Development of a new method to measure environmental Tc-99 in seaweed samples using AMS

by

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Abstract

Since the dawn of the nuclear age, radioactive technetium (Tc)-99 has been released into the environment from nuclear weapons testing, spent fuel reprocessing facilities, and other nuclear activities. Quantifying the measurement, effect, and risk of trace concentrations of Tc-99 is paramount to understanding the isotope's behaviour in human-environment systems. Ground state Tc-99 decays by beta emission (E_{max} — 292 keV) with a half-life ($t_{1/2}$= 2.11 x 10^5 y), while the metastable isomer Tc-99m ($t_{1/2}$ = 6.0 h) decays rapidly by emitting a gamma photon. Technetium-99 is present in the environment in mobile pertechnetate (TcO_4^-) form. Tc-99 is used as an oceanographic tracer to investigate seawater movement and coastal pollution using seaweed as a bioindicator.

The purpose of this study is to develop a sample preparation method to measure low concentrations, down to femtogram levels, of Tc-99 in environmental samples such as seaweed, water and medical Tc-99m waste using an accelerator mass spectrometer (AMS). When present in its soluble form, Tc (VII)can be reduced to Tc (IV) in the presence of a strong reducing agent such as $SnCl_2$, then precipitated out of solution as an iron hydroxide by the addition of an iron carrier. Using AMS to measure precipitates prepared through a simple one-step co-precipitation method show high levels of isobaric interferences by Ruthenium-99 (Ru-99) and impurities by the co-precipitation of other hydroxides. A double-step co-precipitation method was determined to be efficient at reducing interferences of impurities present in the final precipitate. Using Tc-99m as a chemical tracer, the efficiencies of different oxidizing- reducing agents were compared to optimize the yield of Tc-99. The aims and objectives of the study are first: to develop a method for the separation and purification of Tc-99 from Ru-99 by ARS-II with ABEC column. Second: to develop methods for the removal of interferences and extraction of Tc-99 from environmental small size samples, and third: to develop a method to analyze Tc-99 by low energy AMS. Concentrations of Tc-99 were measured in seaweed samples with a newly developed oxidation-reduction method using Tc-99m as a yield tracer. The detection of Tc-99 from seaweed samples follows a two-step procedure. The first step is the oxidation of technetium from Tc (IV) to Tc (VII) oxidation state with H_2O_2 followed by iron hydroxide precipitation. The second step is the reduction of Technetium from Tc (VII) to the Tc (IV) oxidation state with $SnCl_2$ followed by iron hydroxide co-precipitate. The co-precipitate contains the Tc (IV) and is dried at 80°C and then at 200°C to remove excess water, then mixed with PbF_2 to produce TcF_5^- in the AMS ion source. The purification and separation of Ru-99 from Tc-99 is done by ARS-II with ABEC column and measure by AMS. Currently, the most sensitive practical choice for Tc-99 is ICP-MS, with typical LOD at picogram (pg.) levels. This translates to 10-100s of litres required for a seawater sample. AMS has shown potential <10 fg LOD, which translates to volume requirement of sub-litre to litres for seawater samples, this would make the AMS quantification of Tc-99 an incredibly useful and competitive alternative.

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I dedicate my thesis to Prof. Robert Jack Cornett; may he rest in peace.

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ABEC: Aqueous Biphasic Extraction Chromatography

AMS: Accelerator Mass Spectrometry

ARC: University of Ottawa’s Advanced Research Complex

ARS-II: *NorthStar’s* Automated Radionuclide Separator-II

CFLs: Contaminated Food Intervention Levels

CPM: Counts Per Minutes

DPM: Disintegrations Per Minutes

EPA: Environmental Protection Agency

Eh-pH: Eccentric hypertrophy - potential Hydrogen

PEG: Polyethylene Glycol

ICP-MS: Inductively Coupled Plasma Mass Spectrometry

LSC: Liquid Scintillation Counter

TIMS: Thermal Ionization Mass Spectrometer

MS: Mass Spectrometry

MV: Mega Volt

NIST: National Institute of Standards and Technology

NRC: National Research Council of Canada

NSERC: Natural Sciences and Engineering Research Council of Canada

REACT: Research in Environmental, Analytical Chemistry and Toxicology

SPE: Solid-Phase Extraction

SRMs: Standard Reference Material

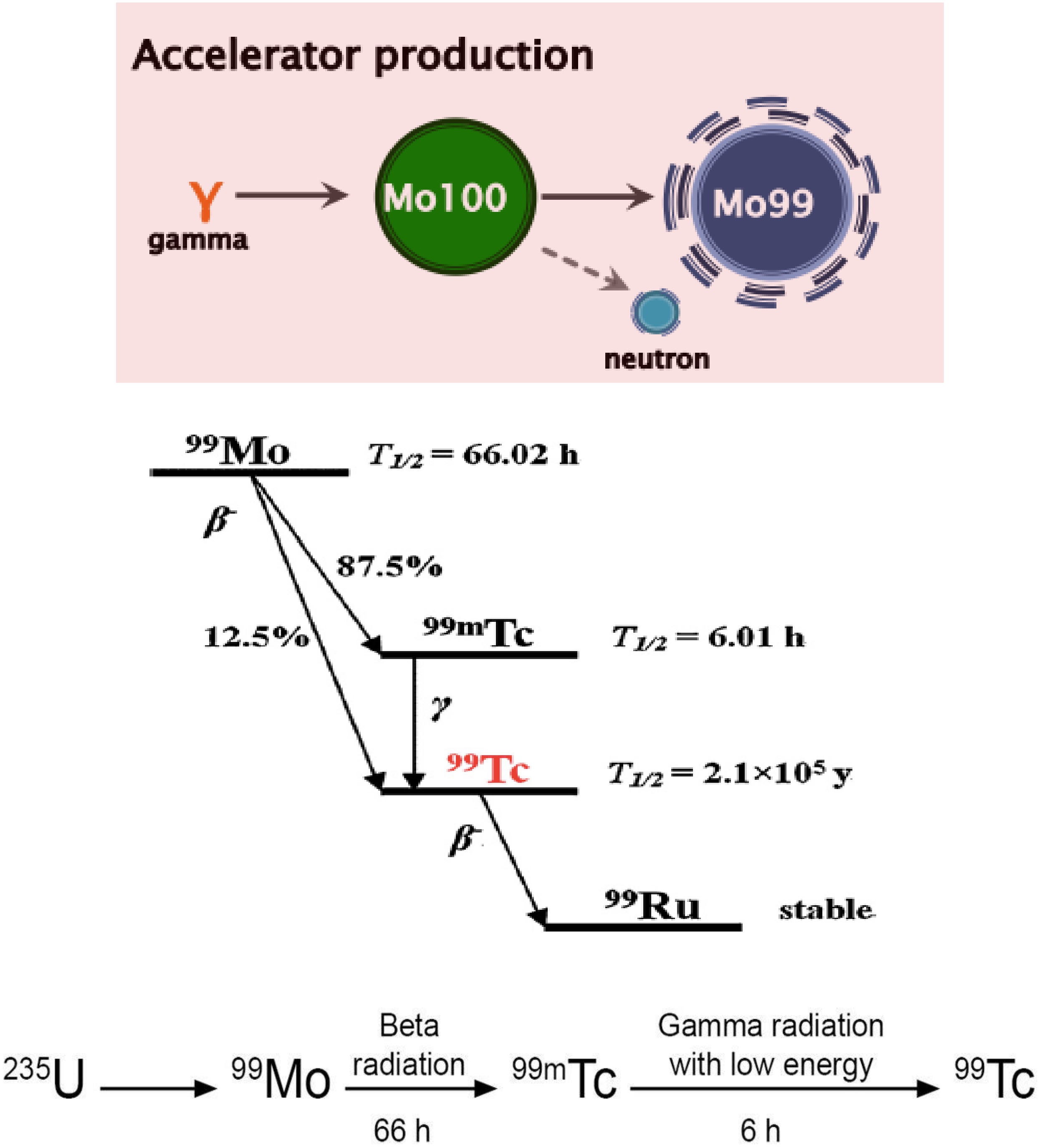
Introduction

Technetium (Tc-99) is an anthropogenic radioisotope that is both beneficial to humans and yet a potential threat to the environment. Its benefits arise for humans and society when metastable Tc-99m is used as a medical diagnostic imaging tool (Tc-99m has a half-life of 6 hours and decays to Tc-99 by emitting a gamma photon). It is also, at low levels, an important tracer of ocean currents and potentially of components of the hydrological cycle. It can, however, be a threat to ecosystems and human health when released into the environment as highly mobile pertechnate, TcO_4^- (Tc-99 has a long half-life of 211,000 years and decays by emitting a beta particle). Research developing analytical methods to quantify Tc-99 will improve our stewardship of this radioisotope and better our understanding of its environmental challenges and impacts on human health and society.

1 Technetium isotopes and production

Technetium, atomic number 47, is found in Group 7 of the Periodic Table between manganese and rhenium. It has no stable isotopes and only three radioisotopes with half-lives longer than a few days. These are Tc-97 ($t_{½}$ = 2.6 million years), Tc-98 ($t_{½}$ = 4.2 million years) and Tc-99 ($t_{½}$= 211,000 years). The ground state Tc-99 is a beta emitter (E_{max} = 292 keV) with a half-life ($t_{½}$= 2.11×10^5 y) decaying to stable Ru-99. Its isomer Tc-99m ($t_{1/2}$ = 6.0 h) emits a gamma photon (Fig-1).

Technetium-99m is used for medical diagnostic and radiopharmaceutical purposes. Tc-99 parent, Mo-99, is produced to supply this important isotope. The method to produce Mo-99 is by bombarding a Mo-100 target with an electron beam from a linear accelerator, the γ/n reaction on Mo-100 to produce Mo-99. (Fig-1)



<u>**Figure 1:Decay chain of Tc-99 showing parent and daughter isotopes (Shi-et al. 2012).**</u>

Molybdenum-99 has half life of 66 hours that decays and generates Tc-99m in a device called a moly cow, which is used to extract the metastable isotope Tc-99m (half life 6 hr.) for medical diagnosis purposes. The relatively long half life of Mo-99 makes it possible to transport a supply of the isotope long distances to hospitals, where it continues to decay and produce Tc-99m (half life 6 hr.) that is extracted from the moly cow for medical diagnostic tests. (Rogers et al, 1996; Shi et al,2012; Galea et al., 2013).

