Matrix Separation of Nickel Isotopes Using Ion-Exchange Chromatography and Analysis with Thermal Ionization Mass Spectrometry

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Thesis Proposal

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DIPLOMA THESIS TOPIC

Author of thesis:	Marissa Rachel Lydia Gutsch
Study programme:	Engineering Ecology
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Language of a thesis:	English

Thesis title:	**Nickel isotope analysis in environmental samples from Northern Norway using Mass Spectrometry with Thermal Ionization (TIMS)**
Objectives of thesis:	The main objective of the thesis is to develop an efficient methodology for Ni isotope analysis by Mass Spectrometry with Thermal Ionization (TIMS). For this purpose matrix separation from the samples must be optimized in order to obtain a pure Ni fraction for the analysis. The method will be developed using environmental samples (i.e. snow, lichens or soil) from Northern Norway, where significant emissions from the Russian Ni-ore industry affect the local environment.
Methodology:	Several types of environmental samples (soil, lichens, snow) as well as Ni-ore, slug from the smelter were collected at the studied area (Norway) and Nickel smelter (Russia). The samples were homogenized and decomposed. The concentration of Ni and other elements was determined by ICP-MS. Aliquots of selected samples will undergo the two-step matrix separation of chromatographic column filled with specific resins. The efficiency of the separation must be higher than 95%. The

second part of the thesis will deal with optimization of the sample loading technique in order to obtain efficient ionization of Ni. The isotope composition will be analyzed by TIMS spectrometer. The isotope data will be used for tracing the source of pollution in different environmental compartments.

The proposed extent of the thesis: 60

Keywords: nickel; isotopes; Norway; matrix separation

Recommended information sources:

1. Komárek, M., Ettler, V., Chrastný, V., Mihaljevič, M., 2008. Environ. Inter. 34, 562-577.
2. Ratié, G., Quantin, C., Jouvin, D., et al., 2016. Applied Geochem. 64, 136-145.
3. Reimann, C., de Caritat, P., Niskavaara, H., et al., 1998. Geoderma 84, 65-87.
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5. Reimann, C., Niskavaara, H., de Caritat, P., et al., 1996. Sci. Total Environ. 182, 147-158.

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Author's Declaration

I, Marissa R. Gutsch, hereby declare that the research and work generated of this thesis is the sole and own work of the author. The work was done in accordance with the Czech University of Life Sciences expectations and guidelines for the completion of a Master's of Science in the Faculty of Environmental Sciences. The research and work was done in cooperation with the Faculty of Environmental Sciences and the Department of Environmental Geosciences.

I confirm that any work of the thesis previously submitted for a degree or other purposes has been clearly stated; that any consultation of published works of other is clearly attributed; the quotation of others work, with the exception of my own work, is appropriately sourced; I have clearly acknowledged all sources of contribution; where any work not done by myself but jointly, it has been made clear what their and my own contributions are; and none of this work has been published or parts of this work has been published in Šillerová, *et al.,* 2017.

Prague, April 2017   Marissa R. Gutsch

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Abstract

A long history of mining and pollution in the Barents portion of the arctic circle (Norway, Russia, and Finland), along with the growing concern of climate change has led to a need to develop an efficient technique to identify and trace pollution deposition in the environment. In the Kola Peninsula of Russia, the mines and processing plants are considered the world's foremost producer of sulphur dioxide and metal emissions creating an industrial desert in this region. Opposite is the Sør-Varanger area of Norway and is under threat of the same pollution effects seen in Russia. This thesis looks at identifying nickel in the Norwegian environment and comparing with the processing plants located in Russia. To source trace the pollution, sampling of snow, moss, bedrock, lichens, and soil was carried out and samples of PM_{10} fraction and smelter slag were acquired and compared at an isotopic level. Samples were prepared through acid digestion and then subjected to a two-stage ion-exchange column chromatography to produce a purified liquid sample of nickel. Purified samples were analyzed at the isotope level using Thermal Ionization Mass Spectrometry. The usage of Thermal Ionization Mass Spectrometry is to determine if the nickel found in the environment is part of a normal background concentration or was accumulated as a result of pollution. Through this work, a methodology can be found to trace metal pollutants in the environment that is less costly and relatively time effective. Additionally, this methodology can help determine the difference between background and non-background concentrations of nickel by using the isotope fingerprint.

Keywords*: Nickel; Isotopes; TIMS; Ion-Exchange Column Chromatography; Pollution.*

Abstrakt

Dlouhodobá těžba nerostů a s tím související znečišťování životního prostředí, například v pobřežních oblastech Barentsova moře (severní část Norska, Ruska a Finska), spolu s rostoucím tlakem na zmírnění následků klimatických změn postupně vedla k vytvoření účinné metody identifikace a sledování depozice znečišťujících látek v životním prostředí. Na poloostrově Kola (Rusko) se nachází značné množství dolů a navazujících zpracovatelských závodů, které patří mezi největší světové producenty oxidu siřičitého a kovů do okolního prostředí. Tyto aktivity navíc vytvářejí v přilehlém regionu tzv. „industriální poušť". Oblast Sør-Varanger, ležící na Norské straně hranic s poloostrovem Kola je ohrožena srovnatelnou mírou zatížení jako zmíněná oblast v Rusku, a tedy stejnými dopady na životní prostředí, jaké jsou pozorovány na Ruské straně hranic. Tato práce je zaměřena na identifikaci niklu v životním prostředí v oblasti Sør-Varanger a porovnání tamního znečištění izotopy Ni se situací na poloostrově Kola. Pro identifikaci míry znečištění byly odebrány vzorky sněhu, mechu, hornin, lišejníků, půdy, frakce PM_{10} z ovzduší, a dále odebrány vzorky strusky z tavících pecí, které byly následně porovnány mezi zájmovými lokalitami. Z odebraných vzorků byl separován čistý tekutý vzorek obsahující Ni frakci pro analýzu izotopů niklu pomocí kyselého rozkladu a dvoustupňové iontové chromatografie na speciálním ionexu. Takto připravené vzorky byly analyzovány pomocí metody TIMS (Thermal Ionization Mass Spectrometry), dle které lze určit, zda je obsah přítomných izotopů niklu v prostředí standardní hladinou či je výsledkem antropogenní činnosti. Tato práce může být do budoucna základem metodiky pro identifikaci a sledování niklu v životním prostředí pomocí méně časově a finančně náročných metod, popřípadě pro určení přirozených a antropogenní činností zvýšených koncentrací polutantů v životním prostředí.

Klíčová slova: *Nikl, Izotopy, TIMS, Ionexová chromatografie, Znečištění*

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1. Introduction

The identification and understanding of pollutants in the environment is critical in environmental sciences and the long-term influences in regards to climate change and environmental degradation. The primary objective of the thesis revolves around the development of a new methodology of isotope analysis using Thermal Ionization Mass Spectrometry (TIMS) of nickel (Ni) post smelting process at a smelter in Russia and its implication for tracing the industrial source of Ni in the Norwegian arctic environment. As no current studies exist in the analysis of Ni using TIMS, it is essential to create a detailed and extensive methodological guide on the topic. The secondary objective of the thesis is determining the Ni isotope composition in collected environmental samples and evaluating isotope fractionation. This study takes place in the Norwegian arctic due to the long history of Ni mining in the area and the identifiable impacts of pollution seen in the arctic (Norseth, 1994; Lindroos *et al.,* 1997). Through the usage of environmental samples (soil, snow, lichens, and mosses) and Ni ore, slug from the smelter, and PM_{10} collected at study sites located in Norway and from the Ni smelter in Russia, the evaluation of the Ni isotope fractionate could be completed. A two-stage ion-exchange column chromatography allows for the efficient matrix separation of the analyte Ni to obtain a pure Ni fraction and removal of organic material and other metals. Ni is important to identify in the environment due to the effects that can occur from Ni accumulating in the environment. Damage to soil microorganisms, nutrient cycling, forest stands, and bioaccumulation in local fauna and flora are some of the environmental affects (Norseth 1994; Lindroos *et al.,* 1997). In addition, Ni can have severe influences on the health of people such as respiratory issues, carcinogenesis, and dermatitis (Smith-Sivertsen *et al.,* 1999; Smith-Sivertsen *et al.,* 2002; Buekers *et al.,* 2015; Raval *et al.,* 2016; Zambelli *et al.,* 2016). The purified Ni fraction can be used for analysis by TIMS to identify natural and anthropogenic sources of Ni deposition in the environment. The development of the matrix separation methodology creates a precedent for further work in the study of pollution tracing in the environment from point and non point

sources. Through TIMS analysis, further research can be tested as well as furthering practices in environmental policy and regulations regarding pollution, monitoring, and remediation techniques.

2. Aims of the Thesis

The aim of this thesis is to develop an efficient methodology to separate and identify Ni isotopes in organic samples and trace the source of Ni to a point source. To achieve this objective, a Ni standard solution must first be tested to determine if the methodology is successful. The first step is the ion-exchange chromatography separation of samples using two matrix separations. The separations will produce a Ni sample free from other metals and organic matter. The second step is the method optimization of using Thermal Ionization Mass Spectrometry to analyze the Ni standard. From these results, a conclusion can be developed suggesting the efficacy of this separation and mass spectrometry analysis of Ni isotopes. The third step is the collection of appropriate environmental samples to compare with background and smelting slag. Collection occurred in Norway between 2015-2016 and soil, snow, moss, bedrock, and lichens were collected in addition to PM_{10} fraction and smelter slag. Samples will undergo acid digestion to be prepared for ion-exchange chromatography. The fifth and final step is the analysis of separated environmental Ni samples with TIMS following the optimized method.

A new and effective methodology for identification is essential to produce accurate point source tracing results. This thesis can lead to similar work being done for other metals being source traced in the environment. Contributions include a better understanding of pollution in arctic environments in terms of spread and depth, as well as contributing to global studies on the effects of pollution in the environment and challenges associated with climate change.

3. Literature Review

3.1. Nickel Properties

Nickel (Ni) is the 24th most abundant natural element found in the Earth's crust that is ubiquitously distributed in the air, soil, and water, and is an essential micronutrient for plant growth and beneficial in animal feed (Cempel and Nikel, 2006; De Brouwere *et al*., 2012; Schaumlöffel, 2012). In the environment, Ni will appear in five natural isotopes, ^{58}Ni, ^{60}Ni, ^{61}Ni, ^{62}Ni, and ^{64}Ni; there are also additional unstable Ni isotopes known to exist (Rosman and Taylor, 1998; Denkhaus and Salnikow, 2002; Cempel and Nikel, 2006). The prevalent oxidation state of Ni is in the +2 valence state, Ni(II), although valence states in -1, +1, +3, and +4 exist but are seen less frequently (Cempel and Nikel 2006). As a transition metal, Ni has a high temperature resistance and resists corrosion by water, air, and alkali but will dissolve readily in dilute oxidizing acids (Cempel and Nikel, 2006). The transition metal attributes and abundance of Ni make it essential in modern infrastructure and technology being used in the stainless steel industry, as an alloy, in transportation, electronics, in batteries or food preparation equipment (Denkhaus and Salnikow, 2002; Mudd, 2011; De Brouwere *et al*., 2012).

Ni is commonly present in the environment in the form of two ore types, sulfide and laterite (Mudd, 2011; Norgate and Jahanshahi, 2011). Sulfide based ores of Ni are derived typically from volcanic or hydrothermal processes and will include metals such as cobalt and copper, and precious metals such as gold or platinum (Mudd, 2011). Pentlandite [$(NiFe)_9S_8$] is the most common of Ni sulfide ores and is typically associated with pyrrhotite, a varying iron sulfide (Warner *et al*., 2007). Laterite based Ni ores occur in tropical or near equator locations with near surface weathering processes of ultramafic rocks and will contain metals such as iron and silica (Mudd, 2011).

3.2. Usage of Nickel

Extraction and usage of Ni has long been practiced across Europe and Asia as a cheap substitute for other metals before it was formally identified as an element in 1751 by Swedish chemist Axel Fredrik Cronstedt (Mudd, 2011). Mining and smelting of Ni has occurred throughout Europe with majority of mines being located in southern Norway by the 1870's until larger deposits were found in Canada and other locations globally causing a Ni boom (Mudd, 2011). Since the 1900's, Ni production has drastically increased from approximately 10,000 t of Ni to 1.6 million t in 2008 (Mudd, 2011; Norgate and Jahanshahi, 2011). Increase in Ni production of the twentieth century occurred primarily by the demands of World War I and II, and the finding of new Ni fields in Russia's Kola and Taimyr Peninsulas, Western Australia, Indonesia, China, and Canada (Mudd, 2011; Norgate and Jahanshahi, 2011). Presently, the Taimyr Peninsula in northern Siberia and the Kola Peninsula of northwestern Russia are the world's leading producer of Ni from Ni sulfide ores (Mudd, 2011). Historically, Ni sulfide ores have been favoured in mining due to a higher ore grade, easy and cost efficient extraction of Ni, and the sulfur can be used as a fuel source (Mudd, 2011; Fukuzawa, 2012). In 2004, it was shown that annual Ni output from Ni sulfide smelters account for 740,000 t or 59% of the global primary Ni production (Warner *et al.* 2007). Russian company Norlisk Nickel in the Kola Peninsula reported ore production of 8,138 kt and 106 kt of Ni produced in 2014 (Norlisk Nickel, 2016).

