Atomic absorption spectrometry — pregnant again after 45 years

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Received 1 June 1999; accepted 4 October 1999

Abstract

Because atomic absorption spectrometry (AAS) seems to be so simple at first glance, its forthcoming end and replacement by more exciting techniques has been forecasted more than once over the past 45 years. However, AAS has received strong impetus again and again, e.g. by the introduction of the graphite furnace technique, and of flow injection, to mention but a few. Although more and more researchers, and even more instrument manufacturers are turning their back on AAS these days, this author believes that AAS is about to give birth to new offspring in the very near future. The most important ones are solid sampling and speciation analysis on the application side, a much deeper exploitation of the potential of flow injection analysis, the use of diode lasers as radiation sources, and the introduction of continuum-source AAS on the instrumental side. The latter could replace conventional line-source AAS in the foreseeable future because of its obvious advantages in essentially all analytical aspects. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Continuum source AAS; Diode laser AAS; Flow injection; Solid sampling; Speciation analysis

1. Introduction

Atomic absorption spectrometry (AAS) is not a technique that one gets excited about at first glance. One has to come a little bit closer and look twice in order to find out about its charm. Maybe this is the reason why, after the first complete description of the processes of absorption and emission of radiation by atoms in flames by Kirchhoff and Bunsen [1–3] in the 1860s, it was optical emission that caught the interest of spectroscopists, and not atomic absorption. And it has taken almost a century until Alan Walsh began to wonder why molecular spectra were usually obtained in absorption and atomic spectra in emission [4]. And he came to the conclusion that there was no good reason for neglecting
atomic absorption spectra; on the contrary, they appeared to offer many vital advantages over atomic emission spectra, and so he started to carry out his first experiments. Even though Alkemade and Milatz [5,6] published two papers about AAS in the same year when Walsh's first paper [7] appeared, it was Alan Walsh who had the vision of a bright future for this technique, and who was supporting and ‘preaching’ AAS with the dedication of a missionary, until it finally found acceptance in the mid-1960s.

However, even with the support of a visionary scientist such as Alan Walsh, AAS is not necessarily exciting at first glance. When Alan, back in 1952, called his colleague John Willis, and showed him his first experiments with the words ‘look, that’s atomic absorption...’ the disappointing response was only ‘so what?’ [4]. This lack of interest continued when an atomic absorption spectrometer was publicly demonstrated for the first time in Melbourne in 1954. The only person who got excited about AAS at first glance in these early years was Boris L’vov, who decided to check the validity of the author’s ideas immediately after he had stumbled over Walsh’s first publication in 1956 [8], which qualifies him as another visionary scientist who could recognize the importance of a discovery that was disregarded by almost everyone else. And L’vov should become another dedicated missionary of AAS, after he had succeeded to slowly escape the ‘splendid isolation’ of the socialist system of his country.

But similar to the experience that Alan Walsh had to make, the excitement of Boris L’vov was not shared by his colleagues, and it is obvious that Alan and Boris were the exception, whereas this author was more the rule, if I may insert some of my personal history. I remember very well my first contact with AAS. It was when I applied for a position as an application specialist for infrared spectroscopy at Bodenseewerk Perkin Elmer in 1966, and they offered me a position as application specialist for AAS instead. ‘Atomic what...?’ was my first question, and when I was digging into Alan Walsh’s paper soon after, there was a complete lack of excitement on my part. You aspirate a solution into a flame and you get a result immediately — something was missing; there is no spectrum that needs interpretation as in molecular spectroscopy. This technique was too simple for me to be exciting, and I really don’t know why I nevertheless accepted the position as an application specialist for a technique that I did not know anything about at that time. However, the excitement came soon, I only had to meet with the two missionaries of AAS, Alan Walsh and Boris L’vov, the latter at the First Atomic Absorption Spectrometry Symposium in Prague, 1967. It was at that conference when the spark of excitement ignited a flame that would continue to burn throughout my career, and that is reflected in more than 250 publications that carry my name, including a book on AAS that just appeared in its third edition [9].

