

THE DETERMINATION OF VERY SMALL AMOUNTS OF MATERIALS BY THE TECHNIQUES OF ATOMIC-ABSORPTION AND ATOMIC-FLUORESCENCE SPECTROSCOPY

T. S. WEST

*Chemistry Department, Imperial College of Science and Technology
(University of London), S. Kensington, London, S.W.7, UK*

ABSTRACT

The dual roles of microanalysis and trace analysis are assessed. The former is generally concerned with the analysis of very small samples for major constituents and the latter with the determination of very minor constituents in samples of normal (or macro) size. This contribution describes a technique of ultramicrotrace analysis in which both principles are combined. Trace constituents are analysed in samples of ultramicro proportions *viz* 1 μ l. A flameless technique of atomic absorption and atomic fluorescence is evolved which allows amounts of some elements to be detected down to 10^{-15} g and to be determined with a precision of 2–3% at 10^{-14} g levels. The samples are evaporated on a resistively heated carbon (graphite) rod and the temperature is then swept up to *ca.* 2600°C by increasing the voltage to *ca.* 12 V. This produces a transient cloud of atoms which are studied by a fast response detection system for atomic absorption or fluorescence signals.

The technique is absolutely specific for each element and allows most elements to be determined with a sensitivity far surpassing that of x-ray fluorescence and challenging and sometimes even surpassing neutron activation analysis, mass spectrometry and electron probe microanalysis using apparatus at a fraction of the cost and generally available, with only slight modification, in almost every inorganic trace analysis laboratory.

INTRODUCTION

The techniques of atomic spectroscopy, e.g. Emission Spectrography and Flame Photometry, have long been regarded by the analytical chemist as belonging to the domain of trace analysis rather than microanalysis. Since the subject matter of this paper is concerned with the application of two of these techniques of atomic spectroscopy to what may more accurately be called 'microanalysis' it is necessary first of all to say a few words about the relationship of trace analysis to microanalysis.

The technique of microanalysis sprang from the pioneer work of two famous Austrian microchemists—Pregl and Emich. Pregl on the organic side was concerned with analysis of small samples of organic compounds for their elemental composition—C, N, O, P, S, etc. This elemental composition was required with a precision of ± 0.2 per cent absolute, i.e. if a compound

contained 50 per cent carbon it was necessary to obtain an answer within 50.2 per cent. Classical microanalysis, therefore, arose from the need to analyse less precise answer was required for hydrogen, e.g. ± 0.2 per cent absolute on a content of, say, 5 per cent hydrogen, i.e. the answer could be 5.2 per cent or 4.8 per cent. Classical microanalysis, therefore, arose from the need to analyse *small* samples with a fair degree of accuracy in some instances, e.g. carbon, and a moderate degree of accuracy in others, e.g. hydrogen. Summarizing, therefore the emphasis in microanalysis has been on small sample size and obtaining as accurate an answer as circumstances permitted in the determination of a major elemental constituent or component. Emich developed the inorganic side of microanalysis and, like Pregl, made use of classical methods of analysis with extremely ingenious miniaturization of apparatus.

Since that time, of course, the techniques of ultramicroanalysis have been developed by others. Here it is not too easy to single out names for special mention, but the work of Alimarin, Belcher, Kirk and Kirsten does perhaps deserve special notice, as does that of another Austrian microchemist, Weisz. The ultramicrochemists have reduced sample sizes to ca. $5\mu\text{g}$ and the same disederata of accuracy apply as in microchemistry.

Trace analysis on the other hand arose from the need to study and account for the influence of impurities or deliberate additions of small amounts of substances on the properties or behaviour of materials. The levels of contamination (or addition) are not clearly defined, but may be considered to lie in the range ≤ 100 ppm, i.e. ≤ 0.01 per cent, although nowadays it is much more common to be concerned with ≤ 1 ppm, i.e. $\leq 10^{-4}$ per cent.

Now the emphasis in trace analysis is commonly not on the size of the sample that is to be analysed, but on the amount of compound or element that is finally being determined or, perhaps most important of all, on its dilution by the sample matrix. In most cases enough material is available to permit 1 gram or more of sample to be used. The principal concern of the trace analyst is to avoid interference by the matrix elements or compounds in the final determination of the constituent which is required. In many cases it is sufficient to know that a harmful trace is less than x ppm or that a beneficial trace constituent lies within the range (say) 1 to 1.5 ppm. On the whole, therefore, the emphasis in trace analysis is much more on the dilution of the constituent and the accuracy of analysis is less important.

In the vast majority of instances, trace analysis involves the use of separation-preconcentration techniques to isolate the component to be determined from other components which might interfere in the final analytical operation and to present the constituent in a sufficiently concentrated form to give an acceptable analytical signal. Almost invariably physicochemical techniques are used rather than classical analytical procedures. In the past, and probably still at the present time, relatively inexpensive and instrumentally simple spectroscopic techniques such as absorption spectrophotometry, or electrochemical techniques such as polarography, have been used almost exclusively. Now, however, more complicated and expensive techniques such as activation analysis (which does not require ca. 100 per cent efficiency in separation procedures) or techniques which require minimal sample handling (e.g. dissolution of sample) such as x-ray fluorescence, electron microprobe analysis, mass-spectrometry, etc. are being increasingly employed in large laboratories.

