Part I: Development of sample preparation
method for analysis of total iodine in air filters.

Part II: Application of Inductively coupled
plasma-mass spectrometry in analysis of
radionuclides-uranium and plutonium

Tiong, Diane Ling Ying

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**NANYANG
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UNIVERSITY**

**Part I: Development of sample preparation method for
analysis of total iodine in air filters**

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Mass spectrometry in analysis of radionuclides-
Uranium and plutonium**

Tiong Ling Ying Diane

SCHOOL OF PHYSICAL & MATHEMATICAL SCIENCES

A thesis submitted to the Nanyang Technological University in fulfilment of the
requirement for the degree of

Doctor of Philosophy in Chemistry

2017

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**Part I: Development of a sample preparation method
for the analysis of total iodine in air filters**

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mass spectrometry in analysis of the radionuclides:
uranium and plutonium**

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Table of contents

ACKNOWLEDGEMENTS	5
TABLE OF CONTENTS	8
ABSTRACT	11
CHAPTER 1	15
DEVELOPMENT OF A SAMPLE PREPARATION METHOD FOR THE ANALYSIS OF TOTAL IODINE IN AIR	
FILTERS	15
<i>1.1. Introduction.....</i>	<i>15</i>
1.1.1. Iodine.....	15
1.1.2. Sample preparation of Iodine analysis.....	17
<i>1.2. Experimental</i>	<i>19</i>
1.2.1 Microwave digestion procedures for filter media	19
1.2.2 Sampling of air filters.....	21
1.2.3 Measurements of iodine samples by quadrupole ICP-MS.....	22
<i>1.3. Results and discussion.....</i>	<i>24</i>
1.3.2 Spiking test on various filter media	27
1.3.2.1. Borosilicate filters (Quartz)	27
1.3.2.2. Cellulose filters.....	29
1.3.2.3. Polypropylene filters	33
1.3.3. Sampling and analysis of iodine in TSP samples collected in Singapore	35
<i>1.4. Conclusions.....</i>	<i>40</i>
REFERENCES.....	42
CHAPTER 2	48
AN INTRODUCTION TO ANALYSIS OF RADIONUCLIDES BY INDUCTIVELY COUPLED PLASMA-MASS	
SPECTROMETRY	48
<i>2.1 Uranium.....</i>	<i>48</i>

2.2 Plutonium.....	49
2.3 Analysis of uranium and plutonium.....	50
2.3.1 Radiometric measurement techniques	50
2.3.2 Mass spectrometric techniques.....	52
2.4 Scope of work.....	53
REFERENCES.....	54
CHAPTER 3.....	57
A RESIN-BASED MATHEMATICAL CORRECTION FOR THE ANALYSIS OF PLUTONIUM-238 USING	
INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY	57
3.1 Background of work.....	57
3.2. Chemical separation technique: Solid Phase Extraction (SPE).....	60
3.3 Experimental.....	63
3.4. Results and Discussion.....	65
3.4.1 Conceptual framework.....	65
3.4.2 Isotopic ratio measurements of Pu with quadrupole ICP-MS	68
3.5 Conclusion	71
REFERENCES.....	72
CHAPTER 4.....	74
ANALYSIS OF URANIUM IN DIFFERENT ENRICHMENT LEVELS USING INDUCTIVELY COUPLED PLASMA	
MASS SPECTROMETRY AND THE CALCULATIONS OF ASSOCIATED UNCERTAINTIES WITHOUT CLEAN	
ROOM FACILITIES.....	74
4.1 Background of work.....	74
4.1.1 Quadrupole ICP-MS.....	76
4.1.2 Sample preparation: Lithium borate fusion.....	78
4.2 Experimental.....	79
4.2.1 Inductively coupled plasma – quadrupole mass spectrometry (ICP-Q-MS)	79
4.2.2. Borate fusion procedure and chemical steps prior to analysis.....	80
4.3. Results and discussion	81

4.3.1 Mechanical processes –overnight standing	81
4.3.2 Filter paper	83
4.3.3 Lithium borate.....	92
4.3.4 Silica gel.....	93
<i>4.4 Analysis of enriched uranium.....</i>	<i>94</i>
4.4.1. Mass bias correction for ICP-MS analysis	94
4.4.2 General Uncertainty Measurement (GUM).....	97
4.4.3 LEU, HEU and WGU analysis with uncertainty measurements	98
<i>4.5 Conclusion.....</i>	<i>103</i>
REFERENCES.....	106
CHAPTER 5	107
CONCLUSION	107
SUPPLEMENTARY DOCUMENTS	110
SUPPLEMENTARY INFORMATION (SI 1).....	111
SUPPLEMENTARY INFORMATION 2(SI 2)	112
SUPPLEMENTARY INFORMATION 3(SI 3)	114
SUPPLEMENTARY INFORMATION 4(SI 4)	115
SUPPLEMENTARY INFORMATION 5(SI 5)	118
SUPPLEMENTARY INFORMATION 6(SI 6)	ERROR! BOOKMARK NOT DEFINED.

Abstract

In Chapter one, an acid assisted closed vessel microwave digestion procedure was developed for the treatment of fine airborne particulate matter that allows elemental iodine to be solubilised simultaneously with metallic elements. This procedure is an improvement over existing methods as it allows the iodine to be safely digested from the filter media (polypropylene or cellulose) in less than one hour and achieve up to 70–100 % recoveries, without requiring an overnight pre-digestion step or the addition of reducing agents, with a microwave temperature of 185 °C and the use of 65 % HNO₃ in the digestion media. A range of filters were investigated to determine the material that has the best properties for microwave digestion that also enabled the deposited iodine present in total suspended particles (TSP) to be rapidly fully digested and quantitatively analysed using inductively coupled plasma-mass spectrometry (ICP-MS). This developed method has shown to be possible in the analysis of metallic elements with iodine of interest without the need of a separate chemical preparation steps.

The following Chapters 3 and 4 are based on the analysis of radioactive isotopes of uranium and plutonium with the use of a quadrupole ICP-MS with a general introduction on radionuclide analysis in Chapter 2. Unlike other mass-spectrometric methods (eg., Sector-field ICP-MS or Multi-collector ICP-MS), the quadrupole ICP-MS is a cost-effective (easier maintenance) analytical instrument with good sensitivity to sub-ppb levels

In Chapter 3, plutonium analysis, in particular ²³⁸Pu, was performed with a non-radiometric method. ²³⁸Pu is an alpha emitter and hence can be analysed successfully with alpha spectrometry, which does not have any spectral interference although it is a very slow alpha emitter and requires a relatively long counting time. However, mass

spectrometric analysis of ^{238}Pu faces isobaric interference with interfering ^{238}U which cannot be resolved. Therefore, in this chapter, a mass spectrometric method that uses an experimentally derived algebraic correction factor was developed that requires sample pretreatment with TEVA and UTEVA resin cartridges to separate the plutonium (TEVA) and uranium (UTEVA) in the sample. The proposed developed method was shown to be more effective when enriched uranium (weapon grade) was added into the sample prior to the resin-based separation steps.

In chapter 4, analysis of uranium isotope samples has usually been performed in a clean-room facility due to the presence of natural uranium in the environment that can potentially contaminate the sample. However, a clean room facility is not available in many laboratories that also carry out ICP analysis. There is also a lack in understanding of the potential contributors to natural uranium contamination, which can be identified through analysis of the process blanks. In this study, the process blanks were analysed in parallel to all samples to enable blank corrections to be performed for every step of the sample treatment processes. A significant portion of the natural uranium contamination was found to derive from reagents and consumables. The capability of analysis of different enrichment levels of uranium samples were evaluated by varying the amount of samples spiked during the sample preparation technique (lithium borate fusion) and assessed with the related relative uncertainties at the various mass point of spiked samples. The thesis ends with a concluding Chapter 5.

List of publication

1. Tiong, L. Y. D.; Pong, B. K.; Webster, R. D., Closed vessel microwave digestion of air filters for measurements of elemental iodine. *Anal. Methods* **2017**, 9 (19), 2909-2914.
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Development of a sample preparation method for the analysis of total iodine in air filters

1.1. Introduction

1.1.1. Iodine

Iodine is a group VII non-metallic naturally occurring element with the most stable natural isotope of iodine is ^{127}I . Iodine determination in biological, food and environmental samples has received considerable attention for the past few decades due to its important role in biological systems.¹ The most important biological use of iodine in humans is in thyroid functions. An adequate intake leads to healthy thyroid function, whereas an excessive iodine intake leads to high-iodine goiter and possibly damage to the nervous system.¹ A daily intake of about 180-200 μg of iodine is recommended to prevent diseases due to iodine deficiency.²

The averaged concentration of iodine in the earth's crust is 0.5 mg kg^{-1} , with approximately $45\text{-}60 \text{ }\mu\text{g l}^{-1}$ in the oceans and $10 \text{ to } 20 \text{ ng m}^{-3}$ in the atmosphere, depending on the proximity to the sea and the types of soil in the region.³ Iodine is deposited into the environment in the form of sea- salt spray or gases. Iodine in the atmosphere can undergo photolytic dissociation, converting molecular iodine into methyl and iodine radicals and producing different iodine forms such as HI, HOI, INO_2 , IONO_2 or OIO .³⁻⁴

Whilst ^{127}I is in close to 100 % natural abundance (National Institute of Standards and Technology, NIST), the most hazardous iodine species are the radioactive

isotopes such as ^{129}I and ^{131}I that form in nuclear reactors. ^{129}I has a longer half-life of 15.7×10^6 years as compared to ^{131}I with a half-life of 8.04 days.⁵ Therefore, it can accumulate in the environment through nuclear weapon testing, nuclear accidents and emissions from nuclear fuel reprocessing plants.⁶ Due to the much longer half-life of ^{129}I , it can potentially enter the food chain via migration in the air and subsequent deposition. Therefore, it is important to have the means of monitoring the amount of iodine present in the air, such as present in small particulate matter (PM) that is circulating in the atmosphere. There has been substantial interest in monitoring atmospheric particulate matter (PM) as it is listed as one of the 5 atmospheric priority pollutants (PM, SO_2 , NO_x , O_3 and CO). It has been continuously monitored by many environmental agencies because of the potential respiratory health problems it can cause.^{7,8,9} There are several sizes of particulate matter of interest, including PM_{10} (particle size $\leq 10 \mu\text{m}$), $\text{PM}_{2.5}$ (particle size $\leq 2.5 \mu\text{m}$) and TSP (Total Suspended Particulates. TSP have aerodynamic diameters of less than $100 \mu\text{m}$ and were studied in this work for the simultaneous analysis of both iodine and 10 other metallic elements present in the sampled TSP filters. The materials deposited on the TSP sampler have a wide range in particle diameters (theoretically it collects particles of all sizes) and therefore, the amount of iodine detected is likely to be higher than solely sampling the finer materials such as $\text{PM}_{2.5}$. The developed method of iodine detection in TSP has been reported in this work and the following sections will discuss the specific results from the proposed methodology.¹⁰

1.1.2. Sample preparation of Iodine analysis

The challenge of analyzing iodine in solid materials lies in the sample preparation required prior to analysis with ICP-MS, because of the tendency of iodine to be lost by volatilization in the form of I_2 .⁶ It has been reported by several groups that the use of an alkaline media such as Tetramethyammonium hydroxide (TMAH) is capable of preventing the losses of iodine from volatilization during the sample preparation steps.^{11,12,13,14} However, the use of TMAH is unfavorable in a closed vessel system such as the microwave digestion method that is used in this work. This is due to the low boiling point of TMAH, which may lead to over-pressurization in a closed vessel environment, and this poses a huge experimental risk.^{11, 15}

Apart from alkaline conditions, mineral acids have been adopted in the sample preparation steps such as with the addition of perchloric acid.^{16,17} This was added to ensure that all the iodine species in the preparation step were converted to the stable iodate species. However, extra precautions are required during the use of perchloric acid to prevent the possibility of an explosion due to contact with oxidizable materials under elevated temperature.¹⁶ Wet ashing of food samples using a pressurized steel bomb system with a mixture of nitric acid and perchloric acid has been reported by Larson et. al.¹⁶ This method requires a sample preparation time of 4 hours at 160 °C where volatile iodine species were reported to be converted to stable iodine species. Other methods include soaking the particulate matter filters collected in KOH with $NaHSO_3$ (or Na_2SO_3) under heating conditions and overnight stirring. This is followed by an hour of reflux prior to ICP-MS analysis.^{18,19}

Microwave-assisted close vessel digestion is one of the most effective sample preparation techniques which utilizes irradiated microwave power supplied to the system for the desired temperature to be attained within a short period of time (within an hour or less). Unlike open systems, where the dissolution of samples is limited by the boiling point of the mineral acids, a closed vessel system allows higher achievable temperatures to be achieved without losses in the volume of the reaction samples.

The microwave-assisted digestion of iodine containing solid samples with nitric acid and the addition of NaHSO_3 as a reducing agent added upon completion of the digestion to reduce volatile iodine to iodide has been reported.⁶ However, such a procedure involves the use of a large amount of reagents such as 20 mL of NaHSO_3 and 12 mL of CHCl_3 for extraction followed by converting the iodine into the form of KI, which further requires an additional 10 mL of KOH solution.

Therefore, in this presented work, the use of a simple mineral acid, HNO_3 is explored to extract/digest spiked iodine air filters using a microwave-assisted digestion system without the need of any hazardous reagents eg: perchloric acid.

Nitric acid has been widely used in many microwave digestion media as it is strong enough to solubilize metals in various samples types including fly ashes.²⁰ Nitric acid is also preferred for ICP-MS analysis as other highly corrosive acids such as hydrofluoric acid are unfavorable for the silica-based glassware of the instrument due to etching, which can lead to signal drift and contamination.²¹ Furthermore, nitric acid matrices are reported to be the best acid medium for ICP-MS analysis because its constituents H_2 , N_2 and O_2 are already present in the

plasma environment, hence the polyatomic ions are not increased significantly with nitric acid matrices.²²

Another aim of this work is to achieve the simultaneous analysis of other elements present in the sampled air filters without the need of an additional sample preparation step. Such a procedure is beneficial as it overcomes the problem of having to process a sample multiple times in order to detect all the elements, especially if there are limited quantities of the sample and time constraints. The use of mineral acids for digestion of particulate matter samples have been widely studied and adopted for air monitoring. Therefore, to achieve the goal of a simultaneous analysis of iodine, an acid-based medium is proposed for sample preparation of the TSP air filters, which avoids additional separate preparation of the filters.^{23,21,24}

Several techniques have been developed for measurements of iodine in food, environmental and biological samples including ion selective electrodes (ISE)²⁵, ion chromatography (IC)^{26,27} and X-ray fluorescence²⁸. However, these techniques are not able to provide good detection limits as compared with ICP-MS. In addition, ICP-MS allows multi-elemental analysis without any mass interference at 127 for stable iodine. The use of ICP-MS is also useful for isotopic analysis, which allows measurements of radioactive isotopes, which currently is a worldwide concern on health after the Fukushima, Japan nuclear accident.

