

# DEVELOPMENTS IN ATOM RESERVOIRS AND LINE SOURCES FOR ATOMIC ABSORPTION AND ATOMIC FLUORESCENCE SPECTROSCOPY

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## ABSTRACT

Up to the present time flame media have been used almost exclusively as atom reservoirs for the purposes of atomic absorption and atomic fluorescence spectroscopy. The merits and demerits of flames in various forms will be discussed against the differing requirements of each technique. Particular attention will be paid to the use of the separated flame in each mode of analysis. Flame emission spectroscopy will also be discussed briefly in relation to this topic.

Several alternatives to the flame have been proposed notably the r.f. plasma torch, Langmuir-torch, the sputtering (hollow cathode lamp) chamber, the Vidale (King) furnace, L'vov furnace and Massmann tube. These devices will be briefly reviewed and the FAR (filament atom reservoir) unit devised at the Imperial College will be discussed more fully. The device fits most commercial equipment in place of the normal flame/nebulizer unit and allows very high sensitivity, e.g.  $10^{-10}$  g Mg in absorption,  $10^{-15}$  g Mg in fluorescence etc. It is self-purging and extremely simple to use in practice. A proposal is made relating to terminology for the sensitivity of non-nebulizing methods of atomic absorption and atomic fluorescence analysis.

The use of microwave-excited electrodeless discharge tubes as spectral line sources for individual elements in atomic absorption and atomic fluorescence spectroscopy will be discussed and the development of multi-element discharge tubes for sequential atomic fluorescence using an integrating flame photometer with automatic flame background correction. The role of continuum sources in atomic absorption and atomic fluorescence spectroscopy will be referred to more briefly.

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## INTRODUCTION

Historically, the laboratory techniques of atomic absorption and atomic fluorescence spectroscopy are closely related to the older technique of flame photometry. Both techniques are instrumentally more complex than flame photometry, but they offer advantages which more than compensate for this. Thus, a light source, chromatic or monochromatic, is required in both and there are quite different requirements for the flame or other atom reservoir used to maintain the population of atomic species during spectral measurement of absorption or fluorescence.

In flame photometry, the energy of the reacting flame gases is used to cause dissociation or atomization of the preatomic species which are introduced in the form of a dilute solution nebulized on the support gas. Following

atomization, further energy must be supplied by the flame to excite the atomic species which then subsequently radiate atomic spectra characteristic of the atomic species as they revert to the ground state of electronic energy. In some instances, where thermal equilibrium does not prevail, e.g. in chemiluminescence emission in the primary region of a flame, the energy requirements are not necessarily so stringent. Generally speaking, however, for elements whose excitation potentials are much greater than approximately four electron volts, the energy availability in most flames is somewhat unsatisfactory. For this reason, in the past, much flame photometry has had to be done in oxyacetylene and oxyhydrogen flames which have had to be burned in a non-premixed manner. In this way the intensely radiating primary reaction between the fuel and oxygen is present throughout the body of the flame and constitutes a very high and noisy background signal against which the measurements of the atomic emissions have had to be made. However, recent work in atomic absorption and atomic fluorescence spectroscopy has shown that it is possible to burn very highly energetic premixed flames such as nitrous oxide-acetylene<sup>1, 2</sup> at a slot or ring burner and thus avoid the problems associated with having to view the high background emission from the primary zone of such a flame. It has also been shown<sup>3, 4</sup> that it is possible to remove or separate the continuum-emitting outer (diffusion) mantle of premixed flames thus reducing the background emission of flames such as air-acetylene by about two or three orders of magnitude over a substantial part of the emission spectrum. These contributions alleviate some of the problems of flame photometry and permit some of the elements which are difficult to excite to be determined somewhat more sensitively and others to be determined where this was scarcely possible. The flame background emission is of relatively minor importance in atomic-absorption and fluorescence measurements because it can be virtually eliminated by modulation of the source and the use of a tuned amplifier. Recently, however, Hermann<sup>5</sup> and his colleagues have also shown that the emission background may be modulated out in flame photometry by pulsing the sample solution fed to the flame. In this way the a.c. amplifier tuned to the pulsing frequency eliminates the virtually d.c. radiation from the flame.

## FLAMES AS ATOM-RESERVOIRS

In atomic absorption and atomic fluorescence spectroscopy, flames are used as atom-reservoirs largely because of their previous use in flame photometry and because they have been fairly convenient for producing atomic populations of many elements. Other atom-reservoirs are now available which appear to offer several advantages over flames, but the latter are likely to be used as a routine procedure for a great number of years, because of their convenience, in the average laboratory.

The only essential requirement for flames in atomic absorption or atomic fluorescence spectroscopy is that they should produce efficient atomization of the inorganic or organo-metallic species under investigation. Excitation of the test element is unnecessary and indeed is undesirable although such atomic emission can be modulated out in the same way as band emission from the flame itself. Such atomic (thermal) emission occurring at the same

wavelength as the absorption or fluorescence signal may, however, add considerably to the noise of the measurement.

With the advent of higher intensity sources it does not matter quite so much now that the *absorption* background of a conventional (50 to 100 mm) length of flame should be fairly high unless high gains still have to be used or scale expansion is being employed. The absorption of flame gases only becomes serious when hydrocarbon flames are being constricted into long tubes or when the absorption of atmospheric oxygen becomes an additional problem, e.g. with arsenic and selenium.

The flame requirements for atomic fluorescence are basically the same as those for atomic absorption. However, because of its inherently higher sensitivity, atomic fluorescence measurements are usually carried out with more dilute test solutions and frequently at maximum gain and maximal slit-width. Because of this, the intensity of the flame background over the spectral band-pass used to isolate an atomic line is generally a more important consideration in atomic fluorescence than in atomic absorption measurements. Even so, the flame background is not so critical a consideration in atomic fluorescence as it is in flame photometry where it is frequently the decisive factor in the feasibility of devising an analytical method.

Unfortunately, in many quarters, there is an obsession in assessing the sensitivity of atomic absorption, atomic fluorescence, and atomic emission with the 'Detection Limit' which is usually, but not invariably, quoted as the concentration in parts per million of an element in solution required to produce an analytical signal to total background noise ratio of one or two, or some other defined ratio. In atomic fluorescence, particularly good detection limits may often be obtained by using low background hydrogen diffusion flames or air-hydrogen flames. But the detection limit in fluorescence, as in absorption or emission, is only an indication of the sensitivity and is, not infrequently, misleading as a measure of the smallest amount of the element which may be determined with a reasonable degree of precision.

Such flames are usually of little use in flame photometry because they are insufficiently energetic to produce excitation of the atoms which they generate.

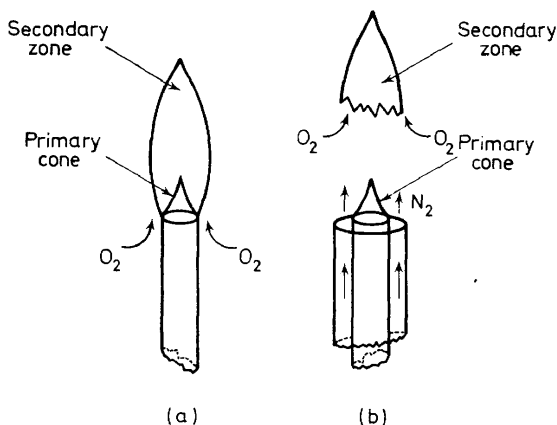
A penalty of using such low temperature flames in atomic fluorescence, despite the attractive detection limits that may be obtained for pure solutions, is that even if the element of interest is efficiently atomized, other compounds which are present in the sample matrix may not be dissociated at such a low temperature. Thus matrix and chemical interferences may abound and the practical value of the fluorescence technique may be overlooked in the process. It is, therefore, beneficial in fluorescence, and even more so in flame photometry, to try to minimize the background emission of the flame rather than to resort to the use of cooler flames of low background.

### SEPARATED FLAMES

The non-premixed flame now plays little part in atomic absorption or atomic fluorescence spectroscopy, and no more will, therefore, be said about it, and reference will be made only to premixed flames burning in a near-laminar flow pattern.

