

1.4 ELECTROTHERMAL ATOMIZERS

The past year has seen continued intense activity in the field of atomizer improvements. There now appears to be a general realization that isothermal heating is necessary for minimum interferences and maximum sensitivity. Towards this end, the graphite platform previously proposed by L'vov (*ARAAS*, 1976, 6, Ref. 1141), has been adopted by many workers and its utility is gaining widespread acceptance. What is however surprising is the *ad hoc* use of various matrix modifiers. It is to be hoped that a more rational use of these aids will develop in the future.

1.4.1 Atomizer Design

Atomic spectroscopic methods have often been criticized in that they are not absolute methods of analysis. The concept of an *absolute method* in ETA, originally expounded by L'vov (see *ARAAS*, 1978, 8, Ref. 1392) is without doubt an attractive one. Chakrabarti and his co-workers (C612, 1057, 1070, C1167, C1458) may have achieved significant progress towards this goal. The capacitively heated anisotropic graphite atomizer reported previously (see *ARAAS*, 1979, 9, 25) is now claimed to be "almost" the ultimate in ETA. The authors state that it is free from all interferences, since all of the sample is atomized. The method requires only single-point calibration, since using appropriate proportionality factors, absorbance is directly related to analyte mass. The papers on this work are of great interest since they may well be describing what is close to the ultimate in electrothermal atomizer design. Such extravagant claims, however, coming in the wake of reality about the ICP, make the publication of an independent appraisal of ETA heated by capacitive discharge an eagerly awaited event.

Much work on attempts to achieve a closer approximation to atomization under *isothermal conditions* is still in evidence. Woodriff and Nichols (C114) have further modified their constant temperature furnace to give greater temperature uniformity (both spatial and temporal). To their "T" shaped atomizer, these workers have added two end posts which conduct current from the electrical connections at the base of the furnace assembly. This modification was claimed to reduce temperature variations significantly along the 26-cm length of the atomizer, giving less than a 30 K temperature gradient. The more isothermal environment was claimed to allow interference free atomization, at often as little as 300 K above the analyte appearance temperature. Similarly, Slavin *et al.* (509, C605) modified a commercial ETA of the Massmann design, by contouring the atomizer tube; in this case the temperature gradient was reduced to 100 K. No significant improvements in sensitivity were recorded by the authors. An interesting modification to the mini-Massmann type atomizer was described by Lawson and Woodriff (1261). By replacing the conventional

centre supports for this furnace by two-pronged supports that held the atomizer tube at both ends, the current was made to flow across the atomizer ends thus heating the centre by conduction only. This resulted in an initial temperature gradient of 700–900 K between the centre and the ends. Interferences on Pb were decreased, presumably due to a reduction in condensation at the tube ends and a hotter vapour-phase environment for atomization.

Use of the *L'vov platform* (see *ARAAS*, 1976, 6, Ref. 1141) continues to be advocated by many workers and Slavin and Manning (1256) have reviewed the "state of the art" regarding this device. The advantages to be gained from the use of this simple modification are now well documented and it has been shown to be a genuinely practical way of reducing molecular interferences. One unforeseen advantage of platform atomization was reported by Ottaway and co-workers (1233, C1724) who found it most effective when measuring AE signals from a graphite furnace. The platform system was used with an echelle spectrometer-based instrument, custom built specifically for emission work. Compared to previous work, improved detection limits were reported for 14 out of the 15 elements studied. Another device designed by L'vov, intended for sampling into a constant thermal environment, was the tungsten loop (see *ARAAS*, 1978, 8, Ref. 1027). This sampling technique has not reached the degree of development of the platform, and Manning and Slavin (C104) described problems associated with tungsten carbide formation resulting in melting of the probe. When they replaced this by a flat graphite rod or probe, higher working temperatures could be used, although analytical precision was poor. The authors attributed this to the variable porosity of the graphite substrate. A modified approach using a similar tungsten-probe sampling system was described by Cedergren *et al.* (C1170). With this device the pyrolysis products, formed during vaporization, were mixed with a gas buffer then passed through two equilibrium zones. Since the residence times of the atoms in this system were of the order of seconds, there appears to be a higher probability of these atoms attaining a state closer to thermal equilibrium. High temperature equilibrium calculations were used to determine the ideal composition of the gas atmosphere.

