Inductively Coupled Plasma Spectrometry and its Applications

Edited by

Steve J. Hill
School of Earth, Ocean and Environmental Sciences
University of Plymouth
Plymouth, UK

Blackwell
Publishing

This page intentionally left blank

Inductively Coupled Plasma Spectrometry and its Applications

Analytical Chemistry

Series Editors: *Alan J. Handley*
John M. Chalmers

A series which presents the current state of the art of chosen sectors of analytical chemistry. Written at professional and reference level, it is directed at analytical chemists, environmental scientists, food scientists, pharmaceutical scientists, earth scientists, petrochemists and polymer chemists. Each volume in the series provides an accessible source of information on the essential principles, instrumentation, methodology and applications of a particular analytical technique.

Titles in the Series:

Spectrochemical Analysis Using Infrared Multichannel Detectors
Edited by Rohit Bhargava

Spectroscopy in Process Analysis
Edited by John M. Chalmers

Atomic Spectroscopy in Elemental Analysis
Edited by Michael Cullen

Extraction methods in Organic Analysis
Edited by Alan J. Handley

Gas Chromatographic Techniques and Applications
Edited by Alan J. Handley

Inductively Coupled Plasma Spectrometry and its Applications 2nd Edition
Edited by Steve J. Hill

Pharmaceutical Analysis
Edited by David C. Lee and Michael Webb

Chemical Analysis of Contaminated Land
Edited by Clive Thompson and Paul Nathanail

Environmental Toxicity Testing
Edited by K. Clive Thompson, Kirit Wadhia and Andreas Loibner

Design and Analysis in Chemical Research
Edited by Roy Tranter

Inductively Coupled Plasma Spectrometry and its Applications

Edited by

Steve J. Hill
School of Earth, Ocean and Environmental Sciences
University of Plymouth
Plymouth, UK

Blackwell
Publishing

Editorial Offices:
Blackwell Publishing Ltd, 9600 Garsington Road, Oxford OX4 2DQ, UK
Tel: +44 (0)1865 776868
Blackwell Publishing Professional, 2121 State Avenue, Ames, Iowa 50014-8300, USA
Tel: +1 515 292 0140
Blackwell Publishing Asia Pty Ltd, 550 Swanston Street, Carlton, Victoria 3053, Australia
Tel: +61 (0)3 8359 1011

First published 2006 by Blackwell Publishing Ltd

ISBN-13: 978-1-4051-3594-8
ISBN-10: 1-4051-3594-8

Library of Congress Cataloging-in-Publication Data is available

A catalogue record for this title is available from the British Library

Set in 10/12 pt Minion by Charon Tec Ltd (A Macmillan Company), Chennai, India
Printed and bound in Singapore by Markono Print Media Pte Ltd

The publisher's policy is to use permanent paper from mills that operate a sustainable forestry policy, and which has been manufactured from pulp processed using acid-free and elementary chlorine-free practices. Furthermore, the publisher ensures that the text paper and cover board used have met acceptable environmental accreditation standards.

For further information on Blackwell Publishing, visit our web site:
www.blackwellpublishing.com

Contents

This page intentionally left blank

Contributors

Dr Lieve Balcaen	Laboratory of Analytical Chemistry, University of Ghent, Proeftuinstraat 86, B-9000 Ghent, Belgium
Mr Malcolm J. Baxter	Central Science Laboratory, Sand Hutton, York, YO41 1LZ, UK
Professor Joseph A. Caruso	Department of Chemistry, University of Cincinnati, PO Box 210172, Cincinatti, OH 45221 0172, USA
Ms Jennifer M. Cook	British Geological Survey, Keyworth, Nottingham, NG12 5GG, UK
Dr Helen M. Crews	Central Science Laboratory, Sand Hutton, York, YO41 1LZ, UK
Dr E. Hywel Evans	School of Earth, Ocean and Environmental Sciences, University of Plymouth, Drake Circus, Plymouth, Devon, PL4 8AA, UK
Dr Andrew Fisher	School of Earth, Ocean and Environmental Sciences, University of Plymouth, Drake Circus, Plymouth, Devon, PL4 8AA, UK
Dr Michael Foulkes	School of Earth, Ocean and Environmental Sciences, University of Plymouth, Drake Circus, Plymouth, Devon, PL4 8AA, UK
Dr Helle R. Hansen	Department of Chemistry, Environmental Chemical Processes Laboratory, University of Crete, Knossou Ave, Heraklion, 71409 Greece