In such flames, the emission background comes from both the intensely

emitting primary cone where the fuel gas and the oxidant undergo reaction and from the outer mantle of the flame, see *Figure 1* (a), where the unburnt residues or products of the initial reaction zone burn by support of the atmospheric oxygen which diffuses in towards the centre of the flame<sup>3</sup>. Normally, with all three techniques, the atomic signals are measured in the



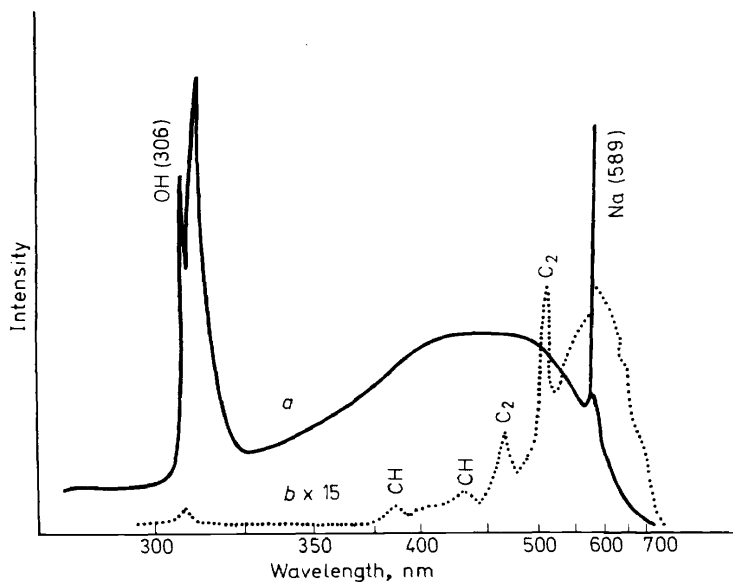
*Figure 1.* Zone structure of premixed flames: (a) Conventional air-hydrocarbon flame supported at open burner port; (b) Same flame with separation of zones by concentric flow of nitrogen gas which prevents combustion of secondary zone in the region surrounding the primary cone.

interconal region immediately above the primary reaction zone. In this way the detector does not view the intense background emission from the primary reaction region of the flame. However, in a conventional flame it cannot avoid viewing the radiation from the outer mantle of the flame. Sometimes this may be very intense relative to the weak atomic signals which are being studied.

Virtually all the hydrocarbons are broken down in the primary reaction zone and carbon monoxide and hydrogen are the main unburnt products which pass through to burn in the outer zone supported by the diffusion of atmospheric oxygen, or by its entrainment at the edges of the flame.

The combustion of both carbon monoxide and of hydrogen result in strong chemiluminescence as shown in *Figure 2* (a)<sup>3</sup>. The OH banding in the 310 nm region is particularly intense whilst that of the carbon monoxide reaction is spread over the bulk of the spectral region shown. When atmospheric oxygen is denied access to the base of the flame either by placing a mechanical obstruction, such as a transparent silica tube in the way, or by blowing an inert gas around the flame, *Figure 1* (b), the combustion of the carbon monoxide, etc. is prevented in the all-important interconal region. Thus it is possible to measure atomic signals of absorption, emission or fluorescence against a virtually non-existent emission background. *Figure 2* (a) shows the spectrum emitted by a premixed air-acetylene flame in the interconal region whilst *Figure 2* (b) shows the emission spectrum of the same region of the same flame after separation by blowing nitrogen concentrically round the flame. The signal strength of the separated flame has

been amplified fifteenfold to make it visible on the same scale as that of the conventional flame. The dramatic reduction in the flame emission background upon separation is extremely beneficial for flame photometry and reduces noise in atomic fluorescence to allow the use of maximum gains, slit-widths and scale expansion, etc. This not only permits better detection limits to be obtained, but produces a genuine increase in sensitivity (i.e. increase in gradient of calibration curves) in both flame photometry and atomic fluorescence measurements.



*Figure 2.* Emission spectra of separated and conventional air-acetylene flame in interconal region: (a) Emission from conventional flame showing strong OH banding *ca.* 310 nm, CO continuum (325–700 nm); (b) Emission from separated flame showing near-elimination of OH and CO bands. *N.B.* The scale of curve *a* is compressed fifteen-fold relative to curve *b*.

At this point it should be mentioned that the removal of the burning outer sheath of gas, upon separation of the two zones of the flame, not unexpectedly produces a slight fall (*ca.* 100 deg.C) in the temperature of the interconal region. This is of virtually no importance as far as absorption or fluorescence measurements are concerned, but has an effect on the absolute strength of atomic (thermal) emission signals because of the critical dependence of emission signals upon temperature. This decrease in the absolute signal strength is, however, offset by the possibility of using higher gains and slit-widths as a result of the considerable drop in the emission background from the flame. The temperature can in fact be restored by enriching the air supply with oxygen if desired<sup>3</sup>.

The removal of the surrounding atmospheric oxygen upon separation also has other beneficial effects. Many elements, for example, emit strongly by oxide or hydroxide band emission in the outer mantle of a flame in which

they are present. They can scarcely do this in a separated flame. In this way many noisy signals can be avoided and even radiative interference. A good visual example is provided by a mixture of copper and lithium sprayed into an air-acetylene flame. The green molecular banding of copper hydroxide in the outer mantle is very intense and virtually obscures the atomic emission of the lithium. When the flame is separated, however, the atomic emission of the lithium can be seen clearly completely unobscured by the band emission due to the copper hydroxide which only appears much higher up where the atmospheric oxygen gains entry to the flame gases.

The prevention of diffusion of atmospheric oxygen is of even more vital concern where the element to be determined forms a refractory oxide. Such elements, e.g. aluminium, beryllium, germanium, silicon etc. are much more efficiently atomized under strongly reducing conditions than in oxidizing conditions. Absorption measurements made in a nitrous oxide-acetylene flame burning at a slot burner show that a greater atomic population is maintained upon separation<sup>6,7</sup>. Separation of a cylindrical flame in emission work for these elements is even more beneficial because the size of the cyanogen zone is considerably increased upon separation. Thus, in addition

Table 1. Effect of flame separation on detection limits in flame photometry

Element	Wavelength, nm	Detection limits, p.p.m.					Improvement on separation, %	
		Air-acetylene*		Nitrous oxide-acetylene†			N	A
		C	N	C	N	A		
Aluminium	391.6	—	—	0.1	0.06	0.05	170	200
Barium	553.6	0.1	0.05	—	—	—	200	—
Beryllium	234.9	—	—	1.5*	0.3	0.15*	500	1000
Bismuth	306.8	20	2	—	—	—	1000	—
Calcium	422.7	0.05	0.002	—	—	—	2500	—
Chromium	425.4	0.08	0.007	—	—	—	1140	—
Cobalt	352.6	0.3	0.04	—	—	—	750	—
Copper	327.4	0.1	0.04	—	—	—	250	—
Iron	372.0	0.5	0.03	—	—	—	1670	—
Lead	405.8	10	0.5	—	—	—	2000	—
Magnesium	285.2	0.1	0.03	—	—	—	3330	—
Manganese	403.3	0.1	0.01	—	—	—	1000	—
Nickel	352.4	0.3	0.05	—	—	—	600	—
Niobium	405.9	—	—	20	0.5	0.3	4000	6670
Platinum	306.4	150	2	—	—	—	7500	—
Silicon	251.6	—	—	60*	10*	6*	600	1000
Strontium	460.7	0.02	0.002	—	—	—	1000	—
Thallium	477.6	0.2	0.04	—	—	—	500	—
Tin	254.6	20	1	—	—	—	2000	—
Titanium	399.8	—	—	0.7	0.23	0.20	300	350
Tungsten	400.8	—	—	10*	0.8*	0.4*	1250	2500
Zirconium	351.9	—	—	7.1	1.13	1.05	630	670

\* All the results given in these two columns were measured on a Unicam SP 900 spectrophotometer (prism).

† All the results given in these three columns were measured on a Techtron AA4 spectrophotometer ( $\frac{1}{2}$  m grating) except those marked (\*) which were measured on a Unicam SP 900.

C denotes conventional flame; N is nitrogen separated flame; A is argon separated flame.

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*Table 2.* Effect of flame separation on detection limits in atomic absorption in a 5 cm nitrous oxide-acetylene flame

<i>Element</i>	<i>Wavelength, nm</i>	<i>Conventional flame, p.p.m.</i>	<i>Nitrogen separated flame, p.p.m.</i>	<i>Improvement on separation, %</i>
Aluminium	309.3	0.24	0.1	240
Beryllium	234.9	0.006	0.003	200
Molybdenum	319.4	0.18	0.1	180
Silicon	251.6	0.45	0.24	190
Vanadium	318.5	0.14	0.04	350

*Table 3.* Effect of flame separation on detection limits in atomic fluorescence spectroscopy with air-acetylene and nitrous oxide-acetylene flames

<i>Element</i>	<i>Wavelength, nm</i>	<i>Air-acetylene, p.p.m.</i>		<i>Nitrous oxide-acetylene, p.p.m.</i>			<i>Improvement on separation, %</i>	
		<i>C</i>	<i>A</i>	<i>C</i>	<i>N</i>	<i>A</i>	<i>N</i>	<i>A</i>
Al	396.1	—	—	0.2	0.18	0.1	110	200
Cd	228.8	0.002	0.0002	—	—	—	—	1000
Mo	313.3	—	—	10.2	0.75	0.46	1340	2220
V	318.5	—	—	1.2	0.88	0.07	130	1720
Zn	213.9	0.002	0.0002	—	—	—	—	2000

C is conventional flame; N is nitrogen separation; A is argon separation.

to an increase in the density of the atomic population, as shown by the absorption measurements, there is an increase in the volume of flame gases in which the atomic emission of the analyte may be observed. We have already shown, in our previous work, that the atomic population of such elements terminates abruptly above the cyanogen zone of the flame.