The study of *atomization surfaces* is of interest now, as workers become more aware of the effects of surface interactions on atomization. Almeida and Seitz (C96) have described a technique for the preparation of carbide-coated tubes. Graphite tubes were soaked in solutions of Mo, Ti or W chlorides under slight negative pressure. The chlorides were then hydrolysed prior to firing the tube at high temperature to form the carbide. Titanium and W carbide coated tubes proved the most successful; tubes coated with Mo tended to deform and chip. Verwolf *et al.* (C100) have advocated the use of vitreous carbon rather than pyrolytic graphite as an atomization substrate. They have studied the physical and electrical properties of vitreous carbon and concluded that only minor design changes would be required to present atomizers to allow the use of this alternative. Another interesting surface modification was described by Bath (C112), *i.e.*, Cu was electroplated on to a standard graphite tube as an aid to the atomization of As. Two-fold enhancements of the As signal were recorded compared to standard tubes, but no enhancements were found when Cu was added to the sample solution.

Papers on the use of *metals as atomizers* were less prevalent this year and only a few workers continue to investigate this alternative. Sychra and co-workers (C1549) have further improved their W tube atomizer to facilitate controlled heating at rates of up to 20 K ms⁻¹. Bezak and Vasiliev (1109) have employed a Ta foil boat (Donega and Burgess, *Anal. Chem.*, 1970, 42, 1521) atomizer operated within a vacuum chamber. Low pressure operation was found to be detrimental to sensitivity.

Other references of interest —

Sample introduction : 1496.

Temperature measurement : 1684.

1.4.2 Atomization and Excitation

L'vov and Pelieva have continued their investigation into the *mechanism of atomization* involving the formation of *gaseous monocyanoïdes* (see *ARAAS*, 1979, **9**, 26). They have calculated the atomization energies for gaseous molecules of alkali-metal monocyanoïdes (895), and Ba, Ca and Sr monocyanoïdes (1342). In the former case, the values calculated agreed well with tabulated dissociation energies of monofluoride, whereas in the latter work, the existence of the metal cyanide molecules was confirmed by identification of their emission and absorption molecular spectra. In further work (1685), a statistical thermodynamic approach was incorporated using a rigid-rotor/harmonic oscillator method to calculate the free-energy function. Equilibrium constants were calculated from integral absorbance values and hence dissociation energies for first row transition-metal monocyanoïdes determined. The author concluded that the gaseous monocyanoïdes were more stable than the chlorides. In a parallel study, L'vov and co-workers (1574) calculated the heat of formation of C_2 molecules in graphite furnaces at 3000–3400 K. They compared two techniques, involving emission and absorption at the edge of the Swan band at 516.5 nm and determined values of 891 ± 37 and 851 ± 37 kJ mol⁻¹. Using error analysis, the absorption method was shown to be inferior in accuracy to the emission technique. Kitagawa *et al.* (472) have calculated degrees of atomization for all atoms extrapolated from experimental measurements of CuCl molecular emission and Cu atomic emission. The degree of atomization was found to be not purely a function of temperature and could be doubled by the introduction of a small percentage of H_2 .

Several *methods and models* have been proposed by numerous workers as an aid to the understanding of *atomization processes*. One of the most comprehensive was that advocated by Frech and co-workers (C1171, C1460) who employed high temperature equilibrium calculations. This approach has been used to advantage to predict the optimum conditions required for the atomization of Si (478) and P (1704). Silicon atoms were formed from SiO(g) or SiC(s) depending on temperature. Phosphorus was shown to be formed *via* its oxide species PO and PO₂, at temperatures below 1800 K, whereas above this, an equilibrium between P₂ and P was predicted. In this study, the molecular spectra were measured to verify the theoretical predictions. Such calculations have been shown to provide reliable results, provided that equilibrium can actually be achieved, *i.e.*, atomizers are operated under isothermal conditions. In commercial non-isothermal atomizers, however, the kinetics of the processes must be considered. Akman *et al.* (1220) described a simplified mathematical analysis of atom formation in such a commercial atomizer, using first order kinetics. A kinetic approach was also used by L'vov and his group (1531) to investigate the atomization mechanism for group IB and VIIIB elements in both graphite and Ta-lined commercial atomizers. The activation energy was shown to be dependent on the nature of the surface but independent of the condition of the surface.

