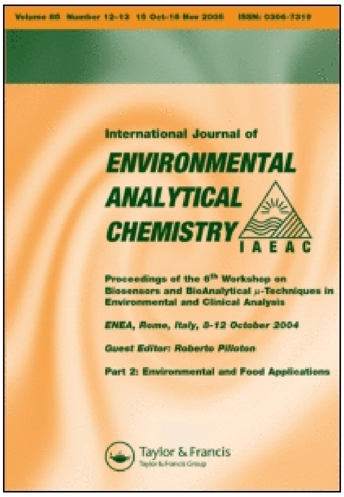

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# Slurry Sampling Electrothermal Vaporization Combined with ICP-AES for Direct Analysis of Environmental Samples

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# SLURRY SAMPLING ELECTROTHERMAL VAPORIZATION COMBINED WITH ICP-AES FOR DIRECT ANALYSIS OF ENVIRONMENTAL SAMPLES

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In this article, a polytetrafluoroethylene (PTFE) slurry was used as a chemical modifier for direct determination of trace elements in environmental samples by electrothermal vaporization inductively coupled plasma atomic emission spectrometry (ETV-ICP-AES) with slurry sampling. The vaporization behaviors of the analytes in slurry and solution were comparatively studied in the presence of PTFE. The main influence factors for this method were examined. Under the optimum operating conditions, the precision of this method was better than 7% with the detection limits varying from 1.7 ng mL$^{-1}$ (Cu) to 203 ng mL$^{-1}$ (Zn). The proposed method has been applied to the direct determination of the trace elements in camphor tree leaves and standard reference material (the combined sample of branch and leaf of shrub, GBW 07603) with satisfactory results.

*Keywords:* Trace metal elements; Slurry sampling; Electrothermal vaporization inductively coupled plasma atomic emission spectrometry; Polytetrafluoroethylene modifier; Environmental samples

## INTRODUCTION

Plants play an important role in the transfer of metals from environmental media, such as soil, water, and atmosphere, into the food chain. For this reason, one of the methods of environmental monitoring is assessment of the effect of polluted ground on chemical composition of plants. Inductively coupled plasma atomic emission spectrometry (ICP-AES) is frequently used to determine trace metals in plant samples [1–4]. However, in most cases, chemical pretreatment is necessary to remove the matrix prior to the measurement. This could lead to a long analysis time, the risk of contamination and loss of analyte, and discharge of pollutants from sample decomposition.

In order to avoid the above problems, direct sampling techniques, including direct insertion [5], powder insertion [6], slurry nebulization [7], laser ablation [8], and electrothermal vaporization (ETV) [9] have been developed for ICP-AES. In addition, several direct instrumental methods, such as laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) [10], electrothermal vaporization inductively coupled

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plasma mass spectrometry (ETV-ICP-MS) [11], electrothermal atomic absorption spectrometry (ETAAS) [12], neutron action analysis (NAA) [13], and X-ray fluorescence (XRF) [14], have drawn growing attention in routine analysis. When compared to the conventional solution sample introduction technique, slurry sampling combined with electrothermal vaporization (ETV) for sample introduction into ICP-AES offers the following advantages: (a) convenient sample preparation; (b) low sample volume requirement; (c) high transport efficiency; (d) easy removal of organic/inorganic matrix; (e) reduction of matrix non-spectral interference; (f) direct analysis of solid samples; (g) improvement of analytical performance using chemical modification techniques; (h) calibration with aqueous standards [15–18]. Our previous studies indicated also that the direct determination of the trace elements in high purity $La_2O_3$ could be carried out by slurry sampling fluorination assisted ETV-ICP-AES [19].

In the present work, slurry sampling coupled with ETV-ICP-AES for the direct analysis of trace elements in the environmental sample (camphor tree leaves) is described. A polytetrafluoroethylene (PTFE) emulsion was used as a chemical modifier to enhance the vaporization properties of analytes for improvement of analytical performances. The accuracy and precision of the proposed method were checked by analyzing standard reference material (the combined sample of branch and leaf of shrub, GBW 07603).

