Method development for the recovery of trace metals from unpreserved water samples

By

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Certificate of Original Authorship

I hereby declare that this thesis has not been submitted, either in the same form or a different form, to UTS or any other university for the award of any other degree. To the best of my knowledge and belief, the thesis contains no material that has been previously published or written by another person except where references are made.

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Wenshuai Tan

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Abstract

Water contamination by trace metals in natural and industrialised environments is a common phenomenon, the analysis of trace metals is therefore a very important process. Trace metal analysis is employed to assess the occurrence and concentration of contaminants thereby providing important data to protect our ecosystems and public health. During trace metal analysis, sample preservation is a critical requirement however it is also subject to numerous difficulties throughout the testing procedure.

The major standard water testing methods to preserve trace metals (as adopted by the USEPA and APHA) use nitric acid (HNO_3) which is added to water samples usually stored in polyethylene bottles. However, in some cases, samples are sent to laboratories unpreserved whereby significant amounts of trace metals may be lost due to being adsorbed in the inner walls of the plastic bottles, leading to a loss of metal concentration in the water samples. The analytical results of analysis could therefore be significantly lower than their true values.

To provide a solution to this problem, this study is focused on the recovery of 19 trace metals – Al, Ag, As, Ba, B, Cd, Cr, Co, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Tl, V and Zn – from unpreserved water samples spiked with trace metals.

First the thesis focuses on deionised (DI) water samples spiked with trace metals. Findings from this work with DI water samples have indicated that sample testing with 1% (v/v) nitric acid plus 0.01% (v/v) hydrochloric acid (HCl) for a 24-hour period enabled efficient re-extraction of 70-110% of trace metals from the tested water samples. However, mercury (Hg) did not yield high recovery results (around 56%) with this method although, with the addition of 10 mg/L Au solution, recovery of Hg was increased to about 70%.

After DI water samples recovery testing, then the thesis focuses on the recovery of trace metals from unpreserved drinking water samples. Tap water samples were studied with

this research method: 1% (v/v) nitric acid plus 1% (v/v) hydrochloric acid for a 24-hour period. This enabled efficient re-extraction of 70-110% of trace metals from the water sample. However, as with tap water sampling, mercury did not yield high recovery results with this method (around 66%) although, with the addition of 1 mg/L Au solution, the recovery of Hg was increased to about 78%. Therefore, it is highly recommended that acidified water samples – those containing 1% (v/v) nitric acid plus 0.01% (v/v) hydrochloric acid – are sent to the laboratory for testing whenever possible to guarantee greatest accuracy in trace metals analyses. If unpreserved tap water samples are received, 1% (v/v) nitric acid plus 1% (v/v) hydrochloric acid can be utilised to recover most trace metals, while 1 mg/L Au solution guarantees greatest accuracy when testing for mercury. Finally, the limitations of this study have been stated with recommendations for future studies and applications which might develop methods for the recovery of trace metals from unpreserved water samples.

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CHAPTER ONE:

INTRODUCTION

Chapter 1. Introduction

1.1 Topic and Thesis

1.1.1 Topic

Method development for the recovery of trace metals from unpreserved water samples.

1.1.2 Thesis

Up to now, most research on trace metal analysis is primarily designed to check for the lost percentages of trace metals in unpreserved samples. It has been shown that significant amounts of trace metals are lost when water samples are stored without acid preservation; however, there is no single research method which can successfully recover 100% trace metal in such samples. To mitigate this problem, and with the aim complying with the ISO recommendation, this research will mainly focus on methods to recover 70-110% of trace metals.

Trace metals are elements such as chromium, cobalt, copper, iron, magnesium, selenium, and zinc and normally occur at very low levels in the environment. Living things need very small amounts of some trace metals but high levels may become toxic (Underwood, 2012).

When considering water analysis procedures, trace metals recovery is of critical importance. This is due specifically to the fact that trace metals are unstable without acid preservation and will yield incorrect results regardless of the analytical methods being applied later. Therefore, appropriate water preservation processes and preparation techniques are of extreme importance in obtaining correct results.

In addition, it is vitally important that water is sampled and preserved correctly in order to ensure that results of analysis accurately reflect the properties and their quantities for

which the testing facility is seeking. Correctly determining the properties and their quantities allows the testing facility to accurately formulate decisions and make recommendations (Schwarz, 2011).

Acidified water samples are usually sent to laboratories in acidified bottles, which are designated as corrosive and dangerous goods. In this case, the client needs to be trained in safety management before handling these goods and extra freight costs are charged from the client. Currently, the major standard water testing methods (as outlined by USEPA and APHA) to preserve trace metals use nitric acid, but mercury is unsuitable in HNO_3 alone as Parker and Bloom (2005) reported that mercury is adsorbed onto inner bottle walls. Therefore, 1% (v/v) nitric acid plus 0.01% (v/v) hydrochloric acid is the recommended acid combination for all trace metals including mercury (Louie et al., 2012).

1.2 Background to the Research

Australian Drinking Water Guidelines (2017) for trace metals in water is in µg/L range and therefore it is of paramount importance that results are accurate and precise at these low concentrations (Quevauviller, 2008).

Currently, the major standard water testing methods as outlined by USEPA and APHA to preserve trace metals use nitric acid, however mercury is unsuitable in HNO_3 alone, because mercury is adsorbed onto inner bottle walls (Parker and Bloom, 2005). The combined use of 1% (v/v) nitric acid and 0.01% (v/v) hydrochloric acid is the recommended procedure for all trace metals (including mercury) when testing water samples (Louie et al., 2012).

In some cases, samples are sent to laboratories unpreserved whereby significant amounts of trace metals are lost due to being stored without acid preservation. Some trace metals are adsorbed on the inner wall of the plastic bottle leading to a loss of metal concentration

in the water (Louie et al., 2012). The analytical results, therefore, are much lower than their true values.

Regardless of advancements in instrumentation development aimed at improving sensitivity, accuracy, and precision for trace metals determination by inductively coupled plasma mass spectrometry (ICP-MS), so far there is yet to be a successful method, which can satisfactorily recover all trace metals in unpreserved water samples.

1.3 Aims and Objectives of This Thesis

Stakeholders:

Australian Scientific Trace Inorganic laboratories

The aims are:

(i) to extract and study trace metals lost from non-acidified water samples;

(ii) to study the effects of pH levels and trace metals recovery from unpreserved water samples;

(iii) to improve sample preservation and preparation processes – this is extremely important because, if incorrectly performed, results will yield errors regardless of the analytical method applied.

The objectives are:

(i) to design and prepare testing methods to locate trace metals lost from non-acidified water samples (using ICP-MS);

(ii) to formulate different methods for recovery of trace metals from unpreserved water samples;

(iii) to avoid the cost of setting up the acid bottle preparation unit (which also includes increased freight costs for buying the acid bottles) and to avoid employment of extra staff in the water sampling process.

The significance of this research is to ensure the highest recovery of trace metals from unpreserved water samples sent from clients to government laboratories, which is daily practice in many countries. The poor recovery of trace metals will lead to erroneous results and have implications for water quality monitoring and potential consequences for public health.

1.4 Statement of the Problem

Most research on trace metal analysis is primarily designed to check for the lost percentages of trace metals rather than recovery. It has been shown that significant amounts of trace metals are lost when water samples are stored without acid preservation; however, there is no single research method, which can successfully recover all trace metals from unpreserved water samples. To mitigate this problem, and with an aim of 70-110% recovery as the ISO recommendation, many methods are already considered as recovery technologies. My research will mainly focus on methods to recover 70-110% of trace metals.

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CHAPTER TWO:

LITERATURE REVIEW

Chapter 2. Literature Review

2.1 Trace Metals

Trace metals are the metals subset of trace elements such as chromium, cobalt, copper, iron, magnesium, selenium, and zinc; that is, metals normally present in small but measurable amounts in animal and plant cells and tissues and that are a necessary part of nutrition and physiology (Underwood, 2012). Living things need very small amounts of some trace metals, but high levels of these same metals can be toxic. For example, Inorganic arsenic is very toxic and can cause serious health problems. Organic arsenic, on the other hand, can be rapidly discharged from the body without causing harm. Prolonged exposure to inorganic arsenic can cause skin pigmentation and lesions that eventually lead to cancer (Saha et al., 1999).

The presence of a safe and adequate supply of trace metals is necessary, because all life forms need trace metals for nutrition and proliferation, and all organisms have evolved mechanisms to harvest the required amount of trace metals from the available pool in their particular environmental niche (He et al., 2005).

2.2 Background for Trace Metals Loss Experiments

Acidification to pH < 2 with nitric acid was found to prevent sedimentation and adsorption of trace metals onto the vessel wall (Louie et al., 2012). The loss of trace metals is directly related to the length of storage time and inversely proportional to the concentration of trace metals (Hatje et al., 2003).

Louie et al. (2012) showed that more than 10% of the mercury was lost within the first 3 days. In 9 days, up to 50% of the mercury was lost and more than 70% of the mercury was lost within 28 days. The trace metals Al, Ag, As, Ba, B, Cd, Cr, Co, Cu, Mn, Mo, Ni,

Pb, Sb, Hg, Se, Tl, V, Zn preserved by a solution of 1% (v/v) HNO_3 plus 0.01% (v/v) HCl were stabilised for 12 months. The recommended acid combination for the simultaneous determination of multi-elements by ICP−MS is therefore 1% (v/v) HNO_3 plus 0.01% (v/v) HCl (Louie et al., 2012).

An investigation from National Exposure Research Laboratory indicated the reliability of 2% HNO_3 as a mercury preservative and reported that mercury had disappeared within a few days. Therefore, it is recommended that 2% HNO_3 with 1 mg/L $AuCl_3$ is used. It was stated that the mercury standard solution stored in this mixture is stable for several years (Louie et al., 2012).

2.3 Trace Metals Analyses

Chemicals are part of our daily lives. All living things and inanimate objects are composed of chemical substances. In fact, every product manufactured includes some combination of chemical substances and many of these chemicals greatly help improve our quality of life, health and wellbeing when used properly. However, some chemicals especially toxic trace metals are very dangerous. They can pollute air, water, and soil and cause great harm to public health. If they are not managed properly, these chemicals can have a lasting, negative impact on our health and environment (Vesilind et al., 2013.). Therefore, aspiring to a better, safer tomorrow means providing valid trace metal analysis capabilities which assist in complying with regulations, ensuring that our drinking water does not contain toxic heavy metals and providing metal analysis solutions for product development, quality control, corrosion control, and other applications (Shannon et al., 2008).

2.3.1 Trace metals analysis

Different metal analysis applications may require different instruments according to

different regulations, concentration ranges, and detection limits. Atomic absorption spectrometry (AAS) and graphite furnace (GF)-AAS are ideal economic tools for analysing a few elements (Bosnak and Grosser, 1996), while inductively coupled plasma optical emission spectrometry (ICP-OES) and ICP-MS are used for multi-element analysis, especially in high-throughput formats. ICP-OES is suitable for tough matrices. However, ICP-MS uses collisional cell technology to remove polyatomic interferences thereby reducing the detection limit to parts per trillion. Using triple quadrupole ICP-MS and high resolution ICP-MS, advanced environmental and geoscience applications can be accurately implemented (Lienemann et al., 2007).

As routine practice for trace metals testing, atomic spectrometry technologies which include AAS, ICP-OES, and ICP-MS, are often used because they provide the sensitivity required by various global regulations (Gomez et al., 2007).

Figure 1. Different analytical instruments for trace metal analysis (Thermofisher Scientific, 2019).

2.3.2 Top four toxic trace metals in water

It is important to analyse the metals in environmental water samples because many heavy metals pose a serious threat to our health. Of the 10 chemicals that are of major concern to public health the top four toxic trace metals in water are arsenic, cadmium, lead and mercury. Due to their toxicity, they are also listed in drinking water regulations by national and international bodies (WHO, 2018).

These four metals threaten human health, especially in children. According to reports, these toxic substances are related to autism and are widely present in drinking water, drugs and toys (Landrigan and Miodovnik, 2011).

(1) Arsenic (As)

Organic arsenic, on the other hand, can be rapidly discharged from the body without causing harm. Prolonged exposure to inorganic arsenic can cause skin pigmentation and lesions that eventually lead to cancer (Saha et al., 1999).

Table 1. Arsenic guideline values from different agencies/countries.

Different agencies / countries	Guideline values
WHO Guidance Values (WHO, 2008)	0.01 mg/L
Australian drinking water guidelines value (ADWG, 2017)	0.01 mg/L
Drinking Water Quality Standards in Japan (2015)	0.01 mg/L
Drinking Water Quality Standards in German (BGBI.I,S.2613,1990)	0.01 mg/L
Drinking Water Quality Standards in China (GB5749-2006)	0.01 mg/L

(2) Cadmium (Cd)

Cadmium often causes kidney disease and stays in our body for between 10 and 30 years. Absorption of cadmium is in the gastrointestinal tract and depends on a variety of factors including the solubility of the ingested compound, but healthy individuals typically absorb 3%-7% of cadmium. (Athar and Vohora, 1995; ADWG, 2017).

Table 2. Cadmium guideline values from different agencies / countries.

Different agencies/countries	Guideline values
WHO Guidance Values (WHO, 2008)	0.003 mg/L
Australian drinking water guidelines value (ADWG, 2017)	0.002 mg/L
Drinking Water Quality Standards in Japan (2015)	0.01 mg/L
Drinking Water Quality Standards in German (BGBI.I,S.2613,1990)	0.005 mg/L
Drinking Water Quality Standards in China (GB5749-2006)	0.005 mg/L

(3) Lead (Pb)

Lead has multiple targets in our body, mainly in bone; lead tests utilise blood, teeth and bones (Papanikolaou et al., 2005). In adults about 10% of lead is absorbed but in children it can be four to five times that level. After absorption, lead is distributed through soft tissues such as those found in the kidney, liver and in bone marrow.

Table 3. Lead guideline values from different agencies/countries.

Different agencies / countries	Guideline values
WHO Guidance Values (WHO, 2008)	0.01 mg/L
Australian drinking water guidelines value (ADWG, 2017)	0.01 mg/L
Drinking Water Quality Standards in Japan (2015)	0.05 mg/L
Drinking Water Quality Standards in German (BGBI.I,S.2613,1990)	0.04 mg/L
Drinking Water Quality Standards in China (GB5749-2006)	0.01 mg/L

(4) Mercury (Hg)

Mercury can remain airborne in the atmosphere for up to a year; in addition, it can also remain stable in marine sediment for millions of years (Schroeder and Munthe, 1998).

Table 4. Mercury guideline values from different agencies/countries.

Different agencies/countries	Guideline values
WHO Guidance Values (WHO, 2008)	0.001 mg/L
Australian drinking water guidelines value (ADWG, 2017)	0.001 mg/L
Drinking Water Quality Standards in Japan (2015)	0.0005 mg/L
Drinking Water Quality Standards in German (BGBI.I,S.2613,1990)	0.001 mg/L
Drinking Water Quality Standards in China (GB5749-2006)	0.001 mg/L

2.4 Drinking Water Guidelines for Trace Metals

2.4.1 Australian drinking water guidelines for trace metals

The Australian Drinking Water Guide (ADWG) aims to provide an authoritative reference to the Australian community and the water industry, explaining the definition of safe, quality water, how to implement it and how to ensure its standards.

The guidelines were developed by taking into account the best scientific evidence along

with a well-managed drinking water supply framework, which was designed to ensure safe usage practices.

For trace metals in drinking water, ADWG defines the characteristics of good quality drinking water, including health and aesthetic characteristics:

A health-related guideline value, which is the concentration or measure of water quality characteristics, which based on current knowledge, does not pose any significant risk to the health of the consumer over a lifetime of consumption;

An aesthetic guideline value, which is the concentration or measurement of water quality characteristics associated with the acceptability of water for consumer use and consumption.

Table 5. Australian drinking water guidelines (2017) value for trace metals (mg/L).

Parameter	Guidelines Value: Aesthetic	Guideline Value: Health
Aluminium	0.2	
Antimony		0.003
Arsenic		0.01
Beryllium		0.06
Barium		2
Boron		4
Bromide		
Cadmium		0.002
Calcium		
Chromium		0.05
Copper	1	2
Iron	0.3	
Lead		0.01
Magnesium		
Manganese	0.1	0.5
Mercury		0.001
Molybdenum		0.05
Nickel		0.02
Potassium		
Selenium		0.01
Silver		0.1
Sodium	180	
Zinc	3	

2.4.2 World Health Organization (WHO) and other guidance values for trace metals

The fourth edition of GDWQ contains 24 inorganic parameters of GV or HBV. Copper, lead and manganese content values have been set in all 104 countries and regions.

Table 6. Different guideline values for trace metals.

Reference	Guideline Values													
	Antimony	Arsenic	Barium	Beryllium	Boron	Cadmium	Chromium	Copper	Lead	Manganese	Mercury	Molybdenum	Nickel	Selenium
WHO Guideline value (mg/L)	0	0	0.7		2.4	0	0.1	2	0		0	0.1	0.1	0
WHO Health-based value (4th edition) *										0.4				
WHO Health-based value (mg/L)				0										
Number of countries and territories setting a regulatory / guideline value (out of 104)	76	102	52	12	73	101	99	104	104	103	100	26	82	96
Number of countries and territories setting a regulatory / guideline value greater than WHO Guideline	1	22	11	1	2	59	3	2	19	19	1	2	3	2
Number of countries and territories setting the WHO Guideline	13	79	35	0	1	38	94	51	84	11	4	22	7	1
Number of countries and territories setting a regulatory / guideline value less than WHO Guideline	62	1	6	11	70	4	1	51	1	73	95	2	72	93
Maximum value set (mg/L)	0.1	0.5	2	0.1	5	0.1	0.5	3	0.1	0.5	0	0.3	0.1	0.1
Minimum value set (mg/L)	0	0	0.1	0	0.2	0	0	0.1	0	0.1	0	0.1	0	0
Median value (mg/L)	0	0	0.7	0	1	0	0.1	1.5	0	0.1	0	0.1	0	0

Antimony levels in most countries and regions (62/76) are lower than GV, with 0.005 mg/L in 50 countries and regions.

Arsenic is one of the value parameters set by most countries and regions (102/104). Most countries (79/102) specified the provisional GV; only one country is less than the provisional GV.

The majority (35/52) of those countries and territories setting a value for barium specified the GV.

Beryllium is one of the least specified parameters; Only 12 of the 104 countries and regions surveyed set value.

No country has set the revised GV of boron in the fourth survey of GDWQ (WHO, 2011); most countries and regions are based on the temporary global value of 0.5mg/L.

As indicated by the median value, cadmium is an inorganic parameter higher than GV specified in most countries and regions. Only four countries and regions specify values below the GV.

Most countries and territories have set the value of total chromium, and most have set up temporary GV.

The GDWQ also noted that copper can cause aesthetic problems including dyeing of clothes with concentrations of more than 1 mg/L. Copper was one of only three inorganic parameters set for all countries and regions in the survey. Most specify GV or the specified lower value. Only two countries have set values more than the GV.

Lead is one of only three inorganic parameters in this survey with values specified by all countries and regions. The majority of GV have been identified and some countries and

regions allow a time of 0.01 mg/L. In countries and regions with a value higher than GDWQ, a maximum of 0.05 mg/L is specified.

All of the countries and regions in the survey set a value for manganese. Most are less than the previous GV. Some countries and regions list these parameters as aesthetics, some inorganic, others both.

Most countries and regions (100/104) set a value for mercury. Only four countries have designated the GV.

For molybdenum, most (22/26) countries and regions are characterized by GV.

Most countries and regions set the nickel value below 0.02 mg/L.

For selenium, only one country specified the new provisional GV of 0.04 mg/L; almost all others specified the previous value of 0.01 mg/L.

2.4.3 Difference between Australian drinking water guidelines and other guidance values

ADWG guideline values are based on the world health organization guidelines on drinking water quality (2004) and subsequent addenda from 2006 and 2008. When the guideline values for chemicals in ADWG are different from those recommended by the world health organization differences usually occur in one of two ways:

The average adult weight of ADWG (2017) is 70 kg, and the WHO value is 60 kg. Using a higher average weight can sometimes yield slightly higher criterion values, but the difference is not significant given the greater safety factor used.

If a defined limit provides adequate protection (i.e. less than 10 times the value determined by health considerations), it is used as a guideline value. If the measured limit is much lower than that determined from health considerations, the lower of the two values is used.

Conversely, if the calculated value is far below the set limit, the calculated value is used but with a note that it is below the actual set limit. These compounds require improved detection limits.

2.4.4 National and international guideline values

For some chemicals, Australian drinking water guidelines may not be available. It is recommended that water suppliers seek advice from the appropriate state or regional health authorities when they detect chemicals with no guidance value in ADWG pertaining to drinking water. In such cases, temporary water quality advice can be obtained from other sources.

The following list details the level of documentation available for finding national and international drinking water guideline values. According to the recommendations of NHMRC and the Environmental Health Committee (enHealth, 2012) on environmental hazards risk assessment (enHealth，2012), these recommendations stem from the relevance to the Australian context and the methodology used to calculate the values of the criteria. Starting at the top of the hierarchy, the most up-to-date version of the document should be consulted until the appropriate temporary guideline value can be found:

a) Australian Guidelines for Water Recycling – Phase 2: Augmentation of Drinking Water Supplies (EPHC, 2008)
b) WHO Guidelines for Drinking-Water Quality, fourth edition (WHO, 2011)
c) Drinking Water Standards for New Zealand, New Zealand Ministry of Health, New Zealand (New Zealand Ministry of Health, 2008)
d) Guidelines for Canadian Drinking Water Quality (Health Canada, 2014)
e) Health Advisories for Drinking Water Contaminants (United States Environmental Protection Agency, various dates)

f) Drinking Water Contaminants Lists (US EPA Office of Water, 2007)

g) Public Health Goal for Chemical Substances in Drinking Water (Office of Environmental Health Hazard Assessment, California Environmental Protection Agency, 2014)

2.4.5 U.S.EPA methods for toxic trace metals

2.4.5.1 Arsenic (Maximum contaminant limit, MCL = 10 ppb)

a) EPA Method 200.5 (ICP-OES axial view)

b) EPA Method 200.8 (ICP-MS)

c) EPA Method 200.9 (GFAAs)

2.4.5.2 Cadmium (MCL = 5 ppb)

a) EPA Method 200.5

b) EPA Method 200.7 (ICP-OES)

c) EPA Method 200.8

d) EPA Method 200.9

2.4.5.3 Lead (Action level, AL = 15 ppb)

a) EPA Method 200.5

b) EPA Method 200.8

c) EPA Method 200.9

2.4.5.4 Mercury (MCL = 2 ppb)

a) cold vapour atomic absorption

b) EPA Method 200.8

2.4.6 Australian drinking water guidelines for handling requirements in samplings

Samples should be analysed within 6 hours of collection. If this is not possible, the samples

must be transported and stored at between 2°C and 10°C. Samples must not be frozen. From Australian Standards AS/NZS 5667.1:1998 and AS/NZS 5667.5:1998, Sampling requirements for trace metals can be found as below:

Table 7. Australian drinking water guidelines for handling requirements in trace metals.

Characteristic	Container	Minimum sample size (mL)	Preservation procedure	Maximum holding period	Comments
Aluminium	P(A), G(A)	100	Add HNO_3 to pH <2	28 days	
Arsenic	P(A), G(A)	500	Add HNO_3 to pH <2	28 days	
Boron	P	100	None required	28 days	Fill container completely to exclude air
Cadmium	P(A), G(A)	100	Add HNO_3 to pH <2	28 days	
Chloride	P, G	100	None required	28 days	
Chromium (total)	P(A), G(A)	100	Add HNO_3 to pH <2	28 days	
Chromium (VI)	P(A), G(A)	100	Refrigerate	24 hours	Sample container should be thoroughly rinsed. Avoiding reagents
Copper	P(A), G(A)	100	Add HNO_3 to pH <2 and refrigerate	28 days	Fill container completely to exclude air. Acidification permits the determination of calcium and other metals from the same sample
Iron	P(A), G(A)	100	Add HNO_3 to pH <2	28 days	
Lead	P(A), G(A)	100	Add HNO_3 to pH <2	28 days	
Manganese	P(A), G(A)	100	Add HNO_3 to pH <2	28 days	
Mercury	G(A)	500	Add HNO_3 to unfiltered sample to pH <1. Add $K_2Cr_2O_3$	28 days	Consult analyst for further instruction
Metals (general)	P(A), G(A)	100	Add HNO_3 to pH <2	28 days	
Metals (filterable)	P(A), G(A)	100	Filter immediately, add HNO_3 to pH <2	28 days	0.45 m filter
Selenium	P(A), G(A)	100	Add HNO_3 to pH <2	28 days	
Sodium	P	100	None required	28 days	
Zinc	P(A), G(A)	100	Add HNO_3 to pH <2	28 days	

Container: P= Plastic (polyethylene or equivalent); G= Glass; P(A), G(A) = Rinsed with 50% HNO_3

2.5 Client Behaviour

Water samples are usually sent to labs in acidified bottles, which are designated as corrosive and dangerous goods. In some cases, water samples are sent to labs unpreserved whereby significant amounts of trace metals are lost due to being stored without acid preservation.

2.5.1 Dangerous goods and cost

For safety purposes, the client requires specialised training. Also, as determined by increased expenses, extra freight costs are charged to the client.

2.5.2 Safety work practice during sample preparation

a) To avoid hazards during transportation of corrosive and dangerous acid bottles (National Research Council US, 1980).
b) To avoid the increased freight costs for purchasing the acid bottles (Phillips, 2005).
c) To avoid acid burn accidents during sample collection (Kolios et al., 2010).
d) To avoid the cost of setting up the acid bottle preparation unit.
e) To avoid employment of extra staff for the water sampling unit.

