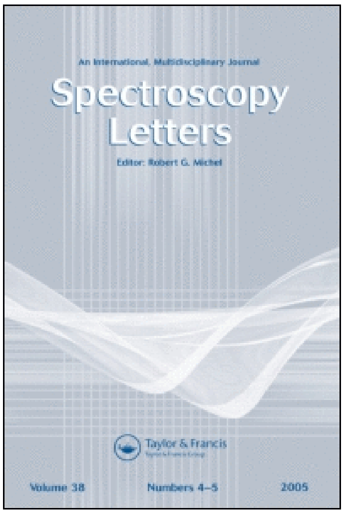

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Preconcentration of Non-Volatile Metal Compounds Using a Thermospray Increased Atomic Absorption Sensitivity

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Preconcentration of Non-volatile Metal Compounds Using a Thermospray Increased Atomic Absorption Sensitivity

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ABSTRACT

A thermospray was used as a metal preconcentration device for flame AAS. With 1.0 mL of sample loading, the AA signal was increased about 15 times and with 2.0 mL of sample loading the signal was increased about 30 times compared to a thermospray flame system and more than two order of magnitude compared to a normal flame system.

INTRODUCTION

A thermospray is a device to convert a stream of liquid into a jet of vapor/aerosol mixture by the combined action of vaporization and nebulization.[1-3] The thermospraying is obtained by forcing a solvent through the heated capillary tubing. The amount of energy applied to the thermospray controls the degree of vaporization, i.e. the ratio of aerosol to vapor, and properties of aerosol, which in turn affect the signal intensity.[4,5]

In previous studies, it was observed that when the amount of energy applied to the thermospray exceeded the energy required for steady solvent vaporization, the vaporization was completed inside the thermospray and a superheated jet of vapor containing little aerosol emerged. No signal was observed with flame AAS. It was suggested that the non-volatile analyte deposited inside the wall of the capillary tubing [3,4].

This property of trapping non-volatile metal compounds in the thermospray has been studied as a possible in situ method of preconcentration leading to increased sensitivity.

EXPERIMENTAL

A. Equipment

1. Atomic Absorption Spectrometer: Perkin Elmer Atomic Absorption Spectrometer model 370A equippped with deuterium background corrector.

2. Solvent Delivery System: Perkin Elmer High Performance Liquid Chromatography solvent delivery system model Series 2 equipped with two sinusoidal dual piston pump.

3. Sample Injector: Waters U6K injector with 2.0 mL sample loop.

4. Recorder: The output from flame AAS was recorded on a Sargent Welch XKR chart recorder.

5. Thermospray: The thermospray nebulizer described previously[4] was used.

The sample solution and solvent were transported from the injector to the thermospray nebulizer through a 0.15 mm i.d. stainless steel capillary tubing.

B. Reagents and Chemicals

Stock solutions, 1000 ppm, of the metals were prepared according to the procedures of Perkin Elmer.[6] All the chemicals used were analytical grade and all the solvents were HPLC grade. A distilled-deionized water was used.

A sample of lake water was collected from a lake located in Baton Rouge, Louisiana (1988). Water was sampled in acid washed Malgene container. The sample was acidified to pH 2.0 with a concentric HCl. After filtration through 0.45 μm membrane filter, sample was passed through the C-18 SepPak column to eliminate the organic constituents.

An air/acetylene flame was used throughout this study.

C. Experimental Procedure

i) Metals in Superheated Vapor

The power of the thermospray nebulizer was set to 140 watt and the solvent flow rate was set at 0.6 mL/min to ensure that all the solvent was converted to superheated vapor. After the thermospray nebulizer was equilibrated under conditions to produce superheated vapor (CSV), 2 mL of test solution was injected and allowed to pass through the thermospray nebulizer. Simultaneously, the thermospray nebulizer was placed inside a 500 mL suction flask which was submerged in an ice bath. The top of the flask was sealed with aluminum foil while the side suction opening was open for ventilation. The superheated vapor was trapped for 5 minutes by cooling. After 5 minutes, power was turned off and the thermospray nebulizer was immediately transferred to another suction flask to cold trap the vapor and aerosol mixture for a further 5 minutes. The amount of analyte in each condensed solution were then measured.

ii) On-line Metal Preconcentration by Thermospray

The thermospray nebulizer was placed to the position in the flame AA burner chamber as described earlier.[4] The energy of thermospray nebulizer was set at 140 watt and solvent flow rate was set at 0.6 mL/min again. After the thermospray nebulizer was equilibrated at this CSV, 1.0 mL of sample solution was injected. After three minutes, the flow rate was increased to 1.5 mL/min abruptly to eliminate the superheated vapor conditon.

