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Flow Injection Techniques

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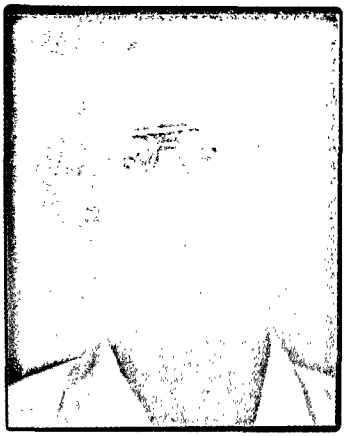
The limitations of annular inductively coupled plasma (ICP) sources in terms of their ability to form atoms or ions from material injected into the central channel are now widely recognized. Consequently, there is growing interest in the use of sample preparation and introduction procedures, appropriate for the material under investigation and the nature of the analytical problem, which can alleviate some of these limitations. Sample preparation and introduction topics formed the basis of numerous presentations at the conference.

The session on flow injection (FI) techniques, held early in the week, was particularly well attended. Topics presented covered the main uses of FI in conjunction with plasma instruments, namely (a) dilution of solutions for calibration purposes and for matrix interference reduction, (b) matrix removal and discrete volumes, (c) chemical vapor generation, and (d) matrix removal and preconcentration. Some of the talks also indicated the possibilities of FI techniques for speciation studies and for field sampling.

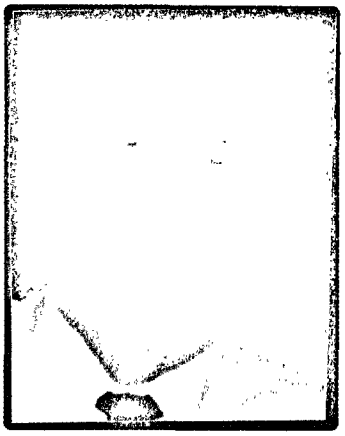
In his opening invited lecture, Professor Jarda Ruzicka (University of Washington, Seattle) once again demonstrated his unfailing ability to continue to produce new ideas for the use of flow injection and sequential injection techniques. He showed some intriguing possibilities for the manipulation of micro-bead reagents in flow systems. His continued enthusiasm for the novel features of sequential injection (SI) is hard to resist and surely at the Winter Conference in 1996, there will be presentations on the use of ICP-based detection with SI sample handling.

Maria Giné (University of Sao Paulo, Piracicaba, Brazil) reported on developments in her laboratory's computer controlled microsampling FI device for ICP-OES. The improved precision obtained with tandem injection (50 aliquots of 5 µl) when the injection was synchronized with roller pressure was clearly demonstrated. Cameron McLeod (Sheffield Hallam University, Sheffield, UK) presented work on the use on micro-columns packed with acidic alumina for field sampling of river waters. In particular, he showed a novel use of the columns for fixing the speciation of selenium at the time of sampling. Elution, back at the laboratory, with dilute ammonia solution followed by concentrated potassium hydroxide solution sequentially released selenium (VI) and selenium (IV), respectively.

The use of solid-phase reagents was a theme also discussed by Jim McLaren (National Research Council of Canada, Ottawa), who described an automated procedure for the determination of several trace elements in sea water. The method was based on the use of 8-hydroxyquinoline immobilized in a silica support and packed into a small high performance liquid chromatography column. In addition to the quantification of some heavy metal pollutants, it was demonstrated that the method also had potential for the measurement of lead isotope ratios and the quantification of the rare earth elements.


Gary Horlick


Julian Tyson


Jarda Ruzicka

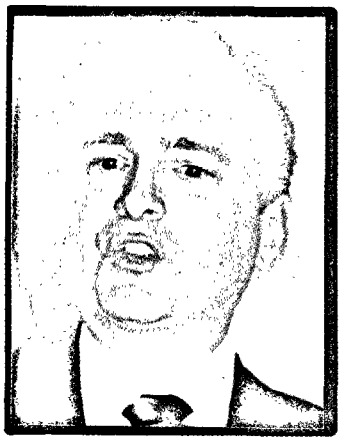

Maria Fernanda Giné

It was necessary to pay particular attention to the purity of the reagents used in this study. On-line purification with appropriate guard columns was shown to be feasible. Another multi-element preconcentration procedure based on solid-phase reagents was described by Mark Hollenbach (RUST Geotech Inc, Grand Junction, CO). In this case, the target analytes were selected radionuclides. Two materials supplied by Eichrom Industries were used. It was noted that the FI procedure generated less laboratory waste than conventional radiochemical procedures. Methods were described for the determination of (a) technetium-99, thorium-234, and plutonium-239 and 240, and (b) uranium-234 and thorium-230 in soils.

