

## ATOMIC ABSORPTION SPECTROSCOPY AND ITS APPLICATIONS - OLD AND NEW

A. Walsh

CSIRO, Division of Chemical Physics, P.O. Box 160, Clayton, Victoria, Australia 3168

Abstract - Atomic absorption methods of analysis are extensively used in the exploration, mining and processing of materials. In such work the most widely used technique involves prior solution of the sample before atomizing in a flame. Methods for the direct analysis of metals and alloys have recently been developed, the atomic vapour of the sample being produced by cathodic sputtering in a glow discharge. The sputtering techniques developed for this work have been applied to the construction of demountable atomic spectral lamps and demountable resonance detectors. It has recently been shown that a separated flame, of the type used in flame fluorescence spectroscopy, can serve as a resonance detector for several elements. By the use of flame-type and sputtering-type resonance detectors, in conjunction with demountable sputtering chambers, it appears possible to develop a general-purpose atomic spectrometer capable of the analysis of solutions or solids by atomic absorption, atomic fluorescence, or atomic emission spectroscopy.

I have been asked to sketch the historical development of atomic absorption methods of analysis, to note their mining and industrial applications as the technique evolved, and to discuss any new developments in which I am participating that are relevant to the theme of this Symposium. It is obvious that, in this one paper, I can not do justice to each of these three aspects of the subject, and so I propose to discuss the first two very briefly and devote most of my paper to a discussion of some new possibilities which have only recently received serious consideration.

As far as the historical development of the subject is concerned, may I remind you that one of the first spectrochemical analyses ever made was based on atomic absorption measurements. This was in 1859 when Kirchhoff showed that the Fraunhofer lines in the sun's spectrum were atomic absorption lines due to the presence of various elements in the sun's atmosphere. It should also be recalled that, in their classic experiments, Kirchhoff and Bunsen showed that various elements in flames gave characteristic emission and absorption spectra. The relationship between these two types of spectra was summarized in Kirchhoff's famous law which states that the ratio of the emissive power to the absorptive power of all bodies at the same wavelength and temperature is a constant. It is a strange feature of the development of spectrochemical methods that, following this early work, the subject for the next 100 years became concerned almost exclusively with emission methods. One can only conjecture as to why this should have happened. I believe that one reason must have been that Kirchhoff and Bunsen's measurements were confined to the visible region of flame spectra and they would therefore see little advantage in using atomic absorption rather than atomic emission measurements. But I believe there is a more subtle reason for the neglect of atomic absorption methods and that is concerned with the wrong interpretation of Kirchhoff's law. It became common to state that this law implied that good radiators are good absorbers and poor radiators are poor absorbers. A brief consideration will show that this is not the case. A black body, for example, is a perfect absorber at all wavelengths and at all temperatures. By contrast, a black body at a low temperature is a poor radiator at all wavelengths, and even at a high temperature it remains a poor radiator at low and at high wavelengths. I believe misinterpretation of Kirchhoff's law led to a widespread confusion regarding the relationship between atomic absorption and atomic emission spectra.

The revival of interest in atomic absorption methods (1,2) was primarily due to the realisation that this confusion had occurred and that atomic absorption methods could offer many potential advantages over emission methods. When I (2) proposed that atomic absorption spectra could provide a promising method of chemical analysis, "with vital advantages over emission methods", the argument I used was a general one. I made no assumptions regarding the method by which the requisite atomic vapour would be produced. As an *example* of the advantages of atomic absorption methods, I pointed out that the type of flames which were then commonly used in emission flame photometry would be extremely good in atomic absorption

for many elements which in the same flames were poor emitters. It then became necessary to consider the problem of making the requisite atomic absorption measurements. The problem lies in the fact that atomic absorption lines are extremely narrow and it is extremely difficult to measure their profiles by conventional absorption methods using a scanning monochromator. My solution to this problem was to use as light source an atomic spectral lamp which would emit lines which were much narrower than the atomic absorption lines to be measured. This approach not only solved the problem but gave the atomic absorption method a very important advantage over emission methods. This lay in the fact that since the resolution was, in effect, provided by the atomic spectral lamp, it was only necessary to use a monochromator which could isolate the appropriate line emitted by the light source from all other elements. Furthermore, since this line was usually one of the strongest of the lines emitted by the lamp, it was usually very easily isolated. The use of a line source instead of a continuous source also greatly reduced any problems due to scattered light within the monochromator. In considering the most appropriate type of atomic spectral lamp, I suggested that the hollow-cathode discharge appeared to offer the best possibilities.

