

T.R.
GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL

**DETERMINATION OF TECHNOLOGY
CRITICAL ELEMENTS (TCEs) IN WASTE
ELECTRONIC AND ELECTRICAL EQUIPMENTS**

DERYA KUTAN

**A THESIS OF MASTER OF SCIENCE
DEPARTMENT OF PHYSICS
METROLOGY PROGRAM**

ADVISOR: PROF. DR. SAVAŞ BERBER

FEBRUARY 2025

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T.C.
GEBZE TEKNİK ÜNİVERSİTESİ
LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

ATIK ELEKTRONİK VE ELEKTRİKLİ
EKİPMANLARDA TEKNOLOJİK KRİTİK
ELEMENTLERİN TAYİNİ

DERYA KUTAN

YÜKSEK LİSANS TEZİ
FİZİK ANABİLİM DALI
METROLOJİ PROGRAMI

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ŞUBAT 2025



MASTER of SCIENCE JURY APPROVAL FORM

A thesis submitted by Derya KUTAN defended on 07/02/2025 before the jury formed with the 03/02/2025 date and 2025/08 numbered decision of the GTU Graduate Administration Board, has been accepted as a MASTER of SCIENCE thesis in the Department of Physics, Metrology Program.

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*To my
Family and
Friends*

ABSTRACT

The recovery and reprocessing of technology-critical elements (TCEs) present in printed circuit boards (PCB) from electrical and electronic waste is essential both for recycling precious elements subject to supply risk and for reducing the environmental impact. Despite the quantitative knowledge of TCEs amounts in end-of-life PCB plays a key role, there are neither matrix certified reference materials nor harmonized analytical methods available to establish the traceability of the results to the international system of units. To fill this gap, a measurement method traceable to system international (SI) was developed and implemented using the triple isotope dilution mass spectrometry method and ICP-MS instrument. PCBs usually contain important TCEs up to several hundreds of mg/kg levels. An SI traceable measurement method is needed to accurately and reliably determine the economic value of electrical and electronic waste (WEEE) such as PCBs.

Methods employing isotopic measurements are commonly used in the measurements of elements in different samples in the fields of environment, food safety, geology and metallurgy, especially at trace levels. Triple Isotope Dilution Inductively Coupled Plasma Mass Spectrometry (triple-ID-ICP-MS) where at least two stable Isotope for analyte in question is needed, is accepted as a primary method of measurement. In many cases, it is possible to choose one of the interference-free isotope of the element interested. The method needs rapid measurement system for the measurement of isotopes to provide reproducible isotope ratio values. This requires less number of isotopes in the monitoring list. Therefore, even though elemental interferences are corrected mathematically, chemical separation of the interfering elements before the measurement provide improved repeatability.

Separation of interferences before introduction to ICP-MS are expected to improve the measurements. Chemical separation of TCEs from interference elements is uniquely challenging due to their nearly identical chemical properties. In this study a reference chemical separation process was developed and validated for traceable measurement of TCEs in PCB samples. The material below 200 μm particle size which is produced in a joint research project was dissolved in 2 ml of 65% (w/w) HNO_3 and 6 ml of 30% (w/w) HCl using microwave digestion system at 200°C for 30 min. Sample blends were prepared by spiking the samples with the isotope enriched reference material before digestion. For the traceability of the measurements, calibration blends were prepared from certified reference materials. High-pressure extraction system (SPE WARE CEREX 48), polypropylene columns (≈ 3 mm i.d. and ≈ 8 cm in length) and lanthanide specific resin (50-100 μm) were used for the chemical separation of TCEs in the digests from Microwave digestion system. The elution process was optimized for the separation of TCEs from the interfering elements.

A bottom-up approach was used for measurement uncertainty calculation for the determination of TCEs in waste PCB material, and measurement uncertainties and uncertainty budgets were calculated according to Guide to the expression of uncertainty in measurement (GUM) approach by using commercial software GUM Workbench.

Keywords: Technology Critical Elements, Waste Electrical and Electronic Equipments, Waste Printed Circuit Board, Triple Isotope Dilution ICP-MS, Neodymium, Recycling, Extraction, Lanthanide Separation, Palladium, Measurement Uncertainty.

ÖZET

Elektrikli ve elektronik atıklardan oluşan baskılı devre kartlarında (PCB) bulunan teknolojik açıdan kritik elementlerin (TCEs) geri kazanılması ve yeniden işlenmesi, hem tedarik riski taşıyan değerli elementlerin geri dönüşümü hem de çevresel etkinin azaltılması açısından büyük önem taşımaktadır. Kullanım ömrü sona ermiş PCB'lerdeki teknolojik açıdan kritik elementlerin (TCEs) miktarlarının niceliksel bilgisi önemli bir rol oynamasına rağmen, sonuçların uluslararası birim sisteminde izlenebilirliğini sağlayacak matriks sertifikalı referans malzemeler veya uyumlu analitik yöntemler bulunmamaktadır. Bu boşluğu doldurmak amacıyla, üçlü izotop seyreltme kütle spektrometrisi yöntemi ve Endüktif Eşleşmiş Plazma Kütle Spektrometrisi cihazı kullanılarak uluslararası sistem (SI) izlenebilir bir ölçüm yöntemi geliştirilmiş ve uygulanmıştır. PCB'ler genellikle birkaç yüz mg/kg seviyesine kadar önemli teknolojik kritik elementleri içerirler. PCB'ler gibi elektrikli ve elektronik atıkların (WEEE) ekonomik değerini doğru ve güvenilir bir şekilde belirlemek için SI izlenebilir bir ölçüm yöntemine ihtiyaç vardır.

Çevre, gıda güvenliği, jeoloji ve metalurji alanlarında, özellikle eser seviyelerde, farklı örneklerdeki elementlerin ölçümlerinde izotopik ölçüm yöntemleri yaygın olarak kullanılmaktadır. Analit için en az iki kararlı izotopun gerekli olduğu durumlarda Üçlü İzotop Seyreltme Endüktif Eşleşmiş Plazma Kütle Spektrometrisi (triple-ID-ICP-MS) birincil ölçüm yöntemi olarak kabul edilir. Birçok durumda, ilgilenilen elementin girişimsiz izotoplarından birini seçmek mümkündür. Tekrarlanabilir izotop oranı değerleri sağlamak için izotopların ölçümüne yönelik hızlı bir ölçüm sistemine ihtiyacı vardır. Buda, izleme listesinde daha az sayıda izotop bulunmasını gerektirir. Bu nedenle, elementel girişimler matematiksel olarak düzeltilse bile, ölçümden önce girişim yapan elementlerin kimyasal olarak ayrılması, tekrarlanabilirliğin artmasını sağlar.

ICP-MS'e geçmeden önce girişimlerin ayrılmasının ölçümleri iyileştirmesi beklenmektedir. TCE'lerin girişim elementlerden kimyasal olarak ayrılması, neredeyse aynı kimyasal özelliklere sahip olmaları nedeniyle oldukça zordur. Bu çalışmada PCB numunelerinde TCE'lerin izlenebilir ölçümü için referans bir kimyasal ayırma işlemi geliştirildi ve doğrulandı. Ortak bir araştırma projesinde üretilen 200 µm'nin altındaki parçacık boyutlu PCB numunesi, 2 ml %65 (w/w) HNO₃ ve 6 ml %30 (w/w) HCl' de 200°C'de 30 dakika boyunca mikrodalga parçalama sistemi kullanılarak çözüldü. Numune çözeltileri, çözünmeden önce numunelere izotop bakımından zenginleştirilmiş referans materyali eklenerek hazırlandı. Ölçümlerin izlenebilirliği için sertifikalı referans materyallerinden kalibrasyon karışımları hazırlandı. Mikrodalga sindirim sisteminden elde edilen çözeltilerden TCE'lerin kimyasal olarak ayrılması için yüksek basınçlı ekstraksiyon sistemi (SPE WARE CEREX 48), polipropilen kolonlar (≈3 mm iç çap ve ≈8 cm uzunluk) ve lantanit spesifik reçine (50-100 µm) kullanıldı. Elüsyon işlemi, TCE'lerin girişim yapan elementlerden ayrılması için optimize edildi.

Atık PCB malzemesindeki TCE'lerin belirlenmesi için ölçüm belirsizliği hesaplamasında aşağıdan yukarıya yaklaşım kullanılmış olup, ölçüm belirsizlikleri ve belirsizlik bütçeleri, ticari GUM Workbench yazılımı kullanılarak Ölçümdeki Belirsizliğin İfadesine İlişkin Kılavuz (GUM) yaklaşımına göre hesaplanmıştır.

Anahtar Kelimeler: Teknoloji Kritik Elementler, Atık Elektrikli ve Elektronik Ekipmanlar, Atık Baskılı Devre Kartı, İzotop Seyreltme ICP-MS, Neodmiyum, Geri Dönüşüm, Ekstraksiyon, Lantanit Ayırma, Paladyum, Ölçüm Belirsizliği.

ACKNOWLEDGEMENTS

Firstly, I want to express my sincere gratitude to my advisors Prof. Dr. Savaş BERBER and Doç. Dr. Oktay CANKUR for the continuous support of my master study and research. Doç. Dr. Oktay CANKUR's guidance helped me in all the time for research and writing of this thesis.

As well as I would like thank the rest of my thesis committee members for motivation, enthusiasm, and immense knowledge.

I would also like to thank TÜBİTAK UME for providing me with the necessary equipment and information for my master's thesis.

This study (20IND01 MetroCycleEU) receive funding from the European Metrology Programme for Innovation and Research (EMPIR) co-financed by the Participating States and from the European Union's Horizon 2020 research and innovation programme

I would also like to thank my mother Sevilay KUTAN, my father Murat KUTAN, my sisters Demet MERCAN and Şeymanur ÖNDER and my cousins who always supported me in pursuing my dreams.

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LIST OF SYMBOLS AND ABBREVIATIONS

BIPM	: Bureau International des Poids et Mesures
CRM	: Certified Reference Material
<i>c</i>	: Percentage
<i>d</i>	: Density
DC	: Direct Current
DRC	: Dynamic Reaction Cell
EMPIR	: European Metrology Programme for Innovation and Research
EC	: European Community
EU	: European Union
g	: Gram
GTÜ	: Gebze Technical University
GUM	: Guide to the Expression of Uncertainty in Measurement
HPLC	: High Performance Liquid Chromatography
HR	: High Resolution
ICP-MS	: Inductively Coupled Plasma Mass Spectrometer
ID-MS	: Isotope Dilution Mass Spectrometer
IRM	: Isotopic Reference Material
ISO	: International Organization for Standardization
IUPAC	: International Union of Pure and Applied Chemistry
kg	: Kilogram
K	: Kelvin
LN	: Lanthanide
LREE	: Light Rare Earth Elements
M	: Molarity
<i>m</i>	: Mass
MW	: Molecular Weight
MR	: Medium Resolution
ml	: Millilitre
<i>m/z</i>	: Mass/Charge
MW	: Microwave System
NIST	: National Institute of Standards and Technology
PCB	: Printed Circuit Board
R_x	: Isotope Ratio of Sample
R_{xy1}	: Isotope Ratio of Sample-Spike
R_z	: Isotope Ratio of NIST CRM Nd 3135a
R_{zy2}	: Isotope Ratio of NIST CRM Nd 3135a -IRM_2
R_{zy3}	: Isotope Ratio of NIST CRM Nd 3135a -IRM_3
REE	: Rare Earth Element
RM	: Reference Material
RSD	: Relative Standard Deviation
RF	: Radio Frequency
SI	: System International
TÜBİTAK	: Turkish Scientific and Technological Research Council
TCE	: Technology Critical Element
TIMS	: Thermal Ionisation Mass Spectrometry
TRU	: Trans Uranium Elements
U	: Expanded Uncertainty

UME	: National Metrology Institute of Türkiye
v	: Volume
W	: Weight
WEEE	: Waste Electrical and Electronic Equipment
μm	: Micrometre



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1. INTRODUCTION

Technology critical elements (TCE) are a group of naturally occurring chemical elements increasingly used in high technology equipment, including energy-efficient lighting, electric car batteries, electronic instruments, computers and mobile phones due to their important characteristics. Obtaining TCE elements from nature is difficult, costly and their resources are limited. Therefore, the recovery of TCE elements in electronic waste is important for both economy and environmental health. A reliable measurement method should be developed to accurately determine the economic value of electronic waste.

In this thesis study, it is aimed to develop a measurement method that can obtain system international (SI) traceable results. For this, ICP-MS instrument was used. Solid printed circuit board (PCB) samples were extracted in the microwave digestion system. Sample solutions were prepared in order to determine the analytes by a high accuracy method, Triple-ID-ICP-MS method. Certified reference materials, CRMs were used to provide the metrological traceability of the measurement result. During the sample preparation method, a matrix separation with suitable resins was developed to prevent element interference in the measurements by ICP-MS.

The results showed that the measurement method was carried out successfully. At the end of the thesis, a method that environmental laboratories, recycling factories and analytical laboratories can benefit from has been obtained from this study. The studies in the thesis will shed light on future reference method development studies.

1.1. Technology Critical Elements

TCE are a group of naturally occurring chemical elements increasingly used in high technology, including energy-efficient lighting, electric car batteries, sensors, electronic instruments, mobile phones and computers, due to their unique characteristics.

These elements are considered as ‘critical’ because of their economic importance in essential technologies and their supply risk. Procuring these elements from nature is difficult and expensive. In 2018, the EU established a list of the critical elements for Europe [5]. The TCE included in the MetroCycleEU project (Cobalt (Co), Gallium (Ga), Germanium (Ge), Indium (In), Tantalum (Ta), Neodymium (Nd), Praseodymium (Pr), Dysprosium (Dy), Gadolinium (Gd), Lanthanum (La), Gold (Au), Platinum (Pt), Palladium (Pd), Rhodium (Rh) and Lithium (Li)) were selected from this list [1]. A method that can measure TCE in electronic wastes at $\mu\text{g/g}$ levels in a reliable and SI traceable manner is required.

MetroCycleEU project is developing and optimising reference methods for the sample preparation and TCE analysis of three urban mine wastes: Printed Circuit Boards (PCB). For method development, a test batch of PCB was crushed and different digestion strategies were assessed by ICP-MS analysis [3]. There are deficiencies in the appropriate reference method for TCE analysis and the digestion method of PCB. Due to the large matrix components of PCB waste, sampling and sample preparation protocols are not available. So, in this thesis study, an appropriate dissolution method was developed for PCB samples using the mw digestion system and various acid mixtures.

1.2. Triple Quadrupole ICP-MS and Working Principle

Working principle of the ICP-MS instrument used to measure TCE elements in PCB is mentioned. ICP-MS is an analytical technique used for elemental determination. In my thesis study, Agilent 8800 ICP-Triple quadrupole instrument was used. The ICP-MS system was developed by Houkand et.al. in 1980, and the first commercial systems were introduced to the market in the early 1980s. Although there were some problems in the first instruments introduced to the market, the method has taken its place as a rapidly developing system because of its sensitivity, speed and ability to reach very low measurement limits. The first commercial ICP-MS systems were quite large, expensive, and had some limited use. Today much smaller instruments can be manufactured with new technology over a wide linear range [6].

ICP-MS is an analytical technique in which samples are sent to high-temperature argon plasma, where molecular bonds are broken and atoms are ionized. ICP-MS instruments consists of two main parts: Inductively Coupled Plasma (ICP) and Mass Spectrometer (MS) which is a high vacuum system where a detector was also located in this part. Once the elements in the sample are ionized in the plasma, they are directed to mass spectrometer, where they are separated and measured based on their mass to charge ratios (m/z).

The sample is introduced as a solution to the nebulizer and spray chamber through the sample entry system. The sample solution is nebulized by argon flow. Only small droplets are transported into the argon plasma. The temperature in the plasma environment is around 8000 – 10000 K [6]. Under the influence of this high temperature, the substances are decomposed and the elements . The atom whose electron is removed from its last orbit becomes single-positively charged, and unwanted ions in the system are separated and removed by various parts. The resulting positively charged ions are separated according to their different mass/charge ratios with the help of a mass filter and sent to the detector. The incoming ions are counted by the detector sequentially. The analytical signal generated by the detector is processed by the electronic parts. The results are given in the requested format, usually as counts per second or evaluated by the software to yield the measurements result as in the amount or ratio format [6].

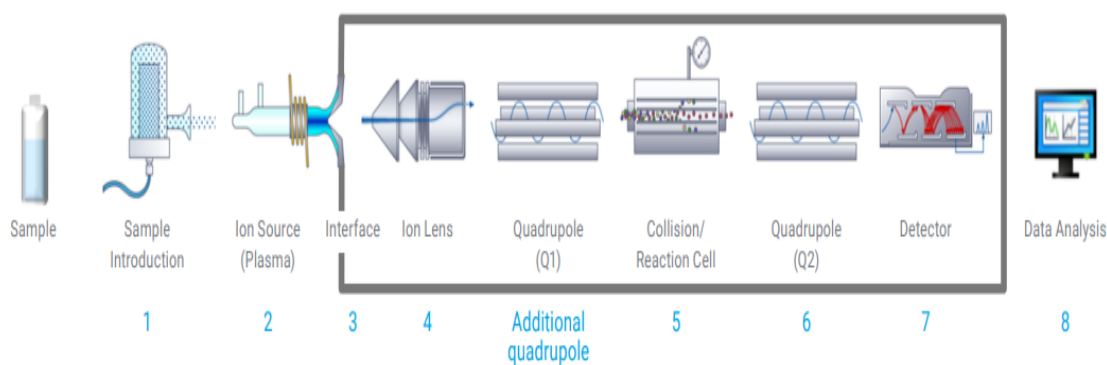


Figure 1.1: Main components of a triple quadrupole ICP-MS instrument [7].

1.2.1. Sample Introduction System

In the ICP-MS instrument, samples are generally introduced to the instrument in the solution form. Solids to be analysed for ICP-MS must be completely digested before analysis. Different acids are used in sample solubilisation. The sample introduction system consists of a peristaltic pump, nebulizer and spray chamber.

When the sample is fed into the system, care should be taken to ensure that there are no solid particles in it. If there are solid particles inside, it may clog the nebulizer tip and thus cause in loss of sensitivity as the solution could not be turned into mist which mix well with the carrier Ar to be transported to the hot part of the plasma for ionization.

Peristaltic Pump

Peristaltic pumps are used to pump the sample solution to the spray chamber by providing constant and stable sample flow. Peristaltic pumps may have several channels. The most commonly used three-channel peristaltic are pumps. While the sample is given through one channel, the excess sample not nebulized in the spray chamber is removed by the other channel which ensures that the large droplets formed and settled down in the spray chamber are sent to waste. Plasma quenching occurs if the liquid sample is administered directly to the torch assembly and thus plasma. The third channel may be used to add internal standards.

Nebulizer

The nebulizer turns the liquid sample into small droplets, called aerosol, with the help of pressurised argon gas. The sample misted by the nebulizer reaches the part called spray chamber. Due to the shape of the spray chamber, large droplets travel downwards. Small droplets move towards the torch and plasma the influence of the nebulizer gas, Argon (Ar).

Atomizer and Ionizer

Analyte atoms transform into ions, forming the plasma that serves as the ion source of the ICP-MS. Argon (Ar) gas is used in plasma because the ionization energy of many elements in the periodic table is lower than the ionization energy of Ar (15.76 eV), the elements can be ionized in plasma. However, Ar cannot ionize the higher energy elements such as halogens and Ne, F and He which has higher ionization energy. Argon gas turns into plasma and reaches 10 000 K. The elements in the sample are ionized and positive charged ions are formed.

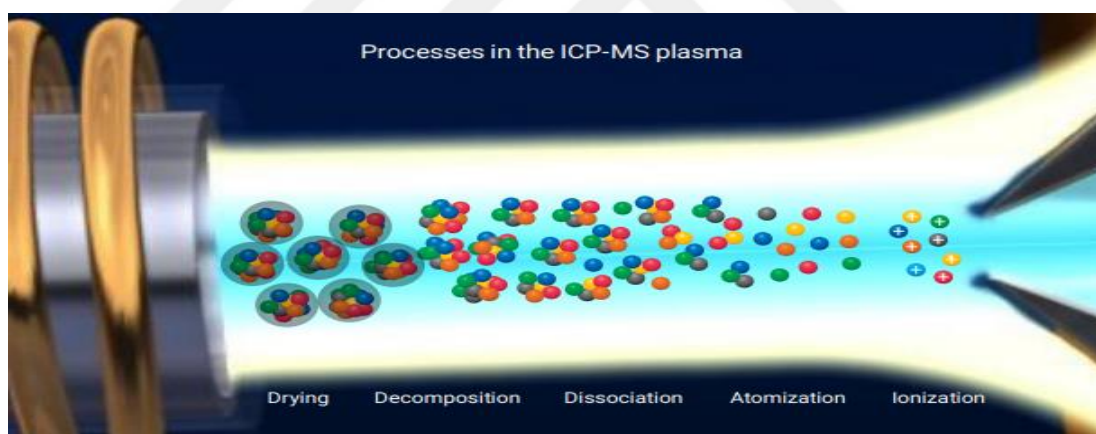


Figure 1.2: Behavior of the solution in plasma [7].

Interface

Interface establishes a connection between the ICP ion source and the mass spectrometer under atmospheric pressure. The plasma ion source and the mass spectrometer are separated by a vacuum interface, which transfers ions from the plasma (at atmospheric pressure) to the mass spectrometer (in a vacuum chamber). The interface consists of a series of cooled metal plates or cones with small holes in them to allow the ions to pass through. The typical arrangement uses a sampling cone

to extract ions from the plasma, followed by a skimmer cone to sample the central portion of the ion beam to pass to the high vacuum region.

Sampler and skimmer cones provide regulated and stepped pressure decrease between atmospheric pressure and the high vacuum part. The extraction lens in the vacuum part accelerates the ions to the mass analyser [7].

Ion Lens

Ion lenses focuses the desired ions and prevents the matrix portion from reaching the mass analyzer (quadrupole or magnet). Depending on the applied voltage, positively charged ions reach the quadrupole in regulated form sequentially and without colliding with each other.

Quadrupole Mass Filter

Most ICP-MS instruments use a quadrupole mass spectrometer to filter ions by mass, or, more accurately, by mass to charge ratio (m/z). The quadrupole mass filter consists of four cylindrical rods. As two pairs of rods; opposite pairs of rods are connected to separate electrical supplies. An out of phase RF voltage and a positive or negative DC voltage is applied to the two pairs of rods. RF and DC voltages filter the ion by mass to charge ratio (m/z), allowing only 1 m/z at a time to pass through the analyzer and reaching to the detector [7].

Collision / Reaction Cell

The isobaric interferences may be encountered in the ICP-MS measurements. In order to eliminate such interferences, usually the quadrupole instruments are equipped with a reaction/collision cell. Either a collision or reaction gas is introduced into the cell where it reacts with interfering ions so that they cannot reach to the detector as the analyte. Such systems can eliminate many plasma-derived polyatomic ions by using the suitable reaction or collision gas. The system becomes capable of measuring the analyte signal with minimized interferent signal and provide much improved sensitivities.