1.2. Experimental

1.2.1 Microwave digestion procedures for filter media

A closed vessel microwave system, EthosONE (Milestone, Italy) with a 10 Teflon vessel capacity was used in this work for the digestion of air filters. The 10 Teflon

vessels are made of high purity Teflon with an internal volume of 100 mL (**Fig. 1.1**).

Figure 1.1. Ethos One microwave system (Source: Milestone).

Recovery test experiments were carried out by spiking the filters with fixed amounts of iodine. Potassium iodide, KI, standard (Accustandard) was prepared at a concentration of $10 \mu\text{g mL}^{-1}$ as a stock solution for the spiking experiments. 0.1 mL of the prepared stock solution was spiked onto the various filter media that were under investigation for suitability in this presented work. The 3 filter media that were studied are cellulose, polypropylene and quartz. The spiking process was performed in a fumehood to ensure consistency of the experimental environment. The spiked filters were left to dry in the fumehood for approximately 30 – 45 minutes. 65 % w/w high purity HNO_3 acid was used as the digestion media and a volume of 8 mL of acidic solution is added into each digestion vessel as the main digestion media for all the filters used in this work. The 8 mL digestion media was made up of 5 mL 65 % w/w HNO_3 (JT Baker, USA) and 3 mL ultrapure water ($18.2 \text{ M}\Omega \text{ cm}$). The digested solution was then diluted further to 100 mL to ensure

that the resulting digested sample was suitable for ICP-MS analysis. The digestion procedure was sufficient for complete digestion of the filter media using the programmable microwave digestion system for a sample size up to 0.2 g. The programmable microwave was optimized based on the spike recovery tests of the filters and validated with replicated recovery tests. The microwave program was set at a power of 1100 W where this amount of energy was irradiated on the microwave vessels to attain a temperature of 185 °C. The following microwave program was set for all the tested filters used in this work: 20 minutes ramping time to 185 °C followed by holding time of 15 minutes at 185 °C, with the cooling period set for 30 minutes. The cooling period is necessary to ensure the vessels were cooled to room temperature and that reduces excessive venting during opening of the vessels.

1.2.2 Sampling of air filters

Total suspended particulate filters that were sampled and collected were stored in the fridge, maintained at 4 °C after 1/8 of the filters were cut and digested. The digested samples were diluted with ultrapure water up to 100 mL prior to ICP-MS analysis. A 0.5 mL aliquot of the diluted digested filter solutions was transferred into 5 mL sample vials for further analysis by ICP-MS.

Polypropylene filters (3M 5739, 460 × 570 mm) were used for the air sampling experiments that were conducted in Singapore. The filters were housed in an anodized aluminum filter cassette to ensure they were well secured during sampling. The air sampling was performed in the School of Physical and Mathematical Sciences (SPMS) at Nanyang Technological University. A high volume air sampler (HiVol 3000, Ecotech, Australia) was located on the level 6

rooftop and operated at a flow rate of $60 \text{ m}^3 \text{ h}^{-1}$. The filters were left to sample the air over a period of 7 days and digested the next day after collection. The analysis was performed on the day of sample preparation to ensure no potential degradation of the samples. A pair of plastic scissors were used to cut 1/8 section of the filter and digested for analysis. The reason for taking a portion of the sampled filters is to ensure that the filter media can be entirely soaked in the digestion media or explosion in the vessels might occur. A total volume of 12 mL was used to ensure the samples were fully soaked with 7.5 mL HNO_3 + 4.5 mL ultrapure water. The larger volume of digestion solution is used for the samples to guarantee the sampled area are fully soaked in the acid medium. A 0.5 mL aliquot of the diluted digested filter solutions were transferred into 5 mL sample vials for further analysis by ICP-MS. This is to ensure that the concentration of the major elements present in the digested sampled TSP filters are not too concentrated which may lead to carry over (or contamination) and will lead to the need for more blank rinses in between sample analysis.

1.2.3 Measurements of iodine samples by quadrupole ICP-MS

An Agilent 7700x (Agilent Technologies, Japan) quadrupole ICP-MS was used in this work for all analysis of iodine samples. The ICP-MS is equipped with a low-flow quartz concentric nebulizer, which introduces the sample into the system with a fine spray of aerosols. The system is also equipped with quartz, Scott-type double-pass spray chamber with Peltier-cooling (3°C), hence eliminating the need of an external cooling water supply. The 7700x ICP-MS is equipped with a collision cell, which removes the interferences present in the samples, which allows accurate measurements of the affected elements. Argon with 99.999 % purity was supplied into the ICP-MS system, which is the source of argide ions for

the formation of the plasma in the instrument. The operating parameters used for the ICP-MS analysis have been listed in the supplementary information (**SI1**).

Calibration solutions were prepared in a concentration range of 0.5-20 ng mL⁻¹ from the KI stock solution (Accustandard). The rinsing solutions used for the samples runs were made up of 5 % HNO₃ (×2 rinses) and ultrapure water (×1 rinse). This combination of rinsing solutions was added after calibration and more stringently for sampled air filters (in between every sampled air filters) to avoid any carry-overs. Memory effects were not observed in this experiment, which have been an issue reported due to the formation of volatile iodine during sample preparation with acids.¹⁶ This could be due to the low concentration levels of the iodine in the samples analyzed in this work and also potentially due to the absence of volatile iodine formation from the presented method. The air particulate samples that were digested were diluted as discussed in section 1.2.2.

1.3. Results and discussion

1.3.1. ICP-MS analysis of iodide standard solutions

Figure 1.2. ICP-MS signal intensity for ^{127}I calibration solutions with 0.2 s integration time during analysis.

Standard calibration solutions were prepared in ultrapure water in 0.5 ppb, 1 ppb, 5 ppb, 10 ppb, 20 ppb and using ultrapure water as the calibration blank. These standard solutions were run under both gas modes (no gas [u] and Helium [He]). Two different integration times for analysis are compared under these two modes and the counts per second do not vary significantly in both gas modes. (n=3) (**Fig. 1.2 and 1.3**).

Figure 1.3. ICP-MS signal intensity for ^{127}I calibration solutions with 0.3 s integration time during analysis.

The use of a longer integration time is to allow for better counts per second (CPS) signals for the elements and hence better counting statistics. The aim of increasing the integration time is to achieve a higher CPS value at the lowest concentration point in the calibration curve. However, with a 0.2 s integration time, the averaged CPS signal for 0.5 ppb found to be 2.65×10^4 CPS with RSD of 6 % under no gas mode and 2.54×10^3 CPS under Helium mode with RSD of 9 %. The use of a longer integration time did not lead to significantly better CPS. 2.66×10^4 CPS with 9.3% RSD under no gas mode and 2.80×10^3 CPS with 8.5% RSD under Helium mode with 0.3 s integration time. The calibration curve with 0.2 s integration time is plotted with triplicate readings for each run with 500 sweeps across the mass range (**Fig 1.4**). The calibration curves for 0.5- 20 ppb of calibration standard solutions led to R^2 values greater than 0.99 (n=3) for both gas modes. The overlapping error bars at each concentration point suggest that there

are no significant differences in the calibration whether it is done under helium or no gas mode.

The 3 masses of iodine isotopes which are of importance and can be found in the environment are ^{127}I , which is the stable and naturally occurring isotope of iodine, and ^{129}I and ^{131}I that are released into the environment due to nuclear activities. There are no reported isobaric interferences at these masses except for mass 131, which suffers interference from ^{131}Xe . Helium mode however, is not useful for the removal of this isobaric interference, which is presently not the mass of interest. The use of collision gas mode (Helium gas) leads to lower signal intensities (approximately 10 times less) than no gas mode. Therefore, no gas mode was used for analysis of spiked iodine samples and TSP collected filters due to the absence of isobaric/polyatomic interferences at m/z 127. However, other metallic elements analyzed simultaneously for sampled TSP filters were analyzed based on the previously optimized mode performed by our laboratory.

Figure 1.4. Calibration curve with integration time of 0.2 s.

1.3.2 Spiking test on various filter media

Filters used for air sampling are selected mainly based on the background metal content which is important for sampling trace levels of elements and as well as the affinity to moisture. Apart from these, the filter media should have the mechanical strength to withstand the prolonged period of air suction through the air sampler. In Singapore's local climate with > 90 % relative humidity, the use of a hydrophobic nature would be preferable to avoid excessive retention of moisture on the filter media. The following sections will discuss the various types of filter media used for spike recovery.

1.3.2.1. Borosilicate filters (Quartz)

Borosilicate filters are one of the commonly used filter media for high-volume air sampling. The other 3 types are cellulose fiber, mixed fiber and polymer membrane filters. Borosilicate filters are commonly used due to their high purities hydrophobic nature, which makes it suitable for use in high moisture content or rainy regions.

The borosilicate filters used in this work were from EMFAB. EMFAB filters have a temperature resistance of up to 500 °C and contain siliceous-containing materials that require the use of hydrofluoric (HF) acid if total digestion is required during sample preparation steps. However, the use of HF acid is undesirable due to its highly corrosive nature as compared to other commonly used acids. Therefore, the use of borosilicate for spiking experiments, only results in extraction of the spiked materials with the filter remaining intact upon subjection to microwave digestion with nitric acid.

0.1 mL of potassium iodide standard solution prepared in a concentration level of $10\ \mu\text{g mL}^{-1}$ was spiked on the various filter media tested and evaporated to dryness prior to digestion in the fumehood. Due to the hydrophobic nature of the filters, KI droplets were observed during the spiking process and no visible droplets were present on the surface after complete drying.

Since the glass filters used do not undergo complete dissolution with the reported microwave parameters and chemical conditions, the main mechanism for preparation of solid samples (filters) prior to ICP-MS analysis would be via an “acid extraction” under elevated temperature and pressure conditions. The ratio of HNO_3 : H_2O added as the digestion media was increased gradually leading to higher acidity of the digestion media (**Table 1.1**, Entries 1-3), but did not lead to improvements in the recovery of KI spiked (**Table 1.1**). The increase in temperature was also shown to have little effect on the recovery of KI. For entries 1-4, the microwave runs were monitored and the digestion occurred at the temperature set for each run. The vessels were irradiated at 1100 W with 5 vessels in each experimental run. The maximum recovery of iodine for microwave digestion under the attempted conditions was only 42 % at a temperature of $190\ ^\circ\text{C}$ with 5 mL of HNO_3 . As there is a factory setting limitation on the operating parameters for the microwave digestion system, the temperature beyond $200\ ^\circ\text{C}$ for 5 vessels has not been tested to ensure safe operations. Another set of experiments were performed at higher microwave power of 1200 W (Supplementary info, **SI 3**) with the same holding time and ramping time in Table 1.1. The microwave system operates with temperature as the main parameter for a successful digestion, with an irradiated power as an aid to achieve that temperature. Therefore, once the desired temperature has been achieved, the irradiated power will drop below the maximum

required value. Since the maximum temperature set of the vessels can be achieved in the pressurized system, the increase in maximum power does not show improvement in the digestion efficiency.

Table 1.1 Variation in microwave conditions for EMFAB filters spiked with KI with irradiated 1100 W.

Entry	HNO ₃ [mL]	Water [mL]	Temperature [°C]	Holding time [mins]	Ramping time [mins]	Yield [%]
1	5	3	180	15	20	37.8
	5	3	190	15	20	42.2
	5	3	195	15	20	22.5
2	6	2	180	15	20	17.9
	6	2	190	15	20	26.1
	6	2	195	15	20	38.6
3	7	1	180	15	20	12.4
	7	1	190	15	20	24.4
	7	1	195	15	20	30.7
4	5	2.5	180	15	20	31.5
	5	2.5	190	15	20	20.9
	5 ^a	2.5	195	15	20	33.1

^a 0.5 mL of 37 % HCl added into the digestion media.

In conclusion, the recovery of iodine spiked onto quartz filter can only be achieved with a maximum recovery of 59 ± 33 % (Supplementary info, **SI 3**) and further exploration for other filter media was necessary which is discussed in section 1.2.2 and 1.2.3.

1.3.2.2. Cellulose filters

Cellulose filters are easily decomposed under acidic conditions and elevated conditions (temperature and pressure). They are also commonly used as an air

sampling filter media as listed in the EPA methods for air monitoring. However, extra caution should be practiced for microwave digestion of cellulose filters, as previously reported, higher temperatures are necessary for heavy matrixes such as cellulose. In addition, cellulose might be more reactive upon complete dissolution and this will increase the internal pressure of the digestion vessels. Hence, extra precautions, such as pre-digestion was investigated to avoid over-pressurization or venting during the digestion process. Based on the experiments performed on blank filters, the filters could be completely digested at 145 °C in 41% HNO₃ with 20 minutes ramping time and a holding time of 15 minutes at a microwave power set at 1000 W. Under such conditions, complete digestion of the filters was achieved with no solid residues. However, to ensure no particulates coarser than 0.2 µm were present in the sample solution for ICP-MS analysis, the samples were passed through a syringe filter (Sartorius, USA) with pore size 0.2 µm prior to ICP-MS analysis.

The filters were weighed to be approximately 0.2 g and there are chances of venting or over pressurization due to the organic components present in cellulose filters. Therefore, to avoid venting during the microwave digestion, an additional step of pre-digestion was performed. This was performed by soaking the filters in the digestion media (HNO₃ acid) for a period of time in the fumehood before performing the actual digestion. However, this only yielded a recovery of 51 % with poor reproducibility of 56 % RSD. The large variation in repeated experiments with same conditions suggest poor robustness of this method and this might due to formation of volatile iodine leading to losses. It was reported by Gómez-Guzmán et al that the addition of a reducing agent is useful for converting volatile iodine into a less volatile anionic form.⁶ Therefore, the use of Na₂SO₃

added into the digestion media in excess (10 mL of 0.0126 g mL⁻¹) was investigated to ensure that all the iodine was able to react with the reducing agent where the volatile I₂ species are reduced. It was found that the addition of the reducing agent improved the recovery to 79 ± 40% (**Table 1.2**, Entry 2). However, poor repeatability still existed (n=15).

