High-accuracy mass spectrometry for isotopic abundances

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Abstract

A measurement program was initiated at the National Bureau of Standards (USA) in 1957 to determine the isotopic abundance of the actinide elements with high accuracy. By 1960 it was apparent that high-accuracy isotopic abundance measurements could provide valuable support for a determination of the Faraday constant and the proposed unified atomic weight scale. Of particular interest was the long-term need for more accurate measurements to resolve differences between chemical and mass spectrometric atomic weight determinations as well as significant differences reported for mass spectrometric measurements on the same element. The methodology developed was based upon the integration of analytical chemistry and mass spectrometry into a single measurement process. Analytical chemistry was utilized to mix accurately known quantities of chemically and isotopically pure separated isotopes to produce standards of known isotopic abundance which were used to calibrate the mass spectrometers. Over a period of more than twenty years high accuracy measurements were made to certify the isotopic abundance of uranium and plutonium and to determine the atomic weight of 14 different elements. The uncertainties of these measurements were reported as overall limits of error at the 95% confidence level and represented the sum of uncertainty components for the ratio determination and the components covering effects of known sources of possible systematic error.

Introduction

From the infancy of mass spectrometry, as benchmarked by "positive ray analysis," instruments have been available to make the three types of measurements which are typically made on a modern mass spectrometer. These measurements may be generally classified as the determination of the relative masses of ions, the determination of relative isotopic abundances, and the study of ionization processes and basic phenomena. Highly accurate mass measurements were made early in the history of mass spectrometry by using either the elements, hydrocarbons, oxides or hydrides of the elements, or combinations of the above, to establish a mass scale. The accuracy of this type of measurement was validated long ago, and is widely accepted and recognized.

With respect to isotopic abundance measurements, the realization of high accuracy was a much slower, and perhaps even more tortuous process. Some of the lack of progress can be attributed to a long-standing perception that highly reproducible relative isotopic abundances were adequate, since there was only limited need for accuracies approaching 1 in 10^4. Another barrier to progress was the limited sensitivity of photographic plates and the early generation of electrical detection systems in characterizing and identifying effects which could bias isotopic abundance measurements by as much as several percent. Many of the measurements made between 1930 and 1960 for specific elements were perceived as self-consistent, although the overall or expanded uncertainties of the measurements were large (several percent) and did not overlap. The practice of reporting only an estimate of the random component of the uncertainty, rather than completely characterizing all known sources of uncertainty and relevant influence factors contributed to the perception that certain types of mass spectrometers were absolute measuring devices. In particular, surface and thermal ionization mass spectrometers were perceived as absolute measuring devices until a series of measurements at the US National Bureau of Standards (NBS; National Institute of Standards and Technology (NIST) since 1988) in the early sixties provided reasonable and credible scientific evidence that isotopic fractionation in the ion source was an effect which had to be evaluated for each element and set of measurement conditions. As the general knowledge of analytical mass spectrometry improved, it was indeed clear that calibration was necessary and essential, if overall or expanded uncertainties approaching 1 in 10^4 were to be realized.

The need for high accuracy

With the advent of the "atomic/nuclear age," there was an immediate and undeniable driving force to realize high accuracy isotopic abundance measurements. It was well recognized that the numerous working standards and reference samples required for the development and application of nuclear energy would have to be underpinned by a smaller number of well characterized Certified Reference Materials (CRMs) and Reference Materials (RMs). From an economic and security point of view, the need for measurement standards was crystal clear in the accounting, control, lease, sale and use of both unprocessed nuclear materials and processed special nuclear materials for defense and non-defense applications. Because of the national and international use of nuclear technologies, a comprehensive system of CRMs and RMs was proposed to link the variety of mass spectrometers and other instruments characterizing the materials produced by

either production or experimental processes to common reference points. In recognition of the needs of the nuclear industry, and at the request of the US Atomic Energy Commission, the NBS established a uranium isotopic standards program in 1957. Although the principal focus of the program was uranium, plutonium, and other actinides, the knowledge gained and the lessons learned would impact an NBS atomic weight program which emerged just a few years later, and thrived for more than two decades.