Detector

The detector used in most ICP-MS systems is a discrete dynode electron multiplier (DDEM). The electron multiplier uses high voltage electrode (or dynode) positioned so that ions that emerge from the quadrupole strike the dynode. Each ion that strikes

the first dynode releases one or more electrons from the dynode surface. These electrons strike the second dynode, releasing further electrons to strike the third dynode and so on down the detector. By the final dynode, the cascade of electrons has built up to a high enough level that it can be recorded as a pulse or count by the electron multiplier electronics [7].

1.2.2. Interferences in ICP-MS Measurements

As with all atomic spectroscopic analytical techniques, various types of interference can occur in routine ICP-MS analysis. In addition, there are interferences that occur when isotopes or elements with the same atomic mass or mass number coexist. Isobaric interferences are probably the largest class of interferences in ICP-MS and are caused by atomic or molecular ions that have the same mass-to-charge ratio as analytes of interest. Current ICP-MS instrument software correct mathematically all known atomic "isobaric" interferences, or interferences caused by compatible isotopes of different elements, but polyatomic interferences cannot be corrected mathematically. Such interferences are caused by polyatomic ions that are formed from precursors having numerous sources, such as the sample matrix, reagents used for preparation, plasma gases, and entrained atmospheric gases. A prior knowledge of polyatomic interferences cited in the literature for a particular analyte mass may be helpful to the analyst for selecting reagents and conditions that would preclude or at least reduce the possibility of their formation [8]. Interference from spectral overlap with isobaric and polyatomic species has long hindered accurate analysis. Diluting the sample to reduce interference is sufficient in some cases, but in others additional sample preparation such as standard addition method and isotope dilution method or advanced instrumentation is required. Interferences depend on the sample matrix and are analysis specific. With the help of the developed approaches, analysis can be done with high accuracy and good precision for elemental determination and isotopic analysis.

1.2.3. Preventing Interference Encountered in the ICP-MS System

1.2.3.1. Writing a Mathematical Equation

The interference of an isotope of any element with another isotope of the same mass is called spectral interference. If the resulting spectral interference is equal to or less than the measured analyte signal, it may be possible to make a correction with mathematical equation. The mathematical correction of ^{144}Sm interference on ^{144}Nd is given in the following example

$$\frac{\text{Sm144}}{\text{Sm149}} = \frac{0.0308 \text{ (natural abundance of Sm144)}}{0.1382 \text{ (natural abundance of Sm149)}} \quad (1.1)$$

$$\text{Total Signal Value at Mass 144} = \text{Nd144} + \text{Sm144} \quad (1.2)$$

$$\text{Nd144} = [\text{Total Signal 144} - \left(\frac{\text{Sm144}}{\text{Sm149}} \times \frac{\text{Signal Sm149}}{\text{Sm149}} \right)] \quad (1.3)$$

In order to write an equation for this type of spectral interference, an isotope of Sm that is devoid of interference is selected and the signal value corresponding to the isotope that causes interference is calculated [9].

1.2.3.2. Using the Reaction Cell

Another way to prevent such interferences is to use ICP-MS equipped with a reaction/collision cell that allow the analyte to react with an active gas and then measured on another mass without interference; this is called mass shift. The reaction gas may also be used to react with the interfering ion to change its m/z ratio or charge neutralize it not to reach the detector as analyte. This is usually needed for eliminating polyatomic interferences. The active gases that can be used are NH_3 , O_2 and H_2 . For example, difficulty in the accurate quantification of Cr by ICP-MS is due to the numerous spectral interferences (e. g. $^{35}\text{Cl}^{16}\text{O}^{1}\text{H}$ or $^{40}\text{Cl}^{12}\text{C}$) created in the plasma on the most abundant Cr isotope, ^{52}Cr . The use of such gases reacts with such chlorinated ions and decreases the background equivalent concentration on ^{52}Cr [10].

1.2.3.3. Using the Collision Cell

ICP-MS systems have included a collision cell to resolve spectral overlaps caused by unwanted ions that appear at the same mass as the analyte ions being measured. By far the most significant spectral overlaps in ICP-MS are caused by molecular (or polyatomic) ions. A polyatomic ion overlap occurs when a combination of atoms forms an ion at the same mass as an analyte of interest. Polyatomic ion overlaps have been a longstanding problem in ICP-MS, so the development of collision cells to address these overlaps was a major factor in improving data accuracy and increasing adoption of ICP-MS across many industries performing routine measurements. In collision mode, the reaction cell is pressurized with a nonreactive gas-usually helium (He) [7]. Separation of interferences by collision is based on molecular size and no chemical reaction occurs in the separation of interferences. Since all polyatomic interferences are larger in size than the analyte they interfere with, they collide with the gas more frequently. Polyatomic ions lose more energy and they cannot reach the energy required to overcome the cell. This is called Kinetic Energy Discrimination (KED) [11]. Helium KED can be considered as a universal collision mode, as the same cell conditions can be used to resolve multiple polyatomic ions overlaps on multiple analyte masses in multiple different sample types.

1.3. HR ICP-MS and Working Principles

High resolution ICP-MS (HR ICP-MS) is a system that can perform quantitative determination of trace elements in solid and liquid samples quickly and with high accuracy.

HR ICP-MS Performance:

- Freedom from interferences through high mass resolution.
- Lowest limits of detection through the highest sensitivity and lowest dark noise of any ICP-MS.
- Routine productivity through full automation and Autotune.
- Exceptional ruggedness and stability.

1.3.1. Variable Mass Resolution

Three fixed resolution settings $R=300$, 4000 and 10000, are available under full computer control. High mass resolution allows interference free measurements from most of the polyatomic interferences that creates serious effects in standard quadrupole ICP-MS instruments.

Because of the enormous number of possible interferences, the ability to identify interfering signals is absolutely crucial to methods development, particularly in new or unknown matrices.

Resolution can be changed rapidly and reproducibly, which combined with the inherently constant transmission results in long term stability without recalibration.

1.3.2. Data Acquisition

Having the ion source at ground potential not only allowed the design of a smaller, simpler and safer instrument, but has profound ramifications for data acquisition; Not only can the magnetic field be changed rapidly, but it is also possible to rapidly change masses by variation of the acceleration voltage with the speed of a quadrupole scan. The ability to make rapid scans and jumps while varying mass resolution gives the analyst unprecedented flexibility and power.

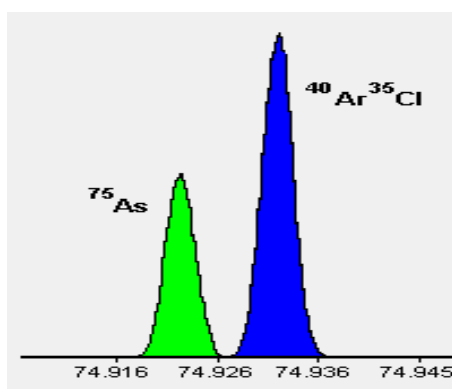


Figure 1.3: Separation of interferences through high mass resolution ($R=10000$).

Magnetic sector mass analyzer is used as the mass analyzer in HR ICP-MS. The magnetic sector field focuses ions with diverging angles of motion from the entrance slit to the intermediate (beta) slit. The magnetic sector field is dispersive with respect to ion energy and mass (exactly: momentum). The electric sector field (ESA) focuses ions with diverging angles of motion from the beta slit on to the exit slit. It is dispersive with respect to ion energy only. Together, if the energy dispersion of magnet and ESA are equal in magnitude but of opposite direction, magnet and ESA focus both ion angles (first focusing) and ion energies (double focusing), while being dispersive for m/z : a mass spectrometer. The order of fields used with HR ICP-MS is called a reverse geometry.

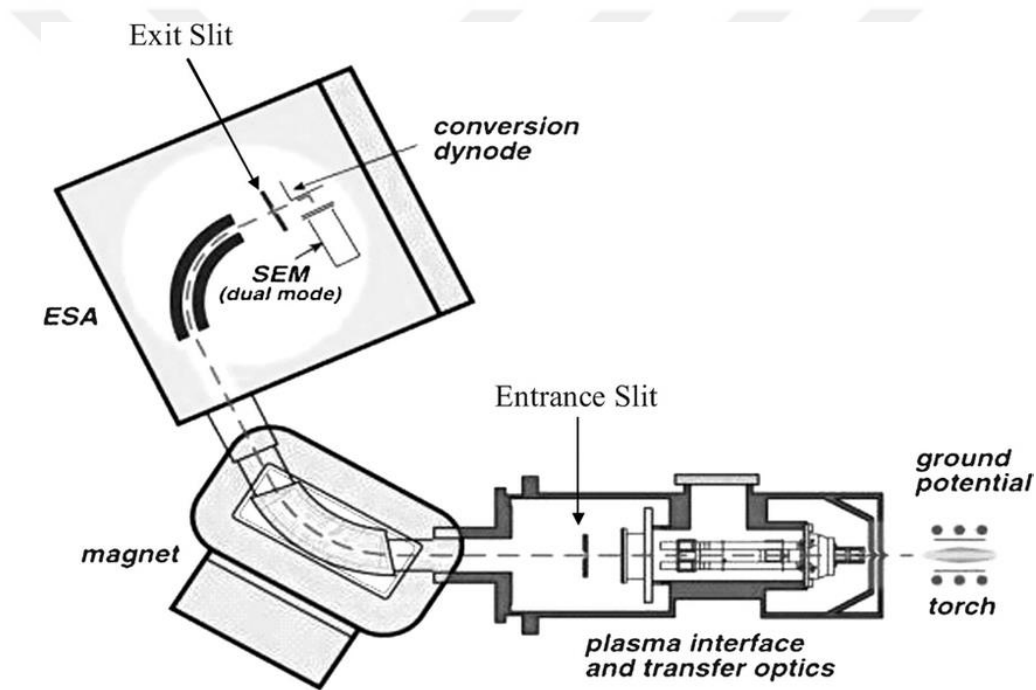


Figure 1.4: Magnetic sector mass analyzer [12].

Resolution is defined as;

$$R = \frac{m}{\Delta m} \quad (1.4)$$

The definition of Δm is different for different types of MS analysers and the magnetic sector MS the 10% valley definition is commonly used.

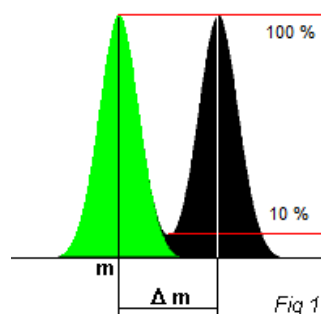


Figure 1.5: 10% valley definition [13].

Magnetic sector instruments like the HR ICP-MS, mass resolution is constant over the whole mass range. This inherent feature differentiates the HR ICP-MS from all ICP-MS based on quadrupole technology [13].

1.4. Calibration Process

Calibration is an important part for providing accurate and reliable measurement results. It is well known that matrix effects can be serious in plasma based atomic spectrometric techniques, due to considerable amounts of matrix ions reaching to the source and can significantly change the analyte signal. Several techniques can be used to minimize these matrix effects, including dilution of the sample, standard addition calibration, isotope dilution or use of matrix separation techniques as elution process before introducing samples to the instruments [11].

1.4.1. External Calibration

The most common method of standardization uses one or more external standards, each of which contains a known concentration of analyte. We call these standards “external” because they are prepared and analyzed separate from the samples.

Limitations to External Calibration: There is a serious limitation, however, to an external standardization. When we determine an analyte's response using external calibration, the analyte is present in the external standard's matrix; that is usually a much simpler matrix than that of "real" samples. When we use an external standardization we assume the matrix does not affect the value of the response (ϵ). However, if the matrix does affect the response, we introduce a proportional determinate error into our analysis. For instance, where we show calibration curves for an analyte in the sample's matrix and in the standard's matrix. In this case, using the calibration curve for the external standards leads to a negative determinate error in analyte's reported concentration. If we expect that matrix effects are important, then we try to match the standard's matrix to that of the sample, a process known as matrix matching. If we are unsure of the sample's matrix, then we must show that matrix effects are negligible or use an alternative method of standardization [26].

- External standard-standards are not in the sample and are run separately
- Generate calibration curve
 - Run known standards and measure signals.
 - Plot vs. known standard amount (concentration, mass, mol).
 - Linear regression via least squares analysis

- Compare response of sample unknown and solve for unknown concentration.
 - All well and good if the standards are just like the sample unknown.
- The solutions are prepared in solvent.
- The signals from the standards should be within the working range should have enough repeatability.
- The concentration range should cover the concentration in the sample.
- Linear range is the most suitable region to work since the sensitivity is the highest.

1.4.2. Standard Addition Method

The standard addition method is a calibration process needed when the content of the sample is a complex mixture and other concomitant components other than the analyte has effect of enhancing or suppression of the analytical signal. These components in the sample matrix or added in the sample preparation stage may change the bulk properties of the sample solution to be introduced into the instrument resulting in a change in the analytical signal. In such cases, a calibration curve prepared based on pure analyte samples will give biased results. The ideal situation is for calibration standards to contain components that are close to the concentrations of both the analyte and other substances in the sample matrix. Thus, the effect of sample matrix on the measured analyte absorbance is minimized [14].

In this method, the analyte concentration in the sample is increased by adding a certain volume of the standard solution of the analyte to a certain amount of sample. The signals before and after addition are measured and the values found are used to calculate the analyte concentration.

The signal is assumed to vary linearly with concentration. To establish an accurate relationship, a large amount of calibration data must be available. Increasing amounts of standard solution are added to the same amounts of samples and measurements are made. No additions are made to the initial sample solution. The signals of these solutions are measured at optimum operating conditions. The analyte concentration in the initial sample is calculated from the intercept on x-axis of the calibration line.

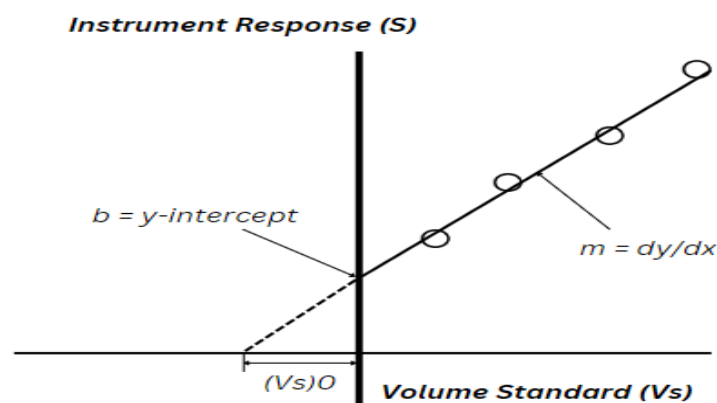


Figure 1.6: Standard addition graph.

$$(V_s) \times C_s = -V_x \times C_x \quad (1.5)$$

$$C_x = -\frac{(V_s) \times C_s}{V_x} \quad (1.6)$$

1.4.3. Isotope Dilution Mass Spectrometer

Isotope dilution mass spectrometry (ID-MS) are usually applied using the formation of positive ions of metals.

The evolution of ID-MS in elemental and organic analysis since the first experiments done in the 1930s and 1940s has depended on three main factors: the availability of isotopically enriched elements and labelled compounds, the developments in mass spectrometry instrumentation and scientific requirements in other disciplines. The technique of isotope dilution mass spectrometry (ID-MS) was initially developed during the 1950s for elemental analysis. In mass spectrometry, unlike spectrophotometric techniques, there is no fixed relationship between the amount, and concentration, of a particular substance and the instrument response. Sensitivity for a particular compound or ion varies with, for example, time and instrumental tune parameters. These variations are in addition to those caused by, for example, sample introduction and chromatography. To achieve even moderately accurate quantification requires the use of an internal standard. An advantage of mass spectrometry lies in its ability to use isotopically enriched analogues (inorganic mass spectrometry) or isotopically labelled analogues (organic mass spectrometry) as internal standards. Indeed, in some instances ID-MS is referred to as 'stable isotope internal standardisation'. Provided the isotopic analogue is added to sample at the very

beginning of the analytical method and it comes into equilibrium with the analyte without losses or isotopic fractionation, it enables exact compensation to be made for errors at all stages of the analysis, from sample digestion/preparation through to the final instrumental measurement.

Initially, ID-MS of inorganic analytes was most frequently performed using thermal ionisation mass spectrometry (TIMS). More recently, inductively coupled plasma mass spectrometry (ICP-MS) based ID-MS has become more prevalent, because it requires much less sample preparation prior to analysis, and can provide results of the required accuracy and precision. The advent of compact and economic instrumentation, such as quadrupole and ion trap mass spectrometers, has led to the increasing use of mass spectrometry in the field of analytical chemistry. As a result, ID-MS is playing an increasingly important role in trace analysis. This also due to its greater accuracy than other calibration methods and its ability to compensate for matrix effects.

1.4.3.1. The Principles of ID-MS

The underlying principle of ID-MS is that an isotopically enriched analogue (inorganic MS) of the analyte compound is used as an internal standard in quantification by mass spectrometry, shown in figure 1.7.

An accurately known amount of the isotopic analogue is added to the sample. The consequent ratio of the amounts of the two isotopes (one resulting from the analyte and the other from the isotopic spike) is measured on a portion of the sample using a mass spectrometer, so enabling the analyte concentration to be calculated.

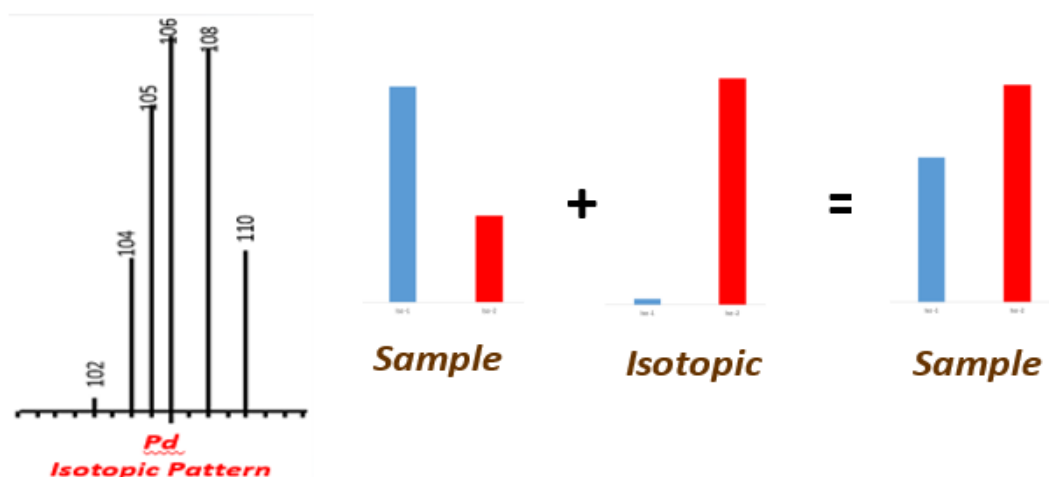


Figure 1.7: A visual explaining ID-MS.

1.4.3.2. Advantages and Disadvantages of ID-MS

Provided that the sample is homogeneous and isotope equilibrium has been reached before measurement, the advantages of ID-MS include:

- It is a definitive method because of its accuracy (precision and trueness) and provision of definable uncertainty values.
- Once equilibration of the spike and analyte isotopes has been achieved, the total recovery of the analyte is not required, because the determined value is based on measuring the ratio between the isotopes, that were chosen for quantification,
- The accuracy of the method is mainly determined by the precision of this ratio measurement and/or the IUPAC isotopic ratio values.
- Loss of analyte during sample preparation is compensated for by use of the isotopic analogue as internal standard.
- The methodology is less time consuming and can provide greater accuracy than standard additions.

Disadvantages of ID-MS:

- Unavailability of standard material enriched for each isotope.
- The prices of enriched standard materials are expensive.

1.4.3.3. Characterisation of Isotopic Analogue

In inorganic ID-MS, prior to spiking the sample with the isotopic analogue it needs to be fully characterised. If a fully characterized i.e. certified isotopic analogue is available the certificate will provide information on the concentration and isotopic abundance. Alternatively, a process known as reverse ID-MS can be used to determine the concentration. In this case the analogue is calibrated against a high purity solution of the natural analyte isotope, prepared from a gravimetric solution of a suitable reference material. If abundance of the isotopic analogue is unknown this needs to be determined by carrying out a separate measurement, commonly referred to as an abundance run. For high accuracy work both of these measurements need to be corrected for instrumental mass bias effects.

1.4.3.4. Addition of Isotopic Analogue

In general, to achieve an isotopic ion abundance ratio measurement with the best precision the ratio of analyte concentration to isotopic analogue concentration should be such as to produce equal ion abundances [2]. The solution for analysis should, therefore, contain similar amounts of the two isotopes. The abundances of all isotopes of the element are examined. The least abundant isotope is added, because it is better to change the isotope ratio by adding less isotopic reference material. Abundance value must be lower than other isotopes. There should be no interference on the isotope. The enrichment percentage must be high.

1.4.3.5. Blank Correction

Ideally an analyte-free matrix material should be used to establish blank levels. In the absence of such a material, a full reagent blank, subjected to all sample preparation steps, should be used to evaluate possible blank contributions [15].

1.4.3.6. Single, Double and Triple Isotope Dilution Mass Spectrometry and Equations and Calibration Strategies

Isotope dilution mass spectrometry (ID-MS) is undoubtedly the most powerful and versatile calibration technique in element analysis. Considering metrological concepts, ID-MS offers the lowest measurement uncertainty, formerly noted as highest accuracy.

This makes ID-MS the primary method of measurement in its fields of application [16].

The basic ID-MS equation 1.7 only consists of isotope ratios, masses of sample and spike as well as known or tabulated quantities (isotope abundances, atomic weights) [17, 18].

$$w_x = w_{yb} \times \frac{M_x \times m_y}{M_b \times m_x \times a_{xb}} \times \frac{(R_y - R_{xy1})}{(R_{xy1} - R_x)} \quad (1.7)$$

In the case where a certified or calibrated spike is used for quantifying the analyte mass fraction in the sample, only Eqn. (1.7) is used and the technique is named single ID-MS or direct ID-MS. This is the most simple and straightforward approach, as the spike with known isotopic composition and elemental concentration is added to the sample, the equilibration step is performed and the isotope ratio is determined in the blend.

In double ID-MS the spike is characterized by a primary assay or so-called back-spike, which contains the analyte element with known (natural) isotopic composition and elemental concentration.

$$w_{yb} = \frac{a_{zb} \times M_b \times m_{z2}}{M_z \times m_{y2}} \times w_{z2} \times \left(\frac{R_{zy2} - R_z}{R_y - R_{zy2}} \right) \quad (1.8)$$

Eqn. (1.7) is replaced by its value from Eqn. (1.8) this yields the equation for double ID-MS Eqn. (1.9) when no isotopic variation occurs between z and x, which means that the sample and the back-spike have the same isotopic composition. Then $M_x = M_z$ and $a_{xb} = a_{zb}$

$$w_x = w_{z2} \times \frac{m_{y1} \times m_{z2}}{m_{x1} \times m_{y2}} \times \left(\frac{R_y - R_{xy1}}{R_{xy1} - R_x} \right) \times \left(\frac{R_{zy2} - R_z}{R_y - R_{zy2}} \right) \quad (1.9)$$

The equation only consists of masses and isotope ratios, as w_{z2} is derived from the weighing processes only. This is the main reason why double ID-MS provides much smaller uncertainties than single ID-MS.

