

# Electrothermal Vaporization Inductively Coupled Plasma Atomic Emission Spectrometry for Direct Multielement Analysis of Solid Food Sample with Slurry Sampling

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## Résumé

Nous avons utilisé la technique du liquide chargé suivie de la vaporisation électrothermique (ETV) pour introduire l'échantillon à analyser par spectrométrie d'émission atomique couplée au plasma inductif (ICP-AES) en vue d'une mesure directe des éléments traces dans des échantillons d'aliments. Nous avons utilisé une émulsion dans le polytétrafluoroéthylène (PTFE) comme agent fluorant servant à promouvoir la vaporisation des substances à analyser. Nous avons étudié en détail les principaux facteurs pouvant affecter le signal analytique. Sous les conditions optimales d'opération, les limites de détection (DL) pour les éléments concernés variaient entre 1.8 ng/mL pour Cu à 215 ng/mL pour Zn. Les écarts-types relatifs se situaient entre 2.6% pour Cu et 7.2% pour Zn. La méthode que nous recommandons a été appliquée avec succès pour déterminer directement V, Cu, Cr, Fe, Zn et La dans le riz, sans aucun prétraitement chimique. Nous avons évalué l'exactitude et la précision de la méthode en analysant un standard certifié (feuilles de thé, GBW 07605) et en comparant les résultats de cette méthode avec ceux obtenus par nébulisation pneumatique (PN) ICP-AES, après décomposition chimique en milieu humide du même échantillon.

## Abstract

*Slurry sampling followed by electrothermal*

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vaporization (ETV) was used as a sample introduction technique in inductively coupled plasma atomic emission spectrometry (ICP-AES) for direct determination of trace elements in food samples. A polytetrafluoroethylene (PTFE) emulsion was utilized as a fluorinating reagent to promote the vaporization of analytes. The main factors affecting analytical signal were investigated in detail. Under optimum operating conditions, the detection limits (DL) for the interesting elements varied from 1.8 ng/ml (Cu) to 215 ng/ml (Zn). The relative standard deviations (RSD) were in the range of 2.6% (Cu) – 7.2% (Zn). The recommended method has been successfully applied to directly determine V, Cu, Cr, Fe, Zn and La in rice without any chemical pretreatment. The trueness and precision were evaluated by the analysis of a standard reference material (tea leaves, GBW 07605) and by comparison of the results for this method with those obtained by pneumatic nebulization (PN) ICP-AES after a wet-chemical decomposition of the same sample.

**Keywords:** Electrothermal vaporization inductively coupled plasma atomic emission spectrometry, trace elements, food, slurry sampling, polytetrafluoroethylene modifier

## Introduction

As is well known, trace elements are essential to human life owing to their participation in a wide variety of metabolic processes, including the synthesis or degradation of carbohydrates, lipids, proteins, and nucleic acids. A deficiency of Zn in the human body causes a

number of diseases, such as stunted growth, taste impediment and male sexual immaturity; Fe is responsible for the transportation of O<sub>2</sub> in blood; Cu has a great influence on arterial strength. Therefore, the analysis of trace elements in foods is an important topic in many areas from nutritional, clinical and biomedical studies to product quality control.

Inductively coupled plasma atomic emission spectrometry (ICP-AES) is a powerful multielement analysis tool that has been widely used for the determination of trace elements in food samples (1-4). Unfortunately, the majority of analyses by ICP-AES are carried out on solutions using a conventional pneumatic nebulizer. This technique has the merits of convenient operation and high precision but, in most cases, chemical pretreatment is necessary to remove the matrix prior to the measurement, as it may be subject to contamination and results in a high blank. In recent years, the application of direct sampling techniques, such as direct sample insertion (5), slurry nebulization (6), laser ablation (7) and electrothermal vaporization (ETV) (8), to ICP-AES for the direct analysis of solid samples have received increased attention because of simple sample pretreatment, low contamination risk, less possibility of analyte loss, and avoidance of corrosive and hazardous chemicals for sample decomposition. Of these techniques, ETV seems to be a very promising approach for solid sample introduction into ICP-AES. This alternative technique to solution nebulization presents several advantages, including high sampling efficiency, small sample requirement, low absolute detection limit, direct analysis of solid sample, and complete or partial removal of organic/inorganic matrix in an ashing step. Furthermore, various chemical modifiers could be utilized to promote the vaporization and transportation of refractory elements for the improvement of their detection limits (9-12). In a previous publication, a polytetrafluoroethylene (PTFE) emulsion chemical modifier was successfully applied for direct ETV-ICP-AES analysis of a high purity material (13).

