The Atomic Weights of the Elements: Review 2000 (IUPAC Technical Report)

J. R. de Laeter, J. K. Böhlke, P. De Bièvre, H. Hidaka, H. S. Peiser, K. J. R. Rosman, and P. D. P. Taylor

Pure and Applied Chemistry
Vol. 75, No. 6, pp. 683–799 (2003)

A consistent set of internationally accepted atomic weights is an essential aim of the scientific community because of the relevance of these values to science, technology, and commerce. Accurate determinations of the atomic weights of certain elements also influence the values of fundamental constants such as the Avogadro, Faraday, and Universal Gas constants.

Various committees or commissions have held responsibility for evaluating and recommending atomic weights of the elements since the late 19th century. This responsibility has resided with IUPAC since it was constituted in 1920. For the last several decades, the Commission on Atomic Weights and Isotopic Abundances (CAWIA) has published updated tables of recommended ("standard") atomic weights and their uncertainties in *PAC* approximately every two years. In *The Atomic Weights of the Elements: Review 2000*, members of CAWIA provide a comprehensive overview of this process in two parts. In the first part, the concept of standard atomic weights, the methods used to determine them, and the basis for making changes are described in a historical review covering the 20th century. In the second part, a detailed summary is provided for each element describing CAWIA decisions that have lead to changes in that element's standard atomic weight and its uncertainty since the 1960s.

Atomic weights were once considered to be constants of nature and were determined by mass-ratio measurements coupled with an understanding of chemical stoichiometry, but they are now based almost exclusively on knowledge of the isotopic composition (derived from isotope-abundance ratio measurements) and the atomic masses of the isotopes of the elements. Technological advances in mass spectrometry and nuclear-reaction energies have permitted measurements of atomic masses with a relative uncertainty of better than 1×10^{-7} and of isotope-abundance ratios of better than 1×10^{-3} in many cases. The improving accuracy and precision of such measurements led to the discovery that many elements exhibit variation in their isotope-abundance ratios (and atomic weights) in different specimens. These variations are caused by a variety of physicochemical and biochemical processes in both natural and industrial systems, place severe constraints on the uncertainties with which some standard atomic weights can be stated, and were once considered a hindrance to the accuracy of chemical measurements. Subsequently, however, these variations have been recognized as powerful tools for investigating important phenomena in physics, chemistry, biology, cosmology, geology, archeology, industry, forensics, and many other fields of study. *The Atomic Weights of the Elements: Review 2000* documents the evolution of two major perspectives in atomic-weight science during the 20th century: increasingly precise measurements of isotope-abundance ratios and atomic weights with ties to the SI (metrology), and discovery and application of isotope-abundance variations in science and technology.

www.iupac.org/publications/pac/2003/7506/7506x0683.html

Critical Review of Analytical Applications of Mössbauer Spectroscopy Illustrated by Mineralogical and Geological Examples (IUPAC Technical Report)

E. Kuzmann, S. Nagy, and A. Vértes

Pure and Applied Chemistry
Vol. 75, No. 6, pp. 801–858 (2003)

A new terminology for Mössbauer pattern analysis has been developed in order to enhance the performance of qualitative analysis by Mössbauer spectroscopy. Mössbauer parameters are considered as a function of a number of externally adjusted experimental parameters at which the spectrum has been recorded. The basis of analytical classification is the microenvironment, which is determined by an assembly of atoms causing the same hyperfine interactions of one particular class of Mössbauer probe atoms. Since Mössbauer spectroscopy measures hyperfine interactions very sensitively, the microenvironment presents itself as a fundamental concept for analytical purposes.

The basic task of any qualitative analysis based on Mössbauer spectroscopy is to identify the individual physical or chemical species from the corresponding patterns present in the spectrum. Ideally, this can be

done if we know the exact correspondence between patterns and species. Such a one-to-one correspondence between species of atoms and individual patterns, however, can be nonexistent for the given set of externally adjusted physical parameters at which the Mössbauer spectrum is recorded. For this reason it is useful to consider all the Mössbauer parameters (P) as a function of a number of externally adjustable physical quantities such as temperature (T), pressure (p), external magnetic field (H), polar angles (Θ,Φ), frequency of high-frequency field (ν), etc.

$$P = P\,(T,p,H,\Theta,\Phi,\nu,\ldots)$$

However, when the whole range of these parameters is considered, we may find points in the space of parameters at which only one pattern is associated with one species and vice versa and thus we can get around the problem of ambiguity.