ATOMIC-ABSORPTION AND ATOMIC-FLUORESCENCE SPECTROSCOPY

Summarizing, therefore, microanalysis is concerned with *small* samples and *major* constituent analysis to a reasonable degree of accuracy and generally there is relatively little need for the application of separation-preconcentration procedures. Trace analysis is not concerned with major, but with *minor* components and with the extent and nature of the dilution of the sought constituent by the matrix in which it is to be found. The sample size is not normally important nor, within limits, is the accuracy with which the determination can be effected. The application of separation-preconcentration procedures is usually a major consideration, however, because of the dilution of the constituent and the chemical complexity of the problem.

In this communication, the author is concerned with the evolution of a technique which can be applied generally for the elemental analysis of ultra-micro samples in the range 10^{-12} to 10^{-15} g, i.e. a technique of *Ultramicrotrace Analysis*.

The techniques of atomic-absorption and atomic-fluorescence spectroscopy were selected for this purpose because they provide virtual specificity of determination and because they can be adapted to the analysis of very small samples as will be shown subsequently in this contribution.

ATOMIC-ABSORPTION AND ATOMIC-FLUORESCENCE SPECTROSCOPY

It is well known that absorption measurements of molecular species in solution are normally made in dilute solutions where the molecules exist chiefly in a free solvated state. When more concentrated solutions are used the linear relationship that exists between absorbance signals and the analytical concentration of the absorbing species as expressed by the Lambert–Beer Law breaks down because of molecular association phenomena, etc. A similar state of affairs exists for molecular fluorescence measurements. Similarly, measurements of absorption or fluorescence of atomic species can only be made with any degree of success under conditions where atoms exist in a free ‘uncondensed’ state. The traditional way of obtaining populations of free atoms is to nebulize a solution containing the sample and pass it into a flame on the support gas. There the heat of the flame, see *Figure 1*, evaporates the small droplets of the solution to small solid particles and these are subsequently caused to dissociate into free atomic species.

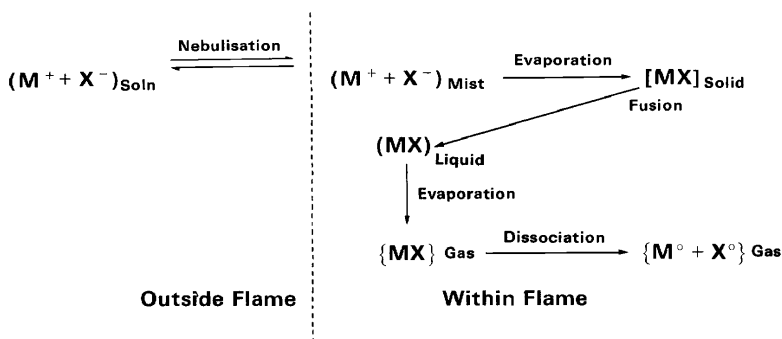


Figure 1. Production of atoms from solutions nebulized into flames.

Measurements of atomic absorption or fluorescence are made by means of a suitable light source which is caused to irradiate the atoms during their transient life and passage through the flame. The limited lifetime of the free atomic species is of little concern as long as a steady state flame is available to generate them continuously and reproducibly in the flame whilst the nebulized solution mist is being fed continuously and reproducibly into the flame.

Because of their complex electronic structures, molecules in solution or in the gas phase show only broad, and generally, featureless absorption or fluorescence bands. These bands normally cover a spectral range of several hundred nanometres. Consequently with only the UV/visible range of ca. 200–800 nm available for absorption measurements, spectral overlap is a serious limitation to the determination of a single molecular species in the presence of several others. A similar state of affairs holds for molecular fluorescence measurements except that fluorescence phenomena are less frequent in occurrence and consequently there are greater possibilities for selective measurement by the fluorescence technique.

Atomic spectra, on the other hand, are much less subject to broadening influences and lines rather than bands are observed.

Each line has a natural width due to the finite lifetime of the atomic species itself, ca. 10^{-8} sec, and consequent application of Heisenberg's principle. There are no broadening influences due to vibration and rotation in chemical bonds as in molecular species, but a degree of line broadening does occur due to the motion of the atom relative to the detector (Doppler broadening, accounting for most of the line width) and to collisions with atomic species of the same kind (Holtsmark broadening) or with other atoms or molecules, etc. (Lorentz broadening). However, even taking these three main broadening influences into account and one or two others which do not normally have much effect in analytical spectroscopy the average half-width of an atomic absorption line is only ca. 0.002 nm. As a result of this extremely narrow absorption profile, overlap of atomic absorption lines is very rare indeed and measurements of atomic absorption phenomena, therefore, present the unique possibility of specific elemental determination yet discovered.

In 1953, Walsh¹ first demonstrated the possibility of making laboratory measurements of atomic absorption in flames by using the cathode glow from a hollow cathode lamp as the source of primary radiation. Because of the minimization of Doppler broadening, Stark broadening, collisional broadening and self-absorption, the lines emitted by a hollow cathode have a much narrower spectral profile than the spectral absorption profile of the atoms in the flame. Each cathode emits atomic lines characteristic of its own species only, plus a small amount of continuum or lines from the filler gas in the cathode lamp envelope. Virtually the only attenuation of the atomic signals from the hollow cathode lamp which can be observed upon passage of the radiation through the flame comes from the atomic species in the flame which are the same as that of the cathode metal*. Consequently, atomic absorption measurements made with a hollow cathode lamp or with a line source emitting lines of similar half-width provides the most delicate lock and key mechanism yet made available for specific analysis. The apparatus is shown schematically in *Figure 2*.

