

A view at the needs of and activities in the analytical atomic spectroscopy community with respect to fundamental reference data

ABSTRACT

This paper discusses why analytical atomic spectroscopists need fundamental reference data, which data they need, and which actions have been undertaken in the recent past to establish the needs, to improve communication about fundamental data, and to expand the databases. As examples of new compilations the paper refers to work in Philips Research Laboratories dealing with the measurement of the physical widths of 350 prominent lines of 65 elements emitted from an inductively coupled plasma (ICP) and "pseudo physically resolved" spectra of rare earth elements (REE), covering 80-pm wide spectral windows about prominent REE lines, also emitted from an ICP. In that context the paper refers to a spectrum simulation program with, *inter alia*, spectral bandwidth as parameter, operational on a personal computer. Finally, the paper discusses the potentials of electronic publications in general and a proposal to start with an electronic supplement of *Spectrochimica Acta*.

INTRODUCTION

The purpose of this paper is to provide information about the needs of fundamental reference data in the analytical spectroscopy community and about some activities aimed at improving a situation, which, needless to say, is not as rosy as one might wish. Analytical atomic spectroscopists use and study plasmas, and therefore we have many interests in common with atomic physicists and astrophysicists. Although our goals, scope, and approaches are different, it appears useful to intensify the contacts between the various communities of scientists concerned with the compilation or application of spectroscopic data.

This may at least increase the awareness of shared needs, on the one hand, and improve access to available, but apparently hidden data, on the other hand.

GOALS AND CHARACTERIZATION OF ANALYTICAL ATOMIC SPECTROSCOPY

The umbrella "analytical atomic spectroscopy" might cover all spectroscopic methods at present used for material characterization, as to both bulk chemical composition and structure. I shall limit the term, however, to spectroscopic methods for elemental analysis covering trace, minor, and major constituents, in solid, liquid, or gaseous samples. I thus exclude from discussion techniques for surface, interface and thin layer characterization.

Main types of spectroscopy used for elemental analysis

- *Classical* optical spectroscopy:
 - atomic emission spectroscopy (AES)
 - atomic absorption spectroscopy (AAS)
 - atomic fluorescence spectroscopy (AFS)
- *Mass* spectroscopy (MS) for inorganic analysis
- *Laser* spectroscopy for inorganic analysis:
 - laser enhanced ionization spectroscopy (LEIS)
 - laser enhanced atomic fluorescence spectroscopy (LEAFS)
 - resonance ionization spectroscopy (RIS)
 - resonance ionization mass spectroscopy (RIMS)
- *X-ray* spectroscopy, such as X-ray fluorescence spectroscopy (XRFS)

Common feature of optical, mass and laser spectroscopies

- Analysis of solids and liquids requires *atomizers*:
 - emission sources (AES)
 - atom reservoirs (AAS, AFS)
 - ion sources (MS)

Global characterization of sources and atom reservoirs

- | | |
|--------------------------|---|
| ● Gas temperature | 2,500 — 10,000 K |
| ● Electron temperature | 2,500 — 50,000 K (?) |
| ● Pressure | 1 torr — 1 atm |
| ● Gaseous atmosphere | Ar He N ₂ O ₂ air |
| ● λ -region used | 160 — 800 nm |
| ● Atomic species used | I II (III) |

Atom reservoirs and sources

● Carbon furnace	AAS	
	LEAFS	
● Flame	AAS	AES
	LEIS	
● Arc	AES	
● Spark	AES	
● Inductively coupled plasma (ICP)	AES	MS
● Microwave induced plasma (MIP)	AES	
● DC plasma (DCP)	AES	
● Laser induced plasma (LIP)	AES	MS
● Glow discharge (GD)	AES	MS
● Hollow cathode discharge (HCD)	AES	
● Hybrid sources (e.g., ICP + LIP)	AES	MS

Basic requirement in analytical atomic spectroscopy

- Control of:
 - sample evaporation/ablation
 - sample introduction into source or atom reservoir
 - sample atomization
 - the interaction of the sample components with the source or atom reservoir
 - the conditions in the source or reservoir (temporal and spatial stability, reproducibility of transients)

Ultimate analytical requirement

- Optimization of all parameters to achieve
 - low detection limits: $\mu\text{g g}^{-1} \rightarrow \text{ng g}^{-1}$ †
 - high precision (= reproducibility): 0.3%
 - high accuracy (= correctness) ‡
 - multielement capability
 - high speed and reliability
 - low cost

† Optimization of detection limits implies minimization of the noise (*i.e.*, the relative standard deviation of the background) and maximization of signal-to-background ratios.