At this point, there are several possibilities that could lead to the non-ideal results of the experiments: cellulose is not a suitable filter media, the long hours of exposure prior to digestion leads to losses or the reducing agent used was not effective in reducing the volatile species of iodine formed in the vessels. Therefore, additional experiments were performed to eliminate the potential causes due to the poor robustness of the experiments. The pre-digestion time was shortened to 0.5 hr with the presence of the same reducing agent (Na₂SO₃). The percentage recovery difference between pre-digestion times of 17 hours and 0.5 hours were significant, 79 % and 89 % recovery, respectively. With shorter pre-digestion time, leading to better recoveries. Therefore, the effect of eliminating the pre-digestion step was explored and quantitative recovery (101 %) was achieved in the presence of a reducing agent with no pre-digestion. In addition, experiments in the absence of a reducing agent were also performed. Good recoveries (92 %) were achieved without a reducing agent with good RSD values of 12% (n=20) (**Fig 1.5**). A summary of the recoveries is presented in Table 3 with n > 3. Iodine could be recovered quantitatively in the presence of a reducing agent under no pre-digestion conditions (**Table 1.2**, Entry 4). The slightly higher than 100 % recovery was noted with 10% variations from averaged triplicate measurements. This could be due to a potential carry-over in the microwave vessels. The recovery obtained without reducing agent was also good and this is useful for experiments that require other

information on other elements present in the filter media as the presence of reducing agent might contain trace elements, which may hinder accurate measurements.

Table 1.2. Recoveries of spiked iodine on cellulose filters with varying conditions.

Entry	Pre-digestion, hours	Recovery $\pm$ RSD (%)
1	Pre-digestion, 17 hrs, no Na ₂ SO ₃	51 $\pm$ 56
2	Pre-digestion, 17 hrs, with Na ₂ SO ₃	79 $\pm$ 40
3	Pre-digestion, 0.5 hrs, with Na ₂ SO ₃	89 $\pm$ 13
4	No Pre-digestion, with Na ₂ SO ₃	101 $\pm$ 10
5	No Pre-digestion, no Na ₂ SO ₃	92 $\pm$ 12

Figure 1.5. Comparison of pre-digestion conditions in the presence of a reducing agent (10 ppb = 100% recovery).

1.3.2.3. Polypropylene filters

One of the main similarities of polypropylene to cellulose filters is the ability to dissolve into a colorless solution after microwave digestion. The temperature required to achieve a homogenous solution had to be ramped up to 185 °C in 20 minutes and with the same holding time of 15 minutes at a microwave power of 1100 W. It has been observed that the addition of reducing agent with no pre-digestion does not affect the recovery of spiked filters, an average value of $70 \pm 7 \%$ without any pre-digestion and reducing agent added (n=5) was achieved with polypropylene filters.

Figure 6 shows the comparison in performance of the three types of filters spiked with KI that were tested for their recoveries after microwave digestion. Borosilicate glass filters (EMFAB) are the most non-ideal filters with low recovery and poor reproducibility. The other two filters, cellulose and polypropylene have

better results with recovery values $\geq 70\%$ with good reproducibility when polypropylene filters were used ($RSD < 7\%$). The nature of polypropylene however, is different from cellulose. Cellulose has a better capacity in absorbing moisture whereas, polypropylene filters are hydrophobic and more time has to be given for the visible droplets of spiked KI to dry. This could possibly be the reason for the lower iodine recoveries than obtained from cellulose as the spiked droplets were exposed to the environment which might result in lowering the pH of the droplets due to the formation of carbonic acid (from CO_2 in air), resulting in the conversion to volatile HF. Nevertheless, the hydrophobic nature of such filters could be essential when air sampling in a humid climate.

Figure 1.6. Comparison of filter performance on spike recovery experiments ($n \geq 5$).

1.3.3. Sampling and analysis of iodine in TSP samples collected in Singapore

TSP samples were sampled and collected in the western part of Singapore in August 2015 for one month. Polypropylene filters were used for air sampling in consideration of Singapore's humid climate and occasional rain events. The treatment of collected samples was performed as outlined in the optimization of recovery tests of polypropylene filter media. The method detection limit (MDL) was determined by the digestion of 7 blank filters under the optimized conditions and measured for iodine content with ICP-MS using the calibration solutions. The MDL was calculated based on 3σ of the 7 blank filters and valued at 0.67 ppb. The values shown in the following **Table 1.3** have been background corrected and normalized based on the volume of air collected during one-week sampling period. Considering the recoveries for polypropylene has an averaged value of 70 %, the values in **Table 1.3** could be 30 % higher.

Table 1.3. Iodine concentration during the month of August 2015 in the western part of Singapore.

Sampling period, 2015	Iodine content [*] [ng m ⁻³]
31 st Jul-5 th Aug	0.956
5 th -12 th Aug	1.58
12 th -20 th Aug	4.61
20 th -28 th Aug	5.63

^{*} The sampled values have been corrected for with blank subtraction.

Based on the values in **Table 1.3**, the sampled amount of iodine present increases significantly during the period of 5th - 28th Aug. During this period, Singapore experienced poor air quality and this can be supported with the Pollutant Standard Index (PSI) index value (NEA, Singapore) which is an indication of air quality in Singapore. In the following (**Fig 1.7**), the TSP iodine content is plotted along with the data from the Singapore PSI. The increase in the PSI value during this period is due to the forest fires in Indonesia and this leads to the hazy conditions. Therefore, there seems to be a positive correlation in the iodine levels present in the sampled air filters and the PSI values during this period. There seems to be a sharp rise in the TSP-iodine concentration pre-dated the noticeable increase in the PSI values by 20 days. This may be due to the high volatility of iodine from the soil-plant-atmosphere system which leads to earlier dispersion than other elements.²⁹ In addition, gaseous species of iodine are expected to be fully volatilized during forest fires, and due to the presence of iodine in the soils and vegetation, it is more likely to be dispersed and transported more rapidly than particulate matter.³⁰ However, this conclusion needs to be verified with a more prolonged period of sampling. At concentration levels lower than the value of 10 ng m^{-3} , stable iodine is not likely to be hazardous to health. However, the scenario is potentially more serious if the plot of land is contaminated with radioactive iodine from a local nuclear power plant or nuclear accident that is then re-released during forest fires.

Figure 1.7. Iodine concentration in TSP (ng m^{-3}) and the PSI values during August 2015 in Singapore.¹⁰

The main objective of exploring an acid-assisted microwave digestion method is to allow simultaneous analysis of elemental metals present in the sampled air. Apart from iodine, metal elements present in particulate matter are of considerable importance due to the health concerns of breathing in toxic material. . Therefore in addition to the iodine measurements, the same digested filters were also examined for 10 commonly monitored transition and main group elements (V, Cr, Mn, Fe, Ni, Co, Cu, As, Se, Cd and Be). These elements are reflective of the actual amount present in the PM in air as they are not present in the filter backgrounds.

From **Table 1.4**, the general trend for all 10 elements measured is an increase in concentration from the period 12th Aug to 28th Aug and this coincides with the period with gradual increase in the PSI readings. The concentrations of the elements ranged from low 0.13 ng/m^3 for Cd which has the lowest concentration among the tested elements during the period of 5th - 12th Aug 2015 which increases

to 0.40 ng/m³ during 20th - 28th Aug 2015. The trend in an increase in the concentration during the period of 20th-28th Aug 2015 follows for all the elements (Table 4). The acidic medium used in the microwave digestion method reported allows complete digestion of the filters, which means zero possibility of elements being trapped on the filters. The acidic medium used has shown low background contribution to iodine and the background of the proposed polypropylene filters are corrected for during each analysis. These reported values were found to be in a similar range for other particulate matter in the same region.³¹

Table 1.4. Elements measured in August 2015 TSP samples with ICP-MS in ng/m³.

	V	Cr	Mn	Fe	Ni	Co	Cu	As	Se	Cd	Be
31 st Jul – 5 th Aug	10.36	2.22	10.70	518.63	6.83	0.30	22.36	29.85	0.86	0.18	68.03
5 th – 12 th Aug	19.66	4.07	16.95	583.06	11.72	0.32	16.52	21.73	1.81	0.13	107.66
12 th – 20 th Aug	44.70	5.17	36.07	1401.16	23.82	0.70	27.43	41.94	4.65	0.30	313.19
20 th – 28 th Aug	33.95	5.76	41.12	1680.48	20.61	0.79	36.18	51.29	6.28	0.40	397.70

1.4. Conclusions

The work in this Chapter has shown that microwave-assisted acid digestion of solid particulate matter samples containing iodine on cellulose and polypropylene filters is effective. Based on the ICP-MS results from digested filters spiked with KI, cellulose was shown to lead to quantitative recoveries (100 % recovery from the spike recovery test) with excellent reproducibility. Polypropylene, on the other hand, despite being able to fully dissolve under higher temperatures than cellulose, shows lower averaged recovery values of 70 % with comparable reproducibility to cellulose filters. Such lower recoveries could be due to analyte loss during the spiking process, as prolonged periods of time is needed for the drying of the spiked solution due to the hydrophobic nature of polypropylene.

Polypropylene filters were used for air sampling in the western part of Singapore. The use of a hydrophobic filter is more favorable to avoid high moisture content in the sampled filters during the one-week sampling period. The proposed method used to prepare the filters for ICP-MS analysis allows the quantification of 10 commonly analyzed metallic elements. This method allows the simultaneous analysis of iodine together with metallic elements under acidic conditions and this avoids the additional need for extra sample preparation for separate analysis of iodine.

Although this work does not involve the detection of ^{129}I , the presented method has shown good recoveries for stable ^{127}I in a closed-vessel acid digestion system, and this sample preparation method may be useful for future airborne particulates sample filters which may contain radioisotopes of iodine.

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Part II: Application of Inductively coupled plasma-
Mass spectrometry in analysis of radionuclides-
Uranium and plutonium.

An introduction to analysis of radionuclides by inductively coupled plasma-mass spectrometry

2.1 Uranium

Natural uranium contains 0.01 % of ^{234}U , 0.72 % of ^{235}U and 99.27 % of ^{238}U . All isotopes of uranium are radioactive and the radioactivity of these isotopes depends on their half-life. The most abundant naturally occurring uranium isotope is ^{238}U which has the longest half-life of 4.47×10^9 years. ^{234}U and ^{235}U have shorter half-life of 2.46×10^5 and 7.04×10^8 years, respectively.^{1,2} Naturally occurring uranium isotopes are weakly radioactive and emit alpha particles which are positively charged ions with weak penetrating power. The uranium isotopes decay to eventually form stable Pb isotopes. The major nuclear use of uranium is as fuel for nuclear reactors and in nuclear weapons. Out of the 3 naturally occurring uranium isotopes, only ^{235}U is fissile, which means the concentration of ^{235}U will be increased during the production of nuclear fuel.

The isotopic composition of uranium may vary and this information allows the identification of the type of category of uranium samples. The categories of uranium are mainly depleted uranium (^{235}U abundance less than 0.72 %), natural uranium ($^{235}\text{U} = 0.72$ %), low enriched uranium (^{235}U abundance higher than 0.72 % and lower than 20 %), high-enriched uranium (^{235}U abundance higher than 20 %) and weapon grade uranium (^{235}U abundance more than 93 %).³ Therefore, whether the sample is natural, depleted or enriched, it can be identified by evaluating the $^{235}\text{U}/^{238}\text{U}$ ratio.

2.2 Plutonium

The plutonium isotopes that are present in the environment are mainly ^{238}Pu , ^{239}Pu , ^{240}Pu , ^{241}Pu and ^{242}Pu and are anthropogenic. Plutonium is produced in a nuclear reactor through neutron capture of uranium and subsequent beta decay.⁴ The most abundant plutonium isotopes are ^{239}Pu and ^{240}Pu , which have half-lives of 24,110 years and 6,584 years respectively and are frequently monitored in environmental studies.^{5,6} ^{238}Pu , ^{239}Pu , ^{240}Pu and ^{242}Pu are long-lived alpha (α) emitters while ^{241}Pu is a beta (β) emitter. They are present in the environment due to nuclear activities in the surrounding area such as nuclear weapon testing, nuclear accidents and reprocessing of nuclear fuels.⁷ The Pu isotope ratio, $^{240}\text{Pu}/^{239}\text{Pu}$, similar to uranium isotopic ratios, provides important information on the samples, and is important as it is a fingerprint for the sources of Pu samples. For reactor grade Pu, the ratio varies from 0.23 to 0.65 according to the irradiation conditions of the fuel.^{5,8} Weapon grade Pu is categorized based on low $^{240}\text{Pu}/^{239}\text{Pu}$ ratios with the amount of ^{240}Pu not greater than 5%.⁹ Therefore, the determination of Pu isotopes have been an important for nuclear safeguards.

Table 2.1. Different grades of plutonium¹⁰

Plutonium grade	^{240}Pu %
Super grade	< 3 %
Weapon grade	< 7 %
Fuel grade	Between 7 % and 18 % included
Reactor grade	>18 %

2.3 Analysis of uranium and plutonium

In recent years, there have been several incidents involving illicit trafficking and smuggling of nuclear material and radioactive sources. These have raised public concerns over the use of such nuclear materials, and with the recent nuclear accidents in Fukushima, Japan, there have been additional concerns over the exposure of such radioactive materials to humans. Therefore, accurate and rapid measurements of radionuclides are important to have a quick access to the amount of harmful radioactive materials present and for decision-makers to take the necessary precautionary actions. Several techniques are available for analysis of radionuclides, particularly uranium and plutonium. The two major techniques can be differentiated as radiometric and mass spectrometric (non-radiometric), which will be discussed in the following sections 2.3.1 and 2.3.2.

