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Atomic Absorption and Atomic Fluorescence Methods of Analysis: Their Merits and Limitations [and Discussion]

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Atomic absorption and atomic fluorescence methods of analysis: their merits and limitations

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Atomic absorption methods involve conversion of the sample into an atomic vapour and measurement of the absorbance of this vapour at a specific wavelength, characteristic of the analyte element. Flames and electrical furnaces are the most widely used means of atomization. Flame atomic absorption methods are rapid and precise, can be carried out on simple equipment, and are applicable to the determination of 67 elements. There have been no major recent advances in such methods. Electrothermal methods of atomization give much better sensitivity and are applicable to much smaller samples. They are generally less precise and slower than flame methods. There have, however, been important recent advances in electrothermal methods and further improvements in the near future are to be expected. There has been some progress in the development of atomization techniques based on cathodic sputtering.

The main limitations of atomic absorption methods are associated with the incomplete atomization of the sample. Simultaneous multi-element analysis is generally not possible since the optimum atomization conditions vary according to the analysis to be carried out. Rapid sequential analysis is, however, now in widespread use.

At present, atomic fluorescence methods are seldom used, possibly because they have most of the limitations of atomic absorption methods and are not so widely applicable. They are, however, superior for some analyses and many of these can be carried out on simple non-dispersive systems that have many attractive features.

In this paper I discuss the merits and limitations of the atomic absorption methods of elemental analysis that have been developed during the past 30 years and are now in widespread use. I also discuss some of the methods developed during this period that involve the measurement of atomic fluorescence, a phenomenon having its origin in atomic absorption. These fluorescence techniques currently find little application in analytical laboratories but merit discussion in view of their many attractive features and their possibilities for further development.

1. Atomic absorption methods

(*a*) *Principles*

Elemental analysis by atomic absorption involves converting a portion of the sample to an atomic vapour and measuring the absorbance of the vapour at a selected wavelength characteristic for each individual element. The measured absorbance is proportional to concentration and analyses are made by comparing this absorbance with that given under the same experimental conditions by reference samples of known composition.

The most commonly used means of atomization are flames and electrical furnaces giving temperatures in the range 1500–3000 °C. It is known that in atomic vapours at these temperatures the great majority of atoms are neutral atoms in the ground state, and these are therefore responsible for most of the light absorption in flame and furnace methods of atomization. The strongest absorption lines are the resonance lines, which involve transitions between the ground state and a low-lying upper level, as shown in figure 1. Atomic absorption methods usually involve measuring absorbance at the wavelength(s) of the strongest resonance line(s). For most elements these lie in the wavelength range extending from the ultraviolet at 200 nm to just beyond the red end of the visible spectrum at 850 nm.

The profiles of the atomic absorption lines in flame and furnace spectra are determined mainly by Doppler broadening due to the temperature of the atomic vapour and pressure broadening due to the ambient gases which are at atmospheric pressure. As a result the half-widths of the atomic absorption lines usually lie in the range 0.002–0.006 nm. It is difficult to record accurately the profiles of such narrow lines. All commercially available atomic absorption spectrometers overcome this difficulty by using, as a light source, an atomic spectral lamp that emits a spectrum of the element to be determined. The lamps are designed to operate at much lower temperatures (about 400 °C) and pressures (about 5 Torr) than those prevailing in flames and furnaces. The emitted lines are therefore much sharper than the absorption lines to be measured, as shown in figure 2. With this arrangement it is possible to make a sufficiently accurate measurement of peak absorbance, without the necessity of using a high-resolution optical system. This concept of 'putting the resolution in the source' is a key feature of modern atomic absorption methods.

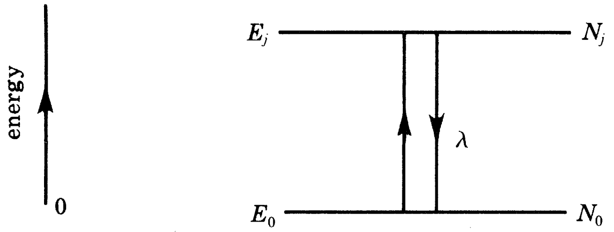

FIGURE 1. Energy-level diagram illustrating transitions involved in the absorption (↑) and emission (↓) of atomic resonance lines.

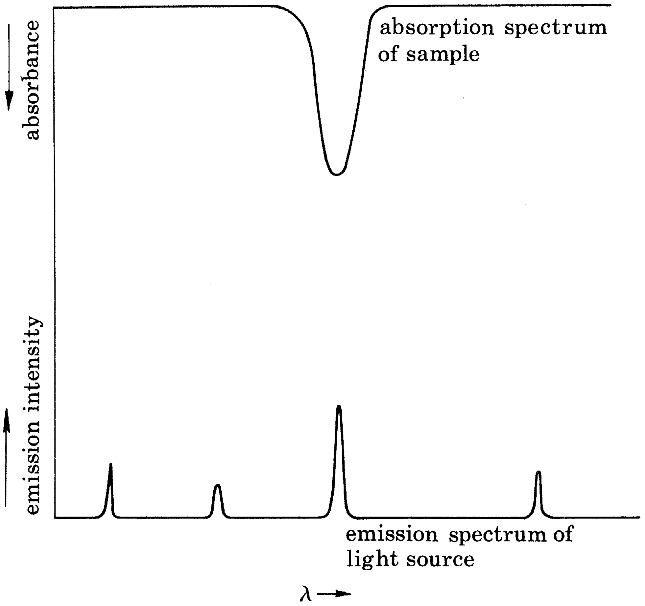

FIGURE 2. Schematic diagram illustrating the use of atomic spectral lamps emitting sharp spectral lines to measure peak absorbance

