workers (5.4) also made use of internal standards. The author however made a detailed study of various internal standards in relation to their behaviour to the platinum group elements and gold in acidic media.

One of the objectives of this study was to show that the analysis of the platinum group elements and gold may be performed in an acidic matrix of 1% (v/v) aqua regia. This is in contrast to the high acidic matrices used by other workers (5.4) (with the exception of a few *[100, 103]*). The higher acidic matrices employed by them is detrimental for the instrument, i.e. corrosion of the sampler and skimmer cones of the ICP-MS.

5.7 Recommendations

The analysis of SARM 7 by means of lead fire assay and ICP-MS proved to be relatively successful for the quantification of Au, Pd and Pt. The analysis procedure followed consisted of three steps *[102]*: 1) separation of the platinum group elements and gold from the matrix and the pre-concentration of the analytes by means of fire assay, 2) the dissolution of the silver beads and 3) detection of the isotopes of the elements by ICP-MS. However, only step 3 was studied in depth in this work. In order to obtain higher recoveries of the platinum group elements and gold from SARM 7, steps 1 and 2 need to be optimised and refined. The following suggestions and recommendations for future work are made:

As suggested by some researchers *[97, 98]* the detection capability of lead fire assay would be enhanced by the purification of flux reagents and dedication of assay equipment (furnaces, crucibles) to the processing of low-level samples only. Thus, improvement in the purity of the flux constituents and equipment would allow advantage to be taken of the excellent sensitivity of ICP-MS in the sense that less impurities would then be available to give rise to possible interferences that might interfere with the detection of the analytes. Also, reagent contamination can be reduced by the use of higher purity reagents and more rigorous clean laboratory procedures. The reagents used in the analysis of the platinum group elements and gold should be analysed for the presence of the analytes before use. Sun, Jain, Zhou and Kerrich *[99]* found their silica flux to be contaminated with Pd.

The assay conditions and parameters of the lead fire assay need to be refined when analysing for the platinum group elements and gold, e.g. some workers choose to fuse at 1000°C for 45-60

minutes and perform cupellation at 900°C for 45-60 minutes, while others fuse at 1050°C for 50-60 minutes and cupel at 950°C for 50-55 minutes *[97]*.

It is further suggested that the dissolution process of the silver beads be refined. The use of sealed tubes *[102]* or Teflon bombs *[99]* for the dissolutions proved to be successful for some researchers.

The lead fire assay procedure as a whole, i.e. flux composition, assay conditions etc. must be optimised for the analysis of samples containing low levels of the platinum group elements and gold.

5.8 Conclusion

From the analysis of the certified reference material, SARM 7, by means of lead fire assay and ICP-MS high recoveries of only Au, Pd and Pt are expected. It was shown that these three elements were indeed extracted and quantified successfully by means of the ICP-MS procedures developed in chapter 3. It was also shown that it was possible to obtain relatively good results with the lower acidic contents of standards and samples (1% (v/v) aqua regia) as employed in this study.

It was also shown that the matrix and drift correction procedures (in the form of the use of internal standards) that were developed in chapter 3 must be applied with caution. The measurements of the drift control sample must first be analysed in order to ascertain whether corrections should be applied. In this analysis of SARM 7 the time used to analyse the samples by means of ICP-MS proved to be too short for instrumental drift to have a significant effect. It was shown that the use of an internal standard was detrimental to the recoveries reported for Au and Pd.

CHAPTER 6

THE QUANTITATIVE DETERMINATION OF ARSENIC IN A CERTIFIED REFERENCE MATERIAL

6.1 Introduction

The validity of the ICP-MS method developed for the analysis of arsenic as developed in chapter 4 may be tested by the analysis of a certified reference material. The reference material Seronorm Trace Elements Urine has a certified value for the amount of arsenic it contains. As urine samples usually have relatively high concentrations of chloride present in the matrix [*79, 80*], the ICP-MS method was tested for the correction of the ArCl interference at *m/z* 75. An attempt was made to accurately determine the arsenic content of the urine samples by means of the developed ICP-MS method, i.e. using arsenic calibration standards prepared in 1% HNO_3, employing La as an internal standard, determining the correction factor at a specific chloride concentration and the application thereof to the intensities obtained at *m/z* 75, as well as the application of drift correction procedures. The urine samples will only be diluted with water. The results of other researchers who also attempted the analysis of arsenic (and specifically in a chloride medium) by means of ICP-MS will also be briefly discussed and compared to the results obtained in this study.