A feature of the measuring technique is that radiation from the atomic spectral lamp is modulated and the signals generated by the photoelectric detector at the exit slit of the monochromator are amplified by an amplifier tuned to the frequency of modulation. The radiation emitted by the flame is not modulated, and therefore gives no resulting output signal.

It was obvious from our first experiments that flames, however useful they might be, were not perfect atomizers and indeed we ended the paper (3) describing our first atomic absorption spectrophotometer with the words:- "This problem of complete atomization of the sample seems to us to be the outstanding problem at the present time". In a paper I wrote in 1962 (4), before any substantial commercial production of atomic absorption equipment had commenced, I enlarged on this problem. I stated that when a flame is used some elements are only partially atomized, "thus resulting in loss in sensitivity and the possibility of chemical interference due to variations of the degree of atomization of one element with the concentration of other elements, radicals or compounds in the solution... This type of interference is present to the same extent in emission and absorption methods and is responsible for serious limitations in flame methods."

In the first applications of the method, reported in 1958, J.E. Allan (5) and D.J. David (6) used a pre-mixed air-acetylene flame. In my opinion the most important single contribution to the development of atomic absorption spectroscopy following these first applications was the development by Willis (7) of the nitrous oxide-acetylene flame. It not only extended the number of elements which could be determined, but it also greatly reduced the interference effects discussed above. Following the introduction of the nitrous oxide-acetylene flame there was a rapid growth in the application of atomic absorption methods, and this created the impression that the subject was making remarkable progress. But it must be remembered that the large number of new applications resulted from straight-forward extensions of the one basic technique. It is salutary to recall that more than 99% of all atomic absorption analyses are still made by a technique which involves the use of a hollow-cathode lamp as light source and a flame as atomizer.

In spite of the atomization problems discussed above, such flame methods have proved immensely useful in the exploration, mining and processing of materials. The applications have indeed been so widespread that it is difficult to select for mention any particular categories. Perhaps it is sufficient to state that in Australia in the sixties, during the greatest mining boom in the country's history, more elemental determinations were carried out by atomic absorption methods than by all other methods combined. It was a remarkable coincidence that just at the time the boom created a demand for millions of analyses, atomic absorption techniques and apparatus of appropriate performance became available.

The only alternative to the flame as a means of atomization that has been adopted to any significant extent is the electrical furnace. Such so-called non-flame atomizers have proved of great value in various biological applications where extremely small amounts of material are available. Whilst the detection limits are indeed impressive, the precision and accuracy of such methods do not yet compare with those obtainable with the flame. I shall not discuss this development further since it is probably not particularly relevant to the theme of this Symposium.

Apart from the atomization problems discussed above, atomic absorption methods using flames have two main limitations. In the first place the sample must be in the form of a solution before it can be analyzed, and secondly, the possibilities of extending the methods to simultaneous multi-element analysis are extremely limited. The necessity to have the sample in solution form also provides a similar limitation to flame fluorescence methods: the latter, however, offer some advantage in the design of multi-element systems. In spite of this and other advantages of flame fluorescence methods, particularly those based on non-dispersive systems, they have found surprisingly little acceptance by analysts. I shall not discuss them further but merely comment that, in my opinion, they merit much further consideration

