1992

Flow Injection Spectrochemical Analysis at the Winter Conference

Julian Tyson

Flow Injection Spectrochemical Analysis at the Winter Conference

Julian Tyson
Department of Chemistry, University of Massachusetts, Amherst, MA 01003

There is currently considerable interest in the analytical possibilities of the combination of flow injection sample introduction for atomic spectrometry. The literature relating to this flow injection atomic spectrometry (FIAS) combination has amounted to some 330 publications up to the end of 1990, of which about 60 are specifically concerned with applications involving inductively coupled plasma (ICP) spectrometry. Although most of these have involved optical emission spectrometry (OES), there has been a steady growth in the number of publications relating to ICP-mass spectrometry (ICP-MS). Much of the earlier published work was concerned with the benefits of the contamination-free micro-sampling characteristics of flow injection sample introduction, the more recent work has been concerned with the interfacing of FI based sample pretreatment with the instrument. For example, of the 50 or so publications appearing in 1990, 13 described solid phase extraction, 8 concerned chemical vapor generation, 5 were about speciation, 7 were descriptions of indirect methods and 6 were concerned with matrix removal.

Flow injection techniques have, over the last 12 months, featured strongly as topics in analytical spectrochemistry conferences and in spectrochemistry streams in more broadly based conferences and this seems set to continue into 1992, if the pattern established in San Diego continues.

For the 3 days prior to the conference, an extremely successful program of intensive short courses was offered during which a well-attended course on Flow Injection Techniques for Plasma Spectrochemistry was organized by Cameron McLeod, Director of the Chemical Analysis Research Centre at Sheffield City Polytechnic in the UK. In this course delegates were introduced to the basic principles of dispersion by fluid flow in narrow bore pipes before being taken through the wide range of sample handling procedures possible with FI. It was interesting to note that many of the delegates had experience with FI or had recently acquired FI equipment. The discussion session concerning the possible applications to real samples containing high dissolved solids was particularly lively and a robust exchange of views took place on the usefulness of solid phase reagents as the basis of speciation studies.

Following the opening plenary on the first day of the conference came a session specifically concerned with flow injection. The session opened with an invited lecture by Professor Jarda Ruzicka of the University of Washington, Seattle in which the thesis of FI as chemical modulation of the impulse injection was developed with reference to a number of examples of relevance to atomic spectrometry including solid phase extraction and vapor generation. Professor Ruzicka also introduced the concept of sequential injection analysis featuring bi-directional fluid flow (by means of a computer-controlled syringe pump) and the stacking of sample and reagent zones in the flow line (by use of a computer controlled) selection valve. It was pointed out that this represents a significant step towards the availability of "keyboard chemistry". Some future areas of application of FI in the Seattle research group were illustrated beautifully by a brief discussion of the enormous potential of flow injection cytometry, an area from which atomic spectroscopists are, alas, currently excluded. Dr. Maria Giné of the Centro de Energia Nuclear na Agricultura in Piracicaba, Brazil described, in her invited lecture, research directed toward the development of a multi-purpose FI system for sample handling for plasma spectrometry. In particular a manifold for performing programmable dilutions and standard additions was described. The basis of this was the development of a concentration profile from an injected solution in a holding coil. By the controlled actuation of some simple 3-way valves, a desired portion of this gradient could be flushed from the holding coil and directed to the spectrometer via a stream confluence point. Thus if sample was injected it could be "diluted" by a version of zone sampling, for which as many sequential zones as desired could be expelled from the holding coil. To implement the standard additions procedure the holding coil was first loaded with standard which was then "zone sampled" as required and merged with a continuous stream of sample at the confluence point. This procedure was validated by the accurate analysis of some plant reference materials.

The basic FI experiment produces a transient signal and thus poses some problems for both multi-element determinations and for the implementation of off-peak background correction. Two approaches for overcoming these problems were outlined by Dr. Brenda Caughlin of Chemex Labs. Ltd., North Vancouver. The first was based on the use of a spectrometer with a diode array detector (the LECO Plasmarray ICP) in which the background and signal were measured simultaneously whereas the second was based on an increase in the data acquisition speed by means of a commercially available modification (Interface Design Inc, Texas). Both approaches were found to equally satisfactorily with the interference of calcium on La but the fast data acquisition system placed an eventual minimum limit on the sample volume injected.

Liquid sample introduction systems for plasma spectrometry in which the solution is nebulized are only a few percent efficient in terms of the fraction of the analyte species that are transported to the atom source. Several alternative solution introduction procedures have been devised, some of which require only small sample amounts and are therefore compatible with a FI sample handling system which produces a zone of analyte species in

volumes typically only a few hundred microliters. Dr. Eric Salin (McGill University, Montreal) described a sample handling and introduction system in which an FI preconcentration/matrix isolation system was combined with a graphite cup direct insertion (DI) device. The FI system utilized a chelating solid-phase extractant Metpac CC1 and Pb, Zn and Cd were the analytes. The spectrometer, a Jarrell Ash model 750, had been modified by the inclusion of a galvanically driven refractor plate so as to be able to handle transient signals. Based on detection limit calculations improvements for the three analytes of factors of 700, 80 and 40, respectively were obtained. The numbers show that the factors due to the FI system and DI device are multiplicative. The improvements were not greater because of the problems with contamination of the reagents. It was considered that if the blank concentrations could be reduced then improvements in detection limits of up to three orders of magnitude would be obtained.