Production of a high quality Ni from a Ni sulfide ore occurs in two steps: smelting and converting to produce a Ni matte suitable for further refining (Warner *et al.* 2007; Crundwell *et al.*, 2011). Two smelting technologies are used in the Ni sulfide ore processing: flash smelting accounting for 70% of Ni produced and electric furnace smelting (Warner *et al.* 2007; Crundwell *et al.*, 2011). The Norlisk Nickel Plant in the Kola Peninsula of Russia operates as an electric furnace smelter and works on a process of roasting, smelting, and converting (Warner *et al.* 2007). Advantages of electric furnace smelting

include high recovery of Ni, ability to attain and control high slag temperatures, and efficiently smelt metal-rich scrap, however, electric furnace smelting consumes a large amount of electricity and produces high volume emissions and waste (Crundwell *et al*., 2011; Fukuzawa, 2012). Ni processing is considered to be highly energy inefficient and has higher carbon dioxide equivalent emissions in comparison to other non-ferrous metals (Norgate *et al*., 2006; Fukuzawa, 2012). Reserves of high-grade Ni ore are progressively declining requiring higher energy consumption and greater impacts from mining and smelting are occurring to compensate for lower grade ore (Norgate *et al*., 2006).

3.3. Nickel Pollution Affects

Environmental issues associated with the Ni industry include air emissions, toxic effluents, and wastes that influence humans, food and crop production, water, soil, flora, and fauna (Denkhaus and Salnikow, 2002; Cempel and Nikel, 2005; Norgate and Jahanshahi, 2011; De Brouwere *et al*., 2012; Fukuzawa, 2012; Solgi and Parmah, 2015). Although Ni is emitted naturally, the anthropogenic activities of humans account for a 1.4 to 1.8 higher rate of release into the environment (Buekers *et al.*, 2015). The combustion of fossil fuels, smelting and refining, steel production, waste incineration, alloy production, and coal combustion are the main contributors to Ni release into the environment (Smith-Sivertsen *et al.*, 1999; Smith-Sivertsen *et al.*, 2002; Buekers *et al.*, 2015). It is estimated by EU27 that total Ni emissions is 1790 t Ni per year and 612 t is released into the air (Buekers *et al.*, 2015). The U.S. Department of Health's Agency for Toxic Substances and Disease Registry determined natural Ni concentration in river and lakes to be less than 0.01 mg/L but in areas where Ni is mined and refined, the concentration to be around 0.072 mg/L, exceeding the set maximum allowable concentration of 0.02 mg/L which can lead to serious health concerns for the environment, fauna, flora, and humans (Ballesteros *et al*., 2016; Raval *et al*., 2016). At a Ni and Cr mine located in northeastern Iran, Ni natural concentrations in the soil range from 10-50 mg/kg and there is a permissible limit of Ni 100 mg/kg but

this ecotoxicological limit is well exceeded in a range of 132 to 550 mg/kg of Ni being found in the soil (Solgi and Parmah, 2015).

Since 1992, research by the Kola Ecogeochemistry Group have studied the effects of pollution in the Kola Peninsula of Russia and the surrounding Norway and Finnish borders through soil, snow, lichen, moss, and groundwater sampling (Niskavaara *et al*., 1996; Reimann *et al*., 1998; Reimann *et al*., 2001). The cumulative impacts of mining can be seen in stark contrast between the Norwegian and Russian border. Extensive studies completed by Gregurek, *et al*., (1998) and Norseth (1994) indicate the extensive damage from the emissions of SO_2 and metals from the Nikel and Zapolarny processing plants. The surrounding plants are considered the cause of an industrial desert that is easily identifiable between the two borders (Figure 1) (Norseth, 1994; Gregurek *et al*., 1998).

Figure 1. The Norlisk smelter located in the Kola Peninsula, Russia as pictured from the Norwegian border (Photo by Marissa Gutsch, 2016).

Although Ni is considered a fundamental micronutrient for plant growth and plays an important biological role for bacteria, archea, and other unicellular eukaryotes, it can cause serious issues for humans through multiple different

pathways of exposure (Cempel and Nikel, 2005; Zambelli *et al.*, 2016). Pathways of Ni exposure to humans is highly diversified from presence in food, jewelry, clothing, money, mobile phones, dental and medical implants, and also through the air, water, and soil (Smith-Sivertsen *et al.*, 1999; Smith-Sivertsen *et al.*, 2002; Buekers *et al.*, 2015; Zambelli *et al.*, 2016). Human exposure to Ni can lead to dermatitis, poisoning, and carcinogenesis (Smith-Sivertsen *et al.*, 1999; Smith-Sivertsen *et al.*, 2002; Buekers *et al.*, 2015; Raval *et al.*, 2016; Zambelli *et al.*, 2016). In the case of Ni mining and refining, workers are at a greater risk to inhalation exposure resulting in the formation of tumors and cellular damage (Buekers *et al.*, 2015; Zambelli *et al.*, 2016). In the Sør-Varanger municipal area of Norway near the Kola Peninsula Ni plants, it was found that Ni allergy of adult women to be three times as high as a control group of Danish women, and that Ni concentrations in tap water and urine samples were significantly higher than in the Russian mining cities of the Kola Peninsula (Smith-Sivertsen *et al.*, 2002). The effects of Ni pollution on humans have been well studied due to the long history of mining in the arctic regions of Norway, Finland, and Russia (Norseth, 1994; Lindroos *et al.*, 1997).

Norseth (1994) reports that at the Monchegorsk smelter and refining plant, 150 metric t per year of Ni was released into the water and 16 000 metric t per year of particles with a 2:1 content of Ni and Cu was released into the air. For local fauna and flora, Ni is easily bioaccumulated in phytoplankton and aquatic plants, which act as sensitive bioindicators for health of the water (Cempel and Nikel, 2005). Damage to soil microorganisms, stand composition, and nutrient cycling of forests near Ni mining and refining operations is reported to be affected by the accumulation of Ni (Norseth 1994; Lindroos *et al.*, 1997). In the case of ruminant species near the Kola Peninsula operations, it was found that reindeer and moose showed high levels of Ni bioaccumulation in their organs and tissue in comparison to other ruminants sampled not in proximity to the Ni operations (Sivertsen *et al.*, 1994).

3.4. Isotope nomenclature

The identification of isotopes of elements has been intimately tied to the rise of mass spectrometry since the beginning of the 19th century (Budzikiewicz and Grigsby, 2006; Hachey, 2016). In 1815, British chemist William Prout proposed his hypothesis on the existence of multiple molecular masses of hydrogen leading to controversy in the development of isotope theories (Budzikiewicz and Grigsby, 2006). The first definition of an isotope was coined in 1913 by Fredrick Soddy and Kazimierz Fajans during their work with radioactive elements (Budzikiewicz and Grigsby, 2006; Hachey, 2016). Soddy and Fajans suggested that atoms of different mass and radioactive properties could have the same essential chemical properties and remain in the same place on the periodic table (Hachey, 2016). In 1919, Francis Aston used a mass spectrograph to identify two isotopes of neon with slightly different atomic masses and continued his work with other nonradioactive elements and their isotopic compositions (Budzikiewicz and Grigsby, 2006; Hachey, 2016). Through Astons work, he published findings in 1925 for the isotopic compositions of over 50 elements. (Budzikiewicz and Grigsby, 2006). Isotope compositions are continuously being updated as techniques improve in mass spectrometry (Budzikiewicz and Grigsby, 2006).

The International Union of Pure and Applied Chemistry (IUPAC) currently defines an isotope as nuclides having the same atomic number but different mass numbers of an element (McNaught and Wilkinson, 1997; Porcelli and Baskaran, 2011; Wiederhold, 2015). Elements typically contain multiple stable isotopes in different fractions making up the atomic mass of the element (Porcelli and Baskaran, 2011; Wiederhold, 2015). When naming an element with the isotope specification each isotope will bear the same element name and will be differentiated by the inclusion of the mass number, for example nickel-60 and the symbol ^{60}Ni (Connelly *et al*., 2005). The expression of an isotope composition is done using the formula:

$$\delta\ (‰) = (R_{sample}/R_{standard} - 1) \times 10^3 \qquad \text{Eq. 1}$$

where δ represents the specific isotope variation and R is the measured abundance ratio of the trace isotope to the standard, such as $\delta^{60}Ni$ and a ratio like $^{60}Ni/^{58}Ni$ (Budzikiewicz and Grigsby, 2006). For the purpose of this thesis, the formula used for the measurement of Ni isotopes during TIMS analysis is measured using $\delta^{60}Ni$:

$$\delta^{60}Ni\ (‰) = (^{60}Ni/^{58}Ni\ 1) \times 10^3 \qquad \text{Eq. 2}$$

3.5. Nickel Isotope Signatures

Thirty-one Ni isotopes have been discovered to date and can be identified between ^{48}Ni to ^{78}Ni (Garofali et al., 2010). This includes five naturally occurring, stable isotopes, 11 proton-rich, and 15 neutron-rich isotopes of Ni (Garofali et al., 2010). The five stable isotopes and corresponding abundances are ^{58}Ni (68.07%), ^{60}Ni (26.22%), ^{61}Ni (1.14%), ^{62}Ni (3.63%), and ^{64}Ni (0.93%) and they are seen naturally in the environment (Rosman and Taylor, 1998; Denkhaus and Salnikow, 2002). In the 1921 paper, "The Constitution of Nickel" by Aston, isotopes ^{58}Ni and ^{60}Ni were first identified with ^{58}Ni showing a greater spectrum than ^{60}Ni (Garofali et al., 2010). As technology improved the remaining isotopes of Ni were discovered or synthesized.

The Earth's upper silicate mantle has a mean concentration of 2000 µg/g of Ni occurring and greater than 99% of the Earth's Ni occurs in this silicate mantle (McDonough and Sun, 1995; Gall et al., 2017). The isotopic composition of the mantle is controlled by differences in mineralogy and provides systematic variations of Ni (McDonough and Sun, 1995; Gall et al., 2017). Typical terrestrial silicate mineral samples analyzed include olivine, orthopyroxene, and clinopyroxene as well as igneous rocks and sediments (Cameron et al., 2009; Gueguen et al., 2013; Gall et al., 2017). In the silicate material it is found that $\delta^{60}Ni$ has a mean compositional value of 0.23 ±

0.13‰ (2 degrees of standard deviation; *n* = 66) in the mantle (Cameron *et al*., 2009; Gall *et al*., 2017).

3.6. Nickel Fingerprinting Methodology

The identification and source tracing of Ni in the environment is difficult due to natural occurring levels found in the bedrock, soil, and plant material (Cempel and Nikel, 2005; Gueguen *et al*., 2012). Through stable isotopes and source tracing techniques, there is a potential for Ni to be identified effectively and efficiently in the environment (Ratié *et al*., 2015a; Wiederhold, 2015). Isotope source tracing technique is based on a comparison of Ni isotope signatures of "background" (natural) and "produced" (anthropogenic) samples (Becker, 2005; Porcelli and Baskaran, 2011). Once the metal and source is identified, then concentration can be used to determine detrimental effects that may be experienced in the environment.

In the case of Ni there are five stable isotopes with the most abundant being ^{58}Ni at 68.07% (Rosman and Taylor, 1998; Gall *et al*., 2012; Gueguen *et al*., 2013). By having multiple stable isotopes, it is possible to view element cycling in the environment through comparison of Ni isotope ratios (Porcelli and Baskaran, 2011; Wiederhold, 2015). The typical Ni isotope ratio measured is ^{60}Ni/^{58}Ni due to the high natural abundance occurring in the Earth's crust (Gueguen *et al*., 2013; Elliot and Steele, 2017; Gall *et al*., 2017). Through two-stage chromatography and mass spectrometry, it is possible to separate different Ni isotope fingerprints occurring in the Earth's bulk silicate material (Gueguen *et al*., 2013). In Gueguen, *et al*. (2013) Ni isotope composition of varying geological reference samples were analyzed using multicollector-inductively coupled plasma-mass spectrometry (MC-ICP-MS) with a double spike correction method. It was found that igneous and mantle derived rocks displayed a range of -0.13 to +0.16% for the ^{60}Ni/^{58}Ni ratio suggesting that Ni isotope fingerprints can be identified in different samples (Gueguen *et al*., 2013).

