Abstract

Theodore W. Richards Redux: Determining Isotope Ratios without Mass Spectrometers

The first American scientist to win the Nobel Prize in Chemistry was Professor Theodore W. Richards, Harvard University, who was honored “in recognition of his accurate determinations of the atomic weight of a large number of chemical elements.” Richards’ painstaking, careful investigations led to highly accurate atomic weights of more than 20 elements, determined in many cases to five significant figures. Richards thought that the atomic weights of the light elements were immutable constants, like the numerical values of e and π but his work on lead from different sources, radioactive and non-radioactive, helped to confirm the existence of isotopes. To quote from his 1914 Journal of the American Chemical Society article[2] “In this paper a description is given of parallel experiments determining the equivalent weights of various samples of lead chloride obtained from different sources. It was found that all of the radioactive specimens possess a lower atomic weight than ordinary lead, as determined under identical conditions, the deficiency in one case amounting to as much as 0.75 of a unit.” Since then, different isotopes, stable and radioactive, have been established to exist for all the elements. Mass spectrometers have been used to determine the most precise values of isotopic weights, abundances, and ratios, but such devices are large, costly, and require operation by experts. In this lecture, I will describe a different approach based on isotopic shifts in the infrared spectra of small molecules. Using the relatively new absorption technique of cavity ringdown spectroscopy, it is possible to measure the isotopic ratio of a few common elements with a precision that rivals that of mass spectrometry.[2,3] Moreover, a cavity ring-down spectrometer can be constructed that is robust, portable, inexpensive, and can run for months without calibration or maintenance. This advance opens the possibility of much more widespread applications of isotope ratio analysis for understanding the origins and provenances of chemical compounds — from geological and atmospheric to agricultural and medical samples.

1. T. W. Richards and M. E. Lembert, “The Atomic Weight of Lead of Radioactive Origin,” *J. Am. Chem. Soc*. **36**, 1329-1344 (1914).

2. E. R. Crosson, K. N. Ricci, B. A. Richman, F. C. Chilese, T. G. Owano, R. A. Provencal, M. W. Todd, J. Glasser, A. A. Kachanov, B. A. Paldus, T. G. Spence, and R. N. Zare, “Stable Isotope Ratios Using Cavity Ring-Down Spectroscopy: Determination of $^{13}C/^{12}C$ for Carbon Dioxide in Human Breath,” *Anal Chem*. **74**, 2003-2007 (2002).

3. R. N. Zare, D. S. Kuramoto, C. Haase, S. M. Tan, E. R. Crosson, and N. M. R. Saad, “High-Precision Optical Measurements of $^{13}C/^{12}C$ Isotope Ratios in Organic Compounds at Natural Abundance,” *Proc. Natl. Acad. Sci*. (USA) **106**, 10928-10932 (2009).