NON-DISPERSIVE SYSTEMS IN ATOMIC ABSORPTION SPECTROSCOPY

A. WALSH

Division of Chemical Physics, CSIRO, Clayton, Victoria, Australia

ABSTRACT

In spectrochemical methods based on atomic absorption measurements the usual procedure is to pass radiation from an atomic spectral lamp through an atomic vapour of the sample and measure the attenuation in the intensity of a selected resonance line, the latter being isolated by means of a dispersion monochromator. In the techniques of selective modulation and of resonance detection, photoelectric signals due to resonance lines are electronically isolated from signals due to other lines and a dispersion monochromator is not required. In flame fluorescence it is also not necessary to provide means for optically resolving and isolating the resonance lines in the fluorescence radiation, provided it is ensured that the atomic spectral lamp which stimulates the fluorescence emits the spectrum of only one of the elements to be determined. For several elements, each of these non-dispersive techniques can yield a performance which is of the same order as, and sometimes superior to, that which can be achieved with a conventional dispersion-type atomic absorption spectrophotometer.

It has recently been demonstrated that these techniques can be successfully adapted to the direct analysis of metals and alloys, by making the sample for analysis the cathode of a selective modulator or resonance detector. The analytical capabilities of such systems are currently being assessed.

---

1. INTRODUCTION

The Japan Society for Analytical Chemistry, whose twentieth anniversary this Congress is commemorating, was formed at a time when some of the potentialities of atomic absorption methods of spectrochemical analysis were first recognized. The widespread adoption of such methods may be illustrated by the fact that the world population of atomic absorption spectrophotometers now exceeds fifteen thousand, and is currently expanding at a rate of three thousand per annum. The method is capable of determining sixty-five different elements and it has been claimed that more determinations of elemental composition are now carried out by atomic absorption methods than by any other technique.

This particular analytical technique would therefore appear to be one giving much cause for satisfaction. Many analytical chemists may well feel astonished when I state that most of those who have worked on the development of this technique are currently feeling a sense of disappointment, even of frustration, at the lack of progress. This is because more than 99.9 per cent

of all determinations now carried out by atomic absorption methods use the same basic technique which was originated twenty years ago. The situation is aggravated by the fact that there have been several interesting new approaches, all of which have either failed to fulfil their early bright promise, or have not found favour with analytical chemists.

In this paper I propose to illustrate the present situation by presenting a progress report on some aspects of recent and current researches aimed at the development of new analytical techniques. In selecting for discussion projects involving the use and development of non-dispersive systems it is by no means intended to imply that other projects being undertaken in various laboratories throughout the world are not of equal or greater significance at the present time. My choice is determined solely by a desire to restrict my comments to projects about which I have some first-hand information and which are probably not familiar to many analytical chemists. It is hoped that the following account will indicate why non-dispersive systems are becoming of increasing interest to our group in Melbourne and draw some of their interesting potentialities to the attention of enterprising analysts and adventurous instrument manufacturers!

Before proceeding to a discussion of non-dispersive systems it is helpful to recall the main characteristics of a typical atomic absorption spectrophotometer of conventional design, as illustrated schematically in *Figure 1*.
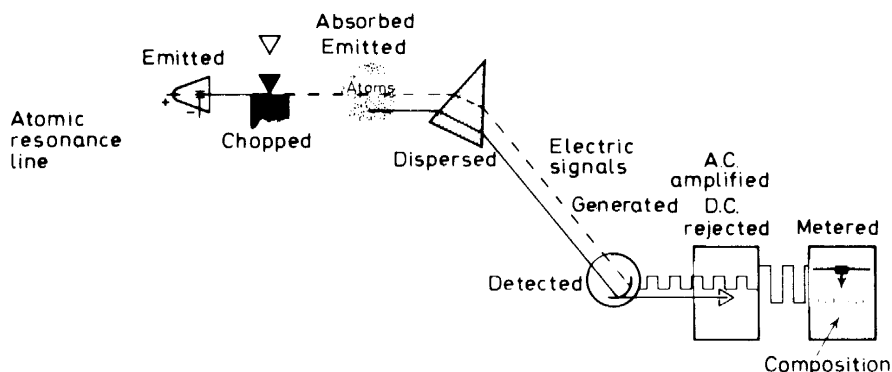

Figure 1. Schematic diagram illustrating conventional atomic absorption spectrophotometer

A portion of the sample is converted into an atomic vapour, and the absorption of radiation by this vapour is measured at a specific wavelength which is characteristic of the element to be determined. The use of a modulated light source and synchronous detection system ensures that unmodulated radiation emitted by the flame gives no signal at the output of the amplifier. The unknown concentration is determined by comparison with absorption measurements on standards of known composition.

It is usual to measure the absorption coefficient at the centre of the absorption line using an atomic spectral lamp which emits lines having a much smaller half-width than the absorption lines so that, to a good approximation, a measurement can be made of peak absorbance, which is linearly

proportional to concentration[1]. The most widely used method of producing the requisite atomic vapour is by spraying a solution into a flame, and the light source is usually a hollow-cathode lamp. *Figure 2* illustrates schematically the different widths of the emission and absorption lines under these conditions. Typically the half-width of the emission lines to be measured is of the order of 0.01 Å, and that of the corresponding absorption line for atomic vapours produced by a flame or furnace is some three to four times greater.
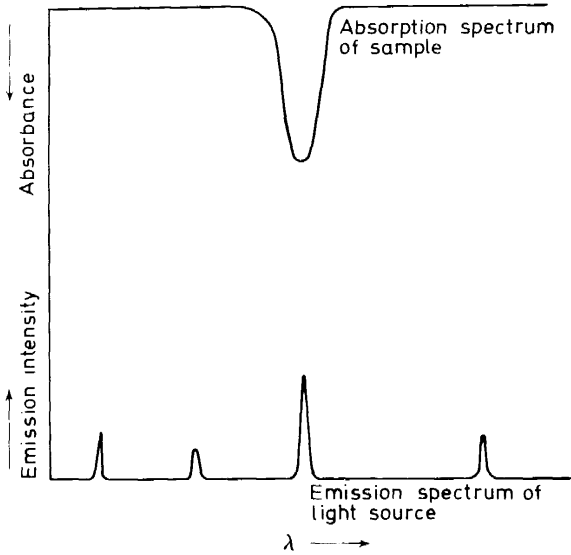

