

# NON-FLAME CELLS IN ATOMIC FLUORESCENCE SPECTROMETRY

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## ABSTRACT

The atomic concentration available for excitation in atomic absorption (AA) and atomic fluorescence (AF) spectrometry can be increased by maintaining a low concentration of species, such as O, OH, etc., to minimize compound formation and maintaining a fairly low temperature to minimize ionization. An effective means of accomplishing this is to use a graphite furnace (at a temperature of about 2000°K). Such a furnace if flushed with argon provides a nearly ideal environment for atomization of the sample. L'vov has used such a system for AA. More recently Massman, and Woodruff, have described similar systems for AA and have obtained excellent sensitivities for elements normally difficult to atomize in flames, e.g. Al and Sn. Massman also used a graphite furnace with hollow cathode discharge tube sources for AF and again obtained good sensitivities for several elements even though his sources were of low intensities. The major difficulties encountered in using graphite cells have been poor reproducibility in sampling and the presence of high background.

A theoretical comparison of the graphite cell and the flame cell for analytical spectrometry is given. Also emission, absorption and fluorescence spectrometry are compared with respect to radiance levels. As a result of the theoretical comparison, the optimum method for trace element analysis would seem to be atomic fluorescence with a graphite cell.

We are using a unique graphite cell system with both continuum and line sources for excitation. We are modulating the exciting radiation and using either a synchronous photon counting or a lock-in amplifier. The sample solution is introduced into the graphite cell via a hypodermic syringe or via a nebulizer.

An argon flush is used to minimize oxidation of the graphite.

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## INTRODUCTION

Since the sensitivity of all atomic spectrometric methods depends directly upon the atomic concentration of the species of concern, many workers have employed a variety of techniques to increase the efficiency of the atom reservoir. Flames have been the most convenient and reliable means of producing atomic vapours. Even so, flames may not be efficient for some elements due to incomplete solute vaporization, compound formation of some elements with flame gas products, e.g. stable monoxides with elements like Zr, Hf, Si, B, etc., and significant ionization with some elements, e.g. Na, K, Rb, Cs, etc. Therefore, many workers have tried to increase the efficiency of aspiration of burner-flame systems by using more efficient nebulizers<sup>1-4</sup> and higher temperature

fuel-rich low-rise velocity flames<sup>5-10</sup>. Nevertheless, even very fuel-rich flames contain sufficient oxygen atom pressure to reduce appreciably the atomic concentration of some elements, e.g. Si, Zr, Hf, U, B, etc., and to limit the applicability of flames for such elements. Therefore, many recent works have involved the use of non-flame cells as atom reservoirs.

The simplest non-flame atom reservoirs for atomic absorption spectrometry have been based on the L'vov graphite furnace<sup>11-13</sup> in an inert atmosphere. More recently variations of the graphite furnace for atomic absorption spectrometry have been described by L'vov<sup>14-15</sup>, by Massman<sup>16-17</sup> and by Woodriff<sup>18-20</sup>. Massman<sup>17</sup> and West and Williams<sup>21</sup> have also used modifications of the graphite furnace for atomic fluorescence studies.

Other methods of producing an atomic vapour in non-flame cells have involved: the use of cathodic sputtering in hollow cathodes<sup>22-26</sup>; the use of laser generated plasma above a solid surface<sup>27</sup>; and the use of rapid vaporization of thin solid materials by an intense flash of radiation from a capacitor discharge lamp<sup>28-31</sup>. In the first device, sampling is rather complex and a lengthy procedure. In the second system, there appear to be considerable matrix effects, results are at best only semi-quantitative, the limits of detection are not great, and the analytical curves are linear only over small ranges in concentration. In the third system, sampling is tedious and lengthy, results are at best only semi-quantitative, and limits of detection are not great.

## THE METHODS

### Atomic spectrometry with flames

In these methods, the analyte solution is continuously introduced into the flame via an aspirator. The flame then converts a fraction of the salt particles introduced into the flames into an atomic vapour. In atomic emission flame spectrometry (AEf), the resulting atomic vapour is excited by the flame. In atomic absorption flame spectrometry (AAf), the atomic vapour is excited by radiation from a source and the fraction of radiation absorbed is measured. In atomic fluorescence flame spectrometry (AFf), the atomic vapour is excited by radiation from a source, and a portion of the radiation emitted when radiational deactivation occurs (called fluorescence) is measured.

### Atomic spectrometry with graphite cells

In these methods, a fixed volume of the analyte solution is pipetted into the graphite cup. A stream of inert gas (generally argon) is present around the graphite cell to minimize deterioration of the cell and to maintain a highly reducing and non-quenching atmosphere. Similar devices can be used for atomic emission (AEg), atomic absorption (AAg) and atomic fluorescence (AFg) spectrometry.

A special non-flame cell, in which analyte solution is placed on a platinum loop in an argon atmosphere and the loop heated to vaporize the analyte, will also be discussed in the experimental section but will not be treated from a fundamental standpoint. Actually the platinum loop could be treated in a similar manner to the graphite cup with fixed volume of analyte solution but this will not be done here.

