

WATER
and WATER
POLLUTION
HANDBOOK

volume **4**

edited by **LEONARD L. CIACCIO**

Water and Water Pollution Handbook

VOLUME 4

Edited by **LEONARD L. CIACCIO**

SCHOOL OF THEORETICAL AND APPLIED SCIENCE
RAMAPO COLLEGE OF NEW JERSEY
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I. Introduction

It is the purpose of this chapter to provide the reader with an insight into a number of the analytical techniques available for the determination

of minor constituents in samples. For purposes of this discussion a minor constituent is considered as any element present in the concentration range between about 100 parts per million and a few per cent. Almost without exception, any analytical technique applicable to the determination of trace constituents will also be applicable to minor element analysis. In addition, trace elements in relatively large samples often can be raised to the minor level by chemical treatment or concentration. Techniques for performing these operations are adequately covered elsewhere in this handbook.

It is obvious that most analytical techniques would therefore be applicable in the concentration range of interest. It would not be possible to cover all techniques within the limits of a single chapter. Consequently, the authors have selected those methods which they feel would be most useful in the determination of minor elements in water samples and which are not covered elsewhere in the book. For this latter reason electrochemical techniques and fluorimetric and spectrophotometric methods are not treated.

The methods to be discussed include flame emission and absorption spectroscopy, atomic fluorescence spectroscopy, emission and X-ray spectroscopy, and activation analysis. Extensive reviews of the applications of each of these methods to water analysis can be found in the annual reviews of the *Journal of the Water Pollution Control Federation* and in the biannual reviews on water analysis which appear in odd years in *Analytical Chemistry*. Since these reviews are extensive and up to date, no attempt is made to duplicate them here. Rather, the general principles of each method are presented along with a discussion of their utility and range of application to allow those not intimately connected with their use to make a judicious selection of the method best suited to a particular problem.

II. Flame Spectrometric Methods

A. Introduction

All flame spectrometric methods involve aspiration of a solution into a flame where the solvent evaporates leaving solute particles. Vaporization and decomposition of the solute particles result in the production of atoms. A portion of these atoms may be raised to an excited state by the thermal energy of the flame. Measurement of the radiation emitted as these atoms return to the ground state is the basis of flame emission

spectroscopy. The ability of the unexcited or ground state atoms in the flame to absorb radiation of a characteristic wavelength is the basis of atomic absorption spectroscopy. The third member of the flame spectroscopy family, atomic fluorescence spectroscopy, involves the measurement of the fluorescence of the atoms excited by a high intensity light source.

Atomic absorption has probably been more widely accepted in a shorter time than any analytical technique ever developed. Although the basic principles of flame emission were first employed about 1860, it wasn't until some 85 years later that flame spectroscopy was extensively used in the analytical community. On the other hand, the first publication on atomic absorption, by Walsh in 1955(1), was followed within a few years with the availability of commercial instruments and widespread use of the technique.

The 13th edition of *Standard Methods for the Examination of Water and Wastewater* lists atomic absorption methods for aluminum, barium, beryllium, cadmium, chromium, copper, iron, lead, magnesium, manganese, silver, and zinc(2). On the other hand, the 12th edition makes no mention of the technique(3).

Atomic fluorescence spectroscopy was first discussed in 1964(4). It has not been as widely accepted as atomic absorption, but there has been considerable discussion about the relative merits of the two methods. Winefordner et al. have presented a critical comparison of the two methods with flame emission(5).

B. Flame Emission

I. GENERAL PRINCIPLES

Flame emission spectroscopy is a technique for determining elemental concentrations based on the measurement of the intensity of the emission spectra of the elements produced by flame excitation. Detailed accounts of the fundamentals of the technique can be found in any number of books on the subject published through the years(6-10).

In general, the flame has to be able to decompose the compounds of interest into gaseous molecules or atoms and excite these decomposition products to emit light. Because of the lower energy of the flame the emission spectra produced are less complex than those produced by arc or spark excitation. Emission spectra resulting from excited atoms consist of lines, while molecules, whose energy characteristics are more complex, result in band emission. The measured intensity of any element

is dependent upon the number of emitting atoms in the flame per unit time and generally will be found to increase linearly with concentration.

The major portion of the atoms in the flame remain in the ground state and are not excited. The relationship between the number of atoms in the excited level, N_j , to the number in the ground state, N_0 , is given by

$$N_j = N_0(P_j/P_0) \exp(-E_j/kT) \quad (1)$$

where P_j and P_0 are the statistical weights for the excited state and ground state, respectively, E_j is the excitation energy of the excited state, k is the Boltzmann constant, and T is the temperature. It can be shown, for example, that for the sodium resonance line at 589.6 nm the value of N_j/N_0 is 9.86×10^{-6} at 2000°K and 4.44×10^{-3} at 4000°K (11). Thus, the number of atoms in the excited state is extremely temperature dependent.