In this work, an investigation of direct multielement analysis of solid powder foods by slurry sampling ETV-ICP-AES was performed using PTFE emulsion as a chemical modifier. The influences of instrument operating conditions, particle size, matrix and PTFE concentration on analytical signals and vaporization behaviors of analytes in both slurry and solution were studied. The proposed method has been applied to the direct determination of

Table 1. Instrument operation parameters for ETV-ICP-AES

Incident power (kW)	1.1
Carrier gas (L/min)	0.5
Coolant gas (L/min)	16
Observation height (mm)	12
Entrance slit width (μm)	25
Exit slit width (μm)	25
Drying temperature (°C)	100 ramp. 10 s, hold 20 s
Ashing temperature (°C)	600 ramp. 10 s, hold 50 s
Vaporization temperature (°C)	2400, 4 s
Clear temperature (°C)	2600, 3 s
Sample volume (μL)	10

V, Cu, Cr Fe, Zn and La in rice and a standard reference material (tea leaves, GBW 07605) with satisfactory results.

## Experimental

### Instrumentation

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

### Reagents

All reagents used in this work were of specpure grade or analytical grade. Twice-distilled water was used throughout. All glassware was soaked in nitric acid for 15 minutes and rinsed with twice-distilled water before

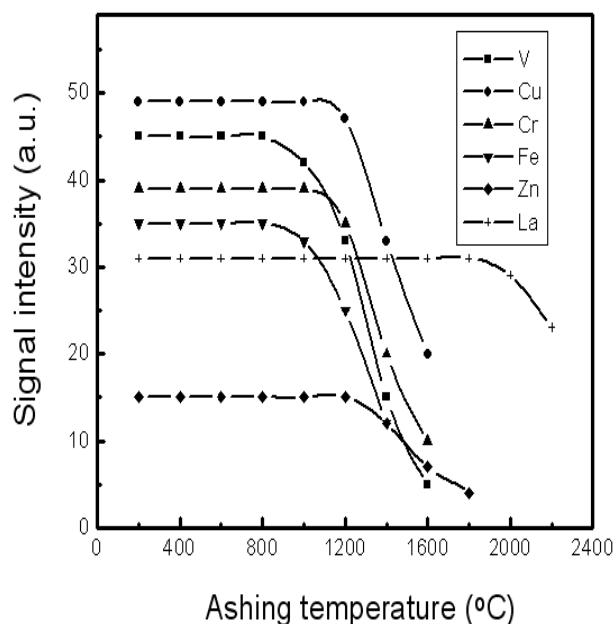


Figure 1. Influences of ashing temperature on emission signal intensity with PTFE: V and Cu, 0.5  $\mu\text{g/mL}$ ; Cr, Fe and La, 0.8  $\mu\text{g/mL}$ ; Zn, 10  $\mu\text{g/mL}$ .

use. The stock standard solutions (1 mg/mL) of V, Cu, Cr, Fe, Zn and La were prepared from their respective oxides by a conventional method before use. A 60% (m/v) PTFE emulsion ( $d < 1\mu\text{m}$ , viscosity,  $7 \times 10^{-3}$ – $15 \times 10^{-3}$  Pa s) was offered by the Institute of Shanghai Organic Chemistry (Shanghai, China).