Figure 2. Schematic diagram illustrating use of a source emitting sharp spectral lines to measure peak absorption

Using this method of measuring peak absorbance, the main function of the dispersion monochromator, which usually provides spectral slit-widths down to about 1 Å, is simply to isolate the line required for measurement from all other lines emitted by the source. Provided this condition is fulfilled it is not essential for the light source to emit a pure spectrum of the element to be determined, and the spectra of hollow-cathode lamps used in conventional atomic absorption spectrophotometers often contain lines due to several different elements. It may also be noted that the spectra of some elements, such as those of Group I and II, are so simple that a low resolution, possibly of several hundred ångströms, is sufficient to isolate the desired line. In such cases the dispersion monochromator can be replaced by an absorption or interference filter. It is, however, important to ensure that the spectral band-pass is not so great that the radiation emitted by the atomic vapour of the sample causes excessive noise in the output signal of the photoelectric detector. This factor is also important in the non-dispersive systems discussed below.

147

2. NON-DISPERSIVE SYSTEMS BASED ON SELECTIVE MODULATION

A well-known method of 'isolating' a given region of a spectrum, illustrated in *Figure 3*, is by means of periodic interposition at a given frequency of an absorbing medium between a light source and a photoelectric detector, thus producing a modulated signal at all wavelengths that lie within the region
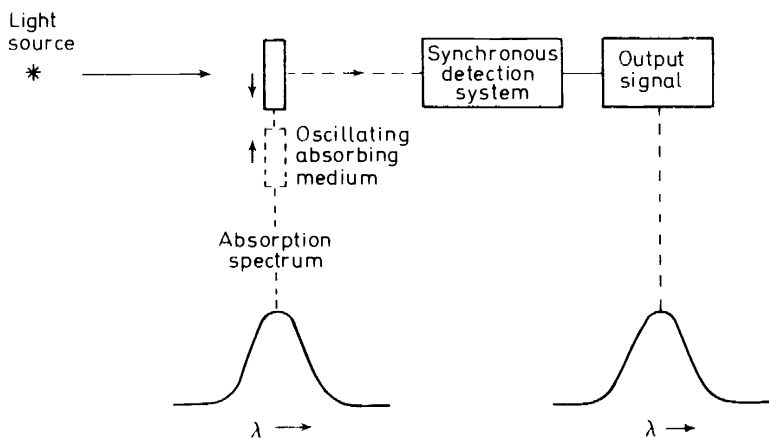

Figure 3. Schematic diagram illustrating the use of a selective-modulation system to produce an output signal *v*. wavelength curve corresponding to an absorption spectrum

of absorption of the medium. By using an a.c. detection system tuned to this modulation frequency an output signal *v*. wavelength curve corresponding to the absorption spectrum is obtained. It will be apparent that in this system any radiation emitted by the absorbing medium gives no resultant mean output provided the same amount of unmodulated radiation falls on the detector for all positions of the absorber. It is important to note, however, that this unmodulated radiation may produce noise at the output of the detection system and this must not be large compared with the modulated signal if satisfactory signal to noise ratios are to be obtained. For this reason it is usual to limit the amount of unmodulated radiation which falls on the detector by means of a filter.

2a. Atomic absorption spectrophotometer incorporating selective modulation by flames

The above type of selective modulation system, often known as the nega-tive-filter method, has been widely used in infrared gas analysers, but the only published application to atomic absorption spectroscopy is that by Alkemade and Milatz[2], who used this type of system to measure the atomic absorption of flames. A rotating chopper was used to obtain periodic passage of light from the spectral lamp through the flame. Using a sodium lamp as light source and an air–propane flame a detection limit of 0.03 ppm sodium was obtained. The possibility of determining 'all metals usually to be deter-

148

mined by flame photometry' was mentioned, but this approach to atomic absorption measurement does not appear to have been investigated further.

This system requires that the light source–filter–detector combination is such that resonance lines of only one element give modulated output signals. Thus, if the filter has a broad spectral band-pass the spectral lamp must be pure.

2b. Atomic absorption spectrophotometer incorporating selective modulation by atomic vapours produced by cathodic sputtering.

