Atomizer, Source, Inductively Coupled Plasmas in Atomic Fluorescence Spectrometry (ASIA)

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clinical samples have now been examined successfully by this GCMS approach. It has confirmed that acetyl-, hexanoyl- and octanoylcarnitine were present in elevated amounts in five cases of infants with a deficiency of MCAD. We have identified isovalerylcarnitine in the urine of a patient with isovaleric acidemia. In all these cases the mass spectra of lactones **2** derived from the various acylcarnitines match those of authentic samples. The method should also be useful for drug metabolism studies. In two instances where infants were known to have had a 3-phenylpropanoic acid load, GCMS showed a component with retention time and mass spectrum consistent with the lactone from the metabolite, 3-phenylpropanoylcarnitine. In the urine of an infant on valproic acid (2-propylvaleric acid) therapy, GCMS revealed a compound consistent with the lactone from 2-propyl-3-oxovalerylcarnitine. 2-Propyl-3-oxovaleric acid is known to be the major metabolite of valproate in man.

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Atomizer, source, inductively coupled plasmas in atomic fluorescence spectrometry (ASIA)

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Atomic fluorescence spectrometry has been an active research area for several years. Interest in the analytical capabilities of the technique has increased recently with the introduction of a commercial instrument based on the hollow cathode lamp excitation of atoms generated in an argon inductively coupled plasma (ICP). An alternative approach has been pioneered at Loughborough involving the use of a second ICP as a light source.

The use of an inductively coupled plasma in atomic emission spectrometry (ICPAES) imparts a number of figures of merit to that technique, namely low detection limits, long linear dynamic range and relative freedom from chemical and ionization effects. However, ICPAES is prone to spectral interference, whereas atomic fluorescence spectrometry (AFS) is not. The ASIA system was assembled to demonstrate that the ICP could be used as both a line source and as an atomizer in AFS and also to demonstrate freedom from spectral interference; in addition, it was hoped to show that the other figures of merit exhibited by ICPAES would be retained.

The poster presentation demonstrated that these desirable aims have been largely achieved. Atomic emission and fluorescence spectra were presented showing that well-known spectral interferences which occur in the emission technique, such as background shifts due to radiative recombination, collisional broadening and direct spectral overlap are absent in the fluorescence technique.

This absence of spectral interference in AFS is due to several factors. (1) The fluorescence spectrum is relatively simple, being confined principally to the resonance lines used in the excitation source. (2) Changes in DC signals (i.e. background shifts) are discriminated against by the use of AC electronics in AFS. (3) Before spectral interference can occur in AFS the absorption profile of the interfering element must overlap with the emission profile of the source. (4) Interference will not occur unless the population of the interfering element in the correct energy level (usually the ground state) is significantly high. (5) Interference will not happen unless the quantum efficiency is significantly high at the wavelength concerned.

Data were presented showing linear dynamic ranges of some five to six orders of magnitude for the ASIA system, evidence of relative freedom from chemical matrix effects and ionization interference and detection limits in the p.p.b. region. It was also demonstrated, by curves of growth, that the ICP is a line source.

Application of furnace atomic non-thermal excitation spectrometry for the determination of non-metals

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Various atomic spectrometry techniques are used for the determination of elemental concentrations in a wide range of samples. Although procedures for the determination of metallic impurities are well established, the development of successful methods for the measurement of non-metal elements at trace levels has proved more difficult. In particular, better methods are required for the determination of B, Cl, P, S, Si, etc., in industrial and clinical samples.

There is currently considerable interest in the development of new types of excitation source for the determination of metals and non-metals by atomic emission spectrometry. Most of the studies involve high-energy helium plasmas which are capable of generating atomic and ionic emission from elements at the level of 1 $\mu g\ g^{-1}$ or 1 $\mu g\ l^{-1}$. One of the main problems encountered in the use of analytical helium plasmas is the disruption of the discharge when the sample material is vaporized. This problem has been addressed in furnace atomic non-thermal excitation spectrometry (FANES) by combining the systems used to atomise and excite the sample components. In FANES, a hollow cathode discharge is generated inside an electrothermal atomizer tube operated at a pressure of 10–20 Torr (*ca.* 1.3–2.7 kPa) (Littlejohn *et al.* 1983; Falk *et al.* 1984). The graphite tube acts as the hollow cathode as well as the vaporizing device. The sample is deposited as a solution (typically 20 μl) into the graphite tube at atmospheric pressure. The solvent is evaporated and the residue charred by electrothermal heating to remove some of the matrix. The atomizer is then evacuated and filled with helium to a pressure of 10–20 Torr, for the establishment of a discharge. Once the plasma is formed, the graphite tube is heated rapidly to temperatures in excess of 2000 °C to vaporize and atomize the sample. Excitation of analyte atoms in the discharge gas is caused mainly by electron collisions and when helium is used as the plasma gas, the