

SOME RECENT DEVELOPMENTS IN ATOMIC FLUORESCENCE SPECTROSCOPY

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Abstract - The merits and demerits of atomic fluorescence spectroscopy as a trace metal analytical technique are compared to those of atomic absorption and emission analysis principally from an inductively coupled RF plasma source. An assessment is made of the possible impact of the use of coherent laser radiation to stimulate atomic fluorescence with the possible onset of super-radiant atomic fluorescence phenomena. The paper also reviews the atomizers most suitable for fluorescence work and the principal instrumental modes of fluorescence.

I should like to use this talk to generalize on Atomic Fluorescence Spectroscopy as a technique of instrumental analysis rather than to use it as a vehicle to discuss specific items of recent research. Secondly, despite the title announced in the programme of the symposium, I will not, except in passing, discuss atomic emission from inductively coupled radiofrequency and microwave plasmas since the former topic is discussed elsewhere in the programme and both have been discussed extensively at recent meetings, *e.g.* at the Colloquium Spectroscopicum Internationale (Prague) August 1977 and the International Symposium on Analytical Chemistry in Birmingham (Britain) July 1977. Their omission does not, however, indicate that I consider them to be less meritorious than atomic fluorescence.

Since its evolution by Walsh<sup>1</sup> in the mid 1950 period, Atomic Absorption Spectroscopy, AAS, has become a well established technique. It has been enormously successful because it is in practice more easily operated than emission spectrometry in arcs, sparks, plasmas or flames. The key-lock mechanism of the emission profile of the hollow cathode source superimposed on the narrow absorption cross section of resonance lines in flames or electrothermal atomizers gives almost complete specificity and the number of interferences or effects that modify the signal are dictated chiefly by the physical characteristics of the atomizer rather than by fundamental spectroscopic limitations such as line overlap<sup>2</sup>. See Table 1. Its chief limitations are that (1) it is basically a single channel technique, (2) absorption techniques are not so easily manipulated to yield higher sensitivities as are emission techniques, and (3) it is generally operated under conditions of relatively low temperature so that the atomization of a small number of elements is inefficient.

TABLE 1. Spectral overlap with source resonance lines in atomic absorption

Source	Emission Wavelength nm	Analyte	Absorption Wavelength nm	Separation nm	Sensitivity ppm
Copper	324.754**	Europium	324.753	0.001	75 (a)
Iron	271.903**	Platinum	271.904	0.001	40 (a)
Silicon	250.690**	Vanadium	250.690	< 0.001	65 (a)
Aluminium	308.215**	Vanadium	308.211	0.004	800 (a)
Gallium	403.298**	Manganese	403.307	0.009	15 (a)
Manganese	403.307**	Gallium	403.298	0.009	25 (a)
Mercury	253.652**	Cobalt	253.649	0.003	100 (a)
Zinc	213.856**	Iron	213.859	0.003	200 (a)

Figures marked (a) are sensitivities calculated from the data given in the papers. Sensitivity is defined here as the concentration in ppm required to produce an absorbance of 0.0044 at the specified wavelength and under the conditions specified in the original papers. Source lines marked \*\* are resonance lines.

Atomic emission techniques such as spectrography or spectrometry from arcs, sparks or plasmas operate at much higher temperatures and are inherently capable of greater sensitivity than AAS. They require very much more sophisticated monochromation and detection systems. Many more atomic lines and ionic lines are emitted by the analyte element than have to be dealt with in AAS and additionally these emission signals are superimposed on and have to be resolved from the considerably greater emission spectrum of the arc, spark or plasma, the electronic temperatures of which are usually many thousands of degrees. In AAS the situation is, of course, simplified because the emission signal of the excitation source can be modulated and demodulated at the detector and the atomizer temperatures are usually only 3000°C or less. Fluctuations in temperature have a significant (exponential) effect on the populations of emitting atoms in high temperature media according to the well known Maxwell Boltzmann Distribution Equation.

