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Ultrasonic nebulizer interface system for coupling liquid chromatography and electrothermal atomic absorption spectrometry

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ABSTRACT

An ultrasonic nebulizer interface for direct "on-line" coupling of high-performance liquid chromatography (HPLC) with atomic absorption spectrometry with electrothermal atomization is described. Two modes of operation were evaluated for measurement of metal-containing chromatographic peaks. In the continuous mode the atomizer was kept at a preselected constant temperature during the chromatographic run while the analyte species were monitored. This mode of operation is suitable only for elements of high and medium volatility and provides poor detection limits. In the collection mode, the effluent from the HPLC column was thermally decomposed so that sample species, adsorbed on the cool parts of the atomizer, were available for subsequent pulse atomization. Only chromatographic peaks of reasonably different retention times can be measured separately in this mode.

The effects of parameters such as effluent flow-rate and composition, aerosol carrier gas flow-rate and collection temperature of the atomizer were investigated. The effects of different matrices on lead and chromium signals were studied. In the collection mode the detection limit of the system was below 1 ng for both chromium and lead.

INTRODUCTION

Determination of species rather than total metal concentrations at trace levels has been recognized to be vital in biochemical, agricultural and environmental studies. This has stimulated the development of so-called "hybrid techniques", which combine the abilities to separate effectively particular species and provide a sensitive element-specific detection. One of the most popular approaches in speciation is to couple liquid or gas chromatography (GC) and one of the spectroscopic techniques. In this instance, flame and electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma (ICP) [1] and laser-stimulated ionization (LEI) [2] have been employed. In most instances, coupling of the two techniques is relatively simple, for example, high-performance liquid chromatography (HPLC)–flame AAS or ICP, but the direct "on-line" measurement of HPLC effluents by ETAAS, which is one of

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the most sensitive techniques, is difficult. To circumvent problems with interfacing, the HPLC effluent has been collected in fractions ranging from 60 μl up to a few millilitres, and subsequently analysed by ETAAS. Most of the papers employing this technique are related to the determination of different copper and zinc blood proteins [3–6] and amino acids [7], but other applications [8–11] have also been published. The major drawback of the technique is that only well separated species can be distinguished.

Brinckman's group at the former National Bureau of Standards developed "well sampler" indirect coupling [12], involving a 50-μl PTFE flow-through cell. The effluent from the HPLC column, continuously passing the cell, is sampled (10–50 μl) at constant time intervals of 40–60 s and atomized in the electrothermal atomizer. This sampling mode has been successfully employed for determination of various organometallic (As, Sn, Hg, Si) compounds [13–15]. The same interface system was used by Fish and co-workers [16–18] in the determination of vanadyl and nickel porphyrin and non-porphyrin compounds in crude oil.

Other similar systems employing a sampling valve, an injector and associated electronics to control the analysis sequence have been developed independently by Vickrey *et al.* [19] and Stockton and Irgolic [20]. These systems delivered 40 μl of column effluent every 30–45 s into an ETAAS system equipped with Zeeman-effect background correction. Organocopper complexes in soil pore water [11] and selenite–selenate in river water [21] were measured by this technique. Both types of interface systems were employed by Brinkman *et al.* [22] for the determination of various arsenic species in soil extracts and drinking water. These two interfaces operate in the so-called "pulsed" mode of sampling, as the atomic absorption data are not continuous in terms of the effluent flow. The frequency of sampling depends merely on the duration of the atomization cycle (30–45 s), and therefore the best results are obtained at low effluent flow-rates and for broad chromatographic peaks. Narrow peaks at high effluent flow-rates can be missed completely by the AA detection system. As an improvement, a "peak storage" interface has been proposed by Vickrey *et al.* [23]. The effluent containing the peak is stored in a capillary tube during the chromatographic run and analysed off-line sequentially by ETAAS. In this way, more measurements can be made per chromatographic peak, which significantly improves the accuracy of the technique. The chromatographic peaks were reported to be broadened, but the resolution can be maintained if the storage tube volume is approximately equal to the peak volume. The concept of Vickrey *et al.* [23] was further modified by Bäckström and Danielsson [24], who connected an extraction system to the interface.