Prof. Gary M. Hieftje Department of Chemistry, Indiana University, Bloomington, IN47405, USA

Prof. Steve J. Hill School of Earth, Ocean and Environmental Sciences, University of Plymouth, Drake Circus, Plymouth, Devon, PL4 8AA, UK

Prof. Jean-Michel Mermet Laboratoire des Sciences Analytiques, Bât. 308, Université Claude Bernard-Lyon 1, 43 bvd du 11 Novembre 1918, 69622 Villeur-banne Cedex, France

Mr Douglas L. Miles British Geological Survey, Keyworth, Nottingham, NG12 5GG, UK

Mr Ciaran O'Connor Analytical Atomic Spectroscopy Group, Department of Chemistry, Loughborough University, LE11 3TU, UK

Dr Gavin O'Connor LGC, Queens Road, Teddington, Middlesex, TW11 0LY, UK

Prof. Spiros A Pergantis Department of Chemistry, Environmental Chemical Processes Laboratory, University of Crete, Knossou Ave, Heraklion, 71409 Greece

Dr Paul Robb Central Science Laboratory, Sand Hutton, York, YO41 1LZ, UK

Dr Baki B.M. Sadi Department of Chemistry, University of Cincinnati, PO Box 210172, Cincinatti, OH 45221 0172, USA

Prof. Jodi R. Shann Department of Biological Sciences, University of Cincinnati, Cincinnati, OH 45221-0006, USA

Dr Barry L. Sharp Analytical Atomic Spectroscopy Group, Department of Chemistry, Loughborough University, LE11 3TU, UK

Dr Karen L. Sutton Procter and Gamble Technical Centres Ltd, Rusham Park, Whitehall Lane, Egham, TW20, 9NW, UK

Dr Philip Taylor Institute for Reference Materials and Measurements, European Commission Joint Research Centre, Retieseweg 111, B-2440 Geel, Belgium

Prof. Frank Vanhaecke Laboratory of Analytical Chemistry, University of Ghent, Proeftuinstraat 86, B-9000 Ghent, Belgium

Dr Anne P. Vonderheide Department of Biological Sciences, University of Cincinnati, Cincinnati, OH 45221-0006, USA

Preface

To undertake to update and revise a book that has been well received is rather a daunting task. Clearly any editor, and indeed all of the authors who contribute, would like the second edition to be even better than the first. The difficulty however is how to achieve that. The first edition of this book was perceived as a handbook for users of inductively coupled plasmas (ICPs) who wanted a better understanding of the theory, yet also wanted a practical insight of how best to approach a range of applications. These key objectives have been retained in the second edition but the focus of the book has changed so that the overall perspective is more forward looking. Much of the historical development behind the use of the techniques described in some detail in the first edition has been minimised and the emphasis is now on state-of-the-art developments and potential developments for the future.

The book has been structured into 11 chapters, each utilising the authors' expertise and experience, and providing enough detail to be useful to both the new and experienced users. The first chapter of the previous edition presented the first full account by Stan Greenfield of the early development of the ICP. This second edition starts at the other end of the spectrum and sets the scene for the rest of the book by providing a thought provoking account of both the strengths and weaknesses of ICP-AES and ICP-MS and how the impact of technology transfer is starting to effect current trends and may impact on future developments. I was delighted when Gary Hieftje accepted the challenge to write this chapter.

The rest of the book follows the same format as the first edition although there have been some important changes. Chapter 2 looks at the fundamental principles of inductively coupled plasma including details of temperature measurement and recent studies employing solid-state detectors to acquire the entire UV-visible spectra for diagnostic studies. Chapter 3 introduces the basic concepts and requirements for precise and accurate practical measurement and then overviews the instrumentation required for ICP-AES. Again however, the focus is on current developments and there are sections on high-resolution spectrometry, microplasmas and plasma on a chip technology. Chapter 4 looks in detail at sample introduction via liquid aerosol generation but also describes other forms of sample transport such as vapour generation techniques, electrothermal vaporisation and solid sample laser ablation. In Chapter 5 the focus turns to ICP-MS, covering fundamental aspects such as ion sampling, mass analysers and ion detection, prior to a more detailed consideration of the use of ICP-MS for isotope ratio measurements, including selected applications, in Chapter 6.

