PROGRESS IN ANALYTICAL ATOMIC SPECTROSCOPY

Volume 1

C. L. CHAKRABARTI

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Editor-in-Chief

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PERGAMON PRESS

OXFORD · NEW YORK · TORONTO · SYDNEY · PARIS · FRANKFURT

U K	Pergamon Press Ltd., Headington Hill Hall, Oxford OX3 0BW, England
U S A	Pergamon Press Inc., Maxwell House, Fairview Park, Elmsford, New York 10523, U.S.A.
C A N A D A	Pergamon of Canada, Suite 104, 150 Consumers Road, Willowdale, Ontario M2J 1P9, Canada
A U S T R A L I A	Pergamon Press (Aust.) Pty. Ltd., P.O. Box 544, Potts Point, NSW 2011, Australia
F R A N C E	Pergamon Press SARL, 24 rue des Ecoles, 75240 Paris, Cedex 05, France
F E D E R A L R E P U B L I C O F G E R M A N Y	Pergamon Press GmbH, 6242 Kronberg-Taunus, Pferdstrasse 1, Federal Republic of Germany

ISBN 0 08 024869 1

First published in *Progress in Analytical Atomic Spectroscopy*, Vol. 1, Nos 1–4, 1978, and supplied to subscribers as part of their subscription. Also available to non-subscribers.

Printed in Great Britain by A. Wheaton & Co. Ltd., Exeter.

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Prog. analyt. atom. Spectrosc. Vol. 1, pp. 1 to 2. Pergamon Press, 1978. Printed in Great Britain

EDITORIAL

The scope and purpose of analytical atomic spectroscopy is growing so fast that even the dedicated scientist cannot follow significant developments which appear in a large number of journals covering many subdisciplines, disciplines, inter-disciplinary and multi-disciplinary areas. This analytical breadth becomes evident when one considers that in addition to many journals of spectroscopy and analytical chemistry where papers in analytical atomic spectroscopy are regularly published, an increasing number of such papers are also published in journals of clinical chemistry, biology, environmental science and technology, marine sciences, forensic science, materials science, mining, geology, metallurgy, fuel science, glass and ceramics, instrumentation, food and drugs, agricultural sciences, biochemistry, geochemistry, biogeochemistry, etc. Analytical atomic spectroscopy has recently experienced an extremely rapid growth in electrothermal atomization in atomic absorption spectroscopy, and in inductively-coupled plasma-optical emission spectroscopy – growth in the latter continues unabated. At present a serious time lag exists between evolution and practice and between the establishment of a technique and the appearance of suitable monographs. This journal aims to bridge this gap by presenting a continuing series of volumes containing contributions from outstanding authorities having intimate knowledge of and experience with their subject. These contributions will be critical reviews embodying comprehensive assessments of analytical techniques and their applications.

The literature of analytical atomic spectroscopy is growing so quickly that it is becoming increasingly difficult for the new research worker to know where to start reading. My personal interest in this journal has stemmed from realization that efficiency of literature-searching by graduate students can be increased significantly by having access to current, comprehensive reviews. The original idea was to publish *Comprehensive Analytical Atomic Spectroscopy* but later it was decided instead to publish a review journal because the latter endeavour would serve our purpose better. I was commissioned to discuss these ideas with international authorities and, if interest seemed promising, to solicit some contributions. Most scientists responded enthusiastically that a review journal was a better idea and that it would fill a real gap and need. Already we have some forty promised reviews. Quick publication by camera-ready copy will enable us to bring review articles in rapidly evolving subject areas. A good review will serve two kinds of readers – the newcomer who wishes to know the salient features and the expert who wishes to hear the latest news. We hope to publish critical comprehensive reviews surveying various topics on a scholarly level satisfying the specialist and nonspecialist alike.

Some of the existing journals occasionally publish critical reviews but such reviews are neither periodic nor can they be comprehensive because of the constraints imposed by limited space and scope. *Annual Reports on Analytical Atomic Spectroscopy*, published by The

Chemical Society, UK, fulfils the need of a synoptic, critical survey of developments in various fields during the past year. Our journal will fill the existing gap and need for a review journal.

