METHOD DEVELOPMENT FOR THE DETERMINATION OF TRACE IMPURITIES IN NUCLEAR GRADE ZIRCONIUM

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DECLARATION

I declare that this dissertation is my own, unaided work. It is being submitted for the Degree of Master of Science at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination at any other University.

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(Signature of candidate)

____27th __day of____October______2020__ in__Johannesburg.

Abstract

Zirconium is currently the most suitable cladding material available for nuclear fuel. Its chemical properties allow thermal neutrons to be transmitted through it with minimal loss of these atom-splitting neutrons. However, the purity of the material is of utmost importance as the presence of impurity elements such as hafnium, boron and cadmium among others, may adversely affect the nuclear fission process, by absorbing thermal neutrons. Removal of these impurities from the material continues to be a persistent challenge and the analysis of the purified material is also a challenge. The immediate challenges with the analysis of the material are inadequate, outdated, ineffective analytical methods which are not standardized. Thus the aim of this study was to develop a functional analytical method for the analysis of nuclear grade zirconium using currently available analytical techniques.

The research approach involved the development and testing of critical steps performed in the analysis of the material, with a particular focus on the sample preparation step. The dissolution of the material using hydrofluoric acid, including the effect of this mineral acid on each of the impurity elements was studied in detail. The preparation procedure for analysis by inductively coupled plasma – atomic emission spectrometry (ICP-AES) was investigated and evidence to support the effectiveness of the preparation procedure was gathered and evaluated on the basis of recoveries obtained from treated solutions.

From this study, the following findings were noted: the use of HF alone will result in non-quantitative determinations of the following elements: Ca, Pb, Sr and the rare earth elements (REEs). The use of a strongly oxidizing acid, $HClO_4$, will prevent the formation of the insoluble fluoride compounds of these elements. Thus, the most effective dissolution media should contain a significant amount of perchloric acid to have a truly quantitative determination of all the elements specified. The preparation and analysis of a reference material was the only means of assessing and validating the effectiveness of the developed method, as there are no available proficiency testing schemes. Lastly, the need to have current literature from others developing similar methods across the world, made available, unhindered by the secrecy that prevails in the nuclear industry.

The developed method has been proven to be fit for purpose based on recoveries (Bias) obtained on the reference material NBS 1212a, with the accuracy and precision of measuring 22 of 27 specified elements being within acceptable recovery range of 80-110% and relative standard deviation < 15% RSD. The developed method has quantification limits, for the specified impurity elements, ranging from 0.026 mg L^{-1} to 0.971 mg L^{-1} for magnesium and uranium respectively. For elements such as B, Cd, Li and U the LOQ's obtained were inadequate. The remaining challenge is to quantitatively determine B, Cd, Li and U, which could not be quantified due to lack of sensitivity, by an alternative technique such as ICP-MS.

In conclusion, the main challenges of unavailability of standard reference materials; standard methods; and collaborative laboratories for determining the impurity elements in nuclear grade zirconium has been overcome. The analytical method as developed can be implemented as a working procedure that will allow for clear product characterization, furthermore, meaningful contribution to the sparsely available literature on the topic can be made.

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List of Abbreviations

NECSA:	Nuclear Energy Corporation of South Africa
AMI:	Advanced Materials Initiative
ICP-OES:	Inductively Coupled Plasma –Optical Emission Spectrometry
IPC-MS:	Inductively Coupled Plasma – Mass Spectrometry
LOD:	Limit of Detection
LOQ:	Limit of Quantification
FAAS:	Flame Atomic Absorption Spectrometry
R&D:	Research and Development
PDZ:	Plasma Dissociated Zircon
SRM:	Standard Reference Material
CRM:	Certified Reference Material
DC:	Direct Current
PSMS:	Plasma Source Mass Spectrometry
GDMS:	Glow Discharge Mass Spectrometry
GDOES:	Glow Discharge Optical Emission Spectrometry
NBS:	National Bureau of Standards
MLOD:	Method Limit of Detection
MLOQ:	Method Limit of Quantification
cps:	Counts per second
CCD:	Charge Coupled Device

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CHAPTER 1

INTRODUCTION

The beneficiation of zircon to nuclear grade zirconium and the uses of zirconium metal in the nuclear industry and its production processes are given in this chapter. The challenges associated with the analysis of nuclear grade zirconium, for certification purposes, are presented with the proposed solution being a newly developed and validated analytical method.

1.1. Background and Motivation

Zirconium is produced mainly from the minerals baddeleyite (94% ZrO_2, 1.2% HfO_2) and zircon ($ZrSiO_4$ (64.2% ZrO_2, 2% HfO_2)) which is found as an impurity in many minerals such as titanates, niobates, tantaloniobates, rare earth silicates etc. (Petrov & Elinson, 1965a) Zirconium compounds are used in many different applications in everyday life including; deodorants, flash bulbs, lamp filaments and artificial gem stones. Zirconium metal finds its greatest use in the nuclear industry where it is used mainly as cladding material for the nuclear fuel, due to its low thermal neutron capture cross section and its outstanding anti-corrosion and mechanical properties (Petrov & Elinson, 1965a) .

The Nuclear Energy Corporation of South Africa (NECSA), through the support of the ‘Advanced Metals Initiative’ (AMI) has been involved in developing a process of manufacturing nuclear grade zirconium using the beneficiated mineral zircon. The material produced will have to be characterized, against a given trace impurity specification, using the available analytical techniques at NECSA.

Nuclear grade or reactor grade zirconium metal has to conform to strict mechanical and chemical specifications, to allow for its safe use in a nuclear reactor. For the chemical specification relating to trace impurities, to be confirmed, a testing method that can deliver accurate and precise results must be in place.

There are very limited documented methods available for the analysis of trace impurities in nuclear grade zirconium. The available literature on the analysis is either outdated or covers only a few of the specified elements (Batistoni, et al., 1985). To add to this, the listed methods employ lengthy sample preparation methods that often require the pre-concentration of some of the analytes due to lack of instrument sensitivity (Pollock, 1963). Other methods require the matrix to be removed using liquid-liquid extractions methods while others still employ sample preparation techniques that produce a sample not suitable for typical modern trace analysis instrumentation such as ICP-OES and ICP-MS (Batistoni, et al., 1985).

The successful analysis of any material that may be produced at NECSA will require the development of a functional method. The desired method should be simple, not time consuming and covering the bulk of the required specified analytes. The method should also ensure minimal loss of analyte and contamination from the laboratory environment and all reagents used. The motivation for this study is the lack of sufficient documented analytical methods for the determination of trace impurities in nuclear grade zirconium using currently available analytical techniques.

1.2. Significance of Research

The documentation of the analysis of most nuclear materials is often done for internal company use and is generally not publicized. For this reason limited literature on the analysis of nuclear grade zirconium is available. The available literature is out dated in terms of analytical techniques that are far behind currently available technologies. This study was conducted with the main targeted analytical technique being ICP-OES.

As no publicly available or published standard method of analysis is available, this project will result in a robust validated analytical method for the determination of trace impurities in nuclear grade zirconium.

The developed method will be simple and efficient using simple sample preparation steps and easily accessible analytical techniques. The majority of the specified impurity elements will also be covered by the developed method, this will add to the current deficiency in the available methods, which cover a few of the specified analytes using tedious and lengthy sample preparation techniques.

Previously utilized analytical techniques, such as ; colorimetric spectrophotometric techniques and Flame Atomic Absorption Spectroscopy (FAAS) have been successfully used, but are limited in contrast to the more modern emission and mass spectrometry techniques, namely ICP-OES and ICP-MS for the determination of trace metals in this matrix.

Analyte selectivity in the analysis using atomic absorption and colorimetric spectrophotometric techniques can be challenging due to the zirconium matrix that is extremely spectrally rich. The rich absorption spectra produced by zirconium makes many of the best analyte absorption wavelengths unusable. Thus for these techniques to be effective matrix removal has been widely used (Hayes & Metcalfe, 1962).

The developed method will also serve as a documented working instruction for the analysis of all R&D samples produced at NECSA and possibly in any material that may be manufactured in South Africa.

1.3. Dissertation Outline

The current chapter is the introductory chapter dealing with the scope of the project and giving some supporting background to the project, the following chapter will deal with the literature available on the subject, which will further support the reason for this study being conducted and the opportunity presented because of inadequate procedures to perform the analysis of the stated material.

Chapter three will deal with the methodology followed in working towards attaining the said goals for the study.

The results coupled with the discussion of all the experimental work done will be presented in the fourth chapter, with each result being discussed immediately after the results are presented. The sequence for the presented results is in the same order presented in the methodology chapter. The concluding chapter will then follow.

Chapter 2

LITERATURE SURVEY

Mineral beneficiation of zircon through the AMI project for the possible benefit of South Africa noted. Available literature on the analysis of nuclear grade zirconium and related topic of method development and validation are discussed.

2.1 Mineral Beneficiation

South Africa is one of the mineral rich countries. With a wide variety of minerals being mined and exported to various countries, usually as the raw mineral. The raw minerals exported are significantly less valuable than the semi- processed form and the final products which are imported into the country. Reasonable income would be generated for the country from the finished or semi-processed products if the minerals were processed and beneficiated in South Africa. (Monnahela, 2008b)

The challenge is to develop processing methods that are efficient and cost effective, processes that would enable the country to be globally competitive. To address this challenge, the government of South Africa has initiated a programme called the Advanced Metals Initiative (AMI). The initiative has four focus areas of research, namely: Ferrous Metals, Light Metals, Precious Metals and New Metals (which include zirconium, hafnium, tantalum and niobium).

The aim of this initiative is to develop, through research and development, processes that will allow South Africa to beneficiate its own minerals and minerals from other African countries, for the economic benefit of Africa.

To date only four countries namely, France, Russia, United States of America and China are capable of manufacturing nuclear grade zirconium metal (Ganguly, 2002). With the demand for nuclear grade zirconium predicted to increase (as more and more countries acquire, and maintain their nuclear capability), countries producing this grade of Zr may be able to benefit greatly.

Beneficiation of the abundantly available mineral, zircon, to nuclear grade zirconium using efficient processes could see South Africa entering a lucrative market to supply a growing demand. The material could be utilized for South Africa's own consumption or for exporting to nuclear capable countries. Nuclear grade zirconium is about 10 times more valuable than non-nuclear grade zirconium (Hendrick, 1999).

2.2 Nuclear Grade Zirconium Production

Nuclear grade zirconium metal is generally considered to be zirconium that contains less than 100 parts per million of hafnium as an impurity, amongst other elements. The complete chemical specification for this material as given in Table 2.1 consists of many more impurity elements than Hafnium. (Monnahela, 2011)

The chemical composition of the metal affects the physical properties and performance of the metal in a nuclear reactor, as such all impurity elements need to be limited to the specified maximum concentrations. Elements that are of high importance are those that significantly inhibit the fission process in a nuclear reactor. These elements include boron, cadmium, lithium, hafnium and the rare earth elements (Energy, 1993).

Hafnium is of a serious concern as it is present in both baddeleyite and zircon (the main sources of zirconium) at low percentage levels. Hafnium, boron and a few other specified elements have the ability to capture the thermal neutrons needed in a reactor (Energy, 1993) thereby inhibiting the fission process. Other elements affect the physical properties of the metal such as tensile strength and some may cause the metal to become brittle and less ductile. Typically the main criterion used to distinguish nuclear grade zirconium from other grades is the hafnium content, which must be less than 100 ppm.

Table 2.1: Chemical specifications for nuclear grade zirconium (ASTM, 1984)

Element	**Maximum Impurities (ppm)**	**Element**	**Maximum Impurities (ppm)**
Aluminium	75	Phosphorus	100
Boron	0.5	Silicon	100
Cadmium	0.5	Tin	100
Calcium	30	Titanium	50
Cobolt	20	Tungsten	50
Copper	50	Uranium	3.5
Chromium	200	Vanadium	50
Hafnium	100	Vanadium	50
Lithium	1.0		
Lead	100		
Magnesium	600	Chloride	1300
Manganese	50	Nitrogen	50
Molybdenum	50	Oxygen	1400
Nickel	70	Carbon	500

The conventional processes used to produce zirconium metal from the mineral zircon are illustrated in Figure: 2.1. There are three typical processes used to release the zirconium from the mineral, namely carbo-chlorination, reaction with sodium hydroxide and fusion with potassium hexa-fluorosilicate.

A modified process which involves the dissociation of the mineral using a thermal plasma, followed by fluorination of the dissociated zircon mineral (PDZ) is followed at NECSA. Various fluorinating agents which include HF and ammonium bifluoride ($NH_4F.HF$) are used. The fluorination process will result in the production of impure zirconium tetra fluoride containing hafnium tetra fluoride equivalent to the hafnium present in the mineral. The ammonium bifluoride is a waste product generated from some of NECSA's manufacturing processes (Monnahela, 2008a).

Since the dissociated zircon is more easily fluorinated at low temperatures than the raw mineral the additional step is beneficial to the process, allowing for better efficiency in the production process.

Once the fluorinated product is formed, the purification of the halide compound may be done via two routes involving either liquid-liquid extraction or vacuum distillation. The purification process is mainly targeted at lowering the hafnium content. The fluorinated zircon may be converted to the chloride compound before reduction to the metal using the Kroll process. The biggest challenge in the whole production/manufacturing process is the purification of the fluorinated or chlorinated zirconium compounds prior to reduction to metallic Zr using magnesium. (Monnahela, 2008a).