Another of the original objectives of this book was to provide a useful starting point when users want to try an approach or technique that is new to them. The latter part of the book is designed to help in this regard. In Chapter 7 alternative and mixed gas plasma are discussed. Some aspects of adding additional gases to the argon plasma are now used routinely in many laboratories (e.g. the addition of oxygen when using organic matrices in ICP-MS). Other approaches have remained more of academic interest but may well offer some advantage for specific applications. The following chapter on electrospray ionisation mass spectrometry again offers something additional to users of plasma spectrometry. Whilst not strictly falling within the remit of the title of this book, this technique has quickly established a major role as a complementary technique for trace metal speciation studies, particularly when there is a need to better characterise important complex metal containing species such as biomolecules. The last three chapters put all of the above into a practical context. These three chapters cover geological, environmental and clinical applications together with a detailed account of plasma spectrometry in food science. All three of these chapters have been extensively revised and updated from the first edition.

Before I finish I must express my sincere thanks to the authors who have contributed to this book. My approach, as with the first edition, was to ask internationally recognised leaders to head up each chapter. Of course such people are also very busy (and not really looking to take on yet another task), and so it is a great honour for me to look down the list of those who agreed to contribute and reflect on their expertise, wealth of experience and standing in the field. Their knowledge and insight is reflected in every chapter. I hope that the combination of all our efforts has resulted in a book that is both timely and informative, and that it provides a useful reference for those engaged in using ICPs to achieve their own scientific goals.

Steve J. Hill

Chapter 1

Introduction – A Forward-Looking Perspective

Gary M. Hieftje

1.1 Introduction

It is a distinct honor and particular pleasure to be asked to prepare the first chapter in this new edition of the popular text edited by Steve J. Hill, 'Inductively Coupled Plasma Spectrometry and Its Applications'. When asked, I was requested to consider what the future might hold for inductively coupled plasma (ICP) spectrometry. However, attempting to forecast the future in this ever-changing field is somewhat daunting. As Niels Bohr once stated, 'making successful predictions is difficult – especially when the predictions are concerned about what will happen in the future'. Moreover, there are no doubt some readers who recall an earlier time in which this author had been asked to predict the future of atomic absorption spectrometry (AAS); with tongue firmly in cheek, he extrapolated recent publications in AAS by fitting the trend to a third-order polynomial, a model that projected the demise of the technique by the year 2000 [1]. Readers are therefore urged to use with some caution the projections offered here and to make a special effort to distinguish true projections from those offered in jest.

There are some established procedures that can be employed to forecast the future. The first is to extrapolate past and current trends, both those within the field of interest (here, ICP spectrometry) and those outside that exert an influence on the directions the field might take. These external influences include those imposed by society, technology, and science. A second approach is to assess the likely impact that might arise directly from other fields of science and technology. This sort of 'technology transfer' is clearly apparent in many past and recent developments in ICP spectrometry, an obvious example being the widespread adoption of array-detector technology for multielement determinations in ICP-atomic emission spectrometry (ICP-AES).

Regrettably for the goals of this chapter, some of the most dramatic changes in any field are wholly unexpected. These 'Eureka' events are impossible to foresee or predict but can change completely the thinking of scientists in the field. Interestingly, some of these breakthrough events require some time before their impact is fully realized. An example in our own discipline is the seminal work involving end-on viewing of the ICP, some 30 years ago [2,3]. Although this pioneering work was ignored for many years, end-on emission measurement from an ICP is now widely utilized.

In this chapter, these predictive tools will be exploited to project a possible future for ICP spectrometry. Greatest emphasis will be placed on likely developments in plasma spectrometric instrumentation, since that is the area of the author's greatest expertise. We will begin with an attempt to assess and extrapolate past and current trends.

1.2 Extrapolation of past and current trends

As the American statesman and President Thomas Jefferson once said, 'I know ought to judge the future, save by the past'. Following Jefferson's lead, let us examine first the external forces that influence the directions our field might take. These influences include those from science, society, politics, and the economy.

1.2.1 Influences from science and technology

Scientific influences dictate where the demand, need, and opportunities for atomic spectrometry exist. These forces were recognized fully by Marvin Margoshes in his classical 1979 paper, 'Demand-Pull and Science-Push in Multielement Analysis' [4]. Margoshes realized that the demand ('pull') for a particular activity (in this case multielement analysis) was dictated by emerging and critical applications, whereas the second factor, a 'push', was provided by scientific innovation and discoveries.

Many of the 'pull' factors in the current environment are clear. Perhaps most prominently, bioscience is driving innovation and providing many of the resources that enable today's research to be performed. Particularly important in this regard is the study of metalloproteins and other metal-containing biologically active compounds. Indeed, the importance of this trend has spawned the new term 'metallomics' to describe the activities [5]. However, also important are materials science and nanotechnology, both of which demand multielemental analysis at every-greater sensitivity, in samples of rapidly decreasing size, and on a spatially resolved basis. Energy needs, too, are pulling our field; the metals content in fossil fuels is already of recognized importance, the nuclear-power industry requires a careful elemental inventory of its feedstock and output, and emerging technologies such as hybrid automobiles and the 'hydrogen economy' will no doubt impose additional demands.