It may well be the apparent simplicity of AAS (that made me wonder back in 1966 if there is anything of interest in this technique) that caused renowned scientists again and again to forecast the end of AAS for the very near future. There must have been a good reason for Alan Walsh to write his article Atomic Absorption Spectroscopy — Stagnant or Pregnant [10] back in 1974, i.e. there must have been rumors in the air about a forthcoming decay of AAS. But obviously, by that time AAS had already given birth to a new kid, the graphite furnace GF which, however, was not yet well understood, and it required the input of L’vov [11], and the introduction of the Stabilized Temperature Platform Furnace (STPF) concept by Slavin et al. [12] before it could become the driving force for AAS in the 1980s.

But at a time when AAS was in use in every laboratory, and research groups all around the world were unveiling atomization and interference mechanisms of GF AAS, and the increasing knowledge made this technique more and more rugged, there was again a renowned scientist predicting the forthcoming end of AAS. Hieftje [13] applied a third order polynomial to the annual number of publications on AAS, and predicted from the extrapolation of that function that ‘with the current rapid growth in ICP atomic emission and ICP mass spectrometry and with new incursions being made by methods based on glow-discharge lamps, AAS is heading for difficult times. If current trends continue, I would not be sur-
prised to see the removal of commercial AAS instruments from the marketplace by the year 2000.' By that time, however, AAS was already pregnant again, and the name of this new offspring was flow injection FI, a technique the input of which can be considered revolutionary in almost all aspects of AAS analysis [14]. It has been shown repeatedly that FI is far more than an elegant sample handling and sample introduction technique, and the potential of FI has not at all been exploited completely, as will be discussed later in this paper.

Obviously only a few milestones in the development have been discussed in this review of the last 45 years of AAS — if 1954, when the first atomic absorption spectrometer was exhibited in Melbourne [10], is taken as the starting point. Zeeman-effect background correction, simultaneous multi-element AAS, and the introduction of solid-state detectors should at least be mentioned as other important contributions. But now, at the end of this millennium, isn’t it time to look for new goals, new challenges, and send AAS to retirement in the same way as this author was sent to retirement, because AAS is an ‘established technique’ that does not justify any more research. Obviously this author has a different opinion and is expecting a whole series of exciting new developments, both in the field of application and in instrumentation. AAS is clearly pregnant again.

2. New fields of application

When new fields of application are discussed, it is necessary also to consider alternate techniques that might be capable of solving the same problem equally well or even better. It must also be kept in mind that there is no single analytical technique that can solve all problems, and that each technique performs best only in its optimum working range, and that the results may deteriorate quickly when it is used outside this range. The practical analyst looks for a solution to his analytical problems and, if he can choose, he selects the analytical technique that offers the best solution with respect to simplicity, time and cost. Obviously, analytical aspects such as accuracy, and frequently also detection power, play an equally important role.

Inductively coupled plasma mass spectrometry (ICP-MS) is undoubtedly the technique that is most en vogue today for trace element analysis, and there is no doubt about its detection power, its multi-element(-mass) capability, and its speed of analysis. The possibility of doing isotope analysis, in addition, offers a unique field of application that is proprietary to MS. On the other hand, ICP-MS is undoubtedly one of the relatively expensive techniques, both in purchase price and in running cost. ICP-MS also requires considerable operator’s skill, and is certainly not free of interferences, particularly in the presence of complex and concentrated matrices. Because of its popularity and competitiveness, ICP-MS will be the prominent technique for comparison with the new fields that AAS may enter soon.

2.1. FI on-line preconcentration and separation for GF AAS

It has been mentioned earlier that the potential of FI has not been fully exploited for its application in AAS. One of these fields is undoubtedly FI on-line preconcentration and separation for GF AAS, using sorbent extraction in packed microcolumns and/or precipitation and collection in knotted reactors (KR). Although the first papers using these techniques already appeared in the early 1990s [15,16], this idea was never really supported by instrument manufacturers. This is surprising because the combination of FI and GF AAS offers ideal conditions for fully automatic ultra-trace analysis in the low ng/l range in complex matrices under normal routine laboratory conditions. Detection limits of GF AAS in samples such as seawater [17,18] or high-purity reagents [19] are lowered by 2–3 orders of magnitude with a relatively minor instrumental requirement, only an insignificant reduction in sample throughput, compared to direct GF AAS analysis, and no need for clean-room facilities.