‡ Generally an analysis is not made in an absolute way, but is based on empirical calibration functions obtained with standards of known composition. A major problem is that standards and samples should behave entirely identically, which, in general, is not so: differences in both chemical composition and physical structure may give rise to differences in the analysis signals between standards and samples for similar concentrations of the elements to be determined (termed "analytes"). The associated

potential errors are designated "interferences" and the responsible components "interferents".

Fundamental knowledge needed for rational "analytical" optimization

- Overall plasma characterization: LTE, pLTE, non-LTE, T , T_e , n_e
- Spatial distributions of T , T_e , n_e , and heavy particle densities
- Atomization, ionization—recombination, and excitation mechanisms
- Particle transport mechanisms
- Accurate composition of the atomic spectra and the background [resolution: physical; dynamic range: $> 10^6$]

Eventually, "analytical plasmas" are always complex chemical systems, because we have to contaminate them with the samples, and these samples usually exert a major influence on the plasma characteristics and the spectra.

Conclusion

On the whole, if we want to approach our problems in a rational, systematic way, we are basically concerned with

- diagnosis of sample conversion,
- plasma diagnostics, and
- spectrum analysis.

Therefore we need fundamental reference data in the same way as other scientists dealing with plasmas.

What did we do with respect to these needs and what are we trying to do?

NEEDS FOR FUNDAMENTAL REFERENCE DATA FOR ANALYTICAL ATOMIC SPECTROSCOPY

Actions organized in the past three years

- Organizers:
 - Prof. Alexander Scheeline, Department of Chemistry, University of Illinois
 - Prof. Paul Boumans, Philips Research Laboratories and Spectrochimica Acta, Part B, Atomic Spectroscopy
- Flags:
 - National Research Council Committee on Line Spectra of the Elements
 - *Titre personnel*

- *Spectrochimica Acta, Part B (SAB)*
- Specification of actions:
 - Worldwide circulated questionnaire (1986)
 - Workshop in Scarborough, Ontario (1987)
 - Edited Workshop Proceedings (including reports of questionnaire and transcribed discussions) published in SAB (No. 1, 1988)
 - Column "News on Fundamental Reference Data", with cooperation of the National Institute of Standards and Technology (NIST), formerly NBS, started in SAB (1989)
 - Symposium on Fundamental Reference Data at the XVIth Meeting (Oct 1989) of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS) in Chicago, with cooperation of NIST
 - Proposal for starting an electronic supplement of *Spectrochimica Acta*

The questionnaire was circulated to help establish the scope of the workshop. Approximately 100 responses from laboratories worldwide were received. These responses ranged from requests for retabulation of data which have been known for many years, to requests for impossibly huge amounts of information.

The results of the questionnaire are summarized in the first two papers of the Proceedings of the Workshop (Boumans, 1988; Scheeline, 1988b), which have been published as a special issue of *Spectrochimica Acta B* (Boumans and Scheeline, 1988); the conclusions have been summarized in the Preface (Scheeline, 1988a).

Discussion during the Workshop did not emphasize new work. Rather, it focused on problems which could not be adequately solved using currently available fundamental data tables of line wavelengths, line shapes, transition probabilities, energy exchange cross-sections, and assorted reaction rate constants. The diversity of the spectrochemical community can be seen from the range of points of view expressed. Some people desire source-specific information. Others want source-independent data. Still others are as concerned with the storage and retrieval of data as with the actual data values. It became clear that the individuals and organizations collecting reference data have been oblivious to the concern of analytical spectroscopists and *vice versa*. One effect of the workshop was to start a dialogue concerning reference data which can only benefit both the producers and consumers of such information.

The start of a column "News on fundamental reference data" in *Spectrochimica Acta B* is a direct

and permanent follow-up of the Workshop (Scheeline and Boumans, 1989; Scheeline, 1989). Important is that we now have established some type of hot line with NIST via Dr. Wiese. The first result is that we can rapidly inform the analytical community about new data compilations and also make them aware of older compilations that may have escaped their attention. Evidently, this initial step primarily concerns an improvement in the access to existing and forthcoming information. In the next stage we hope to be able to exert some influence on the filling of the gaps in the data and on the way in which data are disseminated.

Categorization of needs

- Fundamental analytical spectroscopy
 - Reference information for fundamental studies of emission sources and excitation processes:
 - Wavelengths, Transition Probabilities, Fine Structure Data, Cross Sections*
 - Applied analytical spectroscopy
 - Data on spectral interferences, notably to predict line overlap, for at least 50-pm wide spectral windows centred about 300-400 prominent analysis lines:
 - Wavelengths, Sensitivities, Line Shapes and Widths, Fine Structures*

With respect to fundamental analytical spectroscopy the the following detailed recommendations from the Workshop should be mentioned.