Environmental science is already an important customer of ICP spectrometry and will no doubt continue to be so. Moreover, environmental demands and those from many other fields now require information not only on the elemental composition of samples, but also about the chemical form in which those elements are found. The importance of this 'speciation' is already documented in our community, and is on its way to becoming universally recognized in importance.

These demands (pull) on our field are coming at a time when we can expect a time compression in the life cycle of most analytical methods. Because of rapid technological developments, new techniques and instruments will continue to be introduced, to undergo the traditional development and acceptance phase, and fall into senescence as newer, even more powerful methods replace them. It is, in fact, interesting that the field of AES has endured so long [6]. The reason can be found in the continuing developments that reinforce the field. Fundamental discoveries help us to understand better the components of

our systems, from sample-introduction devices to excitation events that transpire in the ICP. In turn, these findings lead to continuous improvements in sources, sample-introduction equipment, and spectrometric systems. We will return to this point later.

Also, pulling our field along is the growing demand for information-rich methods. Because sample mixtures being examined are increasingly complex, it is now not uncommon to see employed a two-dimensional or three-dimensional separation process before an analytical measurement of each constituent is made. Especially in the bioscience area, we can expect to witness these sorts of complex schemes employed in conjunction with ICP spectrometry. Of course, the danger of such combinations is a data storm, a glut of information that must be converted in some form to knowledge. The newly emerging discipline of *informatics* will no doubt play an important role in this interpretation process.[1]

Other science and technology needs include the desire for unattended and remote operation of instruments, so measurements can be made in hostile or unapproachable sites, and the need for simpler, faster, and continuous analysis. These desires are at odds with the operation of the conventional ICP spectrometer, with its high-power consumption and its need for high volumes of high-purity argon.

Just as science and technology will pull our field along because of its needs, there will also be external scientific trends that provide us with fresh opportunities and 'push' our field in new directions. There will probably be, for example, spin-offs from bioscience, materials science, energy, and the environment that are difficult to foresee. One possibility is the development of low-cost solid-state (diode) lasers that could be used in a number of ways, from simplifying spectral alignment in atomic emission spectrometers, to promoting selective ionization in ICP-mass spectrometry (ICP-MS), to reopening opportunities in ICP measurement by atomic fluorescence. Improvements in battery performance and energy storage might also simplify the design of 'fieldable' ICP spectrometers, and lessons learned from bioscience might make possible the design of miniaturized spectrometers based on mimics of the vision process. In fact, whole new generations of microspectrometers might emerge because of developments now under way in the area of nanotechnology. Combinatorial methods, already very popular in chemistry and materials science, might result in the fabrication of new components for ICP spectrometers that are now difficult to envision; also, such methods might result in the introduction of new, highly selective chelates for specific elements, and in new tools for speciation (perhaps in conjunction with bioscience in the form of highly selective aptamers) [7].

Information-rich methods and informatics itself might also simplify in a number of ways our interpretation of ICP spectrometric data. For example, such methods should make it easier to identify suitable internal standards for most elements, perhaps by combining signals from a number of different internal-standard candidates. They could also be applied to the broad range of atomic emission lines or mass-spectrometry signals that can now be acquired in a virtually simultaneous fashion by modern spectrometers. If applied properly, that broad range of signals could provide diagnostic information that would enable a spectrometer to determine if and why a spectral or matrix interference exists for a particular sample and perhaps even help determine how a spectrometer or the ICP itself could be adjusted to overcome the interference.

[1] For example, consult the web site of the Indiana University School of Informatics http://informatics.indiana.edu/

'Interdisciplinarity' is another 'push' that affects our field. Traditionally, analytical chemists have always functioned best when immersed in a problem they are asked to help solve. However, the importance of this cooperation is now being more widely recognized, something that should help those in atomic spectrometry perform their job better. Similarly, electronic publication, virtually instantaneous communication, and nearly free and ubiquitous computing power will make interdisciplinary collaboration even simpler. It will also foster the ultimate development of a truly self-diagnosing instrument and allow its output to be monitored remotely.