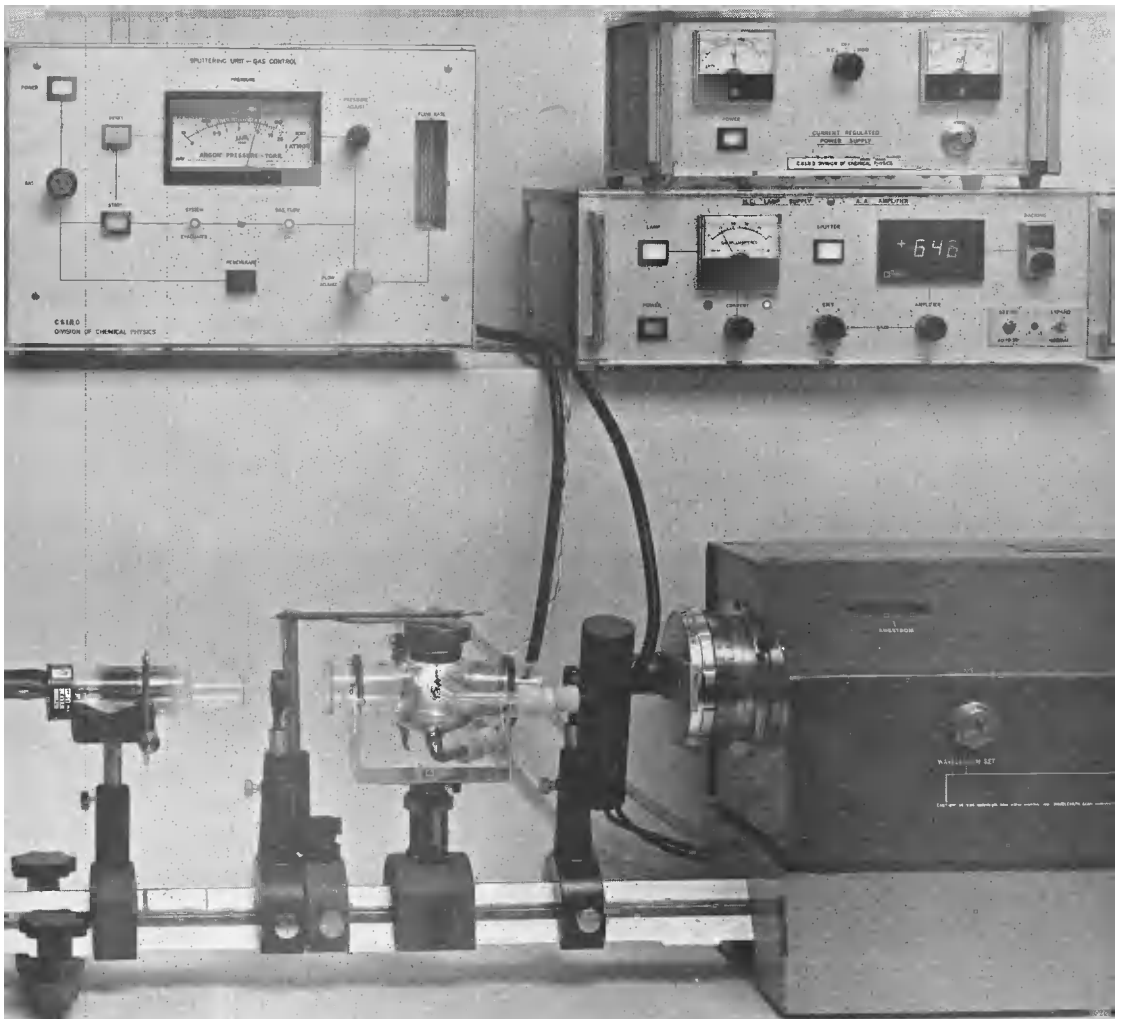


Fig. 1. Atomic absorption spectrophotometer for the analysis of metals. At bottom, atomic spectral lamp, sputtering chamber, and monochromator. At top, gas control unit, power-supplies and amplifier.

Turning now to some recent developments, I would like to refer to work in our laboratory on the development of atomic absorption methods for the direct analysis of metals and alloys (8,9). In the technique we have developed the sample is made the cathode of a low-pressure discharge in a rare gas, and ionic bombardment of the cathode surface results in the liberation of atoms from the cathode surface. We have been working on this problem since 1958 but it is only in the past two years that the technique has been developed to a point where, due mainly to the work of my colleague D.S. Gough (9), it is applicable to the analysis of a wide range of metals and alloys. In principle, the experimental arrangement is extremely simple and consists essentially of a conventional atomic absorption spectrophotometer in which the burner assembly is replaced by a sputtering chamber as shown in Fig. 1. For optimum results, Gough has found it desirable to modify the conventional electronic system so that it provides automatic compensation for background absorption and for any variation in the intensity of the atomic spectral lamp. His system is remarkably effective and I regard it as essential for proper exploitation of the sputtering technique. By far the most important feature of our sputtering chamber is the method used in attaching the sample for analysis to the chamber, and in the manner in which gas flows over the sample surface into the body of the chamber. The specimen, in the form of a metallic disc, is attached to the chamber simply by placing it on the O-ring assembly illustrated in Fig. 2. A water-cooled metal block rests on the sample and prevents over-heating. The silica annulus confines the discharge to a well-defined region of the cathode slightly smaller than the 1 cm diameter hole. Beyond this region the discharge is suppressed by the 0.2 mm gap which is smaller than the width of the cathode dark space for the usual operating conditions of the discharge. This gap is also sufficiently small to prevent diffusion of