## PRINCIPLES

## Advantages of graphite cells instead of flame cells

*Increased atomic concentrations*

The concentration of analyte atoms in a flame (atoms  $\text{cm}^{-3}$ ) is related to the concentration of analyte (moles  $\text{l}^{-1}$ ) in the solution aspirated into the flame<sup>32-34</sup> by

$$n = 1 \times 10^{19} F \varepsilon \beta C / Q e_f \quad (1)$$

where  $F$  denotes solution transport (flow) rate,  $\text{cm}^3 \text{min}^{-1}$ ;  $\varepsilon$  is efficiency of aspiration, i.e. efficiency of producing a gas of the analyte in the flame, no units;  $\beta$  is efficiency of atomization, i.e. efficiency of producing atoms from gaseous analyte, no units;  $e_f$  is the flame gas expansion factor due to increase in temperature of gases from room temperature and increase in number of moles of flame gas products, no units; and  $Q$  is the flowrate of unburnt gases into flame,  $\text{cm}^3 \text{sec}^{-1}$ .

The atomization efficiency,  $\beta$ , is the ratio of the concentration of free analyte atoms in the flame to the total concentration of analyte in all gaseous forms<sup>35</sup>. This factor accounts for incomplete dissociation of the analyte compound introduced into the flame, for formation of compounds resulting between the analyte and flame gas molecules, and for ionization of the analyte atoms in the flame gases.

The aspiration efficiency,  $\varepsilon$ , is the ratio of the number of all gaseous analyte species produced in the flame per unit time to the number of analyte species aspirated per unit time<sup>36</sup>. This factor accounts for volatilization of the solid particles in the flames and also for the transfer efficiency (yield) of the aspirator chambers and associated tubes used with chamber type aspirator burners.

The peak atomic concentration,  $n$ , in atoms  $\text{cm}^{-3}$  of analyte in a graphite cell is related to the analyte concentration,  $C$ , in moles  $\text{l}^{-1}$  introduced into the cell by means of a pipette, by the following equation

$$n = 6 \times 10^{20} V C \varepsilon \beta / V_c \quad (2)$$

if the analyte vaporizes instantly and then diffuses out of the cell slowly. The symbols are:  $V$ , volume of analyte solution introduced into the cell,  $\text{cm}^3$ ;  $\varepsilon$ ,  $\beta$ , degrees of aspiration and atomization of the analyte within the graphite cell, no units; and  $V_c$ , the inner volume of the graphite cell.

Therefore, the ratio of atomic concentrations when the same concentration of analyte,  $C$ , is either introduced into the graphite cell or aspirated into the flame is given by dividing equation 1 by 2, and so

$$R_n = 60 [(V/V_c) (\varepsilon\beta)_g / (F/Q e_f) (\varepsilon\beta)_f] \quad (3)$$

where all terms have been defined above and  $(\varepsilon\beta)_g$  and  $(\varepsilon\beta)_f$  refer to the  $\varepsilon\beta$  value for the analyte introduced into a graphite cell ( $g$ ) and a flame ( $f$ ).

To compare the atom-producing ability of the graphite cell with the atom-producing ability of a flame, several values for the parameters in equation 3 (typical of experimental systems in use in the author's<sup>37</sup> laboratory) will be chosen:  $V \simeq 0.010 \text{ cm}^3$ ;  $V_c \simeq 0.5 \text{ cm}^3$ ;  $(\varepsilon\beta)_g \simeq 1$ ,  $F = 2 \text{ cm}^3 \text{min}^{-1}$ ;  $Q = 100 \text{ cm}^3 \text{sec}^{-1}$ ;  $e_f \simeq 10$ ;  $(\varepsilon\beta)_f = 1$ . For this particular case,  $R_n = 600$ , which

shows that the graphite cell produces atoms more efficiently than the flame cell. The reasons for this result are twofold. First of all, the atomic vapour is maintained in a smaller volume in the graphite cell than in the flame since the graphite cell is essentially a static system and the flame, a dynamic system, and also the flame gases expand about tenfold in most analytical flames. The factor in equation 3 expressing the increased concentration is  $[V/V_c]/(F/Q_e)$ . Secondly, for many analytes,  $(\epsilon\beta)_f$  will be considerably less than unity; particularly for analytes which do not undergo complete vaporization within the flame gases, i.e. solute vaporization interferences<sup>38</sup> and for analyte atoms which form stable monoxides, monohydroxides or other compounds with species present in the flame gases; e.g. Mg, Ba, Zr, Hf, Al, Si, etc.<sup>35</sup>. The factor in equation 3 expressing the efficiency of aspiration-atomization is  $(\epsilon\beta)_g/(\epsilon\beta)_f$ .

#### *Decreased quenching of radiationally excited atoms*

The graphite cell provides a less efficient quenching atmosphere (mainly inert gas molecules) compared to analytical chemical flames (mainly N<sub>2</sub>, CO, CO<sub>2</sub>, etc.). Therefore, due to the reduced quenching in a graphite cell, the signal level of element Z in a graphite cell will be increased with respect to the signal level of element Z in a flame—assuming all other factors are identical—by the ratio  $R_y$ , given by

$$R_y = Y_g/Y_f \quad (4)$$

where  $Y_s$  are the quantum efficiencies (yields) for element Z in the graphite cell ( $g$ ) and in the flame ( $f$ ). The ratio  $R_y$  can be expressed in terms of first order (or pseudo-first order) rate constants<sup>39-47</sup> by

$$R_y = \{k_F + \sum_i(k_{Q_i}n_{Q_i})_g\} / \{k_F + \sum_i(k_{Q_i}n_{Q_i})_f\} \quad (5)$$

where  $k_F$  is the first-order rate constant for radiational deactivation of the resonance level, sec<sup>-1</sup>;  $k_{Q_i}$  is the second-order quenching rate constant for deactivation of the resonance level by collisions of element Z with a quencher  $Q_i$  of concentration,  $n_{Q_i}$ , sec<sup>-1</sup> cm<sup>3</sup>; and  $n_{Q_i}$  is the concentration of quencher,  $Q_i$ , cm<sup>-3</sup>.