Efforts to increase the sensitivity and scope of application of flame emission have resulted in a great deal of study of various types of flames, and many different combustible gases have been used (12, 13). Although flame temperature is of importance in determining the excitability of the elements, it is not the only factor. The oxidation or reduction status of the flame also plays a role, as was indicated by the work which led to the significant increase in detection sensitivity for elements such as niobium, vanadium, titanium, molybdenum, tungsten, and rhenium by the use of a reducing oxyacetylene flame (14, 15). It must be remembered that the hottest available flame is not necessarily the best choice for a particular analytical problem. The choice must depend on the properties of the chemical species involved.

2. INSTRUMENTATION

Flame spectrometers are simple instruments and are of two basic designs, single- or double-beam instruments. The single-beam instrument contains only one set of optics with a single light path and one detector. Light emitted in the flame is collected and focused through optical filters or a monochromator onto a detector. Double-beam instruments possess a second light path with a double set of optics and two detectors. The two detectors are in simultaneous operation with the signal from one opposing the signal from the other. The double-beam system provides for the measurement of the intensity of an internal standard element added to the test solution. One set of optics transmits only the characteristic wavelength of the element to be analyzed and the other transmits the characteristic wavelength of the internal standard. A ratio of the two detectors is developed electrically and this information is used to determine concen-

tration. The internal standard method effectively compensates for instrumental errors and for some interferences.

The flame photometer then must have the ability to vaporize the sample, to select the proper wavelength, and to measure and record the intensity of the emitted light.

a. Sample Vaporization

The reproducible introduction of the sample into the flame is one of the most critical steps in flame emission spectroscopy. Reliable analytical results can be obtained only if a uniform means of sample injection is used.

Two types of atomizers are normally used to deliver the sample solution to the flame. In the drainage-type atomizer the sample solution is reduced to a mist by a blast of air or oxygen which also carries the smaller droplets from the mist to the flame. The larger droplets are carried to waste or in some instances returned to the original solution. This is a relatively inefficient atomizer in that only a small fraction of the sample solution is actually delivered to the flame.

The more practical unit is the total consumption type, in which the atomizer is combined in one unit with the burner. A fine stream of the sample solution is drawn up a small capillary by the venturi effect created by the oxygen or compressed air used to support combustion. The entire liquid is sprayed directly into the flame, permitting the introduction of a large amount of sample per unit time with a corresponding increase in sensitivity.

Although the flame is the most commonly used means of exciting the elements for this method of analysis, a number of nonflame sources have been proposed and investigated(13). However, for water samples the flame to date remains the most convenient excitation source.

b. Optical Systems

The function of the optical system is to collect the light from the flame, to isolate the wavelength of interest from all other emission in the flame and the flame background, and to focus the light onto the detector. The wavelength selection can be accomplished by the use of absorption or interference filters or grating or prism monochromators. The most satisfactory resolution is achieved with the monochromator, which also provides the greatest versatility.

c. Detection Systems

Any photosensitive device may be used as a detector provided it has a response in the wavelength region of interest and possesses the required

sensitivity. Photographic plates, barrier-layer cells, and multiplier phototubes have been used. The latter device is the preferred radiation detector due to its high sensitivity.

3. SENSITIVITY

The limit of sensitivity of flame emission is usually defined as that concentration of an element in solution which produces a signal 1% above the flame background. The practical sensitivity is a function of many variables, such as the type and temperature of the flame, the atomizer-burner efficiency, the efficiency of the optical system, and the sensitivity of the detector. There are many compilations of concentrational sensitivities for the method (5, 6, 16-18) and further repetition is not necessary.

It is obvious from a study of these collections that some 60-70 elements have the potential of being detected in aqueous solutions when present at the parts per million or lower level. Consequently, flame emission spectroscopy has wide potential use for the determination of minor constituents in water samples.

4. INTERFERENCES

Flame photometry can be subject to a number of interferences or factors which can affect the accuracy of the method.

Interference can be caused by the superposition of a continuum or a band spectrum over the line spectra of interest or by the superposition of emission lines from two elements. This type of interference can be minimized by the use of an optical system of high resolution.

Interference can also be caused by the flame background, which would include contributions from the flame and sample matrix. Flame background measurements constitute an important correction factor. In the analysis of routine samples the most convenient means of evaluating the correction is by the use of a synthetic blank containing all constituents except the element to be determined.

The emission intensity of an element in the flame depends on the number of neutral atoms which are raised to an excited state. Therefore, the flame which has sufficient energy to ionize the metals will in effect reduce the number of neutral atoms available for excitation and consequently reduce the emission intensity. This effect becomes more pronounced in hotter flames. Hence an increase in flame temperature is not necessarily followed by a corresponding increase in emission intensity. The ionization effect on the element of interest can be reduced by the addition of a more readily ionized element to the solution.

Another form of interference can occur due to the presence of other