(i) From 180 to 600 nm, all emission lines of He I, Ar I, and either Fe I or Mo I should be observed and tabulated as to wavelength, fine structure, and transition moment. Any properties of continua and line broadening within this range which can be determined should be accurately measured. This will provide reference information for fundamental studies of emission sources and excitation processes. Implicit in this recommendation is further consultation between physicists, astrophysicists, and analytical spectroscopists so that all agree on the quality of the collected data.

Jack Sugar of NIST pointed out that the accuracy of the *known* Fe I transition probabilities is high, and that an additional reference, more or less equivalent to Fe I, may well be the Mo I spectrum, which recently has been investigated with considerable care by Whaling and his co-workers at the California Institute of Technology, Pasadena, CA, using an inductively coupled radio frequency argon plasma (ICP), which also is one of main excitation sources at present used in spectrochemical analysis (*cf.* Scheeline, 1989).

(ii) A clearinghouse, perhaps at NIST, should be established for the collection, confirmation, and

dissemination of atomic reference data. Discrepancies between published and observed data, undocumented spectral lines, and other experimental data would be submitted to this clearinghouse to aid in resolution of conflicting data, confirmation of unexpected results, and notification of the scientific community of significant improvements in measurement. The Office of Standard Reference Data at NIST may already offer such a forum, but the use of the Office as a routine clearinghouse for data is not part of the community's *modus operandi*. Should it be desirable to make it such, means of access should be widely publicized.

(iii) Currently, data are available from NIST, the Joint Institute for Laboratory Astrophysics (JILA), Oak Ridge National Laboratory (ORNL), and individual researchers. A single, central facility should perpetually maintain a list of current data. NIST's Bibliographies of reference data form a solid basis for this central effort. This is a corollary of the need for a data clearinghouse.

Symposium at 1989 FACCS Meeting

The symposium during the forthcoming FACCS Meeting in Chicago, organized by Boumans and Scheeline, lists the following speakers and topics.

- W.C. Martin (NIST): Atomic wavelengths, energy levels, transition probabilities.
- J.W. Gallagher (NIST): Atomic collisions cross-sections.
- J.E. Lawler (Univ. Wisconsin): Laser and Fourier transform techniques for measurement of atomic transition probabilities.
- P.W.J.M. Boumans (Philips): Measurement and simulation of atomic spectra: towards an electronic publication.

MEASUREMENT AND SIMULATION OF ATOMIC SPECTRA

Detection limits

Obviously, in spectrochemical analysis, detection limits form an important issue. In AES, detection limits are dictated by the following factors:

- Intrinsic properties of the lines
→ prominent lines
- Source characteristics
→ optimization of source conditions
- Structure of background spectrum as dictated

by the sample composition → *line interference*
→ remedies:

- high-resolution spectroscopy
- mathematical (chemometric) techniques

However, part of the problems connected with line interference stem from

- (a) the lack of quantitative spectral data appropriate to each of the common excitation sources, and
- (b) the intransferability of available data between different spectrometers.

Spectrum simulation: ab initio approach

The absolute ideal would be to have available the transition probabilities of "all" spectral lines as well as quantitative models for calculating the spectral emission distributions for the various sources. An interesting attempt to spectrum simulation using this approach has been made by Burton and Blades (1986, 1987) for spectra emitted from an ICP. The approach is currently limited by both the lack of accuracy and the limited availability of transition probabilities for all elements. The simulated spectra are only as complete and accurate as the *gA*-values used to generate them.

Spectrum simulation: compilation of new data

In Philips Research Laboratories we also made an approach to spectrum simulation (Boumans *et al.*, 1988b, 1989). We measured high-resolution spectra in 80-pm wide spectral windows about prominent analysis lines, deconvoluted the spectra, stored the physically resolved spectral data in the computer, and simulate spectral scans by convoluting the physical spectra with the instrument function.

To cover a maximum of pitfalls during the design and development of the measuring and simulation procedures we chose the complex spectra of rare earth elements (REE) for the exploration of the approach, which is further specified as follows.