Another method of selectively modulating atomic resonance lines is by means of atomic vapours produced by cathodic sputtering[3–5]. The principle of this method, as applied to an atomic absorption spectrophotometer, is shown in *Figure 4*. In this arrangement radiation from an atomic spectral
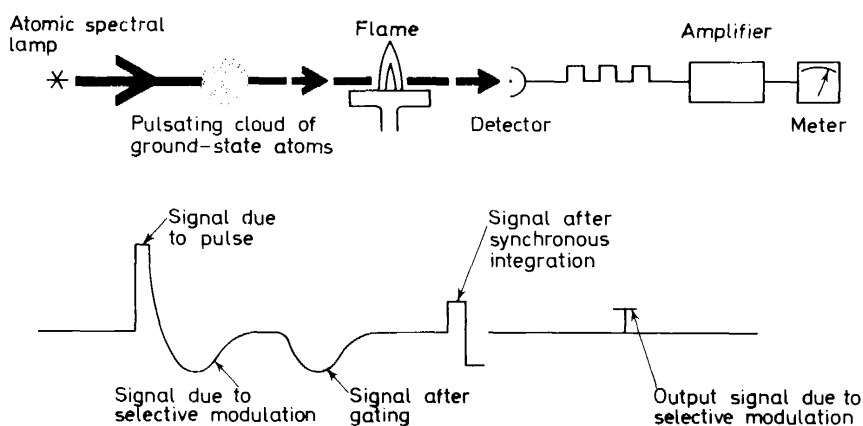

Figure 4. Schematic diagram of an atomic absorption spectrophotometer employing a pulsating cloud of atoms, produced by cathodic sputtering, to selectively modulate atomic resonance lines. The lower portion of the diagram illustrates the waveform of the photoelectric signal as it passes through various stages of the synchronous detection system to the output meter

lamp, such as a hollow-cathode lamp, is selectively modulated, by means of a pulsating cloud of ground-state atoms of the element to be determined. These pulsating clouds are produced by means of a pulsed low-pressure discharge which results in pulsed cathodic sputtering of atoms from the surface of the cathode. The only lines modulated by these atoms and which can therefore give a signal at the output of the synchronous detection system are those which are emitted by the light source and which are absorbed by the atom cloud. A simple gating switch ensures that any light emitted by the pulsed discharge produces no output signal[5]. In practice the modulator electrode is merely a loop of wire of the appropriate metal and the two electrodes of the modulator discharge can readily be accommodated within the housing of the atomic spectral lamp.

In the early applications of the technique the selectively modulated lamp was used in conjunction with a conventional atomic absorption spectrophotometer. Under these circumstances the monochromator, even if operated with wide slits, greatly restricts the amount of unmodulated radiation from the lamp or flame which can fall on the detector and thus favours the generation of modulated signal with a high signal to noise ratio. It has recently been demonstrated[6, 7] that for elements whose resonance lines have wavelengths below 320 nm the monochromator is not necessary if a solar-blind detector is used. For example, the caesium telluride photo-cathode of the Hamamatsu R166 photomultiplier has the sensitivity curve shown in *Figure 5* and it can be seen that it has very low sensitivity in the wavelength
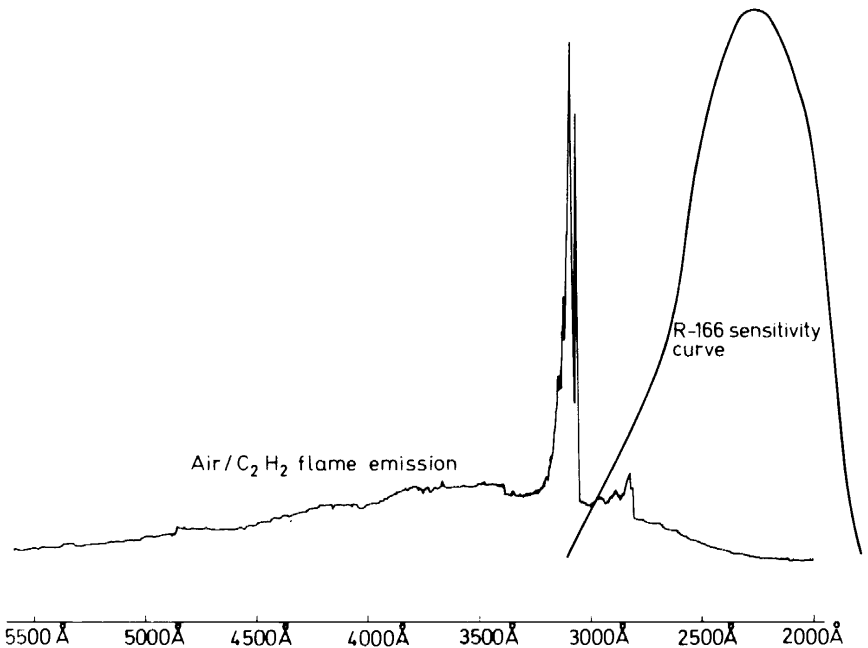

Figure 5. Spectral-sensitivity curve of a caesium telluride solar-blind photomultiplier (Hamamatsu R166) illustrating low sensitivity at wavelengths at which there is high flame emission

region in which maximum flame emission occurs. For wavelengths above 320 nm satisfactory signal to noise can be obtained by using absorption filters to restrict the unmodulated radiation falling on the detector.

My colleague, J. V. Sullivan, is currently preparing for publication a detailed survey of the characteristics and performance of this type of non-dispersive system. For the purposes of the present discussion it is sufficient to note that for many elements the performance is comparable with that of a conventional atomic absorption spectrophotometer. The absence of any slit or wavelength adjustments makes the instrument particularly simple to operate. A pure spectrum of a given element is obtained if either the lamp or

the modulator cathode is pure. If both are slightly impure the resultant spectrum may still be essentially pure since any weak lines due to impurities in the lamp cathode are modulated to such a small extent that the resultant signal due to the impurity becomes negligible.

In spite of the attractions and impressive performance of this system, it has the serious disadvantage that it lacks the versatility of the conventional dispersion system, and no doubt for this reason it has not been considered suitable for commercial exploitation. Nevertheless the work carried out to date has been instructive in demonstrating that high performance can be attained by this method of isolating signals due to atomic resonance lines, and the experience gained is proving invaluable in the development of selective modulation methods for the direct analysis of metals and alloys.

