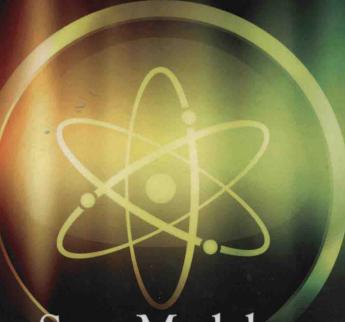
SECOND EDITION

ATOMIC ABSORPTION SPECTROMETRY

ANINTRODUCTION

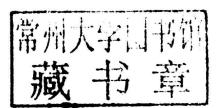


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Atomic Absorption Spectrometry: An Introduction, 2nd Edition

ALFREDO SANZ-MEDEL AND ROSARIO PEREIRO





MOMENTUM PRESS, LLC, NEW YORK

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First published by Momentum Press®, LLC 222 East 46th Street, New York, NY 10017 www.momentumpress.net

ISBN-13: 978-1-60650-435-2 (hardback, case bound)

ISBN-13: 978-1-60650-437-6 (e-book)

DOI: 10.5643/9781606504376

Cover design by Jonathan Pennell Interior design by Exeter Premedia Services Private Ltd., Chennai, India

10987654321

Printed in the United States of America

Atomic Absorption Spectrometry: An Introduction

Preface

More than 50 years have elapsed since the successful introduction of atomic absorption spectrometry (AAS) by Sir Alan Walsh for elemental analysis. At this moment in time it is comparatively rare to find research publications on new AAS fundamentals or even new AAS applications. Conversely, analytical AAS has become an established elemental analysis routine tool applied worldwide. Furthermore, it can be safely said that in today's routine laboratories AAS is the most popular, inexpensive, and easy-to-use technique among all the "workhorses" available for elemental analysis.

It is not surprising then that we have restricted the scope of this tutorial book to the study of fundamentals and practical use of such popular and efficient atomic absorption techniques. An up-to-date account of AAS fundamentals, instrumentation, special techniques, and elemental analysis applications is provided here. To do so, the atomic absorption experiment and the photophysical law governing such photon absorption processes are revised first. Then, the main components or units, that, when adequately assembled, constitute an AAS instrument, are described in detail to set the foundations of modern spectrometers for AAS measurements.

After describing the basic instrumentation for AAS measurements, we have selected those AAS-based techniques that are not only well established now, but of recognized practical value to provide robust and fit-to-purpose analytical results. In order to provide direct, concise material, we utilized the approach of studying progressively complex AAS techniques that have been introduced to solve problems of lack of sensitivity, selectivity, or easy sample handling in elemental determinations, as carried out worldwide today in routine laboratories. A section of carefully selected applications (illustrating the relative merits and strengths of each particular AAS technique) is included at the end of each chapter.

The approach of using a classical flame as atomizer is considered first, while the following chapter deals with flame sensitivity problems and how to overcome them in a general way by resorting to electrothermal (ET) atomization of the sample to be analyzed. The greater sensitivity of ET, coming from a confined and better-controlled atomization of the whole sample (not just the analyte), explains the superior performance of ETAAS in ultratrace determinations (µg/L concentrations of the analyte in the dissolved sample) versus mg/L in conventional flame AAS (FAAS).

The next chapter deals with a rather special chemical, a more restricted alternative to improve the sensitivity of those analytes able to form volatile species at room temperature when the dissolved sample is treated with appropriate reagents; for instance, techniques based on hydride or cold-vapor generation to increase analyte transport. Of course, such higher sensitivity approaches so popular today in AAS are not restricted to atomic absorption (even if they were born and developed mainly using absorption measurements).

Also discussed is flow injection analysis (FIA), a practical technique intended for the automation of serial assays, which has evolved well beyond that original point. At present, FIA offers the most convenient and straightforward approach to not only automate, but also to enhance, all sample pretreatment steps for atomic spectrometric detectors in general and for atomic absorption techniques in particular. Also, the online coupling of chromatographic separations to AAS for elemental detection has demonstrated a great analytical potential, in particular for metal speciation purposes. Therefore, a complete section is dedicated to such couplings and problem solving based on chemical speciation.

The final chapter is devoted to emerging fields of applications (such as the characterization of nanoparticles) and to chemometrics. A section focused on troubleshooting and quality-control guidelines has also been included.