#### Slurry sample preparation

The rice samples used in this study were ground in an agate mortar until they could be completely passed through the different mesh-size polyester sieves. A 10 mg portion of the sample was accurately taken into a micro-test tube with graduation. 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  $\text{L}^{-1}$   $\text{HNO}_3$ , which was previously checked for blanks, were added and diluted to 1 mL with twice-distilled water. Aqueous standard solutions containing 6% (m/v) PTFE were used for calibration. The slurry samples mentioned above were dispersed with an ultrasonic vibrator for 20 minutes, and then the micro-test tubes were shaken prior to any sampling.

#### Recommended procedure

After the plasma had been ignited and stabilized, 10  $\mu\text{L}$  of slurry sample was pipetted into a graphite furnace with a micro-syringe. The graphite furnace was sealed with a graphite cylinder before its heating cycle

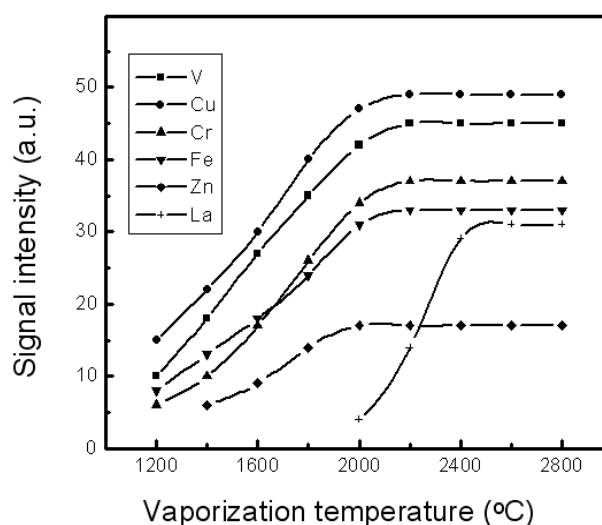


Figure 2. Analytical signal versus vaporization temperature with PTFE: V and Cu, 0.5  $\mu\text{g/mL}$ ; Cr, Fe and La, 0.8  $\mu\text{g/mL}$ ; Zn, 10  $\mu\text{g/mL}$ .

commenced. After being dried and ashed, the analyte was vaporized and carried into plasma by argon gas, and the emission signals of the analytes from the plasma were recorded.

## Results and Discussion

### Optimization of ETV conditions

#### 1) Ashing temperature

The ashing temperature, as an important factor affecting the emission signal, should be considered for direct analysis of food. In general, a higher ashing temperature could lead to analytical signal loss, whereas a lower ashing temperature is not beneficial to the complete elimination of organic matrix. Figure 1 shows the dependence of emission signal intensities of the analytes with addition of PTFE on the ashing temperature. As can be seen, the analytical signal losses of the analytes occur above 800  $^{\circ}\text{C}$ . Thus, in order to completely remove the organic matrix without analytical signal loss, an ashing temperature of 600  $^{\circ}\text{C}$  was selected for the analysis of real samples.

#### 2) Ashing time

The influence of ashing time on the emission signal intensities of the analytes was examined at an ashing temperature of 600  $^{\circ}\text{C}$ . The experimental results showed that the signal intensities of the tested elements remain constant with increasing ashing time from 30 s to 70 s. Therefore, an ashing time of 50 s was used throughout

the experiment.

### 3) Vaporization temperature

At an optimized vaporization time of 4 s, the effects of vaporization temperature on the emission signal intensities of the elements of interest were investigated with PTFE. The results shown in Figure 2 illustrate that the emission signal intensities of the interesting elements are enhanced with increasing temperature, and the signal intensities reached a plateau at a proper vaporization temperature (about 2400 °C) due to the formation of more volatile fluoride with similar vaporization characteristics. In this work, a compromise vaporization temperature of 2400 °C was used for the simultaneous multielement determination.

