

Study on the Simultaneous Determination of Different Volatile Elements in High Purity Zirconium Dioxide by *In situ* Matrix Removal and ETV-ICP-MS

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INTRODUCTION

As a basic substance for the production of advanced functional and structural materials, zirconium dioxide powder has attracted considerable practical interest due to its variety of applications ranging from sensors, insulators, coatings, solid electrolytes for fuel cells, piezoelectric or electro-optic devices, catalysts and engine parts to stationary phases in liquid chromatography (1-3). Several investigations show that the desired properties and applications of ZrO_2 may be strongly influenced by the addition of minor as well as trace elements (4, 5). Therefore, it is essential to develop a simple, rapid, sensitive, and accurate method with minimum chemical pretreatment for the determination of trace elements in high purity ZrO_2 .

Currently, inductively coupled plasma atomic emission spectrometry (ICP-AES), atomic absorption spectrometry (AAS), and inductively coupled plasma mass spectrometry (ICP-MS) still represent the most important routine techniques for elemental analysis (6-11). However, AAS greatly suffers from limited matrix tolerance and single-element detection ability and is generally not suitable for routine analysis of refractory elements such as Zr, Hf, Nb, Ta, and the rare earth elements (REEs). Although ICP-AES allows fast and multielement analysis, it often suffers from the line-rich spectrum interferences of some elements such as Zr, Ta, and REEs.

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ABSTRACT

In this work, a novel method was developed for the simultaneous determination of different volatile elements (refractory Cr, medium volatile Cu, and easily volatile Cd) in high purity zirconium dioxide (ZrO_2) by *in situ* matrix removal and electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS). A polytetrafluoroethylene slurry (PTFE) as a chemical modifier not only enhanced the difference in the volatility between the analytes and the matrix for *in situ* matrix removal, but also results in their similar vaporization behaviors of the different volatile elements (Cr, Cu, and Cd) for their simultaneous determination. Under optimum operating conditions, the detection limits (DLs) for Cr, Cu, and Cd were 2.5, 9.8, and 3.4 ng g^{-1} with relative standard deviations (RSDs) of less than 6.2%, respectively. The calibration graphs of the analytes were linear over three orders of magnitude. This method was applied to the simultaneous determination of the different volatile elements Cr, Cu, and Cd in high purity ZrO_2 , and the results were in good agreement with those obtained by conventional pneumatic nebulization (PN) ICP-MS after separation of the matrix with a solvent extraction procedure.

Relatively, ICP-MS is the most favorable choice for elemental analysis owing to its high sensitivity, multi-element detection capability and lack of line-rich spectral interferences encountered in ICP-AES. However, it is often difficult to

directly determine trace impurity elements in high purity materials by ICP-MS because of very low analyte concentrations and a complex sample matrix. To solve these problems, an effective separation and preconcentration step is often required prior to their determination (12-20). This could lead to a long analysis time, risk of contamination and loss of analytes, and discharge of pollutants from sample pretreatment. In addition, the most popular sample introduction method for ICP-MS is pneumatic nebulization (PN). It is simple and convenient to operate, but PN suffers from low sample transport efficiency and presents some difficulties with viscosity, high salt content, and micro-volume of sample.

Electrothermal vaporization (ETV) as a sample introduction device for ICP-MS has many advantages, including high introduction efficiency, small sample requirement, low absolute detection limit, and partial or complete removal of the organic/inorganic matrix (21-27). However, conventional ETV has disadvantages with respect to very low sensitivity and severe memory effect for refractory and carbide formation elements such as Zr, Ta, V, Ti, Cr, Mo, W, Nb, B, Si, and the REEs. On the other hand, ashing loss may occur in ETV for easily volatile elements such as Cd, Zn, and Pb which results in a decrease of analytical signals. It is obvious that ETV as a sample introduction technique for ICP-MS is difficult for the simultaneous determination of refractory/carbide formation and easily volatile elements. Fortunately, the application of a chemical modifier in ETV to change

the volatility of refractory and volatile elements is an alternate way to solve this problem. The representative chemical modifiers are halogenating reagents, metal salts, and chelating reagents (28-35). Among them, polytetrafluoroethylene as a classical and effective chemical modifier has been used in ETV-ICP-AES/MS because of its attractive features such as high fluorine content, sufficient activity, suitable decomposition temperature (about 415 °C), fewer inorganic impurities, and convenient use (36-38).