The certified reference material used in this study was used to assess the accuracy of the analytical method developed. As only four samples were analysed it was not possible to perform statistical analysis in order to assess the precision and determine detection limits. The results reported here could therefore only be considered as preliminary.

6.2 Certified reference material *[108]*

Seronorm Trace Elements Urine is produced from human urine collected from thoroughly controlled voluntary Norwegian donors. The reference material is stable and is a lyophilised reference urine of human origin for *in vitro* diagnostic use. The material does not contain any preservatives. After reconstitution of the reference material it is considered stable for one month at a temperature of ≤ -20°C, seven days at temperatures of between 2°C and 8°C and for eight hours at temperatures of between 15°C and 25°C. The analytical data of Seronorm Trace Elements Urine have been determined after reconstitution with 5.00 ml pure water.

Seronorm Trace Elements Urine (Lot 403125, 403125x, 403125y) has an analytical arsenic value of 101 μg dm^{-3} with a standard deviation of 3 μg dm^{-3}. It also has a certified analytical value of 4326 mg dm^{-3} with a standard deviation of 15 mg dm^{-3} for chloride. It does not have a certified value for Se.

6.3 Literature survey

McLaren *et al.* [*48*] determined arsenic in the marine sediment certified reference material PACS-1 by means of ICP-MS. They investigated the use of the background ion $^{40}Ar_2^+$ as an internal standard. With no internal standardisation applied they reported a recovery of 92.4% and with the argon dimer, $^{40}Ar_2^+$, as internal standard they achieved a recovery of 96.7%. They reported that the use of the argon dimer to compensate both for suppression (or enhancement) of ion sensitivity by concomitant elements and for induced calibration drift proved to be successful for the determination of arsenic since the mass difference between arsenic and the argon dimer is relatively small. Hydrochloric acid was however not used during sample preparation so it was not necessary to compensate for the $^{40}Ar^{35}Cl$ interference at *m/z* 75. Nitric acid, hydrofluoric acid and perchloric acid were used during sample preparation procedures.

Branch, Ebdon, Ford, Foulkes and O'Neill [*80*] determined the arsenic content of samples with a high chloride content using ICP-MS with the addition of nitrogen to the carrier gas. With the addition of nitrogen to the argon carrier gas, the level of the $^{40}Ar^{35}Cl^+$ polyatomic ion that interferes with the determination of monoisotopic arsenic is reduced to negligible levels. They showed this modification to be effective even for solutions which contain up to 1.13% chloride. All standards and samples were spiked with In to give a final concentration of 100 μg dm^{-3} and made up to volume with 2% nitric acid. The Seronorm urine samples were diluted 10x with 2% nitric acid. Their results are summarised in table 6.1.

Table 6.1: Results of the determination of arsenic in several reference materials by means of ICP-MS.

Sample	**% Recovery of arsenic without nitrogen addition**	**% Recovery of arsenic with nitrogen addition**
NIES CRM No.9 (Sargasso seaweed)	128.7	95.7
Seronorm urine	not determined	103.5
NIST 8431 (Mixed diet)	not determined	102.5
NIST 1573 (Tomato leaves)	not determined	88.9
NRCC DORM 1 (Dogfish muscle)	not determined	100.6

Kershisnik and co-workers [*78*] presented a method for the correcting the ICP-MS $^{40}Ar^{35}Cl$ interference with ^{75}As by using the $^{16}O^{35}Cl$ species. They observed that the signal intensities for the species $^{16}O^{35}Cl$ and $^{40}Ar^{35}Cl$ are proportional over a range of chloride concentrations (0 - 2.84%). They used Y as internal standard. The method is sensitive to the presence of vanadium (mass 51) in solution. They analysed a NIST standard in duplicate and reported recoveries of 102.8% and 105.2%

Branch, Ebdon and O'Neill [*88*] determined arsenic species in fish by directly coupled high performance liquid chromatography-ICP-MS. For total arsenic determinations, nitrogen addition ICP-MS was used to overcome the potential interference from $^{40}Ar^{35}Cl$. In was used as internal standard. The sample preparation procedures did however not involve the addition of hydrochloric acid. The dogfish reference material, DORM-1, was analysed and a recovery of 100.6% was reported.