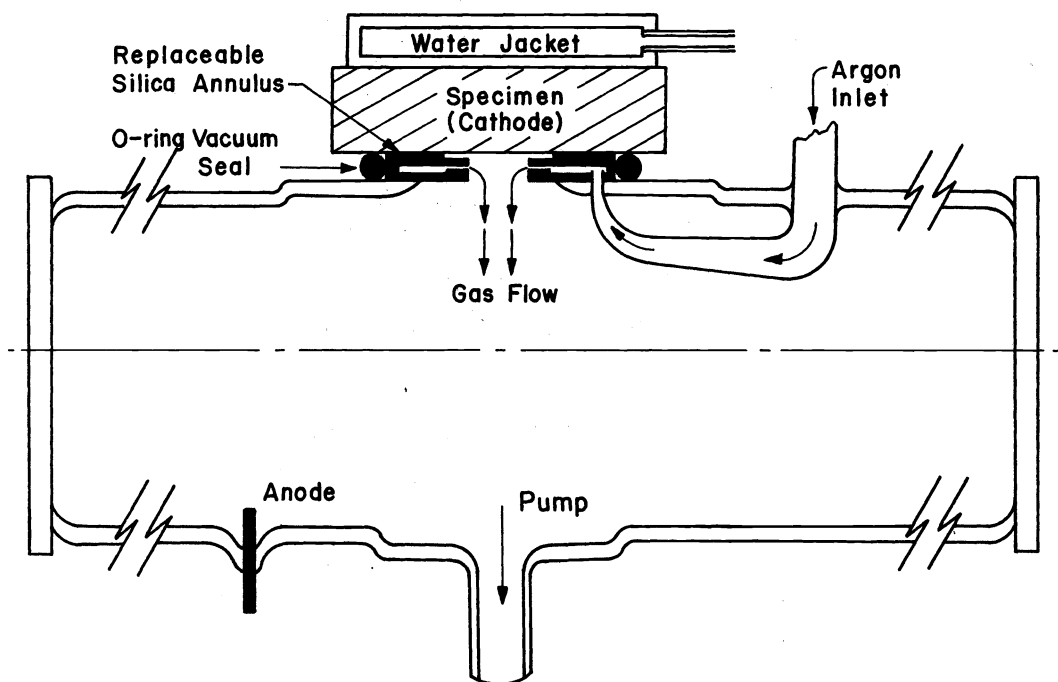


Fig. 2. Schematic diagram of the sputtering chamber.

the sputtered vapour to the region between the annulus and the specimen and thereby enables the cathode to remain electrically isolated from the rest of the chamber, even when the chamber is covered with a sputtered film. Once the sample has been placed in position the chamber is evacuated within about 30 seconds by a rotary pump and argon is then flowed through the system, at a pre-determined flow-rate and pressure with the discharge on. It will be noted from Fig. 2 that the argon flow is such as to sweep the atoms liberated from the surface of the cathode into the body of the chamber. This type of gas flow is an essential feature of the technique.

In a comprehensive report on the performance of such a system, D.S. Gough (9) reports that the time per analysis varies from about 2-3 minutes for brasses and iron alloys, to 5 minutes for zinc alloys and 10 minutes for aluminium alloys. The reproducibility depends on the matrix sputtered and is typically  $\pm 1\%$  for low-alloy steels and copper-base alloys,  $\pm 2\%$  for aluminium alloys, and  $\pm 3\%$  for zinc alloys. Detection limits are in the range 0.0003 to 0.04%. At the present time, one of our sputtering units is in use in a routine analytical laboratory where its performance in the analysis of a wide range of steels is being assessed.

It is also possible to use the same type of sputtering chamber to carry out analyses by fluorescence measurements and the performance of such a system in the analysis of iron-base samples has been reported (10). At the time that work was reported the method was not applicable to the analysis of aluminium- or zinc-base alloys, but the type of gas flow system described earlier has removed this limitation. The detection limits obtainable in fluorescence are significantly better than those we obtained in absorption. However, my colleague R.M. Lowe is at present developing an absorption cell having a much longer absorption path than has been used previously. His results indicate that the long cell may significantly increase the sensitivity obtainable by absorption methods.