Another driving force creating a favorable climate and giving impetus to advances in isotopic abundance measurements was the development and adoption of a unified atomic weight scale. Prior to 1961, two scales were in common use for the reporting of atomic weights. These were designated as the chemical scale, where the natural mixture of oxygen was taken as equal to 16 and the physical scale, where ^{16}O was equal to 16. Effective as of 1961, a new unified atomic weight scale based upon 12 as the assigned atomic mass of ^{12}C was adopted. Values on the chemical scale and the physical scale were systematically reduced by 43 parts per million and 318 parts per million, respectively, to correspond to the ^{12}C scale. All of these changes were included in the 1961 International Table of Relative Atomic Weights which was based on a comprehensive and thorough review of experimental data and evidence reported between 1925 and 1961. At the beginning of this period, atomic weights were determined exclusively by chemical methods. However, by 1961 practically all new values were determined by mass spectrometry. The mass spectrometric values were, with but few exceptions, based on relative isotopic abundances rather than mea-

Figure 1. Analytical methodology for high accuracy isotopic abundance.

surements calibrated for the effects of bias in the mass spectrometry. Consequently, there was a critical need for new data and, if at all possible, calibrated or "absolute" measurements to resolve the differences in mass spectrometric data reported for the same element, as well as discrepancies between chemical and mass spectrometric determinations of atomic weights.

Transition to atomic weights determined by mass spectrometry

Having played a significant role in the adoption of the unified atomic weight scale, and having exercised a similar role in the review process leading to the 1961 International Table of Relative Atomic Weights, NBS had great interest in redetermining the atomic weights of key elements. In particular, the focus was on those elements which could be used to assess the accuracy of many of the chemically determined atomic weights. In fact, NBS had a long and distinguished history of research on the atomic weights of the elements. Noyes (1907) reported the first of these measurements, a value of 1.00783 for the atomic weight of hydrogen based on the classical method of the electrolysis of water. Very shortly thereafter, Noyes & Weber (1907) reported the atomic weight of chlorine. This was of particular importance since contemporary work at Harvard on the ratio of silver to chlorine had led to the determination of the atomic weights of a number of elements based on the atomic weight of chlorine. The work on chlorine was followed a few years later by Weber's (1913) publication reporting the atomic weight of bromine. Between 1913 and 1959, work on the atomic weight of a variety of elements was conducted using classical chemical methods. In 1959, NBS was on the verge of starting a program which would within 5 years result in the atomic weights of silver (Shields *et al.* 1960), chlorine (Shields *et al.* 1962), and bromine (Catanzaro *et al.* 1964). The analytical methodology was based upon the use of isotopic standards of known composition which were prepared by gravimetrically blending chemically pure and very nearly isotopically pure separated isotopes of the elements.