For triple ID-MS a third blend between spike and back-spike is used, yielding Eqn. (1.10). This third blend is used to replace R_y in the equation system.

$$w_{yb} = \frac{a_{z3b} \times M_b \times m_{z3}}{M_{z3} \times m_{y3}} \times w_{z3} \times \left(\frac{R_{zy3} - R_{z3}}{R_y - R_{zy3}} \right) \quad (1.10)$$

w_{yb} from Eqn. (1.9) is identified with w_{yb} from Eqn. (1.10)

$$\frac{a_{z2b} \times M_b \times m_{z2}}{M_{z2} \times m_{y2}} \times w_{z2} \times \left(\frac{R_{zy2} - R_{z2}}{R_y - R_{zy2}} \right) = \frac{a_{z3b} \times M_b \times m_{z3}}{M_{z3} \times m_{y3}} \times w_{z3} \times \left(\frac{R_{zy3} - R_{z3}}{R_y - R_{zy3}} \right) \quad (1.11)$$

Reducing and resolving Eqn. (1.11) for R_y yields Eqn. (1.12), when the isotopic compositions of $z2$ and $z3$ are identical.

$$R_y = \frac{x_2 \times (R_{zy2} - R_z) \times R_{zy3} - x_3 \times (R_{zy3} - R_z) \times R_{zy2}}{x_2 \times (R_{zy2} - R_z) - x_3 \times (R_{zy3} - R_z)} \quad (1.12)$$

R_y in the double ID-MS equation (Eqn. (1.9)) is replaced by its definition in Eqn. (1.12). Reducing and resolving for w_x lead to the triple ID-MS equation (Eqn. (1.13))

$$w_x = \frac{m_{y1}}{m_{x1}} \times (w_{z2} \times \frac{m_{z2}}{m_{y2}} \times \frac{(R_{zy2} - R_z) \times (R_{zy3} - R_{xy1})}{(R_{xy1} - R_x) \times (R_{zy3} - R_{zy2})} + w_{z3} \times \frac{m_{z3}}{m_{y3}} \times \frac{(R_{zy3} - R_z) \times (R_{xy1} - R_{zy2})}{(R_{xy1} - R_x) \times (R_{zy3} - R_{zy2})}) \quad (1.13)$$

There is no need to determine the isotope ratio of spike. This is triple ID-MS's important advantage. The equation consists only of masses and isotope ratio.

Table 1.1: Symbols used for parameters adopted in the Triple ID-MS measurement equations.

Symbol	Quantity
$mz2_1$	Mass of back-spike for blend2-1
$my2_1$	Mass of spike for blend2-1
$mz3_1$	Mass of back-spike for blend3-1
$my3_1$	Mass of spike for blend3-1
$mz2_2$	Mass of back-spike for blend2-2
$my2_2$	Mass of spike for blend2-2
$mz3_2$	Mass of back-spike for blend3-2
$my3_2$	Mass of spike for blend3-2
$mz2_3$	Mass of back-spike for blend2-2
$my2_3$	Mass of spike for blend2-3
$mz3_3$	Mass of back-spike for blend3-3
$my3_3$	Mass of spike for blend3-3
$my1_1$	Mass of spike for blend1-1

Continuation of the **Table 1.1.**

Symbol	Quantity
$mx1_1$	Mass of sample for blend1-1
$my1_2$	Mass of spike for blend1-2
$mx1_2$	Mass of sample for blend1-2
$my1_3$	Mass of spike for blend1-3
$mx1_3$	Mass of sample for blend1-3
$wz2$	Mass fraction element in back-spike solution z2
$wz3$	Mass fraction element in back-spike solution z3
$wy1$	Mass fraction enriched isotope in spike (blend2-1)
$wy2$	Mass fraction enriched isotope in spike (blend2-2)
$wy3$	Mass fraction enriched isotope in spike (blend2-3)
wy	Mean of mass fraction of enriched isotope in spike
$Rzy2_1$	Isotope ratio any isotope of the element / enriched isotope in blend2-1
$Rzy3_1$	Isotope ratio any isotope of the element / enriched isotope in blend3-1
Rx	Isotope ratio any isotope of the element / enriched isotope in back-spike
$Rxy1_1$	Isotope ratio any isotope of the element / enriched isotope in blend1-1
$Ry1$	Isotope abundance ratio any isotope of the element / enriched isotope in spike from blend1
$Rzy2_2$	Isotope ratio any isotope of the element / enriched isotope in blend2-2
$Rzy3_2$	Isotope ratio any isotope of the element / enriched isotope in blend3-2
$Rxy1_2$	Isotope ratio any isotope of the element / enriched isotope in blend1-2
$Ry2$	Isotope abundance ratio any isotope of the element / enriched isotope in spike from blend2

Continuation of the **Table 1.1.**

Symbol	Quantity
$Rzy2_3$	Isotope ratio any isotope of the element / enriched isotope in blend2-3
$Rzy3_3$	Isotope ratio any isotope of the element / enriched isotope in blend3-3
$Rxy1_3$	Isotope ratio any isotope of the element / enriched isotope in blend1-3
$Ry3$	Isotope abundance ratio any isotope of the element / enriched isotope in spike from blend3
Ry	Mean isotope abundance ratio any isotope of the element / enriched isotope in spike
$\sum Rx$	Total isotope ratio in IUPAC
$nx1$	Element amount in sample, blend1
$nx2$	Element amount in sample, blend2
$nx3$	Element amount in sample, blend3
Max	Atomic weight of Nd (IUPAC Value)
$Mx1$	Element amount in solution, blend1
$Mx2$	Element amount in solution, blend2
$Mx3$	Element amount in solution, blend3
$BLANK$	Isotope ratio of any isotope of the element / enriched isotope in blank solution
$wx1$	Mass fraction of element in sample (blend1-1)
$wx2$	Mass fraction of element in sample (blend1-2)
$wx3$	Mass fraction of element in sample (blend1-1)
wx	Mean Mass fraction of element in sample

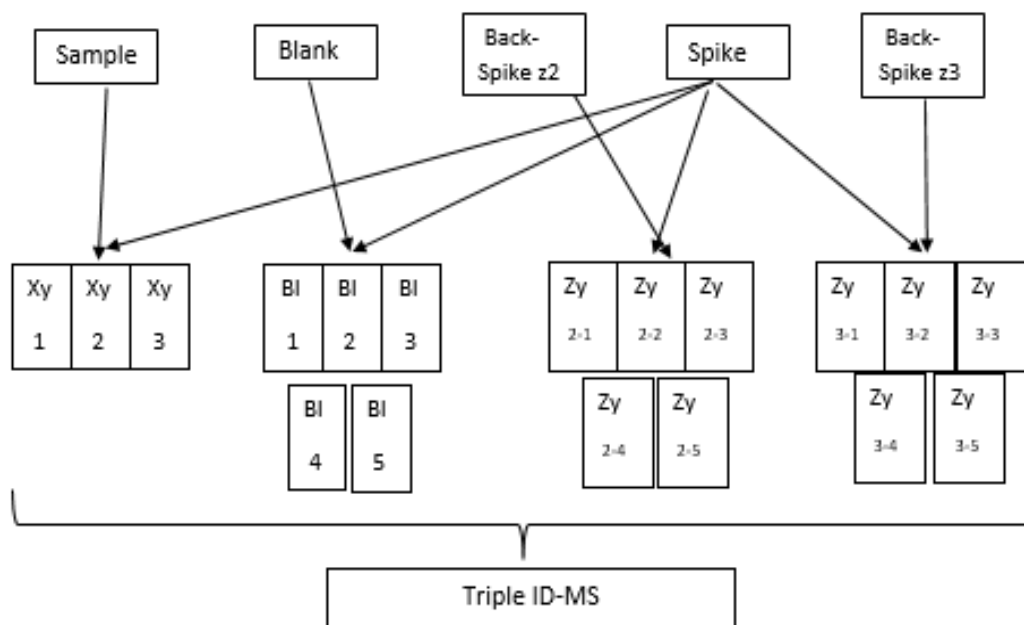


Figure 1.8: Schematics of blend preparation for triple ID-MS.

The major advantage of triple ID-MS is that the isotope abundance ratio of the spike does not need to be determined. Therefore, triple ID-MS is recommended when highly enriched spikes are used whose isotope abundance ratio is difficult to determine, when strong memory effects occur between samples featuring different isotopic composition, or when the ultimate measurement uncertainty is required [19].

1.5. Chemical Separation

Even though elemental interferences are corrected mathematically, chemical separation of the interfering elements before the measurement provide improved repeatability of isotope ratio measurements as the matrix effects are minimized. Furthermore, no need to measure the interfering isotope decreases the measurement time which results in enhanced repeatability. In this thesis, a chemical separation procedure was developed using a high-pressure extraction device, polypropylene column and lanthanide specific resin.

1.5.1. Lanthanide Specific Resin and Extraction Column

The lanthanide specific resin produced by Triskem are used to separate technologically critical elements from each other [4].

Separation of Lanthanides (Ce, La, Pr, Nd, Sm, Eu, Gd, Dy) [20].

Order N°.: LN-R50-S

Particle size: 50-100 μm

Density: LN resin: 0.38 g/ml

The LN resin (LaNthanides) is composed of di (2- ethylh exyl) ortho phosphoric acid (HDEHP) (fig. 1.9) impregnated onto an inert support.

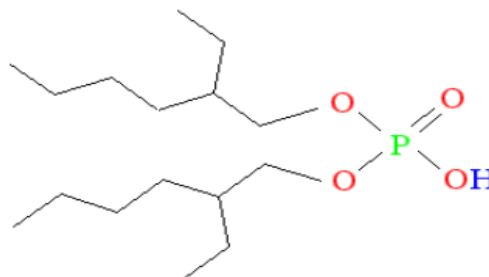


Figure 1.9: Di(2-ethylhexyl) orthophosphoric acid [4].

LN resin is mainly used for separation of lanthanides for a wide range of applications.

LN resin is used for the determination of light rare earth elements.

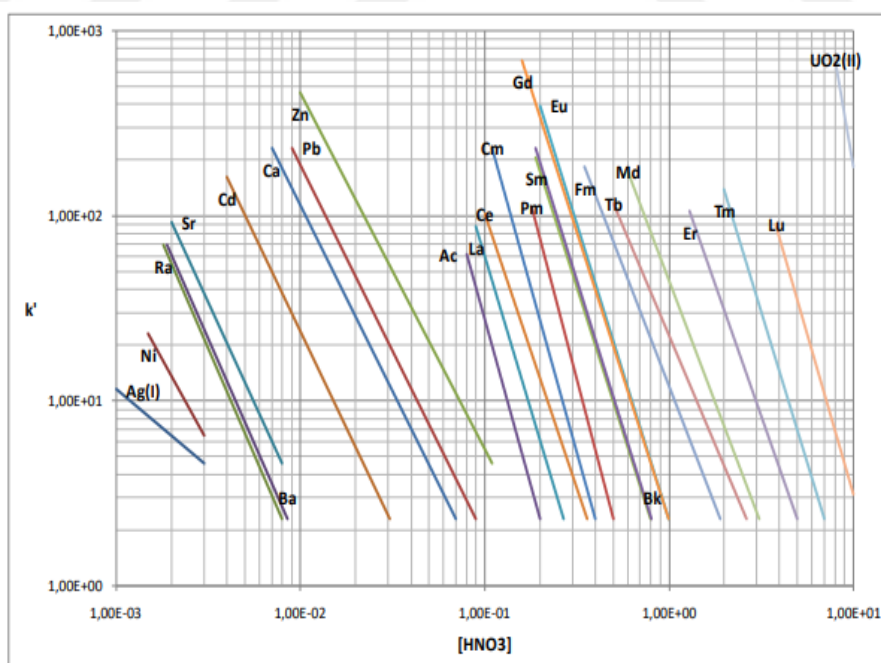


Figure 1.10: Retention of different elements on LN resin as a function of the HNO_3 [18].

The light rare earth elements are eluted with 0.05 mol/L HNO_3 and directly passed onto LN resin, which was previously conditioned with 0.05 mol/L HNO_3 . At this acid concentration the REEs are retained on the LN resin. La, Ce, Pr, Nd are eluted using 0.25 mol/L HCl in the cited order; Sm and Eu are then eluted using 0.75 mol/L HCl . The described separation was performed using 0.3 g of LN resin with a particle size of 50-100 μm .

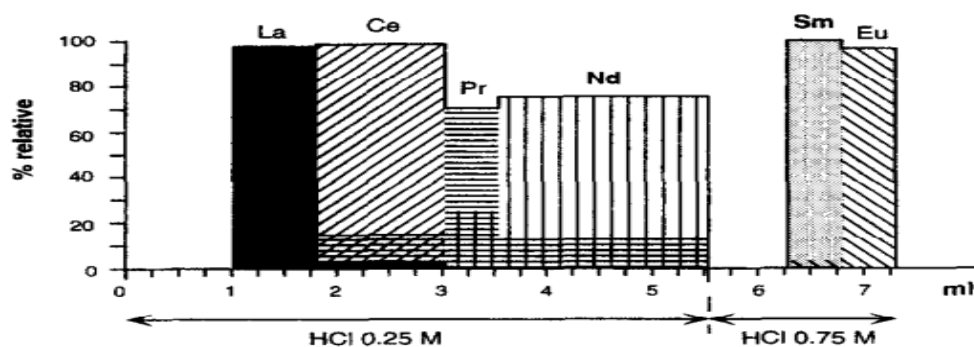


Figure 1.11: Histogram showing the elution profile of Light Rare Earth Elements [21].

In this system, the lightest lanthanides have the lowest extraction coefficients and elute first, and more and more concentrated solutions of HCl or HNO_3 are required to displace the heavier lanthanides.

1.6. Measurement Uncertainty

1.6.1. Principles of Estimation of Measurement Uncertainty

Measurement uncertainty is the parameter associated with the result of a measurement according to the International Vocabulary of Basic and General Terms in Metrology (VIM) source and characterizing the dispersion of values that can be reasonably attributed to the measurand [22]. Uncertainty of a measurement result, non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used. Measurement uncertainty includes components arising from systematic effects, such as components associated with corrections and the assigned quantity values of measurement standards, as well as the definitional uncertainty. Sometimes estimated systematic effects are not corrected for but, instead, associated measurement uncertainty components are incorporated [22].

Sources of Uncertainty

- Sampling
- Sample retention/storage
- Instrument-related effects
- Chemical material purity
- Reaction stoichiometry
- Measurement/environmental conditions
- Sample matrix effect
- Computational effects
- Blind correction
- Operator effect
- Random effects

Reasons for needing measurement uncertainty:

- It is an indicator of measurement quality.
- Defines an appropriate confidence interval.
- It is absolutely necessary to comply with the limits.
- Allows results to be compared.
- It is a requirement for accreditation according to TS EN ISO/IEC 17025.
- It can give an idea about the measurement procedure.
- Providing documentation of the measurement procedure it helps.

1.6.2. Measurement Uncertainty Calculation Approaches

There are two broad approaches to the estimation of uncertainty. One of the, described as top-down, uses some level of replication of the whole measurement procedure to give a direct estimate of the uncertainty for the final result of measurement. This approach called the ‘empirical’ approach in Guide. The second, variously described as bottom-up, aims to quantify all of the sources of uncertainty individually, and then uses as a model to combine them. It will accordingly be referred to as the ‘modelling’ approach. These approaches are not mutually exclusive. Both approaches can usefully be employed together to study the same measurement system, if required [14] [23].

1.6.2.1. Bottom-up approach

The modelling approach, often colloquially known as ‘bottom-up’, has been described for measurement methods in general, and applied to analytical measurements.

It initially identifies all of the sources of uncertainty, quantifies the contributions from each source, and then combines all of the contributions, as a budget, to give an estimate of the combined standard uncertainty.

In the process, the measurement method is separated into all of its individual steps. This can usefully take the form of a cause-and-effect, or ‘fish-bone’, diagram [14].

The uncertainty of measurement generated by each of these steps is estimated independently, either empirically or by other methods. The combined uncertainty is then calculated by combining the uncertainty from all of the steps by appropriate methods. In the bottom-up approach, all details about the method are determined, all factors affecting the result are identified and all effects are calculated.

Advantages

The principal advantage of the modelling approach is that it allows the largest source of uncertainty to be readily identified, if it was in the model. It gives a transparent method showing which components of uncertainty have been considered in the summation of uncertainty. Finally, where prior information is available, modelling approaches can be less costly than extensive experimental studies. It is a scientifically superior approach. Contains information to improve the method. It is evidence that the method is fully understood.

Disadvantages

The disadvantages of the modelling approach include that the theoretical predictions of uncertainty may require detailed prior measurements of the mineralogy, grain size and analyte speciation of the material to be sampled (e.g. soil), and how these vary across the target. Idealised assumptions have to be made therefore about the make up of the material (e.g. mineralogy, grain size and analyte speciation). The modelling approach using sampling theory requires estimates or assumptions about eight types of sampling error, and also how these might vary across the target. Both theoretical and empirical approaches can be relatively time consuming and therefore expensive to implement. Generic estimates may be too general and not reflect the specific circumstances at any particular sampling target. Further, not all of the sources of uncertainty might be identified, leading to an underestimate of the total uncertainty [23]. Determining all the factors requires a lot of research may require. When many factors are involved, a complex model equation can emerge. Risk of some important factors not being identified is higher.

Model Function GUM Approach for Bottom-up Approach

Its value is a function of the quantities that are the measured quantity value of the output quantity of the measurement model when calculated using the known quantity values of the input quantities of a measurement model.

GUM is used as a guide document for uncertainty calculations. In 1993, "Guide to the Expression of Uncertainty in Measurement" (GUM) was prepared and published by ISO as a guide. In 1995, GUM was revised. It was published as a BIPM document in 2008 [25].

1.6.2.2. Top-down approach

The top-down approach is based on the principle that the reproducibility standard deviation obtained in a collaborative study is a valid basis for measurement uncertainty evaluation. This approach is widely used in chemical measurement and testing, where it accepted that a suitably representative standard uncertainty can be obtained by that approach. Measurements made in different laboratories, at different times, with different instruments and personnel are carried out under a well-defined

reproducibility condition measurement. This approach is sometimes known as the ‘pure top-down approach’ [24].

The empirical (top-down) approach is intended to obtain a reliable estimate of the uncertainty, without necessarily knowing any of the sources individually. It relies on overall precision estimates from either in-house or inter-organisational measurement trials. It is possible to describe the general type of source, such as random or systematic effects, and to subdivide these as those arising from the sampling process or the analytical process. Estimates of the magnitude of each of these effects can be made separately from the properties of the measurement methods, such as sampling precision (for random effects arising from sampling) or analytical bias (for systematic effects arising from chemical analysis). These estimates can be combined to produce an estimate of the uncertainty in the measurement result [14].

Sources of uncertainty in Top-Down Approach:

It is possible to consider uncertainty of measurements to arise from four broad sources of error. These four sources are the random errors arising from the methods of both the sampling and analysis, and also the systematic errors arising from these methods. These errors have traditionally been quantified as the sampling precision, analytical precision, sampling bias and the analytical bias respectively.

Table 1.2: Estimation of Uncertainty Contributions in the Empirical Approach [23].

Process	Random Effect	Systematic Effect (Bias)
Analysis	Duplicate analysis gives precision under repeatability conditions	e.g. validation data or crm
Sampling	Duplicate samples	Reference sampling target, inter-organisational sampling trial

The random component of the uncertainty can be estimated by applying analysis of variance (ANOVA) or range calculation to the measurements of concentration on the duplicated samples. Both ANOVA and range calculations can be used for calculations in concentration units [23].

Advantages:

The empirical approach includes all sources of uncertainty, without the scientist having to know their identity in advance. For example, it is automatically applicable to the particular contaminants and mineralogy present at a geological site. The calculations do not require any prior knowledge of the nature of the material (e.g. grain size, analyte speciation, degree of heterogeneity). It is relatively quick and easy to apply practically (especially for the 'duplicate method'). There are at least four options available to allow progressively more accurate (and more expensive) estimates of uncertainty, as appropriate. Some of these methods can allow for systematic error (such as sampling bias) within the estimate of uncertainty. Sampling proficiency tests and reference sampling targets are still in the early stages of development, but already show considerable promise for this application [20] [23]. Top-down approach is generally much easier to implement, especially for routine, frequently repeated measurements and easier to cover all factors because it is based on actual performance.

Disadvantages:

Among the disadvantages of the empirical approach is that it does not necessarily quantify any of the individual components of uncertainty (although this knowledge can be added with limited resolution). It is not based on a theoretical model of particulate sampling, but this may be an advantage in applications to materials that are not particulate in form (e.g. gaseous, liquids, biota). The empirical approach only gives an approximate value of uncertainty, which is assumed to be constant over the target, but this is also true of the modelling approach. Extreme values in the replicate measurements may lead to an overestimate of the uncertainty value, which is not representative of most measurements. This effect minimised, however, by the use of robust statistics [23]. It does not contain information to improve the method. Does not assist in method development phase.

1.6.3 Steps to Calculate Measurement Uncertainty

- The mathematical relationship (model function) between the values of the input quantities and the output quantity value (result) is determined.
- In the measurement conditions, all factors affecting the measurement result are determined.

- A list of uncertainty components due to corrected and uncorrected systematic errors is made.
- For the systematic components of uncertainty, previous distributions and uncertainty studies are used.
- For each systematic component of uncertainty, values are calculated assuming a rectangular, triangular or U-type distribution or assuming a normal distribution (uncertainty obtained from external certifications).
- To calculate the uncertainty of the values obtained as a result of repeated measurements, the experimental standard deviation value and the standard deviation of the mean are first calculated.
- The combined uncertainty value is calculated.
- The Expanded Uncertainty value is calculated.
- Measurement results are reported together with the measured value and the calculated uncertainty value.
- Necessary explanatory statements regarding uncertainty, coverage factor and reliability level are used.

2. PURPOSE OF THE STUDY

Technology critical elements (TCEs) are a group of naturally occurring chemical elements increasingly used in high technology equipment including electrical and electronic instruments, cellular phones, energy efficient lighting, batteries, etc. The most common TCEs for which EC [20] released a list of strategic raw materials includes Co, Ga, Gd, Ge, Li, Nd, Pd, Pt and Rh. The recovery of these critical elements from waste electronic and electrical equipments (WEEEs) such as printed circuit board (PCB) gained importance in recent years due to limited natural resources and high cost of production from primary sources compared to recycling from WEEE where TCEs are at higher concentrations [3]. In recent years, with the developments in recycling technologies of WEEE and TCE, the economic value of these wastes has increased significantly. The accurate determination of economic value of such waste materials requires reliable measurement methods and reference materials. In this study, an ID-MS method was developed for PCB characterization that obtains SI traceable results with measurement uncertainty below 5% and this work is part of the EMPIR 20IND01 MetroCycleEU joint research project that received funding from the EU under Horizon 2020. An SI traceable reference analytical measurement method was developed and implemented for TCEs such as Nd and Pd using the Triple-ID-ICP-MS method. Another aim of the project is to develop a method for CRM certification.