$$N_j = N_0 \frac{P_j}{P_0} \exp - (E_j/kT)$$

but scarcely any effect on the absorbing population of atoms under the lower temperature conditions normally employed in AAS. It is widely accepted that there are many inter-element effects in emission spectrography in arcs/sparks from solid specimens, but there is evidence that the emission technique based on the inductively coupled radiofrequency plasma is considerably freer of these interelement effects than the older established emission techniques, because the sample is supplied as the aerosol of a homogeneous solution as in conventional flame-based AAS or AES. However, though this situation still has to be resolved - as had to be the case for AAS in the early 1960s - the high temperature of the RF plasma with its excellent ability to atomize all species of interest does create problems of ionic excitation, and interelement effects are still encountered.

Atomic fluorescence spectrometry, which should have been much easier to discover<sup>3</sup> and evolve<sup>4</sup> than AAS<sup>5,1,6</sup> since it does not require specially narrow line profiles in the source, is based in the first instance upon AAS and possesses most of its advantages and a substantial number of the attractive features of AES.

As will be seen<sup>7</sup> from the Eqn

$$P_f = \Phi P_\alpha \frac{\alpha \Omega}{4\pi} \beta \gamma (KvLC)$$

it uses the quite invariant ground state population of atoms rather than the more tenuous excited state population. Thus it does not require particularly high temperature atom cells and can, therefore, operate against a relatively low emission background. Furthermore the background problem can be simplified by modulation of the excitation source and synchronous demodulation of the detected signals at the amplifier as in AAS. The biggest improvement over AAS is, however, that a single emission signal is being measured and does not require to be ratioed against the signal from which it arises as in AAS. Thus the benefits of the use of the most sensitive possible detectors and of signal amplification can be maximally utilized. The key to the sensitivity of AFS is, therefore, very much a function of

1. The Line Intensity of the Source
2. The Sensitivity of the Detector
3. The Gain of the Amplifier
4. The Fraction of the Fluorescence received by the Detector

Obviously the use of a source of low intensity, e.g. a conventional hollow cathode lamp can result in much lower sensitivities for AFS than for AAS, but the use of very intense sources, e.g. microwave excited electrodeless discharge lamps or narrow-band pulsed dye lasers can yield AFS sensitivities that are several orders of magnitude greater than those obtainable by AAS.

One now has to ask the question of how far can one go in increasing the sensitivity of AFS by increasing the source intensity. Can one go on indefinitely? The answer is clearly that this is not possible for the following reason. In atomic fluorescence with non-laser sources only a small fraction of the ground state atoms are raised to the excited level. The overwhelming fraction remains in the absorbing ground state. Thus the fluorescence population is a linear function of the radiance of the source. But when the situation arises that the source is sufficiently energetic to pump up 50% of the atoms to the excited state, see Fig. 1, then the supply of ground state atoms becomes the limiting factor and the fluorescence signal eventually becomes completely independent of the radiance of the source. This is apparently as far as the source intensity factor can take us.

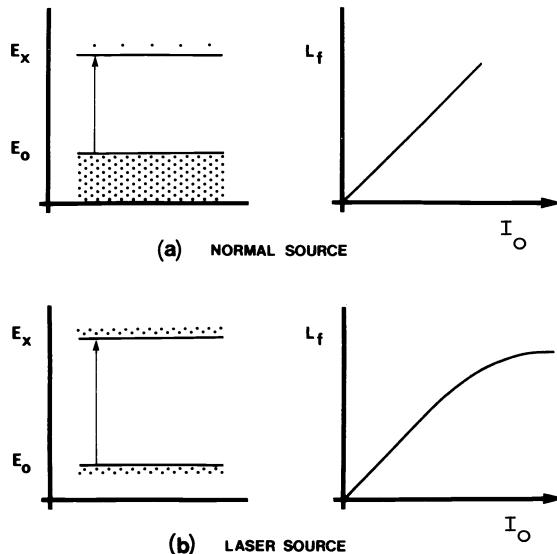
Now let us stop then and ask how does this compare with the atomic emission situation using the most powerful thermal excitation sources known.

