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Flow Injection at the 1996 Winter Conference

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For the first time in several years there were fewer presentations specifically concerned with flow injection (FI) sample introduction. However, this should not be interpreted as a decline in interest in FI techniques, as it became apparent even from the lectures in the opening session, that FI is now considered to be a sample introduction procedure to be used when appropriate. And clearly, many researchers are finding FI procedures to be useful. Thus, even before the start of the session on Monday afternoon devoted to FI, delegates had heard at least three presentations in the Sample Introduction and Transport Phenomena session in which FI was used. In describing recent developments with the oscillating capillary nebulizer, Rick Browner (Georgia Tech) presented results in which FI was used to model for chromatographic procedures. This use of FI was also reported by several other workers and is clearly a relatively widely used practice in HPLC-ICP spectrometry method development. It is also clear that for the various high pressure nebulizer devices, such as those developed by Harald Berndt (Institut fur Spektrochemie and Angewandte Spektroskopie, Dortmund), FI is the basic introduction mode as sample components are never in contact with pump components. Even when low pressure peristaltic pumps are used for propulsion, this is a non-trivial advantage over conventional introduction. Antonio Canals (University of Alicante) described a system which used FI introduction in which the nebulizer and spray chamber were located inside a domestic microwave oven.

The session specifically devoted to FI opened with an update from Professor Cameron McLeod (Sheffield University) on the use of simple chemistry implemented in “The FIA Way” for measurement of inorganic species differentiated by oxidation state. Some further uses of mini-columns for field sampling of ocean and other surface waters were described in which the possibility of speciation was again discussed. A further application of solid-phase extraction was described by Ludwik Halicz (Geological Survey of Israel) for the determination of rare earth elements in Dead Sea water following preconcentration on silica immobilized 8-hydroxyquinoline. A novel manifold for increasing the sensitivity obtained by such a procedure was described by Maria Fernanda Giné (Centro de Energia Nuclear na Agricultura, Universite Sao Paulo, Piracicaba) for the determination of lead and cadmium following preconcentration on two cation exchange columns. The columns were eluted simultaneously and the eluents merged to give one peak whose area was used as the quantitative parameter.

Flow injection was the sample introduction procedure of choice for Henry Foner (Geological Survey of Israel) in a method for the determination of bromine and iodine in natural waters by ICP-MS. Iodine was troublesome because of very long wash-out times and these were considerably decreased for the FI mode. In addition, salt concentrations of up to 2% could be tolerated; a useful feature when the analyte matrix was Dead Seawater. It was clear from the last speaker in this session, Ulrich Greb (Finnigan MAT), that at least one company is taking very seriously the additional capability conferred on ICP-MS performance by the use of some sample introduction accessories such as a flow injection system.

This theme was also picked up during the Panel Discussion which concluded this first day of the conference. It is clear that several of the needs of users that are not yet met by the manufacturers of the instruments were being addressed by companies specializing in sample introduction devices, some of which had the capability of performing on-line chemistry. Some criticism was voiced over the slow rate at which these practical developments were being introduced. In connection with flow injection, it was pointed out that pump technology was not currently capable of providing the performance required in terms of convenient, precise, pulse-free delivery.

It was clear from the revised order of the topics at the conference that there is a sustained and growing interest in the use of plasma spectrometries for chromatographic detection and speciation studies. These topics appeared in the middle of the week. Many such studies define the speciation in terms of the chemistry used as the basis of separation, and it is clear that flow based chemical manipulations plays a key role in this methodology. As the demands of these analyses are orders of magnitude more exacting than those of methods which simply require the total element content of the matrix of interest, it is likely that providing solutions to the problems of speciation at trace and ultra-trace concentrations will be exercising the ingenuity of conference participants for years to come, and thus flow based chemistry will be established in a central role in this area of analytical science.
IL4 ICP ATOMIC AND MASS SPECTROMETRY, THE FIA WAY. Cameron W. McLeod, Centre for Analytical Sciences, Department of Earth Sciences, University of Sheffield, Sheffield S3 7HF, United Kingdom

In ICP spectrometry there has been a continuing interest in devising FIA methodology since reports were first published in 1981. The “FIA Way” brings considerable benefits including improved sensitivity, reduced interferences, high sample throughput, improved long term stability, speciation capability, and cost-effective operation. The versatility of FIA is such that developments are not just confined to the laboratory. For instance a new strategy for environmental waters concerns the integration of microcolumn field sampling and FIA. In this experiment, microcolumns packed with adsorbent are used in the field to isolate trace elements of interest. After field sampling the columns are returned to the laboratory for elution/quantitation. The approach offers considerable potential in speciation research and ultratrace analysis.

