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Atomic Spectrometry: A User's View [and Discussion]

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Atomic spectrometry: a user's view

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Atomic spectrometry is broadly defined as a collection of analytical techniques, whereby total element concentrations are determined through their interaction with electromagnetic radiation. A description is given of the physical basis, the instrumentation, and the analytical characteristics of the four techniques in current general use: flame atomic absorption, graphite furnace atomic absorption, inductively coupled plasma emission, and X-ray fluorescence. Together they cover almost the complete periodic table and allow determinations down to μg/kg in solid samples, although solutions are the more common vehicle. Six other atomic spectrometric methods are also considered, four of which are commercially available, whereas two are still under development. At present, each serves special applications, but ICP-mass spectrometry and total reflection X-ray fluorescence may become contenders for a more general utilization. It is concluded that atomic spectrometry will remain the method of choice for rapid, total-element concentrations in a wide variety of samples.

1. Introduction

The title of this paper reflects a subtle ambiguity. As a scientific discipline atomic spectrometry includes a collection of analytical methods, whereby free, gaseous atoms (and monovalent positive ions) are detected through radiative processes in the UV–visible region of the spectrum. The purpose-oriented user views them as tools for the determination of total element concentrations in his samples and is likely to broaden the definition to include X-ray fluorescence.

Indeed, in any reasonably equipped industrial laboratory the department of atomic analysis will possess the four techniques that represent the state of the art: flame atomic absorption, graphite furnace atomic absorption, inductively coupled plasma emission, and X-ray fluorescence. Within the narrower frame of bulk trace analysis the three vapour phase methods have a definite edge (figure 1), which justifies their more prominent place in the following discussion. For a proper assessment of their position mutually and collectively, X-ray fluorescence will be included in the comparison.

The fact that the four techniques have coexisted peacefully during the past ten years demonstrates that they are complementary rather than competitive, each serving a particular need in the broad spectrum of applications. Of more concern is the observation that there are no indications that the situation will change over the next ten years. Apparently, current development of the field is evolutionary rather than revolutionary and newly emerging offsprings (and some older ones) may fill particular niches, but do not threaten the position of the big four.

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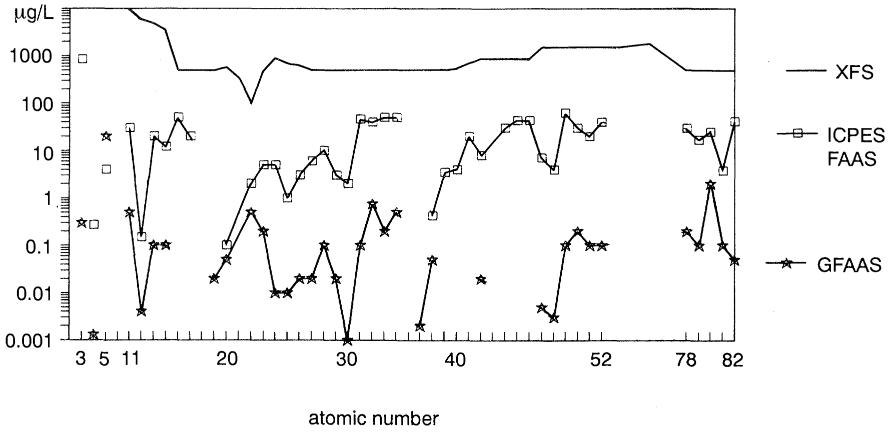

Figure 1. Detection limits in aqueous solutions. For X-ray fluorescence the same values apply to solid samples (µg/kg). Flame atomic absorption gives figures similar to inductively coupled plasma, but for fewer elements. Note the large variations of data for vapour phase methods in comparison with the smooth curve for XFS.

2. Physical basis

Because virtually all samples are originally in a condensed state (solid, liquid or dissolved), they must be converted to a free atomic vapour before they can be analysed by optical spectrometry based on the radiative processes of valence electrons. The importance of this step is emphasized by the observation that the different methods are distinguished primarily by their means of generating a vapour of free atoms, and only secondarily by the observation technique. Thus we distinguish flames, furnaces and plasmas as sources of free atoms, their communal property being an elevated temperature ranging from 2500 to 7000 K. Although other means of liberating atoms from condensed samples have been proposed, such as laser ablation or spark volatilization, the ubiquitous technique is the transfer of thermal energy generated by chemical reactions (flame) or electrical power (furnace, plasma).

The purpose of the phase transition is to create a proportionality between the concentration, c, of an element in the condensed phase and the concentration, n, of the corresponding atoms in the vapour phase:

$$n = Kc. \tag{1}$$

Ideally, the vapour composition is an exact parallel of the solution, which means that the proportionality constant, K, is equal for all elements and independent of the sample composition. Despite many attempts to the contrary, the truth is that this ideal is approached (not realized!) more closely when the sample is a liquid in the form of a fairly dilute (1 % w/w) solution.