At first sight the answer is obviously virtually the same because depletion of the population of ground state atoms will again be the limiting parameter. But, there is another factor to

be thought of for thermal emission techniques such as those involving inductively coupled RF plasmas. [I use the word "thermal" to distinguish this type of excitation from photon excitation, although it is appreciated that we are not necessarily dealing with equilibrium processes in such high energy (thermal) sources]. This is that the energy supplied by them is not quantized and may, therefore, deplete the ground state analyte population not only by transfer to excited atomic states, but significantly to ionic states, and there is no way of avoiding this except by using a less energetic source. Palliative measures such as the addition of alkali metal halides may, of course, be used but the presence of such salts may induce other complications. Ionic fluorescence can of course also be stimulated by photon sources, but there is the possibility of resolving such radiation before it is incident on the atom cell and to select only the resonance radiation to

Fig. 1

**REGULATION of FLUORESCENCE**



(a) Normal source. Bulk ground state population; linear dependence of fluorescence upon population/intensity.

(b) Laser source. 50% depletion of ground state population; invariance of fluorescence signal with intensity.

provide key-lock excitations of the atomic state. So on this basis, atomic fluorescence has possible advantages in sensitivity over atomic emission analysis. There is, however, another factor which can apply in laser excited AFS which can take the sensitivity of measurement well over the apparent upper limit imposed by the saturation level shown schematically in Fig. 1(b). This is the phenomenon of super-radiance<sup>8</sup>. A narrow-line single transverse mode laser behaves as a diffraction-limited plane-wave generator and the coherence of its photon flux can radically alter the photon-atom interaction predicted by classical quantum mechanics. Groups of excited atoms produced by the laser in constant phase relation to each other may interact mutually as co-operating clusters and spontaneously emit coherent fluorescence radiation. The radiant power of such co-operating clusters should be *ca.* 3-4 orders of magnitude greater than the normal (summed) fluorescence contribution of the same atoms behaving in the normal quantum mechanistic way. Thus super-radiant atomic fluorescence, SAF, may add a completely new dimension to atomic fluorescence in the future. Present-indirect evidence for SAF in our work arises from the observation that saturation is much more difficult to achieve than predicted. This would arise because the spontaneous emission of SAF will pump excited atoms back to the ground state. The life-time of the superradiant excited atoms is *ca.* 2-3 ps compared with a typical (dephasing) collision time of *ca.* 35 ps. Because the life-time of superradiant excited atoms is so short the half-line width of the SAF is typically much broader than normal AF. Other features to be expected from SAF are (1) anisotropic emission of radiation depending on the direction and polarisation of the source and the geometry of the atom cloud which would of course allow good signal to noise ratios to be obtained, and (2) dependence of the signal strength on  $N_o^2$  rather than  $N_o$  which will at low levels of  $N_o$  rather vitiate the sensitivity gain that would otherwise be expected.

It may be calculated that it would be necessary to use lasers capable of delivering more than  $10^7 \text{ W cm}^{-2}$  to work in this area of supersaturation so the situation is well within the bounds of exploitation in the not-too distant future. Improved tuning capability could also be of very great benefit.

## SOURCES FOR FLUORESCENCE

The discussion of atomic fluorescence excitation sources such as continuum types, *e.g.* 150-500 W Xenon arc lamps, high intensity hollow cathode lamps, microwave excited discharge lamps, etc. is well known and need scarcely be gone over again since it has been reviewed extensively in the literature. It is fairly clear that the continuum source can yield surprisingly high sensitivities and that it is useful in producing scanning atomic fluorescence techniques<sup>9</sup>. Pulsed hollow cathode lamps have been used by several authors and are particularly satisfactory in non dispersive techniques where losses due to monochromator luminosity are not encountered. They have also been used to good effect in multi-channel semi-dispersive systems<sup>10,11</sup>. However, there is little doubt that the microwave excited discharge lamp is probably the most generally useful excitation source. A very significant contribution has been made by thermal stabilization of the EDL<sup>12</sup>. It is certainly our experience<sup>13</sup> that much greater intensities are possible, and greater stability often showing small, but practicable intensity *vs* input power (and temperature) plateaus, where the fluorescence signal is relatively free from fluctuations in these latter two parameters. See Figs. 2, 3. The temperature-controlled EDL can generally be operated at much lower powers than previous EDLs and therefore show longer running lifetimes.