In elegant studies on *analyte ionization*, using microwave attenuation methods, Sturgeon *et al.* (C609, C1150, 1378, C1459) determined the electron concentrations in both graphite and Ta atomizers. They obtained values of 2.5×10^{11} to 7.8×10^{12} cm⁻³ in the temperature range 2470–3000 K in graphite atomizers and 1.1×10^{12} to 8.7×10^{12} cm⁻³ in the range 2413–2743 K for Ta. Ionization, it was concluded, was negligible for elements of ionization potential greater than 4.2 eV in Ta atomizers and 4.5 eV in graphite atomizers.

Ishibachi and Kibuchi (520) have studied *diffusion effects* for atoms in various sheath gases in furnace atomizers. Using Al, Co and Cu as test elements, the effect of Ar, He, N₂ and mixtures of these with H₂ were studied. It was found that the gas flow-rate was directly related to the logarithm of the absorption signal and that, overall, Ar provided the best sensitivity. Falk and Thann (1229) have continued their investigations into the expansion

processes occurring in the vapour cloud above open atomizers and resolved that these processes could not be fully explained in terms of diffusion alone. L'vov and Polzic (1326) calculated the atom distribution in open atomizers with horizontally and vertically extended atom sources. A simple method was developed to predict the analytical signal, based on diffusion effects in two directions.

The effect of hyperfine structure on Zeeman splitting and line crossing, in *atomic Faraday spectroscopy* was described by Kitagawa *et al.* (2). A theoretical approach was developed that closely agreed with experimental observations. This described the dependence of transmitted intensity on the magnetic field strength for line crossings between two Zeeman components. Atomic Faraday spectroscopy was concluded to be comparable in sensitivity to conventional AAS.

Results of investigations into *calibration graph curvature* in carbon furnace AES were reported by Littlejohn and Ottaway (1121). Self absorption was found to be the most common cause and was shown to be independent of temperature. Self reversal however was only significant at concentrations greater than 1000 times the detection limit and then only for light elements. Curvature in calibration graphs for refractory elements was shown to be due primarily to atomization effects.

1.4.3 Interferences

Without doubt, the most important contribution to the alleviation of interferences has been the trend toward attaining a more isothermal heating environment in ETA. In this context there have been many papers expounding the general utility of *graphite platforms* (C1475, C1477, C1168, C1169). Slavin and Manning (C113) found improvements in the determinations of Al, Cd, Mn and Tl in the presence of halide matrices. Sukhoveeva and co-workers (1328) fabricated platforms from discs cut from graphite electrodes and reported reductions of interferences for Ga and In in chloride media. Better results were however obtained when the discs were pre-treated with solutions of 1% *m/V* ascorbic acid. Tantalum-coated platforms were fabricated in batches by Koirtjohann *et al.* (C103) and used in Ta-coated tubes, prepared according to the procedure of Zatka (ARAAS, 1978, 8, Ref. 950). These platforms were capable of accepting up to 50 μl of solution. In tests using low, medium and high volatility elements in synthetic and natural water matrices; improved performance, close to pure aqueous standards, was achieved. As in the previous reference (1328), the use of a matrix modifier, in this case 0.5% $\text{NH}_4\text{H}_2\text{PO}_4$, reduced all matrix effects to less than 10%. The conclusion to be drawn from studies such as these is that the attainment of a more constant thermal environment during atomization is necessary in order to minimize interference.

Despite the fact that there appears to be a "witches brew" approach to the use of *matrix modification* for the reduction of interferences in ETA, the effectiveness of the technique is reflected in the number of applications in which it has appeared. Itsuki and Ibeda (529) found the addition of La to be advantageous in the removal of interferences occurring from the presence of various cations and organic acids during the atomization of Sn. Various combinations of matrix modifiers and atomization surfaces were investigated by Sefflova and Komarek (1527) in order to find an optimum for the determination of Pb in waters and particulate matter. A combination of atomization from a Ta carbide coated surface in the presence of 1% *m/V* La solution was found to give minimal interferences from phosphate, sulphate and chloride. Soluble organic acids have been previously reported to reduce interference effects in sea-water analysis, and Hydes (991) confirmed that the use of 1% *m/V* ascorbic acid was advantageous in removing such interference effects on Ca, Cu and Mn. Goss (C97) reported that the use of NaBH_4 removed interference effects in the determination of Pb in drinking water, and that this was a superior modifier to ascorbic

acid or La. Matsusaki *et al.* (481) removed chloride interferences on Cr by the addition of an EDTA salt, and Cooksey and co-workers (C101) have advocated the addition of O₂ to the purge gas during ashing, as an effective matrix modifier.