The first real "on-line" coupling of HPLC to a continuously heated graphite atomizer was described by Nygren *et al.* [25], who employed a thermospray interface. The performance of this was evaluated for speciation of tri- and dibutyltin using ion-exchange chromatography. The only limitation of the system was the relatively low effluent flow-rate (up to 0.2 ml/min) which could be tolerated. However, recent developments in designing "thermospray" devices for aerosol production in flame AAS [26] and ICP [27,28] indicate wider possibilities for this type of interface.

The aim of this work was to design and evaluate an interface which would tolerate the higher effluent flow-rates normally used in HPLC and yet provide continuous detection of metal-containing chromatographic peaks by ETAAS. An ultrasonic nebulizer spray chamber–aerosol desolvation system was constructed for this purpose and connected to a graphite atomizer. A similar system has been described recently [29] for interfacing HPLC to a flame photometric detector.

EXPERIMENTAL

Description of the interface

The main components of the ultrasonic nebulizer interface are shown in Fig. 1. The ceramic piezoelectric transducer (Channel Products, Chesterland, OH, U.S.A.) was clamped into the PTFE body by means of a PTFE nut. To prevent nebulizing solution entering the rear of the transducer, a sealing ring was placed in front of it. A brass ring and the centrally positioned brass container provide electrical contacts to the transducer. In order to ensure efficient heat exchange and good electrical contact, the surface of the brass container touching the transducer was polished and the container was spring loaded. The latter permitted relatively free vibration of the transducer.

The transducer temperature was maintained between 50 and 60°C by circulating tap water through the brass container. The transducer was powered by a commercial ultrasonic humidifier (Burg, SIBE International, Spånga, Sweden), which was modified to operate at a resonant frequency of 1.35 MHz. A maximum of 45 V was applied to the transducer. The effluent from the chromatographic column flowed continuously onto the working side of the transducer via a stainless-steel needle (1.1 mm O.D.). A small (17-ml) conical spray chamber, 140 mm long, was held in the PTFE nut, a tight connection being provided by a rubber sealing ring. Constant aerosol transport was maintained by directing a fixed argon flow through the chamber. The effluent condensing in the chamber was removed continuously through the drain tube. The conical part of the spray chamber, which ended in a 105 mm × 6 mm I.D.

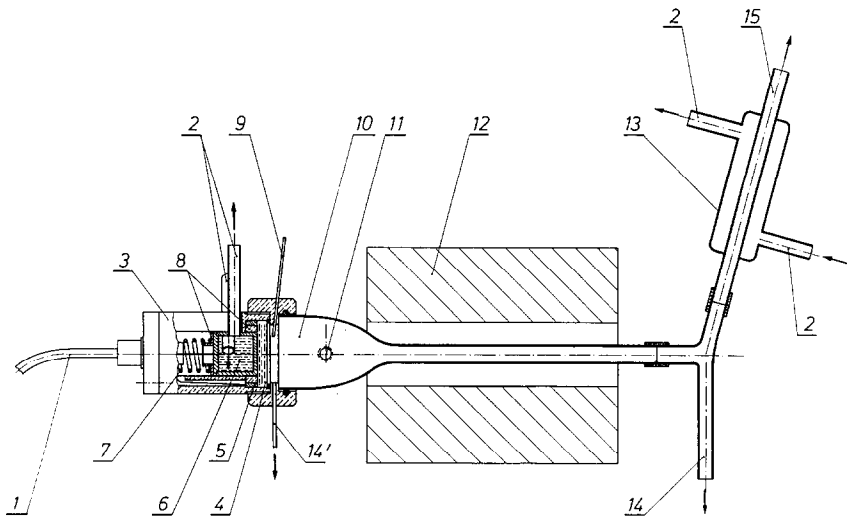

Fig. 1. Ultrasonic nebulizer interface. 1 = Electrical connection (50 V maximum, 1.35 MHz); 2 = cooling water circulating systems; 3 = PTFE body; 4 = piezoelectric transducer; 5 = brass ring providing electrical contact to the front side of the transducer; 6 = brass container for cooling water providing electrical contact to the rear of the transducer; 7 = spring; 8 = PTFE insulation; 9 = inlet tube for HPLC effluent; 10 = glass chamber; 11 = inlet for aerosol carrier gas; 12 = furnace; 13 = glass cooler; 14 = drain; 14′ = drain connected to peristaltic pump; 15 = aerosol supply to the graphite atomizer.

tube, was inserted into an electrically heated oven. The end of the spray chamber was connected to the cooler via a T-piece which provides an outlet for drainage of the condensed solvent. The dry aerosol was injected into the furnace through a 26 mm × 2.0 mm I.D. glassy carbon tube (Ringsdorff-Werke, Bonn, Germany). The latter was inserted into the enlarged sampling hole (3.2 mm diameter) of the atomizer tube so that it did not obstruct the light beams from the hollow-cathode lamps.