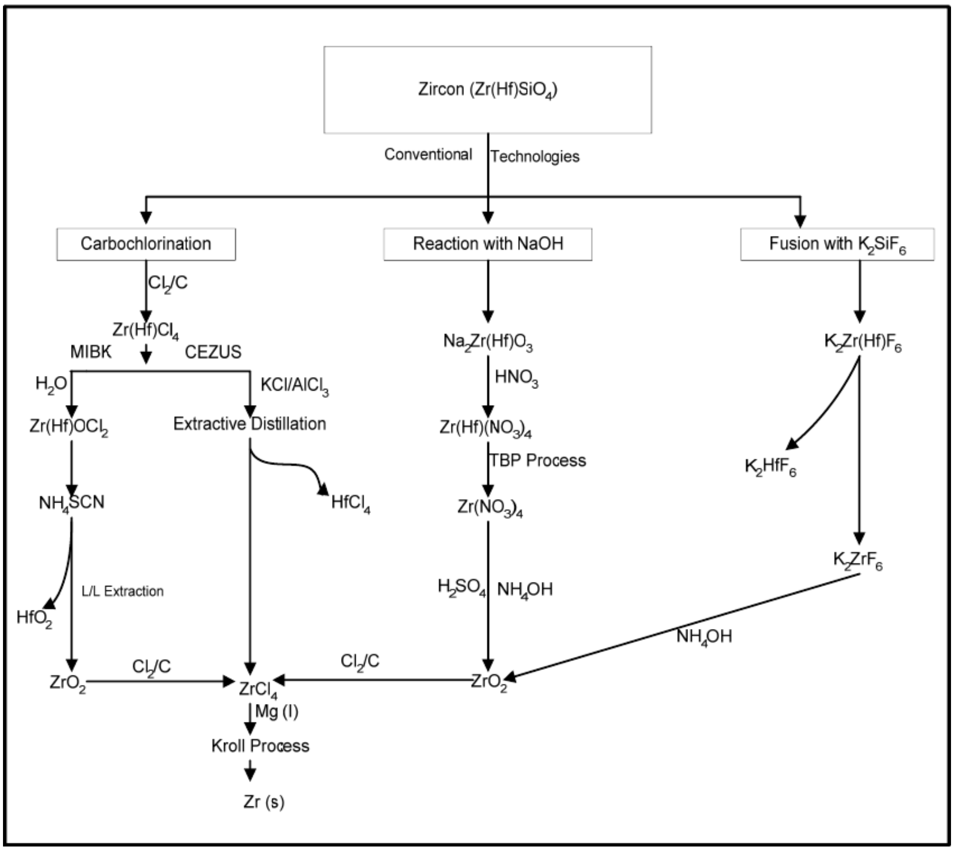

Figure 2.1: Illustration of the Zirconium Production Process **(Monnahela, 2008a)**

2.3 General Aspects of Method Development

For the characterization of the produced metal an analytical method that is proven or validated is needed. The development of an analytical method and the validation thereof are interlinked and are often done concurrently (Chauhan & Mittuharti, 2015). Method development and validation is a systematic process of testing that an analytical procedure in the laboratory is indeed capable of producing accurate and precise results that may be traceable to a primary standard. (Magnusson & Onermauk, 2014a)

The method development and validation process may require the design of experiments to test various parameters around the method including but not limited to; sampling, sample handling and storage, sample preparation, sample preservation and analytical instrument conditions (Heshmatollah, et al., 2019). The outcome of the experiments ultimately gives the evidence that can lead to confidence, that the final procedure developed is capable of consistently producing reliable results.

Two approaches to method validation exist; the inter-laboratory comparison approach and the single laboratory approach (Magnusson & Onermauk, 2014). When a method is needed but is not available as a published standard method, the single laboratory approach is considered. This approach is considerable in other instances where there is no general interest in the method or laboratories using the method are competitors.

In the development of a manufacturing process for nuclear grade zirconium or many other materials, the chemical analysis of various materials ranging from raw materials (zircon), to intermediate products, to the final product is critical. Characterization of these materials should occur without exception.

Analytical results from a chemical laboratory are an integral part of the development of the manufacturing process and give valuable information about the efficiency of the process at various stages of production. These results are an invaluable tool that may be used to improve the process being developed. Chemical analysis in the development of a beneficiation process should also enable the researcher to refine the processes when undesired systematic errors are discovered.

The primary objective of a chemical analysis is to achieve an accurate result which can be reproduced consistently. Analytical methods which are used must be refined to achieve this primary goal. The secondary objective of chemical analysis is to be able to deliver these results in a cost effective and speedy manner (Li, et al., 2019). In short the ultimate purpose of method development is to create analytical methods that can deliver accurate and precise results at a reasonable cost in the shortest time possible using resources available to a testing laboratory.

The development of such methods is an important task involving elimination of any unproven assumptions about the behavior of the material under inspection, testing and proving that each of the functions performed in carrying out the analysis produces the desired outcome. To prove or disprove any assumptions made in the method procedures a one variable at a time approach is often used, where one variable is studied while all other parameters are kept constant (Anthony, 2003).

2.4 Method Validation

Analytical figures of merit and other terms used to describe a method's capabilities are obtained from the method validation process. These may include the following: limits of detection (LOD), limits of quantitation (LOQ), sensitivity, ruggedness, robustness, working and analytical range.

Method validation is always done to determine the suitability of the method in determining the analytes required or specified, at the concentration levels needed in a given matrix. When a method is developed in the laboratory without the use of a standard method (as a basis), method validation is also normally part of the development process. (Magnusson & Onermauk, 2014a)

Standard methods of analysis (which are preferred methods) have been published and used throughout the world, but even these cannot assure that different laboratories will produce the same, or even similar, results when analyzing the same material. Before these can be used they have to be verified using known or characterized materials. These methods still have to be adjusted and optimized to suit each laboratory's environment. For the determination of trace impurities in nuclear grade zirconium, there are no standard methods available.

Considering the two main objectives behind developing a method; namely accuracy and precision, a very useful tool in the form of Standard Reference Materials or Certified Reference Materials is often available. One SRM 'NBS 1212a' (appendix A), sourced by NECSA and CRM solutions of the impurity analytes were available and used for this study.

Standard Reference Materials (SRM's) are materials with a similar matrix as the materials to be analysed, with certified parameters that include the uncertainty associated with the measurement of the certified parameter. Due to the involvement of many participants in determining these parameters the certified values are acquired by means of consensus.

Certified reference materials (CRM's) which are materials with certified parameters that are traceable to a metrological standard are also available. These may not have the same matrix as the material under study but may be used to spike the material under study. They have certified concentrations of the analytes of interest in a different matrix.

Both these materials may be used to give definite assurance that the analytical method used is able to deliver accurate results (Vieira, et al., 2019). Thus in developing an analytical method these are very useful, and their use where possible is highly recommended to validate the results produced by a method. If standard materials are available then the non-use of standard methods is not too critical as the standards will ultimately prove the suitability of the developed or tested method.

2.5. Analytical Figures of Merit (Performance Characteristics)

A developed method needs to be proven to be fit for its intended use. This is done by comparing the methods' performance characteristics against pre-determined criteria. For this study the criteria used is the acceptable accuracy and precision of measurement as laid out in 'Trends in Analytical Chemistry' (Taveniers, et al., 2004).

The performance of a method may be expressed in the form of its analytical figures of merit such as accuracy (bias), precision, limits of detection (LOD) limits of quantification (LOQ) and Sensitivity (Magnusson & Onermauk, 2014).

Accuracy has been defined as the closeness of a single measurement to a reference value. In this study this parameter has been expressed as relative recovery (Recovery (%)) and relative spike recovery (Spike Recovery (%)), calculated using the formulae below: (Magnusson & Onermauk, 2014b)

$$Recovery(\%) = \frac{\bar{x}}{x_{ref}} \times 100 \qquad \text{(Eq 1)}$$

$$Spike\ Recovery(\%) = \frac{\bar{x}\prime - \bar{x}}{x_{spike}} \times 100 \qquad \text{(Eq 2)}$$

Where: $\bar{x}$ is the mean concentration of the analyte in solution.

$\bar{x}'$ is the mean concentration of the analyte in a spiked solution.

x_{ref} is the reference value for the analyte from SRM.

x_{spike} is the added analyte concentration.

Precision has been defined as a measure of how close measurements are to each other and is typically expressed in statistical terms which describe the spread of the results such as standard deviation and relative standard deviation. The amount of random error present in a method is simply indicated by the magnitude of this characteristic. Relative standard deviations used for this study were calculated according to the formula below:

$$\%RSD = \frac{StDEV}{Mean} \text{ X } 100 \qquad \text{(Eq 3)}$$

Where: StDev is the standard deviation from replicate measurements

Limit of detection (LOD) is simply defined as the lowest concentration of an analyte that can be detected in a sample, using the developed method and with a defined level of confidence. Similarly Limit of quantification (LOQ) is the lowest concentration of analyte that can be quantified in a sample with acceptable performance (Magnusson & Onermauk, 2014c). These characteristics have been determined in two ways: Analysis of blanks and more recently regression analysis on Microsoft Excel. The latter means were employed in this study and the LOD and LOQ were calculated using the following formulae: (Kombath & Balde, 2015)

$$LOD = 3 \times \frac{standard\ calibration\ error\ (S\frac{y}{x})}{slope(x\ variable)} \qquad \text{(Eq 4)}$$

$$LOQ = 10 \times \frac{standard\ calibration\ error\ (S\frac{y}{x})}{slope(x\ variable)} \qquad \text{(Eq 5)}$$

These two parameters alone are the most important parameters to establish for an analytical method, they are directly related to the sensitivity (slope) of the instrument. The approach used to calculate these characteristics take more than the error that can be found when only a blank sample is used. This is the preferred approach in many industries including the nuclear industry.

2.6. **Analysis of Nuclear Grade Zirconium**

The analysis of nuclear grade zirconium has been done by various analytical techniques, due to the nature of the matrix and the analytes (Brookes & Townshend, 1970). The concentration ranges specified for the impurities makes it necessary to use different analytical techniques, techniques which have good selectivity and appropriate sensitivity for each analyte.

For instance, elements with the lower specified maximum impurity concentrations require an instrument or technique that has high sensitivity or a sample preparation procedure that does not result in a highly diluted analyte concentration. Typically solid state analytical techniques such as DC-Arc, X-ray fluorescence, Plasma Source Mass Spectrometers, Glow Discharge Mass Spectrometers or Optical Emission Spectrometers etc. have been used (Brown & Hillier, 1975).

When the sample preparation step in the analysis results in the sample being diluted, effectively diluting the analyte, a highly sensitive technique such as Inductively Coupled Plasma-Mass Spectrometry would be required or pre-concentration of the analyte with matrix removal to allow for these elements to be analyzed using a less sensitive technique. ICP-MS (Li, et al., 2019) has significantly higher sensitivity and would be able to quantify analytes from diluted liquid samples with ease compared to ICP-OES (Khan, et al., 2013)

The general principles applied for trace element analysis need to be strictly followed when the analysis is done. The nature and concentration of the analyte dictate that all precautions should be taken to avoid contamination of the sample; this may require specialized equipment, procedures and environments. Even when all has been reasonably done to secure the integrity of the sample material, the use of blanks in the analysis is normally required.

The production route employed in the production process may introduce certain challenges or advantages with regards to analysis. For the material produced at NECSA the use of fluorine instead of chlorine in the process will result in some of the analytes reacting differently and forming fluoride compounds that are highly insoluble such as the rare-earth elements, uranium, and volatile compounds which would be lost such as the fluoride or oxy-fluoride compounds of boron, silicon, chromium and phosphorus.

The analysis of zirconium made at NECSA may also introduce new analytical challenges as the material manufactured via the fluoride route may contain certain trace analytes not typically analysed for or elements that are specified at much higher concentrations. Elements that have a strong interaction with fluorides (such as the rare earth elements) may be found at higher concentrations in the produced material.

The possible advantage of the fluoride route in the production of Zr, is the possible loss of analytes such as Cr, Si, B and P during the intermediate production steps which may result in the produced material having lower concentrations of these elements.

2.7. **Instrumentation**

2.7.1. ICP-OES Principles

Inductively coupled plasma optical emission spectrometry (ICP-OES) is a trace element analysis technique that is based on the spontaneous emission of photons from atoms and ions that have been excited in a plasma (Hou & Jones, 2000).

Dissolved samples solutions are converted into an aerosol by means of a nebulizer; this sample aerosol is then directed to the central channel of the plasma. At the core of the plasma temperatures approximately 10 000 K are maintained and the sample aerosol is readily vaporized releasing analyte atoms as free atoms in a gaseous state. Enough energy is present in the plasma to convert the atoms to ions and even ions to higher excitation states, thus both atomic and ionic excited species of an analyte atom may be present in the plasma. (Hou & Jones, 2000)

The excited species would then relax back to their ground state via the emission of a photon. The wavelength of this photon can be used to identify the element from which it was emitted, while the number of photons emitted is directly proportional to the concentration of the element it came from.

A portion of the emitted photons are collected using a lens or a concave mirror, these are then resolved into their different wavelengths using either a monochromator or a polychromator. The resolved photons are then converted to an electrical signal by a photo detector. The signal is amplified and processed by the detector electronics then displayed or stored on a personal computer. (Hou & Jones, 2000)

2.7.2. ICP-OES Components

The instrument used for this study was the SPECTRO Arcos with axially viewed plasma. The basic components of this instrument are displayed in Figure 2.2.