The significant event that moved NBS away from a narrow focus on the isotopic abundances of uranium and plutonium to other elements of the periodic table was a broad based program in science to improve our knowledge of the fundamental constants. High accuracy determinations of the Faraday constant were of particular interest because of its relationship to Avogadro's constant. Historically, the Faraday was determined by reacting a pure substance electrolytically with an assumed efficiency of 100%. While the electrochemical data of the time were evaluated as self-consistent, they did not agree as well as needed with the Faraday calculated by combining other fundamental constants. In an effort to bring some clarity to this situation, Craig *et al.* (1960) conducted experiments leading to a determination of the electro-chemical equivalent of high purity silver and a value for the Faraday using a silver perchloric acid coulometer. The work of Craig and his coworkers had critical implications for Avogadro's constant, the Faraday constant and the atomic weights of a number of elements as determined chemically by their combining
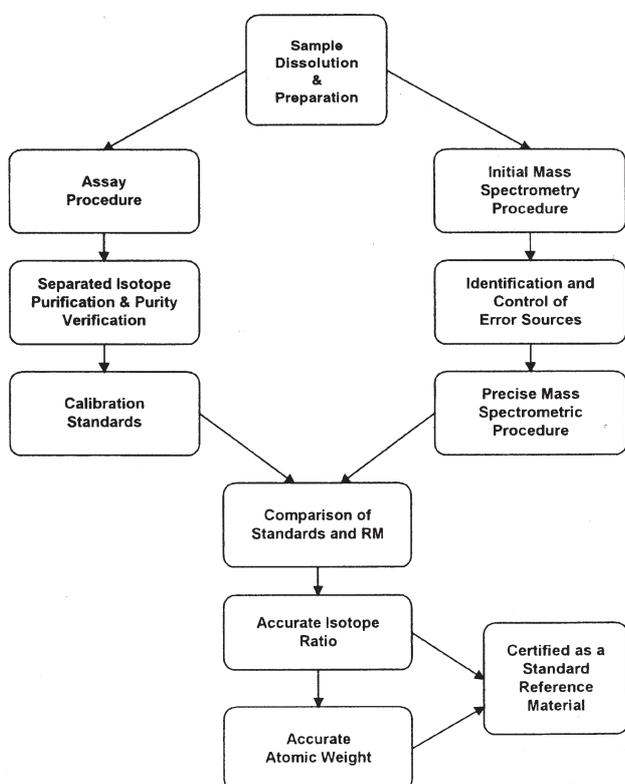
weight ratios. The initial task for mass spectrometry at NBS was to give assurance that the process used to purify the silver for Craig's measurements had not produced either an isotopically enriched or depleted high-purity silver sample. Because mass spectrometry gave credible evidence that some enrichment of the light isotope did occur, it was deemed necessary to do the following;

(1) establish the absolute isotopic abundance of silver used in the electrochemical determination of the Faraday;

(2) establish limits for natural isotopic variations of silver; and

(3) shed some light on the nearly 8% range in mass spectrometric data reported between 1948 and 1959. At the conclusion of these measurements, the extension of the program to the atomic weights of chlorine, bromine and other elements was an obvious outcome.

The methodology for high accuracy

By 1960, all of the essential and critical technologies for high accuracy were in place and tested. The nuclear community had served as a great incubator for analytical chemistry, mass spectrometry and instrumentation advances. The proof of principle in blending highly enriched separated isotopes to produce standards of known isotopic abundance had been conclusively and routinely demonstrated at uranium diffusion plants where mass spectrometers equipped with electron impact ion sources had made measurements with expanded uncertainties between 5 in 10^4 and 2 in 10^4. The most critical technology for the development of high accuracy uranium isotopic abundance measurements was the availability of relatively large amounts (kilograms) of highly enriched separated isotopes of uranium. The electromagnetic separation technology which produced these nuclear materials also resulted in the availability of economically affordable, but in some cases still very expensive, highly enriched and chemically pure separated isotopes of many other elements. These separated isotopes were the key ingredient for preparing standards of known isotopic abundance to calibrate mass spectrometers for the effect of bias for a wide range of elements other than those of critical and immediate importance to the nuclear industry.

The methodology to determine the isotopic abundance of an element with high accuracy (Fig 1) is in fact a combination of analytical chemistry and mass spectrometry. The least recognized, and perhaps least appreciated component, is the analytical chemistry. The ultimate products from the analytical chemistry are;

(1) a high purity Reference Material to be calibrated, and

(2) a series of "calibration standards" with known isotopic ratios covering the range of isotopic ratios of the Reference Material to be characterized.

The critical components and potential sources of uncertainty in the analytical chemistry are sample dissolution, stoichiometry, chemical purification, interfering ions, gravimetry and high precision assay of the separated

isotope solutions for the analyte element. Using gravimetric procedures, weighed aliquots of the separated isotope solutions are blended to produce the calibration standards. Knowing the assay or concentration of the analyte element in the separated isotope solutions, the weight of aliquots blended to produce the standards, and the composition of the separated isotopes from mass spectrometric analysis, the isotopic abundance of the calibration standards can be calculated. Ideally, it is desirable to know the calibration standards with an expanded uncertainty of 1 in 10^5. More realistically, the uncertainty contribution from the calibration standards was 1 to 2 in 10^4.