## EXPERIMENTAL

### Instrumentation

A 27 ± 3 MHz ICP spectrometer with a power of 2 kW (Beijing Second Broadcast Equipment Factory, Beijing, China) and a conventional plasma silica torch were used. A WF-1-type heating cycle with graphite furnace vaporizer (Beijing Second Optics, Beijing, China) was used as the vaporization device. The radiation from the plasma was focused as 1 : 1 straight image on the entrance slit of a WDG-500-1A monochromator (Beijing Second Optics, Beijing, China) having a reciprocal linear dispersion of $1.6\,\mathrm{nm\,mm^{-1}}$. The evolved components were swept into the plasma excitation source through a 0.5-m Teflon tube (4-mm i.d.) by a stream of carrier gas. The transient signals were detected with a R456-type photomultiplier tube (Hamamatsu, Japan) and a home-built direct current amplifier, and recorded by a U-135 recorder (Shimadzu, Japan). The instrumentation and operation conditions are listed in Table I.

TABLE I ETV-ICP-AES operating conditions

| | |
|---|---|
| Incident power (kW) | 1.2 |
| Carrier gas (Ar) flow rate ($\mathrm{L\,min^{-1}}$) | 0.6 |
| Coolant gas (Ar) flow rate ($\mathrm{L\,min^{-1}}$) | 18 |
| Observation height (mm) | 12 |
| Entrance slit width (μm) | 25 |
| Exit slit width (μm) | 25 |
| Drying temperature (°C) | 100, ramp, 10 s, hold, 20 s |
| Pyrolysis temperature (°C) | 700, ramp, 10 s, hold, 40 s |
| Vaporization temperature (°C) | 2400, 4 s |
| Clear-out temperature (°C) | 2700, 3 s |
| Sample volume (μL) | 10 |

## Reagents

All reagents used in this study were of specpure or analytical grade. The stock standard solution (1 mg mL$^{-1}$) for Y, Cu, Cr, Cd, Pb, and Zn were prepared from their oxides (Shanghai, China) by the conventional method. A 60% (m/v) PTFE emulsion ($d < 1\,\mu m$, viscosity, $7 \times 10^{-3}$–$15 \times 10^{-3}$ Pa s) was purchased from the Shanghai Institute of Organic Chemistry, China. Doubly distilled, de-ionized water was used throughout. All glass and polypropylene wares were kept in 10% (v/v) nitric acid for at least one night and then rinsed with 1% nitric acid (v/v) and subsequently with twice-distilled water before use.

## Sample Preparation

The sample (10 mg of camphor tree leaf) with a particle size of 140 mesh was accurately weighed into a graduated micro-testtube. Then 0.1 mL 60% (m/V) PTFE slurry, 0.1% agar, 0.1% Triton X-100 solution and $1.0 \times 10^{-4}$ mol L$^{-1}$ $HNO_3$ were added and diluted to 1 mL with twice-distilled water. The resulting mixture (1% (m/V) slurry) was dispersed with an ultrasonic vibrator for 20 min and then the bottles were shaken prior to any sampling. An aqueous standard solution containing 6% (w/v) PTFE was used for calibration.

## Procedures

After the plasma had been stabilized, 10 µL of sample was pipetted into the furnace. After being dried and ashed, the analyte was vaporized and carried into the plasma by the argon carrier gas. The emission signals from the plasma were recorded.

# RESULTS AND DISCUSSION

## Optimization of ICP Discharge Parameters

The ICP discharge parameters were chosen with the standard solution of the analytes, using signal-to-background rates (S/B) as observation index. The results showed that 1.2 kW power, 0.6 L min$^{-1}$ flow rate of carrier gas and 12 mm observation height could yield the optimum S/B.

## Verification of Temperature Programming

### *Pyrolysis Temperature*

In the presence of PTFE, the dependences of the signal intensities of the analytes on the pyrolysis temperature are given in Fig. 1. It can be seen that analytical signal losses of the target elements occur at above 1200°C. Therefore, a pyrolysis temperature of 700°C was used in this work.

### *Pyrolysis Time*

The effects of pyrolysis time on the analytical signal intensities of the analytes were optimized. The experimental results show that no significant influences are observed in the range of 30–70 s. To ensure the removal of as much matrix as possible, an appropriately long pyrolysis time of 40 s was chosen.