I believe that methods based on absorption and fluorescence measurements on sputtered atomic vapours are now sufficiently developed to be usefully applied to a wide range of metallurgical analyses. It is also to be expected that the same methods can be extended to the analysis of powders by incorporating them in metallic pellets as in emission methods using the Grimm low-pressure discharge.

The sputtering techniques and apparatus described above have other useful applications. In the first place, they can obviously be applied to the construction of demountable atomic spectral lamps having a hollow cathode, or a flat-surface cathode as in Fig. 2. Furthermore

it has now been demonstrated by my colleague R.M. Lowe (11) that a secondary boosting discharge (12) can be incorporated in demountable lamps, and produce a significant increase in intensity without sacrifice in line width. Such demountable high-intensity lamps are not only useful as light sources in atomic absorption and atomic fluorescence spectroscopy but also, as Lowe has demonstrated, in emission spectroscopy.

The sputtering chamber described can also be readily adapted to serve as a demountable resonance detector (for which IUPAC has tentatively proposed the name "resonance spectrometer"). Such detectors can serve as a substitute for optical monochromators. They consist essentially of means for producing an atomic vapour of a given element under conditions which favour the production of fluorescence, or resonance, radiation when the vapour is illuminated. Such fluorescence can only occur for incident radiation at wavelengths characteristic of, and highly specific to, that element.

The application of resonance detectors in atomic absorption spectroscopy, using the apparatus illustrated schematically in Fig. 3, has been reviewed (13). Their application in atomic emission spectroscopy was first reported by L.R.P. Butler (14). He and his colleagues (15) used a sputtering-type resonance detector to isolate resonance lines emitted by a Grimm low-pressure discharge, using the apparatus illustrated schematically in Fig. 4.

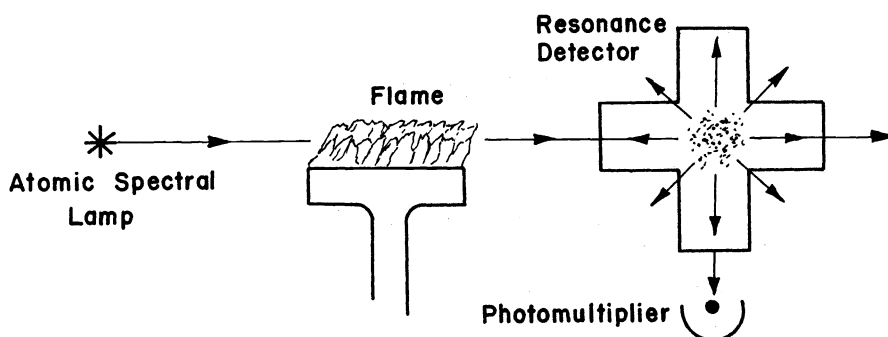


Fig. 3. Schematic diagram of atomic absorption spectrophotometer incorporating a resonance detector.

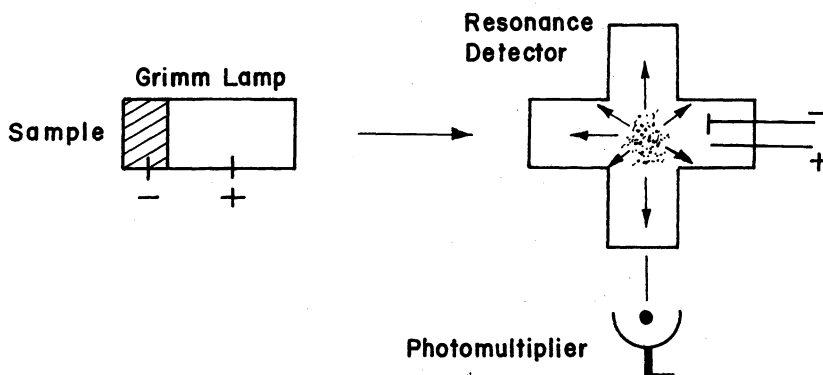


Fig. 4. Schematic diagram of apparatus for emission spectroscopy incorporating a resonance detector (14,15).

The most widely applicable method of producing the requisite atomic vapour is by cathodic sputtering. The original resonance detectors were of the sealed-off type and a separate chamber was required for each element. The demountable sputtering chamber described above can serve as a resonance detector for any selected element simply by appropriate choice of cathode material. The demountable resonance detector has an additional advantage over the sealed-off type in the improved signal-noise ratio. This results from the gas-flow conveying some of the atomic vapour sputtered from the cathode to a relatively dark region of the discharge. Thus fluorescence measurements can be made on an atomic vapour which emits less radiation than the atomic vapour in a static system. Consequently there is less noise superposed on the fluorescence signal. I believe the use of such demountable sputtering-type resonance detectors in atomic absorption and atomic emission spectroscopy merits a detailed investigation.