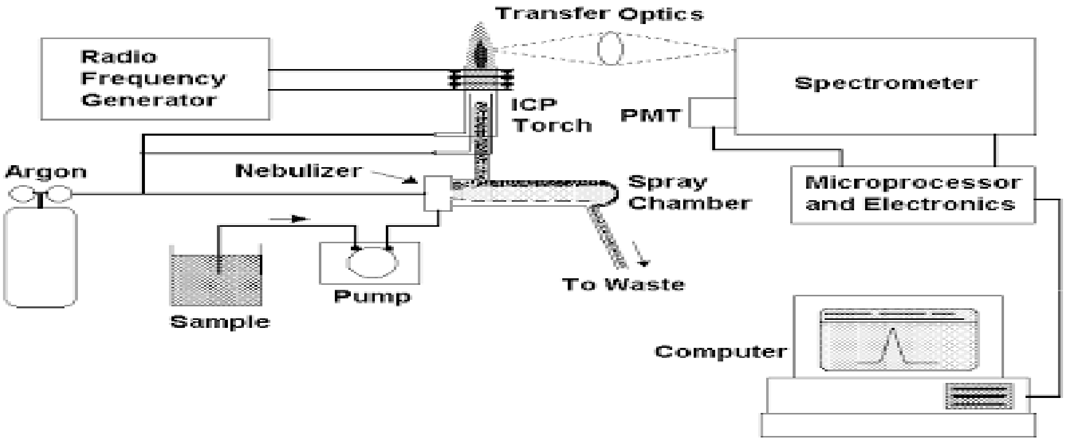

Figure 2:2 Components of the instrument (Michael, 2004)

The instrumentation is composed of the following components:

Sample introduction system, consisting of a nebulizer, spray chamber and torch. The optical interface and the optics or spectrometer, and the detector which is coupled to a readout device connected to a computer.

2.7.3. ICP-OES Advantages and Disadvantages

Analysis of trace metals in various matrices has been achieved with the use of a variety of analytical techniques including but not limited to ICP-OES and ICP-MS. ICP-OES as the more affordable option is utilized more frequently for the analysis of trace elements in liquid solutions (Li, et al., 2019), Table 2.2 list some of the advantages and disadvantages or this Technique.

Table 2.2: Advantages and Disadvantages of ICP-OES

Advantages	Disadvantages
High matrix tolerance	Limited sensitivity with general use introduction system
Simultaneous determination of multiple elements per sample	Sample preparation all sample has to be dissolved
Complementary analysis technique to XRF	
Large dynamic range	

2.8. **Trace element quantification limitations to consider**

The analysis of pure materials for trace element constituents presents many interesting challenges. Firstly, the availability of instrumentation that possesses the ability to measure very low concentrations of one compound in the presence of high concentrations of any given matrix (Li, et al., 2019). The analytical techniques required should be both sensitive and selective to the analyte of interest.

Secondly, the handling (including preparation) of the sample material to be analysed may require special procedures and conditions to be followed. The storage of the sample should preserve the integrity of the sample; the storage conditions should not have high concentration levels of the element to be quantified or have environmental conditions that could cause loss of the analyte. The sample preparation process should not introduce the analyte into the sample from any external source neither should it cause any loss of analyte. (Magnusson & Onermauk, 2014c)

2.9. **Overall Method Performance**

The ability of a method to deliver correct results is affected by the following parameters: Sensitivity of the instrument, instrument detection and quantification limits (an instrument's ability to distinguish between noise and analyte signal) and Instrument linearity. Other parameters are not dependent only on the instrument, such as precision which can be affected by other processes outside of the final measurement on the instrument.

Accuracy and precision of the method are the two most critical characteristics of a method and these are influenced by the parameters mentioned above and the efficiency of sampling, storage, preparation and introduction of the sample solution into the instrument.

The performance characteristics need to be summarized and expressed as the method performance characteristic which will incorporate the whole analysis process including sample preparation. i.e. the LOD and LOQ must be exclusively expressed as method LOD (MLOD) and method LOQ (MLOQ). The following were considered in developing the method; Sample preparation, instrument conditions, instrument performance LOD, LOQ & sensitivity, Interferences, instrument selection based on sensitivity and LOQ. (Magnusson & Onermauk, 2014d)

Sampling was not addressed as this is under the control of the manufacturer. The practical determination of LOQ for the low specified elements in the matrix was done by spiking a real sample with increasing concentrations of the analyte and using the spike recovery values obtained to select the appropriate level of quantification.

2.10. **Research Aim and Objectives**

The main aim of the research is to develop and validate an analytical method for the determination of metallic impurities in nuclear grade zirconium using the available analytical techniques.

The aim was achieved by the following objectives:

- To optimize the sample preparation method for analysis by ICP-OES or ICP-MS.
- To evaluate the performance of the instrumentation used with respect to figures of merit.
- To verify the method using standard reference materials and samples spiked with certified traceable material.

2.11. **Research Questions**

- Can the analysis of the metallic impurities be done to satisfactory standards against the given nuclear grade specification?
- Can a method that is simplified and functional (utilizing resources available at NECSA) be developed for the analysis of nuclear grade zirconium?

2.12. **Research Hypothesis**

A simple, quick and cost effective analysis method for the determination of trace impurities in nuclear grade zirconium can be developed and validated at NECSA.

Chapter 3

METHODOLOGY

The research approach employed in this study including the specific instrumentation and analytical methodology is given in this chapter.

3.1 Procedure

3.1.1 Instrumentation

- ICP-OES Spectrometer – with Multiple CCD detectors
- Make: SPECTRO
- Model: ARCOS FHE12
- Serial Number: 76004553

Table 3.1: Instrument Conditions

Parameter	Setting
RF Power	1400W
Coolant Flow	13L/min
Auxiliary Flow	1L/min
Carrier Flow	1L/min
Spray Chamber	Cyclonic- Tracey TFE
Nebulizer	Mira mist
Viewing Mode	Axial
Viewing Depth	5mm

3.1.2 Equipment

- Aluminium Digestion Block and Hotplate
- PTFE Beakers
- 50mL and 15mL Graduated plastic tubes
- Centrifuge

3.1.3 Reagents

- $HClO_4$ 70% (m/v)
- HNO_3 65% (m/v)
- HF 40% (m/v)
- 10000 mg L^{-1} Zr standard
- 1000 mg L^{-1} Scandium standard.
- 1000 mg L^{-1} Standards, single and multi-element standards containing all the specified elements.
- Demineralized water

3.2 Recovery Tests for Sample Preparation

Sample preparation as a preceding step to the chemical analysis of any material is critical and deserves significant attention in the method development process. As the analysis performed will only be as good as the sample preparation (Moldoveanu & David, 2015).

The first step in sample preparation is the dissolution of the zirconium metal using a suitable solvent. For zirconium the most effective mineral acid to use is hydrofluoric acid, thus the initial test performed was with HF only. This acid is effective for the dissolution of the matrix but may adversely affect some of the analytes that need to be quantified. Thus the stability of the entire elements to be analyzed was studied in great detail.

A zirconium matrix was spiked with a known concentration of the analytes and then treated with HF. The treated solution was then analyzed to determine the recoveries of each of the analytes. The recoveries for the concentration levels used were then used to decide on the effect of the acid on the analyte (Eq1 & Eq2). Analytes found to be within the acceptable recovery range as stated in (Taveniers, et al., 2004) were accepted as being unaffected by the acid while those that fell outside of this range were considered as adversely affected.

3.4 Achieving Complete Dissolution of Sample Matrix and Analytes

To overcome the effect of the Hf on some of the analytes the use of a strongly oxidizing acid (perchloric acid) for analytes that were lost due to the formation of insoluble fluoride compounds that precipitated out of solution was investigated. A mixture of HF and $HClO_4$ was used and the similar experiment repeated to assess the recoveries on those elements that are affected by the HF.

The $HClO_4$ was added to the sample after the HF. A volume of 1 mL was added resulting in a v/v concentration of 2% $HClO_4$ in a final volume of 50mL (Yokoyama, et al., 1999). The aim of these tests was to achieve good recoveries for all the elements of interest, including those that were adversely affected by HF.

3.5 Instrument Performance

The analysis of nuclear grade zirconium using ICP-OES needed the confirmation that the instrument will be capable of reaching the desired levels specified in the material. The tests conducted next focused on three characteristics, namely limit of detection, limit of quantification and sensitivity that the instrument would have for each of the specified elements; Al, B, Ca, Cd, Co, Cr, Cu, Dy, Eu, Fe, Gd, Hf, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Si, Sm, Sn, Sr, Th, Ti, U, V, W and Zn in a clean Matrix and a zirconium matrix. Table 3.2 gives the determined instrumental detection limits obtained using a clean matrix.The zirconium matrix was taken as a solution containing 2000 mg L^{-1} Zr .

The instrument conditions used were kept to the standard or normal operating conditions, without any modifications. For each of the analytes the correct measurement conditions were confirmed with respect to;

- Wavelength selection
- Instrument parameters (as stated under instrument conditions)
- Interferences
- Need for background correction

Table 3.2: Selected wave lengths and determined instrumental detection limits for the Spectro Arcos ICP-OES using a clean matrix.

Element	Analyte Wavelength (nm)	Instrumental Detection Limit (mg L^{-1})	Element	Analyte Wavelength (nm)	Instrumental Detection Limit (mg L^{-1})
Al	167.078	0.002	Na	589.592	0.006
B	182.641	0.005	Ni	231.604	0.007
Ca	317.933	0.011	P	177.495	0.015
Cd	214.438	0.004	Pb	220.353	0.021
Co	238.892	0.001	Sb	206.833	0.020
Cr	267.716	0.002	Si	251.612	0.177
Cu	324.754	0.006	Sm	359.260	0.005
Dy	353.170	0.001	Sn	242.949	0.010

Element	Analyte Wavelength (nm)	Instrumental Detection Limit (mg L^{-1})	Element	Analyte Wavelength (nm)	Instrumental Detection Limit (mg L^{-1})
Eu	420.505	0.001	Sr	407.771	0.001
Fe	259.941	0.005	Th	401.913	0.005
Gd	342.247	0.003	Ti	334.941	0.001
Hf	277.336	0.007	U	385.958	0.025
Li	370.780	0.005	V	309.311	0.012
Mg	279.553	0.001	W	207.911	0.039
Mn	260.569	0.001	Zn	206.200	0.041
Mo	202.095	0.008			

Using the standard cooperating conditions on the instrument the recoveries obtained on a spike matrix gave confirmation of the applicability of the selected wavelengths and the presence of significant interferences. Where acceptable recoveries were obtained the absence of interference was confirmed. Unacceptable recoveries were taken as an indication of the presence of interferences and the need to confirm the usability of the selected wavelength or the need for more complex background corrections.

The instrument performance figures of merit, namely limit of detection, limit of quantification and sensitivity were then determined, using Microsoft Excel ANOVA. The quantification limit was also determined practically using incremental concentrations (0.01, 0.05 and 0.10 mg L^{-1}) of all the analytes spiked into the Zr matrix,. The practically determined LOQ was taken as the lowest concentration that could be determined with acceptable recoveries and precision (Magnusson & Onermauk, 2014d, p. 25). The comparison of Instrumental detection limits, ANOVA calculated limits and practically determined limits was necessary, as true confirmation of the method’s ability to quantify the impurity elements present in zirconium was necessary. Also instrumental detection limits are too modest for practical use.

Based on the results for these test the decision could be made of the suitability of the technique for the determination of all the elements as related to the given specification. For Those elements that the technique was found to be less than adequate an alternative technique was proposed.

3.6 Final Preparation Procedure.

A mass of Zr metal was directly weighed into a 50mL plastic tube. To the tube 10mL of demineralized water was added and a stoichiometric amount of HF acid equivalent to 10% excess was slowly added, followed by 1mL of $HClO_4$. The solution was allowed to react until no solid material was visible. After cooling the solution was made up to volume with demineralized water with scandium internal standard added.

3.7 Final Sample Analysis

The prepared solutions of the SRM, spiked and unspiked, were analysed on the ICP after the instrument was calibrated. The instrumental conditions stated in Table 2 were used, with adequate rinsing applied between each solution aspirated.

3.8 Final Method Validation Decision

Once the sample preparation and the instrument conditions had been evaluated, the final confirmation of the efficiency of the analysis was achieved using SRM

NBS 1212a (Appendix A), results for these are found in Table 4.7 expressed as Recovery %.

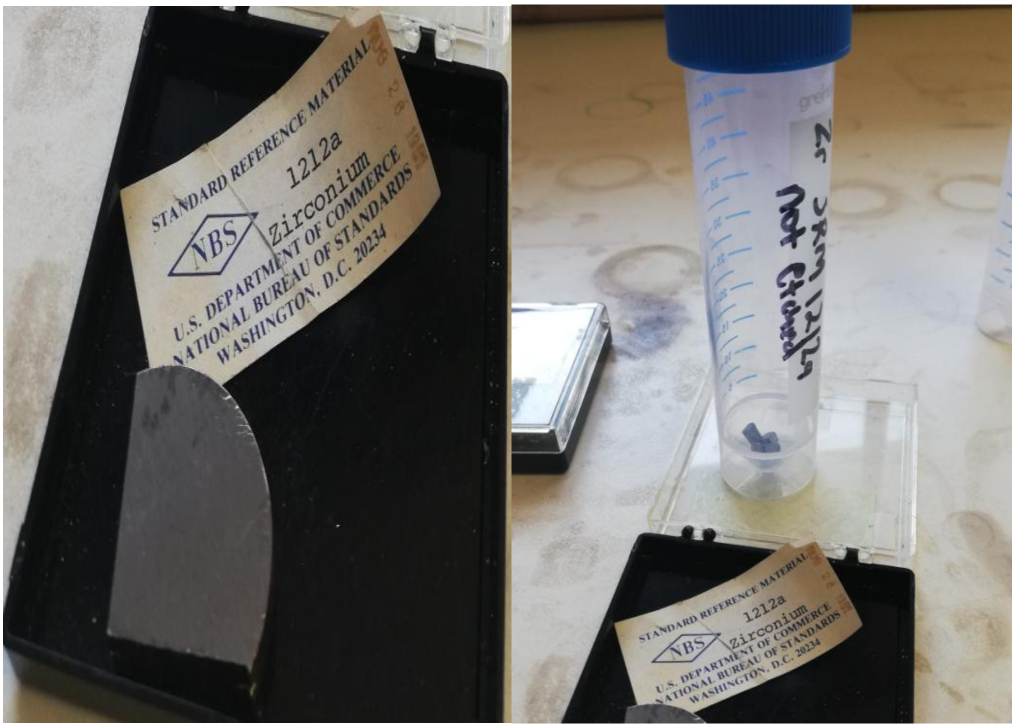

Figure 3.1: Zirconium NBS 1212a SRM

The standard reference material was divided into small pieces weighing approximately 0.2 g. The SRM was then taken through the preparation process and analysed under the stated conditions using a slight excess of HF and HClO4. The dissolved sample was split and part thereof was spiked with elements not certified for, in the material. Scandium equivalent to 1 mg L-1 was added to all solutions as an internal standard to compensate for possible volume variations.