The presentation will chart the impact of FIA on ICP spectrometry and in particular highlight developments in element speciation and field sampling. For example new manifold designs utilizing direct injection nebulization, microconcentric nebulization, and ultrasonic nebulization will be specified for target species - As, Br, Cr, Hg and Se. The scope for ultratrace determination of actinides in seawater (pg/l) will be considered.

M9 ON-LINE ICP-MS ANALYSES OF REE IN HIGHLY SALINE BRINES. Ludwik Halicz, Ittai Gavrieli, and Ethel Dorfman, Geological Survey of Israel, 30 Malkhei Yisrael St., Jerusalem 95501, Israel

ICP-MS has been used successfully for the direct determination of rare earth elements (REE) in geological materials. However, its application for REE determination in seawater and highly saline brines remains limited. This is due to the extremely low REE concentrations in seawater and saline brines, which are below the detection limits, and to the high matrix concentration of these solutions.

A previously reported on-line ICP-MS determination method of heavy metals in seawater [1, 2] has been re-examined and modified to determine REE in seawater and Dead Sea brine (salinity above 30%). The method is based on the separation of the REE from the brine by adsorption on a small column of silica-immobilized 8-hydroxyquinoline (1-8-HOQ), followed by their removal with a small volume of acid for their introduction into the ICP-MS. Analyses were carried out with a Perkin-Elmer Sciex ELAN 6000 ICP-MS (with excellence limit of detection) equipped with a FIAS 400 sample introduction system. An additional Dionex injection valve fitted with a 3-ml sample loop was added to the latter and controlled by the ELAN 6000 software.

The on-line preconcentrations were done using micro-column (length 25 and ID 2.5 mm) filled with 1-8-HOQ (80–100-μm grain size) synthesized following Sturgeon et al. [3]. The procedure developed yielded REE peak height sensitivity about 10 times higher than that of continuous nebulization. The peak shape is comparable with that obtained with a high-pressure, Dionex, on-line preconcentration system [2], although the full widths at half maximum height increased from 7 to 10 s. Calibration was done with a water standard that included 14 REE at concentrations of 100 ng/l. Recovery
experiments were carried out with complex matrices (seawater and diluted 1:1 Dead Sea water). Blanks were under the ng/l range, and the limit of detection ranged between 0.06 to 0.6 ng/l. The results obtained for the NASS-1 and NASS-2 (no certified values available) are comparable with seawater levels found in the literature. The concentrations of the REE found in the Dead Sea are comparable with those previously determined by isotope-dilution thermal ionization mass spectrometry ([4], Figure 1).


**M10 AUTOMATED ON-LINE PRECONCENTRATION SYSTEM FOR PLASMA SPECTROMETRY.** Ana Paula Packer, Maria Fernanda Giné, Carlos E.S. Miranda, and Boaventura F. dos Reis, Centro de Energia Nuclear na Agricultura, CENA-USP, C.P. 96, 13400-970, Piracicaba-SP, Brazil

The main parameters involved in a flow system with ion-exchange columns to attain appropriated enrichment factors for water sample analysis and to work on-line with ICP-AES or ICP-MS were studied. In the proposed flow design the sample is loaded simultaneously by small columns inserted in parallel channels so that the sampling time is reduced. The sampling step is performed with the columns off-line from the plasma to avoid the inlet of sample matrix. To elute the analytes the columns are placed-on-line with the nebulizer. The elution solution flows in a reverse direction simultaneously by the columns, and the released species are merged before reaching the nebulizer. Both improvements have as their purpose the minimal dispersion of the concentrated analytes solution. Results demonstrated that there is a real gain in preconcentration efficiency. Enrichment factors from 5 to 100 were correlated to the sample loading time of 0.6 to 3 min. The transient signal obtained by the proposed system is characterized by higher peak area than the equivalent obtained with one column. This is an advantageous feature for scanning mass by ICP-MS or sequential emission detection ICP-AES and is applied to determine traces of Cd and Pb in water samples by ICP-MS.

