

# THE APPLICATION OF NEW TECHNIQUES TO SIMULTANEOUS MULTI-ELEMENT ANALYSIS

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## ABSTRACT

The application of atomic absorption methods to simultaneous multi-element analysis is generally difficult, since the various elements to be determined may require not only the use of different flame lengths but also different fuel mixtures. However, the use of resonance detection, selective modulation and flame fluorescence, either individually or collectively, in conjunction with one or more flames, permits the development of simple multi-element systems which can be successfully applied to some important classes of analytical problem. Measurement of the intensity of the resonance radiation produced by illuminating atomic vapours generated by cathodic sputtering offers a possible approach to the direct simultaneous determination of several elements in metals and alloys.

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## INTRODUCTION

During recent years increasing attention has been directed to the development of atomic absorption spectrophotometers for the simultaneous determination of several elements<sup>1-3</sup>. These efforts have had only limited success, as may be illustrated by the fact that of the ten thousand atomic absorption spectrophotometers now in operation throughout the world, probably less than fifty are capable of making simultaneous determinations of two or more elements.

The reasons for the difficulty in designing multi-channel instruments suitable for application to a wide range of analytical problems have been discussed in detail elsewhere<sup>3</sup>, and may be summarized as follows: (a) One set of working conditions can only be used over a concentration range of about 1:10 if precise results are to be obtained; (b) for several elements the number of absorption lines available for measurement is extremely small, and the two most sensitive lines may give sensitivities varying by more than 1:100, so that a range of absorption path lengths and/or sample dilutions becomes necessary if analyses over a wide concentration range are required; (c) the optimum fuel mixture varies from element to element; (d) the height of the absorption path above the burner which gives minimum chemical interference also varies from element to element; (e) all channels must be kept in correct wavelength adjustments, and this may require more stringent control of room temperature than is necessary for the successful operation of a single-channel instrument.

There are, of course, many analytical problems for which one absorption path in a given flame can be used for the determination of several elements and in such cases the design of a multi-channel instrument is straightforward. In general, however, this is not so and at the present time the prospects for developing a multi-channel instrument of wide applicability do not appear to be promising. This paper describes four approaches to the problem which my colleagues and I have studied in an attempt to overcome some of the difficulties listed above.

## MULTI-CHANNEL SPECTROPHOTOMETERS EMPLOYING RESONANCE DETECTORS

The multi-channel instrument described below was the outcome of the successful application of resonance detectors in single-channel instruments for the routine determination of magnesium, calcium, copper and nickel and described in recent publications by J. V. Sullivan *et al.*<sup>4-7</sup>. It has been demonstrated that for these elements the techniques can yield results of the same precision and accuracy as those obtainable by conventional atomic absorption spectrophotometers employing optical monochromators for the isolation of atomic resonance lines.

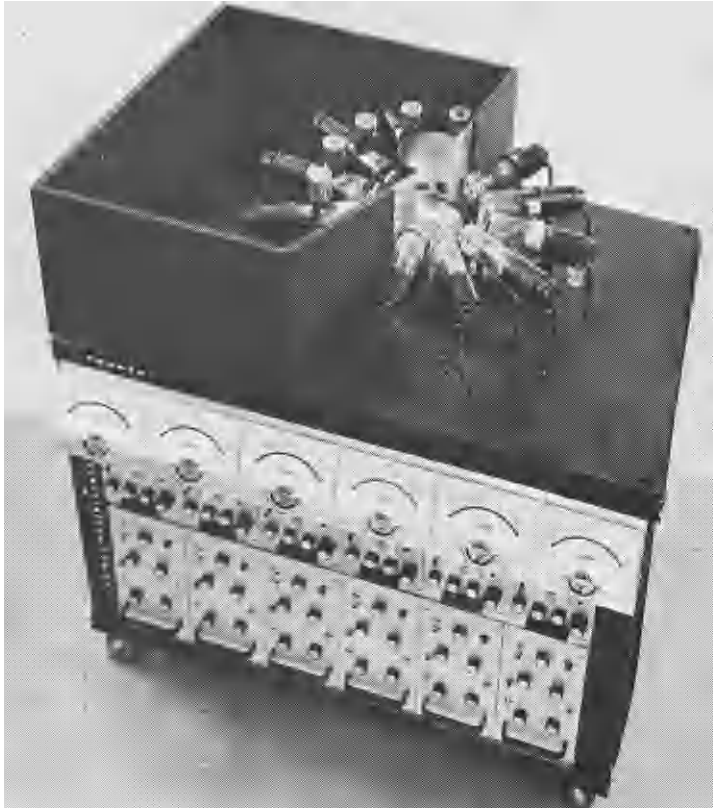
The factors determining the design and performance of atomic absorption spectrophotometers incorporating resonance detectors have been discussed in detail in a recent review<sup>8</sup>. The outstanding characteristic of a resonance detector is that it cannot be put out of adjustment by changes in room temperature and pressure, and it is virtually unaffected by mechanical vibrations. The use of resonance detectors in multi-channel instruments thus offers a solution to the problem of maintaining each channel correctly 'tuned' to the resonance wavelength(s).