I wish now to refer to a completely different approach to resonance detection. This is based on the surprisingly belated realization (16,17) that a "separated" flame, of the type commonly used in flame fluorescence spectroscopy, can provide a useful resonance detector for many elements. In such a flame a sheath of inert gas surrounds the flame and separates the primary and secondary combustion zones by a region of low luminosity. The main attraction of using a flame-type detector is that the element which is detected is determined simply by spraying into the flame a pure solution of the required element. It is therefore possible to change from the detection of one element to another in a matter of seconds.

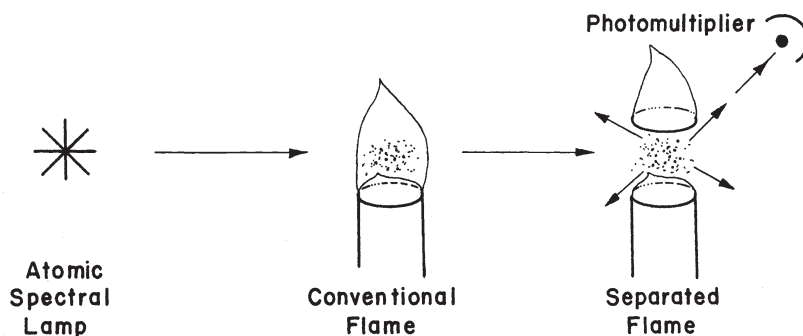


Fig. 5. Schematic diagram of atomic absorption spectrophotometer incorporating a flame-type resonance detector.

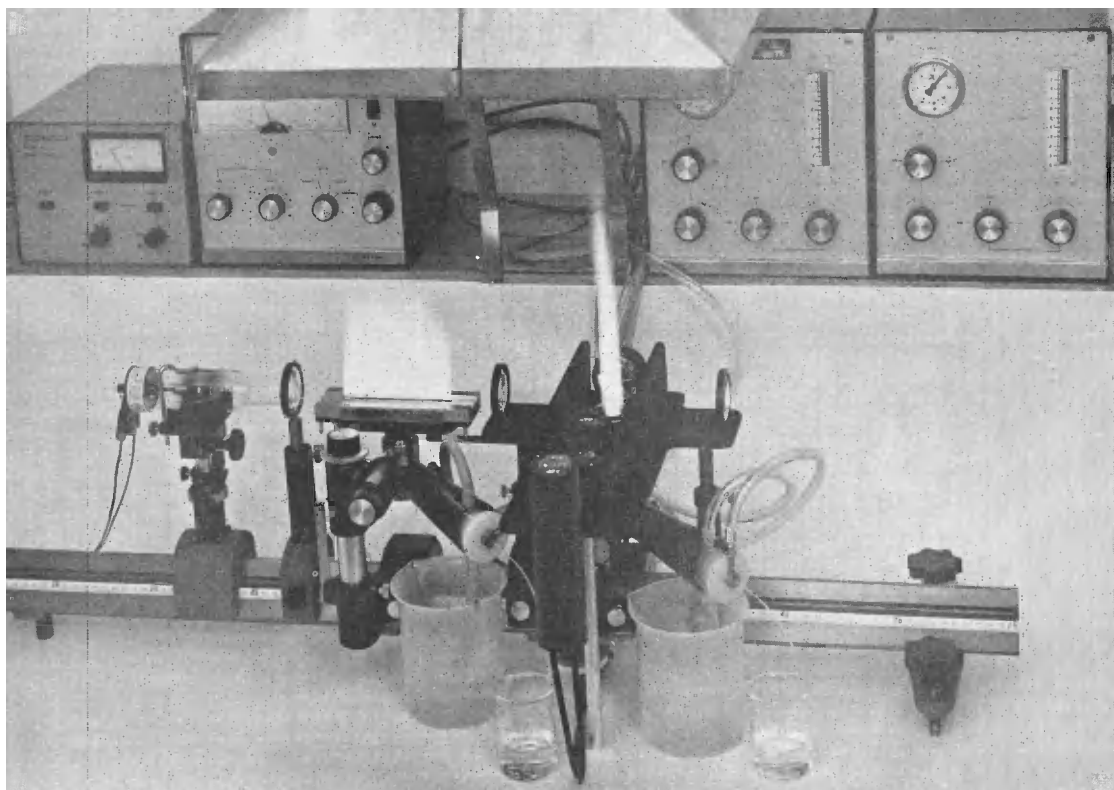


Fig. 6. Photograph of atomic absorption spectrophotometer incorporating a flame-type resonance detector.