Description of the graphite atomizer

The two-step atomizer used in this work has been described in detail previously [30] and incorporates integrated contact (IC) tubes [31] and IC cups. The tube and cup can be heated independently of each other by two separate power supplies. A laboratory-constructed power supply equipped with an optical feed-back system [32] to provide temperature control was used to heat the IC tube. The cup was heated using a Perkin-Elmer HGA-500 power supply. Some measurements were carried out using IC tubes without the cup.

The atomizer was installed in a research spectrometer system [30,31] incorporating a Varian Techtron AA-6 monochromator complete with a hydrogen lamp for background correction. A Tecmar Labmaster with 12-bit ADC was used to interface the spectrometer with an Ericsson PC with a Facit 4513 A4 matrix printer.

Temperature measurements of the inner tube surface and of the inner cup bottom were made using a disappearing filament pyrometer (Keller Spezialtechnik Pyrowerk, Model PBO 6A F3) above 1300 K and otherwise with a NiCr–Ni thermocouple. Hamamatsu hollow-cathode lamps were used as light sources.

Instrumental parameters are listed in Table I.

TABLE I

INSTRUMENTAL PARAMETERS

Parameter	Pb	Cr
Wavelength (nm)	283.3	357.9
Spectral band width (nm)	0.7	0.2
Lamp current (mA)	4	8
Continuous mode of operation		
Atomization temperature (°C)		
Cup	1300[a]	–
Tube	1300[a]	–
Collection mode of operation		
Collection temperature (°C)		
Cup	2200[a]	2500
Tube	Not heated[a]	Not heated[a]
Atomization temperature (°C)		
Cup[b]	1800	2500
Tube[c]	1300	2050

[a] If not stated otherwise.
[b] Heating commenced 2 s after the start of the tube heating.
[c] Atomization time varied between 8 and 15 s.

Reagents and materials

$Pb(NO_3)_2$ and K_2CrO_4 aqueous solutions containing 1 mg/ml of metal were used for measurements of lead and chromium, respectively. Lower standards were prepared freshly in different water–methanol mixtures. Chromium standard solutions contained in addition $5 \cdot 10^{-4}$ *M* tetrabutylammonium phosphate (Supelco, Bellefonte, PA, U.S.A.).

In the interference study, 0.1 *M* NaCl (Merck, Darmstadt, Germany) and 1 *M* NH_4NO_3 (Merck) were used. All solutions were prepared from reagents of the highest available purity. The gas employed for the furnace and as an aerosol carrier was spectroscopic-grade argon. IC tubes and IC cups were manufactured from single pieces of RW0-quality graphite and coated with pyrolytic graphite (Ringsdorff-Werke). The IC tubes had a wall thickness of 0.6 mm and were of 5.7 mm I.D. and 19 mm long (round tubes) or of 5 mm square internal section and 24 mm long. Cups were 8 mm long, 7 mm in depth, of 5.2 mm O.D. and 2.8 mm I.D.

Operating procedure

The interface and electrothermal atomizer could be operated in two different modes:

(1) The "continuous mode", in which the ETA was held at a constant temperature during the whole period of the chromatographic separation. While the effluent was nebulized and transferred to the ETA, the absorbance was monitored continuously. In this mode, a two-step atomizer is not essential and a simpler commercially available system can be employed.

(2) The "collection mode". When the effluent containing the chromatographic peak of interest enters the interface, the atomizer tube or cup was heated to a preselected temperature, characteristic of the element of interest, and maintained constant for a period of time equivalent to the width of the chromatographic peak. Subsequently, the condensed species were atomized by the "pulse technique". The integrated absorbance can be used as a measure of the total metal content in a particular chromatographic peak.