1.2.2 Influences from society, politics, and the economy

Let us now turn to external influences on our field other than those imposed by science and technology. These factors include societal, political, and economic. Unfortunately, there is at present a widespread disaffection with science. Smaller numbers of science majors are found each year in universities throughout the world, a situation that will translate into fewer scientists in the future. These shortages will place demands on every surviving laboratory and will require those who remain to be more innovative and more efficient.

Another regrettable trend that affects our field especially is low funding. A widespread misconception about atomic spectrometry is that the ICP is a 'solved problem' and that innovation in atomic spectrometry in general is lacking. Fewer and fewer in our discipline are being funded by major federal agencies, and graduate students considering academic careers are urged to pursue other scientific endeavors. I see no clear solution to this problem, but believe it can be mitigated by education and mutual support. Our colleagues in other areas must be made aware not only of the past achievements of ICP spectrometry but also of its continuing improvement, evolution, and excitement. Young people must be particularly encouraged and urged to introduce atomic spectrometry into other areas where its impact can be appreciated.

The ever-expanding world population will also have an influence on every aspect of science, our own work included. The global population is roughly 6 billion now and is expected to be 9 billion by the year 2050. This larger population will place, again, greater weight on efficiency, energy, and the environment, opening new opportunities (but also new responsibilities) for us.

The fact that we will have fewer students and probably scientists will increase the need for automation and better diagnostics. It might also lead to longer times for students to complete their doctoral studies, a regrettable but perhaps unavoidable trend. Lower funding by federal agencies and from the private sector will place greater demands on resources, potentially leading to stagnation. These funding shortfalls will require selective investment in only the best science.

Finally, there is the aging of the world's population to consider. In our own field, the 'graying of spectrochemical analysis' could lead to a loss of our knowledge base. Already, those of us long in the field witness the reinvention of many things, an efficiency that will become more and more impossible to tolerate. There is a tendency, with the powerful literature search engines that now exist and the desktop availability of journals, to ignore the past literature (except, perhaps, for citation purposes). Every effort will have to be made to compensate for the loss of our knowledge base by exploiting the Internet and developments in

informatics more efficiently. Another impact of population aging will be elevated costs of healthcare and difficulties faced by those on fixed incomes. Again, this situation will no doubt pose problems for our discipline, but also provide it with new opportunities to improve efficiency and develop new tools that provide high-quality multielemental and speciation information but at lower cost.

1.2.3 Past and current trends in atomic spectrometry

There are several ways in which trends in atomic spectrometry can be used to predict its future. The most straightforward way, of course, is to track current or recent changes and simply to extrapolate them to future performance, figures of merit, and instrumental developments. However, an even more effective approach is to assess the strengths and weaknesses of currently available systems and to suggest how the strengths might be improved and the weaknesses overcome. In this approach, it is particularly useful to establish an 'ideal' standard with which the performance of existing systems can be compared [8]. Such an ideal system provides a fixed, immutable standard for comparison, and also serves to indicate not only which weaknesses are most worrisome but also how much existing strengths can be improved. In strengthening attributes and lessening shortcomings, it is appropriate to consider the impact of newly emerging or introduced technologies.

As was suggested earlier, tracing the growth and decline of individual analytical methods is valuable in gauging where a field is headed [6]. The questions that naturally emerge are: (1) What methods have endured? (2) What methods have died? and (3) What are the reasons for these changes? In the field of atomic spectrometry, the changes are fairly easy to define. Flame emission spectrometry, which was dominant in the 1950s and early 1960s, was supplanted by flame atomic absorption spectrometry (FAAS), in part because of improved nebulizer-burner systems that were introduced for FAAS but in part also because of the simplicity of locking onto desired atomic lines by means of the narrow-band emission from a hollow cathode lamp. In turn, FAAS was largely replaced by electrothermal vaporization (ETV)-AAS and by ICP-AES. ETV-AAS offered better detection limits and the ability to handle microliter sample volumes, while ICP-AES provided a considerably broader dynamic range, lower detection limits, and truly multielement capability. More recently, we have seen some of the workload traditionally handled by ETV-AES taken over by ICP-MS, again because it offers truly multielement capability and extraordinarily low detection limits.