2.6 Fact Sheets for Trace Metals in Drinking Water

2.6.1 Aluminium

2.6.1.1 Australian drinking water guidelines

The concentration of acid soluble aluminium in drinking water should not exceed 0.2 mg/L. It is strongly recommended that water authorities reduce the concentration of acid soluble aluminium as much as possible, preferably less than 0.1 mg/L (ADWG, 2017).

2.6.1.2 Overview

Aluminium may exist in water through natural leaching of soil and rocks or by utilisation of aluminium salts as coagulants in water treatment (Srinivasan, 1999).

Aluminium is used in many industrial and household products, including antacids, antiperspirants and food additives, and vaccines (Krewski et al., 2007). It is often used by the food industry in food containers and packaging, and many cookers are made of aluminium (Coles et al., 2003).

The United States and the United Kingdom show that the aluminium concentration in natural water sources is 0.014-1.2 mg/L (ADWG, 2017). Some Australian water sources are likely to be much higher because of the presence of clay minerals (Bigham and Nordstrom, 2000). The residual aluminium concentration in the treated water depends on the concentration in the water source, pH and filtration efficiency (Srinivasan et al., 1999).

2.6.1.3 Australian drinking water typical values

In the main Australian network supply the concentration of aluminium is normally 0.01 mg/L to 0.9 mg/L, however the typical concentration of consumable materials is about 0.1 mg/L (ADWG, 2017).

2.6.1.4 Analytical method

Acid soluble aluminium is determined after acidification of the sample to pH 1.5-2, followed by membrane filtration of 0.45µm. If the filtrate's normal analysis method (such as GF-AAS, APHA Method 3500-Al Part B, 1992) provides a result value above the guideline value, the filtrate using catechol violet should be reanalysed by the colorimetric method (APHA method 3500-Al Part E, 1992), which provides a better estimate of the active aluminium components. The determination limit of the latter method is approximately 0.01 mg/L.

2.6.1.5 Health effects

It is estimated that, for adults in Australia, the intake of aluminium from food and drink is approximately 5-7 mg/day (Greger, 1992). Drinking water accounts for less than 2% of the total daily intake, while only 0.3-0.4% of the aluminium in water is absorbed by the body

(Reinke et al., 2003; ADWG, 2017; Spungen, 2005). Recent studies have shown that the bioavailability (i.e. blood absorption) of aluminium in drinking water is similar to food (Stauber et al., 1999).

Some aluminium accumulates in bone, liver, and brain tissues but most are removed from the blood and excreted (Priest, 1993.). In healthy adults, the total aluminium accumulation is about 35mg. There is considerable evidence that aluminium is neurotoxic (DeVoto and Yokel, 1994; Perez-Granados and Vaquero, 2002; ADWG, 2017). A kidney dialysis patient's intestinal barrier, which is bypassed can accumulate aluminium in the blood leading to an encephalopathy called dialysis dementia. A study has found that there was a correlation between the concentration of aluminium in the water used to prepare the dialysis fluid and the incidence of dialysis dementia (Reinke et al., 2003).

Elevated aluminium concentrations were found in the anatomical human brain of an Alzheimer's sufferer and the brain area contained a large number of neurofibrillary tangles, which are characteristic of the disease; aluminium has been proposed as one of a number of causal agents (Perl and Brodie, 1980). There are many epidemiological studies to determine if aluminium in drinking water plays a role in Alzheimer's disease. Although some studies showed that a temporary link may exist, more recent evidence (Martyn et al., 1997) suggests that aluminium in drinking water is not associated with an increased risk of Alzheimer's disease.

2.6.2 Antimony

2.6.2.1 Australian drinking water guidelines

For health reasons, the concentration of antimony in drinking water should not exceed the determination limit of 0.003 mg/L (ADWG, 2017).

2.6.2.2 Overview

Antimony is found as the trivalent (Sb(III)) or pentavalent (Sb(V)) salt, which has been detected in natural water (Filella et al., 2002). In the vicinity of lead or copper smelting operations the occurrences are more common. Antimony-tin solders are beginning to replace lead solders so contact with potable water in the future may increase. Antimony alloys and compounds are used in semiconductors, batteries, friction reducers, ammunition, cable jackets, and flame retardants. Antimony salts are mainly used in the manufacture of glass, ceramics and pottery (ADWG, 2017).

2.6.2.3 Australian drinking water typical values

Drinking water supplies in Australia have not routinely been monitored for antimony.

2.6.2.4 Analytical method

The concentration of antimony in drinking water is analyzed by atomic absorption spectrometry. The limit of the determination is approximately 0.001 mg/L. In addition, GF-AAS can be used to determine 0.003 mg/L (APHA Method 3500-Sb Part B, 1992).

2.6.2.5 Health effects

The International Agency for Research on Cancer has concluded that antimony trioxide is possibly carcinogenic to humans by the inhalation route (Group 2B, inadequate evidence in humans, sufficient evidence in animals); and antimony trisulfide is not classifiable due to its carcinogenicity to humans (Group 3, inadequate evidence in humans and limited evidence in animals) (IARC, 1989; Tylenda et al., 2015; ADWG, 2017).

Studies using mice have shown that about 15% of the antimony is absorbed by the gastrointestinal tract. It is mainly distributed in the liver, spleen and heart, as well as in the thyroid and adrenal glands, excreted in faeces and urine.

There are many studies on the effects of long-term human exposure to antimony. More than half of the exposed workers suffered from dermatitis. Other studies have reported abnormal heartbeats, lung cancer, and spontaneous abortions among female employees (Bircher, 2018).

2.6.3 Arsenic

2.6.3.1 Australian drinking water guidelines

For health reasons, the concentration of arsenic in drinking water should not exceed 0.01 mg/L.

2.6.3.2 Overview

Arsenic is a natural element that can be introduced into water by dissolving minerals and ores (mainly in the form of sulphides) (Lajçi et al., 2017; Essington, 2015), or from industrial wastewater, atmospheric deposition (by burning fossil fuels and waste incineration) (Manahan, 2017), draining from disused gold mines (Mpofu and Mpofu, 2017). Natural resources can make a significant contribution to the concentration of arsenic in drinking water (Dummeret al., 2015). Arsenate (i.e. pentavalent (As(V)) is usually the most common form of oxygenated surface water and drinking water but under reduced conditions (as found in deep lake sediments or groundwater) the trivalent form (As(III), arsenite) predominates (Flora, 2015).

Arsenic compounds have commercial and industrial uses in the manufacture of transistors, lasers and semiconductors, and in the processing of glass, pigments, textiles, paper, metal adhesives, ceramics, wood preservatives, ammunition, and explosives. They are also used in the hide-tanning process and, as feed additives, pesticides and drugs (Karcioğlu et al., 2017). Although inorganic forms of arsenic are the most common, organic arsenic compounds are also used (Taylor et al., 2017).

The concentration of arsenic is generally less than 0.005 mg/L in surface and groundwater that are not affected by arsenic deposits or contamination.

2.6.3.3 Australian drinking water typical values

In Australia's drinking water supply, typical arsenic concentrations range from < 0.001 mg/L to 0.03 mg/L.

2.6.3.4 Analytical method

The concentration of arsenic in drinking water can be determined by atomic absorption spectrometry. The limit of the determination is approximately 0.001 mg/L. In addition, GF-AAS can also be used and its measurement limit is about 0.005 mg/L (APHA Method 3500-As Part B, 1992).

2.6.3.5 Health effects

Health considerations apply primarily to inorganic arsenic compounds because they are more easily present in drinking water (James et al., 2015; Hagiwara, et al., 2015; Lamm et al., 2015).

Soluble arsenic salts are easily absorbed by the gastrointestinal tract (Poor et al., 2017). After absorption, inorganic arsenic binds to haemoglobin and deposits in the liver, kidneys, lungs, spleen and skin (Ahmad et al., 2017). Inorganic arsenic does not seem to cross the blood-brain barrier, but it can cross the placenta.

An extensive review of the arsenic toxicity data for human and animal was conducted (IPCS2001, WHO 2003, IARC 2004, Health Canada 2006, ATSDR 2007) and the results showed that an increase of arsenic in drinking water was related to the development of cancer in several sites, especially skin, bladder and lungs (Oberoi et al., 2014). Cancer is considered to be the most sensitive toxic end point for setting arsenic guidelines for drinking water but

the mechanism or mode of action of arsenic on cancer has not been clearly clarified (Tchounwou et al., 2015; Abdul et al., 2015; WHO, 2003).

The sequential reduction and methylation of inorganic arsenic leads to the formation of monomethylarsinic acid (MMA) and dimethylarsinic acid (DMA). This metabolism is considered to be biologically active arsenic and is more toxic (ADWG, 2017). The sub-populations where arsenic poisoning may pose a greater risk are those with genetic variants of arsenic metabolism and whose urine has a higher proportion of MMA (Chen et al., 2009; Smith and Steinmaus, 2009).

The International Agency for Research on Cancer concluded that there is sufficient evidence that arsenic in drinking water causes bladder, lung, and skin cancers, and that arsenic in drinking water is listed as carcinogenic to humans (Group 1) (IARC, 2004).

2.6.4 Beryllium

2.6.4.1 Australian drinking water guidelines

For health reasons, the concentration of beryllium in drinking water should not exceed 0.06 mg/L.

2.6.4.2 Overview

Beryllium can enter water sources through the weathering of rocks, atmospheric deposition and discharge. The main source of beryllium in the environment is the burning of fossil fuels. Other, less prominent sources are slag and ash heaps (Manahan, 2017).

The concentration of beryllium in drinking water is usually very low, normally less than 0.001 mg/L. For example, the concentration of beryllium in drinking water, based on a survey of 1577 drinking water samples taken from a broad area of the United States, showed

that beryllium was detected in 5.4% of samples with an average concentration of 0.00019 mg/L and a maximum concentration of 0.00122 mg/L (0.19 and 1.22 μg/L) (ADWG, 2017).

Atmospheric exposure to beryllium is usually less than food or water but poses a greater danger. Smokers are exposed to higher concentrations than non-smokers (Mroz et al., 2018).

2.6.4.3 Australian drinking water typical values

Drinking water supply in Australia has not been routinely monitored for beryllium.

2.6.4.4 Analytical method

The concentration of beryllium in drinking water can be determined by ICP-AES (APHA Method 3500-Be Part B or C, 1992). The limit of determination is about 0.002 mg/L.

2.6.4.5 Health effects

Beryllium compounds are not easily absorbed by the gastrointestinal tract because they are often insoluble in the intestinal pH (Boschi and Willenbring, 2016). A large proportion of the absorbed beryllium that is incorporated into bones has a biological half-life of more than one year (ADWG, 2017).

The US Environmental Protection Agency (USEPA, 1998), WHO (2001) and US Agency for Toxic Substances and Disease Registry (ATSDR, 2002) conducted a review of the toxicology of beryllium. There is no reliable data showing the health effects of beryllium. Inhalation data led the International Agency for Research on Cancer to conclude that beryllium and beryllium compounds are carcinogenic to humans (Group 1, sufficient evidence of carcinogenicity in humans and sufficient evidence in animals) (IARC, 1993).

2.6.5 Boron

2.6.5.1 Australian drinking water guidelines

For health reasons, the concentration of boron in drinking water should not exceed 4 mg/L.

2.6.5.2 Overview

Boron can be found in drinking water through the natural leaching of boron-containing minerals or the contamination of water sources (Tagliabue et al., 2014). The environmental chemistry of boron is not well understood. In water, the main form may be boric acid (ADWG, 2017).

Boron compounds are used in glass manufacturing, wood and leather preservatives, flame retardants, cosmetics, preservatives and occasionally food preservatives. In other countries, the concentration of boron in unpolluted water sources is usually less than 1 mg/L. In groundwater supplies, the concentration is as high as 6.5 mg/L (ADWG, 2017).

Boron is naturally present in many foods and is found in high levels in plant-derived foods, especially fruits, leafy vegetables, nuts, and beans. It is estimated that the boron intake from food is about 10 times that of water. The daily consumption of boron is 10-25 mg. In the United States, for example, the average adult intake is 0.87-1.34 mg/day. In Australia, the estimated boron intake is 2.2 mg/day (Samman et al., 1998).

2.6.5.3 Australian drinking water typical values

In Australia's drinking water supply, boron is not often monitored, but limited information indicates that the boron concentration is less than 0.1 mg/L.

2.6.5.4 Analytical method

The boron concentration in drinking water can be determined by ICP-AES (APHA Method 4500-B Part D, 1992). The limit of determination is about 0.05 mg/L.

2.6.5.5 Health effects

After ingesting high-dose foods, a large number of poisoning reports have occurred with symptoms including: gastrointestinal disorders, skin rashes, central nervous system

stimulation, and depression. Prolonged exposure to boron can cause similar symptoms (ADWG, 2017).

The tolerated daily intake (TDI) of 0.16 mg/kg body weight (mg/kg) was obtained by the WHO (2004a).

Mutagenicity tests using bacteria and mammalian cells were mostly negative. In mammalian cells, neither boric acid nor borate induced chromosomal aberrations (Ince et al., 2017).

Boron is suspected to be a trace nutrient in mammals and some authors believe that this plays an important role in humans (Nielson, 1996). However, recent reviews suggest that an apparent biological function of human boron has not yet been established (IOM, 2001; USEPA, 2008b).

Although boron is a basic trace element of plants, some plants (such as citrus fruits, stone fruits, some nut trees) are very sensitive to boron toxicity if the irrigation water concentration is higher than 0.5 mg/L (Lazarova et al., 2005).

2.6.6 Cadmium

2.6.6.1 Australian drinking water guidelines

For health reasons, the concentration of cadmium in drinking water should not exceed 0.002 mg/L.

2.6.6.2 Overview

Contamination of cadmium may be caused by zinc in galvanized pipes or in solder used in the fittings, water heaters, water coolers, and faucets (ADWG, 2017). Cadmium can also be released into the environment through the pollution of fertilizers and via the metallurgical industry (Mahar et al., 2015).

Cadmium compounds are commonly used as pigments in plastics, batteries and some electronic components (Banerjee and Bhardwaj, 2016).

The concentration of cadmium in unpolluted natural water bodies abroad is usually less than 0.001 mg/L. Food is the main source of cadmium. Estimates of the average dietary intake of Australian adults are about 0.03 mg daily. Smoking is an important source of cadmium (ADWG, 2017).

2.6.6.3 Australian drinking water typical values

In major Australian networks, the cadmium concentration is usually less than 0.002 mg/L.

2.6.6.4 Analytical method

Determination of cadmium in drinking water is by GF-AAS (APHA Method 3500-Cd Part B, 1992). The limit of determination is about 0.0002 mg/L.

2.6.6.5 Health effects

Absorption of cadmium is in the gastrointestinal tract and depends on a variety of factors including the solubility of the ingested compound, but healthy individuals typically absorb 3%-7% of cadmium. This figure may be higher in people who lack iron, calcium or protein. Cadmium accumulates in the kidneys and releases slowly. In a period of 10-15 years, human biological half-life will be prolonged (Athar and Vohora, 1995; ADWG, 2017).

An extensive review and summary of human and animal toxicity data for cadmium was conducted (IPCS, 1992). In humans, long-term exposure can lead to the excretion of proteins in the urine. In a certain proportion of people this happens if the cadmium content exceeds 200 mg/kg of renal cortical tissue; an estimated 10% of the population has this sensitivity. Other effects include osteomalacia (bone softening). Cases of Itai-Itai disease have been

reported in the Japanese population among elderly women exposed to highly contaminated food and water. Symptoms are similar to osteomalacia and cadmium poisoning.

The International Agency for Research on Cancer has concluded that cadmium may be carcinogenic to humans (Group 2A, limited evidence of carcinogenicity in humans and sufficient evidence for animals) (IARC, 1987).

2.6.7 Chromium

2.6.7.1 Australian drinking water guidelines

For health reasons, the concentration of hexavalent chromium (VI) in drinking water should not exceed 0.05 mg/L. If the total chromium concentration exceeds this value a separate analysis of hexavalent chromium should be performed.

2.6.7.2 Overview

In the trivalent (Cr(III)) and hexavalent (Cr(VI)) states, chromium is present in the environment. Trivalent chromium is the most common naturally occurring state (Kotas and Stasicka, 2000). Most soils and rocks contain a small amount of chromium oxide and weathering, oxidation and bacterial action convert this insoluble compound into a soluble Cr(III) salt (Dhal et al., 2013).

Hexavalent chromium compounds are used in the metallurgical industry for the production of chromium alloy and as an oxidant in the chemical industry (Zayed and Terry, 2003; Saha et al., 2011; Kimbrough et al., 1999).

The total chromium concentration in drinking water is usually less than 0.005 mg/L, but the concentration has been reported in foreign countries from 0.06 mg/L to 0.12 mg/L (ADWG, 2017)

2.6.7.3 Australian drinking water typical values

In major Australian networks, the total chromium concentration is 0.03 mg/L, and the typical concentration is usually less than 0.005 mg/L.

2.6.7.4 Analytical method

The total chromium concentration in drinking water can be determined by ICP-AES or GF-AAS (APHA Method 3500-Cr Part B or C, 1992). The limit of determination is about 0.01 mg/L.

Hexavalent chromium (Cr(VI)) can be determined with a colorimetric method using diphenylcarbizide (APHA Method 3500-Cr part D, 1992). The limit of determination is about 0.005 mg/L.

2.6.7.5 Health effects

The absorption of chromium after intake is low, depending on the valence state. Hexavalent chromium is more easily absorbed through the gastrointestinal tract than trivalent compounds. It penetrates the cell membrane where it is reduced to Cr(III) and forms a complex with proteins and genetic material (Costa, 1997; Kerger et al., 1996).

Epidemiological studies have found a link between inhaled hexavalent chromium compounds and lung cancer, especially in humans exposed during chromate production. There is no evidence that organs other than the lungs are affected or that the intake of hexavalent chromium compounds can cause cancer (Cohen et al., 1993; Costa, 1997).

2.6.8 Copper

2.6.8.1 Australian drinking water guidelines

For health reasons, the concentration of copper in drinking water should not exceed 2 mg/L.

For aesthetic reasons, the concentration of copper in drinking water should not exceed 1 mg/L.

2.6.8.2 Overview

Copper is widely distributed in rocks and soils as carbonate and sulphide minerals (ADWG, 2017). Copper has strong corrosion resistance and is suitable for domestic water supply pipes and fittings. It is also used in electroplating and the chemical industry as well as in many household items (Oliphant, 2003).

In unpolluted surface water, the concentration of copper is very low, usually less than 0.01 mg/L. When water with lower pH and hardness comes in contact with copper pipes and fittings, the concentration may increase significantly (Georgopoulos et al., 2001). The taste threshold of copper is in the range of 1-5 mg/L, depending on the purity of the water. Concentrations above 1 mg/L may cause blue or green stains on sanitary ware. Such stains may also be due to slow water leakage. Copper corrosion occurs over a long period of time and does not necessarily result from high concentrations of copper in drinking water (ADWG, 2017).

2.6.8.3 Australian drinking water typical values

In the main Australian network supply the total copper concentration range is 0.8 mg/L, with a typical concentration of 0.05 mg/L.

2.6.8.4 Analytical method

The copper concentration can be determined by ICP-AES (APHA Method 3500-Cu Part C, 1992) with a measured value of 0.01 mg/L. Flame or graphite furnace atomic absorption spectrometry (APHA 3500-Cu Part B, 1992) can also be used to determine 0.05 mg/L and 0.005 mg/L, respectively.

2.6.8.5 Health effects

Copper is an essential trace element in the human body. It is estimated that the requirements of adults are 2-3 mg per person per day. High doses of copper (over 50 mg/kg body weight) can be fatal (ADWG, 2017).

The gastrointestinal absorption of copper ranges from 25% to 60% depending on many factors, including the formation of copper and the dietary status of copper (Olivares et al., 1998). Copper is stored in the liver, brain and muscle tissue. High concentrations can also be found in the kidneys, heart and hair. Copper is mainly excreted in bile.

Many cases of copper poisoning have been reported, including cases of poisoning in children whose food is prepared in copper containers or pots (Tanner, 1998). Copper poisoning has resulted in cirrhosis of the liver and, in extreme cases, death. Other mild symptoms associated with drinking water containing 3-5 mg/L copper are gastrointestinal symptoms such as nausea, abdominal pain, and vomiting (Pizarro et al., 1999). In genetic disorders, Wilson's disease and idiopathic copper poisoning, patients are particularly susceptible to copper (Lonnerdal and Uauy, 1998).

2.6.9 Iron

2.6.9.1 Australian drinking water guidelines

According to the aesthetic considerations of iron precipitating from solution and causing taste, the concentration of iron in drinking water should not exceed 0.3 mg/L.

There are no health-based guideline values for iron.

2.6.9.2 Overview

In water, it exists in the oxidised form of ferric (Fe(III)) or ferrous (Fe(II)) compounds (Zhang, 2003). In aerated surface water iron is usually found combined with organic

substances such as humic material or adsorbed on suspended substances (Voelker, 1997). The concentration of iron in uncontaminated surface water is usually less than 1 mg/L; however, the concentration of water provided by rusted iron pipes can reach 5 mg/L or higher. In oxygen-depleted groundwater, the recorded iron concentration is as high as 100 mg/L (ADWG, 2017).

The water content of iron is approximately 0.3 mg/L and levels over 3 mg/L will cause adverse reactions (ADWG, 2017). High iron concentrations give the water an undesirable rust-brown appearance, which can lead to contamination of laundry and plumbing fittings, ion exchange softener contamination, and blockages in irrigation systems. The growth of iron bacteria, which causes iron concentrates, can cause taste and odour problems, leading to pipe restriction, blockages and corrosion (DeZuane, 1997).

2.6.9.3 Australian drinking water typical values

In the main Australian network supply, the total iron concentration range is 4 mg/L, with a typical concentration of 0.1 mg/L.

2.6.9.4 Analytical method

Determination of iron concentration in drinking water is by ICP-MS or GF-AAS (APHA Method 3500-Fe Part B or C, 1992). The measurement range was 0.01 mg/L and 0.005 mg/L respectively. Another method is the phenanthroline colorimetric method (APHA 3500-Fe Part D, 1992), which has the limits of measurement 0.01 mg/L. Flame atomic absorption spectroscopy is not sensitive enough.

2.6.9.5 Health effects

Iron is an essential trace element for humans. The minimum daily requirement varies by age and gender. For example, females aged 11-50 years need about 14 mg a day, but this requirement needs to be doubled for pregnant women, while men need 7 mg a day. Iron

deficiency is common and affects many people around the world (Goldhaber, 2003; ADWG, 2017).

According to individual needs and the source of iron, the amount of iron absorbed by the gastrointestinal tract varies from 1% to 20%. It is used to produce haemoglobin, myoglobin, and many enzymes and is stored in the spleen, liver, bone marrow, and muscles (Fairbanks and Beutler, 1995; ADWG, 2017).

A large number of cases of iron poisoning have been reported, mainly in children taking adult iron supplements. The physiological regulation of iron absorption has a high protective effect on iron toxicity (Fine, 2000; Andrews, 1999; Heath and Fairweather-Tait, 2003).

2.6.10 Lead

2.6.10.1 Australian drinking water guidelines

For health reasons, the concentration of lead in drinking water should not exceed 0.01 mg/L.

2.6.10.2 Overview

Lead can be found in drinking water because of dissolved natural resources or plumbing systems that contain lead. These systems may include lead in pipes or solders for sealing joints (Schock et al., 2008). The amount of lead dissolved depends on a number of factors including pH, water hardness, and water retention time (Delpla et al., 2009).

Lead is the most common of heavy metals and is widely mined around the world (Jarup, 2003). It is mainly used in lead-acid batteries, solder, alloys, cable sheaths, paint pigments, ammunition, glaze and plastic stabilizers. Organic lead compounds tetramethyl and tetraethyl lead are widely used as anti-knock and lubricating compounds in gasoline (ADWG, 2017).

In foreign countries, the concentration of lead drinking water is usually lower than 0.002 mg/L, but the concentration of 0.1 mg/L has been reported in Scotland where lead pipes and acidic water are the influencing factors (ADWG, 2017).

About 80% of daily lead intake comes from food, dirt and dust. Food contains a small amount of lead, which increases when acidic food is stored in lead-glazed pottery or lead soldered cans. Lead-free solder is widely used in the food processing industry. The average Australian adult consumes about 0.1 mg of lead per day (ADWG, 2017).

2.6.10.3 Australian drinking water typical values

In the main Australian network, the total lead concentration range is 0.01 mg/L and the typical concentration is lower than 0.005 mg/L.

2.6.10.4 Analytical method

Determination of lead in drinking water is by GF-AAS (APHA Method 3500-Pb Part B, 1992). The limit of determination is 0.005 mg/L.

2.6.10.5 Health effects

Lead can be absorbed by the body through inhalation, ingestion or placental metastasis (Neeti and Prakash, 2013). In adults about 10% of lead is absorbed but in children it can be four to five times that level. After absorption, lead is distributed through soft tissues such as those found in the kidney, liver and in bone marrow. In less than 40 days it has a biological half-life in adults where, in bones, it can persist for 20 to 30 years (ADWG, 2017).

In human, lead is a cumulative poison that severely affects the central nervous system (Finkelstein et al., 1998). Pregnant women are the most vulnerable. Placental metastasis occurs in humans as early as the 12th week of pregnancy and continues throughout the development process (ADWG, 2017).

Many epidemiological studies have been conducted on the effects of lead exposure on children's intellectual development. Despite some contradictory results, studies have shown that exposure to lead can adversely affect intelligence (Lanphear et al., 2005; Schnaas et al., 2006; Koller et al., 2004).

These results are supported by experiments with young primates in which exposure to lead led to the same types of behavioural and learning difficulties observed in human children (Wiener, 2004). Other adverse effects associated with high lead exposure include kidney damage, red blood cell interference, and calcium metabolism, which is needed for bone formation (Patrick, 2006).