#### Investigation of fluorination vaporization behavior

The typical signal profiles of V, Cu, Cr, Fe, Zn and La in both slurry and solution prepared from the same sample were investigated with and without PTFE. The experimental results showed that, in the absence of PTFE, weak emission signals with trailing for the refractory elements (V, Cr and La) and medium volatile elements (Cu and Fe) were observed for the slurry or the solution, and the residual signals obtained after empty firing were almost the same as the original signals. However, after the addition of the fluorinating reagent PTFE, sharper and more intense emission signals without trailing were recorded, and there were no memory effects in the empty firing process. Moreover, the appearance time, height and profile of the analytical signals from the slurry were extremely similar to those from the solution. From the experimental results stated above, it could be concluded that, for the refractory elements and medium volatile elements, the addition of PTFE not only eliminates the differences in the form in which samples exist, but also greatly promotes the vaporization efficiency and improves the analytical sensitivity because of the formation of the corresponding volatile fluorides. In other words, the analytes in either slurry or solution have similar vaporization behaviors in the presence of PTFE. As an exception, sharp and intense emission signal profiles of Zn were obtained and no memory effect existed with or without PTFE. The possible reason for this is that Zn does not form a thermally stable oxide or carbide. Hence, it is feasible to employ aqueous solution standards for the calibration of slurry samples, and the systematic errors of the analytical results can be ignored.

Table 2. Influence of the particle size on the relative vaporization rates (%) (n=3)

Particle size (mesh)	Element					
	V	Cu	Cr	Fe	Zn	La
>270	101.1±2.0	99.1±1.7	99.1±2.0	100.8±1.4	102.1±2.5	98.1±2.8
270-230	99.5±2.4	102.7±2.9	98.0±3.1	98.6±2.9	98.4±3.0	96.9±3.9
230-200	98.2±3.0	97.8±4.2	97.6±3.7	97.4±3.5	98.3±4.1	96.7±4.4
200-170	96.7±4.3	96.5±4.5	95.7±5.5	97.8±4.9	96.4±5.5	94.8±5.3
170-140	94.0±4.9	96.3±5.7	93.3±7.1	95.4±5.8	96.8±6.1	93.5±7.3
140-100	88.7±8.0	83.4±9.4	80.6±14.3	84.1±10.3	82.2±7.9	76.2±15
100-70	75.6±12.5	69.4±15.3	65.9±18.1	72.8±13.5	71.5±9.4	55.3±23

#### Effect of particle size

The particle size of the solid sample used to make the slurry can influence the stability of the slurry and the vaporization efficiency of the analytes, which in turn can influence the trueness and precision. Thus, the effect of particle size on the determination of the analytes was investigated by measuring the relative vaporization rate (R) of the interesting element in different slurries prepared from the same sample with different particle sizes. The relative vaporization rate is defined as the ratio of the signal intensity of an element in the slurry to that in a solution containing the same concentration under the optimized conditions as expressed in percentage with PTFE. The experimental results in Table 2 show that when the average particle size of the sample is smaller than 0.105 mm (140 mesh), the relative vaporization rate is larger than 93%, with a relative deviation between a single determined value and the average value being smaller than ±10%. In this work, samples with a particle size less than 0.105 mm (140 mesh) were used.

#### Effect of matrix amount

With PTFE as a chemical modifier, the effects of the common matrix elements (Na, K, Ca and Mg) in food samples on the emission signal intensities of the elements of interest were investigated by ETV-ICP-AES. The experimental results demonstrated that the amount of the matrix elements ranging within 2 mg/mL - 5 mg/mL does not affect the emission signal intensities of the examined elements. In other words, the addition of PTFE slurry as a chemical modifier in ETV-ICP-AES could remarkably reduce the matrix effects. Thus, the systematic errors resulting from matrix effects can be ignored. Further studies on the removal of matrix

Table 3. Detection limit and precision (n=9)

Element	Wavelength (nm)	Detection limit (ng/ml)	RSD (%)
V	290.882	2.6	3.9
Cu	324.754	1.8	2.6
Cr	267.716	2.3	4.2
Fe	259.940	3.5	3.6
Zn	334.502	215	7.2
La	333.749	8.0	5.8

interferences by means of PTFE slurry are being undertaken.