Fractionation of Ni isotopes is a relatively new study for terrestrial samples with the bulk of studies focusing on meteorite samples (Regelous et al., 2008; Gueguen et al., 2013; Gall et al., 2017). The abundance of ^{61}Ni, ^{62}Ni, and ^{64}Ni in meteorites occur in ratios with each other and account for their corresponding terrestrial abundances (Regelous et al., 2008; Elliot and Steele, 2017; Gall et al., 2017). Assessing Ni fractionation in natural materials is difficult due to inter-mineral equilibrium fractionation factors are relatively unknown for Ni (Lazar et al., 2012). However, kinetic fractionation can be observed for Ni if exposed to high temperatures during smelting of Ni minerals but is unlikely (Herzog et al., 1994; Lazar et al., 2012). The observed natural fractionation of terrestrial Ni can be explained through biotic and abiotic processes (Cameron et al., 2009; Gueguen et al., 2013; Elliot and Steele, 2017; Gall et al., 2017). Abiotic fractionation of Ni isotopes includes weathering processes, chemical precipitation, and adsorption in aqueous systems such as oceans and rivers (Gueguen et al., 2013; Elliot and Steele, 2017; Gall et al., 2017). Biotic fractionation of Ni occurs through microorganism assimilation for the purposes of methanogensis (Cameron et al., 2009; Gueguen et al., 2013; Elliot and Steele, 2017; Gall et al., 2017).

Tracing Ni in the environment to its pollution source has been explored using concentration analysis in terrestrial samples (Adamo et al., 1996). Ni is a highly mobile metal and often associates with inorganic oxides or to clay surfaces, however, concentration analysis does not provide an appropriate history of Ni deposition (Adamo et al., 1996). In a study on laterite ores and ultramafic rocks, Ni isotope fractionation through weathering processes lead to promising results on using Ni isotopes as a tracer for biogeochemical cycling (Ratié et al., 2015b). However, challenges associated with the source tracing of Ni is identified by Ratié et al (2015a) in the study of Ni isotope fractionation during laterite Ni ore smelting. While enrichment of soils near a smelting and refining plant was discovered, the discerning of anthropogenic and natural Ni isotopes is difficult due to weathering processes causing fractionation and a large global range of published δ^{60}Ni values (Ratié et al., 2015a).

3.7. Nickel Isotope Analysis

Isotope analysis of metals is an emerging practice within the last two decades in environmental sciences due to advancements in methodology and analytical tools (Becker, 2005; Porcelli and Baskaran, 2011). Many metals, Ni included, are involved in biological cycling such as translocation and uptake in plants, assimilation, or the formation of organic complexes in the soil (Gall *et al*., 2012; Wiederhold, 2015).

Before isotopes analysis can begin, samples must be prepared using a matrix separation technique to provide an aqueous, purified sample for best results (Cook *et al*., 2007; Gall *et al*., 2012; Gueguen *et al*., 2013; Wiederhold, 2015). The separation of Ni is relatively difficult due to chemically similar behavior of several elements, such as Fe, Cu, Mg, and Ca; thus requiring an effective separation methodology (Gall *et al*., 2013). Ion-exchange chromatography is an effective method of sample separation purification as it will ensure removal of undesirable organics and inorganics that may provide interference when analyzing by mass spectrometry (Cook *et al*., 2007; Gall *et al*., 2012; Gueguen *et al*., 2013). By using an anion exchange resin with an acid activation, it is possible to remove unwanted cations, such as Fe or Ca, from solution while maintaining Ni in solution (Cook *et al*., 2007; Gall *et al*., 2012; Gueguen *et al*., 2013). A second column can then be used with a Ni specified resin that will allow other ions to pass through solution and Ni to remain adhered to the resin (Cook *et al*., 2007; Gueguen *et al*., 2013). Ion-exchange chromatography is essential to remove any isobaric interference by chemically similar elements, such as Fe before mass spectrometry analysis (Cook *et al*., 2007; Gall *et al*., 2012; Gueguen *et al*., 2013).

The measurement of stable isotopes in the environment can be undertaken by usage of mass spectrometry (Becker, 2005; Porcelli and Baskaran, 2011). Mass spectrometry is based on the counting of atoms through separation that is achieved by diverting charged particles travelling across a magnetic field (Porcelli and Baskaran, 2011; Georgiou and Danezis, 2015). All ions of

an element will have the same charge and are therefore subjected to the same magnetic field and the same velocity meaning the path of radii are a function of mass (Porcelli and Baskaran, 2011; Georgiou and Danezis, 2015). Ions of the same element will then exit the magnetic field according to their atomic mass and the ion of interest will remain in the magnetic field for analysis (Porcelli and Baskaran, 2011; Georgiou and Danezis, 2015). Mass spectrometry is utilized as it provides highly sensitive measurements of element concentrations (Becker, 2005; Porcelli and Baskaran, 2011; Georgiou and Danezis, 2015). In the case of Ni, Multicollector Inductively-Coupled Plasma Mass Spectrometry (MC-ICP-MS) is used for analyzing isotopes in the environment, however in this thesis, Thermal Ionization Mass Spectrometry is used for Ni analysis.

Thermal Ionization Mass Spectrometry (TIMS) is a methodology where samples are manually loaded onto a metal filament inside a vacuum source (Porcelli and Baskaran, 2011; Georgiou and Danezis, 2015). During the thermal processing, the metal is resistance heated and atoms are evaporated (Porcelli and Baskaran, 2011; Georgiou and Danezis, 2015). A portion of the atoms are ionized and will travel down a flight tube into a magnetic field where analysis can be done (Porcelli and Baskaran, 2011; Georgiou and Danezis, 2015). While TIMS provides an ion beam with a narrow range of energies and generates high precision data, it is a time-consuming process and the proportion of vaporizing atoms that can ionize can be low for elements with high ionization energy (Porcelli and Baskaran, 2011; Georgiou and Danezis, 2015). The ionization energy (eV) of Ni is dependent upon its ion charge and will increase in ionization energy as the ion charge increases. Starting at an ion charge of zero, Ni I, has an eV of 7.639, Ni II with an ion charge of +1 the eV is 18.168, and Ni III with an ion charge of +2 the eV is 35.187 (Kramida *et al.*, 2015). As the most common form of Ni is the +2 valence state, the ion energy is relatively high for TIMS.

For MC-ICP-MS, samples are introduced in a solution into an Argon plasma for efficient ionization of ions (Porcelli and Baskaran, 2011; Georgiou and Danezis, 2015). Ions are then transferred from the plasma into the vacuum

system of the analyzer (Porcelli and Baskaran, 2011; Georgiou and Danezis, 2015). However, ions exit much more rapidly than in TIMS and require corrections to the ion beams such as adding more magnets or an electrostatic field to create precise results (Porcelli and Baskaran, 2011; Georgiou and Danezis, 2015).

Usage of TIMS or MC-ICP-MS in isotope analysis can determine the Ni isotope signature in the environment. However, issues with instrumental mass discrimination occur when using either TIMS or MC-ICP-MS. Mass discrimination is the result of an analyzer detecting ions more efficiently than another (Wiederhold, 2015). This is problematic as Ni isotope fractionation occurs by natural processes that can lead to a discrepancy in results (Gall *et al*., 2012). Correction of mass discrimination in TIMS analysis is best done by using a double spike method. A double spike will determine the mass discrimination and allow for correction of measured delta values to accurately represent the Ni isotope composition of a sample (Holmden 2005; Gall *et al*., 2012; Wiederhold, 2015). When corrected, identification of Ni will show the origins of the sample by comparison between pre-existing background conditions and a potential pollution source.

4. Methodology

4.1. Site Description

The study and sampling takes place in the Barents region of Northern Norway bordering northern Finland and northwestern Russia. The sampling sites are more precisely located in the Sør-Varanger area of Norway within the vicinity of the large smelter plant located in Russian. The Sør-Varanger area is a coastal rugged landscape with mountains reaching elevation of 700 m above sea level and a glacial morainal terrain (Reimann *et al*., 2001; Uhlig and Junttila, 2001). Bedrock geology is diversified with sea sediments and quaternary deposits of till and peat with relatively young, nutrient poor podzolic soils (Niskavaara *et al*., 1996; Reimann *et al*., 2001; Karlsen *et al*., 2008). Climatically, the yearly average temperature is -1 °C, precipitation occurring primarily between September and January with mild winters due to coastal influences (Reimann *et al*., 2001). The vegetation of the area is three part transitional between boreal, boreal to subarctic, and subarctic tundra (Karlsen *et al*., 2008; Niskavaara *et al*., 1996; Reimann *et al*., 2001; Uhlig and Junttila, 2001). Common vegetation found in the region includes ericaceous (*Empetrum nigrum*) and heather (*Calluna vulgaris*) shrubs, lichens (*Caldonia* sp.), terrestrial mosses (*Hylocomium splendens* and *Pleurozium schreberi*), pines (*Pinus sylvestris*), and birches (*Betual pubescens*) (Reimann *et al*., 2001; Uhlig and Junttila, 2001; Karlsen *et al*., 2008).

4.2. Sampling Techniques

Samples were obtained using a line transect technique across approximately 200 km^2 in the Sør-Varanger area. A total of 17 sample sites were chosen as a function of geography, prevailing wind direction, and distance from the smelters, and were split into three transects (Figure 1). The first transect runs southwest for approximately 50 km and is sites 1, 2, 3, 4, and 5. The second

transect runs northwest for approximately 90 km and is sites 6, 7, 8, 9, and 13. The third transect runs approximately 40 km to the northeast and is sites 10, 11, 12, 14,15,16, and 17. The closest sampling point is approximately 8 km (site 5) and the furthest is 90 km (site 6) from the smelter.
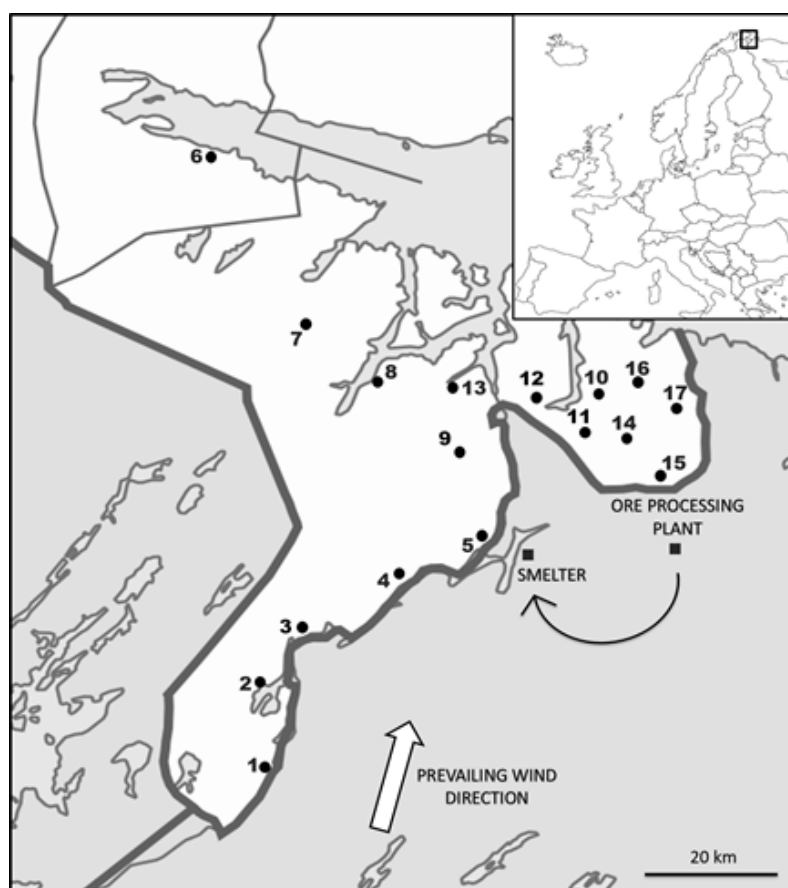

Figure 1. Map of sampling sites in the Sør-Varanger region, Norway. A total of 17 sites were picked from 3 different transects. The closest site to the smelter is Site 5 and the furthest is Site 6 (Šillerová et al., 2017).