Comprehensive reviews occupy a special place in scientific literature – intermediate between the concise original papers of scientific journals and the exhaustive treatment allowed by books. Such reviews will give the author space and opportunity to expound ideas, and to give his personal evaluation after he has "weighed", "digested" and "balanced" the available evidence, some of which may be conflicting.

The scope of this journal includes atomic absorption spectroscopy, optical emission spectroscopy with excitation by arc, spark and other sources especially by high-temperature plasmas, atomic fluorescence spectroscopy, X-ray and electron beam techniques. The scope will be flexible and broad. The journal will serve the modern analytical scientists whose profession each day demands broader perspective and solution of problems with increased complexity. In solving problems posed by new materials and new technology, the analytical chemist (whose responsibilities include both characterization and quantification), is increasingly required to be fully conversant with a wide variety of techniques that are available so that he can use the most appropriate technique or techniques to solve a particular problem.

Our reviews will be solicited and contributed. Authors are encouraged to submit draft manuscripts to the Editor-in-Chief or any member of the Board of Advisory Editors for consideration. All contributions will be refereed by experts in the field who will be asked to comment on any errors or omissions. We seek critical and authoritative contributions from all sources but must insist on the English language.

From time to time an entire volume (such as this volume) will be devoted to a single topic and will embody recent developments made in the author's laboratories. Such contributions may not be critical reviews but have the merit of presenting significant developments in a critical, comprehensive manner. Furthermore, it is our intention at a later date to produce a major work 'Comprehensive Analytical Atomic Spectroscopy' using up-dates of selected articles from this journal supplemented with others that will be specially commissioned.

Book reviews will be included from time to time and any books for review should be sent to the Editor-in-Chief.

"Forthcoming Events" will be a regular feature. This will enable readers to know well in advance the dates of relevant meetings. Conference organizers are asked to note this facility which is offered to them free of charge. Brief details of planned meetings should be sent to the Editor-in-Chief as early as possible.

Comments and suggestions from readers are welcome and maybe sent to any of the members of the Board of Advisory Editors or to the Editor-in-Chief.

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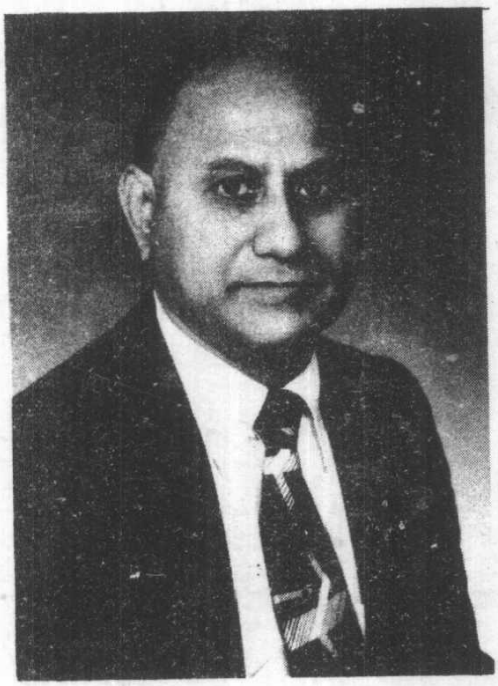
Prog. analyt. atom. Spectrosc. Vol. 1, p. 3. Pergamon Press, 1978. Printed in Great Britain

BIOGRAPHIES

Chuni L. Chakrabarti received the M.Sc. degree from the University of Birmingham in 1960 and the Ph.D. degree from the Queen's University of Belfast in 1962. He has been on the faculty of Carleton University since 1965, and is a professor of chemistry.

Dr. Chakrabarti's research interests are in analytical chemistry and environmental chemistry, with special interests in the development of analytical atomic spectroscopy, trace and ultratrace analysis, and metal-organic interactions in the aquatic environment. He is a consultant to Exxon Production Research Company, Houston, USA and some other companies. He is Editor-in-Chief of *Progress in Analytical Atomic Spectroscopy*, Associate Editor of *Canadian Journal of Spectroscopy*, a member of the Editorial Board of *Spectrochimica Acta*, Part B, and *Annual Reports on Analytical Atomic Spectroscopy*, published by The Chemical Society, UK. He is a Fellow of the Chemical Institute of Canada, Fellow of the Royal Institute of Chemistry, and The Chemical Society, UK, and a member of the American Chemical Society. He is the 4th recipient of the Herzberg Award of the Spectroscopy Society of Canada – the award was given in recognition of his outstanding contribution to spectroscopy.