2c. Selective-modulation system for the direct analysis of metals and alloys

An interesting type of selective-modulation system is obtained by combining the arrangements described in Sections 2a and 2b to give the system shown in *Figure 6*. In this case the sample for analysis is made the modulator cathode so that a pulsating cloud of atoms of the sample is produced. Thus the resonance line(s) of a given element emitted by the atomic spectral lamp is modulated to an extent proportional to the concentration of that element in the sample. This system therefore provides a method for the direct analysis of metals and alloys. It merits investigation since it may offer significant advantages over conventional methods of measuring the absorption of atomic vapours produced by cathodic sputtering[8-11]. In particular, the selective-modulation approach provides a single-beam system which does not require the high stability of light-source intensity, which would normally be required for measuring very small values of absorption. Furthermore there is the possibility of using a non-dispersive system in cases where an atomic spectral lamp emitting a pure spectrum of the element to be determined is available.
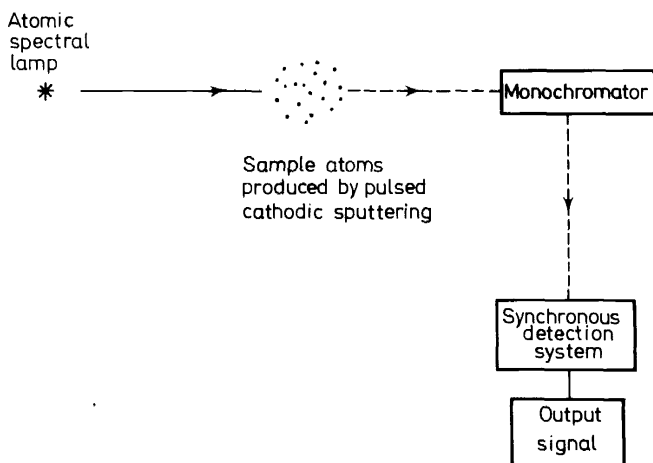

Figure 6. Schematic diagram of an atomic absorption spectrophotometer for the analysis of metals and alloys

151

Lowe, McDonald and Walsh[12] have recently reported some preliminary results obtained with a system, illustrated in *Figure* 7, in which a sputtering chamber replaces the flame in a conventional atomic absorption spectrophotometer. A flat surface of the sample for analysis is prepared by grinding and polishing on wet-and-dry paper, and the sample is sealed to the glass sputtering chamber by an O-ring. The chamber is evacuated to a pressure of 10^{-3} torr by means of a rotary pump. Dry-tank argon, which has first passed through a cold trap and a zeolite column, is then flowed through the system and the pressure adjusted to approximately 3 torr. The sputtering chamber and gas-handling procedure are similar in principle to those used by Grimm[13] in his work on atomic emission spectra from low-pressure discharges.
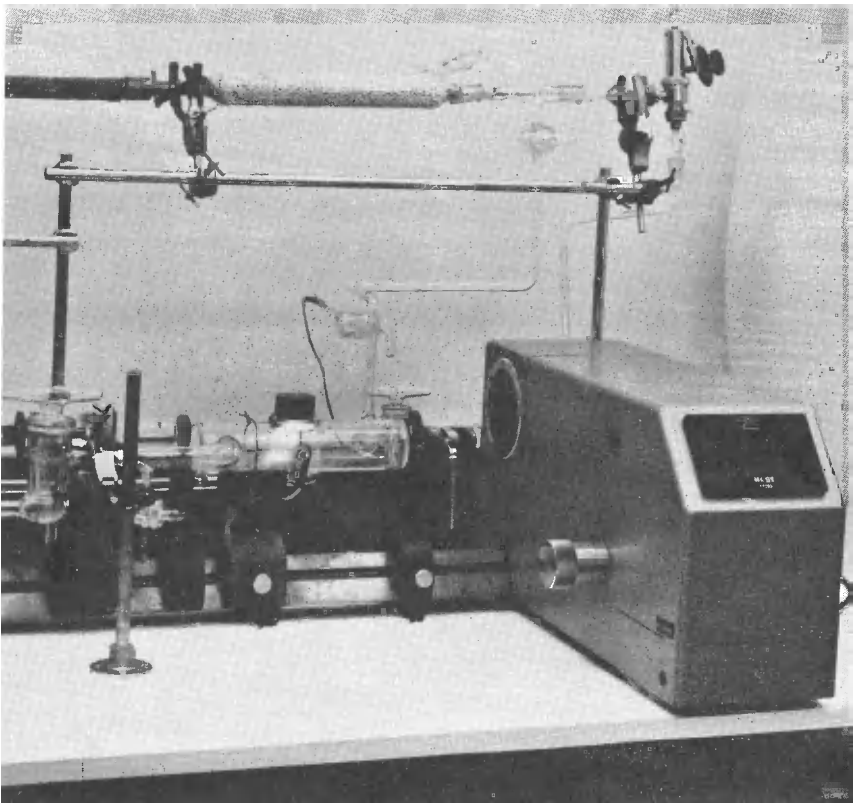

Figure 7. Photograph of apparatus used for the direct analysis of metals by the selective-modulation technique

When the final pressure has been precisely adjusted to the required value, the sample surface is cleaned by a d.c. sputtering discharge of about 50 mA for 1 min. The pulsed discharge is then switched on. Typically the pulses are in the range 50–75 mA for a period of 1–3 ms, followed by an off-period of 40 ms. The light source is operated from a regulated d.c. supply. The syn-

chronous detection system is similar to that described by Lloyd and Lowe[14].