In this work, PTFE was used as a chemical modifier for ETV-ICP-MS to convert the refractory matrix (Zr) and the different volatile analytes (refractory Cr, medium volatile Cu, and easily volatile Cd) into their fluorides. The formation of the fluorides greatly changes their vaporization behaviors. This strategy was not only used for *in situ* matrix removal, but also for the simultaneous determination of different volatile elements. This method was applied to the simultaneous determination of the different volatile elements Cr, Cu, and Cd in high purity ZrO₂ with satisfactory results.

EXPERIMENTAL

Instrumentation

An X-7 ICP-MS system (Thermo Elemental Corporation, USA), equipped with a modified commercially available WF-4C graphite furnace (Beijing Analysis Instrument Factory, Beijing, P.R. China) as an electrothermal vaporizer, was used for the determination of the analytes. The optimum operating conditions of ETV-ICP-MS are summarized in Table I.

Standard Solutions and Reagents

The standard solutions (1.0 mg mL⁻¹) of Cr, Cu, and Cd were prepared by dissolving their oxides in

dilute HNO₃ and bringing it to a certain volume with doubly distilled water. A 60% (m/v) polytetrafluoroethylene emulsion (diameter <1 μm, viscosity 7×10⁻³-15×10⁻³ Pa s) was purchased from the Shanghai Organic Chemistry Institute (Shanghai, P.R. China). All other reagents were of analytical grade or better. High purity deionized water (18.2 MΩ), obtained from a Milli-Q® A10 system (Millipore Corporation, USA), was used throughout this work.

Sample Preparation

An amount of 0.0675 g of ZrO₂ powder, 0.3377 g of (NH₄)₂SO₄, and 1.0 mL of concentrated H₂SO₄ was added into a 10-mL quartz beaker, then heated until the solution was clear. The mixture was evaporated to dryness and kept at this temperature for decomposition of excess (NH₄)₂SO₄ for 10 minutes. The residue was dissolved with 2.0 mL of 6.0 mol L⁻¹ HNO₃ solution, then 0.5 mL of 60% (w/v) PTFE slurry was added, and finally

diluted to 5.0 mL with high purity deionized water. The resultant mixture was dispersed with an ultrasonic vibrator for 15 minutes before use. Aqueous standard solutions containing 1.5% (w/v) PTFE were used for calibration. The blank was prepared in the same way as the sample.

Recommended Procedure

After the ETV unit was connected to the ICP-MS and the system stabilized, a 10-μL volume of sample was injected into the graphite furnace. During the drying and pyrolysis steps, the dosing hole of the graphite furnace was kept open to remove the water and other vapors. The dosing hole was sealed with a graphite cone for about 10 seconds before the high temperature vaporization step, then the analytes were vaporized and carried into the plasma excitation source by argon carrier gas. The peak-hop transient mode of data acquisition was used for ICP-MS detection.

TABLE I
Operating Parameters for ETV-ICP-MS

ICP-MS System	
Plasma Power	1300 W
Plasma Argon Flow Rate	14.5 L min ⁻¹
Auxiliary Argon Flow Rate	0.76 L min ⁻¹
Nebulizer Argon Flow Rate	0.92 L min ⁻¹
Sampler Orifice (nickel)	1.1 mm
Skimmer Orifice (nickel)	0.7 mm
Acquisition Mode	Peak jumping
Number of Sweep	100
Dwell Time	10 ms
Acquisition Time	40 s
Number of Measurements per Peak	3
Isotopes	⁵² Cr, ⁶⁵ Cu, ¹¹³ Cd, and ⁹⁰ Zr
ETV	
Sample Volume	10 μL
Carrier Gas Flow Rate	0.43 L min ⁻¹
Drying Temperature	100 °C, ramp 10 s, hold 20 s
Pyrolysis Step	800 °C, ramp 10 s, hold 80 s
Vaporization Step	2200 °C, hold 4 s