The phase transition then consists of a sequence of the following steps (Alkemade *et al.* 1982):

(*a*) the nebulization of the solution into a spray of tiny (5 µm) droplets, or the dosing of a single such droplet;

(*b*) the desolvation of the droplet(s) by vaporization of the solvent;

(*c*) the vaporization of the tiny solid residue of each droplet to molecules;

(*d*) the dissociation of the molecules into free atoms;

(*e*) the ionization of some atoms to singly charged, positive ions.

In view of the large number of physical properties contained in these processes (solvent viscosity, boiling points of solvent and dissolved sample, dissociation and ionization energies), it is remarkable that the ideal of a single proportionality constant in (1) can be attempted at all. Obviously, the temperature of the atom source plays a decisive role and the higher it is, the more closely the ideal is approached. It is for this reason, that the high-temperature inductively coupled plasma has gained its current popularity.

Once the free atoms and ions are formed, we have three radiative processes at our disposal to observe them. Historically the oldest is optical emission of atomic radiation denoted by the simplified expression

$$I_0 = A \exp(-hc/kT)\, n, \tag{2}$$

where A denotes the basic strength of the transition, and the exponential Boltzmann factor stresses the need for a high temperature, T. For practical purposes the emission process offers two advantages. Simultaneous observation of many transitions, and hence elements, is simple and the zero blank signal is instrumental in achieving a long dynamic range (five orders). Against this counts the disadvantage that the emission spectrum is also very crowded, necessitating considerable optical resolution to avoid overlapping signals.

Because absorption of radiation is virtually restricted to ground state transitions, the absorption spectrum is much cleaner. In addition, the primary source of radiation needed for the absorption measurement is an atomic line source automatically tuned to the wavelength of interest. For these two reasons atomic absorption spectrometry is an instrumentally and operationally simpler technique. Quantitative applications are based on Beer's law for atomic transitions

$$A = \ln(I_0/I) = abn, \tag{3}$$

where a again denotes the strength of the transition, and b is the path length in the atom source (ignored in (2)). To derive the absorbance A, the sample intensity, I, is ratioed to the blank intensity, I_0, and this accounts for a practical dynamic range of only three orders.

In principle we can have the best of two worlds (clean spectrum, long dynamic range and multielement capabilities) in fluorescence spectrometry, where the simplified expression takes a slightly different form, depending on whether the observed sample is optically thin or infinitely thick

$$I_{\mathrm{F}}(\mathrm{UV/vis}) = \Phi I_0\, abn, \quad I_{\mathrm{F}}(\text{X-ray}) = (\Phi I_0/a)\, c, \tag{4}$$

where Φ is the fluorescence yield factor. In optical atomic fluorescence spectrometry the first expression applies, but practical realization has always been hindered by the lack of sufficiently intense sources of primary radiation. Continuum sources required for simultaneous multielement observations are much too weak and even boosted line sources are barely adequate. Therefore, the technique has never gained popularity. By contrast, in the X-ray region we can use electron bombardment to create an intense continuum source. Perhaps the greatest advantage of X-ray fluorescence spectrometry is the possibility to observe solid samples directly, because the fluorescent radiation arises from the inner shell electrons. As a result, the penetration depth is only 100 μm, and for ordinary samples the second expression applies.

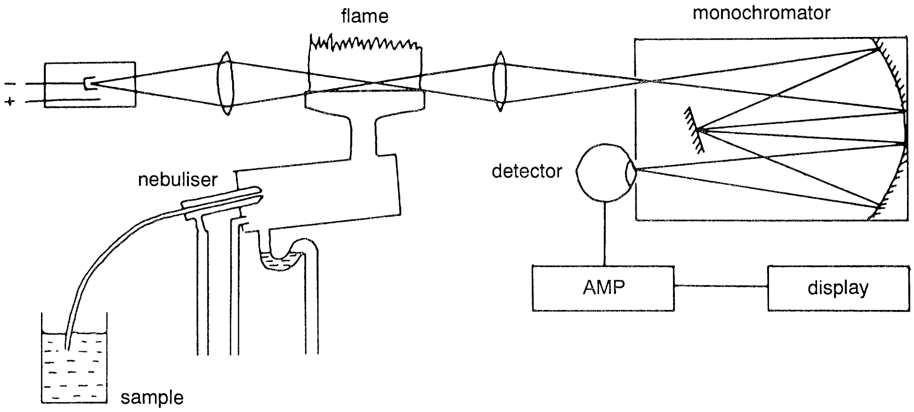

Figure 2. Schematic lay-out of a flame atomic absorption spectrometer.