The natural abundance of technetium is exceedingly low, produced by the spontaneous fission of uranium isotopes and calculated to be on the order of perhaps two hundred thousand tons in the crust. It is, however, produced anthropogenically through fission of U-235 and Pu-239 in nuclear reactors and is part of spent nuclear fuel. Tc-99 is produced in ton quantities in nuclear reactors, it is adding to the environmental burden of radioactive waste. The enormous amounts of Tc-99 radioactive material produced and disposed of make it an important environmental consideration.

2 Chemistry of Technetium

In 1869 Mendeleev published the Periodic Table (Mendeleev's Archive, 1951) and reported a gap, which was predicted for element 43 between Mo-42 and Ru-44. The isotope Tc-99 was first discovered in 1937 following the invention of the cyclotron in an experiment where atoms of molybdenum were bombarded with deuterium by Carlo Perrier and Emilio Segre, producing Mo-99 and its daughter Tc-99. (Perrier and Segre, 1939).

Tc in solid form is a silvery-gray metal that dissolves in HNO_3, aqua regia and concentrated H_2SO_4, but is not soluble in any strength of HCl solution. Technetium-99 is present in the environment as pertechnetate (TcO_4^-). Technetium exhibits nine oxidation states from −1 to +7, with +4, +5, and +7 being the most common and stable. In the reductive stage, Tc (IV) is the stable oxidation state and hydrolyzes in aqueous solutions and is stable as TcO_2 in the absence of water (Lieser, 2001).

In an aqueous solution, Tc exists in different oxidation states eg Tc(II), Tc(IV), Tc(V), Tc(VI) and Tc(VII) (Schwochao, 2000; Hu, 2010). In the environment, Tc is present in two oxidation states, Tc(IV) and Tc(VII). Tc-99 exists as a pertechnetate ion (TcO_4^-) in an aqueous solution or as volatile Tc_2O_7 in the absence of water in oxidizing conditions. Tc_2O_7 melts at 119.5°C and boils at 311°C. It is hygroscopic and dissolves in water to form $HTcO_4$ (Schwochao, 2000; Hu, 2010).

TcO_4^- is stable in water over a wide pH range in the absence of reducing substances. (Schwochao, 2000; Hu, 2010). Seaweeds, like the *Fucus genus*, show the ability to accumulate Tc-99 from seawater and so it is used as biological indicators for monitoring the levels of Tc-99 (Schwochao, 2000; Hu, 2010).

The Eh-pH diagram of Tc (Figure 2) indicates areas in which the different oxidation states of technetium predominate. Tc exists in two oxidation states (Tc (VII) and Tc (IV)) in the environment. In the oxidized state, Tc exists as the pertechnetate ion (TcO_4^-) in an aqueous solution or as volatile Tc_2O_7 in the absence of water (Hu, 2010). Tc $(OH)_2$ and TcO_2 are the stable forms of Tc (IV) and are insoluble in water. TcO_4^- is an important inorganic anion of Tc-99 in the environment which is stable in aquatic solutions at different pH in the absence of reducing substances (Wigley, 2000, Schwochao, 2000; Hu, 2010).

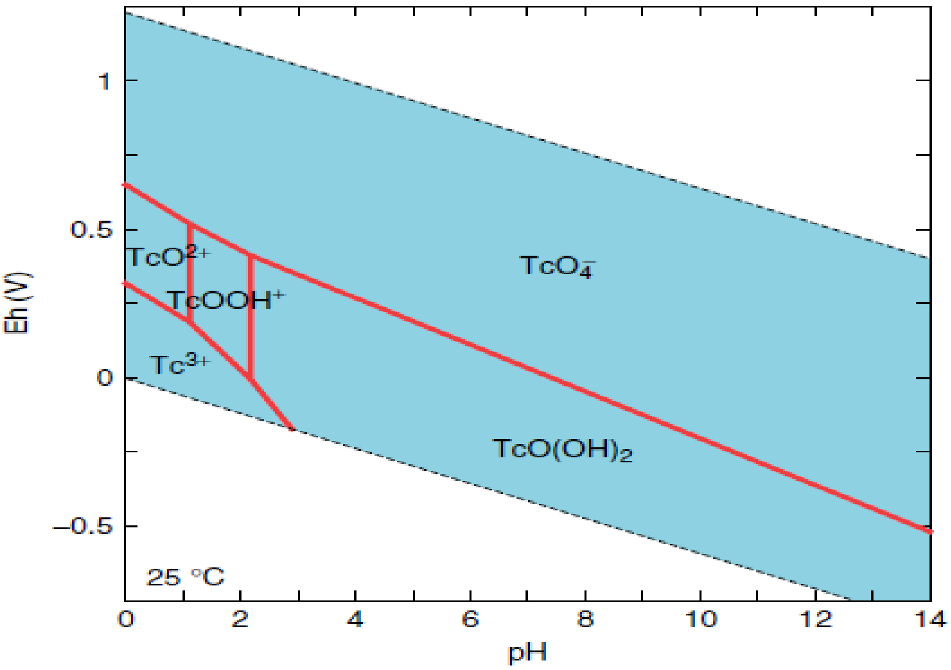


Figure 2: Eh-pH diagram of technetium obtained at 25 °C in aqueous media without other complexion reagents and adopted from reference (Hu,2010)

Tc-99 can also be found in organic complexes. It can combine with organic ligands (e.g., EDTA and humic acid) or bio-macromolecules, and concentrated by matrix materials. The formation of Tc-complexes with organic ligands is stable at different pH (Hattic, 2000).

3 Technetium in the environment

While some Tc-99 found in the environment is due to nuclear weapons testing or from the Chernobyl and Fukushima accidents, the main sources of anthropogenic Tc-99 come from spent-fuel reprocessing plants such as Sellafield (United Kingdom) and La Hague (France). These discharges are released into the Irish Sea (from Sellafield) and English Channel (from La Hague). Tc-99 discharges are as pertechnate, TcO_4^-, and are transported to the North Sea and further northwards through the Norwegian Sea to the Arctic and the Greenland Sea. (Meena et al., 2017). The water exchange between the North Sea and the Baltic Sea causes Tc-99 transport to the Baltic Sea. Seawaters in these areas have high concentrations of Tc-99. The concentrations of Tc-99 in aquatic plants (e.g. seaweed) and animals (e.g. shellfish) are higher in the contaminated area than in uncontaminated areas. The major global releases of Tc-99 into the environment have been summarized in Table 1.

Table 1: Main source of Tc-99 in the environment (Meena, et al 2017)

Source	**Tc-99 released (×10^{12} Bq=1TBq)**
1-Sellafield nuclear reprocessing plant	1720 TBq
2- La Hague nuclear reprocessing plant	154 TBq
3- Global weapons fallout (the 1940s–1970s)	140 TBq
4- Nuclear accident in Chernobyl	0.75 TBq
5- An estimated nuclear accident in Fukushima	>0.25 TBq
6- Estimated medical application (99Mo–99mTc generator)	<0.02 TBq

Plants, animals, seaweed, and marine animals (such as lobsters and crabs) can become contaminated with Tc-99 to levels above the CFIL limit of 1,250 Bq per kilogram (EPA). Because of its long half-life, Tc-99 can remain in the environment for hundreds of thousands of years. Tc-99 enters the food chain due to uptake in aquatic plants and marine animals. Seaweed can concentrate Tc-99. The mechanism is that TcO_4^- in seawater is first taken up through foliar absorption, and then reduced to Tc(IV) in the chloroplast. The reduced Tc-99 is afterwards absorbed with organic ligands in seaweed and fixed (Hattink, 2000).

Animals and humans can become exposed to Tc-99 through the consumption of contaminated water or ingestion of contaminated food. Tc-99 could then concentrate in the thyroid gland and gastrointestinal tract, causing cancer and other adverse health effects (Hattink, 2000).

Tc-99 is a challenging radionuclide in radioactive waste management that creates problems related to safe disposal because of its high mobility and volatility in an environmentally stable form of pertechnetate (TcO_4^-) (Hattink, 2000).

Research on Tc-99 is important to get accurate concentration information at trace levels that will help us to understand the impact and mobility of Tc-99 on the environment, health, and human society. Measurement of T-99 is important because knowledge of correct concentrations of Tc-99 helps to fix regulations for environments and human health. Tc-99 is also used as an oceanographic tracer to investigate seawater movement but requires large volumes of water for analysis by radiometric methods. Coastal pollution can be assessed using seaweed as a bioindicator, but analysis remains difficult and requires large samples.

Research on analytical methodology of Tc-99 is essential for understanding Tc-99 behaviour in ecosystems were low to trace concentrations present analytical challenges. This is done by assessing environmental samples that are pretreated for separation and purification of Tc-99 before analysis. Measurement of Tc-99 at low levels concentration in environmental samples can be achieved radiometrically using liquid scintillation counting (LSC) for beta activity, gamma counting (GM) or by mass spectrometry using inductively coupled plasma mass spectrometry (ICP-MS) and accelerator mass spectrometry (AMS).

4 Objectives

The objectives of this research work are to first establish rapid and accurate analytical methods for determination of Tc-99 by AMS in environmental samples such as seaweed, and second develop an approach for the calibration of Tc-99 analysis by AMS, considering that there is no stable Tc isotope that can be used to normalize Tc-99 measurements (Fifield et al. 2000, Litherland et al,2011).

Literature review for analysis of Tc-99

Due to the extremely low concentration of Tc-99 in environmental samples, the sample preparation, pre-concentration, chemical extraction, separation, and purification for removal of interfering matrix effects for detection of Tc-99 are the most important steps to provide an accurate determination of Tc-99. Chemical separation is a key issue to obtain accurate analytical results. The reported analytical procedures for the determination of Tc-99 in environmental samples are complicated, intrinsic, and time-consuming (Shi et al., 2012). There is a requirement for accurate analysis of low concentrations of technetium in environmental samples, this requires the use of AMS for the analysis of Tc-99 to get an accurate result. Major challenges include the separation, purification, and determination of Tc-99 in environmental samples with high efficiency and low detection limit (LOD) using AMS (Fifield et al. 2000; Hellborg and Scog,2008; Litherland et al,2011; Shi et al. 2012; Kutschera,2016). The measurement methods of Tc-99 are explored, with a focus on Tc concentration in seaweed. According to the types of samples, different pre-treatment methods have been tested (Shi et al. 2012), including dry ashing and acid leaching for solid samples as well as co-precipitation of technetium using ferrous hydroxide from large-volume water samples. From these approaches, methods are developed to separate and purify technetium from the sample matrix and other interferences before measurement of Tc-99 by AMS. Ru and Mo interferences are common to all MS. For MS methods of analysis, the interferences of ruthenium and molybdenum are mitigated using extraction chromatographic techniques, specifically with SPE, TEVA and ABEC columns. (Shi et al., 2012). Table-3 provides background information and a literature review on Tc-99 separation and determination.