2.3.1 Radiometric measurement techniques

Radioisotopes undergo decay into their final state and this process occurs at a specific rate, which is unique to individual radioisotopes and called the decay constant. When the radioisotopes decay to achieve stability, they emit energies in the form of particles (such as alpha and beta) and/or electromagnetic radiation (gamma emission). Traditionally, radiometric methods such as alpha (α) spectrometry, gamma (γ) spectrometry and liquid scintillation counting (LSC) are used for measurements of radionuclides. These methods have been used to complement each other to obtain complete information on the radionuclides present in the samples.¹¹

Alpha spectroscopy as the name suggests, measures the alpha particles emitted by the radioactive isotopes during its decay reaction. During an alpha decay, an alpha

particle, which is exactly the same as a stable helium nucleus, is emitted. It is commonly used to measure plutonium isotopes, particularly ^{238}Pu , ^{239}Pu and ^{240}Pu . The alpha activity for ^{238}Pu is the strongest among the Pu nuclides, hence given the same number of moles of the isotopes of Pu, ^{238}Pu will give the highest counts (or signal intensity). The decay of ^{238}Pu via alpha emission leads to the formation of ^{234}U . Therefore, alpha spectrometry is a powerful tool for determination of ^{238}Pu .¹² Alpha spectrometry faces limitations when the alpha energies emitted by the isotopes overlap and cannot be resolved. The energies of ^{239}Pu and ^{240}Pu isotopes are represented as $^{239+240}\text{Pu}$ as these two isotopes emit similar energies.¹³ This limitation can be overcome with the use of ICP-MS where the isotopes can be resolved based on the mass-to-charge ratio.

Gamma spectrometry, on the other hand, is a measurement of the gamma rays emitted during the decay of a radioactive isotope. Unlike alpha spectrometry, gamma spectrometry is a non-destructive technique as the samples does not need any treatment before counting and thus is useful for the first screening of samples prior to further investigations and minimizes the potential contamination during sample preparation. Liquid Scintillation Counting (LSC) technique measures the sample's emission of beta particles. For example, ^{241}Pu is not sensitive for alpha spectrometry measurement however; LSC is usually used for ^{241}Pu measurements due to its sensitivity to beta decay. Similar to alpha spectrometry, sample preparation is required although it has a relatively simpler sample preparation than alpha spectrometry.

Radiometric methods are useful for strong emitters and usually for radioactive isotopes with short half-lives. However, radioactive isotopes with generally much longer half-lives will result in weaker signals and this leads to a longer analysis

time required for quantification. Therefore, the use of a mass spectrometry method, which is an ion counting technique, can be more sensitive for long-lived radionuclides.

2.3.2 Mass spectrometric techniques

Inductively coupled plasma mass spectrometry (ICP-MS) is one of the most suitable methods for routine uranium isotopic ratio measurements as it is able to provide sufficient sensitivity, accuracy and most importantly, it has short analysis time for long-lived radionuclides.^{14,15} The ICP-MS has another advantage when compared to radiometric methods in that it has the capability of multi-elemental analysis. A single injection of sample allows other mass numbers of interest to be determined. In addition to the above-mentioned advantages of measuring radionuclides using ICP-MS, the sample preparation protocols for ICP-MS are generally simpler than for radiometric measurement techniques.¹⁶

There are several types of ICP-MS instruments and in nuclear forensics, high resolution ICP-MS such as the sector-field ICP-MS and multi-collector ICP-MS are typically used due to their high sensitivity and accuracy in isotopic ratio measurements. However, the sector field mass spectrometers are expensive, require frequent maintenance and are typically not available in a routine analytical laboratory. Despite the high sensitivity of sector field and multi-collector mass spectrometers, the isobaric interferences faced by ^{238}Pu cannot be resolved. The presence of interfering ^{238}U in samples is a challenge and has made analysis of ^{238}Pu impossible by mass spectrometric methods. Hence, the use of alpha spectrometry is always needed for plutonium analysis.

Apart from ICP-MS techniques, the use of thermal ionization mass spectrometry (TIMS) for determination of isotopic ratios of radioactive samples with high precision is widespread.^{17,18,19,20} However, this technique is limited only to elements with low 1st ionization energies and long analysis times with extensive sample preparation are required for this technique.¹⁵ The analysis with TIMS is also complicated by time dependent mass fractionation effects, which are corrected for by using two other isotopes with known ratios.^{15,21} Other mass spectrometric techniques such as resonance ionization mass spectrometry (RIMS) and accelerator mass spectrometry (AMS) are also used for radionuclides measurement.^{22,23} However in this work, the use of a quadrupole ICP-MS (ICP-Q-MS) is the main focus due to the ease of accessibility to an ICP-Q-MS.

2.4 Scope of work

The work in this thesis focuses on the use of a quadrupole ICP-MS that is commonly found in analytical laboratories. The quadrupole ICP-MS was utilized for analysis of uranium and plutonium isotopic ratios of liquid samples. Prior to analysis, precise sample preparation is needed to be performed which is discussed in detail in the following individual chapters. Challenges faced during the analysis of radionuclides are addressed in the following two chapters and methods to overcome these challenges are proposed (Chapters 3 and 4). Chapter 3 focuses on the analysis of plutonium isotopes, particularly on ²³⁸Pu, which suffers isobaric interferences in mass spectrometric analysis. In Chapter 4, the main focus of the study is on the analysis of uranium samples and the capability of analyzing the enriched uranium samples with a quadrupole ICP-MS without elaborate facilities such as the clean room.

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A resin-based mathematical correction for the analysis of plutonium-238 using inductively coupled plasma mass spectrometry

3.1 Background of work

Plutonium analysis has been of great interest for the past few decades as it is released during nuclear power plant accidents, weapon testing or due to unauthorized release of nuclear waste into the environment. The important plutonium isotopes produced in a reactor are ^{238}Pu (half-life: 87.7 years), ^{239}Pu (half-life: 24110 years), ^{240}Pu (half-life: 6560 years) and ^{241}Pu (half-life: 14.35 years).¹ Since plutonium is an anthropogenic element, which exists due to man-made activities, it is formed typically as a by-product in a nuclear reactor through a neutron capture and subsequent β -decays.

The isotopic composition of these plutonium isotopes is important in providing information on the category of the plutonium material; categorization of plutonium requires the determination of all of the above-mentioned plutonium isotopes. For example, weapon-grade plutonium has an isotopic composition of around 93.5 % ^{239}Pu , less than 6 % of ^{240}Pu and 0.5 % of ^{241}Pu with minor amounts of ^{238}Pu and ^{242}Pu .² Therefore, the Pu isotopic composition can provide a “fingerprint” of different sources and is used in identifying potential misuse of the nuclear fuel.³

In age determination of a nuclear material, four parent/daughter relations can be used.⁴ They are $^{238}\text{Pu}/^{234}\text{U}$, $^{239}\text{Pu}/^{235}\text{U}$, $^{240}\text{Pu}/^{236}\text{U}$ and $^{241}\text{Pu}/^{241}\text{Am}$. Thus, the information on ^{238}Pu is equally important as the use of these several parent-

daughter ratios alleviates systematic errors in age determination instead of using only one of the ratios in age-determination. Ideally, with the use of an ICP-MS, the masses of interest: ^{238}Pu , ^{234}U , ^{239}Pu , ^{235}U , ^{240}Pu , ^{236}U can be obtained with a single run.

Various methods are used for plutonium isotopic determination, including radiometric methods such as alpha spectrometry and liquid scintillation counting (LSC). Traditionally, analysis of actinides has been determined by radiometric methods. The use of radiometric methods however, often suffers from serious interferences due to the similarity in energy, for example, ^{238}Pu , ^{241}Am and ^{228}Th have alpha energies of 5.499, 5.486, 5.423 MeV, respectively. The main drawback in solely plutonium analysis is however, the similar alpha energies of ^{239}Pu and ^{240}Pu which are 5.15 MeV and 5.18 MeV, respectively.⁵ Another drawback of alpha spectrometry is the long counting time required for samples with low-activity with the amount of time required up to several days or months.⁶ However, alpha spectrometry is particularly useful for measurements of ^{238}Pu due to its relatively short half-life. Apart from measurements of ^{238}Pu with alpha spectrometry, the use of other mass spectrometric methods such as Resonance Ionization Mass Spectrometry (RIMS) or Accelerator Mass Spectrometry (AMS) have been widely used.⁷⁻⁹ Liquid Scintillation Counting (LSC) has been a useful method to determine ^{241}Pu which is a slow beta emitter.^{10,11} Therefore, for a complete analysis of all the plutonium isotopes, alpha spectrometry (^{238}Pu), liquid scintillation (^{241}Pu) and ICP-MS (^{239}Pu and ^{240}Pu) will be required.

On the other hand, Thermal Ionization Mass Spectrometry (TIMS) suffers the same drawbacks as ICP-MS due to the isobaric interferences in ^{238}Pu measurement from the ubiquitous ^{238}U present in the environment.¹¹ The main disadvantage of

the TIMS source compared to the ICP-MS source is the lower ionization efficiency of the sample for ion production which is important for measuring low-level amounts of plutonium, particularly for measurements of isotopes having low abundance, such as ^{241}Pu and ^{242}Pu .¹² The use of TIMS for a complete plutonium analysis had been demonstrated with the use of an Interfering Element Correction (IEC) method reported by Aggarwal et. al.¹³ Despite being a successful method, a time frame of 2 weeks is required to determine the ^{238}Pu present. In addition, considering the availability of this instrument, analytical costs and operating skills involved, it is definitely not ideal in a common analytical laboratory.

Apart from the drawbacks faced by radiometric methods, the mass spectrometric methods, primarily ICP-MS analysis faces serious isobaric interferences, which is discussed and overcome in this chapter. At m/z 238, isotopes of uranium ^{238}U and plutonium, ^{238}Pu are both not differentiable by mass spectrometric methods. Therefore, it is a common practice to use both alpha spectroscopy and ICP-MS for the complete analysis of plutonium isotopes present in the sample. One advantage, apart from the shorter analysis time, is the shorter sample preparation time required for ICP-MS. For liquid samples, a separation extraction technique prior to analysis can be performed to either remove possible interferences or to pre-concentrate the samples to achieve higher signal intensity. For alpha spectrometry however, electroplating of the samples onto a stainless steel planchet is required. Prior to that process, several other chemical steps are also required, which results in approximately 1-2 days of preparation time. Extra caution is needed during the electroplating process as a thin and homogenous film of the samples have to be achieved on the planchet to ensure a good energy resolution spectra. This makes the sample preparation for alpha spectrometry more tedious. The quadrupole ICP-

MS has shown to be able to measure plutonium contents with sufficient precision and accuracy, satisfying the International Atomic Energy Agency requirements.^{2,14} This gives the quadrupole ICP-MS relevance in its application in plutonium and uranium quantification without a high cost model such as the sector field ICP-MS. In this chapter, ²³⁸Pu analysis with quadrupole ICP-MS is explored and the performance of the analysis were satisfactory using a numerical correction approach. The use of the quadrupole ICP-MS allows a shorter analysis time with simple preparation required i.e. chemical separations using resins.

3.2. Chemical separation technique: Solid Phase Extraction (SPE)

Chemical separation is required to separate uranium and plutonium due to the interferences in analysis by ICP-MS. Apart from the main interferences faced in analysis, the amount of plutonium and uranium present in the environment is low. Therefore, a chemical extraction process also allows a pre-concentration of the isotopes of interest in order for an accurate analysis to occur.

The separation of plutonium and uranium from the sample bulk can be performed using two resin cartridges purchased from Eichrom Technologies. They are named as TEVA[®] and UTEVA[®]. The TEVA resins contain an active component, which is an aliphatic quaternary amine. The following figure shows the acid dependency of the actinides in a TEVA resin from HNO₃ and HCl acids. Maximum uptake occurs in the range of 2-4 M HNO₃ (**Fig 3.1**, Left). In this range, the difference in retention factors for U, Np and Am are huge as compared to Pu which has the highest retention factor among the other elements. This property can be exploited to retain the tetravalent plutonium while the uranium present in the samples will not be retained well in the TEVA resins. Although the retention factor for uranium

is small, this does not necessary mean that no uranium will be trapped in TEVA. Therefore, samples can be loaded into the resins with 3 M HNO_3 and the plutonium will be retained in the TEVA resin while the majority of the uranium will be passed through into the next stacked UTEVA resin. HCl can be used to elute Th from the TEVA resin, while Pu and Np will remain in the column due to their much higher retention (k') values. However, HCl extraction was not necessary in this work, as thorium analysis was not investigated.

Figure 3.1. Acid dependency curve of TEVA resins for actinides at varying acid concentrations of HNO_3 (Left) and HCl (Right). (image credit: Eichrom Technologies).

UTEVA resins consist of diamyl amylphosphonate (DAAP) and form nitrate complexes with the actinides. The retention increases with increasing concentration of nitric acid, which is used to dissolve the sample. **Fig 3.2** shows the uptake of actinides with varying HNO_3 concentrations.

Figure 3.2. Acid dependency curve of UTEVA resins for actinides at varying acid concentrations of HNO_3 (Left) and HCl (Right). (image credit: Eichrom Technologies)

There is a strong retention for most of the tetravalent actinides and hexavalent uranium. Since the tetravalent plutonium has firstly been removed from the sample through the use of TEVA resins, the uranium present in the eluted solution passing

through the TEVA resin will then be retained in the UTEVA resin. For both TEVA and UTEVA resins, the elution was performed using 0.1 % HEDPA for the elution of Uranium from UTEVA as described by Nygren et. al.¹⁵ (1-hydroxyethylidene diphosphonic acid) (see experimental **section 3.3**). In this case, we did not perform any elution for TEVA as we are concerned with uranium in this chapter.

3.3 Experimental

Mass spectrometric analysis was performed on an Agilent 7700x ICP-MS with a quartz cross-flow nebulizer and a quadrupole mass analyzer. The following certified reference materials were used: (a) IRMM-086 containing 3.75×10^{-6} mol g⁻¹ of ²³⁹Pu (97.8 % ²³⁹Pu, 2.19 % ²⁴⁰Pu, 0.024 % ²⁴¹Pu, 0.0074 % ²⁴²Pu and 0.003 % ²³⁸Pu in 5 % HNO₃), (b) IRMM-054 containing 3.95×10^{-6} mol g⁻¹ of ²³⁵U (0.995 % ²³⁴U, 93.176 % ²³⁵U, 0.418 % ²³⁶U and 5.41 % ²³⁸U in 5 M HNO₃) and (c) IRMM-073/15 with 6.38×10^{-9} mol g⁻¹ of ²³⁵U (50 % ²³⁵U and 50 % ²³⁸U in 1.6 M HNO₃). The above IRMM reference solutions were purchased from the Institute for Reference Materials and Measurements (IRMM, Belgium).