The summation is taken over all quenchers and the subscripts  $g$  and  $f$  denote the gaseous medium. Since graphite cells (argon atmosphere) should contain few active quenchers,  $k_F \gg \sum_i(k_{Q_i}n_{Q_i})_g$  and so

$$R_y \simeq k_F / \{k_F + \sum_i(k_{Q_i}n_{Q_i})_f\} \quad (6)$$

In most common analytical flames<sup>39-47</sup>,  $k_F \simeq 0.1 \sum_i(k_{Q_i}n_{Q_i})_f$  and so  $R_y$  should be of the order of ten, i.e. an atom emits its resonance line ten times more intensely in a graphite cell than in a flame if the same atomic concentration in each is radiationally excited.

Since fluorescence radiation does not affect the sensitivity of measurement in atomic absorption studies<sup>46</sup> and fluorescence is negligible in atomic emission studies<sup>48</sup>, there is no comparable factor to  $R_y$  in AA or AE.

#### *Geometry factor*

If it is assumed that the same radiant power, in erg sec<sup>-1</sup>, is incident upon the flame in AA or AF, whether a graphite cell or a flame is used, then there

is no need to consider a geometry factor for the absorption process. For convenience, it will also be assumed that the area of the source image incident upon the flame in AA is the same as the flame area imaged upon the monochromator entrances in AE. Therefore, the only real difference between the use of a graphite cell and a flame in atomic spectrometry occurs in the measured fluorescence area in AF. The geometry factor relating the signal in AF<sub>G</sub> to the signal in AF<sub>F</sub> assuming the previous factors  $R_n$  and  $R_y$  are unity is given by

$$R_G = \xi\eta \quad (7)$$

where  $\xi$  is the ratio of fluorescence area in the flame to fluorescence area in the graphite cell (area in direction of measurement system), no units; and  $\eta$  is the fractional fluorescence from the graphite cell measured by the measurement system, no units.

The above expression is only valid if the slot in the graphite cell and the fluorescence area in the flame exceed the dimensions of the entrance slot of the monochromator. For our graphite cell and flames<sup>37</sup>,  $\xi$  is about ten and  $\eta$  is about 0.03, and so  $R_G \simeq 0.3$ . Thus the geometry of our flame is more ideal than the geometry of our graphite cell for AF. This is a rather likely result for an open system (flame) versus a confined system (graphite cell).

#### Noise considerations

The major sources of noise in AF<sub>F</sub> or AE<sub>F</sub> are flame flicker noise and photo-tube shot noise. Since measurements can sometimes be made in the non-luminous part of low-background hydrogen-based flames<sup>49, 50</sup> in AF<sub>F</sub>, flame flicker noise is then comparable to shot noise. However, in the higher temperature fuel-rich flames, flame background flicker noise can be several orders of magnitude greater than shot noise. Source scattering noise in AF<sub>F</sub> can be made quite small compared to other noises<sup>49, 50</sup> *despite many statements to the contrary* by other writers. The major sources of noise in AA<sub>F</sub> are source flicker noise and flame flicker noise, especially when using high temperature fuel-rich flames, e.g. acetylene-based flames. When using a properly baffled graphite cell in AA and AF, the major sources of noise should be source flicker noise in AA and shot noise in AF. When using a graphite disc in AE, there will probably be appreciable background flicker noise as well as shot noise. Therefore, the noise level when using graphite cells instead of flames should be considerably smaller in all these atomic spectrometric methods (AA, AE and AF).

#### Summary

The graphite cell should offer a greater advantage as an atom reservoir in AF than in AA or AE. The gain in signal in AA and AE is approximately  $R_n$  whereas the gain in signal in AF is approximately  $R_n R_y R_G$  when using a graphite cell instead of a flame ( $R_n R_y R_G$  should generally be greater than unity). In any event, there certainly appears to be ample justification for using the graphite cell as an atom reservoir in atomic spectrometry. Since the signal levels should be greatly increased due to greater atomic concentrations and since the noise levels should be smaller when using graphite cells rather than flame cells, the limits of detection with graphite cells in AA

and AE as well as AF should be substantially lower (say two or more orders of magnitude). Also, it should be noted that the intersection point of the analytical curves, i.e. the intersection of the low and high concentration lines, will also shift to lower concentrations. Finally it should be pointed out that there is an additional factor present in AEg and AEf, namely the ratio of the Boltzmann factors,  $\exp(-E_u/kT_g)/\exp(-E_u/kT_f)$ , where  $E_u$  is the excitation energy of the resonance line,  $k$  is the Boltzmann constant, and  $T_g$  and  $T_f$  are the temperature of the atomic vapour in the graphite cell (g) and flame (f), respectively. Since  $T_g > T_f$ , this ratio may be significantly greater than unity. Therefore, AEg has the additional advantage over AEf of increased excitation as well as increased atomic concentration.

The greatest disadvantage to use of graphite cells instead of flames seems to arise from the greater sampling errors on transferring small volumes to the cell and the need for occasional replacement of the graphite cell. For limited sample sizes, the small volume of sample needed for the graphite cell is an additional advantage. Of course, solutions can be nebulized<sup>18-20</sup>.