*Table 4.* Atomic absorption sensitivities in long path separated air-acetylene flame

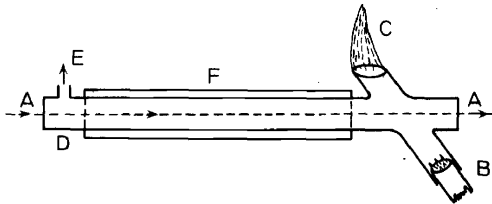
<i>Element</i>	<i>Wavelength, nm</i>	<i>Absorbance, cm<sup>-1</sup>, flame path, μg<sup>-1</sup> min<sup>-1</sup>, of sample entering flame</i>	<i>Sensitivity,* p.p.m.</i>
Ag	328.1	0.011	0.016
Cu	324.7	0.004	0.042
Fe	248.3	0.0015	0.120
Hg	253.7	0.050	0.040
Mg	285.2	0.020	0.008
Zn	213.9	0.070	0.003

\* Concentration for one per cent absorption, ignoring length of flame and solution uptake rate.

Some results obtained for measurements in separated and unseparated flames are shown in *Tables 1 to 3*. These data show that detection limits in flame photometry and atomic fluorescence are commonly improved by

2- to 10-fold, and by *ca.* 2-fold for refractory oxide forming elements in atomic absorption in a nitrous oxide–acetylene flame.

Another interesting aspect of separated flames in atomic absorption spectroscopy is their use in long tube reservoirs. In the conventional long tube devices, such as those first described by Fuwa and Vallee<sup>8</sup>, hydrogen is used as the fuel gas and aqueous sample solutions are aspirated in the usual way. Serious problems arise, however, when organic solvents are aspirated or when hydrocarbon fuels are substituted for hydrogen. The absorption background due to carbon species in these constricted flames becomes unacceptably high. If, however, an air–acetylene flame is separated by a silica shield provided with a long side arm, see diagrammatic representation in *Figure 3*, it is possible to draw the interconal gases along a 400 to 500 mm path by gentle suction and to make atomic absorption measurements in the side arm without difficulty. The use of the separated constricted flame<sup>9</sup> allows use to be made of the Lambert–Beer law in atomic absorption, thus permitting increased sensitivity of measurement for elements which have low atomization efficiencies or, more particularly, low transition probabilities.



*Figure 3.* Long tube separated flame atom reservoir for atomic absorption measurements (schematic): A Silica end windows, B Burner head showing primary cones on perforated plate of burner. This is sealed into the reservoir by an asbestos washer, C Secondary zone of flame, D 400 mm side arm, E To exhaust (gentle suction), F Split tubular furnace *ca.* 1000°C.

Some results obtained by this device are shown in *Table 4*. It should be noted that an unconventional method is used to express the increased sensitivity of these measurements.

Flame separation increases the actual sensitivity of determination in flame photometry and atomic fluorescence in most instances, but in absorption only in the nitrous oxide–acetylene flame when refractory oxide forming elements are being determined or where atmospheric oxygen causes absorption of weak resonance lines.

### ATOM RESERVOIRS OTHER THAN FLAMES

Many reservoirs, other than flames, have been described in the atomic absorption literature. These include the hollow cathode sputtering chamber, flash heating devices, variations of the King furnace, as modified by Vidale<sup>10</sup>, the laser microprobe, radio frequency plasma torch, electron beam furnace



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and the electronically heated carbon (graphite) tube device of L'vov<sup>11</sup> and Massmann<sup>12</sup>. It is beyond the scope of this brief survey to discuss these. As a generalization it may be said that the hollow cathode sputtering chamber, laser microprobe, electron beam furnace and, to a lesser extent perhaps, the radio frequency plasma torch and flash heating devices are most suited to the analysis of solid specimens. Some of these reservoirs produce very high background emissions and are, therefore, somewhat unattractive at first sight though developmental research may overcome such difficulties.

The electrically heated carbon (graphite) tube reservoirs of L'vov<sup>11</sup> and Massmann<sup>12</sup> are particularly attractive devices in the sense that they require only minute samples and produce very high atomization efficiencies. We have found several technical problems in using such tube reservoirs, e.g. variation of temperature of tubes as they are used over a period of time, difficulties due to the continuum emitted by the white hot tube, limited life-time of tubes and difficulties in preparing the tubes from graphite rods in

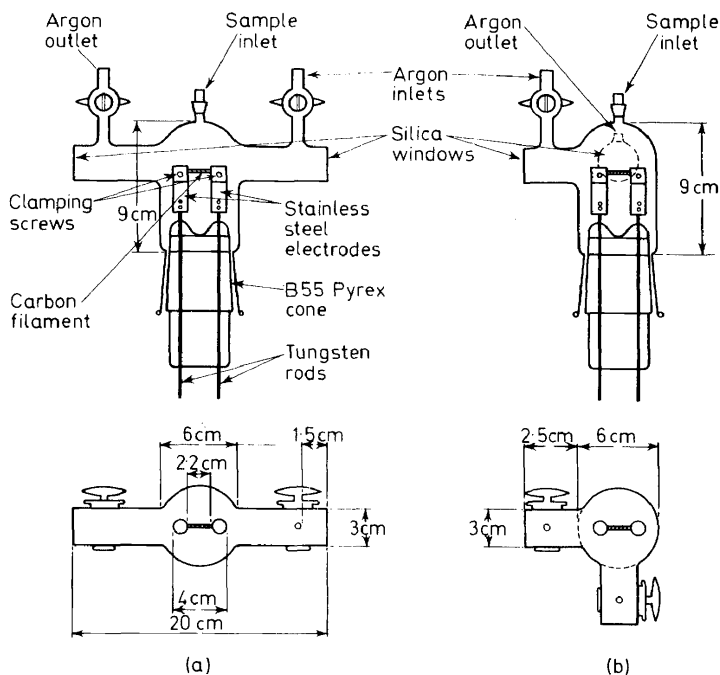


Figure 4. Filament atom reservoir: (a) FAR for atomic absorption, (b) FAR for atomic fluorescence.

a conventional machine workshop. In addition, the current/voltage requirements were rather demanding.

A rather simpler device has been constructed in this Department<sup>13</sup>. Briefly, it consists of a 1.5 to 2 mm diameter filament or rod of carbon (graphite) of ca. 40 mm length clamped between two stainless steel electrodes

mounted on tungsten rods which are sealed through a large conventional ground glass joint.

A covering glass head with linearly disposed side arms with silica end-windows is used for absorption or a right angle arrangement for fluorescence, see *Figure 4* (a) and (b). The filament atom reservoir unit is placed so that the filament occupies the space normally occupied by the primary zone of a flame on a slot burner and the space above the filament is irradiated with a line source such as a high intensity hollow cathode lamp, using the absorption or fluorescence mode of the unit as appropriate. A ( $10^{-1}$  sec f.s.d.) recorder is then set running to monitor the source signal or to receive a fluorescence signal when it is generated. Argon or nitrogen is passed through the cell at *ca.* 4 litres per minute to purge out atmospheric oxygen and provide a reproducibly dynamic atmosphere within the cell. A measured drop of solution (1 to 5  $\mu$ l) is placed on the centre of the filament and a momentary current is passed through the cell to remove the water from the sample and pass it out of the cell. The current (*ca.* 100 A at 5 to 6 V) is then switched on fully and the absorption or fluorescence signal which is obtained within two or three seconds is registered as a peak on the recorder chart. The peak height is related directly to the concentration of the test ion in the solution. In this way, we have determined silver and magnesium down to  $10^{-11}$  g in absorption and to  $10^{-13}$  and  $10^{-15}$  g in fluorescence. We have studied the effects of interferences on these ions and have shown that none of the elements that would be expected to interfere by matrix effects, e.g. Al, Th, Ti etc. in flame media, does so even at 1000-fold concentration ratio on the filament. We have, however, observed<sup>14</sup> unexpected depressive effects from Cu, Hg, Pb and Bi on Ag and from K, Ba and Sr on Mg. These depressions are currently of the order of 20 to 30 per cent in most instances. The reasons for this are not clear yet, though atomic nucleation in the gas phase above the filament is the probable cause of interference. But it does appear that in some instances it may be possible to overcome these depressions by selective volatilization of the troublesome element at a lower temperature than the test element. Compound formation is not suspected, but there does appear to be a possibility of some elemental interaction, i.e. condensation on abundant nuclei, in the gas phase. The filament itself is self-purging and shows no memory effects with the elements so far tested, i.e. either a positive (cumulative) memory effect for the element itself or a negative memory effect for the few depressive effects so far encountered. This device shows very high promise for atomic absorption, but is even more advantageous for atomic fluorescence measurements because of the complete absence of an emission background.

## ATOM LINE SOURCES

The conventional hollow cathode lamp, which was in widespread use before the introduction of the newer high-brightness hollow cathode lamp, was satisfactory for the absorptiometric determination of most atomic species in flames except possibly for As and Se where absorption from atmospheric oxygen caused problems, particularly the heated oxygen in the environment of the flame. Generally, the intensity of these sources was

insufficient to yield analytically worthwhile atomic fluorescence signals. The newer high brightness lamps are, however, in some cases usable for fluorescence excitation.

Much of the earlier work on atomic fluorescence was done using metal vapour discharge lamps of the sodium street lamp variety and these gave good sensitivity for the very limited range of elements for which they were available, except for Hg for which the source was badly self-reversed.