RESULTS AND DISCUSSION

Comparison of Signal Profiles for Analytes

In order to compare the signal profiles of the different volatile elements, the vaporization behaviors of the analytes were investigated with (Figure 1A) and without (Figure 1B) PTFE. As can be seen from Figure 1, the addition of PTFE greatly changes the vaporization behavior of the refractory element Cr. Compared with no PTFE (a'), an intense analytical signal was obtained with PTFE (a). For the easily volatile element Cd, intense signals were observed (e and e') and there were no memory effects (f and f'), no matter whether the PTFE was used or not in the experiments. The signal with PTFE is more intense than without PTFE for the medium volatile element Cu (c and c'), indicating that the vaporization behavior of Cu is between Cr and Cd. It is worth noting that for Cr and Cu, no memory effects were observed with PTFE (b and d), while there were severe memory effects without PTFE (b' and d'). In conclusion, in the presence of PTFE, the different volatile elements have similar vaporization behaviors in the furnace. Therefore, the simultaneous determination of elements with different volatilities is possible by ETV-ICP-MS.

Investigation of *In situ* Matrix Removal

As a classically refractory element, Zr is difficult to vaporize and to determine directly by conventional ETV-ICP-MS even at a high temperature because the boiling points of Zr, its oxide, and its carbide are about 4377 °C, 5000 °C, and 5100 °C, respectively, which are much higher than 2800 °C as provided commonly by conventional ETV. In the presence of PTFE, however, the matrix and analytes were changed into their fluorides in the ETV. Among them, zirconium fluo-

ride is one of the most volatile compounds (boiling point: ZrF_4 , 600 °C; CrF_2 , 1200 °C; CuF_2 , 1449 °C; CdF_2 , 1750 °C). Therefore, a rational selection of ashing temperature and time is key to the possibility of separating the matrix *in situ* from the analytes. For this reason, the effect of ashing temperature and time on the signal intensities of the analytes was investigated and the results are presented in Figures 2 and 3,

respectively. As shown in Figure 2, with the addition of PTFE, the emission signal loss of the matrix (Zr) occurs at 600 °C, but above 1100 °C for the analytes. It is especially worth noting that for the easily volatile element Cd, the addition of PTFE greatly enhanced its thermal stability. As a result, signal loss occurs for Cd above 1400 °C in the presence of PTFE, while at about 400 °C without PTFE (39). Further-

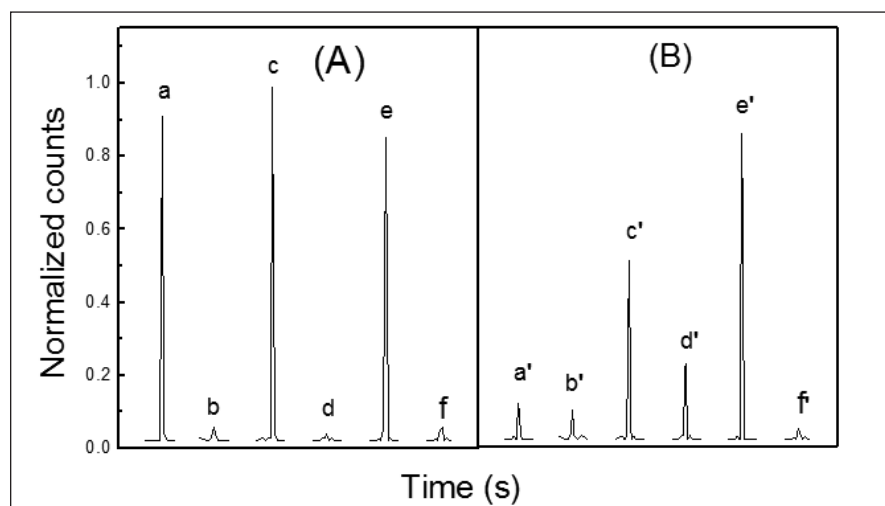


Fig. 1. Comparison of signals for the analytes. With PTFE (A) and without PTFE (B): a, a' 5.0 ng mL⁻¹ Cr; c, c' 5.0 ng mL⁻¹ Cu; e, e' 5.0 ng mL⁻¹ Cd; b, d, f, b', d', and f' are their residual signals of the empty firing, respectively.