Analytical grade HNO₃ (65 %, EMSURE[®] ISO, Merck) and HCl (37%, EMSURE[®] ISO, Merck) were used. 60 % 1-Hydroxyethylidene-1,1-diphosphonic acid (HEDPA) in water was obtained from Tokyo Chemical Industry, Japan. TEVA and UTEVA resins (100-150 µm) were obtained from Eichrom Technologies, USA. Uncertainty calculations were performed as these provided an indication of confidence on the experimental results. Uncertainties calculations were performed on the General Uncertainty Measurement (GUM) software with k factor =1. The GUM workbench evaluates the uncertainty in measurement based

on the user defined model equation which is used in calculating the final experimental value in each set of the experiments.

TEVA and UTEVA resins (100-150 μm , Eichrom Technologies, USA) were used to chemically separate U and Pu prior to analysis by ICP-MS. These resins are unstackable, thus the sequence for separation is to have samples first passing through the TEVA resins, which traps primarily tetravalent actinides, then followed by the UTEVA resins, which have high selectivity for U (VI). Both resins were conditioned by passing 5 mL of 3 M HNO_3 before loading of the sample into the TEVA resin. 6 mL of sample passing through the resin (TEVA) is made up of 4.9 mL sample of interest (IRMM-086), 0.1 mL of uranium sample [natural uranium (NU), highly enriched uranium (HEU) or weapon grade uranium (WGU)] and 1 mL of concentrated nitric acid were passed through the TEVA resin to extract the plutonium isotopes. The Pu-stripped sample was next passed through the UTEVA resin to extract the uranium isotopes. The TEVA resin was rinsed with 10 mL of 9 M HCL (to remove Th that may be present in soil samples, if such samples were to be analyzed) and followed by 20 mL of 3 M HNO_3 (to remove traces of U).¹⁴ The trapped plutonium was eluted out with 5 ml of 0.1 % HEDPA. Note that although the TEVA resin traps primarily tetravalent actinides (e.g. the Pu isotopes); it has a finite affinity for the uranium isotopes; the TEVA fraction was hence ‘contaminated’ with a small but significant amount of uranium.

The UTEVA resin was rinsed sequentially with 10 mL of 5 M HCL (to remove any Th) followed by 5 mL of 3 M HNO_3 (to remove any trace Am) and U was eluted from the UTEVA resin with 5 ml of 0.1 % HEDPA. Due to the high retention of Pu by the TEVA resin in the previous step, the UTEVA fraction is free from Pu isotopes and contains only uranium. A procedural blank was performed

for each experimental set. 6 mL of 3 M HNO₃ was treated as the sample blank, passing through both TEVA and UTEVA resins and eluted in the same manner as described for the samples. The analysis was performed on an ICP-MS with 1000 sweeps and integration time of 0.1 s for the masses of interest; 238, 239, 240 and 241. Each run had 3 replicate measurements and the signal counts per second (CPS) reflected are an averaged of the repeated readings.

3.4. Results and Discussion

3.4.1 Conceptual framework

Figure 3.3. Schematic diagram of how the amount of m/z 238 is differentiated from the natural ^{238}U .

Figure 3.3 shows the calculations involved after the analysis of the eluted samples by ICP-MS after passing through the SPE cartridges. TEVA and UTEVA resins both trap uranium but TEVA traps Pu primarily with a better retention factor, hence samples were passed through the TEVA resin first to separate the Pu before passing through the UTEVA resin which traps the uranium.

In this method, we use the principle that ^{235}U and ^{238}U will be trapped equally in both TEVA and UTEVA resins. The isotope ratio value from the UTEVA resin is important as this fraction is not interfered with by Pu, as the Pu in the samples have been chemically separated by the TEVA[®] resins in the first step of the separation procedure.

Since the uranium isotope ratio of ^{238}U and ^{235}U in UTEVA was readily determined (**Step 1**), the same isotopic ratio of $^{238}\text{U}/^{235}\text{U}$ can be applied to the TEVA eluted fraction (**Step 2**). As there is no isobaric interference at m/z 235, this allows the measurement of ^{235}U present in the TEVA fraction by ICP-MS and account for the ^{238}U present in the TEVA fraction as shown in **Equation 1**.

$$Pu238_{TEVA} = Total\ 238_{TEVA} - \frac{U238_{UTEVA}}{U235_{UTEVA}} U235_{TEVA} \quad \text{Equation (1)}$$

The above-proposed numerical correction potentially allows analysis of Pu samples without the need for alpha spectrometry as it accounts for the isobaric interference by ^{238}U . The determination of Pu by using only ICP-MS was validated using IRMM-086 solution and the results will be discussed in section 3.4.2. The main contributors to the overall uncertainty in the calculated isotopic ratio of $^{238}\text{Pu}/^{239}\text{Pu}$ comes from the m/z 235 in TEVA from ^{235}U . The value of ^{238}U in TEVA comes from the ^{235}U in TEVA. Hence, the higher the error in ^{235}U in TEVA leads to higher error in the calculated ^{238}U in TEVA which hence affects $Pu238_{TEVA}$ in equation 1. Therefore, it is noted that the uncertainty contributions obtained from GUM has a reported uncertainty index % of 87.8% when no enriched uranium is added and it decreases to 1.6% when enriched uranium (WGU) is added. Although in this case the uncertainty % index increases for

TEVA_{total 238}, based on the experimental data on the isotopic ratio uncertainty, it suggested that the overall uncertainty is more sensitive towards the TEVA₂₃₅ counts. Detailed equations that are used to derive the related uncertainties contributed to the final uncertainty in isotopic ratio of $^{238}\text{Pu}/^{239}\text{Pu}$ are presented in the supplementary information **SI 4**. The range of values for the experimentally determined ^{238}Pu in **equation 1** ranges from 9483 cps to 2173 cps (Total 238_{Teva}) and the subtraction of the signal attributing from ^{238}U in TEVA ranges from 8017 cps to 340 cps. The difference between the subtractions of these two parameters increase as the uranium enrichment increases in the loading sample (spiked WGU). An attempted measurement of the $^{238}\text{Pu}/^{239}\text{Pu}$ was performed without any correction proposed in this work.

For instance, the IRMM-086 was diluted to ensure “trace” levels of ^{238}Pu and natural uranium in 1 ppm concentration was added to illustrate the importance of correcting for the natural uranium counts. Results showed that the isotopic ratio calculated based on ICP-MS analysis with correction is 5.02×10^{-3} and the certified ratio given is 3.10×10^{-5} . Without the corrections proposed in Fig.3 and Eqn 1, the experimental $^{238}\text{Pu}/^{239}\text{Pu}$ calculated was 0.75. The corrected ratio has a lower percentage bias compared to the uncorrected ratio, however, the corrected data is inaccurate and further adjustments have to be made. The raw data of this example can be found in the supplementary information (**SI 4**). More notably, with the corrections, the m/z value at 238 will not be “mistaken” to be ^{238}Pu in excess, leading to a wrong categorization of the plutonium samples. For instance, IRMM-086 is a weapon grade sample, however, without the corrections, the IRMM-086 gives a ratio expected for reactor-grade based on the $^{239}\text{Pu}/^{\text{Total}}\text{Pu}$ calculated to be of smaller value due to the higher $^{\text{Total}}\text{Pu}$ where ^{238}U is mistaken for ^{238}Pu .

Therefore, the use of Eqn.1 for the determination of ^{238}Pu in samples containing natural uranium is applied. The applied correction will lead to correct determination of the plutonium samples comparing with the certified ratio. Nevertheless, there is still poor accuracy for the $^{238}\text{Pu} / ^{239}\text{Pu}$ ratio and this is likely due to insufficient amount of ^{235}U being trapped in the TEVA resins leaving to a large uncertainty of the value.

3.4.2 Isotopic ratio measurements of Pu with quadrupole ICP-MS

Results were not satisfactory when the original IRMM-086 solution samples were loaded directly, due to low amount of ^{235}U present in the loading solution. Therefore, the addition of extra natural uranium standards were made based on increasing the concentrations of the spike (500 ng/mL and 1000ng/ml). The results of experiments are given in Table 1, Entries 1-5. However, the amount of ^{235}U present was still not sufficient for an accurate calculation. Therefore, subsequent experiments were performed with an attempt to increase the amount of ^{235}U present in the samples (Table 1, Entries 6-10) using more highly enriched uranium.

Table 3.1. Amount of ^{235}U and ^{238}U added into SPE load solutions are varied by spiking 100 μl of U isotopes in varying ratios.

Entry	^{235}U in spiked in load [ng/mL]	^{238}U spiked in load [ng/mL]	Experimental($^{238}\text{Pu}/^{239}\text{Pu} \times 10^{-5}$) $\pm$ relative uncertainty %	Certified $^{238}\text{Pu}/^{239}\text{Pu}$ ($\times 10^{-5}$)
1	5.98E-02	8.24	1.40 $\pm$ 182	3.10
2	5.98E-02	8.24	2.90 $\pm$ 110	3.10
3	5.98E-02	8.24	6.20 $\pm$ 22	3.10
4	0.12	16.60	1.00 $\pm$ 700	3.10
5	0.12	16.60	2.00 $\pm$ 400	3.10
6	12.5	12.5	3.60 $\pm$ 25	3.10
7	12.5	12.5	3.10 $\pm$ 29	3.10
8	1.55	8.99E-02	3.63 $\pm$ 6	3.10
9	3.10	0.18	3.34 $\pm$ 11	3.10
10	7.75	0.45	3.53 $\pm$ 9	3.10

The amount of ^{235}U added into the sample was shown to lead to improvements in the percentage relative uncertainty of the $^{238}\text{Pu}/^{239}\text{Pu}$ calculated experimentally. This trend can be explained with reference to Equation 1. The amount of ^{238}U present in column containing the TEVA resin is accounted for based on the ratio of ^{235}U and ^{238}U being trapped in the column containing the UTEVA resin, which traps primarily uranium. The column containing the TEVA resin has the capability to trap uranium, apart from its primary use for separating Pu from samples, although the retention capability is low with $k' < 10$. Therefore, the amount of uranium in the TEVA resin has to be sufficient for the numerical corrections to be carried out. Based on the above table, the amount of ^{235}U present has to be at least 1.55 ng/mL (Entries 8-10, **Table 3.1**) and ^{238}U to be present in at least 0.09 ng/mL. Based on **Table 3.1**, the amount of enriched uranium spiked into the load sample

will have to lie in the weapon grade category in order for the mathematical corrections to have a reasonable uncertainty.

This method hinges on the fact that the $^{235}\text{U}/^{238}\text{U}$ isotope ratio in the TEVA fraction would be identical to that in the UTEVA fractions. Another requirement is that the UTEVA fraction is free from any plutonium isotopes, which could be achieved with treating the sample with TEVA resins in the first step of the separation procedure. The above-proposed numerical correction potentially allows analysis of plutonium samples without the need for alpha spectrometry as it accounts for the isobaric interference by ^{238}U . The categorization of plutonium using only ICP-MS was validated using IRMM-086 solution and comparing to the certified value provided. The calculated uncertainty measurement for $^{238}\text{Pu}/^{239}\text{Pu}$ was performed using GUM workbench with a coverage factor of $k=1$.

3.5 Conclusion

In this Chapter, the addition of enriched uranium i.e. weapon grade to plutonium samples has been shown to improve the measurement of ^{238}Pu using the proposed mathematical correction (**equation 1**). The analysis was performed with a quadrupole ICP-MS leading to a relatively small 10 % bias from certified value (**Table 3.1**, entry 9). This allows a complete analysis of the plutonium isotopes without the potential need of radiometric methods. The analysis can be performed within a single day and thus is useful for samples that require rapid information on the nature of the plutonium samples (grade of plutonium). The sample preparation required for such analysis is simple and requires less amount of reagents, and is often less laborious than alpha spectrometry analysis. In addition, the time required upon completion of the sample preparation for analysis is reduced significantly.

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Analysis of uranium in different enrichment levels using inductively coupled plasma mass spectrometry and the calculations of associated uncertainties without clean room facilities

4.1 Background of work

The analysis of enriched uranium is critical as it determines the grade of uranium samples (discussed in Chapter 2). Long-lived radionuclides generally emit weaker radioactive decay products (alpha, beta particles and gamma rays) therefore measurements by radiometric techniques will not be optimum, as more samples are required to achieve better results. The use of non-radiometric techniques such as ICP-MS is a powerful tool for quantifying the long-lived radionuclides and obtaining isotopic ratio information. ICP-MS is able to simultaneously provide isotopic information on the sample without multiple injections. Hence isotopic information on ^{234}U , ^{235}U and ^{238}U can be obtained in a single injection. There are several types of ICP-MS and the most commonly used ICP-MS in a routine analytical lab is the quadrupole ICP-MS. It has a relatively lower cost than other high-resolution ICP-MS such as the sector-field ICP-MS (SF-ICP-MS) and the multi-collector (MC-ICP-MS). In addition, the maintenance of a quadrupole ICP-MS is less complex and the time required for running each sample is shorter as additional time is required for adjustments in the magnet used in the high resolution ICP-MS. This makes the quadrupole ICP-MS a rapid and high

throughput technique. However, in terms of sensitivity, the quadrupole ICP-MS has a lower sensitivity as compared to a Sector field ICP-MS and MC-ICP-MS.

The other major type of ICP instrument is an ICP-optical emission spectrometer (ICP-OES), which faces spectral interferences that are more serious than the isobaric interferences faced by ICP-MS, which can typically be resolved with the use of a collision gas for removal of interferences. ICP-OES measures the emission wavelengths emitted by the elements of interest and this technique is unfortunately not suitable for radiometric measurements. The isotopes of the same elements cannot be differentiated because their emissions occur at very similar wavelengths, leading to serious overlapping of the emission lines. However, with recent developments in ICP-OES, a high-resolution instrument is available in the market with reported ability to provide information on the U isotopic composition with a satisfactory measurement uncertainty.¹

Uranium is ubiquitous in the environment and this makes the analysis of uranium under normal laboratory conditions problematic, as contamination of samples from the environment is inevitable. Identifying the sources of contamination is important as this can allow suitable modifications to the procedures involved in sample preparation to reduce the interference and hence improve the sensitivity of the technique.

In this chapter, uranium samples in varying enrichment levels were analyzed with the use of a suitable sample preparation step, namely LiBO₂ fusion. The final sample was analyzed by quadrupole ICP-MS and the overall relative uncertainties involved in the analysis was calculated with the use of desktop General Uncertainty Measurement (GUM) software. Prior to this, a study involving the

identification of the potential sources of uranium contamination was performed. The main outcome of this work is to understand the analytical performance of a quadrupole ICP-MS in a normal laboratory environment without clean room facilities for analyzing uranium samples.