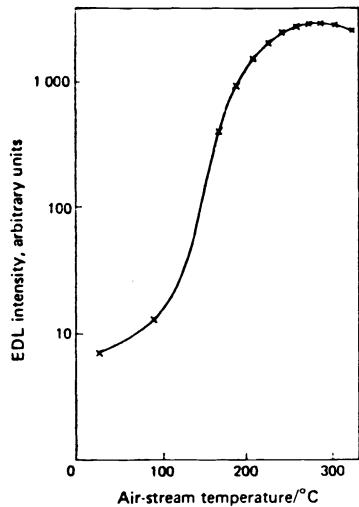


Fig. 2. Variation of lamp intensity at 228.8 nm for a cadmium electrodeless discharge lamp operated in a  $\frac{1}{4}$ -wave resonant cavity as a function of the surrounding air-stream temperature.

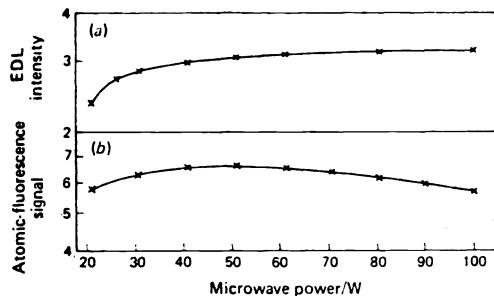


Fig. 3. Variation of lamp intensity and fluorescence response for cadmium at 228.8 nm as a function of applied power using a temperature-controlled electrodeless discharge lamp at 300°C: (a) lamp intensity; and (b) atomic fluorescence signal for a cadmium solution. A  $\frac{1}{4}$ -wave resonant cavity was used.

Usually they also give lower noise levels, greater signal-to-background characteristics in fluorescence, lower susceptibility to tuning changes and position within the resonant cavity. There is ample evidence in the literature that for a great number of elements AFS using EDL excitation and electrothermal atomizers such as the carbon rod can compete in sensitivity with sophisticated techniques such as neutron activation, X-ray fluorescence and, dare I say it, arc/spark source mass spectrometry and AE from inductively coupled radio-frequency plasmas. It is, however, at present very much a do-it-yourself technique due to the studied indifference of instrument manufacturers who are all too ready to ride the not too demanding and very profitable bandwagon of AAS or those of the more expensive and sophisticated techniques mentioned above

## ATOMIZERS FOR FLUORESCENCE

There has been considerable discussion of atomizing sources for AAS and AFS in the literature, *e.g.* premixed flames based on hydrogen and hydrocarbons, separated flames, hydrogen diffusion flames and electrothermal devices such as carbon tubes, cups or rods as well as variants such as ribbons and loops and rods of metal such as tantalum, tungsten, etc. There is, therefore, little need to discuss the situation in detail and only a few broad generalizations are necessary.

Much atomic fluorescence work has been done in the hydrogen diffusion flame which has an extremely low background level since the hottest parts of it are only *ca.* 1000°C and the bulk *ca.* 350-400°C. This permits spectacular detection limits to be obtained because of

the very low background, but in practice analysis in these flames suffers seriously from matrix effects and such flames are only really useful for relatively pure solution work or following separation preconcentration/isolation operations. The higher temperatures of premixed hydrogen and hydrocarbon flames gives much better atomization of many species, but considerably higher backgrounds. Separated hydrocarbon flames retain the same good atomization characteristics, but yield much lower backgrounds, particularly in the area of the OH emission band *ca.* 310 nm<sup>14</sup> *cf.* Fig. 4. They are, in the author's experience, unquestionably the best type of chemical flame for AFS work. Inductively coupled radio-frequency plasmas may be and indeed have been used but would probably be preferred only where difficult-to-atomize elements are concerned because of their generally high emissive background. The type of plasma discharge when the charged ion plasma is bent magnetically, or otherwise, at right angles to its initial direction thus allowing neutral, *i.e.* uncharged species to continue on into a relatively dark space might prove very useful indeed for such work.