My colleagues D. C. McDonald, P. Lloyd and J. V. Sullivan have collaborated with C. Macliver and D. Sampey (Sampey Exploration Services, Western Australia) in the design and construction of an instrument for the simultaneous determination of copper, silver, nickel, zinc, lead and cobalt in ores. The general layout of the instrument is shown in *Figure 1*. The light sources are on the right and the resonance detectors on the left. In operation, the lid of the instrument covers and makes light-tight the compartment housing the detectors. The resonance radiation from the six detectors falls on six photomultiplier tubes below the detectors. The amplifiers, power supplies and read-out systems of the six channels are housed beneath the optical system.

*Figure 2* shows a close-up of the burner and light sources. The perforations in the burner top are so arranged as to provide the appropriate absorption path length and an adequate width for each element. The optical system for each channel can be arranged to select the optimum height above the burner.

High-intensity hollow-cathode lamps<sup>9</sup> are used as light sources for the determination of zinc and nickel, whilst conventional hollow-cathode lamps are used for copper, silver and lead channels. Sputtering-type detectors are used for all channels except zinc and lead, for which a thermal type detector has proved superior. No combination of lamp and detector has yet given a satisfactory signal-to-noise ratio for the determination of cobalt.

Using the type of burner illustrated in *Figure 2* it has only been possible to use an air-propane flame. It is advisable to use an air-acetylene flame in



*Figure 1.* Six-channel atomic absorption spectrophotometer incorporating resonance lamps as monochromators.



*Figure 2.* Arrangement of light sources and burner in six-channel spectrophotometer.

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order to minimize chemical interferences, but all efforts to design a satisfactory burner for use with an air-acetylene flame have so far failed.

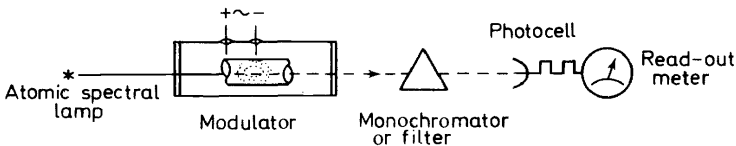
However, preliminary tests indicate that the performance of the instrument is capable of providing analytical results to an accuracy of  $\pm 5$  per cent which is adequate for the determination of zinc, lead, copper, silver and nickel in ores. The various path lengths can be adjusted so that for each element the absorbance is in the appropriate range.

For the preliminary tests the output of each channel is recorded on a separate meter. All channels can be automatically set on full scale before the sample is sprayed into the flame, and the results of the five determinations can be stored and read on the meters. When the instrument is put into routine operation the answer will be fed into a computer and the instrument is designed to carry out an analysis for up to six elements every twelve seconds.