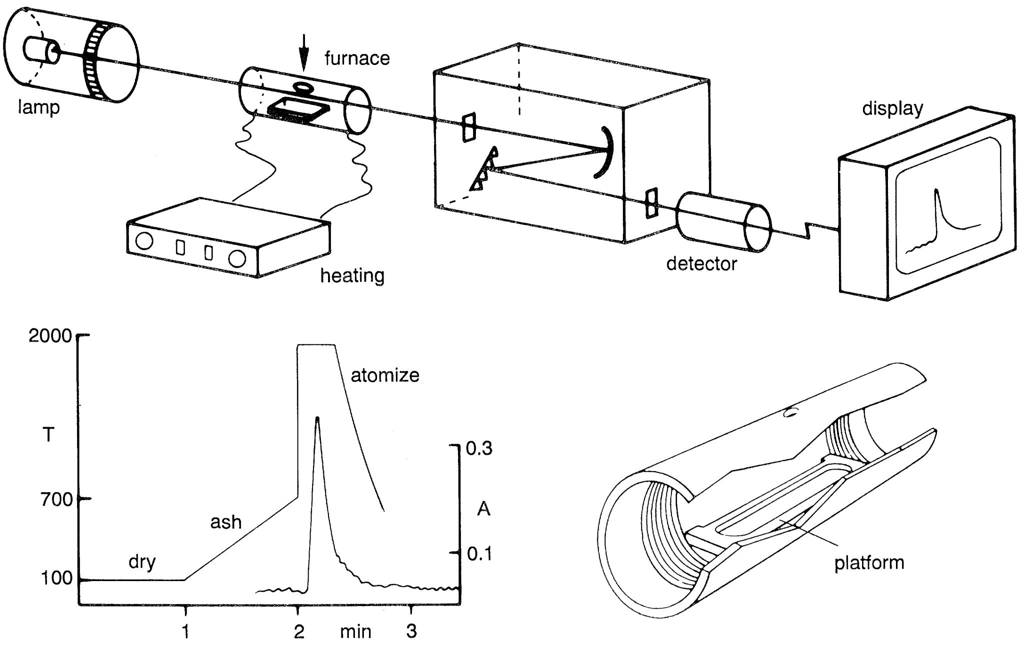

Figure 3. Schematic lay-out of a graphite furnace atomic absorption spectrometer (top) with an enlarged drawing of the furnace (bottom right) and a typical heating curve with transient absorption signal (bottom left).

The combination of (2) with either of the other three defines the calibration curve between radiative signal and sample concentration, c, that forms the basis of quantitative analysis.

3. Instrumentation

An optical atomic spectrometer consists of a source of primary radiation (in the case of absorption measurements), an atom source, a device for selecting and detecting the radiation, and a computer for controlling the instrument and processing the data. Rather than discussing them in this order, the components will be recognized in the description of the standard instruments.

3.1. *Flame atomic absorption spectrometry* (FAAS)

The primary source of radiation is a hollow-cathode lamp designed to emit the atomic spectral lines of the element to be measured. It provides optimum sensitivity and guarantees automatic tuning of the wavelength to the transition of interest, but also implies a separate lamp for each analyte, so that the technique is inherently single-element. Because each measurement takes only a few seconds, this is less of a problem when not too many elements must be determined in a sample. With the advent of multielement emission techniques this is the usual application of FAAS (Welz 1976).

The conversion of a fine spray of dissolved sample to gaseous atoms takes place in a flame, where acetylene is burned with air (2500 K) for volatile elements or with nitrous oxide (3000 K) for the more refractory elements. The moderate flame temperatures help to suppress emission of radiation, which would raise the signal noise, and the ionization of elements, which would reduce the free atom fraction. However, they also account for incomplete dissociation of the molecular sample fragments and, hence, so-called chemical interferences are a serious source of errors. Fortunately, over the years a number of correction procedures have been collected in standard protocols.

After passage through the flame the radiation is selected by a simple monochromator and detected by a photomultiplier (figure 2). Current hollow-cathode lamps are so stable that double-beam instruments are no longer required. Modern instruments are operated from a keyboard with microprocessors used for signal processing (including calibration and reporting) and for the control of sample changers, wavelength selection, flame composition, etc.

The strength of flame atomic absorption technique is its simplicity and reliability. Some 40 elements – all metallic – can be determined down to 0.01 mg l^{-1} at best. With total salt contents of 1% being easily acceptable, the typical concentrations determined in solid samples range from 1 to 1000 mg kg^{-1}. Particularly in the less affluent laboratory FAAS remains indispensable for rapid total element determinations.