Continuum sources, such as the xenon arc lamp, are also useful for atomic fluorescence since most of the radiation passes through the flame unabsorbed. The narrow cross sections of radiation absorbed by atoms in the flame are then re-radiated as resonance or direct-line fluorescence etc. Since the detector does not view the source, the restrictions which apply to the use of continuum sources in absorption do not apply in fluorescence measurements. It is, of course, apparent that the energy available from a continuum source under the area of any absorption line in a flame will be much smaller than when a specific line source is used. Consequently high sensitivities are not to be expected, but the practical possibility of using a single source to excite fluorescence signals for many elements is an attractive one. The chief problem is to be aware of just how many spectroscopic interferences will be encountered. That is to say, the situation will closely parallel the problem encountered in flame photometry except that one will be relying on a much denser participating population of atoms. We have recently made an examination of this problem using a 500 W d.c. xenon arc lamp in conjunction with an integrating d.c. flame photometer with a 1 mm slit and automatic background correction<sup>15</sup>. The limitations of using an unmodulated instrument for fluorescence work are obvious, but we were more concerned with comparing the selectivity of AFS using a continuum source with flame photometry done on the same instrument than with sensitivity. For it must never be forgotten that selectivity of determination is almost invariably a more important consideration than sensitivity. This of course is why even sodium is quite frequently determined by atomic absorption although it is obviously much more sensitively determined by flame photometry. Atomic fluorescence with a line source possesses the same freedom from spectroscopic interference as atomic absorption, but this is not to be expected from the use of a continuum source which may obviously excite atomic fluorescence in all elements present in the analyte. The selectivity is, therefore, limited by the resolving power of the monochromator as in flame photometry.

*Table 5* shows some of the results obtained in air-acetylene by this study. It will be seen that the fluorescence results are in the p.p.m. range and are commonly about ten times less sensitive than flame photometry measurements made on the same instrument. This is as expected.

Generally, the spectral interference pattern in these fluorescence measurements (arising from added foreign ions) is similar to that for flame photometry on the same instrument. There are, however, some interesting differences, which generally show a selectivity advantage for fluorescence even with the continuum source.

Silver interfered in fifty-fold excess with the determination of copper at 327.40 nm (Ag 328.07 nm line) and copper similarly interfered with the determination of silver at 328.07 nm by either flame photometry or atomic

Table 5. Atomic fluorescence detection limits using a 500W continuum source. Comparison with flame photometry on the same integrating flame photometer (air-acetylene flame)

Element	Line, nm	$g_f$	AE detn† limit, p.p.m.	AF detn† limit, p.p.m.
Cu	324.75	0.64	0.25	3
Cu	327.40	0.31	0.15	2
Ag	328.07	0.53	0.20	3
Ag	338.29	0.23	0.20	4
Ga	403.30	0.24	0.20	—
Ga	417.21	0.53	0.15	—
In	410.18	0.47	0.30	20
In	451.13	0.66	0.20	15
Tl	377.57	0.22	0.25	6
Tl	535.05	0.92	0.50	20
Zn	213.86	1.30	—	10
Cd	228.80	0.92	6	10
Cd	326.11	0.0014	5	—
Ca	422.67	0.28	0.02	0.5
Mg	285.21	1.10	0.30	3
Cr	357.87	1.60	1.5	3*
Cr	359.35	1.40	2.0	
Cr	360.53	1.00	2.5	
Cr	425.43	0.54	1.5	20*
Cr	427.48	0.41	0.5	
Cr	428.97	0.26	0.4	
Mn	279.48	0.97	0.50	2.5
Mn	279.83	0.78		
Mn	280.11	0.57		
Mn	403.08	0.33	0.05	4
Mn	403.31	0.23		
Mn	403.45	0.13		
Co	350.23	2.0	1.0	—
Co	350.26	0.066		
Co	240.73	2.20		
Co	242.49	1.90	—	20
Ni	323.00	0.86		
Ni	341.48	1.00		
Ni	352.45	0.85	0.8	5
Ni	361.94	1.50	1.5	—

\* Although the resolution was sufficient to resolve these lines by thermal emission at minimum monochromator bandpass (0.15 nm) no resolution was possible at the maximum bandpass (6 nm) used for this and all other fluorescence measurements.

† Detection limit taken as the concentration at which the signal is twice the standard deviation at that concentration.

fluorescence using the continuum source. On the other hand 1000 p.p.m. of As, Bi, Ca, Cd, Co, Cr, Fe, In, K, Mn, Na,  $\text{NH}_4^+$ , Pb, Sn or Te did not interfere in the determination of 20 p.p.m. of silver by either technique at 328.07 or 338.29 nm.

No interference was encountered from 1000 p.p.m. of tin in the fluori-

metric determination of 100 p.p.m. of indium (continuum source) at 410.18 nm, but the same amounts of tin caused 32 per cent enhancement in the flame photometry of 10 p.p.m. of indium at the same wavelength due to the SnO molecular emission in the flame. 1000 p.p.m. of Co gave about 60 per cent enhancement in flame photometry and about 88 per cent in fluorescence with the continuum source.

No interference was encountered from 1000 p.p.m. of barium in the fluorimetric (continuum source) determination of 80 p.p.m. of thallium, but the analytical signal by flame photometry was increased by more than 100 per cent because of BaO emission. Iron interfered seriously in the determination of thallium by both techniques at 377.57 nm. Nickel did not interfere in the fluorimetric determination of thallium at 377.57 nm, but interfered seriously in the determination by flame photometry.

Although good fluorescence signals were obtained for zinc in the air-acetylene flame using the continuum source no thermal emission signals were obtained and so no comparison of interference could be made. The situation was reversed for gallium where no fluorescence signals were available using the continuum source, though quite sensitive results were available by flame photometry.

Nickel was found to interfere quite seriously with the fluorimetric determination of cadmium at 228.80 nm using the continuum source, but only slightly in flame photometry at 228.80 nm or 326.11 nm. The chromium line at 425.43 nm interfered with the fluorimetric determination of calcium (continuum source) at 422.67 nm, as it did also in flame photometry. In the latter instance, however, the slits could be closed down to provide sufficient resolution to eliminate the radiative interference from chromium.

On the other hand 1000 p.p.m. of iron and cobalt interfered by doubling the flame photometry signal for 20 p.p.m. of chromium at 357.87 nm, whereas neither interfered with the determination of chromium by fluorescence. The manganese lines at 279.48, 279.83 and 280.11 nm were virtually free from radiative interferences by either technique. Potassium (1000 p.p.m.) gave about 12 per cent enhancement by both techniques for determination of 20 p.p.m. of manganese at 403 nm. The same concentration of gallium yielded 60 per cent enhancement in flame photometry of 20 p.p.m. of manganese at 403.31 nm, but did not interfere in the fluorimetric determination.

The flame photometric determination of cobalt at 350.23 to 350.26 nm was subject to strong radiation interferences from nickel and manganese. No fluorescence of cobalt was detected at this wavelength using the continuum source. The same excesses of these elements did not interfere in the determination of cobalt by measurement of its resonance fluorescence at 240.73 and 242.49 nm where, unfortunately, the flame photometry signal of cobalt was too weak to permit comparison to be made.

1000 p.p.m. of cobalt completely predominated over the flame photometric determination of 20 p.p.m. of nickel at 341.48 nm, but there was no interference in fluorescence. 1000 p.p.m. of manganese gave about 50 per cent enhancement in flame photometry at 352.45 nm, but no interference was detected in fluorescence at the same wavelength. No comparison was possible for the interference of 1000 p.p.m. of iron and chromium at the nickel line at 361.94 nm, where flame photometry showed fivefold and

4.5-fold enhancements respectively, because no fluorescence signals were obtained for nickel at this wavelength.

This study of the relative interferences in flame photometry and atomic fluorescence under its most unfavourable circumstances (i.e. use of a continuum source) shows, not unexpectedly, that a similar radiative interference pattern exists, but that the molecular emission interferences which are predominant in the former technique are without effect in atomic fluorescence measurements. These results also substantiate Goodfellow's observations<sup>16</sup> that atomic fluorescence is not significantly affected by energy transfers between radiatively excited atomic species in flame media.

Unquestionably, however, the best way to excite atomic fluorescence is to use a line emitting source and moreover one which exhibits maximum emission under the area of the atomic absorption line in the flame, or whatever other atom reservoir is being used. The line in this instance need not be as narrow in profile as the source line used in atomic absorption measurements where a very narrow line must be used so that signal attenuation can be measured at or near the centre of the absorption line in the atom reservoir. A much more important feature of the ideal type of source for fluorescence is that the lines should be very intense. Broadening influences within the source or within the flame are of much less importance in fluorescence than in absorption measurements.

Nothing much need be said here of the use of vapour discharge lamps of the sodium street lamp variety. These are generally very good sources for the excitation of atomic fluorescence. The number of these lamps is unfortunately rather limited. They provide specific methods of very high sensitivity for zinc, cadmium and one or two other elements. The calibration curves are usually nearly linear over a thousand-fold concentration range as opposed to the tenfold concentration range of atomic absorption. In this respect the calibration curves are similar to those of flame photometry. Normally the upper limit of the calibration curve is about the same as for the corresponding atomic absorption determination, but the lower end is usually about one or two orders of magnitude down the concentration scale. The specificity of these methods is well established<sup>17-18</sup>; none of the sixty potential interferences examined showed any effect on the determination of cadmium or zinc, for example.