Epidemiological studies have not found a link between lead and cancer rates. However, kidney tumours have been reported in rats, mice and hamsters but only at doses above 27 mg/kg each day. Gliomas (brain tumours) have also been reported in studies with rats. In addition, lead salts taken orally also increased the carcinogenic activity of known carcinogens (ADWG, 2017).

The International Agency for Research on Cancer has concluded that lead may cause cancer in humans (Group 2B, inadequate human data but sufficient evidence in animals for inorganic lead compounds) (IARC, 1987).

2.6.11 Manganese

2.6.11.1 Australian drinking water guidelines

According to aesthetic considerations, the concentration of manganese in drinking water should not exceed 0.1 mg/L. If the concentration exceeds 0.5 mg/L, manganese will be considered a health concern.

2.6.11.2 Overview

Manganese is present in the environment in the divalent (Mn(II)), tetravalent (Mn(IV)), and heptavalent (Mn(VII)) states. Most divalent compounds are soluble in water. The most common tetravalent compound, manganese dioxide, is insoluble however the heptavalent permanganate is soluble (ADWG, 2017).

Manganese is mainly used in the manufacture of steel and alloy products (Polmear, 1994). Unpolluted rivers and streams have low levels of manganese which range from 0.001 mg/L to 0.6 mg/L. High concentrations can occur in polluted rivers or under anoxic conditions, such as found in deep reservoirs or lake bottoms, or groundwater. In cases of a concentration of more than 0.1 mg/L, manganese will have an adverse effect on water and will contaminate the plumbing and laundry. Even when the concentration is 0.02 mg/L, manganese will form a coating on the pipe, which can be removed as black ooze. It is estimated that the daily intake of manganese is 2 to 4 milligrams (ADWG, 2017).

2.6.11.3 Australian drinking water typical values

In the main Australian network, the manganese concentration can reach 1.41 mg/L however the typical concentration is lower than 0.01 mg/L.

2.6.11.4 Analytical method

The manganese concentration in drinking water can be determined by ICP-AES or GF-AAS (APHA Method 3500-Mn Part B or C, 1992). The measurement range is 0.005 mg/L and 0.001 mg/L respectively.

2.6.11.5 Health effects

Manganese is a basic element necessary for the normal growth of mammals. Manganese deficiency affects the reproduction of bones and the brain in many animal species. Although there are no specific symptoms in humans it is suggested that manganese deficiency may be

associated with anaemia and bone disease in children (Soetan et al., 2010; Underwood, 2012; ADWG, 2017).

Because of the low solubility of manganese in gastric juice, only 3%-8% of manganese is absorbed by the gastrointestinal tract. After absorption, it concentrates in the liver and eventually excretes in the faeces. In humans, it has a relatively short half-life of 13 to 37 days (ADWG, 2017).

The human and animal toxicity data of manganese were reviewed and summarized extensively (IPCS, 1981). In humans, the toxicity of manganese is mainly due to long-term inhalation of manganese dust. Manganese is considered to be one of the least toxic elements by the oral route.

In a case involving a large number of highly contaminated wells, symptoms included lethargy, increased muscle tension, tremors and mental disorders. Manganese concentration exceeded 14 mg/L, however the concentration of other metals was also high and the impact of the report may not have been entirely caused by manganese (ADWG, 2017).

2.6.12 Mercury

2.6.12.1 Australian drinking water guidelines

For health reasons, total mercury in drinking water should not exceed 0.001 mg/L.

2.6.12.2 Overview

Naturally-releasing mercury into drinking water is extremely low level but pollution may be caused by industrial emissions or leaks (Wang et al., 2014). Mercury compounds can be classified into two types: inorganic mercury salts, many of which are quite insoluble in water; organic mercury compounds, most notably methylmercury. Inorganic mercury can be

converted to methylmercury, which may be caused by bacteria in the sediment and easily enters the food chain (ADWG, 2017).

The concentration of mercury in natural water is usually so low that accurate analysis is difficult (Horvat et al., 1993). Overseas studies have reported that concentrations were lower than 0.0005 mg/L and some sources were lower: 0.00003 mg/L. In some Japanese wells, the maximum value was 0.0055 mg/L (ADWG, 2017).

2.6.12.3 Australian drinking water typical values

In the main Australian network, the total mercury concentration is 0.001 mg/L and the typical concentration is usually less than 0.0001 mg/L.

2.6.12.4 Analytical method

The concentration of total mercury in drinking water can be determined by the cold vapour atomic absorption method (APHA 3500-Hg Part B, 1992). The limit of determination is 0.0001 mg/L.

2.6.12.5 Health effect

Less than 15% of inorganic mercury in drinking water is absorbed by the gastrointestinal tract. Inorganic mercury compounds accumulate in the kidneys and have a long biological half-life, possibly many years in duration (Jarup, 2003). The human and animal toxicity data of inorganic mercury have been extensively reviewed and summarized (IPCS, 1991). A number of studies have looked at workers who have been exposed to mercury at work and have reported health effects including tremors, mental disorders and gingivitis (inflammation of the mucosa around the teeth). The main toxic effect was kidney failure. Organic mercury compounds are unlikely to be found in uncontaminated drinking water; however, toxicity is more serious than inorganic mercury. The human and animal toxicity data of methyl mercury have been extensively reviewed and summarized (IPCS, 1990). Methylmercury is almost

completely absorbed by the gastrointestinal tract (Gochfeld, 2003). The main effects of methylmercury poisoning are severe irreversible neurological and mental disability. These compounds accumulate in fish and are then eaten by humans (Ekino et al., 2007; ADWG, 2017).

2.6.13 Molybdenum

2.6.13.1 Australian drinking water guidelines

For health reasons, the concentration of molybdenum in drinking water should not exceed 0.05 mg/L.

2.6.13.2 Overview

Molybdenum is found in ground and surface water and the concentration is very low, usually below 0.01 mg/L. There is normally a high level of concentration near molybdenum mining operations. Fly ash from coal-fired power plants may be an important source of molybdenum. The application of chemical fertilizer can also increase the concentration of molybdenum in ground and surface water supplies (ADWG, 2017).

2.6.13.3 Australian drinking water typical values

Australia's drinking water supply does not regularly monitor molybdenum.

2.6.13.4 Analytical method

The concentration of molybdenum in drinking water is determined by ICP-AES or GF-AAS (APHA Method 3500-Mo Part B or C, 1992). The measurement range is 0.005 mg/L and 0.04 mg/L.

2.6.13.5 Health effects

Molybdenum is an essential trace element for humans and other animals. It is estimated that adult demand is between 0.15 mg/day and 0.5 mg/day.

Approximately 30-70% of dietary molybdenum is absorbed in the gastrointestinal tract. The highest concentrations of molybdenum are found in the liver, kidneys and bones. There is no biological accumulation of molybdenum in the body. About 90% of molybdenum is excreted in urine. In human long-term and short-term molybdenum toxicity data is scarce: one study found that two years of no-adverse reaction was found in drinking water with 0.2 mg/L of molybdenum (ADWG, 2017).

2.6.14 Nickel

2.6.14.1 Australian drinking water guidelines

For health reasons, the concentration of nickel in drinking water should not exceed 0.02 mg/L.

2.6.14.2 Overview

Drinking water usually contains very low concentrations of nickel. Nickel is used in the electroplating industry and in alloys for chemical, marine, nuclear and aerospace industries. It is used as a catalyst in the industrial process. The main emissions found in the environment come from the burning of fossil fuels and the discharge of waste from the electroplating industry (ADWG, 2017).

2.6.14.3 Australian drinking water typical values

In the main Australian network, the concentration range of nickel is 0.03 mg/L and the typical concentration is lower than 0.01 mg/L.

2.6.14.4 Analytical method

Nickel concentration in drinking water is determined by ICP-AES or GF-AAS (APHA Method 3500-Ni Part B and C, 1992). The limit of determination is 0.02 mg/L and 0.005 mg/L respectively.

2.6.14.5 Health effects

The intestinal absorption of soluble nickel in drinking water is up to 27% compared with just 0.7% in food. After absorption, nickel seems to be distributed to most organs with higher levels found in the kidneys, lungs and liver. It can pass through the human placenta (ADWG, 2017).

The human and animal toxicity data of nickel were reviewed and summarized extensively (IPCS, 1991). In humans, prolonged exposure may have a toxic effect on the kidneys. Increased beta-macroglobulin concentration was reported among electroplating workers exposed to large amounts of nickel.

Nickel is a common skin allergen that causes dermatitis, especially in young women. When skin is sensitive, oral low doses (0.0083 mg/kg.day) may cause contact dermatitis in sensitive people. Several epidemiological studies have shown that inhaling nickel can lead to lung cancer, sinus and nasal cancer. There is no evidence that other organs are affected or that nickel is carcinogenic when ingested (ADWG, 2017).

The International Agency for Research on Cancer concluded that nickel compounds are carcinogenic to humans (Group 1, sufficient evidence of carcinogenicity in humans) (IARC, 1990).

2.6.15 Selenium

2.6.15.1 Australian drinking water guidelines

For health reasons, the concentration of selenium in drinking water should not exceed 0.01 mg/L.

2.6.15.2 Overview

Selenium and selenium salts are ubiquitous in the environment. Selenium is released from natural and human-made sources (Berkowitz et al., 2014); the main source is coal combustion. Selenium is also a by-product of sulfide ore processing, mainly in the copper refining industry (ADWG, 2017).

The main purpose of selenium is to make electronic components. It is also used in several other industries: selenium compounds may be used in some insecticides, used as an anti-dandruff agent, and as a nutrient feed additive for poultry and livestock (Fordyce, 2013).

The concentration of selenium in the source water is usually very low, depending on local geochemical, pH values, and iron salts. The concentrations found in drinking water overseas are usually below 0.01 mg/L; however, the concentration of groundwater in the United States can be as high as 6 mg/L, as reports have shown (ADWG, 2017).

2.6.15.3 Australian drinking water typical values

In Australia's main network supply, the selenium concentration is lower than 0.005 mg/L. In Australia the concentration of selenium in groundwater is not a problem, as it can be in some overseas supplies.

2.6.15.4 Analytical method

The concentration of selenium in drinking water can be determined by hydride generation and atomic absorption spectrometry (APHA Method 3500-Se Part C, 1992). The limit of determination is 0.001 mg/L.

2.6.15.5 Health effects

Selenium is an important element in many species, including humans. Signs of selenium deficiency are not clear but may include a chronic disorder of the heart muscle, other heart

diseases and some cancers. The recommended dietary intake for Australians is approximately 0.001 mg/kg body weight per day (ADWG, 2017).

Most water-soluble selenium compounds are significantly absorbed by the gastrointestinal tract. Selenium is then distributed to most organs with the highest concentrations found in the kidneys, liver and spleen (Zachara et al., 2001).

The human and animal toxicity data of selenium were reviewed and summarized extensively (IPCS, 1987). There are many reports which provide evidence supporting short and prolonged exposure to selenium can cause adverse effects. Most of these effects are due to occupational exposure or accidental poisoning; however, acute or chronic nutritional toxicity is rare. Taking more than 1 mg/day over a long period can lead to nail deformities. Other features of excessive selenium intake include nonspecific symptoms such as gastrointestinal disturbances, dermatitis, dizziness, lassitude and a garlic odour to the breath.

The International Agency for Research on Cancer has concluded that selenium is not classifiable as to its carcinogenicity in humans (Group 3, inadequate evidence in humans and in animals) (IARC, 1987).

2.6.16 Silver

2.6.16.1 Australian drinking water guidelines

For health reasons, the silver concentration in drinking water should not exceed 0.1 mg /L.

2.6.16.2 Overview

The silver concentration in natural water sources is usually very low, below 0.0002 mg/L. In some countries, silver and silver salts are used for disinfection and preservation of water, which may lead to higher concentrations of silver (ADWG, 2017).

Silver is a precious metal used in the production of tableware, jewellery and coins. It is also used in batteries, mirrors, chemical catalysts (Purcell and Peters, 1998).

2.6.16.3 Australian drinking water typical values

Australia's drinking water supply is not routinely monitored for silver concentration levels.

2.6.16.4 Analytical method

The concentration of silver in drinking water is determined by GF-AAS or ICP-AES (APHA Method 3500-Ag Part B or C, 1992). The measurement range is 0.001 mg/L and 0.01 mg/L respectively.

2.6.16.5 Health effects

Although silver can be found in many biological substances, it is not a necessary trace element for mammals. It is estimated that less than 10% of dietary silver is absorbed by the gastrointestinal tract. Silver is mainly stored in the liver and skin and can be combined with amino acids and proteins (ADWG, 2017).

The most famous clinical symptom of silver poisoning is that it causes a bluish-grey metallic discolouration of the skin, hair, mucous membranes, mouth and eyes. Most cases are related to the self-management of silver preparations or occupational exposure to silver and silver compounds (ADWG, 2017).

2.7 Methodology

2.7.1 Scope

ICP-MS is utilised in the determination of Al, Ag, As, Ba, B, Cd, Cr, Co, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Tl, V and Zn in fluid bases such as water (or other comparative aqueous solution) due to its high precision and suitability during testing.

For those elements which do not appear above, calibration standard solutions demonstrating suitable testing characteristics are utilised for their determination; results are then verified by the various, qualified reference literature / materials which are appropriately certified for this purpose.

2.7.2 Principle

Treatment of water is necessary before analysis: dilute nitric acid or mixture of nitric acid and hydrochloric acid is utilised. For analysis, ICP-MS is employed to determine elemental concentration levels.

2.7.2.1 Definitions

A Laboratory Control Sample (or LCS) is a reference standard solution or sample spike prepared from that solution. Requirements dictate that it is necessary for the LCS to be taken from an alternative source than that of the calibration standards. An LCS may be prepared in-house (using AR Grade chemicals) or purchased from a supplier which stocks suitable standard solutions however it is imperative that it be from a different batch than the calibration standard solution being used. Purchase of a LCS from an alternative supplier can alleviate any concerns if there is doubt.

2.7.2.2 Reagents

Redistilled nitric acid concentrated ($\rho 20 = 1.42$ g/mL) or IQ (Instrument Quality) nitric acid (Seastar).

Redistilled hydrochloric acid ($\rho 20 = 1.19$ g/mL) or IQ (Instrument Quality) hydrochloric acid (Seastar).

Deionised (DI) water of > 18 mega ohm-cm resistance was used for all reagent preparations.

2.7.2.3 Standard solutions for ICP-MS

Following are the most commonly utilised standard solutions currently in use:

Mixed Stock Standard Solution (100 mg/L), QCS-26 (High Purity Standards).

This mixed standard solution contains the following elements Ag, Al, B, Ba, As, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Sb, Se, Tl, V, Zn, Ca, Mg, Na, K, Fe, Si and Ti.

Mercury Stock Standard Solution (10 mg/L).

2.7.3 Sample Preparation

Water samples were spiked with a multi-element standard solution in separate HDPE bottles.

One was acidified with 1% (v/v) nitric acid plus 0.01% (v/v) hydrochloric acid, the other two bottles were not acidified (neutralised to pH 6.5–7.5).

Samples were analysed by ICP-MS as soon as possible and in consecutive days.

Nitric acid was added to one of the two non-acidic samples several days after preparation. It was allowed to stand overnight.

All samples – the original acidic samples, one non-acidic sample and the freshly acidified sample – were analysed together.

One of the non-acidified samples was analysed as control.

Two types of waters were analysed: a potable water from UTS and a clean Milli-Q water.

LCS = 10 mL of a certified reference solution at 0.001, 0.01 or 0.1 mg/L.

2.7.4 Selection of isotopes (for portable water)

Table 8. The recommended isotopes.

Elements	Mass	Elements	Mass
Al	27	Hg	201
Ag	107	Mg	24
As	75	Mn	55
B	11	Mo	95
Ba	137	Na	23
Ca	43,44	Ni	60
Cd	111	Pb	206, 207, 208
Co	59	Sb	121
Cr	52	Se	78
Cu	63	Tl	205
Fe	56	V	51,53
K	39	Zn	66

2.7.5 Quality Control Samples

Each batch of analysis should include at least:

a) Reagent blanks (1% HNO_3)

b) 1 blank spike

c) 1 matrix spike

d) 1 LCS

e) 1 duplicate (or at the rate of 1 in 20 samples)

f) 1 Check standard in every 10–20 samples dependent on sample size

Faculty of Engineering and Information Technology

CHAPTER THREE:

TRACE METAL ANALYSIS

IN DEIONISED WATER SAMPLES

Chapter 3. Trace Metal Analysis in Deionised Water Samples

3.1 Introduction

Trace metals contamination in water supplies is being observed and successfully regulated on a worldwide scale. However, to achieve continually high standards of water quality management within these networks, the process of trace metals analysis has taken on an important role designed to identify occurrences and concentrations of these trace metals. Results of these tests allow governments and institutions to monitor and protect our ecosystems and ensure public health and safety.

Sample preservation is a key step in trace metals analysis, but it is, in fact, difficult to perform. The main standard water quality detection methods for preserving trace metals (used by USEPA and APHA) use nitric acid, which is to be added to water samples normally stored in polyethylene bottles.

Some heavy metals are very dangerous and cause great harm to public health. In order to meet the environmental monitoring standards of various regulatory bodies such as drinking water guidelines and requirements of environmental protection agencies, it is necessary to determine the detection limit of trace elements in water samples.

Most guidelines for trace elements in water are in the mg/L range. For example, the guideline for mercury levels in healthy Australian drinking water is 0.001 mg/L, while the guideline for lead levels in healthy Australian drinking water is 0.01 mg/L. Most other trace elements range from 0.002 mg/L to 0.1 mg/L. Natural waters typically contain low concentrations of mercury (up to 0.001 mg/L). Therefore, at these low concentrations, the accuracy of test results is most crucial (Louie et al., 2012).

Regardless of how to improve the determination of trace elements by ICP-MS instrument sensitivity, accuracy and precision, there seems to be limited research data on preservation techniques for trace elements, including mercury. Most analytical laboratories dealing with water samples will follow a standard method of programming.

The two most commonly used standard methods for the determination of multiple elements for ICP-MS recommend the addition of nitric acid until the pH value of the water sample is < 2.0. The USEPA method recommends 1.5 mL of concentrated nitric acid per 1 litre of water. The holding time for mercury is recommended as 28 days while other trace elements in water are recommended as 6 months.

The preparation of standard solution for trace elements determination by ICP-MS is also conducive to the use of nitric acid (1%-2% nitric acid is commonly used). Nitric acid is superior to other acids e.g. hydrochloric acid, perchloric acid and sulfuric acid, because they may cause significant polyatomic interference in the determination of trace elements in ICP-MS due to the formation of molecular ions.

Australian and international standards also recommend the use of nitric acid to preserve trace elements for ICP-MS measurements. These two standards mention the need to use hydrochloric acid to stabilize mercury and potentially hydrosoluble elements Mo, Sb, and Bi, however no detailed studies or confirmed results have yet been reported. In some cases, water samples are sent to the laboratory without acid preservation whereby large amounts of trace metals are lost. Some trace metals are absorbed into the inner wall of the plastic bottle resulting in the loss of metal concentration in the water. Therefore, the test analysis result is far lower than the real value.

There have been many studies to evaluate some of the ways to preserve trace metals in water samples. Mercury within the range of 0.001 mg/L to 0.050 mg/L is stable in seawater when

stored at 0.6% HNO_3. This suggests that chlorides may play an important role in preserving mercury in water (Gardner and Gunn, 1997). The recommendation of long-term storage samples to be measured for total and single methylmercury should be kept in 0.4% HCl (v/v) and stored in a dark environment. All mercury can be recovered quantitatively by adding BrCl at least 24 hours prior to analysis when mercury is adsorbed in the inner wall of the bottle (Parker and Bloom, 2005). It also reported the addition of trace amounts of chlorinated gold to 1%-2% nitric acid to preserve mercury, and the simultaneous determination of mercury and other elements by ICP-MS (Allibone et al., 1999).

Trace metal concentrations can be measured using different monitoring instruments. ICP-MS is a recommended method to measure low trace metal concentrations, therefore Agilent 7900 ICP-MS has been chosen for sampling purposes. In this chapter, trace metals lost from unpreserved DI water samples have been analysed and a few methods to recover the trace metals have been applied. The research studies were assessed based on: (1) DI water spike trace metals carried out, (2) trace metals loss studied at pH 6.5-7.5, (3) recovery methods with focus on different acid, different acid concentration and chlorinated gold solution, (4) a comparison of different recovery methods.

3.2 Experimental Methods

3.2.1 Sampling

All of the reagents used were of ultra-high purity and were prepared in deionised water of > 18 M ohm resistance. The concentration 0.01 mg/L was chosen for this study as the health guidelines for most trace elements in drinking water are quite low, usually in the range of 0.001-0.1 mg/L. Therefore, it is important to monitor the stability of low concentrations to investigate any significant loss. HDPE containers (250 mL capacity) were used in the study

as they are most commonly utilised for storing water samples due to their ease of availability and low cost and were well proven to be free from trace element contamination.

DI water samples (200 mL) were spiked respectively with a multi-element standard solution containing 0.01 mg/L of Al, Ag, As, Ba, B, Cd, Cr, Co, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Tl, V and Zn. They were preserved in various combinations and concentrations of acids and stored in 20 HDPE bottles.

Bottle 1 was acidified with 1% (v/v) nitric acid plus 0.01% (v/v) hydrochloric acid while the remaining 19 bottles were not acidified (neutralised to pH 6.5-7.5).

Figure 2. DI water samples (200 mL) were spiked with a multi-element standard solution.

3.2.2 Monitoring instruments and sampling campaigns

An Agilent 7900 ICP-MS coupled to an Agilent SPS 4 auto-sampler was used for the determination of multi-elements in water samples. Platinum sampler and skimmer cones

were used. Samples were introduced to the plasma by means of a peristaltic pump, via a cross-flow nebulizer and a Scott type spray chamber. The operation of the ICP-MS was fully automated.

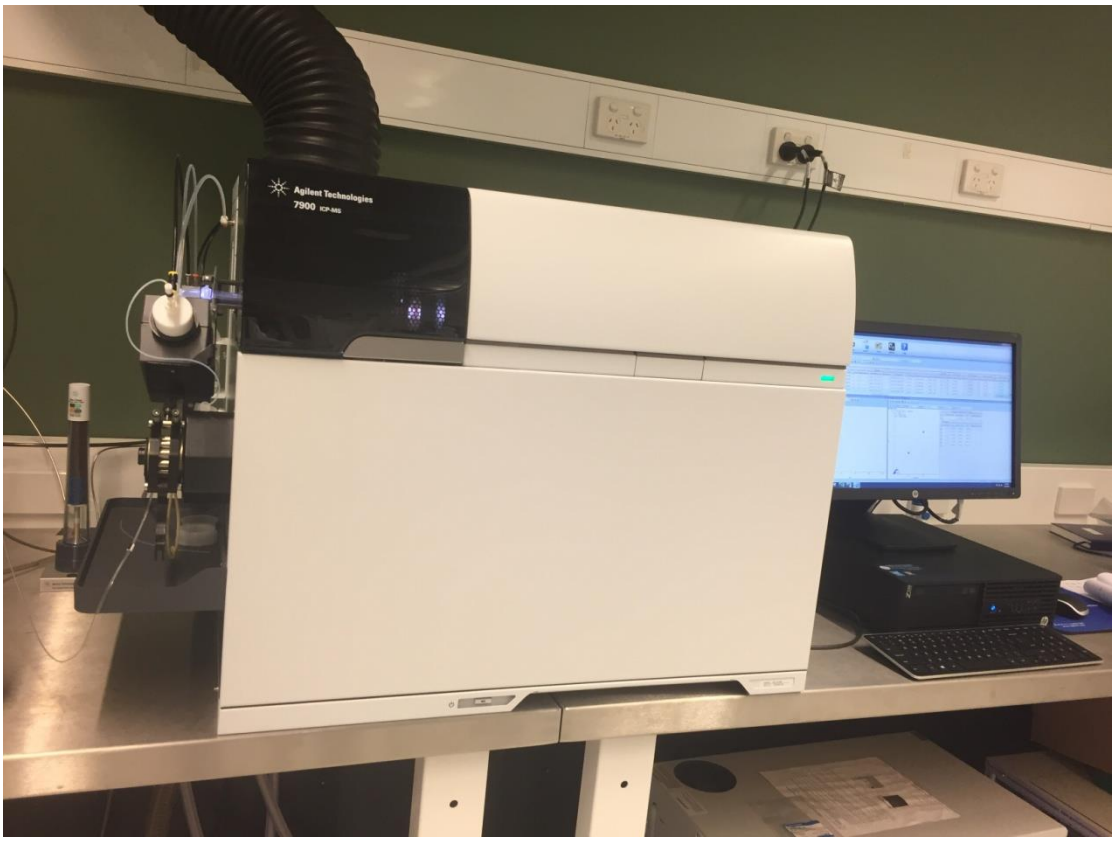


Figure 3. Agilent ICP-MS 7900 used for trace metal concentration measurements.

The ICP-MS was optimised before use in accordance with the manufacturer's instructions to ensure correct performance and that the instrument was in optimal functional condition. Argon and Helium gas levels and pressures needed to be checked before use. Optimisation involved plasma alignment, mass calibrations and auto-tuning with a multi-element tuning solution.

The operational criteria for ICP-MS are as described in the instrument's Operation Manual with minor modification as indicated below:

Table 9. ICP-MS operational criteria.

Instrument settings	Operational criteria
Scans/replicate	20
Number of replicates	3
Sample uptake	40 s
Stablilize	40 s
Scan mode	Peak hopping Sample uptake delay40s Stabilisation delay 40s
Rinse time (fast)	40 s
Nebulizer flow rate	0.3 L/min
Curve type	Linear through blank

The sampling campaign was carried out during October 2017 to March 2018 period. Samples were analysed by ICPMS after 4 hours of storage and then on consecutive days. Details of the samples are shown as below:

Table 10. Details of all DI water samples.