Mass spectrometry instrumentation and procedures

For most of the high-accuracy work at NBS, solid sample, thermal or surface ionization mass spectrometers were used. A notable exception was by Barnes *et al.* (1975) for the isotopic abundance of a reference sample of high purity silicon by electron impact ionization of a gaseous sample. The other notable exception was the use by Gramlich *et al.* (1973) of a double magnetic stage instrument arranged in an "S" configuration and equipped for pulse counting detection. For the atomic weight determination of nickel by Gramlich *et al.* (1989), a commercially designed multicollector instrument was used. Otherwise, all mass spectrometers were single focussing, magnetic sector instruments, either 15 cm or 30 cm radius of curvature, and/or 60°, 68°, or 90° sectors. These instruments (Shields *et al.* 1967) were equipped with interchangeable and nearly identical electronic components, the same basic design of a multi-element, deep-bucket Faraday cup collector, and either a standard Nier type ion source (prior to 1964) or a thin lens "z" focussing ion source (after 1964).

Mass spectrometric procedures for all elements were based upon:

(1) a knowledge of the sources of uncertainty in the measurement process;

(2) control of the parameters and influence factors which could contribute to the uncertainty or bias the measurement;

(3) identifying and selecting the critical analytical parameters; and

(4) establishing an acceptable tolerance specification for each parameter which would be the same for all analyses.

Because of isotopic fractionation effects in the ion source of a thermal ionization mass spectrometer, it was critical to develop a methodology which yielded precisely the same isotopic fractionation pattern for each analysis. The goal was to quantify the correction for this effect as an experimentally determined constant which was unique for the analytical conditions of the measurement. In general, three types of isotopic fractionation trends or patterns were observed for the ratio of the lighter to heavier isotope of an element:

(1) constant and non-changing with time;

(2) decreasing with time; and

(3) increasing with time.

For some elements and matrices, all three patterns could be observed in the same analysis. By controlling the time base for each analysis and the other critical parameters of the measurement process, it could be demonstrated that the same correction for isotopic fractionation could be applied to each analysis. In addition to isotopic fractionation, it was necessary and essential to characterize the effect of secondary electrons in the collector as well as non-linear effects in the entire measuring system. Complete characterization of the measurement uncertainty from the mass spectrometry included an evaluation of possible sources of uncertainty, influence factors and suspected influence factors in the sample handling system, the ion source, analyzer, ion detector, and the data handling system. A graphic representation of the general scheme used to completely characterize the uncertainty is shown in (Fig 2), including an allowance for the use of judgment-based limits. Knowledge of influence factors and suspected influence factors was integrated into the measurement process as a modification or refinement of control procedures or specifications for control of a parameter.
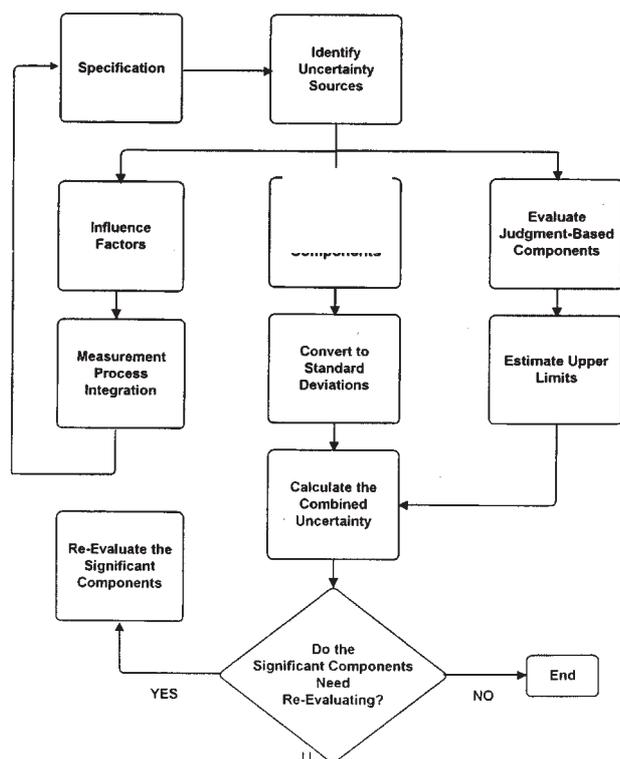
Figure 2. Characterization of measurement uncertainty.