3. EXPERIMENT

The material used to develop the measurement method is provided by the French Geological Survey (BRGM), one of the MetroCycleEU project partners who was in charge of the preparation of the material. Approximately 500 kg of waste printed circuit board collected in an industrial sorting chain by the waste recovery company “Envie 2E Midi-Pyrenees” (France). The material is processed to decrease its particle size below 200 μm particle size. Then, PCB powder was sent to TUBITAK UME for the development of the analytical methods [3].

Since no matrix certified reference materials made from PCB are available to check the recovery yield of the digestion methods, the digestions were optimized in using ICP-MS based on experience and in house digestion protocols.



Figure 3.1: PCB sample.

3.1. Measurement of Nd

3.1.1. Preliminary Analysis to Roughly Determine Element Concentrations in PCB Sample

In the triple ID-MS method, the analyte concentrations in the PCB sample must be known even if they are only estimated. For this purpose, matrix-made calibration solutions were prepared and analyte concentrations were calculated by the standard addition method. PCB reference material was used to calculate Nd concentration in the analysis. Samples were prepared by digesting and dissolving at least 3 replicates samples of 200 mg in Milestone Ethos SEL microwave digestion system. PCB material below 200 μm particle size which is produced in a joint research project was dissolved in 6 ml of 65%

(w/w) HNO₃ and 2 ml of 30% (w/w) HCl using microwave digestion system. Digestion was done in two step microwave (MW) program using the microwave digestion system with high pressure (HP) 10/1000 rotor.

Table 3.1: Digestion Method for Nd.

Step	Temperature, °C	Ramp Time, min	Hold Time, min	Power, Watt
1	150	15	0	500
2	180	15	30	1000
Cool down and vent the vessels				
3	150	10	0	1000
4	180	10	0	1000
5	200	10	20	1000

After the digestion process, the solutions were taken into falcons.

Preparation of calibration solutions:

Equal amounts from the digested sample solutions were combined in a test tube to represent the sample matrix which was used for the preparation of matrix-matched addition calibration solutions. Each calibration solution contained the same amount sample solution adjusted to have optimum analyte concentration for introduction to the instruments. Standard mixture solution containing Nd element was prepared and added in increasing volumes. While preparing the calibration solutions, 1 ppm Scandium and Thallium solution an internal standard was added to the solutions. Calibration solutions were prepared in increasing concentrations. The total volume was determined as 10 ml and 1% HNO₃ was used to dilute the solutions. A total of 8 standard solutions were prepared in increasing concentrations. Prepared samples and calibration solutions were read on the ICP-MS instrument.

Table 3.2: Signal and Concentration to Calibration Solutions.

	Signal	Concentration
Standard 0	0.03399	0.0000
Standard 1	1.95216	8.9465
Standard 2	3.75235	17.5101
Standard 3	7.37518	34.6526
Standard 4	13.29773	64.7508
Standard 5	21.69477	109.1416
Standard 6	32.89463	174.0930
Standard 7	44.43154	260.7473

Calibration graph were drawn using the concentrations corresponding to the signals and the slope was calculated. The slope was calculated as 0.2117.

$$\text{Concentration} = \frac{\text{Signal of sample}}{\text{Slope}} \times \text{Dilution Factor} \quad (3.1)$$

The concentration of Nd was calculated using the formula above.

Table 3.3: Nd Concentration

	Nd Concentration mg/kg
First PCB Sample	43.8895
Second PCB Sample	42.7858
Third PCB Sample	43.1637
Mean Nd Concentration	~43 mg/kg

3.1.2. Nd Sample Preparation for the Triple ID-MS Analysis

3.1.2.1. Selection of Isotopes for ID-ICP-MS Measurements

There are some critical considerations for selection of isotopes to be used. The isotope with low absorbance value should be selected. Abundance value must be lower than other isotopes.

Table 3.4: Amount Fraction Nd in IUPAC.

Amount Fraction	
¹⁴² Nd	0.27152
¹⁴⁴ Nd	0.23798
¹⁴⁵ Nd	0.08293
¹⁴⁶ Nd	0.17189
¹⁴⁸ Nd	0.05756
¹⁵⁰ Nd	0.05638

Table 3.5: Interferences on Nd isotopes.

Neodymium	Natural	Interference				
142	0.27152	Ce	¹⁰² Ru ⁴⁰ Ar	¹⁰² Pd ⁴⁰ Ar	¹²⁶ Te ¹⁶ O	
143	0.12174		¹⁰³ Rh ⁴⁰ Ar	¹⁰⁷ Ag ³⁶ Ar	¹²⁷ I ¹⁶ O	
144	0.23798	Sm	¹⁰⁴ Pd ⁴⁰ Ar	¹⁰⁴ Ru ⁴⁰ Ar	¹²⁸ Xe ¹⁶ O	¹²⁸ Te ¹⁶ O
145	0.08293		¹⁰⁹ Ag ³⁶ Ar	¹⁰⁵ Pd ⁴⁰ Ar	¹²⁹ Xe ¹⁶ O	¹²⁷ I ¹⁸ O
146	0.17189		¹⁰⁶ Pd ⁴⁰ Ar	¹⁰⁶ Cd ⁴⁰ Ar	¹³⁰ Xe ¹⁶ O	¹³⁰ Te ¹⁶ O
148	0.05756	Sm	¹⁰⁸ Pd ⁴⁰ Ar	¹⁰⁸ Cd ⁴⁰ Ar	¹³² Xe ¹⁶ O	
150	0.05638	Sm	¹¹⁰ Cd ⁴⁰ Ar	¹¹⁰ Pd ⁴⁰ Ar	¹³⁴ Ba ¹⁶ O	¹³⁴ Xe ¹⁶ O

The enrich percentage must be high and there should be no interference on the isotopes. ¹⁴⁸Nd abundance value is less than ¹⁴⁵Nd but there are interferences on ¹⁴⁸Nd. Considering these features, ¹⁴⁵Nd isotope was chosen in the study. According to the ID-MS method: Addition of an isotopically enriched standard to the sample changes the natural isotope ratio of the analyte. The amount of analyte in the sample is calculated by measuring the new isotope ratio. But there is no certified *R_y* and *w_y* value of the isotopically enriched reference material for the ¹⁴⁵Nd isotope. For this reason the samples were prepared according to the triple ID-MS method. Because the triple ID-MS equation consists only of added masses and measured isotope ratios, it is not necessary to know the isotope ratio and concentration of the isotope-enriched

reference material to calculate the concentration of the sample. The samples were spiked with isotopically enriched material to change the ratio of selected isotopes Nd. The isotope ratios of the calibration blends to be prepared were adjusted to be 5-2% below and above the sample blend. One sample blend and two calibration blends were prepared for triple ID-MS analysis.

Table 3.6: Isotope Abundance and Isotope Ratio Nd in isotopic reference material and corresponding values as published by IUPAC.

	Isotopic Reference Material Abundance	$^{144}\text{Nd}/^{145}\text{Nd}$	IUPAC Abundance	$^{144}\text{Nd}/^{145}\text{Nd}$
^{142}Nd	0.0033	0.003626	0.2715	3.274087
^{143}Nd	0.0472	0.051868	0.1217	1.467985
^{144}Nd	0.0106	0.011648	0.2379	2.869649
^{145}Nd	0.9100	1.000000	0.0829	1.000000
^{146}Nd	0.0271	0.029780	0.1718	2.072712
^{148}Nd	0.0012	0.001319	0.0575	0.694079
^{150}Nd	0.0006	0.000659	0.0563	0.679850

The following tables show the mass and volume amounts to be added and the targeted isotope ratio values for the sample blend and calibration blend 1 and 2.

Table 3.7: The Theoretical Isotope Ratio of the Sample Blend.

Sample Blend	
Isotope 1	^{144}Nd
Isotope 2	^{145}Nd
Sample isotope ratio, natural	2.86965
Spike isotope ratio, isoflex	0.01165
Sample weight PCB, kg	0.00020
Spike weight, kg	0.00059
Balance for 10 ml	9.999
Isotope Ratio of the Sample Blend	0.6525

Table 3.8: Isotope Ratio for Calibration Blend 1.

Calibration Blend 1	
Isotope 1	^{144}Nd
Isotope 2	^{145}Nd
Sample isotope ratio, (IRM)	0.011648
Spike isotope ratio, (NIST SRM 3115a)	2.869649
Sample weight, kg	0.00010
Spike weight, kg	0.00053
Balance for 10 ml	9.999
Isotope Ratio for Calibration Blend 1	0.5858

Table 3.9: Isotope Ratio for Calibration Blend 2.

Calibration Blend 2	
Isotope1	¹⁴⁴ Nd
Isotope2	¹⁴⁵ Nd
Sample isotope ratio, (IRM)	0.011648
Spike isotope ratio, (NIST SRM 3115a)	2.869649
Sample weight, kg	0.00010
Spike weight, kg	0.00069
Balance for 10 ml	9.999
Isotope Ratio for Calibration Blend 2	0.7163

3.1.2.2. Digestion Method for Nd

Samples were prepared by digesting and dissolving at least 3 replicates samples of 200 mg in Milestone Ethos SEL microwave digestion system. PCB material below 200 μm particle size which is produced in a joint research project was dissolved in 6 ml of 65% (w/w) HNO_3 and 2 ml of 30% (w/w) HCl using microwave digestion system. Digestion was done in two step microwave (MW) program using the microwave digestion system with high pressure (HP) 10/1000 rotor. All preparation were gravimetrically.



Figure 3.2: Milestone ETHOS SEL with HP 10/1000 rotor.

The samples were prepared according to the triple ID-MS method. The isotopic of the selected Nd isotopes which would be monitored is varied by adding the enriched isotopic CRM (iCRM) to obtain a precalculated isotopic ratio which is suitable for the optimum relative responses for the calculations and the uncertainties as well as the easiness of the preparation. The sample has a natural isotope ratio, there is an isotopic ratio in isotope firm. Sample blends were prepared by spiking the isotopic RM (enriched ^{145}Nd) (IsoFlex) before digestion and NIST CRM 3135a reference material was used for providing the metrological traceability in Nd measurement.



Figure 3.3: NIST CRM 3135a reference material and isotopic RM enriched ^{145}Nd .

Sample blends were prepared by spiking the iCRM (Enriched ^{145}Nd) before digestion. NIST CRM 3135a standard solution was used for providing the metrological traceability in Nd measurement. Calibration blends at two level were prepared by spiking iCRM and NIST Nd 3135a before digestion and dissolved in 6 ml of 65% (w/w) HNO_3 and 2 ml of 30% (w/w) HCl using microwave digestion system. Sample blend and calibration blend 1 and 2 solutions were prepared in 3 parallels. Digestion was done in two step MW program using Milestone ETHOS SEL with HP 10/1000 rotor.

Table 3.10: Digestion Method for Nd.

Step	Temperature, °C	Ramp Time, min	Hold Time, min	Power, Watt
1	150	15	0	500
2	180	15	30	1000
Cool down and vent the vessels				
3	150	10	0	1000
4	180	10	0	1000
5	200	10	20	1000

Dilution procedures were applied to the dissolved samples in the required proportions before introduction to ICP-MS.

3.1.2.3. Matrix Separation

ICP-MS is one of the major techniques used in the measurements of elements, but it suffering from isobaric interferences due to other elements of molecules produced in the plasma. Since chemical separation provides a matrix-free sample, the effects of the matrix in the plasma are reduced and reproducibility increases. Potential attempts are

prevented, this is important for isotope dilution. The elements separated; Nd, Sm, Ce, La, Pr, Gd, Dy, Eu. Especially Sm, Ce, Nd are difficult to separate from each other. Some of the elements present in PCB sample creates interferences during Nd measurements, for example some of the isotopes of Nd has been interfered by those of Ce, Sm and also some others argides. In order to remove such potential interferences from the matrix, a matrix separation method with elution was developed for separation of Nd from those interfering elements. Chemical separation of Nd from these elements is uniquely challenging due to their very similar chemical properties. Interferences must be separated before introduction to ICP-MS instrument analysis; for this purpose, extraction chromatography, separation column and LN resin were used in the studies. The chemical separation was done by using a pressurized extraction system and using lanthanide specific resin Triskem LN, 50-100 μ m placed in polypropylene microcolumn (~ 3 mm i.d. and ~8 cm long).

LN resin was mixed with water in a container and made aqueous, and the prepared LN resin was poured into the column, taking care to avoid air bubbles. In this study, an triple-ID-ICP-MS method employing chemical separation of Nd from sample matrix was developed and validated for traceable measurement of Nd in waste PCB material.

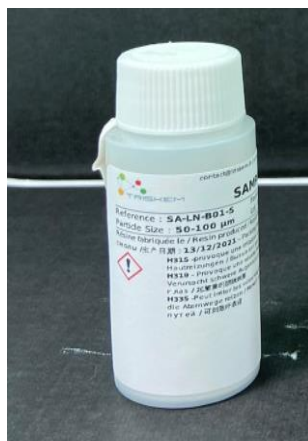


Figure 3.4: Triskem LN, 50-100 μ m.



Figure 3.5: Extraction System and PP microcolumn
(~ 3 mm i.d. and ~8 cm long).

3.1.2.4. Elution Process Method

The elements to be separated are: La, Ce, Nd, Sm, Eu, Gd, Dy.

The first trials for separation of elements were done by synthetic solution total volume 30 ml and this solution containing 667 ng/L Nd, 667 ng/L Sm, 233 ng/L La, 73 ng/L Pr, 20 ng/L Gd, 17 ng/L Dy and 667 ng/L Ce.

An aqueous solution of these elements was prepared in accordance with their concentrations in there all sample.

- Dilute the sample 200 times

In order for the element stored in the resin, the acidity must be less than

0.05 mol/L and calculated the acidity of the sample and diluted the sample 200 times.

Calculating the molarity of the acids used:

HNO₃:

$$m = \frac{c \times d \times v}{100} \quad (3.2)$$

$$m = \frac{60 \times 1.51 \times 1000}{100} = 906 \text{ g}$$

$$M = \frac{m \times 1000}{M_w \times V} \quad (3.3)$$

$$M = \frac{906 \times 1000}{63 \times 1000} = 14.38$$

HNO₃ ~14 mol/L

HCl:

$$m = \frac{c \times d \times v}{100} \quad (3.2)$$

$$m = \frac{30 \times 1.18 \times 1000}{100} = 354 \text{ g}$$

$$M = \frac{m \times 1000}{M_w \times V} \quad (3.3)$$

$$M = \frac{354 \times 1000}{36.5 \times 1000} = 9.70$$

HCl~10 mol/L

Table 3.11: Symbols used for parameters in calculated Molarity

Symbol	Quantity
m	Mass
c	Percentage
d	Density
v	Volume
M_w	Molecular Weight
M	Molarity

Amounts of acid used in the digestion method: 6 ml of 65% (w/w) HNO₃ and 2 ml of 30% (w/w) HCl.

$$\left(\frac{14 \times 6 + 10 \times 2}{30} \right) = 2.8 \text{ mol/L}$$

$$\frac{28}{200} = 0.014 \text{ mol/L} < 0.05$$

The acidity in the prepared solution was 2.8 mol/L, and the samples were diluted 200 times to make the value less than 0.05 mol/L.

- Wash the column with 3 ml of 1.5 mol/L HCl
- Condition with 8 ml of 0.05 mol/L HNO₃
- Load 3 ml of sample into the column, decide on this volume according to whether the concentration of the elements is measurable or not.
- Rinse undesired cations 5 ml of 0.05 mol/L HNO₃
PCB sample contains high amount of matrix such as Fe, Cu, Pb, reducing the effect of these matrices is important to obtain results with low uncertainty.
- Elute La, Ce with 2.5 ml 0.1 mol/L HCl
- Elute Pr, Nd with 7.5 ml .025 mol/L HCl
- Elute Sm with 5 ml 0.50 mol/L HCl
- Elute Gd with 5 ml 0.75 mol/L HCl
- Elute Dy with 2.5 ml of 1 mol/L HCl and 2.5 ml of 2 mol/L HCl

After the whole elution procedure total of 50 fractions of 0.5 ml were collected. The collected fractions were measured on the ICP-MS instrument using the autosampler of the HPLC instrument and the following graphs were drawn with the obtained data.



Figure 3.6: Autosampler tray of HPLC used for the introduction of effluents.

Table 3.12: The elution volume of Nd from LN column for sample blend and calibration blends.

	Elution volume, mL
Sample blend	5-11
Calibration blend	5.5-10.5
Sample	5-10.5

Neodymium is eluted from the column between 5 and 11 ml and slight differences in the elution volume is observed between the blends. Which may be attributed to matrix or counter ion effects from the solutions. Samarium comes after the eleventh milliliters. (22nd fraction and the volume of one fraction is 0.5 ml.).

The sample were measured by using Agilent 8800 QQQ ICP-MS in "no-gas" mode.

3.1.3. Instrumental Parameters ICP-MS for Nd Measurements

The sample were measured by using Agilent 8800 QQQ ICP-MS in "no-gas" mode. Isotope ratio measurements of Nd by Triple Quad ICP-MS/MS. The experimental parameters are given in the following table.

Table 3.13: ICP-MS Measurement Procedures for Nd.

Agilent 8800 Triple Quadrupole ICP-MS	
Nebulizer	Micromist glass nebulizer
Spray chamber	Scott type-double pass
Sampler/Skimmer Cone	Ni
RF applied power (Watt)	1550
Sampling depth (mm)	6.7
Nebulizer pump (rps)	0.2 / Self Aspiration
Scan Type	MS/MS
Carrier gas flow rate (L min ⁻¹)	No gas mode
Extract 1 (V)	-45.0
Extract 2 (V)	-190
Omega Bias (V)	-80
Omega Lens (V)	0.9
Octopole Bias (V)	-10
Wait Time Offset (ms)	0
Sample Intake, s	60
Stabilization, s	35
Sweeps/Replicate	400
Integration Time, s	0.999
Number of Replicates	10
Total Analysis Time, min	176
Rinse Time, s	130
Detection Mode	Pulse
Internal Standard	Tl-Sc
Rinse	1% HNO ₃

3.2. Measurement of Pd

3.2.1. Preliminary Analysis to Roughly Determine Pd

Concentrations in PCB Sample

Samples were prepared by digesting and dissolving at least 3 replicates samples of 200 mg in Milestone Ethos SEL microwave digestion system. PCB material below 200 μm particle size which is produced in a joint research project was dissolved in 2 ml of 65% (w/w) HNO_3 and 6 ml of 30% (w/w) HCl using microwave digestion system. Digestion was done in two step microwave (MW) program using the microwave digestion system with high pressure (HP) 10/1000 rotor.

Table 3.14: Digestion Method for Pd.

Step	Temperature, $^{\circ}\text{C}$	Ramp Time, min	Hold Time, min	Power, Watt
1	150	15	0	500
2	180	15	30	1000
		Cool Down		
3	150	10	0	1000
4	180	10	0	1000
5	200	10	30	1000

After the digestion process, the solutions were taken into falcons.

Preparation of calibration solutions:

Equal amounts from the digested sample solutions were combined in a test tube to represent the sample matrix which was used for the preparation of matrix-matched addition calibration solutions. Each calibration solution contained the same amount sample solution adjusted to have optimum analyte concentration for introduction to the instruments. Standard mixture solution containing Pd element was prepared and added in increasing volumes. While preparing the calibration solutions, 1 ppm Scandium and Thallium solution an internal standard was added to the solutions. Calibration solutions were prepared in increasing concentrations. The total volume was determined as 10 ml and 1% HNO_3 was used to dilute the solutions. A total of 8 standard solutions were prepared in increasing concentrations. Prepared samples and calibration solutions were read on the ICP-MS instrument.

Table 3.15: Signal and Concentration to Calibration Solutions.

	Signal	Concentration
Standard 0	5,63881	0,0000
Standard 1	6,38013	1,2476
Standard 2	6,95755	2,4419
Standard 3	8,24311	4,8311
Standard 4	10,35477	9,0299
Standard 5	13,26882	15,2205
Standard 6	17,03846	24,2784
Standard 7	20,96242	36,3629

Calibration graph were drawn using the concentrations corresponding to the signals and the slope was calculated. The slope was calculated as 0.5344.

$$\text{Concentration} = \frac{\text{Signal of sample}}{\text{Slope}} \times \text{Dilution Factor} \quad (3.1)$$

The concentration of Pd was calculated using the formula above.

Table 3.16: Pd Concentration.

	Pd Concentration mg/kg
First PCB Sample	16.7542
Second PCB Sample	16.1965
Third PCB Sample	17.3324
Mean Nd Concentration	~17 mg/kg

3.2.2. Sample Preparation for the Triple ID-MS Analysis

3.2.2.1. Selection of Isotopes for Pd ID-ICP-MS Measurements

Choosing the Pd Isotope for ID, some points to consider when choosing isotope:

-At least 2 stable isotope is needed

-Potential interferences on the isotopes should be taken into account

The enrich percentage must be high and there should be no interference on the isotopes.

-Cost and availability

Table 3.17: Amount Fraction Pd in IUPAC.

Amount Fraction	
^{102}Pd	0.0102
^{104}Pd	0.1114
^{105}Pd	0.2233
^{106}Pd	0.2733
^{108}Pd	0.2646
^{110}Pd	0.1172

Table 3.18: Interferences on Palladium.

Palladium		Interference				
102	Ru	$^{86}\text{Sr}^{16}\text{O}$	$^{62}\text{Ni}^{40}\text{Ar}$			
104	Pb^{+2}	$^{64}\text{Ni}^{40}\text{Ar}$	$^{64}\text{Zn}^{40}\text{Ar}$	$^{88}\text{Sr}^{16}\text{O}$		
	Ru					
105	Bi^{+2}	$^{65}\text{Cu}^{40}\text{Ar}$	$^{69}\text{Ga}^{36}\text{Ar}$	$^{89}\text{Y}^{16}\text{O}$		
106	Cd	$^{66}\text{Zn}^{40}\text{Ar}$	$^{90}\text{Zr}^{16}\text{O}$	$^{88}\text{Sr}^{18}\text{O}$		
108	Cd	$^{68}\text{Zn}^{40}\text{Ar}$	$^{92}\text{Mo}^{16}\text{O}$	$^{90}\text{Zr}^{18}\text{O}$		
110	Cd	$^{70}\text{Ge}^{40}\text{Ar}$	$^{70}\text{Zn}^{40}\text{Ar}$	$^{74}\text{Ge}^{40}\text{Ar}$	$^{94}\text{Zr}^{16}\text{O}$	$^{94}\text{Mo}^{16}\text{O}$

Interferences due to dimers produced Cu (12%), Zn (3%) and Ni (1%)

The enrich percentage must be high and there should be no interference on the isotopes. According to the ID-MS method: Addition of an isotopically enriched standard to the sample changes the natural isotope ratio of the analyte. The amount of analyte in the sample is calculated by measuring the new isotope ratio. But there is no certified R_y and w_y value of the isotopically enriched reference material for the ^{104}Pd isotope. For this reason the samples were prepared according to the triple ID-MS method. Because the triple ID-MS equation consists only of added masses and measured isotope ratios, it is not necessary to know the isotope ratio and concentration of the isotope-enriched reference material to calculate the concentration of the sample. The samples were spiked with isotopically enriched material to change the ratio of selected isotopes Pd.