The measured peak absorbance, $A_{\max}$, is proportional to $N_a f$, where N_a is the number of absorbing atoms in the atomic vapour, and f, the oscillator strength of the absorption line, is a measure of the transition probability for the two levels involved in the transition responsible for the absorption. As examples, $f = 0.7$ and 2 for the strongest lines of the atoms in Groups 1 and 2, respectively, and lies in the range 0.1 to 0.5 for the strongest lines of many of the other common metals.

The main components and mode of operation of an atomic absorption spectrometer are shown schematically in figure 3 (Alkemade & Milatz 1955; Walsh 1955). Radiation from the atomic spectral lamp, which emits the spectrum of the element to be determined, is passed through an atomic vapour of the sample. The emerging beam of radiation passes through a monochromator, which isolates the selected spectral line of the element, and is detected by a photo-electric detector, the output from which is measured on a meter or recorder. Since the atomic vapour may be emitting appreciably at the wavelength at which the absorbance measurement is to be made, it is essential to compensate for any signal due to such emission.

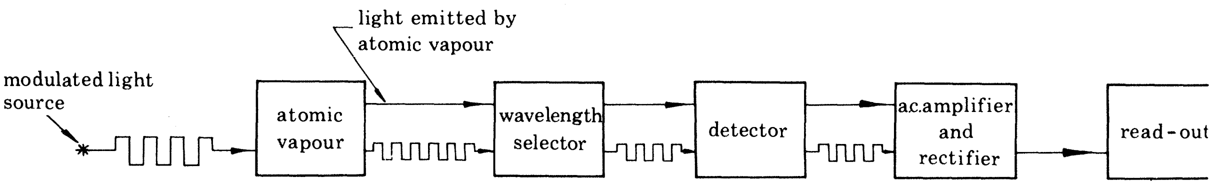

FIGURE 3. Schematic diagram illustrating the use of a modulated light source and a.c. detection system for measuring the absorbance of atomic vapours that are emitting radiation.

This is usually achieved by modulating the power supply to the spectral lamp and using an a.c. amplification system that responds only to signals at the modulation frequency. Thus any radiation from the atomic vapour gives no signal at the output of the amplification system since it is not modulated.

The most widely used light source is the hollow-cathode lamp, but electrodeless lamps and laboratory-type discharge lamps are superior, and are frequently used, for the determination of some of the elements with lower melting points. The modulation frequency is usually in the range 50–500 Hz. The atomic vapour is generated by a flame or furnace in a manner to be discussed later. The function of the monochromator is merely to isolate the required resonance line from other lines and a resolution of the order 0.1 nm is sufficient for this purpose. Photomultipliers are used as detectors and the photoelectric signal is fed to an a.c. amplifier tuned to the modulation frequency. Synchronous demodulation provides a d.c. signal, which is fed to an output meter. This is usually arranged to read directly in concentration.

The operation of such an instrument is extremely simple. For any given determination it is merely necessary to select the appropriate lamp and adjust the current, select the appropriate atomizing conditions, and set the monochromator to the wavelength of the resonance line to be measured.

(b) *Atomization by flames*

For flame atomization a pre-mix laminar flow burner of the type illustrated in figure 4 is generally used. The most widely used fuel mixture is air–acetylene, but nitrous-oxide–acetylene is essential for the determination of elements that form refractory compounds in the flame, and it is advantageous for some other determinations.

Flame methods are more widely used than any other method, and 67 elements can be determined on equipment that is relatively inexpensive and simple to operate. The method of obtaining high effective resolution by using sharp-line light sources results in great ease and certainty in the selection of the appropriate resonance line. An absorbance measurement requires only a few seconds. The precision obtainable is usually good, and may be as high as ± 0.1% in favourable cases.