5 Analytical methods for Tc-99

Radiometric and mass spectrometric techniques have been used for the measurement of Tc-99, these techniques include β counting using GM gas flow counter and LSC, neutron activation analysis, ICP-MS, TIMS, RIMS and AMS. GM gas flow counter and ICP-MS are the most used techniques. A summary of the literature on the analysis of Tc-99 is given below in Table 2 and Table-3.

Table 2: Main analytical methods with detection limit used to measure Tc-99

Method	Detection Limit	Determination time	References
GM Counter	10^{-11}-10^{-12} g	Days	Holm et al.,1984; Chen et al.,1994
LSC	10^{-10}-10^{-11}g	Hours	Banavali et al.,1995; Wigley et al.,1999; Nevissi et al.,1994
ICP-MS	~ 10^{-12} g	Minute to hours	Kim et al.,1989; Song and Probst,2000; Mass et al.,2004.
AMS	~10^{-15} g	Minute to hours	Wacker et al.,2004; Fifield et al.,2000

As a pure beta-emitter, Tc-99 can be detected by beta counting using a gas ionization detector or LSC. Compared to the MS techniques, these methods have lower cost, relatively higher reliability, and easier operation. However, counting time is much longer than with MS techniques, and the detection limit of LSC is higher compared with mass spectrometric methods, due to the high background level.

6 Liquid Scintillation Counting

The LSC method is used to count beta decays from Tc-99 (a pure beta-emitter with a maximum energy of 0.294 MeV) (Wigley 2000, Egorov et al, 1998). The advantage of LSC is its simple source preparation and short counting time but the main disadvantage is the higher detection limit. Due to the high detection limit, quench impacts are significant during LSC measurements. Acid, alkali, and salt in the sample solution are the common quench reagents (Jordan et al, 1995).

7 Geiger-Mueller counter (GMC)

Gas ionization detection by a gas flow Geiger-Mueller counter is a technique that can be used to detect beta particles emitted by the decay of Tc-99. The detection limit of the GM counter technique depends on the count rate of blanks and the counting time. The detection limit of a gas flow GM detector is 10^{-12} g of Tc-99. (Chen et al, 1990, Kramer,1983). The advantages of gas flow GM detectors are a relatively low detection limit, low cost and easy to measure but the disadvantage is a long counting time for low activity samples. This technique provides a reliable analytical result because of the high separation efficiency of interferences from other radionuclides, but the technique is time-consuming.

8 Inductively coupled plasma-mass spectrometry (ICP-MS)

Mass spectrometric (MS) methods have the advantages of high sensitivity and short analysis time. MS has been applied to measure Tc-99 in low-activity environmental samples (Tatami et al., 1995). The measurement of Tc-99 has been carried out by using ICP-MS. Different types of MS techniques are used to measure Tc-99 from environmental samples such as AMS and ICP-MS (Tagami et al., 1995, Gomez et al., 2001). ICP-MS has the advantages of short analytical time from several minutes per sample, with high sensitivity (Eroglu et al,1998, Shi et al., 2012, Ihsanullah and East,1994). ICP-MS detection limit is 10^{-12} g (about 1 mBq) (Shi et al., 2012).

9 Accelerator mass spectrometry (AMS)

AMS is an analytical technique based on ion accelerator mass spectrometry. After chemical separation of the element from material and loaded as a target in the ion source, the ion beam is accelerated and analyzed. Isotopes are identified and counted individually with ion detectors. (Figure; 3 and 4) (Litherland et al,2011, Kieser et al,2015).

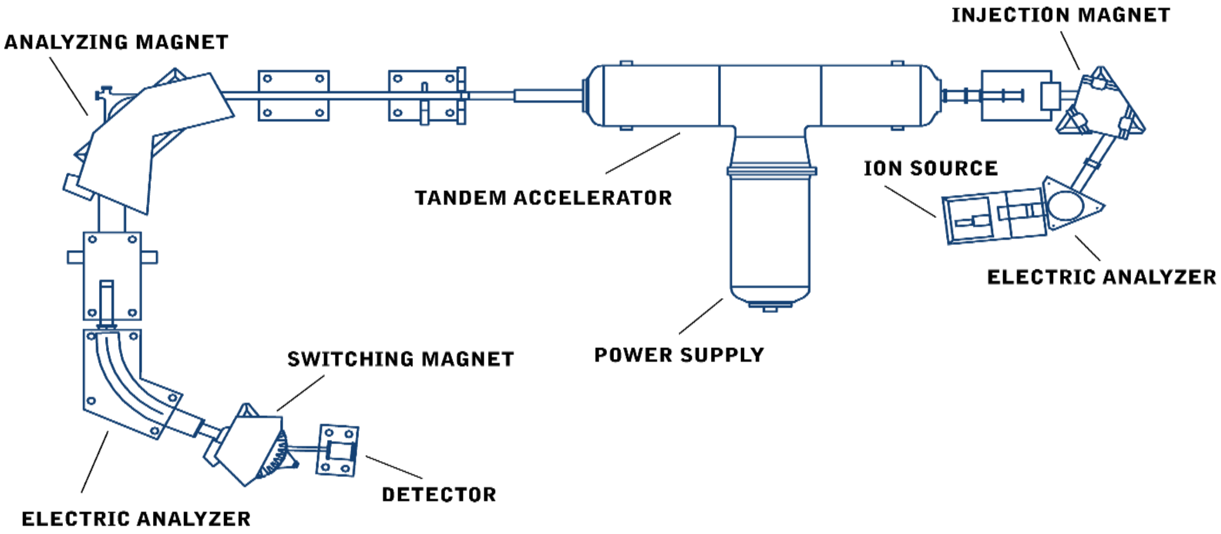


Figure 3: Accelerator Mass Spectroscopic (AMS) (Litherland et. Al, 2011).

1-The ion source produces a beam of ions that are emitted from a few milligrams of solid material. The element is first chemically extracted from the sample e.g.: seaweed sample, then it is loaded into a copper holder and inserted into the ion source through a vacuum lock. Atoms are sputtered from the sample by cesium ions that are produced on a hot, spherical ionizer. Negative ions are extracted along a voltage gradient from the ion source and injected as an ion beam into the first magnet.

2-The injector magnet bends the negatively charged ion beam by 120° to select the mass of the ion of interest.

3-The tandem accelerator is made of two accelerating gaps with a positive voltage terminal in the middle. The negative ions are accelerated along the beam tube towards the positive terminal. At the terminal negative ions pass through an electron stripper, either a gas or a very thin carbon foil, and emerge as positive ions. The positive terminal repels and accelerates the cations towards ground potential at the exit from the accelerator. Molecular isobars are broken apart and eliminated in the terminal stripper.

4-The analyzing and switching magnets select the mass of the radionuclide eg-Tc-99 and separate it from abundant isotopes. The isotope ratios are measured by bouncing between the stable and radioisotopes with the injector and analyzing magnets.

5-The electrostatic analyzer is a pair of metal plates at high voltage that deflects the beam to the left by 65 degrees. This selects particles depend on their energy and removes any isobaric interfering ions that may have regenerated following from the accelerator.

6-The gas ionization detector counts the rare radioisotope ions one at a time from the beam line. The ions are slowed down in isobutene gas, releasing electrons impact. Then these electrons are collected on metal plates, amplified, and read into the computer. For each atom, the computer determines the rate of energy loss of each atom and identify the nuclear charge (element atomic number) to recognize interfering isobars.

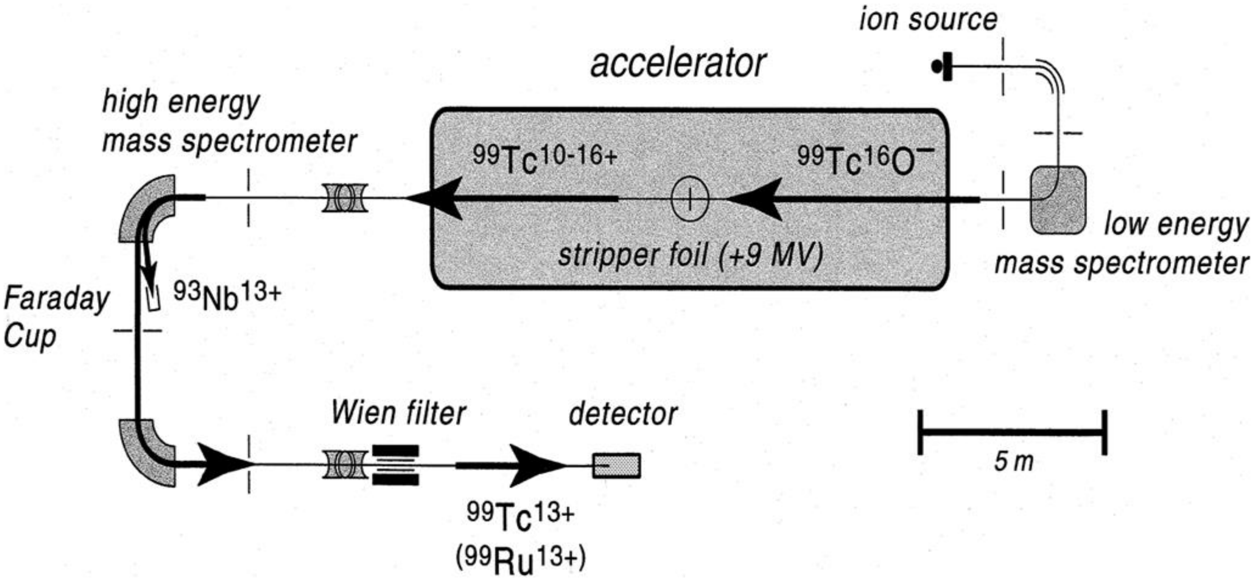


Figure 4: Schematic of Tc-99 analysis by AMS (Shi et al., 2012)

AMS is a highly sensitive method for the determination of Tc-99, a low-level radionuclide in the environmental samples. The major advantage of the AMS method is to analyses Tc-99 with high sensitivity and a small amount of sample. The challenge with the AMS measurement of isotopes is the potential for counting interfering isobars. For Tc-99 the principle isobaric interference is stable Ru-99 (Litherland et al,2011, Walker et al 2004). As isotopes are separated in the analyzing magnet on the basis of their mass to charge ratio (m/z), other isotope of different mass can also interfere. For Tc-99, the isotope of ytterbium, Yb-173 is an interference of concern at the 7+ charge state (173/7 = 24.71; 99/5 = 24.75).