Several important interference studies have been reported concerning the effect of the atomizer surface. Erspamer and Niemezyk (102) concluded that the physical and chemical properties of the atomizer surface play a key role in determining the degree to which the matrix effects the atomization mechanism. Veillon *et al.* (1519) have used a radio-tracer technique with ⁵¹Cr to demonstrate how that element was irreversibly retained by graphite furnace tubes and that the degree of retention varied with matrix and tube condition. Penetration of analyte solution into the graphite tube during the drying stage was cited by Dabeka (C1163, C1404) as being detrimental to analytical accuracy. In this work, the author proposed the theory that previously reported matrix effects are in fact related to problems associated with the drying temperature. The authors however failed to mention the effect of drying rate.

Miller and Sgontz (C559) have noted that poor precision may result from fluctuation in the gas flow between the charring and atomization steps. They proposed the inclusion of a flow stabilization cycle to improve precision.

Other references of interest —

Double peaks : C98, C611, C1149, C1461.

Halide interferences : 189, 1264, 1664.

Isothermal sampling : 429, 902.

Ionization : 521.

Response times : 1275.

1.4.4 Advances in Methodology

One of the main areas of interest this year has been the *interfacing of chromatographic systems*, in particular HPLC systems to conventional electrothermal atomizers. The problems of interfacing HPLC or an ion-exchange column to an electrothermal atomizer were discussed by Chau *et al.* (C1179) who demonstrated the applicability of such techniques to speciation studies of alkyl compounds of As, Pb, Se and Sn. Arsenical pesticide residues and some of their metabolites were similarly determined by Woolson and Ahronson (1622) by coupling an HPLC to the automatic sampler accessory of an electrothermal atomizer. Such systems have been shown to be simple to automate, as was demonstrated by Brinckman (1618) who again determined various alkyl As compounds in soils and drinking water. Various HPLC techniques such as size exclusion and reverse bonded phase were used by the same group (984) to study Si and Sn macromolecules. Tetra-alkyl Pb compounds were separated by conventional GC by De Jonghe *et al.* (486). These authors described an alternative way of interfacing the GC to an electrothermal atomizer, whereby the eluate from the column was run directly into the inner gas purge stream of the graphite furnace, which was maintained at 2000 °C.

Some advances in dealing with problems associated with the atomization of *biological fluids* have been evident. Frigieri and Trucco (1200) concluded that the only effective background correction system for such applications was that based on the inverse Zeeman effect. Similar conclusions were reached by Magyar and Vonmont (1206) who found O₂ source background correction inadequate for the determination of Hg in urine. An alternative to conventional AA analysis of biological fluids was proposed by Ottaway *et al.* (C213, C1725, 1736). These workers reported improved detection limits when graphite furnace AE was used in an instrument employing an echelle spectrometer with wavelength modulation for background correction. An interesting indirect method for the determination of F⁻ in urine and blood

was described by Fuwa and co-workers (1318). The tube was pre-treated with Al and the molecular absorption of AlF was used as a measure of the F⁻ concentration. Results were compared with ion-selective electrode techniques and agreement was found for F in urine but not in blood, where the authors concluded that some F was protein bound.

Carbide-coated tubes are gaining in popularity. L'vov *et al.* determined platinum group metals (383) down to 0.1 ng and Y in steels (821) down to 0.001% using Ta-coated tubes. The necessity for such tubes when determining refractory metals was emphasized by Hanamura (C93), who determined Zr using a Zeeman AA system. Metal carbide tubes have also been used to advantage by Harrison *et al.* (C569) who determined organometallics of groups IVA, VA and VIA. The modified surface was claimed to decrease analyte carbide formation and reduce molecular volatilization.

Other references of interest —

Automated analysis : 87, C1410.

Marine samples : 600, 601, 1659, 1705.

Solid sampling : C827, 883, 1245, C1462, C1561.