- Excitation source: inductively coupled plasma
- Prominent lines: 26 lines of the most abundant rare earths: Ce, La, Nd, Pr, Sm
- Interferents: all rare earths
- Dynamic range: 6 orders of magnitude
- Number of lines of interferents: 1100

To cover also very weak lines we exploited a dynamic range as large as 10^6 , but this demanded some sacrifice from the resolution, so that we

eventually obtained what we called "pseudo physically resolved spectral data", which for the time being are entirely adequate and can be treated in convolutions as truly physically resolved data, except at very small spectral bandwidths. This approach was feasible as a result of exploiting the basic outcomes of the measurement of the shapes and physical widths of 350 prominent lines of 65 elements emitted from an ICP (Boumans and Vrakking, 1986).

The publications (Boumans *et al.*, 1988b, 1989) describe the approach and cover assessments of the results for internal consistency and vis-à-vis classical data compilations (Gatterer and Junkes, 1945; Norris, 1960; Harrison, 1969; Meggers, Corliss, and Scribner, 1969) and a recent compilation for another ICP (Tielrooy, 1987; Boumans *et al.*, 1988a). This assessment demonstrates the poverty and, in fact, the definitive bankruptcy of the classical tables!

ELECTRONIC PUBLISHING IN SPECTROSCOPY

The publications on spectrum simulation (Boumans *et al.*, 1988b, 1989) describe the approach and its evaluation, show examples, and cover the underlying data. The only shortcoming is that the reader is doomed to passiveness whereas the subject urges him to activity! The reader would absorb the quintessence of the approach far more easily if he could himself specify parameters, choose examples from the infinite variety of possibilities, and watch the outcome on the computer screen. Not only would this facilitate his job as a reader, it could also fruitfully contribute to the development of new ideas and induce cross-fertilization.

Recognizing that this wealth of spectroscopic data including the simulation program may be important for the spectroscopy community as a benchmark and milestone as well as for its didactical value, we have redesigned and extended the program and data to make it operational on personal computers (PC) using a compiled version on diskette.

These are the main features of this potential "electronic publication":

- *Compiled program*: operational directly from "floppy" on IBM compatibles.
- *Simulates* about 240 REE spectra (80-pm) centred about 26 wavelengths.
- *Parameters*: Doppler temperature, a -parameter of Voigt profile, spectral bandwidth, interferent

concentration.

- Covers simulation of interferent *plus* analyte spectra.
- Covers *superposition* of spectra of various interferents without or with analyte.
- Provides a multiplicity of *numerical data*, either appended to the graphics or in separate tables.

Obviously, the simulation program is only one example out of a plethora of potential electronic publications in spectroscopy. Generally speaking, I believe that there should be established adequate and "well structured" ways for readers to obtain programs and data on electronic media in order that they can explore published approaches more efficiently and incorporate them effectively in their own research work.

As Editor-in-Chief of *Spectrochimica Acta B*, I'm therefore considering the feasibility of starting with an electronic supplement of *Spectrochimica Acta*: SAE, *Spectrochimica Acta Electronica* (Boumans, 1989). A prerequisite for such a proposal is to establish the market of attractable electronic manuscripts in the authors' domain and the market of subscriptions in the readers' domain.

I do not see an electronic publication as a replacement of classical journal publications, but as an extension (Boumans, 1989), and I am not the first to consider such a possibility. One example is: *Tetrahedron Computer Methodology*, TCM (Wipke, 1988), which may be featured as follows.

- TCM focuses on new computer methods for handling chemical information, representing chemical entities, designing algorithms, and solving problems relating to organic chemistry.
- TCM is published and distributed as hardcopy journal plus floppy disks.
- The disks contain texts and, where possible, graphics of the printed version, and also additional key information such as executable programs, source code, data files, and parameter sets.
- Readers can reproduce published computer chemistry "experiments", apply a new algorithm to their own data, or use their own three-dimensional display software to view a molecular model, published in TCM, in ways not pictured in the printed article.
- The electronic version of TCM *text* offers the reader on a PC full text search capability.
- The readers can easily transfer references, molecules, reactions, and figures into their own personal documents or databases.

A major problem for research workers in an industrial organization may be the odium that sticks on "making software available to third parties", where the sting is in the term "software". Making a clear distinction between "electronic publication" and "software" appears indispensable to pull down possible "psychological and political barriers". The following definitions and explanations may be helpful to settle this point.