The precision and accuracy of the method was then determined from this test. For certified values these could be used to directly determine the accuracy using (Eq 1), for uncertified values the spike recoveries were used. Results for the impurity elements falling within the certified concentration range were confirmation of the methods ability to satisfactorily quantify these elements. The final method validity decision was based on these results.

Chapter 4

RESULTS AND DISCUSSION

The results for experiments performed in the method development and validation are presented in this chapter. Each experiment is discussed in detail where the results are presented with in the chapter.

4.1 The effect of HF on impurity analytes in sample preparation

The dissolution or digestion of Zr metal with aqueous HF requires a slight excess of the acid to be used, thus when the metal is completely dissolved by the mineral acid, there will remain in solution some unreacted HF. This unreacted HF will also react with any available reactive elements, including the trace contaminants in the metal. During this dissolution process heat is released and the temperature of the solution rises above room temperature

Three sets of 6 test solutions containing 2 mg L^{-1} of the analytes and 5 mg L^{-1} Sc internal standard were prepared. To five of the prepared solution in each set the following additions of 40% supra-pure HF was made: 0.5, 1.0, 1.5, 2.0 and 2.5% (v/v) labeled as Samples; B2, B3, B4, B5 and B6 respectively. All solutions were diluted to the 50mL mark with demineralized water.

The test solutions were analysed on the same day the solutions were prepared as well as the following 2 days. The effect of the different concentrations of aqueous HF added on the analyte and the time taken to perform the analysis was then studied, and the results are shown in Figure 4.1 to 4.4, with figure 4.4 being the summary of only those elements showing a noticeable trend.

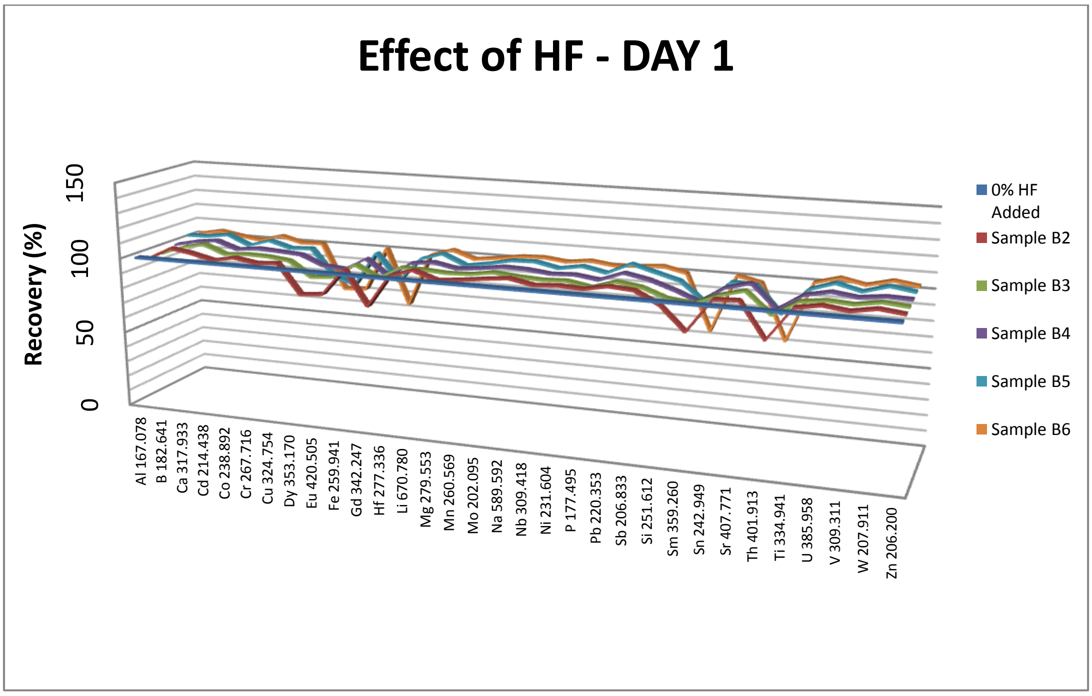

Figure 4.1: Effect of HF on Impurity Analytes Day 1.

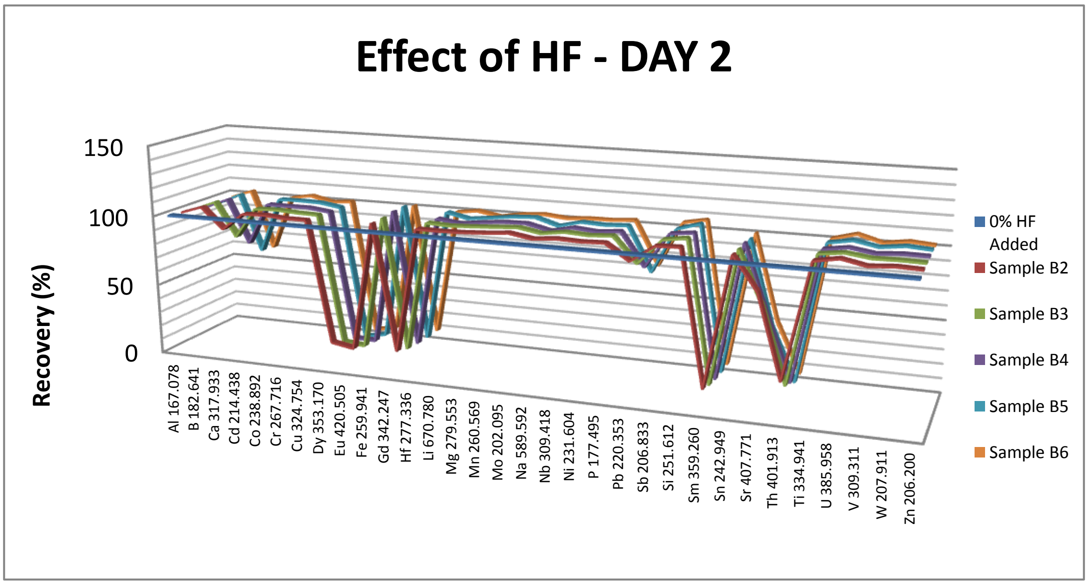

Figure 4.2: Effect of HF on Impurity Analytes Day 2.

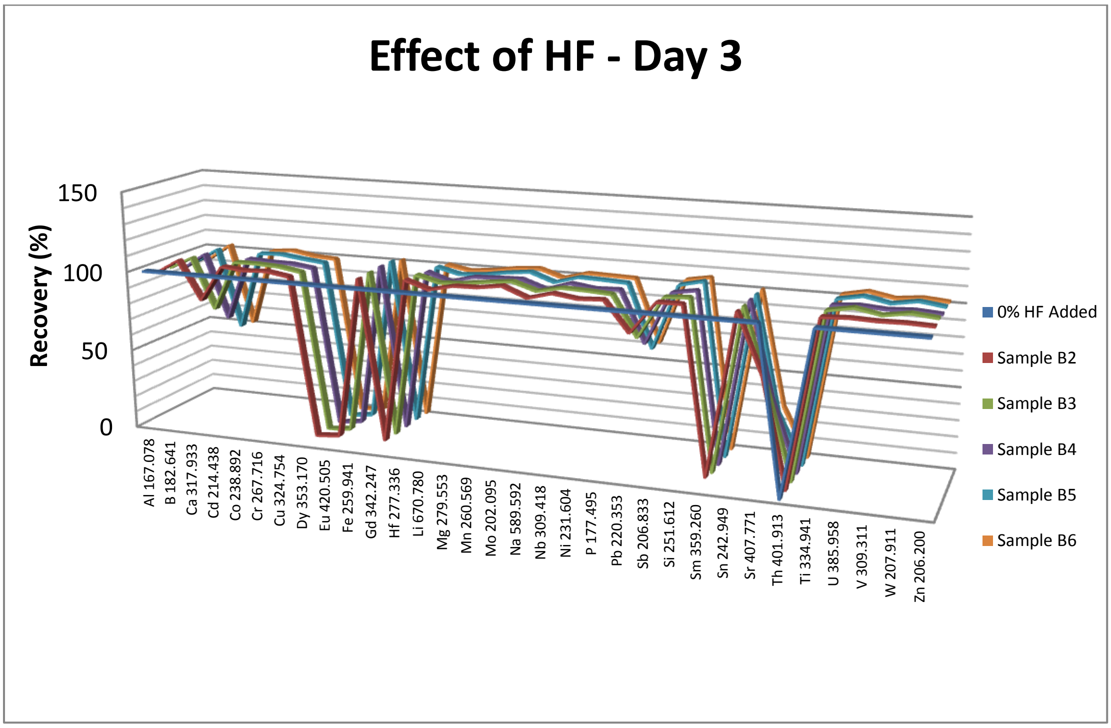

Figure 4.3: Effect of HF on Impurity Analytes Day 3.

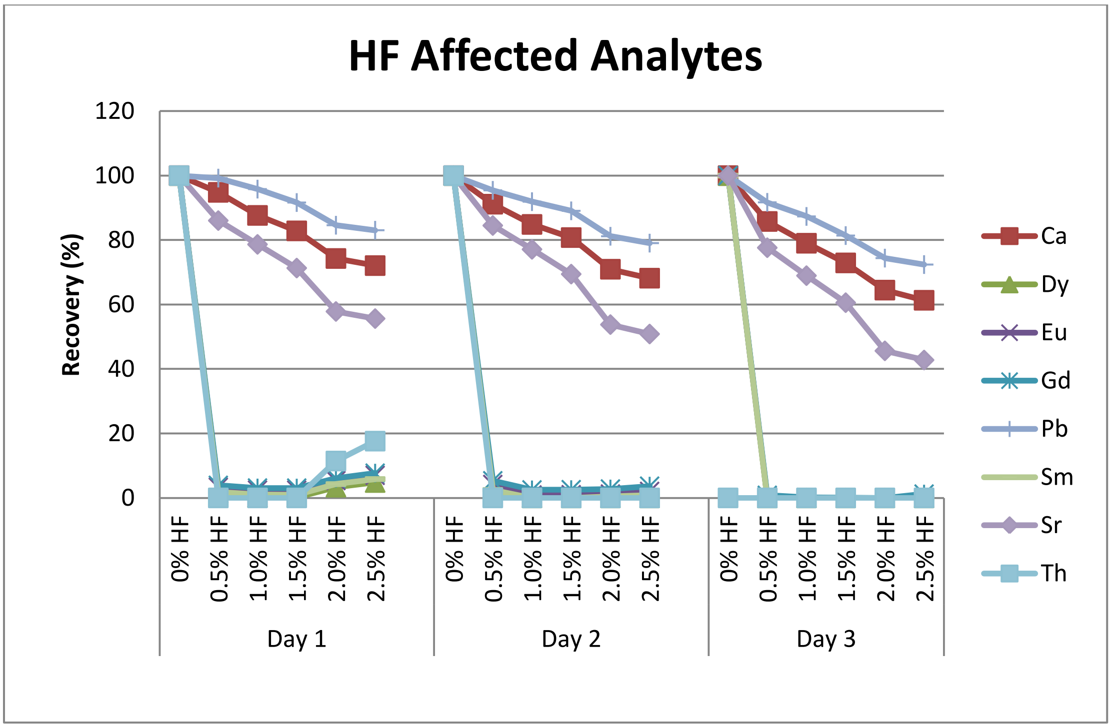

Figure 4.4: Analytes Adversely Affected by HF.

Discussion of Results

The stability of the analytes in solution was also determined by analyzing the test solutions over a period of three days. The results of the analysis from day one as shown in Figure 4.1 indicated a loss for the rare earth elements in comparison to the other elements. By the second day Figure 4.2 the losses experienced for the rare earth elements was significant with almost all of these having less than 10% recoveries. Thorium and the rare-earth elements were completely lost from the solution by the 3rd day. Irrespective of the HF concentration present all of the rare earth elements were completely lost by the 3rd day. These results were however not surprising since it is well known that the rare earth metal fluorides such as: DyF_3, $EuF_{3,}$ $GdF_{3,}$ and SmF_3, and are highly insoluble.

From Fig 4.2 to Fig 4.3 a developing trend with the following elements; Ca, Sr, and Pb, is evident. These elements are impacted by both time and HF content in the prepared solutions as an increase content of HF results in greater losses as shown by the lowest recoveries obtained in sample B6. Other metal fluorides with low solubility in water and HF include CaF_2, SrF_2 and PbF_2 hence the declining concentration of these analytes over time (Weast, 1980). The results clearly indicated that other digestion techniques should be used as an alternative to HF digestion for accurate determination of certain impurity elements including the rare earth elements in Zr for its nuclear applications.

All the impurity elements specified for nuclear grade zirconium were studied. The results expressed in Figure 4.4 revealed that Ca, Pb, Sr and the rare earth elements Eu, Dy, Gd, Sm as well as Th were affected by the presence of HF. The other elements were unaffected by even the highest concentration of HF added.