The isotope ratios of the calibration blends to be prepared were adjusted to be 5-2% below and above the sample blend. One sample blend and two calibration blends were prepared for triple ID-MS analysis.

Table 3.19: Isotope Abundance and Isotope Ratio Pd in isotopic reference material and corresponding values as published by IUPAC.

	Isotopic Reference Material Abundance	$^{105}\text{Pd}/^{104}\text{Pd}$	IUPAC Abundance	$^{105}\text{Pd}/^{104}\text{Pd}$
^{102}Pd	0.0010	0.001139	0.0102	0.091562
^{104}Pd	0.8780	1.000000	0.1114	1.000000
^{105}Pd	0.0880	0.100228	0.2233	2.004488
^{106}Pd	0.0240	0.027335	0.2733	2.453321
^{108}Pd	0.0070	0.007973	0.2646	2.375224
^{110}Pd	0.0020	0.002278	0.1172	1.052065

The following tables show the mass and volume amounts to be added and the targeted isotope ratio values for the sample blend and calibration blend 1 and 2.

Table 3.20: The Theoretical Isotope Ratio of the Sample Blend.

Sample Blend	
Isotope 1	^{105}Pd
Isotope 2	^{104}Pd
Sample isotope ratio, natural	2.00448
Spike isotope ratio, isoflex	0.100228
Sample weight PCB, kg	0.00020
Spike weight, kg	0.00020
Balance for 10 ml	9.9960
Isotope Ratio of the Sample Blend	0.8243

Table 3.21: Isotope Ratio for Calibration Blend 1.

Calibration Blend 1	
Isotope 1	^{105}Pd
Isotope 2	^{104}Pd
Sample isotope ratio, (IRM)	0.100228
Spike isotope ratio, (NIST SRM 3115a)	2.00448
Sample weight, kg	0.00010
Spike weight, kg	0.00150
Balance for 10 ml	9.9984
Isotope Ratio for Calibration Blend 1	0.8634

Table 3.22: Isotope Ratio for Calibration Blend 2.

Calibration Blend 2	
Isotope1	^{105}Pd
Isotope2	^{104}Pd
Sample isotope ratio, (IRM)	0.100228
Spike isotope ratio, (NIST SRM 3115a)	2.00448
Sample weight, kg	0.00010
Spike weight, kg	0.00125
Balance for 10 ml	9.9986
Isotope Ratio for Calibration Blend 2	0.7818

3.2.2.2. Digestion Method for Pd

Samples were prepared by digesting and dissolving at least 3 replicates samples of 200 mg in Milestone Ethos SEL microwave digestion system. The first PCB sample sent by BRGM was used for Pd analysis. The samples were prepared according to the triple ID-MS method. The isotopic of the selected Pd isotopes which would be monitored is varied by adding the enriched isotopic CRM (iCRM) to obtain a precalculated isotopic ratio which is suitable for the optimum relative responses for the calculations and the uncertainties as well as the easiness of the preparation. The sample has a natural isotope ratio, there is an isotopic ratio in isotope irm. Sample blends were prepared by spiking the iCRM (Enriched ^{104}Pd) before digestion. NIST SRM 3138 Palladium Standard Solution was used for providing the metrological traceability in Pd measurement. Calibration blends at two level were prepared by spiking iCRM and NIST NIST SRM 3138 Palladium Standard Solution before digestion and dissolved in 2 ml of 65% (w/w) HNO_3 and 6 ml of 30% (w/w) HCl using microwave digestion system. Sample blend and calibration blend 1 and 2 solutions were prepared in 3 parallels. Digestion was done in two step MW program using Milestone ETHOS SEL with HP 10/1000 rotor. All preparation were gravimetrically.

Table 3.23: Digestion Method for Pd.

Step	Temperature, °C	Ramp Time, min	Hold Time, min	Power, Watt
1	150	15	0	500
2	180	15	30	1000
Cool Down				
3	150	10	0	1000
4	180	10	0	1000
5	200	10	30	1000

3.2.3. Instrumental Parameters HR-ICP-MS for Pd Measurements

Measurements were done by Thermo Element2 HR-ICP-MS using Medium Resolution (MR) and High Resolution (HR) modes. Many isobaric interferences arising from Argides of Zn, Cu and Ni are separated from Pd isotopes 104, 105, and 106.

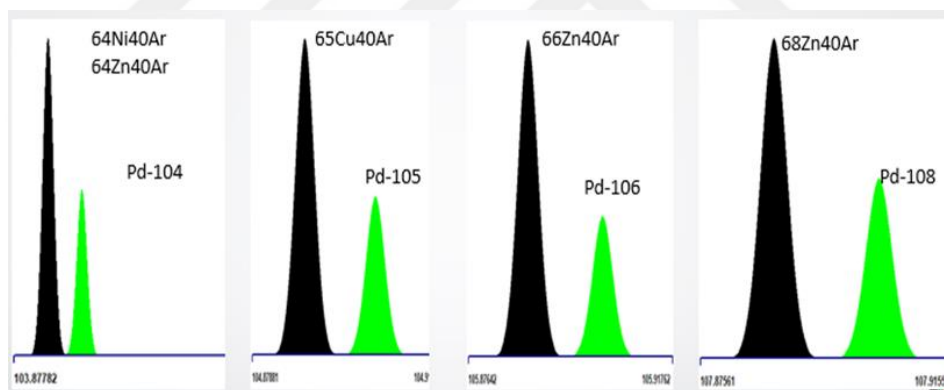
**Figure 3.7:** Pd peaks at even HR mode.

Table 3.24: HR ICP-MS Measurement Procedures for Pd.

	Medium Resolution	High Resolution
Mass Resolution	400	1000(10% valley)
Signal Stability	Better than 1% over 10 minutes	Better than 1% over 10 minutes
Dark Noise	<0.2 counts/second (cps)	<0.2 counts/second (cps)
Quad 1 Lens (V)	2.54	4.87
Quad 2 Lens (V)	6.66	4.60
Focus Quad 1 (V)	-8.44	-12.42
Detector Type	Magnetic Sector Mass Filter	Magnetic Sector Mass Filter
Cool gas flow rate (L min ⁻¹)	44	44
Auxiliary gas flow rate (L min ⁻¹)	0.04	0.04
Sample gas flow rate (L min ⁻¹)	0.018	0.018
Additional gas 2 flow rate (L min ⁻¹)	0.066	0.066
Fore Vacuum (mbar)	2.31×10 ⁻⁰⁰⁴	2.31×10 ⁻⁰⁰⁴
High Vacuum (mbar)	6.45×10 ⁻⁰⁰⁸	6.45×10 ⁻⁰⁰⁸
Argon Middle (bar)	2.80	2.80
Argon Max (bar)	6.07	6.07
Res. Switch Delay (s)	2	2
Wash time (s)	60	60
Take-up time (s)	120	120
Dead time (ns)	30	30
Rinse (v/v)	1% HNO ₃	1% HNO ₃

4. RESULTS

4.1. Results from the Preliminary Analysis to Roughly Determine the Element Concentrations in the PCB Sample

Table 4.1: Element concentrations obtained in the preliminary analysis.

Nd Concentration	
mg/kg	~43 mg/kg
Pd Concentration mg/kg	~17 mg/kg

Before analysis is performed by isotope dilution mass spectrometry, the concentrations of the elements in the analyte must be known, at least roughly. Therefore, the concentrations of Nd and Pd elements were calculated using the standard addition method. In this method, a certain volume of the standard solution of the analyte is added to a certain amount of sample to increase the concentration of the analyte in the sample. The signals before and after the addition are measured and the values found are used to calculate the analyte concentration. The PCB sample, which is a reference material candidate, was used for the Nd element analysis, and the first PCB sample from the BRGM institute was used for the Pd element analysis. Different digestion methods were tried for both Nd and Pd elements. Calibration solutions for Pd element were prepared using NIST SRM 3138 Palladium Standard Solution in increasing concentrations. Calibration solutions for Nd element were prepared using NIST Nd 3135a Standard Solution in increasing concentrations and these were read on the ICP-MS instrument and the concentrations were calculated.

4.2. Evaluation of Elution Process

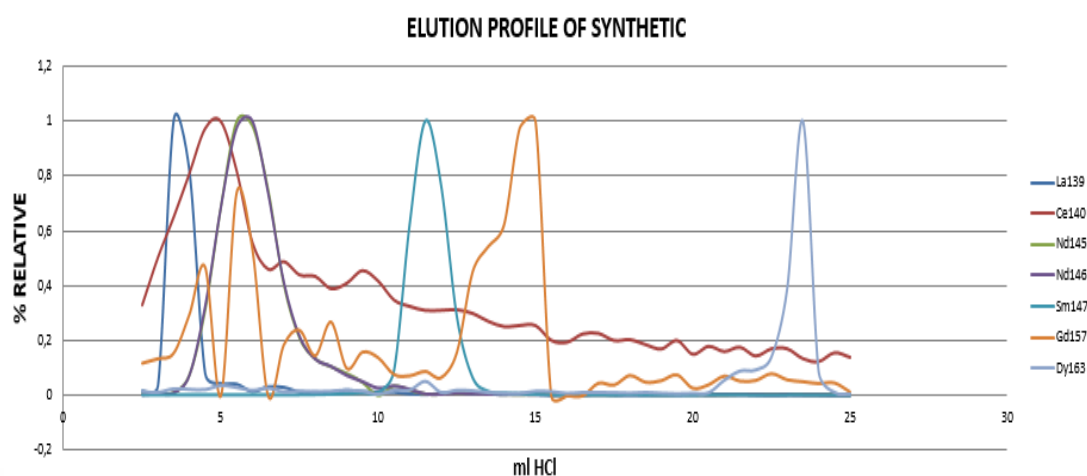


Figure 4.1: Elution profile of synthetic.

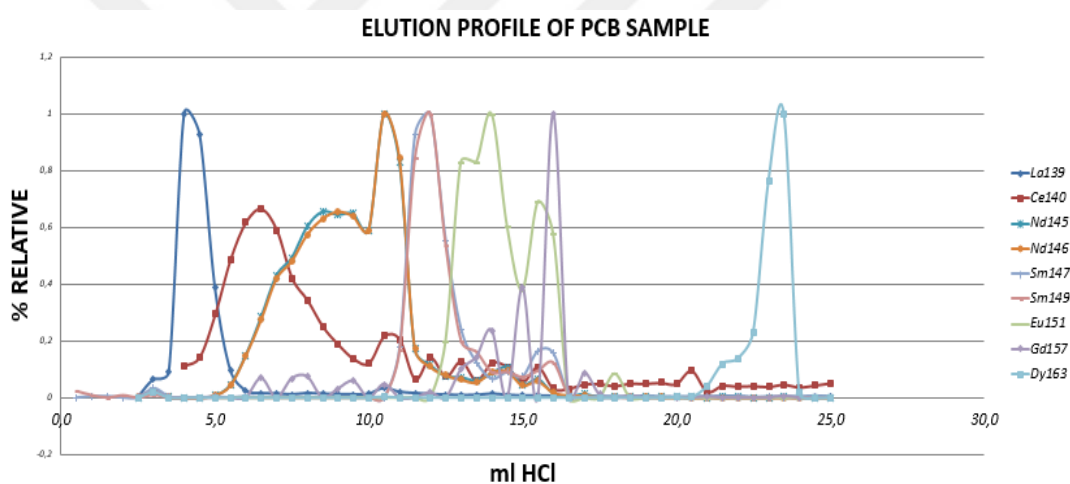


Figure 4.2: Elution profile of PCB sample.

Elution processes were tried for two samples. One of these samples is an original PCB and the other is a synthetic sample prepared with the required concentrations of the trace elements. As it can be seen on the Figure 4.1 and Figure 4.2, the synthetic sample and the PCB sample create different elution profiles. This is due to the high concentration of Sn and Cu elements in PCB sample.

Table 4.2: Parameters of the elution process.

Parameters	Explanation
The elements to be separated	La, Ce, Nd, Sm, Eu, Gd, Dy
Column	Polypropylene Column (~ 3 mm i.d. and ~8 cm long)
Resin	Lanthanide specific resin Triskem LN, 50-100 μ m
Sample Volume	3 ml
Wash the column	3 ml of 1.5 mol/L HCl
Condition the column	8 ml of 0.05 mol/L HCl
The range of acid concentrations over which the fractions are collected	0.1 mol/L HCl-2 mol/L HCl
Flow rate	1.42 ml/min
Total number of fractions	50

As a result of the analysis the elution process with the best elemental separation was developed. The elution process developed for the Nd element is described in section 3.1.2.4.

Listed below tried until optimum separation conditions were achieved. These;

- The sample was passed through the column too quickly (1.42 ml/min) and no distinction could be observed between the elements.
- 2 ml of 1.5 mol/L HCl was used to wash the column, but from the complex peaks obtained as a result of the measurement, it was decided that this amount of acid was not sufficient to clean the column.
- When we separated between 0.25 mol/l HCl and 1 mol/l HCl, Ce, La, Nd elements were not separated from each other. Therefore, I started the separation process with 0.1 mol/l HCl. The separation time was longer, but the elements were separated from each other better.
- When I completed the separation using 1 M HCl, I was not able to collect the Dy element, so I increased the acid concentration and collected the Dy element from the column using 2 mol/L HCl.
- I did the first experiments by collecting a total of 40 fractions between 0.25 mol/L HCl and 0.75 mol/L HCl. The analysis results were examined and understood that fractions should be collected at concentrations above and below these acid concentrations.

4.3. Calculation to Element Concentrations of Nd and Pd using the Triple ID-MS Model Equation

4.3.1. Calculation of Nd Concentration and Complete Uncertainty Budget of triple ID-MS in Waste PCB Sample

Table 4.3: Result for Nd.

IR Used in the Calculation	PCB Sample Weight, mg/kg	%RSD (n=3)	U (k=2)
$^{142}\text{Nd}/^{145}\text{Nd}$	42.87	1.5%	0.81%
$^{144}\text{Nd}/^{145}\text{Nd}$	41.69	0.5%	0.81%
$^{146}\text{Nd}/^{145}\text{Nd}$	41.47	0.9%	0.92%
Std Addition	~43 mg/kg		

Calculation of Nd concentration and complete uncertainty budget of triple ID-MS;

Calculation of Nd concentration using ^{142}Nd , ^{144}Nd and ^{146}Nd enriched isotope ^{145}Nd . The notations used in the equation are given in Table A.1, Table A.2, Table A.3 (Appendix-A).

Calculation final concentration of sample wx , $wx1$, $wx2$, $wx3$;

$$wx = \frac{wx1 + wx2 + wx3}{3}; \quad (4.1)$$

$$wx1 = \frac{Mx1 - BLANK}{1000}; \quad (4.2)$$

$$wx2 = \frac{Mx2 - BLANK}{1000}; \quad (4.3)$$

$$wx3 = \frac{Mx3 - BLANK}{1000}; \quad (4.4)$$

Calculation of element amount in solution $Mx1$, $Mx2$, $Mx3$;

$$Mx1 = (Max \times nx1) \times 10^6 \quad (4.5)$$

$$Mx2 = (Max \times nx2) \times 10^6 \quad (4.6)$$

$$Mx3 = (Max \times nx3) \times 10^6 \quad (4.7)$$

Calculation of $nx1$, $nx2$, $nx3$;

$$nx1 = wy \times \frac{my1_1}{mx1_1} \times \frac{Ry - Rxy1_1}{Rxy1_1 - Rx} \times \sum Rx \quad (4.8)$$

$$nx2 = wy \times \frac{my1_2}{mx1_2} \times \frac{Ry - Rxy1_2}{Rxy1_2 - Rx} \times \sum Rx \quad (4.9)$$

$$nx3 = wy \times \frac{my1_3}{mx1_3} \times \frac{Ry - Rxy1_3}{Rxy1_3 - Rx} \times \sum Rx \quad (4.10)$$

Calculation of total isotope ratio;

$$\sum R_X = (R_{142.145}X + R_{143.145}X + R_{144.145}X + R_{145.145}X + R_{146.145}X + R_{148.145}X + R_{150.145}X) \quad (4.11)$$

$$\sum R_X = 3.2740 + 1.4680 + 2.8694 + 1 + 2.0727 + 0.6941 + 0.6799 = 12.0584 \quad (4.12)$$

Calculation of wy , wy1, wy2, wy3;

$$wy = \frac{wy1 + wy2 + wy3}{3} \quad (4.13)$$

$$wy1 = \left(wz2 \times \frac{mz2_1}{my2_1} \right) \times \frac{\frac{Rx - Rzy2_1}{Rzy2_1 - Ry}}{\sum Rx} \quad (4.14)$$

$$wy2 = \left(wz2 \times \frac{mz2_2}{my2_2} \right) \times \frac{\frac{Rx - Rzy2_2}{Rzy2_2 - Ry}}{\sum Rx} \quad (4.15)$$

$$wy3 = \left(wz2 \times \frac{mz2_3}{my2_3} \right) \times \frac{\frac{Rx - Rzy2_3}{Rzy2_3 - Ry}}{\sum Rx} \quad (4.16)$$

Calculation of Ry , Ry1, Ry2, Ry3;

$$Ry = \frac{(Ry1 + Ry2 + Ry3)}{3} \quad (4.17)$$

$$Ry1 = \frac{\left(\frac{mz2_1 \times wz2}{my2_1} \right) \times (Rzy2_1 - Rx) \times Rzy3_1 - \left(\frac{mz3_1 \times wz3}{my3_1} \right) \times (Rzy3_1 - Rx) \times Rzy2_1}{\left(\left(\frac{mz2_1 \times wz2}{my2_1} \right) \times (Rzy2_1 - Rx) - \left(\frac{mz3_1 \times wz3}{my3_1} \right) \times (Rzy3_1 - Rx) \right)}; \quad (4.18)$$

$$Ry2 = \frac{\left(\frac{mz2_2 \times wz2}{my2_2} \right) \times (Rzy2_2 - Rx) \times Rzy3_2 - \left(\frac{mz3_2 \times wz3}{my3_2} \right) \times (Rzy3_2 - Rx) \times Rzy2_2}{\left(\left(\frac{mz2_2 \times wz2}{my2_2} \right) \times (Rzy2_2 - Rx) - \left(\frac{mz3_2 \times wz3}{my3_2} \right) \times (Rzy3_2 - Rx) \right)}; \quad (4.19)$$

$$Ry3 = \frac{\left(\frac{mz2_3 \times wz2}{my2_3} \right) \times (Rzy2_3 - Rx) \times Rzy3_3 - \left(\frac{mz3_3 \times wz3}{my3_3} \right) \times (Rzy3_3 - Rx) \times Rzy2_3}{\left(\left(\frac{mz2_3 \times wz2}{my2_3} \right) \times (Rzy2_3 - Rx) - \left(\frac{mz3_3 \times wz3}{my3_3} \right) \times (Rzy3_3 - Rx) \right)}; \quad (4.20)$$

The equation consists of only of masses and isotope ratios. There is no need to determine the isotope ratio of spike and this is the most important advantage of triple ID-ICP-MS. The concentration of Nd was calculated using this model equation.

The elution parameters were optimized for the separation of Nd from the interfering elements. The measurement uncertainty for determination of Nd in waste PCB material was estimated according to GUM bottom-up approach, and all its component are quantified using commercial software GUM Work Bench.

The uncertainty value was calculated using the GUM Work Bench program. The values are shown in Table 4.3.

In Table A.1., Table A.2., and Table A.3 (Appendix-A) the effect of each parameter on uncertainty is shown as a percentage. The parameters that most affect uncertainty are; The ratios of elemental isotopes and the masses of the added certified reference material and the masses of the added isotopic reference material.

As a result, a measurement method with a high analysis level and low uncertainty value was developed for the Nd element.

In the project, the PCB material developed to be a reference material for PCB samples was used as a standard sample.

4.3.2. Calculation of Pd Concentration and Complete Uncertainty Budget of triple ID-MS in Waste PCB Sample

Table 4.4: Result for Pd used Medium Resolution ($m/\Delta m \approx 4000$).

Weight, mg/kg	Weight, mg/kg	U (k=2)
$^{105}\text{Pd}/^{104}\text{Pd}$	15.30	3.4%
$^{106}\text{Pd}/^{104}\text{Pd}$	18.40	2.2%
$^{108}\text{Pd}/^{104}\text{Pd}$	15.08	0.48%
Std Addition	≈ 17	

Table 4.5: Result for Pd used High Resolution ($m/\Delta m \approx 10000$).

Weight, mg/kg	Weight, mg/kg	U (k=2)
$^{105}\text{Pd}/^{104}\text{Pd}$	20	3.8%
$^{106}\text{Pd}/^{104}\text{Pd}$	14	5.4%
$^{108}\text{Pd}/^{104}\text{Pd}$	15.57	0.37%
Std Addition	≈ 17	

Calculation of Pd concentration using ^{105}Pd , ^{106}Pd , ^{108}Pd , and enriched isotope ^{104}Pd at MR mode HR ICP-MS and HR mode HR ICP-MS. The notations used in the equation are given in Table B.1, Table B.2, Table B.3, Table B.4, Table B.5, Table B.6 (Appendix-B). The calculation method is the same for all three isotopes.