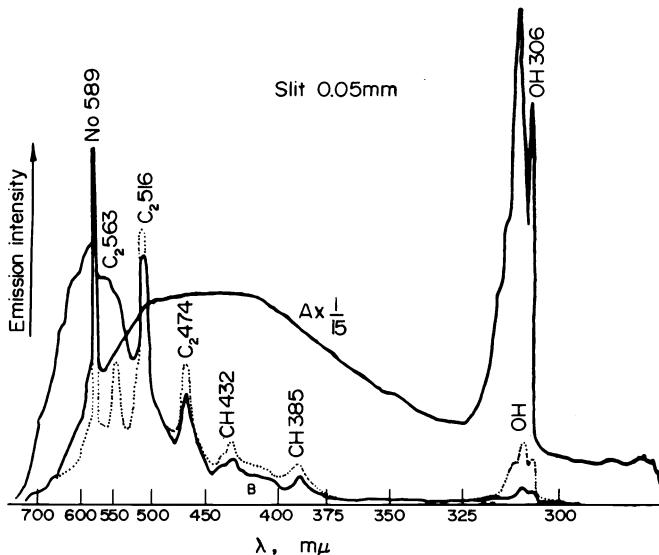


Fig. 4. Background emission from unseparated (A) and separated (B) flame. The ordinate of A should be multiplied by 15 to compare absolute intensities. Dotted line shows effect of decreased fuel flow-rate on emission spectrum from separated flame.

However, whilst for most routine purposes where plenty of sample is available and the utmost in sensitivity of determination is required the separated flame is the most useful atomizer, there is little doubt that the electrothermal atomizer based on a graphite rod (or cup) is nearer the ideal because it allows denser than normal populations of atomic species to be excited in a free standing cloud in an inert low-quenching argon atmosphere, against an almost radiationless background. This permits sensitivities that are at least one or possibly, on occasion, two orders of magnitude better than in a flame and allows nanogram, picogram and sometimes even femtogram amounts of metal ion to be detected and determined<sup>15</sup>, see Table 2. At present the detection limits and sensitivity of analysis on these carbon rod electrothermal atomizers are limited chiefly by the atomizers' tendency to eject glowing particulate carbon at or near their optimum temperatures (*ca.* 3000°C), but design studies could improve this capability very considerably.

Hollow cathode chambers, etc. are other near ideal atomizers for fluorescence work, but so far have only been used to a limited extent, *e.g.* for solid metallic specimens, though they show very considerable promise and may become much more widely used in the future.

#### INSTRUMENTAL MODES OF FLUORESCENCE

Briefly, and in conclusion, it is appropriate to survey in summary the available instrumental modes of fluorescence. The main sub-divisions are those of Single Channel and Multichannel Fluorescence. In the former a monochromator is tuned to the resonance, direct-line or stepwise fluorescence frequency most suited to the measurement. This is analogous to the situation in molecular fluorescence work in solution media. In the non-dispersive single channel mode a spectrally pure line source is used and since the number of AF spectral overlaps is very limited indeed the monochromator is dispensed with since only the absorbing species fluoresces. Usually a solar blind photomultiplier is used for UV work. The equipment can be very simple indeed and is capable of much higher

sensitivity than that obtainable using a monochromator. Multichannel continuous scanning fluorescence using either a continuum or better still a selected number of intense line sources such as single or multielement EDL yields excellent results for routine analytical

