

BOOKS IN SOILS AND THE ENVIRONMENT

SOIL ANALYSIS

Instrumental Techniques and Related Procedures

Edited by KEITH A. SMITH

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Edited by KEITH A. SMITH
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Preface

The last twenty years have seen the rapid development of instrumental methods of analysis. These have virtually replaced the traditional methods and have made it possible to undertake on a routine basis some determinations that could not be attempted previously.

The rate of adoption of instrumental techniques has been very uneven even in different scientific fields and has been heavily influenced by the size of budgets, by traditions, and even by legislation prescribing that a particular analysis be carried out in a particular way. However, many changes have occurred in the last few years, and much instrumentation that previously might have been found only in industrial or medical laboratories is now commonplace in agricultural and environmental laboratories in which analysis focuses mainly on soils and plant material.

In spite of these developments the research soil scientist or the analyst working in governmental or commercial soil testing services generally has to make do with books covering traditional methods of analysis and specialist monographs on individual instrumental techniques. The latter are usually not written with soil or plant analysis specifically in mind, and are often inadequate in their consideration of the particular problems arising from the nature of the materials being analyzed. This book attempts to fill the gap between the two extremes, by covering the principles of the major instrumental techniques currently of relevance to soil analysis, together with discussions of sample preparation and matrix problems and critical reviews of applications in soil science and related disciplines. It will, I hope, be of value to scientists who wish to make a critical evaluation of available techniques in order to select the most appropriate ones for their needs, whether in terms of speed, cost, sensitivity, or other criteria, and also to the teachers and students of postgraduate courses in soil chemistry and soil analysis.

The principles underlying the various analytical techniques described by the contributors to this volume will continue to apply, irrespective of changes in the actual instrumentation available. However, the pace of development of this instrumentation has dramatically increased with the advent of microprocessor-based control systems. This phenomenon has occurred since this book was first conceived, and many significant innovations have appeared even since individual chapters were written and rewritten. It is therefore appropriate to supplement the information given in individual chapters with some mention here of recent developments in microprocessor control to illustrate the potential of this new approach. It is a safe bet that within a year or two there will be little analytical instrumentation commercially available that does not have some element of microprocessor-based control of operations or data processing facilities.

In the latest generation of gas chromatographs and liquid scintillation counters, for example, the operating parameters are set up not by operation of switches or dials on control panels, but by an interactive computer program; that is, the operator responds to questions displayed on a screen (or printer roll) by typing in appropriate answers via a keyboard. Invalid responses are not accepted, and, if no response is made, the system may automatically enter a preset stored value. After each acceptable response, the next question is posed and the process repeated. A "library" of standard programs may be available, or, alternatively, programs specifically tailored to fit a unique requirement may be written. Microprocessor-controlled instruments will normally be able to print out a list of all the operating parameters contained in a particular library program or those entered via a keyboard.

Many instruments (including those with some degree of automation) currently in service have simple analog output devices such as chart recorders, or digital meter displays or printers. Any further processing of data, whether it be colorimetric absorbance, chromatographic peak height, or electrode voltage, requires the intervention of the user, either through manual calculation or through transferring the data to a computer. In contrast, a major feature of the latest instruments is the ability to perform such functions as storing standard readings, calculating response curves and then calculating sample values, subtracting backgrounds, and calculating means and standard deviations of replicate samples. Furthermore, day-to-day or month-to-month variation in instrumental performance can be automatically monitored by comparison of fresh standard readings with earlier ones stored in the memory. Where further computer processing or data filing is necessary, there is a major reduction in the quantity of data to be handled, as a result of the initial processing within the microprocessor-based instrument, and the computer-compatible output of this instrument avoids manual handling of the data with the associated risk of transcription error. In many laboratories where existing instruments devoid of such facilities as those described have years of useful life in them, microprocessor-

based attachments are now being constructed to up-grade the instruments at a fraction of the cost of complete replacement.

There has been a dramatic "leveling up" of features available in instruments from different branches of analytical science. We now see the humble pH meter equipped with the sort of sophisticated circuitry that was previously limited to complex instruments such as pulse height analyzers or mass spectrometers. Before long we may expect to reach an equilibrium stage where no analytical instrument is manufactured without the incorporation of some microprocessor-based facilities; but until then the instrumentation available in any one field is likely to change from month to month, rather than year to year. This is a small price to pay for what is, by any criterion, a major revolution in chemical analysis. The versatility, convenience, and improved quality control of the new generation of instruments is to be wholeheartedly welcomed. All we users need now is the funds with which to reequip ourselves!