### Comparison of AF with AE and AA<sup>51</sup>

#### Measured signals

The ratio of measured signals for dilute atomic vapours in atomic absorption spectrometry (AA) or in atomic emission spectrometry (AE) with respect to atomic fluorescence spectrometry (AF) can be obtained by use of the intensity expressions (see Appendix 1) given by Zeegers, Smith and Winefordner<sup>34</sup> assuming the conditions and assumptions given in Appendix 1 are valid. The signal ratios are given by:

$$S_{AAC/AFC} \approx 1/Y(\Omega/4\pi) \quad (8)$$

$$S_{AAL/AFL} \approx 1/Y(\Omega/4\pi) \quad (9)$$

$$S_{AE/AFL} \approx (B_{\lambda_0}^B/B_{\lambda_0}^C)(1/Y\{\Omega/4\pi\}) \quad (10)$$

$$S_{AE/AFL} \approx (B_{\lambda_0}^B \Delta\lambda_D/B^L \delta)(1/Y\{\Omega/4\pi\}) \quad (11)$$

where the third letter of each subscript refers to the use of a continuum (C) or a line (L) source and the entire subscript gives the ratio of interest and where:  $Y$  denotes quantum efficiency for transition, no units;  $(\Omega/4\pi)$  is the fractional solid angle of excitation radiation collected by entrance optics and impinging on atomic vapour, no units;  $B_{\lambda_0}^B$  is the spectral radiance of a black body at peak absorption (emission) wavelength,  $\lambda_0$ ,  $\text{erg sec}^{-1} \text{cm}^{-2} \text{\AA}^{-1}$ ;  $B_{\lambda_0}^C$  is the spectral radiance of a continuum source (L) at  $\lambda_0$ ,  $\text{erg sec}^{-1} \text{cm}^{-2} \text{\AA}^{-1}$ ;  $B^L$  is the integrated radiance of the line source,  $\text{erg sec}^{-1} \text{cm}^{-2}$ ;  $\Delta\lambda_D$  is the Doppler half-width of the absorption line,  $\text{\AA}$ ; and  $\delta$  is a correction factor to account for the shape and width of the exciting line in AA or AF and for the broadening of the absorption line by collisional as well as Doppler broadening (see Appendix 1), no units.

The above equations are valid for either flames or graphite cells, i.e. both methods in the ratio utilize the same atom reservoir and have the same instrumental system satisfying conditions given in Appendix 1. If different atom reservoirs are used, then the considerations in the previous section on increased atomic concentration must be accounted for.

Since  $Y$  in analytical flames is of the order of 0.1 for many elements and should be of order unity for the same elements in graphite cells containing an inert atmosphere and since  $\Omega_A/4\pi$  is of the order of 0.01 for flames and graphite cells,  $S_{AAC/AFC}$  and  $S_{AAL/AFL}$  should be of the order of  $10^3$  for flames and  $10^2$  for graphite cells. This is reasonable since absorption must occur before fluorescence can occur. In fluorescence there are two solid angles—one for excitation and one for fluorescence measurement—whereas, in absorption (and emission) there is just one solid angle for excitation (and measurement of emission). Thus for all excitation sources ( $C$  denotes xenon arc lamp;  $L$  is a hollow cathode discharge tube or electrodeless discharge tube), the signals in AA will be greater than the corresponding fluorescence signals. On the other hand, the signals in AF (see Appendix 1) may exceed those in AE if  $B_{\lambda_0}^C$  exceeds  $B_{\lambda_0}^L$  or if  $B^L$  exceeds  $B_{\lambda_0}^B \Delta\lambda_D/\delta$  by more than  $Y(\Omega/4\pi)^{-1}$ . This will only be expected at short wavelengths, i.e. less<sup>50</sup> than about 4000 Å when using common excitation sources.

The ratio of detection limits in AFC or AFL with respect to the detection limits in AAC, AAL or AE is given by the quotient of the above ratios for the signal levels divided by the corresponding ratios for the noise levels:

$$G_{AAC/AFC} = S_{AAC/AFC}/N_{AAC/AFC} \quad (12)$$

$$G_{AAL/AFL} = S_{AAL/AFL}/N_{AAL/AFL} \quad (13)$$

$$G_{AE/AFC} = S_{AE/AFC}/N_{AE/AFC} \quad (14)$$

$$G_{AE/AFL} = S_{AE/AFL}/N_{AE/AFL} \quad (15)$$

Since source flicker and all background (especially flame) flicker noises are dominant in AA and shot noise and cell background flicker noise (flame mainly) are dominant in AF, when using either flames or graphite cells (source flicker noise generally greatly exceeds all background flicker noise), the noise ratios  $N_{AAC/AFC}$  and  $N_{AAL/AFL}$  will always exceed unity and, in fact, near the limits of detection  $N_{AAC/AFC}$  and  $N_{AAL/AFL}$  will generally exceed  $S_{AAC/AFC}$  and  $S_{AAL/AFL}$ , respectively, as long as sources of sufficient intensity<sup>51</sup> are available. Therefore, for all cases in which good sources are available, e.g. Zn, Cd, Hg, Cu and Ag, experimental limits of detection in AFL (with either atomizer) should be greatly superior to those in AAL.