To facilitate the optimization of the interface and ETA performance, the HPLC effluent flow was simulated by a peristaltic pump and a range of flow-rates (0.5–2.0 ml/min) normally encountered in HPLC were investigated. The chromatographic peak width and the total mass of element in a particular peak were varied by introducing samples into the stream of eluent over different time periods (5–20 s) and changing the concentration of the element in the solution.

RESULTS AND DISCUSSION

Continuous mode of operation

For this mode of operation the flow-rate of the carrier gas affects both aerosol transport efficiency and residence time of atoms in the detector. At very small flow-rates the residence time of droplets in the aerosol chamber becomes relatively long and, owing to the high rate of coalescence, considerable deposition losses of the effluent occur. This reduction in sample transport efficiency is, however, outweighed by an increase in detector sensitivity at lower flow-rates. The dependence of the detector sensitivity on aerosol carrier gas flow-rate is shown in Fig. 2. To achieve

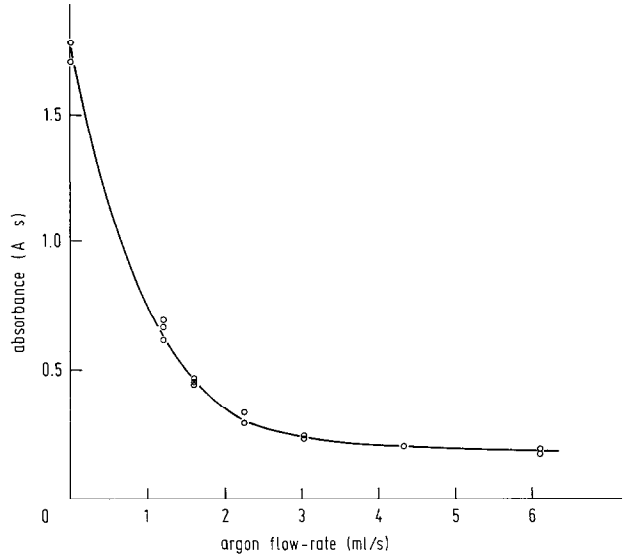

Fig. 2. Sensitivity of the detector varied by the aerosol carrier gas flow-rate (10 ng Pb).

reasonable precision, flow-rates below 1.0 ml/s should be avoided. For further experiments we used a flow-rate of 2.3 ml/s, thus lowering the sensitivity to *ca.* 20% of its maximum value.

The influence of effluent flow-rate on the sensitivity (sample throughput) was investigated in separate experiments, and very little variation in the signal magnitude was found in the range of flow-rates from 0.8 to 1.8 ml/min; 1 ml/min was chosen for further experiments.

The sensitivity of measurements employing the continuous mode was found to be relatively poor owing to the low sample transport efficiency of the interface and the detrimental effect of argon flow-rate on atom residence time in the graphite tube. In addition, the variations of the blank values were large because of long integration times and resulted in poor detection limits compared with previously described interface techniques [12–23].

Further, the 13-ml dead volume of the interface caused postcolumn chromatographic peak broadening of less than 20%. Another difficulty associated with the continuous mode of operation arises when elements requiring high atomization temperatures are monitored. In this instance the atomizer has to be kept at temperatures exceeding 2000°C for extended periods of time, which means that special furnaces have to be designed. To obviate these problems, an alternative method of chromatographic peak measurement was sought. In a recent paper, Demarin *et al.* [33], while determining various organogermanium and organosilicon species by GC–ETAAS, proposed a technique by which these compounds were decomposed and collected on the wall of the furnace and subsequently atomized in the "pulse mode". Detection limits 7–8 times lower than those in the continuous mode of operation were reported.

A similar approach was therefore investigated for the HPLC–ETAAS combination.

Collection mode of operation

The necessary requirement to employ this mode of operation is that the retention times (t_r) and approximate widths of the chromatographic peaks are known. The difference in the t_r values of two subsequent species of interest should be large enough to permit atomization of the first species collected before the collection parameters are re-established.

In order to collect analyte species efficiently, it is important that aerosol particles are vaporized before they are carried out of the atomizer by the convective gas stream. In contrast to aerosol particles, vapours will be trapped more readily, in particular if large temperature gradients exist in the graphite atomizer. Therefore, the use of the two-step atomizer was regarded as advantageous, as either the cup or the tube can be heated to vaporize the aerosol. Collection of the vapour species can then take place at the graphite parts which are not heated. It should be emphasized that the temperature required to vaporize the aerosol depends on its thermochemical properties, hence optimum temperatures have to be selected for a particular analyte and the matrix.

