

Is it still possible, necessary and beneficial to perform research in ICP-atomic emission spectrometry?

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Introduction

"Nothing tends so much to the advancement of knowledge as the application of a new instrument".

Sir Humphry Davy

It is often said that there is no more need for research in atomic emission spectrometry (AES), and that it is a dead-end street. Therefore, a question could be raised: Is it still possible, necessary and beneficial to perform research in atomic emission spectrometry? Actually this question contains some keywords. "Possible" implies that financial support may be obtained to conduct research regardless of the origin of the support, *i.e.*, national or international agencies, instrument companies, or industry. "Necessary" means that strong needs can be defined by users or instrument companies, or are required because of new regulations. "Beneficial" means that this type of research is recognized through conferences, scientific journals and awards, and that students preparing a PhD thesis on this subject would easily find a job corresponding to their expertise. More complex is what should be "research" in analytical chemistry, and in particular in AES. In contrast to what non-analysts think, research cannot be confined to the use of an analytical method, as sophisticated as it might be. It is similar with computers: using complex softwares does not mean that we are computerists.

Interest in AES

"Atomic emission spectrometry" is a field that academic people may consider as old fashioned compared with

ICP-MS, as AAS could have been once with AES. It is true that AES is one of the oldest analytical instrumental techniques, as the early work started in the 1800s. Almost every principle had been already described during the 19th century, *i.e.*, line specificity and quantitative analysis, along with instrument developments such as the pneumatic nebulizer, although most physical concepts could not be understood because of the lack of knowledge of physics. For instance, the discovery of the electron was only made in 1897 by Thomson. Except probably the concept of internal standardization by Gerlach,¹ and that of limit of detection by Kaiser,² most improvements were related to the technique: development of new radiation sources, more efficient and reliable sample introduction systems, the introduction of gratings in the dispersive systems and photo-electric detection such as the photomultiplier tube (PMT) in 1935, and charge transfer device detectors in the 1980s.³

The advantages of AES are well known: photons can easily travel and be collected with simple optics, they do not exhibit memory effects or degrade detectors, and various detectors are available, including array or 2D detectors. Besides, depending on the radiation source, the spectrum of each element present in the sample can be obtained, which results in an inherent multi-element technique. AES is widely used for elemental analysis in the routine laboratory. The need for elemental analysis will remain for ever as the determination of elements in various matrices will always be a request. The only change will be a trend to determine more and more elements with lower and lower concentrations, in more and more complex matrices, with a demand for more information such as speciation (for bioavailability and toxicity reasons) and structure. Because there are not so many multi-element techniques, there is still room for AES, provided that it will be the subject of further improvements.

Interest in ICP-AES

Many radiation sources have been described with the following being the most popular: spark, glow discharge, laser-produced plasma, electrical field-produced plasmas such as the microwave induced plasma and the inductively coupled plasma (ICP). Each of them has its own advantages, but an ICP has some definitive advantages. An ICP is a highly efficient atomization source, which means that every molecule should be dissociated provided that operating conditions are optimized for this purpose. The ionization efficiency is also high, which justify the use of ICP as an ionization source in inorganic mass spectrometry. Besides, because of the skin effect, the sample is confined along a central channel, which facilitates photon probing, regardless of the viewing mode, radial or axial. Also, the ICP exhibits an excellent tolerance to high salt concentration: as a consequence, limits of detection in a solid prior to digestion are excellent.