RESULTS AND DISCUSSIONS

a) Studies of the analyte/superheated vapor separation

The volume of the condensed solution confirmed the complete recovery of the vapor by the cold trap using suction flask.

The superheated vapor contained virtually no metals as shown in Table 1. This clearly explained the reason for no analyte AA signal when the thermospray nebulizer was operated at superheated condition.

Table 1

Amount of analyte in Superheated Vapor and in Thermospray Nebulizer Tubing, n = 3

Total Amount of Metal Injected	Amount of Metal in Superheated Vapor	Amount of Metal Left in Tubing
2.0 μg Mg	0.02 μg (1%)	2.0 μg (100%)
5.0 μg Cd	0.05 μg (1%)	5.0 μg (100%)
10.0 μg Cu	0.20 μg (2%)	9.7 μg (97%)
10.0 μg Ca	0.20 μg (2%)	9.9 μg (99%)
100.0 μg Ca	3.0 μg (3%)	95.0 μg (95%)

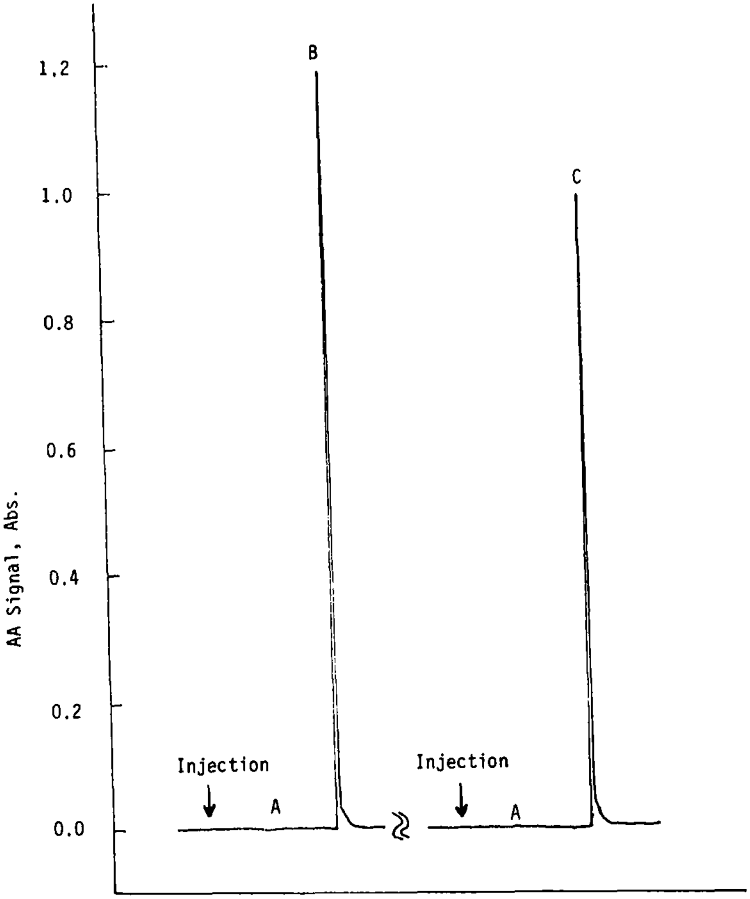

Fig. 1 AA Signal obtained at CSV

A: analyte accumulation period
B: signal from 1.0 ml of 0.5 ppm Cu solution
C: signal from 1.0 ml of 0.5 ppm Ca solution

When the thermospray nebulizer was run at non-CSV conditions almost all the metal that was trapped was eluted from the thermospray nebulizer as shown in Table 1. The metal trapping efficiency was higher than 97% except in the presence of high salt content.

Figure 1 indicates that no AA signal was observed when the thermospray nebulizer was operated at CSV but large and sharp AA peaks were observed by increasing solvent flow rate presumably redissolving the deposited analyte.