Sample NO.	Sample Type	Days of Test for Trace Metals Lost	Days of Test for Trace Metals Recovery
1	DI water spiked 0.01 mg/L trace metals preserved	4 hours-30 days	N/A
2	DI water spiked 0.01 mg/L trace metals preserved	4 hours-30 days	N/A
3	DI water spiked 0.01 mg/L trace metals unpreserved	4 hours-30 days	N/A
4	DI water spiked 0.01 mg/L trace metals unpreserved	4 hours-30 days	N/A
5	DI water spiked 0.01 mg/L trace metals unpreserved	4 hours-30 days	N/A
6-20	DI water spiked 0.01 mg/L trace metals unpreserved	N/A	30 days

3.2.3 ICP-MS standard solution and preparation procedures

a) Stock standards most commonly utilised in this method are as follows:

Multi-element stock standard solution, QCS-26, 100 mg/L (High Purity Standards) containing Ag, Al, B, Ba, As, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Sb, Se, Tl, V, Zn, Ca, Mg, Na, K, Fe, Si and Ti.

Table 11. Intermediate-1 (0.5 mg/L) Multi-elements QCS-26.

Stock QCS-26 100 mg/L	HNO_3	Final Volume	Final Concentration
mL	mL	mL	mg/L
0.5	1	100	0.5

Table 12. Intermediate-2 (5 mg/L) Multi-elements QCS-26.

Stock QCS-26 100 mg/L	HNO_3	Final Volume	Final Concentration
mL	mL	mL	mg/L
5	1	100	5

Table 13. Intermediate-3 (1.0 mg/L) Hg.

Stock Hg 10 mg/L	HCl	Final Volume	Final Concentration
mL	mL	mL	mg/L
5	0.5	50	1.0

b) Working Calibration Standards for ICP-MS.

This solution contains: Ag. Al, As, B, Ba, Be, Cr, Co, Cu, Pb, Mn, Mo, Ni, Sb, Se, Tl, Ti, V, Zn and Hg.

Table 14. Preparation of standards.

Std ID	Inter Std-1 QCS-26 (0.5 mg/L)	Inter Std-2 QCS-26 (5 mg/L)	Inter Std-3 Hg (1.0 mg/L)	HNO_3 Concentration	HCl 1% v/v	Final Volume	Final Concentration Multi elements	Final Concentration Hg
	mL	mL	mL	mL	mL	mL	mg/L	mg/L
Blk				1	1	100		
1	1		0.1	1	1	100	0.005	0.001
2	1		0.25	0.5	0.5	50	0.01	0.005
3	2		0.5	0.5	0.5	50	0.02	0.01
4		1	1	0.5	0.5	50	0.1	
5		2	2	0.5	0.5	50	0.2	

These standards contain 1% (v/v) HNO_3 and 0.01% (v/v) HCl.

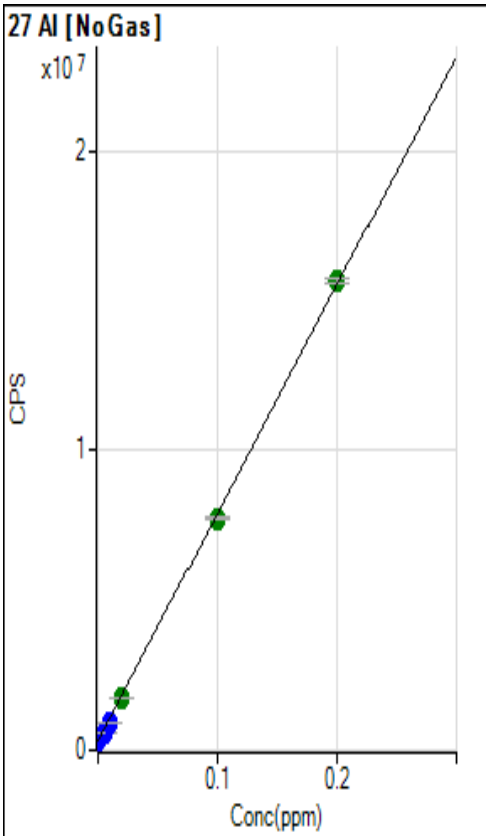
3.2.4 Calibration

Calibration standards

Calibration multi-element standard solutions (consisting of 0, 0.005, 0.01, 0.02, 0.1, 0.2 mg/L) were prepared in 1% (v/v) nitric acid and 0.01% (v/v) hydrochloric acid. Results of ICP-MS calculations were determined by comparison with these multi-element standard solutions as automated by the instrument's computer. All test results were compared with the control and adjusted accordingly and all solutions were analysed in at least duplicates.

Table 15. Details of calibration standard concentration.

Standard ID	Standard Set (mg/L)
Level-1	0
Level-2	0.005
Level-3	0.01
Level-4	0.02
Level-5	0.1
Level-6	0.2



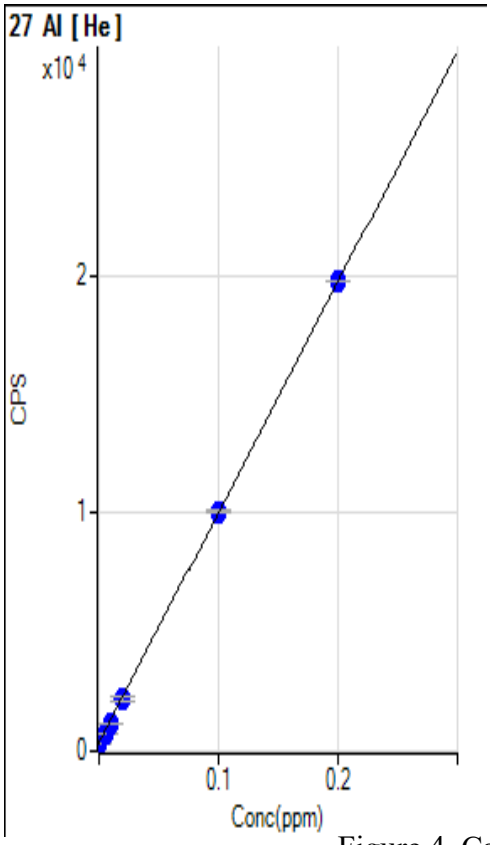
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	307334.38		P	1.1
2		0.00500	0.00370	588859.60		P	1.4
3		0.01000	0.00776	897572.80		P	0.4
4		0.02000	0.01867	1727601.59		A	0.3
5		0.10000	0.09759	7731730.72		A	0.8
6		0.20000	0.20148	15635809.35		A	1.1

$y = 76078178.7656 \times x + 307334.3800$

R = 0.9999

DL = 0.0001371

BEC = 0.00404



	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	356.69		P	11.3
2		0.00500	0.00382	726.71		P	5.7
3		0.01000	0.00837	1166.75		P	2.6
4		0.02000	0.01905	2200.23		P	5.5
5		0.10000	0.10026	10060.29		P	1.5
6		0.20000	0.20007	19719.80		P	0.2

$y = 96779.9175 \times x + 356.6867$

R = 1.0000

DL = 0.001253

BEC = 0.003686

Figure 4. Calibration graphs for Al.

3.3 Results and Discussion

3.3.1 Trace metals loss tests

Trace elements Al, Ag, As, Ba, B, Cd, Cr, Co, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Tl, V and Zn were analysed. When compared to the acidified samples, significantly lower concentrations of trace metals Al, Ag, As, Cr, Hg, Pb, Se, V and Zn indicated losses of more than 10% in the non-acidified samples 4 hours-20 days after preparation.

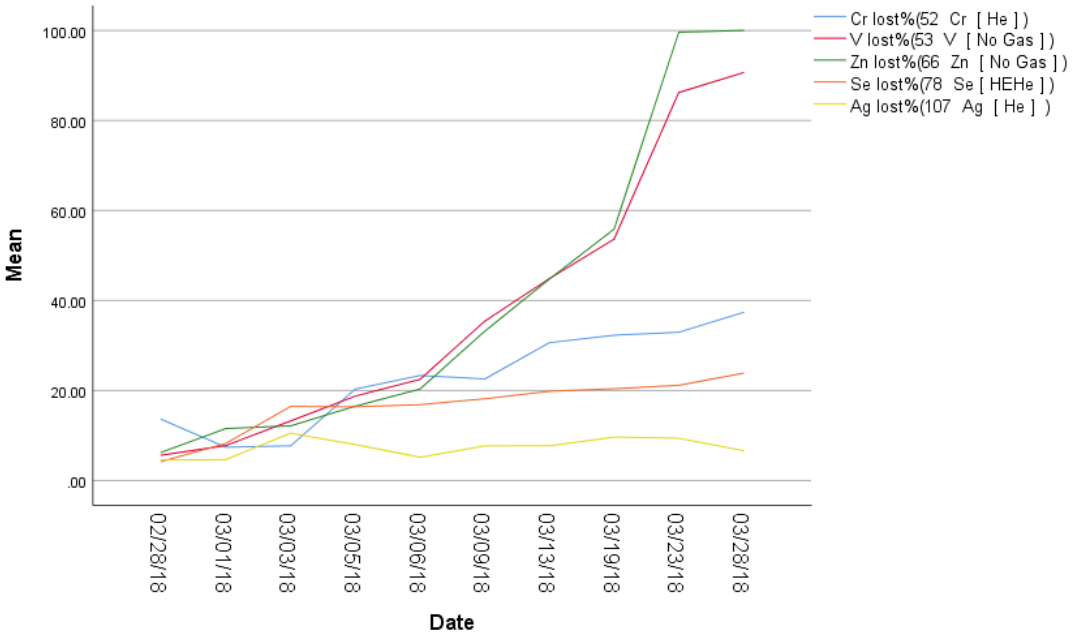


Figure 5. Some trace metals indicated losses of more than 10%.

Table 16. Three metals from the top four toxic trace metals with losses of more than 10%.

Times lapsed after preparation	Conc.	^{75}As	^{201}Hg	^{207}Pb
4 hours	mg/L	1%±0.02%	5%±0.01%	3%±0.01%
1 day	mg/L	3%±0.02%	9%±0.01%	6%±0.01%
2 days	mg/L	3%±0.02%	15%±0.01%	13%±0.02%
3 days	mg/L	4%±0.02%	9%±0.01%	16%±0.02%
4 days	mg/L	4%±0.02%	9%±0.01%	23%±0.03%
5 days	mg/L	5%±0.03%	28%±0.01%	16%±0.02%
6 days	mg/L	6%±0.03%	21%±0.01%	18%±0.02%
7 days	mg/L	8%±0.03%	29%±0.01%	25%±0.03%
8 days	mg/L	8%±0.03%	24%±0.01%	26%±0.03%
10 days	mg/L	11%±0.05%	36%±0.01%	44%±0.04%
12 days	mg/L	17%±0.05%	35%±0.01%	39%±0.04%
14 days	mg/L	18%±0.04%	40%±0.01%	50%±0.05%
16 days	mg/L	14%±0.05%	40%±0.01%	40%±0.04%
18 days	mg/L	19%±0.05%	37%±0.01%	47%±0.04%
20 days	mg/L	19%±0.05%	39%±0.01%	50%±0.05%
22 days	mg/L	20%±0.06%	40%±0.01%	49%±0.04%
24 days	mg/L	22%±0.06%	52%±0.01%	63%±0.06%
27days	mg/L	24%±0.06%	58%±0.01%	64%±0.06%
30 days	mg/L	25%±0.06%	60%±0.01%	64%±0.06%
38 days	mg/L	20%±0.06%	67%±0.01%	71%±0.06%

Figure 6. Three metals from the top four toxic trace metals with losses of more than 10%.

3.3.2 Methods to recover trace metals

(1) 1% (v/v) nitric acid

(2) 3% (v/v) nitric acid

(3) 5% (v/v) nitric acid

(4) 1% (v/v) nitric acid plus 0.01% (v/v) hydrochloric acid

(5) 1% (v/v) nitric acid plus 0.02% (v/v) hydrochloric acid

(6) 1% (v/v) nitric acid plus 1% (v/v) hydrochloric acid

(7) 3% (v/v) nitric acid plus 3% (v/v) hydrochloric acid

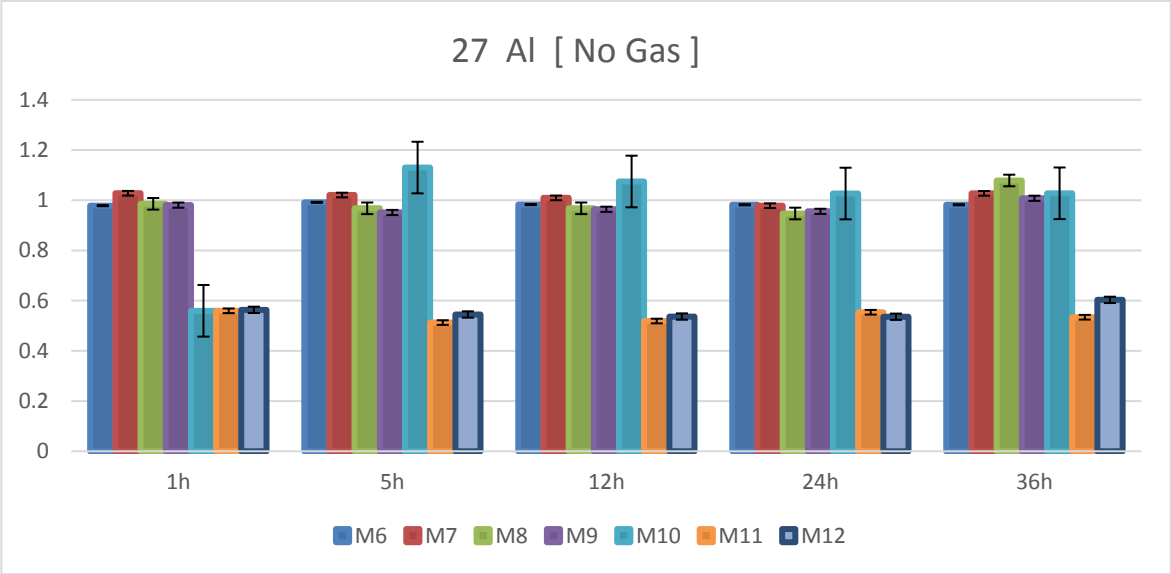
(8) 5% (v/v) nitric acid plus 5% (v/v) hydrochloric acid

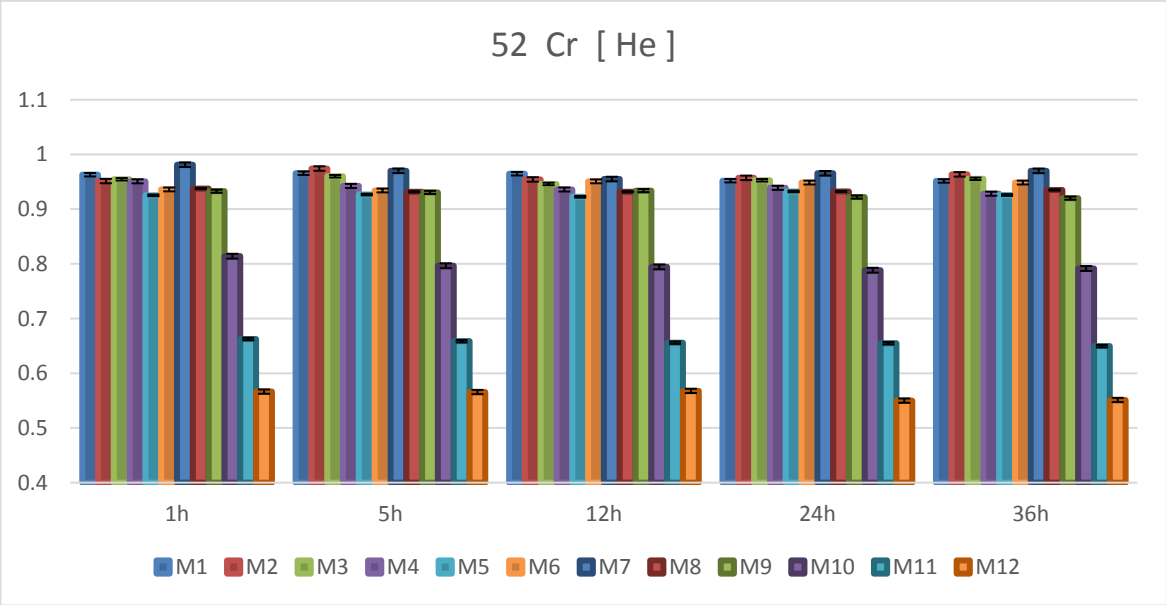
(9) 10 mg/L Au

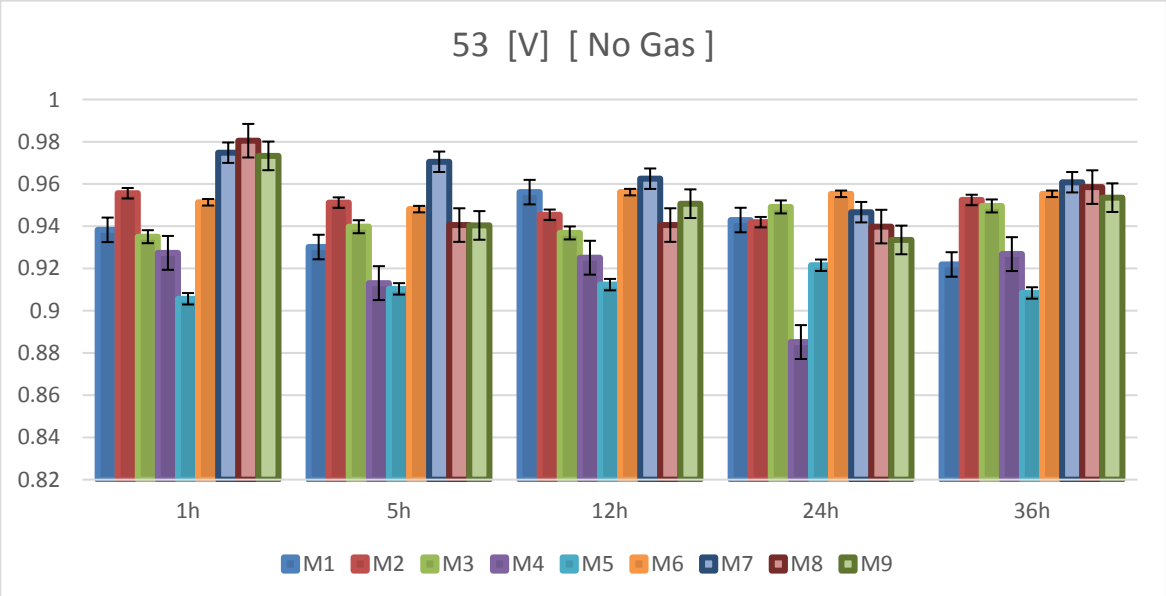
(10) 100 mg/L Au

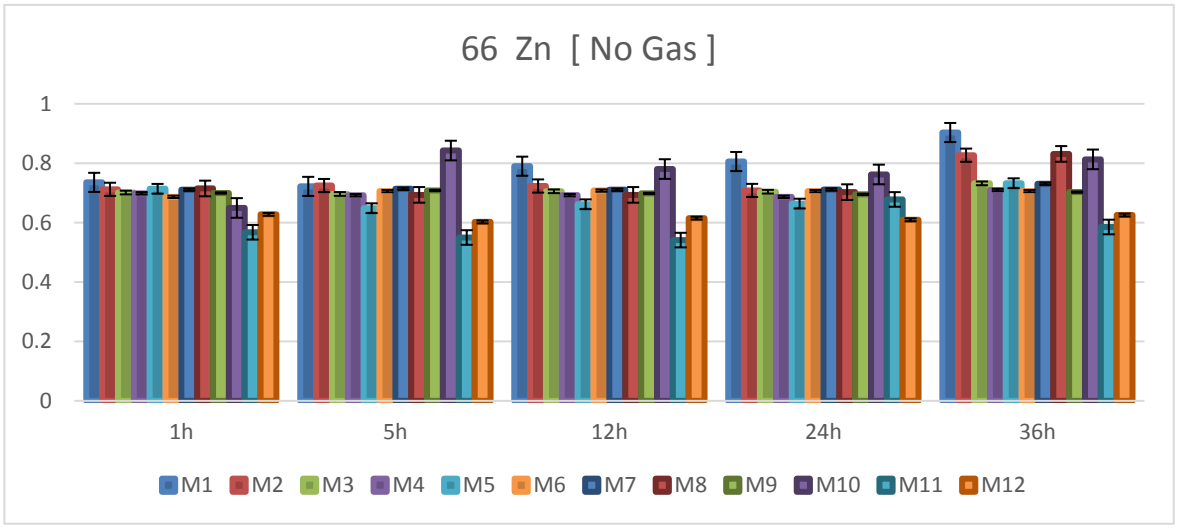
3.3.3 Recovery of trace metals from unpreserved DI water samples

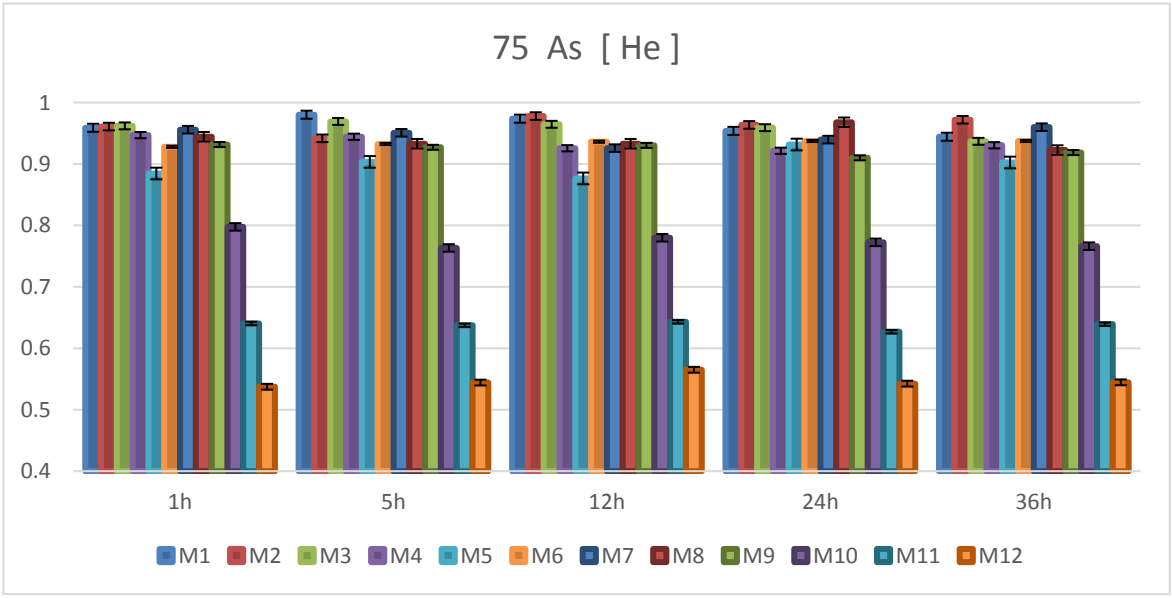
After adding solutions above to the non-acid preserved samples and allowed to stand 1hour, 5 hours, 12 hours, 24 hours, 36 hours, recovered concentrations of trace metals were tested.