Julian Tyson (University of Massachusetts, Amherst, MA) described a novel closed loop recirculating manifold for the dilution of samples and standards. In contrast to many other FI procedures for dilution, no controlled timing of any operation was required. The dilution factor is set by the total volume of the loop and the volume sub-sampled by the injection valve. Repetitive actuation of the valve at appropriate intervals (as short as 40 s) provides serial dilution of an initial concentrated solution. In this way, with even a modest dilution factor (of say 2), several orders of magnitude of concentration may be covered in a matter of minutes. Results for the dilution of lead and magnesium solutions showed precisions on the order of 1-3%, relative standard deviation. A novel method of achieving homogenization in the loop was described based on the destructive interference of the concentration oscillations at the confluence point of a two-line network of unequal lengths. The need for reliable and easily implemented dilution procedures was underlined by extensive quotation from two EPA methods involving ICP-MS, for which several of the QC procedures involved dilution and reanalysis as a check on the magnitude of matrix interference effects.


Cameron McLeod **Jim McLaren**

The beneficial effects of injection of the sample into a segmented air/water carrier stream was shown by Diane Beauchemin (Queen's University, Kingston, Ontario, Canada). In comparison with the water carrier of the conventional FI introduction process, the peaks were larger (both in height and area) and narrower, giving rise to improved sensitivity and throughput. This was considered to be due to the reduced longitudinal dispersion in the carrier stream and an increased nebulization efficiency, arising from the presence of air in the carrier delivered to the nebulizer. It was also shown that further improvements in the analytical characteristics could


Mark Hollenbach


Diane Beauchemin


Paul Ek


Graham Kimber

be obtained with the aid of mixed gas plasmas. The effect of the introduction of air, nitrogen or hydrogen into the central channel was studied. It was found that the segmented stream did not deliver enough gas to have a significant effect on the plasma and that addition of the gas to one or more of the argon supplies was required.

An ingenious use of a motor driven piston buret as both pump, reaction vessel and gas liquid separator for the generation of the hydrides of arsenic and selenium was described by Paul Ek (Åbo Akademi University, Åbo, Finland). In effect, the procedure is one of sequential injection as the sample and reagents are drawn into the reaction vessel by aspiration. Following reaction, the gaseous reaction products are removed by compression of the head space vapor and forcing the gas through a capillary for transport to the DC plasma detector. This procedure avoids the use of an additional stripping gas (usually argon) and therefore has the potential for higher sensitivity, as this source of gas-phase dilution is avoided. For a reaction chamber volume of 50 ml, a calibration over the range 1-10 ppb was possible. It will be of interest to see how well the system handles interferences by transition metals.

Finally in this session, the mysteries of the discontinuous flow analysis (DFA) procedure were clarified by Graham Kimber (Queensland University of Technology, Brisbane, Australia). The system consists of several pumps working in opposition. When there is a flow rate discrepancy between pumps, sample solution may be aspirated at an appropriate confluence point. Following changing of valve positions, the sample slug may be manipulated in the flow manifold in much the same way as in merging stream FI procedures, but with the additional feature that the delivery of fluids may be flow-rate gradient programmed. This allows implementation of the analog of the FI electronic dilution procedure as well as a gradient calibration procedure. Precise operation of the syringe pumps used is provided by optical encoders and appropriate electronic control. The system incorporates an on-line mixing device, the details if which were not disclosed, but which from the results shown would appear to give rapid radial mixing.

The use of flow injection procedures was to be found in presentations dispersed longitudinally throughout the six days of the conference, and it was gratifying to note that in any discussion of sample introduction topics, FI was mentioned routinely alongside such techniques as ultrasonic or direct insertion nebulization, electrothermal vaporization (ETV), and laser ablation (LA) as member of this group. It is clear that FI is now fully accepted as a legitimate method for sample handling and introduction on plasma spectrochemistry. It should be borne in mind that many of the concepts of FI can also be applied to the techniques of ETV and LA, which to a first approximation, are vapor-phase FI procedures. And, as has been pointed out before, flow analysis procedures also encompass the techniques of chromatography (of which numerous examples were described) and of capillary zone electrophoresis, the coupling of which to ICP instrumentation was reported at this conference for the first time.

The need for instruments to have the capability to handle transient events of all sorts and to process the resulting signals with appropriate, user-friendly soft-ware was clearly of considerable interest to many of the delegates as is the ability to interface a number of sample introduction accessories easily to any given instrument.