From calculations of  $G$  values (using equations 12 to 15) assuming identical instrumentation for all three methods and assuming the use of a flame atomizer, it is found that AFL (assuming use of sources with intensities comparable to those for the Zn, Cd, Hg, Cu and Ag electrodeless discharge tubes are used) should give similar or lower limits of detection than AAL for nearly all elements with resonance lines below about 3250 Å. On the other hand, AE should give lower limits of detection for nearly all elements with resonance lines greater than about 3250 Å.

From a survey of the literature<sup>51</sup> for all elements experimentally measured by AAL, AFL, and AE using *flame* atomizers: AAL gives greatly superior limits of detection for only three elements: Be, Mg and Rh; AFL gives greatly superior limits of detection for: Ag, Cu, Cd, Hg and Zn; and AE gives greatly superior limits of detection for Cs, Ga, In, K, Li, Na, Rb and Sr. 'Superior' means here that the detection limit is threefold or more lower by the desig-

nated method. For As, Au, Bi, Cu, Fe, Ni, Pb, Sb, Si, Sn and Te, AAL and AFL are currently experimentally equivalent and superior to AE. For Ca and Cr, AAL and AE are experimentally equivalent but superior to AFL, and for Ge, Mn and Tl, all three methods are similar. Since reliable experimental data for other elements determined by AFL were not available in the literature, no other elements are listed in the comparison. Therefore, experimental studies tend to confirm the predictions, i.e. good sources<sup>52</sup> are currently not available for Be, Co, Cr, Mg, Ca and Ge and only fair sources are available but can undoubtedly be improved for As, Au, Bi, Fe, Mn, Ni, Pb, Sb, Si, Sn, Te and Tl.

The use of a graphite furnace cell rather than a flame in AA and AF will probably not change the relative detection limits (actually AF will probably be aided more than AA—see previous sections—and could cause a few more elements to be added to the AF list) but more importantly should lower the detection limits for all elements relative to those in flames. The use of a graphite furnace in AE rather than a flame could have even more striking effects because of the Boltzmann factor ratio,  $\exp(-E_u/kT_g)/\exp(-E_u/kT_f)$  which could greatly exceed unity if  $T_g \gg T_f$  as well as the increase in atomic concentration ( $R_n$ ). Therefore, the crossover point between AFL and AE could be substantially below 3250 Å which is the approximate crossover point for detection limits with flames in AFL or AE.

#### *Optimum methods (s) for trace metal analysis*

From the foregoing comments, it is evident that the graphite cell atomizer should produce considerably greater signals for all elements measured by AA, AE or AF than can be obtained using the same concentration in a flame atomizer. The improvement should be significant for the more volatile elements, e.g. Cd, Zn, Tl, Hg, Se, Te, Ga, In, etc., but should be immense for the less volatile elements, e.g. Be, Si, Al, Zr, Hf, Mo, W, etc.

When using either flame or graphite cell atomizers, the combination of AFL and AE should be an optimum in terms of sensitivity, i.e. lower limits of detection should result by using AFL and AE than by AA. With flames, AFL should produce lower limits of detection for elements with resonance lines less than about 3250 Å and AE should produce lower limits of detection for elements with resonance lines above about 3250 Å.

An additional advantage to the combination of AFL with AE for trace element analysis is that the same instrument can be optimally used for both methods. In fact, since both methods are based on low level light emission, the optimum detection system of photon counting can be used. The major source of noise in such a system should be statistical noise, i.e. the signal-to-noise ratio is equal to the square root of total counts, if the signals are a result of integration. By means of a discriminator on the input signal, it is possible to eliminate leakage current, stray pickup, and dynode pulses as well as to minimize the effect of cosmic ray pulses on the total signal. With such a system in AF, a correction would be necessary for thermal emission. Actually the ideal system for AF would involve the use of a modulated source and a reversible counter so that the counter would count in the positive direction during excitation and in the negative direction during non-excitation (periods of excitation equal periods of non-excitation). In this manner, the

thermal emission signal, due to the element of interest, would be minimized. This latter system is called synchronous photon counting and would be similar in principle to the analogue method consisting of a chopper and lock-in amplifier.