At the present stage of its development the apparatus is not functioning reproducibly, and the reasons for this have not yet been identified. *Figures 8*
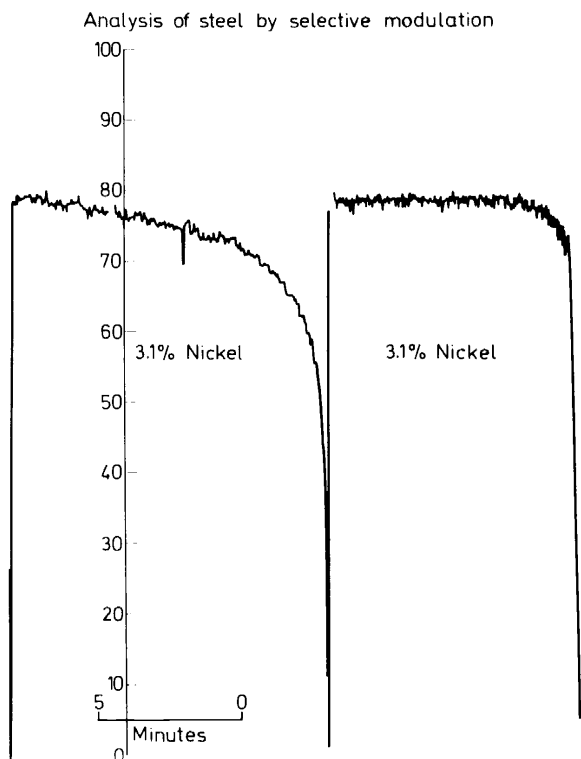

Figure 8. Representative performance obtained with the selective-modulation technique for the direct analysis of metals and alloys. The left-hand trace illustrates poor performance and the right-hand trace good performance

and 9 give results illustrative of present performance. It can be seen that a typically 'good' performance is adequate for many analytical requirements, but a typically 'poor' performance falls well short of that usually required. It is probable that the erratic behaviour is associated with insufficient cleanliness of the gas, specimen chamber and/or sample. Consistent behaviour is expected to be achieved once the cleanliness requirements have been clearly established. It is known that these will be even more severe in the case of aluminium samples.

At the moment the situation is encouraging and there is a good prospect of developing a method which will be applicable to the direct analysis of many metals and alloys.
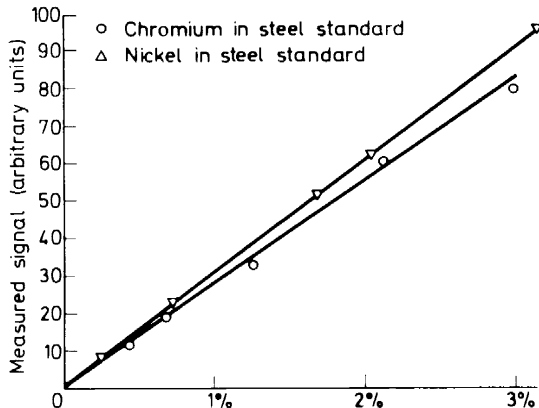
153

Figure 9. Calibration curves obtained using the selective-modulation technique applied to the direct analysis of low-alloy steels

3. NON-DISPERSIVE SYSTEMS BASED ON ATOMIC FLUORESCENCE

The second type of non-dispersive system to be discussed exploits the characteristics of the well-known phenomenon of atomic fluorescence. This occurs when an illuminated atomic vapour absorbs some incident radiation and subsequently re-emits some of the absorbed energy as radiation. When an atom in the ground state is optically excited and returns to the ground state, the fluorescence is generally referred to an resonance radiation. The technique discussed below is mainly concerned with this special type of fluorescence, which was first discovered by Wood[15] in 1905, and subsequently used by him as a means of isolating resonance lines[16, 17].

If an atomic vapour is illuminated by an atomic spectral lamp, then the spectrum of the fluorescence radiation will only contain lines due to atoms which are present in the lamp and in the atomic vapour. In particular, the spectrum of the fluorescence radiation is specific to one element if, by appropriate combination of lamp and vapour, the latter only absorbs lines of that element. For example, the vapour may contain only one atomic species capable of absorbing any of the radiation emitted by the lamp. Alternatively the lamp may emit spectral lines of only one atomic species capable of being absorbed by the vapour. The following techniques are based on this simple method for producing fluorescence specific to a given element, thus obviating the need for a dispersion monochromator to isolate a given spectral line.

3a. Atomic absorption spectrophotometer using atomic fluorescence as a means of isolating resonance lines of a given element

One obvious application of an atomic fluorescence system is as a replacement for a monochromator in an atomic absorption spectrophotometer[3–5, 18, 19]. This type of system is illustrated in *Figure 10*. The most generally applicable method for generating an atomic vapour of a given
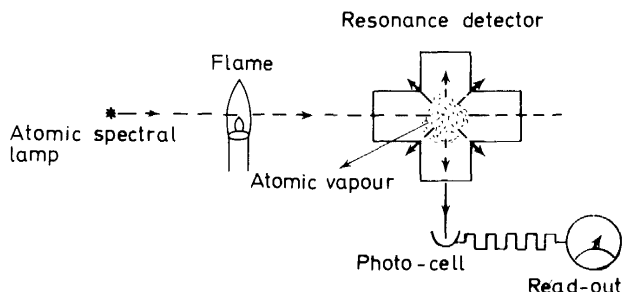
Figure 10. Schematic diagram of an atomic absorption spectrophotometer incorporating a resonance detector

element is by means of cathodic sputtering, which liberates atoms from the cathode of a low-pressure discharge in a rare gas. In this technique it is inevitable that the production of atomic vapour will be accompanied by the emission of radiation, and it is essential to isolate signals due to this from those due to fluorescence radiation. This is readily achieved by modulating the radiation emitted by the source and using a synchronous detection system which responds only to signals of this frequency. Any radiation emitted by the d.c. sputtering discharge thus produces no signal at the output of the detector.