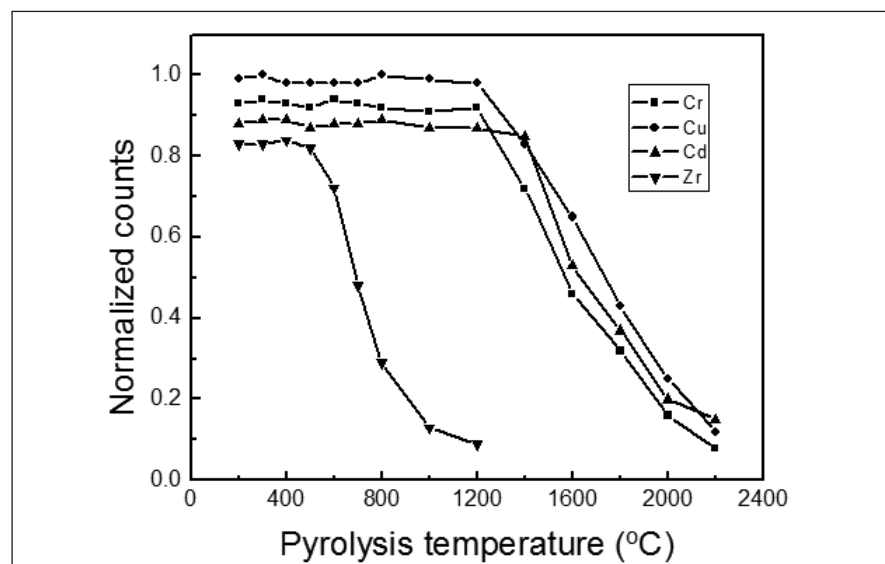


Fig. 2. Dependence of signal intensity on pyrolysis temperature with PTFE. Cr, Cu, Cd, and Zr: 5.0 ng mL⁻¹.

more, the results in Figure 3 indicate that the signal intensities of the analytes do not decrease by prolonging the ashing time at the selected ashing temperature. To the contrary, the signal intensity of the matrix (Zr) decreases significantly owing to the formation of the highly volatile ZrF_4 .

Based on the above experimental results, it appears possible to remove the matrix (Zr) by selecting an appropriate ashing temperature and ashing time prior to the vaporization of the analytes. Thus, an ashing temperature of 800 °C and an

ashing time of 80 seconds were used in this work.

Selection of Vaporization Temperature

Figure 4 illustrates the variation in the signal intensities of the analytes at different vaporization temperatures with (Figure 4A) and without (Figure 4B) PTFE. The following conclusions could be drawn: (a) the higher the vaporization temperature, the stronger the signal intensity whether with or without PTFE; (b) with the addition of PTFE, the signal intensities for

Cr, Cu, and Cd reach a plateau above a proper temperature of 2200 °C in comparison with conventional vaporization (no PTFE), and the vaporization temperature of Cr and Cu is obviously lowered in the presence of PTFE; (c) it is an exception for Cd that compared with the absence of PTFE, the presence of PTFE could not enhance its signal intensity because it does not form highly thermally stable oxides or carbides. The experimental facts mentioned above can be due to the fluorides of the different volatile elements having similar vaporization characteristics in the presence of PTFE. In this work, a vaporization temperature of 2200 °C and a vaporization time of 4 seconds were used for the simultaneous determination of the analytes.

Effect of Matrix Concentration

The matrix effects were studied by measuring the signal intensities for the solutions with variable concentrations of Zr (from 0 to 500 $\mu\text{g mL}^{-1}$) and keeping the concentrations of the analytes constant at 5.0 ng mL^{-1} . The matrix effect was defined as the difference between the signal intensities from spiked and unspiked Zr solutions. The experimental results show that with the use of PTFE as the chemical modifier, the largest tolerable matrix concentrations are 300 $\mu\text{g mL}^{-1}$ for the analytes at an ashing temperature of 800 °C and an ashing time of 80 seconds. However, once the matrix (Zr) concentration surpasses that amount, the analytical signals are found to increase or decrease. The increase could be produced by spectroscopic interference, while the decrease could be attributed to the occurrence of two competitive reactions, one taking place between the analytes and PTFE, and the other between the matrix (Zr) and PTFE, leading to an incomplete vaporization of the analytes.