Results

Atomic weight determinations, certification of the isotopic abundances of uranium and plutonium, and trace element analysis by isotope dilution mass spectrometry were the broad areas where high accuracy isotopic abundance measurements were made at NBS from 1960 to 1985. The scope of this paper does not permit full attention to either of these areas, so atomic weights will be used as the prime example. During the period in question, the atomic weights of 14 different elements were determined. These measurements included; silver (Shields *et al.* 1960); chlorine (Shields *et al.* 1962); copper (Shields *et al.* 1964); bromine (Catanzaro *et al.* 1964); chromium (Shields et al. 1966); magnesium (Catanzaro *et al.* 1966); lead (Catanzaro *et al.* 1968); rubidium (Catanzaro *et al.* 1969); boron (Catanzaro *et al.* 1970); rhenium (Gramlich *et al.* 1973); silicon (Barnes *et al.* 1975); potassium (Garner *et al.* 1975); Thallium (Dunstan *et al.* 1980); silver (Powell *et al.* 1981) and strontium (Moore *et. al.* 1982). After the period in question, the absolute isotopic abundance ratios and the atomic weight of gallium (Machlan *et al.* 1986) and nickel (Gramlich *et al.* 1989) were reported. The absolute isotopic abundance ratios for a representative number of these elements are shown in Table 1.

Table 1.

Absolute isotopic abundance ratios by thermal ionization mass spectrometry.

Element	Year	Ratio	Value
Ag	1960	107Ag/109Ag	1.0755 ± 0.0013
Ag	1961	107Ag/109Ag	1.07597 ± 0.00135
Br	1964	79Br/81Br	1.02784 ± 0.00190
Cu	1964	63Cu/65Cu	2.2440 ± 0.0021
Rb	1969	85Rb/87Rb	2.59265 ± 0.00170
Re	1973	185Re/187Re	0.59738 ± 0.00039
Tl	1979	205Tl/203Tl	2.38714 ± 0.00101
Ag	1981	107Ag/109Ag	1.07638 ± 0.00022

The uncertainty of an isotopic ratio was reported as an overall limit of error and was determined by summing the 95% confidence limits of the uncertainty components. The overall or expanded uncertainty of the measurement included terms to cover random effects as well as possible systematic error. Each overall or expanded uncertainty included a random component for the "mass spectrometric analytical error," a component for "possible systematic error in composition of separated isotopes," and a component for "possible systematic error in chemical analysis." The only notable exception was the atomic weight of silver by Shields *et al.* (1960) which included a component for nuclidic masses, since at that time it was not clear as to whether the unified atomic weight scale would be adopted. Because rounding-off could have impact on the atomic weight calculation, most ratios were reported to one figure beyond significance.

While there is some uniqueness about each of the measurements in the atomic weight series, silver is considered in a separate niche because;

(1) it had the distinction of being the "pathfinder element" (Shields *et al.* 1960) of the series;

(2) the only element for which additional measurements were made and data published beyond the original measurements (Shields *et al.* 1961); and

(3) the only element for which a completely independent redetermination was made by a different team of scientists (Powell et al. 1981).

In addition, silver was the only element for which the expanded uncertainty was perceived to be very near the limits achievable with the instrumentation, analytical chemistry and measurement process then developed.