Sheppard and co-workers [*93*] developed a single microwave digestion procedure for the determination of arsenic, cadmium and lead in seafood products by ICP-AES and ICP-MS. As seafood products normally have significant chloride levels, they applied the following correction at *m/z* 75 in order to obtain the intensity due to arsenic: $I_{As} = I_{75} - (3.1278 \times I_{77}) + (1.0177 \times I_{78})$ where I_n is the intensity at $m/z = n$. They analysed the dogfish muscle and liver reference material, DORM-1, and the lobster hepatopancreas marine reference material, TORT-1. They reported arsenic recoveries of 94.9% and 121.5% respectively for the two reference materials.

Larsen and Stürup [*109*] added carbon as methanol or ammonium carbonate to aqueous analyte solutions in combination with increased power input and enhanced the ICP-MS signal intensities of arsenic and selenium. They proposed that an increased population of carbon ions or carbon-containing ions in the plasma facilitates a more complete ionisation of analytes lower in ionisation energy than carbon itself. They used antimony as internal standard. The enhanced detection power for arsenic was applied to arsenic speciation by high-performance liquid chromatography ICP-MS and made possible the detection of arsenocholine (AsC) in extracts of shrimp. No reference material was analysed.

Whilst participating in some preliminary As speciation studies organised by the European Unions' Measurement and Testing group Campbell *et al.* [*79*] observed that total As levels were in excess of their certified or indicative values. They reported that the ratio of the mass to charge ratios at 75 and 77 indicated that the observed excess was not due to the formation of an isobaric polyatomic interference ($^{40}Ar^{35}Cl$) with ^{75}As. They presented evidence to support an element-specific enhancement of the As signal in the presence of a carbon matrix. They identified the source of this error as arising principally from differences in acidity between the samples and external calibrants. They obtained results using a matrix matching technique that minimised differences in acidity and carbon loading. They used microwave solubilisation (nitric acid) and mineralisation (nitric, sulphuric and perchloric acids) procedures. They analysed certified reference material CRM 422 (cod mussel) and candidate reference materials T28 (mitilus) and T25 (tuna fish). Y was used as internal standard. The presence of the polyatomic interference $^{40}Ar^{35}Cl$ was detected when a low dilution factor was employed, i.e. high matrix loading occurred. The data was then corrected on the basis of the signals at *m/z* 83 (^{83}Kr), 82 (^{82}Se + ^{82}Kr) and 77 (^{77}Se + $^{40}Ar^{37}Cl$), respectively, to derive the contribution of $^{40}Ar^{35}Cl$ to the apparent ^{75}As signal. Tables 6.2 and 6.3 show the results they obtained using external calibration, standard additions, matrix matched standards and acid matched standards.

Table 6.2: Comparison of ICP-MS results for As in certified reference and candidate reference materials by external calibration following mineralisation or solubilisation with HPLC-ICP-MS.

Sample	**Solubilisation**	**Mineralisation**	**% Recovery of arsenic by ICP-MS**	**% Recovery of arsenic by HPLC- ICP-MS**
CRM 422		x	147.4	100.0
CRM 422	x		114.2	97.2
CRM 422	x		104.3	-
T25	x		102.3	100.0
T25		x	318.2	102.3
T28		x	150.0	100.0
T28	x		136.0	97.8
T28		x	268.4	-

Table 6.3: Comparison of different calibration strategies for As in certified reference and candidate reference materials by ICP-MS. (* Denotes As values after correction for the polyatomic interference $^{40}Ar^{35}Cl$ due to high matrix-loading.)