Collection of samples was carried out several times between 2015 to 2016 of snow, lichens, soil, bedrock, and moss, while PM_{10} fraction was obtained from two monitoring stations provided by the Norwegian Institute for Air Research. In addition representative samples of smelter slag and feeding material were obtained for analysis. The collected samples were homogenized and decomposed in a mixture of acids including HNO_3, HCl, and HF to produce a liquid sample. Snow samples were reduced by evaporation on a hot plate to approximately 25 mL and then subjected to the

acid digestion into duplicates. Approximately 250 mg of lichen, moss, and soil, and 100 mg of bedrock, feeding material, and smelter slag was digested and were digested in triplicates. After digestion the samples were evaporated to near dryness and taken up to 2% HNO_3 for purification using a Ni specific matrix separation.

4.3. Nickel Matrix Separation and Purification

The separation of matrix from the Ni sample occurred using ion-exchange chromatography columns as adapted from Gueguen *et al.* (2012) through a two-stage procedure. Before separation of Ni, two mesh sizes of the BioRad anionic resin AG 1-X8 were tested. Mesh size refers to the particle space in between resin beads allowing for solution to pass through. Sizes of the AG1-X8 resin tested were 100-200 mesh and 200-400 mesh. A 100-200 mesh would allow for particles between 74-149 μm to pass through and a 200-400 mesh would allow for particles 37-74 μm to pass through the column. Three tests were completed with the resin and loaded onto the column using a pipette. The volume of the first test resin bed size, 100-200 mesh, and the second test resin bed, 200-400 mesh, was 2 mL and a third test at 200-400 mesh was 1 mL. The three tests then had a Ni standard solution passed through to determine the fastest and most effective mesh size for the experiment. Once the appropriate mesh size was determined, the other mesh sizes were discarded. The ideal mesh size was found to be the 100-200 and was used for the remainder of the experiment.

The first stage of ion-exchange chromatography (Figure 2) involved the loading 2 mL of the BioRad anionic resin AG 1-X8 in the chloride form (100-200 mesh) in the column (summary of crucial steps in Table 1). Columns were washed in a three-step process using reservoirs of ultra-pure water, 2% HNO_3, and ultra-pure water in preparation of fraction loading. The column is then activated by the addition of 10 mL of 6 M HCl and is prepared for sample passage. Nickel samples were first evaporated to near dryness at a temperature of approximately 100°C based on a specific aliquot ratio. At near

dryness, the samples are removed from heat and a few drops of concentrated HNO_3 and a few drops of H_2O_2 are added to the samples and left for twenty minutes. After twenty minutes, the samples were evaporated a second time to near dryness at a lower temperature approximately 60°C. Once evaporated to near dryness, 2 mL of 6 M HCl is added to the samples to be loaded on the AG 1-X8 column. Each sample was then added to a column with an additional 10 mL of 6 M HCl to ensure sample has passed through the resin completely. The samples were collected in individual labeled savillex vessels and evaporated to near dryness. Post sample collection, AG 1-X8 columns were rinsed using 10 mL 0.1 M HCl in preparation for another separation.
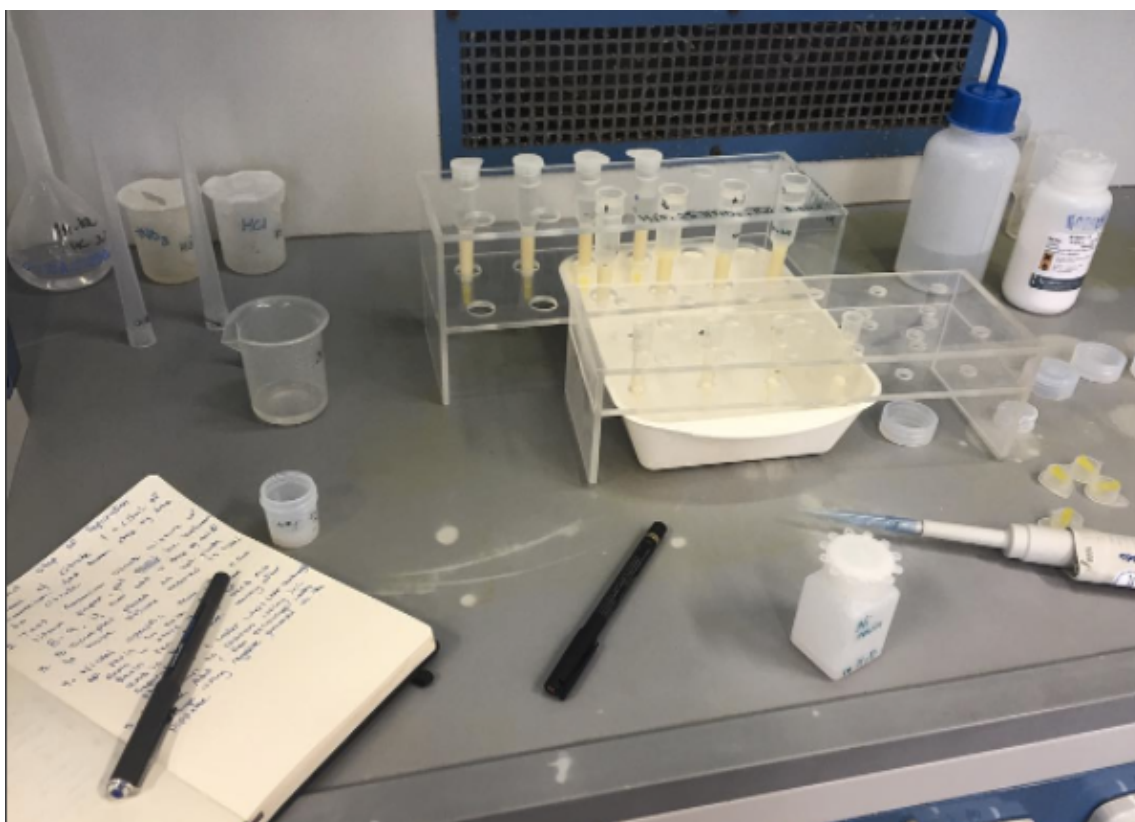

Figure 2. Columns of AG 1-X8 resin and Ni-DMG resin used in the separation procedure (Photo by Marissa Gutsch, 2016).

The second stage of ion-exchange chromatography used a Ni specific resin by Trisken International made of polymethacrylate with a dimethylglyoxime (DMG) molecule to form a Ni-DMG complex at pH 8-9 (Gueguen *et al.* 2012) in a second set of columns (Figure 2). The Ni resin grade is between 100-

150 µm. Approximately 0.5 mL of the Ni-resin (wet volume) is added to the columns. Column preparation, post loading of the resin, involved activation through washing with 2 reservoirs of ultra-pure water, 1 reservoir of 2% HNO_3, and 2 additional reservoirs of ultra-pure water. Once the samples are at near dryness, they are removed from heat and a few drops of concentrated HNO_3 and a few drops of H_2O_2 are added to the samples and left for twenty minutes. After twenty minutes, samples were evaporated to near dryness at a lower temperature approximately 60°C. The evaporated samples then had 1 mL of 0.24 M HCl added. Ammonium citrate is prepared using 40 mL of $(NH_4)_2C_6H_6O_7$ and approximately 5 mL of NH_4 at a pH range of 8-9 and is used to activate the Ni-resin and is added to the samples. The Ni-resin is activated using 2 mL of the ammonium citrate and is prepared for samples. The samples have 0.3 mL of ammonium citrate added and must be a pH 8-9. If the samples are not the desired pH, then additional NH_4 and 0.24 M HCl can be added drop by drop until ideal pH is achieved.

The samples are loaded onto the activated Ni-resin and not collected. An additional 4 mL of ammonium citrate and then 4 mL of ultra pure H_2O are passed through the columns to ensure all material has passed through. The last step is the addition of 8 mL of 3 M HNO_3 to break up the Ni-resin complex and is collected in labeled savillex vessels. The samples are then evaporated to near dryness at an approximate temperature of 100°C. Once evaporated to near dryness, a few drops of concentrated HNO_3 and a few drops of H_2O_2 are added to the samples and once again left for twenty minutes before being evaporated at an approximate temperature of 60°C until near dryness.

Eluent	Volume (mL)	Eluted
2 mL **Biorad AG 1-X8** anion exchange resin (100-200 mesh)[a]		
2% HNO_3 (resin cleaning)	10	
Ultra Pure H_2O (resin cleaning)	10	
6 M HCl (resin activation, conversion to Cl^- form)	10	
6 M HCl (sample solution)	2	Matrix
6 M HCl (resin rinse)	10	Matrix
0.24 M HCl (sample solution)	1	
0.5 mL **Ni-DMG** anion exchange resin[b]		
Ultra Pure H_2O (resin cleaning)	4	
2% HNO_3 (resin cleaning)	2	
Ultra Pure H_2O (resin cleaning)	4	
Ammonium Citrate (pH 8-9, resin activation)	2	
Ammonium Citrate (pH 8-9, sample solution)	0.3	
Ammonium Citrate (pH 8-9, resin rinse)	4	
Ultra Pure H_2O (pH 8-9, resin cleaning)	8	
3 M HNO_3 (resin break up)	8	Ni

Table 1. Summary of ion-exchange separation steps.

[a] Resin re-used following resin wash procedure of 2% HNO_3 and ultra pure H_2O.

[b] Resin discarded after break up with 3 M HNO_3.

4.4. TIMS Analysis

The analysis of Ni samples post ion-exchange column chromatography separation is undertaken using Thermal Ionization Mass Spectrometry (TIMS). Before the separated samples of Ni are analyzed using TIMS, the methodology for sample loading onto a special filament. Consequently an aliquot of 1 ug of Ni from NIST 986 standard, Ni double spike and NIST and double spike mixture must be analyzed to set up measurement protocol as well as the instrumental mass bias correction.

4.4.1. Optimization of Sample Loading and Nickel Ionization

The loading of samples was tested using a Ni standard solution, NIST 986 and different activators such as boric acid (H_3BO_3, 0.1 N) or phosphoric acid (H_3PO_4, 0.1 N), silica gel and Al. The sample together with selected activators are loaded in a small drop onto a Re (rhenium) filament (Figure 3a) and evaporated to dryness by passing a current (~1800 A) through the filament (Figure 3b). Both single and double filament technique was tested (Figure 4). The aim was to find an optimal chemical cocktail that will ensure stable and intense (minimum 30 minutes, and signal of 1.5 V on ^{58}Ni) ion beam for Ni isotope analysis.
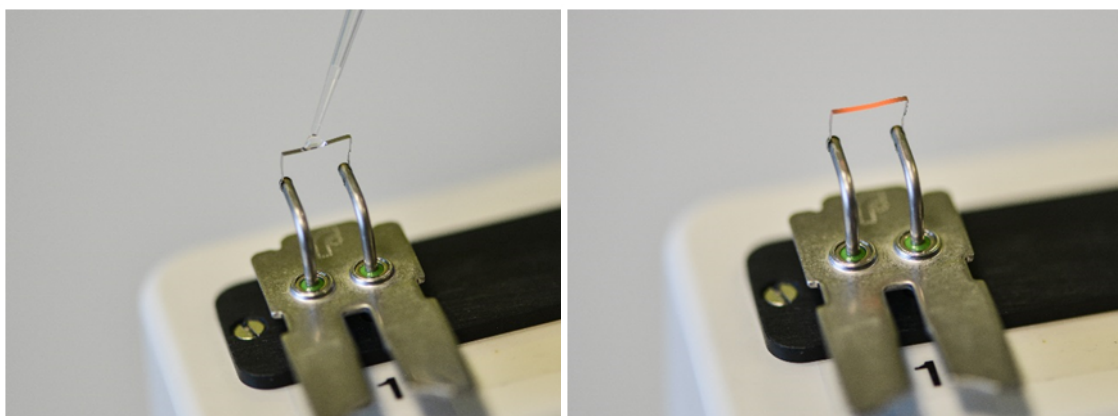

Figure 3. Sample loading onto a Re filament (a) and heating of the filament by passing a current (b) (Photo by Tom Junek, 2016).

