Thermal Ionization Mass Spectrometry

(TIMS)

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Introduction

Thermal Ionization Mass Spectrometry (TIMS) is a powerful analytical technique used for precise measurements of isotope ratios, giving it applications in geochronology, nuclear forensics, and stable isotope analysis. The extreme precision achieved by TIMS is accomplished by having an extremely stable ion emission from the filament, allowing for very low uncertainty when measuring the intensity of the beam as well as calibrations using standards of known isotope ratios. However, the major advancement in accuracy and precision came when multiple ion beam collectors were implemented into the system as this greatly improves the percentage of ions collected, and reduces errors produced by instability in the beam that were impossible to correct for when only one collector was in use.

Although TIMS is exceedingly useful for determining isotopic ratios, which can be used in defining many characteristics about a sample, there are some drawbacks to the method. Sample preparation is labor intensive, often requiring many elemental separation and purification steps, and extreme diligence must be exercised in ensuring background contamination is accounted for and minimized. A limitation of any mass spectrometer, intrinsic to certain elements/systems, is isobaric interference which could only be overcome by increasing the resolving power in the MS, or the ability to separate ion beams based on their mass to charge ratio (Carlson, 2014).

History

The mass spectrometer has experienced many innovations since its introduction in 1913 by JJ Thomson and the foundations for modern TIMS had been laid out as early as 1918. Dempster built off Thomson's work and conducted a series of experiments aimed at enhancing the intensity and later, the resolving power of existing designs. By this time, most of the major components of a modern TIMS unit were already being used in a recognizable way. Dempster's description of his experimental setup included ion production across a filament, magnets that directed and separated the ions, a curved flight tube for the ions to traverse under high vacuum, and a conductive metal plate connected to a voltmeter to read the signal produced by the ion beam (Dempster, 1918).

In the years following Dempster's work, significant advancements were made in the field of mass spectrometry. The 1930s saw the development of the sector field mass spectrometer by Kenneth Bainbridge and later Alfred Neir, and the invention of the quadrupole mass spectrometer, important in the improvements of resolving power in later iterations, by Wolfgang Paul (De Laeter and Kurz, 2006; Paul and Steinwedel, 1954). These innovations greatly improved the resolution and sensitivity of mass spectrometry, paving the way for the development of TIMS.

The actual development of TIMS as a distinct technique began in the mid-20th century. Alfred Nier, a physicist at the University of Minnesota, is often credited with the development of the first TIMS instrument. Nier's design was capable of very high precision measurements, making it ideal for isotope ratio determinations (De Laeter and Kurz, 2006).

In the 1950s and 1960s, TIMS was further refined and became a standard method for the precise measurement of isotopic ratios, particularly in the fields of geology and cosmochemistry. The technique was predominantly used to determine the age of rocks and minerals, and to study the isotopic composition of meteorites. Eventually Claire C. Patterson determined the age of the earth at around 4.5×10^9 years by way of lead isotope analysis (Patterson, 1955)

The advent of solid-state electronics in the 1970s and 1980s led to further improvements in TIMS. The introduction of multi-collector systems allowed for simultaneous measurement of multiple isotopes, significantly increasing the speed and precision of analyses (White et. al., 2000).

In recent years, TIMS has continued to evolve with advancements in technology. Modern TIMS instruments are computer-controlled and equipped with sophisticated software for data acquisition and processing. Despite the development of other mass spectrometry techniques, TIMS remains a powerful tool for high-precision isotope ratio measurements (Carlson, 2014).

Theory

Thermal Ionization Mass Spectrometry is primarily used for high-precision measurement of isotope ratios. The isotopic ratios of radionuclides are used to get an accurate measurement for the elemental analysis of a sample (Griffiths, 2008). Most analyses done by TIMS look to determine the age, source, and/or history of the sample. However, occasionally it can be used to find environmental tracers or cross reference materials from across the planet (Kavasi and Sahoo, 2024).

Working Principle

In TIMS, singly charged ions of the sample are formed by the thermal ionization effect. A chemically purified liquid sample is placed on a metal filament which is then heated to evaporate the solvent. The filament is chosen based on the melting point of the metal, the analyte of interest, and cost. Filaments are made out of extremely pure samples and are most often made from the following elements; Re, Pt, W, Fe, Ni, and Au. The removal of an electron from the purified sample is achieved by heating the filament enough to release said electron, which then ionizes the atoms in the sample (Carlson, 2014).