AMS is a relative analytical method, i.e., it gives a ratio of two isotopes, normally the target isotope and another isotope of the same element (e.g., I-129/I-127 for I-129 measurement and Pu-239/Pu-242 for Pu-239 measurement, Tc-99/Tc-97for Tc-99 measurement.

The very small difference in the atomic mass of Ru-99 and Tc-99 (Δ m = 0.0003154 u) makes the isolation of Ru-99 from Tc-99 in AMS difficult, and therefore Ru-99 is the major interference in the AMS measurement of Tc-99. Removal of Ru-99 from Tc-99 by chemical separation is needed before the AMS measurement of Tc-99 (Shi et al.,2012, Kutschera,2005).

A small difference in the energy loss of Tc-99 and Ru-99 ions in the gas ionization chamber has been used to discriminate Ru-99 from Tc-99, using multiple anodes for measurement of the energy loss of the ions as they slowdown in the gas ionization chamber. This is only effective when the ion energy is at least 120 MeV (Litherland et al,2011, Shi et al., 2012).

Fifield et al. (2000) found a method to eliminate the interference of Ru-99 by quantifying and subtracting the contribution of Ru-99 from Tc-99 by accounting for Ru-101 and using the natural ratio of Ru-99/Ru-101. The detection limit of AMS for Tc-99 could be as low as 10^{-15} g using this method (Fifield et al. 2000, Litherland et al,2011, Shi et al., 2012).

Negative ions of T-99 in both form Tc^- and TcO^- can be formed in the ion source with similar prolificacy but the yield of Ru− is much higher than that of the RuO^- ion (the Ru^-/RuO^- yield ratio is about 6). The Ru-99 signal can be suppressed to some extent using oxide ions, so the negative oxide ion TcO^- is applied as the analyte for Tc-99 measurement by AMS (Litherland et al,2011). The advantage of AMS is to provide a better detection limit for Tc-99 measurement with small sample size, but it suffers a higher cost and less availability of AMS, limiting the use of AMS for the routine measurement of Tc-99(Litherland et al,2011).

There are challenges related to the lack of a stable Tc-99 isotope and measurements of Tc-99 with isobaric interference Ru-99 (Fifield et al. 2000). AMS is a combination of the high-efficiency mass spectrometry and suppression of isobar and molecular interferences. This is due to negative ions, dissociating molecular ions and stripping atomic ions in the sample to high positive charge states and identification of individual ions in accelerator. The equipment used for AMS is based on the electrostatic tandem accelerator (Shi et al., 2012).

Table 3: Background and Literature review of Tc-99 separation and determination.

SN	Samples	Sample size	Yield monitor	Separation and purification	Recovery	Determination Method	Reference
1-	Seawater	200-400 ml	Tc99m	Anion exchange with AGI-X4 and Solvent extraction with TIOA/Xylene	70%	GM counter (Gas flow)	Chen et al, 1990
2-	Seawater	14 ml	Re	Anion exchange with IRA 400 resin	85%	ICP-MS	Tagami et al 1995
3-	Seawater	0.25-5ml	Tc-95m	Solid-phase extraction with TEVA	-	AMS	Walker et al 2004
4-	Water sample	500ml	Tc-95m	Co-precipitation with Fe (OH)2 and solid-phase extraction with TEVA	50-80%	ICP-MS	Seki et al., 2005
5-	Water sample	5-30ml	Tc95m	Solvent extraction with TIOA/Xylene and Anion exchange with Dowex1-X8	65%	ICP-MS	Ihsanullah and East,1994

SN	Samples	Sample size	Yield monitor	Separation and purification	Recovery	Determination Method	Reference
6-	Drinking water	1-2ml	Re	Solvent extraction with TIOA/Xylene and solid-phase extraction with TEVA	100%	ICP-MS	Gomez et al., 2001
7-	Contaminated water	-	Tc-99m	Solid-phase extraction with TEVA	85-98%	ETV-ICP-MS	Skipperud et al., 2007
8-	Soil	3-6 g	Re	Online flow injection separation with extraction chromatography using TEVA	62-73%	FIHR-ICP-MS	Kim et al., 2002
9-	Soil	1-20g	Tc-95m	Solvent extraction and anion exchange with Dowex 1-X8	84-92%	HR-ICP-MS	Yamamoto et al., 1995
10-	soil	10g	Re	Anion exchange with Dowex1-X8 and solid-phase extraction with TEVA	-	ICP-MS	Eroglu et al., 1998

SN	Samples	Sample size	Yield monitor	Separation and purification	Recovery	Determination Method	Reference
11-	Soil	0.25g	Re	Solid-phase extraction with TEVA	93%	FI-ICPMS	Hollenbach et al., 1994
12-	soil	10-100g	Tc-99m	Co-precipitation with Fe (OH)2 and Solvent extraction with TBP	50-80%	Gas flow GM counter	Holm et al.,1984
13-	soil	50g	Tc-95m	VolatizatiSolid-phase has extraction with TVA	62-73%	ICPMS	Tagami et al., 1995
14-	Seaweed	10mg	Tc-99m	Anion exchange with Dowex 1-X8 and Solvent extraction with TIOA/Xylene	70-95%	LSC	Wigley et al.,1999
15-	Seaweed	10g	Tc99m	Recrystallization and solid-phase extraction with TEVA	50-80%	ICP-MS	McCartney et al.,1999

SN	Samples	Sample size	Yield monitor	Separation and purification	Recovery	Determination Method	Reference
16-	Biota	15-100g	Tc-99m	Coprecipitation with Fe (OH)2 and solvent extraction with TBP	50-80%	GM gas flow	Holm et al.,1984
17-	Lobster	10g	Tc-99m	Anion exchange with Dowex 1-X8 and Solvent extraction with TIOA/Xylene	70-95%	LSC	Wigley et al., 1999
18-	Tank waste sample	1ml	Tc-99m	Online sequential injection and separation with TEVA	-	SI-LSC	Egorov et al., 1998
19-	Vegetation	25g	Tc-95	Anion exchange with Dowex 1-X8 and solvent extraction witcyclohexanean	80%	NAA	Fotet et al., 1972

SN	Samples	Sample size	Yield monitor	Separation and purification	Recovery	Determination Method	Reference
20-	Geological sample	2.5-15g	Tc-97	Solvent extraction with CHCl3 and anion exchange with AGMP1X8	10-80%	TIMS	Dixoet et al., 1997
21-	Radioactive waste	1-10g	Tc-99m	Co-precipitation with Fe (OH)2 and solvent extraction with CHCl3	90%	LSC/Proportional counter	Chet et al., 1989
22-	Urine	200ml with CuS	Ammonium pertechnate NH4(TcO4)	Precipitate dissolved in Ammon acid peroxide to remove Cu (II).	80%	Gas proposal counter	-Garry H. Kramer, 1983
				Tc-99 is extracted with 2 butanone.		The limit limitation is 20mBq.	
						Time of measurement 20 minutes.	

10 ARS-II with ABEC column used to develop Tc-99 standard

For the measurement of Tc-99 by mass spectrometry (ICP-MS and AMS), suppression or elimination of isobaric interferences is critical. Furthermore, for radioisotopes like Tc-99 which have no stable isotope for ratio measurement, normalization to establish a concentration in the sample itself poses a challenge. One approach is to build a calibration curve on the AMS using targets prepared with a standard sample diluted to precise concentrations of Tc-99. These two considerations were the objectives of this research project.

The goal is to develop a method for the effective chemical separation of Tc-99 in a sample from isobaric interferences and providing a high chemical yield of Tc-99. The interferences from isobaric and molecular ions in the mass of 99 (^{98}Mo^{1}H, Ru-99, Mo-99) are the main challenge for Tc-99 separation and measurement by a mass spectrometer (ICPMS, AMS). For the separation and purification of Tc-99 from other base and transition metals, many techniques can be used. The most common are co-precipitation, solvent extraction, ion-exchange chromatography, extraction chromatography or a combination of two or more methods (Shi et al., 2012).

Ru-99 interference with Tc-99 can be a problem during analysis by AMS and must be removed before target preparation. Ru-99 poses the major interference with Tc-99 during AMS measurement, due to the very small difference in atomic mass of Ru-99 and Tc-99 ($\Delta m = 0.0003154$ u). The research experiment required the NorthStar ARS-II unit with ABEC column for separation of Ru-99 from Tc-99m. The Tc-99m was provided from a local hospital. (Shi et al., 2012; Galea et al., 2013).

Different types of methods used to separate Ru-99 from Tc-99 include precipitation to separate Ru-99 and precipitation of Tc-99 with rhenium (Re) carrier by using $C_{20}H_{16}N_4$ (Nitron)

(Perrier and Segre, 1937) and using tetraphenyl arsonium chloride. Distillation was used for Ru reduction as insoluble RuO_2 by perchloric acid and alcohol and followed by distillation from sulphuric acid. A chemical separation method involves the separation of Tc-99 from Ru-99, using a series of coprecipitations with rhenium (Re) by ferric hydroxide. An extraction method uses pyridine to selectively extract Tc-99 which does not extract Ru-99. Finally, a solvent extraction method is used to extract or separate Tc-99 from Ru-99 such as tri-iso-octylamine (TiOA), tributyl phosphate (TBP) and cyclohexanone. (Shi et al., 2012; Galea et al., 2013).

Anion exchange resin column chromatography is the most frequently used separation technique for Tc-99, with resins such as (I)-Strong basic anion exchange resin like Dowex 1 or Bio-Rad AG1 which have very high selectivity for TcO_4^- anion in a wide range of pH, as the affinity of TcO_4^- to the resin is much higher as compared with RuO_4^-. (II)-Macro-pore anion exchange resins like Bio-Rad AG MP-1 and IRA-400. AG MP-1 resin is useful to remove Ru-99 from Tc-99. (III)- Amberlite IRA-400 anion exchange resin is effective to remove Mo and Ru, both form important interfering anions of $TcO_4^{-.}$ (IV)-Cation exchange Poly Ethylene Glycol (PEG) resins (ChemMatrix) were used to separate Tc-99m and molybdenum in 4N NaOH. (V)-Extraction chromatographic resin TEVA® for separation of Ru-99 from Tc-99 in anion exchange extraction chromatography. (VI) ABEC-resin of PEGS. (Galea et al., 2013).

TEVA resin is used for the separation of Tc from Ru , based on the great difference in the affinity of TcO_4^- to TEVA compared with RuO_4^-. The function group on TEVA resin is Trialkyl methylammonium salt, also called Aliquat® 336. This is mainly used to separate tetravalent actinides and Tc. The separation of Tc using TEVA resin is based on the high affinity of TcO_4^- to TEVA resin in a low concentration of acid. Washing the column with a high concentration of HNO_3 increases the removal of Ru-99 from Tc-99. The affinity of Tc on TEVA resin decreases with increasing HNO_3 concentration and therefore a high concentration of HNO_3 is used to elute Tc from the resin (Shi et al., 2012; Galea et al., 2013).