Collection of lead

In the first approach the tube was heated to various temperatures to vaporize the aerosol, which in this instance can be assumed to be present as lead nitrate particles. The analyte species were subsequently collected on the cool cup wall, which was not directly heated. As can be seen from Fig. 3, optimum collection efficiencies were obtained for tube temperatures between 650 and 750°C. Lead nitrate decomposes at 470°C, however, and the higher temperatures needed for best collection should be ascribed to effects caused by the convective argon flow, which will cool the gas phase of the tube and shorten the residence time of particles therein. Therefore, at insufficiently high temperatures particles might leave the tube only being partly vaporized. On the

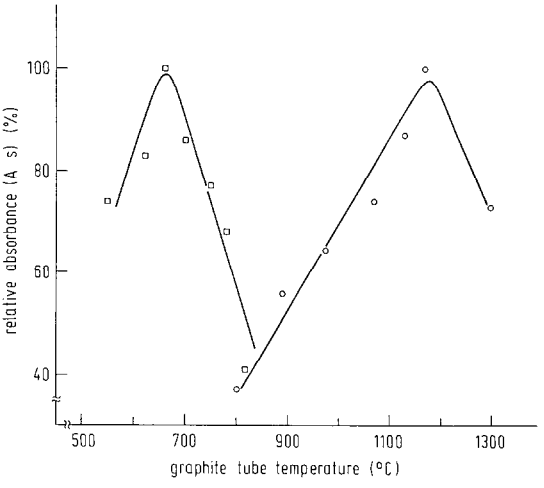

Fig. 3. Collection efficiency for 68.7 ng of lead (□), and 11 ng chromium (○) as a function of the graphite tube temperature. A two-step atomizer and a 19 mm long IC tube was used for lead and chromium, respectively. Solutions contained methanol–water (1:1, v/v). The effluent flow-rate was 1 ml/min. Aerosol carrier gas flow-rates of 2.6 ml/s (Pb) and 9.7 ml/s (Cr) were employed.

other hand, at too high temperatures a fraction of the analyte will be lost by re-evaporation.

In the second approach, the possibility of trapping the analyte species resulting from lead nitrate on the atomizer tube surface was investigated. In this instance, the cup was heated and the optimum temperature was found to be between 2200 and 2400°C. In this range the sensitivity and hence transport and/or collection efficiencies were 2–3 times higher than in the first approach and variations of the cup temperature in this temperature interval only slightly changed the sensitivity. Therefore, in subsequent experiments only the mode with the cup heated was investigated.

Collection of chromium

The temperature dependence of the collection of chromium species was investigated using IC tubes only or the two-step atomizer with the cup heated and the tube kept cool. The results are shown in Fig. 3 and it can be seen that collection efficiencies are strongly temperature dependent.

Effect of carrier gas flow-rate on sensitivity

An increase in the carrier gas flow-rate is expected to improve the transport efficiency of the aerosol from the spray chamber to the graphite atomizer and will, at the same time, reduce the residence time of the analyte species in the atomizer. The velocity of the gas through the graphite tube is in addition dependent on the applied collection temperature. This effect will be more pronounced if the tube is heated during aerosol collection. In this instance, it can be generally expected that lower flow-rates of carrier gas will be required for optimum collection, in contrast to the situation where the cup is heated. In the latter arrangement the aerosol particles are ejected from the entrance port at high speeds directly to the hot cup bottom where vaporization takes place. The convective flow of argon is maintained predominantly through the atomizer tube arms and thus an increase in the flow-rate does not influence to the same extent the removal of analyte species from the cup.

The effect of the argon flow-rate on the sensitivity of lead when the cup was heated for collection is shown in Table II. The optimum argon flow-rate extends over a fairly wide range, between 14 and 18 ml/s.

Effect of effluent flow-rate and matrix composition on transport efficiency and analytical signal

In HPLC, effluents containing various concentrations of organic solvents are usually obtained at flow-rates of 0.1–2 ml/min. Methanol, as one of the most frequently used mobile phases, was employed in this work. The effects of varying the composition of the methanol–water mixture and of the effluent flow-rate on the absorption signal were studied. In addition, the influence of some salt matrices was also examined.

