

## Summaries of Papers in this Issue

### Development and Optimisation of Atom Cells for Sensitive Coupled Gas Chromatography - Flame Atomic-absorption Spectrometry

The development of four novel atom cells for the determination of volatile organometallic compounds by coupled gas chromatography - flame atomic-absorption spectrometry is described. Tetraalkyllead compounds provided a model system in the optimisation of the four atom cells by the variable step-size simplex method. The effects of the various parameters on analytical performance are discussed. In the most sensitive system presented the effluent from the chromatograph was fed to a small hydrogen diffusion flame and the atoms from this flame were swept into a flame-heated ceramic tube. This simple, readily demountable arrangement enjoys the advantages of continuous operation associated with flames but, because of the relatively long atomic residence times, gave detection limits of 17 pg for both tetraethyl- and tetramethyllead. These limits are superior to any previously reported for a gas chromatographic - atomic-absorption spectrometric technique, including those employing electrothermal atomisation.

*Keywords:* Gas chromatography; flame atomic-absorption spectrometry; simplex optimisation; trace metal speciation; alkyllead compound determination

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### Study of the Use of Soil Suspensions for the Determination of Iron, Manganese, Magnesium and Copper in Soils by Flame Atomic-absorption Spectrometry

A method is described for the direct, routine atomic-absorption spectrometric determination of copper, iron, manganese and magnesium in soil samples of the terra rossa and peat types. An investigation was made of the factors influencing the atomisation efficiency of these elements when suspensions of soil samples were aspirated into the flame. Particle size, flame temperature and position in the flame were found to be critical in determining the fractions of particular elements atomised. Special emphasis was given to the preparation of the soil suspensions, which is the most critical step in the whole analytical procedure. Magnetic and ultrasonic devices were used for stirring purposes. The latter proved to be more efficient, particularly when suspensions of high clay content soils are being prepared. An average standard sample made for each soil type was used for calibration. Test analyses of two sets of soil samples showed that the majority (80-90%) of samples can be analysed with an accuracy of  $\pm 20\%$ . This should be acceptable in most applications where a large number of samples are to be analysed. Considerable amounts of time and chemicals can be saved. The method was also found to be suitable for the determination of lithium, calcium, strontium, barium, aluminium, chromium and titanium.

*Keywords:* Iron, manganese, magnesium and copper determination; soil samples; soil suspensions; flame atomic-absorption spectrometry

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**Rapid Hydride Evolution - Electrothermal Atomisation  
Atomic-absorption Spectrophotometric Method for Determining  
Arsenic and Selenium in Human Kidney and Liver**

A rapid semi-automated electrothermal atomisation atomic-absorption spectrophotometric procedure has been developed for the determination of arsenic and selenium in human liver and kidney specimens. The sample is digested with a mixture of nitric and perchloric acids. The nearly dry residue is taken up in hydrochloric acid. The arsenic or selenium in the hydrochloric acid solution is converted into its hydride with sodium tetrahydroborate(III). The hydride is decomposed and atomised in an electrically heated silica furnace, and the atomic-absorption signal is measured at the appropriate resonance wavelengths of arsenic and selenium. Both of the elements can be determined in the biological samples in the range 50–500 ng per gram of wet sample. The method was applied to the determination of arsenic and selenium in about 40 autopsy samples of human kidney (cortex and medulla) and liver taken from Canadian adults living in the Great Lakes Region of Ontario. The arsenic levels in all of the samples analysed were found to be  $\leq 10$  ng per gram of wet sample; the median selenium levels in the cortex, medulla and liver were found to be 0.84, 0.31 and 0.39 mg per kilogram of wet sample, respectively.

*Keywords: Arsenic and selenium determination; hydride evolution; electrothermal atomisation; atomic-absorption spectrophotometry; human kidney and liver*

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**Reduction of Matrix Interferences in the Determination of Lead in  
Aqueous Samples by Atomic-absorption Spectrophotometry with  
Electrothermal Atomisation with Lanthanum Pre-treatment**

A previous paper described a lanthanum pre-treatment procedure for overcoming matrix interferences in the determination of lead in drinking water. In this paper, the amounts of lanthanum and nitric acid employed have been optimised such that the technique is now applicable to a wide range of aqueous samples, for example river waters, borehole waters, sewage effluents and trade effluents. The technique has been tested and found to be satisfactory for samples containing up to 1150 mg l<sup>-1</sup> of chloride, 1420 mg l<sup>-1</sup> of sulphate, 760 mg l<sup>-1</sup> of sodium and 1530 mg l<sup>-1</sup> total hardness (as calcium carbonate). The optimum pre-treatment conditions for samples was 1% V/V nitric acid and 0.05% m/V of lanthanum (as lanthanum chloride), which completely overcame suppressive interferences in the determination of lead, and gave a furnace tube lifetime of approximately 600 firings. This investigation enabled a close study to be made of the processes by which interferences are overcome by nitric acid - lanthanum matrix modification, and some possible mechanisms are presented and discussed.