An example of the capability of this technique
Table 1: Determination of four elements in doubly deionized water (DDW) and in NASS 2 open ocean sea water standard reference material (National Research Council Canada) using flow-injection on-line sorbent extraction separation and pre-concentration for GF AAS

<table>
<thead>
<tr>
<th>Element</th>
<th>Sample</th>
<th>DDW found</th>
<th>NASS 2 found</th>
<th>NASS 2 certified</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td></td>
<td>24 ± 1</td>
<td>28 ± 1</td>
<td>29 ± 4</td>
</tr>
<tr>
<td>Pb</td>
<td></td>
<td>18 ± 2</td>
<td>41 ± 2</td>
<td>39 ± 6</td>
</tr>
<tr>
<td>Cu</td>
<td></td>
<td>34 ± 5</td>
<td>101 ± 4</td>
<td>106 ± 11</td>
</tr>
<tr>
<td>Ni</td>
<td></td>
<td>73 ± 12</td>
<td>282 ± 14</td>
<td>257 ± 27</td>
</tr>
</tbody>
</table>

*a All values in ng/l; S.D. of \( n = 10 \) (data taken from Sperling et al. [17]).

is given in Table 1, which shows the determination of four trace elements in a sea water reference material by GF AAS after on-line sorbent-extraction preconcentration and separation. The results demonstrate first of all that the technique is capable of obtaining accurate results in the ng/l range in a complex and concentrated matrix such as sea water. Secondly it is shown that all commonly occurring elements can be determined in doubly deionized water (DDW), making an on-line purification of reagents a necessity. Thirdly, by comparing the standard deviation obtained in the sea water sample and in DDW it becomes apparent that it is no longer the matrix that determines the precision, but obviously the lamp flicker noise (nickel is well known to be a noisy lamp). This means the matrix has been separated completely and has no more influence on the determination.

FI on-line preconcentration and separation clearly brings GF AAS detection limits close to those of ICP-MS, and it even surpasses the capabilities of the latter technique when the matrices are considered in which the detection limits are obtained. Obviously, FI on-line preconcentration and separation could also be coupled to ICP-MS, but not with the same ease, considering the eluents that are typically used (organic solvents) and their volume which is usually <0.1 ml. Last, but not least, the running cost for the GF AAS

Fig. 1. Determination of thallium in rock samples by direct solids analysis. (a) Atomization signals are dependent on the tube temperature; 1 — 1100°C, sample sinters; 2 — 1400°C, sample melts; 3 — 1700°C, sample begins to volatilize. (b) Correlation of the AAS signals with neutron activation analysis (NAA) (from Welz [9]).
approach is probably an order of magnitude lower than that for the comparable ICP-MS system.

2.2. Solid sampling for GF AAS

Although Alan Walsh in his first approach proposed ‘that the sample is dissolved and then vaporized in a Lundegardh flame’ [5], which for good reasons became the preferred technique in the 1960s and 1970s, solid sampling is as old as AAS [20]. Boris L’vov used a graphite furnace and a few crystals of sodium chloride in his first experiment back in 1957 to demonstrate the principle of AAS, and several other groups developed a variety of furnaces for solid sample analysis in the following years. Fig. 1 shows an early application of solid sample analysis that was carried out in our laboratory using a prototype of what was later called the HGA-70, and that was presented at the International Atomic Absorption Spectroscopy Conference in Sheffield, 1969. Although the conditions were very primitive at that time, with no reliable tools for solid sample introduction into the furnace and no means for background correction, the results were surprisingly good.