The application of such flame detectors in atomic absorption spectroscopy has been studied by P.L. Larkins and A. Walsh (18) using apparatus illustrated in Figs. 5 and 6. It consists essentially of a conventional atomic absorption spectrophotometer in which the optical monochromator has been replaced by the sheathed flame which serves as the resonance detector. The burner for the detector flame and the photomultiplier-amplifier system are exactly the same as those used by P.L. Larkins (19) for non-dispersive flame fluorescence spectrometry.

The concentration of the solution sprayed into the detector flame is not critical; it is slightly less than that which gives the maximum fluorescence signal. It has been found that the performance of such a system conforms to expectations. For elements such as zinc, cadmium and magnesium for which the resonance spectrum consists predominantly of one line, the calibration curves are closely similar to those obtained by conventional atomic absorption spectrometers. For elements having more complex fluorescence spectra, the difference in the calibration curves is due to the fluorescence spectrum of the detector flame consisting of several lines, so that the final measurement is a resultant absorbance measurement for an assemblage of lines. This aspect of the use of resonance detectors has been discussed previously (12).

It may be noted that in the arrangement discussed above the effective resolution of the system varies with the operating conditions of the atomic spectral lamp. When the latter is operated at a low current, as in atomic absorption spectroscopy, then the lamp will determine the line width. However when it is operated at higher currents, as in the experiments described above, there is appreciable broadening of the emitted atomic resonance lines and these widths may become wider than the absorption lines in the separated flame. Consequently the latter determine the effective resolution of the optical system. Irrespective of the widths of the lines emitted by the lamp, this resolution cannot be inferior to that corresponding to the widths of the lines absorbed by the detector flame. Thus it is possible to use a continuum source without undue loss in sensitivity. Some preliminary results have shown that a xenon lamp can be used for the determination of several elements.

The main limitation of the flame as a resonance spectrometer is that it is not suitable for the detection of elements such as aluminium and silicon which require high-temperature flames for their atomization, and these flames are too luminous to serve as satisfactory resonance detectors.

The use of flames as detectors in emission spectroscopy is particularly attractive because the effective resolution is much better than can be achieved with typical dispersion-type monochromators. The method has been applied to the analysis of metals using a boosted low-pressure discharge as light source. It has already been shown that many important metallurgical analyses, such as the determination of nickel and manganese in low-alloy steels, can be carried out using this simple system.

Of even greater interest is the extension of the techniques described above to provide a general-purpose spectrometer of the type shown in Figs. 7 and 8. Examples of the type of operation which is possible with this system are as follows.

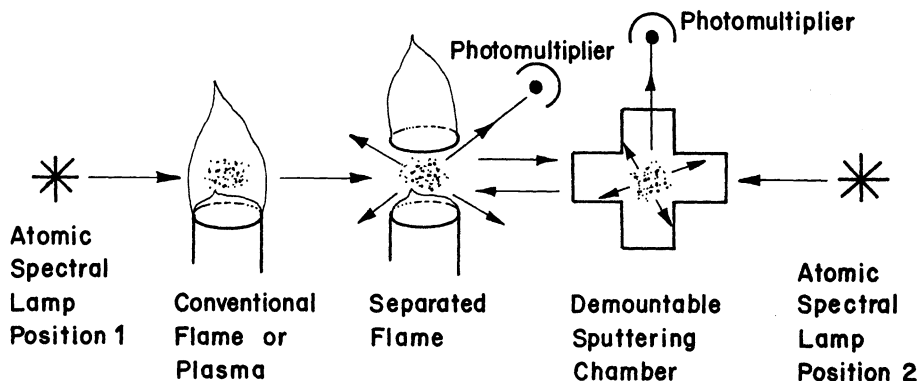


Fig. 7. Schematic diagram of general-purpose atomic spectrometer.

With the atomic spectral lamp in position (1) absorption or fluorescence measurements of solutions may be obtained by spraying the sample in the absorbing flame or in the separated flame, respectively. If the lamp is of the demountable type, it can also be used as the light source in emission spectroscopy.