For Ca, Pb and Sr the losses increase with time and concentration HF added. There was no loss experienced for B, Si and P in the presence of HF even after heating, this proves that under the experimental conditions used the formation of volatile fluoride compounds, such as BF_3, PF_5 and SiF_4, does not occur. In all the HF acidified samples a fine white precipitate was observed.

Conclusion of Results

Sample preparation for the analysis of trace contaminants in Zr metal using aqueous HF will result in the loss of Ca, Sr, Pb, Th and the rare earth elements ; , Eu, Dy, Gd, and Sm. Even with a minimal concentration of HF of 0.5% (v/v) losses >5% are possible for Ca, Pb, Sr. The elements of major importance B, Cd and Hf and the rest of the elements specified are not lost.

The results clearly indicated that sample preparation using only HF is not ideal for the quantitative determination of the rare earths elements and an alternative dissolution method must be considered.

The further treatment of the HF dissolved sample with $HClO_4$ in a two stage digestion could possibly dissolve any precipitate that is formed. Thus a preparation where after the addition of HF, $HClO_4$ is added could be a solution to achieving quantitative determination of all the impurity analytes. Other acids like H_2SO_4 will form less soluble compounds with the same analytes that are lost due to the presence of HF and would not be suitable, while it and aqua-regia (1:3, HNO_3:HCl) may be able to dissolve the Zr they would both not be suitable for the determination of all analytes.

4.2 Total Dissolution using $HClO_4$

The determination of Ca, Pb, Sr and the REE's, required the use of a strongly oxidizing acid '$HClO_4$. A mixture of HNO_3, HF and $HClO_4$ was used to treat impurity spiked solutions containing 2000 mg L-1 Zr. Both treated and untreated solutions were analysed to assess the effect of the added $HClO_4$ From the recoveries obtained. The Effect of the addition on the other elements is reported in Tables 4.8 and 4.9 and discussed with the analysis of a real sample in section 4.9.

Table 4.1: Recoveries for adversely affected elements treated with $HClO_4$

Sample	Ca	Pb	Sr	Sm	Dy	Eu	Gd
	%	%	%	%	%	%	%
UNTREATED	93(4)	98(4)	95(3)	0	0	0	0
$HClO_4$ treated	105(0.6)	105(0.8)	107(0.7)	86(0.7)	92(0.4)	88(0.5)	89(0.3)

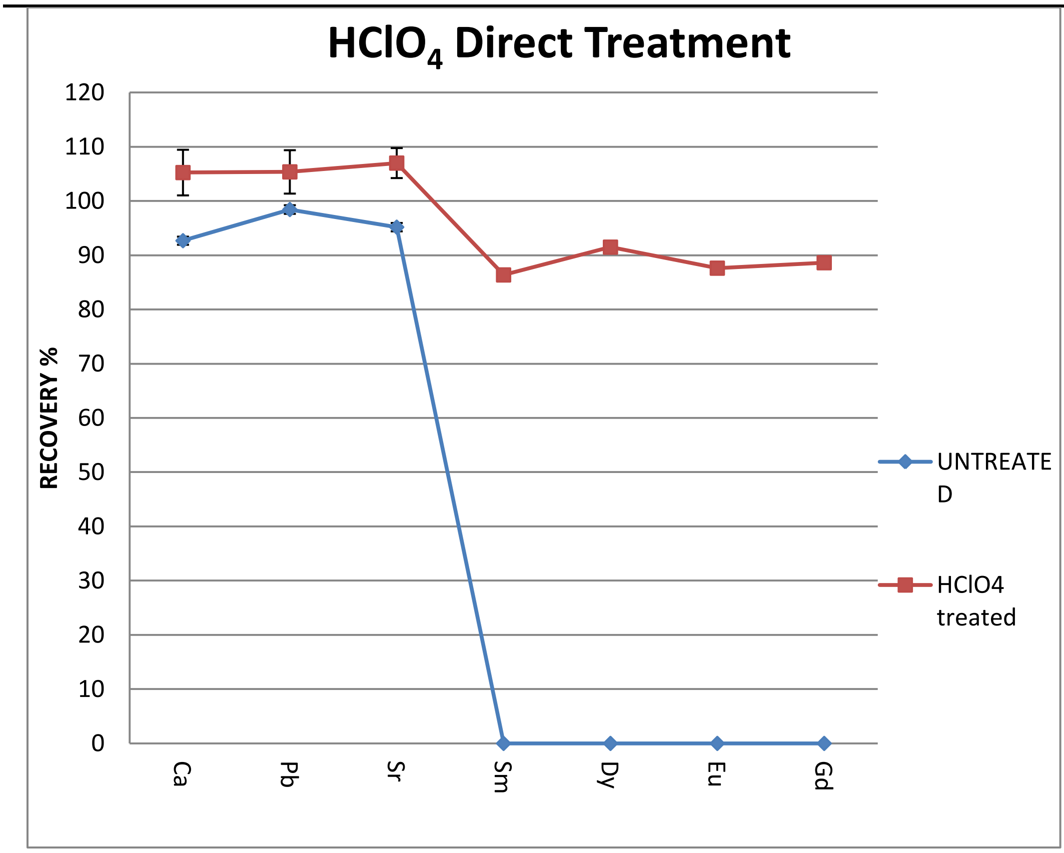

Figure 4.5: $HClO_4$ Treated Solutions

Discussion of Results

Table 4.1 and Figure 4.5 show the effect of adding $HClO_4$ on the elements identified as adversely affected by HF. The results obtained for all the treated samples show acceptable recoveries between 90% and 110%. This is a clear indication that the addition of $HClO_4$ to the sample prevents the formation of the insoluble fluorides this simple step will allow for the quantitative determination of Ca, Sr, Pb, and the rare-earth elements by ICP-OES or ICP-MS, from a single preparation.

The quantitative analysis of the rare earth elements and thorium in zirconium using the hydrofluoric acid (HF) digestion method will require further treatment of the digested sample as these form insoluble fluorides in the presence of HF (Hettel & Fassel, 195).

The specified impurity limits for the nuclear fuel could realistically be extended to the cladding material, as the effect of these elements on the performance of any nuclear reactor is similar whether they are present in the fuel, the cladding material or the cooling water.

Conclusion of Results

The quantitative determination of the rare earth elements Gd, Dy, Eu, Sm, Th, as well as Ca, Sr and Pb by ICP-OES in Zr metal can be done successfully following a simple digestion procedure. The combined use of perchloric and hydrofluoric acid in the dissolution of Zr metal will result in a sample solution that is free of any undesired precipitate that could contain the rare earth elements, thorium, Ca, Sr, and Pb. Should the unspecified elements like the rare-earth elements and Sr be included in future revisions of the nuclear grade specification the method developed will be able to deliver acceptable results for these.

4.3 Instrument Performance

The most practical measure of the instruments performance is the LOD and LOQ that can be obtained under the defined operating conditions. With these two related characteristics the true ability of the instrument to measure Trace levels of the analytes is given. Both LOD and LOQ are typically derived from the regression data meaning they are strongly dependent on the quality of the calibration standard solutions. Since matrix matched liquid standards are not commercially available, assurance that clean standards that would be used in the calibration of the instrument, would yield the desired results had to be given.

Calibration standards were prepared using both nitric acid matrix (clean) and zirconium matrix (2000 mg L^{-1}). The data from these calibrations were compared in terms of the LOD's and LOQ's obtained (Appendix D).

Table 4.2: ICP-OES Regression LOD's and LOQ's in mg L^{-1}

Analyte	**LOD** (3% HNO_3)	**LOQ** (3% HNO_3)	**LOD** (2000 Zr)	**LOQ** (2000 Zr)
Al	0.007	0.025	0.016	0.052
B	0.015	0.050	0.016	0.052
Ca	0.011	0.038	0.030	0.101
Cd	0.010	0.034	0.016	0.054
Co	0.012	0.039	0.020	0.068
Cr	0.011	0.036	0.016	0.053
Cu	0.010	0.033	0.013	0.043
Fe	0.010	0.032	0.015	0.050

Analyte	LOD	LOQ	LOD	LOQ
	(3% HNO_3)	(3% HNO_3)	(2000 Zr)	(2000 Zr)
Gd	0.008	0.026	0.061	0.204
Li	0.031	0.104	0.028	0.092
Mg	0.018	0.059	0.008	0.026
Mn	0.008	0.028	0.012	0.038
Na	0.048	0.161	0.004	0.012
Ni	0.010	0.033	0.040	0.133
Pb	0.014	0.047	0.013	0.043
Sm	0.008	0.026	0.028	0.092
Sr	0.010	0.034	0.002	0.006
Th	0.011	0.037	0.194	0.645
U	0.044	0.148	0.291	0.971
Zn	0.010	0.033	0.010	0.034
Hf	0.005	0.017	0.030	0.099
Mo	0.029	0.097	0.010	0.034
Nb	0.020	0.066	0.018	0.061
P	0.022	0.073	0.011	0.036
Si	0.016	0.055	0.019	0.065
Sn	0.019	0.063	0.018	0.059
Ti	0.009	0.029	0.026	0.087
V	0.017	0.055	0.018	0.060
W	0.020	0.068	0.012	0.039

Table 4.3: ICP-OES sensitivity in cps / mg L^{-1} and standard calibration error in cps

Analyte	Sensitivity	Error Sy/x	Sensitivity	Error Sy/x
	(3% HNO_3)		(2000 Zr)	
Al	982342	2433	940670	4924
B	58898	294	62549	326
Ca	777610	2964	641057	6474
Cd	572445	1925	506695	2735
Co	279487	1077	272412	1852
Cr	227894	810	215443	1134
Cu	671555	2215	764611	3289
Fe	449690	1432	428477	2148
Gd	564040	1478	465024	9466
Li	6000000	60541	6648627	61384
Mg	15986564	94372	14947885	39272
Mn	1709438	4763	1625127	6234
Na	934040	15024	1277617	1527
Ni	158083	528	1001814	13287
Pb	31540	148	30091	130
Sm	158921	409	141283	1306
Sr	19128172	64340	18801001	11801
Th	114070	418	81957	5289
U	81830	863	50801	4935
Zn	232782	757	204324	694
Hf	126749	215	119816	1186
Mo	38678	961	89428	303
Nb	676535	4498	627471	3806
P	23222	170	22428	81
Si	137475	753	153504	997
Sn	13684	86	12734	75
Ti	4000000	10817	3518004	30567
V	13903	152	1717736	10316
W	33434	227	30415	119

Discussion of Results

Table 4.2 shows a general decrease in sensitivity when measurements are done in the sample matrix, resulting in a higher LOQ's for most of the elements. For the following elements an increase in sensitivity was noted: Li, Na, P, W and Sr. This is probably due to ionization suppression for the group 1 elements.

The LOD's and LOQ's were calculated using (Eq 4 and Eq 5) respectively. Since the LOD and LOQ are performance parameters derived from both the sensitivity of the instrument and the error of the measurement (mainly calibration error). They are inversely proportional to the sensitivity and directly proportional to the calibration error, thus Lower calibrations errors will also produce lower (favorable) LOD's and LOQ's.

The general increase in LOD and LOQ as shown in Table 4.3 indicates a decrease in sensitivity mainly due to increased calibration error as the sensitivity between the two solutions is comparable. The increase in calibration error is due to increased background from the Zr matrix.

The increase in sensitivity for Li, Na, P, W and Sr may imply that there could be some instrumental parameters that could be better optimized to give better figures. One such parameter is plasma conditions. By decreasing the power output of the plasma, one may create conditions within the plasma where elements suffering from excessive ionization may be less affected. Another parameter is the nebulizer flow, which may also be adjusted to limit the residence time of these analytes in the plasma.

Conclusion of Results

The increase in sensitivity in six of the elements was confirmed. The increase in sensitivity would however not be sufficient to allow the quantification of Li (a low maximum specification element) by ICP-OES.

As the sample preparation will produce a Zr solution containing approximately 2000 mg L^{-1}, the LOQ found using the 2000 mg L^{-1} calibration must be used. For the majority of the analytes, the difference in LOQ's obtained from the clean and matched calibration solutions is in the same order of magnitude, thus it will be possible to conduct the analysis without matrix matched calibration standards.

4.4 Suitability for Trace Element Impurity Analysis by Alternative Technique

The elements specified for nuclear grade zirconium may not be quantifiable using just one technique. Some elements specified at very low concentrations may require a more sensitive technique. The limitations of ICP-OES in terms of the LOQ's attained show that some of the elements require a more sensitive technique for quantification.

Table 4.4 and 4.5 gives a summary of the elements that may be quantified using the recommended techniques, based on the attainable LOQ as given in Table 4.2 for a typical sample prepared by dissolving a sample mass of approximately 0.1g into a final volume of 50 ml (1-500 Preparation) .