Extraction chromatography has the advantages of both solvent extraction and chromatography, i.e., combining the selectivity of solvent extraction with the high separation efficiency of the chromatographic method. Besides TEVA, some other types of extraction chromatographic resins such as AnaLig® Tc-02 gel, and C18 Silica have also been investigated and applied for separation of Tc-99 from sample matrixes used C18 Silica to purify Tc-99 from the sample solution (Shi et al., 2012; Galea et al., 2013).

NorthStar ARS-II with ABEC column was used to separate the Tc-99m in the NRC, a Government of Canada lab. The separation process based on the aqueous biphasic extraction chromatography (ABEC) column and implemented in the ARS-II separator has eliminated all these limitations and provides automated separation of Tc-99m from a solution containing low specific activity Mo-99. Adsorption of Tc-99 on aqueous biphasic extraction chromatographic (ABEC) sorbent used Eichrom's ABEC column (10 cc cartridge) made of PEGs (polyethylene Glycols). Eichrom already characterized the behaviour of the pertechnetate ion (TcO_4^-) on ABEC resin at a low flow rate (<4 mL/min) column study (Galea et al., 2013).

Materials and methods:

Materials and methods are divided into two-parts. (1) Purification and separation of Tc-99 and (2) Develop methods for extraction of Tc-99 from seaweed and calibration and analyses from the AMS method. In part-1, Tc-99 is purified by using *Northstar's* ARS-II, containing ABEC columns, as a separator. This experiment provides high purity Tc-99 for the analysis purpose in AMS.

There is a requirement for separating Tc-99m after the production from Mo-100 (n, γ reaction). Although, many separation methods are available but use of ABEC column system for the separation of Mo/Tc is valuable for Good Manufacturing Practice (GMP) regulatory environment purpose, Solid phase extraction (SPE) with PEG as stationary phase is automated method for separating molybdate and pertechnetate Tc in ABEC column. Hydrophobic adsorbents in ABEC column coated with PEG is used for Mo and Tc separation. The TcO_4^- adsorption depends on the amount of PEG coated in the ABEC column (ABEC resins of 50−100 mesh size) as hydrophobic resin. For ARS-II, purpose ABEC sorbent with particle size of 125–250 µm was used from NorthStar and produced by Eichrom Technologies (Rogers etal,1996).

11 ARS-II with ABEC column for the separation and purification of Tc-99 from Mo-99 and Ru-99

11.1 Tc-99 separation in ARS-II

Molybdenum-99 may be obtained or produced by neutron irradiation (neutron activation of n,γ reaction) in a high neutron flux reactor or nuclear reactor, which have target of highly enriched uranium-235 (HEU-235). Mo-99 may also be produced with a cyclotron; a particle accelerator invented by Ernest O. Lawrence in 1929 that is used to produce short lived radioisotopes (e.g., Tc-99m) for medical purpose. Medical cyclotrons produce proton beams which are used to prepare radioisotopes in medical diagnosis areas. Radioisotopes produced in cyclotron decay by positron emission or electron capture. (Rogers et al., 1996; Shi et al., 2012; Galea et al., 2013).

The separation and purification of Tc-99 from samples containing Mo-99 and Ru-99 made use of NorthStar's Automated Radionuclide Separator II (ARS-II), Liquid Scintillation Counting (LSC), and gamma ray spectroscopy. Tc-99m was separated from the solution using the NorthStar automated radionuclide separator ARS-II. The key element of the separator is a column containing an ABEC resin (Galea et al., 2013) which retains Tc-99. The automated separation cycle, which takes about 45 min, passes the parent solution over the column, and then rinses the retained Tc-99 into a product vial using about 5 mL (0.9%) of normal saline (NaCl) solution. The separation efficiency of the ARS-II was obtained using γ-ray spectroscopy and ionization chamber measurements (Galea et al., 2013).

11.2 Standardization of ARS-II with ABEC column and Alumina column

In the ARS-II, fixed ABEC (Separation column) and Alumina (Guard column) columns are used. It was then to run a buffer solution to check ARS-II working status before loading Tc-99m for separation.

11.3 Tc-99m verification

Tc-99m was produced by medical cyclotron in hospital and supplied for test and purification purpose in standard lab. The specific activity and purity of Tc-99m was checked by LSC. The standard parameter for Tc-99m is pH between 5 and 9, concentration less than 10ppm and purity 95%. A buffer solution and 0.9% saline solution were prepared and used to dilute the Tc-99m sample for purification and separation with the ARS-II. First load solution Mo/Tc in NaOH (5M) onto ABEC column, then adjusts pH with Acetic acetate buffer (pH ~6), rinse with saline and collect effluent for further analysis (Galea et al.,2013).

11.4 Tc-99 m standard to produce a purified Tc-99 standard by ARS-II

National Institute of Standards and Technology (NIST) is a source of well-characterized materials certified for a given chemical or physical property. These Standard Reference Materials (SRMs) are used to calibrate measuring instruments and evaluate methods. (Galea et al., 2013).

The parent solution (63pg/g in 30 ml, NaOH 3.9x 10^{11}a/g; concentration of Tc-99m, 370 MBq/30 ml; Number of atoms1.2 x10^{13}) was received from source Mo/Tc (NIST traceable standard reference material for radioactivity measurements) with Ru-99 in a 1 ml syringe.

The diluted parent solution was put into 5M NaOH up to 30 ml for ARS-II purification and then 25 ml was processed in ARS-II (Galea et al.,2013). This was repeated three times and left for 10 days to decay to Tc-99. Analysis of Tc-99 samples was performed by AMS as per availability and requirement for future research.

12 Experimental design and methodology for Tc-99 measurement in seaweed.

For testing analytical approaches to measure technetium in environmental samples, seaweed was chosen as a starting test material. Seaweed is organic and therefore taken as representative of other plants and biological materials. Furthermore, it is known to be enriched in anions absorbed from the water column, such as iodine and can be anticipated to hold elevated concentrations of technetium.

We have tested a method to measure Tc-99 in seaweed samples by AMS using samples with low environmental activities. The seaweed samples are digested in concentrated nitric acid. For method development, we used Tc-99m as a yield tracer to monitor the subsequent chemical preparation of the AMS target. This method excludes the use of Tc-99m during routine use due to potential contamination by ground state Tc-99 present in the Tc-99m stock solution. We found significant interference from Yb-173, during AMS analysis which means Tc-99 and Yb-173 are extracted from seaweed in the analytical sample. As a rare earth element, stable Yb-173 is found in low concentrations in all-natural material. It becomes an interference to Tc-99 as it is abundant in the 7+ charge state leaving the accelerator, which together with Tc^{4+} interferes at the common mass/charge value of 24.7. It`s concentration in a sample depends on its removal during sample preparation chemistry to see how strong or weak it shows up when detecting Tc-99^{+4} ions. To overcome this Yb-173 issue, an option is to select Tc-99^{+2} rather than the usual Tc-99^{+4}. In this case we only need to concern Ru-99. Sample chemistry no longer needs to worry about reducing Yb-173, just need to reduce Ru-99. So, an AMS methodology must be developed to isolate Tc-99 from Yb-173 compound for analysis (Cornett et al, 2019), as illustrated in Figures 10 to 13 (further discussed below).

12.1 Selection of materials

To check and verify different types of seaweed that are suitable for Tc-99 extraction method development, three different types of market seaweed were used: 1-Raw Seaweed -Kombu Koyo comp. (2215 CPM) 2- Roasted Seaweed -Yanki Nori comp. (2155 CPM) 3- Organic Seaweed-GimMe comp. (2291 CPM) (Fig-6).

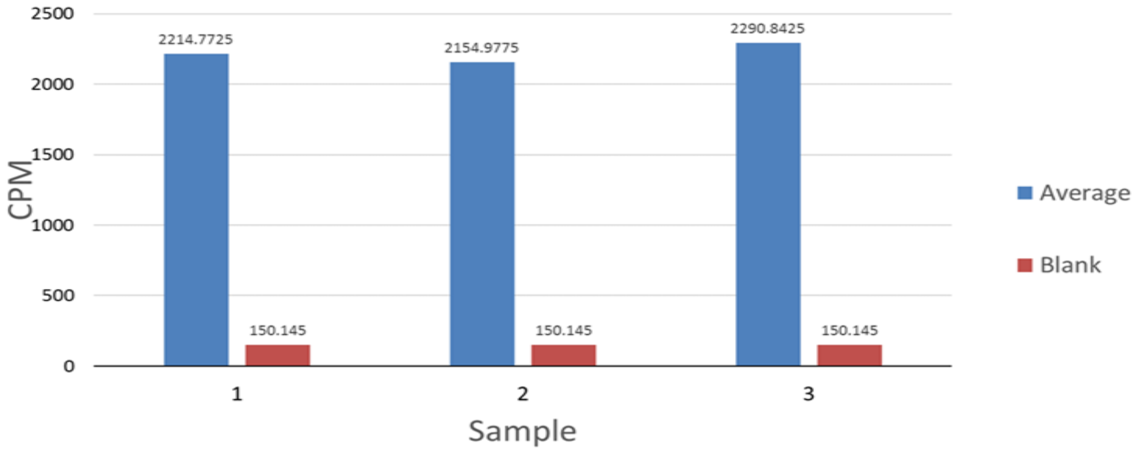


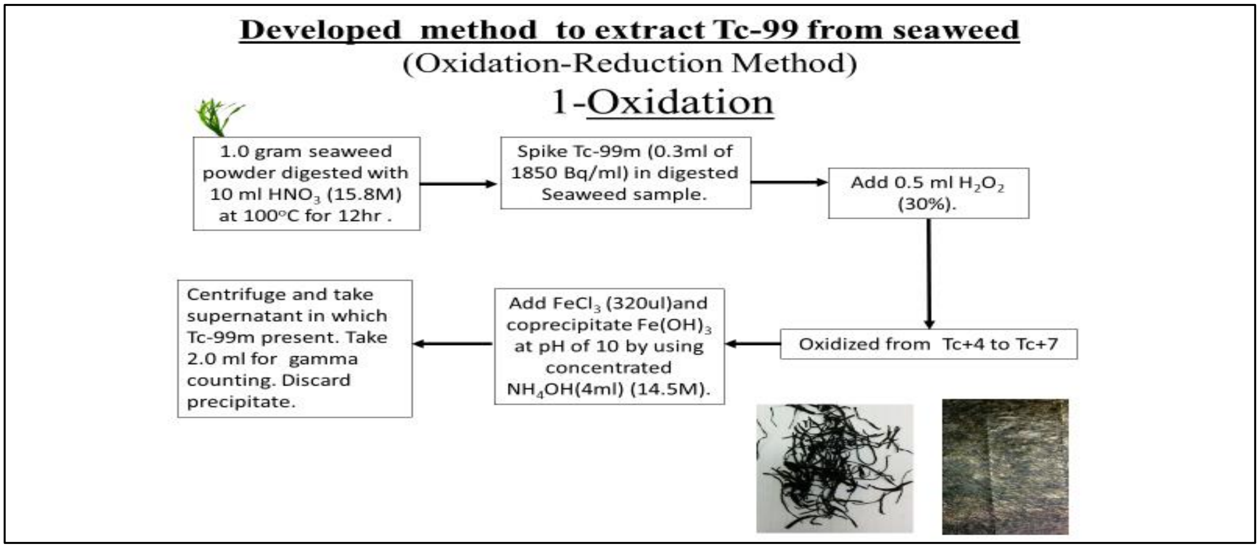
Figure 5: Analysis of three different types of raw Seaweed from market (after spike Tc-99m)-Kombu Koyo comp. (2215 CPM) 2- Roasted Seaweed -Yanki Nori comp. (2155 CPM) 3- Organic Seaweed- GimMe comp. (2291 CPM)