These changes appear at first glance to support the concept involved in Velmer Fassel's 'Seven Stages of an Analytical Method' [9]. These stages are outlined in Table 1.1

I would argue that Fassel's list does not fully account for the evolutionary changes in atomic spectrometry that have occurred. In particular, it seems unlikely that immediately after we secure an improved understanding of the fundamental principles of a method, then it becomes outdated. Rather, I would modify Fassel's Seven Stages as shown in Table 1.2. In this modified series of steps, the main change is that an improved understanding of fundamental principles leads to better instrumentation and methods which, in turn, generate better figures of merit and new systems that are introduced into the marketplace, enjoy general acceptance and widespread use, and spur further characterization of the fundamental features of the method. Only when this iterative improvement produces systems

Table 1.1 Seven stages of an analytical method

1. Conception of idea
2. Design and construction of first operating apparatus
3. Successful demonstration of idea; first publication
4. Improvement of instrumentation; figures of merit
5. Maturity; general acceptance; automation
6. Improved understanding of fundamental principles
7. Old age and senescence

Adapted from Fassel, V.A., Fresenius', Z. (1986) *Anal. Chem.*, **324**, 511.

Table 1.2 Seven stages of an analytical method (modified)

1. Conception of idea
2. Successful demonstration and publication of idea
3. Improvement of instrumentation; figures of merit
4. Maturity; general acceptance; automation
5. Improved understanding of fundamental principles; introduction of new instrumentation
6. Iteration of steps 3–5
7. Old age and senescence

that fail to compete with new techniques and technologies does the method then enter its period of old age and senescence. At that point, it will of course be supplanted by the newer technologies. We will consider this issue in somewhat more detail shortly.

1.3 Influence of technology transfer

Advances made in other fields of science and technology will no doubt have an almost immediate impact on ICP spectrometry. Let us deal with a few of these ongoing changes and their likely impact.

1.3.1 Electronics and data manipulation

Electronic systems are being made ever faster, smaller, and less expensive. This will lead to smaller, cooler-running systems that are more likely to be portable. Further, power supplies should become more efficient and therefore less critical. At present, power supplies constitute one of the most expensive components of commercial ICP-AES or ICP-MS systems. In addition, *fast data acquisition* will become more powerful and simpler, making it possible to read detector-array chips even more rapidly and making it more straightforward to perform multielemental analysis on transient samples such as those produced by laser ablation, flow-injection, or chromatography. Fast data acquisition will be particularly important, of course, for inherently high-speed techniques such as time-of-flight mass spectrometry (TOFMS).

On-board data manipulation by *digital signal processing* (DSP) chips will make it possible for an instrument to process increasingly complex data arrays and to devise strategies

for characterization that permit samples to be characterized more fully and immediately. The low cost of electronic systems and *virtually free computing power* will encourage the use of redundancies so instruments become more robust. Further, as outlined earlier, *self-diagnosis* of instrumentation will become common. Lastly, the *human–computer interface*, which has already undergone a revolution of its own, will improve even further. Data displays are likely to evolve from current models that show tables and one-dimensional plots to those that display more complex patterns, more easily recognized by humans. Examples can be found in the field of informatics, in which complex data arrays are being expressed in the form of human-like faces, whose subtle expressions we as human beings have come to recognize immediately. In a similar vein, complex-data patterns are now being expressed by audible signals, in varying tones of pleasantness or dissonance, according to the 'quality' of incoming information. Even tactile feedback seems reasonable; just as an experienced automobile driver benefits from 'road feel', operators of future ICP spectrometers might obtain a sense of how an instrument is performing or the nature of a sample by means of pressure, vibration, or force applied to the operator's hand.

1.3.2 Metal-binding structures

As it was suggested before, novel *lock-and-key structures* useful for elemental or speciation analysis might emerge from both materials' science and bioscience activities. An example is the use of aptamers [7]. Simply viewed, aptamers are single-strand DNA structures that have been intentionally evolved to interact selectively with specific moieties. Most commonly applied to protein analysis, aptamers are also now being explored as vehicles for the selective tagging of smaller molecules or structures and might some day be applied to metal ions, oxyanions, and other chemical systems currently of interest to ICP spectrometrists. This capability would be a tremendous aid in speciation, since the aptamer would entrap the original species in its native state, thereby avoiding alterations in speciation such as now occur in chromatography or when other conventional methods of separation are used.

Single-strand DNA aptamers are evolved by a repeated process of selection and amplification. A combinatorial sort of approach is initially employed to produce a broad range of DNA structures, which are then collectively allowed to interact with the target species. Those DNA structures that successfully bind with the target are then trapped by a suitable method, while the others are discarded. The DNA species that had been trapped are then denatured, to release the target species, and the DNA strands themselves amplified by the polymerase chain reaction (PCR). The expanded group of DNA molecules is then 'renatured' and allowed to interact once again with the target species. This process of amplification and selectivity refinement then continues until the desired degree of specificity is achieved.