**M12 DETERMINATION OF BROMINE AND IODINE IN NATURAL WATERS AND RELATED MATERIALS BY ICP-MS AND FIAS-ICP-MS.** Henry A. Foner, Ludwik Halicz, Olga Yaffe, and Sarah Ehrlich, Geochemistry Division, Geological Survey of Israel, 30 Maltke Yisrael St., Jerusalem 95501, Israel, and Ramon M. Barnes, Department of Chemistry, Lederle Graduate Research Center, University of Massachusetts, Amherst, MA 01003-4510

A number of methods for determining bromine and iodine using ICP-AES and/or ICP-MS have been published. Some of the authors of these methods have experienced great difficulty with memory effects especially in the case of iodine. In the past this has been the experience of some of the present authors too. In fact, the memory effect of iodine was so marked that it was impossible to use ICP-MS to determine this element at all. Using a SCIEX Elan model 250 ICP-MS spectrometer with a Scott type glass spray chamber, iodine signals were still significantly above background levels after 30 minutes of washing out. This contrasted with the signal decay curves for bromine and strontium which behaved normally. With signal decay times as long as this, it was obviously impossible to develop a practical analytical method for iodine. The memory effect has been attributed to adsorption of iodine or iodide on the glass surfaces or on the tubing of the sample introduction system [1, 2].

Using the Elan 250 instrument mentioned above, we attempted to reduce washout times by washing out with solutions containing acids, ammonia, reducing agents and complexants - all to no avail. Washing with acid caused an iodine "blip" on the decay curve, but did not significantly affect the washout time. Exchanging the glass spray chamber for a Teflon one, however, significantly reduced the washout time.

We have recently attempted to develop a method for the determination of bromine and iodine in natural waters and related materials by ICP-MS using a Perkin Elmer/Sciex Elan 6000 ICP-MS. We have chosen to use the ICP-MS technique and not ICP-AES because the sensitivity of the latter is not sufficient for the concentrations of these elements in our water samples. With this instrument the memory effects with iodine are reduced - but still significant. At low concentrations washout times are reasonable (a few minutes) but at higher concentrations the memory effect is again in evidence, although it is much less pronounced than in the Elan 250. The concentration range between possible and impossible working conditions is surprisingly small, about 1:3. The Elan 6000 has a plastic ("Pyton", polyphenylene sulfide) spray chamber. The experiments to reduce washout times which were carried out on the Elan 250 were essentially repeated on the Elan 6000 - with the same disappointing results.

At this stage of the project, we decided to use Flow Injection Analysis for the determination. The instrument used was a FIAS 400 unit with an AS 90 auto sampler (both kindly loaned by Perkin Elmer GmbH). This system does not suffer from any obvious memory effects and iodine signals drop rapidly to background levels in about 2 minutes. This is presumably because of the small amount of sample introduced into the system. Another advantage of this system is that quite a concentrated sample solution can be used (up to 1 to 2% total solids) without causing blockage or build up on the sampler cone.

Detection limits using the FIAS-MS system are 120 ng 1· for iodine and 800 ng 1· for bromine. Results have been validated by the use of spiked samples and by independent analysis using XRF. Results will be presented for a range of natural samples.

M13 THE ANALYSIS OF SMALL SAMPLE VOLUMES BY HIGH RESOLUTION ICP-MS. Ulrich Greb and Lothar Rottmann, Finnigan MAT GmbH, Barkhausenstr. 2, D-28197 Bremen, Germany

HR ICP-MS is a very attractive method for a complete multi-element analysis of samples, even for difficult sample matrices. Very often, however, the sample volume is only limited, sometimes to below 1 mL. We will show that the new generation of fast high resolution ICP-MS and the new generation of high performance nebulizers allow the multi-element analysis of sample volumes down to 100 µL.

Direct injection of the sample into the plasma is one technique used to efficiently nebulize the sample and introduce it into the plasma. The sample introduction efficiency reaches 100%. Due to the relatively small surface involved and the missing requirement for a spray chamber, the sample memory can be decreased considerably and a fast washout can be assured.

The second technique used is the Micro-Concentric Nebulizer (MCN, CETAC). Here the sample introduction efficiency is very high, too. This is due to the formation of very small droplets with a very narrow size distribution. This leads to a very high probability of the droplet finding its way into the plasma, without condensing in the spray chamber. The sample introduction efficiency thus reaches approximately 90%.

The third technique is µ-sampling by the introduction of small sample volumes into the discharge. Important considerations are the use of inert materials for the switching valve, the sample loops etc. The µ-sampler can be used to combine the sample introduction technique with trace/matrix separation, on-line dilution, standard addition and other sample preparation techniques. The full computer control allows the automatization of these sample preparation steps for small or “difficult” samples.

The µ-sampling can of course be combined with the MCN to provide a complete analysis for interfered and uninterfered elements from sample volumes as low as 100 µL or even less. This is of considerable interest for a variety of applications, where the sample volume is very limited.