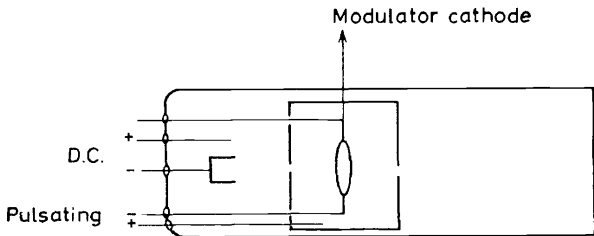
The instrument is expected to be in routine operation in the near future and a full report on the performance of this instrument will be submitted for publication.

### MULTI-CHANNEL SPECTROPHOTOMETERS EMPLOYING SELECTIVE MODULATION

An alternative to the resonance detection technique described above would be to isolate the resonance line(s) for each channel by the selective modulation technique<sup>10, 11</sup>, the principle of which is illustrated in *Figure 3*. Radiation from an atomic spectral lamp emitting the spectrum of a given element passes through a pulsating vapour of atoms of the same element, thus giving rise to selective modulation of the atomic resonance lines emitted by the lamp. Thus by using an a.c. detection system tuned to the frequency of this modulation only signals due to resonance lines are recorded.



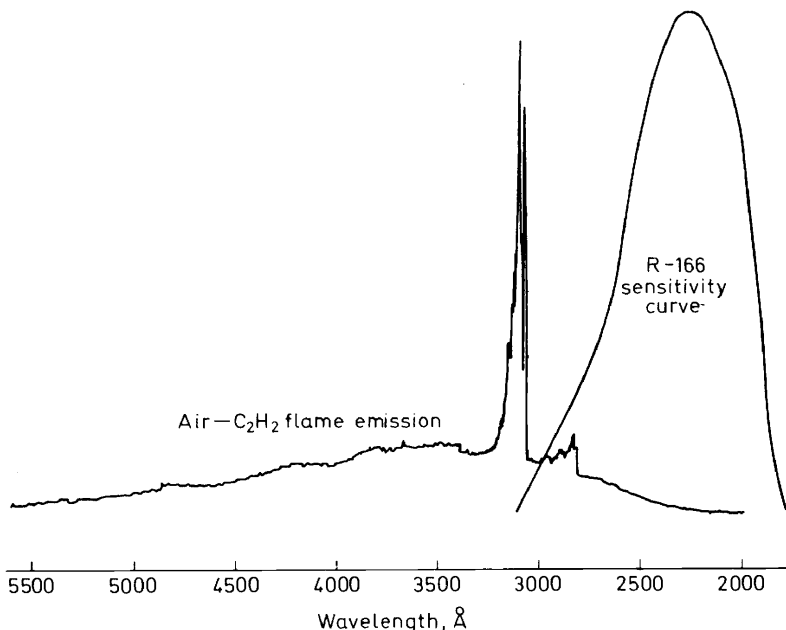
*Figure 3.* Schematic diagram illustrating the apparatus for isolating atomic resonance lines by selective modulation with a pulsating atomic vapour produced by cathodic sputtering.



*Figure 4.* Schematic diagram of hollow-cathode lamp incorporating a selective modulator.

In early experiments exploiting this technique for atomic absorption measurements the pulsating vapour was produced by a modulated hollow-

cathode discharge. In order to avoid excessive noise due to light emitted by the discharge, it was necessary to use a high-intensity hollow-cathode lamp as light source. A modern version<sup>8</sup> of this technique is illustrated in *Figure 4* and consists of a conventional hollow-cathode lamp together with a modulating cathode in the form of a loop. Pulses of short duration are applied to provide the modulation, and a gating circuit in the detection system ensures that the latter is inoperative whilst the modulation discharge is on, thus avoiding any difficulties due to light emitted by the modulator. In a typical arrangement the modulation frequency is 70 Hz whilst the pulsed current is 100 mA for a duration of 0.5 msec, the gating width being 2 msec.



*Figure 5.* Spectral sensitivity curve of caesium-telluride solar-blind photomultiplier R-166.