3.2. *Graphite furnace atomic absorption spectrometry* (AAS)

When we replace the flame in the atomic absorption instrument by a small graphite tube connected to an electrical power supply, the same observation technique gains a new analytical perspective. The sample solution can no longer be introduced continuously, but is injected as a single 20 μl droplet onto a platform inside the cold furnace (figure 3). Physical processes of desolvation, matrix volatilization and analyte atomization that proceed uncontrolled in a flame can now be carefully sequenced by time-programming the temperature of the furnace until a final burst of heat creates a temperature of maximally 3000 K. The sample atoms released at this stage almost completely displace the protective argon inside the small tube, so that the analytical sensitivity is very high. By far the strongest point of electrothermal atomization AAS is, therefore, the extremely low limits of detection that can be achieved: typically 0.01 μg l^{-1} in solution or 1 μg kg^{-1} in originally solid samples (Slavin 1984).

The price to be paid is the much longer analysis time; the complete cycle including automated sample introduction, sequential heating and cooling of the graphite tube typically takes 150 s, during which time only one element is determined with conventional instrumentation. Attempts to accelerate the heating programme by either skipping the ashing step or by introducing the sample into a preheated furnace have met with limited success. Favourable examples invariably refer to simple, clean samples, but for the average sample shortcutting the temperature programme carries a serious risk of interferences and, hence, unacceptable inaccuracy.

The situation would be improved if we could raise the upper temperature of the furnace, but the melting point of the tube material imposes an obvious limitation and explains the preference for graphite. Another advantage of graphite is its inertness, although the tendency of some metals to form carbides restricts the number of elements that can be conveniently determined by graphite furnace AAS to some 30, again all metallic.

As in all extreme trace analyses, the accuracy of the determinations has been the hardest problem to solve and it has taken many years of gradual improvement to reach the current state of the art. Salient contributions have been made by careful tube design and material (total pyrolytic graphite), by the inclusion of a small platform, by controlled and rapid heating during the final atomization stage, and by adequate correction for background scatter (Zeeman technique). Persistent interferences are being combatted with chemical ingenuity: the addition of modifiers to influence the relative volatility of the matrix and the analyte. At present, the precision and accuracy of electrothermal atomization AAS are acceptable, certainly for trace analysis, but still slightly inferior to the figures reached by other atomic spectrometric techniques.

3.3. *Inductively coupled plasma emission spectrometry* (*ICPES*)

The modest temperature of chemical flames is adequate for the dissociation of most molecules, but not sufficient to excite the liberated atoms into emitting intense radiation, even though the flame spectrometer was originally developed for that purpose. The replacement of the two classical emission sources, arc and spark, awaited the invention of a source of equally high temperature, but inherently more stable and versatile. The answer was the inductively coupled plasma (Montaser & Golightly 1987). Generated by a high-frequency (40 MHz) coil around a silica tube in a flow of argon, the white-hot ring-shaped plasma can reach temperatures of 8000 K. Similar to the flame, a fine spray of solution droplets is carried with a second flow of argon into the centre of the plasma rendering it its typical doughnut shape.

The dynamic character of the system and the use of solutions account for its stability, whereas the high temperature permits efficient phase transition and release of intense radiation from liberated atoms and singly charged positive ions. Radiation is observed 1 cm above the coil, where the temperature is typically 6000 K.

The unravelling of the intricate emission spectra of transition elements requires a monochromator with a much better resolution than in atomic absorption spectrometry. Two types are used. Large monochromators with a fixed grating, and an array of carefully positioned photomultipliers behind multiple exit slits allow the simultaneous observation of up to 40 spectral lines each representing another element. With a new sample every minute, the amount of data generated per day is immense, but flexibility is obviously minimal. The alternative is a much cheaper monochromator with a rotating grating scanning the spectrum across a single exit slit. Consequently, spectral lines (i.e. elements) are measured sequentially, but efficient wavelength peak-hopping provides equal speed for up to five elements. This is the preferred arrangement for the determination of a limited number of varying elements. The wealthy laboratory may acquire a combination of the two (figure 4).

Simultaneous (or rapid sequential) analysis is facilitated by the possibility of defining a single set of operating conditions (electrical power, argon flows, observation height) that is close to optimal for nearly all elements and independent of the sample matrix, although it differs for aqueous and organic solvents. Also, the large dynamic range of the emission technique permits observation of elements with widely different concentration in one dilution. The detection limits are similar to FAAS (0.01 mg l^{-1}), but the high plasma temperature significantly broadens the range of elements that can be determined: some 50 including virtually all metals as well as S and P, but again excluding the halogens and the permanent gases. The greatest limitation to the analysis of complex samples, such as rare earths, is the remaining danger of line-overlap, for which adequate correction procedures are still lacking.

3.4. X-*ray fluorescence spectrometry* (XRF)

Although the basic lay-out of a fluorescence spectrometer can be recognized, the changeover to the X-ray region of the electromagnetic spectrum dictates the use of completely different components. The primary source of radiation is a vacuum tube provided with a tungsten or chromium anode, which releases a strong continuum X-ray spectrum under bombardment by high-energy electrons.