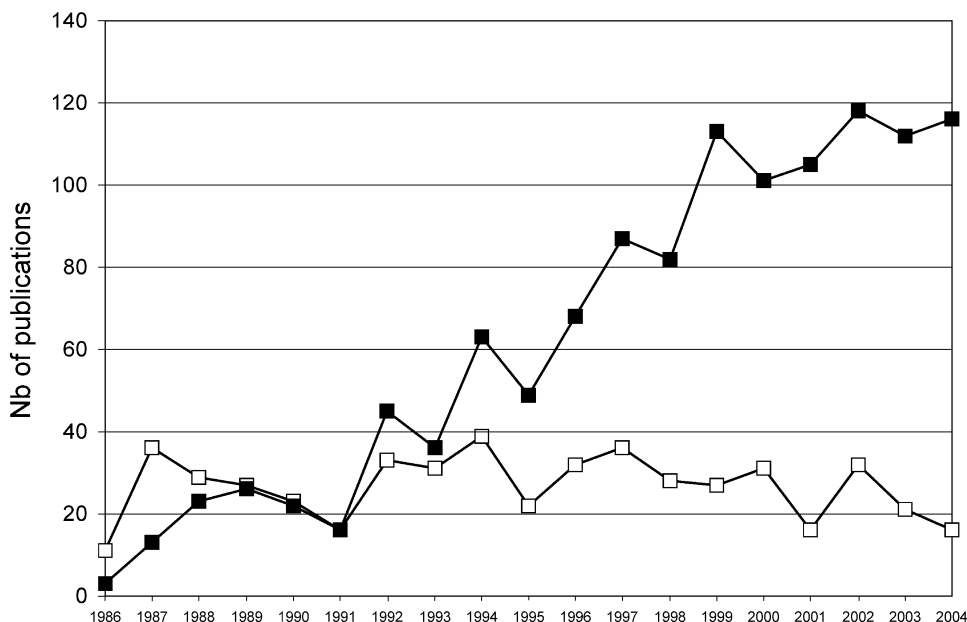


Fig. 1 Number of publications per year published in *JAAS*: □, ICP-AES; ■, ICP-MS.

However, ICP-AES suffers from some limitations: the LOD are excellent for light elements, but are not satisfactory enough for elements such as As, Se, Pb... Spectral interferences due to spectrum richness, line broadening and insufficient resolution can hamper the analysis with matrices such as Co, Fe, Mo, Nb, Ta, U, V, W and some rare earth elements. Non-spectral matrix effects are usually low, but present, which makes them dangerous as the effects are not always obvious. This last limitation is probably the most crucial one.

On the whole, the use of ICP-AES in routine and research laboratories is perfectly justified, which is illustrated by the worldwide market that is about 1400 units a year, corresponding to a turnover of about 120M\$.

In terms of publications, it could be thought that the introduction of ICP-MS led to a decrease in the number of ICP-AES papers. If we select a journal such as *JAAS*, where a large number of ICP-MS papers are published, it is interesting to see that, although the number of ICP-MS publications is still growing, the number of ICP-AES papers has not varied drastically over the past 20 years (Fig. 1).

Basically, an ICP-AES system has remained the same since its introduction: a hf generator, a pneumatic nebulizer associated with a spray chamber, a torch, a dispersive system, a detector and a computer for data acquisition and processing. The system can be partially or fully computer-driven. Major changes have centred on the detection level, with some consequences on the optical mounting of the dispersive system. Before the 1990s, dispersive systems were either monochromators (so-called sequential systems) or polychromators (so-called simultaneous systems). Both types were equipped with PMTs. Most polychromators were based on the Paschen-Runge optical mounting, with the PMTs set up on the Rowland circle. The commercial introduction of solid state detectors, first of the photodiode type, then of the CTD type, either CCD or CID, has revived echelle grating-based dispersive systems, with most of them making use of a post-cross-dispersion to obtain a 2D spectrum. Even the Rowland circle is now equipped with a linear assembly of CCD arrays. As a consequence, conventional polychromators, *i.e.*, those equipped with PMTs, almost disappeared from the market, and sequential systems, which represented about two-third of the market at the end of the 1980s, were overpassed by the new polychromator generation in 1992-1993. Note that there is a dispersive system intermediate between a monochromator and polychromator: the system

is making use of a multichannel CTD detector, and instead of a single narrow bandpass at a time, a more or less wide spectral window is selected and moves sequentially.

Research in ICP-AES

Research may include: (i) search for new physical/chemical processes that can be used for analytical chemistry; (ii) understanding of the processes; (iii) development of the method; and (iv) method validation. More details are given in Table 1. Note that an efficient research study should also imply transfer and dissemination of knowledge and results to students, users, instrument companies, normalization bodies...