Ralph E. Sturgeon received his B.Sc. in 1973 and his Ph.D. degree in 1977 from Carleton University. His Ph.D. research was done on electrothermal atomization in graphite furnace atomic absorption spectroscopy under the supervision of Dr. C.L. Chakrabarti. He is currently a Research Associate at the National Research Council of Canada.



C.L. Chakrabarti

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0160-4139/78/0801-0005$05.00/0

RECENT ADVANCES IN ELECTROTHERMAL ATOMIZATION IN GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

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INTRODUCTION

A flame is the most widely used medium for atomizing samples in atomic absorption spectrometry (AAS). However, the demand for better sensitivity and detection limits, the necessity for more economical use of samples and the fundamental limitations of flame techniques have led to the development of a variety of electrothermal atomizers as alternatives to flames. These electrothermal atomizers have utilized heated graphite tubes, carbon rods and filaments, sampling boats and cups, loops, and metal filaments. Comprehensive reviews of these atomizers have been published by Kirkbright [1], Syty [2] and Woodriff [3], and recent developments have been reviewed by Hieftje *et al.* [4].

Electrothermal atomizers are more difficult to build, cost more to purchase and are physically more bulky than a typical nebulizer-burner (flame), as they require a large and elaborate power supply and fairly sophisticated equipment to record the analytical signals. The most commonly used electrothermal atomizers (graphite tubes and rods) offer tremendous analytical advantages and further potential for development over atomization by the flame technique, as shown below.

(1) Electrothermal atomizers require only a few microlitres of sample per injection.

(2) Viscous liquids that are difficult to nebulize in the flame can be conveniently handled with electrothermal atomizers.

(3) Analysis of samples in the vacuum ultraviolet is possible with electrothermal atomization (using a system purged free of air), whereas such a measurement with a flame is prevented by the intense absorption by oxygen.

(4) Electrothermal atomizers produce a low background signal, resulting in superior signal-to-noise ratios (i.e. better detection limits) to those given by the flame technique.

(5) The chemical and thermal environment of the atomic vapour can be much better controlled when electrothermal atomizers are employed.

(6) The efficiencies of vaporization and atomization in electrothermal atomizers are usually superior to those in the flame, especially in the cases of elements which tend to form thermally stable oxides. This is a consequence of the smaller volume of the electrothermal atomizer, the absence of dilution of the analyte by expanding flame gases, the highly reducing environment inside an incandescent graphite tube and the more complete vaporization and dissociation.

(7) Enhancements in sensitivity of the order of 10^4-10^5 over the flame technique are attainable with electrothermal atomizers as a result of the above characteristics and the increased lifetime of the atomic vapour within the analytical volume.

(8) The capability of direct solid sampling exists when electrothermal atomizers are used.

(9) The speed of analysis by flame and electrothermal techniques is similar.

The possibility of determining a large number of elements ($\sim$ 70) with high sensitivity, selectivity, accuracy and speed, coupled with the simplicity, relatively low cost of apparatus

and low cost of analysis (per element), makes AAS with electrothermal atomization potentially ideal for trace and ultratrace analysis. It is therefore not suprising that the technique has been shown to be of considerable value for the detection and quantitative determination of trace amounts of metals in a variety of matrices [2–4].