Standard samples, a double spike solution, and standard samples mixed with the double spike solution were analyzed for TIMS optimization. Usage of a double spike mixed with the Ni standard simulates a real sample and ensures that the Ni standard will ionize efficiently and when compared against other ratios. Each load of Ni standard, double spike, and the standard with double spike was analyzed through a sequence of runs using the same filament load of 1 µg of Ni. One sequence of 3-6 runs (150-300 cycles of measurements and ratios) constitutes a single mass spectrometer analysis.
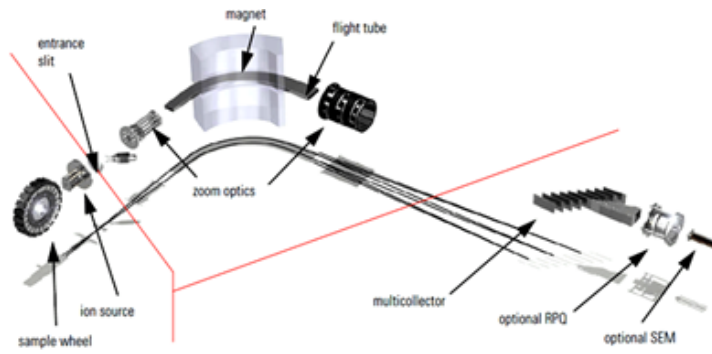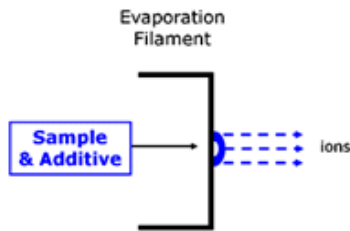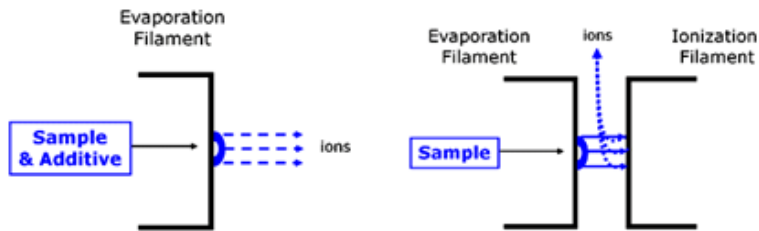
Figure 4. Single and Double Filament techniques used for sample analysis with TIMS.

4.4.2. Isotope Integration

Analysis of isotopes conducted by TIMS was interpreted using analytical software. The software allowed for different configurations in integration time and the number of integrations for each analysis (Figure 5). Integration time was analyzed at 4, 8, 16, and 33 seconds and the number of integrations at 1, 3, and 5 times. Testing of integration time and number of integrations is to optimize results of δ^{60}Ni to produce the most stable signal for good analytical statistics. The aim was to produce the most consistent result based on 150-300 cycles.
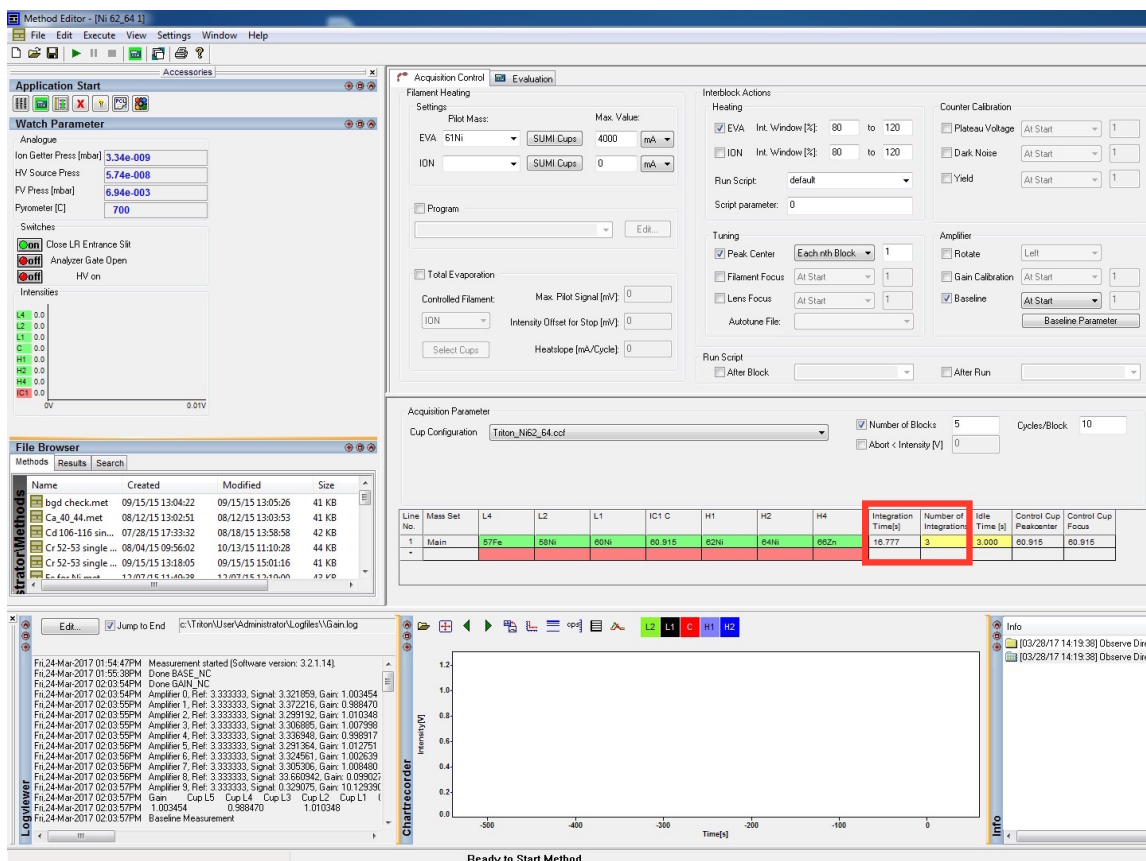
Figure 5. Acquisition parameters - Number of integrations and integration time setting (highlighted in red).

Once optimal integration time and number of integrations is set, the TIMS software will designate Faraday cup configurations for each of the different isotopes of Ni to be tested and any potential interferences from other elements. In Figure 6, there are 9 detectors for the different isotopes of Ni, and interferences from Fe and Zn. The ratio of one Faraday cup to another is compared to calculate the precise isotope ratios.
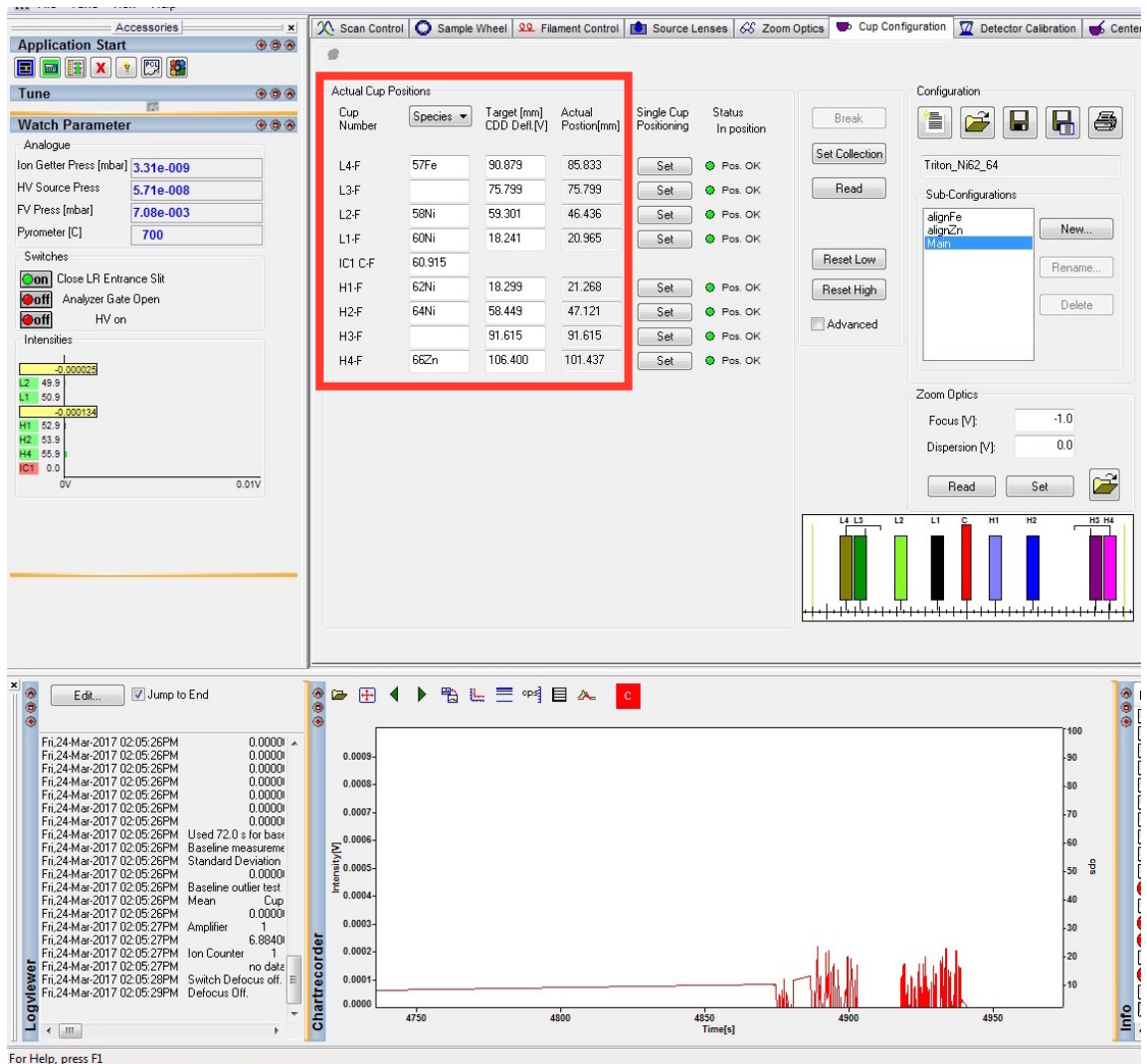
Figure 6. Faraday cup configurations for TIMS analysis. Each detector analyzes a different Ni isotope (^{58}Ni, ^{60}Ni, ^{61}Ni, ^{62}Ni, and ^{64}Ni) as well as potential interferences from ^{57}Fe and ^{66}Zn (highlighted in red).

5. Results

5.1. Nickel Separation Efficiency From AG1-X8

The separation of Ni was first tested using two different mesh sizes of the AG 1-X8 resin at three different volumes in the column. Sizes of the AG 1-X8 resin included 100-200 mesh and 200-400 mesh. For the 100-200 and 200-400 mesh size, the column had 2 mL loaded, and 1 mL was loaded for the 200-400 size and is denoted by 200-400 ½. It was found that on average the least amount of Ni separated occurred using the 100-200 mesh resin with 1.2% being removed and 98.8% of Ni remained in the sample for the second stage of separation. The resins at 200-400 showed 1.6% removed and 98.4% remaining, and 200-400 ½ at 8.9% removed and 91.1% remaining of Ni (Table 1). Table 1 shows the efficiency in the removal of the metals Pb, Cr, Co, Cu, Zn, and Fe found in the samples by each resin size. Removed metals are maintained in the ionic resin and Ni is successfully separated into a solution for the next stage of separation.

Resin Type (mesh)	Metals Removed						
	Fe	Zn	Cu	Co	Ni	Pb	Cr
AG 1-X8 (100-200)	82.9	99.1	81.4	36.4	1.2	15.9	2.4
AG 1-X8 (200-400)	70.1	99.3	93.0	29.9	1.6	19.1	2.7
AG 1-X8 (200-400) 1/2	94.8	99.1	39.7	19.3	8.9	9.1	11.9

Table 1. Efficiency of removal of metals during first stage of ion-exchange column chromatography using three different resin sizes, AG 1-X8 100-200 m, 200-400 m, and 200-400 m ½ to determine most efficient resin size for maintaining at minimum 95% of Ni in the sample for second stage ion-exchange column chromatography.

Based on the results of the first stage separation, the AG 1-X8 resin at 100-200 mesh was used for all further first stage separations. This was to ensure a minimum 95% recovery of Ni during the separation stages. As the 100-200 mesh resin only allowed for 1.2% of Ni to be removed during separation, it

matched the minimum requirements and was the resin of choice for the first step of separation.

5.2. Nickel Separation Efficiency of Ni-DMG

After completion of the first stage of separation, samples were then prepared for the second stage of separation using the Ni-DMG specific resin. Ni was maintained in the Ni-DMG resin and metals were separated into a solution that was discarded. The break up of the resin yielded an 8.1% loss of Ni into the separated solution (Table 2).

Metal	DMG Resin (% removed)
Fe	64.2
Cu	91.3
Co	89.2
Ni	8.1
Zn	96.7
Pb	98.5
Mg	92.2
Ca	61.8
K	83.1
Na	79.7
Cr	93.1
Mn	93.4

Table 2. Efficiency of removal of each element found in samples using the specific Ni-DMG resin during the second stage of ion-exchange column chromatography.