One of the problems associated with the resonance and selective modulation techniques for the isolation of resonance lines is that the resultant signal may be due to several lines of different oscillator strength. This may result in marked curvature of the calibration curve and also in some loss of sensitivity. A useful improvement can often be obtained by the use of a solar-blind photomultiplier having a spectral sensitivity curve of the type shown in *Figure 5*<sup>12</sup>. This provides a simple method of isolating signals due to lines of wavelength below about 3000 Å from signals due to lines of higher wavelength. For example, the sensitive group of nickel lines in the region near 2320 Å can be isolated from the less sensitive group in the region near 3414 Å. A further advantage of the use of a solar-blind photomultiplier in the selective modulation technique is that it greatly reduces any noise due to light emitted by the flame since, as can be seen from *Figure 5*, most of the latter consists of radiation at wavelengths greater than 3000 Å. Thus, for elements having resonance

lines below  $3000\text{\AA}$  the radiation from the atomic spectral lamp, after passage through the flame, may fall directly on a solar-blind photomultiplier. For lines above  $3000\text{\AA}$  a filter is usually required.

The type of spectrum isolated by this selective modulation technique has been discussed previously<sup>9</sup>. For most of the elements we have studied including copper, silver, magnesium, gold and nickel, the calibration curves obtained were those to be expected from a knowledge of the resonance lines isolated by selective modulation. For iron, however, the sensitivity has been unaccountably poor and no satisfactory explanation of this effect has yet been found.

An alternative to the selective modulation technique described above has been developed by R. M. Lowe<sup>13</sup>, who has shown that selective modulation may be achieved by appropriate operation of a conventional hollow-cathode lamp. In this method the hollow-cathode is operated at a steady d.c. level, and superimposed on this is a series of short high-current pulses. The increased sputtering due to each pulse causes a cloud of atoms of the cathode material to be formed inside and in front of the hollow-cathode, and by adjusting the pulse height and width it is possible to make the vapour cloud sufficiently dense to cause almost complete absorption of the resonance lines emitted by the lamp when operated at a low d.c. level. The absorption of the vapour cloud decreases between the pulses and the output intensity of the resonance lines rises again to that of the d.c. level. The detection circuit is so arranged that there is a gating switch on the output side of the photomulti-

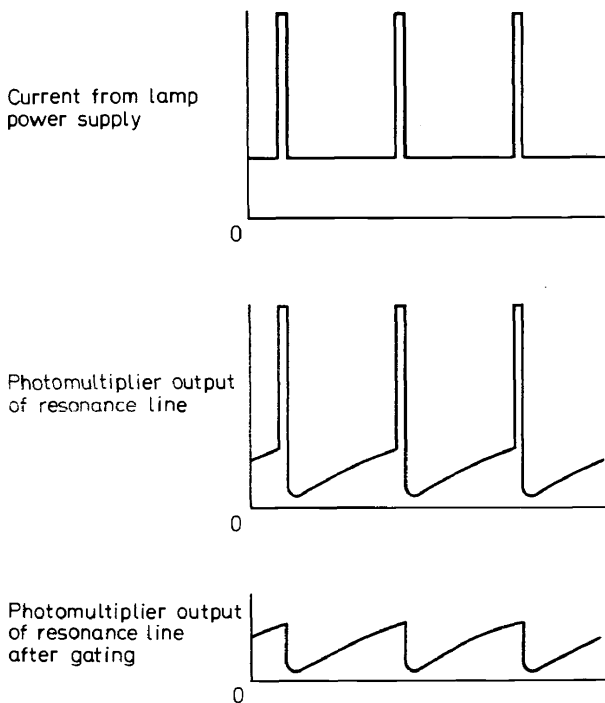


Figure 6. Waveforms illustrating Lowe's method of obtaining selective modulation of resonance lines by pulsed operation of a hollow-cathode lamp.

plier which is triggered by the onset of each pulse. This switch cuts out the very large increase in signal which would otherwise occur when the pulse is on. *Figure 6* illustrates the manner in which the modulated signal is obtained.

