

## Volatile Species Generation in Flow injection for the On-line Determination of Species in Environmental Samples by Electrothermal Atomic Absorption Spectrometry

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### Abstract

This review presents the different vapor generation compounds techniques within flow injection manifolds for the determination of species of environmental interest by electrothermal atomic absorption spectrometry. Its possibilities and potential advantages when the volatile analyte is either determined in a pre-heated furnace or it is previously collected by trapping on stable coating of the atomizer are discussed.

**Keywords** Flow injection, environmental analysis, electrothermal atomic absorption spectrometry, sample pre-treatment, automated analysis.

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### 1. Introduction

The environment may be considered as the surrounding conditions, influences, or forces that influence or modify the whole complex of climatic, edaphic, and biotic factors that act upon an organism or an ecological community. The rapid growth in agriculture and industrial activity has resulted in chemical pollution of different worldwide environment scenarios. Therefore, great efforts are made to evaluate the entire range of the environmental factor that directly influence and are affected by man's activities. The complexity of the real samples and the diversity of analytes typically encountered in environmental studies hampers the direct analysis of key components by use of a specific detection technique. In environmental analysis, the most interesting samples consist of

powders and particles (sediments, soil, airborne dust), dried organic substances (from animals or plants), gases and liquids or solutions containing the analytes to be analysed. In this respect, flow injection (FI) have proven useful for handling contaminated complex samples and for direct pretreatment of solids and liquids with harsh chemical matrices [1,2].

The main objective of this work is to bring the analyst's attention to the potential use of the generation of volatile compounds in FI systems combined with ETAAS detection modes in the control of environmental pollution.

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## 2. Interfacing atomic spectroscopy (AS) with a FI preconcentration system

The different FI preconcentration approaches for AS techniques so-far described by the literature are depicted in Fig. 1. Successful analyte preconcentration and matrix or interferences separation can be achieved by on-line sorption on a solid phase, preconcentration & coprecipitation reactions, on-wall retention processes, volatile generation and liquid-liquid extraction. The main consideration is to ensure that the manifold produces an appropriate degree of mixing between the sample and the reagent solutions so that the desired process proceeds. The detector should be able to [3]: (i) have a fast response to cope with the high sampling rates achieved in FI systems; (ii) respond linearly over a wide concentration range of components transported to the detector as reaction products from the manifold system are used; (iii) be repeatable over extended periods of time so that frequent calibration runs to detector weaknesses are not required; (iv) have a low noise characteristics; (v) have a very low memory effect; (vi) be sensitive enough to yield the lowest possible detection limit; and (vi) be compatible with data processing system.

A FI-AS system is made up of three major components, the FI manifold, the spectrometer unit and the programmer. The liquids delivery unit, injectors, reactors, the atomizer and the programmer can be located depending upon the analysis performed by the analyst. The spectacular advances in micromechanics, microelectronics and microcomputer science allow to program the physical mixing and the chemical reactions

which takes place in the FI system to occur at specified times [4].

## 3. Chemical vapor generation and preconcentration on the atomizer

The VG generation approach, including hydride generation (HGAAS), cold vapor and other vapor generation/volatilization methods, is now a well established sub-discipline of AAS [5,6]. While most of the work reported so far has been performed in conjunction with a heated quartz tube atomizer, it has been found possible to trap the volatile analyte species on the interior of a graphite furnace thereby allowing a preconcentration prior to atomization. In the early stages of development, the volatile analyte was introduced into a pre-heated furnace (at temperatures above 100 °C) and atomized during its transit time through the device. This approach has greatly limited the use of these systems, probably due to low collection efficiencies [7]. However, since the analyte collection was retained using in-situ trapping on stable coatings, a growing interest is apparent because it is a clean, an efficient way to preconcentrate the analyte and an elegant approach for its separation from other matrix components. In particular, the “in situ” collection of generated hydrides in a furnace using the electrostatic deposition methodology is an attractive approach for the determination of different metal species with good sensitivity [8]. Naturally, the sensitivity for on-line atomization is generally lower than with in situ trapping. Thus, the coupling of most graphite furnace with “in situ” collection of the analytes can readily provide detection limits down to parts per

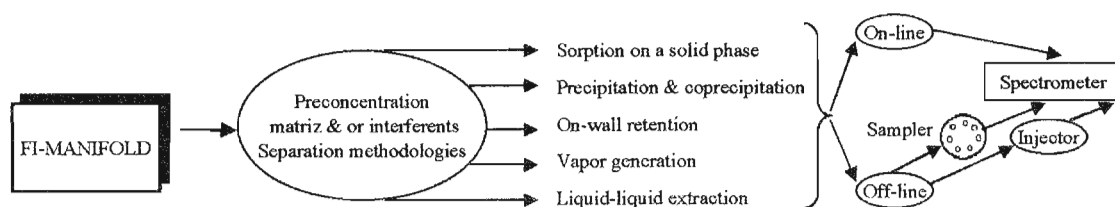


Fig 1 Preconcentration techniques used for FI-AS determinations

trillion concentrations. The nature of the graphite tube is expected to affect greatly the efficiency of the volatile species adsorption. It has been shown that the efficiency of adsorption increases in the order new normal graphite tubes < old pyrolytic graphite tubes < old normal graphite tubes [6,9].