### ELECTRODELESS DISCHARGE LAMPS

Most of the pioneer work in the use of microwave excited electrodeless discharge lamps (EDL) as atomic spectral line sources for atomic fluorescence and atomic absorption measurements has been done by Winefordner and his colleagues at the University of Florida and by ourselves at the Imperial College, London. These EDL can now be made for most elements, see *Figure 5*, and sufficient data are available for a fair number of these to show that they are generally very satisfactory for both atomic fluorescence and atomic absorption measurements.

Generally, these sources are made very conveniently in the laboratory by hermetically sealing about 10 mg of the appropriate metal and 1 to 2 mg of iodine in a very well degassed silica tube under *ca.* 1-2 torr of argon or

ATOM RESERVOIRS AND LINE SOURCES FOR ATOMIC ABSORPTION

neon filler gas. When these EDL are operated at *ca.* 2450 MHz (125 mm wave) in a  $\frac{3}{4}$  or  $\frac{1}{4}$  wave tuned cavity of the type shown in *Figure 6* at a power rating of 20 to 80 W they produce line intensities which are *ca.* 100 to 1000-fold better than those of the corresponding conventional hollow cathode lamps, 10 to 100 times better than the newer high brightness lamps (narrow bore cathodes, etc.) and commonly 1 to 10 times better than the high intensity lamps of the Sullivan and Walsh variety<sup>19</sup>.

H																			He
	Be										B		N	O					Ne
Na	Mg										Al	Si	P	S	Cl				Ar
K	Ca		Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br			Kr
Rb			Zr	Nb	Mo					Pd	Ag	Cd	In	Sn	Sb	Te	I		Xe
Cs			Hf		W					Pt	Au	Hg	Tl	Pb	Bi				
					U														

	Pr	Nd																	
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Figure 5. Elements for which electrodeless discharge lamps have been prepared up to July 1969.

Generally the line to background signal ratio is very much better in EDL than in the corresponding hollow cathode lamps. In our experience their warm-up time is usually better as is their short and long term stability when they are properly operated.

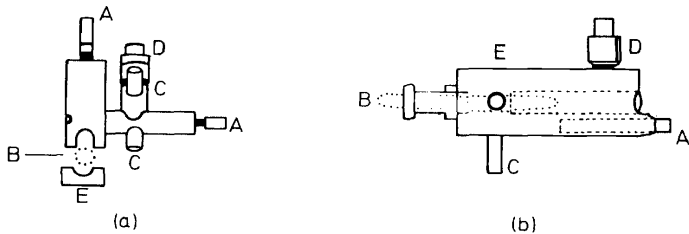


Figure 6. Microwave resonant cavities for EDL: (a) Quarter wave cavity, (b) Three-quarter wave cavity. (A) Tuning probes, (B) Position of EDL, (C) Cooling inlets or outlets, (D) Coaxial connections for generator, (E) Viewing port for EDL emission.

Some comparative data for stability, intensity, line to background ratios, warm-up time etc. are shown for a few elements in *Tables 6* and *7*. These data show that, with the exception of silver, *Table 7*, the EDL are usually considerably brighter at the resonance lines than the corresponding hollow cathode lamps (HCL). At the same time, their reproducibilities, drift rates,

Table 6. Comparison of intensities of hollow cathode lamps and electrodeless discharge lamps

Element	Wavelength, nm	HCL current,* mA	Relative intensities†	
			HCL	EDL
Tin	224.6	12	1	820
	286.3	12	220	275000
Lead	217.0	15	1	8
	283.3	15	3200	120000
Thallium	276.8	10	1	60
	377.5	10	4	380
Mercury	253.6	7	1	910
Silver	328.1	8	1	1

\* Maximum recommended operating current.

† Intensities are uncorrected for the spectral response characteristics of the instrument and are taken relative to the weakest absorption line from the hollow cathode lamp in those instances in which more than one resonance line is used for atomic absorption.

Table 7. Source characteristics of hollow cathode and electrodeless discharge lamps

Element	Wavelength, nm	Warm-up time,* min		Noise level on signal, %	
		HCL‡	EDL‡	HCL	EDL
		Tin	224.6	15	3
Lead	217.0	12	10	1	0.5
Thallium	276.8	12	10	1	1
Mercury	253.6	12	5	1	1
Silver	328.1	6	6	0.5	0.5

	Av. drift rate, %/h <sup>-1</sup>		Reproducibility of output  , %	
	HCL	EDL	HCL	EDL
	Tin	8	1	6
Lead	3	3	4	1
Thallium	3	2	5	3
Mercury	4	4	5	3
Silver	3	1	6	2

\* Time taken for recorder to reach an equilibrium value.

† Hollow cathode lamp.

‡ Electrodeless discharge lamp.

§ With no external damping on the system.

|| Reproducibility of output on re-initiation 15 min after being switched off.

noise levels etc., Table 6, are as good as, or better than, those of the corresponding hollow cathode lamps. Some similar data are shown diagrammatically in Figures 7 to 12. Figure 7, for the lead sources, shows that the intensity and purity of the EDL spectra are better than those for the HCL and that the signal to background noise ratio is very much better. Figure 8 gives some stability plots for silver sources, again showing a superior reproducibility



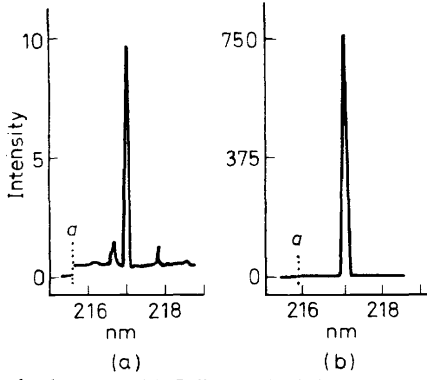


Figure 7. Emission spectra for lead sources: (a) Hollow cathode lamp, (b) Electrodeless discharge lamp; (a) Denotes opening of shutter.

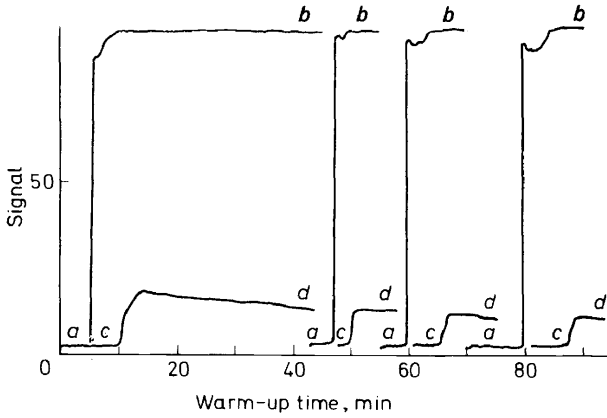


Figure 8. Comparison of stabilities, reproducibilities and output of silver line sources at 328.1 nm: (a) EDL switched on; (b) EDL switched off; (c) HCL switched on; (d) HCL switched off.

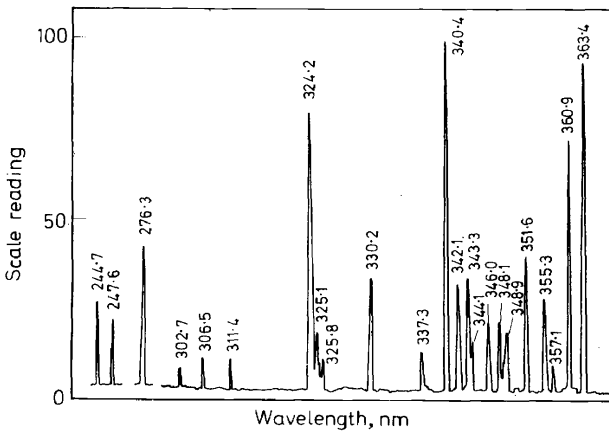


Figure 9. Complex spectra emitted by Pd EDL in quarter wave cavity at 2450 MHz and 40 W.

