

## FLOW INJECTION INDUCTIVELY COUPLED PLASMA MASS SPECTROSCOPY (FI-ICPMS)

Steven F. Durrant

Laboratório de Processos de Plasma, Departamento de Física Aplicada,  
Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas  
13083-970, Campinas, SP, Brazil

### ABSTRACT

Flow injection is a versatile sample introduction method in combination with inductively coupled plasma mass spectrometry for elemental analysis. Advantages of the technique include small sample volumes and the ability to analyze solutions of high dissolved solids content. Applications of FI-ICPMS are illustrated from recent literature.

### 1. INTRODUCTION

Since its inception (1), flow injection has become well established for liquid sample introduction in atomic spectrometry. In this technique a known volume of sample solution is injected into a continuously flowing stream (which may be a diluent or chemical reagent or both) in narrow-bore

rates of diffusion experienced at the front and rear boundaries of the sample plug, the sample and reagent are soon mixed, at which time the product is typically passed to a suitable detector.

Always an attractive method in combination with elemental detection, FI has recently been employed with inductively coupled plasma mass spectrometry (ICPMS). The pros and cons of this combination, FI-ICPMS, for multielemental analysis are addressed here.

### 2. FLOW INJECTION

A simple FI system is shown in Fig. 1. Sample solution is injected into the carrier and mixed before being passed to the detector, in this case an ICP-mass spectrometer. In practical applications

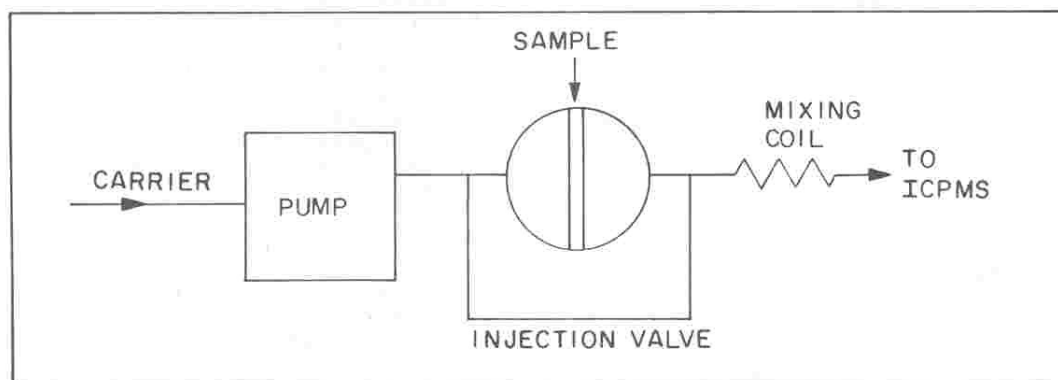


Figure 1. Simple flow injection system

nonwetting tubing. Such conditions produce laminar flow, whereby the molecules of fluid flow in stream lines parallel to the walls of the tubing. A parabolic velocity gradient exists across the diameter of the tubing such that at the center the molecules of the fluid travel at twice the average linear velocity, and at the walls of the tube the particle velocity is zero. Owing to these conditions the sample solution is quickly dispersed into a volume in the form of "an extremely long hollow needle" (2). As a result of different

complex, tailor-made systems involving several reagents and valves may be necessary.

A typical response from an analyte contained in the sample plug injected into a carrier stream is shown in Fig. 2. Although the signal is transient, it typically lasts for several tens of seconds, which is sufficient for many scans across a chosen mass range (or set of mass ranges) by an ICP-mass spectrometer. Thus quasi-simultaneous multielemental analysis is possible.

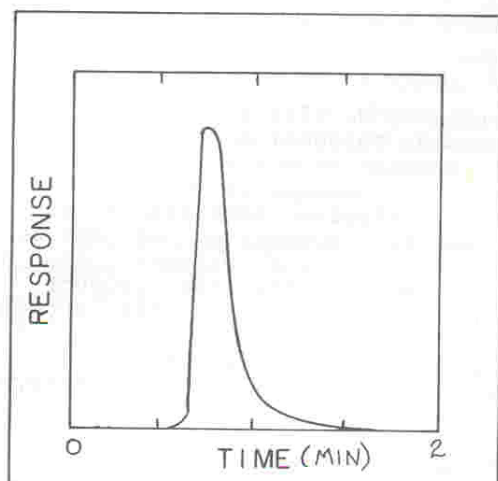


Figure 2. Typical response from an analyte in an injected sample (see (15))

The method of FI offers several significant advantages: small sample volumes (tens of  $\mu\text{L}$ ); small reagent volumes; remote manipulation of the sample solution; on-line dilution or preconcentration; analysis of samples with high dissolved solids content; simple or complex chemical treatment. Thus for samples that are difficult to obtain and only available in small volumes, such as cerebrospinal fluid, FI offers direct quantitative analysis. For routine analysis, important economies on reagents may be made. The possibilities of sample treatments are also important.

