Aspects of the determination of the platinum group elements and arsenic by inductively coupled plasma mass spectrometry

by

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Submitted in partial fulfilment
of the requirements for the degree

Philosophiae Doctor

in the Faculty of Natural and Agricultural Sciences
University of Pretoria

Pretoria
January 2001

ACKNOWLEDGEMENTS

The author wishes to thank the following:

Professors CJ Rademeyer and CA Strydom for their guidance.

The Foundation for Research and Development, the University of Pretoria and her parents for financial assistance.

The Forensic Science Laboratory of the South African Police Service for the use of their equipment and instrumentation.

Her husband, Heinrich Schmidt, for his advice and assistance.

Her family for their encouragement.

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Aspects of the determination of the platinum group elements and arsenic by inductively coupled plasma mass spectrometry

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Inductively coupled plasma mass spectrometry is an extremely sensitive analytical technique for the detection of the isotopes of the elements.

The principles of the technique and the instrumentation associated with it were discussed with emphasis being placed on the inductively coupled plasma, ion extraction, ion focusing, quadrupole mass spectrometers and ion detection.

In order to set up a procedure for the optimisation of the inductively coupled plasma mass spectrometer and due to the complex nature of the technique a study was made of the effects of instrument parameters on the signals of the light elements, the heavy elements, the background intensities and the formation of interferences, for example polyatomic oxides and doubly charged ions. The parameters investigated include torch adjustment in the *x*, *y* and *z* directions, the coolant and auxiliary gas flow rates, the power, the aerosol carrier gas flow rate as well as ion lens settings.

An attempt was made to optimise and refine the method of quantitative determination of the platinum group elements (iridium, palladium, platinum, rhodium, ruthenium) and gold by means of inductively coupled plasma mass spectrometry. Selected isotopes of argon, scandium, yttrium and lanthanum were considered as possible internal standards for such determinations. The effect of the concentration of aqua regia present in solution on the ratios of the isotopes of the analytes to the isotopes of the internal standards was determined. Extensive regression data were compiled for calibrations involving the isotopes of the platinum group elements and gold with the mentioned isotopes as internal standards. The accuracy of quantitative determinations using these calibration curves was then determined in matrices comprising of various concentrations of aqua regia.

The quantitative determination of mono-isotopic arsenic in acidic matrices was investigated. Interferences render the quantitative determination of arsenic in a chloride containing matrix almost impossible. The reason for this is the fact that the argon isotope of mass 40, which is present due to the plasma, and the chlorine isotopes of masses 35 and 37, which is usually present due to the sample matrix or introduced via reagents, combine to form polyatomic ions at masses 75 and 77. The only naturally occurring isotope of arsenic is detected at mass 75. Various procedures for the correction of these polyatomic interferences on the analyte signal of arsenic were investigated in an attempt to make the accurate detection of low levels of arsenic by means of inductively coupled plasma mass spectrometry possible. In order to test the viability of using these correction procedures and to verify the accuracy thereof, molecular correction factors, employing the formation of polyatomic ions at masses 75 and 77, were determined in a number of acidic matrices. The effects of these correction factors combined with the use of several isotopes of chlorine, argon, scandium, yttrium and lanthanum as internal standards, on the quantitative determination of arsenic in various acidic matrices, including nitric acid, hydrochloric acid and combinations thereof, were monitored.

Certified reference materials were analysed in order to verify the validity of the developed methods.

SAMEVATTING

Aspekte van die bepaling van die platinum groep elemente en arseen deur middel van induktief gekoppelde plasma massaspektrometrie

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Induktief gekoppelde plasma massaspektrometrie is 'n baie sensitiewe analitiese tegniek vir die bepaling van die isotope van die elemente.

Die basiese beginsels van die tegniek en die instrumentasie wat daarmee geassosieer word, is bespreek en klem is gelê op die induktief gekoppelde plasma, ioon-ekstraksie, ioon-fokusering, kwadrupool massaspektrometers en ioon-deteksie.