Sample	**Solubilisation**	**Mineralisation**	**% Recovery of As (standard additions)**	**% Recovery of As (matrix matched standards)**	**% Recovery of As (acid matched standards)**
CRM 422	x		114.7*	107.1	-
CRM 422	x		115.6*	103.8*	-
CRM 422	x		-	108.5	104.3
CRM 422	x		-	100.5	-
CRM 422	x		105.2	96.7	-
CRM 422	x		-	105.2	-
CRM 422		x	100.5	100.0	97.2
CRM 422		x	-	-	96.7
CRM 422		x	-	-	99.5
T28	x		-	102.2	-
T28	x		-	105.1	-
T28	x		-	104.4	109.6
T28	x		-	106.6	-
T28	x		-	105.9	-
T28		x	100.0	-	91.9

Lasztity *et al.* determined the total arsenic in environmental, biological and food samples by ICP-MS [*94*]. Various sample preparation procedures were followed, e.g. 1) dry ashing with conventional and microwave heating and $Mg(NO_3)_2$ as ashing aid, 2) closed vessel microwave heated dissolution and 3) high temperature, pressure vapour phase acid digestion. In and Ge were used as internal standards. The following reference materials with certified As concentrations were analysed: oyster tissue (NIST SRM 1566), orchard leaves (NIST SRM 1571), pine needles (NIST SRM 1575), urban particulate matter (NIST SRM 1648), mussel

tissues (NIES no. 6) and soil (IAEA soil 7). Table 6.4 shows the recoveries of arsenic they obtained from the reference materials.

Table 6.4: Recoveries of As from reference materials by means of ICP-MS.

Sample	**Sample preparation procedure**	**% Recovery of arsenic**
Oyster tissue	Closed vessel microwave heated digestion	97.0
	High temperature, pressure vapour phase acid digestion	103.7
	Thermal furnace dry ashing	94.8
	Microwave heated ashing furnace	97.8
Orchard leaves	Closed vessel microwave heated digestion	109.0
	High temperature, pressure vapour phase acid digestion	108.0
	Thermal furnace dry ashing	102.0
	Microwave heated ashing furnace	97.9
Pine needles	Microwave heated ashing furnace	95.2
Mussel tissues	Microwave heated ashing furnace	98.2
Soil	Closed vessel microwave heated digestion	100.7
Urban particulate matter	Closed vessel microwave heated digestion	100.6
	Thermal furnace dry ashing	103.9

Nixon and Moyer [*81*] determined arsenic in urine and whole blood by ICP-MS. In order to minimise or eliminate the interference of $^{40}Ar^{35}Cl$ on arsenic they examined the classic $^{40}Ar^{37}Cl/^{82}Se/^{83}Kr$ correction and other empirical corrections, including $^{16}O^{35}Cl$. They analysed the following materials which have certified arsenic concentrations: NIST SRM 2670 (Toxic metals in freeze-dried urine, low and elevated concentrations), Lyphochek urine metals control (level 2), Lyphochek whole blood control (level 2), Urichem urine chemistry control (human level II), Sernorm whole blood III. (During preliminary investigations urine-based standards with Y as internal standard and the $^{40}Ar^{37}Cl/^{82}Se/^{83}Kr$ correction resulted in arsenic values that were 20% higher than the certified concentrations.) Isobaric correction for $^{40}Ar^{35}Cl$ was made

by measurement of the counts per second at mass 51 ($^{16}O^{35}Cl$). The intensity of $^{16}O^{35}Cl$ is approximately ten times the intensity of $^{40}Ar^{35}Cl$ and is linear with increasing chloride concentrations. The corrected As signal was obtained by subtraction of the $^{40}Ar^{35}Cl$ signal (as calculated from the $^{16}O^{35}Cl$ signal) from the total signal measured at mass 75. Results for urine analysis for As were about 13% high with the $^{16}O^{35}Cl$ correction and with Y as internal standard. Ga was then used as internal standard for the determination of As. Table 6.5 shows the arsenic results they obtained with Ga and Y as internal standards and table 6.6 shows the arsenic results after a period of seven days.

Table 6.5: % Recoveries for As in certified urines by means of ICP-MS using the $^{16}O^{35}Cl$ isobaric correction procedure.

Certified reference material	**% Recovery of As Internal standard: none**	**% Recovery of As Internal standard: Ga**	**% Recovery of As Internal standard: Y**
Urine metals control (level 2)	130.6	95.2	95.2
NIST SRM 2670	130.4	102.3	102.3

Table 6.6: Results for arsenic analyses over a seven day period. The material were analysed once a day by means of ICP-MS using the $^{16}O^{35}Cl$ isobaric correction procedure and Ga as internal standard.