Calculation final concentration of sample w_x , and w_{x1} , w_{x2} , w_{x3} ;

$$w_x = \frac{w_{x1} + w_{x2} + w_{x3}}{3}; \quad (4.1)$$

$$w_{x1} = \frac{M_{x1} - BLANK}{1000}; \quad (4.2)$$

$$w_{x2} = \frac{M_{x2} - BLANK}{1000}; \quad (4.3)$$

$$w_{x3} = \frac{M_{x3} - BLANK}{1000}; \quad (4.4)$$

Calculation of element amount in solution M_{x1} , M_{x2} , M_{x3} ;

$$M_{x1} = (Max \times nx1) \times 10^6 \quad (4.5)$$

$$M_{x2} = (Max \times nx2) \times 10^6 \quad (4.6)$$

$$M_{x3} = (Max \times nx3) \times 10^6 \quad (4.7)$$

Calculation of $nx1$, $nx2$, $nx3$;

$$nx1 = w_y \times \frac{my1_1}{mx1_1} \times \frac{R_y - R_{xy1_1}}{R_{xy1_1} - R_x} \times \sum R_x \quad (4.8)$$

$$nx2 = wy \times \frac{my1_2}{mx1_2} \times \frac{Ry - Rxy1_2}{Rxy1_2 - Rx} \times \sum Rx \quad (4.9)$$

$$nx3 = wy \times \frac{my1_3}{mx1_3} \times \frac{Ry - Rxy1_3}{Rxy1_3 - Rx} \times \sum Rx \quad (4.10)$$

Calculation of total isotope ratio;

$$\sum R_X = (R_{102.104}X + R_{104.104}X + R_{105.104}X + R_{106.104}X + R_{108.104}X + R_{110.104}X) \quad (4.21)$$

$$\sum R_X = 0.0915 + 1 + 2.0044 + 2.4533 + 2.3752 + 1.0520 = 8.9767 \quad (4.22)$$

Calculation of wy , wy1, wy2, wy3;

$$wy = \frac{wy1 + wy2 + wy3}{3} \quad (4.13)$$

$$wy1 = \left(wz2 \times \frac{mz2_1}{my2_1} \right) \times \frac{\frac{Rx - Rzy2_1}{Rzy2_1 - Ry}}{\sum Rx} \quad (4.14)$$

$$wy2 = \left(wz2 \times \frac{mz2_2}{my2_2} \right) \times \frac{\frac{Rx - Rzy2_2}{Rzy2_2 - Ry}}{\sum Rx} \quad (4.15)$$

$$wy3 = \left(wz2 \times \frac{mz2_3}{my2_3} \right) \times \frac{\frac{Rx - Rzy2_3}{Rzy2_3 - Ry}}{\sum Rx} \quad (4.16)$$

Calculation of Ry, Ry1, Ry2, Ry3;

$$Ry = \frac{(Ry1 + Ry2 + Ry3)}{3} \quad (4.17)$$

$$Ry1 = \frac{\left(\frac{mz2_1 \times wz2}{my2_1} \right) \times (Rzy2_1 - Rx) \times Rzy3_1 - \left(\frac{mz3_1 \times wz3}{my3_1} \right) \times (Rzy3_1 - Rx) \times Rzy2_1}{\left(\left(\frac{mz2_1 \times wz2}{my2_1} \right) \times (Rzy2_1 - Rx) - \left(\frac{mz3_1 \times wz3}{my3_1} \right) \times (Rzy3_1 - Rx) \right)}; \quad (4.18)$$

$$Ry2 = \frac{\left(\frac{mz2_2 \times wz2}{my2_2} \right) \times (Rzy2_2 - Rx) \times Rzy3_2 - \left(\frac{mz3_2 \times wz3}{my3_2} \right) \times (Rzy3_2 - Rx) \times Rzy2_2}{\left(\left(\frac{mz2_2 \times wz2}{my2_2} \right) \times (Rzy2_2 - Rx) - \left(\frac{mz3_2 \times wz3}{my3_2} \right) \times (Rzy3_2 - Rx) \right)}; \quad (4.19)$$

$$Ry3 = \frac{\left(\frac{mz2_3 \times wz2}{my2_3} \right) \times (Rzy2_3 - Rx) \times Rzy3_3 - \left(\frac{mz3_3 \times wz3}{my3_3} \right) \times (Rzy3_3 - Rx) \times Rzy2_3}{\left(\left(\frac{mz2_3 \times wz2}{my2_3} \right) \times (Rzy2_3 - Rx) - \left(\frac{mz3_3 \times wz3}{my3_3} \right) \times (Rzy3_3 - Rx) \right)}; \quad (4.20)$$

The uncertainty value was calculated using the GUM Work Bench program. The values are shown in Table 4.4 and 4.5.

In Table B.1., Table B.2., Table B.3, Table B.4, Table B.5, Table B.6. (Appendix-B) the effect of each parameter on uncertainty is shown as a percentage. The parameters that most affect uncertainty are; The ratios of elemental isotopes and the masses of the added certified reference material and the masses of the added Isotopic reference material.

As a result, a measurement method with a high analysis level was developed for the Pd element.

There are interferences of Pb^{+2} , Bi^{+2} , Zn, Ru and Cd elements on the Pd element. These interferences could not be eliminated in the medium resolution method and the high resolution method was tried. Interferences were eliminated in the high resolution method. ^{106}Cd interference was corrected mathematically.

5. CONCLUSION

In case of Nd, the interfering elements Ce and Sm and potentially Ar dimers from concomitant elements Ag, and Cd. By developing the matrix separation method for Nd element, elution process was possible to separate elements such as La, Ce, Sm, Nd, Gd, Dy, Eu in the PCB before measurement with the ICP-MS instrument and elemental attempts were prevented. Thus, after the Nd was eliminated from the Sm interference, Nd was measurement correctly in ICP-MS.

Pb^{+2} , Bi^{+2} , Zn interferences were eliminated on Pd with using the high resolution method, and Cd interference corrected mathematically.

Concentrations of Nd, Pd elements were measured accurately using the triple ID-MS method.

Looked at the uncertainty calculation made with the GUM program using the analysis results, it was seen that the biggest effects on the uncertainty were caused by the added masses and isotope ratios.

Finding from analysis:

- During the sample preparation phase, the dissolution method was tried separately with low and high pressure vessels, and it was decided that the dissolution process with high pressure vessels provided better dissolution.
- Sample dissolution was done in two steps because it was seen that dissolution in one step was not sufficient.
- Several acid mixtures were tried in the sample dissolution part, for example, 2 ml HCl-1ml HF- 6 ml HNO_3 and 2 ml HCl- 6 ml HNO_3 and 6 ml HCl – 2 ml HNO_3 . It was decided that the dissolution process with 2 ml HCl – 6 ml HNO_3 gave better results.
- A targeted elution process was developed to minimize elemental interference before ICP-MS measurement.
- In the triple-ID-MS section, triple-ID-ICP-MS 63analyses were started with the aim of the isotope ratios of Calibration Blend _1, Calibration Blend_2 and Sample Blend to be $\pm 2\%$ different from each other, but when the data obtained was examined, it was seen that this range could not be achieved and samples

were prepared so that this ratio was $\pm 5\%$ different. ID-ICP-MS analysis was performed and the targeted results were achieved.

- After the triple-ID-ICP-MS analysis, element concentrations were calculated, and it was seen that the estimated element concentrations were measured correctly.
- When all parts were combined, a measurement method with a high level of analysis and low uncertainty was obtained for PCB.

As a result, considering all analysis results, a measurement method with a low measurement uncertainty and a high level of analysis was developed. The developed analysis method will be used in CRM certification [28].



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BIOGRAPHY

Derya KUTAN completed primary and secondary school at Cumhuriyet Primary School, receiving a certificate of outstanding achievement. She studied high school in the Chemistry department of Lafarge Aslan Çimento Technical High School and graduated from high school in 2011, receiving the title of valedictorian. In the same year, she was accepted to the Chemical Engineering department at Gazi University Faculty of Engineering and Architecture in Ankara. She was entitled to receive a success scholarship from the Türk Eğitim Vakfı in her third year of university. She did her university laboratory internship at TÜBİTAK UME. She completed her undergraduate education with 3.24 GPA in 2016 and started living in Gebze. She worked as an analysis supervisor in an environmental laboratory for approximately two years and had the opportunity to participate in many comparisons and inspections. In 2017, she was accepted to the Metrology (100% English) program of Gebze Technical University, which is a joint master's program with TÜBİTAK UME. Due to some problems experienced at that time, she took a break from her master's degree and returned to the university to complete her education in 2022. She received training on metrology from experts in the field at TÜBİTAK UME. During her master's degree, she worked on the MetroCycleEU project, a European Union project, as a TÜBİTAK UME master's scholar. During her master's education, she attended the 12th International Analytical Chemistry Congress and made a poster presentation about her master's thesis. During the congress, she had the opportunity to meet many successful analytical chemistry professors and researchers. The international article of the project she worked on at TÜBİTAK UME she was took part.

PUBLICATIONS AND PRESENTATIONS FROM THE THESIS

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APPENDICES

APPENDIX-A: RESULTS AND COMPLETE UNCERTAINTY BUDGET TABLES OF TRIBLE ID-MS FOR ND

Table A.1: Results and Complete Uncertainty Budget of Tribble ID-MS for $^{142}\text{Nd}/^{145}\text{Nd}$.

Quantity	Unit	Value	Expanded Uncertainty	Description	Index
$mz2_1$	(kg)	5.3070×10^{-4}	1.94×10^{-6}	Mass of back-spike for blend2-1	0.3%
$my2_1$	(kg)	1.0350×10^{-4}	2.08×10^{-6}	Mass of spike for blend2-1	7.7%
$mz3_1$	(kg)	6.8890×10^{-4}	1.94×10^{-6}	Mass of back-spike for blend3-1	0.4%
$my3_1$	(kg)	1.0400×10^{-4}	1.94×10^{-6}	Mass of spike for blend3-1	0.2%
$mz2_2$	(kg)	5.3430×10^{-4}	1.94×10^{-6}	Mass of back-spike for blend2-2	0.2%
$my2_2$	(kg)	1.0370×10^{-4}	1.94×10^{-6}	Mass of spike for blend2-2	5.6%
$mz3_2$	(kg)	6.9000×10^{-4}	1.94×10^{-6}	Mass of back-spike for blend3-2	0.4%
$my3_2$	(kg)	1.0420×10^{-4}	1.94×10^{-6}	Mass of spike for blend3-2	19%
$mz2_3$	(kg)	5.3840×10^{-4}	1.94×10^{-6}	Mass of back-spike for blend2-2	0.2%
$my2_3$	(kg)	1.0340×10^{-4}	1.94×10^{-6}	Mass of spike for blend2-3	5.1%
$mz3_3$	(kg)	7.0250×10^{-4}	5.77×10^{-3}	Mass of back-spike for blend3-3	4.2%
$my3_3$	(kg)	1.0370×10^{-4}	1.94×10^{-6}	Mass of spike for blend3-3	18%
$my1_1$	(kg)	6.1700×10^{-1}	1.73×10^{-6}	Mass of spike for blend1-1	1.0%
$mx1_1$	(kg)	2.0080×10^{-1}	5.77×10^{-3}	Mass of sample for blend1-1	1.1%
$my1_2$	(kg)	6.1720×10^{-1}	1.73×10^{-6}	Mass of spike for blend1-2	1.0%
$mx1_2$	(kg)	2.0170×10^{-1}	5.77×10^{-3}	Mass of sample for blend1-2	1.0%
$my1_3$	(kg)	6.1180×10^{-1}	1.73×10^{-6}	Mass of spike for blend1-3	1.0%
$mx1_3$	(kg)	2.0370×10^{-1}	5.77×10^{-3}	Mass of sample for blend1-3	1.0%
$wz2$	(mol/kg)	1.6197×10^{-5}	23.9×10^{-9}	Mass fraction Nd in back-spike solution z2	0.3%
$wz3$	(mol/kg)	1.6197×10^{-5}	23.9×10^{-9}	Mass fraction Nd in back-spike solution z3	1.0%

<i>wy1</i>	(mol/kg)	24.7×10 ⁻⁶	4.3×10 ⁻⁶	Mass fraction Nd ¹⁴⁵ in spike (blend2-1)	Intermediate result
<i>wy2</i>	(mol/kg)	25.1×10 ⁻⁶	4.4×10 ⁻⁶	Mass fraction Nd ¹⁴⁵ in spike (blend2-2)	Intermediate result
<i>wy3</i>	(mol/kg)	24.2×10 ⁻⁶	4.1×10 ⁻⁶	Mass fraction Nd ¹⁴⁵ in spike (blend2-3)	Intermediate result
<i>wy</i>	(mol/kg)	24.7×10 ⁻⁶	4.2×10 ⁻⁶	Mean of mass fraction of Nd ¹⁴⁵ in spike	Intermediate result
<i>Rzy2₁</i>		0.7164	4.62×10 ⁻³	Isotope ratio 142/145 in blend2-1	1.2%
<i>Rzy3₁</i>		0.8659	4.62×10 ⁻³	Isotope ratio 142/145 in blend3-1	2.6%
<i>Rx</i>		3.274	209×10 ⁻⁶	Isotope ratio 142/145 in back-spike	0.0%
<i>Rxy1₁</i>		0.8142	4.04×10 ⁻³	Isotope ratio 142/145 in blend1-1	5.7%
<i>Ry1</i>		0.02	0.19	Isotope abundance ratio 142/145 in spike from blend1	Intermediate result
<i>Rzy2₂</i>		0.7098	4.97×10 ⁻³	Isotope ratio 142/145 in blend2-2	1.4%
<i>Rzy3₂</i>		0.8617	5.77×10 ⁻³	Isotope ratio 142/145 in blend3-2	4.4%
<i>Rxy1₂</i>		0.7990	4.04×10 ⁻³	Isotope ratio 142/145 in blend1-2	5.5%
<i>Ry2</i>		-0.02	0.25	Isotope abundance ratio 142/145 in spike from blend2	Intermediate result
<i>Rzy2₃</i>		0.7377	4.97×10 ⁻³	Isotope ratio 142/145 in blend2-3	1.1%
<i>Rzy3₃</i>		0.8977	5.77×10 ⁻³	Isotope ratio 142/145 in blend3-3	4.1%
<i>Rxy1₃</i>		0.8208	4.04×10 ⁻³	Isotope ratio 142/145 in blend1-3	5.5%
<i>Ry3</i>		0.01	0.24	Isotope abundance ratio 142/145 in spike from blend3	Intermediate result
<i>Ry</i>		0.001	0.13	Mean isotope abundance ratio 142/145 in spike	Intermediate result
$\sum Rx$		12.05850	780×10 ⁻⁶	Total isotope ratio in IUPAC	0.0%
<i>nx1</i>		301.3×10 ⁻⁶	6.9×10 ⁻⁶	Element amount in sample, blend1	Intermediate result
<i>nx2</i>		292.6×10 ⁻⁶	6.6×10 ⁻⁶	Element amount in sample, blend2	Intermediate result
<i>nx3</i>		297.7×10 ⁻⁶	6.8×10 ⁻⁶	Element amount in sample, blend3	Intermediate result
<i>Max</i>	(g/mol)	144.241595	1.00×10 ⁻⁶	Atomic weight of Nd (IUPAC Value)	0.0%

<i>Mx1</i>	($\mu\text{g/kg}$)	43460	990	Element amount in solution, blend1	Intermediate result
<i>Mx2</i>	($\mu\text{g/kg}$)	42200	960	Element amount in solution, blend2	Intermediate result
<i>Mx3</i>	($\mu\text{g/kg}$)	42940	980	Element amount in solution, blend3	Intermediate result
<i>BLANK</i>		0.0094	1.28×10^{-3}	Isotope ratio of $^{142}/^{145}$ in blank solution	0.0%
<i>wx1</i>	(mg/kg)	43.46	0.99	Mass fraction of Nd in sample (blend1-1)	Intermediate result
<i>wx2</i>	(mg/kg)	42.20	0.96	Mass fraction of Nd in sample (blend1-2)	Intermediate result
<i>wx3</i>	(mg/kg)	42.94	0.98	Mass fraction of Nd in sample (blend1-1)	Intermediate result
<i>wx</i>	(mg/kg)	42.87	0.81	Mean mass fraction of Nd in sample with expanded uncertainty (k=2)	-

Table A.2: Results and Complete Uncertainty Budget of Triple ID-MS for $^{144}\text{Nd}/^{145}\text{Nd}$.

Quantity	Unit	Value	Expanded Uncertainty	Description	Index
<i>mz2₁</i>	(kg)	5.3070×10^{-4}	1.94×10^{-6}	Mass of back-spike for blend2-1	0.4%
<i>my2₁</i>	(kg)	1.0350×10^{-4}	2.08×10^{-6}	Mass of spike for blend2-1	10.9%
<i>mz3₁</i>	(kg)	6.8890×10^{-4}	1.94×10^{-6}	Mass of back-spike for blend3-1	0.3%
<i>my3₁</i>	(kg)	1.0400×10^{-4}	1.94×10^{-6}	Mass of spike for blend3-1	0.1%
<i>mz2₂</i>	(kg)	5.3430×10^{-4}	1.94×10^{-6}	Mass of back-spike for blend2-2	0.4%
<i>my2₂</i>	(kg)	1.0370×10^{-4}	1.94×10^{-6}	Mass of spike for blend2-2	9.4%
<i>mz3₂</i>	(kg)	6.9000×10^{-4}	1.94×10^{-6}	Mass of back-spike for blend3-2	0.3%
<i>my3₂</i>	(kg)	1.0420×10^{-4}	1.94×10^{-6}	Mass of spike for blend3-2	12.0%
<i>mz2₃</i>	(kg)	5.3840×10^{-4}	1.94×10^{-6}	Mass of back-spike for blend2-2	0.4%
<i>my2₃</i>	(kg)	1.0340×10^{-4}	1.94×10^{-6}	Mass of spike for blend2-3	12.0%

$mz3_3$	(kg)	7.0250×10^{-4}	5.77×10^{-3}	Mass of back-spike for blend3-3	2.5%
$my3_3$	(kg)	1.0370×10^{-4}	1.94×10^{-6}	Mass of spike for blend3-3	11.3%
$my1_1$	(kg)	6.1700×10^{-1}	1.73×10^{-6}	Mass of spike for blend1-1	0.9%
$mx1_1$	(kg)	2.0080×10^{-1}	5.77×10^{-3}	Mass of sample for blend1-1	1.0%
$my1_2$	(kg)	6.1720×10^{-1}	1.73×10^{-6}	Mass of spike for blend1-2	0.9%
$mx1_2$	(kg)	2.0170×10^{-1}	5.77×10^{-3}	Mass of sample for blend1-2	1.0%
$my1_3$	(kg)	6.1180×10^{-1}	1.73×10^{-6}	Mass of spike for blend1-3	1.0%
$mx1_3$	(kg)	2.0370×10^{-1}	5.77×10^{-3}	Mass of sample for blend1-3	1.0%
$wz2$	(mol/kg)	1.6197×10^{-5}	23.9×10^{-9}	Mass fraction Nd in back-spike solution z2	0.5%
$wz3$	(mol/kg)	1.6197×10^{-5}	23.9×10^{-9}	Mass fraction Nd in back-spike solution z3	0.6%
$wy1$	(mol/kg)	23.9×10^{-6}	4.3×10^{-6}	Mass fraction Nd ¹⁴⁵ in spike (blend2-1)	Intermediate result
$wy2$	(mol/kg)	24.2×10^{-6}	4.4×10^{-6}	Mass fraction Nd ¹⁴⁵ in spike (blend2-2)	Intermediate result
$wy3$	(mol/kg)	23.2×10^{-6}	4.0×10^{-6}	Mass fraction Nd ¹⁴⁵ in spike (blend2-3)	Intermediate result
wy	(mol/kg)	23.8×10^{-6}	4.1×10^{-6}	Mean of mass fraction of Nd ¹⁴⁵ in spike	Intermediate result
$Rzy2_1$		0.6437	4.62×10^{-3}	Isotope ratio 142/145 in blend2-1	2.4%
$Rzy3_1$		0.7804	4.62×10^{-3}	Isotope ratio 142/145 in blend3-1	2.2%
Rx		2.870	112×10^{-6}	Isotope ratio 142/145 in back-spike	0.0%
$Rxy1_1$		0.7125	4.04×10^{-3}	Isotope ratio 142/145 in blend1-1	6.8%
$Ry1$		0.0005	0.18	Isotope abundance ratio 142/145 in spike from blend1	Intermediate result
$Rzy2_2$		0.6392	4.97×10^{-3}	Isotope ratio 142/145 in blend2-2	2.8%
$Rzy3_2$		0.7740	5.77×10^{-3}	Isotope ratio 142/145 in blend3-2	3.5%
$Rxy1_2$		0.7091	4.04×10^{-3}	Isotope ratio 142/145 in blend1-2	6.7%
$Ry2$		-0.0103	0.23	Isotope abundance ratio 142/145 in spike from blend2	Intermediate result
$Rzy2_3$		0.6648	4.97×10^{-3}	Isotope ratio 142/145 in blend2-3	2.3%
$Rzy3_3$		0.8065	5.77×10^{-3}	Isotope ratio 142/145 in blend3-3	3.3%

R_{xy1_3}		0.8208	4.04×10^{-3}	Isotope ratio 142/145 in blend1-3	6.7%
R_{y3}		0.0130	0.22	Isotope abundance ratio 142/145 in spike from blend3	Intermediate result
R_y		0.001057	0.12	Mean isotope abundance ratio 142/145 in spike	Intermediate result
ΣR_x		12.05850	780×10^{-6}	Total isotope ratio in IUPAC	0.0%
$nx1$		290.3×10^{-6}	6.9×10^{-6}	Element amount in sample, blend1	Intermediate result
$nx2$		287.3×10^{-6}	6.6×10^{-6}	Element amount in sample, blend2	Intermediate result
$nx3$		289.4×10^{-6}	6.8×10^{-6}	Element amount in sample, blend3	Intermediate result
Max	(g/mol)	144.241595	1.00×10^{-6}	Atomic weight of Nd (IUPAC Value)	0.0%
$Mx1$	($\mu\text{g/kg}$)	41900	1000	Element amount in solution, blend1	Intermediate result
$Mx2$	($\mu\text{g/kg}$)	41400	1000	Element amount in solution, blend2	Intermediate result
$Mx3$	($\mu\text{g/kg}$)	41750	990	Element amount in solution, blend3	Intermediate result
$BLANK$		0.0168	808×10^{-6}	Isotope ratio of 142/145 in blank solution	0.0%
$wx1$	(mg/kg)	41.9	1.0	Mass fraction of Nd in sample (blend1-1)	Intermediate result
$wx2$	(mg/kg)	41.4	1.0	Mass fraction of Nd in sample (blend1-2)	Intermediate result
$wx3$	(mg/kg)	41.75	0.99	Mass fraction of Nd in sample (blend1-1)	Intermediate result
wx	(mg/kg)	41.69	0.81	Mean mass fraction of Nd in sample with expanded uncertainty (k=2)	-

Table A.3: Results and Complete Uncertainty Budget of Triple ID-MS for $^{146}\text{Nd}1/^{145}\text{Nd}$.