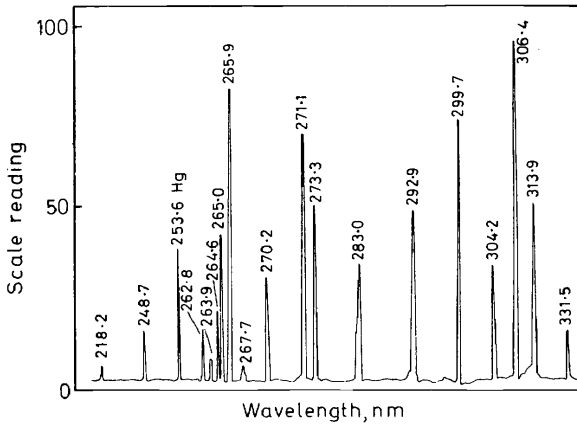


Figure 10. Complex spectra emitted by Pt EDL in quarter wave cavity at 2450 MHz and 40 W.

and stability for the EDL. Similarly, *Figures 9 to 11* show the spectra emitted by platinum and palladium EDL and illustrate their stability in operation. *Figure 12* shows the same data for a completely different type of metal—sodium. Reference to these tabular and diagrammatic data for a variety of different types of metal are generally indicative of the superiority of EDL to HCL as spectral line sources for atomic fluorescence or atomic absorption spectroscopy. The first comparative study to be made showed that considerable advantage may be gained from the use of EDL, rather than HCL for atomic absorption measurements<sup>20</sup> particularly where the line intensity from a hollow cathode lamp tends to be weak and where the resonance line is surrounded by non-resonance lines, e.g. iron, so that a wide slit has to be used and excessive curvature results from the presence of the unabsorbed lines. Here the use of the EDL source somewhat increases sensitivity and extends the range of linearity of the analytical calibration curve. Earlier

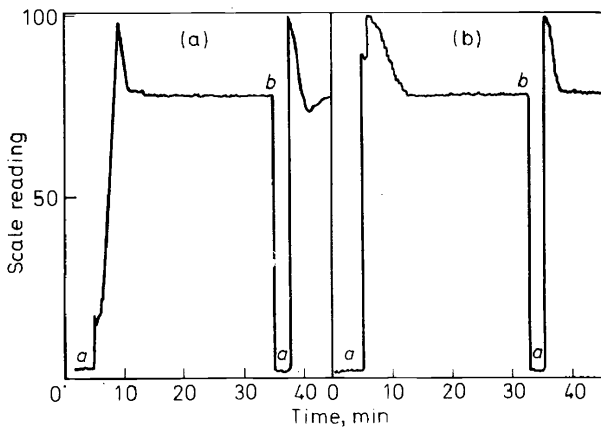


Figure 11. Warm-up times, stability and reproducibility of platinum metal EDL: (a) Pd EDL at 340.4 nm; (b) Pt EDL at 306.4 nm; (a) Power on; (b) Power off.

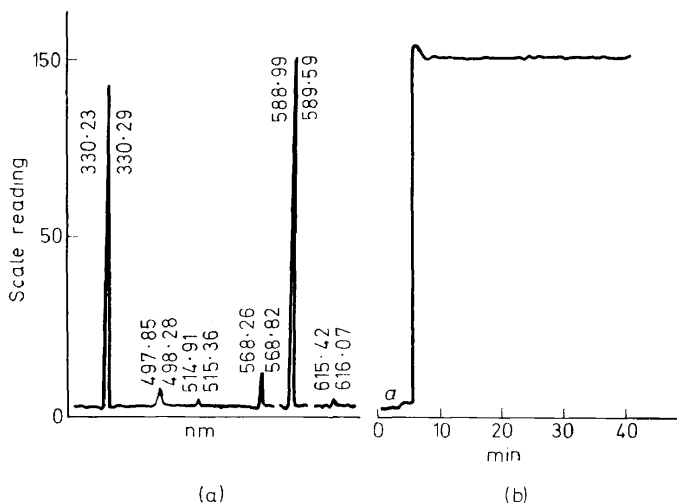


Figure 12. Emission spectra and stability plot for sodium EDL: (a) Emission spectra showing unresolved doublets measured on Unicam SP900; (b) Warm-up time and stability plot for Na EDL at 589 nm doublet line; (a) Power switched on

work has also shown that the intensity of the EDL is also particularly advantageous in the u.v. region where atmospheric oxygen causes attenuation of resonance lines, e.g. Se at  $196.1 \text{ nm}^{21}$  so that the signal from a HCL is excessively weak. Sensitivity is once again increased slightly. Additionally, on general grounds, the use of EDL rather than HCL for atomic absorption spectroscopy is advantageous in that much lower instrumental gains can be used. This produces much quieter and less noisy signals because the detector noise level arising from the d.c. radiation from the flame is minimized. This is particularly advantageous with intensely emitting flames such as fuel-rich air-acetylene or nitrous oxide-acetylene. The use of the flame separation technique, q.v., in conjunction with EDL does, of course, present maximum benefit. Slit widths may also be reduced to their minimum values when EDL are used for atomic absorption measurements. The use of EDL consequently produces better than normal detection limits ( $S:N$  ratios). Because of their high operating powers, EDL are more subject to line broadening or self-reversal than HCL. They should, therefore, be used in a lower intensity mode for AAS than they are for AFS.

It is, however, in atomic fluorescence spectroscopy that the outstanding advantage of the EDL becomes apparent, because the fluorescence signal is proportional to the source intensity whereas, within limits, the absorption signal does not reflect any proportional advantage.

### MULTI-ELEMENT ELEMENT ANALYSES VIA ELECTRODELESS DISCHARGE LAMPS

In his paper to this symposium Dr Alan Walsh developed the theme of multi-element analysis and pointed out that this is one of the areas where

flame photometry tends to be more flexible than atomic absorption spectroscopy. Our work<sup>15</sup>, pp 109 to 112 has tended to show that, even with a continuum source, atomic fluorescence spectroscopy may be a little more selective than flame photometry. The use of the continuum source permits such flexibility (scanning technique) in fluorescence, but of course the sensitivity is not nearly so good. On the whole, multi-element hollow cathode lamps for atomic absorption have, with a few notable exceptions, not been very successful largely because of preferential sputtering of certain metals which gradually tend to predominate over all the others as the multi-element HCL is used. This problem should, however, not arise in multi-element EDL because all the discharge carrying material can be maintained completely in the gas phase during the operation of the tube. We have done a considerably amount of developmental work on multi-element electrodeless discharge lamps and have found them to be easy to prepare and operate and to be generally as satisfactory as the individual element EDL<sup>22</sup>. Furthermore, we have operated them for atomic absorption and for atomic fluorescence with very satisfactory results. Provided that one selects groups of elements that have approximately the same vapour pressures, i.e. similar running conditions in an EDL and which do not have resonance lines so close together that the lines for two of the elements lie within the band-pass of the monochromator being used, there appears to be no reason why, say, five or six elements should not be grouped together in the same EDL envelope. At the present time we have prepared several dual element EDL and one tri-element EDL which operate very successfully. These multi-element EDL permit a scanning technique of atomic fluorescence for the group elements incorporated in the source. Alternatively a multi-channel, i.e. polychromator. technique. may be used with the sensitivity characteristic of a single element EDL and almost with the flexibility of atomic fluorescence with a continuum source or of flame photometry, but at the same time virtually free from the radiative interferences which may be found in these two techniques.

We have also found that these multi-element EDL have shelf lives and running lives which are at least as good as those of the single element EDL. Thus, they permit the sensitivity and specificity of atomic fluorescence spectroscopy using specific element sources with a good measure of simultaneous or scanning multi-element analyses.

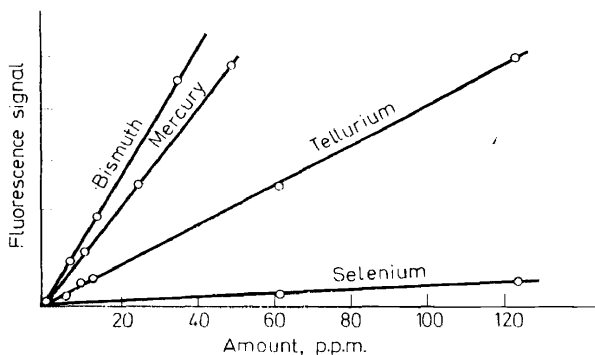
Typical groupings which we have looked at, so far, include Se-Te-Hg; In-Ga; Zn-Cd; As-Sb. The Se-Te-Hg source is fabricated from the elements plus iodine. The elements Se and Hg both function perfectly satisfactorily in the lamp in the elemental state, but Te is somewhat involatile and is best used as the iodide<sup>21</sup>. The presence of the iodine reduces the volatility of the Se (as selenium iodide) and slightly impairs the emission of the Se lines in comparison with a selenium EDL on its own. The reduction in intensity is very marginal, however, and the intensity of the Te and Hg lines is as good as in the individual EDL. All tubes containing iodides emit the 206.16 nm non-resonance iodine line. This line has sufficient coincidence with the 206.17 nm bismuth line to permit Bi to be determined by atomic absorption using the EDL or by resonance atomic fluorescence at the same wavelength or even more sensitively by direct-line fluorescence at 269.7 and 302.5 nm.