The remaining available purified Ni accounted for 91.9% and was in acceptable parameters of the experiment. The metals removed by the Ni-DMG separation stage include in order of highest removal Pb, Zn, Mn, Cr, Mg, Cu, Co, K, Na, with Fe and Ca having the lowest removal rate during separation (Table 2). With the separation of Ni standard falling within

acceptable efficiency range, the samples can be prepared for an application of UV light before analysis with TIMS.

5.3. TIMS Isotope Analysis

Initial analysis of Ni (NIST 986, double spike and NIST 986+double spike) serve to ensure that Ni instrumental fractionation is mass dependent (MDF) and can be corrected by a double spike method. Mass dependent fractionation results in a line when plotting two different ratios (^{61}Ni/^{58}Ni vs. ^{60}Ni/^{58}Ni or ^{62}Ni/^{58}Ni vs. ^{60}Ni/^{58}Ni). It is seen in Figure 1.a. and Figure 1.b. with Filament 1 and Filament 2 displaying linear dependence between the Ni ratios. Over time the amount of isotope ^{58}Ni decreases and the amount of isotopes ^{61}Ni (Figure 1.a.) and ^{62}Ni (Figure 1.b.) increases indicating the Ni ionization to be successful and the Ni isotope fractionation mass dependent.
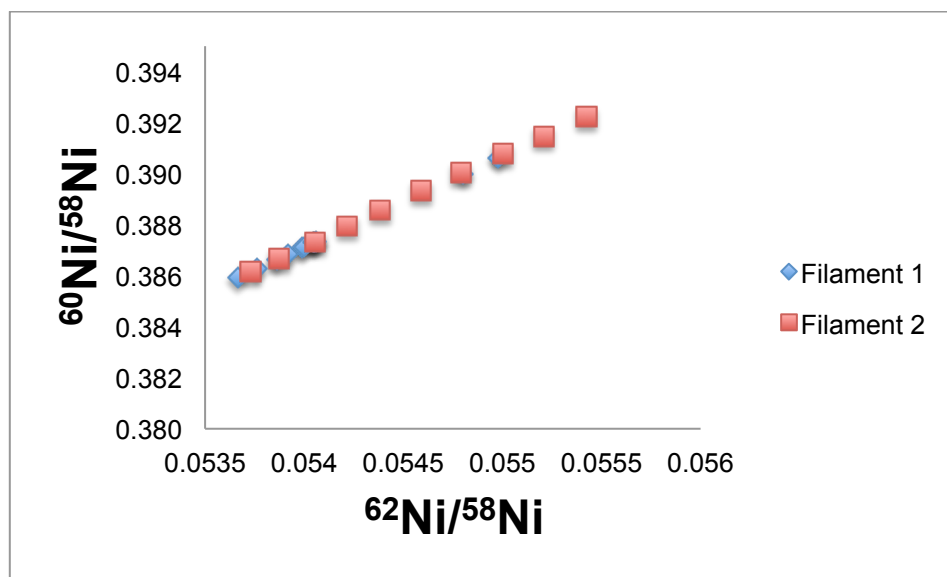

Figure 1.a. Measured Ni isotope ratios during analysis of two independent filaments loaded with NIST 986 showing linear dependence between the ratios ^{60}Ni/^{58}Ni vs. ^{62}Ni/^{58}Ni.
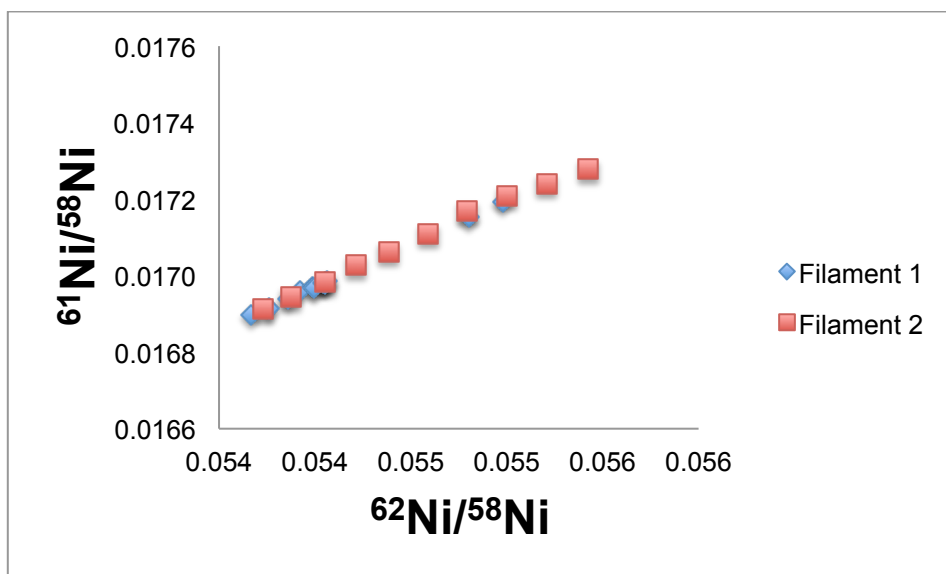
Figure 1.b. Measured Ni isotope ratios during analysis of two independent filaments loaded with NIST 986 showing linear dependence between the ratios $^{61}Ni/^{58}Ni$ vs. $^{62}Ni/^{58}Ni$.

After testing the NIST 986, the Ni isotope composition of the double spike was analysed on 4 independent filaments and the ratios $^{60}Ni/^{58}Ni$, $^{61}Ni/^{58}Ni$, and $^{62}Ni/^{58}Ni$ were compared as seen in Figure 2.a., 2.b., 2.c., and 2.d.
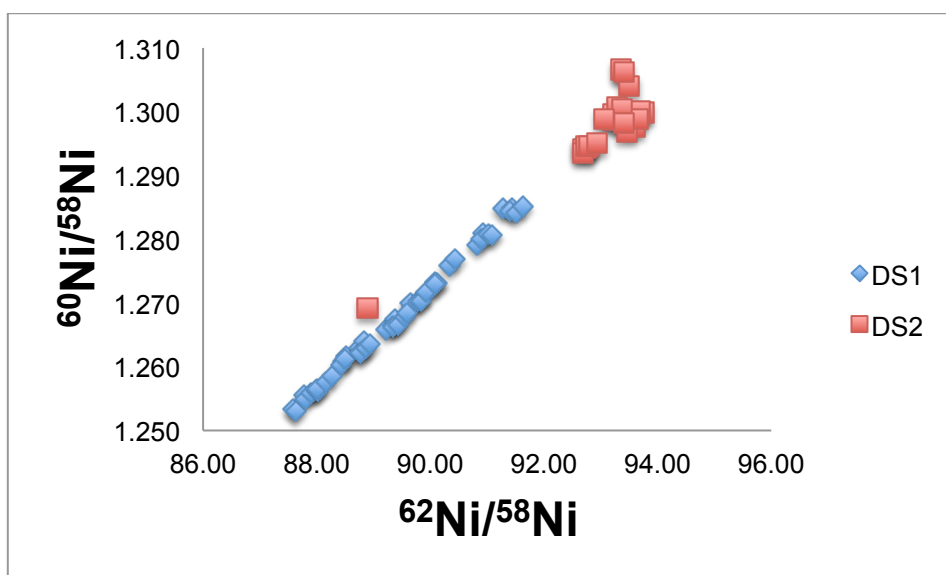

Figure 2.a. Measured Ni isotope ratios during analysis comparing double spike 1 (DS1) and double spike 2 (DS2) methods and Ni ratios $^{60}Ni/^{58}Ni$ vs. $^{62}Ni/^{58}Ni$.

Figure 2.b. Measured Ni isotope ratios during analysis comparing double spike 3 (DS3) and double spike 4 (DS4) methods and Ni ratios ^{60}Ni/^{58}Ni vs. ^{62}Ni/^{58}Ni.

Figure 2.c. Measured Ni isotope ratios during analysis comparing double spike 1 (DS1) and double spike 2 (DS2) methods and Ni ratios ^{61}Ni/^{58}Ni vs. ^{62}Ni/^{58}Ni.
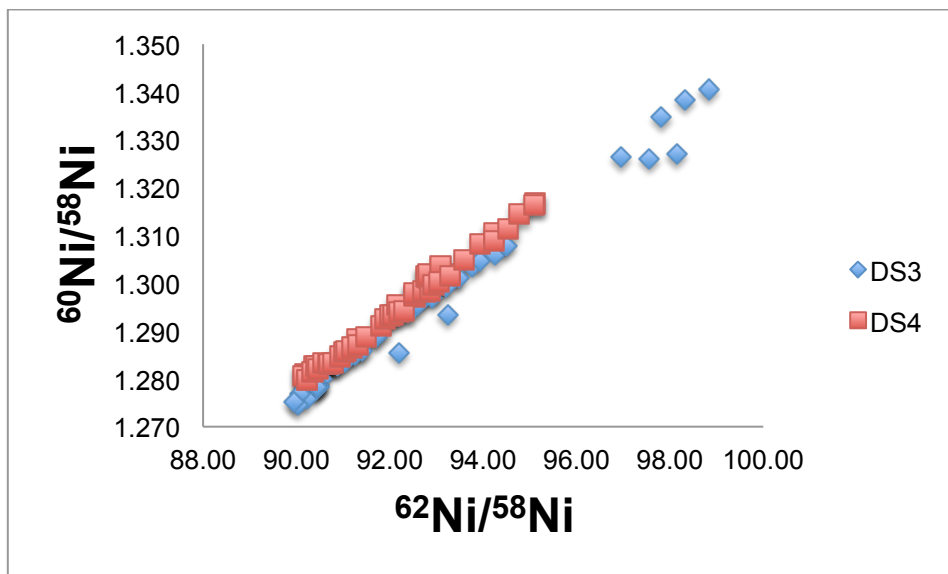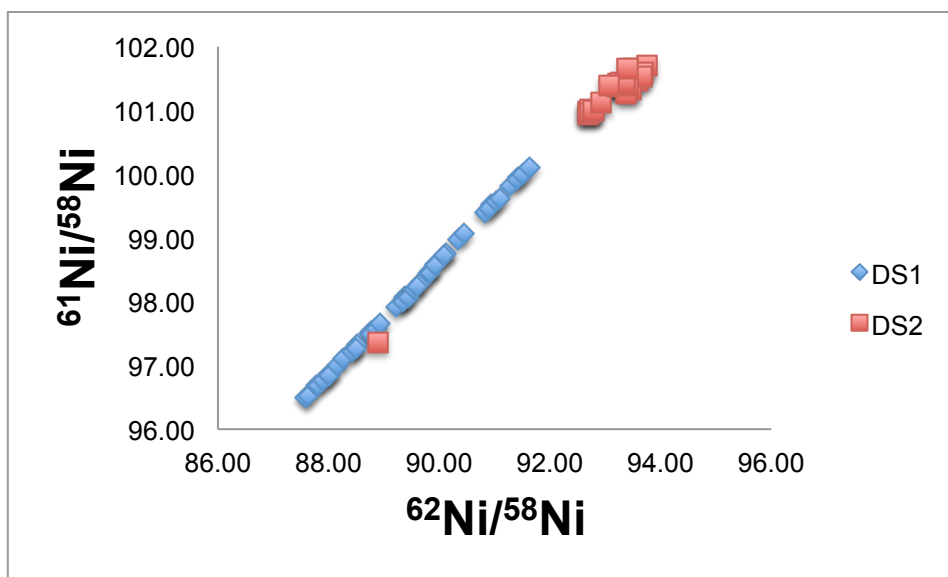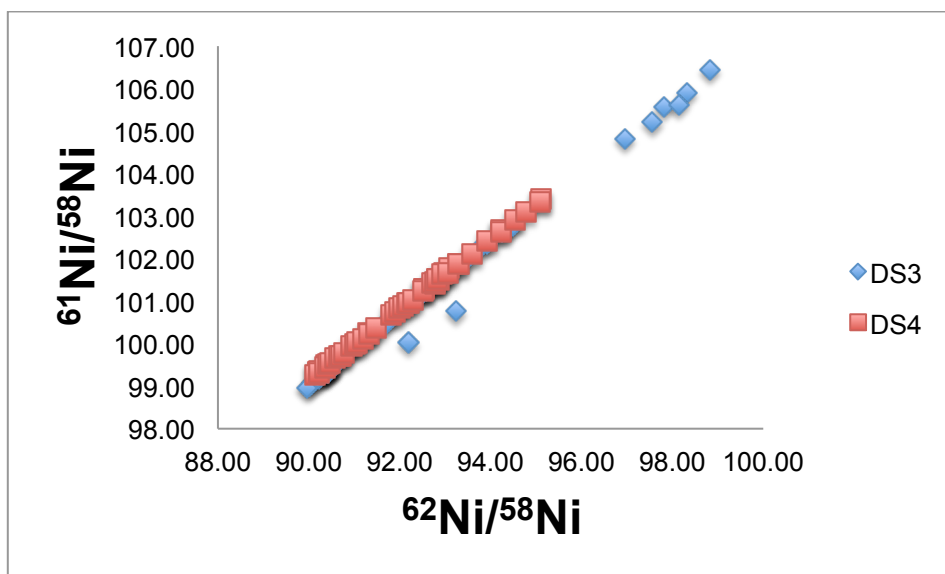
Figure 2.d. Measured Ni isotope ratios during analysis comparing double spike 3 (DS3) and double spike 4 (DS4) methods and Ni ratios ^{61}Ni/^{58}Ni vs. ^{62}Ni/^{58}Ni.