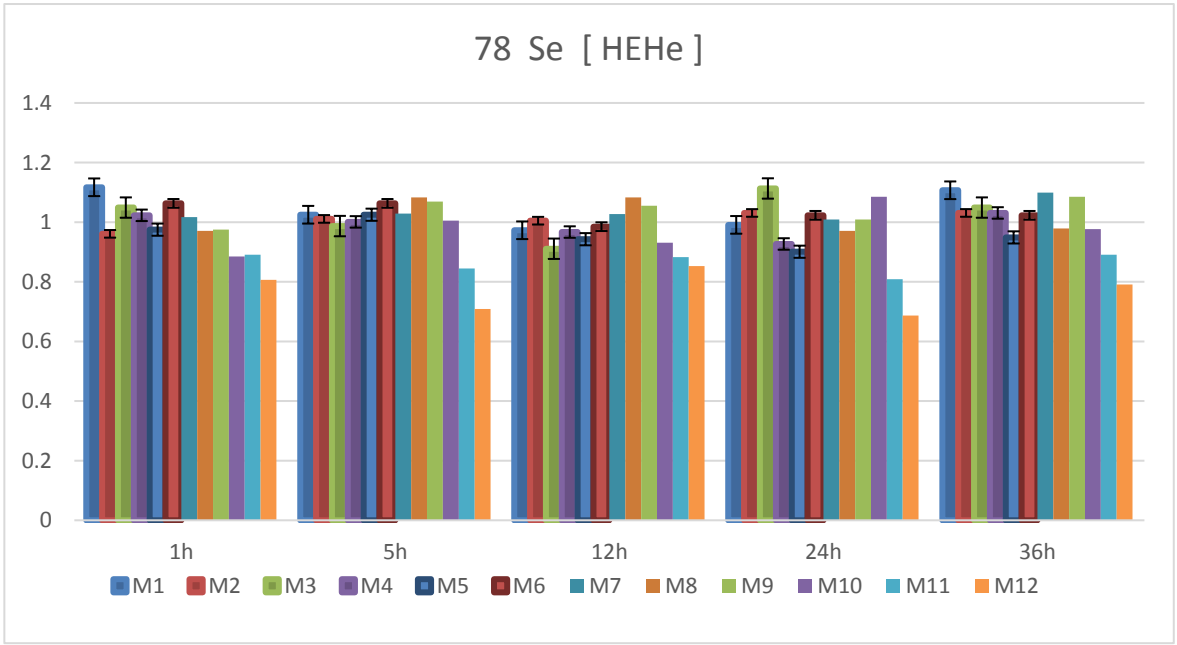

27 Al [No Gas]
1.4
1.2
1
0.8
0.6
0.4
0.2
0
1h
5h
12h
24h
36h
M6 M7 M8 M9 M10 M11 M12


52 Cr [He]
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
1h
5h
12h
24h
36h
M1 M2 M3 M4 M5 M6 M7 M8 M9 M10 M11 M12


53 [V] [No Gas]
1
0.98
0.96
0.94
0.92
0.9
0.88
0.86
0.84
0.82
1h
5h
12h
24h
36h
M1 M2 M3 M4 M5 M6 M7 M8 M9


66 Zn [No Gas]
1
0.8
0.6
0.4
0.2
0
1h
5h
12h
24h
36h
M1 M2 M3 M4 M5 M6 M7 M8 M9 M10 M11 M12


75 As [He]
1
0.9
0.8
0.7
0.6
0.5
0.4
1h
5h
12h
24h
36h
M1 M2 M3 M4 M5 M6 M7 M8 M9 M10 M11 M12


78 Se [HEHe]
1.4
1.2
1
0.8
0.6
0.4
0.2
0
1h
5h
12h
24h
36h
M1 M2 M3 M4 M5 M6 M7 M8 M9 M10 M11 M12

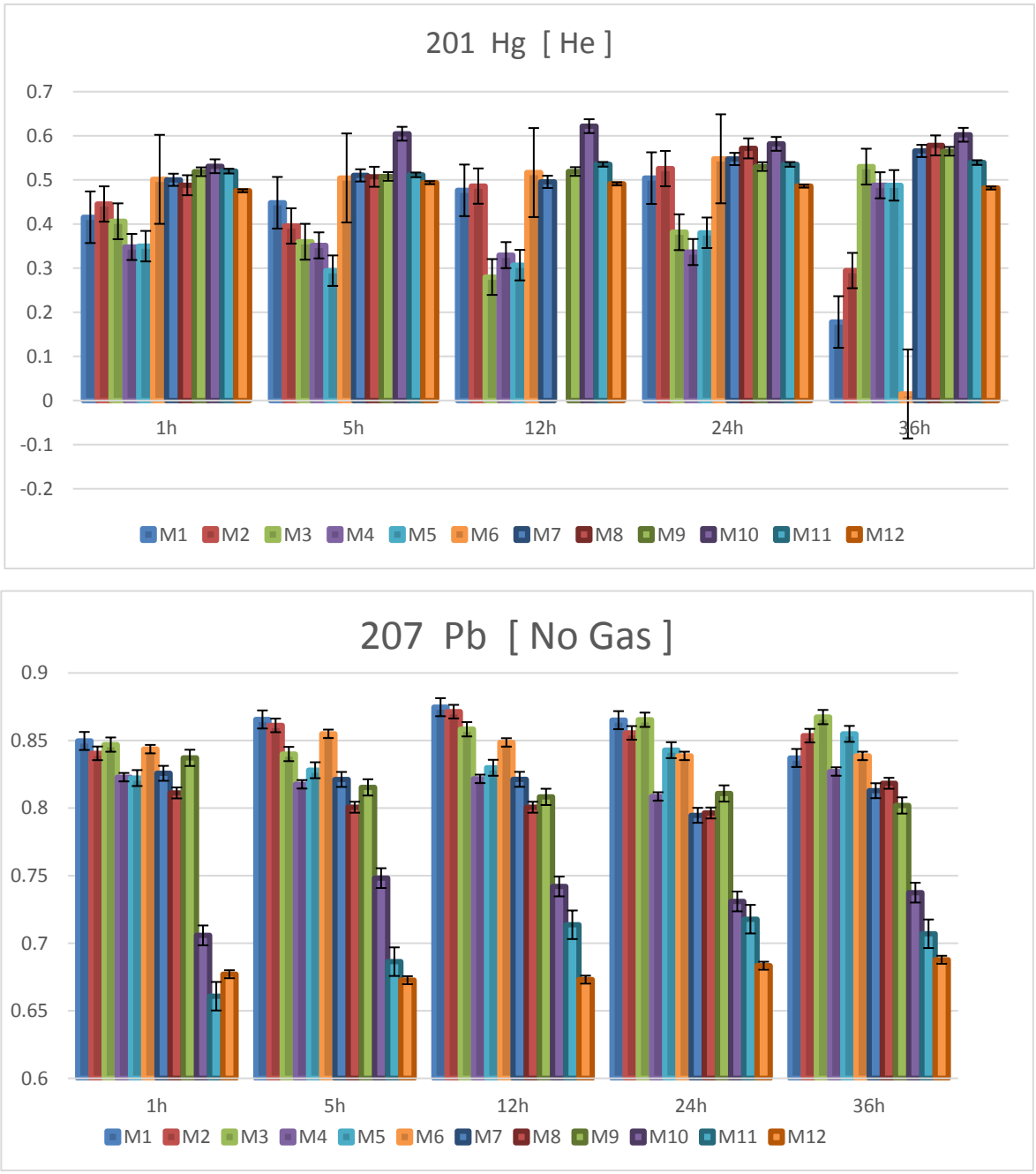


Figure 7. Different methods to recover Al, Cr, V, Zn, As, Se, Hg, Pb.

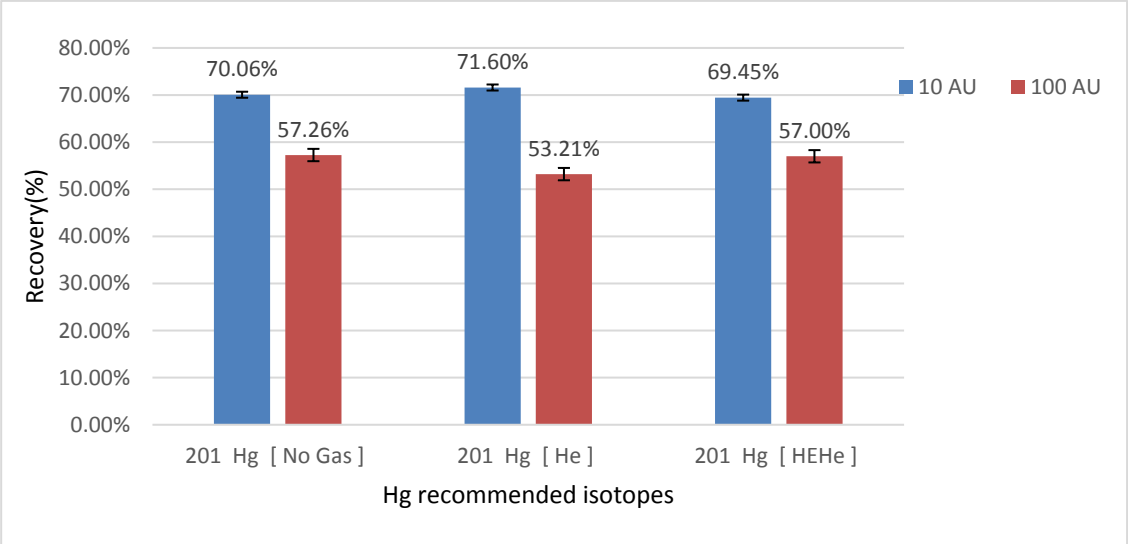


Figure 8. Recovery of Hg by using 10 mg/L and 100 mg/L Au solutions.

3.4 Summary

The satisfactory recovery of trace metals in the non-acidified samples was achieved when 1% (v/v) nitric acid plus 0.01% (v/v) hydrochloric acid was added for a 24-hour period. This process enabled efficient re-extraction of 90% of trace metals from the water samples. However, mercury did not yield high recovery results (only 56%) with this method; with 10 mg/L Au solution 71.6% recovery was obtained.

For the next step of the experiments using tap water spiked trace metals, 1 mg/L Au solution proved suitably efficient for recovery and testing.

Faculty of Engineering and Information Technology

CHAPTER FOUR:

TRACE METAL ANALYSIS

IN DRINKING WATER SAMPLES

Chapter 4. Trace Metal Analysis in Drinking Water Samples

4.1 Trace Metals in drinking water

The occurrence of trace metals in drinking water has increased considerably in the last century, which is, in itself, an indication of the progressive industrialisation of the modernised world. Aside from the many natural sources of trace metals, small amounts are needed for survival while high levels can often be toxic. Some trace metals in drinking water are known to cause a wide range of adverse health issues in human. Trace metals are non-degradable, thus elevated concentrations of these pollutants may cause serious health problems and can adversely impact the environment. Human exposure to heavy metals is through inhalation and ingestion pathways, which can cause moderate to serious health problems due to the bio-accumulation of these metals inside the human body (Kampa and Castanas, 2008). Therefore, the determination of the sources of these substances is a very important issue in relation to epidemiological and toxicological studies.

In Chapter 3, DI water spiked with trace metals had been analysed and a few of the methods to recover those trace metals were applied. This chapter will therefore cover the trace metals analysis in drinking water samples, using tap water from UTS.

4.2 Sampling Methodology

For trace metals loss analysis, drinking water sample (200 mL) collection was collected at UTS environmental laboratory on the 5th April 2018. The 0.01 mg/L trace metals were spiked, including Al, Ag, As, Ba, B, Cd, Cr, Co, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Tl, V and Zn. They were preserved in various combinations and concentrations of acids and stored in 22 HDPE bottles.

Bottle 1 and bottle 2 were tap water; bottles 3 to 22 were tap water spiked 0.01 mg/L trace metals. Bottles 1 to 4 were acidified with 1% (v/v) nitric acid plus 0.01% (v/v) hydrochloric acid while the remaining 18 bottles were not acidified (neutralised to pH 6.5-7.5).

Figure 9. Drinking water samples (200 mL) spiked with a multi-element standard solution.

The sampling campaign was carried out during the period April to June 2018. Samples were analysed by ICP-MS after 4 hours of storage and then on consecutive days.

Details of the samples are shown in Table 17.

Table 17. Details of all drinking water samples.

Sample NO.	Sample Type	Days of Test for Trace Metals Loss	Days of Test for Trace Metals Recovery
1	Drinking water preserved	4 hours-30 days	N/A
2	Drinking water preserved	4 hours-30 days	N/A
3	Drinking water spiked 0.01 mg/L trace metals unpreserved	4 hours-30 days	N/A
4	Drinking water spiked 0.01 mg/L trace metals unpreserved	4 hours-30 days	N/A
5-7	Drinking water spiked 0.01 mg/L trace metals unpreserved	4 hours-30 days	N/A
7-22	Drinking water spiked 0.01 mg/L trace metals unpreserved	N/A	30 days

4.2.1 Monitoring instruments and calibration

An Agilent 7900 ICP-MS coupled to an Agilent SPS 4 auto-sampler was used for the determination of multi-elements in water samples.

The calibration multi-element standard solutions (consisting of 0, 0.005, 0.01, 0.02, 0.1, 0.2 mg/L) were prepared in 1% (v/v) nitric acid and hydrochloric acid.

4.2.2 ICP-MS analysis

Once the sample preparation process has been completed, samples are then ready for trace metal concentration analysis by ICP-MS which is a modern spectrometry technique offering precision and accuracy in results analysis with miniscule detection limits. The process lasts for three minutes (per sample) and results are then available to view on the attached desktop. In this case, concentrations of 19 metals were analysed; selection of these metals was based on the QCs and detection limits for the ICP-MS unit in all samples. It should be noted that the detection limits in the ICP-MS method vary depending on the element therefore their

respective concentration measurements are excluded from this study. For each sample, concentrations of Al, Ag, As, Ba, B, Cd, Cr, Co, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Tl, V and Zn were measured. Metal concentration results will be utilised in Chapter Five as recommendations in future work.

Spiked samples and blanks were analysed in at least triplicates by ICP-MS on the day of preparation to confirm their expected concentrations and then on subsequent days and as often as possible for at least 30 days.

4.2.3 Quality assurance and calibration

As mentioned before, duplicate samples analyses were regularly performed during the experiments which indicated that all concentration results obtained were within 10% of each other for the same extracted sample. As part of the calibration process, internal standards and quality control blanks for the 19 metals were used. Each element was calibrated using six points linearity curves; all correlation coefficients yielded for the 19 metals were more than 0.99 (Appendix A-1).

4.3 Results and Discussion

The results obtained for the four hours of analysis for all solutions indicated the prepared concentrations of various elements were correct (within plus or minus 10% of the expected values).

4.3.1 Trace metals loss tests

Trace elements Al, Ag, As, Ba, B, Cd, Cr, Co, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Tl, V and Zn were analysed. When compared to the acidified samples, significantly lower concentrations of trace metals Al, Ag, Cr, Hg, and Pb indicated losses of more than 20% in the non-acidified samples 4 hours-35days after preparation.

The results of trace metals determination by ICP-MS were calculated by reference to the standard solutions described above. Calculation of results was automated by the instrument's computer.

Without acid preservation, the samples were analysed over 35 days and results are illustrated in Table 18. Each result is the mean of triplicate analysis.

Table 18. The loss of trace metals over 35 days study period.

Times lapsed after preparation	Unit	^{27}Al	^{52}Cr	^{107}Ag	^{201}Hg	^{207}Pb
4 hours	mg/L	0%±0.01%	8%±0.01%	3%±0.01%	12%±0.01%	12%±0.01%
1 day	mg/L	16%±0.01%	13%±0.01%	2%±0.01%	9%±0.01%	17%±0.01%
3 days	mg/L	15%±0.01%	31%±0.01%	3%±0.01%	14%±0.01%	29%±0.02%
5 days	mg/L	18%±0.01%	36%±0.01%	3%±0.01%	18%±0.01%	35%±0.03%
7 days	mg/L	19%±0.01%	35%±0.01%	6%±0.01%	26%±0.01%	41%±0.04%
9 days	mg/L	20%±0.02%	40%±0.01%	6%±0.01%	21%±0.01%	39%±0.03%
11 days	mg/L	20%±0.02%	40%±0.01%	8%±0.01%	26%±0.01%	41%±0.04%
13 days	mg/L	15%±0.01%	40%±0.01%	8%±0.01%	26%±0.01%	42%±0.04%
15 days	mg/L	19%±0.01%	40%±0.01%	12%±0.01%	33%±0.02%	45%±0.04%
17 days	mg/L	16%±0.01%	42%±0.01%	13%±0.01%	28%±0.02%	42%±0.04%
21 days	mg/L	13%±0.01%	41%±0.01%	15%±0.01%	31%±0.02%	44%±0.04%
25 days	mg/L	20%±0.02%	42%±0.01%	22%±0.02%	38%±0.02%	46%±0.04%
31 days	mg/L	14%±0.01%	42%±0.01%	25%±0.02%	44%±0.02%	49%±0.04%
35 days	mg/L	25%±0.01%	45%±0.01%	28%±0.02%	44%±0.02%	50%±0.05%

Figure 10. Two metals from the top four toxic trace metals with losses of more than 10%.

4.3.2 Methods to recover trace metals

(1) 1% (v/v) nitric acid

(2) 1% (v/v) nitric acid plus 0.01% (v/v) hydrochloric acid

(3) 1% (v/v) nitric acid plus 1% (v/v) hydrochloric acid

(4) 1 mg/L Au plus 1% (v/v) nitric acid

(5) 0.1% EDTA (v/v)

(6) 0.1% EDTA (v/v) plus 1% (v/v) nitric acid

4.3.3 Recovery of trace metals from unpreserved drinking water samples

After adding solutions, above, to the non-acid preserved samples and allowed to stand 1 hour, 12 hours, 24 hours, recovered concentrations of trace metals were tested.

Table 19. Percentage to recover trace metals from tap water.

Times lapsed after preparation	Unit	^{27}Al	^{52}Cr	^{107}Ag	^{201}Hg	^{207}Pb
Method 1-1 hour	mg/L	109%±0.04%	91%±0.01%	87%±0.02%	57%±0.02%	91%±0.06%
Method 1-12 hours	mg/L	90%±0.03%	91%±0.01%	89%±0.02%	59%±0.02%	91%±0.06%
Method 1-24 hours	mg/L	76%±0.01%	93%±0.01%	94%±0.02%	53%±0.02%	90%±0.06%
Method 2-1 hour	mg/L	86%±0.02%	93%±0.01%	84%±0.02%	55%±0.02%	91%±0.06%
Method 2-12 hours	mg/L	86%±0.02%	92%±0.01%	85%±0.02%	55%±0.02%	91%±0.06%
Method 2-24 hours	mg/L	82%±0.02%	92%±0.01%	91%±0.02%	52%±0.02%	91%±0.06%
Method 3-1 hour	mg/L	103%±0.04%	83%±0.01%	90%±0.02%	39%±0.01%	83%±0.05%
Method 3-12 hours	mg/L	91%±0.03%	87%±0.01%	93%±0.02%	46%±0.01%	88%±0.05%
Method 3-24 hours	mg/L	88%±0.02%	88%±0.01%	98%±0.02%	44%±0.01%	88%±0.05%
Method 4-1 hour	mg/L	90%±0.01%	83%±0.01%	97%±0.02%	78%±0.02%	109%±0.06%
Method 4-12 hours	mg/L	91%±0.03%	84%±0.01%	93%±0.02%	75%±0.02%	101%±0.06%
Method 4-24 hours	mg/L	86%±0.02%	84%±0.01%	96%±0.02%	71%±0.02%	98%±0.05%
Method 5-12 hours	mg/L	95%±0.03%	86%±0.01%	76%±0.01%	65%±0.02%	94%±0.05%
Method 5-24 hours	mg/L	102%±0.04%	87%±0.01%	67%±0.01%	60%±0.02%	79%±0.03%
Method 6-12 hours	mg/L	106%±0.04%	86%±0.01%	77%±0.01%	53%±0.02%	76%±0.03%
Method 6-24 hours	mg/L	89%±0.02%	86%±0.01%	78%±0.01%	48%±0.01%	73%±0.03%

4.4 Summary

In this chapter, trace metals loss and recovery were determined by employing acid addition, followed by the ICP-MS analytical method. Samples were analysed for 30 days to check trace metals loss and 6 methods were applied to recover trace metals. A total number of 22 samples were analysed and the following conclusions have been derived from this chapter:

- From the results of method 4, the recovery of trace metals in the non-acidified tap water samples, was achieved as the aim of 70%-110% as the ISO recommendation when 1 mg/L Au plus 1% (v/v) nitric acid was added after a 1-hour period.
- From the results of method 3, the recovery of trace metals in the non-acidified tap water samples, was achieved as the aim of 70%-110% as the ISO recommendation when 1% (v/v) nitric acid plus 1% (v/v) hydrochloric acid was added for a 24-hour period except Hg recovery which was 66%.
- This proves that un-acidified water samples can be sent to the laboratory for testing total acid extractable metals, provided 1 mg/L Au plus 1% (v/v) nitric acid is added to the samples in the original container to allow adsorbed metals to leach back into the water.
- It is highly recommended that acidified water samples – those containing 1% (v/v) nitric acid plus 0.01% (v/v) hydrochloric acid – are sent to the laboratory for testing whenever possible to guarantee accuracy of all trace metals analyses.
- This study has shown that the simultaneous determination of multi-elements in the same run by ICP-MS under routine laboratory operating conditions can produce good recovery and precision of the listed elements to meet health-based guidelines.

Faculty of Engineering and Information Technology

CHAPTER FIVE:

CONCLUSIONS, LIMITATIONS AND RECOMMENDATIONS FOR FUTURE WORK

Chapter 5. Conclusions, Limitations and Recommendations for Future Work

5.1 Summary of the Recovery of Trace Metals from Unpreserved Drinking Water Samples

An efficient and accurate extraction method, followed by ICP-MS analysis, was developed for the recovery of trace metals from unpreserved water samples. If non-acidified water samples are sent to the laboratory the addition of 1% (v/v) nitric acid plus 1% (v/v) hydrochloric acid for a 24-hour period will enable efficient re-extraction of 70%-110% of trace metals from tap water samples except Hg recovery which is 66.11%. However, with the addition of 1 mg/L Au solution plus 1% (v/v) nitric acid, Hg recovery was increased to 78%. Therefore, it is highly recommended that acidified water samples are sent to the laboratory whenever possible to guarantee precise accuracy of all trace metals. If unpreserved water samples are received from the client, the addition of 1% (v/v) nitric acid plus 1% (v/v) hydrochloric acid for a 24-hour period, or 1 mg/L Au solution plus 1% (v/v) nitric acid, will enable recovery of trace metals.

5.2 Limitations of the Current Study

Trace metals Al, Ag, As, Ba, B, Ca, Cd, Cr, Co, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Tl, V and Zn were analysed by ICP-MS and Al, Ag, As, Ba, B, Cd, Cr, Co, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Tl, V and Zn were chosen as research elements because some elements cannot be measured accurately with the ICP-MS test (e.g. Ca). In addition, instrument stability can be unreliable with some batches. More experimentation methods with different acids, different acid concentrations, and different Au solution concentration are needed.

The rate and amount of trace metals loss in each experiment was not identical indicating the

active sites for adsorption varied from bottle to bottle. It is to be expected that HDPE bottles from different batches will behave differently and the size of the bottles will play a role in the loss of trace metals.

As an update to the analysis, trace metals were spiked to DI water and tap water. From the test results, DI water spiked with trace metals had a higher loss percentage than tap water spiked trace metals and some elements were lost from DI water but stable in tap water. Therefore, this research also has limitations with sample type.

5.3 Recommendations for Future Research

The trace metals studies have shown that the trace metals had significant loss without sample preservation, and there is limited study for trace metals recovery from unpreserved water samples.

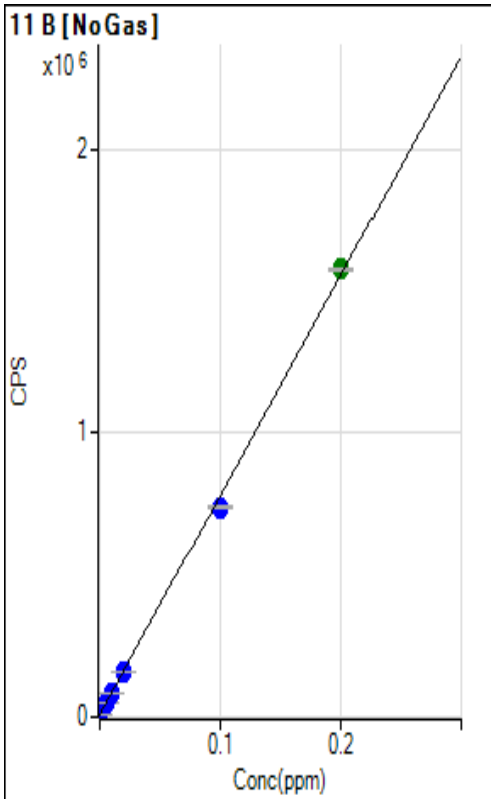
Trace metals lost from non-acidified water samples have been analysed and a few methods to recover the trace metals have been applied; proximate and ultimate analysis of trace metals lost, which use DI water and tap water to spike trace metals, has been carried out and now there is a need to carry out further characterization for raw water and wastewater with trace metals spike. Trace metals loss has been studied at pH 7. More focus will need to be given in the recovery methods with different acids, varying acid concentrations, and pH adjustments, with Au solution or other methods such as hot water.

The rate and amount of trace metals loss in each experiment was not identical indicating that the active sites for adsorption varied from bottle to bottle. It is to be expected that HDPE bottles from different batches will behave differently and the size of the bottles will play a role in the loss of trace metals. More focus can be given to different HDPE bottles.

1% (v/v) nitric acid plus 1% (v/v) hydrochloric acid for a 24-h period was found to be

suitable for metal recovery, which enabled efficient re-extraction of 70-110% of trace metals from the water sample. However, as with tap water sampling, mercury (Hg) did not yield high recovery results with this method (around 66%) although, with the addition of 1 mg/L Au solution, recovery of Hg was increased to about 78%. Varying concentration of Au solution should be applied to check its impact on the recovery of trace metals especially Hg from unpreserved water samples.