The relationship which exists between the atomic absorption signal A and the

* In this it is assumed that the spectrometer is zeroed on the flame plasma absorption.

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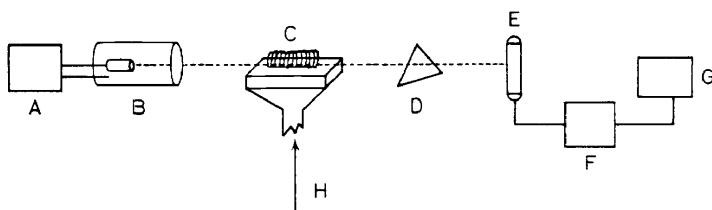


Figure 2. Schematic outline of apparatus used for measuring atomic absorption in flame media.

- A Stabilized (modulated) power supply
- B Hollow cathode lamp
- C Laminar (premixed) flame
- D Monochromator
- E Photomultiplier
- F A.C. amplifier
- G Readout
- H Fuel gas and support gas carrying nebulized solution.

analytical concentration C of the measured element in the test solution may be conveniently expressed by analogy with the simple Lambert–Beer relationship in conventional (molecular) absorptiometry via

$$A = \log I_0/I = \epsilon_A \cdot l \cdot C \cdot \alpha$$

where I_0 and I represent the intensities of the selected resonance line from the hollow cathode glow before and after entry to the atomic population in the flame, ϵ_A represents an atomic absorptivity coefficient corresponding to the probability of absorption taking place for that particular line and species, l represents the absorption path length through the atomic population and α represents a conversion factor which includes the efficiency of nebulization and the efficiency of atomization within the flame gases.

Each atomic species–resonance line pair has a limited possibility to undergo photon capture and consequently atomic absorption measurements have a limited sensitivity for determination, i.e. value of ϵ_A . The path length l can be increased by constricting the flame gases within a narrow tube but this has only a limited success because of the absorption background of the flame gases, etc. Similarly there is little to be gained by increasing I_0 since the effect is ratioed out by I . α can only be increased to a limited extent by using more efficient nebulization or by use of a more efficiently atomizing flame.

Atomic absorption spectroscopy is, therefore, not as sensitive a technique as many people believe it to be. It is capable of determining parts per million of most metals in solution and in many cases fractions of a part per million with a precision of ± 2 –5 per cent. Its chief merits lie in its simplicity of apparatus and ease of application, its range of analysis, see *Table 1*, and its virtual specificity.

Every atom that absorbs radiation should be capable of emitting fluorescence. Indeed, the re-emission of radiation in this way can be regarded as the normal de-excitation process for atomic species in a flame since apart from collisional de-activation, there is no other process akin to the vibrational rotational shedding mechanism which prevails in molecular species. Gaydon² has calculated that the average number of potentially quenching collisions undergone by a typical molecular species in its passage through a flame burning at atmospheric pressure is only of the order of 10–1000. This is a very small number and it is to be expected that an atom would suffer fewer collisions than a molecule.

Table 1. Elements determined by atomic absorption

	Li	Be																	
	Na	Mg																	
	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se			
	Rb	Sr	Y	Zr	Nb	Mo		Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te			
	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi				
				Th	Pa	U													
				Ce	Pr	Nd		Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		

ATOMIC-ABSORPTION AND ATOMIC-FLUORESCENCE SPECTROSCOPY

To excite atomic fluorescence it is not necessary to use an atomic line source. The atoms in the flame gases will absorb only those quanta from the source which correspond to their own atomic absorption profiles. The rest of the radiation will pass unabsorbed through the flame. In fluorescence measurements, see *Figure 3*, the detector does not 'view' the source but merely the atoms which are caused to fluoresce in the flame. Quite sensitive analysis can be

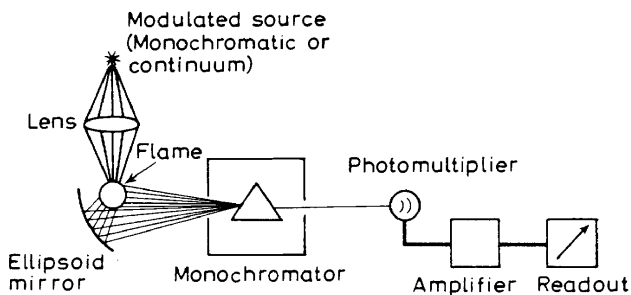


Figure 3. Schematic outline of apparatus used for measuring Atomic fluorescence in flame media.

obtained in this way by means of fluorescence measurements with continuum source excitation, see *Table 2*, but it is of course possible to promote simultaneous fluorescence from several elements and if the emitted lines of the other elements lie within the bandpass of the monochromator at the selected wavelength, specific analysis will not be possible. Yet again, the energy which is emitted by a continuum source is spread throughout the spectrum and the amount which is available within the absorption profile of an atom in a flame is therefore correspondingly small. As a result the sensitivity of determination by atomic fluorescence measurements with a continuum source is not very great though most elements can be determined with a sensitivity approaching that of atomic absorption measurements using individual hollow cathode lamps for each element.