Continuous HG combined with in-situ trapping of the species [11] preceded the development of FI-VP-ETAAS systems. The principles for design of FI-VG systems in order to perform a wide variety of on-line functions, such as: gas diffusion separation, matrix modification, sensitivity enhancement and suppression of interferences have been described by Fang [10]. The various possibilities with their typical achievable enhancement factors reflecting the state-of-the-art of FI-VP-ETAAS combinations have undergone rapid developments. All the papers in Table 1 concern applications of on-line FI-VP-ETAAS. Initial reports dealt with the use of FI systems as a mere alternative to the on-line generation of the volatile species [28]. However, the key steps for automation, which are the transference of the analyte to the furnace and its subsequent in situ concentration were manually done [26], with an appreciable reduction of sample throughput. Besides, the complete automation of the FI-

VP-ETAAS technique has been hampered because the graphite tubes were initially impregnated with not or relatively stable trapping species, which required of the insertion of the trapping species prior to each measurement using also the manual technique.

However, the increasing use of: (i) microcomputers to control the measurement procedure and data acquisition and (ii) "permanent" sequestering reagents [29-31] have permitted the fully operation of most FI-VP-ETAAS preconcentration modes.

Haug and Liao have used the commercially available Perkin-Elmer FIAS-400 FI system for the determination of Sn [32], As, Sb, Bi [15], Se and Te [33] using in-situ trapping on stable coatings, which required only a single application on the atomizer surface. Trapping temperatures curves indicate higher signals for trapping of Sn at 500-600 °C, As at 750-800 °C, Sb at 450-800 °C and Bi at 100-500 °C on Zr-coated tubes, whereas, Ir- and Ir/Mg-coated tubes showed a higher response for trapping of Se and Te at 550-800°C and for Sb and Bi at lower temperatures. However, based on signal stability and reproducibility the better performance was found with the Zr-coated tubes with the characteristic masses of about 17, 16, 15 and 9 pg for Sn, As, Sb and Bi, respectively.

Whereas, the characteristic mass was about 11 pg for Se and 12 pg for Te. Changes in the AAS software allowed controlled hot injection of the gaseous hydride above 200°C. Also, Haug [20] has found that the stability and reproducibility of lead signals were better at 200-300°C after the tubing coating with either W or Zr. A characteristic mass of about 21 pg was readily obtained. An important step toward automation of the in situ trapping procedure was the hydride transfer into the graphite tube via the quartz capillary mounted in place of the PTFE capillary tubing on the sample dispenser arm, and the automatic insertion through the sample hole of the graphite tube [15,20].

Erber and Cammann [34] have presented a sensitive method for the on-line determination and preconcentration of nickel using the coupling of a FI system with transversely heated atomizer. The method, which was applied for the nickel determination in synthetic rain and certified water samples, was based on the volatilization of nickel as nickel tetracarbonyl and its in situ trapping on the pre-heated graphite furnace. Two tubes with reagents for the carbonyl generation were connected to the chemifold in which nickel tetracarbonyl is formed after reducing the nickel with sodium tetrahydroborate(III). An inert gas and the carbon monoxide needed transported the products from a gas-liquid separator to the atomizer. Because of the large amounts of carbon monoxide needed, two pumps were necessary to achieve a high flow of gas. The linear range for the determination of nickel varied from 0.1 up to 30  $\mu\text{g Ni l}^{-1}$  with a detection limit of 0.0018  $\mu\text{g Ni l}^{-1}$ .

Tyson and co-workers [25] have preconcentrated selenium from aqueous samples on an anion-exchange resin in order to improve the sensitivity and to allow the separation of the analyte from potentially interfering matrix compounds; also, the stripping of the hydrogen selenide was facilitated by the inclusion of glass beads in the gas-liquid separator. Recently, a standard double-line FI manifold was presented for a Perkin-Elmer FIAS-200 FI unit to generate lead hydride for the determination of lead in calcium supplements [21]. In the later, the hydride was trapped on the interior surface of a transversely heated graphite atomizer pre-treated with iridium; the quartz tipped transfer probe was inserted into the graphite atomizer such that the tip was about 1 mm above the L'vov platform. In all cases, the outlet of the block-type gas liquid separator was passed through a Nafion<sup>R</sup> dryer tube to remove moisture from the hydrogen|argon|hydride gas mixture before being delivered to the Ir-pretreated furnace via a quartz tube.