4.1.1 Quadrupole ICP-MS

The quadrupole ICP-MS is a cost effective mass spectrometric instrument, which is commonly found in analytical laboratories. The ICP part of the instrument is the source of ionization while the MS part of the instrument is responsible for differentiating the different mass numbers present and allowing quantification with the use of an external calibration or internal standard. The source of ionization of the ICP-MS is made up of Ar^+ ions maintained at a temperature as high as 8000 K. Argon has a 1st ionization potential of 15.75 eV and is one of the highest elemental 1st ionization potentials except for He, Ne and F. The 2nd ionization potential of Ar however is lower than most of the elements in the periodic table, with some exceptions such as notably Ca, Sr and Ba. This means that Ar^+ is able to ionize most of the elements in the periodic table to their first singly positively charged ions (M^+). Since Argon has a low 2nd ionization potential, it means that there is insufficient energy for 2nd ionization to happen for most of the elements, with some exceptions.

One of the commonly used ICP-MS for sample introduction is the laser-ablation ICP-MS (LA-ICPMS) where solid samples can be directly determined without any chemical preparation. This method is timesaving however; radionuclide, which may be present in trace amount, will suffer from matrix suppression. However this can be overcome with a chemical separation of the samples such as Solid Phase

Extraction (SPE) to separate the elements of interest from the matrix and also serve as a pre-concentration of the elements of interest. In this work, a quadrupole ICP-MS with a liquid sample introduction system was adopted hence sample preparations prior to analysis is required (especially for solid samples).

Once the liquid sample is injected into the system, 5 key processes take place in the ICP-MS: nebulization, desolvation, vaporization, atomization and finally ionization into a singly positively charged ion.

Figure 4.1. Key processes in plasma interface of the ICP-MS.

The ion beam leaving the plasma is subsequently directed into the mass spectrometer for mass/charge separation. The mass spectrometer is made up of precisely aligned square array of 2 pairs of rods. Ions of certain m/z ratios are able to pass through the quadrupole. Upon hitting the detector, a certain voltage is generated which is then converted to the amount of ions hitting the detector (Counts per second, CPS) during the window frame opened for that particular m/z value. The working mass range of the quadrupole ICP-MS covers from 2-260 amu giving a mass spectrum of most of the elements and information can be obtained simultaneously with different masses of interest in a single injection of sample. For the absolute amount of sample present to be obtained, the use of an internal

standard is adopted in this work, which also allows any instrumental drift to be detected.

For this study, a fusion method for solid samples was adopted for prior to analysis and will be further discussed in the subsequent section 4.1.2.

4.1.2 Sample preparation: Lithium borate fusion

There are several commonly used sample solubilisation treatment methods such as microwave digestion, borate fusion and acid dissolution. Fusion is usually used to decompose samples that are hard to dissolve in acid dissolution. Samples such as soils and silicates require the use of fusion to ensure total dissolution. For fusion, the flux material together with the sample is heated under high temperature (~1000 °C), which is sufficiently high to melt the flux into a molten state, and where the sample mixture will react. Microwave digestion operates under pressurized conditions at elevated temperature in a closed-vessel system. Under pressurized conditions, the temperature in the vessel is able to reach above the boiling of the digestion media (eg: HNO₃, HCl, etc) within a short period of time (approx. 15-20 mins), allowing complete digestion to be achieved. However, microwave digestion often requires the use of dangerous acid, HF for complete digestion of siliceous samples mainly soil and sand. The use of HF acids in sample preparation is often not desirable as it can cause etching of the glass surfaces of the ICP-MS during analysis. HF acid is also difficult to handle as it is highly corrosive and poses a high safety risk to researchers. Therefore, the use of Lithium borate fusion is more desirable for environmental samples such as soil.

4.2 Experimental

4.2.1 Inductively coupled plasma – quadrupole mass spectrometry (ICP-Q-MS)

A 7700x Agilent Technologies ICP-Q-MS equipped with a quartz concentric nebulizer was used in this work. A covered integrated autosampler (I-AS) offering 89 sample vials capacity with 3 rinse vials was connected to the ICP-MS. The operating parameters of the ICP-MS in no gas mode are summarized in the following Table 1.

Table 4.1. Operating parameters for 7700x ICP-MS.

RF power [W]	1550
S/C temperature [°C]	2.0
Sample uptake [rps]	0.1
Carrier gas [Lmin ⁻¹]	1.15-1.20
Integration time [sec]	0.1
Sample depth [mm]	10
Omega lens [V]	8.5
Omega bias [V]	-95
Extract 1 [V]	2.7
Extract 2 [V]	-200
Plate bias [V]	-50
Deflect [V]	11.8
Number of replicates	3
Dead time [ns] ^a	30

^a ICP-MS calibrated dead time.

The 3 rinse vials consists of (i) 5 % HNO₃, (ii) millipore ultrapure water (18.2 MΩ cm⁻¹), and (iii) tuning solution. The ICP-MS was equipped with platinum sampling and skimmer cones and a peri-pump with tygon tubing with internal diameter 1.02

mm for sample delivery. ^{233}U was added into the sample preparation fusion step to account for losses and quantification of the uranium isotopes.

4.2.2. Borate fusion procedure and chemical steps prior to analysis

0.1 mL of IRMM (Institute for Reference Materials and Measurements) solutions were spiked as samples into 2 g of flux consisting of silica and lithium metaborate, LiBO_2 in the ratio of 1:4.5. 0.1 mL of ^{233}U was spiked as an internal standard for the determination of U isotopes. The IRMM solutions used in this work were: IRMM 073-15 containing $6.38 \times 10^{-9} \text{ mol g}^{-1} {}^{235}\text{U}$, IRMM-054 with $3.95 \times 10^{-6} \text{ mol g}^{-1} {}^{235}\text{U}$ and ES2-1 (CMX-4) which is a lowly enriched uranium solution with 2.15 % of ^{235}U which amounts to $1.92 \times 10^{-11} \text{ mol g}^{-1} {}^{235}\text{U}$. The sample flux was contained in a carbon crucible and subjected to 1050 °C for 15 minutes. Glassy pellets were formed and dissolved by stirring in 100 mL of 1.4 M HNO_3 . Upon complete dissolution, 0.36 g of polyethylene glycol (PEG-2000) was added into solution to flocculate the silicates and the solution left stirring at 140 °C until the total volume was halved. The concentrated solution was left to stand overnight for cooling. The solution was passed through a filter paper to remove the precipitated silica. 5 mL of 2.8 M HNO_3 was added into the beaker for rinsing to ensure complete transfer of the samples. The key step in this procedure lies in the filtering process. Prior to filtering, the filter paper has to be washed with 50 mL 2.8 M HNO_3 . The reason for this will be further discussed in the following section 4.3.

In this work, the situation was mimicked where there might potentially be both Pu and U present in the samples. Hence, chemical separation of Pu and U was performed using commercial extraction chromatographic resins, UTEVA (Eichrom Technologies, USA) which is made up of a neutral organophosphorous diamyl

amylphosphonate extractant mounted onto an inert polyacrylamide support. However, small amounts of Pu can also be trapped by this resin, therefore, an extraction with TEVA (Eichrom Technologies, USA) resin is necessary to remove the Pu from the samples before passing the samples through the UTEVA resins. Chemical separation of U and Pu by these commercially available resins have been widely reported.^{5,6}

The TEVA and UTEVA resins were conditioned with 5 mL of 3 M HNO₃ prior to sample loading. Both TEVA and UTEVA were eluted with 5 mL 0.01 % 1-Hydroxyethylidene diphosphonic acid (HEDPA). The above fusion protocol was recommended by the FOI (Sweden) radiochemistry team and the above-mentioned method is a commonly used technique for solid samples preparation (soil in particular) prior to analysis.

4.3. Results and discussion

The following sections include the results of this study where the sources of natural uranium contamination during the process of sample preparation to analysis were identified. The approach of this work is by a process of elimination to find the procedures that might have introduced uranium contamination.

4.3.1 Mechanical processes –overnight standing

The glassy solid pellets that were dissolved in 100 mL of 1.4 M HNO₃ and evaporated to half the volume of 50 mL were left to stand overnight. The standing of solution overnight was investigated for any contributions of uranium coming from the fume hood environment. The presence of uranium in the environment might introduce contamination causing inaccurate isotopic ratio measurements. To determine the effect of overnight cooling of the solution on the overall blank

natural uranium content, duplicate experiments were performed with overnight standing of the solution upon addition of PEG and evaporation. Another set of experiments was conducted where the solutions were left to cool in an ice bath for approximately 2 hours to allow the precipitation of the silicates followed by allowing the solution to warm to room temperature (n=2). In these experiments, the solutions were filtered with a disposable plastic cased syringe filter (Sartorius, PES membrane, 0.2 μm) instead of the filter paper to avoid additional potential contribution of uranium and the acid blank solutions were passed through the PES syringe filters which were found to have no contribution to the samples (signal counts per second were equivalent to direct analysis of acid blanks). Based on the data in **Fig 4.2**, it can be seen that the overnight standing of the heated solution to room temperature followed by the standard experimental procedures stated in section 4.2. showed that there is no additional introduction of natural uranium into the solution comparing to the results for ice-bath.

Figure 4.2. Comparison of amount of natural uranium when solutions are left overnight and in an ice bath.

4.3.2 Filter paper

The filtering process to remove the precipitated silicates was found to be a source of natural uranium when Grade 1 Cellulose (Whatman, USA) was used during the sample preparation steps (Figure 2). The Grade 1 cellulose filters were found to leach natural uranium into the solution with increasing acidity. This can be further supported by the processing of the filter paper by microwave digestion (EthosOne, USA). The Whatman grade 1 cellulose filter paper was digested in 10 mL of 40.6 % HNO_3 under 1000 W with a ramping time of 20 mins to reach the desired temperature of 185 °C, which was held at that temperature for 15 mins to ensure complete dissolution of the filter paper. Upon complete digestion, the digested samples were diluted to 100 mL volume with UPW. The uranium content was calculated with reference to the 0.1 mL of internal standard, ^{233}U added to the 5 mL sample vial for analysis by ICP-MS. The uranium content of half of the filter paper was found to be 2.06 ng of ^{238}U and 0.02 ng of ^{235}U (n=2) and these are calculated based on the internal standard ^{233}U . This suggests that a half Whatman grade 1 cellulose filter is expected to introduce a uranium content of approximately 4.79 ng per gram of filter.

Figure 4.3. Increasing concentration of HNO_3 shows increase in concentration of natural uranium.

Another supporting experiment to show that natural uranium leaches the most from filters in contact with HNO_3 with increasing molarity. At 0 M, which means only ultrapure water passes through the filter paper, 0.004 ng/mL of natural uranium is calculated to be present in the filtrate solution. However, when acid passes through, the amount of uranium present in the filtrate is calculated to contain 0.10 ng/mL of ^{238}U for 0.7 M of HNO_3 to 0.12 ng/mL for 2.8 M of HNO_3 . The choice of filter paper is therefore important to ensure leaching of uranium from the filter paper is avoided. The contribution of the analytical grade HNO_3 acid in this work does not have significant influence in the uranium contribution as the amount of uranium contributed has a signal intensity of <500 CPS for a 5 % HNO_3 rinsing solution.

Grade 1 Whatman cellulose filters (Qualitative grade) were used to filter the sample solution after overnight standing. The overall amount of natural uranium,

^{238}U present in the solution passed through the filter was found to be present at a concentration value of 2.78 ng/mL (n=3). Another set of experiments was performed by rinsing of the filters prior to filtering. The filters were rinsed by passing 1.4 M HNO_3 acid 5 times prior to filtering. The amount of ^{238}U was found to reduce by twice the amount to 1.35 ng/mL (n=6). The results are summarized in Figure 3. Rinsing of the filters prior to filtering of the sample solution was found to reduce ^{238}U leaching out of the filters. This also confirms that the Grade 1 cellulose filters are a source of uranium.

Figure 4.4. Comparison of overall ^{238}U concentration unwashed cellulose filters and cellulose filters washed with nitric acid.

Hence, further rinsing experiments were performed with the Grade 1 cellulose filters. A single cellulose filter paper was rinsed several times and the filtrate was analyzed by ICP-MS to check on the rinse times required to achieve ^{238}U CPS as low as possible. The filter papers were taken from the top, middle and bottom layer of the box and multiple rinses were performed. 50 mL of 2.8 M HNO_3 was passed through each time and analyzed by ICP-MS. The rinses required to reduce the natural uranium leaching were as many as 5 times (**Fig 4.5**). After the 5th rinse, the amount of uranium that was found to have leached into the solution was 0.12 ng/mL. Rinsing beyond the 5th time was not performed. However, multiple rinses are not desirable as they made the filter water fragile and hence increased the risk of tearing when the samples with precipitate pass through.

Figure 4.5. Three filters of cellulose grade were rinsed 5 times with 2.8 M HNO₃ and the filters were taken from the top, middle and bottom layers of the same box.

Therefore, the use of a pre-treated filter is necessary and this leads to the proposal of ashless grade filters. This particular grade of filter has already been acid-washed, hence should have lesser amount of natural uranium leaching out when an acidic medium passes through. The use of ashless grade (Whatman, USA and Ahlstrom, Finland) filters does lead to a huge reduction in the natural uranium background. Top, middle and bottom samples from a box of the ashless (Whatman, USA and Ahlstrom, Finland) filters were rinsed 5 times (**Fig 4.6** and **4.7**).

Figure 4.6. Three ashless (Whatman) filters were rinsed with 2.8 M HNO₃ and individual rinses were analyzed.

Figure 4.7. Three ashless (Ahlstrom) filters were rinsed with 2.8 M HNO₃ and individual rinses were analyzed.

Both Whatman and Ahlstrom brands for ashless grades filter did not show any significant difference in the natural uranium background present in the solution that was passed through after the 1st rinse with 50 mL of 2.8 M HNO₃. Multiple rinses were found to be unnecessary as the CPS does not further decrease significantly after multiple rinses (**Fig 4.6 and 4.7**). The solution in the 1st rinse, contributes 0.2 ng/mL of natural uranium and the amount after the 2nd rinse subsequently decreases to 0.02 ng/mL, while Ahlstrom ashless filters leached 0.042 ng/mL after the second rinse. The amount of uranium leaching through the filters remains reasonably constant after the first rinse suggesting the bulk of uranium leachable has been removed. Therefore, a single rinse will be sufficiently good for removing the majority of the uranium that is “leachable” out of the filter. The results are summarized in **Figure 4.8** for the filtering experiments performed. **Figure 4.8** shows that ashless filters have lesser variations in the uranium leaching out after the 1st rinse whereas, cellulose have a huge variation in the “leachable” uranium after the 5th rinse. This is not desirable as this will lead to a huge variation in the uranium content determined if cellulose filters were adopted in the procedure.