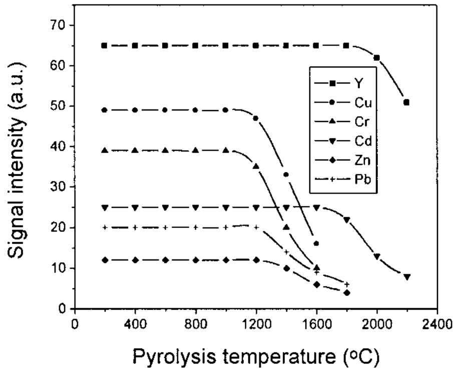

FIGURE 1 Influence of pyrolysis temperature on signal intensity with PTFE. Y, 1.0 μg $mL^{-1}$; Cu and Cr, 0.5 μg $mL^{-1}$; Cd, 10 μg $mL^{-1}$; Pb and Zn, 20 μg $mL^{-1}$.

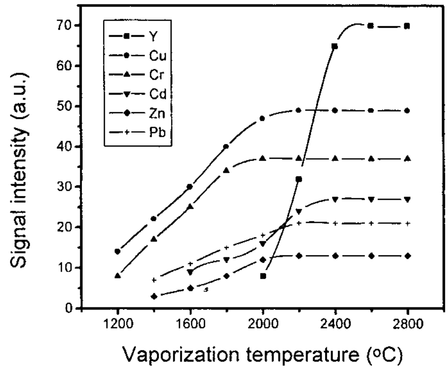

FIGURE 2 Analytical signal *versus* vaporization temperature with PTFE. Y, 1.0 μg $mL^{-1}$; Cu and Cr, 0.5 μg $mL^{-1}$; Cd, 10 μg $mL^{-1}$; Pb and Zn, 20 μg $mL^{-1}$.

### *Vaporization Temperature*

Figure 2 illustrates the effects of vaporization temperature on the analytical signal intensities of the elements with PTFE. As can be seen, the higher the vaporization temperature, the stronger the emission signals, and the emission signal intensity increment reached a plateau above *ca.* 2400°C. In this work, 2400°C was selected as a compromise vaporization temperature.

### *Matrix Interferences*

The effects of the common matrix elements (Na, K, Ca, and Mg) in plants on the signal intensities of the target elements were investigated. The experimental results in Table II show that when the concentration of the main matrix elements (Na, K, Ca, and Mg) lies between 2 mg $mL^{-1}$ and 5 mg $mL^{-1}$, there are no obvious effects on the determination of the target elements.

## Choice of PTFE Concentration

The optimum amount of PTFE was tested. It has been found that with a concentration of PTFE up to 5% (m/V), the signal intensities of the target elements (Y, Cu, and Cr)

TABLE II Effect of matrix concentration

| *Element* | *Wavelength* (nm) | *Tolerable amount of matrix element* (mg mL$^{-1}$) | | | |
|---|---|---|---|---|---|
| | | *K* | *Na* | *Ca* | *Mg* |
| Y | 371.030 | 5.0 | 5.0 | 5.0 | 5.0 |
| Cu | 324.754 | 5.0 | 5.0 | 5.0 | 5.0 |
| Cr | 267.716 | 5.0 | 5.0 | 5.0 | 5.0 |
| Cd | 228.567 | 4.0 | 4.0 | 3.0 | 3.0 |
| Pb | 220.353 | 4.0 | 4.0 | 3.0 | 3.0 |
| Zn | 334.502 | 5.0 | 5.0 | 2.0 | 2.0 |

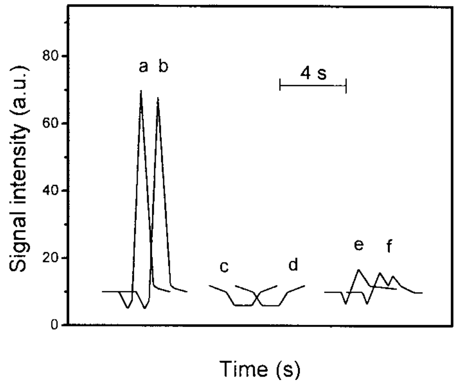

FIGURE 3 Typical signal profiles of the element Y. With PTFE: a, in the solution; b, in the slurry; c and d, are their residual signals of the empty firing, respectively. Without PTFE: e, in the solution; f, in the slurry.

do not increase with increasing PTFE concentration. However, the PTFE showed no effect on the signal intensities of Cd, Pb, and Zn owing to their greater volatilities. In this study, 6% PTFE was therefore used.

