Determination of Trace Rare Earth Impurities in Tantalum Pentaoxide by Electrothermal Vaporization ICP-MS Using *in situ* Volatilization for Matrix Removal

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INTRODUCTION

As a basic substance for advanced functional and structural materials, tantalum pentaoxide is widely used in the electrical, mechanical, steel, optical, aviation, and semiconductor industries owing to its excellent properties (1, 2). The properties and applications of high purity materials in the high-tech fields depend not only on the characteristics of the basic substances, but also on the purity of the compounds (3, 4). Thus, the development of a rapid, sensitive, accurate, and direct method for the determination of trace impurities in high purity Ta₂O₅ is an important research topic.

The most common methods for the determination of trace impurities in high purity materials are inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), and atomic absorption spectrometry (AAS) (5-10). However, the conventional methods for the determination of trace impurities in high purity materials may suffer from insufficient sensitivity and matrix effects, especially spectral interferences from the line-rich spectrum of Ta. Therefore, separation and pre-concentration techniques, such as liquid-liquid extraction, coprecipitation, ion exchange, electrodeposition and chromatography, are generally required prior to the

ABSTRACT

In this paper, an *in situ* matrix separation method has been developed for the determination of trace rare earth impurities in high purity tantalum pentaoxide (Ta₂O₅) by electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS). A polytetrafluoroethylene (PTFE) slurry was used as a chemical modifier to convert both the matrix (Ta) and the rare earth elements (REEs) into their fluorides, with different volatilities, at high temperature in a graphite furnace. The more volatile TaF₅ was removed *in situ* by selective vaporization prior to the determination of the analytes, eliminating matrix effects.

Under optimum operating conditions, the detection limits (DLs) for La, Eu, and Yb were found to be 4.2, 1.9, and 3.5 ng g⁻¹, with relative standard deviations (RSDs) less than 5.0%. The recommended method was successfully applied to the determination of trace impurities (La, Eu, and Yb) in Ta₂O₅, and the results were in good agreement with those obtained by pneumatic nebulization (PN) ICP-MS after separation of the matrix using a solvent extraction procedure.

determination for the elimination of matrix interferences and improvement of analytical sensitivity (11-15). However, these additional steps could lead to low sample throughput, risk of contamination, loss of analyte, and discharge of pollutants from sample pretreatment. Electrothermal vaporization (ETV) as a sampling technique

could offer the following advantages: (a) small sample requirement, (b) high transport efficiency, (c) low absolute detection limits, and (d) direct analysis of solid samples. Furthermore, the application of various chemical modifiers in ETV not only enhances the analytical sensitivity for refractory and carbide-forming elements (such as Zr, V, Ti, Cr, Al, and rare earth elements), but also effectively separates the matrix constituents from the analytes by suitable selection of furnace temperature programs. The representative examples are the application of halogenating reagents, metal salts, alkylating reagents, and chelating reagents (16-22). Among the chemical modifiers, a polytetrafluoroethylene (PTFE) slurry has drawn growing attention owing to the following attractive features: (a) high fluorine content, (b) sufficient activity to react with refractory material, (c) suitably high decomposition temperature (about 415 °C), (d) few inorganic impurities, and (e) convenient use. PTFE has been applied for the direct analysis of high purity and refractory materials (23,24).

The present work is aimed at converting both the matrix (Ta) and the rare earth elements (REEs) in Ta₂O₅ into their corresponding fluorides, characterized with different volatilities, at a high temperature in a graphite furnace using a polytetrafluoroethylene (PTFE) slurry as a fluorinating reagent. Prior to the transport of the analytes to the plasma, the more easily volatile tantalum fluoride

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(boiling point: 230 °C) can be vaporized and separated *in situ* from the fluorides of the analytes (boiling points: about 2200 °C) in the ashing step. Based on the facts mentioned above, a novel method for the analysis of Ta₂O₅ via *in situ* separation of the matrix from the analytes has been developed by ETV-ICP-MS. The proposed method is characterized by simplicity, speed, small sample requirement, and limited chemical pretreatment.

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. A Model Ethos T microwave system (Milestone, Italy) was used for sample digestion.