When an intense atomic line source is used, however, such as a Sullivan and Walsh³ high intensity hollow cathode lamp^{4, 5, 6, 7} or a microwave excited electrodeless discharge lamp⁸, almost all the energy from the lamp is supplied in the atomic lines where it is most beneficial. Consequently some very highly sensitive determinations can be achieved. Solutions containing only nanograms per ml can be determined in this way^{4, 5}.

The basic relationship between the analytical signal F in atomic fluorescence spectroscopy and the analytical concentration of the species to be determined in the test solution may be expressed by analogy to the absorption equation as

$$F = Q \cdot I_0 \cdot \epsilon_A \cdot l \cdot C \cdot \alpha \cdot \rho$$

Where Q denotes the quantum efficiency of the fluorescence mechanism, ρ is a geometric factor which denotes the fraction of the emitted radiation which can be accepted by the detector and the other symbols have the same meaning as in the previous (absorption) equation.

In this instance, it will be seen that the analytical signal is proportional to the

Table 2. Detection limits in atomic fluorescence spectroscopy with a 500 watt xenon arc continuum source.

Element	Line (nm)	gf	AF detn.* limit (ppm)	Energy levels	
				Lower (eV)	Upper (eV)
Cu	324.75	0.64	3	0	3.817
Cu	327.40	0.31	2	0	3.786
Ag	328.07	0.53	3	0	3.778
Ag	338.29	0.23	4	0	3.664
In	410.18	0.47	20	0	3.022
In	451.13	0.66	15	0.274	3.022
Tl	377.57	0.22	6	0	3.283
Tl	535.05	0.92	20	0.966	3.283
Zn	213.86	1.30	10	0	5.795
Cd	228.80	0.92	10	0	5.417
Ca	422.67	0.28	0.5	0	2.932
Mg	285.21	1.10	3	0	4.346
Cr	357.87	1.60	3*	0	3.463
Cr	359.35	1.40		0	3.449
Cr	360.53	1.00		0	3.438
Cr	425.43	0.54	20*	0	2.913
Cr	427.48	0.41		0	2.899
Cr	428.97	0.26		0	2.889
Mn	279.48	0.97		0	4.433
Mn	279.83	0.78		2.5	0
Mn	280.11	0.57	4	0	4.423
Mn	403.08	0.33		0	3.075
Mn	403.31	0.23		0	3.073
Mn	403.45	0.13		0	3.072
Co	240.73	2.20		0	5.149
Co	242.49	1.90	20	0	5.111
Ni	232.00	0.86	8	0	5.342
Ni	341.48	1.00	5	0.025	3.655
Ni	352.45	0.85	5	0.025	3.542

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

line intensity of the source and that the sensitivity of determination will therefore be enhanced by using as intense a source as possible. The gain of the electronic system can also be increased to increase the sensitivity of measurement within the limits imposed by electronic noise. Again, efficient light collection ρ and the use of wide slits, etc. may be very beneficial. Taking these factors into account it will be seen that inherently atomic-fluorescence should be considerably more sensitive than atomic-absorption measurements. This is almost invariably found to be so.

We have as yet found no evidence of interelement quenching in atomic fluorescence signals measured in flames, i.e. a specific reduction of fluorescence sensitivity caused by the presence of other elements in the test solution. Where reductions of signal have been observed, they are invariably shown to be due to reduction in the atomic population, as revealed also by absorption measurements, and not due to quenching. Partial quenching does of course occur from the flame gases, but this is a constant factor in any given steady-state flame, and it may be almost entirely avoided by using non-flame cells.

Atomic fluorescence with an atomic line source has the same precise lock

and key mechanism as atomic absorption spectroscopy and it is, therefore, virtually specific in its application to elemental analysis as is atomic absorption spectroscopy but in general the sensitivity of determination is usually at least ten times higher. Spectral line sources can of course be run at much higher powers for atomic fluorescence measurements since a fair degree of line-broadening can be tolerated because measurements are effectively integrated over the whole profile of the absorption line in the flame.

Much remains to be done on the evolution of high intensity spectral line sources such as the microwave excited electrodeless discharge lamp and on detector systems for fluorescence signals, but the present position shows very favourable prospects. Flame photometry is particularly sensitive for those elements with atomic lines in the visible region of the spectrum, e.g. the alkali metals and the alkaline earths and it is doubtful if even fluorescence measurements will achieve the sensitivity of flame photometry for such elements. Where both atomic absorption and fluorescence offer most advantage is, however in the author's experience, the considerably greater freedom from interelement effects and the ease with which they may be applied by relatively unskilled staff.

SAMPLE SIZE AND ATOMIC SPECTROSCOPY

Most experiments in atomic spectroscopy involve making up sample solutions to a volume of 50 or 100 cm³, although smaller volumes are occasionally used. The smallest volume that can conveniently be analysed in the standard types of apparatus currently available is ca. 2 cm³. This provides just sufficient sample mist to flush out and precondition the walls of the nebuliser chamber, and the pipework that leads the mist into the flame and to provide a reasonable trace on a recorder. At the 1 ppm level this means that an amount of constituent must be available corresponding to 2 µg or at the 0.1 ppm level, 0.2 µg and so on.