## Comparative Investigation of Vaporization Behavior

For comparison of the vaporization behaviors of the analytes in slurry and solution, the following experiments were carried out. Two sample aliquots were separately weighed into two micro-testtubes. One of them was directly used for the preparation of the slurry, and the other for the preparation of the slurry after wet-chemical digestion using the method described above. The signal profiles obtained for Y under the selected conditions are plotted in Fig. 3. It can be seen that in the absence of PTFE, the signals of Y are very weak in both the solution and the slurry. In the presence of PTFE, however, intense signals were recorded; the height, appearance times, and peak shapes of the emission signals in the slurry are very similar to those in solution, and there are no memory effects. The same results were observed for Cr and Cu. It should be pointed out here that PTFE does not affect the signals of the more volatile elements Cd, Pb and Zn. Thus, standard solutions can be used for the calibration of slurry samples.

## Detection Limits and Precision

The detection limits calculated as three times the standard deviation and precisions expressed as relative standard deviations (RSDs) for the nine replicate measurements are summarized in Table III.

TABLE III Detection limits and relative standard deviations ($n = 9$)

| *Element* | *Wavelength* (nm) | *Detection limits* (ng mL$^{-1}$) | *RSD* (%) |
|---|---|---|---|
| Y | 371.030 | 3.1 | 2.8 |
| Cu | 324.754 | 1.7 | 2.5 |
| Cr | 267.716 | 2.5 | 5.4 |
| Cd | 228.567 | 9.4 | 4.6 |
| Pb | 220.353 | 65 | 6.1 |
| Zn | 334.502 | 203 | 6.5 |

TABLE IV The contents of the target elements in the camphor leaf ($n = 5$)

| *Element* | *ETV-ICP-AES* | | | *PN-ICP-AES* |
|---|---|---|---|---|
| | *Calibration curve method*[a] (μg g$^{-1}$) | *Standard addition method*[a] (μg g$^{-1}$) | *Calibration curve method*[b] (μg g$^{-1}$) | *Calibration curve mehtod*[b] (μg g$^{-1}$) |
| Y | 1.52 ± 0.21 | 1.40 ± 0.30 | 1.46 ± 0.15 | 1.61 ± 0.25 |
| Cu | 9.85 ± 1.24 | 10.9 ± 1.5 | 11.4 ± 2.0 | 12.3 ± 1.0 |
| Cr | 2.47 ± 0.51 | 2.61 ± 0.43 | 2.55 ± 0.38 | 2.65 ± 0.24 |
| Cd | 1.12 ± 0.19 | 1.03 ± 0.21 | 0.94 ± 0.17 | 1.21 ± 0.13 |
| Pb | 8.41 ± 1.25 | 9.54 ± 1.31 | 7.82 ± 1.16 | 8.19 ± 1.08 |
| Zn | 42.3 ± 4.6 | 46.1 ± 5.5 | 43.8 ± 3.9 | 45.4 ± 4.7 |

[a]Direct analysis with slurry sampling. [b]Analysis after digestion with $HNO_3 + HClO_4$.

TABLE V The concentration of target elements in standard reference material of the combined sample of branch and leaf of shrub (GBW 07603) ($n = 5$)

| *Element* | *Found*[a] (μg g$^{-1}$) | *Certified* (μg g$^{-1}$) |
|---|---|---|
| Y | 0.75 ± 0.08 | 0.68 ± 0.02 |
| Cu | 5.7 ± 0.81 | 6.6 ± 0.4 |
| Cr | 3.2 ± 0.51 | 2.6 ± 0.1 |
| Cd | 0.44 ± 0.07 | 0.38 |
| Pb | 42 ± 3.5 | 47 ± 2 |
| Zn | 60 ± 4.9 | 55 ± 2 |

[a]Calibration curve method with slurry sample.

### Sample Analysis

The contents of Y, Cu, Cr, Cd, Pb, and Zn in camphor tree leaf were directly determined using the standard addition and working curve method. The analytical results are listed in Table IV. In addition, the results obtained by the proposed approach were compared with those obtained by pneumatic nebulization (PN)-ICP-AES. As can be seen, they are in good agreement.

In order to confirm the accuracy of the method, the standard reference material of the combined sample of branch and leaf of shrub (GBW 07603) was analyzed (see Table V). The results obtained are in good agreement with the certified values.

## CONCLUSIONS

The proposed method reduces the risk of contamination, is less time consuming, and has the advantage of small sample requirement. Moreover, calibration could be carried out by the standard addition method with aqueous standards owing to the elimination of differences in the chemical forms of analytes in the presence of PTFE. Therefore, it provides a reliable and fast routine determination method for direct analysis of solid environmental samples.

## *Acknowledgments*

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