The book ends with:

- Appendix A—Buyer's Guide: a listing of manufacturers worldwide of atomic absorption spectrometers and information about companies marketing AASbased instruments;
- Appendix B—Glossary: definitions of specialized terms;
- Appendix C—Standards: selected examples of standards for chemical analysis
 of different samples by AAS (from the British Standards Institution and the
 International Standards Organization) are provided; and
- References: A full list of the research articles, review articles, and books that were cited in each chapter.

KEYWORDS

atomic absorption spectrometry (AAS); characterization of nanoparticles; chemometrics; chromatographic separations; cold vapor generation; electrothermal (ET) atomization; elemental analysis; flow injection analysis (FIA); hydride vapor generation

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An Introduction to Analytical Atomic Spectrometry

In this introductory chapter, the basic interactions of ultraviolet-visible photons with atoms (spontaneous emission, stimulated absorption, and stimulated emission) are reviewed using self-explanatory diagrams. Furthermore, the important characteristics of the atomic lines, constituting the atomic spectra, are considered in detail paying particular attention to main effects and phenomena in an atomizer that gives rise to the broadening of atomic lines and brings about the final spectral width of an atomic line.

It ends with a critical comparison of the main analytical techniques based on atomic spectrometry (absorption, emission, fluorescence, and mass spectrometry) for the analysis of dissolved samples as well as for the direct analysis of solids.

1.1. BASIC INTERACTIONS OF ELECTROMAGNETIC RADIATION WITH ATOMS FOR CHEMICAL ANALYSIS

Most of the molecular spectroscopy-based analytical methods currently used take advantage of the differential features of interacting photons of radiation with the matter to be analyzed. In particular, the interaction of photons with electrons of the molecules of matter is observed and measured. The photons most frequently used for such analytical purposes extend from the ultraviolet (UV: 190–390 nm) to the visible (Vis: 390–750 nm) regions of the electromagnetic spectrum; these interact easily with valence electrons. Of course, the infrared (IR: 750–2,500 nm) region is also very useful in molecular analysis.

Three main basic photon-electron interactions of the molecules are analyzed: absorption, emission, and fluorescence. If the energy of photons, $E = h \cdot v$, is equal to the energy gap between electronic energy states 1 and 2 ($\Delta E = E_2 - E_1 = h \cdot v$), the so-called resonance condition is fulfilled and the photon disappears as its energy is absorbed to promote the electron to the higher-energy state 2 (excited state of the electron). Furthermore, the electron may be promoted to an excited state by other types of energy (thermal, electric, etc.). Once excited, the electron is not stable at the higher energy level and tends to fall back to the lower energy (nonexcited) level. In doing so, the energy difference $\Delta E = E_2 - E_1$ can be emitted as electromagnetic radiation of frequency $v = \Delta E/h$ (h is the Planck's constant: 6.63×10^{-34} J s). When the energy used to promote the electron to the excited state is in the form of photons (photoexcitation), the spontaneous emission occurring is called fluorescence.

This tutorial book deals with analytical atomic spectrometry. In this case, the analyzed matter (sample) must be in the form of atoms in the gas phase, but the main interactions we make use of for the analysis are the same: that is, absorption, emission, and fluorescence. From an analytical point of view, the fact of having the sought elements of the sample in the form of gaseous atoms is most convenient because we obtain atomic spectra. Such spectra (graphs of the measured absorption, emission, or fluorescence versus the energy of the photons used in the experiment) are consequently much simpler to interpret than molecular spectra.

The interaction processes between UV-Vis photons and outer electrons of the atoms of the sought elements can be studied and understood through the quantum mechanics theory. In the thermodynamic equilibrium between matter and interacting electromagnetic radiation, according to the radiation laws postulated by Einstein, three basic processes (quantized transitions) between the two stable energy levels 1 and 2 are possible. These three processes, which can be defined by their corresponding transition probabilities, are summarized in Figure 1.1:

- (a) Spontaneous emission of photons. This process refers to a spontaneous transition of the electron from the excited state 2 to the lower energy state 1 with emission of a photon of frequency $v_0 = (E_2 E_1)/h$. The probability of such a transition is usually represented by A_{21} (and corresponds to the inverse value of the lifetime of the excited state 2).
- (b) Stimulated absorption of photons. In this case, the electronic transition takes place from state 1 to state 2 in response to the action of an external radiation of the appropriate frequency. The probability of such transitions can be represented by B_{12} .
- (c) Stimulated emission of photons. This process consists of electronic transitions from the excited energy level to the lower one stimulated or in response to an external radiation of the adequate frequency $(E_2 E_1)$ /h. The probability of these transitions is termed B_{21} (of course, a given transition only has a given probability and so $B_{21} = B_{12}$).