Appendix A-1



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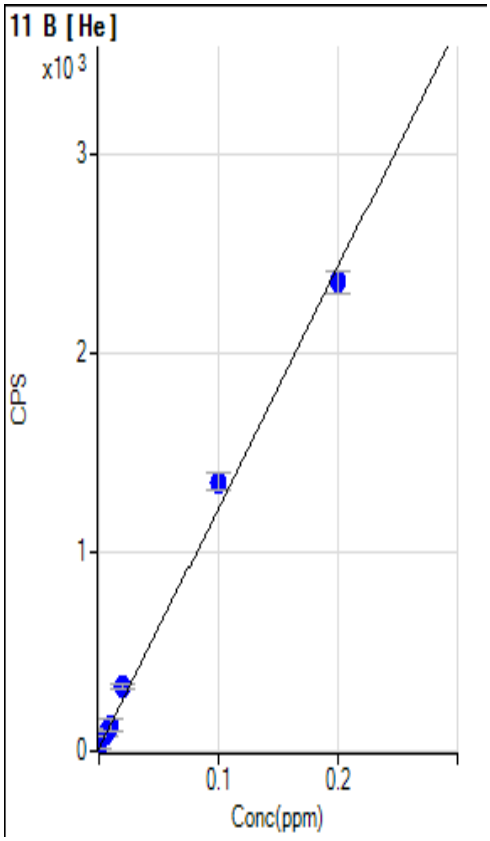
1		0.00000	0.00000	8559.29		P	13.7
2		0.00500	0.00491	46483.80		P	0.7
3		0.01000	0.00939	81061.43		P	0.7
4		0.02000	0.01929	157571.70		P	0.6
5		0.10000	0.09427	736672.62		P	1.2
6		0.20000	0.20297	1576134.67		A	0.4

$y = 7723331.0068 \times x + 8559.2933$

R = 0.9994

DL = 0.0004567

BEC = 0.001108



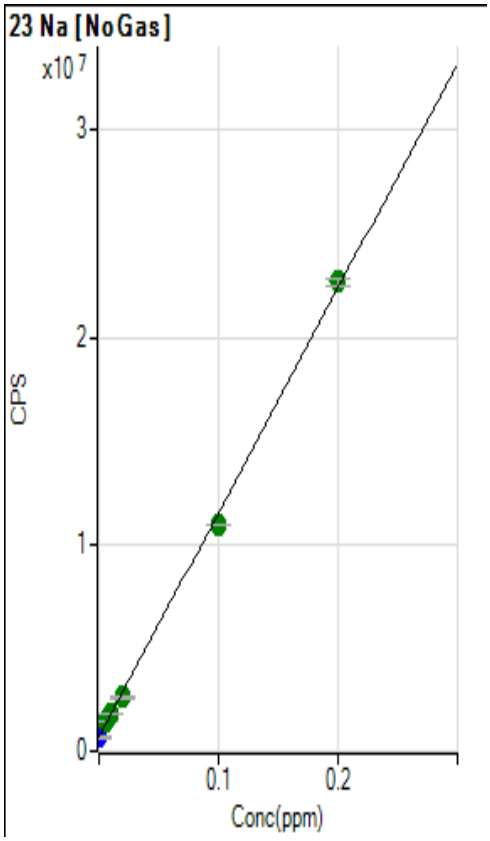
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	13.33		P	43.3
2		0.00500	0.00661	93.33		P	43.3
3		0.01000	0.00964	130.00		P	46.8
4		0.02000	0.02562	323.35		P	7.8
5		0.10000	0.11100	1356.77		P	7.3
6		0.20000	0.19392	2360.25		P	4.6

$y = 12102.7801 \times x + 13.3333$

R = 0.9975

DL = 0.001431

BEC = 0.001102



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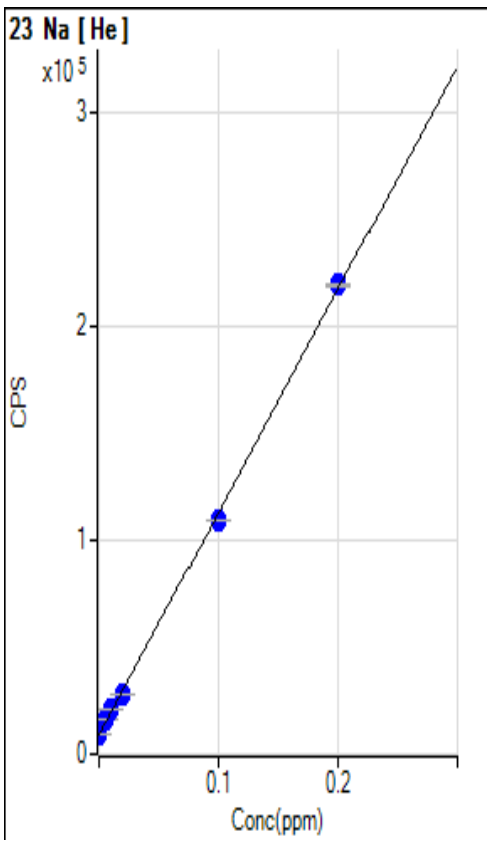
3		0.01000	0.01055	1831842.94		A	0.4
4		0.02000	0.01751	2585781.99		A	0.6
5		0.10000	0.09471	10955624.84		A	0.7
6		0.20000	0.20283	22675998.00		A	1.4

$y = 108408064.3394 \times x + 688027.5667$

R = 0.9993

DL = 0.002323

BEC = 0.006347



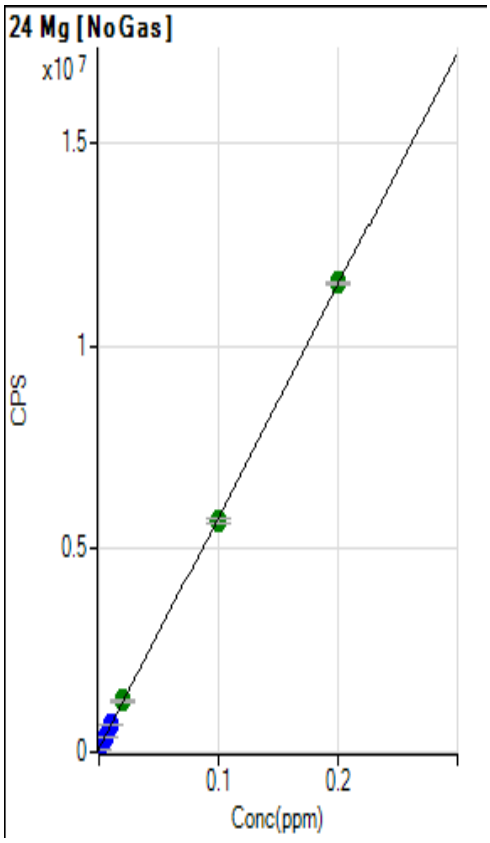
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	8946.17		P	4.1
2		0.00500	0.00677	16005.53		P	2.9
3		0.01000	0.01118	20600.96		P	1.4
4		0.02000	0.01828	27996.08		P	2.4
5		0.10000	0.09617	109191.86		P	0.5
6		0.20000	0.20198	219478.30		P	0.8

$y = 1042332.2329 \times x + 8946.1733$

R = 0.9996

DL = 0.001043

BEC = 0.008583



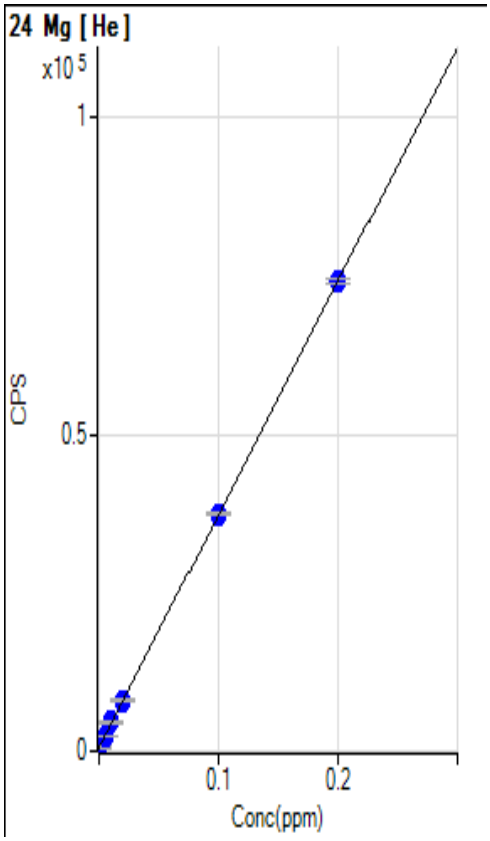
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	82766.11		P	0.7
2		0.00500	0.00524	382070.83		P	1.0
3		0.01000	0.01001	654783.38		P	0.1
4		0.02000	0.02058	1258278.60		A	1.7
5		0.10000	0.09798	5679495.54		A	1.8
6		0.20000	0.20095	11561298.16		A	0.8

$y = 57122341.4095 \times x + 82766.1100$

R = 0.9999

DL = 2.884E-05

BEC = 0.001449



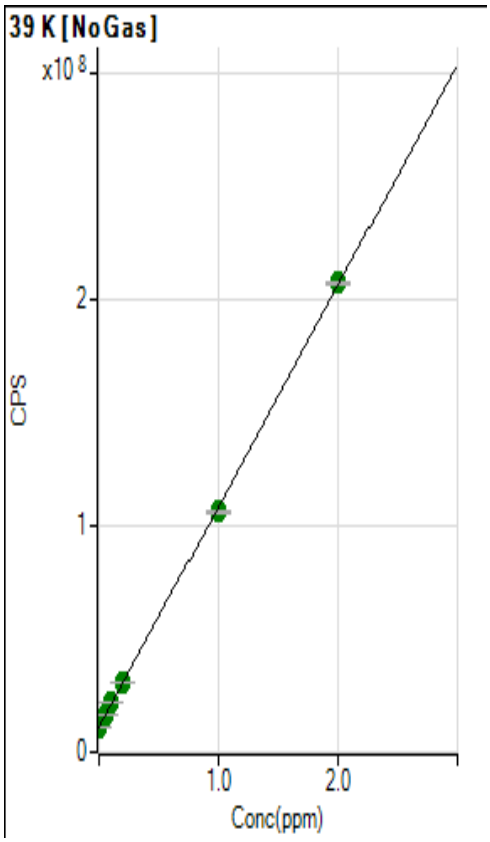
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	556.70		P	15.1
2		0.00500	0.00492	2363.59		P	3.9
3		0.01000	0.01086	4547.50		P	2.4
4		0.02000	0.02015	7962.36		P	4.6
5		0.10000	0.10029	37422.86		P	1.3
6		0.20000	0.19980	74001.15		P	1.1

$y = 367591.5250 \times x + 556.6967$

R = 1.0000

DL = 0.0006845

BEC = 0.001514



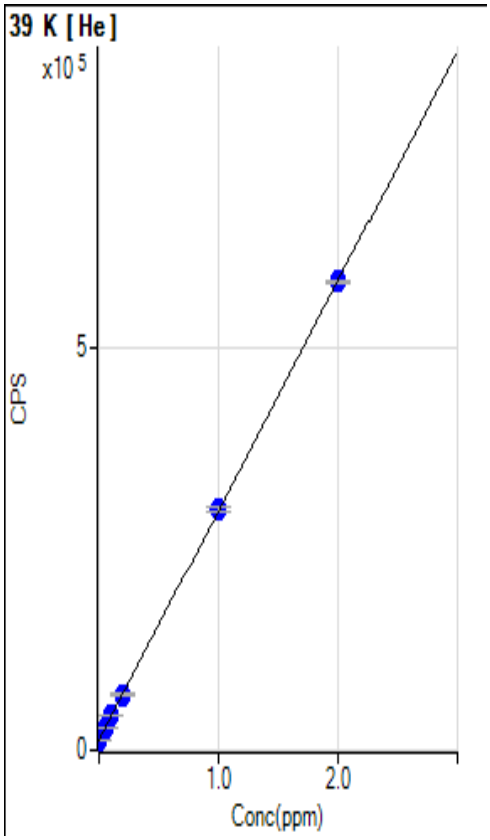
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	11007721.51		A	0.5
2		0.05000	0.05829	16695496.83		A	0.2
3		0.10000	0.10991	21732143.85		A	0.2
4		0.20000	0.20311	30826446.21		A	0.3
5		1.00000	0.97444	106091218.42		A	0.7
6		2.00000	2.01177	207311943.58		A	0.7

$y = 97577935.0817 \times x + 11007721.5067$

R = 0.9998

DL = 0.001678

BEC = 0.1128



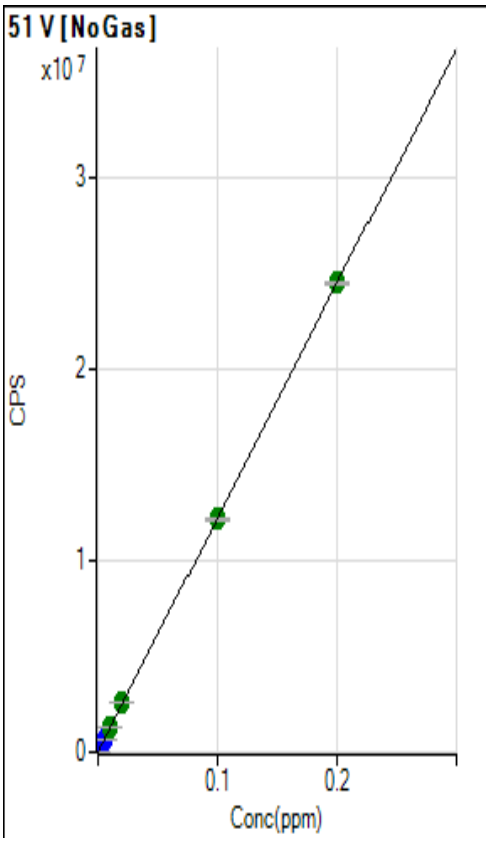
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	12689.00		P	1.4
2		0.05000	0.05344	27919.44		P	0.8
3		0.10000	0.10645	43024.87		P	1.0
4		0.20000	0.19835	69217.51		P	1.5
5		1.00000	1.00498	299098.30		P	1.6
6		2.00000	1.99727	581888.99		P	0.3

$y = 284989.6274 \times x + 12688.9967$

R = 1.0000

DL = 0.001814

BEC = 0.04452



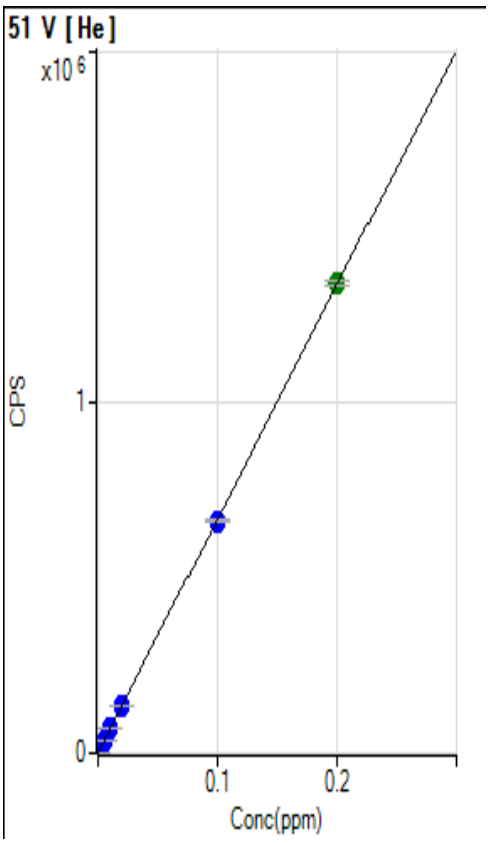
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	16176.38		P	22.6
2		0.00500	0.00530	663459.80		P	0.7
3		0.01000	0.01053	1301994.25		A	1.3
4		0.02000	0.02086	2563951.86		A	0.8
5		0.10000	0.09928	12138669.47		A	0.8
6		0.20000	0.20024	24467398.52		A	0.4

$y = 122108735.1011 \times x + 16176.3833$

R = 1.0000

DL = 9E-05

BEC = 0.0001325



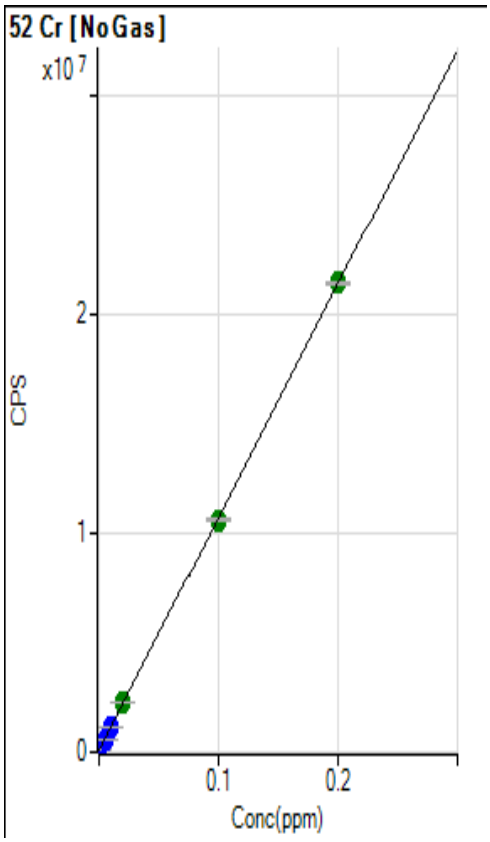
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	233.34		P	23.6
2		0.00500	0.00506	34025.53		P	3.9
3		0.01000	0.01022	68505.51		P	1.0
4		0.02000	0.02039	136489.49		P	2.7
5		0.10000	0.09915	662695.59		P	0.9
6		0.20000	0.20037	1338954.20		A	1.0

$y = 6681191.5177 \times x + 233.3433$

R = 1.0000

DL = 2.473E-05

BEC = 3.493E-05



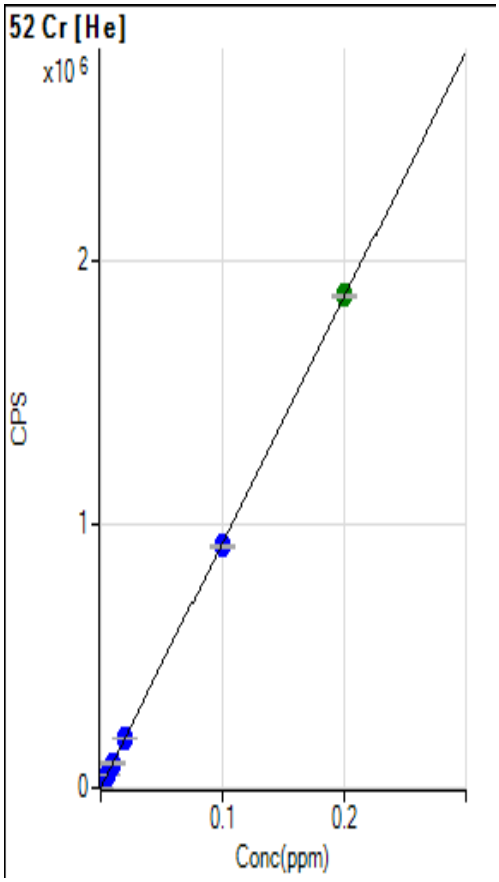
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	60752.93		P	1.1
2		0.00500	0.00523	618026.81		P	0.3
3		0.01000	0.01015	1142237.27		P	0.8
4		0.02000	0.02067	2264088.25		A	1.7
5		0.10000	0.09891	10604179.01		A	1.3
6		0.20000	0.20046	21429225.51		A	0.5

$y = 106594854.8718 \times x + 60752.9333$

R = 1.0000

DL = 1.963E-05

BEC = 0.0005699



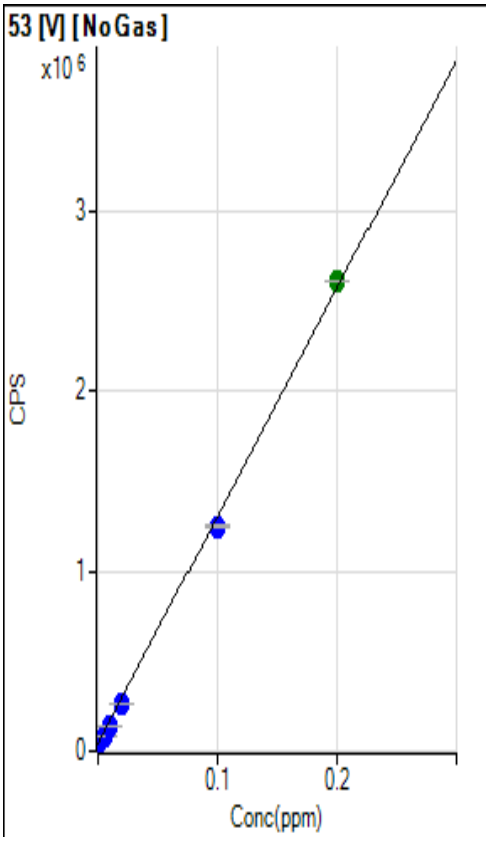
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	1073.41		P	14.1
2		0.00500	0.00509	48274.47		P	0.6
3		0.01000	0.00998	93723.37		P	1.5
4		0.02000	0.02003	186996.20		P	1.1
5		0.10000	0.09848	915052.30		P	0.6
6		0.20000	0.20076	1864248.67		A	0.3

$= 9280829.3554 \times x + 1073.4067$

R = 1.0000

DL = 4.896E-05

BEC = 0.0001157



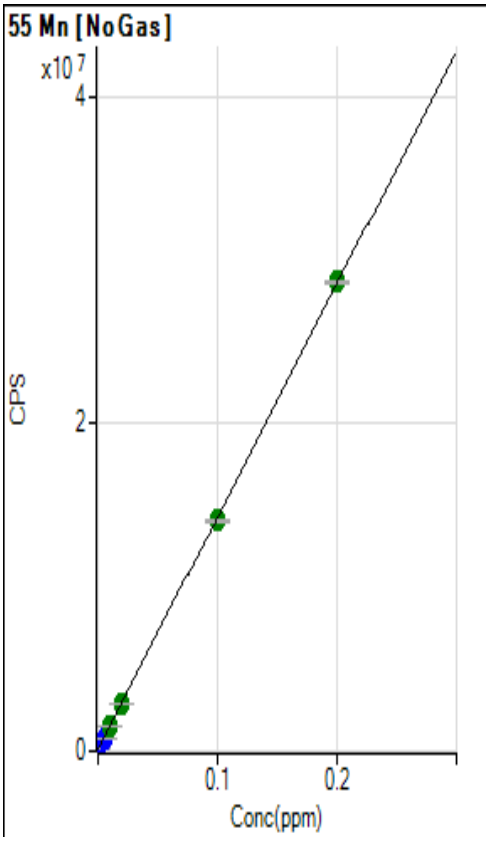
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	43152.54		P	3.3
2		0.00500	0.00307	82050.14		P	1.5
3		0.01000	0.00775	141249.66		P	0.7
4		0.02000	0.01771	267226.89		P	0.9
5		0.10000	0.09509	1246540.53		P	1.3
6		0.20000	0.20284	2610156.31		A	0.1

$y = 12655051.9502 \times x + 43152.5400$

R = 0.9996

DL = 0.0003396

BEC = 0.00341



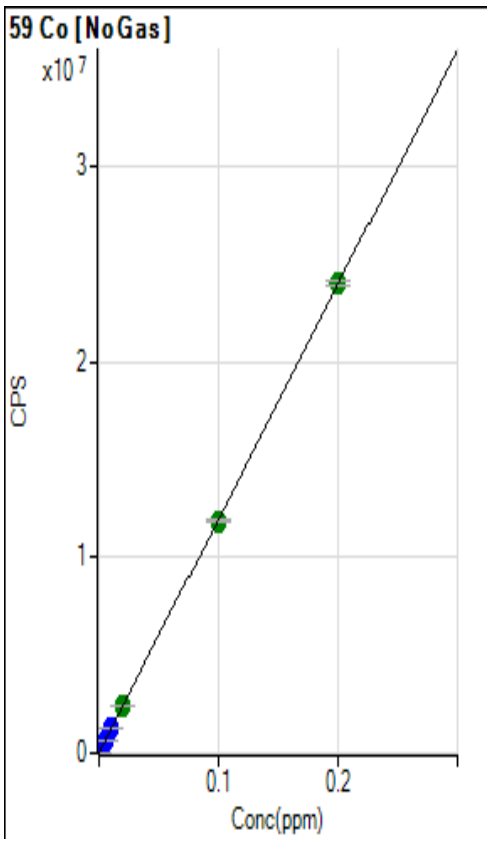
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	108945.68		P	0.8
2		0.00500	0.00461	763714.42		P	0.4
3		0.01000	0.00980	1501655.76		A	0.8
4		0.02000	0.01997	2947449.85		A	0.3
5		0.10000	0.09817	14065219.79		A	0.6
6		0.20000	0.20094	28675147.91		A	0.6

$y = 142164055.0836 \times x + 108945.6833$

R = 0.9999

DL = 1.948E-05

BEC = 0.0007663



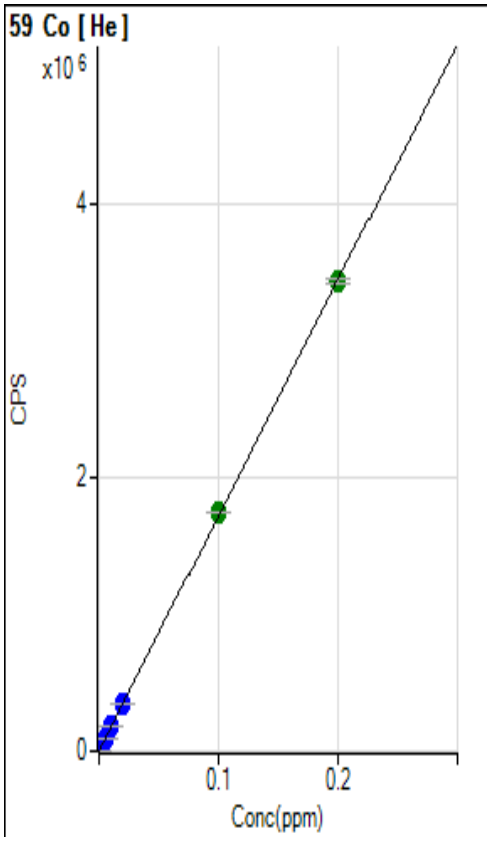
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	866.72		P	13.9
2		0.00500	0.00518	621038.97		P	0.6
3		0.01000	0.01013	1212175.89		P	0.6
4		0.02000	0.02057	2461508.46		A	0.5
5		0.10000	0.09926	11873481.49		A	1.6
6		0.20000	0.20030	23960532.98		A	1.0

$y = 119616457.4953 \times x + 866.7233$

R = 1.0000

DL = 3.013E-06

BEC = 7.246E-06



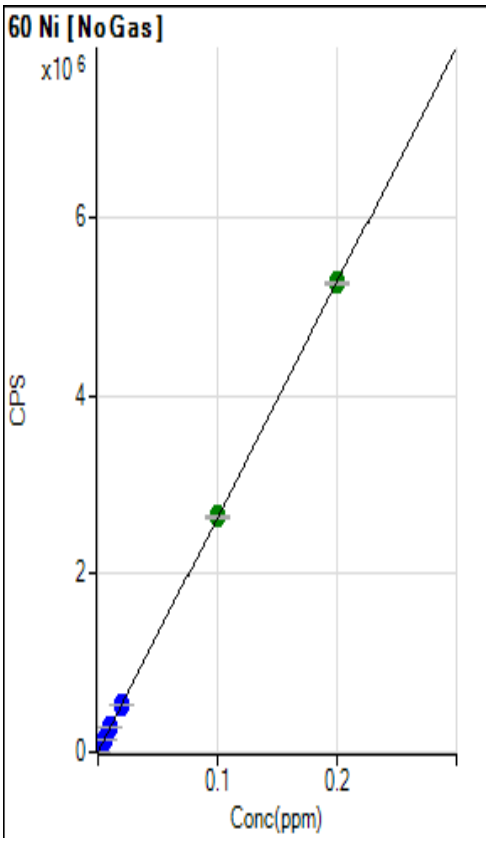
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	86.67		P	35.3
2		0.00500	0.00518	89264.68		P	0.2
3		0.01000	0.01016	174897.11		P	1.0
4		0.02000	0.02027	348737.30		P	1.7
5		0.10000	0.10149	1745905.44		A	0.6
6		0.20000	0.19921	3426789.53		A	1.0