Discussion

The single unifying concept which brought together the critical elements of analytical chemistry and mass spectrometry to yield high accuracy isotopic abundance measurements was the concept of measurements as a process. Pontius & Cameron (1967) first documented this concept in describing mass measurements as a production process. A fundamental assumption of this concept is that measurement is analogous to a production or manufacturing process. When a production process is in a state of control, the product is uniform and reproducible, reflecting the degree of control of the process. Analogous to the industrial production process, the product of an isotopic abundance measurement process is an isotopic ratio. When the entire process is in a state of statistical control, the associated uncertainty of the process is valid and predictable. When the measurement process is out of statistical control, predictability is lost and the uncertainty of the measurement under control conditions is not applicable to the out-of-control condition.

In conjunction with measurement as a process, the concept of measurement assurance was the other general principle which underpinned the pathway to high accuracy isotopic abundance measurements. This process was perceived and implemented as a continuous improvement process. The technique for mass spectrometry included but was not limited to;

(1) the use of sound experimental design principles so that the entire measurement process, its components and relevant influencing factors could be well characterized, monitored and controlled;

(2) complete experimental characterization of the uncertainty for the measurement process to include statistical variations, contributions from all known or suspected influence factors, imported uncertainties, judgment based components, and the propagation of uncertainties throughout the measurement process; and

(3) continuously monitoring the performance and state of control of the complete measurement process, both analytical chemistry and mass spectrometry, with locally tested and proven quality control or process control techniques to include the measurement of stable isotopic abundance check standards along with the normal workload.

The state of statistical control observed for an element did not preclude the measurement assurance requirement to continuously monitor, control, and evaluate the process. After completion of a unique or distinct set of measurements such as an atomic weight determination, then it was appropriate to study, evaluate, test and experiment with the measurement process. The results and findings would then become the basis for changing, improving, redesigning or even developing a substantially different process. After the next set of unique or distinct measurements the cycle was repeated. Where applicable, knowledge gained about one element was utilized in developing and evaluating the measurement process for other elements.

Perhaps the best illustration of the value of a sound measurement assurance program was the first attempt to determine the atomic weight of bromine in 1962. An independent, third-party statistical analysis of the data, a practice which was followed in all of the high accuracy isotopic measurements, revealed an out-of-control statistical condition during the preparation of the calibration mixes. Re-evaluation of the analytical chemistry revealed that the separated isotopes were not blended over a short time span of hours but a period of several days. As a result the isotopic abundances of the calibration standards were dependent on the time of mixing and it was necessary to void the entire set of isotope ratio measurements. This hard-earned lesson became a cornerstone of the methodology for all future measurements in which solutions were blended to prepare calibration mixes or to perform isotope dilution.

Summary

The products of isotopic abundance mass spectrometry are the value for the abundance ratio(s) and the uncertainty associated with the ratio. Initial isotopic ratio measurements by thermal ionization mass spectrometry at NBS between 1958 and 1960 were made with an expanded uncertainty of 2% over the ratio range 1:20 to 20:1. With major developments and improvements in instrumentation and measurement process, the expanded uncertainty was reduced to 0.5% for the ratio range 1:100 to 100:1. The breakthrough to an expanded uncertainty of 1 or 2 in 10^4 as a realistic limit for high accuracy isotopic abundance measurements by thermal ionization mass spectrometry occurred when it was realized that the best strip chart recorders available were a limiting factor. When performing to manufacturer's specification, strip chart recorders measured a full scale output signal to ± 0.5 %. By modifying the strip chart recorder to operate in an expanded scale measuring mode, the contribution to the uncertainty of the measurement was reduced by a factor of 10. With improvements in the measurement process and the advent of digital measurement systems, the ultimate accuracy for thermal ionization mass spectrometry was realized for the determination of the atomic weight of silver (Powell *et al.* 1981).

In looking at the future from a 1995 perspective, the potential for ultra high accuracy measurements of 1 in 10^5 is still over the horizon. Assuming ideal conditions of equal atom ratio measurements, ultra high enriched separated isotopes of 99.9999%, highly reproducible isotopic fractionation, and ideal ion current intensities, ultra high accuracy is not a practical goal without major breakthroughs or different approaches in the analytical chemistry and mass spectrometry.

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