### 3. INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

Quickly following its introduction as a research tool (3), ICPMS was successfully commercialized and there are now several manufacturers in the field. The technique, which has been described in detail elsewhere (4-6), is capable of routine elemental analysis of a wide range of elements at the sub ng/mL level.

Isotope ratios may also be determined (7). A linear dynamic range of up to ten orders of magnitude is possible. Spectra are typically simple, and calibration may be made using simple aqueous solutions of known concentration.

Various difficulties of fully-quantitative analysis are encountered with practical samples, including matrix effects and various types of spectral

interference, and these have been described in the literature (8-10). Note however, that experience over the last ten years has revealed many ways to overcome, or at least alleviate, these difficulties (11). Some of these problems, as they relate to FI-ICPMS, are addressed in the following section.

### 4. FI-ICPMS

As early as 1983, Houk and Thompson (12) described a FI system for use with ICPMS. Samples were injected manually using a pipette. It was possible, using this method, to determine Mg and Ni isotope ratios with precisions of 1-3%, at concentrations in the range 2-40  $\mu\text{g/mL}$  in volumes of 50-200  $\mu\text{L}$ . As shown by the same authors (13), the FI technique is also important in combination with separation devices for speciation, such as chromatographs. Speciation is topical but is not dealt with here; readers interested in this subject are directed elsewhere (14).

Beauchemin *et al* (15) described a procedure for the extraction of organomercury from the reference materials dogfish muscle (DORM-1) and lobster hepatopancreas (TORT-1). The final solutions contained more than 4% sodium, a concentration too high for regular analysis by ICPMS using conventional pneumatic nebulization (PN). Successful analysis was possible, however, using FI, with detection limits of a few ng/mL.

Several other applications of the technique have been undertaken in recent years (16-25). For example, Peng *et al* (22) determined Ge, Pd and Pt at trace levels in solutions of 2.5 M phosphoric acid and 1.5 M ammonium nitrate employing the method of standard additions. Detection limits based on the isotopes  $^{72}\text{Ge}$ ,  $^{74}\text{Ge}$ ,  $^{105}\text{Pd}$ ,  $^{108}\text{Pd}$ ,  $^{194}\text{Pt}$  and  $^{195}\text{Pt}$  were 1, 0.2, 0.3, 0.2, 0.3 and 0.3 ng/mL, respectively. Also, Eaton *et al* (23) showed that the dissolved solids content of samples for analysis could be increased from the 0.2 - 2% W/V typically possible with PN to 5 - 10% W/V with sample introduction by FI. Platinum-group metals were determined in the standard reference peridotite PCC-1 at concentrations in the range 0.03 - 0.3 ng/g.

Metals have also been analyzed using FI-ICPMS. For example, Mochizuki *et al* (19) optimized the carrier flow rate, injection volume and sample



concentration for the determination of Tl, Pb and Bi in nickel-base alloys. In this case better accuracies and precisions were obtained with FI than with PN. Detection limits were in the range 1 to 40 ng/g.

Flow injection with cation-exchange using a column on-line for trapping major elements and Hf has been reported for geological samples (21). Hafnium had to be removed because it caused suppression, and spectral interference via HfO.

Preconcentration by anion exchange of gold as a cyanide complex,  $(Au(CN)_2)^-$ , and using  $^{195}Au$  radiotracer to monitor recoveries has been reported (25). The samples were of sea water from the Atlantic, Pacific and Mediterranean Oceans.

## 5. CONCLUSIONS

FI-ICPMS offers rapid multielemental analysis of small sample volumes with high dissolved solids contents. Excellent detection limits, ng/mL or better, are typically obtained. As the FI system is closed, risk of elemental contamination or loss is small. Sample pretreatment, preconcentration or dilution may be implemented.

Although there are numerous works describing analysis by FI-ICPMS, the method might be still more widely exploited, particularly considering its numerous advantages over pneumatic nebulization ICPMS.

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