## EXPERIMENTAL RESULTS ON ATOMIC FLUORESCENCE IN NON-FLAME CELLS

### Previous work

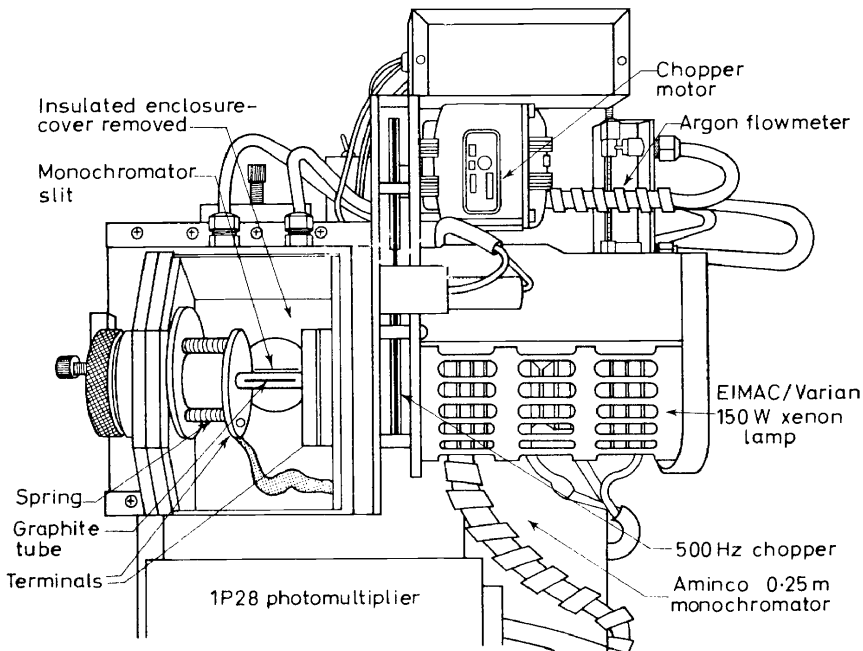
Massman<sup>17</sup> first demonstrated the usefulness of graphite cells for atomic fluorescence spectrometry. With a heated graphite cell ( $T = 2873^\circ\text{K}$ ) in an argon atmosphere, he was able to detect  $4 \times 10^{-14}$  g of Zn,  $2.5 \times 10^{-13}$  g of Cd,  $1.5 \times 10^{-12}$  g Ag, (high intensity sources were available for Zn, Cd and Ag),  $2 \times 10^{-10}$  g of Sb,  $3 \times 10^{-9}$  g of Fe,  $2 \times 10^{-9}$  g of Tl,  $3.5 \times 10^{-11}$  g of Pb,  $3.5 \times 10^{-12}$  g of Mg,  $4.5 \times 10^{-10}$  g of Cu (fairly intense sources were available for the remaining elements). Since high intensity sources were not available for Sb, Fe, Tl, Pb, Mg and Cu, atomic fluorescence gave poorer limits of detection than atomic absorption. The relative standard deviations for both atomic absorption and atomic fluorescence were between 4 and 12 per cent. Sample sizes for absorption and fluorescence were 100  $\mu\text{l}$  or less and 30  $\mu\text{l}$  or less, respectively. If an integrated signal were measured (peak area measured) rather than an instantaneous signal (peak height measured), then the results were essentially independent of the matrix composition. Since the monochromator was apparently not well shielded from the glowing graphite cell, the fluorescence signal was superimposed on a huge background when using a signal-beam unmodulated system. The background was minimized by use of a modulated source and a frequency selective amplifier. Although no results were obtained in the vacuum u.v. region, a major advantage of the graphite cell system was that measurements could have been made in the short wavelength region ( $< 1950 \text{ \AA}$ ) since the vaporized sample was in an argon atmosphere.

West and Williams<sup>21</sup> more recently constructed a carbon filament (1 to 2 mm diameter) within a chamber with quartz windows. Atomization of small samples of aqueous solution (5  $\mu\text{l}$ ) pipetted upon the filament was achieved by passage of a current of about 100 A for about five seconds (the carbon filament was at about  $2000^\circ$  to  $2500^\circ\text{K}$ ). The carbon filament was flushed with argon to maintain an inert atmosphere. The limits of detection for magnesium and silver were about  $10^{-15}$  g and  $10^{-10}$  g respectively, and a precision of better than 30 per cent was obtained for magnesium samples above the limit of detection. The advantages stressed by West and Williams were increased atomization, simplicity and safety of operation, small sample size compared to flames, a lack of memory effects, and probably no matrix effects. The disadvantages of the system appear to be the poor precision, the sampling difficulties, and the relatively poor linearity of analytical curves.

### Our work on a graphite cell furnace for atomic fluorescence

Mr Fraser in my laboratory has constructed a graphite cell system for atomic fluorescence studies<sup>37</sup>. The system is shown schematically in *Figure 1*. Sample solutions are introduced into the cell by means of a hypodermic syringe and needle inserted through a rubber septum in the front of the cell housing.

Therefore, samples can be introduced without opening the front door on the cell compartment, and so time per determination is short and only a minimum flowrate of argon is needed to maintain a continuously flushed cell. New graphite tubes (see *Figure 2*) can be introduced into the cell housing by opening the front door of the housing and releasing a spring mechanism holding the tube in place. The monochromator is a  $\frac{1}{4}$ m Czerny-Turner grating system. A 1P28 multiplier phototube is used as the detector. The



*Figure 1.* Schematic drawing of graphite cell system in atomic fluorescence

source is a 150 W concentrated xenon arc lamp from EIMAC. Also electrodeless discharge tubes will be used. The source radiation is modulated at 500 Hz by a mechanical chopper which also modulates a reference signal used to gate the photon counter detection system with a low level discriminator. The graphite tube has slits cut in such a manner that any black body radiation emitted by the inner back wall of the tube does not reach the monochromator entrance slit. In addition, there is a baffle in front of the graphite tube to minimize pick up of black body radiation by the monochromator. The graphite tube is heated by an ordinary electric welder capable of a 300 A output.

At the time of this report, no results had been obtained using the above system.