Lowe's experience to date indicates that his method gives a performance similar to that obtained by the use of a separate modulator electrode and it has the great merit of requiring no special lamps. *Figure 7* shows the compact arrangement which is possible using the selective modulation technique.

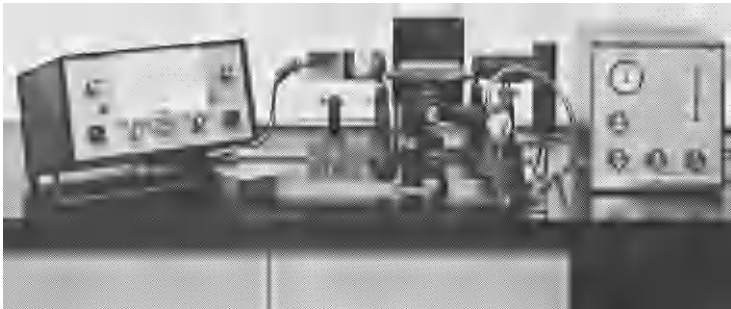
It is obvious that the multi-channel resonance instrument illustrated in *Figure 1* could be converted to a simpler system if the atomic spectral lamps were selectively modulated and the light transmitted by the flame allowed to fall directly on to solar-blind photomultipliers or, for isolating lines having wavelengths greater than  $3000\text{\AA}$ , through filters on to appropriate photomultipliers. It would also be possible to use much narrower beams through the flame than is possible with resonance detectors.

The major limitation in the performance of resonance and selective modulation instruments of the type described is imposed by the burner, and such instruments can obviously have only restricted application until the problem of designing burners suitable for operation on air-acetylene, and preferably also on nitrous oxide-acetylene, has been solved. In addition, it is apparent that neither system can be inexpensive and may, indeed, be no more economical than one using optical monochromators to isolate the resonance lines.

### MULTI-CHANNEL INSTRUMENTS USING FLAME FLUORESCENCE

One of the most important developments of the past few years has been the demonstration of the possibility of measuring flame absorption by measuring the amount of absorbed energy which is re-emitted subsequently by the flame<sup>14-16</sup>. Such so-called flame fluorescence measurements are of tremendous promise, particularly from the point of view of obtaining high sensitivities, and with the continuing development of light sources of high intensity it may well prove that for many analyses this is the best approach to atomic absorption measurements on flames. Attention has recently been drawn to the possibilities of making flame fluorescence measurements using a solar-blind photomultiplier as detector, thereby making unnecessary for many determinations the use of a monochromator<sup>17</sup>. The successful operation of this type of simple system depends on the fact that, as can be seen from *Figure 5*, most of the light emitted by the flame lies mainly outside the sensitivity response curve of the photomultiplier and therefore produces no noise. This technique also has the advantage that it permits collection of fluorescence radiation over a much wider angle than is possible when using a monochromator, and avoids the restriction of an entrance slit. It also has the advantage of recording the total signal of all fluorescence lines lying within the sensitivity curve of the detector, thus enhancing the sensitivity of the method. Thus in flame fluorescence the low oscillator strengths of the lines in complex spectra, such as those of the transition elements, can be compensated for to some extent if several of these can be recorded simultaneously. This offers an advantage over conventional atomic absorption methods in which maximum sensitivity can only be obtained by isolating the line having the maximum oscillator strength.





*Figure 7.* Atomic absorption spectrophotometers employing selective modulation to isolate resonance line(s).



*Figure 10.* Seven-channel atomic fluorescence spectrophotometer.