The direct analysis of solid samples, using all kinds of furnaces and devices for sample introduction was continued throughout the past 30 years, as reviewed in a recent book, edited by Kurfürst [21], but it was typically supported by isolated research groups only. This is surprising because GF AAS is an ideal technique for direct solid sample analysis, because it is very flexible with respect to the sample size, which can range from approximately 0.01 mg up to almost 100 mg [22], and also with respect to the form in which the sample is presented. This is among other things due to the way the sample is introduced, e.g. on a platform, the thermal pretreatment in the graphite furnace, and the long residence time of the atoms in the atomizer. The introduction of a commercial system for automatic slurry sampling [23], based on the extensive work of Miller-Ihli [24], could have been the turning point, but the acceptance was not as expected.

More recently, however, there appears to be an increasing market requirement for solid sample analysis, coming predominantly from the producers of modern high-tech materials, such as hard metals, superalloys and ceramic superconductors, etc. All these materials have two things in common: their quality depends extremely on their purity with respect to a number of critical trace elements, and they are very difficult to bring into Table 2

Limits of detection in ng/g (based on 3 s) achievable in analysis of tungsten blue oxide by solid sampling ET AAS (SS-ETAAS) in comparison with those of solution ET AAS (sol-ETAAS), slurry-ETAAS, ion chromatography (IC), coupled to ICP OES, and glow discharge mass spectrometry (GDMS)

<table>
<thead>
<tr>
<th>Element</th>
<th>SS-ETAAS</th>
<th>sol-ETAAS</th>
<th>slurry-ETAAS</th>
<th>sol-ETAAS</th>
<th>IC-ICP OES</th>
<th>GDMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>0.05</td>
<td>0.2</td>
<td>0.4</td>
<td>0.09</td>
<td>1.7</td>
<td>0.3</td>
</tr>
<tr>
<td>Co</td>
<td>0.2</td>
<td>0.4</td>
<td>0.4</td>
<td>0.09</td>
<td>1.7</td>
<td>0.3</td>
</tr>
<tr>
<td>Cr</td>
<td>0.4</td>
<td>0.2</td>
<td>0.2</td>
<td>0.09</td>
<td>1.7</td>
<td>0.3</td>
</tr>
<tr>
<td>Cu</td>
<td>0.09</td>
<td>0.4</td>
<td>0.4</td>
<td>0.09</td>
<td>1.7</td>
<td>0.3</td>
</tr>
<tr>
<td>Fe</td>
<td>1.7</td>
<td>0.4</td>
<td>0.4</td>
<td>0.09</td>
<td>1.7</td>
<td>0.3</td>
</tr>
<tr>
<td>K</td>
<td>0.3</td>
<td>0.2</td>
<td>0.2</td>
<td>0.09</td>
<td>1.7</td>
<td>0.3</td>
</tr>
<tr>
<td>Mg</td>
<td>0.02</td>
<td>0.4</td>
<td>0.4</td>
<td>0.09</td>
<td>1.7</td>
<td>0.3</td>
</tr>
<tr>
<td>Mn</td>
<td>0.07</td>
<td>0.4</td>
<td>0.4</td>
<td>0.09</td>
<td>1.7</td>
<td>0.3</td>
</tr>
<tr>
<td>Na</td>
<td>0.01</td>
<td>0.2</td>
<td>0.2</td>
<td>0.09</td>
<td>1.7</td>
<td>0.3</td>
</tr>
<tr>
<td>Ni</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.09</td>
<td>1.7</td>
<td>0.3</td>
</tr>
<tr>
<td>Zn</td>
<td>0.01</td>
<td>0.2</td>
<td>0.2</td>
<td>0.09</td>
<td>1.7</td>
<td>0.3</td>
</tr>
</tbody>
</table>

\(a\) from Hornung and Krivan [27].
\(b\) Digestion procedure: HF/HNO\(_3\).
\(c\) Digestion procedure: H\(_2\)O\(_2\).
\(d\) Digestion procedure: NH\(_3\).
solution. It was particularly the group of Viliam Krivan in Germany who did excellent pioneering work in that field, demonstrating that detection limits of solid sampling GF AAS are superior to all other techniques available for this kind of analysis, including ICP-MS, simply because the risk of contamination associated with any acid digestion technique, is avoided [22,25–27]. A typical example is shown in Table 2 for the detection limits achievable for a number of elements in the analysis of powdered tungsten trioxide and tungsten blue oxide, using a variety of analytical techniques [27].