Certified reference material	**% Recovery of arsenic**
Urine chemistry control (human level II)	121.3
Urine metals control (level 2)	95.2
NIST SRM 2670	102.3
Sernorm whole blood III	125.2

Madeddu and Rivoldini analysed plant tissue for arsenic by means of ICP-MS. They used a microwave digestion procedure with nitric acid and hydrofluoric acid. They used Rh and Re as internal standards. They analysed the following certified reference materials: GSV-1 and

GSV-2 (bush twigs and leaves), GSV-3 (poplar leaves) and GSV-4 (tea). Their results are shown in table 6.7.

Table 6.7: % Recoveries of arsenic from plant tissues by means of ICP-MS.

Certified reference material	**% Recovery of arsenic**
GSV-1	113.7
GSV-2	118.4
GSV-3	110.8
GSV-4	117.9

Wang, Jeng and Shieh [*110*] determined arsenic in airborne particulate matter by means of ICP-MS. They tested two closed-vessel digestion methods, i.e. high-pressure bomb digestion and microwave digestion with NIST SRM 1648 (urban particulate matter). Their results are shown in table 6.8.

Table 6.8: Comparison of As determinations in airborne particulate matter, NIST SRM 1648, by closed-vessel digestion methods under different conditions.

Digestion method	**Amount of acid mixture in ml**	**Digestion time**	**% Recovery of arsenic**
High-pressure bomb digestion:			
HNO_3	10	5 h	74.5
HNO_3-$HClO_4$	10 (1+1)	5 h	82.0
HNO_3-$HClO_4$/HF	10 (3+5/2)	7 h	96.4
HNO_3-$HClO_4$/$HClO_4$-HF	10 (3+3/2+2)	7 h	101.3
Microwave digestion:			
HNO_3-$HClO_4$-HF	5 (3+5+2)	18 min	140.2
HNO_3-$HClO_4$/$HClO_4$-HF	5 (3+3/2+2)	18 min	107.4

Sakao and Uchida [*111*] determined arsenic levels in shellfish tissue samples by ICP-MS. They analysed the following certified reference materials: NIST (USA) SRM 1566 (oyster tissue) and NIES no. 6 (mussel) with Co, Y and Bi as internal standards. They also used a sealed bomb

decomposition method (nitric acid) as a sample preparation procedure. They also employed a high resolution ICP-MS in order to overcome interferences from polyatomic ions. Table 6.9 shows their results.

Table 6.9: % Recoveries for As from oyster tissue and mussel by ICP-MS.

Technique	**% Recovery of arsenic from oyster tissue**	**% Recovery of arsenic from mussel**
Quadrupole ICP-MS	124.6	140.2
High resolution ICP-MS	103.1	103.3
Sealed decomposition method (with quadrupole ICP-MS)	-	97.2

6.4 Experimental

6.4.1 *Reconstitution of Seronorm Trace Elements Urine [108]*

The lyophilised material is sealed to ensure stability. In order to reconstitute the material, the screw cap was opened and the rubber stopper was carefully lifted without removing it completely and the air was let to enter the vial through the groove of the lower part of the stopper avoiding the loss of dry material. The rubber stopper was then removed. 5.00 ml high purity water was then added to the vial, the vial was carefully closed and let to stand for 30 minutes. The content of the vial was completely dissolved by gentle swirling, avoiding the formation of foam.

6.4.2 *ICP-MS procedure*

Preparation of sample and standard solutions for analysis by ICP-MS

The content of the vial was diluted 50x by transferring 1 ml of the solution to a 50 ml volumetric flask and making it up to the mark with distilled water. La was also added to the solution as internal standard before making it up to the mark. The chloride content of the solution to be analysed by ICP-MS was approximately 87 mg dm^{-3}.

The standards were prepared as set out in chapter 4 with La as internal standard. A solution that was blank with respect to arsenic and contained 200 mg dm^{-3} chloride (10 μl HCl transferred to

a 50 ml volumetric flask) was prepared in order to assess the correction factor to be applied to the intensities at *m/z* 75.