Flames have been used as atom reservoirs for metal ions in solution without introducing the sample mist on the support gas of the premixed gases. White⁹, for example, takes up a sample of a few microlitres on a platinum wire loop and introduces it mechanically through the side of a premixed air-acetylene flame. The solution boils off and the solid dissociates quickly. The atomic vapours are retained within a nickel tube in the flame momentarily to allow a measurable absorption signal to be obtained. In this way a reproducibility of ± 5 per cent was obtained on certain elements and limits of detection of 10⁻⁹ g and 10⁻¹⁰ g were found respectively for lead and cadmium. Danielson and Ulfendahl¹⁰ have used an integrating technique to overcome the problem of variable sample release from a similar device.

Another device uses a platinum or tantalum boat to hold the solid or liquid specimen. This is again introduced horizontally through the wall of the flame and absorption measurements are made in the conventional way. Both these methods are very successful for the relatively volatile elements but there are serious problems of thermal capacity for most other elements particularly with the boat technique.

In addition, the flame is not an ideal medium for producing populations of free atoms of many elements particularly those which form refractory oxides. This arises because of the presence of oxygen in the burning flame medium. The nitrous oxide-acetylene flame¹¹ which is strongly reducing in nature was a

notable advance as was the introduction of the separated flame technique which cuts out the entry of atmospheric oxygen into the important interconal region of the flame¹². Both these developments and their combination¹³ considerably increase the sensitivity with which these elements may be determined by either fluorescence, absorption or emission, but does not provide any great advance in the possibility of determining very small samples.

Finally, although the band and continuum emission signals produced by burning flames are considerably reduced by flame separation¹², the emissions are received by the detector. They do not appear as a recorded signal because of source modulation and the use of suitably tuned amplifiers but they still constitute a measurable noise level on the analytical signal in absorption and fluorescence measurements.

For all of these reasons, but particularly from the point of view of being able to handle very small samples the use of non-flame cells is particularly important for the development of ultramicrotrace analysis.

NON FLAME CELL METHODS IN ATOMIC SPECTROSCOPY

1. The Hollow Cathode Sputtering Chamber

Gatehouse and Walsh¹⁴ have described the use of a hollow cathode sputtering chamber as a means of producing atomic populations for absorption measurements. The method is well suited to the analysis of metallic alloy specimens where a reasonable amount of alloy is available for preparation of a suitable cathode. The sample is drilled out as an open-ended cylinder and is used as the cathode in a demountable hollow cathode lamp device. When a discharge is struck in the lamp, excited filler gas cations, e.g. Ar^+ , are produced. These are accelerated towards the cathode and upon striking it, they sputter metal atoms from the inner surface of the cathode. The atoms thus produced within the cavity of the cylindrical cathode cause attenuation of the signal from a conventional hollow cathode lamp which has its radiation directed down the axis of the cylindrical specimen onto the entrance slit of a conventional atomic absorption arrangement.

This type of atomiser is not well suited to ultramicrotrace analysis as it stands, but Goleb and Brody¹⁵ have suggested modifications whereby solutions may be handled by evaporating them on the surface of a suitable open-ended cylindrical cathode. This modification shows considerable promise for the handling of ultramicro-sized samples. It tends to be somewhat unwieldy and slow in use because of the need to establish a vacuum after the addition of each sample.

2. Flash Chamber Reservoir

Nelson and Kuebler¹⁶ described a flash chamber device which also shows promise for the analysis of small specimens. Basically their device consists of a silica tube chamber fitted with end windows and situated within the coils of a xenon flash tube. Arrangements are made to purge the chamber with an inert gas such as argon. Mounted within the chamber of the cell is a flat strip of silica or carbon on which the sample to be analysed is situated. The light beam from a hollow cathode lamp is directed through the windows of the cell in the area immediately above the specimen holder and the selected resonance line is

monitored by means of a conventional detector set-up. The sample is vaporized by an intense 10 KW/cm^2 flash from the capacitor discharge lamp around the cell and the signal attenuation from the hollow cathode lamp is measured as usual.

This device is very attractive for the handling of ultramicro samples and it is somewhat surprising to find that it does not appear to have been applied by other workers to such problems. In theory, at least, it should be more rapid in use than the sputtering chamber device though it is possible that problems might exist with the evaporation of small samples of involatile compounds.

Vidale¹⁷ has described a closely similar form of the King furnace, but he used an evacuated chamber previously purged by an inert gas such as argon and the whole device was heated by a wire-wound furnace to ca. 1100°C . Samples down to 10^{-10} g were determined in this way but once again the cell is somewhat cumbersome and is probably less useful for routine purposes than the flash chamber.

3. The Laser Shot

Mossotti, Laqua and Hagenah used a flash from a ruby laser to vaporize samples of solid specimens for the purposes of atomic absorption measurement¹⁸. The laser causes vaporization of the metallic or other specimen over a very small area. Because of the intensity of the laser plume the decay of the white hot incandescent material, thrown out from the pit caused by the laser shot, the atomic absorption measurement has to be made at an interval shortly after the laser plume, etc. has died down, but before condensation of the atoms. With many elements, the number of atoms outlasting the laser plume was sufficient to permit semi-quantitative measurement of atomic absorption at sub-microgram levels. Matrix effects were encountered with solid specimens, but there appears to be no reason why this interesting development could not be applied to the analysis of very small samples of solutions evaporated on preprepared laser cavities in, for example, a carbon plate.

This device again appears to have considerable promise for extension to ultramicrotrace analysis and should be particularly well suited to the development of atomic methods for the non-metals which cannot be determined in flame media for a variety of reasons which need not be detailed here.