Even more important for the practical analysis is that the efforts of Krivan and his group have resulted in the recent introduction of commercial equipment that automates solid sampling GF AAS and makes it accessible for routine application (Fig. 2). It has been shown that modern furnace technology using platform atomization in a transversely heated graphite tube, and integrated absorbance for signal evaluation, has increased accuracy dramatically, making solid sample analysis possible with calibration against simple aqueous standards [22,25–27].

2.3. Speciation analysis

In the 1960s, determination of summation parameters such as total heavy metals in water by sulfide precipitation and gravimetry, was replaced by the determination of the individual elements, as it was recognized that the various heavy metals differ significantly in their toxicity. One of the driving forces at that time was the introduction of AAS which made these determinations easy. In the meantime it is well established that the total content of an element does not give sufficient information, as several elements may be essential for humans or animals, and may be toxic at the same time, depending not only on their concentration, but even more importantly on their oxidation state or the chemical form in which they are present. A typical example is chromium, which is essential in its trivalent form, but carcinogenic in its hexavalent compounds. Another example is arsenic, the inorganic forms of which are well known to be highly toxic, whereas organic compounds, such as arsenobetain, which are found in high concentration in some seafood, are non-toxic, and may even be essential.

A limiting factor for the introduction of speciation analysis into routine use is undoubtedly that most of the research work in that field is currently done using high-pressure liquid chromatography (HPLC) as a separation technique, and ICP-MS for detection. This combination, although very powerful, is far too expensive for routine use, considering that a fast multi-element system is typically waiting 10–20 min for a few species of a single element arriving at the detector. There is no doubt that this kind of research has to be carried out in order to gain all the knowledge necessary for speciation analysis. However, for routine purposes, a good percentage of speciation analysis can be done without prior separation of the individual compounds by chromatography [28]. A simple procedure has, for example, been proposed to distinguish between ‘toxic’, i.e. inorganic, mono- and di-methylated arsenic, and non-toxic
arsenobetaine using hydride generation (HG) AAS [29]. FI on-line column preconcentration and separation is typically selective for one oxidation state of an element only, and may hence be used for the separation of redox species, as was demonstrated for the differential determination of Cr(VI) and total chromium in water [30]. Another example of speciation analysis by on-line separation and preconcentration is shown in Fig. 3 for an activated alumina microcolumn, which at pH 2 selectively preconcentrates Cr(VI), whereas Cr(III) is retained selectively at pH 7 [31]. There is no question that this field of routine speciation analysis is far from being completely explored.

In addition, AAS with a quartz tube atomizer is an extremely attractive detector for gas chromatography (GC), as already proposed back in 1976 by Van Loon and Radziuk [32]. This door was, however, closed by instrument manufacturers with the introduction of digital electronics in the 1980s that no longer permitted the recording of a series of peaks over an extended period of time, i.e. the duration of a chromatogram. It should not be difficult to open this door again, and AAS could then become a sensitive, highly specific, and not too expensive detector for GC [33], and after post-column derivatisation, even for HPLC [34–36]. This aspect of AAS as an attractive detector for chromatography in speciation analysis will be brought up one more time in connection with diode laser AAS (see Section 3.2).

3. Instrumental developments

As in the previous chapter, this author does not intend to consult a crystal ball to see the distant future, but simply wants to analyze the ongoing research for its potential to become attractive for routine application within the next few years. Obviously, as the instrumental developments, even more than the applications, depend on the decision of instrument manufacturers to invest in a particular field, it is not easy to predict if those developments that appear most promising to this author, will really become commercial products.