$y = 17201176.7947 \times x + 86.6667$

R = 1.0000

DL = 5.328E-06

BEC = 5.038E-06



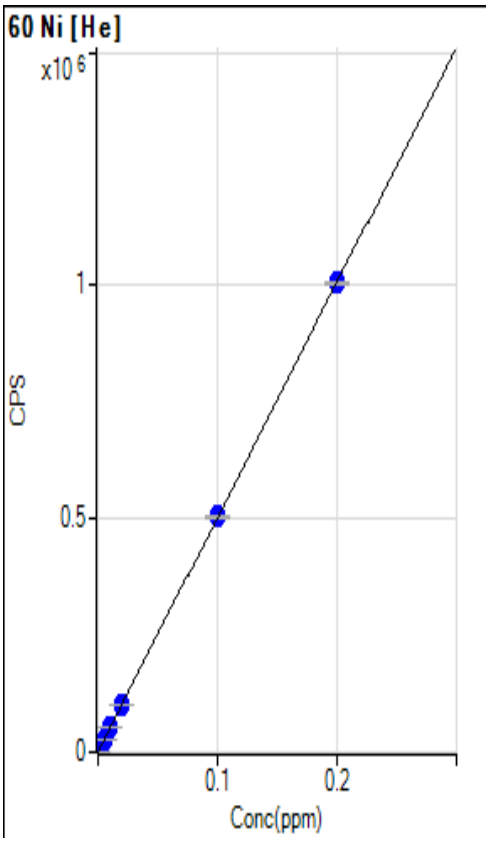
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	1316.76		P	5.1
2		0.00500	0.00526	140027.89		P	1.5
3		0.01000	0.01030	273009.73		P	1.6
4		0.02000	0.02036	538354.10		P	0.6
5		0.10000	0.10026	2645363.92		A	1.0
6		0.20000	0.19981	5270555.55		A	0.5

$y = 26371176.7458 \times x + 1316.7633$

R = 1.0000

DL = 7.576E-06

BEC = 4.993E-05



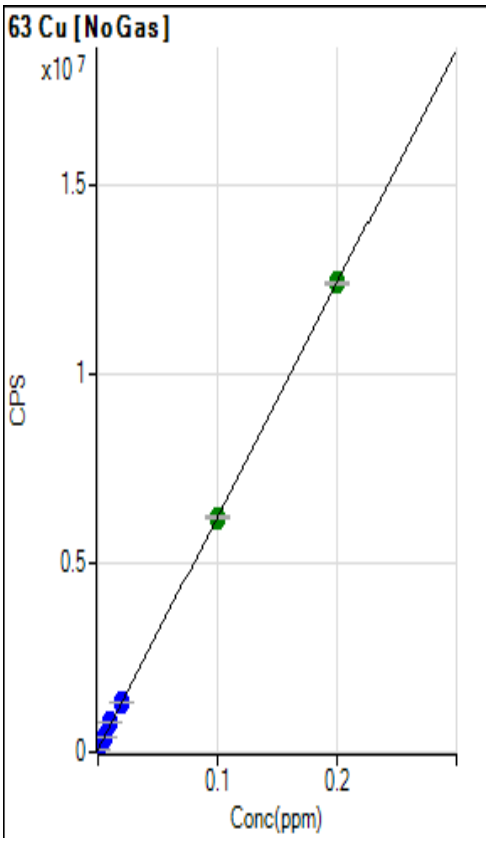
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	213.34		P	27.5
2		0.00500	0.00525	26667.70		P	2.2
3		0.01000	0.01006	50853.25		P	0.5
4		0.02000	0.02038	102824.21		P	1.9
5		0.10000	0.10025	504901.63		P	0.6
6		0.20000	0.19983	1006174.60		P	0.6

$y = 5034180.4562 \times x + 213.3433$

R = 1.0000

DL = 3.492E-05

BEC = 4.238E-05



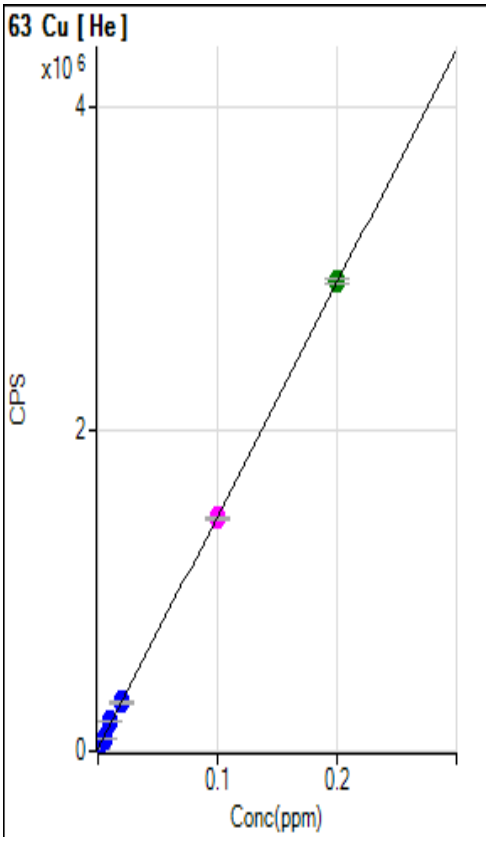
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	60713.87		P	1.6
2		0.00500	0.00492	364566.24		P	1.2
3		0.01000	0.01154	773429.75		P	0.9
4		0.02000	0.02013	1304502.43		P	0.9
5		0.10000	0.09950	6207391.99		A	1.3
6		0.20000	0.20016	12425693.98		A	0.8

$y = 61775082.1762 \times x + 60713.8667$

R = 1.0000

DL = 4.646E-05

BEC = 0.0009828



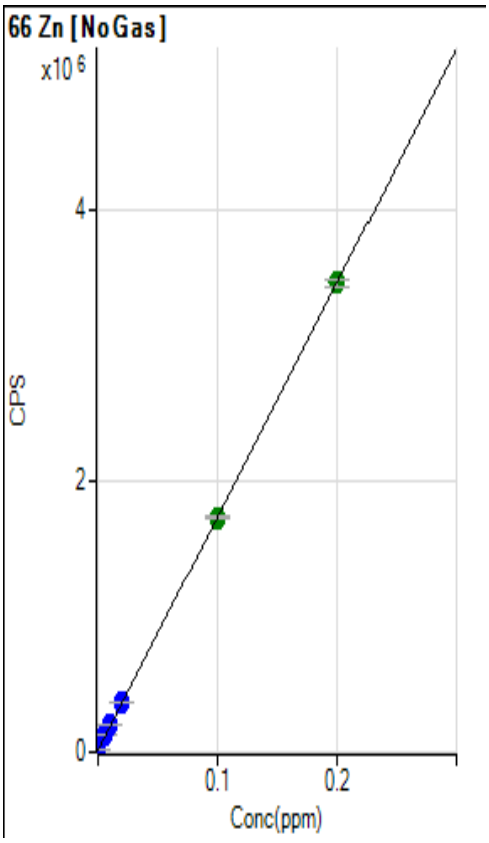
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	13633.32		P	3.2
2		0.00500	0.00477	82841.95		P	0.7
3		0.01000	0.01157	181283.94		P	1.6
4		0.02000	0.01997	303045.85		P	2.0
5		0.10000	0.09911	1450170.03		M	1.4
6		0.20000	0.20037	2917895.37		A	0.9

$y = 14494149.0246 \times x + 13633.3233$

R = 0.9999

DL = 8.923E-05

BEC = 0.0009406



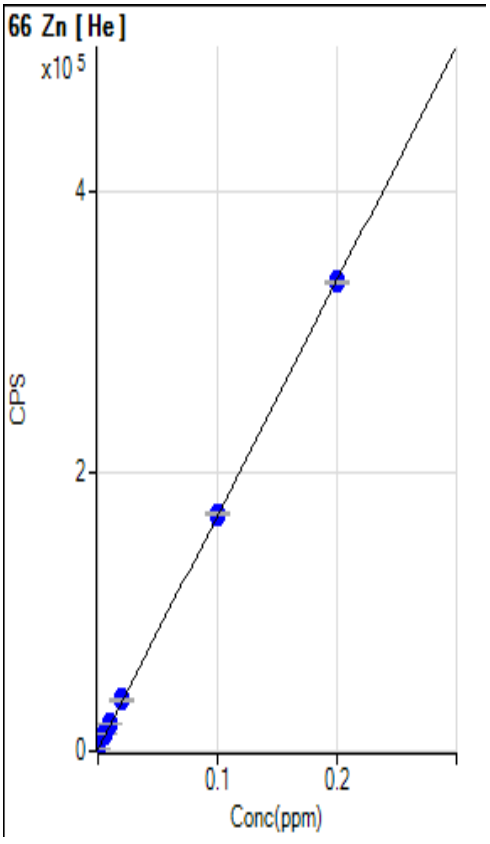
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	12702.40		P	2.4
2		0.00500	0.00625	120522.99		P	0.6
3		0.01000	0.01060	195474.00		P	0.9
4		0.02000	0.02056	367232.46		P	1.1
5		0.10000	0.09970	1731810.86		A	1.8
6		0.20000	0.20003	3461930.37		A	1.3

$y = 17243223.3643 \times x + 12702.3967$

R = 1.0000

DL = 5.385E-05

BEC = 0.0007367



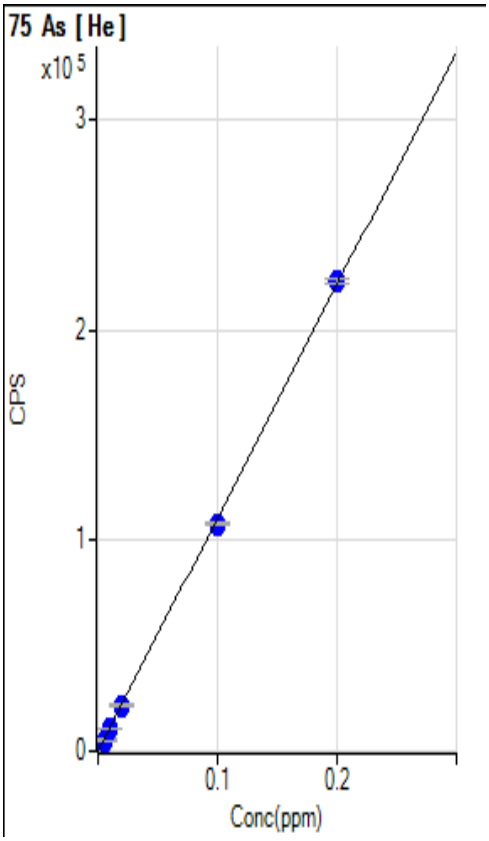
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	1110.08		P	10.4
2		0.00500	0.00636	11791.71		P	1.1
3		0.01000	0.01083	19296.28		P	1.6
4		0.02000	0.02128	36832.83		P	1.9
5		0.10000	0.10054	169877.82		P	0.8
6		0.20000	0.19952	336016.65		P	0.5

$y = 1678531.6939 \times x + 1110.0767$

R = 1.0000

DL = 0.0002061

BEC = 0.0006613



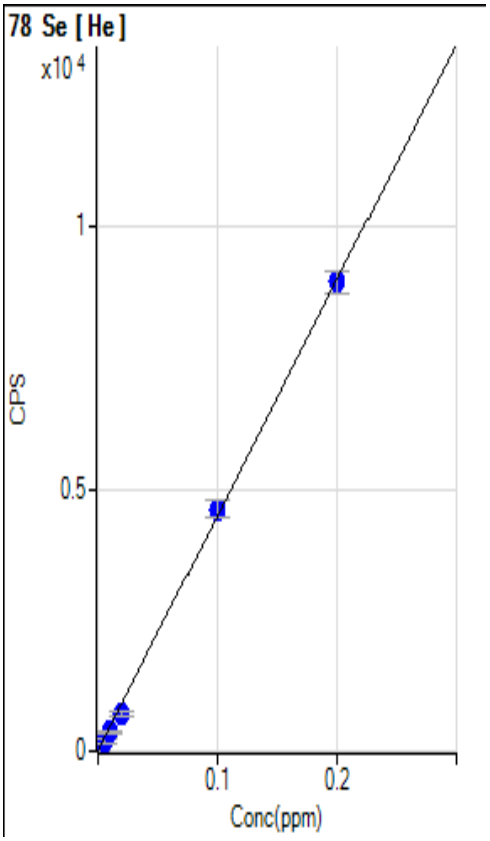
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	133.34		P	22.9
2		0.00500	0.00466	5287.77		P	4.2
3		0.01000	0.00912	10220.51		P	1.6
4		0.02000	0.01933	21509.49		P	3.4
5		0.10000	0.09755	107980.27		P	1.8
6		0.20000	0.20135	222740.48		P	0.9

$y = 1105596.9870 \times x + 133.3400$

R = 0.9999

DL = 8.291E-05

BEC = 0.0001206



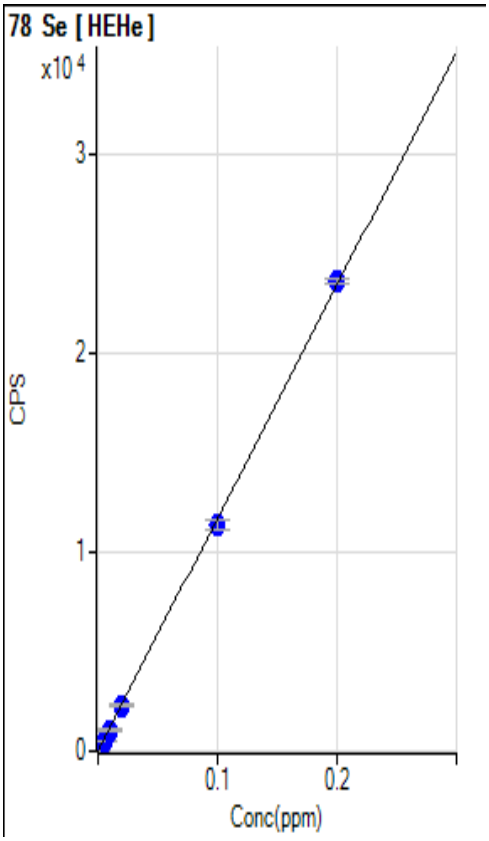
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	6.67		P	86.6
2		0.00500	0.00408	190.01		P	43.1
3		0.01000	0.00795	363.35		P	12.4
4		0.02000	0.01597	723.37		P	13.6
5		0.10000	0.10273	4617.53		P	7.6
6		0.20000	0.19917	8946.28		P	4.6

$y = 44885.2324 \times x + 6.6667$

R = 0.9997

DL = 0.0003859

BEC = 0.0001485



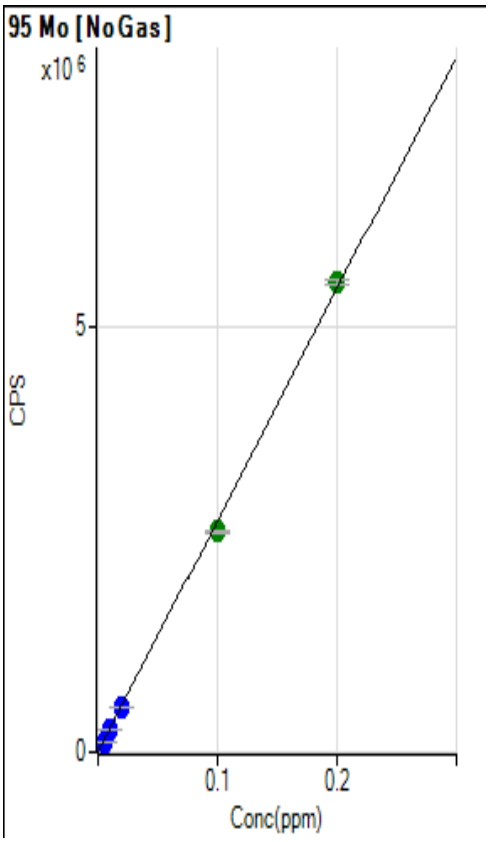
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	3.33		P	173.2
2		0.00500	0.00450	530.03		P	10.0
3		0.01000	0.00882	1036.73		P	7.0
4		0.02000	0.01961	2300.26		P	3.8
5		0.10000	0.09720	11388.03		P	3.6
6		0.20000	0.20151	23606.17		P	1.0

$y = 117129.0239 \times x + 3.3333$

R = 0.9999

DL = 0.0001479

BEC = 2.846E-05



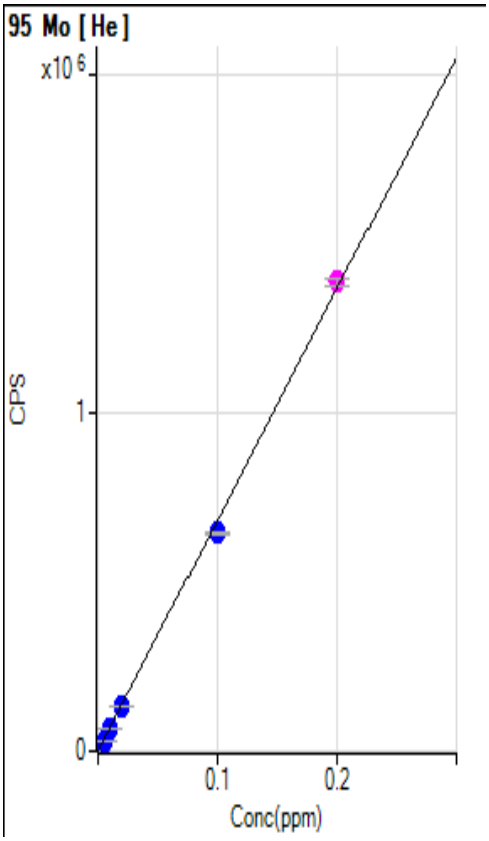
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	1920.18		P	8.7
2		0.00500	0.00457	126459.47		P	0.9
3		0.01000	0.00921	252770.56		P	1.2
4		0.02000	0.01905	520723.65		P	1.2
5		0.10000	0.09512	2591890.07		A	1.4
6		0.20000	0.20258	5517714.50		A	0.9

$y = 27227374.9857 \times x + 1920.1833$

R = 0.9996

DL = 1.841E-05

BEC = 7.052E-05



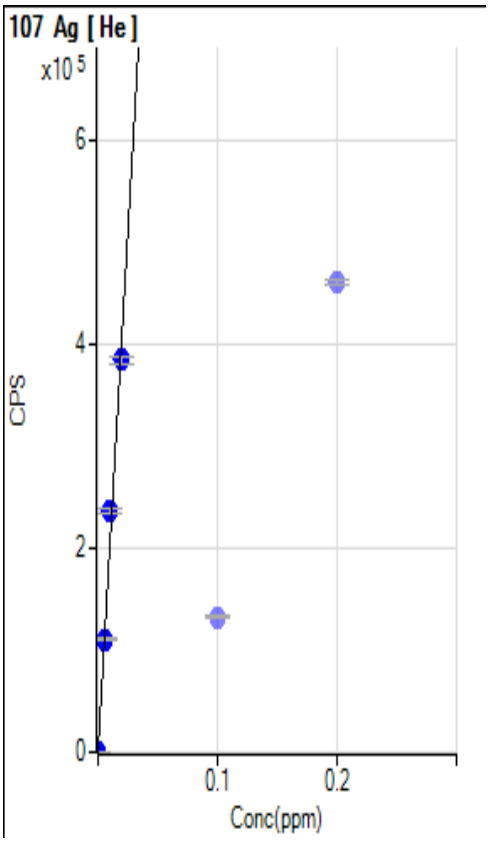
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	450.02		P	27.8
2		0.00500	0.00443	30696.08		P	3.1
3		0.01000	0.00927	63799.37		P	0.7
4		0.02000	0.01904	130605.60		P	1.9
5		0.10000	0.09419	644156.78		P	1.0
6		0.20000	0.20305	1388219.36		M	1.5

$y = 6834485.4491 \times x + 450.0233$

R = 0.9994

DL = 5.5E-05

BEC = 6.585E-05



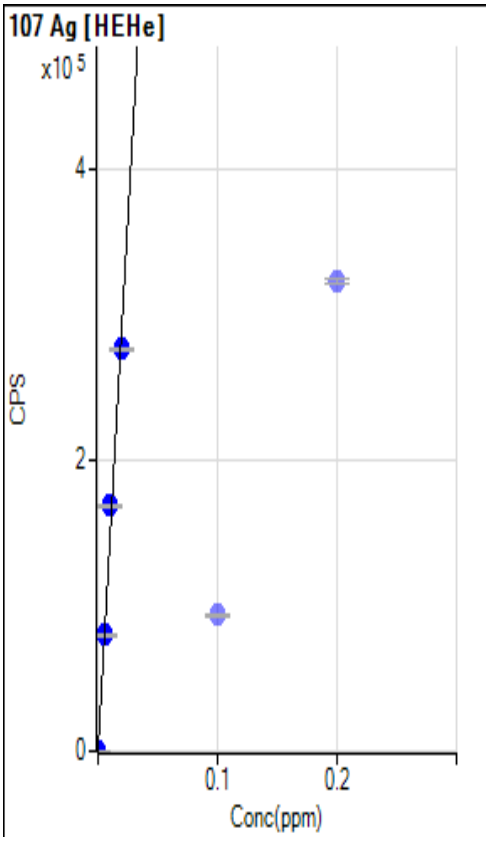
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	210.01		P	9.5
2		0.00500	0.00547	110917.71		P	0.8
3		0.01000	0.01172	237599.21		P	1.7
4		0.02000	0.01902	385345.33		P	1.6
5	✓	0.10000		132863.16		P	0.7
6	✓	0.20000		461092.40		P	1.0

$y = 20247879.8413 \times x + 210.0100$

R = 0.9919

DL = 2.963E-06

BEC = 1.037E-05



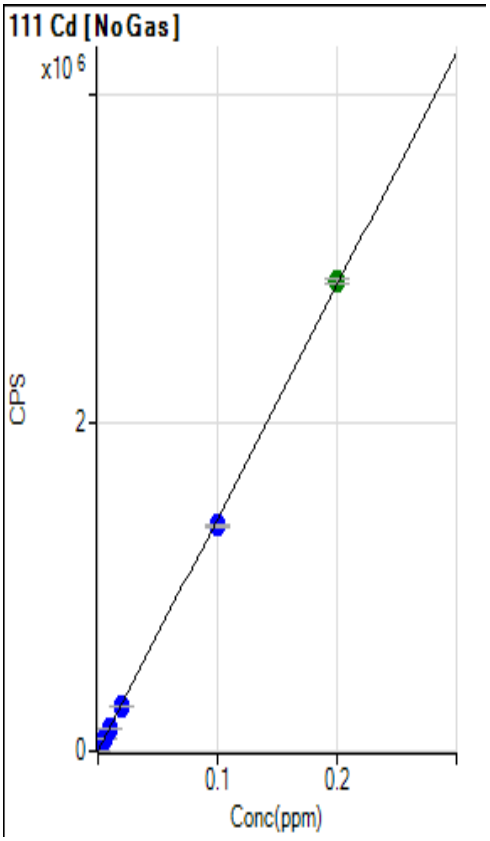
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1	☐	0.00000	0.00000	126.67		P	16.4
2	☐	0.00500	0.00548	79433.68		P	1.5
3	☐	0.01000	0.01162	168149.59		P	1.7
4	☐	0.02000	0.01907	275928.48		P	0.5
5	☑	0.10000		93067.66		P	1.8
6	☑	0.20000		321992.33		P	0.9

$y = 14462476.8254 \times x + 126.6700$

R = 0.9928

DL = 4.319E-06

BEC = 8.759E-06



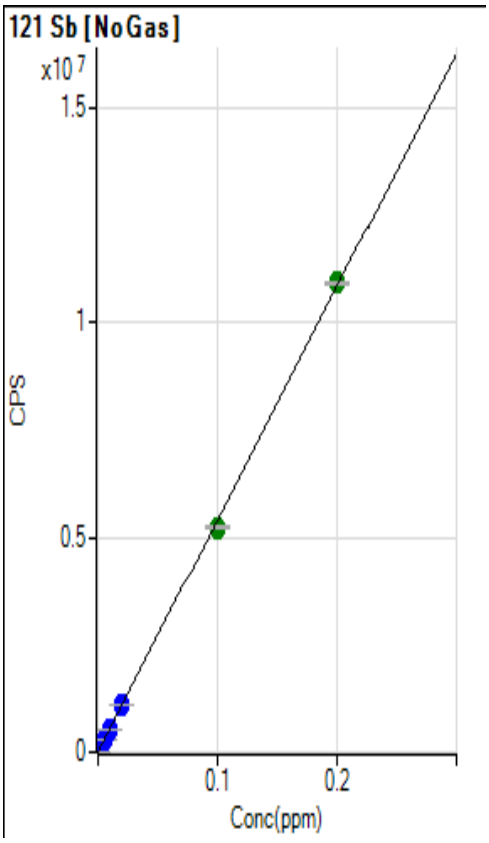
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1	☐	0.00000	0.00000	30.00		P	33.3
2	☐	0.00500	0.00506	71668.40		P	1.8
3	☐	0.01000	0.00974	138033.18		P	2.2
4	☐	0.02000	0.01951	276263.87		P	0.6
5	☐	0.10000	0.09689	1372221.02		P	1.1
6	☐	0.20000	0.20161	2855237.56		A	1.0