13 Method development

13.1 Sample preparation and measurement of Tc-99m

The seaweed samples were digested in concentrated HNO_3 then weighed and spiked with Tc-99m (TcO4-) at 6hr with gamma activity at 178 Kev. To oxidize the sample 0.5 ml 30% H_2O_2 was added and left for 5 minutes to assure conversion of Tc^{+4} to Tc^{+7} (oxidized in HNO_3) (Figure-6a). A first precipitation was performed by adding Fe $(OH)_2$ and NH_4OH at pH 10. At this stage, Tc remains in the supernatant. The precipitate was centrifuged at 3000 rpm for 15 minutes and the supernatant was retained, and the precipitate discarded. Two ml of the supernatant was taken for gamma counting within 6 hours to test the yield of Tc-99m remaining in solution. The weight of the remaining supernatant is then measured. For reduction, 0.009-gram of tin chloride ($SnCl_2 \cdot H_2O$) is added to reduce Tc^{+7} to $Tc^{+4.}$ Figure (7). A second precipitation was performed by adding Fe $(OH)_3$ and NH_4OH at pH 10. Then centrifuge at 3000rpm for 15 minutes and take 2ml supernatant in gamma vial for measurement on a gamma counter. In this supernatant, there is no Tc-99m. The precipitate was then dried at 80°C for 12 hr and put in the furnace for 12 hr before preparation as a target for AMS analysis. The sample consisting of Tc-99 with Fe $(OH)_3$ was mixed with PbF_2 for the production of fluoride anions in the sputter source. The mixture was then prepared as a target for AMS analysis. The counts per minute (CPM) of the spiked solution in the gamma counter provide the yield results (Figure 5) of three different sample types, showing that there is high spike yield with no significant difference. Thus, all three seaweed samples are suitable to use for the development of the Tc-99 extraction method in the lab.

13.1.1 Sample preparation for AMS analysis: Presented in diagram 6,7,8



Developed method to extract Tc-99 from seaweed

(Oxidation-Reduction Method)

1-Oxidation

1.0 gram seaweed powder digested with 10 ml HNO_3 (15.8M) at 100°C for 12hr .

Spike Tc-99m (0.3ml of 1850 Bq/ml) in digested Seaweed sample.

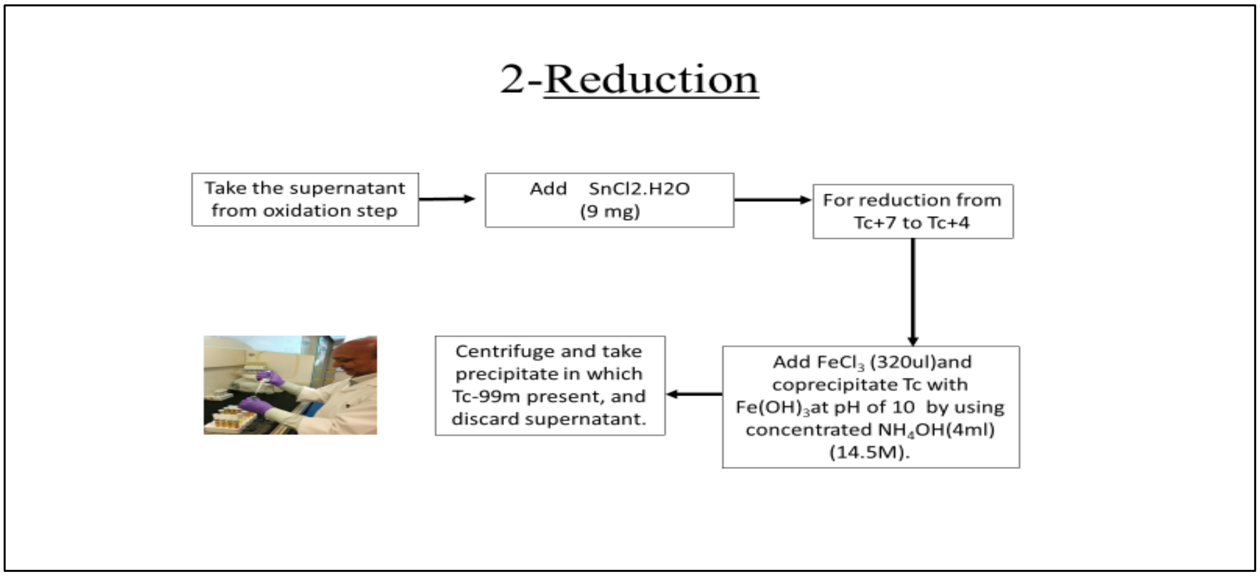
Add 0.5 ml H_2O_2 (30%).

Oxidized from Tc+4 to Tc+7

Add $FeCl_3$ (320ul)and coprecipitate $Fe(OH)_3$ at pH of 10 by using concentrated NH_4OH(4ml) (14.5M).

Centrifuge and take supernatant in which Tc-99m present. Take 2.0 ml for gamma counting. Discard precipitate.

Figure 6: Oxidation process during extraction of Tc-99 from Seaweed



2-Reduction

Take the supernatant from oxidation step

Add SnCl2.H2O (9 mg)

For reduction from Tc+7 to Tc+4

Add $FeCl_3$ (320ul)and coprecipitate Tc with $Fe(OH)_3$at pH of 10 by using concentrated NH_4OH(4ml) (14.5M).

Centrifuge and take precipitate in which Tc-99m present, and discard supernatant.

Figure 7: Reduction process during extraction of Tc-99 from Seaweed

13.2 Calibration of AMS for Limit of Detection (LOD)

The purpose of this experiment is to prepare a target for the calibration of AMS (Figure-8). The method used for target preparation for calibration curve was to first take a centrifuge vial (50 mL) and add 20 ml deionized water then add 5 mL $FeCl_3$ (500 mg Fe). In a second step, a spike of Tc-99 (2 µL) is mixed with 15 mL NH_4OH and kept at pH 10. The precipitate is centrifuged at 2500 rpm for 15 minutes, removed of supernatant water and placed in the oven at 80°C for 6 h and then remove from oven, dry and powder. This was then mixed and placed in a furnace for 12 h at 200°C as a final part before mixing with 50 mg of Fe $(OH)_2$ powder. For the preparation of AMS targets, this material was mixed with PbF_2 in a 1:10 ratio and packed into 3 AMS copper target set for AMS analysis. Variable blank to sample mixtures were prepared for a calibration curve, according to the mass ratios presented in Table 4 and Figure 9.

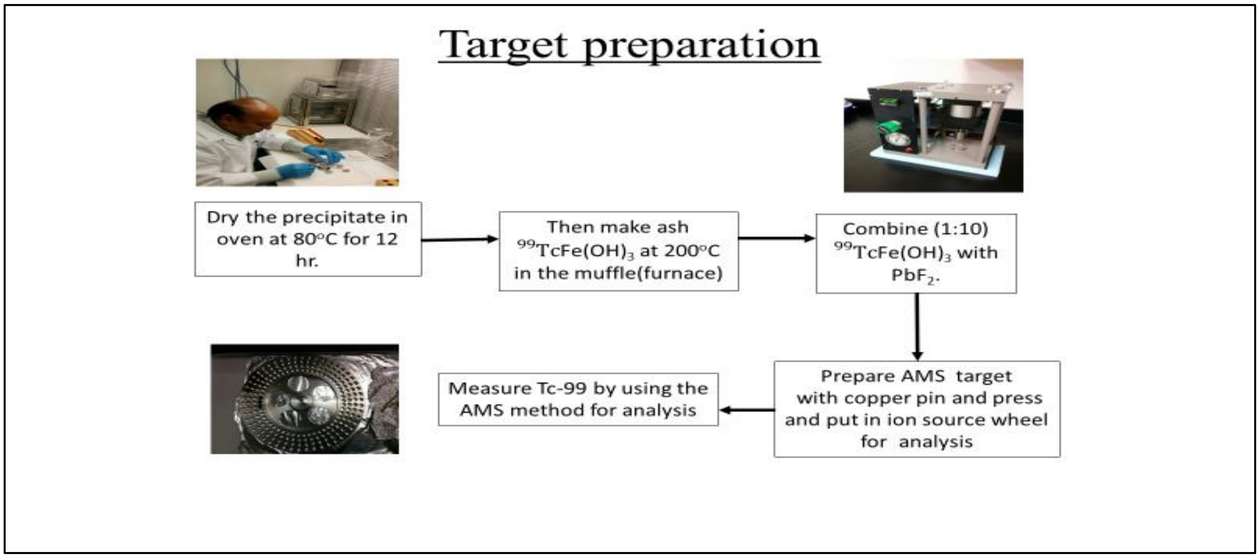


Figure 8: Tc-99 target preparation for AMS analysis

Table 4: Preparation of solutions (Fe (OH)3 +Tc-99) for the calibration curve

A	**B**	**PJ-2 stock of Tc99**
Fe $(OH)_3$	Fe $(OH)_3$ +Tc99	Tc99
50mg	50mg + 12.5pg	2ul = 12.5pg Tc99 in PJ2 stock

Sample	**A**	**B**	**PbF_2**
1	15 mg	0 mg	150 mg
2	12mg	3mg	150mg
3	9mg	6mg	150mg
4	6mg	9mg	150mg
5	3mg	12mg	150mg
6	0 mg	15mg	150mg