3.1. FI gradient ratio calibration

Flow injection has been discussed several times already in this paper as a revolutionary technique for sample handling, sample introduction, and for on-line preconcentration and separation for AAS. However, there are many more application possibilities for this technique, particularly because of the very high repeatability of the transport properties and the dispersion of the sample bolus in the FI system. It has been demonstrated that this high repeatability of all events over time can be used successfully to correct for a number of limitations of conventional AAS, including the limited linear working range, and the influence of concomitants on the analyte signal in FAAS [37]. With this ‘gradient ratio calibration’ the entire transient signal produced by the sample bolus is stored in a computer and used for calibration. The ratio of the absorbance of the calibration solution and the test sample solution is formed at the reading frequency of the spectrometer. If no interference is present, and the measurement solutions are all in the linear range, the ratio will not change during the entire measurement. If the maximum absorbance of a test sample solution is outside the linear range, however, the absorbance
ratio changes as soon as the linear range is exceeded. This is recognized and corrected by the computer. The same situation occurs if an interference is present which decreases with increasing dilution (dispersion), as shown in Fig. 4a for the interference of phosphate on the determination of calcium. If the computer program is used to extrapolate the signal ratio over the entire absorbance profile against absorbance $A = 0$, the interference can be eliminated by calculation (Fig. 4b).

A major significance of this procedure is certainly that not only can non-spectral interferences in many cases largely be eliminated by calculation, but more importantly that it can recognize interferences. The possibility is thus given of issuing a warning signal that permits the analyst to thoroughly examine the trueness of the result determined by the computer. This opens completely new perspectives for quality assurance with respect to trueness of analytical results. Techniques like this one, which essentially only require software development, and which belong already in the area of expert systems, should become more and more part of future instruments, as computer capacity is no longer a limiting factor.

3.2. Diode laser AAS

Tunable dye lasers have been proposed as radiation sources for AAS already some 20 years ago [38]. However, in spite of their extremely good spectroscopic properties — they can be set to virtually any atomic line between 213 nm and 900 nm with a bandwidth corresponding to the natural width of an atomic line — they have not found their way into common use because of a number of practical and economic reasons: these laser systems are expensive, frequently unreliable, and difficult to operate. In contrast to dye lasers, diode lasers (DL) appear to be more suitable to one day replace hollow cathode lamps (HCL) and electrodeless discharge lamps (EDL). Semicon-
ductor laser diodes are nowadays mass produced for compact disc players, laser printers, optical data storage systems, and telecommunication equipment, and hence they are cheap, reliable, easy to operate and they have long lifetimes. A number of these diodes have excellent spectroscopic properties which make them attractive sources for spectrochemical analysis [39].

Firstly, the power of presently available commercial DLs is between one and several orders of magnitude higher than what is provided by the best HCLs. In addition, DLs show exceptional stability, both in terms of wavelength and intensity. These two factors together make it possible to measure extremely low absorbances if optimal experimental conditions are realized and the fundamental shot-noise limit is achieved. But even in conventional ‘routine’ atomizers, such as flames and furnaces, detection limits were achieved that were 1–2 orders of magnitude lower than those obtained with HCLs [39,40].

Secondly, the typical linewidth of a commercial DL is approximately two orders of magnitude less than the width of absorption lines in flames and furnaces. This makes possible the expansion of the dynamic range of calibration to high analyte concentrations by measuring the absorption on the wings of the absorption line, where optically thin conditions prevail [40]. In addition, a DL, under normal operating conditions, emits one single narrow line, which dramatically simplifies the spectral isolation of the absorption signal. One does not need the monochromator which is necessary with HCLs for isolation of the analytical line from the other spectral lines emitted by the HCL, and the photomultiplier could be replaced by a simple semiconductor photodiode [39,41].

Thirdly, the wavelength of DLs can be easily modulated at frequencies up to GHz by modulation of the diode current. Wavelength modulation of the DL with detection of the absorption at the second harmonic of the modulation frequency, 2f, greatly reduces low-frequency (flicker) noise in the baseline, providing improved detection limits [39,40]. In addition, wavelength modulation of the radiation source provides an ideal correction of non-specific absorption and significantly improves the selectivity of the AAS technique.