Figure 4.8. The averaged concentration of 3 filters taken from the top, middle and bottom layer of each box of filter type- Ashless (Whatman) and cellulose.

The impact on the uranium procedural blank signal using untreated grade 1 cellulose and ashless grade filters are summarized in **Figure 4.9**, where the entire sample preparation procedure was described in section 4.2.2. The use of a cellulose unwashed filter resulted in 2.78 ng/mL of natural uranium present in the procedural blank. After 5 times rinses with 50 mL of 2.8 M HNO_3 , the natural uranium in procedural blank was reduced to 1.35 ng/mL, which is still higher than using unwashed ashless filter which has 1.02 ng/mL of uranium present in the blank.

Figure 4.9. Three different filters are used in the procedure for preparing solid samples prior to ICP-MS analysis (n=2). *Filters that are washed x5 were shown on the left with 1.4 M HNO_3 . ** Filters with one rinses .

The use of a washed (50 mL 2.8 M HNO_3) ashless (Whatman or Ahlstrom) filter resulted in uranium contents of 0.98 and 1.05 ng/g in the first-rinsed solution, respectively. The use of an ashless grade filter is hence better for the analysis of uranium samples with 50 mL of 2.8 M HNO_3 rinsing off any natural uranium from the filters. From the above Figures 4.6 and 4.7, we can also conclude that the rinsing of ashless filters more than twice has partial impact on reducing the natural uranium present in the procedural blank and this leads us to the next component of the chemical procedure which may further reduce the amount of the uranium present in the blank process.

4.3.3 Lithium borate

The lithium borate is used in the fusion step. It is an effective technique for decomposing minerals without the need for hazardous hydrofluoric acid (HF). The lithium metaborate (LiBO_2) is available commercially from Claisse (Canada) in two main grades: trace metal and ultrapure. Following the use of ashless grade filters in **section 4.3.2**, the use of trace metal and ultrapure grade of LiBO_2 were compared (**Fig 9**).

Figure 4.10. The use of a trace metal and ultrapure grade LiBO_2 is compared. Natural Uranium is found to be lesser with the use of ultrapure grade.

The use of ultrapure LiBO_2 is favorable as this reduces the overall natural uranium present in the blank by approximately 2.5-fold. This is equivalent to approximately 0.98 ppb natural uranium present in the overall procedural blank without the use of an ultra-pure LiBO_2 , which is reduced to 0.40 ppb of natural uranium present in the procedural blank when ultrapure LiBO_2 is used.

4.3.4 Silica gel

The silica gel used in this sample represents the potential environmental samples such as sand and soil. Si atoms in the presence of the fusing agent, LiBO_2 form Si- LiBO_2 bonds, which allows the sample to form a glassy pellet. Silica is typically produced by purifying sand and it is likely to contain natural uranium. Experiments were performed to prove that the addition of silica into the fusion process contributes to the overall process blank for the fusion process. These experiments were performed by reducing the amount of silica in the fusion mixture, since analysis of silica itself is not possible without the use of HF acid. If silica is indeed contributing to the natural uranium contamination, there should be a reduction in the CPS for natural uranium in the overall process blank when the amount of silica in the fusion mixture is reduced.

Figure 4.11. The reduction of silica gel in the fusion flux has showed a decrease in the amount of natural uranium.

When the amount of silica was reduced, a corresponding reduction in the CPS of process blank ^{238}U was also observed. Halving the amount of Si resulted in a

corresponding reduction of 0.069 ng/g of ^{238}U . For experiments performed without any Si, the amount of ^{238}U was further reduced by 0.062 ng/g comparing with experiments with halved the amount of Si. The amount of ^{238}U contained in a flux mixture with no silica but going through the whole fusion process was calculated to be 0.19 ng/g. In comparison, the control experiments with 0.36 g of Si added (Section 4.2.2) showed the presence of 0.33 ng/g of ^{238}U .

4.4 Analysis of enriched uranium

4.4.1. Mass bias correction for ICP-MS analysis

Mass bias is encountered in ICP-MS analysis when different ion masses are transmitted through the spectrometer with different efficiencies. This leads to varying sensitivity across the mass range, hence affecting the accuracy of isotopic ratio measurements.² The occurrence of mass bias in a quadrupole ICP-MS is typically from the space charge effect where lighter mass ions are deflected by the heavier mass ions present in the sample at the interface region. Space charge is caused by a net charge imbalance by an excess of charged particles which in the ICP-MS the positive ions experience a mutual repulsion which results in a loss in the ion transmission efficiency and sensitivity.³ The loss in sensitivity is due to the defocusing effect of the ion flow and is a function of the ion's kinetic energy.⁴ Since the ion kinetic energy is directly proportional to the mass of the ions ($\text{KE} = \frac{1}{2} mV^2$, where V is the speed of ions). Therefore, the heavier mass ions are preferred and the lighter ions get defocused to a bigger extent and leads to inaccurate isotopic ratio measurements. To correct this discrimination, known materials with accurately determined isotopic composition are used to calculate the correction factor for mass bias. The solution used for mass bias in this work is

IRMM 073-1 containing ^{233}U , ^{235}U and ^{238}U in approximately equal number of moles. An aliquot of this solution is run at the start of the sample analysis and a duplicate done at the end of the sequence to check for any drift in the mass bias correction factor. The mass bias correction factor, k is calculated based on the following equation:

$$k = \frac{R_{true}}{R_{obs}}$$

The mass bias corrections are performed for every single data analysis by applying a correction factor for each mass analyzed (Δm) with reference to the smallest mass in the solution to obtain the R_{true} . Table 2 shows the k correction factor for the different Δm . The exponential and power model for mass bias corrections are more widely used for mass bias corrections in MC-ICP-MS analysis.^{6,8} However, the linear model shown in the above equation has shown successful corrections for a quadrupole ICP-MS.^{6,8} For the k factor value to be determined, a plot of $\frac{R_{true}}{R_{obs}}$ against Δm is plotted and a best fit line is drawn with a $y=mX+C$ relationship established for the determination of k value at different Δm (Figure 4.12).

Figure 4.12. Plot between $\frac{R_{true}}{R_{obs}}$ against Δm for determination of k values.

Table 4.2. Correction factor, k for mass bias corrections (calculated for 7700x ICP-MS used in this work).

Δm	k factor value
1	1.0139
2	1.0278
3	1.0417
4	1.0556
5	1.0695

4.4.2 General Uncertainty Measurement (GUM)

The first step in a GUM procedure is to establish a model for the calculations involved in the experimental procedure. The model is expressed in the form of a series of mathematical equations. The calculation of the results and its associated standard uncertainties is obtained by applying the equation model and the uncertainty propagation involved in each step will be represented in the final answer.

The model equation for calculating the uncertainty in measuring the isotopic ratio of $^{235}\text{U}/^{238}\text{U}$ is described as follow:

$$I_{\text{blankmassbias235}} = I_{\text{blank235}} \cdot \Delta 2;$$

$$I_{\text{blankmassbias238}} = I_{\text{blank238}} \cdot \Delta 5;$$

$$I_{\text{massbiascorr235}} = I_{\text{Exp235}} \cdot \Delta 2;$$

$$I_{\text{massbiascorr238}} = I_{\text{Exp238}} \cdot \Delta 5;$$

$$\text{Conc_U235} = (\text{Conc_U233}/I_{\text{Exp233}}) \cdot I_{\text{massbiascorr235}};$$

$$\text{Conc_U238} = (\text{Conc_U233}/I_{\text{Exp233}}) \cdot I_{\text{massbiascorr238}};$$

$$\text{Concblank_U235} = (\text{Conc_U233}/I_{\text{blank233}}) \cdot I_{\text{blankmassbias235}};$$

$$\text{Concblank_U238} = (\text{Conc_U233}/I_{\text{blank233}}) \cdot I_{\text{blankmassbias238}};$$

$$\text{Conc_NET235} = \text{Conc_U235} - \text{Concblank_U235};$$

$$\text{Conc_NET238} = \text{Conc_U238} - \text{Concblank_U238};$$

$$\text{IR_LEU}^a = \text{Conc_NET235}/\text{Conc_NET238};$$

Where I refer to intensity of the m/z value from ICP-MS (counts per second) and $\Delta 2$, 5 refers to the mass bias correction constant. ^a IR_LEU represents the enriched uranium samples (LEU, HEU and WGU).

4.4.3 LEU, HEU and WGU analysis with uncertainty measurements

From the presented study, sources of natural uranium are identified and rectified to minimize the incorporation of natural uranium into the fusion preparation prior to ICP-MS analysis. At present, the overall amount of natural uranium present in the fusion process is 0.40 ± 0.04 ng/mL of ^{238}U and $(34.9 \pm 9.3) \times 10^{-4}$ ng/mL of ^{235}U (n=35) (Table 4.4). This process blank value is attained with the modifications used: one time-rinsing of ashless filters + ultra-pure lithium metaborate. For each analysis of enriched uranium samples, parallel blanks were performed such that an overall averaged blank concentration was subtracted from the enriched uranium data. Three certified reference materials; lowly enriched uranium (LEU), highly enriched uranium (HEU) and Weapon grade uranium (WGU) are analyzed and the isotopic ratio of $^{235}\text{U}/^{238}\text{U}$ was determined from the ICP-MS data. Uncertainty measurements for each isotopic ratio determined experimentally were calculated using GUM with $k = 2$ at a confidence level of 95 %. LEU samples containing 2.14 % ^{235}U were analyzed with varying amount of LEU samples spiked into the sample preparation process. Results for LEU samples are summarized in the following Figure 12. The following **Table 4.3** shows the results of the amount of samples prepared affects the calculated expanded uncertainty.

Table 4.3. Summary of data on masses of ^{235}U and ^{238}U in final 5 mL volume with expanded uncertainties for LEU samples.

Mass of ^{238}U [ng]	Mass of ^{235}U [ng]	Isotopic ratio of $^{235}\text{U}/^{238}\text{U}$	Expanded uncertainty
0.42	0.009	0.0212	4.90E-04
0.21	0.004	0.0214	5.70E-04
0.07	0.002	0.0217	1.80E-03
0.04	0.0009	0.0253	4.20E-03
0.03	0.0005	0.0186	5.60E-03
0.02	0.0004	0.0186	6.60E-03

Figure 4.13. Calculated LEU ratios with calculated expanded uncertainties by ICP-MS analysis.

The masses of LEU samples prepared with the fusion procedure were varied and it was found that with lower masses of samples, the related uncertainties in the calculated experimental isotopic ratio of $^{235}\text{U}/^{238}\text{U}$ increases. This is because for lower amounts of the LEU samples, the amount of ^{235}U present is lesser and this

means the CPS signal for ^{235}U is low which resulted in higher RSD% for the CPS.

For a confidence level of 95 %, 0.05 ng of IRMM LEU sample is required to achieve an uncertainty below 15 %.

Table 4.4. Concentration of 35 procedural blank sample runs with standard deviation.

	Conc U235 [ng/mL] $\times 10^{-3}$	Conc U238 [ng/mL] $\times 10^{-1}$
	2.87	3.67
	3.81	3.98
	3.30	4.09
	3.81	3.98
	2.73	3.54
	3.81	3.98
	2.35	3.36
	2.96	4.10
	2.87	3.68
	3.81	3.98
	2.74	4.17
	2.70	3.60
	3.50	3.77
	3.65	4.74
	2.70	3.60
	2.98	3.56
	3.50	3.77
	3.79	3.49
	3.39	4.18
	2.65	3.80
	2.70	3.60
	3.63	3.94
	5.11	4.25
	3.63	3.94
	5.11	4.25
	4.16	4.42
	2.93	3.73
	3.65	4.74
	2.88	3.99
	2.93	3.73
	3.39	4.18
	2.88	3.99
	2.93	3.73
	6.30	4.26
	6.20	4.80
Averaged	3.49	3.96
Std dev	0.93	0.37

Table 4.4. Summary of data on masses of ^{235}U and ^{238}U in final 5 mL volume with expanded uncertainties for HEU samples.

Mass of ^{238}U [ng]	Mass of ^{235}U [ng]	Isotopic ratio of $^{235}\text{U}/^{238}\text{U}$	Expanded uncertainty
1.58	1.50	9.49E-01	3.80E-03
0.05	0.05	1.05E+00	8.30E-02
0.03	0.03	1.08E+00	1.70E-01
0.02	0.02	9.49E-01	2.60E-01
0.01	0.01	9.93E-01	0.42

Figure 4.14. Calculated HEU ratios with calculated uncertainties by ICP-MS analysis.

Similarly for HEU samples, the uncertainty of the calculated ratio increases when lower amount of HEU samples was analyzed (**Fig 4.14**). 0.1 ng of IRMM HEU sample is required for uncertainty to fall below 15 %. For WGU samples, 0.47 ng of sample will result in uncertainty below 15 %. Higher amounts of WGU are required as compared to the other grades of uranium as the amount of ^{238}U is now the minor isotope and the presence of ^{238}U in the blank will overpower the ^{238}U in the sample if the amount of WGU is too little, resulting in inaccurate isotopic ratio

measurement with high uncertainty (**Fig 4.14**). At 0.47 ng of WGU samples, the amount of ^{238}U present is 0.03 ng, which is approximately the same level with reference to the amount of HEU required to achieve an uncertainty of less than 15 % (0.1 ng of HEU, 0.05 ng of ^{238}U). On the contrary, LEU samples are dominated by the amount of ^{235}U present because ^{238}U is the dominant species; hence the uncertainty value calculated is more sensitive towards the amount of ^{235}U present in the sample.

Table 4.5. Summary of data on masses of ^{235}U and ^{238}U in final 5 mL volume with expanded uncertainties for WGU samples.

Mass of ^{238}U [ng]	Mass of ^{235}U [ng]	Isotopic ratio of $^{235}\text{U}/^{238}\text{U}$	Expanded uncertainty
0.65	10.44	1.60E+01	0.12
0.12	2.02	1.62E+01	0.47
0.06	1.06	1.64E+01	0.98
0.03	0.45	1.71E+01	2.1
0.02	0.22	1.26E+01	2.5

Figure 4.15. Calculated WGU ratios with calculated uncertainties by ICP-MS analysis.