AMS Analysis Parameters

Injected ion	$^{99}TcF_4$-
Accelerator Terminal Voltage	2.5 MV
High Energy Analyzer-ion selected	$^{99}Tc^{4+}$

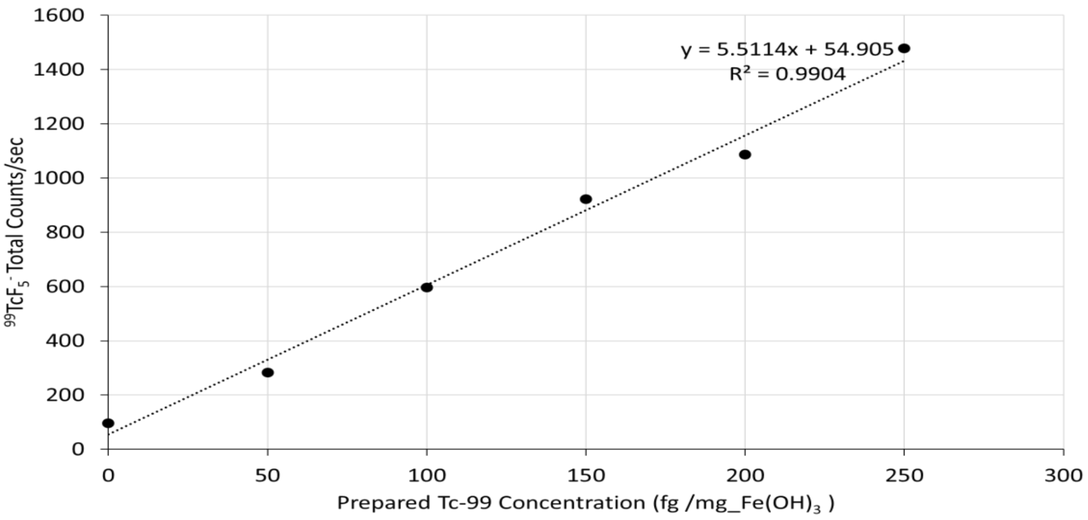


Figure 9: Calibration curve of Tc-99 plot showing the limit of detection (LOD) 10 fg/mg

13.3 Analysis of Tc-99 by AMS:

The use of AMS (Accelerator Mass Spectrometry) generally requires that the radioisotope of interest is measured as a ratio to a stable isotope of that element. For example, ^{129}I is measured as a ratio with its stable isotope, ^{127}I which is measured by other means for total concentration in the original sample. This then allows the total concentration of ^{129}I in the sample to be established. Where the concentration of the stable isotope is too low for extraction and manipulation during target production, a measured spike of the stable isotope can be added as a carrier. In the case of Tc-99, there is no stable isotope for this ratio measurement. In these types of experiments, a spike of Tc-95 can be added to the sample which, measured by gamma counting, provides a hard value that can be then used to normalize the measured amount of Tc-99. The purpose of this experiment was to analyse Tc-99 by AMS to get spectrum and information of interferences such as Ru-99 and Yb-173.The method and procedure used in section 4.5 for this experiment for the preparation of the AMS target. That analysed and gave results in spectra presented in Figures 10 to 13.

Results and discussion of Tc-99 analyzed by AMS

The spectrum measured in Figure 10 from a pure Tc-99 [50 fg/mg Fe $(OH)_3$] target shows minimum interferences of the signal of Tc-99 and Ru-99 together in the black region of interest with minimal interference of Yb-173 in the higher energy region above. The spectrum measured in Figure 10 from a seaweed blank sample shows an example of the maximum interference of Yb-173 at energies above Tc-99 (and Ru-99) bleeding into the black region of interest for Tc-99 counts. The same maximum interference is shown in the spectrum of Figure 11, a seaweed sample spiked with Tc-99 seaweed target showing maximum interference of Yb-173. In both Figures 10 and 11, high counts of Yb-173 interfere with the counting of Tc-99 and Ru-99. After separation and purification of Tc-99 from seaweed the by newly developing oxidation-reduction ion method we found less interference of Yb-173 (See Figure 12) allowing for more accurate measurement of Tc-99. Oxidation and reduction method help to reduce Yb-173 concentration. This method can be improved by reducing the background Tc-99 in the reagents and eliminating the scattering Yb-173. The other method, such as Solid-phase extraction methods will also help to reduce Yb-173 concentration.

Energy spectrum of Tc-99 measured by the accelerator mass spectrometer(AMS)
Pure Tc-99 (m/z= 99/4=24.75) [50 fg/mg Fe(OH)$_3$] target showing minimum interferences of Yb-173 (m/z=173/7=24.75).

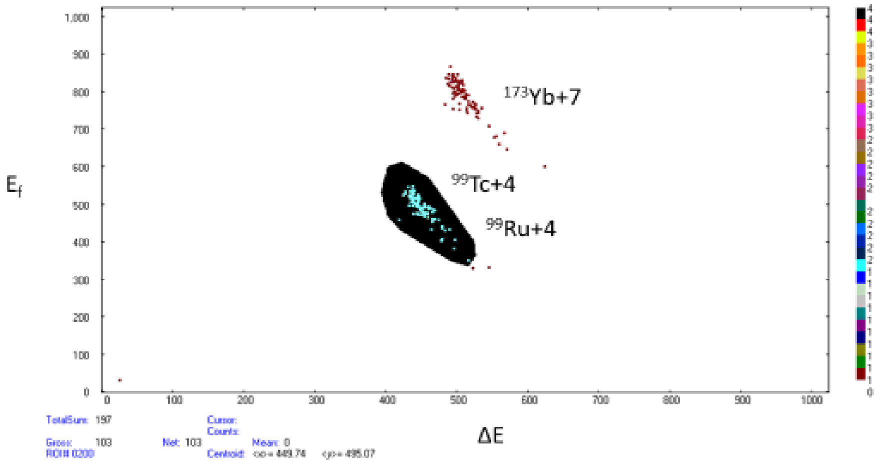


Figure 10: Pure Tc-99 [50 fg/mg Fe (OH)3] target showing minimum interferences of Yb-173 (brown dots)

Blank seaweed target showing maximum interferences of Yb-173

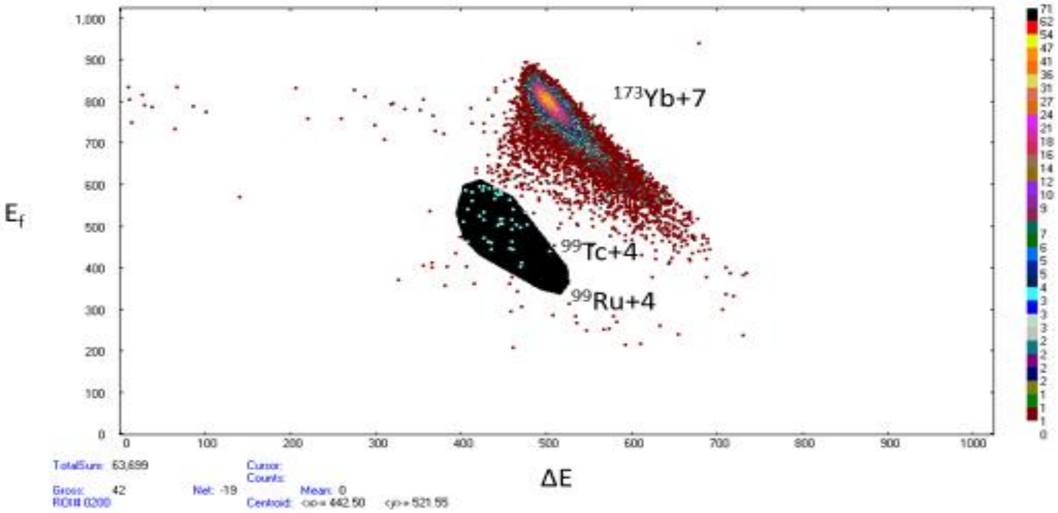


Figure 11: Blank seaweed target showing maximum interferences of Yb-173

Spiked Tc-99 seaweed target showing maximum interference of Yb-173.