Quantity	Unit	Value	Expanded Uncertainty	Description	Index
$mz2_1$	(kg)	5.3070×10^{-4}	1.94×10^{-6}	Mass of back-spike for blend2-1	0.3%
$my2_1$	(kg)	1.0350×10^{-4}	2.08×10^{-6}	Mass of spike for blend2-1	9.2%
$mz3_1$	(kg)	6.8890×10^{-4}	1.94×10^{-6}	Mass of back-spike for blend3-1	0.2%
$my3_1$	(kg)	1.0400×10^{-4}	1.94×10^{-6}	Mass of spike for blend3-1	0.0%
$mz2_2$	(kg)	5.3430×10^{-4}	1.94×10^{-6}	Mass of back-spike for blend2-2	0.3%
$my2_2$	(kg)	1.0370×10^{-4}	1.94×10^{-6}	Mass of spike for blend2-2	7.8%
$mz3_2$	(kg)	6.9000×10^{-4}	1.94×10^{-6}	Mass of back-spike for blend3-2	0.2%
$my3_2$	(kg)	1.0420×10^{-4}	1.94×10^{-6}	Mass of spike for blend3-2	8.2%
$mz2_3$	(kg)	5.3840×10^{-4}	1.94×10^{-6}	Mass of back-spike for blend2-2	0.3%
$my2_3$	(kg)	1.0340×10^{-4}	1.94×10^{-6}	Mass of spike for blend2-3	7.0%
$mz3_3$	(kg)	7.0250×10^{-4}	5.77×10^{-3}	Mass of back-spike for blend3-3	1.7%
$my3_3$	(kg)	1.0370×10^{-4}	1.94×10^{-6}	Mass of spike for blend3-3	8.2%
$my1_1$	(kg)	6.1700×10^{-1}	1.73×10^{-6}	Mass of spike for blend1-1	0.7%
$mx1_1$	(kg)	2.0080×10^{-1}	5.77×10^{-3}	Mass of sample for blend1-1	0.8%
$my1_2$	(kg)	6.1720×10^{-1}	1.73×10^{-6}	Mass of spike for blend1-2	0.7%
$mx1_2$	(kg)	2.0170×10^{-1}	5.77×10^{-3}	Mass of sample for blend1-2	0.7%
$my1_3$	(kg)	6.1180×10^{-1}	1.73×10^{-6}	Mass of spike for blend1-3	0.7%
$mx1_3$	(kg)	2.0370×10^{-1}	5.77×10^{-3}	Mass of sample for blend1-3	0.7%
$wz2$	(mol/kg)	1.6197×10^{-5}	23.9×10^{-9}	Mass fraction Nd in back-spike solution z2	0.4%
$wz3$	(mol/kg)	1.6197×10^{-5}	23.9×10^{-9}	Mass fraction Nd in back-spike solution z3	0.5%
$wy1$	(mol/kg)	22.7×10^{-6}	4.5×10^{-6}	Mass fraction Nd^{145} in spike (blend2-1)	Intermediate result
$wy2$	(mol/kg)	22.9×10^{-6}	4.5×10^{-6}	Mass fraction Nd^{145} in spike (blend2-2)	Intermediate result
$wy3$	(mol/kg)	22.2×10^{-6}	4.3×10^{-6}	Mass fraction Nd^{145} in spike (blend2-3)	Intermediate result
wy	(mol/kg)	22.6×10^{-6}	4.3×10^{-6}	Mean of mass fraction of Nd^{145} in spike	Intermediate result

<i>Rzy2₁</i>		0.4899	4.62×10 ⁻³	Isotope ratio 142/145 in blend2-1	3.6%
<i>Rzy3₁</i>		0.5903	4.62×10 ⁻³	Isotope ratio 142/145 in blend3-1	2.8%
<i>Rx</i>		2.073	112×10 ⁻⁶	Isotope ratio 142/145 in back- spike	0.0%
<i>Rxy1₁</i>		0.5385	4.04×10 ⁻³	Isotope ratio 142/145 in blend1-1	9.6%
<i>Ry1</i>		0.0116	0.15	Isotope abundance ratio 142/145 in spike from blend1	Intermediate result
<i>Rzy2₂</i>		0.4887	4.97×10 ⁻³	Isotope ratio 142/145 in blend2-2	4.2%
<i>Rzy3₂</i>		0.5874	5.77×10 ⁻³	Isotope ratio 142/145 in blend3-2	4.5%
<i>Rxy1₂</i>		0.5347	4.04×10 ⁻³	Isotope ratio 142/145 in blend1-2	9.4%
<i>Ry2</i>		0.0075	0.19	Isotope abundance ratio 142/145 in spike from blend2	Intermediate result
<i>Rzy2₃</i>		0.5043	4.97×10 ⁻³	Isotope ratio 142/145 in blend2-3	3.5%
<i>Rzy3₃</i>		0.6097	5.77×10 ⁻³	Isotope ratio 142/145 in blend3-3	4.3%
<i>Rxy1₃</i>		0.5488	4.04×10 ⁻³	Isotope ratio 142/145 in blend1-3	9.4%
<i>Ry3</i>		0.0108	0.19	Isotope abundance ratio 142/145 in spike from blend3	Intermediate result
<i>Ry</i>		0.009990	0.10	Mean isotope abundance ratio 142/145 in spike	Intermediate result
ΣRx		12.05850	780×10 ⁻⁶	Total isotope ratio in IUPAC	0.0%
<i>nx1</i>		288.5×10 ⁻⁶	8.3×10 ⁻⁶	Element amount in sample, blend1	Intermediate result
<i>nx2</i>		284.5×10 ⁻⁶	8.2×10 ⁻⁶	Element amount in sample, blend2	Intermediate result
<i>nx3</i>		289.4×10 ⁻⁶	8.2×10 ⁻⁶	Element amount in sample, blend3	Intermediate result
<i>Max</i>	(g/mol)	144.241595		Atomic weight of Nd (IUPAC Value)	0.0%
<i>Mx1</i>	(µg/kg)	41600	1200	Element amount in solution, blend1	Intermediate result
<i>Mx2</i>	(µg/kg)	41000	1200	Element amount in solution, blend2	Intermediate result
<i>Mx3</i>	(µg/kg)	41700	1200	Element amount in solution, blend3	Intermediate result
<i>BLANK</i>		0.0334	1.28×10 ⁻³	Isotope ratio of 142/145 in blank solution	0.0%

<i>wx1</i>	(mg/kg)	41.6	1.2	Mass fraction of Nd in sample (blend1-1)	Intermediate result
<i>wx2</i>	(mg/kg)	41.0	1.2	Mass fraction of Nd in sample (blend1-2)	Intermediate result
<i>wx3</i>	(mg/kg)	41.70	1.2	Mass fraction of Nd in sample (blend1-1)	Intermediate result
<i>wx</i>	(mg/kg)	41.47	0.92	Mean mass fraction of Nd in sample with expanded uncertainty (k=2)	-

APPENDIX-B: RESULTS AND COMPLETE UNCERTAINTY BUDGET TABLES OF TRIBLE ID-MS FOR PD

Table B.1: Results and Complete Uncertainty Budget of Tribble ID-MS for MR ¹⁰⁵Pd/¹⁰⁴Pd.

Quantity	Unit	Value	Expanded Uncertainty	Description	Index
<i>mz2₁</i>	(kg)	1.5021×10 ⁻³	1.10×10 ⁻⁶	Mass of back-spike for blend2-1	0.0%
<i>my2₁</i>	(kg)	1.0080×10 ⁻⁴	577×10 ⁻¹²	Mass of spike for blend2-1	0.0%
<i>mz3₁</i>	(kg)	1.3457×10 ⁻³	416×10 ⁻⁶	Mass of back-spike for blend3-1	0.0%
<i>my3₁</i>	(kg)	1.0090×10 ⁻⁴	5.77×10 ⁻⁹	Mass of spike for blend3-1	0.0%
<i>mz2₂</i>	(kg)	1.5000×10 ⁻³	1.10×10 ⁻⁶	Mass of back-spike for blend2-2	0.0%
<i>my2₂</i>	(kg)	1.0080×10 ⁻⁴	577×10 ⁻⁹	Mass of spike for blend2-2	0.0%
<i>mz3₂</i>	(kg)	1.0090×10 ⁻⁴	416×10 ⁻⁶	Mass of back-spike for blend3-2	0.0%
<i>my3₂</i>	(kg)	1.0090×10 ⁻⁴	5.77×10 ⁻⁹	Mass of spike for blend3-2	0.0%
<i>mz2₃</i>	(kg)	1.5039×10 ⁻³	1.10×10 ⁻⁶	Mass of back-spike for blend2-3	0.0%
<i>my2₃</i>	(kg)	1.0080×10 ⁻⁴	577×10 ⁻¹²	Mass of spike for blend2-3	0.0%
<i>mz3₃</i>	(kg)	1.3510×10 ⁻³	416×10 ⁻⁶	Mass of back-spike for blend3-3	0.0%

<i>my3₃</i>	(kg)	1.0090×10 ⁻⁴	5.77×10 ⁻⁹	Mass of spike for blend3-3	0.0%
<i>my1₁</i>	(kg)	2.0200×10 ⁻¹	200×10 ⁻⁶	Mass of spike for blend1-1	0.0%
<i>mx1₁</i>	(kg)	2.0320×10 ⁻¹	418×10 ⁻⁶	Mass of sample for blend1-1	0.0%
<i>my1₂</i>	(kg)	2.0200×10 ⁻¹	200×10 ⁻⁶	Mass of spike for blend1-2	0.0%
<i>mx1₂</i>	(kg)	2.0320×10 ⁻¹	418×10 ⁻⁶	Mass of sample for blend1-2	0.0%
<i>my1₃</i>	(kg)	2.0140×10 ⁻¹	200×10 ⁻⁶	Mass of spike for blend1-3	0.0%
<i>mx1₃</i>	(kg)	2.0200×10 ⁻¹	418×10 ⁻⁶	Mass of sample for blend1-3	0.0%
<i>wz2</i>	(mol/kg)	9.5454×10 ⁻⁶	577×10 ⁻¹²	Mass fraction Nd in back-spike solution z2	0.0%
<i>wz3</i>	(mol/kg)	9.5454×10 ⁻⁶	57.7×10 ⁻¹²	Mass fraction Nd in back-spike solution z3	0.0%
<i>wy1</i>	(mol/kg)	30.000×10 ⁻⁶	660×10 ⁻⁶	Mass fraction Nd ¹⁴⁵ in spike (blend2-1)	Intermediate result
<i>wy2</i>	(mol/kg)	30.000×10 ⁻⁶	660×10 ⁻⁶	Mass fraction Nd ¹⁴⁵ in spike (blend2-2)	Intermediate result
<i>wy3</i>	(mol/kg)	30.000×10 ⁻⁶	660×10 ⁻⁶	Mass fraction Nd ¹⁴⁵ in spike (blend2-3)	Intermediate result
<i>wy</i>	(mol/kg)	30.000×10 ⁻⁶	660×10 ⁻⁶	Mean of mass fraction of Nd ¹⁴⁵ in spike	Intermediate result
<i>Rzy2₁</i>		0.9149	7.19×10 ⁻³	Isotope ratio 142/145 in blend2-1	43.2%
<i>Rzy3₁</i>		0.9063	0.0135	Isotope ratio 142/145 in blend3-1	0.0%
<i>Rx</i>		2.004	189×10 ⁻⁶	Isotope ratio 142/145 in back-spike	0.0%
<i>Rxy1₁</i>		0.9034	5.18×10 ⁻³	Isotope ratio 142/145 in blend1-1	0.2%
<i>Ry1</i>		0.8300	0.34	Isotope abundance ratio 142/145 in spike from blend1	Intermediate result
<i>Rzy2₂</i>		1.1386	0.0719	Isotope ratio 142/145 in blend2-2	0.0%
<i>Rzy3₂</i>		0.8659	0.0135	Isotope ratio 142/145 in blend3-2	0.0%
<i>Rxy1₂</i>		0.9271	5.18×10 ⁻³	Isotope ratio 142/145 in blend1-2	0.2%
<i>Ry2</i>		0.8400	0.29	Isotope abundance ratio 142/145 in spike from blend2	Intermediate result
<i>Rzy2₃</i>		0.9321	0.0719	Isotope ratio 142/145 in blend2-3	0.0%
<i>Rzy3₃</i>		0.8659	0.0135	Isotope ratio 142/145 in blend3-3	0.0%
<i>Rxy1₃</i>		0.9244	5.18×10 ⁻³	Isotope ratio 142/145 in blend1-3	0.2%

<i>Ry3</i>		-0.5000	6.7	Isotope abundance ratio 142/145 in spike from blend3	Intermediate result
<i>Ry</i>		0.4000	2.2	Mean isotope abundance ratio 142/145 in spike	Intermediate result
ΣRx		8.9767	2.6×10^{-6}	Total isotope ratio in IUPAC	0.0%
<i>nx1</i>		140×10^{-6}	25×10^{-6}	Element amount in sample, blend1	Intermediate result
<i>nx2</i>		146×10^{-6}	67×10^{-6}	Element amount in sample, blend2	Intermediate result
<i>nx3</i>		146×10^{-6}	52×10^{-6}	Element amount in sample, blend3	Intermediate result
<i>Max</i>	(g/mol)	106.4153	1.00×10^{-6}	Atomic weight of Nd (IUPAC Value)	0.0%
<i>Mx1</i>	($\mu\text{g/kg}$)	15000	2700	Element amount in solution, blend1	Intermediate result
<i>Mx2</i>	($\mu\text{g/kg}$)	15600	7100	Element amount in solution, blend2	Intermediate result
<i>Mx3</i>	($\mu\text{g/kg}$)	15500	5600	Element amount in solution, blend3	Intermediate result
<i>BLANK</i>		0.3881	0.0493	Isotope ratio of 142/145 in blank solution	0.0%
<i>wx1</i>	(mg/kg)	15	2.7	Mass fraction of Nd in sample (blend1-1)	Intermediate result
<i>wx2</i>	(mg/kg)	15.6	7.1	Mass fraction of Nd in sample (blend1-2)	Intermediate result
<i>wx3</i>	(mg/kg)	15.5	5.6	Mass fraction of Nd in sample (blend1-1)	Intermediate result
<i>wx</i>	(mg/kg)	15.3	3.4	Mean mass fraction of Nd in sample with expanded uncertainty (k=2)	-

Table B.2: Results and Complete Uncertainty Budget of Tribble ID-MS for MR $^{106}\text{Pd}/^{104}\text{Pd}$.

Quantity	Unit	Value	Expanded Uncertainty	Description	Index
<i>mz2₁</i>	(kg)	1.5021×10^{-3}	1.10×10^{-6}	Mass of back-spike for blend2-1	0.0%
<i>my2₁</i>	(kg)	1.0080×10^{-4}	577×10^{-12}	Mass of spike for blend2-1	0.0%

$mz3_1$	(kg)	1.5600×10^{-6}	416×10^{-6}	Mass of back-spike for blend3-1	0.0%
$my3_1$	(kg)	1.0090×10^{-4}	5.77×10^{-9}	Mass of spike for blend3-1	0.0%
$mz2_2$	(kg)	1.5000×10^{-3}	1.10×10^{-6}	Mass of back-spike for blend2-2	0.1%
$my2_2$	(kg)	1.0080×10^{-4}	577×10^{-9}	Mass of spike for blend2-2	0.0%
$mz3_2$	(kg)	1.3475×10^{-3}	1.5600×10^{-6}	Mass of back-spike for blend3-2	0.2%
$my3_2$	(kg)	1.0090×10^{-4}	5.77×10^{-9}	Mass of spike for blend3-2	0.0%
$mz2_3$	(kg)	1.5039×10^{-3}	1.10×10^{-6}	Mass of back-spike for blend2-2	0.0%
$my2_3$	(kg)	1.0080×10^{-4}	577×10^{-12}	Mass of spike for blend2-3	0.0%
$mz3_3$	(kg)	1.3510×10^{-3}	1.5600×10^{-6}	Mass of back-spike for blend3-3	0.0%
$my3_3$	(kg)	1.0090×10^{-4}	5.77×10^{-9}	Mass of spike for blend3-3	0.0%
$my1_1$	(kg)	2.0200×10^{-1}	200×10^{-6}	Mass of spike for blend1-1	0.0%
$mx1_1$	(kg)	2.0190×10^{-1}	418×10^{-6}	Mass of sample for blend1-1	0.0%
$my1_2$	(kg)	2.0200×10^{-1}	200×10^{-6}	Mass of spike for blend1-2	0.0%
$mx1_2$	(kg)	2.0320×10^{-1}	418×10^{-6}	Mass of sample for blend1-2	0.0%
$my1_3$	(kg)	2.0140×10^{-1}	200×10^{-6}	Mass of spike for blend1-3	0.0%
$mx1_3$	(kg)	2.0200×10^{-1}	418×10^{-6}	Mass of sample for blend1-3	0.0%
$wz2$	(mol/kg)	9.5454×10^{-6}	577×10^{-12}	Mass fraction Nd in back-spike solution z2	0.0%
$wz3$	(mol/kg)	9.5454×10^{-6}	57.7×10^{-12}	Mass fraction Nd in back-spike solution z3	0.0%
$wy1$	(mol/kg)	6.10×10^{-6}	13×10^{-6}	Mass fraction Nd ¹⁴⁵ in spike (blend2-1)	Intermediate result
$wy2$	(mol/kg)	6.10×10^{-6}	13×10^{-6}	Mass fraction Nd ¹⁴⁵ in spike (blend2-2)	Intermediate result
$wy3$	(mol/kg)	6.10×10^{-6}	13×10^{-6}	Mass fraction Nd ¹⁴⁵ in spike (blend2-3)	Intermediate result
wy	(mol/kg)	6.10×10^{-6}	13×10^{-6}	Mean of mass fraction of Nd ¹⁴⁵ in spike	Intermediate result
$Rzy2_1$		1.0639	0.0188	Isotope ratio 142/145 in blend2-1	3.3%
$Rzy3_1$		1.0397	0.0144	Isotope ratio 142/145 in blend3-1	0.0%
Rx		2.4530	189×10^{-6}	Isotope ratio 142/145 in back-spike	0.0%

<i>Rxy1₁</i>		1.2456	0.0168	Isotope ratio 142/145 in blend1-1	1.0%
<i>Ry1</i>		0.7900	0.61	Isotope abundance ratio 142/145 in spike from blend1	Intermediate result
<i>Rzy2₂</i>		1.1272	0.0188	Isotope ratio 142/145 in blend2-2	69.3%
<i>Rzy3₂</i>		0.9973	0.0144	Isotope ratio 142/145 in blend3-2	22.8%
<i>Rxy1₂</i>		1.2865	5.18×10 ⁻³	Isotope ratio 142/145 in blend1-2	1.1%
<i>Ry2</i>		-7	80	Isotope abundance ratio 142/145 in spike from blend2	Intermediate result
<i>Rzy2₃</i>		1.0817	0.0719	Isotope ratio 142/145 in blend2-3	0.6%
<i>Rzy3₃</i>		0.9954	0.0135	Isotope ratio 142/145 in blend3-3	0.3%
<i>Rxy1₃</i>		1.3020	5.18×10 ⁻³	Isotope ratio 142/145 in blend1-3	1.2%
<i>Ry3</i>		-0.8	2.5	Isotope abundance ratio 142/145 in spike from blend3	Intermediate result
<i>Ry</i>		-2	27	Mean isotope abundance ratio 142/145 in spike	Intermediate result
$\sum R_x$		8.9767	2.6×10 ⁻⁶	Total isotope ratio in IUPAC	0.0%
<i>nx1</i>		167×10 ⁻⁶	18×10 ⁻⁶	Element amount in sample, blend1	Intermediate result
<i>nx2</i>		174×10 ⁻⁶	23×10 ⁻⁶	Element amount in sample, blend2	Intermediate result
<i>nx3</i>		177×10 ⁻⁶	24×10 ⁻⁶	Element amount in sample, blend3	Intermediate result
<i>Max</i>	(g/mol)	106.4153	1.00×10 ⁻⁶	Atomic weight of Nd (IUPAC Value)	0.0%
<i>Mx1</i>	(μg/kg)	17800	1900	Element amount in solution, blend1	Intermediate result
<i>Mx2</i>	(μg/kg)	18500	2400	Element amount in solution, blend2	Intermediate result
<i>Mx3</i>	(μg/kg)	18900	2600	Element amount in solution, blend3	Intermediate result
<i>BLANK</i>		0.3938	0.0666	Isotope ratio of 142/145 in blank solution	0.0%
<i>wx1</i>	(mg/kg)	17.8	1.9	Mass fraction of Nd in sample (blend1-1)	Intermediate result
<i>wx2</i>	(mg/kg)	18.5	2.4	Mass fraction of Nd in sample (blend1-2)	Intermediate result

$wx3$	(mg/kg)	18.9	2.6	Mass fraction of Nd in sample (blend1-1)	Intermediate result
wx	(mg/kg)	18.4	2.2	Mean mass fraction of Nd in sample with expanded uncertainty (k=2)	-

Table B.3: Results and Complete Uncertainty Budget of Tribble ID-MS for MR $^{108}\text{Pd}/^{104}\text{Pd}$.

Quantity	Unit	Value	Expanded Uncertainty	Description	Index
$mz2_1$	(kg)	1.5021×10^{-3}	1.10×10^{-6}	Mass of back-spike for blend2-1	0.0%
$my2_1$	(kg)	1.0080×10^{-4}	577×10^{-12}	Mass of spike for blend2-1	0.0%
$mz3_1$	(kg)	1.5600×10^{-6}	416×10^{-6}	Mass of back-spike for blend3-1	0.0%
$my3_1$	(kg)	1.0090×10^{-4}	5.77×10^{-9}	Mass of spike for blend3-1	0.0%
$mz2_2$	(kg)	1.5000×10^{-3}	1.10×10^{-6}	Mass of back-spike for blend2-2	0.1%
$my2_2$	(kg)	1.0080×10^{-4}	577×10^{-9}	Mass of spike for blend2-2	0.0%
$mz3_2$	(kg)	1.3475×10^{-3}	1.5600×10^{-6}	Mass of back-spike for blend3-2	0.0%
$my3_2$	(kg)	1.0090×10^{-4}	5.77×10^{-9}	Mass of spike for blend3-2	0.0%
$mz2_3$	(kg)	1.5039×10^{-3}	1.10×10^{-6}	Mass of back-spike for blend2-2	0.0%
$my2_3$	(kg)	1.0080×10^{-4}	577×10^{-12}	Mass of spike for blend2-3	0.0%
$mz3_3$	(kg)	1.3510×10^{-3}	1.5600×10^{-6}	Mass of back-spike for blend3-3	0.0%
$my3_3$	(kg)	1.0090×10^{-4}	5.77×10^{-9}	Mass of spike for blend3-3	0.0%
$my1_1$	(kg)	2.0200×10^{-1}	200×10^{-6}	Mass of spike for blend1-1	0.0%
$mx1_1$	(kg)	2.0190×10^{-1}	418×10^{-6}	Mass of sample for blend1-1	0.2%
$my1_2$	(kg)	2.0200×10^{-1}	200×10^{-6}	Mass of spike for blend1-2	0.0%
$mx1_2$	(kg)	2.0320×10^{-1}	418×10^{-6}	Mass of sample for blend1-2	0.2%
$my1_3$	(kg)	2.0140×10^{-1}	200×10^{-6}	Mass of spike for blend1-3	0.0%
$mx1_3$	(kg)	2.0200×10^{-1}	418×10^{-6}	Mass of sample for blend1-3	0.2%

wz2	(mol/kg)	9.5454×10 ⁻⁶	577×10 ⁻¹²	Mass fraction Nd in back-spike solution z2	0.0%
wz3	(mol/kg)	9.5454×10 ⁻⁶	57.7×10 ⁻¹²	Mass fraction Nd in back-spike solution z3	0.0%
wy1	(mol/kg)	1×10 ⁻⁶	18×10 ⁻⁶	Mass fraction Nd ¹⁴⁵ in spike (blend2-1)	Intermediate result
wy2	(mol/kg)	1×10 ⁻⁶	18×10 ⁻⁶	Mass fraction Nd ¹⁴⁵ in spike (blend2-2)	Intermediate result
wy3	(mol/kg)	1×10 ⁻⁶	18×10 ⁻⁶	Mass fraction Nd ¹⁴⁵ in spike (blend2-3)	Intermediate result
wy	(mol/kg)	1×10 ⁻⁶	18×10 ⁻⁶	Mean of mass fraction of Nd ¹⁴⁵ in spike	Intermediate result
Rzy2 ₁		1.0444	0.0232	Isotope ratio 142/145 in blend2-1	43.2%
Rzy3 ₁		1.0170	0.0140	Isotope ratio 142/145 in blend3-1	0.0%
Rx		2.375	189×10 ⁻⁶	Isotope ratio 142/145 in back-spike	0.0%
Rxy1 ₁		1.0565	0.0121	Isotope ratio 142/145 in blend1-1	4.9%
Ry1		0.7300	0.75	Isotope abundance ratio 142/145 in spike from blend1	Intermediate result
Rzy2 ₂		1.1181	0.0232	Isotope ratio 142/145 in blend2-2	40.2%
Rzy3 ₂		0.9747	0.0140	Isotope ratio 142/145 in blend3-2	0.0%
Rxy1 ₂		1.0950	5.18×10 ⁻³	Isotope ratio 142/145 in blend1-2	5.4%
Ry2		-90	310	Isotope abundance ratio 142/145 in spike from blend2	Intermediate result
Rzy2 ₃		1.0536	0.0232	Isotope ratio 142/145 in blend2-3	0.0%
Rzy3 ₃		0.9753	0.0144	Isotope ratio 142/145 in blend3-3	0.0%
Rxy1 ₃		1.0901	0.0121	Isotope ratio 142/145 in blend1-3	5.4%
Ry3		-0.5	2.6	Isotope abundance ratio 142/145 in spike from blend3	Intermediate result
Ry		-30	100	Mean isotope abundance ratio 142/145 in spike	Intermediate result
ΣRx		8.9767	2.6×10 ⁻⁶	Total isotope ratio in IUPAC	0.0%
nx1		139.4×10 ⁻⁶	4×10 ⁻⁶	Element amount in sample, blend1	Intermediate result
nx2		142.9×10 ⁻⁶	5.8×10 ⁻⁶	Element amount in sample, blend2	Intermediate result
nx3		142.8×10 ⁻⁶	5.4×10 ⁻⁶	Element amount in sample, blend3	Intermediate result

<i>Max</i>	(g/mol)	106.4153	1.00×10^{-6}	Atomic weight of Nd (IUPAC Value)	0.0%
<i>Mx1</i>	(µg/kg)	14840	430	Element amount in solution, blend1	Intermediate result
<i>Mx2</i>	(µg/kg)	15210	620	Element amount in solution, blend2	Intermediate result
<i>Mx3</i>	(µg/kg)	15190	570	Element amount in solution, blend3	Intermediate result
<i>BLANK</i>		0.3553	0.0613	Isotope ratio of $^{142}/^{145}$ in blank solution	0.0%
<i>wx1</i>	(mg/kg)	14.84	0.43	Mass fraction of Nd in sample (blend1-1)	Intermediate result
<i>wx2</i>	(mg/kg)	15.21	0.62	Mass fraction of Nd in sample (blend1-2)	Intermediate result
<i>wx3</i>	(mg/kg)	15.19	0.57	Mass fraction of Nd in sample (blend1-1)	Intermediate result
<i>wx</i>	(mg/kg)	15.08	0.43	Mean mass fraction of Nd in sample with expanded uncertainty (k=2)	-

Table B.4: Results and Complete Uncertainty Budget of Tribble ID-MS for HR $^{105}\text{Pd}/^{104}\text{Pd}$.