Table III shows that a fairly low flow-rate of solution in the range 0.5–0.7 ml/min results in the most efficient sample transport. Towards lower or higher flow-rates the nebulization efficiency decreased for the vertically positioned transducer which was used here. The reason is that at very low flow-rates the sample makes contact with only a relatively small area of the vibrating surface, resulting in poor and irregular nebulization. At higher flow-rates the crystal surface is entirely covered by a regular

TABLE II

PEAK-AREA ABSORBANCES FOR 34 ng OF LEAD IN METHANOL–WATER (1:1) AS A FUNCTION OF AEROSOL CARRIER GAS FLOW-RATE

Cup temperature during collection, 2400°C.

Argon flow-rate (ml/s)	Peak area (A s)	Argon flow-rate (ml/s)	Peak area (A s)
5.0	0.185	14.5	0.588
6.8	0.235	16.8	0.586
10.7	0.435	18.3	0.620
12.5	0.539	20	0.518

liquid film, which will increase [34] in thickness so that the proportion of larger droplets formed will increase [35], reducing the transport efficiency.

It is well known that the diameter and the number of droplets formed during the nebulization process are merely dependent on the viscosity and surface tension of the nebulized solution [35]. This means that a change in the concentration of methanol is likely to affect the transport efficiency in the interface used in this work. However, measurements of lead using methanol–water solutions showed no systematic variation of peak-area absorbance on changing the methanol content from 50% to 90%. In a similar experiment, an increase in absorbance equal to twice the standard deviation of measurements was observed for chromium. This indicates that the interface can be used successfully for chromatographic separations using gradient elution. In order to check the extent to which the analytical results are affected by salt matrices, lead in the presence of 0.1 *M* NaCl and 1 *M* NH_4NO_3 was investigated. As can be seen from Table IV, 80 mg/ml of NH_4NO_3 did not alter the sensitivity of lead, whereas a ten times lower concentration of NaCl increased the signal significantly. It has been shown in previous studies [36] that ultrasonic nebulizers can tolerate fairly high salt concentrations in the solution without affecting the nebulization rate. The reason for the observed effect of 0.1 *M* NaCl present in methanol–water (1:1) effluent on the lead absorbance signal should therefore be sought in some other phenomena. It should be noted that a background signal, caused by NaCl, was observed during the atomization

TABLE III

NORMALIZED PEAK AREA FOR LEAD IN METHANOL–WATER (1:1) AS A FUNCTION OF EFFLUENT FLOW-RATE

Aerosol carrier gas flow-rate, 14.5 ml/s; collection temperature, 2200°C.

Effluent flow-rate (ml/min)	Peak area per ng Pb (A s)	Effluent flow-rate (ml/min)	Peak area per ng Pb (A s)
0.28	0.0147	1.00	0.0164
0.55	0.0225	1.43	0.0117
0.77	0.0191	1.96	0.0089

TABLE IV

MATRIX INTERFERENCE EFFECTS ON 30 ng OF LEAD

Effluent flow-rate, 1 ml/min; collection time, 10 s; carrier gas flow-rate, 14 ml/s; cup temperature, 2200°C.

Matrix	Peak area (A s)	Matrix	Peak area (A s)
H_2O	0.690 ± 0.020	H_2O	0.808 ± 0.064
1 *M* NH_4NO_3	0.726 ± 0.079	0.1 *M* NaCl	1.077 ± 0.085

of lead (see Fig. 4). If it is assumed that the atomization efficiency of lead is decreased in the presence of sodium chloride, the positive effect of this matrix on aerosol transport and/or collection would be even more pronounced. It is also evident from the signals shown in Fig. 4 that the major part of the analyte is not collected on the tube surface but on the cup surface which was heated during the collection. In the mode in which the graphite atomizer was operated, the upper part of the cup which is in direct contact with the cool tube will attain relatively low temperatures in comparison with the remainder of the cup. Sample vapours may therefore predominantly condense at the vicinity of the top, *i.e.*, on the rim of the cup. It is also reasonable to assume that convective gas flows are lower in the cup than in the tube, which favours condensation in the cup.