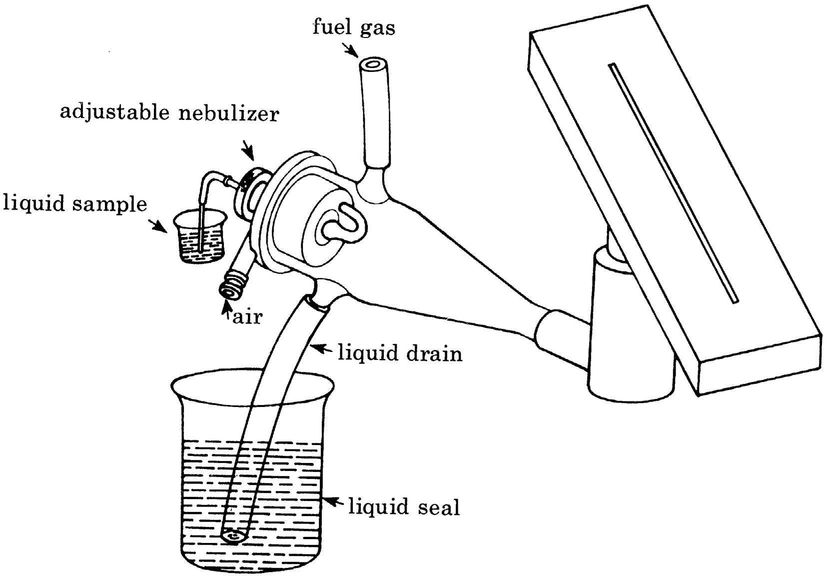

FIGURE 4. Schematic diagram illustrating the main features of nebulizer, spray-chamber and burner assembly.

The main limitations of such methods are associated with the fact that flames are not ideal atomizers. For several elements atomization is incomplete, resulting in a loss in sensitivity and the production of matrix interferences. The latter are now well understood and can generally be overcome by simple chemical treatment of the sample, but this is time-consuming and different treatments are necessary according to the particular analysis being undertaken.

The range of concentration that can be accurately measured under one set of experimental conditions by using atomic absorption methods is also limited. This limited dynamic range is an inherent characteristic of most methods based on absorption measurements. The combination of limited dynamic range and the fact that optimum flame conditions and any chemical treatment of the sample may be different from one element to another also make atomic absorption methods not generally adaptable to simultaneous multi-element analysis. To date, the only useful approach in overcoming this limitation has been to develop atomic absorption methods for automatic sequential determination of several elements. These are now in widespread use and their development represents a most important recent advance.

The prospects for reducing the present limitations of flame methods are not encouraging. The last major advance was the introduction of the nitrous-oxide–acetylene flame by Willis (1965). Possibly the most useful advance since then has been the development of the hydride generation technique, which has greatly improved the sensitivity in the determination of elements that form gaseous covalent hydrides, e.g. arsenic, selenium, tellurium, bismuth and antimony (Holak 1969). The hydrides can be atomized in a low-temperature flame, but a silica furnace is now generally preferred.

(*c*) *Electrothermal methods of atomization*

The most important advance in atomic absorption spectrometry during the past decade has undoubtedly been the further development of electrothermal methods of atomization of the type originated by L'vov (1961). The essence of L'vov's method is to vaporize totally a small quantity of sample in a graphite tube furnace. Commercial developments of L'vov's equipment are based on a simplified version due to Massman (1968). Figure 5 illustrates schematically the main features of a L'vov–Massman furnace. The furnace tube is of graphite and is electrically heated. It is continually flushed with a stream of nitrogen, to exclude oxygen. A small quantity of sample, such as 1–50 μl of solution or 10–500 μg of powder, is introduced through a small hole on top of the furnace. The heating cycle of the furnace, as shown in figure 5, consists of three stages during which the sample is dried, ashed and atomized. The absorption signal is a transient one, so integrated or peak absorbance is measured. This contrasts with flame techniques where a steady absorption signal is measured.