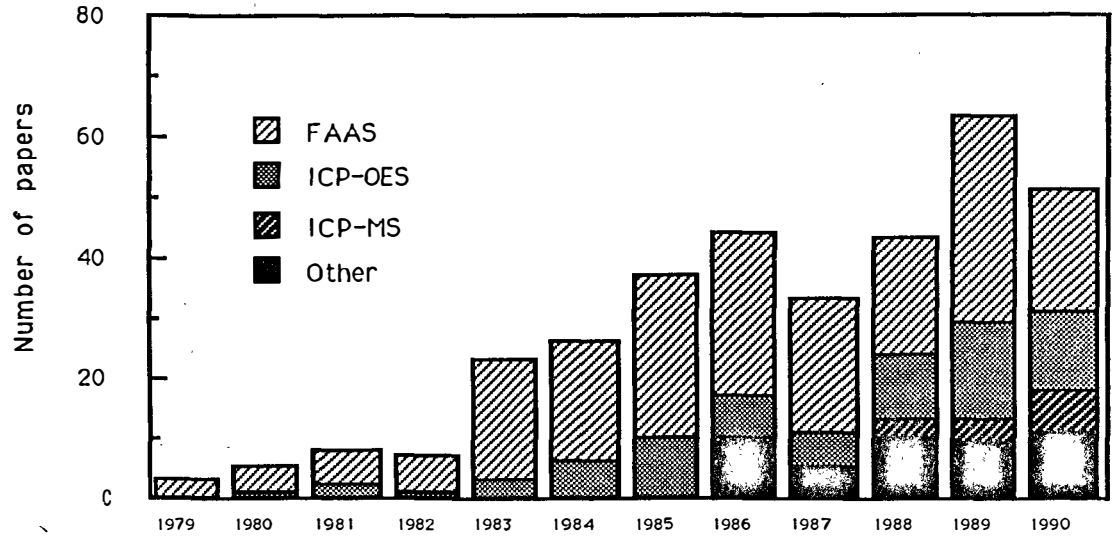
Solid phase reagents for sample pretreatment also featured in the work presented by Dr. Cameron McLeod of the Sheffield, City Polytechnic, UK. In particular columns of reagent had been used as part of a field sampling procedure. A number of surface waters (river and ocean) had been sampled by drawing a known volume of sample through a solid phase cartridge which stabilized the element species at the time of sampling. The reagents used included alumina and sulphydryl cotton. This latter reagent was used in a protocol for measuring methyl mercury. The loaded columns are returned to the laboratory for subsequent analysis by incorporation in a FI manifold for elution and detection.

In the final talk in this lecture stream, Professor Rick Browner (Georgia Institute of Technology), provided a critical overview of the present understanding of aerosol generation and transport. Professor Browner argued that many of the long-established models for describing aerosol characteristics, such as the Nukiyama-Tanasawa or Kelvin-Lang equations, did not describe the situation with regard to aerosol generation in plasma spectrometers very accurately. He reported that the aerosol velocity distribu-tion in the spray chamber was Gaussian in character which should give pause for thought for those who had consid-ered the spray chamber to be adequately described by models based on well-stirred tanks with simple velocity distributions. Clearly there is still some way to go before an accurate description of the FI peak shape may be obtained from mathematical models of the various transport proc-esses.

Flow Injection techniques made a brief appearance in the lively panel discussion session under the direction of Professor Les Ebdon (Polytechnic South West, Plymouth, UK) as the obvious procedure to be adopted when sample volumes were limited. The themes of this session are reported in more detail elsewhere in this journal.

Several presentations later in the week featured flow injection as the basis of the sample pretreatment including, for example "Application of Inductively Coupled Plasma Mass Spectrometry to an Acid Mine Drainage Contamina-tion Study using Chelation Concentration Chromatogra-phy" by Lynda Faires of the US Geological Survey, Arvada, CO and "A Novel Desolvation System for the Analysis of Organic Solvents by Flow Injection Inductively Coupled Plasma Mass Spectrometry", by James Hartley (co-au-thors P. Goodall, Les Ebdon and Steve Hill) of Polytechnic Southwest, to highlight one of the best poster presenta-tions and one of the best oral presentations by a graduate student, respectively.

Of course, the numbers of flow injection presentations would be increased substantially if the various chromatography-plasma spectrometry combinations were placed in this category. Maybe that's a suggestion too radical for 1992, but what will be the position in 1994?



Growth of the Flow Injection Atomic Spectrometry Literature