The samples of Ni double spike analyzed by TIMS produced comparable results. Variations from the mean data can be explained with slight differences in sample purity, filament shape and conductive properties, and differences in chemical mixture composition. In all samples, it can be seen that over time, the amount of δ^{58}Ni decreases and it's corresponding ratio, either δ^{61}Ni or δ^{62}Ni, increases suggesting that the double spike will correct any potential mass discrimination effect that may occur during TIMS.

The final test before Ni environmental sample can be analysed is analysis of a mixture of NIST 986 and the double spike. This mixture simulates real sample, except that its isotope compostion is known. The method together with the Ni ratios ^{60}Ni/^{58}Ni, ^{61}Ni/^{58}Ni, and ^{62}Ni/^{58}Ni as seen in Figures 3.a. and 3.b. As seen in the figures, the Ni ionization was successful and the Ni isotope fractionation mass dependent. Moreover, δ^{60}Ni values corresponds with the certificated Ni isotope composition on NIST 986 indicating that the instrumental fractionation is corrected by the double spike addition.
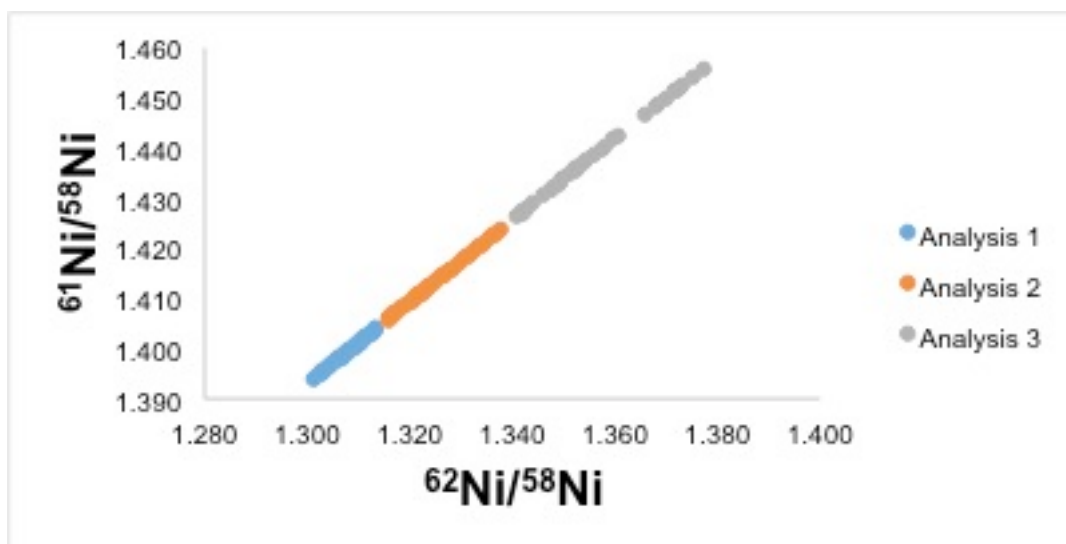
Figure 3.a. Measured Ni isotope ratios during TIMS analysis comparing Ni ratios $^{61}Ni/^{58}Ni$ vs. $^{62}Ni/^{58}Ni$ using the double spike and NIST 986.
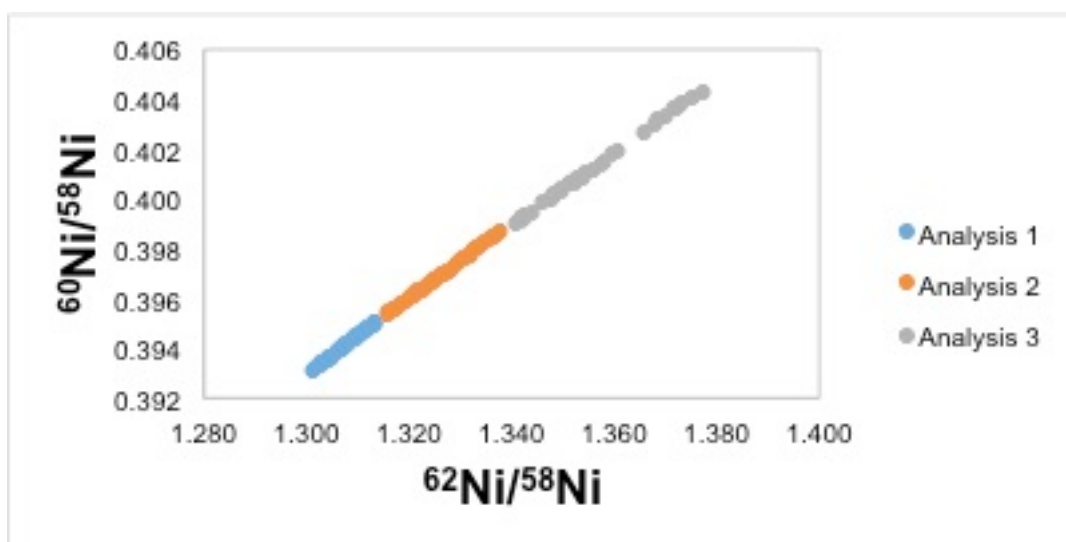
Figure 3.b. Measured Ni isotope ratios during TIMS analysis comparing Ni ratios $^{60}Ni/^{58}Ni$ vs. $^{62}Ni/^{58}Ni$ using the double spike and NIST 986.

To ensure good analytical statistics several acquisition parameters such as integration time and number of integrations was tested to find the lowest standard deviation of a set of $\delta^{60}Ni$ within a single analysis (150-300 cycles = 150-300 $\delta^{60}Ni$) Ni isotope (Figure 4).

Figure 4. Measured isotope ratios with respect to integration time (seconds) and number of integrations (highlighted in red). The number of blocks and cycles results in total number of measured Ni isotope ratios during 1 sample analysis.
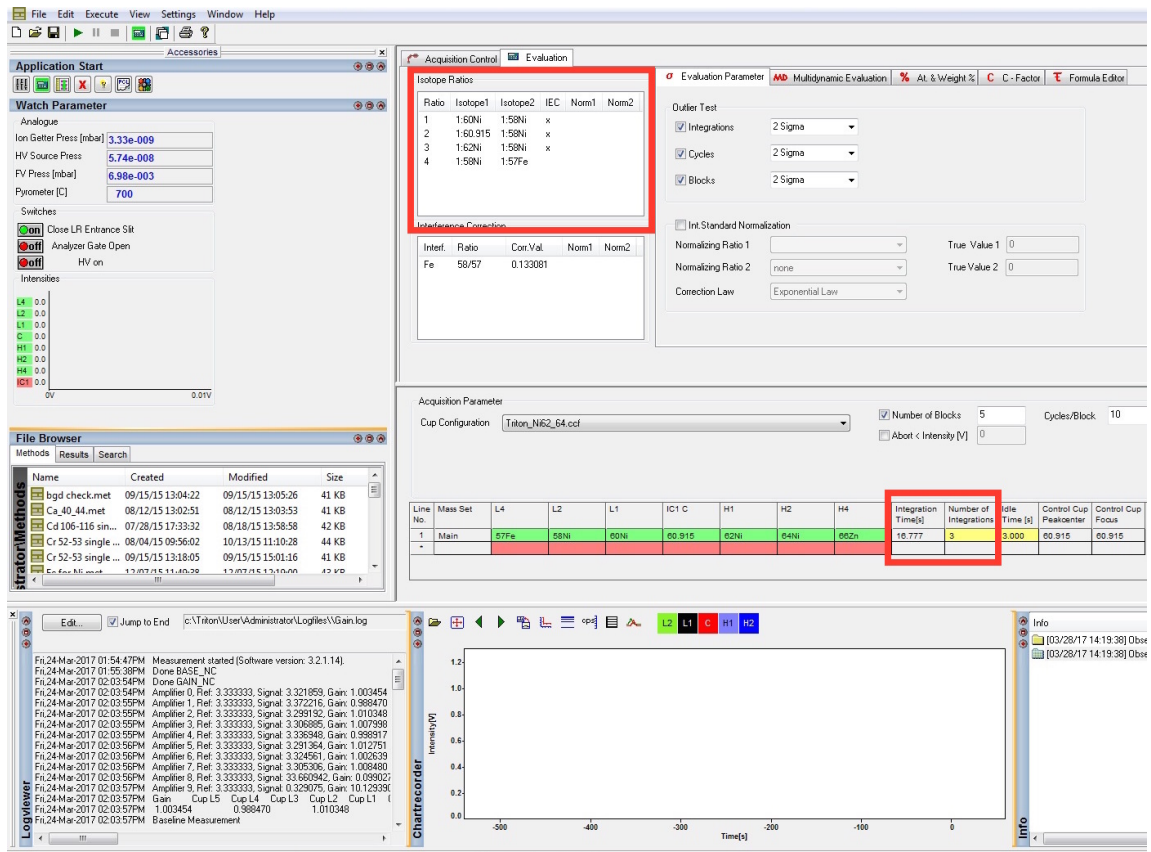
Variations in integration time and number of integrations led to method optimization (Table 3) for best possible statistics of a single analysis. One analysis of the signal intensity of Ni is measured between 150-300 cycles and will produce a calculation of the desired isotope ratio average. From the average Ni isotope ratio, any mass bias seen can be corrected and δ^{60}Ni can be calculated according to Equation 2. Through optimization, the standard deviation can be minimized during the 150-300 cycles to produce ideal ratios and calculations of δ^{60}Ni. An integration time of 16 seconds combined with 3 integrations within one cycle produced the lowest standard deviation of calculated δ^{60}Ni of 0.10186. An integration time of 33 seconds with 3 integrations had a standard deviation δ^{60}Ni of 1.024 that is similar to the integration time of 16 seconds and 3 integrations, however, when analyzing samples, the lower integration time is preferred. Therefore an integration time

of 16 seconds and 3 integrations is ideal for the analysis of Ni isotopes using TIMS.

Integration Time (seconds)	Number of Integrations	
	1	
	$\delta^{60}Ni$	STD $\delta^{60}Ni$
4	4.38786	0.544250544
16	9.191437129	0.200186258
33	11.16344651	0.169
	3	
	$\delta^{60}Ni$	STD $\delta^{60}Ni$
8	11.12584	0.15619
16	15.51178	0.10186
16 - 12.4.16	5.535062714	0.200
16 - 13.4.16	3.860611956	0.313
16 - 19.4.16	8.10E-01	0.145
16 - 20.4.16	1.41E+01	2.60E-01
16 - 21.4.16	-1.11E+01	0.143
33	-3.64E+00	0.1024
	5	
	$\delta^{60}Ni$	STD $\delta^{60}Ni$
8	4.45106	0.19930

Table 3. Method of Optimization of TIMS Analysis. Determining the best integration time and the number of integrations to produce the lowest standard deviation of $\delta^{60}Ni$.