Upon striking the solid sample, the incident X-rays eject electrons from the inner shells of atoms in a thin surface layer, a process exploited analytically in electron spectroscopy. When next the electron holes are reoccupied, energy is released through the emission of either secondary electrons of fluorescent X-rays. The former process predominates for light elements (and is used in Auger spectrometry), whereas from sodium upwards the latter process prevails. The characteristic K- and L-lines of the sample elements are dispersed by a suitable crystal and measured with a scintillation detector. It is a singular property of Bragg's law that only one spectral line is diffracted at a time, so that a simultaneous X-ray spectrometer requires as many detectors and crystals as the number of elements to be determined. Therefore, the sequential arrangement is the more common with a single detector rotating at twice the speed of the diffraction crystal (figure 5).

The dispersion of the crystal is orders of magnitude less than the resolution offered by optical gratings, but fortunately the X-ray spectrum is very simple because each element emits only a few strong lines regularly ordered according to its position in the Periodic Table. Persistent overlap can be removed by electronic means or corrected with deconvolution algorithms. The measurement of spectral lines thus being fairly straightforward, their conversion to element concentrations is extremely complex. Indeed, the absorption coefficient in the denominator of equation (4) depends not only on the analyte, but also and strongly upon instrumental factors and the composition of the sample, suggesting the need for carefully matched standards. Fortunately, this is no longer true (Tertian & Claisse 1982).

It is a tribute to the scientists and the instrument designers that correction algorithms have been developed that are so robust that a few calibration standards suffice to reach an accuracy that matches the unsurpassed precision of the method (better than 1 %).

From a practical point of view the greatest challenge is to ensure that the 100 μm surface layer of the sample is homogeneous and representative of the bulk material.

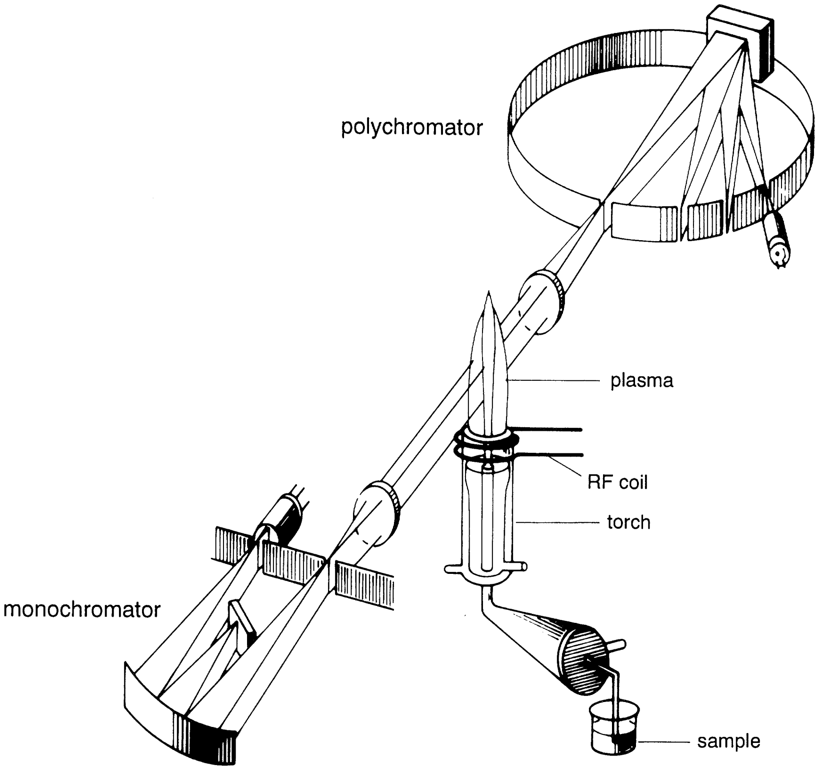

Figure 4. Inductively coupled plasma emission spectrometer. Radiation can be collected with a polychromator for simultaneous measurement or with a scanning monochromator for sequential observation.

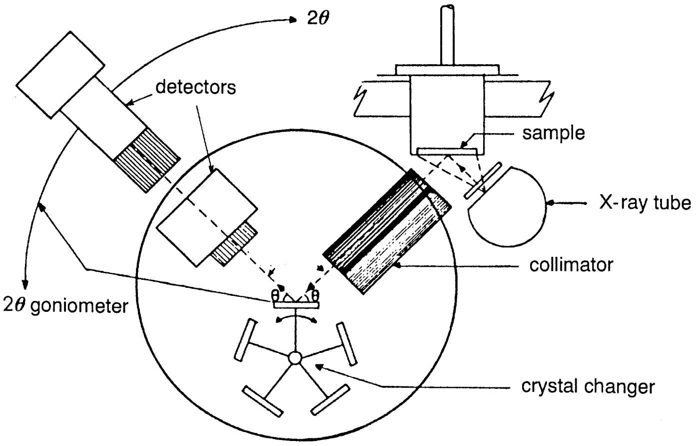

Figure 5. Schematic lay-out of an X-ray fluorescence spectrometer with selectable crystals and two detectors placed in tandem.