4. Carbon Furnace Methods of L'Vov and Massmann

In 1961 L'Vov described a non-flame cell for use in atomic absorption spectroscopy which shows very considerable promise¹⁹. It consists of a hollow graphite cylinder which is clamped between two water-cooled electrodes connected to a transformer capable of passing ca. 500 amps at 10/12 volts through the graphite tube and thus heating it to ca. 3000°C . The inside of the graphite tube was lined with tantalum foil to prevent over-rapid diffusion of atomic vapours through the carbon. Later developments tend to suggest, however, that the liner is not necessary. In his original experiments L'Vov analysed solution samples by evaporating them onto a plug of graphite which fitted into a cavity in the middle of the under-surface of the tube. The whole assembly is maintained in an argon atmosphere. A D.C. discharge is struck from an auxiliary electrode onto the sample-containing plug for up to 4 seconds. This causes the sample to be vaporized into the white hot carbon tube where atomic absorption signals may

be measured by directing the beam from a hollow cathode lamp along the axis of the graphite tube. The sample is atomized and disperses very quickly but the peak absorption signal registered on a recording trace of the hollow cathode lamp allowed elements such as aluminium and titanium to be determined in a concentration range of 1–50 ppm. Analytical signals down to 10^{-8} and 10^{-11} g were recorded for some elements.

Massmann²¹ simplified L'Vov's original apparatus by dispensing with the auxilliary electrode and by depositing the sample solution directly into a small hole in the upper surface of the graphite tube by means of a micropipette. A similar graphite cuvette was devised for fluorescence measurements. As a primary source he used Sullivan and Walsh high intensity hollow cathode lamps and he made a comparison of the sensitivities of the absorption and fluorescence techniques by measuring the detection limits. For zinc these were 4×10^{-14} g fluorescence, 8×10^{-13} g absorption; cadmium 2.5×10^{-13} g fluorescence, 2×10^{-12} g absorption; silver 1.5×10^{-12} g fluorescence, 8×10^{-13} g absorption. For the other six elements, viz. antimony, iron, thallium, lead, magnesium and copper for which measurements were made, better signals were obtained in absorption than in fluorescence. This was attributed by Massmann to the lack of line intensity in the sources available to him and he comments that the fluorescence signals *should* provide higher sensitivities than those from absorption. Sample sizes of 5–200 μ l were used for absorption and 5–50 μ l for fluorescence measurements.

The electrical current requirements for the L'Vov and Massmann devices are both rather severe and there are serious problems associated with the passage of light beams along a restricted cylindrical passage surrounded by walls of white hot carbon. Our experiments have shown that there is a distinct tendency for memory effects to occur in such graphite tubes and we have therefore abandoned them in favour of a simpler, less restrictive, electrically heated graphite filament device.

5. The Graphite Filament Atom Reservoir

The filament atom reservoir (FAR) was first described by West and Williams²³. In its early form, see *Figure 4*, the filament atom reservoir consisted of a 1.5–2 mm, 4 cm long graphite filament mounted between two steel electrodes on the ends of two tungsten rods sealed through a large ground glass stopper. This was connected to a welding transformer/Variac unit capable of delivering up to ca. 100 amps at 5–10 volts. The sample of 1–5 μ l was placed on the centre of the cylindrical filament and a glass dome as shown in the figure was placed over the ground glass stopper with side arms appropriate to (a) absorption, or (b) fluorescence measurements as required. Argon was then passed through the cell at 1–4 litres per minute to displace atmospheric oxygen and the water in the solution was evaporated by brief passage of a current at a low voltage. The water vapour was thus passed out of the cell. The filament was then flash heated to ca. 2000–2600°C as appropriate in 2–3 seconds by passage of ca. 80 amps at 5–10 volts and the absorption or fluorescence measurements were made on a strip chart recorder by surveying the area immediately above the graphite filament. In these early experiments, absorption signals down to 10^{-10} g were recorded for silver and magnesium and down to 10^{-13} and

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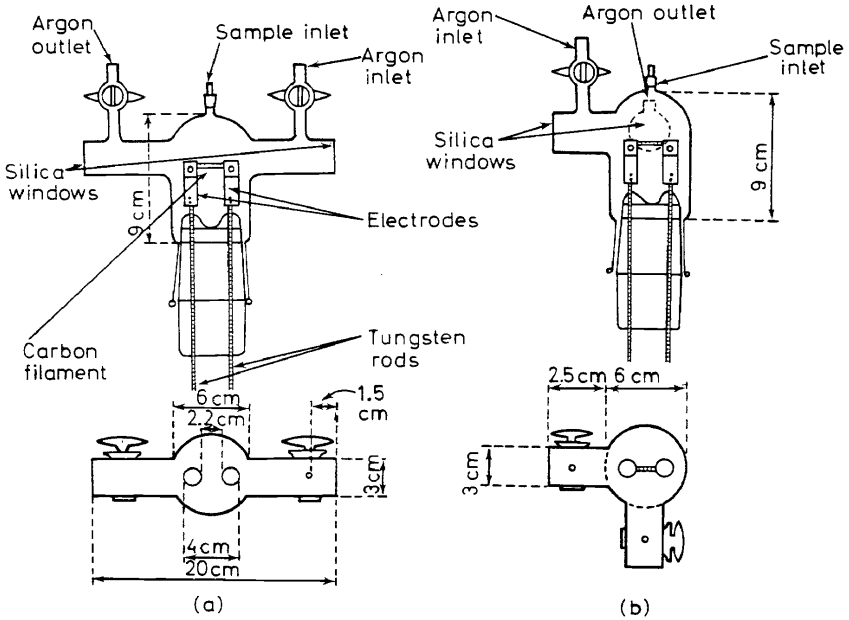


Figure 4. Filament atom reservoir device (Mark I). (a) FAR unit for AAS. (b) FAR unit for AFS

10^{-15} g respectively in fluorescence. High intensity hollow cathode lamps of the Sullivan and Walsh pattern were used in both instances.