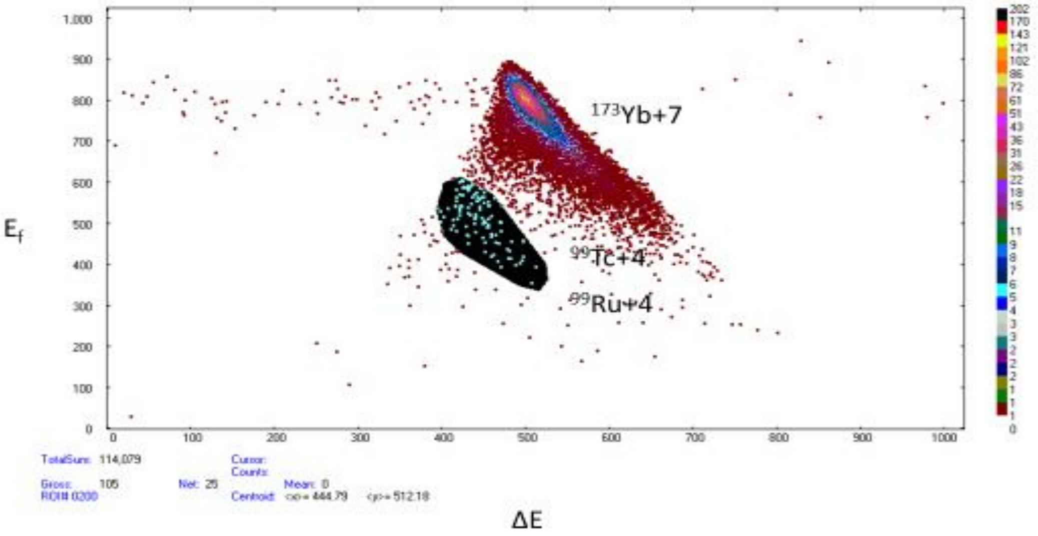


Figure 12: Spiked Tc-99 seaweed target showing maximum interference of Yb-173

Spiked Tc-99m and Tc-99 purified and extracted seaweed target showing minimum

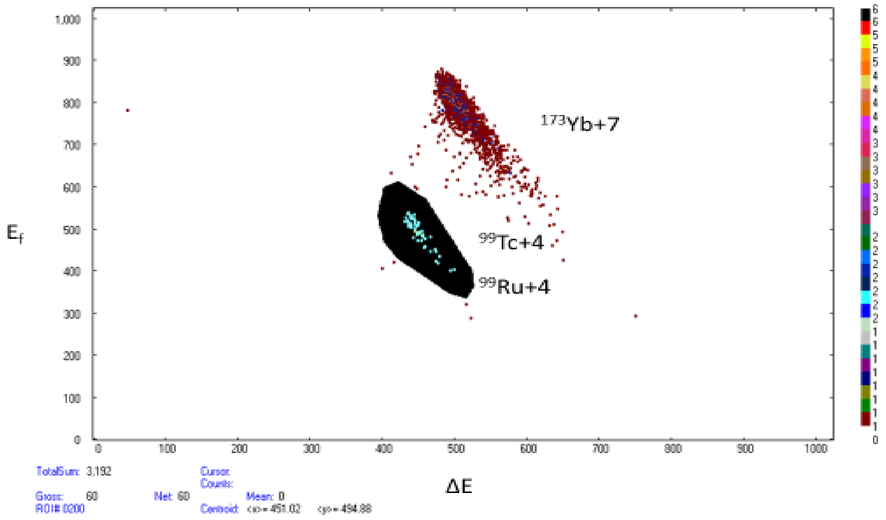
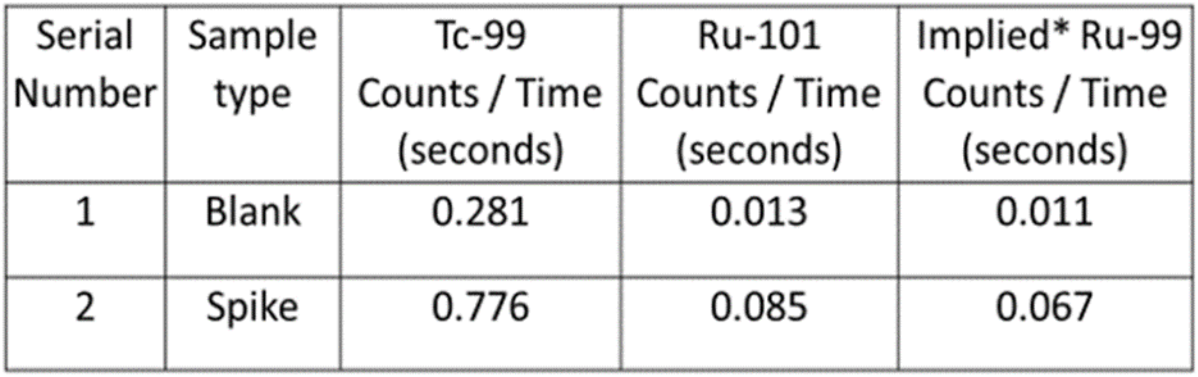


Figure 13: Spiked Tc-99m and Tc-99 purified and extracted seaweed target showing minimum interference of Yb-173

Table 5: Seaweed counts in AMS



Serial Number	Sample type	Tc-99 Counts / Time (seconds)	Ru-101 Counts / Time (seconds)	Implied* Ru-99 Counts / Time (seconds)
1	Blank	0.281	0.013	0.011
2	Spike	0.776	0.085	0.067

*Calculated from isotopic ratio Ru-99/Ru-101

The background concentration of Tc-99 and Ru-99 is about 30 fg/mg originating from Ru-99 and the small amount of Tc-99m (about 2fg in the Tc-99m solution) was added to the sample as a yield monitor. The scattering is caused by Yb-173 that needs to remove by using a solid-phase extraction method.

The oxidation-reduction method provides a simple way to estimate low levels of Tc-99 in samples of biota collected from the environment. This method can be further improved by reducing the background Tc-99 in the reagents and eliminating the scattering Yb-173 by using a solid-phase extraction method in future experiments. The radiochemical method for the detection of Tc-99 from seaweed is based on a two-step procedure and uses Tc-99m as a yield tracer. The first step is the oxidation of technetium from Tc^{+4} to Tc^{+7} oxidation state with H_2O_2 followed by iron hydroxide precipitation. The second step is the reduction of technetium from Tc^{+7} to the Tc^{+4} oxidation state with $SnCl_2$ followed by iron hydroxide precipitate. This precipitate contains the Tc^{+4} and is dried at 80°C and then at 200°C to remove excess water then mixed with PbF_2 to produce TcF_5^- in the AMS ion source. Fluoride anions are extracted, and the Tc is stripped to produce Tc^{4+}. The advantage of using AMS to measure Tc-99 is that it provides a 1000 times greater sensitivity than beta counting methods. The count rate in AMS is about 5 counts per second for a target containing 1 picogram of Tc per mg of the dried precipitate. The background is about 30 fg/mg level, and it comes from Ru-99 and the small amount of Tc-99m (about 2 fg plus an unknown amount of Tc-99 already in the Tc-99m solution) that was added to the sample as a yield monitor (table 5). As the result, we found significant interference from Yb-173. However, following an oxidation and reduction protocol, we found Yb-173 as greatly reduced. This method can be improved by reducing the background Tc-99 in the reagents and eliminating the scattering Yb-173. Also, we can reduce Ru-99 and Yb-173 by solid-phase extraction.

Summary of methods

The aims and objectives of the study were to develop methods for the removal of interferences and extraction of Tc-99 from small environmental samples and develop a method to calibrate then analyze a standardized solution of Tc-99 on a low energy AMS.

AMS is a method for the determination of Tc-99, a low-level radionuclide in environmental samples. The major advantage of the AMS method is to analyse Tc-99 with high sensitivity and a small amount of sample. The challenge with the AMS measurement of Tc-99 is the isobaric interference of Ru-99. Calibration of Tc-99 involved work at NRC using a traceable primary radiometric standard of Tc-99 from NIST. First, we test the Tc-99 standard solution directly to confirm the presence of Ru-99 and second, we clean it and standardize the Tc-99 by using ARS-II with ABEC column (Galea et al., 2013). The very small difference in the atomic mass of Ru-99 and Tc-99 ($\Delta m = 0.0003154$ amu) makes the isolation of Ru-99 from Tc-99 in AMS difficult, and therefore Ru-99 is the major interference in the AMS measurement of Tc-99.

We have developed and tested a method to measure Tc-99 in seaweed with environmental seaweed samples from market by AMS. (Akram, et al., 2017; Cornett, et al., 2017). The seaweed samples are digested in concentrated nitric acid and dried to prepare a sample for AMS analysis.

For method development, we used Tc-99m as a yield tracer to monitor the subsequent chemical preparation of the AMS target. This method excludes the use of Tc-99m during routine use due to potential contamination by ground state Tc-99 present in the Tc-99m stock solution. In the procedure development, H_2O_2 is added to the sample solution to ensure that all the Tc is oxidized before $FeCl_3$ is added. The pH is adjusted with NH_4OH to pH 10 where TcO_4– is stable and Fe will precipitate potential interferences such as rare earth elements that also digested in the seaweed matrix. Subsequently, the precipitate is washed and discarded, and the supernatant is reduced using $SnCl_2$ so that the Tc forms $TcO\ (OH)_2$ precipitate. This form of Tc can then be co-precipitated in a second $Fe\ (OH)_3$ precipitation step. The iron precipitate is dried at 80^{o}C and then at 200^{o}C to remove excess water. ARS-II with ABEC column used to develop Tc-99 standard.

The dried iron with Tc-99 was mixed with PbF_2 to produce TcF_5^- in the AMS ion source. The anions are extracted, and the Tc is converted in the accelerator to Tc^{4+} for measurement. The count rate is about 5 counts per second for a target containing 1 picogram of Tc per mg of the finally dried precipitate. The background is on the 30 fg/mg level, and it comes from Ru-99 and the small amount of Tc-99m (about 2fg plus an unknown amount of Tc-99 already in the-99m solution) that was added to the sample as a yield monitor.

The result, we found significant interference from Yb-173. When we follow oxidation and reduction methods, we found Yb-173 to be greatly reduced. This method can be improved upon by reducing the background Tc-99 in the reagents and further eliminating the scattering Yb-173. Also, we can use Column extraction methods to reduce Yb-173 by solid-phase extraction.

Conclusion

The purpose of this research work is to develop a sample preparation method (oxidation-reduction method) to detect Tc-99 at low levels in environmental samples through the analysis of AMS. This technique provides a simple way to estimate low levels of Tc-99 in samples of seaweed collected from the environment. The advantage of using AMS to measure Tc-99 is that it provides greater sensitivity than other analytical instruments such as: beta counting and ICP-MS methods. The major points of conclusion are the following-

1- Pre-treatment and extraction of Tc-99 from solid seaweed sample, is an important step. The release and transfer of Tc-99 from solid seaweed sample to solution is carried out by the oxidation-reduction method and ashing technique.

2- Transferring Tc to TcO_4^- is an important step due to the highly soluble properties of TcO_4^-. During experiment, we used oxidation-reduction method to co-precipitation and pre-concentrated Tc-99 from seaweed samples.

3- Before going for AMS analysis, we need to do calibration of AMS to determine a limit of detection (LOD). Variable blank - sample mixtures were prepared for a calibration curve, based on the mass ratios presented in Table 4 and Figure9.

4- Analysis by AMS requires that the radioisotope of interest is measured as a ratio to a stable isotope of that element. But in the case of Tc-99, there is no stable isotope for this ratio measurement. So, in these types of experiments, a spike of Tc-95 can be added to the sample which is then measured by gamma counting.

5- The aim of this type of experiment was to analyse Tc-99 by AMS to get spectrum (Fig-8,9,10 and 11) and information of interferences such as Ru-99 and Yb-173 in the prepared sample for AMS analysis.

The objectives of research into the AMS technique and applications are to use different types of oxidation-reduction agents to get Tc-99 in a small size sample. It is important to develop the method for precipitation of Tc-99 to prepare a solid sample for AMS analysis. In the AMS analysis of Tc-99, the scattering is caused by Yb-173 that needs to work to remove interference by using a solid-phase extraction (SPE) method. To apply the developed method in real environmental small size samples (water, seaweed and medical used Tc-99m waste) and to extract and analyze Tc-99 in AMS to prove the validity of the newly developed method. The main aims and objectives of this research work with AMS to establish rapid and accurate methods for extraction and determination of Tc-99 in small size environmental samples (e.g., seaweed, water and hospital used waste).

Presentation and publication of research work

1. Presented research work at AMS -14 conference at uOttawa in 2017 and published in AMS-14 conference journal.
2. Presented in NSERC CREATE-REACT conference-2017 at Laval university, Quebec.
3. Presented research work at ASER -2018 conference at University of Ottawa and published in ASER-2018 conference journal.
4. Presented in NSERC CREATE-REACT conference-2019 at Carleton university, Ottawa.

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