Table 4.4: ICP-MS Recommended Elements

Analyte	Maximum specification	ICP-OES LOQ	1-500 preparation
	mg kg^{-1}	mg L^{-1}	mg L^{-1}
B	0.5	0.052	0.001
Ca	30	0.101	0.060
Cd	0.5	0.054	0.001
Co	20	0.068	0.040
Li	1.0	0.092	0.002
U	3.5	0.971	0.007

Table 4.5: ICP-OES Recommended Elements

Analyte	Maximum specification	ICP-OES LOQ	1-500 preparation
	mg kg^{-1}	mg L^{-1}	mg L^{-1}
Al	75	0.052	0.150
Cr	200	0.053	0.400
Cu	50	0.043	0.100
Fe	1500	0.050	3.000
Mg	600	0.026	1.200
Mn	50	0.038	0.100
Na	50	0.012	0.100
Ni	70	0.133	0.140
Pb	100	0.043	0.200
Mo	50	0.034	0.100
P	100	0.036	0.200
Si	100	0.059	0.200
Sn	100	0.087	0.200
Ti	50	0.028	0.100
V	50	0.060	0.100
W	50	0.039	0.100

Table 4.6: Unspecified Elements

Analyte	Maximum specification	LOQ	1-500 preparation	Proposed Technique
	mg kg^{-1}	mg L^{-}	mg L^{-1}	
Dy	15	0.069	0.030	ICP-MS
Eu	15	0.109	0.030	ICP-MS
Gd	15	0.204	0.030	ICP-MS
Sm	15	0.092	0.030	ICP-MS
Nb	-	0.061	-	ICP-MS
Sr	-	0.006	-	ICP-OES/MS
Th	-	0.645	-	ICP-MS
Zn	-	0.034	-	ICP-OES/MS

Discussion of Results

Table 4.4 to 4.6 gives the confirmed LOQ’s for ICP-OES and the required LOQ’s for the indicated sample preparation. In considering the adequacy of the analytical technique to be recommended, the ICP-OES LOQ was compared to the 1-500 preparation, which is the probable impurity concentration that would be in solution. LOQ’s above the 1-500 preparation indicate that the technique is not suitable and an alternative technique must be used.

Table 4.4 lists 6 elements that require a more sensitive technique for the prepared solutions. ICP-OES under the standard operating conditions will not have adequate sensitivity to quantify these. Table 4.5 lists all the elements that may be adequately quantified using the stated sample preparation and ICP-OES, while table 4.6 lists all the unspecified elements and the recommended technique. The recommended techniques are given only on the basis of the sensitivity they have.

Of the unspecified elements tested only strontium and zinc may be considered for analysis by ICP-OES should the required limits be similar to those of associated elements. The rare earth elements and thorium ,which could have limits similar to those of Cd, B and U, would be more fitted for analysis by ICP-MS. Should limits be specified for these elements ICP-MS would be able to quantify them at levels comparable to limits set for U and B.

Conclusion of Results

The capability of ICP-OES to quantify the specified elements satisfactorily is limited to 17 of the 23 elements. The six elements requiring a more sensitive technique are boron, calcium, cadmium, cobalt, lithium and uranium. The advantage of the preparation method is that the same solutions prepared for the ICP-OES are also suitable for ICP-MS. Thus it would be possible to quantify these elements in the prepared solutions by ICP-MS as this technique typically may have sensitivity 1000 fold greater than that of ICP-OES.

4.5 Sensitivity Enhanced by Increasing Matrix

Comparison of the results obtained for the 2000 mg L^{-1} Zr solution (Table 4.2) indicated a possible increase in sensitivity for six elements (Li, Na, P, Sr, and W). The possibility of matrix enhanced LOQ was investigated, to rule out the possibility of this being abnormal behavior, with the following results being obtained.

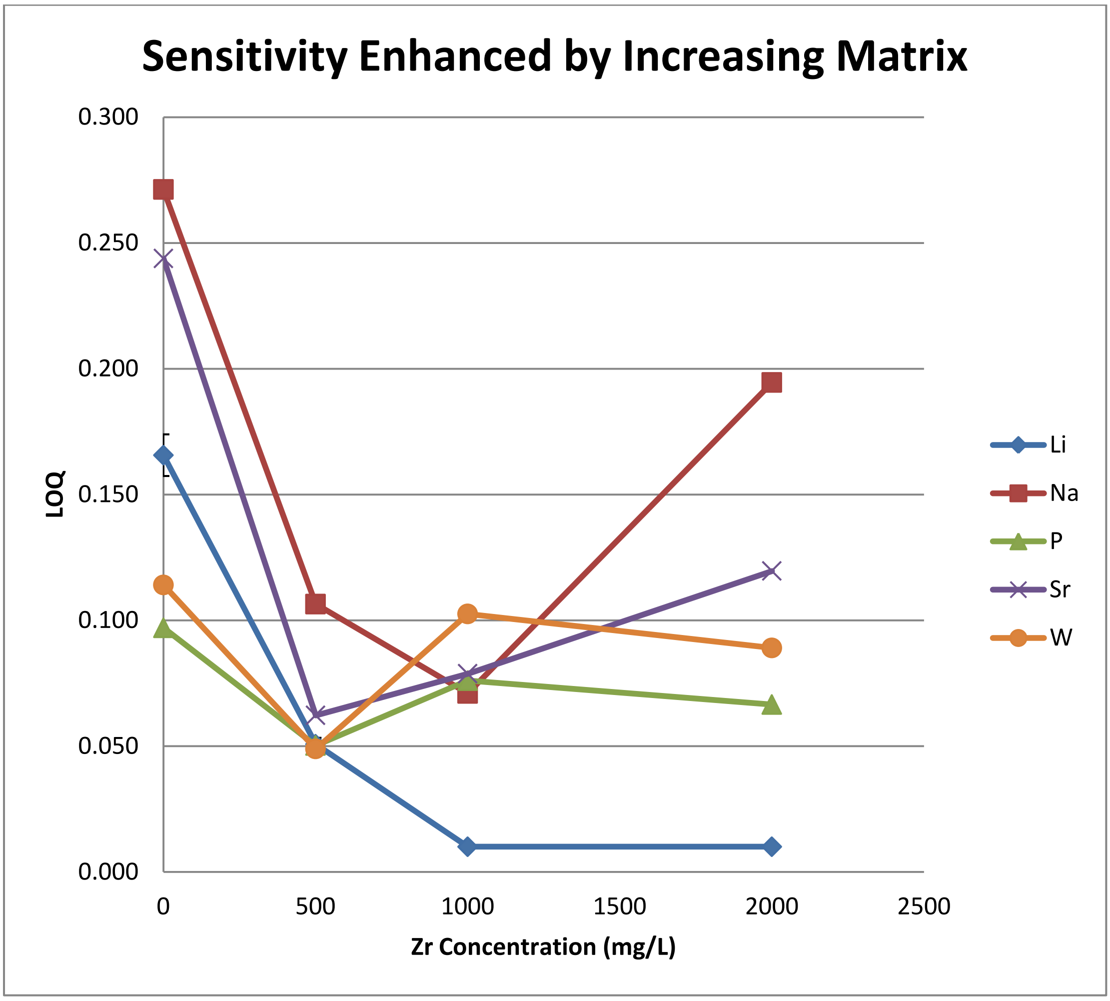

Figure 4.6: Zr Matrix Concentration vs LOQ

Discussion of Results

The LOQ's experience a large drop indicating a significant increase in sensitivity up to 500 mg L^{-1} Zr. Above this concentration the sensitivity begins to drop. At 2000 mg L^{-1} Zr the LOQ are not significantly better for P and W. The other elements Li, Na and Sr have a significant gain in sensitivity.

The gain in sensitivity due to increased matrix observed, may be due ionization suppression of the ionic species of these elements formed in the plasma. As these elements remain in the atomic state within the plasma this allows for the atomic emission lines to be more dominant than the ionic line, resulting in greater emission intensities being detected.

Conclusion of Results

The matrix increase will only affect two of the listed specified analytes (Li & Na). The determined LOQ for these analytes in a sample solution containing 2000 mg L^{-1} Zr are correct and not an anomaly. The increased sensitivity is not sufficient for the quantification of lithium.

The increase in sensitivity is due to ionization suppression as alkali elements are easily ionized in the plasma, resulting in lower emission intensities, when ionization to higher oxidation states is suppressed emission intensities, at the wavelengths used, increase. This results in better sensitivity.

4.6 Direct Determination of LOQ

The Limit of quantification obtained with the use of Microsoft Excel (Analysis Toolpak) may be modest as some measurements can be reliably made at concentrations much lower than calculated. For this reason it is often useful to determine the limit of quantitation experimentally.

This was done by preparing standards in a clean matrix and calculating the recoveries obtained. The limit of quantitation was redefined as the concentration that is read back with acceptable accuracy and precision. The typical acceptable accuracy was used as 80 to 110% recoveries for all concentrations below 1 mg L^{-1}.

Table 4.7: The LOQ in 2000 **mg L^{-1}** Zr, based on spike recoveries (n=8).

Analyte	Calculated LOQ / mg L^{-1}	Experimental LOQ / mg L^{-1}	Required LOQ (1 g-500 mL prep) / mg L^{-1}
Al	0.052	0.05	**0.15**
Co	0.068	0.05	**0.04**
Cr	0.053	0.05	**0.40**
Cu	0.043	0.05	**0.10**
Fe	0.050	0.05	**3.00**
Hf	0.099	0.05	**0.20**
Mn	0.038	0.05	**0.10**
Mo	0.034	0.05	**0.10**
Ni	0.133	0.05	**0.14**
Pb	0.043	0.05	**0.20**
Si	0.059	0.10	**0.20**
Ti	0.028	0.05	**0.10**
V	0.06	0.05	**0.10**
W	0.039	0.05	**0.10**
B	0.052	0.05	**0.001**
Ca	0.101	0.05	**0.06**
Cd	0.054	0.05	**0.054**
Li	0.092	0.05	**0.002**
Mg	0.026	0.05	**1.2**
Na	0.012	0.05	**0.1**
P	0.036	0.05	**0.2**
Sn	0.087	0.05	**0.2**

Discussion of Results

Experimentally determined limits of quantification could be a more realistic measure of the methods capabilities. These limits would also bring higher confidence in reported results. Though the calculated values are widely accepted in industry, confirmation of these values may be done practically, to give more assurance.

When the matrix of a sample is considered in the method’s capabilities, the LOQ’s calculated from the regression data may differ significantly, as is the case with Hf, Ni, Si, Ca, Li, Na and Sn that have an LOQ that differs by around a factor 2. The Experimentally determined LOQ’s show an improvement for the mentioned elements excluding Si which has a decreased LOQ of 0.10 mg L^{-1} from a calculated LOQ of 0. 059 mg L^{-1}.

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Conclusion of Results

Experimentally determined LOQ’s for the following elements were found to noticeably lower than the calculated LOQ’s; Co, Ca, Hf, Ni and Li. The results presented support the values calculated as the experimentally determined LOQ’s do not differ significantly to the calculated values. Calcium which was calculated to have an inadequate LOQ may now be quantifiable using ICP-OES, making the total quantifiable elements by ICP-OES to 18 of the specified 23.

The practically determined limits of quantitation are to be considered along with the calculated LOQ’s, to allow for the accurate quantification of a total of 18 elements including calcium. The calculated LOQ’s for the specified elements have been confirmed to be achievable.

4.7 Analysis of Real Sample

The analysis of a real sample with certified concentrations for the specified elements was the most effective tool of assessing the method's performance. From such an analysis one may obtain critical data on the accuracy of the method. The available standard material used did not have certified concentrations for the following elements: B, Cd, Ca, Li, Mg, Na, P, Sn, Sr and Zn.

To assess the methods capability for the quantification of these elements in the Zr matrix the prepared solutions of the SRM where spiked with varying concentrations (0.05, 0.01, 0.10, 0.50 and 1.00 mg L^{-1}) of the uncertified element at concentrations similar to the required LOQ, the concentrations where acceptable recoveries (80-110%) where obtained were used to conclude the capability of the method in quantifying these elements.

Table 4.8: SRM 1212a Results

Analyte	Units	NBS 1212a	Certified values	Certified Range	NBS Recovery
Al	mg kg^{-1}	261	240	-	109
Co	mg kg^{-1}	74	80	-	93
Cr	mg kg^{-1}	634	630	610-640	101
Cu	mg kg^{-1}	169	150	140-170	113
Fe	mg kg^{-1}	756	710	700-730	106
Hf	mg kg^{-1}	261	260	-	101
Mn	mg kg^{-1}	292	300	280-330	97
Mo	mg kg^{-1}	118	120	110-130	99
Ni	mg kg^{-1}	419	430	400-480	97
Pb	mg kg^{-1}	303	280	-	108
Si	mg kg^{-1}	370	350	320-390	106
Ti	mg kg^{-1}	163	150	140-160	108
U	mg kg^{-1}	52	100	80-130	52
V	mg kg^{-1}	117	150	-	78
W	mg kg^{-1}	112	140	120-170	80

Table 4.9: Spiked NBS 1212a results

Analyte	Acceptable recovery spike/ µg L^{-1}	NBS 1212a Recovery %	Acceptance decision
B	100	86	Acceptable
Ca	100	87	Acceptable
Cd	10	100	Acceptable
Li	10	110	Acceptable
Mg	5	100	Acceptable
Na	10	90	Acceptable
P	50	116	Acceptable
Sn	50	112	Acceptable
Sr	50	106	Acceptable
Zn	50	88	Acceptable

Table 4.10: t-test data for NBS 1212a (Appendix G)

Analyte	**t-Calc**	**t-Tcrit**
Al	-1.23	12.71
Co	0.72	12.71
Cu	-0.52	12.71
Cr	-0.91	4.30
Fe	-2.27	4.30
Hf	0.09	12.71
Mn	0.51	12.71
Mo	0.17	12.71
Ni	0.52	12.71
Pb	-0.82	12.71
Si	-0.16	12.71
Ti	-1.24	12.71
U	2.87	4.30
V	2.21	12.71
W	1.33	12.71

Discussion of Results

The recoveries obtained from the certified and uncertified elements are acceptable ranging from 78% to 116% with the exception of uranium (Table 4.9). Uranium recoveries are so low due to lack of sensitivity. For the elements recommended for a more sensitive technique like B, Li, Co and Cd it is possible to perform the analysis with samples that may contain higher concentration of these elements.