In subsequent work²⁴, we have modified the filament atom reservoir cell by water cooling the steel electrodes to ensure more reproducible electrical contact

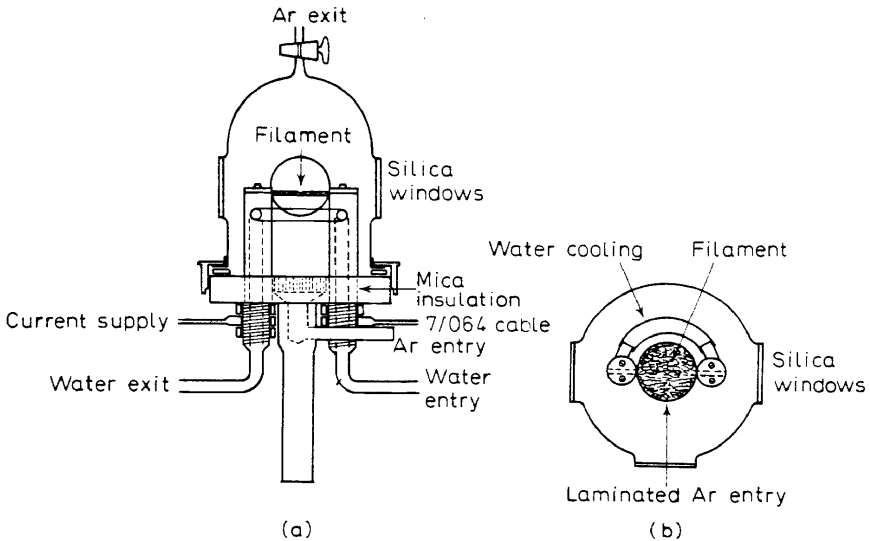


Figure 5. Filament atom reservoir device (Mark II). (a) Front view, (b) plan view.

Table 3. Atomic fluorescence data with modified FAR (Mark II) unit and a techtron AA4 spectrophotometer

Element and Line (nm)	Lamp	Filament Voltage	Argon flowrate (1 min ⁻¹)	Detection limit	Concentration Sample = 1 µl	Max. determinable amount	Previously reported detection limit in flames
Mg (285.2)	HIL	9.0 V	3.3	10 ⁻¹² g	0.001 ppm	10 ⁻⁹ g	0.002 ppm
Ag (328.1)	HIL	10.8 V	0.6	10 ⁻¹² g	0.001 ppm	2 × 10 ⁻⁹ g	0.002 ppm
Pb (405.8)	HIL	8.4 V	1.1	1.5 × 10 ⁻¹¹ g	0.015 ppm	1.5 × 10 ⁻⁷ g	0.5 ppm
Zn (213.9)	EDL	7.2 V	1.7	2 × 10 ⁻¹⁴ g	0.00002 ppm	4 × 10 ⁻¹⁰ g	0.00004 ppm
Bi (306.8)	EDL	9.0 V	2.5	10 ⁻¹¹ g	0.01 ppm	10 ⁻⁸ g	0.7 ppm
Tl (377.6)	EDL	9.0 V	1.7	5 × 10 ⁻¹¹ g	0.05 ppm	2 × 10 ⁻⁹ g	0.008 ppm
Sb (231.2)	EDL	9.6 V	2.5	10 ⁻⁹ g	1.0 ppm	3 × 10 ⁻⁸ g	0.1 ppm
Ga (417.2)	EDL	9.0 V	1.7	10 ⁻⁹ g	1.0 ppm	10 ⁻⁸ g	1.0 ppm
Cu (324.7)	HIL	12.0 V	1.1	2 × 10 ⁻¹² g	0.002 ppm	2 × 10 ⁻⁹ g	0.003 ppm
Mn (279.5)	HCL	10.8 V	2.5	5 × 10 ⁻¹² g	0.005 ppm	2 × 10 ⁻⁹ g	0.006 ppm
Cd (228.8)	EDL	7.2 V	2.5	10 ⁻¹⁵ g	0.000001 ppm	2 × 10 ⁻¹² g	0.000001 ppm
Hg* (253.7)	EDL	12.0 V	1.7	5 × 10 ⁻¹¹ g	0.05 ppm	10 ⁻⁸ g	0.1 ppm

* DC System.

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with the carbon filament and to speed up the cooling down of the filament between analyses so that they can be carried out at the rate of ca. one every two minutes. We have also led the purging gas directly into the bottom of the cell and have designed a single glass dome to replace the two previously used for either absorption or fluorescence measurements, see *Figure 5*. In addition, we have replaced the slow response amplification system of the commercial flame photometer and the strip-chart pen recorder by an operational amplifier system and a fast response UV recorder so that the transient signals can easily be recorded at full intensity and distinguished from the continuum signal from the glowing carbon of the filament. Some of the results we have obtained in this way can be seen from *Table 3*.