#### *Influence of PTFE concentration*

The influence of PTFE concentration on the emission signal intensities of the interesting elements was investigated by varying PTFE percentage (m/v) from 0.5% to 10%. The experimental results showed that the emission signal intensities of V, Cu, Cr, Fe and La were enhanced with increasing PTFE concentration and reached constant values at a PTFE concentration of about 5%. However, the PTFE showed no effect on the emission signal intensity of Zn. Taking into account that the PTFE could be consumed by matrix in a real sample analysis, a properly higher PTFE concentration of 6% was used in this work.

#### *Calibration, detection limit and precision*

The analytical performance of the proposed method was tested using aqueous standard solutions and the optimized parameters listed in Table 1. The slopes of the calibration curves for analytes were linear over a concentration range of three orders of magnitude and had correlation coefficients better than 0.998. The detection limit (DL) is defined as the concentration corresponding to three times the standard deviation of the blanks. The detection limits for the elements of interest and the relative standard deviations (RSDs) of the proposed method obtained for nine replicate determinations at a concentration of 0.2 µg/mL V, Cu, Cr, Fe, La and 2.0 µg/mL Zn, are reported in Table 3.

#### *Sample analysis*

The proposed method was applied to the direct determination of V, Cu, Cr, Fe, Zn and La in rice using the standard addition method and working curve method. The same samples were also analyzed by PN-ICP-AES after wet chemical decomposition of the samples. All data are summarized in Table 4. As can be seen, they are in good agreement. In order to verify the reliability of the proposed procedure, a reference standard material of tea leaves (GBW 07605) was analyzed, and the results given in Table 5 indicate good agreement with the certified values.

Table 4. Analytical results of the interest elements in rice (n=5)

Sample	Element	FETV-ICP-AES		PN-ICP-AES	
		Calibration curve method <sup>a</sup>	Standard addition method <sup>a</sup>	Calibration curve method <sup>b</sup>	Calibration curve method <sup>b</sup>
Rice (µg/g)	V	0.47±0.07	0.58±0.09	0.51± 0.05	0.60± 0.04
	Cu	4.35± 0.48	4.17± 0.55	4.47±0.40	4.60±0.25
	Cr	0.34±0.06	0.40±0.07	0.47±0.05	0.43±0.04
	Fe	15.4±2.3	13.9±2.5	14.0±1.8	15.8±1.2
	Zn	26.5±3.1	24.6±3.7	25.0±2.9	26.9±2.0
	La	0.87±0.16	0.83±0.15	0.90±0.12	0.77±0.05

<sup>a</sup>Direct analysis with slurry sampling. <sup>b</sup>Analysis after conventional acid digestion.

Table 5. The concentration of interest elements in the standard reference material of tea leaves (GBW 07605)(n=5)

Element	Found <sup>c</sup> (μg/g)	Certified (μg/g)
V	0.98±0.14	0.86
Cu	18.9±2.5	17.3±1.0
Cr	0.71±0.10	0.80±0.02
Fe	280±21	264±10
Zn	29.1±3.9	26.3±0.9
La	0.53±0.07	0.60±0.03

<sup>c</sup>Calibration curve method with slurry sample

## Conclusion

Slurry sampling combined with ETV for sample introduction into ICP-AES has been developed for direct determination of trace elements in solid powder food samples. The calibration of slurry samples could be performed by using aqueous standards because, in the presence of PTFE, the vaporized analytes from the slurry have similar vaporization characteristics to those from a solution. The possible reason for this is that the analytes, which exist in either slurry or solution, could be converted into the volatile fluoride when using PTFE as chemical modifier. In addition, in comparison with the conventional nebulization of solution, the proposed method has the advantages of eliminating sample pretreatment, reducing sample contamination, small sample requirement and no discharge of pollutants from sample decomposition.

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