The t-test (Table 4.10) performed on the results for the SRM analysis show that there is no significant difference between the means obtained and the certified values for all but one analyte, as all calculated t-values are less than the critical t-values. Assuming Unequal variance the calculated t value of 2.87 for Uranium is less than the critical value of 4.30 showing that the method could be capable of quantifying uranium. However the uncertainty of such result for uranium may be unacceptably high due to lack of sensitivity.

Conclusion of Results

The accuracy of the method has been established and demonstrated through the recoveries obtained from the SRM, by making use of the certified concentration ranges. The values obtained for the real samples that fall within this range are taken as positive confirmation of the methods' capabilities. Spike recoveries of the SRM that gave acceptable recoveries are also a confirmation of the methods ability to measure the uncertified elements.

Chapter 5

CONCLUSION AND RECOMMENDATIONS

The conclusion with regards to the study performed with respect to the aim of the study given in chapter 2 is given in this chapter. Recommendations to further improve on the work done are also given.

5.1 Overall Conclusion

The development of an analytical method for the determination of trace impurities in nuclear grade zirconium has been achieved. Through the use of SRM NBS 1212a the accuracy of the method, the sample preparation procedure and the chosen instrumental conditions have been validated to be able to deliver the required results for the given specifications of.

The study has shown that it is possible to have a method that is simple, quick and cost effective. The method is uncomplicated, efficient requiring resources available at NECSA. Following basic principles of method development and applying the understanding of the chemistry of the matrix and targeted impurity elements has made it possible to have a functional method, which can be utilized by NECSA or anyone else in the nuclear industry, developed.

The study has also shown that modern instrumentation for trace element analysis is capable of performing the analysis for multiple analytes on a single solution with good accuracy and precision, without the need for matrix removal or analyte pre-concentration.

5.2 Recommendations

From the study it was shown that some of the elements given in the chemical specification of nuclear grade zirconium cannot be quantified at the required concentration by ICP-OES. ICP-OES has limitations with regard to sensitivity and an alternative technique such as ICP-MS is recommended. Future work could involve the analysis of similar material with specific attention given to Li, B, Cd and U, as these could not be quantified at the given specification.

The current specification for nuclear grade zirconium does not contain limits for the rare-earth elements. Revision of this specification may have to be reviewed as other potential sources of the minerals used to produce zirconium, such as monazite and Niobates, may contain significant amounts of these elements.

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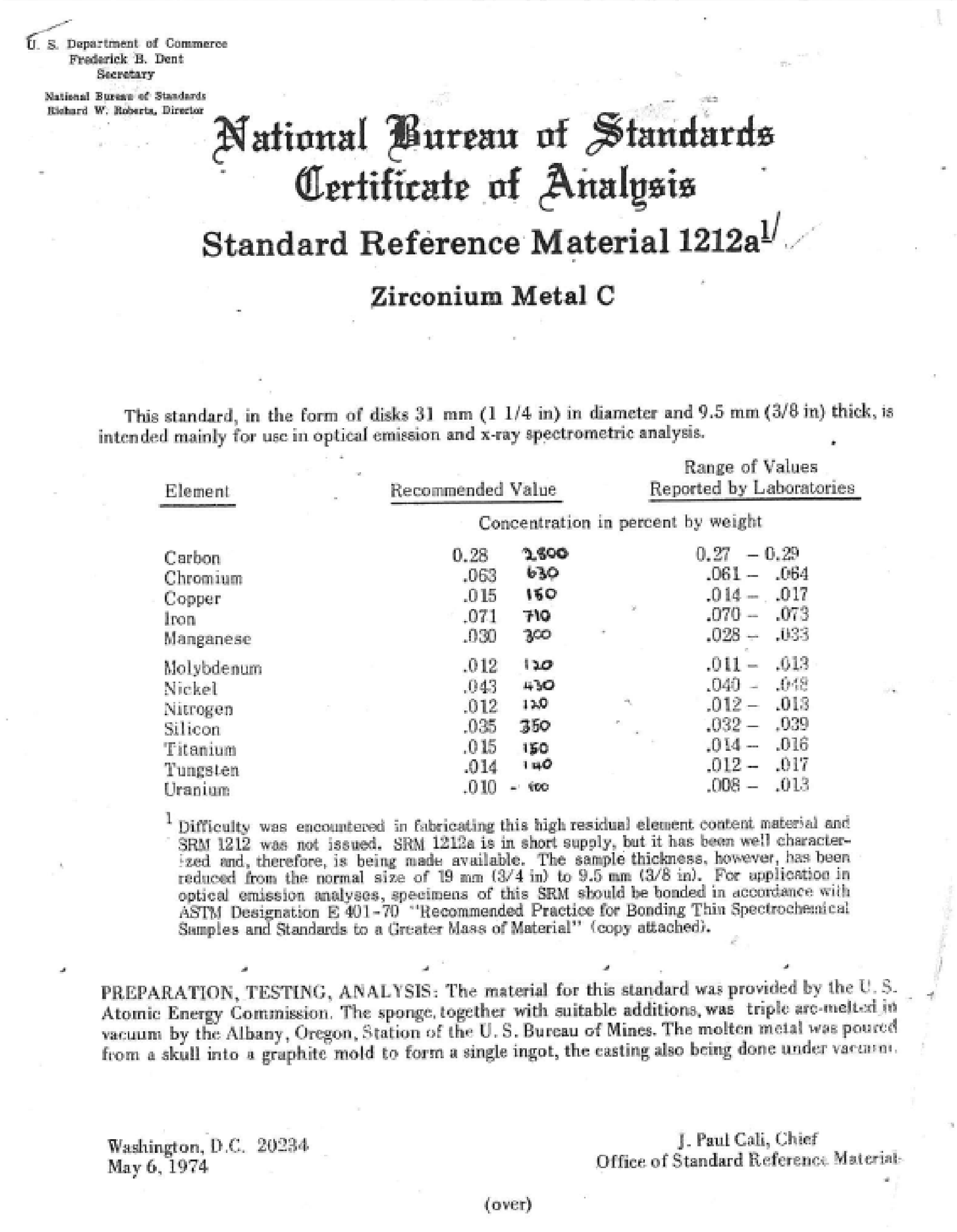
Appendices

Appendix A- NBS 1212a Certificate



U. S. Department of Commerce
Frederick B. Dent
Secretary

National Bureau of Standards
Richard W. Roberts, Director

National Bureau of Standards
Certificate of Analysis

Standard Reference Material 1212a[1/]

Zirconium Metal C

This standard, in the form of disks 31 mm (1 1/4 in) in diameter and 9.5 mm (3/8 in) thick, is intended mainly for use in optical emission and x-ray spectrometric analysis.

Element	Recommended Value		Range of Values Reported by Laboratories
	Concentration in percent by weight		
Carbon	0.28	2800	0.27 – 0.29
Chromium	.063	630	.061 – .064
Copper	.015	150	.014 – .017
Iron	.071	710	.070 – .073
Manganese	.030	300	.028 – .033
Molybdenum	.012	120	.011 – .013
Nickel	.043	430	.040 – .048
Nitrogen	.012	120	.012 – .013
Silicon	.035	350	.032 – .039
Titanium	.015	150	.014 – .016
Tungsten	.014	140	.012 – .017
Uranium	.010	- 100	.008 – .013

[1] Difficulty was encountered in fabricating this high residual element content material and SRM 1212 was not issued. SRM 1212a is in short supply, but it has been well characterized and, therefore, is being made available. The sample thickness, however, has been reduced from the normal size of 19 mm (3/4 in) to 9.5 mm (3/8 in). For application in optical emission analyses, specimens of this SRM should be bonded in accordance with ASTM Designation E 401-70 "Recommended Practice for Bonding Thin Spectrochemical Samples and Standards to a Greater Mass of Material" (copy attached).

PREPARATION, TESTING, ANALYSIS: The material for this standard was provided by the U. S. Atomic Energy Commission. The sponge, together with suitable additions, was triple arc-melted in vacuum by the Albany, Oregon, Station of the U. S. Bureau of Mines. The molten metal was poured from a skull into a graphite mold to form a single ingot, the casting also being done under vacuum.

Washington, D.C. 20234
May 6, 1974

J. Paul Cali, Chief
Office of Standard Reference Materials

(over)

After cropping top and bottom, the ingot was cut lengthwise to remove the center section (approximately one-fourth of the ingot) which was also discarded. The remaining sections then were fabricated to rods, annealed, and centerless ground to 31 mm (1 1/4 in) in diameter.

Homogeneity testing was performed by spectrochemical and chemical analyses at the National Bureau of Standards, Washington, D. C., and by the following cooperating laboratories:

Columbia-National Corp., Pensacola, Fla.
Reactive Metals Inc., Ashtabula, Ohio
Westinghouse Electric Corp., Bettis Plant, Pittsburgh, Pa.

Chemical analyses, and spectrochemical analyses relative to carefully prepared synthetic standards, were made on millings cut from the cross section of the rods by the following laboratories:

National Bureau of Standards, Washington, D. C.
General Electric Co., Knolls Atomic Power Laboratory,
Schenectady, N. Y.
Ledoux and Co., Teaneck, N. J.
Metals and Control Inc., Attleboro, Mass.
Oregon Metallurgical Corp., Albany, Ore.
U. S. Atomic Energy Commission, New Brunswick Lab.,
New Brunswick, N. J.
U. S. Department of the Interior, Bureau of Mines,
Albany, Ore.
Westinghouse Electric Corp., Bettis Plant,
Pittsburgh, Pa.
Westinghouse Electric Corp., Atomic Fuels Dept.
Cheswick, Pa.

Chemical analyses were also made by:

United Nuclear Corporation, New Haven, Conn.

Spectrographic analyses were also made by:

The Carborundum Co., Akron, N. Y.

ADDITIONAL INFORMATION ON THE COMPOSITION: The following values are not certified and are included for information only:

Element	Percent by Weight	
Aluminum	(0.024)	240
Cobalt	(.008)	80
Hafnium	(.026)	260
Lead	(.028)	280
Vanadium	(.015)	150

Appendix B – Raw data – Sensitivity enhanced concentration

Sample	Conc	Li 670.780	Na 589.592	P 177.495	Sr 407.771	Ti 334.187	W 207.911
		cps	**cps**	**cps**	**cps**	**cps**	**cps**
BLANK	0.000	73932	40099	-67	2253	-210	584
0.001 PPM	0.001	86025	45871	-7	7901	455	592
0.005 PPM	0.005	204469	101583	-75	36046	3264	648
0.010 PPM	0.010	120799	55453	71	71275	6119	682
0.050 PPM	0.050	223818	82289	770	350936	30027	1714
0.100 PPM	0.100	352282	117561	1561	660905	59786	2988
0.50 PPM	0.500	1457970	429640	8118	3234670	298554	13006
1.00 PPM	1.000	2711550	796954	15497	5677620	539043	23993

Sample	**Conc**	**Li 670.780**	**Na 589.592**	**P 177.495**	**Sr 407.771**	**Ti 334.187**	**W 207.911**
		cps	**cps**	**cps**	**cps**	**cps**	**cps**
500 PPM ZR 0.000	0.000	-1954	17503	-78	11596	-2082	468
500 PPM ZR 0.001	0.001	226	8068	-111	18082	-298	447
500 PPM ZR 0.005	0.005	14015	10596	0	47757	1977	662
500 PPM ZR 0.010	0.010	27269	15266	18	77843	4361	639
500 PPM ZR 0.050	0.050	165126	52226	874	396481	31390	1917
500 PPM ZR 0.100	0.100	308534	89066	1727	731211	59677	3203
500 PPM ZR 0.500	0.500	1448050	398482	8474	3209960	288803	12997
500 PPM ZR 1.000	1.000	2960860	830467	16765	6315790	571402	25752
Sample	**[Conc]**	**Li 670.780**	**Na 589.592**	**P 177.495**	**Sr 407.771**	**Ti 334.187**	**W 207.911**
		cps	**cps**	**cps**	**cps**	**cps**	**cps**

1000 PPM ZR 0.000	0.000	-2433	8002	-61	17605	-1798	381
1000 PPM ZR 0.001	0.001	450	15547	-50	24624	-249	522
1000 PPM ZR 0.005	0.005	12564	16495	15	50526	153	539
1000 PPM ZR 0.010	0.010	25599	16372	93	78810	3672	795
1000 PPM ZR 0.050	0.050	149459	45312	833	347159	27907	1809
1000 PPM ZR 0.100	0.100	308839	88492	1773	715365	59159	3208
1000 PPM ZR 0.500	0.500	1588870	413813	9351	3323530	310472	14557
1000 PPM ZR 1.000	1.000	3179770	844099	18006	6365980	595442	27142
2000 PPM ZR 0.000	0.000	5477	18690	-87	29442	5109	273
2000 PPM ZR 0.001	0.001	598	15643	30	41377	-10826	521
2000 PPM ZR 0.005	0.005	13657	16304	3	64918	-11540	510
2000 PPM ZR 0.010	0.010	29824	21655	99	99627	-3823	580
2000 PPM ZR 0.050	0.050	172709	58401	944	371546	15487	1712
2000 PPM ZR 0.100	0.100	307666	85945	1647	643973	49219	2860
2000 PPM ZR 0.500	0.500	1675670	426473	9357	3175820	287834	14248
2000 PPM ZR 1.000	1.000	3642340	930926	19300	6755630	631092	29353

Appendix C – Raw Data for $HClO_4$ Treated samples (figure 4.5)