During atomization, the tube is heated first and then, after a selected delay time, the cup. In this mode of operation the upper part of the cup will be heated to some extent by the tube and when cup heating commences the entire cup will approach spatial isothermality.

In separate experiments, the effect of the power setting on the transducer performance was investigated. An increase in power resulted in a higher aerosol output. However, for long-term operation it is not recommended to use the highest settings because of the risk for overheating the transducer.

Dependence of peak width on sensitivity

In order to ensure an accurate determination of the analyte present as various species, separated by HPLC procedures, employing the interface in the collection mode, the influence of the chromatographic peak width on the sensitivity was examined. In this experiment the mass of lead was varied between 20 and 340 ng while the peak half-width, equivalent to the time of sample introduction, was varied between 5 and 20 s. The results showed a linear relationship between integrated absorbance and mass of lead, regardless of peak half-width.

Detection limits and reproducibility

Detection limits for chromium were measured on several occasions using both the two-step atomizer and the IC tube without a cup. The values obtained, based on three times the standard deviation for samples containing 7–14 ng of chromium corrected for blank values, were in the range 0.4–1.2 ng. In each series, blanks and samples were run alternately and each value reported is based on 10–15 measurements.

The detection limit for lead was determined using only the two-step atomizer with the cup heated for collection. The value obtained for samples containing 1.1 ng of

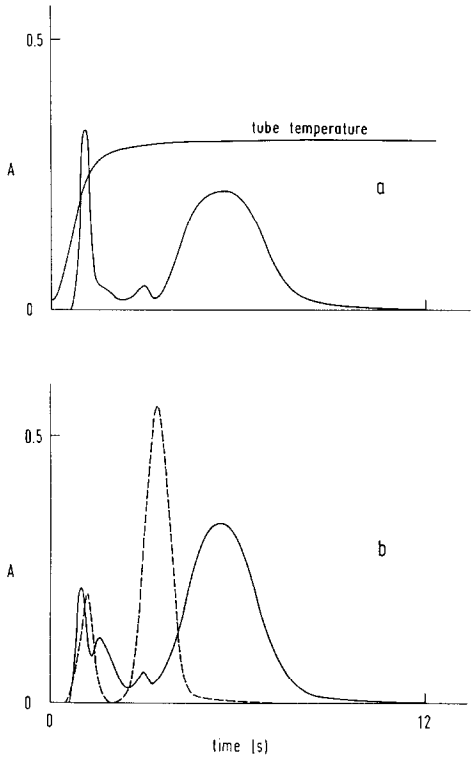

Fig. 4. Signal traces for 30 ng of lead trapped with the two-step atomizer (the cup was heated for collection). (a) Aqueous solution; (b) lead in 0.1 *M* NaCl. The dashed line denotes the background absorption.

lead was 0.3 ng using the above criteria for calculation. In both instances methanol–water (1:1) was employed.

The relative standard deviations of measurements were typically between 3 and 10%. If larger masses of chromium (above 100 ng) were determined, the signals started to tail resulting in poor reproducibility and memory effects. This problem is caused by the glassy carbon capillary inserted in the tube (even during atomization). The capillary does not reach a sufficiently high temperature for complete removal of large masses of chromium during the atomization step. This memory effect is eliminated by introducing an additional atomization sequence without sample.

CONCLUSIONS

The interface system described here facilitates "on-line" coupling of an HPLC column to an ETAAS system. Various effluents at flow-rates commonly encountered in HPLC can be employed without problems. Two modes of operation are proposed, a continuous and a collection mode, both yielding approximately the same sensitivity. The convective flow of argon through the atomizer in the continuous mode and incomplete trapping of the analyte in the graphite atomizer during collection are the limiting factors.

However, in the collection mode the detection limits are substantially improved (typically by one order of magnitude), and in addition the measured signals are not affected by the dispersion of the chromatographic system and/or postcolumn peak broadening. The system should be applicable to a large number of elements and the detection of less than 1 ng of analyte present in one chromatographic peak is possible.

Many inter-element variables critically affect the performance of the interface–graphite atomizer and hence optimization of the system for a particular chromatographic separation is necessary. In this respect it is desirable to investigate separately effects of effluent composition on processes such as nebulization, aerosol transport, trapping and atomization of the analyte.

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