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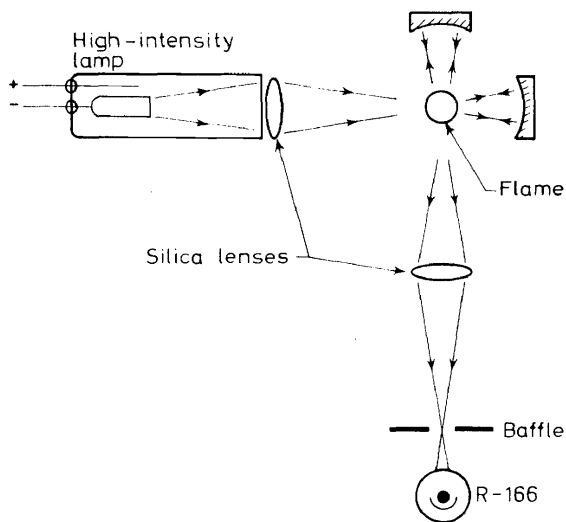


Figure 8. Schematic diagram of flame fluorescence apparatus employing a solar-blind photomultiplier.

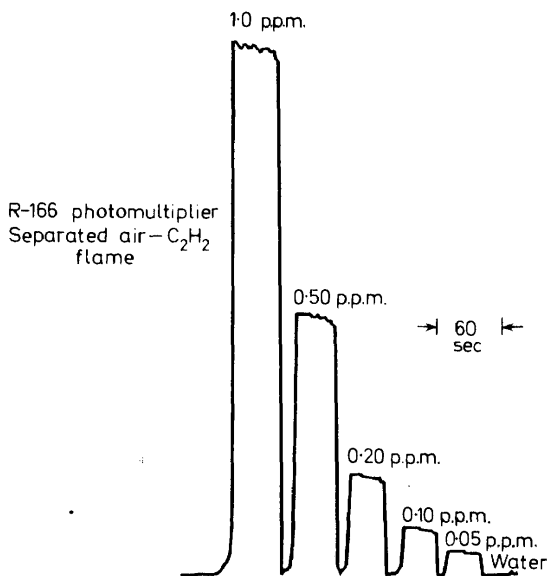


Figure 9. Atomic fluorescence measurements for nickel using a solar-blind photomultiplier R-166 with no monochromator or filter. Air-acetylene flame

Table 1. Detection limits ( $S/N = 1$ ) by flame fluorescence using a solar-blind photomultiplier as detector

Element	p.p.m.	Element	p.p.m.
Au	0.01	Mg	0.0002
Ni	0.004	Co	0.04
Fe	0.02	Cd	0.0005
Zn	0.0005	Hg	0.5

The detection limits obtained by P. L. Larkins<sup>18</sup> using the apparatus illustrated in *Figure 8*, are listed in *Table 1*. For these experiments the light source was an improved high-intensity hollow-cathode lamp developed by R. M. Lowe<sup>19</sup>. *Figure 9* shows a typical recording obtained using this technique. It is proposed to investigate the use of thermal high-intensity lamps<sup>9</sup> as light sources for elements of low melting-point.

The successful operation of this technique obviously demands the use of light sources each of which emits only a spectrum of the element to be determined. In general this requirement presents no difficulties but with nickel for example there is a possibility that it may be difficult to obtain a nickel spectrum completely free of the magnesium line at 2852Å. There may also be difficulties with samples having a high solids content since these may result in a scatter signal which is of the same order of magnitude as the fluorescence signal. Neither of the above limitations appears to be fundamental and this technique offers considerable promise.

Over and above the merits of such a system for single-channel analysis is the possibility of developing extremely simple equipment for the simultaneous determination of those elements which can be determined by the solar-blind technique. It is expected that the elements which could be determined would include the elements listed in *Table 1* together with Mn, Ga, Pd, Pt, Ir, Sn, Sb, Pb and Bi. It should also prove possible to extend the method to As, Se and Te, provided suitable high-intensity thermal lamps can be developed.

The multi-element system P. L. Larkins and P. D. Lloyd are investigating is illustrated in *Figure 10* and is a simple extension of the single-channel equipment. The light sources are Lowe's improved high-intensity lamps, which are switched on sequentially (pulse duration 1 ms, pulse separation 0.125 ms) and a time-sharing system is used. This multi-element system is similar to that described by Mitchell and Johansson<sup>23</sup> but does not require a series of filters for line isolation.