If the atomic spectral lamp is placed in position (2) it becomes possible to carry out absorption or fluorescence analysis of solids by making the sample the cathode of the demountable sputtering chamber. Finally, the demountable sputtering chamber can also serve as a resonance detector for absorption or emission measurements using the light source in position (1). This type of resonance detector can then be used for those elements for which the flame detector is not satisfactory.



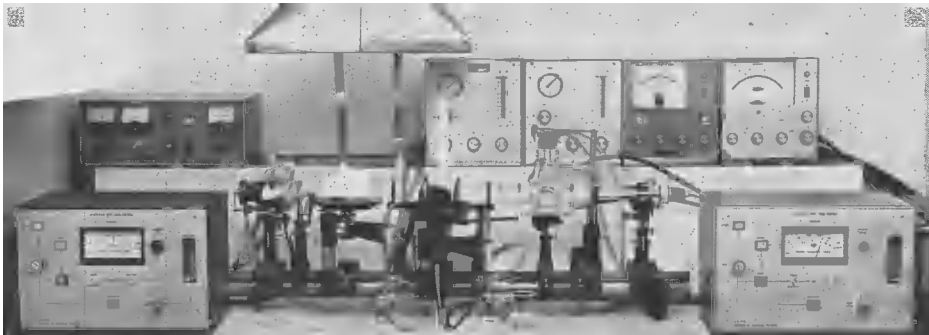


Fig. 8. Photograph of general-purpose atomic spectrometer.

The photograph in Fig. 8 shows all the components, apart from the vacuum pump and gas supplies, for a general-purpose atomic spectrometer. At the bottom of the photograph, from left to right, are:- control box for automatically adjusting argon gas-flow and pressure in demountable atomic spectral lamp, demountable atomic spectral lamp, conventional flame, detector flame, sputtering chamber, atomic spectral lamp and a second control box for automatically adjusting argon gas-flow and pressure in sputtering chamber. At the top from left to right are:- power supply for atomic spectral lamps and sputtering chamber, control boxes for flame gases, and amplification and readout systems.

It now appears possible, by appropriate combination of atomic spectral lamps, sputtering chambers and flames, to develop a non-dispersive atomic spectrometer which is applicable to the analysis of solutions and solids by atomic absorption, atomic fluorescence or atomic emission measurements. In my opinion this type of system merits a detailed investigation.

#### REFERENCES

1. C.T.J. Alkemade and J.M.W. Milatz, *Appl. Sci. Res.* B4, 289 (1955).
2. A. Walsh, *Spectrochim. Acta* 7, 108 (1955); Erratum, *ibid.* 7, 252 (1955).
3. B.J. Russell, J.P. Shelton and A. Walsh, *Spectrochim. Acta* 8, 317 (1957).
4. A. Walsh, *Proc. Xth Colloquium Spectroscopicum Internationale*, p. 127, Spartan Books, Washington (1962).
5. J.E. Allan, *Analyst* 83, 433 (1958).
6. J.E. Allan, *Spectrochim. Acta* 18, 605 (1962).
7. J.B. Willis, *Nature* 107, 715 (1965).
8. A. Walsh, *Appl. Spectrosc.* 27, 335 (1973).
9. D.S. Gough, *Anal. Chem.* (in press).
10. D.S. Gough, P. Hannaford and A. Walsh, *Spectrochim. Acta* B28, 197 (1973).
11. R.M. Lowe, *Spectrochim. Acta* (in press)
12. J.V. Sullivan and A. Walsh, *Spectrochim. Acta* 21, 721 (1965).
13. J.V. Sullivan and A. Walsh, *Appl. Optics* 7, 1271 (1968).
14. L.R.P. Butler, Paper presented at Ninth Australian Spectroscopy Conference, Canberra, Aug. 13-17 (1973).
15. L.R.P. Butler, Kröger and C.D. West, *Spectrochim. Acta* 30B, 489 (1975).
16. A. Walsh, *Analyst*. 100, 764 (1975).
17. A. Walsh, *Proc. Roy. Aust. Chem. Inst.* 42, 297 (1975).
18. P.L. Larkins and A. Walsh, *Proceedings of International Conference on Heavy Metals in the Environment*, Toronto, Oct. 27-31 1975 (in press).
19. P.L. Larkins, *Spectrochim. Acta* 26B, 447 (1970).