Table 1. *Brief characterization of atomic spectrometric methods of analysis*

method	det. limit in solid sample	precision (%)	speed/s	elements
FAAS	< mg/kg	1	10/elem	40 metals
ETAAAS	< µg/kg	3	150/elem	30 metals
ICP emiss	> µg/kg	1	60/run	50 metals
ICPMS	µg/kg	5	60/run	60 (non)metals
XRF	> mg/kg	0.5	300/run	all after Ne

Dissolution is an obvious answer, but the modest sensitivity of XRF makes this a less attractive option.

Fusion and pelletizing are more commonly used. Then the analyst is rewarded with a technique that allows fully automatic determinations of all elements heavier than neon with detection limits in the solid sample around 1 mg/kg.

4. Performance

4.1. *Scope*

The main characteristics of the above four methods are summarized in table 1. It is clear that all offer roughly similar precision although optimum performance may be a little more difficult to reach with graphite furnace AAS than with the other three. Obviously, all four are also relative methods of analysis that require calibration with appropriate standards. Fortunately, the resistance to matrix interferences has improved so much that accurate matching of the standards is no longer necessary. ICP is the least demanding from this view, but even with graphite furnace AAS the cumbersome standard addition technique is no longer used.

The selection of the most suitable method of the four is based on differences in sensitivity, in the range of elements, and in the physical state of the sample. Thus, X-ray fluorescence is the method of choice for non-metallic elements and for determinations in the g/kg range in originally solid samples.

At the other end of the scale, the low throughput and somewhat inferior precision of graphite furnace ASS are readily accepted for extreme trace analysis down to µg/kg. In between, FAAS and ICP emission are used for mg/kg determinations in readily dissolved samples, the latter having the edge when many elements must be determined or elements, such as boron and phosphorus, that are beyond the capability of FAAS.

4.2. *Sample pretreatment*

Sometimes, the nature of the sample is such that it can be submitted to the instrument directly, for example surface waters. Generally, however, more or less elaborate pretreatments are necessary.

Even in the case of X-ray fluorescence spectrometry solid samples must usually be pelletized or fused with lithium metaborate to achieve the necessary homogeneity. Significantly more elaborate procedures are needed before solid samples can be analysed by any of the three optical methods, because they accept only solutions. Time-consuming wet ashing or fusion techniques seriously impair the potentially large sample throughput of FAAS and ICP emission. Direct introduction of solid samples in the form of slurries has been proposed, but the need for extremely small particle size (less than 5 μm) restricts the technique to the rare cases of very brittle, readily grinded materials.

It is a characteristic common to all atomic spectrometric methods of analysis that they determine only total element concentrations, regardless of the chemical environment. In many cases that may be counted as an advantage, but especially in environmental analysis the interest may be in a particular molecular species (organic mercury, inorganic arsenic). To achieve such speciation the sample is subjected to pretreatment before it is submitted to the atomic spectrometer. Selective extraction of valence states, vaporization of volatile species and, most comprehensive, complete separation by either gas or liquid chromatography are widely used. In such hyphenated techniques the atomic spectrometer serves as the sensitive detector of the species of interest.

4.3. *Automation*

In recent years advances in automation have had a large impact. Here we can distinguish between hardware and software. With respect to hardware the origin lies in the fifties with the construction of multichannel instruments allowing simultaneous measurement of many elements. The space-demanding design of multiple slits positioned along the Rowland circle has withstood the test of time, because photodiodes or charge coupled devices lack the sensitivity and stability of the classical photomultiplier tube. Another important step was the introduction of fully automated sample changers with capacities for 40–100 samples. As remarked above, however, much human labour is spent in preparing and dissolving the samples before they can be loaded into the sample changer. Laboratory robots are slowly entering this field, but it will be a long time before they match the flexibility and intelligence of human beings.

In software three stages can also be distinguished. The first addressed the calibration and calculus to convert the primary intensity readings to element concentrations. Apparently simple, it did take some time before the computer acquired the ability to handle nonlinear calibration curves correctly. The next step was the inclusion of algorithms that correct for matrix interferences and line overlap. Here the limitation was not the computer, but the understanding of the complex phenomena. In view of the near-perfection reached in X-ray fluorescence, it remains puzzling why the optical methods, especially ICP emission, are proving so difficult. The problem must be solved before the final step can be taken, whereby the result of the analysis is automatically validated.