TABLE 2. Atomic-fluorescence detection limits by carbon filament technique

Species	Detection limit/g	Upper linear range/g
Sb	$10^{-9}$	$3 \times 10^{-8}$
Bi	$10^{-11}$	$10^{-8}$
Cd	$10^{-15}$	$5 \times 10^{-12}$
Co	$2 \times 10^{-11}$	$6 \times 10^{-9}$
Cu	$10^{-12}$	$4 \times 10^{-9}$
Ga	$5 \times 10^{-11}$	$10^{-8}$
Au	$4 \times 10^{-12}$	$5 \times 10^{-10}$
Pb	$10^{-11}$	$1.5 \times 10^{-7}$
Mg	$10^{-12}$	$10^{-9}$
Mn	$5 \times 10^{-12}$	$2 \times 10^{-9}$
Hg ( $Hg^{2+}$ )	$5 \times 10^{-11}$	$1 \times 10^{-8}$
Ni	$5 \times 10^{-12}$	$2 \times 10^{-9}$
Ag	$10^{-12}$	$2 \times 10^{-9}$
Tl	$5 \times 10^{-11}$	$2 \times 10^{-9}$
Zn	$2 \times 10^{-14}$	$4 \times 10^{-10}$

problems<sup>16</sup>, see Fig. 5. A technique of interrupted scanning, *i.e.* jumping the monochromator from one selected line to the next permits more rapid analysis<sup>11</sup>. Semi-dispersive fluorescence allows carefully selected line sources to be used with narrow band filters instead of a monochromator as this is inherently capable of greater sensitivity in pure solution work and with real samples<sup>17</sup>. Lastly, mention should be made of the time-resolved non-dispersive atomic fluorescence technique made possible by the use of continuous source or selected single or multielement EDL used in conjunction with a graphite filament atomizer. Because the temperature of the atomizer is a function of time, different species on the filament are atomized at different moments in time and, therefore, have their fluorescence peak signals dispersed in time. The fluorescence signals can, therefore, be detected with a single detector in a non-dispersive mode<sup>18</sup>. Figure 6 shows the time resolved signals for two elements that atomize at temperatures that are rather close together, *i.e.* Cd and Tl.

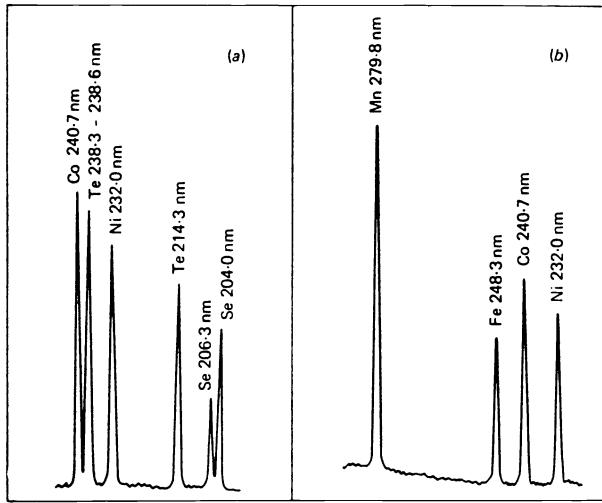


Fig. 5. Spectral scans for: (a) a flame containing selenium, tellurium, nickel and cobalt irradiated with two EDLs (selenium-tellurium and cobalt-nickel); (b) as (a), but with nickel-cobalt and iron-manganese.

Finally the author wishes to express his regrets that so many topics in AFS have had necessarily to be excluded from this review. Their omission was made necessary by the limitation of time. The material selected for review is, therefore, a blend of the requirements of historical perspective and an assessment of what is thought to be most relative at the present and likely to be so in the foreseeable future.

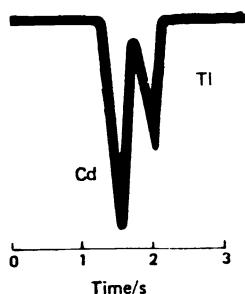


Fig. 6. Oscilloscope trace of time-resolved non-dispersive atomic-fluorescence signals for 5 ng of cadmium and 5 ng of thallium. Two single-element sources were used.

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