Quantity	Unit	Value	Expanded Uncertainty	Description	Index
<i>mz2₁</i>	(kg)	1.5021×10^{-3}	1.10×10^{-6}	Mass of back-spike for blend2-1	0.0%
<i>my2₁</i>	(kg)	1.0080×10^{-4}	577×10^{-12}	Mass of spike for blend2-1	0.0%
<i>mz3₁</i>	(kg)	1.5600×10^{-6}	416×10^{-6}	Mass of back-spike for blend3-1	0.0%
<i>my3₁</i>	(kg)	1.0090×10^{-4}	5.77×10^{-9}	Mass of spike for blend3-1	0.0%
<i>mz2₂</i>	(kg)	1.5000×10^{-3}	1.10×10^{-6}	Mass of back-spike for blend2-2	0.1%
<i>my2₂</i>	(kg)	1.0080×10^{-4}	577×10^{-9}	Mass of spike for blend2-2	0.0%
<i>mz3₂</i>	(kg)	1.3475×10^{-3}	1.560×10^{-6}	Mass of back-spike for blend3-2	0.0%

$my3_2$	(kg)	1.0090×10^{-4}	5.77×10^{-9}	Mass of spike for blend3-2	0.0%
$mz2_3$	(kg)	1.5039×10^{-3}	1.10×10^{-6}	Mass of back-spike for blend2-2	0.0%
$my2_3$	(kg)	1.0080×10^{-4}	577×10^{-12}	Mass of spike for blend2-3	0.0%
$mz3_3$	(kg)	1.3510×10^{-3}	1.560×10^{-6}	Mass of back-spike for blend3-3	99.6%
$my3_3$	(kg)	1.0090×10^{-4}	5.77×10^{-9}	Mass of spike for blend3-3	0.0%
$my1_1$	(kg)	2.0200×10^{-1}	200×10^{-6}	Mass of spike for blend1-1	0.0%
$mx1_1$	(kg)	2.0190×10^{-1}	418×10^{-6}	Mass of sample for blend1-1	0.0%
$my1_2$	(kg)	2.0200×10^{-1}	200×10^{-6}	Mass of spike for blend1-2	0.0%
$mx1_2$	(kg)	2.0320×10^{-1}	418×10^{-6}	Mass of sample for blend1-2	0.0%
$my1_3$	(kg)	2.0140×10^{-1}	200×10^{-6}	Mass of spike for blend1-3	0.0%
$mx1_3$	(kg)	2.0200×10^{-1}	418×10^{-6}	Mass of sample for blend1-3	0.0%
$wz2$	(mol/kg)	9.5454×10^{-6}	577×10^{-12}	Mass fraction Nd in back-spike solution z2	0.0%
$wz3$	(mol/kg)	9.5454×10^{-6}	57.7×10^{-12}	Mass fraction Nd in back-spike solution z3	0.0%
$wy1$	(mol/kg)	20×10^{-6}	330×10^{-6}	Mass fraction Nd^{145} in spike (blend2-1)	Intermediate result
$wy2$	(mol/kg)	20×10^{-6}	180×10^{-6}	Mass fraction Nd^{145} in spike (blend2-2)	Intermediate result
$wy3$	(mol/kg)	20×10^{-6}	250×10^{-6}	Mass fraction Nd^{145} in spike (blend2-3)	Intermediate result
wy	(mol/kg)	20×10^{-6}	250×10^{-6}	Mean of mass fraction of Nd^{145} in spike	Intermediate result
$Rzy2_1$		1.0788	9.58×10^{-3}	Isotope ratio 142/145 in blend2-1	0.0%
$Rzy3_1$		1.0170	0.0140	Isotope ratio 142/145 in blend3-1	0.0%
Rx		2.4530	189×10^{-6}	Isotope ratio 142/145 in back-spike	0.0%
$Rxy1_1$		1.2456	0.0168	Isotope ratio 142/145 in blend1-1	0.0%
$Ry1$		0.5900	0.64	Isotope abundance ratio 142/145 in spike from blend1	Intermediate result
$Rzy2_2$		1.1115	9.58×10^{-3}	Isotope ratio 142/145 in blend2-2	0.0%
$Rzy3_2$		0.9973	0.0144	Isotope ratio 142/145 in blend3-2	0.0%
$Rxy1_2$		1.2865	0.0168	Isotope ratio 142/145 in blend1-2	0.0%
$Ry2$		0.9890	0.095	Isotope abundance ratio	Intermediate result

				142/145 in spike from blend2	
<i>Rzy2₃</i>		1.1001	9.58×10 ⁻³	Isotope ratio 142/145 in blend2-3	0.2%
<i>Rzy3₃</i>		0.9954	0.0144	Isotope ratio 142/145 in blend3-3	0.2%
<i>Rxy1₃</i>		1.3020	0.0168	Isotope ratio 142/145 in blend1-3	0.0%
<i>Ry3</i>		-21	3.6	Isotope abundance ratio 142/145 in spike from blend3	Intermediate result
<i>Ry</i>		-0.2	1.2	Mean isotope abundance ratio 142/145 in spike	Intermediate result
ΣRx		8.9767	2.6×10 ⁻⁶	Total isotope ratio in IUPAC	0.0%
<i>nx1</i>		180×10 ⁻⁶	290×10 ⁻⁶	Element amount in sample, blend1	Intermediate result
<i>nx2</i>		190×10 ⁻⁶	380×10 ⁻⁶	Element amount in sample, blend2	Intermediate result
<i>nx3</i>		190×10 ⁻⁶	410×10 ⁻⁶	Element amount in sample, blend3	Intermediate result
<i>Max</i>	(g/mol)	106.4153	1.00×10 ⁻⁶	Atomic weight of Nd (IUPAC Value)	0.0%
<i>Mx1</i>	(μg/kg)	19000	31000	Element amount in solution, blend1	Intermediate result
<i>Mx2</i>	(μg/kg)	20000	40000	Element amount in solution, blend2	Intermediate result
<i>Mx3</i>	(μg/kg)	21000	44000	Element amount in solution, blend3	Intermediate result
<i>BLANK</i>		0.3938	0.0666	Isotope ratio of 142/145 in blank solution	0.0%
<i>wx1</i>	(mg/kg)	19	31	Mass fraction of Nd in sample (blend1-1)	Intermediate result
<i>wx2</i>	(mg/kg)	20	40	Mass fraction of Nd in sample (blend1-2)	Intermediate result
<i>wx3</i>	(mg/kg)	21	44	Mass fraction of Nd in sample (blend1-1)	Intermediate result
<i>wx</i>	(mg/kg)	20	3.8	Mean mass fraction of Nd in sample with expanded uncertainty (k=2)	-

Table B.5: Results and Complete Uncertainty Budget of Tribble ID-MS for HR $^{106}\text{Pd}/^{104}\text{Pd}$.

Quantity	Unit	Value	Expanded Uncertainty	Description	Index
$mz2_1$	(kg)	1.5021×10^{-3}	1.10×10^{-6}	Mass of back-spike for blend2-1	0.0%
$my2_1$	(kg)	1.0080×10^{-4}	577×10^{-12}	Mass of spike for blend2-1	0.0%
$mz3_1$	(kg)	1.5600×10^{-6}	416×10^{-6}	Mass of back-spike for blend3-1	0.0%
$my3_1$	(kg)	1.0090×10^{-4}	5.77×10^{-9}	Mass of spike for blend3-1	0.0%
$mz2_2$	(kg)	1.5000×10^{-3}	1.10×10^{-6}	Mass of back-spike for blend2-2	0.0%
$my2_2$	(kg)	1.0080×10^{-4}	577×10^{-9}	Mass of spike for blend2-2	0.0%
$mz3_2$	(kg)	1.3475×10^{-3}	1.560×10^{-6}	Mass of back-spike for blend3-2	0.0%
$my3_2$	(kg)	1.0090×10^{-4}	5.77×10^{-9}	Mass of spike for blend3-2	0.0%
$mz2_3$	(kg)	1.5039×10^{-3}	1.10×10^{-6}	Mass of back-spike for blend2-2	0.0%
$my2_3$	(kg)	1.0080×10^{-4}	577×10^{-12}	Mass of spike for blend2-3	0.0%
$mz3_3$	(kg)	1.3510×10^{-3}	1.560×10^{-6}	Mass of back-spike for blend3-3	96.5%
$my3_3$	(kg)	1.0090×10^{-4}	5.77×10^{-9}	Mass of spike for blend3-3	0.0%
$my1_1$	(kg)	2.0200×10^{-1}	200×10^{-6}	Mass of spike for blend1-1	0.0%
$mx1_1$	(kg)	2.0190×10^{-1}	418×10^{-6}	Mass of sample for blend1-1	0.0%
$my1_2$	(kg)	2.0200×10^{-1}	200×10^{-6}	Mass of spike for blend1-2	0.0%
$mx1_2$	(kg)	2.0320×10^{-1}	418×10^{-6}	Mass of sample for blend1-2	0.0%
$my1_3$	(kg)	2.0140×10^{-1}	200×10^{-6}	Mass of spike for blend1-3	0.0%
$mx1_3$	(kg)	2.0200×10^{-1}	418×10^{-6}	Mass of sample for blend1-3	0.0%
$wz2$	(mol/kg)	9.5454×10^{-6}	577×10^{-12}	Mass fraction Nd in back-spike solution z2	0.0%
$wz3$	(mol/kg)	9.5454×10^{-6}	57.7×10^{-12}	Mass fraction Nd in back-spike solution z3	0.0%
$wy1$	(mol/kg)	20×10^{-6}	340×10^{-6}	Mass fraction Nd^{145} in spike (blend2-1)	Intermediate result
$wy2$	(mol/kg)	20×10^{-6}	340×10^{-6}	Mass fraction Nd^{145} in spike (blend2-2)	Intermediate result
$wy3$	(mol/kg)	20×10^{-6}	340×10^{-6}	Mass fraction Nd^{145} in spike (blend2-3)	Intermediate result
wy	(mol/kg)	20×10^{-6}	340×10^{-6}	Mean of mass fraction of Nd^{145} in spike	Intermediate result

<i>Rzy2₁</i>		0.9285	0.0153	Isotope ratio 142/145 in blend2-1	0.5%
<i>Rzy3₁</i>		0.9102	0.0141	Isotope ratio 142/145 in blend3-1	0.0%
<i>Rx</i>		2.004	189×10 ⁻⁶	Isotope ratio 142/145 in back- spike	0.0%
<i>Rxy1₁</i>		0.9034	8.78×10 ⁻³	Isotope ratio 142/145 in blend1-1	0.0%
<i>Ry1</i>		0.7300	0.55	Isotope abundance ratio 142/145 in spike from blend1	Intermediate result
<i>Rzy2₂</i>		0.9811	0.0153	Isotope ratio 142/145 in blend2-2	0.6%
<i>Rzy3₂</i>		0.8671	0.0141	Isotope ratio 142/145 in blend3-2	0.0%
<i>Rxy1₂</i>		0.9331	8.78×10 ⁻³	Isotope ratio 142/145 in blend1-2	0.1%
<i>Ry2</i>		0.8580	0.097	Isotope abundance ratio 142/145 in spike from blend2	Intermediate result
<i>Rzy2₃</i>		0.9492	0.0141	Isotope ratio 142/145 in blend2-3	1.1%
<i>Rzy3₃</i>		0.8686	0.0141	Isotope ratio 142/145 in blend3-3	1.0%
<i>Rxy1₃</i>		0.9126	8.78×10 ⁻³	Isotope ratio 142/145 in blend1-3	0.0%
<i>Ry3</i>		-1.4	4.3	Isotope abundance ratio 142/145 in spike from blend3	Intermediate result
<i>Ry</i>		0.1	1.4	Mean isotope abundance ratio 142/145 in spike	Intermediate result
ΣRx		8.9767	2.6×10 ⁻⁶	Total isotope ratio in IUPAC	0.0%
<i>nx1</i>		128×10 ⁻⁶	18×10 ⁻⁶	Element amount in sample, blend1	Intermediate result
<i>nx2</i>		135×10 ⁻⁶	99×10 ⁻⁶	Element amount in sample, blend2	Intermediate result
<i>nx3</i>		130×10 ⁻⁶	41×10 ⁻⁶	Element amount in sample, blend3	Intermediate result
<i>Max</i>	(g/mol)	106.4153	1.00×10 ⁻⁶	Atomic weight of Nd (IUPAC Value)	0.0%
<i>Mx1</i>	(µg/kg)	13600	1900	Element amount in solution, blend1	Intermediate result
<i>Mx2</i>	(µg/kg)	14000	10000	Element amount in solution, blend2	Intermediate result
<i>Mx3</i>	(µg/kg)	13800	4300	Element amount in solution, blend3	Intermediate result
<i>BLANK</i>		0.3881	0.0493	Isotope ratio of 142/145 in blank solution	0.0%

<i>wx1</i>	(mg/kg)	13.6	1.9	Mass fraction of Nd in sample (blend1-1)	Intermediate result
<i>wx2</i>	(mg/kg)	14	10	Mass fraction of Nd in sample (blend1-2)	Intermediate result
<i>wx3</i>	(mg/kg)	13.8	4.3	Mass fraction of Nd in sample (blend1-1)	Intermediate result
<i>wx</i>	(mg/kg)	14	5.4	Mean mass fraction of Nd in sample with expanded uncertainty (k=2)	-

Table B.6: Results and Complete Uncertainty Budget of Tribble ID-MS for HR $^{108}\text{Pd}/^{104}\text{Pd}$.

Quantity	Unit	Value	Expanded Uncertainty	Description	Index
<i>mz2₁</i>	(kg)	1.5021×10^{-3}	1.10×10^{-6}	Mass of back-spike for blend2-1	0.0%
<i>my2₁</i>	(kg)	1.0080×10^{-4}	577×10^{-12}	Mass of spike for blend2-1	0.0%
<i>mz3₁</i>	(kg)	1.5600×10^{-6}	416×10^{-6}	Mass of back-spike for blend3-1	0.0%
<i>my3₁</i>	(kg)	1.0090×10^{-4}	5.77×10^{-9}	Mass of spike for blend3-1	0.0%
<i>mz2₂</i>	(kg)	1.5000×10^{-3}	1.10×10^{-6}	Mass of back-spike for blend2-2	0.0%
<i>my2₂</i>	(kg)	1.0080×10^{-4}	577×10^{-9}	Mass of spike for blend2-2	0.0%
<i>mz3₂</i>	(kg)	1.3475×10^{-3}	1.560×10^{-6}	Mass of back-spike for blend3-2	0.0%
<i>my3₂</i>	(kg)	1.0090×10^{-4}	5.77×10^{-9}	Mass of spike for blend3-2	0.0%
<i>mz2₃</i>	(kg)	1.5039×10^{-3}	1.10×10^{-6}	Mass of back-spike for blend2-2	0.0%
<i>my2₃</i>	(kg)	1.0080×10^{-4}	577×10^{-12}	Mass of spike for blend2-3	0.0%
<i>mz3₃</i>	(kg)	1.3510×10^{-3}	1.560×10^{-6}	Mass of back-spike for blend3-3	0.0%
<i>my3₃</i>	(kg)	1.0090×10^{-4}	5.77×10^{-9}	Mass of spike for blend3-3	0.0%
<i>my1₁</i>	(kg)	2.0200×10^{-1}	200×10^{-6}	Mass of spike for blend1-1	0.0%

$mx1_1$	(kg)	2.0190×10^{-1}	418×10^{-6}	Mass of sample for blend1-1	0.3%
$my1_2$	(kg)	2.0200×10^{-1}	200×10^{-6}	Mass of spike for blend1-2	0.0%
$mx1_2$	(kg)	2.0320×10^{-1}	418×10^{-6}	Mass of sample for blend1-2	0.3%
$my1_3$	(kg)	2.0140×10^{-1}	200×10^{-6}	Mass of spike for blend1-3	0.0%
$mx1_3$	(kg)	2.0200×10^{-1}	418×10^{-6}	Mass of sample for blend1-3	0.3%
$wz2$	(mol/kg)	9.5454×10^{-6}	577×10^{-12}	Mass fraction Nd in back-spike solution z2	0.0%
$wz3$	(mol/kg)	9.5454×10^{-6}	57.7×10^{-12}	Mass fraction Nd in back-spike solution z3	0.0%
$wy1$	(mol/kg)	9.8×10^{-6}	8.8×10^{-6}	Mass fraction Nd ¹⁴⁵ in spike (blend2-1)	Intermediate result
$wy2$	(mol/kg)	9.6×10^{-6}	8.5×10^{-6}	Mass fraction Nd ¹⁴⁵ in spike (blend2-2)	Intermediate result
$wy3$	(mol/kg)	9.7×10^{-6}	8.6×10^{-6}	Mass fraction Nd ¹⁴⁵ in spike (blend2-3)	Intermediate result
wy	(mol/kg)	9.7×10^{-6}	8.6×10^{-6}	Mean of mass fraction of Nd ¹⁴⁵ in spike	Intermediate result
$Rzy2_1$		0.9285	0.0153	Isotope ratio 142/145 in blend2-1	16.2%
$Rzy3_1$		0.9102	0.0141	Isotope ratio 142/145 in blend3-1	0.1%
Rx		2.3750	189×10^{-6}	Isotope ratio 142/145 in back-spike	0.0%
$Rxy1_1$		0.9034	8.78×10^{-3}	Isotope ratio 142/145 in blend1-1	13.6%
$Ry1$		0.7800	0.53	Isotope abundance ratio 142/145 in spike from blend1	Intermediate result
$Rzy2_2$		0.9811	0.0153	Isotope ratio 142/145 in blend2-2	21%
$Rzy3_2$		0.8671	0.0141	Isotope ratio 142/145 in blend3-2	3.3%
$Rxy1_2$		0.9331	8.78×10^{-3}	Isotope ratio 142/145 in blend1-2	15%
$Ry2$		-1.2	2.8	Isotope abundance ratio 142/145 in spike from blend2	Intermediate result
$Rzy2_3$		0.9492	0.0141	Isotope ratio 142/145 in blend2-3	24%
$Rzy3_3$		0.8686	0.0141	Isotope ratio 142/145 in blend3-3	12.3%
$Rxy1_3$		0.9126	8.78×10^{-3}	Isotope ratio 142/145 in blend1-3	14.6%
$Ry3$		-2.7	6.0	Isotope abundance ratio 142/145 in spike from blend3	Intermediate result

<i>Ry</i>		-0.1	2.2	Mean isotope abundance ratio 142/145 in spike	Intermediate result
ΣR_x		8.9767	2.6×10^{-6}	Total isotope ratio in IUPAC	0.0%
<i>nx1</i>		143×10^{-6}	4.4×10^{-6}	Element amount in sample, blend1	Intermediate result
<i>nx2</i>		148.8×10^{-6}	5.4×10^{-6}	Element amount in sample, blend2	Intermediate result
<i>nx3</i>		147.1×10^{-6}	5.0×10^{-6}	Element amount in sample, blend3	Intermediate result
<i>Max</i>	(g/mol)	106.4153	1.00×10^{-6}	Atomic weight of Nd (IUPAC Value)	0.0%
<i>Mx1</i>	(µg/kg)	15210	470	Element amount in solution, blend1	Intermediate result
<i>Mx2</i>	(µg/kg)	15830	570	Element amount in solution, blend2	Intermediate result
<i>Mx3</i>	(µg/kg)	15650	530	Element amount in solution, blend3	Intermediate result
<i>BLANK</i>		0.3492	0.0575	Isotope ratio of 142/145 in blank solution	0.0%
<i>wx1</i>	(mg/kg)	15.21	0.47	Mass fraction of Nd in sample (blend1-1)	Intermediate result
<i>wx2</i>	(mg/kg)	15.83	0.57	Mass fraction of Nd in sample (blend1-2)	Intermediate result
<i>wx3</i>	(mg/kg)	15.65	0.53	Mass fraction of Nd in sample (blend1-1)	Intermediate result
<i>wx</i>	(mg/kg)	15.57	0.37	Mean mass fraction of Nd in sample with expanded uncertainty (k=2)	-