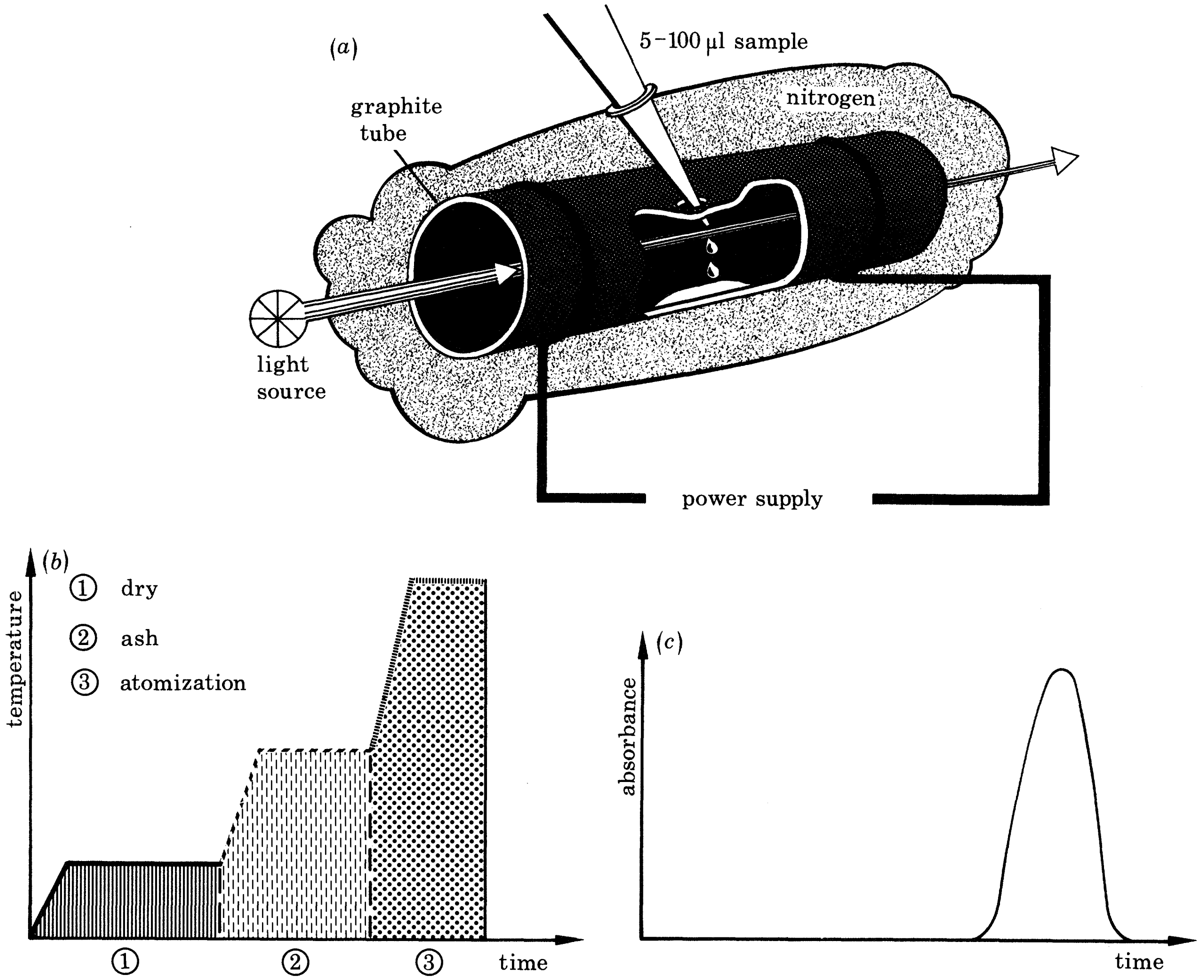

FIGURE 5. Diagram illustrating (*a*) main features of a L'vov–Massmann furnace; (*b*) heating cycle; (*c*) absorption signal.

In furnace spectra there is often a very high background absorbance and this must be measured to allow the desired atomic absorbance to be obtained. This has usually been achieved by means of a continuum source such as a deuterium lamp. In recent years various methods of background correction have been developed that are based on the Zeeman effect, i.e. the splitting of spectral lines into various components by a magnetic field. Such Zeeman methods are based on the assumption that, while atomic absorption is affected by magnetic fields, background absorption is not. Thus, by measuring the absorbance of the furnace in the presence and the absence of a magnetic field, it becomes possible to correct the absorbance due to background. Much improved results for many analyses have been obtained with such Zeeman systems, which have recently been reviewed by de Galan & de Loos-Vollebregt (1979).

Other important advances have also recently been made in furnace design, graphite preparation, furnace power supplies and furnace operation. In particular, it has been demonstrated that in many analyses matrix interferences are greatly reduced by arranging for the furnace to have approached temperature equilibrium before volatilization of the analyte commences. Various methods of achieving this have been described by L'vov (1978), by Lawson & Woodriff (1980) and by Chakrabarti *et al.* (1980). The simplest is that due to L'vov (1978) in which the sample is deposited on a small graphite platform that makes poor thermal contact with the furnace walls. The platform is therefore heated primarily by radiation from the furnace wall, thus resulting in an appreciable time-delay between the heating of the tube and the sample. It has been demonstrated, by Slavin & Manning (1979, 1980) for example, that this simple platform technique can greatly reduce or eliminate matrix effects in some analyses where they are severe by conventional atomization from the furnace wall.

Furnace atomization has three great merits. In the first place the detection limits for many elements are up to two orders of magnitude better than can be achieved by flame methods. Secondly, it is possible to analyse much smaller samples than those required for flame atomization. Thirdly, it is capable of analysing many biological samples, such as whole blood, without pretreatment. Furnace methods have the same limitation as flames with respect to limited dynamic range and the need to use different atomization conditions for different analyses, thus preventing the development of methods for simultaneous multi-element analysis. In addition, furnace methods are slower and less precise than flame methods, the maximum precision being of the order of $\pm 1\%$ compared with $\pm 0.1\%$ for flames. The equipment required is also more expensive, since it is more complex. The operation can, however, be automated. Until recently matrix effects in furnace methods have been much greater than those encountered in flame methods, and not nearly so well understood. However, the combination of new techniques of furnace atomization with improved methods of background correction has dramatically changed this situation. It seems likely that in the near future many of the limitations associated with matrix effects will be further reduced or eliminated. This confidence is encouraged by the better understanding of the complex processes occurring in furnace atomization that has been obtained in the past few years (L'vov *et al.* 1981).