Sample	Ca 317.933 mg/l	Pb 220.353 mg/l	Sr 407.771 mg/l	Sm 359.260 mg/l	Dy 353.170 mg/l	Eu 420.505 mg/l	Gd 342.247 mg/l
UNTREATED 1	1.9	2.0	1.9	0.0	0.0	0.0	0.0
UNTREATED 2	1.7	1.9	1.8	0.0	0.0	0.0	0.0
UNTREATED 3	1.9	2.0	1.9	0.0	0.0	0.0	0.0
UNTREATED 4	1.9	2.0	1.9	0.0	0.0	0.0	0.0
UNTREATED Average	**1.9**	**2.0**	**1.9**	**0.0**	**0.0**	**0.0**	**0.0**
Std Dev	**0.1**	**0.1**	**0.1**	**0.0**	**0.0**	**0.0**	**0.0**
% RSD	**4.2**	**4.0**	**2.8**				
UNTREATED + HCLO4 1	2.1	2.1	2.2	1.7	1.8	1.8	1.8
UNTREATED + HCLO4 2	2.1	2.1	2.1	1.7	1.8	1.8	1.8
UNTREATED + HCLO4 3	2.1	2.1	2.2	1.7	1.8	1.8	1.8
UNTREATED + HCLO4 4	2.1	2.1	2.1	1.7	1.8	1.7	1.8
UNTREATED + HCLO4 Average	**2.1**	**2.1**	**2.1**	**1.7**	**1.8**	**1.8**	**1.8**
Std Dev	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**
% RSD	**0.61**	**0.81**	**0.66**	**0.73**	**0.45**	**0.55**	**0.28**

Appendix D – Raw Data for LOQ in Zr Matrix

Sample Name	concentration	Al 167.078 cps	B 182.641 cps	Ca 317.933 cps	Cd 214.438 cps	Co 238.892 cps	Sr 407.771 cps
BLANK 2000Zr	0	2267	1090	12358	320	3073	84862
0.001PPM 2000Zr	0.001	3313	1382	598	919	3363	108818
0.005PPM 2000Zr	0.005	7837	1982	15370	3280	4812	202569
0.010PPM 2000Zr	0.010	11606	2135	19670	5456	5734	272127
0.050PPM 2000Zr	0.050	47846	4540	39259	25233	16274	1008860
0.100PPM 2000Zr	0.100	94291	7826	63300	49874	29112	1969410
0.500PPM 2000Zr	0.500	460940	32067	321732	247241	134928	9484870
1.000PPM 2000Zr	1.000	946898	64193	651626	509297	276926	18890700

Sample Name	concentration	Cr 267.716 cps	Cu 324.754 cps	Dy 353.170 cps	Eu 420.505 cps	Fe 259.941 cps	Th 401.913 cps
BLANK 2000Zr	0	10935	20990	25548	33779	1502	54102
0.001PPM 2000Zr	0.001	11600	20797	26651	40631	1971	56363
0.005PPM 2000Zr	0.005	13086	24950	35337	50067	4150	62489
0.010PPM 2000Zr	0.010	13050	27088	39145	57045	5777	53162
0.050PPM 2000Zr	0.050	21069	57074	92523	148633	22371	56968
0.100PPM 2000Zr	0.100	31926	94943	157758	253171	43613	64064
0.500PPM 2000Zr	0.500	116471	394857	684931	1169440	210700	106457
1.000PPM 2000Zr	1.000	227364	787335	1294670	2171650	431763	134040

Sample Name	concentration	Gd 342.247 cps	Li 670.780 cps	Mg 279.553 cps	Mn 259.373 cps	Mn 260.569 cps	U 385.958 cps
BLANK 2000Zr	0	6189	-584	32792	117673	5858	94452
0.001PPM 2000Zr	0.001	9515	5601	61063	124508	7223	98369
0.005PPM 2000Zr	0.005	24868	33872	116037	138289	14223	106879
0.010PPM 2000Zr	0.010	18504	60926	185861	132662	17970	94789
0.050PPM 2000Zr	0.050	31762	309044	771090	196349	68503	94472
0.100PPM 2000Zr	0.100	48329	619948	1542190	277214	131369	100299
0.500PPM 2000Zr	0.500	259365	3174900	7602060	925467	642588	119515
1.000PPM 2000Zr	1.000	470333	6691210	14952300	1747890	1284050	149073

Sample Name	concentration	Na 589.592 cps	Ni 231.604 cps	Pb 220.353 cps	Pb 283.305 cps	Sm 359.260 cps	Zn 206.200 cps
BLANK 2000Zr	0	6787	2076	707	3	-3651	-306
0.001PPM 2000Zr	0.001	9287	2193	685	44	-3490	-126
0.005PPM 2000Zr	0.005	15062	3041	936	-431	-2159	739
0.010PPM 2000Zr	0.010	17008	3442	1025	-521	-838	1658
0.050PPM 2000Zr	0.050	51723	9095	2132	125	5158	9724
0.100PPM 2000Zr	0.100	96940	16542	3739	2000	12398	19980
0.500PPM 2000Zr	0.500	477139	75230	15469	9991	70372	100173
1.000PPM 2000Zr	1.000	1018740	150362	30901	22797	137555	204561

Appendix E – Accuracy and precision data for unspecified elements.

	2000 ppm Zr +0.05			2000 ppm Zr +0.1	
Element	**% RSD**	**Recovery**		**% RSD**	**Recovery**
Al	**1.1**	**99**		**0.9**	**101**
B	**1.1**	**97**		**1.1**	**97**
Ca	**9.3**	**71**		**5.4**	**78**
Cd	**0.0**	**82**		**0.6**	**85**
Co	**0.8**	**97**		**0.5**	**97**
Cr	**0.6**	**96**		**1.2**	**96**
Cu	**2.9**	**113**		**1.1**	**114**
Fe	**3.9**	**98**		**0.8**	**96**
Hf	**2.6**	**101**		**2.9**	**92**
Li	**0.9**	**106**		**0.8**	**105**
Mg	**0.0**	**98**		**0.0**	**97**
Mn	**0.0**	**98**		**0.8**	**98**
Mo	**1.3**	**87**		**1.4**	**90**
Na	**1.1**	**91**		**0.7**	**94**
Ni	**0.9**	**96**		**1.9**	**95**
P	**4.8**	**93**		**2.5**	**96**
Pb	**2.5**	**107**		**2.1**	**102**
Si	**10.2**	**34**		**2.8**	**74**
Sn	**5.0**	**89**		**1.5**	**91**
Ti	**0.6**	**94**		**0.3**	**92**
V	**1.0**	**95**		**0.0**	**95**
W	**2.2**	**89**		**1.4**	**91**
Zn	**1.4**	**83**		**1.5**	**86**

Appendix F – SRM preparation data

	Rep- 1	Rep- 2	Rep- 3	Rep- 4	Rep- 5
sample mass	0.3212	0.3331	0.3674	0.3743	0.3546
HF Conc	0.4	0.4	0.4	0.4	0.4
HF Density	1.13	1.13	1.13	1.13	1.13
n Zr	0.0035	0.0037	0.0040	0.0041	0.0039
N HF	0.0211	0.0219	0.0242	0.0246	0.0233
Mass HF	0.4225	0.4382	0.4833	0.4924	0.4665
Mass HF (40-48)	1.0563	1.0955	1.2083	1.2310	1.1662
Volume HF (mL)	0.935	0.969	1.069	1.089	1.032
Volume Used + 10%	1.028	1.066	1.176	1.198	1.135
	1.028	1.066	1.176	1.198	1.135
Vol excess	0.093	0.097	0.107	0.109	0.103
% excess in 50mL	0.2	0.2	0.2	0.2	0.2

Appendix G t- test data for Certified elements in SRM NBS 1212a

Al

t-Test: Two-Sample Assuming Unequal Variances

	Variable 1	*Variable 2*
Mean	236	260.8149561
Variance	800	14.06727384
Observations	2	3
Hypothesized Mean Difference	0	
df	1	
t Stat	-1.233538653	
P(T<=t) one-tail	0.21683804	
t Critical one-tail	6.313751514	
P(T<=t) two-tail	0.433676079	
t Critical two-tail	12.70620473	

Co

t-Test: Two-Sample Assuming Unequal Variances

	Variable 1	*Variable 2*
Mean	80	74.18558464
Variance	128	1.200392645
Observations	2	3
Hypothesized Mean Difference	0	
df	1	
t Stat	0.724540519	
P(T<=t) one-tail	0.300417489	
t Critical one-tail	6.313751514	
P(T<=t) two-tail	0.600834978	
t Critical two-tail	12.70620473	

Hf

t-Test: Two-Sample Assuming Unequal Variances

	Variable 1	*Variable 2*
Mean	264	261.3263041
Variance	1800	45.80309405
Observations	2	3
Hypothesized Mean Difference	0	
df	1	
t Stat	0.088376734	
P(T<=t) one-tail	0.47194171	
t Critical one-tail	6.313751514	
P(T<=t) two-tail	0.943883419	
t Critical two-tail	12.70620473	

Mn

t-Test: Two-Sample Assuming Unequal Variances

	Variable 1	*Variable 2*
Mean	305	292.1724879
Variance	1250	49.66585159
Observations	2	3
Hypothesized Mean Difference	0	
df	1	
t Stat	0.506436956	
P(T<=t) one-tail	0.350781449	
t Critical one-tail	6.313751514	
P(T<=t) two-tail	0.701562898	
t Critical two-tail	12.70620473	

Cr

t-Test: Two-Sample Assuming Unequal Variances

	Variable 1	*Variable 2*
Mean	625	633.6841482
Variance	450	157.7279957
Observations	2	3
Hypothesized Mean Difference	0	
df	1	
t Stat	-0.521238243	
P(T<=t) one-tail	0.347054173	
t Critical one-tail	6.313751514	
P(T<=t) two-tail	0.694108347	
t Critical two-tail	12.70620473	

Cu

t-Test: Two-Sample Assuming Unequal Variances

	Variable 1	*Variable 2*
Mean	155	168.856526
Variance	450	22.74847296
Observations	2	3
Hypothesized Mean Difference	0	
df	1	
t Stat	-0.908584953	
P(T<=t) one-tail	0.265234372	
t Critical one-tail	6.313751514	
P(T<=t) two-tail	0.530468743	
t Critical two-tail	12.70620473	

Mo

t-Test: Two-Sample Assuming Unequal Variances

	Variable 1	*Variable 2*
Mean	120	118.2462093
Variance	200	14.21663004
Observations	2	3
Hypothesized Mean Difference	0	
df	1	
t Stat	0.171365661	
P(T<=t) one-tail	0.44597735	
t Critical one-tail	6.313751514	
P(T<=t) two-tail	0.891954701	
t Critical two-tail	12.70620473	

Ni

t-Test: Two-Sample Assuming Unequal Variances

	Variable 1	*Variable 2*
Mean	440	418.8983817
Variance	3200	72.47256107
Observations	2	3
Hypothesized Mean Difference	0	
df	1	
t Stat	0.523602472	
P(T<=t) one-tail	0.346462969	
t Critical one-tail	6.313751514	
P(T<=t) two-tail	0.692925938	
t Critical two-tail	12.70620473	

Fe

t-Test: Two-Sample Assuming Unequal Variances

	Variable 1	*Variable 2*
Mean	715	755.7579028
Variance	450	290.935286
Observations	2	3
Hypothesized Mean Difference	0	
df	2	
t Stat	-2.271425206	
P(T<=t) one-tail	0.075545672	
t Critical one-tail	2.91998558	
P(T<=t) two-tail	0.151091343	
t Critical two-tail	4.30265273	

Si

t-Test: Two-Sample Assuming Unequal Variances

	Variable 1	*Variable 2*
Mean	355	360.7728402
Variance	2450	17.11731941
Observations	2	5
Hypothesized Mean Difference	0	
df	1	
t Stat	-0.1647083	
P(T<=t) one-tail	0.448038255	
t Critical one-tail	6.313751514	
P(T<=t) two-tail	0.89607651	
t Critical two-tail	12.70620473	

Pb

t-Test: Two-Sample Assuming Unequal Variances

	Variable 1	*Variable 2*
Mean	280	302.9140317
Variance	1568	19.36618618
Observations	2	3
Hypothesized Mean Difference	0	
df	1	
t Stat	-0.81500979	
P(T<=t) one-tail	0.282331272	
t Critical one-tail	6.313751514	
P(T<=t) two-tail	0.564662544	
t Critical two-tail	12.70620473	

Ti

t-Test: Two-Sample Assuming Unequal Variances

	Variable 1	*Variable 2*
Mean	150	162.7465422
Variance	200	15.02885263
Observations	2	3
Hypothesized Mean Difference	0	
df	1	
t Stat	-1.243878178	
P(T<=t) one-tail	0.215539432	
t Critical one-tail	6.313751514	
P(T<=t) two-tail	0.431078864	
t Critical two-tail	12.70620473	

U

t-Test: Two-Sample Assuming Unequal Variances

	Variable 1	*Variable 2*
Mean	105	17.42894354
Variance	1250	911.3042185
Observations	2	3
Hypothesized Mean Difference	0	
df	2	
t Stat	2.873471872	
P(T<=t) one-tail	0.051388759	
t Critical one-tail	2.91998558	
P(T<=t) two-tail	0.102777518	
t Critical two-tail	4.30265273	

V

t-Test: Two-Sample Assuming Unequal Variances

	Variable 1	*Variable 2*
Mean	150	116.7294879
Variance	450	6.794792976
Observations	2	3
Hypothesized Mean Difference	0	
df	1	
t Stat	2.20695396	
P(T<=t) one-tail	0.135421713	
t Critical one-tail	6.313751514	
P(T<=t) two-tail	0.270843426	
t Critical two-tail	12.70620473	

W

t-Test: Two-Sample Assuming Unequal Variances

	Variable 1	*Variable 2*
Mean	145	111.7069153
Variance	1250	12.20460439
Observations	2	3
Hypothesized Mean Difference	0	
df	1	
t Stat	1.327410256	
P(T<=t) one-tail	0.205513433	
t Critical one-tail	6.313751514	
P(T<=t) two-tail	0.411026867	
t Critical two-tail	12.70620473	