Full details of the construction and characteristics of this type of spectro-photometer have been fully discussed by Sullivan and his co-workers, who have also reported on their application to various analytical problems[20–23]. The publications of Sullivan *et al.* indicate that such systems can give the same performance as a conventional spectrophotometer and are suitable for routine operation. For example, Sullivan, Timms and Young[15] used an instrument over a period of six months to determine nickel in 10,000 ore samples. They state: 'The fact that this instrument cannot be put out of adjustment due to changes in the ambient temperature or pressure, or by small mechanical vibrations, is a particularly attractive feature of the instrument since there is no adjustment corresponding to 'tuning-in' to a given line. The instrument is extremely simple and rapid in operation. The instrument has been entirely trouble-free and has proved itself well suited to the routine determination of nickel in ore samples'.

In spite of these promising results, this type of system is no longer used and is not now produced commercially. The reason for this is that the system is more expensive than a conventional spectrophotometer, and becomes prohibitively so if more than one element is to be determined. The main significance of this work has been to clearly demonstrate the feasibility of this type of measurement for the determination of a wide range of elements, and to show that the resonance radiation, which can be stimulated by illuminating atomic vapours produced by cathodic sputtering, is of sufficient intensity to yield photoelectric signals of high signal to noise ratio.

The excellent results obtained with such systems suggested the possibility of developing atomic fluorescence methods for the analysis of metals and alloys described in Section 3c.

155

3b. Non-dispersive flame fluorescence spectrophotometer

Atomic fluorescence from flames was first reported in 1923[24–26], but it is only in recent years that methods of chemical analysis based on measurements of such fluorescence have been developed. In 1961 Robinson[26] observed weak fluorescence from a magnesium flame, and in 1962 Alkemade[27] drew attention to the characteristics of flame fluorescence, particularly to the difference in photo-detector noise for fluorescence and absorption measurements. The first paper on analytical applications of flame photometry by Winefordner and Vickers[28], was published in 1964. Since that time the development of this method of chemical analysis has been almost entirely due to Professor Winefordner's group at the University of Florida and to Professor West and his colleagues at the Imperial College of Science and Technology in London. Authoritative reviews of the subject have recently been published by members of these groups[29, 30].

In much of the published work on flame fluorescence the fluorescence radiation has been passed through a dispersion monochromator to isolate one or more lines for measurement. This is not necessary and may even be undesirable if the light source emits the spectrum of only one of the elements present in the flame. In this case the only reason for restricting the radiation falling on the detector is to prevent excessive noise in the output signal from the photoelectric detection system. This can be achieved by means of an appropriate filter or by using a detector such as a caesium telluride solar-blind photomultiplier (Section 2a). It thus becomes possible to use the simple arrangement shown in *Figure* 11.
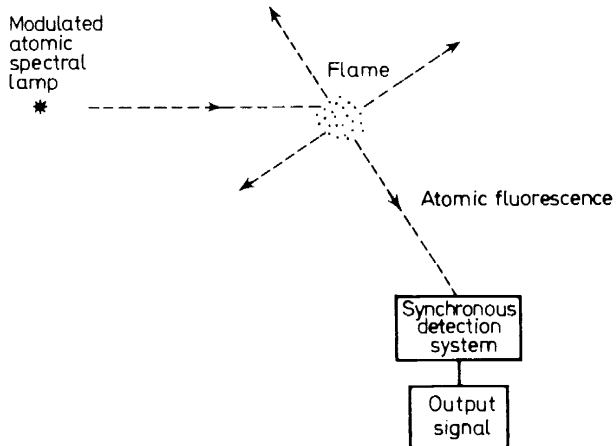

Figure 11. Schematic diagram of non-dispersive atomic flame fluorescence spectrophotometer

Larkins[31] has recently reported on the performance of this type of non-dispersive instrument using 'pure' high-intensity hollow-cathode lamps as light source[32], and a separated air–acetylene flame sheathed by nitrogen in the manner described by Hobbs *et al.*[33]. Larkins concludes that this simple

Table 1. Detection limits obtained by Larkins[31] using a non-dispersive flame fluorescence spectrophotometer compared with the best reported results for atomic absorption

| Element | Limit of detection (μg/ml) | | Wavelength (nm) |
	Atomic fluorescence	Atomic absorption	
Au	0.005	0.02	242.80
Bi	0.25	0.05	223.06
Cd	0.0002	0.005	228.80
Co	0.0015	0.005	240.72
Fe	0.003	0.005	248.33
Ga	6.0	0.1	287.42
Hg	0.07	0.5	253.65
In	1.0	0.05	303·94
Mg	0.0002	0.005	285.21
Ni	0.002	0.005	232.00
Pb	0.15	0.01	283.31
Pd	2.0	0·02	247.64
Pt	0.3	0.1	265.95
Sb	0.04	0.2	217.58
Sn	3.0	0.06	224.60
Tl	0.3	0.2	276.79
Zn	0.0003	0.002	213.86

arrangement generally gives better detection limits than can be obtained using a monochromator. For nine of the seventeen elements studied the limits of detection, given in *Table 1*, are superior to those obtained using a conventional atomic absorption spectrophotometer.