ICP-MS: Instrument optimisation and method used

The instrument was optimised as set out in chapter 2. After the instrument was calibrated with the prepared standards, the prepared samples were analysed. The 5.00 μg dm^{-3} arsenic calibration standard was used to monitor the drift of the instrument at *m/z* 75.The method used for analysis was as developed in chapter 4.

6.5 Results and discussion

Although the number of samples analysed by ICP-MS was small, the drift of the instrument at *m/z* 75 was monitored over a time period of 150 minutes on the day of the analyses. The 5.00 μg dm^{-3} standard were analysed at intervals of approximately 50 minutes. In the case of no internal standard being applied the measurements were 4.73 μg dm^{-3}, 4.47 μg dm^{-3}, 5.31 μg dm^{-3}, 5.48 μg dm^{-3} and the drift correction equation was calculated to be ($y = -2.278e\text{-}6x^3 + 5.596e\text{-}4x^2 - 2.756e\text{-}2x + 4.734$). In the case of La as internal standard the measurements were 4.63 μg dm^{-3}, 4.60 μg dm^{-3}, 5.88 μg dm^{-3}, 6.19 μg dm^{-3} and the drift correction equation was calculated to be ($y = -2.961e\text{-}6x^3 + 7.054e\text{-}4x^2 - 2.861e\text{-}2x + 4.630$).

The interference correction factor at *m/z* 75 was calculated as set out in chapter 4: The intensities at *m/z* 75 and *m/z* 77 were monitored for a solution consisting of water only as well as for a solution containing a small amount of chloride. The ratio of the intensities of the last solution is determined after the intensities of the water solution have been subtracted from those of the last solution. The correction factor was calculated to be 4.352. Although the interferent is usually depicted to be $^{40}Ar^{35}Cl$ it should be borne in mind that $^{38}Ar^{37}Cl$ may also be contributing to the intensity at *m/z* 75. It is therefore imperative that the interference correction factor be determined before the analyses of the samples to take into account instrument conditions and the formation of polyatomic interferences at *m/z* 75. The results of the analyses of the arsenic content of Seronorm Trace Elements Urine are shown in table 6.10.

Table 6.10: Results of the determination of the arsenic content of Seronorm Trace Elements Urine by means of ICP-MS.

Drift correction	**Internal standard**	**Interference correction**	**% Recovery of As**
Not applied	None	Not applied	110.1
Not applied	La	Not applied	120.1
Not applied	None	Applied	87.7
Not applied	La	Applied	88.2
Applied	None	Not applied	126.4
Applied	La	Not applied	137.6
Applied	None	Applied	100.3
Applied	La	Applied	101.0

From table 6.10 it may be seen that when only drift correction or interference correction was applied, unacceptable results were obtained. The recoveries that were obtained after both drift correction and interference correction were applied proved to be acceptable with and without the use of an internal standard.

6.6 Recommendations

A dilution factor of 50 was employed for the urine samples in this study. Although this reduced carbon loading as element-specific enhancement of the As signal might occur in the presence of a carbon matrix [*79*], it is recommended that smaller dilution factors are also used with the proposed method in order to test the validity of the method in matrices with a higher carbon content.

In this study the interference correction factor was determined with a solution that contained approximately the same amount of chloride (200 mg dm^{-3}) than the sample solutions (87 mg dm^{-3}). It is however recommended that the chloride content of unknown samples is determined beforehand (e.g. potentiometrically) and that the chloride content of the solution be matched exactly to those of the sample solutions.

Selenium is usually present together with arsenic in biological matrices [*79*]. The certified reference material analysed in this study did not have a certified Se content. A detailed study should be made of the effect of ^{77}Se on the interference correction procedure and the method should be modified to take into account the contribution of selenium to *m/z* 77.

6.7 Conclusion

It was shown to be possible to successfully determine the arsenic content of a biological sample that has a significant chloride concentration by means of ICP-MS. The method may be summarised as follows: 1) arsenic calibration solutions was prepared in 1% (v/v) HNO_3 and external calibration was used, 2) the interference correction factor was determined with a solution that contained a small amount of chloride and water, 3) La was used as internal standard, 4) drift correction procedures were employed and 5) the sample solutions were diluted 50x in order to reduce the carbon loading of the plasma.