- *Software* is a commercial product, which is brought onto the market with the purpose of making money.
- Software should fulfil a particular specification and the vendor should guarantee the customer that the software does what the specification promises.
- The "power" of the software package and the degree of development are reflected in the price.
- An *electronic publication* is *not* the author's commercial product, but an extension and partial replacement of a classical publication, having the purpose to provide the "reader" (*not* the "customer" or "user") with information that may or may not be communicated in printed form, but can be far more effectively or even exclusively disseminated in electronic form to enable the reader picking up the thread of the work immediately and manipulating the author's data in the way described by the author.
- The reader gets the electronic publication as part of his subscription to the journal.
- The reader gets the same guarantees as a classical publication provides him: the author did his best to perform the research work in a scientifically correct and reliable way and the editor consulted reviewers to separate the wheat from the chaff.

Types of information that might be covered by a possible electronic supplement of *Spectrochimica Acta*:

- Programs with data that enable the reader to become actively involved in the communicated work, with a minimum of additional programming.
- Data such as transition probabilities, tables of normal-coordinate calculations, and whatever atomic or molecular spectral data in either numerical or graphical form.
- A gradually built, efficient subject index for *Spectrochimica Acta*, with text search capability,

possibly extended to other Pergamon journals, such as *Progress in Analytical Spectroscopy* (rebaptized as *Spectrochimica Acta Reviews*) and *Journal of Quantitative Spectroscopy and Radiative Transfer*.

An important issue is that the leading scientists of the various Spectroscopy Communities seriously reflect about the proposal and help defining concrete examples where this approach could enrich scientific communication.

CONCLUSION

We need more, and more accurate data, we should communicate better about the existing data and the needs for new data, and we should more and more exploit the media that befit communication in the Electronocento (Boumans, 1989).

REFERENCES

- Boumans, P.W.J.M., 1988 — *Spectrochim. Acta*, **43B**, 5–13.
- Boumans, P.W.J.M., 1989 — The dissemination of the results of scientific research in the era of electronic media. In "Future Trends in Spectroscopy", eds Paul Boumans, Sidney Kettle, Walter Slavin, and Jeffrey Steinfeld, *Spectrochim. Acta*, **44**, Golden Jubilee Supplement.
- Boumans, P.W.J.M., and A. Scheeline, eds, 1988 — Needs for Fundamental Reference Data in Analytical Atomic Spectroscopy, Proceedings of a Workshop held in Scarborough, Ontario, Canada, 19–21 June 1987. *Spectrochim. Acta*, **43B**, 1–127.
- Boumans, P.W.J.M., and J.J.A.M. Vrakking, 1986 — *Spectrochim. Acta*, **42B**, 1235–1275.
- Boumans, P.W.J.M., J.A. Tielrooy and F.J.M.J. Maessen, 1988a — *Spectrochim. Acta*, **43B**, 173–199.
- Boumans, P.W.J.M., J.J.A.M. Vrakking and A.H.M. Heijms, 1988b — *Spectrochim. Acta*, **43B**, 1365–1404.
- Boumans, P.W.J.M., He ZhiZhuang, J.J.A.M. Vrakking, J.A. Tielrooy and F.J.M.J. Maessen, 1989 — *Spectrochim. Acta*, **44B**, 31–93.
- Burton, L.L., and M.W. Blades, 1986 — *Spectrochim. Acta*, **41B**, 1063–1074.
- Burton, L.L., and M.W. Blades, 1987 — *Spectrochim. Acta*, **42B**, 513–519.
- Gatterer, A., and J. Junkes, 1945 — *Atlas der Restlinien*, Vol. II, *Spektren der seltenen Erden*. Specola Vaticana, Vatican City.

- Harrison, G.R., 1969 — *M.I.T. Wavelength Tables*. The M.I.T. Press, Cambridge, MA / London.
- Meggers, W.F., C.H. Corliss, and B.F.Scribner, 1975 — *Tables of Spectral-Line Intensities*, N.B.S. Monograph 145. U.S. Government Printing Office, Washington, DC.
- Norris, J.E., 1960 — *Wavelength Tables of Rare-Earth Elements and Associated Elements*. Oak Ridge National Laboratory, Oak Ridge, TN, ORNL-2774.
- Scheeline, A., 1988a — *Spectrochim. Acta*, 1–4.
- Scheeline, A., 1988b — *Spectrochim. Acta*, 15–20.
- Scheeline, A., 1989 — *Spectrochim. Acta*, 129–130, 427–430, 725–728.
- Scheeline, A., and P.W.J.M. Boumans, 1989 — *Spectrochim. Acta*, 125–126.
- Tielrooy, J.A., 1987 — *Ph.D. Thesis*, University of Amsterdam.
- Wipke, W.T., editor-in-chief, 1988 — *Tetrahedron Computer Methodology* (Pergamon Press, Oxford). Thimann Laboratories, University of California, Santa Cruz, CA 95064.

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