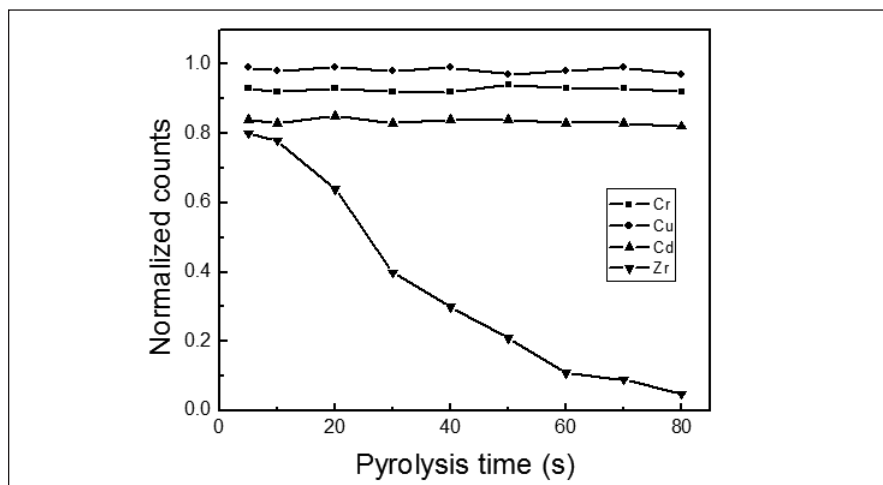


Fig. 3. Effect of pyrolysis time on signal intensity with PTFE. Cr, Cu, Cd and Zr: 5.0 ng mL^{-1} .

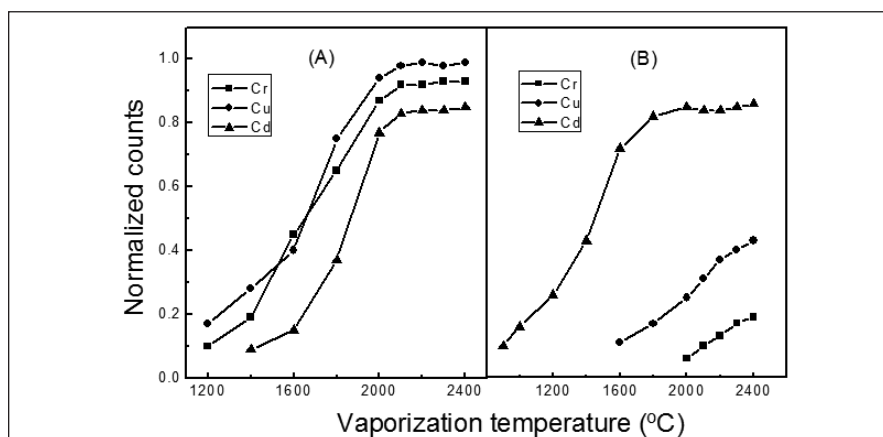


Fig. 4 (A and B). Influence of vaporization temperature on signal intensity with (A) and without (B) PTFE. Cr, Cu, and Cd: 5.0 ng mL^{-1} .

In order to explore the reasons of the reduced matrix effects, the investigation on vaporization behavior of the analytes (Cr, Cu, and Cd) and the matrix (Zr) was carried out by this method. The results given in Figure 5 showed that the analytical signals successively appeared in the sequence of Zr, Cr, Cu, and Cd. In other words, the selective volatilization among the elements examined took place in the vaporization process. This selective volatilization behavior is beneficial to decrease the matrix effects.

Influence of PTFE Amount

The effect of the amount of PTFE was investigated by varying its percentage (m/v) from 0.2% to 2.0%.

The experimental results showed that the signal intensities of the analytes increased by increasing the chemical modifier amount and reached a constant value at about 1.0%. Since the chemical modifier could be consumed by the matrix in a real sample analysis, a suitably higher polytetrafluoroethylene concentration of 1.5% was used in this work.