Scatter problems using a pre-mix burner are negligible provided there are no elements in the solution which form refractory particles in the flame. When such elements are present the scatter problem with a non-dispersive system is more severe than when a monochromator is used, since many more scattered lines fall on the detector. In fluorescence, as in atomic absorption, correction for such scattering effects is essential if accurate results are to be obtained. The scatter problem is less for higher temperature flames such as those using acetylene–nitrous oxide but in this case the fluorescence technique does not give as good detection limits as atomic absorption methods[34].

In spite of the many attractions and advantages of this and other flame fluorescence methods, there are very few published descriptions of their application to routine analysis, and little commercial equipment is available. Possibly the biggest obstacle to progress is the unsatisfactory situation regarding the intense atomic spectral lamps which are essential for exploiting the full potentialities of the method. Electrodeless discharge lamps are not sufficiently reliable for many elements whilst the high cost and complexity of high-intensity hollow-cathode lamps and their associated power supplies restrict their usefulness. Mitchell and Johannson[35] have used pulsed hollow-cathode lamps in their multi-channel flame fluorescence spectrophotometer and this is possibly the most attractive approach to the light-source problem. At the present time there is conflicting evidence regarding the performance of lamps operated in this manner and some workers have found the operating life of the lamp to be drastically curtailed under pulsed operation.

Even in its present state of development the flame fluorescence technique provides analysts with a powerful method of trace analysis, and simple non-dispersive systems of the type described above would appear to be particularly attractive.

3c. Non-dispersive atomic fluorescence spectrophotometer for the direct analysis of metals and alloys

The excellent results obtained with the systems described in Sections 3a and 3b have suggested an investigation of the combination shown in *Figure 12.* In this arrangement an atomic vapour of a metal sample for analysis is produced by cathodic sputtering and the intensity of fluorescence from this vapour is used as a measure of concentration.
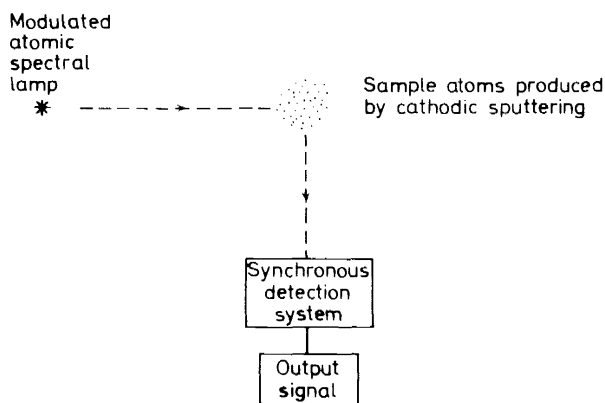

Figure 12. Schematic diagram of non-dispersive atomic fluorescence spectrophotometer for the direct analysis of metals and alloys

Gough, Hannaford and Walsh[36] have recently reported some preliminary results obtained with the apparatus shown in *Figure 13.* The apparatus for sealing the sample to the sputtering chamber, evacuating and producing the argon-flow is as described in Section 2c. In this case, however, the light source is a modulated 'pure' high-intensity lamp of the type described by Lowe, and the sputtering discharge is operated from a regulated d.c. supply, giving an output of up to 100 mA and 1000 V. For elements having their strongest lines below 3200 nm the fluorescence is allowed to fall directly on a solar-blind photomultiplier. For elements whose resonance lines lie in the wavelength range 3200–4000 nm a photomultiplier having a 5.5 response, such as a Hamamatsu R106, is used in conjunction with a Schott UG.5 filter.

To assess the performance of this method in the analysis of steels, measurements have been made on a series of spectroscopic low-alloy steel standards supplied by the Bureau of Analysed Samples Ltd., England. Representative results are given in *Figures 14* and *15.* The former shows a typical fluorescence signal $v.$ time curve for a standard containing 1.7 per cent Ni. Repeat measurements show that the signal obtained after two minutes sputtering is reproducible to better than ± 2 per cent.

Figure 13. Photograph of non-dispersive atomic fluorescence spectrophotometer for the direct analysis of metals and alloys, showing the sample being placed in position on the sputtering chamber

1.7% Ni in Fe (fresh surface)

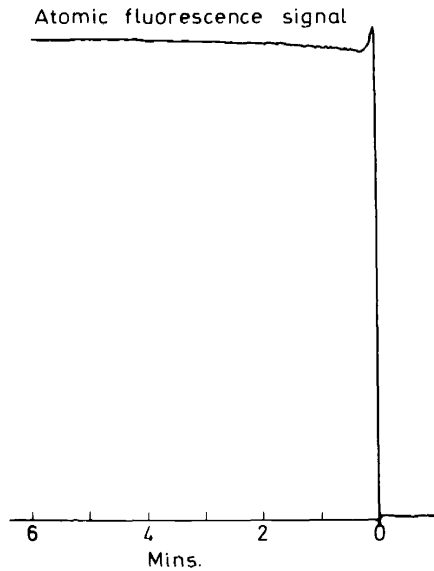Atomic fluorescence signal

6   4   2   0

Mins.