6. Discussion

6.1. Ion-Exchange Separation of Nickel

The methodology adapted from Gueguen *et al.* (2012) while informative and provided the step-by-step approach for separation and purification of Ni isotopes using ion-exchange chromatography columns, issues were found with the samples organic nature. The organic matter found comes from the samples being collected in soil, lichens, moss, bedrock, and snow where potential to form organo complexes is high. Gueguen *et al*. (2012) was able to ionize Ni samples as MC-ICP-MS is capable of ionizing samples due to trace organic matter not being problematic for the inductively coupled plasma that is lacking in TIMS. Complexes between organic sample material and metals such as Fe and Ni were found to be problematic during separation and required further additional steps to achieve the 95% acceptable pure sample. Ni-organo complexes are problematic as they are stable and will not ionize efficiently during TIMS analysis making these organo complexes essential to remove during separation. This problem was initially addressed using an acidic solution. The first step is the evaporation of the aliquot to near dryness and then removing the sample from heat. Once removed from heat, a few drops of concentrated HNO_3 and a few drops of H_2O_2 are added to form a nitrogen peroxy acid and is used to oxidize any organic matter present and prevent reduction of metals (Dauphas and Rouxel, 2006). It is essential in this step to allow the sample to cool before addition of H_2O_2 as heat decomposes peroxide quickly and will prevent interaction with organic matter. The sample is then evaporated a second time and 6 M HCl is added to the samples for loading on the AG 1-X8 column (Gueguen *et al.* 2012) for the retention of Ni and separation of other metals present. However, the presence of any remaining HNO_3 when mixed with HCl is unwanted; the presence of remaining HNO_3 causes a yellow-orange fuming liquid of nitric gases (Cannon, 1961). To remove residual HNO_3 completely, a few drops of concentrated HCl should be added causing a visible colour change from yellow to a transparent colour. Once the colour change has occurred, the 6 M

HCl is added and the separation is continued. As noted by Dauphas and Rouxel (2006), Fe will oxidize when presented with a high molarity HCl and sorption will occur with an HCl activated anionic resin. This will allow Fe to be included in the Ni solution resulting in samples not within the accepted parameters for the second stage of separation. The prevention of Fe reduction requires a reverse solution with a 2:1 HNO_3:HCl solution (Cook *et al*., 2007) with a lower molarity HCl before the 6 M HCl is added. The 6 M HCl added to a sample can still cause the reduction of Fe and it may still be present despite necessary precautions taken. This problem was consistent throughout the separation procedure due to determining the correct concentration of HNO_3 to HCl before column separation.

In addition to the separation issues with organic matter, contamination of lab materials provided further complications in the first and second stages of separation. Contamination with Fe of the stock acids, prepared solutions, and lab materials was found and likely added further issues with the separation results. Contamination could be prevented by more diligent laboratory procedures in cleaning and maintenance of stock acids and solutions needed for the separation. As the separation methodology is sensitive, attention to detail is required to ensure desired results. All the chemicals must be of the highest quality (ROTIPURAN Ultra, Carl Roth) and stored in Teflon bottles.

For the removal of organic matter, other methods than the usage of HNO_3 and H_2O_2 might have been used to prevent the formation of aqua regia when the HCl was added. Removal of dissolved organic matter from liquid samples can be achieved through a few different approaches that may work for this experiment. One example is the usage of a sodium hydroxide (NaOH) solution and acetone to produce a double liquid layer where the dissolved organic matter would remain in the NaOH and the metals would migrate into the acetone as discussed in Huber *et al*. (2012). This methodology could work for the liquid samples as acetone is a ketone, or organic solvent, and will only dissolve the organic matter present. The NaOH solution is inorganic and when mixed with an acid, a metal precipitate can form that can be further reduced back into a liquid metal sample (Huber *et al*., 2012). A second

methodology is the usage of bromine oxidation reaction for organic matter removal (Mitchell and Smith, 1974). Unlike treatment with H_2O_2 and HNO_3, a bromine oxidation is rapid, inexpensive, requires no evaporation, will not oxidize the metals, and will not produce an undesirable by-product (Mitchell and Smith, 1974). A third methodology that was tested with the samples was the usage of UV light (<280 nm) to degrade organics. UV light degradation is an oxidation reaction that works by using light absorption of a molecule and sufficient energy to change the energetic state of a molecule. This methodology was found to be successful when separating the samples and is the recommended action for future separations.

The separation of Ni also face challenges due to the nature of metals and the complexes that can be formed in the environment. During the first stage of separation, 98.8% of Ni passed through the resin, however 17.1% of Fe and 18.6% of Cu also passed. The second stage of separation accounted for 91.9% of Ni remaining in the resin but 35.8% of Fe also remained in the resin suggesting a relationship between Ni and Fe. This relationship might be explained by the increased deposition of Ni and SO_2 by the processing plants in the environment of the Sør-Varanger area (Niskavaara *et al*., 1996; Lindroos *et al*., 1997; Boyd *et al*., 2009). When SO_2 is present in the soil from acid rain deposition, the mobility of metals such as Ni and Fe will increase as will their affinity for organic matter (Uren, 1992; Mellis *et* al., 2004). The increased mobility and affinity can lead to the creation of a Ni hydroxy species that may form with chelation to produce a NiFeOH complex (Uren, 1992; Trotochaud *et* al., 2014). Trotochaud, *et al.* (2014) found that Fe readily incorporates with NiOH with no applied potential and to obtain a high purity NiOH it must be developed through precipitation with an electrolyte to remove any Fe impurities. This suggests that the environmental samples collected may have had a NiFeOH complex and when subjected to initial acid digestion the mobilized metals were able to remain in the sample.

To reiterate, the precise separation of samples must be completed before analysis by TIMS. Ion-exchange chromatography using a chloride activated resin and a Ni-DMG specific resin with removal of organics using a UV light

will ensure 95% pure Ni samples, as the nitrogen peroxy acid solution cannot break apart the stable Ni-organo complexes. This is essential for TIMS analysis to remove any interference and ascertain accurate results.

6.2. TIMS Analysis Efficacy

Analysis of Ni isotope composition using TIMS was found to be largely successful when all necessary considerations for separation and sample loading were met. Efficacy of sample ionization was highly dependent on multiple factors such as the sample loading mixture, purity of the sample (Fe, Cu, and organic contaminants), and filament shape. To guarantee best possible results from TIMS, additional steps were taken in developing the methodology. The loading of samples onto the filament was done through a trial and error approach to derive the optimal chemical mixture for best ionization results. Mixtures of different activators such as boric acid (H_3BO_3, 0.1 N), phosphoric acid (H_3PO_4, 0.1 N), silica gel, and Al were combined. An optimal mixture will allow Ni to be ionized slowly and to produce a stable and lasting signal for analysis. The initial amount loaded on each filament was 1 µg of Ni, however there were issues with ionization and it was changed to 2 µg of Ni to improve results. A further step to ensure ionization success was the running of a standard between each sample to identify any problems and allow for calibration if a problem existed.

From the data presented it can be see that with a double filament method with addition of a double spike and an integration time of 16 seconds with 3 integrations proved to be successful for Ni ionization analysis by TIMS. When samples are prepared carefully and necessary corrections are made, it is possible to analyze Ni isotopes effectively despite the higher ionization energy of Ni and potential interferences from organics and similar elements. As the samples tested in TIMS were the Ni standard, the next step in research is the analysis of the collected environmental samples. Once TIMS analysis of the collected samples is complete, they can be compared to samples analyzed by MC-ICP-MS as done in Šillerová *et al*. (2017).

6.3. Comparison of TIMS to MC-ICP-MS

Mass spectrometer analysis of elements such as Ni are typically undertaken using MC-ICP-MS due to the relatively high ionization energy of Ni and the precise ability to measure isotope variability (Walcyzk, 2004; Becker, 2005; Gall *et al*., 2013). MC-ICP-MS is relatively time efficient, provides proficient analysis accuracy, and is not as susceptible to organic matter interference (Walcyzk, 2004; Becker, 2005). However, issues with MC-ICP-MS include the high cost of the Argon gas, chemically similar interferences, and analysis of isotopes can result in a mass discrimination by an order of 4 times higher than desired (Walcyzk, 2004; Becker, 2005). To guarantee precision when using MC-ICP-MS, matrix separation of Ni samples are undertaken to prevent any interferences from similar elements resulting in better accuracy (Walcyzk, 2004; Gall *et al*., 2013; Gueguen *et al*., 2013; Šillerová *et al*. 2017). The usage of a double spike method can correct the mass discrimination effect that MC-ICP-MS analysis is susceptible too (Walcyzk, 2004; Becker, 2005). Addition of matrix separation and a double spike reduces the overall time efficiency of MC-ICP-MS.

In comparison to MC-ICP-MS, TIMS is less susceptible to isotope fractionation, provides precise and accurate isotope ratio measurement, and does not require expensive Argon gas (Walcyzk, 2004; Becker, 2005). Similarly, to provide the most accurate results, matrix separation and a double spike are done with TIMS. Unlike MC-ICP-MS, TIMS analysis of isotopes faces challenges associated with organic matter and isobaric interference from similar element isotopes (Walcyzk, 2004; Becker, 2005). Presence of organic matter not removed from separated samples can generate ion interferences preventing Ni from ionizing efficiently. Secondly, inorganic material, such as Fe or Zn, can reduce the ionization efficiency when present in large quantities due to their similarity to Ni (Gall *et al*., 2012; Gueguen *et al*., 2012; Šillerová *et al*., 2017). Thirdly, TIMS is commonly used for isotopes with a low ionization potential and Ni has a higher ionization potential than what is typically used for TIMS analysis (Becker, 2005;

Gueguen *et al.*, 2012). With these factors, it is essential that careful separation and loading of samples be completed to ensure success of TIMS analysis. As indicated in the results of this thesis, when separation is completed methodically along with a double spike solution, it is possible for TIMS to analyze Ni effectively and accurately regardless of the slightly higher ionization energy,

Currently, isotopic studies of Ni from environmental samples are undertaken using a MC-ICP-MS method as evident in Gall *et al.* (2013), and Gueguen *et al.* (2013), and most recently Šillerová *et al.* (2017). Using a matrix separation and a double spike methodology, as described in this thesis, with MC-ICP-MS, favourable results were found for identifying Ni in the Norwegian arctic (Šillerová *et al.*, 2017). Through isotopic analysis, δ^{60}Ni was found to have similar isotopic composition to feeding material and/or smelter slag in lichen, snow, and soil samples; lighter δ^{60}Ni isotope values were found in the bedrock (Šillerová *et al.*, 2017). This indicates anthropogenic input of δ^{60}Ni in collected samples, but a wide range of δ^{60}Ni values was found in the soil suggesting natural fractionation process are occurring (Šillerová *et al.*, 2017). With these results and the success of using TIMS to analyze NIST 986 as presented in this thesis, the collected environmental samples should be analyzed by TIMS and compared to the results from MC-ICP-MS. If a favourable comparison of results is found, it can be shown that TIMS is a reliable, efficient, and effective tool for isotopic analysis of Ni in source tracing of contaminants as MC-ICP-MS. Further, other elements with similar ionization energies might also be able to be analyzed by TIMS and can create new protocols in source tracing. Adaptations of this methodology may be necessary depending on samples collected and availability of reference material, however, the potential outweighs most setbacks.

7. Conclusion

Source tracing of contaminants is an essential practice for understanding pollution in the environment. Through quantitative methods, identifying the source of a contaminant can help in the development of policy, implementation of technological best practices, and identify current and future effects that are seen. Pollution from a contaminant like Ni can extensively damage local fauna and flora, disrupt biological processes, and cause health concerns for humans working and living in a polluted area. To properly assess contamination of Ni in the region, it is necessary to develop a methodology that can identify background concentrations versus anthropogenic-inputted concentrations of Ni. To date, most studies identifying Ni revolves around isotope analysis using MC-ICP-MS. While this method is relatively effective, limitations exist such as high cost and mass discrimination effects. Using TIMS there is potential to identify Ni isotopes at a lower cost and efficiently to provide an alternative to MC-ICP-MS.

Through ion-exchange chromatography and a double spike method, results can be optimized for Ni isotope analysis by TIMS. Separation of Ni through ion-exchange chromatography resulted in good separation results, 90% retention of Ni, and removal of organics and the sample matrix was completed by the specific resins and UV light exposure. The pure Ni samples can then be effectively analyzed with TIMS using the double spike method and integration optimization of the Ni standard deviation. This suggests that TIMS can be used for Ni isotope analysis instead of MC ICP-MS following the methodological guideline as outlined in this thesis.

Overall, the aims of the defense thesis were met in the matrix separation methodology and TIMS analysis of Ni standard samples. Through meticulous ion-exchange separation practices and methodical optimization of a double spike and integration time and numbers in TIMS provided favourable results for future work in Ni isotope analysis. However, the results presented are based on a NIST 986 solution and not the collected environmental samples.

Establishment of TIMS as a reliable analytical tool for Ni source tracing is dependent upon if collected environmental samples provide ideal results. Collected samples should be tested with TIMS and then compared to MC-ICP-MS results to determine the overall success of this new methodological guideline. Through testing of the presented TIMS methodology in this thesis, there is potential to expand this work further into other transition elements with similar ionization energies.

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