The major limitation of DL AAS at this point in time is that, although a commercial blue laser diode was introduced earlier this year, the lower wavelength limit for mass-produced DLs is approximately 630 nm, which means that even with frequency doubling in non-linear crystals, the important wavelength range for AAS of 190–315 nm cannot be attained yet with this technique. However, this need not necessarily be a major limitation for the successful introduction of DL AAS into routine application, as this technique, in the opinion of this author, is ideally suited for dedicated instruments for special purposes and as low-cost detectors for GC or HPLC. One example for such an application is the HPLC–DL AAS system for speciation analysis of Cr(III)/Cr(VI) proposed by Groll et al. [42]; another example is the tungsten coil atomizer DL AAS system for the determination of aluminum and chromium described by Krivan et al. [41], which is shown in Fig. 5. Another very interesting aspect is that with DLs as radiation sources, the determination of non-metals such as halogens, sulfur, or even noble gases comes within reach of AAS. All these elements have long-lived excited states from which strong absorption transitions can be induced by the red and near-IR radiation of LDs [39]. Zybin et al. [43], for example reported about a determination of chlorine by GC-microwave induced plasma-DL AAS with a detection limit some two orders of magnitude lower than the best values obtained by optical emission spectrometry.

In the opinion of this author, DL AAS should at this point in time not be considered a competitor of the conventional AAS with HCLs and EDLs, but as a very attractive expansion of the capabilities of AAS that opens entirely new fields of application at relatively low cost. The first-generation instruments and modules for DL AAS that became commercially available recently [44] offer an excellent opportunity to exploit the potential of this technique not only in research but already in routine application.

3.3. Continuum source AAS

In his early work of 1952, Walsh essentially ruled out the use of a continuum source (CS) for
AAS because the required resolution of approximately 2 pm was far beyond the capabilities of the best spectrometer available in his laboratory at the time. He concluded that ‘one of the main difficulties is due to the fact that the relationships between absorption and concentration depend on the resolution of the spectrograph...’ if a regular monochromator is used [10]. Hence, line sources (LS), such as HCLs and EDLs were used almost exclusively for routine application of AAS over the past 45 years, as their stable, narrow-line emission guarantees high analyte specificity, even with the use of low-resolution monochromators, as well as good detection limits, and a working range of 2–3 orders of magnitude. The fact, however, that the use of LSs in essence makes AAS a one-element-at-a-time technique (although the simultaneous determination of more than one element has in the meantime been realized) has stimulated researchers again and again to investigate the feasibility of CS AAS [45].

Only recently, however, have these efforts shown convincing results with the availability of high-resolution échelle spectrometers [46], solid-state array detectors [47,48], and continuum sources that have a sufficiently high emission intensity within the small spectral interval under consideration over the entire wavelength range of AAS. Fig. 6 depicts such a system with a Xenon short-arc lamp, a double-échelle monochromator (DEMON), and a CCD detector, providing a spectral resolution of approximately 2 pm/pixel [49]. The resolving power of this setup is impressively demonstrated in Fig. 7, which shows the integrated absorbance spectrum around the cadmium resonance line at 228.802 nm.

Obviously, instruments for CS AAS can be designed in several different ways, and their fea-
Fig. 6. Experimental setup for CS AAS with double echelle monochromator (DEMON); (1) Xenon short-arc lamp; (2) hollow cathode lamp for emission measurements; (3) off-axis ellipsoid mirrors; (4) longitudinal Zeeman graphite furnace module; (5) entrance slit; (6) off-axis parabolic mirrors; (7) Littrow prism; (8) deflection mirrors and intermediate slit; (9) echelle grating (75 grooves/mm, blaze 76°); and (10) linear CCD array detector (from Heitmann et al. [49]).