As a result of these advances all four atomic methods of analysis can run without human supervision for many hours. The operator loads the sample changer, selects the appropriate analysis program from the computer library and returns at the end of the day to collect the data sheets and analysis reports. In fact, X-ray fluorescence and possibly graphite furnace AAS can run unattended overnight. It is for fear of accidental fire that most laboratories are wary of running FAAS and ICP emission overnight.

5. Rivals and developments

In this section attention will be paid to existing and emerging techniques that have not found general utility, but have proven their value in special cases, or may do so in the future.

5.1. *Glow discharge*

At least in the developed world the classical arc emission spectrometer has ceased to be used. This is not true for the spark discharge, which remains valuable for the rapid analysis of conductive materials (metals and alloys), particularly in the steel industry. The strong matrix effects remain a nuisance, however, and alternatives have been proposed.

The most promising appears to be the glow-discharge, where a conductive sample is sealed in a vacuum tube and bombarded with positively charged argon ions. Sample atoms are sputtered into the discharge area where they emit their characteristic spark-like spectrum. Matrix effects are markedly reduced, but the need for a low pressure retards sample change and has prevented the glow-discharge from replacing the spark. However, it has found another interesting application: the sputtering process slowly erodes the sample and releases atoms from successively deeper layers, thus permitting depth profiling.

5.2. *Inductively coupled plasma mass spectrometry* (ICPMS)

The observation that many elements in the inductively coupled plasma discharge are ionized to a significant extent has led to the development of mass spectrometric detection instead of the optical emission procedures discussed above (Douglas & Houk 1985). The interfacing of a hot, atmospheric plasma with the deep vacuum of the mass spectrometer called for some ingenuity, but once realized the benefit is a hundredfold increase in sensitivity. The instrument, therefore, promises to combine the low detection limits of graphite furnace AAS with the range of elements and the speed of ICP emission.

Yet, the acceptation of ICPMS by the general laboratory has been slower than can be explained by price considerations alone. One reason is, of course, that such high sensitivity is not always needed and the mass spectrometer is a more delicate instrument than the optical spectrometer. Also, the precision of the analysis is somewhat lower than desired, but that may improve with further development. A more serious obstacle are the frequent peak overlaps, not only from the background spectrum of the acidic solvent, but also from molecular fragments of other elements. Despite the apparent simplicity of the mass spectrum, the resolution of the quadruple spectrometer is not sufficient to distinguish the oxide of one element from the 16 a.m.u. heavier neighbour.

Reported applications refer mainly to relatively clean samples, such as rain, surface and sea water, and to geological applications, where ICPMS offers unrivalled possibilities for the extremely sensitive determination of the rare earths.

5.3. *Total reflection* X-*ray spectrometry*

The modest sensitivity of conventional X-ray fluorescence spectrometry arises from the relatively strong background of Compton and Rayleigh scattering. Both effects may be reduced by several orders of magnitude in a completely different instrument design. Here the incident beam of primary X-rays strikes the sample at such small angle (a few minutes of arc) that it is totally reflected. Similar to other regions of the spectrum (e.g. IR) the totally reflected beam penetrates the surface to approximately one wavelength, which for X-rays corresponds to a few nanometres. Secondary X-rays emitted from the thin top layer are collected simultaneously and sorted according to their photon energy by an energy dispersive detector. In comparison with conventional XRF the detection power is stunning: 10 pg absolute or μg l^{-1} for solutions (Klockenkämper 1989).

The collection of radiation from only a few nanometres poses obvious practical problems in sample handling. Protection from contamination is essential. Solutions are analyses as thin films deposited or freeze-dried onto a very clean and optically flat surface, e.g. quartz. Even then, heavy matrices must be avoided and detection power is comparable with ICP emission. Solid samples must be equally smooth, polished even, and the thin surface can never claim to be representative of the bulk. Clearly, the technique offers exciting possibilities for surface analysis of, for example, semiconductors.

5.4. *Microwave induced plasma emission spectrometry*

The success of the radio-frequency inductively coupled plasma has stimulated the exploration of other frequency domains for generating plasma discharges, notably the microwave region (2450 MHz). The preferred medium is helium, flowing gently through a few millimetres wide silica tube, positioned in the centre of a microwave cavity. At moderate power (100 W) the plasma resides entirely within the tube and assumes a pink colour from background helium radiation. The fact that helium lines can be observed at all is remarkable and must probably be attributed to direct excitation by energetic electrons. As a result, the plasma performs better for noble gases and metalloids than for metallic elements.

Because halogens, carbon, nitrogen and oxygen are notoriously difficult to determine by other atomic spectroscopic techniques, the interest in the microwave plasma is easily understandable.