Figure 14. Representative performance obtained with the fluorescence technique for the direct analysis of low-alloy steels

These results are extremely promising and indicate that this method will prove to be applicable to the analysis of low-alloy steels. It is expected that the method will be equally applicable to the analysis of many non-ferrous
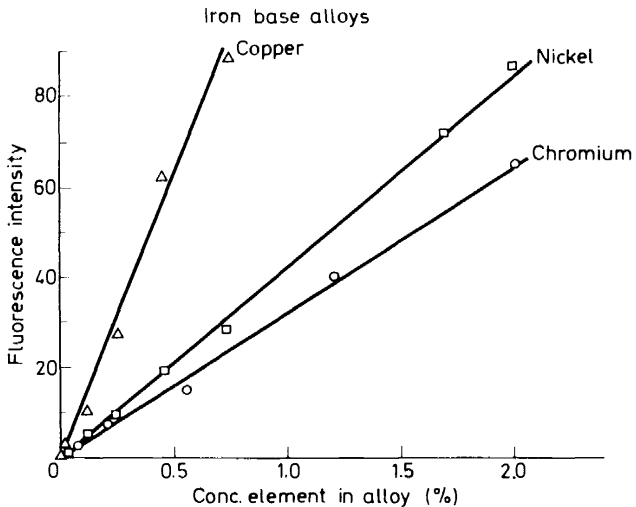

Figure 15. Calibration curves obtained by the fluorescence technique applied to the analysis of low-alloy steels.

alloys but it is known that aluminium alloys present a difficult problem owing to the oxide film on the surface.

4. SUMMARY AND CONCLUSIONS

For many analyses non-dispersive systems based on selective modulation and resonance detection have been shown to be capable of a performance comparable with, and in some cases better than, that obtained using conventional atomic absorption methods. They also provide promising new approaches to the analysis of metals and alloys.

REFERENCES

[1] A. Walsh, *Spectrochim. Acta,* 7, 108 (1955).
[2] C. T. J. Alkemade and J. M. W. Milatz, *Appl. Sci. Res.,* B4, 289 (1955).
[3] J. A. Bowman, J. V. Sullivan and A. Walsh, *Spectrochim. Acta,* 22, 205 (1966).
[4] J. V. Sullivan and A. Walsh, *Appl. Opt.,* 7, 1271 (1968).
[5] P. A. Bennett, J. V. Sullivan and A. Walsh, *Anal. Biochem.* 36, 123 (1970).
[6] P. L. Larkins, R. M. Lowe, J. V. Sullivan and A. Walsh. *Spectrochim. Acta,* 24B, 187 (1969).
[7] A. Walsh, *ASTM, Special Technical Publication,* 443 (1969).
[8] B. J. Russell and A. Walsh, *Spectrochim. Acta,* 15, 883 (1959).
[9] B. M. Gatehouse and ·A. Walsh, *Spectrochim. Acta,* 16, 602 (1960).
[10] J. A. Goleb, *Anal. Chim. Acta,* 34, 135 (1966).
[11] C. Bordonali and M. A. Biancifiori, *XV Colloquium Spectroscopicum Internationale,* p. 269, Madrid (1969); Hilger: London (1970).
[12] R. M. Lowe, D. McDonald and A. Walsh, *Spectrochim. Acta,* in the press.
[13] W. Grimm, *Spectrochim. Acta,* 24B, 443 (1968).
[14] P. D. Lloyd and R. M. Lowe, *Spectrochim. Acta,* in the press.
[15] R. W. Wood, *Phil. Mag.,* 10, 513 (1905).
[16] R. W. Wood, *Phil. Mag.,* 23, 689 (1912)
[17] R. W. Wood, *Physical Optics,* Macmillan, New York (1934).
[18] J. V. Sullivan and A. Walsh, *Spectrochim. Acta,* 21, 727 (1965).
[19] J. V. Sullivan and A. Walsh, *Spectrochim. Acta,* 22, 1843 (1966).
[20] J. V. Sullivan, A. B. Timms and P. A. Young, *Proc. Australasian Inst. Mining Met.,* No. 226, 31 (1968).
[21] B. S. Rawling and J. V. Sullivan, *Trans. Instn. Mining Met. (London),* 76, 238 (1967).
[22] P. L. Boar and J. V. Sullivan, *Fuel (London),* 46, 47 (1967).
[23] P. L. Boar and J. V. Sullivan, *Fuel (London),* 46, 230 (1967).
[24] E. L. Nicholls and H. L. Howes, *Phys. Rev.,* 22, 425 (1923).
[25] E. L. Nicholls and H. L. Howes, *Phys. Rev.,* 23, 472 (1924).
[26] J. W. Robinson, *Anal. Chim. Acta,* 24, 254 (1961).
[27] C. Th. J. Alkemade, *Proceedings of Tenth Colloquium, Spectroscopicum Internationale,* p. 143, Spartan Books, Washington D.C. (1963).
[28] J. D. Winefordner and T. J. Vickers, *Anal. Chem.,* 36, 161 (1964).
[29] J. D. Winefordner and R. Smith, *Analytical Flame Spectroscopy,* Ch. 11 (ed. R. Mavro-dineanu), Macmillan, London (1970).
[30] T. S. West, *Minerals Sci. Eng.,* 2, 31 (1970).
[31] P. L. Larkins, *Spectrochim. Acta,* 26B, 477 (1971).
[32] R. M. Lowe, *Spectrochim. Acta,* 26B, 201 (1971).
[33] R. S. Hobbs, G. F. Kirkbright, M. Sargent and T. S. West, *Talanta,* 15, 997 (1968).
[34] P. L. Larkins and J. B. Willis, *Spectrochim. Acta,* 26B, 491 (1971).
[35] D. G. Mitchell and A. Johansson, *Spectrochim. Acta,* 25B, 175 (1970).
[36] D. S. Gough, P. Hannaford and A. Walsh, *Spectrochim. Acta,* in the press.

161