In most cases, emphasis in research concerning atomic absorption spectrometry with electrothermal atomizers has been placed on the construction of electrothermal atomizers and their application to practical analytical problems; thus, there is a body of largely empirical studies without an adequate background framework of theory. Only a relatively few authors have done a systematic study of the fundamental aspects of electrothermal atomization. This is in striking contrast to the large amount of theoretical material which has been published on the flame technique. The primary reason for the difficulty in explaining the behaviour of atomic populations produced by electrothermal atomizers lies in the transient nature of the atomic vapour. The distribution of free, gaseous atoms and their lifetime depend not on the equilibrium temperature of the atomizer but on the rate of atomization of analyte compounds or their decomposition products from the graphite surface. An understanding of the processes of vaporization and atomization is important since it will ultimately enable prediction of optimum conditions for analysis based on theoretical principles (as opposed to empirical studies), and provide information about the mechanism of interference from concomitants in the analyte matrix. The nature of the signal profile is also important because proper recording of the atomic absorption signal (which depends on the correct design of equipment) is a prerequisite to obtaining accurate and precise analytical data. In order to understand the processes occurring in electrothermal atomizers, a fundamental study of the time-dependent processes which occur during the atomization of an analyte in graphite (tube-type) electrothermal atomizers was undertaken. During the time this research was in progress, the following topics were reported in the literature: characterization of atomic absorption signals and various methods of their measurement [5], the influence of the response time of the amplifier-recorder system on the signals [5–8], the influence of the rate of heating of the atomizer on the analytical sensitivity [8–10], the effects of atomizer geometry and construction material on the signals [11–14], the mechanism of atom formation [10, 12, 15–17], the temperature of the atomic vapour within the atomizer [18], and the interferences due to compound formation and the composition of the matrix [19–24]. By far the most important work to date is that by L'vov [11], who has explained the phenomenon of production of atomic vapour and the concept of the temporal signal profile.

CHAPTER 1

CHARACTERIZATION OF TRANSIENT SIGNALS AND THEIR MEASUREMENT

Analytical signals obtained with electrothermal atomizers are, in general, curves having peaks [2], their exact shape for a given element being determined by the physical and chemical properties of the matrix, by the properties of the sample cell (geometry, construction material), by the heating rate of the atomizer and by the distortion of the signal caused by the finite response time of the amplifier-recorder system used. The selection of an optimum method of atomization in atomic absorption spectrometry is therefore a complicated problem which still remains largely unresolved, the main reason for this being the purely empirical approach to its solution taken by the majority of the investigators in this field.

The most widely used method of measuring signals given by electrothermal atomizers is the measurement of the maximum or peak absorbance attained [11]. An alternative method is to measure the integrated absorbance, obtained by summing the absorbance values over the time period during which free atoms reside within the analytical volume (defined by the beam of radiation from the emission source).

Theory of Signal Shape

To assess the relative merits of the peak and integration methods of measurement of signals from a theoretical viewpoint and to consider the influence of various physicochemical factors on the analytical characteristics of the signals, L'vov [5, 25] and L'vov *et al.* [26, 27] devised a mathematical model to describe the time-dependent characteristics of the atom population within an isothermal cuvette. For the sake of simplicity, only the processes of the transfer of sample vapour through the analytical volume were considered; all intermediate stages in the transformation of the sample before it entered the analytical volume (i.e. the mechanism of atom formation) were not taken into account. The following assumptions were made in constructing the mathematical model: the element to be determined is completely atomized; all of the atoms of the element enter the analytical volume; the removal of atomic vapour from the analytical volume is determined solely by diffusion under a concentration gradient. The following variables are introduced: N_0 is the number of atoms of the element to be determined in the sample; N is the total number of atoms of the element within the analytical volume at the moment of time t; τ'_1 is the atomization time – the time duration of transfer of atoms into the analytical volume; τ'_2 is the residence time of atoms within the cuvette – the mean length of time spent by an atom within the analytical volume, and τ_3 is the length of time during which the signal is recorded ($\tau_3 = \tau'_1 + 5\tau'_2$).

The change in the number of atoms within the analytical volume at any instant of time t is determined by the difference between the number of atoms entering the analytical volume, $n_1(t)$, and the number of atoms escaping from it $n_2(t)$, in unit time:

$$dN/dt = n_1(t) - n_2(t). \tag{1.1}$$

With a diffusional mechanism of vapour loss, the function $n_2(t)$ may be approximated by:

$$n_2(t) = N/\tau'_2. \tag{1.2}$$

Introduction of sample into the analytical volume takes place via a process of accelerated vaporization of the sample due to the continuously rising temperature of the evaporation surface. Hence, $n_1(t)$ may be approximated by:

$$n_1(t) = At. \tag{1.3}$$

From the condition of normalization, A may be determined:

$$\int_0^{\tau'_1} n_1(t)dt = N_0. \tag{1.4}$$

Hence

$$n_1(t) = (2N_0/\tau'^2_1)t \tag{1.5}$$

and equation (1.1) becomes:

$$dN/dt = (2N_0/\tau'^2_1)t - N/\tau'_2. \tag{1.6}$$

This is a general linear first-order differential equation which may be solved with the aid of an integration factor $[\exp(t/\tau'_2)]$ to yield the following integral:

$$N_{t\leqslant\tau'_1} e^{t/\tau'_2} = (2N_0/\tau'^2_1)\int te^{t/\tau'_2}dt + C. \tag{1.7}$$