It is obvious that the vast majority of publications is related to applications. To illustrate the various fields of research, Fig. 2 gives the number of publications for some fields such as fundamentals, *i.e.*, non-spectral matrix effects, excitation mechanisms and internal standardization, and instrumentation, *i.e.* axial viewing, micronebulization, laser ablation, hydride and vapour generation, and electrothermal vaporization. Also, as an example of data processing, the number of papers related

Table 1 Possible fields of research in atomic emission spectrometry

Search for new physical/chemical processes	
Understanding of the processes	Diagnostics
	Mechanisms Modelling Non-spectral matrix effects Internal standardization
Development of the method	Instrumentation
	Data processing, information retrieval, chemometrics Analytical results Optimization Applications to illustrate the potential and the current limits of the methods
Method validation	Analytical performance Uncertainty and traceability Linearity of the calibration graph

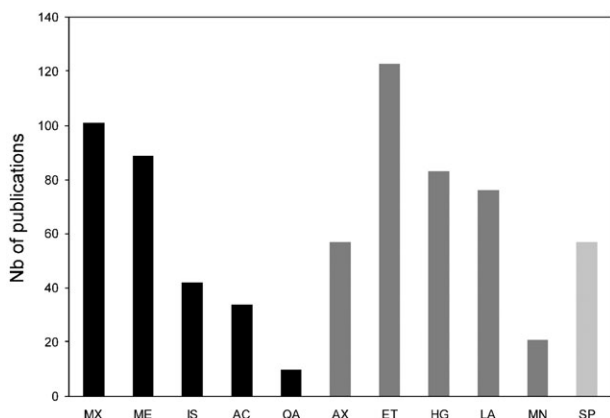


Fig. 2 Number of ICP-AES publications related to matrix effects (MX), mechanisms (ME), internal standardization (IS), acid effects (AC), qualitative analysis (QA), axial viewing (AX), electrothermal atomization (ET), hydride and vapor generation (HG), laser ablation (LA), micronebulization (MN) and speciation (SP).

to qualitative analysis is given. These figures were extracted from over 2300 ICP-AES publications stored in my own database.

Over this number of publications, a similar number of roughly 500 ICP-AES publications have been published in the *Journal of Analytical and Atomic Spectrometry* and in *Spectrochimica Acta, Part B* (Fig. 3).

Note that the classification was not based on keywords, but on my own perception of the contents of the papers. However arbitrary it might be, it is nevertheless an indicator of the past research in ICP-AES. A hundred papers on non-spectral matrix effects means that less than 5% of those papers have been related to this field. It can be easily understood that only very few laboratories have the expertise to run diagnostics based on Thomson scattering because of the complex set-up, along with the need to adapt the instrument for this purpose. In contrast, most of the studies on matrix effects, at least in terms of results, could be performed on commercially available instruments by any analyst willing to do it. Interesting to note is that axial viewing is the default viewing mode for most systems that are currently commercialized. However, less than 60 papers dealt with the influence or the role of such a viewing mode.

A large number of papers are concerned with alternative sample introduction systems such as laser ablation, micronebulization, volatile species generation, electrothermal vaporization. First, a need exists for the replacement of the conventional pneumatic nebulizer. Then, it is probably the easiest part to modify on a commercially available system. Early research in the 1960s was based on the availability of a hf

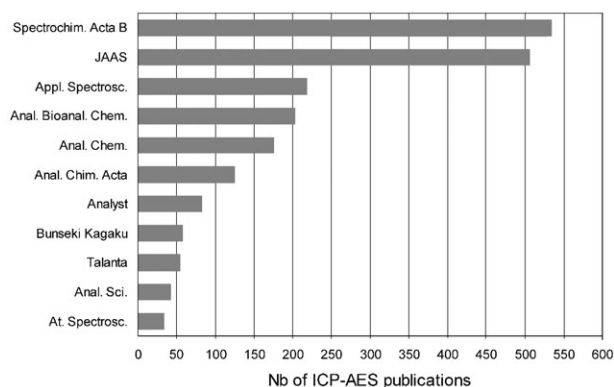


Fig. 3 Number of ICP-AES publications against the scientific journal. Note that the figure for *Anal. Bioanal. Chem.* contains also publication from the former *Fresenius' Z. Anal. Chem.* and *Fresenius' J. Anal. Chem.*

generator either designed for inductive heating (usually with a free-running technology) or for broadcasting (crystal-controlled technology), a dispersive system equipped with photomultiplier tube(s), and a simple acquisition system, for instance a picoammeter associated to a chart recorder. Because systems were not computer driven with the absence of firmwares, and consisted of separated parts, it was relatively simple to modify the instrument configuration. Currently, apart the sample introduction system, it is far more complex to modify a commercially available system.

Evidently, applications are numerous and this field is currently the most popular and justifies the success and the high citation index of scientific journals such as *JAAS*. Surprisingly enough, speciation has been the subject of almost 60 papers, although it could be thought that ICP-MS is the most appropriate instrument for this purpose. In contrast, the number of papers related to method validation, and in particular to the estimation of uncertainty budget, is almost below the limit of detection.