#### **Our work on a heated platinum loop for atomic fluorescence**

By simple electrical heating in an inert atmosphere of a platinum loop with analyte solution, atomization of many elements can be effected<sup>53</sup>. A schematic

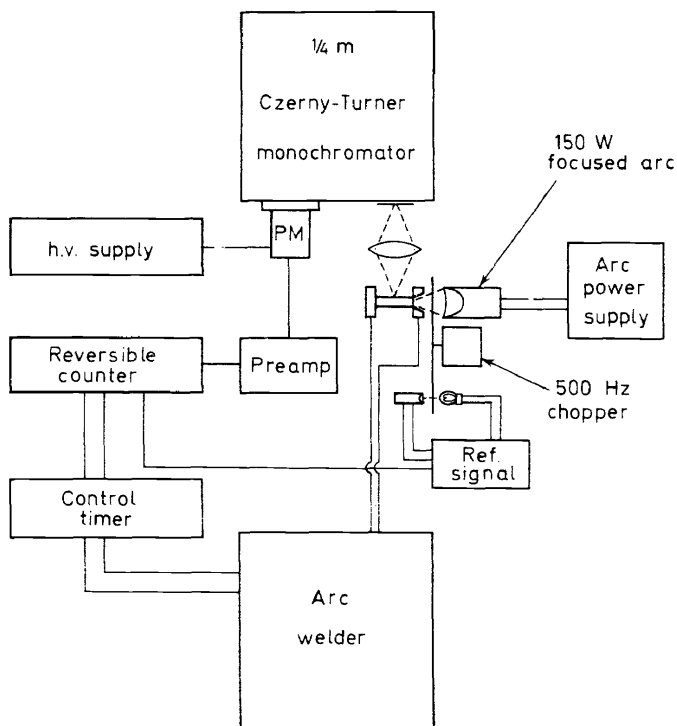


Figure 2. Schematic drawing of cell housing of graphite cell system in atomic fluorescence

diagram of the system is given in *Figure 3*. The resulting atomic vapour is then excited by means of radiation from electrodeless discharge tubes and the transient atomic fluorescence signal measured using a d.c. electrometer recorder system<sup>54</sup>. Samples are applied to the loop either by means of a Hamilton syringe or by dipping the loop into the appropriate solution

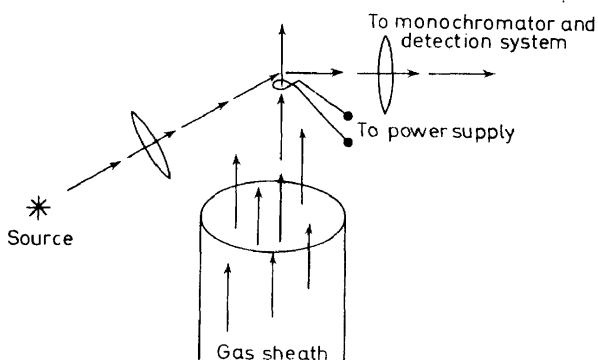
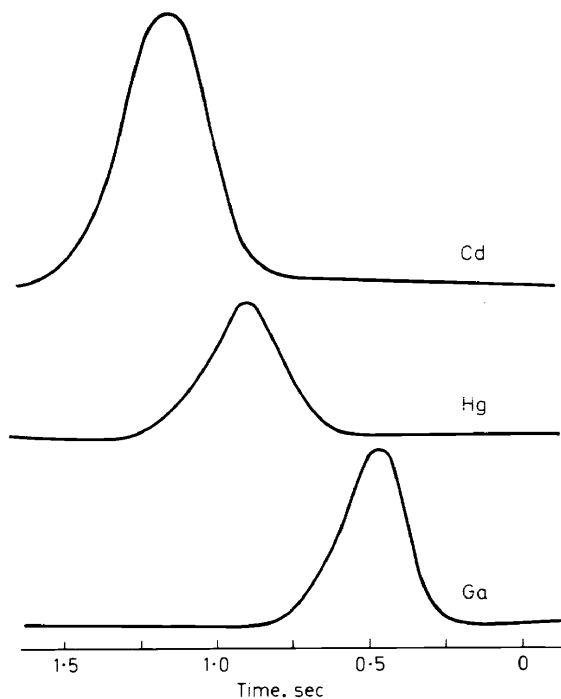


Figure 3. Schematic drawing of platinum loop device for atomic fluorescence

(precision of  $\pm 8$  per cent). The platinum loop was heated by means of a current through the loop. The rate of vaporization and atomization was dependent upon the element, e.g. gallium compounds vaporized almost instantaneously, whereas cadmium and mercury required about one second before a signal was observed (see *Figure 4*). Several sheath gases (oxygen, nitrogen, argon,



*Figure 4.* Vaporization rate of aqueous solutions [10  $\mu$ l of Cd (1 p.p.m.), Hg (10 p.p.m.), and Ga (100 p.p.m.)] using the platinum loop method

air, carbon dioxide) were used for cadmium, mercury and gallium and for all three metals, the atomic fluorescence signal in argon was greatest. The relative signals for the Cd 2288 Å line in argon, nitrogen, air, carbon dioxide, nitrous oxide and oxygen were: 1.00, 0.68, 0.28, 0.24, 0.18 and 0.06, respectively. The relative signals for the Hg 2537 Å line in the same gases were 1.00, 0.81, 0.02, 0.34, 0.00 and 0.00, respectively. The relative signals for the Ga 4033 Å in argon, carbon dioxide, nitrous oxide, oxygen, nitrogen and air were: 1.00, 1.18, 0.93, 0.85, 0.83 and 0.83. The relative signals for the Ga 4172 Å line were approximately the same. The sheath gas has two major effects: variation of non-radiative deactivation processes; and variation of oxygen content of the atmosphere.