Integrating, and evaluating C from the boundary condition $N = 0$ at $t = 0$ yields:

$$N_{t\leqslant\tau'_1} = 2N_0\frac{\tau'^2_2}{\tau'^2_1}\left[\frac{t}{\tau'_2} - 1 + e^{-t/\tau'_2}\right]. \tag{1.8}$$

When the sample has been completely atomized ($t = \tau'_1$), N_t attains a maximum:

$$N_{t=\tau'_1} = 2N_0\frac{\tau'^2_2}{\tau'^2_1}\left[\frac{\tau'_1}{\tau'_2} - 1 + e^{-\tau'_1/\tau'_2}\right]. \tag{1.9}$$

At $t \geqslant \tau'_1$, equation (1.1) must be modified to account for the fact that the sample introduction step has been completed and only diffusional loss follows, i.e.

$$dN/dt = -N/\tau'_2, \tag{1.10}$$

$$\int_{N_{\tau'_1}}^{N_t} \frac{dN}{N} = \int_{\tau'_1}^{t} -\frac{dt}{\tau'_2} \tag{1.11}$$

$$N_{t \geqslant \tau'_1} = N_{\tau'_1} e^{(\tau'_1 - t)/\tau'_2}. \tag{1.12}$$

Substitution of the value of $N_{\tau'_1}$ given by equation (1.9) results in equation (1.13).

$$N_{t \geqslant \tau'_1} = 2N_0 \frac{\tau'^2_2}{\tau'^2_1} \left[\frac{\tau'_1}{\tau'_2} - 1 + e^{-\tau'_1/\tau'_2} \right] e^{(\tau'_1 - t)/\tau'_2}. \tag{1.13}$$

Equations (1.8) and (1.13) describe the kinetics of change in the number of atoms in the analytical volume as a function of time. A graphical representation of this is shown

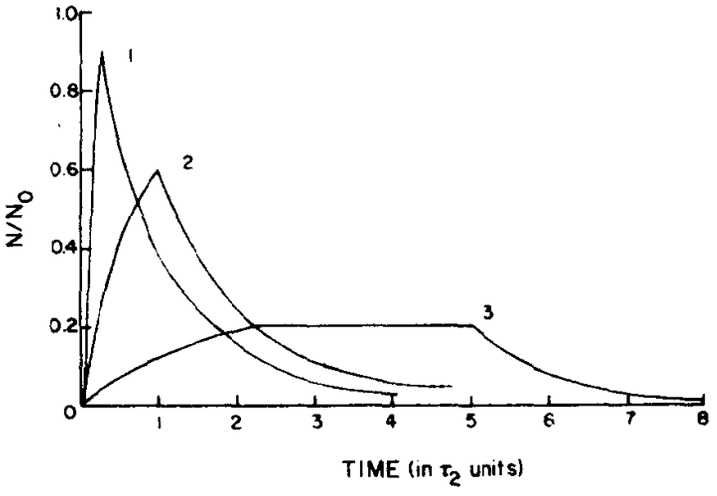

Fig. 1. Variation in the number of atoms in an analytical volume for different τ'_1/τ'_2 ratios. $1 - \tau'_1/\tau'_2 = 0.2; 2 - \tau'_1/\tau'_2 = 1.0; 3 - \tau'_1/\tau'_2 = 5.0$.

in Fig. 1 where the pulse shapes for various τ'_1/τ'_2 ratios have been plotted according to equations (1.8) and (1.13).

Methods of Recording Atomic Absorption

The pulses shown in Fig. 1 may be conveniently characterized by two quantities; the peak value, N_p, corresponding to the peak of the pulse, and the area under the pulse, Q_N.