Remaining challenges in ICP-AES

Several reviews have been already devoted to the future of ICP-AES and related techniques.⁴⁻⁷ The question has often been raised as to whether the future would be evolution or revolution.⁴ It is certainly easier to verify whether the current needs are fulfilled than to anticipate technological gaps. Most gaps are inherently unpredictable. However, it is always possible to dream, and, for instance, if a fully tunable UV-visible diode laser were to become available, it would revolutionize atomic fluorescence spectrometry, while a multicathode PMT would allow the design of a dispersive system with sequential windows, keeping the advantages of a PMT when compared to CTD detectors.

To extrapolate current research, it is convenient to define an ideal system for elemental analysis and to verify where the

Table 2 Quality of the analytical results, analytical quality of the system, instrument operation characteristics, and economical aspects

Quality of the analytical results	Accuracy and precision (including repetability, intermediate precision and the various reproducibilities) Uncertainty and traceability using the metrology approach
Analytical quality of the system	Number of elements which can be determined by the system, mostly related to the wavelength range Sensitivity and low limits of detection and quantitation Long-term stability Selectivity, <i>i.e.</i> , the ability to separate the analyte line from concomitant lines, which is related to the practical resolution Robustness, <i>i.e.</i> , the absence of non-spectral matrix and interelement effects High linearity and dynamic range
Instrument operation characteristics	Ease of operation Ease of maintenance Intelligent and fully automated system Use of any form of the sample, solid, liquid or gas Low sample consumption if any Low size and low floor space of the system
Economical aspects	Fast analysis and high sample throughput Reliability Safety Low capital investment Low running cost

Table 3 Remaining fields of research in ICP-AES

Plasma generation	Mixed-gas plasma
Sample introduction system	Total-consumption system Chemical vapor generation Direct solid analysis
Photon collection and detection	Axial viewing
Intelligent software	Reduction in shot noise Improved solid-state detection Automatic (multi)line selection Semi-quantitative analysis True self-diagnostics
Analytical performance	Improvement in limits of detection Origin and minimization of matrix effects
Method validation	Guideline Uncertainty budget

missing features are located. A system may be characterized by the quality of the analytical results, the analytical quality of the system, the instrument operation characteristics, and the economical aspects. Details are given in Table 2.

Considering that the analyst is a problem solver and needs accurate and precise results, along with low limits of detection and quantitation, some challenges remain in ICP-AES and are summarised in Table 3.

Hf generator design

There is a need to design a hf generator that can easily accept significant changes in the load, *e.g.*, wet *versus* dry aerosol, vapors, volatile organic solvents, large amounts of foreign gases, or simply change in the matrix nature or concentration in aqueous solutions, without a change in the plasma characteristics such as temperature, electron number density or spatial distribution. Note that the design may be adequate, but the final tuning may have a drastic influence. Warm-up time and long term stability are still of concern for obvious reasons.

Sample introduction systems

Clearly, sample introduction system is a field where there is the need for more flexibility and less sensitivity as regards the sample form. It seems surprising that most ICP-AES analysts are still using a concentric pneumatic nebulizer very similar in design to that described by Gouy at the end of the 1800s. Although specifications are different, diesel engines have been the subject of significant improvements, mostly because of the very high-pressure introduction system. We probably need to have a closer look at the research performed in the aerosol formation field.⁸ There is a demand to design sample introduction systems with a trend to total-consumption devices, producing either smaller droplets or directly vapor or volatile species, along with noise reduction.⁹ This is justified by the coupling with separation methods (need for low flow rates), by the small amounts of sample in some fields such as biology and forensic sciences, and the need to suppress hazardous waste.

Direct injection is probably a way to pursue, if some current limitations can be overcome: too a large solvent loading, and large size and high velocity of the droplets. An alternative is to modify the role of the spray chamber, so that the chamber acts as an evaporation cavity. This is possible because of the availability of efficient micronebulizers.