1.3.3 Novel separations methods

The need to analyze samples of ever-increasing complexity might require atomic spectrometrists to become familiar with and employ additional separations' methods in the future. Especially in the field of metallomics, high-efficiency, multi-dimensional separations will no doubt be necessary. In protein characterization, for example, instruments are now being used

that begin with a two-dimensional separation by means of liquid chromatography (LC). In this process, a first LC column that provides a relatively slow separation is followed by a second column that separates on a much faster time scale but by means of an alternative mode of affinity. As a peak elutes from the first column, it is rapidly sent through the second, and overlapping constituents thereby hopefully resolved. The result, of course, is a much more highly defined chromatogram, a greatly increased plate capacity, and much less likely overlap of co-eluting species. Nevertheless, this preliminary two-dimensional separation, which occurs on a time scale of seconds, is now being followed by electrospray ionization and a gas-phase separation by means of ion mobility spectrometry (IMS). Unlike LC, which separates on the basis of the differential affinity of a compound for a stationary and mobile phase, IMS separates compounds on the basis of their gas-phase collisional cross-sections, and on a millisecond time scale. Consequently, even proteins having the same primary structure (amino acid sequence) but different folding (tertiary structure) can be distinguished [10]. Even this degree of separation is today not considered to be adequate, for recent practice is to follow the first IMS stage with a collision cell and a second, faster IMS unit [11,12]. Just as two-dimensional LC provides more information and greater benefits than a single stage of LC, the dual-IMS makes it far less likely that two co-emerging proteins will occur. Moreover, a collision region between the two IMS units permits proteins to be fragmented or altered to provide an additional degree of selectivity.

Conveniently, even this four-dimensional complex stage of protein analysis could be coupled to an ICP system for the analysis of a metalloprotein mixture. It should be straightforward to feed the output from the second IMS system directly into an ICP and to analyze the ICP output by either emission or high-speed MS.

1.3.4 Detector technologies

Continuing improvement in detector technologies has already had an enormous impact on ICP spectrometry and will continue to do so. Pixel densities keep on increasing, costs are lower, readout speeds are faster, sensitivities are higher, all while noise continues to drop. Moreover, technologies intended originally for optical imaging are likely to find their way into mass spectrometers. A recent example is our own work [13] in which a multiplexed array of integrating amplifiers, originally designed for use in infrared detection, was employed in conjunction with a double-focusing mass spectrometer. The result, at present, is a 128-channel detector array that is capable of examining a broad mass range at once, of interrogating each mass location in either a destructive or non-destructive way, in any mass order desired, and of integrating the incoming signal continuously. Even early generations of the array offered sensitivity that equals or betters that of conventional mass-spectrometric detectors based on electron multiplication. Similar developments in electronics and detector-array technology are likely to benefit MS in the future.

1.4 Strengths and weaknesses of ICP-AES and ICP-MS

Before listing the strengths and weaknesses of each of the ICP spectrometric techniques, it is useful to compare the two methods on the basis of the signals they generate and the relative difficulty of measuring those signals above a finite background. Modern ICP-MS

instruments produce signal levels on the order of 10^8 counts per second (cps) when a 1 part per million (ppm) solution of a given element is introduced into them. This signal level would appear to be remarkably high, until it is recalled that a 1 ppm solution of an element having a hypothetical atomic weight of 100, introduced into a nebulizer at a rate of 1 ml min^{-1}, involves the consumption of ~10^{14} atoms s^{-1}. In other words, the efficiency of even a modern ICP-MS instrument is only approximately 10^{-4} %.

However, important is that the background in a typical ICP-MS instrument is extremely low, on the order of 1 cps or less. Consequently, the signal-to-background ratio of an ICP-MS instrument is on the order of 10^8 for a 1 ppm solution. Because background noise follows a Poisson distribution, the noise in the background should be equal to the square root of the background itself, which in the present case is also 1, making the signal-to-noise ratio expected of an ICP-MS instrument equal to 10^8 for a 1 ppm solution. If the spectrometric system behaves linearly, and it is expected to do so, the signal-to-noise ratio should therefore be unity at a concentration of 10^{-8} ppm, or 0.01 ppt. Because detection limits are ordinarily defined at a S/N = 3, this calculation would suggest a detection limit of 0.03 ppt for an ICP-MS instrument, roughly what is commonly quoted.