$y = 14161771.7018 \times x + 30.0000$

R = 0.9998

DL = 2.118E-06

BEC = 2.118E-06



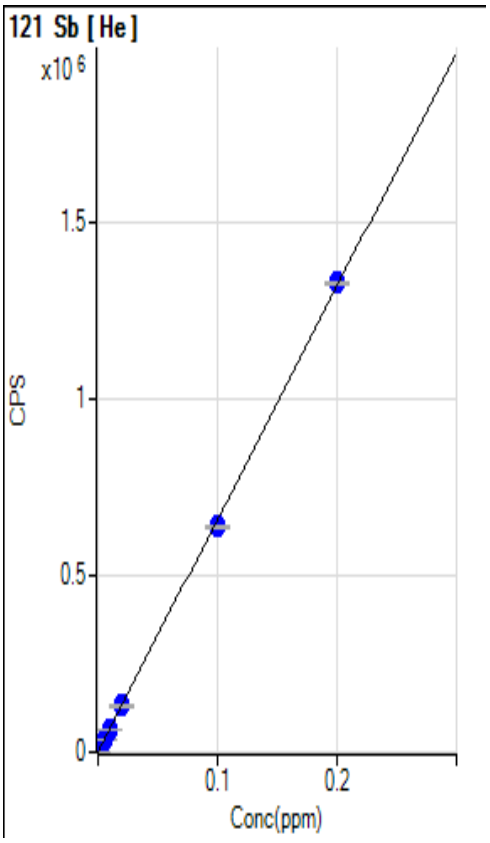
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	923.40		P	5.5
2		0.00500	0.00510	277090.29		P	0.5
3		0.01000	0.01000	542956.89		P	1.1
4		0.02000	0.02013	1091807.36		P	0.4
5		0.10000	0.09662	5235866.49		A	0.9
6		0.20000	0.20167	10927635.26		A	0.4

$y = 54180218.3008 \times x + 923.3967$

R = 0.9998

DL = 2.787E-06

BEC = 1.704E-05



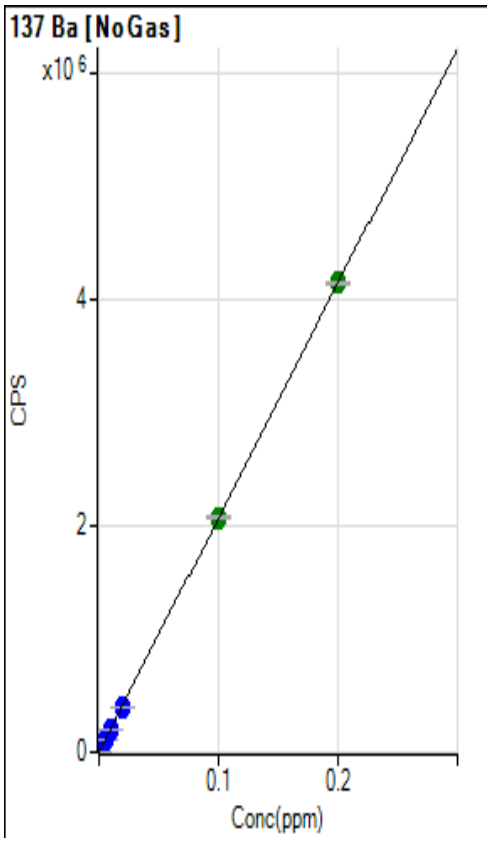
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	86.67		P	13.3
2		0.00500	0.00495	32691.28		P	2.4
3		0.01000	0.00988	65087.76		P	1.1
4		0.02000	0.01980	130373.34		P	1.1
5		0.10000	0.09698	638271.57		P	0.7
6		0.20000	0.20154	1326247.48		P	0.2

$y = 6580295.3010 \times x + 86.6667$

R = 0.9998

DL = 5.264E-06

BEC = 1.317E-05



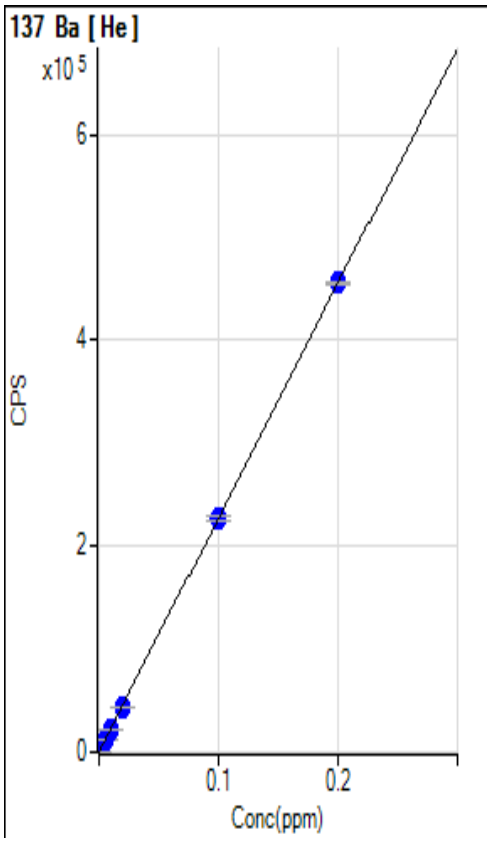
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	1553.47		P	7.2
2		0.00500	0.00494	103961.66		P	1.0
3		0.01000	0.00958	200139.22		P	0.9
4		0.02000	0.01913	397929.30		P	0.9
5		0.10000	0.09977	2069188.51		A	1.0
6		0.20000	0.20022	4150913.59		A	0.2

$y = 20723620.8088 \times x + 1553.4733$

R = 1.0000

DL = 1.615E-05

BEC = 7.496E-05



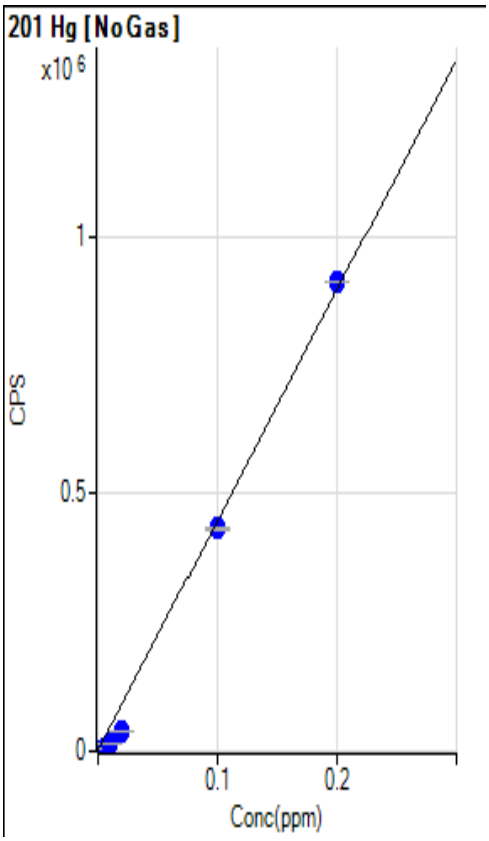
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	176.68		P	8.6
2		0.00500	0.00496	11464.93		P	1.7
3		0.01000	0.00962	22074.42		P	1.8
4		0.02000	0.01922	43908.55		P	0.8
5		0.10000	0.09972	227061.99		P	1.1
6		0.20000	0.20024	455774.22		P	0.3

$y = 2275271.5840 \times x + 176.6767$

R = 1.0000

DL = 2.014E-05

BEC = 7.765E-05



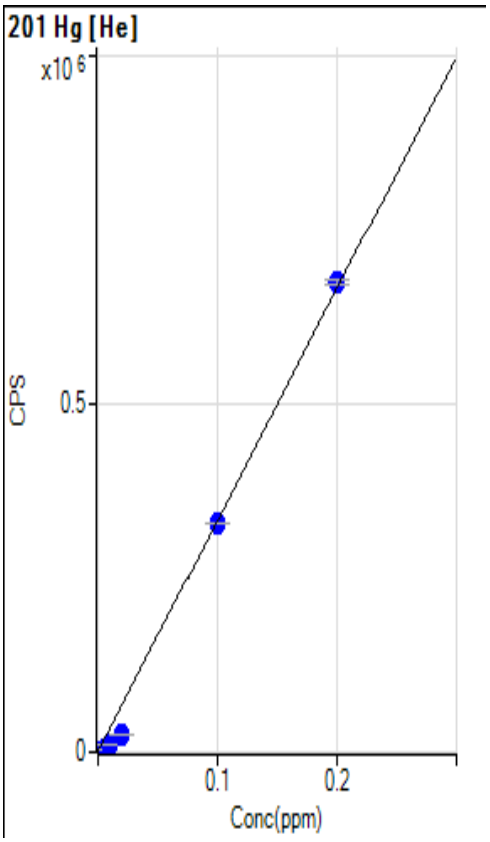
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	1353.45		P	15.0
2		0.00500	0.00050	3580.59		P	8.2
3		0.01000	0.00304	14958.70		P	4.6
4		0.02000	0.00796	36954.30		P	1.2
5		0.10000	0.09661	433495.08		P	1.6
6		0.20000	0.20336	910975.06		P	0.1

$y = 4472987.4574 \times x + 1353.4500$

R = 0.9987

DL = 0.0001359

BEC = 0.0003026



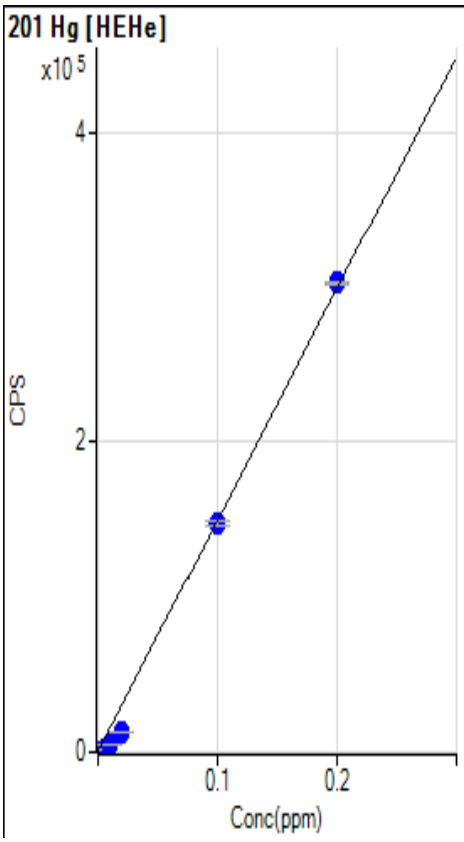
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	746.72		P	17.1
2		0.00500	0.00041	2103.57		P	8.6
3		0.01000	0.00312	11121.58		P	6.1
4		0.02000	0.00758	25928.86		P	4.3
5		0.10000	0.09837	327630.11		P	0.2
6		0.20000	0.20252	673730.95		P	1.0

$y = 3323094.7455 \times x + 746.7167$

R = 0.9987

DL = 0.000115

BEC = 0.0002247



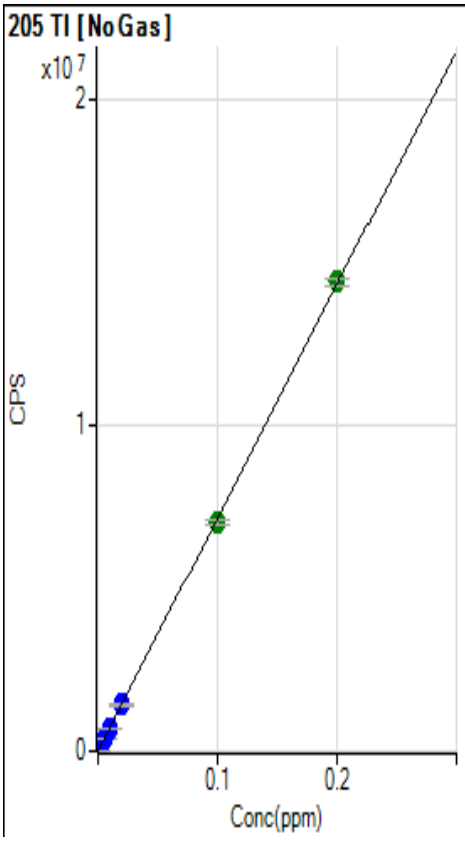
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	406.69		P	1.4
2		0.00500	0.00041	1016.74		P	16.6
3		0.01000	0.00318	5147.82		P	1.1
4		0.02000	0.00828	12766.41		P	1.6
5		0.10000	0.09827	147140.32		P	2.5
6		0.20000	0.20249	302752.72		P	0.4

$y = 1493126.6785 \times x + 406.6867$

R = 0.9988

DL = 1.16E-05

BEC = 0.0002724



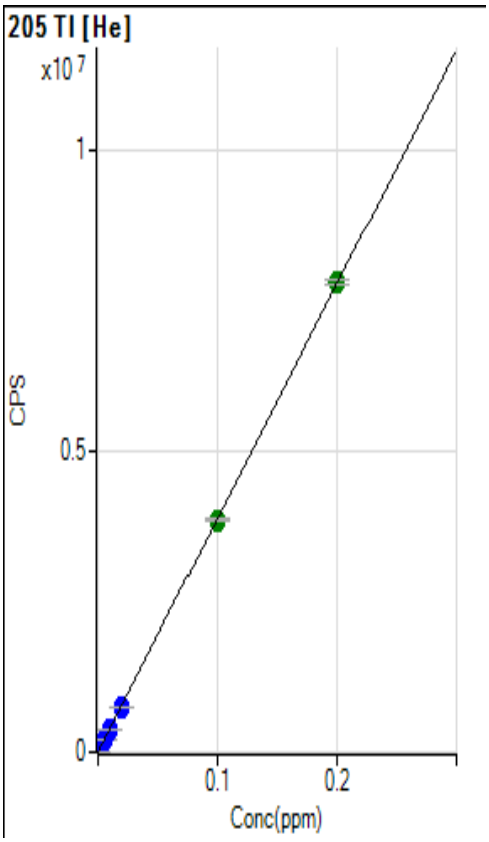
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	1506.80		P	6.6
2		0.00500	0.00497	358039.84		P	1.2
3		0.01000	0.00976	701357.44		P	0.9
4		0.02000	0.01972	1415412.58		P	1.1
5		0.10000	0.09793	7021358.02		A	2.3
6		0.20000	0.20107	14414901.45		A	1.4

$y = 71681807.8159 \times x + 1506.8000$

R = 0.9999

DL = 4.193E-06

BEC = 2.102E-05



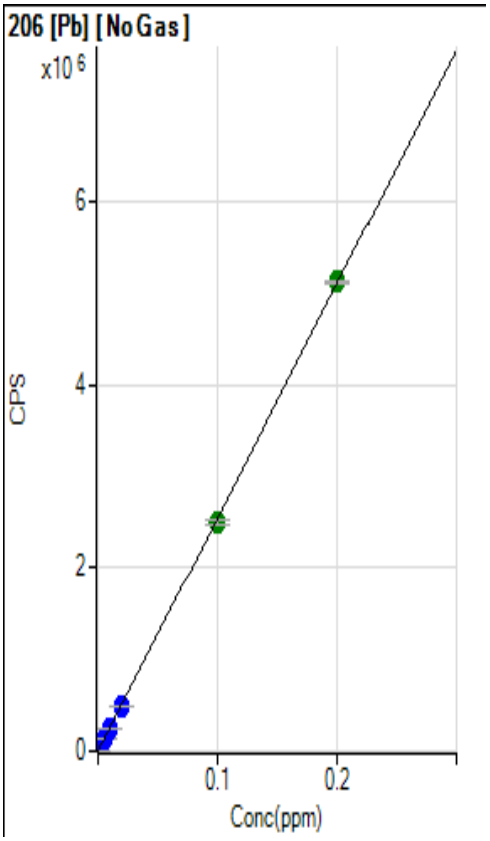
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	753.38		P	2.8
2		0.00500	0.00491	191755.83		P	1.3
3		0.01000	0.00954	371492.95		P	1.2
4		0.02000	0.01931	751378.01		P	1.4
5		0.10000	0.09905	3850535.78		A	0.9
6		0.20000	0.20057	7796465.72		A	1.0

$y = 38867800.2263 \times x + 753.3833$

R = 1.0000

DL = 1.607E-06

BEC = 1.938E-05



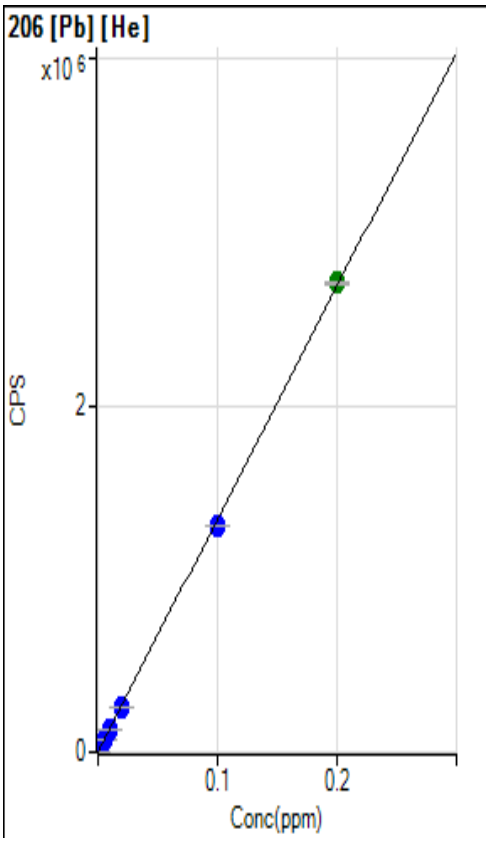
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	1750.18		P	2.6
2		0.00500	0.00492	127285.89		P	2.0
3		0.01000	0.00970	249274.22		P	1.8
4		0.02000	0.01937	495997.54		P	0.9
5		0.10000	0.09824	2507889.96		A	1.8
6		0.20000	0.20096	5128278.36		A	0.6

$y = 25510291.5633 \times x + 1750.1800$

R = 0.9999

DL = 5.39E-06

BEC = 6.861E-05



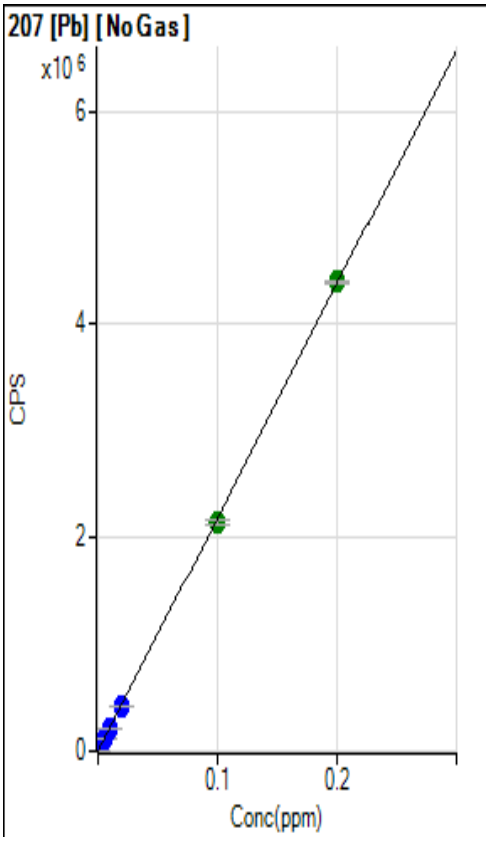
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	846.72		P	1.4
2		0.00500	0.00483	65743.05		P	2.1
3		0.01000	0.00936	126653.79		P	0.8
4		0.02000	0.01892	255066.08		P	1.2
5		0.10000	0.09735	1309051.07		P	0.3
6		0.20000	0.20147	2708291.42		A	0.5

$y = 13438422.8237 \times x + 846.7233$

R = 0.9999

DL = 2.578E-06

BEC = 6.301E-05



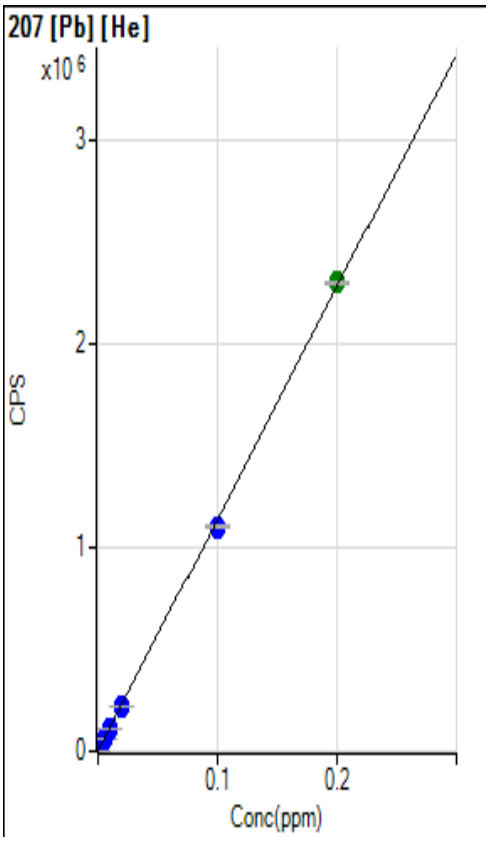
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	1453.47		P	3.2
2		0.00500	0.00492	109066.19		P	1.9
3		0.01000	0.00973	214427.48		P	1.9
4		0.02000	0.01931	424292.56		P	1.3
5		0.10000	0.09833	2154204.19		A	2.3
6		0.20000	0.20092	4399980.56		A	0.4

$y = 21892233.0787 \times x + 1453.4667$

R = 0.9999

DL = 6.33E-06

BEC = 6.639E-05



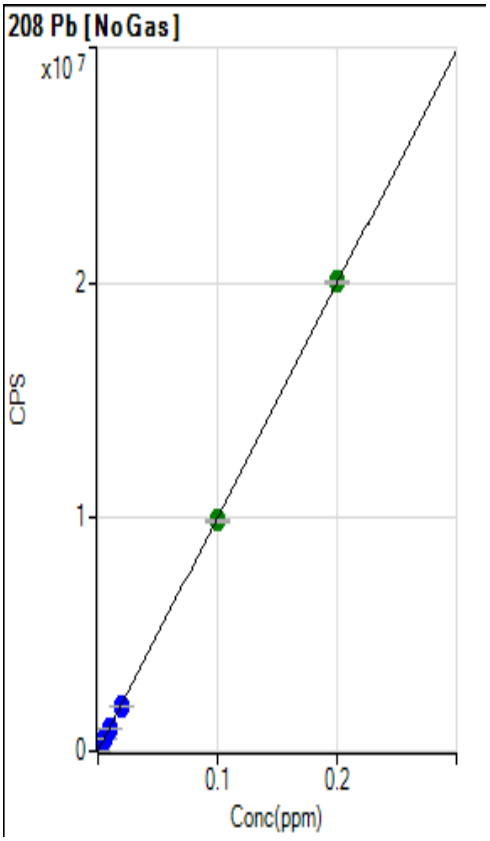
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	683.38		P	11.9
2		0.00500	0.00487	56110.02		P	1.3
3		0.01000	0.00948	108656.03		P	0.7
4		0.02000	0.01892	216066.18		P	1.2
5		0.10000	0.09666	1101115.09		P	1.2
6		0.20000	0.20181	2298239.24		A	0.9

$y = 11384836.3942 \times x + 683.3767$

R = 0.9998

DL = 2.146E-05

BEC = 6.003E-05



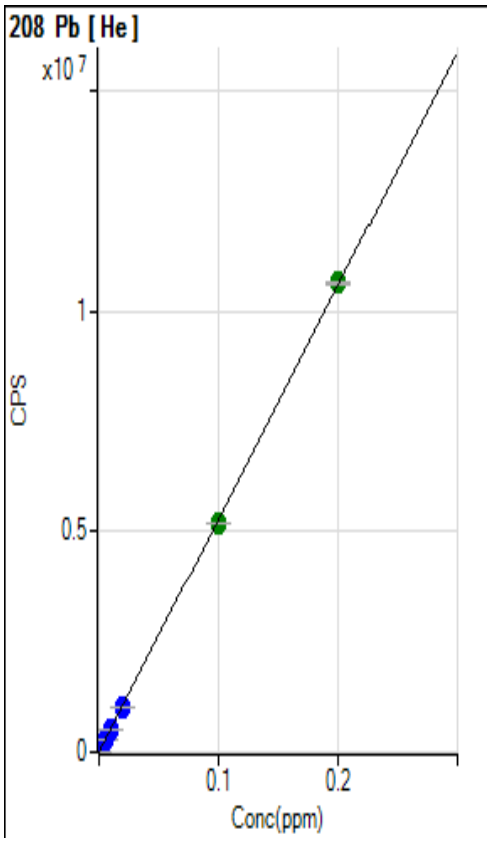
	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	6904.29		P	0.2
2		0.00500	0.00499	504130.20		P	0.8
3		0.01000	0.00983	986264.83		P	1.6
4		0.02000	0.01952	1952254.18		P	0.5
5		0.10000	0.09844	9816265.22		A	1.7
6		0.20000	0.20084	20020356.27		A	0.7

$y = 99649940.0287 \times x + 6904.2933$

R = 1.0000

DL = 4.596E-07

BEC = 6.929E-05



	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.00000	0.00000	3490.32		P	0.9
2		0.00500	0.00487	261335.05		P	1.0
3		0.01000	0.00949	505935.60		P	0.7
4		0.02000	0.01914	1016567.81		P	1.5
5		0.10000	0.09786	5183646.74		A	0.6
6		0.20000	0.20119	10653326.41		A	0.7

$y = 52935340.6432 \times x + 3490.3200$

R = 0.9999

DL = 1.7E-06

BEC = 6.594E-05

Figure 11. Calibration graphs for Ag, As, Ba, B, Cd, Cr, Co, Cu, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Tl, V and Zn.

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