Chemical vapor and volatile species generation is a growing field. There is no more need for evaporation, and it is possible to separate the analyte from the matrix. At least half of the elements of the periodic table have a volatile chemical form. Besides hydrides, it may be possible to form chelates, halides (AsCl₃), oxides (OsO₄), carbonyl ((Ni(CO)₄), alkyls with Cd,

Hg, Pb, Se, Sn, S-containing compounds (H₂S). Hydride generation has been extended to unconventional elements such as Ag, Au, Cd, Co, Cu, Ni, Sn, Zn, Os, Pd,¹⁰ with Cd appearing as one of the most successful generations.¹¹ Probably the most challenging research is to allow the simultaneous formation of several volatile species to keep the multi-element capability of the ICP-AES. Moreover, as mentioned above, study of plasma characteristics with a sample in the form of a vapor and with possible excess of foreign gas such as H₂ should be conducted as water no longer acts as a load buffer.

Because the expertise in wet chemistry is disappearing, particularly when trace elements are of concern, the demand for direct solid analysis is growing. Laser ablation ICP-AES is one of the possibilities. It is evident that if a single or a few shots are performed, ICP-MS is more relevant because of its higher sensitivity. In contrast, LA-ICP-AES is highly suited to solid bulk analysis, because a large amount of ablated material can be injected into the plasma without the risk of blocking or having memory effects, as observed with an ICP-MS. However, the key point remains calibration. Even moving to the UV and to very short pulses, LA-ICP-AES (or MS) is still sensitive to matrix mismatch. As there is lack of matrix-matched and homogeneous standards, in particular for exotic samples, *e.g.*, composite materials, polymers, glasses, ceramics, and environmental samples, calibration remains problematic for most samples when a high accuracy is requested. Considering the cost of a certified reference element (CRM), particularly if trace element and homogeneity at the few micrometres scale are a request, only a limited number of CRMs can be released. It is then necessary to develop a far more flexible calibration procedure, which means that the analytical process should not be too sensitive to the composition and the nature of the matrix. Alternative calibration methods, such as the use of wet aerosols, imply that atomization and excitation mechanisms should be similar regardless of the sample form. Note that diagnostics based on AES are more informative than those performed in ICP-MS, because of the access to different ionization states, excitation levels and optical transitions.

Photon collection and detection

It took decades to optimize a torch for radial viewing, including space between the outer and the intermediate tubes, inner diameter of the injector, and carrier gas flow rate. When using axial viewing, besides setting up the torch horizontally, the only change seems to be in slightly larger inner diameters of the injector, *i.e.*, larger than 2 mm. So far, no evidence has been given about the influence of the probing volume, *i.e.*, its shape and location. Besides, the circular shape of the central channel is usually imaged onto a rectangular entrance slit. The aim of axial viewing is evidently to keep the limit of detection enhancement while lowering matrix effects to the level observed for radial viewing.

A PMT presents some major advantages, such as a large wavelength range, including the UV region down to 120 nm, a noise that is usually negligible at room temperature, thus not requiring any cooling device, and a high amplifier gain. However, compared with a photographic plate, the major drawback of a PMT is to be a single-channel detector. AES implies the emission of the spectrum of each element, which means that the use of a single channel detector leads to a drastic waste of information, even when several detectors are set up in a polychromator. There is then a need for a detector that associates photon-current conversion of a photoelectric detector and the richness of information of a photographic plate: this can be obtained by using a solid-state multichannel detector. This type of detector has progressively replaced the PMT since the beginning of the 1990s. In ICP-AES, multichannel detectors used with commercially available ICP-AES systems are currently based on charge transfer technology. Both

charge-coupled device (CCD) and charge-injected device (CID) detectors are in use. Two dimensional CCD and CID detectors, or an association of linear CCD arrays, currently equip commercially available ICP-AES systems and permit a fast acquisition of the entire uv-visible spectrum. An alternative is the use of a solid-state detector leading to a spectral window of several nm, which is sequentially moved through the spectrum.

Benefits, or at least potential benefits, of multichannel detection may be divided into two groups. A first group is related to the richness of the acquired information, *i.e.*, the entire uv-visible spectrum: (i) full flexibility in analytical line selection; (ii) use of several lines of the same element to extend the dynamic range; (iii) use of a large number of lines of the same element to improve accuracy and to verify possible matrix effects or spectral interferences; (iv) qualitative analysis; and (v) fast diagnostics. The second group is related to true simultaneous measurements: (i) speed of analysis; (ii) time correlation between lines of different elements to improve repeatability by internal standardization; and (iii) time correlation between line and adjacent background intensities to improve limits of detection and limits of quantitation.