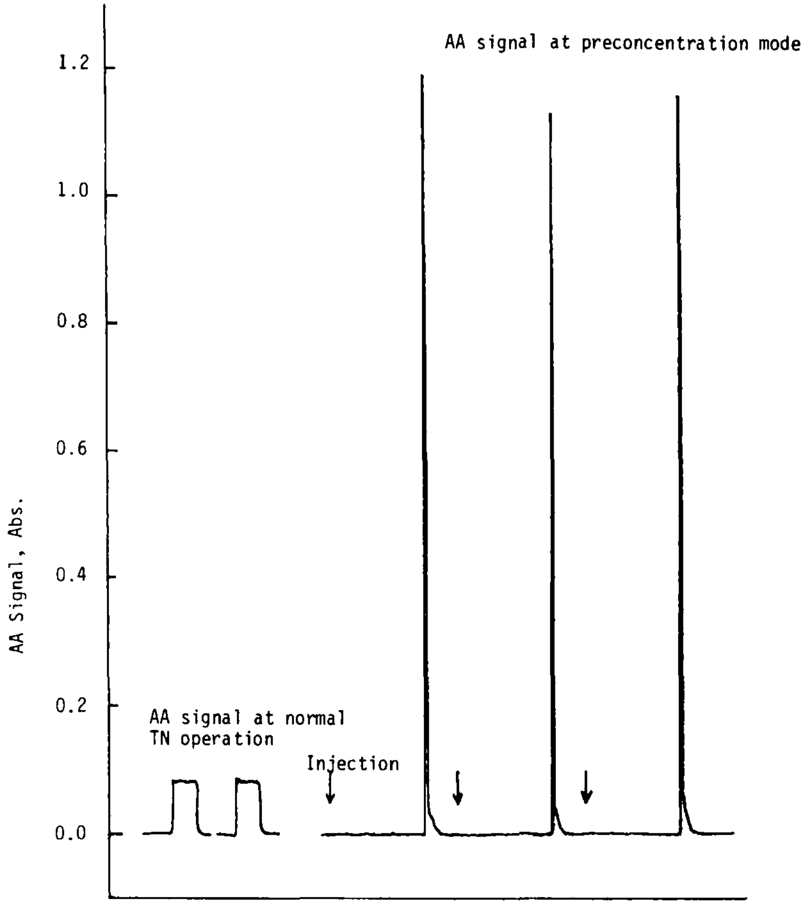

Fig. 2 Comparison of signals obtained from normal operation and preconcentration mode. 1.0 ml of 0.5 ppm Cu solution was tested.

This confirmed that the metal deposited inside the thermospray nebulizer when superheated vapor was produced and was washed off when the condition was removed.

In a simple explanation, it appears that deposition of the non-volatile analyte appeared to be an evaporation phenomenon, i.e. a non-volatile salt remained preferentially in solution phase and finally dried on the solid surface of the inner wall of the capillary tubing. The results of complete analyte

Table 2

Analyte Preconcentration Factor at Superheated Condition
Absorbance Signal
Volume Injected: 1.0 mL

Sample	Normal Burner[1]	No Preconcentration with Thermospray[2]	After Preconcentration with Thermospray[3]	Increased Sensitivity vs. Normal Burner[4]
0.5 ppm Cu	0.025	0.079	1.15 ± 0.08	X 46
0.5 ppm Ca	0.024	0.060	0.72 ± 0.06	X 30
0.05 ppm Mg	0.030	0.081	1.20 ± 0.05	X 40
0.05 ppm Mg + 10 mM NaCl	0.030	0.080	1.00 ± 0.08	X 33
0.05 ppm Mg + 50 mM NaCl	0.028	0.079	0.70 ± 0.08	X 25
0.1 ppm Cu*	0.005	0.017	0.46 ± 0.02	X 92

[1] Signal obtained at optimum operation
[2] Signal obtained at normal operation at 1.8 mL/min
[3] Signal obtained after preconcentration step, n = 10
[4] Preconcentration factor
* 2 mL injection

recovery indicated that it was a reversible physical process in which the deposited analyte could be redissolved and injected into the flame.

b) On-line Metal Preconcentration Mode

The ability of the thermospray nebulizer to trap the non-volatile metal under superheated vapor conditions raises the possibility of using this property as on-line metal preconcentration step for flame AAS. To study this, the thermospray nebulizer was operated at CSV and the sample was injected. The sample passed through the thermospray nebulizer and the analyte deposited inside the nebulizer walls. After all the sample had passed through the system the solvent flow rate was increased from 0.6 ml/min to 1.8 ml/min and CSV conditions were eliminated. The deposited analyte redissolved, and was swept into the flame producing a large signal.