It is too early to assess the merits of this arrangement but the results to date have been encouraging and there are good prospects that this method can be successfully applied to those elements which can be determined using an air-acetylene flame, and which have their sensitive wavelengths below 3000Å.

Some initial experiments on the determination of elements such as silver, copper and chromium using a photomultiplier with  $S_4$  response (Hamamatsu R-106) and a filter<sup>24</sup> indicates that these three elements could be satisfactorily

determined by this arrangement. At the present time the important question is whether or not this technique can be satisfactorily extended to those elements which require a nitrous oxide-acetylene flame for satisfactory atomization. We have not yet investigated this question.

Whilst the flame fluorescence approach described above appears to be extremely promising and certainly offers the possibility of an extremely simple instrument we still have the basic difficulty associated with the fact that the optimum fuel mixture will not be the same for all elements. If the above approach is adopted then it may be necessary to use at least two arrays of lamps and two burners using air-acetylene and nitrous oxide-acetylene respectively. It may often happen, of course, that it will not be possible to determine a required concentration range of one element simultaneously with required concentration ranges of other elements. This problem appears to be basic to all absorption and fluorescence methods in which the atomic vapour is produced from the sample by means of a flame.

### **MULTI-CHANNEL SPECTROPHOTOMETERS FOR THE DIRECT ANALYSIS OF METALS AND ALLOYS**

Many of the limitations of the spectrophotometers described above are associated with the use of a flame for the production of an atomic vapour from the sample. It has therefore seemed worthwhile to re-examine an alternative method for producing the requisite atomic vapour, and the technique of cathodic sputtering<sup>20, 21</sup> is therefore being investigated further. One of the main attractions of this technique is that it offers the possibility of direct analysis of metals and alloys without prior solution. It is also the only technique, other than complete thermal vaporization, which offers any possibility of producing an atomic vapour of the same composition as the sample for analysis. Furthermore the power required to produce atomic vapour by cathodic sputtering is extremely small.

Early experiments indicated that it was possible to carry out analysis by the cathodic sputtering technique but there were many practical problems which had to be solved before the method could be considered suitable for routine analysis. The only published application of this method to real analysis is that by Goleb<sup>22</sup> on the determination of uranium isotopes. This of course is a special problem and does not require the provision of standards in the normal sense.

The experiments my colleague P. Hannaford is carrying out are not aimed immediately at the production of an analytical instrument but instead an attempt is being made to determine whether, in a specific case, it is possible to produce an atomic vapour which has the same composition as the basic metal and for study a typical stainless steel has been selected (knowing full well that this may represent a favourable case). The initial investigations are concerned primarily in investigating the effect of various electrode configurations, different gas pressures of argon, neon, krypton and xenon, and different discharge currents. Experience with resonance detectors has also encouraged an investigation of the measurement of atomic absorption from measurements of the intensity of resonance radiation. The sputtered vapour can be simultaneously excited by chromium, nickel and iron lamps, the resonance radiation being allowed to fall on a solar-blind photomulti-

plier and on a conventional photomultiplier tube. The three lamps are modulated at different frequencies and the output signals due to each are isolated by synchronous demodulation. At the moment, Dr Hannaford's experiments are insufficiently advanced to justify any conclusion except to say that it now appears that with stainless steel the atomic vapour produced is certainly not markedly different in composition from that of the solid alloy. Furthermore, it seems possible by this technique to obtain extremely high signal-to-noise ratios. It may be noted that the fluorescence signal can be calibrated by means of an absorption measurement. One attractive feature of this method is that the atomic concentration can be altered simply by altering the discharge current, and in this respect offers a marked advantage over a flame.

It will be apparent that the development of an analytical technique based on the type of experimental measurement described above will be by no means easy. However, it is I believe a distinct possibility which is well worthy of further investigation since it offers some chance of a method of analysis which would not require a whole range of standard alloys but only the availability of pure metals to calibrate the instrument. It also offers some hope of producing a far simpler apparatus than any comparable emission equipment and the precision and sensitivity of such methods may well exceed those of any other method.

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