The use of CTD detectors has revolutionized AES. However, these detectors still suffer from some limitations related to pixelation, UV response, dynamic range and shot noise. Because the spectral bandpass of a pixel is larger than the physical line width, the pixelation phenomenon results in the difficulty of obtaining a fair measurement of the peak intensity, and summation of pixels must be performed to the detriment of the practical resolution. When UV response is of concern, several techniques have to be used: lumogen coating, open electrode technology and backside illumination. Dynamic range, *i.e.*, the ratio between the full well capacity and the readout noise, needs to be increased in order to facilitate the simultaneous measurement of lines with different intensities. This increase may be obtained by reducing the readout noise down to a few electrons RMS. Another significant limitation is the shot noise. For low signals such as background in the UV, the systems are usually shot noise limited, which necessitates long integration times to significantly decrease the relative standard deviation of the signal. This is particularly true when determining limits of detection. Moreover, time correlation between signals can only be observed if the non-correlated shot noise is not a limitation. In order to minimize shot noise, it would then be necessary to improve photon collection, regardless of the viewing mode, radial or axial. It may be said that there is no doubt that multichannel detection is highly beneficial to AES. At least for the time being, CCD and CID are appropriate detectors but not yet ideal.

Intelligent software

The ideal would be to have an autonomous instrument,¹² with an intelligent software to take full benefit of the potential of CTD detectors, as mentioned previously: automatic line selection, efficient semiquantitative analysis, true self-diagnostics and feedback, optimization of the operating parameters, which implies an efficient use of chemometrics and information retrieval.¹³ Automatic line selection should include several to many lines per element, taking into account matrix spectral interferences and relative concentrations, with, when possible, a pool of lines covering different ionization states, excitation energies, optical transitions, so as to carry out an automatic survey of spectral and non-spectral interferences. This selection can be based on an available data base,¹⁴ or use stored single-element spectra and combination.¹⁵

The use of chemometrics should significantly improve data processing, and several publications have already shown the potential benefit of advanced statistics,⁷ based on the use of principal component analysis, multiple linear regression, fuzzy logic, artificial neural networks, and multivariate calibration.

Implementation of chemometrics in software and better knowledge of matrix effects should result in the introduction of an ideal software that should ask a limited number of questions such as: (i) What is your matrix? (ii) Which elements do you want to determine? (iii) What are the expected concentrations? (iv) What precision is required? From the answers, and based on a data base, the software should suggest several sets of analytical lines and appropriate operating conditions, *i.e.*, power, nebulizer gas flow rate and integration time, at least for the most common matrices.

Analytical performance

Improving limits of detection has always been a challenge in analytical chemistry. Acquisition of ICP-MS is often justified by the lower limits of detection that can be achieved when compared with ICP-AES, at least in solution. If LODs could be improved by one or two orders of magnitude, particularly for the so-called heavy elements, because of the advantages of ICP-AES mentioned previously, there would be a return to ICP-AES. There is, then, a need to fill the missing gap between current ICP-AES systems and quadrupole-based ICP-MS. Following the IUPAC LOD approach, two ways can be explored to improve LODs, *i.e.*, either an increase in the signal or a decrease in the noise of the background. Increasing the signal has its own limitations. For instance, use of ultrasonic nebulization does increase the amount of aerosol, but to such an extent that solvent loading is too large, at least with the forward power currently in use. A desolvation process is then required to eliminate a significant part of the solvent. The limitation is the dew point, which implies that not all the water is eliminated, except if an additional device such as membrane desolvation is used. Although promising, these various devices mainly apply to relatively clear solutions, while users want to analyze complex and highly concentrated solutions. It remains to develop at a reasonable cost a flexible and universal device to improve the original analyte/solvent ratio, to consequently increase the analyte signal.

There has been some work on signal modulation.¹⁶ Because of the availability of direct injection nebulizers, the damping effect of the spray chamber no longer exists as a problem, and a signal modulation would be easier to perform.