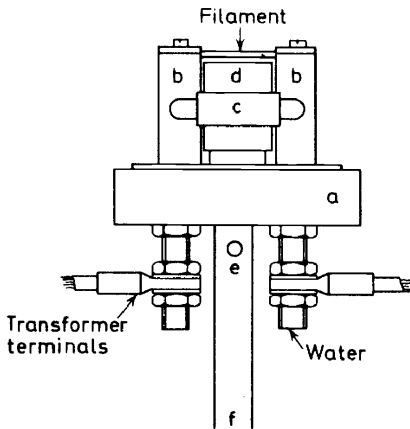


Figure 6. Filament atom reservoir modified for use in open atmosphere. (a) Base, (b) water-cooled electrodes, (c) water link between electrodes, (d) laminar flow box, (e) inlet for shield gas, (f) support stem for reservoir.

These results show that very sensitive limits of detection may be obtained using high intensity hollow cathode lamps (HIL) or electrodeless discharge lamps (EDL) as primary sources. The decrease in detection limits for magnesium and silver is attributed to the age of the lamps which have now undergone several hundred hours of continuous operation since the preliminary experiments were carried out on the original FAR cell device. It is also suspected that the EDL used for Tl, Sb and Ga were not of maximum intensity. This is borne out by the detection limit and also by their restricted range of applications as compared to the other elements.

More recently²⁵ we have even dispensed with the use of an enclosing glass dome for the apparatus. This is simply done by leading a laminar flow of the inert gas up around the filament, see *Figure 6*. This allows the FAR unit to be used open to the atmosphere and allows for very quick repetitive analyses to be carried out with the FAR unit mounted in place of a conventional burner and adjusted so that the filament is in the position normally occupied by the primary combustion zone of the flame. With cadmium we have studied the effect of various 'inert' gases. Variations of gas are practically without effect in absorp-

tion measurements but quenching and enhancing effects are easily demonstrated in fluorescence, see *Table 4*. We have also been able to demonstrate atomic phosphorescence signals for cadmium at 326.1 nm when none are obtained in a flame media.

Table 4. Effect of sheathing gas on fluorescence signals during FAR spectroscopy.

<i>Sheath Gas</i>	<i>Fluorescence (228.8 nm)</i>	<i>Fluorescence (326.1 nm)</i>
Ar	100	3
N ₂	50	50
N ₂ O	11	0
CO ₂	9	0
H ₂ *	2.5	0

* A protective dome was used to prevent combustion of the hydrogen.

The effect of potential interferences in those atomic absorption and fluorescence studies with the filament atom reservoir device is now being actively studied at a 1000 fold concentration level. It appears that at this level interferences occur from a selected number of elements which are sometimes close in property characteristics to the element being determined. The interference occurs in both absorption and fluorescence, demonstrating that the effect is most probably due to a more rapid than normal removal of free atoms from the space immediately above the filament. We have every reason to suspect that this is due to an induced condensation of the free atoms of the sought element on the cloud of rapidly condensing atoms of the interferent element in the cold atmosphere above the filament surface. Support is given to this by some experiments in which we have run two filaments alongside each other, one containing the solution of the test element alone and the other the interfering element. Interference still occurs showing that the atom depletion phenomenon occurs in the gas phase above the rod²⁶. Subsequent experiments have shown that the interference can largely be diluted out and even further minimized by making measurements as low down as possible immediately above the surface of the filament so that the free atoms are measured before much condensation can occur on the rapidly nucleating interferent atoms. The fairly specific nature of the interference, e.g. only Sr, Ba and Cu with magnesium; Bi, Hg, Cu and Pb with silver and so on lends some support to the co-crystallization or nucleation theory. The boiling points of the metals are also similar and simple condensation by physical rather than chemical processes may offer a better explanation.

The detection limits quoted in *Table 3* are for 1 μ l samples. The largest single sample that may conveniently be added directly to the filament is 5 μ l. Thus the detection limits quoted can be directly reduced five-fold since the solution is evaporated directly on the filament in the preliminary operation of analysis. It is of course also possible to concentrate solutions by repeated addition of 5 μ l samples to the filament simply by flicking the transformer switch on between sample additions to boil off the water. In this way, a 5-fold 5 μ l addition would reduce the detection limits in *Table 3* by 25-fold. This is a facility which is not available for atomic absorption or fluorescence measurements in flames.

Organic samples, e.g. oils, blood plasma, etc. which smoke when heated

directly on the filament and thus cause spurious absorption or fluorescence signals may be suitably diluted with a non-smoke producing diluent before deposition on the filament. This is frequently possible because of the extreme sensitivity of these analyses by the FAR technique. We have also found it possible in several instances to pretreat chemically the sample directly on the filament and in other instances to smoke off the organic constituents without loss of the element to be determined.

This technique of ultramicrotrace analysis combines a sensitivity of determination which challenges and in many cases surpasses that of activation analysis, x-ray fluorescence and mass spectrometry with virtually complete specificity of determination. It has freedom from toxic hazards, flames and explosions and can be carried out on apparatus which costs very little by modern standards. It is well within the budget of even the smallest analytical laboratory and can be applied to the determination of almost any element in the periodic table.

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