4.5 Conclusion

The analysis of uranium in samples is impaired by the presence of natural uranium in the laboratory environment so that very careful handling of the samples is essential for accurate measurements of the uranium isotopic ratios. For trace amounts of uranium, the presence of natural uranium will greatly affect the ability for accurate isotopic ratio measurements and the confidence level of analysis will be poor. The process of sample preparation for solid samples or samples with a mixture of plutonium and uranium present will require the fusion process prior to ICP-MS analysis and potentially increase the natural uranium in the sample blank. In the above-mentioned work, sources of uranium contamination were identified. The overall uranium content was found to have a significant contribution coming from the silica gel used for the fusion process to form the glassy solid pellets for dissolution. This component itself has a 50 % contribution to the overall uranium content and the remaining 50 % of the natural uranium present comes from the other contributors such as the filter paper, LiBO_2 , SPE processes as well as handling process which may contribute to the uranium background. Sources of uranium coming from the surrounding environment without clean room facilities are mainly originating from the chemicals and consumables used, which can be minimized through correction factors or through chemical pretreatments. In addition, there are several cost-effective measures such as using HEPA cabinets for storing the chemicals and minimizing natural uranium being introduced into the bottles and such less expensive alternatives that could help to maintain consistency in the natural uranium background while keeping the cost low.

It has been reported that with the double focusing sector-field ICP-MS, the analysis of the ultra-purity water achieved a detection limit for uranium (^{238}U) in

the low range of fg/mL. ⁶ In the case of the single-quad ICP-MS, the analysis of our ultra-pure water in 7 separately dispensed ultra-pure samples, we managed to achieve a 0.11 ppt (based on 3 σ) instrumental detection limit for ²³⁸U. However, the detection limit achieved based on the procedural blanks for the fusion process was 0.11 ppb for ²³⁸U and 0.28 ppb for ²³⁵U, which means that samples of interest will need to have amounts higher than the method detection limit and not instrumental detection limit. The natural contamination from the environment plays a crucial role as the more contributions derived from the environment will lead to an increase in the method detection limit, which is undesirable for trace analysis. Low uranium contamination with < ppt amounts is most likely to be not detected by quadrupole ICP-MS measurements due to detection limit limitations and requires a more sensitive technique such as the sector-field ICP-MS to pick up the environmental fluctuations in natural uranium contamination other than the reported sources from this work (and chapter).

The following **Table 4.6** gives an overview of the sensitivity comparison of the ICP-MS instruments.

Table 4.6. ICP-MS detection limit comparison table.

	ICP-MS (single quad)	ICP-SF	ICP-OES	ICP-QQQ
Detection limit (DL)	ppt level	Typically pgL ⁻¹	Low ppb (~Single ppb)	sub ppt range

For sector field ICP-MS, the high sensitivity and lower background gives better detection limits, typically in the pgL^{-1} range although this is also limited by the blank signal for the element of interest.⁷ In addition to the good detection capability, the main benefit of magnetic-sector instruments is their capability to measure quantitatively with high precision.⁷ However, for sector-field ICP-MS, as the resolution increases, the ion transmission decreases and the detection limit will be compromised under high precision analysis.

On the other hand, the quadrupole ICP-MS has been known to perform poorer than the SF-ICP-MS in terms of sensitivity. It has been reported that the SF-ICP-MS instrument sensitivity range from 10^9 (for U) per $\mu\text{g/mL}$ in low resolution mode, however, with recent advancements in technology, values of more than 10^8 cps per $\mu\text{g/mL}$ have been reported for in for quadrupole ICP-MS.⁸

Therefore in this chapter, we have determined the contamination contributions during our sample preparation procedures and the analysis was performed with the quadrupole ICP-MS. After removal of the natural uranium sources, the amount of enriched uranium samples required have been determined.

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Conclusion

The first portion of this thesis focused on the challenge of sample preparation of iodine containing solid samples, which have been commonly prepared in alkaline media. The method reported in this work utilizes an acidic medium under closed-vessel microwave digestion conditions. The main aim of developing an acidic sample preparation is to allow the simultaneous determination of metallic elements present in suspended airborne particulate samples, which will save the amount of sample and reagents required for sample preparation. This method can also potentially be used for monitoring airborne iodine radionuclides suspended in the atmosphere with the use of polypropylene filters for sampling, which were found to achieve a good recovery for iodine solutions spiked on filters. The analysis of iodine was performed with ICP-MS which is also a common technique used for the remaining two other projects discussed in this thesis.

Regardless of the analytical techniques for determination of radionuclides, it is desirable that the technique is able to provide sufficient sensitivity, accuracy, be rapid, be simply to operate and of low cost (and low maintenance costs). In the presented plutonium and uranium analysis, the use of a quadrupole ICP-MS is able to satisfy the above-mentioned requirements to a large extent. The relative sensitivity in comparison to the other high-end mass spectrometric techniques such as sector-field ICP-MS and multi-collector ICP-MS may be lower. However, the cost of operations and maintenance in the very high-end instruments is problematic for many laboratories. The quadrupole ICP-MS that was used in this study was found to function adequately for uranium analysis without being housed in a clean

room. The natural uranium contaminants present in process blanks were found to originate mainly from the chemicals used, such as the purity of the reagents and the consumables. The environmental contributions to the process blanks were not significant for the quadrupole ICP-MS analysis. However, the sensitivity of the quadrupole ICP-MS might be insufficient to detect the environmental contributions from natural uranium.

For the analysis of plutonium, the use of a high-resolution ICP-MS or a quadrupole ICP-MS will not solve the isobaric interference problems. The use of radiometric technique as such alpha spectrometry is required for complete categorization in plutonium samples. Nevertheless, the use of two instruments leads to more time required to obtain the results. Hence, a numerical correction has been proposed in this thesis to allow ^{238}Pu to be measured, using data collected by first processing the samples through resins that selectively concentrate plutonium or uranium. This sample pre-treatment method allowed good agreement with the certified values from standard isotopic materials with reasonable uncertainties. This method will allow samples to be analyzed using the ICP-MS for a quick screening of the type of plutonium samples. The addition of a small quantity of weapon grade uranium is required for this method to work, as the amount of natural ^{235}U trapped in the TEVA resin is too low, hence the addition of the enriched uranium allows better confidence in the data.

The use of the quadrupole ICP-MS in this thesis has shown the versatility of the instrument in measuring isotopic and environmental samples. The key to multiple applications of ICP-MS for different element lies in developing a suitable and efficient sample preparation method combined with data analysis.

Given the advancements in mass spectrometric methods, the possibility of using a triple quadrupole ICP-MS for plutonium and uranium analysis should be explored. The use of reactive gases such as ammonia gas for Pu and U analysis by the ICP-QQQ-MS has been studied however, other less toxic gases such as CO₂ have been mentioned but there is a lack of experimental data on the possibility for Pu and U analysis.

In the current market, there is an automated fusion oven that allows direct pouring of the samples into the acidic solution without the formation of glassy pellets. Such process would suggest that silica is not required as the formation of glassy pellet is not required for an automated fusion oven. This should be able to lower the overall process blank of the sample preparation prior to ICP-MS analysis. Hence, future studies on using the current advancements in instrumentation might lead to a “cleaner” preparation process and improve the method detection limits.

Supplementary documents

Supplementary information (SI 1)

Table 1. General 7700x ICP-MS operating parameters for iodine analysis.

RF power [W]	1550
S/C temperature [°C]	2.0
Sample uptake [rps]	0.1
Carrier gas [Lmin ⁻¹]	1.15-1.20
Integration time [sec]	0.1
Sample depth [mm]	10
Omega lens [V]	8.5
Omega bias [V]	-95
Extract 1 [V]	2.7
Extract 2 [V]	-200
Plate bias [V]	-50
Deflect [V]	11.8

Supplementary information 2(SI 2)

The following calibration curves in SI 2. was obtained from the ICP-MS analysis of the TSP sample filters obtained during the sampling period.

Figure 1. Calibration graphs for V, Cr, Mn, Fe, Co, Ni, Cu, As and Se with $R^2 > 0.99$.

Figure 2. Calibration graph Be with $R^2 > 0.99$.

Figure 3. Calibration graph Cd with $R^2 > 0.99$.

Figure 4. Calibration graph Pb with $R^2 > 0.99$.

Supplementary information 3(SI 3)

Table 1. Microwave power at 1200 W for EMFAB filters spiked with KI with higher temperatures (n=5).

Entry	Temperature [°C]	Holding time [mins]	Ramping time [mins]	Averaged recovery ± RSD [%]
1	185	15	20	41 ± 19
2	195	15	20	59 ± 33

Supplementary information 4(SI 4)

Table 1. Example of experimental calculations of diluted IRMM solution with 1 ppm of natural uranium added to illustrate the importance of m/z 238 corrections.

UTEVA	cps	isotopic composition
U-235	7069.142	0.61
U-238	1160393.988	99.39

TEVA	cps	isotopic composition	Expt	Certified
Pu-238	5.29E+04	n(Pu-238)/n(Pu-239)	7.52E-01	0.00003105
Pu-239	7.04E+04			
Pu-240	1.53E+03	n(Pu-240)/n(Pu-239)	2.17E-02	0.022434
Pu-241	0.00E+00	n(Pu-241)/n(Pu-239)	0.00E+00	0.0002485
Pu-242	8.00E+00	n(Pu-242)/n(Pu-239)	1.14E-04	0.0000757
Total Pu	1.25E+05			

Isotopes	Atomic mass	Mass fraction	Expt	mass fraction	Expt	Certified
Pu-238	238.0495601	m(Pu-238)/m(Pu-239)	7.484E-01	m(Pu-238)/Total m(Pu)	4.23E+01	3.023E-03
Pu-239	239.0521636		1.000E+00		5.65E+01	9.776E+01
Pu-240	240.0538138	m(Pu-240)/m(Pu-239)	2.184E-02	m(Pu-240)/ Total m(Pu)	1.23E+00	2.202E+00
Pu-241	241.0568517	m(Pu-241)/m(Pu-239)	0.000E+00	m(Pu-241)/ Total m(Pu)	0.00E+00	2.449E-02
Pu-242	242.0587428	m(Pu-242)/m(Pu-239)	1.151E-04	m(Pu-242)/ Total m(Pu)	6.50E-03	7.494E-03
Total m(Pu)=			1.770E+00			

Table 1. (cont'd)

m(Pu-239)/m(Pu)	56.49 %	> 97% --> super weapon grade
m(Pu-240)/m(Pu)	1.23 %	< 3% --> super weapon grade
m(other Pu)/m(Pu)	42.28 %	

Table 2. Corrections were done based on equation

UTEVA	cps	isotopic composition
U-235	7069.142	0.61
U-238	1160393.988	99.39

TEVA	cps
U-235	320.18
U-238	52556.63

TEVA	cps	isotopic composition	Expt	Certified
Pu-238	3.54E+02	n(Pu-238)/n(Pu-239)	5.02E-03	0.00003105
Pu-239	7.04E+04			
Pu-240	1.53E+03	n(Pu-240)/n(Pu-239)	2.17E-02	0.022434
Pu-241	0.00E+00	n(Pu-241)/n(Pu-239)	0.00E+00	0.0002485
Pu-242	8.00E+00	n(Pu-242)/n(Pu-239)	1.14E-04	0.0000757
Total Pu	7.23E+04			

Isotopes	Atomic mass	Mass fraction	Expt	mass fraction	Expt	Certified
Pu-238	238.0495601	m(Pu-238)/m(Pu-239)	5.002E-03	m(Pu-238)/m(Pu)	4.87E-01	3.023E-03
Pu-239	239.0521636		1.000E+00		9.74E+01	9.776E+01
Pu-240	240.0538138	m(Pu-240)/m(Pu-239)	2.184E-02	m(Pu-240)/m(Pu)	2.13E+00	2.202E+00
Pu-241	241.0568517	m(Pu-241)/m(Pu-239)	0.000E+00	m(Pu-241)/m(Pu)	0.00E+00	2.449E-02
Pu-242	242.0587428	m(Pu-242)/m(Pu-239)	1.151E-04	m(Pu-242)/m(Pu)	1.12E-02	7.494E-03
		Total m(Pu)=	1.027E+00			

m(Pu-239)/m(Pu)	97.38	> 97% --> super weapon grade
m(Pu-240)/m(Pu)	2.13	< 3% --> super weapon grade
m(other Pu)/m(Pu)	0.50	

Supplementary information 5(SI 5)

The following model equations are used in the GUM software for the uncertainty calculations for the experimentally determined $^{238}\text{Pu}/^{239}\text{Pu}$.

Corrected with blank subtraction

TEVA238_Pu

TEVA239_Pu

TEVA238_U

TEVA235_U

UTEVA238_U

UTEVA235_U

Definitions

TEVA_TOTAL238 : Total m/z 238 cps from TEVA fraction

TEVA235_Ublank: Blank TEVA m/z 235 cps

TEVA239_Publack: Blank TEVA m/z 239 cps

TEVA238_Publack: Blank TEVA m/z 238 cps

UTEVA235_Ublank : Blank UTEVA m/z 235 cps

UTEVA238_Ublank: Blank UTEVA m/z 238 cps

TEVA235_Uraw, TEVA239_Puraw, UTEVA235_Uraw, UTEVA238_Uraw:

Experimental raw data from ICP-MS

Model equation(s):

$$\text{TEVA235_U} = \text{TEVA235_Uraw} - \text{TEVA235_Ublank};$$

$$\text{TEVA239_Pu} = \text{TEVA239_Puraw} - \text{TEVA239_Publank};$$

$$\text{UTEVA235_U} = \text{UTEVA235_Uraw} - \text{UTEVA235_Ublank};$$

$$\text{UTEVA238_U} = \text{UTEVA238_Uraw} - \text{UTEVA238_Ublank};$$

$$\text{IR_235U} = \text{UTEVA235_U} / (\text{UTEVA235_U} + \text{UTEVA238_U});$$

$$\text{IR_238U} = \text{UTEVA238_U} / (\text{UTEVA235_U} + \text{UTEVA238_U});$$

$$\text{TEVA238_U} = \text{TEVA235_U} * \text{IR_238U} / \text{IR_235U};$$

$$\text{TEVA238_Pu} = \text{TEVA_TOTAL238} - \text{TEVA238_U} - \text{TEVA238_Publank};$$

$$\mathbf{RATIO238Pu239Pu} = \text{TEVA238_Pu} / \text{TEVA239_Pu}$$