I would like to offer my thanks to the other contributors to this volume for their efforts, to Gordon Finnie and Jackie Calder for producing many of the illustrations, to Ruth Easton for checking the manuscript, and, not least, to the members of my family for their tolerance while this project struggled toward completion.

Keith A. Smith

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1

Atomic Absorption and Flame Emission Spectrometry

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I. INTRODUCTION

Since the independent realization in 1955 by Walsh [1] and by Alkemade and Milatz [2] of the analytical potential of atomic absorption spectrometry in flames, and the pioneering work of Walsh and his colleagues [3,4] in designing a practical atomic absorption instrument, there have been almost two decades of research and development. The first applications of the technique were to soils, plant ash, and other agricultural materials [5-7], while the use of solution samples, nebulized into a flame, derives from the earlier use of flame emission spectrometry largely by Lundegårdh [8], again in an agricultural context. The history of these developments and earlier work has been comprehensively reviewed [9]. At present, atomic absorption spectrometry is established as the principal analytical technique for elemental analysis in agricultural and environmental laboratories.

Atomic emission spectrometry using flame photometers with photoelectric detectors was of considerable importance in the 1950s and 1960s, but its use, except for the determination of the alkali metals and the alkaline earths, has to a large extent been superseded by atomic absorption spectrometry. More recently, however, there has been a revival of interest in atomic emission spectrometry, due to the development of high temperature sources such as the nitrous oxide/

acetylene flame [10-12], various types of high-frequency plasma [13], and, in particular, radio-frequency inductively coupled plasma (ICP) sources [14-18]. This interest stems not only from the high sensitivity of the ICP sources: It is due also to the increasing realization of the advantages of simultaneous multielement analysis offered by atomic emission and atomic fluorescence spectrometry. Atomic absorption spectrometry remains essentially a single-element technique.

This account will be concerned mainly with atomic absorption spectrometry (AAS) and its use and potential in the analysis of soils and other environmental materials, but reference will be made where appropriate to atomic emission spectrometry (AES) and to atomic fluorescence spectrometry (AFS). In this connection it is important to realize that most commercial atomic absorption spectrometers, using conventional atomic absorption burners, make excellent flame photometers and an emission mode of operation is usually provided. Most instruments can be adapted for AFS but specialized flames or electrothermal atomizers will usually be required. Initial discussion of the principles of AAS will be in terms of flame atomizers, but electrothermal atomization using graphite tube furnace and carbon-rod techniques will also be considered, together with other nonflame methods of analysis.

II. BASIC PRINCIPLES

In its simplest sense atomic absorption spectrometry makes use of the fact that free atoms of an element absorb light at wavelengths characteristic of that element and that the extent of the absorption is a measure of the concentration of these atoms in the light path. The production of atoms from chemical compounds requires a source of energy such as a flame which can vaporize and dissociate the sample compounds into the gaseous elemental state in which *atomic absorption* of radiation can take place. In favorable circumstances, this light energy absorbed by the atoms can subsequently be re-emitted as light of characteristic wavelengths whose intensity can form the basis for analysis by *atomic fluorescence spectrometry*. The function of the flame, therefore, in atomic absorption and fluorescence spectrometry, is to produce atoms from the sample compounds, i.e., to act as an *atomizer*. For atomic emission spectrometry, on the other hand, additional energy is required from the flame to excite the emission of atomic spectra, again characteristic of the element, whose intensity is not only a function of the atomic concentration in the flame but also of the temperature of the flame. The energy required for the production of atomic emission spectra increases as the wavelength decreases, and practical chemical flames such as air/acetylene, and even nitrous oxide/acetylene, are of little value for elements whose analytical wavelengths are lower than about 250 nm. Atomic absorption and fluorescence spectrometry, on the other hand, do not have this limitation and are

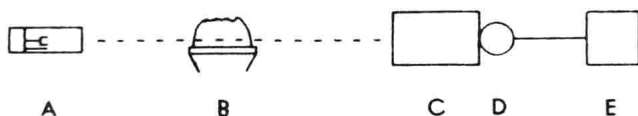


Figure 1 Schematic diagram of a single-beam atomic absorption spectrometer comprised of a hollow-cathode lamp, A; a burner/nebulizer, B; a monochromator, C; a photomultiplier detector, D; and an output device, E.

successfully used even at wavelengths below 200 nm. The extremely high temperatures attained by the radio-frequency plasma sources, as distinct from chemical flames, are sufficient to produce emission spectra with excellent sensitivity for elements whose spectral lines lie well below 200 nm.