Despite many attempts, including a change to argon as the carrier gas, the introduction of a solution spoils many of the favourable characteristics and reveals persistent matrix effects. The reason is that the microwave plasma is essentially a cold discharge combining a high electronic excitation temperature with a low gas kinetic temperature. Hence, condensed samples cannot be accommodated and acceptable results are only obtained with gaseous samples. In turn, it explains why so far the only commercial exploitation of the MIP has been as an element-specific detector for gas chromatography (Uden 1986).

5.5. *Furnace atomization non-thermal emission spectrometry* (*FANES*)

The realization that the phase transition of condensed samples to a gas requires a high kinetic temperature, whereas emission of radiation is boosted by a high excitation temperature has led to a combination best known by its acronym FANES (Falk *et al.* 1984). The experimental set-up resembles that of graphite furnace AAS, but with two differences. The graphite tube is not only electrically heated, but also kept at a strong negative potential; and after the sample droplet has been introduced and allowed to dry, the pressure inside the enclosed tube is reduced. As a result, the sample atoms released during the final heating stage are excited by colliding electrons and produce strong emission spectra.

Indeed, the detection limits reached in this emission mode are equally impressive as in graphite furnace AAS, with the added possibility of simultaneous multielement determinations. Because the technique has not yet proceeded beyond the research stage, it is difficult to assess its full potential.

5.6. *Continuum source atomic absorption spectrometry*

As remarked above, the single-element character and long cycle time of graphite furnace AAS conspire to reduce the analytical throughput of the technique.

A reduction of the cycle time not being generally feasible, the alternative remedy is a more efficient utilization of the cycle time by increasing the number of elements determined. Realization first requires that the hollow-cathode line source is replaced by a continuum lamp. To maintain adequate sensitivity the resolution of the monochromator must be increased drastically to achieve a band width comparable with the atomic absorption line width of a few picometres. The solution is found in the echelle grating used in very high order. Indeed, with such an arrangement the possibility of simultaneous multielement AAS has been convincingly demonstrated (Harnly & O'Haver 1981).

In fact, it is now even possible to overcome another limitation of conventional AAS. By scanning the complete absorption profile measurements need not be restricted to the maximum, but can also be made at carefully defined positions in the line wing, thereby reducing the sensitivity and increasing the dynamic range of the technique.

Unfortunately, there are two limitations. One is the weak intensity of the primary continuum source in the far UV, which deteriorates the signal-to-noise ratio and, hence, the detection limits of many elements with transitions below 300 nm. The other is more fundamental. Simultaneous measurement of several elements requires a single temperature programme for the graphite furnace, whereas experience has shown that each element, if not each sample type, prefers its own. Compromise conditions, so common for the inductively coupled plasma, do not come easily with the graphite furnace. Until that situation is improved, simultaneous graphite furnace AAS will not become generally applicable, but restricted to a few sample types.

6. Conclusions

Over the past thirty years the four main representatives of atomic spectrometry have developed into reliable, convenient analytical methods for the determination of practically all elements in the periodic table (N, O, F, and noble gases excepted) in a wide variety of samples.

So far their dominant position has not been seriously challenged, although total reflection X-ray fluorescence and ICPMS may become strong contenders. Completely different alternatives, such as electrochemical methods or ion exchange chromatography, still fall short in general utility and convenience. For rapid, selective total element determinations atomic spectrometric methods of analysis will remain the method of choice for many years to come.

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Discussion

L. Ebdon (*Plymouth Analytical Chemistry Research Unit, U.K.*). I feel Professor de Galan has underestimated the significant role ICPMS already plays in atomic spectrometry and increasingly will play. In particular there seems to be an underestimation of its capability in comparison with electrothermal atomization atomic absorption spectrometry (ETAAAS). I believe ICPMS will dominate the field in the coming decade because in comparison with ETAAAS it offers: equivalent limits of detection; greater freedom from interferences; longer linear working ranges; multielement, multi-isotopic capability and above all much greater speed of analysis, perhaps 60 times faster.

L. de Galan. Although Professor Ebdon may be right, I have tried to indicate the promise of the technique, and I still believe there are problems with interferences and high concentration solutions. It appears to be another technique which is very good for clean samples.

L. Ebdon. I feel I really must attempt to destroy the myth that ICPMS is prone to many interferences. There are some well-known ones for a very few elements but these are now well characterized and solutions for several of the problems are known, for example our own work on nitrogen addition to reduce the $ArCl^+$ interference on arsenic. Neither is it true to say that it is not possible to look at high concentrations by ICPMS, as evidenced by our own published work on concentrated coal slurries. In particular the use of flow injection coupled to ICPMS enables higher concentration solutions to be analysed as the absolute mass reaching the cones is more significant than the concentration. Clearly such coupled techniques have a large potential in atomic spectrometry.

L. de Galan. Coupled techniques do have considerable potential but the way to avoid interference problems is better software.