TIMS utilizes a magnetic sector mass analyzer to separate the ions based on their mass to charge ratio. The ions gain velocity by an electrical potential gradient and are focused into a beam by electrostatic lenses. The ion beam then passes through the magnetic field of the electromagnet where it is partitioned into separate ion beams based on the ion's mass/charge ratio. These mass-resolved beams are directed into a detector where it is converted into voltage. The voltage detected is then used to calculate the isotopic ratio (Carlson, 2014).

Limitations

Despite its high precision and sensitivity, TIMS has several limitations. Not all elements are easily ionized, which restricts applications to elements with low ionization potential. Ionization is not equally efficient for all elements and is generally less than 1%. TIMS is only effective on metals, there are no applications for non-metals or noble gases. Additionally, mass fractionation may continually change with temperature throughout analysis. This can affect the accuracy and precision of the measurements but can be corrected by way of standards (Carlson, 2014).

While TIMS is a powerful tool for isotope ratio measurements, it is important to consider its limitations when interpreting the results. Understanding these limitations can help guide the selection of appropriate samples and elements for analysis and ensure the accuracy and precision of the data obtained.

Applications

The application of Thermal Ionization Mass Spectrometry (TIMS) spans a wide range of fields, as demonstrated by the following case studies:

1. **Measurement of ^{90}Sr and ^{87}Sr/^{86}Sr isotope ratio in Japanese cow milk sample using thermal ionization mass spectrometry**: This study by Kavasi and Sahoo (2024) demonstrates the use of TIMS in food chemistry. The researchers developed a rapid ^{90}Sr analysis protocol using TIMS for milk samples to track radiation from nuclear disasters in Japan. With improved sample preparation, 1 mL of milk with a minimal effective concentration of ^{90}Sr well below the standard of safety. Sr separation, and a newly developed TIMS method, they were able to analyze 18 milk samples in less than 30 hours. This study highlights the potential of TIMS in relatively rapid, when compared to other sample preparation procedures, and precise isotope ratio analysis in food samples, despite the normally associated challenges with sample preparation.
2. **184Os/188Os and 186Os/188Os measurements by Negative Thermal Ionization Mass Spectrometry (N-TIMS): Effects of interfering element and mass fractionation corrections on data accuracy and precision**: Luguet, Nowell, and Pearson (2008) conducted a detailed study of the effects of polyatomic interferences, mass fractionation, and correction procedures on the quality of Os isotope data obtained using the N-TIMS method. Their research highlights the importance of TIMS in geochemistry, particularly in the precise and accurate measurement of isotope ratios, and the ongoing need for methodological refinements to overcome analytical challenges that arise at the edge of our current understanding.
3. **Multi-step TIMS and CA-TIMS monazite U–Pb geochronology**: In this study, Peterman, Mattinson, and Hacker (2012) found that optimal TIMS results are provided by slow, partial dissolution of monazite in weak acid to remove exterior zones that may have

been altered in some way. This research showcases the versatility of TIMS in geochronology and the potential for methodological innovations to enhance data quality.

These case studies illustrate the broad applicability of TIMS in various fields, from food chemistry to geochemistry and geochronology. They also highlight the ongoing need for methodological advancements to overcome the inherent limitations of the technique and expand its utility.

Conclusion:

Thermal Ionization Mass Spectrometry (TIMS) has proven to be a robust and precise analytical technique, particularly in the fields of geochronology, nuclear forensics, and stable isotope analysis. The technique's strength lies in its ability to achieve extreme precision through stable ion emission from the filament and the use of standards for calibration. The implementation of multiple ion beam collectors has significantly enhanced the accuracy and precision of TIMS, improving ion collection and reducing errors caused by beam instability.

However, despite its strengths, TIMS is not without its limitations. The tedious and time-consuming nature of sample preparation, coupled with the cost of purchasing filaments, can be a deterrent. Furthermore, the technique is susceptible to isobaric interference, although this can be mitigated through careful sample preparation and analysis.

In optimal situations, TIMS is currently used when the precise measurement of isotope ratios is required, despite the challenges associated with sample preparation and potential isobaric interference. In the future, the technique holds promise for further applications as improvements continue to be made in overcoming its limitations. The exploration of methods to streamline sample preparation and reduce costs associated with filament purchase could broaden the accessibility and applicability of TIMS. Additionally, continued research into methods for overcoming isobaric interference and expanding elemental coverage could further enhance the technique's utility and precision. As such, the future of TIMS in geochemistry and other fields appears promising, with ample opportunities for continued refinement and application.

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