(*d*) *Atomization by cathodic sputtering*

I wish now to refer briefly to attempts to develop methods of atomization by cathodic sputtering in a glow discharge. Most work has been concerned with the direct analysis of metals and alloys by using the sputtering chamber shown schematically in figure 6. In operation, the glow discharge results in the metal sample being bombarded by high-velocity positive ions and neutral atoms, and these cause the sputtering of atoms from the surface of the cathode. The method is of interest because it involves atomization by a non-thermal process. Gough (1976) has surveyed the results obtained for a wide range of metallurgical analyses. He quotes detection limits in the range 0.01–0.001% and precisions in the range ± 1 to ± 3%. The results are encouraging but the method is not yet competitive with emission methods. As will be seen later, however, a different application of the same sputtering technique is more promising.

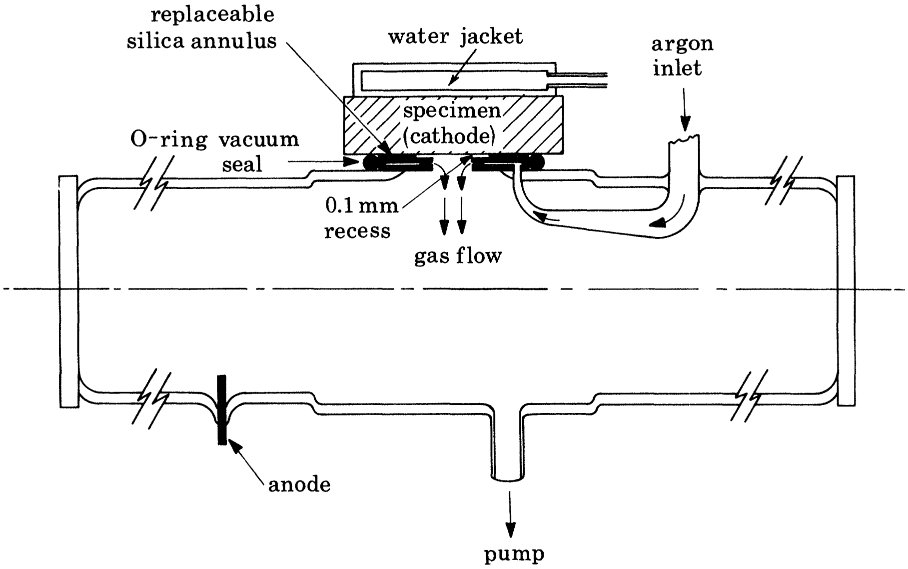

Figure 6. Schematic diagram illustrating a sputtering chamber.

There is a small but interesting set of applications of sputtering atomization in the field of isotopic analysis. To understand the principle of this method, it must be realized that very few atomic spectral lines have a simple profile of the type illustrated in figure 2. Most lines not only have a hyperfine structure due to the interaction of nuclear spin with the motions of electrons, but they may also have additional fine structure due to the presence of more than one isotope. There are two types of isotope effect on atomic spectra. One is due to the different masses and is greatest for the light elements; the other is due to the different nuclear charge distributions and is greatest for the heavy elements. Thus the isotopic effect is difficult to observe except for elements with a very low or a very high atomic number. In cases where the lines due to different isotopes are sufficiently resolved from each other, the use of the appropriate isotopic spectral lamps permits the determination of isotopic composition from atomic absorption measurements. In such work atomic vapours generated by cathodic sputtering are highly advantageous because their low temperature and pressure ensure very narrow absorption lines, which facilitate spectral isolation of the components due to different isotopes. The atomic absorption method has now been successfully applied to the isotopic analysis of mercury by Osborn & Gunning (1955), of lithium by Zaidel & Korennoi (1961), of uranium by Goleb (1963), of lead by Brimhall (1969) and Kirchof (1969), and of boron by Hannaford & Lowe (1977).

2. METHODS INVOLVING THE MEASUREMENT OF ATOMIC FLUORESCENCE

(*a*) *Principles*

I wish now to consider some spectrochemical methods that involve the measurement of atomic fluorescence. In most cases the measured fluorescence results from ground-state neutral atoms absorbing radiation at the resonance-line wavelength and the excited atoms produced then emitting radiation of the same wavelength, as illustrated in figure 1.

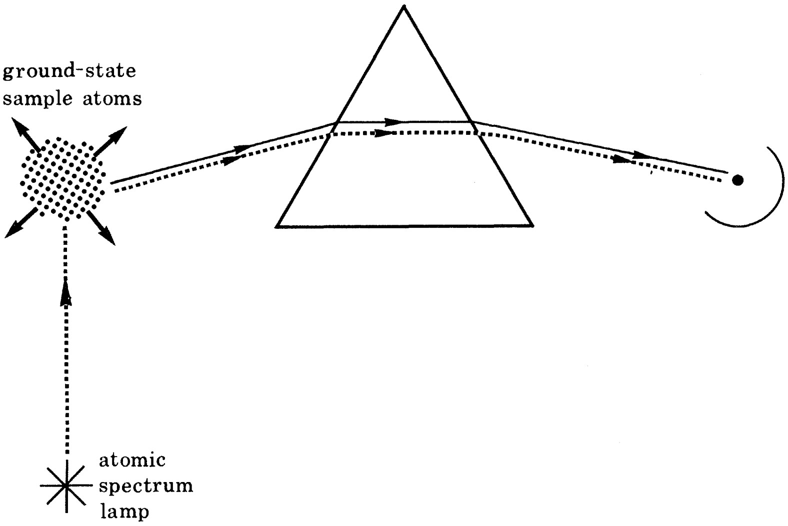

FIGURE 7. Schematic diagram illustrating the technique for measuring atomic fluorescence.