The other way is to reduce the background noise. There are three major causes of noise: flicker (multiplicative) noise, mostly originating at the sample introduction level (fluctuations of the aerosol cloud at the exit of the spray chamber/tip of the injector), shot noise due to the random emission and detection of the photons, and detector noise (dark current and readout noise in the case of solid-state detectors). Shot noise can usually be minimized by increasing the exposure/integration time. However, for limits of detection, integration time up to 1 min may be necessary as mentioned above, which, associated with a significant number of replicates, may lead to a real time penalty. Because the detector noise is negligible with PMTs and made negligible with solid-state detectors by cooling them to reduce dark current noise, and by selecting a detector with a low readout noise, the ultimate limitation should be flicker noise. It can be reduced by using a sample introduction system with less fluctuations. Several decades ago, a 1% RSD was estimated as a reasonable value for the background fluctuations, while values as low as 0.2% can be currently achieved. However, another possibility is based on truly simultaneous measurements. In this case, possible time correlation between signals can be used to reduce background noise. For that, shot noise should be negligible against flicker noise, as has been previously emphasized.

As regards non-spectral matrix interferences, I would like to quote the conclusions of a recent paper.¹⁷ "Since the beginning of the studies on ICP-AES, non-spectral matrix interferences have been the subject of numerous publications. It can be easily

understood that the selection of a limited number of lines and elements can lead to various conclusions, according to the selection, the operating parameters, the viewing mode, and the ICP type. It is probable that the generator design and its tuning play a role in the magnitude of matrix effects. Use of a large number of lines per element illustrates how complex matrix effects are. Several processes may be involved, including possible different spatial distributions for these mechanisms. Knowledge of the origin of matrix effects remains probably one of the last challenges in ICP-AES in order to obtain highly accurate results. Not only should a large number of lines be used, but the same experiments should be performed on different ICP-AES instruments, probably through a collaborative study." Because there is a large diversity of ICP-AES systems, with different generator technologies, torch designs, observation modes . . . , no single laboratory can cover this variety. It would be most worthwhile to define some key experiments with a well-defined protocol, including test elements, given matrices, range of operating conditions, diagnostics of the plasma . . . , which would be performed through several laboratories. This is certainly one of the most important remaining challenges, because the first quality that an analyst expects is accuracy, which cannot be obtained if calibration leads to a bias.

Method validation

There is a strong request for method validation with the emphasis on uncertainty, because of regulations such as EPA norms or ISO 17025. So far, users have been mostly interested in conventional analytical performance, such as accuracy (or trueness), precision (repeatability and various reproducibilities), and limits of detection. However, more information is requested about budget uncertainty and traceability, which is certainly a difficult and poorly mastered subject. Regardless of the approach, step-by-step or global, the ICP users really need support. Statistical tools are ready but guidelines dedicated to ICP-AES would be most helpful. Most ICP users have no idea of the magnitude of uncertainty that they should obtain, and would appreciate the availability of reliable data for different types of applications.

Other topics

Sampling, sample transport and storage, and sample preparation along with sample homogeneity, are still the ultimate limitations in analytical chemistry. Needless to say, as excellent as an instrument can be, it can only provide results about the analytical sample.

Miniaturization was not mentioned so far. Significant work has been devoted to microplasmas.¹⁸ However, miniaturization of the whole system is far more difficult. Compact dispersive systems have been described,⁶ but to the detriment of practical resolution, which is still a major concern in AES.

Conclusions

Evidently, this paper reflects a personal view of the research in ICP-AES and contains an arbitrary selection of items related to my background and my experience in this field.

Many remaining challenges are related to instrumentation and should be, therefore, solved by R&D teams in instrument companies, with the possible collaboration of academic teams. However, there has been a drastic change in the strategy of companies where most efforts are directed to sales and not to an improvement in instrumentation and applications.¹⁹ This has been clearly reflected in recent conferences where almost no R&D papers were given by instrument companies. A decade or two ago, scientists with international recognition could work and publish while working for an instrument company, but it seems difficult to observe that nowadays. Therefore, can we perform more fundamental and applied research without the support of instrument companies, and if not, which body is able/willing to support this research?

Whatever the use of chemometrics, if matrix effects are present, accuracy will be poor. Their studies are interesting for any research group as most research topics are involved: diagnostics, mechanisms, role of the parameters, viewing mode, efficient use of internal standardization, influence of the sample introduction system, *i.e.*, including fundamental, instrumental and application aspects. This raises another question about the relation with instrument companies: can companies take full benefit of the academic research?

As ICP-AES is still a most appropriate technique for elemental analysis, with some unique features and still subject to significant improvements, the reply to the question "is it still possible, necessary and beneficial to perform research in atomic emission spectrometry?" is clearly "yes".

A last comment concerns the ICP-MS users. They should read results obtained in ICP-AES and not rediscover the wheel when considering plasma characteristics and capabilities.

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