Detection Limits and Precision

According to the definition of IUPAC, the detection limit (DL) is defined as the concentration corresponding to three times the standard deviation of the blanks. Under the optimum conditions, the detection limits for Cr, Cu, and Cd were 2.5, 9.8, and 3.4 ng g⁻¹, respectively. The precision for Cr, Cu, and Cd,

expressed as the relative standard deviations (RSDs), was 5.0, 5.8, and 6.2%, respectively (n=11, c=1.0 ng mL⁻¹). The calibration graphs of the analytes were linear over three orders of magnitude.

Analysis Application

This method was applied to the determination of the different volatile elements Cr, Cu, and Cd in ZrO₂ using external calibration and the standard addition method. The same sample was also analyzed by PN-ICP-MS after removal of the matrix by a solvent extraction procedure (40). The analytical results are summarized in Table II and show good agreement among the three analytical schemes.

CONCLUSION

Conventional electrothermal vaporization (ETV) as a sample introduction technique inherits the disadvantages with respect to very low sensitivity and severe memory effects for refractory and carbide-forming elements. On the other hand, ashing loss may occur in ETV for easily volatile elements. Thus, it is difficult for the simultaneous determination of refractory/carbide formation and easily volatile elements. In this work, PTFE was used as a chemical modifier for ETV-ICP-MS to convert the refractory matrix (Zr) and different volatile analytes into their fluorides. The formation of the fluorides greatly changes their vaporization behaviors. This strategy was not only used for *in situ* matrix removal, but also for the simultaneous determination of different volatile elements (refractory Cr, medium volatile Cu, and easily volatile Cd). In addition, this method offers the following advantages: (a) decrease of sample pre-treatment, (b) small sample requirement, (c) simple and rapid operation, (d) reduction of sample contamination, and (e) no need for matrix matching. Therefore, it is

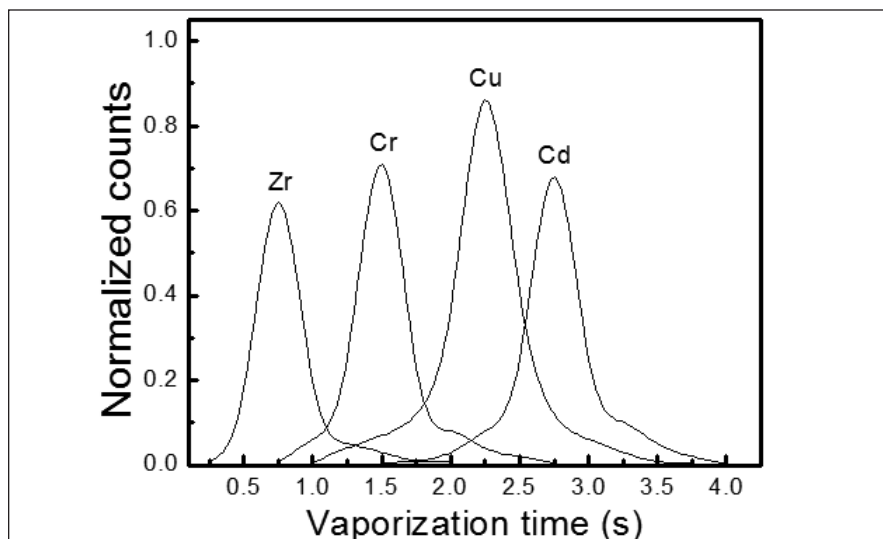


Fig. 5. Analytical signals versus vaporization time with PTFE. Zr, Cr, Cu and Cd: 5.0 ng mL⁻¹, respectively.

TABLE II
Analytical Results of Trace Impurities in ZrO₂ (n=5)

Element	Calibration Curve Method (μg g ⁻¹)	Standard Addition Method (μg g ⁻¹)	PN-ICP-MS ^a (μg g ⁻¹)
Cr	1.3 ± 0.09	1.1 ± 0.10	1.2 ± 0.08
Cu	4.5 ± 0.34	4.8 ± 0.29	5.0 ± 0.32
Cd	1.9 ± 0.13	2.2 ± 0.17	2.0 ± 0.11

^a Analysis after matrix removal by solvent extraction.

likely to become an effective method for the simultaneous determination of trace/ultra-trace impurities in Zr-based powder samples.

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