The development of methods based on the measurement of flame fluorescence resulted from a suggestion made by Alkemade (1963). To understand the basis for his proposal it must be noted that all signals from photoemissive detectors, such as photomultipliers, have a noise component known as 'shot' noise, which increases with the flux of radiation falling on the detector. Alkemade pointed out that in flame fluorescence measurements, for example, the detector receives only weak radiation from the flame whereas in absorption the detector also receives the much stronger radiation from the light source. The difference in the 'shot' noise in the two systems can therefore be significant and result in fluorescence being more sensitive than absorption for some analyses.

The development of flame fluorescence methods of analysis was almost entirely due to groups led by J. D. Winefordner and T. S. West. These pioneering experiments have been described by Winefordner and Smith (1970) and by West (1970). A typical experimental arrangement for atomic fluorescence methods of analysis is shown schematically in figure 7. The sample is converted into an atomic vapour that is illuminated by radiation from an intense atomic spectral lamp. The ground-state atoms absorb at the wavelength of the resonance lines and the fluorescence radiation passes through a monochromator that selects the resonance line(s) falling on the photoelectric detector. As in atomic absorption, a modulated lamp and a.c. detection system is used. This isolates fluorescence signals from any signals due to radiation emitted by the atomic vapour of the sample.

(*b*) *Fluorescence from flames*

Most atomic fluorescence investigations have been concerned with fluorescence from flames. It has been established that for some analyses the detection limits and dynamic range are superior to those obtained by using atomic absorption methods. However, when the sample solution contains elements forming refractory compounds in the flame the scattered light not only gives a false signal, correction for which is difficult, but also increases the 'shot' noise. The detection limits are therefore correspondingly worse. These problems due to scattered light possibly constitute the main reason for flame fluorescence methods finding few applications in analytical laboratories.

All atomic fluorescence methods, however, have a unique attraction, which arises from the fact that the phenomenon of fluorescence itself provides a method of isolating resonance lines. For example, if we refer to figure 7, atomic fluorescence can only be produced by atomic species that are present in the lamp and in the atomized sample. Thus, if a 'pure' light source for the analyte element is used, the fluorescence can only be due to lines of the analyte element. Thus no monochromator is necessary for line isolation and the fluorescence radiation can pass directly to the detector. It is, however, essential to avoid any excessive noise due to radiation emitted by the atomic vapour. In flame fluorescence, this is achieved by using flames of low luminosity such as the 'sheathed flame', as used by Alkemade, in which a curtain of argon or nitrogen separates the regions of primary and secondary combustion, thus providing a region in the flame that is relatively 'dark'. In addition an optical filter or spectrally selective photodetector further selectively attenuates any emission signals. Such simple non-dispersive systems permit the use of high-aperture light beams that result in greater sensitivity than that obtainable from a monochromator (Larkins 1971; Larkins & Willis 1974). Furthermore, the change to the detection of another element only requires switching to the appropriate lamp, so changeover can be extremely rapid, thus facilitating the simultaneous or sequential determination of several elements.

In non-dispersive methods, however, the problem due to scattered radiation is even more acute than when using a monochromator, since the detection system receives radiation of a much wider spectral range. These simple methods are therefore only applicable where scattering is relatively small. In such cases, simple non-dispersive systems are extremely effective. An interesting recent application is the determination of elements such as selenium, arsenic, bismuth and antimony by the hydride generation technique, with which scattering problems are generally not encountered (Tsujii & Kuga 1974; Nakahara *et al.* 1978, 1979). As in atomic absorption methods, the metal hydrides are dissociated by a flame or furnace.

(*c*) *Fluorescence from inductively coupled plasmas*

An interesting recent development in non-dispersive atomic fluorescence has been reported by Demers & Busch (1981). They describe an instrument for simultaneous multi-element analysis that uses an inductively coupled plasma for atomization, pulsed hollow cathode lamp for excitation and optical interference filters to isolate the required lines. Molecular fluorescence interferences are claimed to be absent and particulate light scattering interferences are said to be rare.