Fig. 7. Time-integrated absorbance spectrum around the Cd resonance line at 228.802 nm, measured with CS AAS and DEMON; spectral resolution 2.3 pm/pixel (from Becker-Ross et al. [50]).

tures depend on their particular design. The setup shown in Fig. 6 is still of the monochromator type, i.e. designed for the determination of one element at a time. However, it provides a variety of advantages over conventional LS AAS. Firstly, the atomic absorption can not only be measured at the center of the absorption line (with maximum sensitivity) but also at its wings (with reduced sensitivity), thus greatly increasing the dynamic range to approximately 5–6 orders of magnitude.

Fig. 6. Experimental setup for CS AAS with double echelle monochromator (DEMON); (1) Xenon short-arc lamp; (2) hollow cathode lamp for emission measurements; (3) off-axis ellipsoid mirrors; (4) longitudinal Zeeman graphite furnace module; (5) entrance slit; (6) off-axis parabolic mirrors; (7) Littrow prism; (8) deflection mirrors and intermediate slit; (9) echelle grating (75 grooves/mm, blaze 76°); and (10) linear CCD array detector (from Heitmann et al. [49]).

Fig. 7. Time-integrated absorbance spectrum around the Cd resonance line at 228.802 nm, measured with CS AAS and DEMON; spectral resolution 2.3 pm/pixel (from Becker-Ross et al. [50]).
magnitude in concentration or mass. This, together with detection limits that according to recent reports [45] tend to be even better than those obtained with LS AAS, and with the expectation of further improvement, eliminates one of the classical disadvantages of AAS — its limited dynamic range.

Secondly, the setup shown in Fig. 6 with a CCD detector provides a lot of information about the spectral neighborhood around the analytical line, which eventually results in a much more reliable and accurate background correction, as essentially any pixel or set of pixels may be used for that purpose, depending on the nature of the background. In addition, as this wavelength-resolved absorbance is measured over time with each pixel, a three-dimensional absorbance pattern is obtained eventually, as shown in Fig. 8 for the background signal of 5 μl of urine in the vicinity of the palladium line at 247.642 nm. This kind of structured background makes a correction with a deuterium lamp impossible, and presents a problem even for Zeeman-effect background correction [50]. In the case of the CS AAS, however, it was possible to eliminate the background almost completely by a least-squares background correction with the normalized spectra of PO and Na [50].

To extend the capabilities of CS AAS to its full capability, that is simultaneous multi-element AAS, requires the replacement of the one-dimensional array detector by a two-dimensional multi-array detector. This would obviously have a significant impact on the cost and the complexity of the whole instrument, if all the above-described features are to be retained. A sacrifice in information obtained by significantly reducing the number of pixels per array could be a compromise which, however has yet to be investigated. However, as also pointed out by Harnly [45], this author believes that the advantages of CS AAS over LS AAS, even for the determination of one element at a time, with respect to detection limit, dynamic range, spectral information, and background correction capabilities, are so convincing that it is about time for CS AAS to replace conventional LS AAS step by step. The simultaneous multi-element version will then fol-

Fig. 8. Absorption spectrum of an undiluted human urine sample, spiked with 25 pg Pd, recorded with CS AAS and DEMON. Linear dispersion: 2.6 pm/pixel; time resolution: 16.7 ms/scan (from Becker-Ross et al. [50]).
low with the increasing acceptance of CS AAS, and as prices for two-dimensional array detectors drop.

4. Conclusion

Atomic absorption spectrometry is without doubt pregnant, and will give birth to new offspring very soon, provided the instrument manufacturers are prepared to give their assistance. Some of the application-oriented innovations could be incremented at a comparably small effort; others, such as solid sampling for GF AAS are already available, and only wait for their more general acceptance. Diode laser AAS is still a small niche market, but there is hope that the most rewarding fields of application for this technique, i.e. dedicated instruments, detectors for chromatography, and determination of non-metals, will be exploited soon and introduced into the market properly. Obviously, the manufacturers of laser diodes have to recognize the importance of the analytical and sensor market before further progress can be expected. Continuum source AAS, finally, has the greatest potential in the opinion of this author, and it only requires the decision of a courageous instrument manufacturer to re-design the image of AAS, making it young, bright, and prosperous again.

References


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