The same set of calculations for an ICP-AE spectrometer yields rather different results. Initially, one might expect that an emission measurement would be more efficient than MS. After all, in MS each ion can be detected only once, whereas a free atom or atomic ion can be repeatedly excited at rates typically approaching 10^8 times per second. Thus, 10^{14} atoms s^{-1} (the consumption rate for a 1 ppm solution) should produce as many as 10^{22} photons s^{-1} if the atoms could all be captured and detected. In contrast, measurements made in our laboratory and confirmed elsewhere suggest a more typical count rate of 10^6 per second from a high-quality photomultiplier tube, when a 1 ppm solution is introduced into the ICP. Accordingly, the efficiency of an ICP-AES system is even lower than that of ICP-MS! The reason, of course, lies in the limited time that is available to observe each atom or ion as it passes through the observation zone in the plasma (about 10^{-4} s), the relatively small solid angle of radiation that is captured (~0.01 sr), optical losses, and the relatively low quantum efficiency of even the best photomultiplier tubes. In both ICP-AES and ICP-MS systems, of course, there are additional losses imposed by the sample-introduction system, diffusion in the plasma, and the finite efficiencies of atom and ion formation.

Of importance also is the background that is encountered in ICP-AES. Produced in part by recombination of argon ions and electrons and by the Lorentzian wings of the many atomic spectral lines found in the plasma, this emission background in a typical spectrometer is on the order of 2×10^4 counts s^{-1}. Combined with the signal level of 10^6 cps, this calculation yields a signal-to-background ratio of 50, which is commonly encountered. The signal-to-noise ratio of the system can then, once again, be obtained by recognizing that the background should be Poisson in its statistical characteristics, to yield a noise level of just over 10^2, and a S/N of 10^4. This value for a 1 ppm solution then dictates a detection limit in the range of 0.3 ppb, approximately what is found.

From these crude calculations, it appears that ICP-MS enjoys an advantage in S/N over ICP-AES of a factor of 10^4, which experience shows is about the same as the relative limits of detection. However, other conclusion can be derived:

(1) Both systems are rather inefficient, with ICP-AES being extraordinarily so.
(2) ICP-AES signal levels are only a factor of two or so weaker than those in ICP-MS.

(3) Background levels in ICP-MS are far lower than those in ICP-AES.
(4) Signal and noise characteristics are all highly dependent on instrumentation and therefore should be able to be controlled.

1.4.1 Strengths and weaknesses of ICP-AES

With these considerations as a backdrop, let us now examine the strengths and the weaknesses of each of the ICP spectrometric methods. The strengths of ICP-AES are listed in Table 1.3, but deserve some elaboration. As the foregoing signal analysis indicated, a sufficiently energetic environment (such as that provided by the ICP) can cause each atom to emit as many as 10^8 photons per second. This high count rate enables each atom to be examined many times, unlike in MS, and fundamentally might lead to greatly enhanced sensitivity. Indeed, this is one of the traditional reasons why atomic fluorescence spectrometry (AFS) has been offered as an alternative to emission or AAS.

In addition, ICP-AES produces an extremely line-rich spectrum, permitting spectral lines to be chosen that are ideally free from spectral overlap with those from other species and, as outlined below, can also be used for diagnostic purposes. These lines can come, of course, from either neutral atoms or atomic ions, again providing further information not only about the sample but also about the ICP itself.

Unlike in atomic MS, spatial averaging is trivial to achieve in ICP-AES. In turn, spatial averaging can improve precision, one of the principal reasons ordinarily given for employing end-on viewing and also allowing a region to be selected that is relatively free from matrix interferences [14].

The fact that some modern AES spectrometers can measure virtually all analyte atom and ion lines simultaneously from the ICP, along with emission features from the solvent, intrinsic plasma species, and those entrained from the atmosphere, opens a broad range of options for diagnostics. For example, gas-kinetic ('finger-burning') temperatures (T_g) can be estimated from the Doppler width of some lines, if a sufficiently high-resolution spectrometer is employed, or can be approximated by fitting emission features of molecular species to a Boltzmann distribution based on their rotational or vibrational progressions. Similarly, atomic or ionic excitation temperatures (T_{exc}) can be determined for analyte species such as iron or for intrinsic plasmas species such as argon, merely by fitting the normalized intensities of electronic states to the Boltzmann distribution. Electron number densities, another

Table 1.3 Strengths of AES

- 10^8 counts s^{-1} per atom
- Rich spectrum; choice of spectral lines
- Atom, ion lines
- Straightforward spatial averaging
- Convenient diagnostics
  - T_g, T_{exc}, n_e, M(II)/M(I), MO, etc.
- Simple instrumentation
  - Alignment (visual), familiarity