A FI-HG-ETAAS method was developed by Zhu and Xu [35] for the determination of thallium at the ng  $\text{l}^{-1}$  levels. The acidified sample solution containing Pd and Rhodamine B (to increase the HG efficiency further) merged with the aqueous sodium tetrahydroborate solution at room temperature. The generated gaseous phase was separated in a gas-expanded gas-liquid separator and was led directly into the quartz tube atomizer at 1000°C via the Ar carrier gas for detection by AAS.

**Table 1** Volatile species generated in FI manifolds followed by their on-line in situ trapping within a graphite furnace.

Species	Trapping species	Sample	Comments <sup>a</sup>	Ref.
As	Pd	Water	L-cysteine improved recovery. Thiourea reduced the interferent effect of Ni and Pt. The LOD = 36 pg.	11
	Zr	Aqueous standard solutions	The Zr coating was relatively stable, allowing ca. 80 firing.	12
	Pd	Aqueous standard solutions	As species were selectively determined using the Fleitmann reaction. The arsine was generated in an electrically heated tube filled with a rolled foil of metallic aluminium. The LOD = 10 pg.	13
Alkyl lead	None	Organolead compounds (dialkyl- and trialkyllead compounds)	With a 1.5 sample volume the LOD was about 7 ng l <sup>-1</sup> , but it could be lowered if larger sample volumes were used.	14
Bi	Zr	Water samples and low-alloy steel materials	The Zr coating allowed 400 trapping and atomization cycles. The detection limit was of 0.027 ng.	15
Hg	Ir	Water	After collection of Hg on a gold-platinum gauze, it was direct re-evaporated after amalgamation in the graphite furnace. The LOD for 10 and 25 ml samples were 35 and 70 pg, respectively. Sampling rate = 300 h <sup>-1</sup> .	16,17
Ge	Pd	Tap water and geological reference samples	The FI unit was controlled by a computer independent of the spectrometer. The FI system was kept in the standby mode before the and during the hydride collection. The LOD = 0.004 µg l <sup>-1</sup> using a 4.5 ml sample. Sampling frequency 18 h <sup>-1</sup> .	18
	Zr	Sediment and geological materials	A commercial FI unit was used. LOD = 18 pg for 1 ml sample volume.	19
Pb	W, Zr	Sediment certified reference material	The FI-HGAAS was accomplished using a continuous vapour generation accessory. The W and Zr coating allowed over 400 trapping and atomization cycles. The LOD = 0.25 ng	20
	Ir	Calcium  magnesium  zinc and calcium carbonate from crushed	The instrument was controlled by a commercially available software. The LOD = 0.03 µg l <sup>-1</sup> using 1 ml sample volume.	21

oyster shells  
supplements

Sb	None	Potable and surface waters	The measurement procedure and data acquisition were fully automated. The detection limit was of 5 ng l <sup>-1</sup> using 5 ml sample volumes.	22
Se		Water	The interferences from As, Bi, Sb and Sn were on-line eliminated.	23
	Zr	Aqueous standard solution	The Zr coating was relatively stable, allowing ca. 80 firing.	24
	Ir	Water	The analyte was preconcentrated using an Amberlite IRA-410Stron anion-exchange resin for 60 s. The LOD was 4 ng l <sup>-1</sup> for a 20-ml sample volume.	25
Sn	Pd	River sediment and orchard leaves	The stannane was manually transferred to the furnace. The LOD = 7 ng l <sup>-1</sup> for a 10-ml sample.	26
	Pd	Tap water and geological samples	On-line ion-exchange pre-concentration allowed a detection limit of 10 ng l <sup>-1</sup> using a 10.7 ml sample volume. Sampling rate = 30 h <sup>-1</sup> .	27
Tl	Pd	Water samples	The LOD = 3.3 ng l <sup>-1</sup> was obtained with a sample volume of 500 µl. The precision was 0.9% RSD, with a sampling frequency of 120 h <sup>-1</sup> .	35

<sup>a</sup>RSD = relative standard deviation, LOD = limit of detection.

#### 4. Conclusions

Most preconcentration procedures can be potentially used for the evaluation of volatile species with on-line FI-ETAAS instrumentation. However, up-to-date, the main limitations for on-line liquid/liquid, precipitation and coprecipitation and on-wall preconcentration procedures are the chemical reactions

involved in a particular assay, that would eventually require the fully automation of the overall operations. Nevertheless, the advantages of FI and sequential injection analysis (SIA) would offer different

possibilities for speciation studies and for the determination of successive parameters of environmental interest by ETAAS. These novel approaches should incorporate a computer to control the sequences of the well defined periods of time in order to achieve a reproducible process.

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