(*d*) *Fluorescence from sputtered vapours*

A non-dispersive fluorescence instrument has also been developed for the direct analysis of metals and alloys (Gough *et al.* 1973; Gough & Meldrum 1980). The sample is atomized by cathodic sputtering with the same type of sputtering chamber as that shown in figure 6, but including a side-arm through which fluorescence radiation passes to the detector. In this system there is some scattering from small aggregates that are present, but it is not sufficient to impair sensitivity and Gough & Meldrum describe a simple method for its correction. This system has been applied to the determination of several elements in steels, aluminium alloys, brass and other copper-based alloys. The precision is typically ± 2% and the detection limits, in the range 1–100 μg g^{-1}, are lower than those obtained from atomic absorption measurements. For some metallurgical analyses this simple non-dispersive fluorescence method is possibly more sensitive than any other.

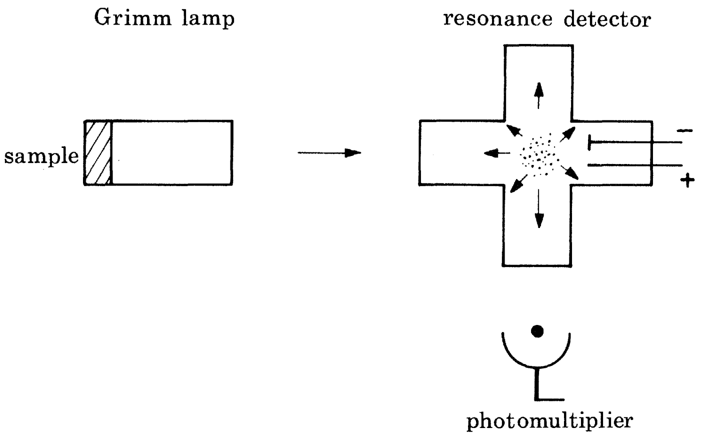

FIGURE 8. Schematic diagram illustrating the use of a sputtering-type fluorescence cell to measure the intensity of resonance lines in emission spectra.

Butler *et al.* (1975) use the inverse of the above method, their apparatus being illustrated in figure 8. In this arrangement the metal sample for analysis is made the cathode of a glow discharge of the type developed by Grimm (1968) for use as a light source for emission spectroscopy. A sputtering-type fluorescence cell is then used as a resonance detector to isolate resonance lines in the emission spectrum of the sample. This system has been developed for the determination of carbon, sulphur and phosphorus in steel, each of these elements having its strongest resonance lines in the vacuum ultraviolet. Whereas conventional emission methods necessitate the use of a vacuum monochromator, which is inevitably expensive, the fluorescence chamber to detect resonance lines is simple and can be housed in the same chamber as the light source. This work is now at an advanced stage of development and it seems likely that the performance obtainable from this simple type of system will meet the requirements of many important classes of metallurgical analysis. This is a most interesting development since it brings to emission spectroscopy one of the most attractive features of atomic absorption and atomic fluorescence methods, i.e. the ease and certainty with which one can isolate the line(s) for measurement. As in all the non-dispersive atomic fluorescence systems I have mentioned, the simplicity of the experimental arrangement is most attractive.

3. SUMMARY OF RECENT ADVANCES

From the above discussion of the merits and limitations of atomic absorption and atomic fluorescence methods of elemental analysis, it has been seen that the most important advances in atomic absorption methods since their introduction in 1955 have been:

(*a*) the introduction of the nitrous-oxide–acetylene flame;

(*b*) the introduction and development of electrothermal methods of atomization, which have been greatly improved in recent years, particularly by better methods of furnace operation and the use of Zeeman methods of background correction;

(*c*) the development of rapid methods of automatic sequential analysis;

(*d*) the development of methods based on the hydride generation technique.

It has been seen that atomic fluorescence methods currently find little application in analytical laboratories. The following appear to be the most important advances:

(*a*) the demonstration that atomic fluorescence methods are superior to atomic absorption methods for some analyses;

(*b*) the development of non-dispersive systems in which the sample is atomized by a flame, by a plasma, or by cathodic sputtering in a glow discharge;

(*c*) the development of non-dispersive fluorescence systems for use in conjunction with the hydride generation technique.

In conclusion it may be noted that this paper has been concerned only with methods used in analytical laboratories. It should not be forgotten, however, that atomic absorption and atomic fluorescence techniques have made, and continue to make, important contributions in many physical investigations in which it is required to measure or monitor the concentration of ground-state atoms. Typical examples are the determination of the vapour pressure of the elements, the measurement of coefficients of diffusion, and the study of the concentration of atoms in electrical discharges. But possibly the most interesting recent contribution is the determination of atomic radiative lifetimes from measurements of the fluorescence decay of sputtered vapours. These techniques are applicable to highly refractory elements and have led, for example, to a new determination of the oscillator strengths of various zirconium lines, and in turn to a new estimate of the abundance of zirconium in the Sun (Hannaford & Lowe 1981; Biémont *et al.* 1981). I feel that it is appropriate to mention this particular contribution at this Royal Society Discussion Meeting, since it was a Fellow of this Society, W. H. Wollaston (1802), who first detected dark lines in the solar spectrum and thereby made, unknowingly, the first observation of an atomic absorption spectrum.