Thus the Se-Te-Hg-I source becomes an EDL for Se-Te-Hg-Bi which can be used for atomic absorption or atomic fluorescence measurements<sup>22</sup>. In our studies we used a 'Southern Analytical' A1740, integrating flame photometer for fluorescence measurements. Unfortunately, the grating of the instrument was blazed at 500 nm and we therefore, had to use second order diffraction for Se, Te, Hg and two of the bismuth lines. This was counter-balanced, to a certain extent, by using an integration period of 20 seconds under each line at a narrow slit width with automatic background correction. We found that when a solution containing Se, Te, Hg and Bi was aspirated into the air-propane flame it was possible, using the multi-element EDL, to determine each element in turn in the sample simply by adjusting the monochromator to the appropriate wavelength. No spectral (radiative) or chemical interferences were observed, see *Table 8* and *Figure 13*. The low

*Table 8.* Determination of known amounts of selenium, tellurium, mercury and bismuth in the presence of each other by atomic fluorescence using a multi-element EDL

Mercury, p.p.m.		Bismuth, p.p.m.		Tellurium, p.p.m.		Selenium, p.p.m.	
Taken	Found	Taken	Found	Taken	Found	Taken	Found
50.0	49.1	36.3	36.5	62.5	63.4	125	121
50.0	48.7	36.3	38.2	62.5	61.8	125	123
25.0	26.2	36.3	35.4	12.6	12.7	62.5	61.6
25.0	25.4	14.5	16.1	12.5	12.5	62.5	63.0
25.0	26.1	14.5	14.2	6.2	6.0		
12.5	13.0	14.5	15.0	6.2	6.3		
12.5	12.2	1.4	1.7				
5.0	5.2	1.4	1.0				
5.0	6.1	1.4	1.5				

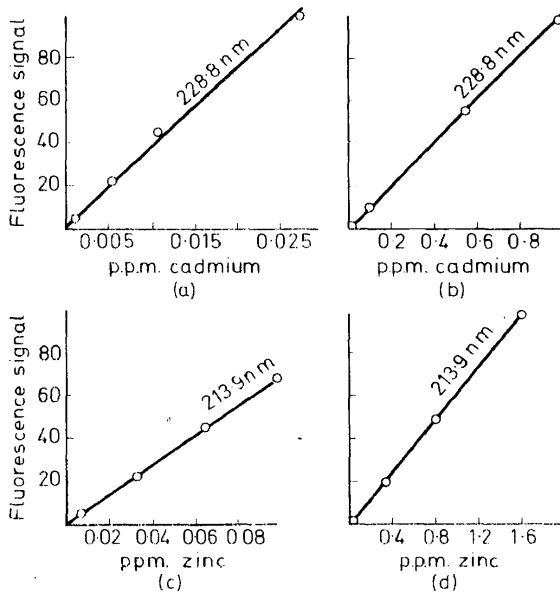
sensitivity for selenium shown in *Figure 13* arises mainly from the facts that Se has a considerably lower sensitivity in AFS (or AAS) than any of the other elements and that particularly unfavourable second order diffraction had to be used. The good sensitivity for bismuth is particularly noteworthy



*Figure 13.* Fluorescence calibration curves for bismuth, mercury, tellurium and selenium using multi-element EDL.

in view of the fact that spectral overlap excitation is being used in conjunction with direct-line emission.

The Zn–Cd lamp was prepared from the metals since both metals have appreciable vapour pressures (*ca.* 1 torr) at 400° to 450°C. Because the grating of the spectrometer used was blazed at 500 nm, second order diffraction and 20 second integration had again to be used. Once again, no spectral interference was found when the dual element EDL was used whilst spraying a solution containing both elements with the monochromator set at either of the wavelengths. The line output performance of the dual-element Zn–Cd EDL was comparable to that of individual EDL for zinc or cadmium. The Zn–Cd EDL was also compared to Wotan discharge lamps of the sodium street lamp type for Zn and Cd. It was 40 times brighter on the 228.8 nm Cd resonance line than the Wotan lamp, see *Figure 14* (a), and 10 times



*Figure 14.* Comparison of fluorescence curves for cadmium and zinc using dual element Cd/Zn EDL with those obtained using metal vapour discharge lamps: (a) Cadmium, EDL; (b) Cadmium discharge lamp; (c) Zinc, EDL; (d) Zinc, discharge lamp

brighter on the 213.9 nm Zn resonance line, (b). Even though second order diffraction was being used, the detection limit (twice the standard deviation) for Cd at 228.8 nm was  $3 \times 10^{-4}$  p.p.m. For Zn at 213.9 nm the corresponding amount was  $2 \times 10^{-3}$  p.p.m.

Indium and gallium both have rather low vapour pressures. Accordingly, these metals were used as their iodides in the EDL envelope. Because their resonance lines are well into the visible region of the spectrum, it was possible to use the A 1740 grating in first order in this instance. Once again, it was found that there was no spectral interference when a solution containing indium and gallium was aspirated into the air–propane flame whilst irradiat-

ing with the In-Ga EDL and with the monochromator set at 417.2 nm for gallium, or at 451.1 nm for indium. Since they are elements that are fairly easily excited, both gallium and indium emit quite strongly by 'thermal' excitation in the flame at the same wavelengths at which they fluoresce, see Figure 15. The A1740 instrument employed d.c. amplification and these

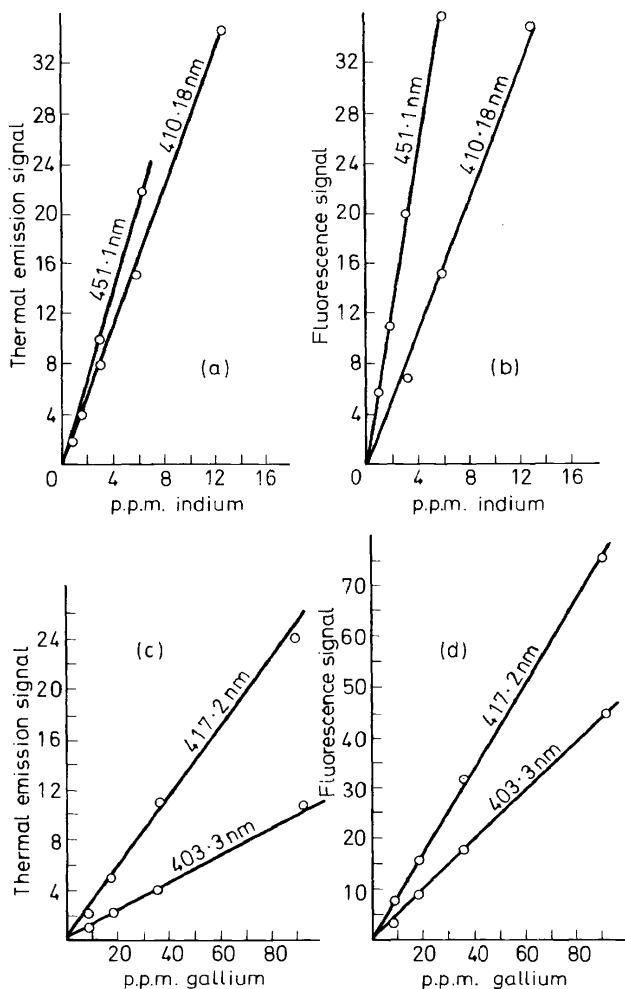


Figure 15. Comparison of flame photometry curves and atomic fluorescence curves obtained using dual In/Ga EDL: (a) Indium, flame emission; (b) Indium, atomic fluorescence; (c) Gallium, flame emission; (d) Gallium, atomic fluorescence

'thermal' emission signals were, therefore, recorded along with the fluorescence signals. To find the net fluorescence signal, the total fluorescence and 'thermal' emission signal was measured and the EDL source was cut off. The thermal emission signal was then deducted to obtain the fluorescence signal.

With a.c. amplification and a pulsed (or chopped) source only the fluorescence signal would have been recorded of course.

At 417.2 nm, gallium yielded detection limits (twice standard deviation) of 1 p.p.m. by atomic fluorescence and 4.6 p.p.m. by flame photometry. At 451.1 nm, indium gave similar detection limits of 0.2 p.p.m. by fluorescence and 0.6 p.p.m. by flame photometry. Much better detection limits could of course be obtained with better optical equipment, but the luminosity of the monochromator and the detection characteristics of the equipment were the same for both techniques. It is, therefore, interesting to note that, even at 450 nm, the fluorescence technique is here more sensitive than flame photometry. From a purely analytical point of view, it should be noted that the combined fluorescence and 'thermal' emission signals for indium (or gallium) provide twice the sensitivity of either technique alone for both these elements.

Work on the Sb-As source<sup>23</sup> is not yet completed, but it is being studied in conjunction with air-acetylene flames. Preliminary results have also included interference studies with about 30 other elements at 100-fold excess concentrations over the As or Sb content of the test solution. As before, with the other couples, there is no mutual interference between the arsenic and antimony and the only radiative interference found from the other elements is with cadmium. There is sufficient coincidence between the arsenic line at 228.81 nm and the cadmium line at 228.80 nm to permit spectral overlap excitation of cadmium fluorescence by means of the As-Sb source. Apart from this, there was no interference and once more it was shown that the use of a multi-element EDL did not introduce any *extra* radiative interference relative to the use of single element sources.

### PRACTICALITY OF ATOMIC FLUORESCENCE AS AN ANALYTICAL TECHNIQUE

Atomic fluorescence spectroscopy has at present been studied almost exclusively in academic laboratories and there appears to be an erroneous impression afoot that it is chiefly a laboratory curiosity. This is not so. It is a technique that generally offers greater sensitivity than atomic absorption and for elements which have their principal resonance lines  $\leq 320-340$  nm, it is almost always more sensitive than flame photometry.