The basic principles of atomic absorption spectrometry are illustrated in Fig. 1, which shows, schematically, the basic components of a simple single-beam instrument. A hollow-cathode discharge lamp, A, whose cathode is made of the element (copper, for example) that is to be determined, emits a spectrum characteristic of the cathode element (copper). This light is passed through the atomizer in the form of a flame, B, into which a fine mist of a solution of the analyte (copper) is sprayed by a pneumatic nebulizer. Atoms of copper are formed from the sample mist by thermal processes in the flame and absorb some of the light from the hollow-cathode lamp at the wavelength of an absorbing (resonance) copper line. The light passed through the flame is received by a monochromator, C, set to accept and transmit radiation of this wavelength. By means of the adjustable, ganged entrance and exit slits the bandwidth of the monochromator is made narrow enough to reject lines of other wavelengths emitted by the hollow-cathode lamp. The light emerges from the monochromator exit slit and falls on the photocathode of a photomultiplier detector, D, and an output current, proportional to the incident light intensity, is amplified, processed electronically, and finally presented to a readout device, E, such as a moving-coil meter, a pen recorder, or digital display.

If the light intensity measured in the absence of copper atoms in the flame is I_0 and the intensity when copper atoms from a nebulized sample solution are present is I_T , then

$$\%T = \text{percentage transmission} = \frac{100 \times I_T}{I_0} \quad (1)$$

$$\%A = \text{percentage absorption} = \frac{100 \times (I_0 - I_T)}{I_0} \quad (2)$$

$$\text{Absorbance} = \log \frac{100}{\%T} = 2 - \log \%T \quad (3)$$

The atomic concentration in the flame is proportional to the measured absorbance and from this the element concentration in the sample solution can be found by standardization (see Sec. IV.B).

The function of the monochromator in atomic absorption spectrometry is merely to isolate the required line from the remainder of the emitted hollow-cathode lamp spectrum, which is usually simple. The effective bandwidth of the absorption measurement is determined by the line width (ca. 0.001 nm) of the spectral lines emitted by hollow-cathode lamps. It is this excellent monochromation which contributes to atomic absorption spectrometry its remarkable freedom from spectral, superpositional interference.

The situation is quite different in atomic emission spectrometry where isolation of the desired line from the emitted spectrum is dependent on the monochromator resolution, which cannot approach the equivalent resolution of atomic absorption spectrometry.

III. THE ATOMIC ABSORPTION SPECTROMETER

A. Introduction

The block diagram of a simple, single-beam, atomic absorption spectrometer, Fig. 1, serves to illustrate the basic components of the measuring system whose various functions are discussed below. An example of a commercial single-beam instrument (Varian Techtron AA6) is shown in Fig. 2, in which these basic components are also indicated.

Since the atomic absorption measurement near the detection limit is the measurement of a small reduction in the initially large signal from the hollow-cathode lamp, this detection limit is determined largely by the stability of the lamp output and by variations in the sensitivity of the detector and electronics. One method of optimizing the detection limit is to use averaging output devices such as pen recorders or signal integrators. Another approach is to use a double-beam instrument in which the light from the hollow-cathode lamp is split into two beams, one passing through the flame and the other, the reference beam, passing outside the flame. The atomic absorption measurement made, by a common detector, is in this case the ratio of the two beam intensities so that lamp and detector noise and instability are considerably reduced. In addition, instrument warmup time, normally about 15 min with a single-beam spectrometer, is virtually eliminated. However, because of the requirement to divide the light beam for double-beam operation, the available light energy at the detector is reduced and this can present some small disadvantage. Double-beam instruments can perhaps more readily incorporate background correction continuum sources (see Sec. VI) but some instruments may sacrifice double-beam operation in the process. Double-beam instruments are necessarily more complicated and their maintenance more difficult but,