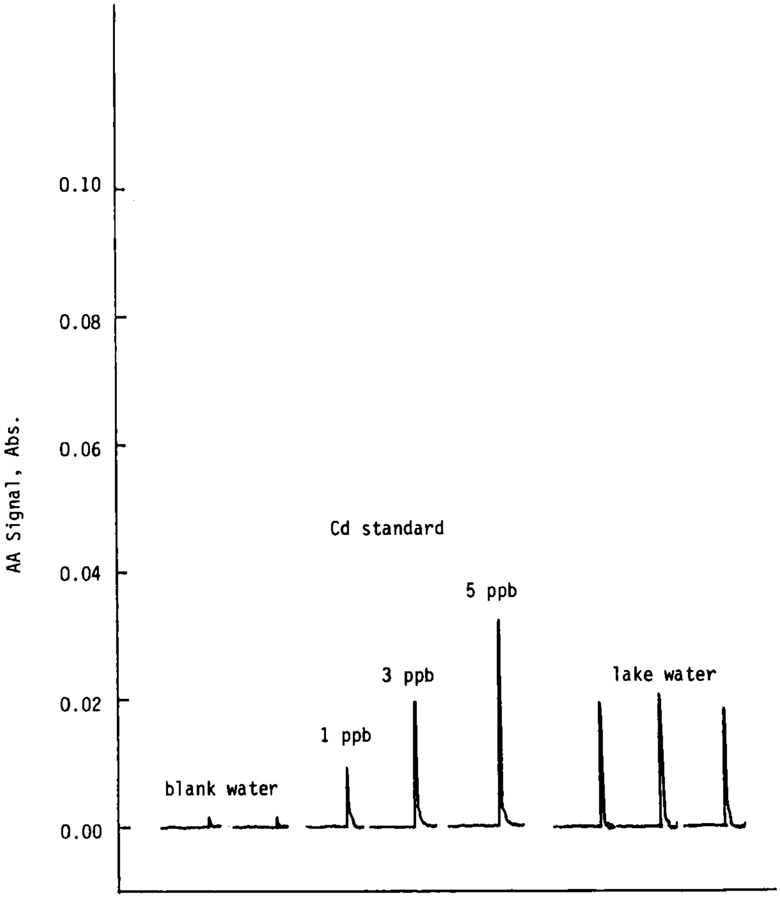

Fig. 3 [Cd] in lake water. Signal was obtained from 2.0 ml of sample at preconcentration mode.

Figure 2 shows the AA signal obtained from 1.0 mL or 0.5 ppm Cu solution when the thermospray nebulizer was operated at preconcentration mode. This was compared with the signal of 0.5 ppm Cu solution obtained at normal thermospray nebulizer operation.

A strong sharp signal was observed. Table 2 lists the results obtained with other metals. The preconcentration factor was about 15 times using a 1.0 mL and 27 times using a 2.0 mL sample injection.

Unfortunately, due to the narrow diameter and short length of current thermospray nebulizer tubing, the total amount of analyte that could be accumulated in this way was limited. In the presence of large amounts of salt, some fraction of analyte and salts were blown out by the vapor; thus, the preconcentration factor was reduced and reproducibility was poor.

With the wider and long capillary tubing, it is believed that more analyte can be loaded and high preconcentration factor can be achieved. This approach is being further investigated.

c) Cd Concentration in Lake Water

To extend this on line preconcentration mode to real sample, the lake water was collected and tested for the presence of cadmium. Figure 3 shows the results after 2.0 mL loading. It is estimated that this lake contained about 3 ppb cadmium. The results agreed with results obtained using a graphite furnace AAS.

d) Thermospray Nebulizer Washing Method

It was noted that operating the thermospray nebulizer at CSV caused an increase in backpressure, resulting in the blockage of the thermospray nebulizer eventually. The reason is not clear. Perhaps some of the metal compounds that deposited in the thermospray nebulizer were not washed off even when the superheating condition was removed, leaving trace amount of non-volatile analyte inside the tubing wall. Another possibility is the pyrolyzation of non-volatile organic constituent. Such traces of analyte may be cumulative unless it was removed by a cleaning solvent. Once the thermospray nebulizer was blocked up, it was almost impossible to clear it up again. Therefore, in general use, it was necessary to operate the thermospray nebulizer at the condition where not superheated vapor was produced.

It was helpful to wash the thermospray nebulizer, whenever some backpressure was noticed, with a weak citric acid or EDTA solution to remove deposited metals. Typically, 0.5 mM of citric acid solution or 0.5 mM EDTA solution was run through thermospray nebulizer with 10 W energy input for about one hour, followed by deionized water.

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