*Keywords: Lead determination; aqueous samples; lanthanum pre-treatment; electrothermal atomisation; interference mechanisms*

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### A Study of Pneumatic Nebulisation Systems for Inductively Coupled Plasma Emission Spectrometry

The analytical performance of different pneumatic nebulisers and cloud chambers for inductively coupled plasma emission spectrometry is reported. A vortex cloud chamber and a double-pass cloud chamber were compared for use with concentric glass nebulisers. An all-plastic double-pass cloud chamber was preferred. Two new nebulisers for solutions containing high levels of dissolved solids or slurries are described. One of these, machined entirely from inert plastic, gave an improved performance compared with a glass concentric nebuliser and no problems were encountered with the nebulisation of solutions containing 20% *m/V* of dissolved solids or slurries.

*Keywords:* Pneumatic nebulisers; inductively coupled plasma; atomic-emission spectrometry; cloud chambers; slurries

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### Apparent and Real Reducing Ability of Polypropylene in Cold-vapour Atomic-absorption Spectrophotometric Determinations of Mercury

Experiments undertaken with polypropylene reaction flasks in connection with the Perkin-Elmer MHS-1 Mercury/Hydride System show that polypropylene very quickly adsorbs tin(II) chloride, which is not then removed by usual routine rinsing. This can cause mercury to be lost rapidly from solutions stored in uncleaned flasks as well as giving signals for mercury in cold-vapour atomic-absorption methods even if reductant is not added. This apparent ability of polypropylene to reduce mercury(II) is rapid and ceases with careful cleaning of the apparatus. This apart, the polypropylene reaction flasks have a real, relatively slow, but considerable ability to reduce mercury(II), which was especially conspicuous if solutions without preservatives were agitated in them.

*Keywords:* Mercury(II) determination; reduction by polypropylene; atomic-absorption spectrophotometry; cold-vapour method

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### 1,2,4,6-Tetraphenylpyridinium Perchlorate as a Reagent for Ion-association Complex Formation and Its Use for the Spectrophotometric Determination of Thallium

The synthesis, characteristics and applications of 1,2,4,6-tetraphenylpyridinium perchlorate (TPPP) as a reagent for the formation of ion-association complexes is described. This reagent forms a 1:1 complex with  $\text{TiCl}_4^-$  ( $\lambda_{\text{max}}$ , 310 nm, molar absorptivity  $3.14 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ ) that is slightly soluble in water and can be extracted with isopentyl acetate with an extraction efficiency of 97.9%. The  $\text{TiCl}_4^-$  - TPP<sup>+</sup> complex obtained is useful for the spectrophotometric determination of thallium in the concentration range 0.05–0.8 p.p.m., and the method is applicable to the determination of thallium in sphalerites and zinc concentrates.

*Keywords:* 1,2,4,6-Tetraphenylpyridinium perchlorate; ion-association complex; thallium determination; spectrophotometry

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### **Spectrophotometric Determination of Nitrate in Vegetable Products Using 2-sec-Butylphenol**

A procedure is described for the determination of nitrate in vegetable products, based on the quantitative reaction of nitrate and 2-sec-butylphenol in sulphuric acid (5 + 7), and the subsequent extraction and measurement of the yellow complex formed in alkaline medium. The colour reaction is sensitive and stable and absorbances measured at 418 nm obey Beer's law for concentrations of nitrate-nitrogen between 0.13 and 2.50  $\mu\text{g ml}^{-1}$ . Various possible interferences in vegetable products do not interfere with the nitration of 2-sec-butylphenol. Recoveries of nitrate from vegetable products were satisfactory and the standard deviation for the whole procedure was 1.41% for the 42 determinations; the detection limit of the method is 1.3 p.p.m. for nitrate-nitrogen.

*Keywords:* Nitrate determination; vegetable products; 2-sec-butylphenol; spectrophotometry

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### **Determination of Thiol Concentrations in Haemolysate by Resonance Raman Spectrometry**

A simple and sensitive method for determining the thiol concentration in haemolysate, using the resonance Raman spectrum of the product of the reaction of the lysate with 5,5'-dithiobis(2-nitrobenzoic acid) (Ellman's reagent), is described. The method uses a signal due to the haem ring of haemoglobin as an internal calibrant. In six separate determinations of the thiol concentrations in the lysate from a normal male volunteer, the average thiol concentration was 1820  $\mu\text{M}$  and the relative standard deviation was 4.5%. Standard addition of glutathione to four lysate samples confirmed this result and indicated an acceptable precision. To obtain a comparison with another technique, clear lysates were prepared by precipitation of haemoglobin and addition of sufficient glutathione to maintain thiol levels comparable to those of coloured lysates. Agreement between the resonance Raman method and a spectrophotometric method was acceptable in this instance. The method is relatively free from the standard interferences found for spectrophotometric assays and is selective. The mean value for the lysate from six normal male volunteers ( $1920 \pm 88 \mu\text{M}$ ) and from seven patients with rheumatoid arthritis ( $3240 \pm 774 \mu\text{M}$ ) were significantly different, suggesting that this measurement may have relevance in the study of disease processes.

*Keywords:* Thiol determination; haemolysate; resonance Raman spectrometry

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