The influence of several interferents upon the peaks of the signal versus time distribution were also studied. The effect of  $10^2$ ,  $10^3$  and  $10^4$ -fold excess of carbonate, silicate, sulphate and phosphate on the atomic fluorescence of Ga, Cd and Hg was investigated. Carbonate at any of the above excesses did

not interfere. Silicate ( $10^4$ -fold excess) caused a reduction of about one third in the peak size. A  $10^3$ -fold excess of silicate did not interfere. A  $10^3$ -fold excess of sulphate resulted in about a 67 per cent increase in signal and a  $10^4$ -fold excess an increase of about fivefold. A  $10^3$ -fold excess of phosphate caused a four-to-five-fold increase in the signal but a  $10^4$ -fold excess caused no interferences. The limits of detection for cadmium, mercury and gallium were:  $10^{-15}$  g,  $10^{-8}$  g and  $10^{-7}$  g, respectively.

## APPENDIX 1

### Intensity Expressions for Dilute Gases in Atomic Spectrometry

For the following equations to be valid, the following conditions and assumptions must be valid.

(i) The same metal resonance line broadened only Lorentzian (collisions with foreign species) and Doppler (thermal motion) broadening is considered for each method. The assumption allows the use of well-known expressions<sup>34</sup> for the limiting case of a dilute atomic gas.

(ii) The cell has a constant concentration of atomic vapour in the measured volume. The temperature of the vapour in the measured region is also constant and the gases are essentially in thermodynamic equilibrium.

(iii) In absorption and fluorescence, the atomic vapour is uniformly illuminated. In fluorescence, fluorescence radiation is measured along the entire width of excited vapour. In absorption, emission and fluorescence, it will be assumed that the same fraction of absorbed, emitted and fluoresced radiation is measured. The fraction measured depends directly upon cell design, entrance optics to the monochromator, the monochromator entrance slit and the monochromator optics.

(iv) In the case of absorption and fluorescence, either a line (L) or continuum (C) source is used for excitation of the vapour. The line source has a half-width of the order of or narrower than the absorption line half-width. The continuum source is essentially constant in intensity across the width of the absorption line and across the spectral band-width of the monochromator.

(v) The same instrumental system entrance optics, monochromator, photodetector and measurement electronics are used for all three methods.

From the review by Winefordner, Svoboda and Cline<sup>51</sup>, the radiant flux expressions for atomic absorption (AA), atomic emission (AE), and atomic fluorescence (AF) spectrometry with the same atom reservoir assuming the atomic vapour is dilute are given by:

$$\Phi_{AA(C)} = \Theta_E \kappa_0 I \Omega_A B_{\lambda_0}^C n_0 / 2(\ln 2)^{\frac{1}{2}} \quad (16)$$

$$\Phi_{AA(L)} = \Theta_A \kappa_0 I \delta \Omega_A B^L n_0 \quad (17)$$

$$\Phi_{AE} = \Theta_E \kappa_0 I \Omega_E B_{\lambda_0}^B n_0 \cdot 2(\ln 2)^{\frac{1}{2}} \quad (18)$$

$$\Phi_{AF(C)} = \Theta_A \kappa_0 I \Omega_A B_{\lambda_0}^C n_0 Y \Omega_F / 8 \{ \pi \ln 2 \}^{\frac{1}{2}} \quad (19)$$

$$\Phi_{AF(L)} = \Theta_A \kappa_0 I \delta \Omega_A B^L n_0 Y \Omega_F / 4\pi \quad (20)$$

where  $\Phi$  denotes radiant power absorbed in AA, emitted in AE or fluoresced

in AF from atomic reservoir,  $\text{erg sec}^{-1}$ ;  $\Theta_E, \Theta_A$  are areas over which emission occurs and absorption occurs respectively,  $\text{cm}^2$ ;  $\kappa_0$  is the specific absorptivity at line centre for pure Doppler broadening, i.e.  $\kappa_0 = k_0/N_0$ ,  $\text{cm}^{-1} \text{cm}^3$ ;  $k_0$  is the peak absorption coefficient at  $\lambda_0$  for pure Doppler broadening,  $\text{cm}^{-1}$ ;  $n_0$  is the concentration of ground state atomic species of concern,  $\text{atoms cm}^{-3}$ ;  $\Omega_A, \Omega_E, \Omega_F$  are the solid angles over which excitation is effected in AA, emission is measured in AE and fluorescence is measured in AF.  $\Omega_A = \Omega_E = \Omega_F = \Omega$ ;  $B_{\lambda_0}^B$  is the spectral radiance of a black body radiator at temperature,  $T$ , of the atom reservoir and at the peak emission wavelength,  $\lambda_0$ ,  $\text{erg sec}^{-1} \text{cm}^{-2} \text{\AA}^{-1} \text{sr}^{-1}$ ;  $B_{\lambda_0}^C$  is the spectral radiance of a continuum source at the peak absorption wavelength,  $\lambda_0$ ,  $\text{erg sec}^{-1} \text{cm}^{-2} \text{\AA}^{-1} \text{sr}^{-1}$ ;  $B^L$  is the radiance of a line source at  $\lambda_0$ ,  $\text{erg sec}^{-1} \text{cm}^{-2}$ ;  $l$  is the path length over which absorption occurs in AA and AF and over which emission occurred in AE;  $\Delta\lambda_D$  is the Doppler half-width of the absorption line,  $\text{cm}$ ;  $\delta$  is the correction factor to account for the shape and width of the exciting line in AA or AF and for broadening of the absorption line by collisional as well as Doppler broadening<sup>55</sup>, no units; and  $Y$  is the quantum yield of resonance transition, no units.

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