From the analytical point of view we can introduce useful terminology classifying Mössbauer patterns. A **spontaneous pattern** is a Mössbauer spectrum measured at a given set of externally adjusted parameters (usually under standard conditions). The spontaneous pattern can be either a simple spectrum called an **elementary pattern**, reflecting only a hyperfine interaction at one particular microenvironment or a complex spectrum called **superimposed pattern**, which consists of a number of subspectra. Here we refer to a family of Mössbauer nuclei experiencing the same hyperfine interaction as a **microenvironment**. An **induced pattern** is a Mössbauer spectrum obtained under conditions other than the (mostly standard) ones selected for measuring the spontaneous pattern. In this case, the differences between the induced and spontaneous pattern can provide an important contribution to the analysis. The **transformed pattern** is obtained from the measured Mössbauer spectrum by mathematical transformation (e.g., by Fourier transformation). The magnetic hyperfine field distribution and the quadruple splitting distribution are transformed patterns. The transformed pattern can give a better resolution for the analysis.

Our approach can also contribute to the systematization of Mössbauer data for the identification of individual physical or chemical species from the corresponding patterns present in the spectrum. This new concept can also be generally applied on the field of analytical methods other than Mössbauer spectroscopy, and examples in the field of mineralogy and geology are included.

www.iupac.org/publications/pac/2003/7506/7506x0801.html

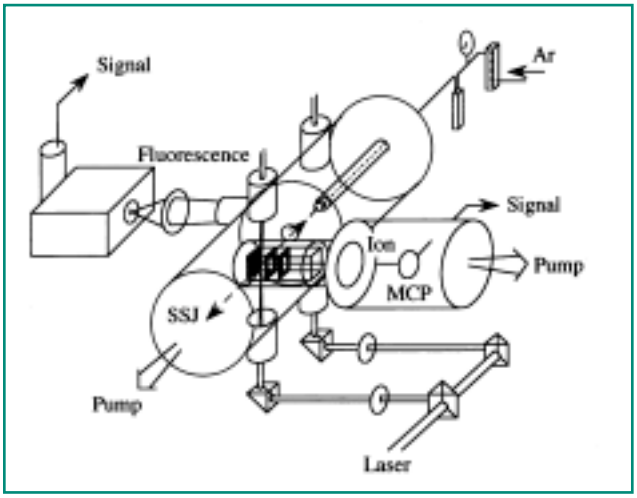
Critical Assessment: Use of Supersonic Jet Spectrometry for Complex Mixture Analysis (IUPAC Technical Report)

T. Imasaka, D. S. Moore, and T. Vo-Dinh

Pure and Applied Chemistry
Vol. 75, No.7, pp. 975–991 (2003)

Numerous chemical substances are present in an authentic sample. Therefore, it is necessary to develop an analytical instrument with high selectivity. However, absorption or excitation/fluorescence spectrometry currently used for analysis of the sample in the condensed phase at room temperature provides a broad band in the spectrum. Therefore, it is difficult to apply it to complex mixture analysis.

When the analyte molecule is cooled to a temperature of a few K using supersonic jet expansion into a vacuum, a molecule exists in the lowest vibrational level of the ground electronic state and is isolated at collision-free conditions. The absorption or excitation/fluorescence spectrum is then greatly simplified when transitions occur from this single vibrational level to a limited number of vibrational levels in the excited electronic state. This method, called supersonic jet spectrometry, is a powerful analytical technique because of its high selectivity, since the chemical species can be accurately identified and



A typical analytical instrument for supersonic jet spectrometry, which allows detection by fluorescence excitation /emission and multiphoton ionization/mass spectrometries simultaneously. Source: T. Imasaka, M. Hozumi, N. Ishibashi. Anal. Chem. *64, 2206 (1992).*