*Selectivity* is, however, generally more important to trace analysis than sensitivity and it is this aspect that makes fluorescence such an attractive proposition for practical analyses because it combines the freedom from radiative interference of atomic absorption spectroscopy with the flexibility and sensitivity of the emission technique. Using a scanning technique (with a continuum source) or a multi-channel system (with multi-element EDL) it also permits simultaneous analyses to be performed with ease. It can be applied directly to practical analytical problems just as easily as atomic absorption. We, for example, have applied it to the direct determination of silicon in steel<sup>24</sup>, beryllium in aluminium salts<sup>25</sup> etc. and the dearth of practical applications in the literature arises largely from the fact that no atomic fluorescence spectrophotometers are yet produced commercially and because, relatively speaking, the technique is still in its infancy. There is



also little doubt that the phenomena of scatter and of quenching are two factors that cause many potential users of fluorescence techniques to hesitate. Fortunately, these reservations can easily be dispelled.

Scatter of incident radiation is highly exceptional in atomic fluorescence spectroscopy when laminar flow flames are used in conjunction with efficient nebulization. We, for example, have conducted experiments where we have aspirated 50000 p.p.m. of materials such as sodium chloride, sodium tungstate etc. into flames without detecting scatter signals. It is true, however, that a few spurious fluorescence signals have been reported in the literature which have been due to scatter signals arising from the use of total consumption burners. These latter devices tend to produce some large clotlets of such dimensions that their gasification in the flame may not be realized with refractory substances. Scatter signals can also arise in using laminar-flow flames with indirect pneumatic nebulization, but only when the matrix is very refractory and where the solids content of the test solution is high.

Quenching exists in all flames due to collisions between flame gas molecules and excited atoms, but is a constant factor for a given flame. Experiments which have been done indicate that when an air-based flame is replaced by an (oxygen-argon) flame, sensitivities can be increased by a factor of *ca.* 2-4-fold due to the replacement of diatomic nitrogen molecules by monatomic argon. Such quenching effects would of course be virtually absent in devices such as the filament atom reservoir<sup>13</sup> or the Massmann cuvette<sup>12</sup>. Gaydon has remarked<sup>26</sup> that the number of collisions undergone by a typical molecule in its passage through an ordinary flame burning at atmospheric pressure is *ca.* 10-1000. This is not a very great number when all things are considered and suggests that the quantum efficiency of most atomic fluorescence processes should be fairly high. However, the really significant question relative to quenching is to ask whether the presence of other elements in the analyte causes quenching of fluorescence. During our four years work in fluorescence in this laboratory we have not yet encountered any instance of inter-element or matrix quenching. This does not mean that inter-element quenching (i.e. energy transfers from radiatively excited metal atoms to other metal atoms simultaneously introduced into the flame) does not exist, but rather that it must be a relatively rare phenomenon.

Thus neither scatter nor quenching is to be regarded as a normal or even hazardous eventuality in applying atomic fluorescence spectroscopy to everyday analytical problems. A much more significant factor is the choice of atom reservoir for atomic fluorescence measurements. The tendency for researchers to use relatively cool diffusion flames or air-hydrogen flames wherever possible is understandable because such flames tend to have very low backgrounds and consequently yield very attractive detection limits where the test element is sufficiently well atomized by the energy available in the flame.

But the detection limit is a rather deceptive butterfly which should be chased warily. Chemistry, and in particular analytical chemistry, is a *practical* science based on quantification. Practical analytical samples almost invariably contain matrix substances other than the trace element being studied. If a trace element is to be found in the presence of a matrix compound, it is also important that a flame be chosen which has sufficient energy not

only to atomize the test element but also to (at least) gasify and, preferably, atomize the matrix salts. Otherwise the test element may not be released because of chemical or physical binding in the matrix salts. Thus flames which are sufficiently hot or reducing in their nature must also be explored for atomic fluorescence spectroscopy, e.g. air-acetylene, nitrous oxide-acetylene, even if they offer less favourable detection limits than quieter flames. It has sometimes been found in atomic absorption work in the past that the flame should be chosen to suit atomization of the matrix elements rather than of the test element. For example, in determining traces of cobalt in an aluminium matrix we have found that although cobalt is most sensitively determined in an (ordinary) air-propane flame it is more sensitively determined in the presence of aluminium salts by using a (reducing) fuel-rich nitrous oxide-acetylene flame in which pure cobalt solutions yield a much inferior detection limit<sup>27</sup>. Separation of such flames considerably reduces their background emissions and enhances their atomizing efficiency for those elements that form refractory oxides.

## CONCLUSIONS

It is apparent that atomic absorption will continue to be used for many years to come as a trace technique *par excellence* and that flames will continue to be used as atom reservoirs because of their convenience and their generally satisfactory nature for most elements.

Nevertheless, atomic fluorescence offers higher sensitivity along with the same freedom from radiative inter-element effects. The introduction of continuum source atomic fluorescence offers a scanning technique of lower sensitivity and which, of course, is more prone to interference (though apparently somewhat less so than flame photometry) but not requiring individual sources. Multi-element EDL offer the possibilities of multi-element atomic fluorescence or atomic absorption spectroscopy whilst the introduction of a simple compact, inexpensive graphite static atom reservoir device such as the filament atom reservoir permits higher sensitivity by avoiding dilution of the atomic population, by using the entire sample and probably by being more efficient than flames in producing atoms in some instances. High intensity hollow cathode lamps of the Sullivan and Walsh type also offer very intense atomic line sources, but electrodeless discharge lamps appear to be considerably more intense and can now be made for a great number of elements. The possibility of pulsing or lasing these electrodeless discharge lamps offers enormous possibilities for the future of atomic spectroscopy and for many other avenues of scientific research.

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### APPENDIX

During the final open meeting which was held at the close of the symposium one or two speakers suggested that atomic absorption was generally inferior to flame photometry, but that atomic fluorescence might possibly be more sensitive for a few elements (by inference a very few) whose resonance lines lay in the u.v. region below *ca.* 320 nm. I disagree with these remarks and with the inference that sensitivity is the prime consideration of trace analysis. I would, however, like to draw attention to the fact that, of the 66 elements

Table 9. Resonance wavelengths for atomic absorption spectroscopy and flame photometry

Element	Absorption* line, nm	Emission† line, nm	Element	Absorption* line	Emission† line
Al	309.27	396.15	Ni	232.00	341.8§
Sb	217.58	231.15	Nb	334.91	405.89
As	193.70	—	Os	290.90	—
Ba	553.55	553.55	Pd	247.64	363.5
Be	234.86	234.86	Pt	265.95	265.95§
Bi	223.06	223.06	K	766.49	766.49
B	249.77	—	Re	346.05	346.05
Cd	228.80	228.80	Rh	343.49	343.49
Cs	852.11	852.11	Rb	780.02	780.02
Ca	422.67	422.67	Ru	349.89	372.75
Cr	357.87	425.43	Sc	391.18	402.04§
Co	240.73	341.25	Se	196.03	—
Cu	324.75	324.75	Si	251.61	251.61
Ga	287.42	417.21	Ag	328.07	338.29
Ge	265.16	265.16	Na	589.00	589.00
Au	242.30	267.60	Sr	460.73	460.73
Hf	307.29	—	Ta	271.47	—
In	303.94	451.13	Te	214.28	—
Ir	263.97	—	Tl	276.79	377.57
Fe	248.33	371.99	Sn	224.61	235.48
La‡	550.13	579.13	Ti	364.27	399.86§
Pb	217.00	405.8	W	255.14	400.88§
Li	670.78	670.78	U	358.49	—
Mg	285.21	285.21	V	318.40	437.92§
Mn	279.48	403.1	Yt	410.24	407.74
Hg	253.65	253.65	Zn	213.86	213.86
Mo	313.26	379.82§	Zr	360.12	360.12§

\* Data from Varian-Techtron Chart.

† Data from R. Herrmann and C. Th. J. Alkemade, *Chemical Analysis by Flame Photometry*. Interscience: New York (1963).

‡ Other 12 lanthanides  $\lambda > 335.96$  nm in absorption.

|| Data from E. Dean, *Flame Photometry*. McGraw-Hill: New York (1960).

§ Data from E. E. Pickett and S. R. Koirtiyohann, *Spectrochim. Acta*, **23B**, 235 (1968).

listed in Table 9; 34 have their *resonance* lines below 320 nm and would by this argument be more sensitive by atomic fluorescence than by flame photometry, i.e. 50 per cent of the elements. The eight alkali and alkaline earth elements plus 13 lanthanides together with 17 others (38 in all) have their most sensitive *emission* wavelengths at values greater than 320 nm. Even at the present time, however, we know that several of the elements, e.g. Ag at 328/338 nm<sup>29</sup> are more sensitively determined by atomic fluorescence than by flame photometry. Examples are even to be found in the present paper, e.g. gallium at 417.2 nm and indium at 451.1 nm where fluorescence is found, even at 450 nm, to be more sensitive than flame photometry<sup>22</sup>. Furthermore, the phenomenon of stepwise and direct line fluorescence permits atoms to absorb energy from radiative sources at very energetic (short) wavelengths and re-emit longer wavelength radiation where detectors are more sensitive in their response. The fluorescence technique is not tied to the energy of the flame to achieve its sensitivity, but rather to the energy which may be pumped into an excitation source external to the flame. Improvements in microwave cavity design will undoubtedly improve source brightness and stability and, as already mentioned, pulsing or lasing of EDL may well cause spectacular improvements in fluorescence capability.

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