Ten einde 'n prosedure daar te stel vir die optimisering van die induktief gekoppelde plasma massaspektrometer en as gevolg van die komplekse aard van die tegniek, is 'n studie gemaak van die effek van instrument veranderlikes op die seine van die ligte elemente, die swaarder elemente, die agtergrond intensiteite en die vorming van steurders, byvoorbeeld poli-atomiese oksides en dubbel gelaaide ione. Die veranderlikes wat ondersoek is, is onder andere verstelling van die fakkel in die *x*-, *y*- en *z*-rigtings, die vloeitempo's van die verkoelings- en plasmagasse, die plasmadrywing, die vloeitempo van die verstuiwergas asook die verstellings van die ioon-lense.

'n Poging is aangewend om die metode van kwantitatiewe bepaling van die platinum groep elemente (iridium, palladium, platinum, rodium, rutenium) en goud deur middel van induktief gekoppelde plasma massaspektrometrie te optimiseer en te verfyn. Sekere isotope van argon, skandium, yttrium en lantaan is oorweeg as moontlike interne standaarde vir sodanige bepalings. Die effek van die konsentrasie van koningswater teenwoordig in oplossing op die verhoudings van die isotope van die analiete tot die isotope van die interne standaarde, is bepaal. Omvattende regressie data vir kalibrasies van die isotope van die platinum groep elemente en goud met die genoemde isotope as interne standaarde, is bepaal. Die akkuraatheid van kwantitatiewe bepalings deur van hierdie kalibrasie kurwes gebruik te maak, in matrikse wat uit verskeie konsentrasies van koningswater bestaan, is vasgestel.

Die kwantitatiewe bepaling van arseen, wat slegs een isotoop het, in verskillende suurmatrikse is ondersoek. Steurders maak die kwantitatiewe bepaling van arseen in 'n chloried-bevattende matriks bykans onmoontlik. Die rede hiervoor is die feit dat die argon-isotoop van massa 40, teenwoordig as gevolg van die plasma, en die chloor-isotope van massas 35 en 37, teenwoordig as gevolg van die monster se matriks of as gevolg van reagense gebruik, kombineer om poli-atomiese ione van massas 75 en 77 te vorm. Die enigste isotoop van arseen wat natuurlik voorkom, word waargeneem by massa 75. Verskeie prosedures om die korreksie van hierdie poli-atomiese steurders op die analiet-sein van arseen te bewerkstellig, is ondersoek. Dit is gedoen in 'n poging om die akkurate bepaling van lae vlakke van arseen deur middel van induktief gekoppelde plasma massa spektrometrie moontlik te maak. Om die haalbaarheid van hierdie korreksie-prosedures te toets en die akkuraatheid daarvan te verifieer, is molekulêre korreksie-faktore, wat berus op die vorming van poli-atomiese ione van massas 75 en 77, bepaal in 'n aantal suurmatrikse. Die effek van hierdie korreksie-faktore, gekombineer met die gebruik van verskeie isotope van argon, chloor, skandium, yttrium en lantaan as interne standaarde, op die kwantitatiewe bepaling van arseen in verskeie suurmatrikse, insluitende salpetersuur, soutsuur en kombinasies daarvan, is vasgestel.

Gesertifiseerde verwysingsmateriale is geanaliseer om die geldigheid van die ontwikkelde metodes te toets.

LIST OF ABBREVIATIONS USED

ICP-MS:	Inductively coupled plasma mass spectrometry or Inductively coupled plasma mass spectrometer
ICP-AES:	Inductively coupled plasma atomic emission spectrometry or Inductively coupled plasma atomic emission spectrometer
RF:	Radio frequency
RSD:	Relative standard deviation
XRF:	X-ray fluorescence spectrometry
AAS:	Atomic absorption spectrometry
GFAAS:	Graphite furnace atomic absorption spectrometry