Water-Quality Principles
QW1022–TEL

Lesson 6—Trace Elements

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Hem, J.D., 1995, Study and interpretation of the chemical characteristics of natural water: U.S. Geological Survey Water Supply Paper 2254, p. 129–130.

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Minor and Trace Constituents (p. 129)

The terms "minor" and "trace" used in reference to solutes in natural water cannot be precisely defined. Commonly, the terms are used for substances tht always or nearly always occur in concentrations less than 1.0 mg/L. Although it is reasonable to suppose that all the naturally occurring elements are present in most natural waters, the sensitivity of most analytical procedures is not adequate to detect those present at concentrations much below 1.0 or 0.1 μg/L.

The crustal abundances of elements listed in table 1 have a range of some eight orders of magnitude. The concentrations of solutes in water analyses given in this book cover a similar range—from hundreds of thousands of milligrams per liter to less than 0.01 mg/L (10 μg/L). However, the element with lowest reported concentration in water in many of the analyses is iron—the third most

abundant in igneous rock. This emphasizes the fact that chemical properties can be more important in controlling concentrations of an element in water than its availability, suggested by average abundance in rocks. Elements that are rare to begin with, and that tend to form compounds of low aqueous solubility, may thus be expected to occur in the nanogram- or picogram-per-liter concentration ranges. For some elements, detection at these levels is possible by mass spectrometry or by radiochemical techniques; for most inorganic constituents, however, the analytical detection limit is above 0.10 μg/L when conventional instrumental and wet chemical procedures are used. Hydrogen ion activity (pH) is measurable over a range of some 14 orders of magnitude. It represents a special type of solute that is not considered in this section.

Specific organic compounds, mostly manmade, related to waste disposal, water treatment, and environmental pollution have received considerable recent attention, and techniques exist and are being developed for detecting these at extremely low levels in water.

The history of research on minor constituents of natural water is punctuated by discoveries that some supposedly insignificant trace constituent was actually or potentially of vital importance to human health, plant nutrition, or other areas of general interest. Some of these discoveries have already been cited—for example, the relation of fluoride concentration in drinking water to the occurrence of tooth decay was discovered in the 1930's, and prior to that time fluoride concentrations in water were rarely determined. Other discoveries relating to minor constituents can be expected in the future, as more is learned about their occurrence and importance. Elements that have recently received special attention include mercury, lead, and selenium.

Availability of Analytical Data

Much of the improvement in sensitivity of determinations of minor metals and metaloid elements in water has stemmed from improved spectroscopic instruments. The emission spectrograph measures the intensity of light emitted at the specific wavelengths characteristic of each element when it is heated to a very high temperature. This information is interpretable in terms of concentration in the sample when the instrument is calibrated with a standard of known composition. Many of the trace-element data for water obtained prior to about 1960 were obtained with a type of spectrograph in which the residue from a dehydrated sample was vaporized in an electric arc. This technique was not altogether convenient, nor highly accurate for water samples and was partly supplanted by flame photometry in which a portion of the water sample was atomized directly into a high-temperature gas flame and the intensity of emitted light measured at the desired wavelength. Instruments available before about 1970 were of limited value because the temperature of the flame was not high enough to give good sensitivity for more than a few elements.

During the 1960's the atomic-absorption flame photometer became the most widely used instrument for determination of dissolved metals. In this device the absorption of light energy at certain wavelengths by the sample vaporized in the gas flame was measured. This principle gives a greatly enhanced sensitivity for most elements and a much better freedom from interferences. The atomic-absorption procedure also was adaptable to samples vaporized by heating in other ways, which permits a longer optical path and further enhancement in sensitivity. In the later 1970's improved emission spectrographs lowered detection limits for some elements even more. These instruments vaporize the sample in a high temperature plasma. Optical methods of these kinds have provided much of the information on minor element composition of natural water that has become available in the past two decades.

The high sensitivity of radiochemical techniques has been mentioned. Induced radioactivity can be imparted by exposing the sample to a neutron flux. The neutron-activation technique has some unique capabilities, and the literature contains many papers on the subject. However, there are some problems in applying this procedure to the determination of trace constituents in water, and it has not been used widely for this purpose.

The principal tool used for low-level organic analysis has been the gas chromatograph, which has been refined to a very high degree by the use of a mass spectrograph as the readout device to determine the composition of the chromatographic fractions. The mass spectrograph determines relative amounts of atoms of the same mass present in the sample. This instrument, of course, can also be used in inorganic analysis.

Other methods used in trace-element analysis include wet chemical and instrumental methods, such as ultraviolet fluorescence and other forms of spectrophotometry, and various forms of polarography. Regardless of the methodology used, the accuracy of data obtained also depends critically on the care used in sample collection, pretreatment, and preservation.

Sample Collection and Treatment

If proper care is not taken to avoid sample contamination or loss of the minor constituents during manipulation, misleading results will be obtained. Any analyst familiar with minor-element analysis is aware of these problems. Water samples for minor-element analysis are usually acidified after collection to minimize loss of metals by adsorption on container walls. If the container is not carefully cleaned or the acid used is impure, contamination results.