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Discussion

J. C. Rivière (*A.E.R.E., Harwell, U.K.*). I was particularly interested in the variation of the atomic absorption spectroscopic technique in which the specimen was sputtered in an argon discharge. This would seem to be complementary to the glow-discharge optical spectroscopy technique, in which the optical *emission* spectrum is measured and used for surface characterization. If this is correct, then is not the sputtering variation of a.a.s. also a quasi-surface analytical technique?

Sir Alan Walsh. I think atomic absorption spectroscopy, and atomic fluorescence spectroscopy using a sputtering cell, are complementary to the glow-discharge emission techniques used for surface characterization. However, since sputtering does not begin until the surface has been cleaved by atomic and ionic bombardment due to the discharge, it is difficult to know the relation between the surface that finally sputters and the original surface.

T. S. West (*The Macaulay Institute for Soil Research, Aberdeen, U.K.*). Sir Alan has indicated that flame-based atomic absorption spectroscopy (a.a.s.) has reached the status of an established technique where there are few signs of any significant development in the immediate future, and has pointed out that the most noteworthy contribution of recent years has been the introduction of the electrothermal atomizer in place of the flame, thereby increasing the sensitivity of a.a.s. by *ca.* one or two orders of magnitude.

One of the reasons why the flame lacks sensitivity in comparison with the electrothermal atomizer is that the nebulization process with a pneumatic atomizer is *ca.* 10% efficient at best. A second reason is that the atomic species that are generated at or near the base of the flame (in most cases) are propagated through the flame at a speed of *ca.* 10^3 cm s^{-1}. Several years ago it occurred to some of us that we could increase the sensitivity of flame a.a.s. considerably if we could concentrate or collect the atoms within the flame before measurement of their 'concentration' by atomic absorption spectroscopy.

Recently, my colleagues and I have succeeded in doing this for several elements by a process which we call atom trapping atomic absorption spectroscopy (Khalighie *et al.* 1979, 1980, 1981, 1982). A water-cooled silica tube is situated above the primary reaction zone of an (a.a.s.) air–acetylene flame. This causes the atoms generated in the flame to condense out as metallic films (oxides, etc.) on the cool surface of the collector tube with a very high degree of efficiency. When sufficient atoms have been collected in this way the water supply through the tube is shut off and the water is ejected from the tube by a blast of air. The surface (i.e. skin) of the tube then warms up within a few seconds and releases the atomic species into the flame gases as a transient population whose atomic absorption can be measured immediately above the surface of the tube. In this way we have found it possible to determine several biosignificant trace elements, e.g. Cu, Cd and Se, at levels well below their detection limit by the normal a.a.s. technique and with detection limits improved by *ca.* one to two orders of magnitude. The sensitivity is, within limits, proportional to the collection time. We have studied interferences and applied the method to the determination of plant-available trace elements in soils.

Since the thermal coefficient of expansion of silica is very low it is possible to repeat the collect–release cycle many times without removing the silica tube from the flame or without extinguishing the latter. A tube may be used for a great number of analyses. We postulate that the release of condensed species from the surface of the collector tube may involve a mechanism of sputtering or thermal scouring by energetic species in the flame as well as direct thermal evaporation in the usual way.

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Sir Alan Walsh. The development that Dr West has described is extremely interesting and may prove to be of great importance. I had not heard of it previously and I am delighted at the prospect of a dramatic improvement in flame atomic absorption spectroscopy using the simple method described by Dr West.

A. F. Fell (*Heriot-Watt University, Edinburgh, U.K.*). In view of the rapid development in multi-element analysis with continuum sources with the echelle device by Professor T. C. O'Haver's group (*Analyt. Chem.* **53**, 1291–1298 (1981)), what is Sir Alan's impression of the contribution of this approach to multi-element analysis in atomic spectrometry? Does he consider that the optical multichannel detectors, such as the linear diode array and the vidicon tube, have much to contribute in this area?

Sir Alan Walsh. I think the system that Professor O'Haver and colleagues have developed is a very interesting one, and the determination of several elements is, of course, attractive. However, in my experience the central problem in developing atomic absorption methods for simultaneous multi-element analysis is related to the fact that the optimum atomization conditions vary from element to element. As I see it, Professor O'Haver's system does not solve this problem.

As far as diode arrays are concerned, the latest information available to me is that the silicon diode is still inferior in performance to a photomultiplier.

A. F. Fell. As regards the sensitivity of optical multichannel devices, recent work has demonstrated that the intensified silicon intensified target vidicon tubes are capable of single-photon detection in u.v.-visible spectrometry (Y. Talmi (ed.) *Optical multichannel detectors*, American Chemical Society Monograph no. ACS 102 (1979)). So it would appear that at least in the research laboratory, the multichannel detector is capable of adequate sensitivity for use in atomic spectrometry, as exemplified recently by Busch and colleagues (K. W. Busch, B. Malloy & Y. Talmi, *Analyt. Chem.* **51**, 670 (1979)). It would appear that such devices present significant potential for industrial quality control with, for example, the inductively coupled plasma source.