Reagents

The standard solutions (1.0 mg mL⁻¹) of La, Eu, and Yb were prepared by dissolving their high purity oxides in 2.0 mol L⁻¹ HNO₃, and made up to 25.0 mL volume with doubly distilled water. A 60% (m/v) PTFE emulsion (d<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 Milli-Q™ A10 system (Millipore Corporation, USA) was used throughout this work.

Sample Preparation

A sample portion of 0.1000 g Ta₂O₅ (Shanghai Reagent Factory, Tianjin, P.R. China) was accurately

weighed into a 100-mL Teflon® microwave digestion vessel, to which 2.0 mL of concentrated HNO₃ and 3.0 mL concentrated HF were added. The samples were heated in a microwave oven at 200 °C (ramp: 10 minutes, hold: 30 minutes) at 1.0 kW power. After the digestion had been completed, the vessels were cooled to room temperature and vented carefully. The resulting solutions were transferred to a PTFE beaker and heated to near dryness for removal of HF. The residues were dissolved in 2.0 mL of 0.1 mol L⁻¹ HNO₃. Next, 0.10 mL of 60% (w/v) PTFE slurry was added, followed by dilution to 4.0 mL with deionized water. The resultant mixture was dispersed with an ultrasonic vibrator for 15 minutes before use. Aqueous standard solutions containing 6% (w/v) PTFE were used for calibration. The blank was prepared in exactly 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. The sample inlet hole was blocked with a graphite cone. After being dried and ashed, the analyte was vaporized and carried into the plasma by the carrier gas (argon) for ICP-MS determination.

RESULTS AND DISCUSSION

Investigation of Vaporization Behavior of Analytes

Rare earth elements (REEs) are difficult to vaporize and determine directly by conventional ETV-ICP-MS, even at a high temperature, because the boiling points of both the REEs and their oxides are above 3000 °C, which is much higher than the 2800 °C commonly provided by conventional ETV. In order to solve this problem, application of a chemical modifier to form a more volatile species is an

TABLE I
Operating Parameters for ETV-ICP-MS

ICP-MS Plasma	X-7 ICP-MS system
Plasma power	1300 W
Plasma argon flow rate	14.5 L min ⁻¹
Auxiliary argon flow rate	0.78 L min ⁻¹
Nebulizer argon flow rate	0.95 L min ⁻¹
Sampler orifice (nickel)	1.1 mm
Skimmer orifice (nickel)	0.7 mm
Acquisition mode	Peak-jumping
Number of sweeps	100
Dwell time	10 ms
Acquisition time	40 s
Number of measurements per peak	3
Isotopes	139 La, 153 Eu, 172 Yb, and 181 Ta
ETV -----	
Sample volume	10 μL
Carrier gas flow rate	0.50 L min ⁻¹
Drying temperature	100 °C, ramp: 10 s, hold: 20 s
Ashing step	600 °C, ramp: 10 s, hold: 50 s
Vaporization step	2600 °C, hold: 4 s

effective way to increase the sample introduction efficiency and to improve the analytical performance. Figure 1 shows the typical signal profiles of Yb with and without PTFE. In the presence of PTFE, a sharper and more intense signal from Yb was detected without memory effect (a, b), while the contrary is observed in the absence of PTFE (c, d). Similar results were also obtained for Ta and the other REEs. The results mentioned above can be explained by the fact that the ETV temperature is not high enough to vaporize the refractory elements. However, when using PTFE as a chemical modifier, its decomposition products can strongly react with the refractory elements to form the corresponding fluorides whose boiling points are lower than those of their metals, oxides, or carbides, thus leading to an improved vaporization and transport efficiency. In addition, Figure 1 also gives the signal of the blank solution (e).

In situ Separation of Matrix from Analytes

Due to the different volatility of tantalum fluoride (matrix) with REE

fluorides (analytes), a rational selection of ashing temperature and time would be the key to *in situ* separation of the matrix from the analytes in the graphite furnace. Therefore, the effect of ashing temperature and time on the signal intensities of the matrix and analytes was investigated with PTFE (shown in Figures 2 and 3), in which La, Eu, and Yb were chosen as the representatives of the light, medium, and heavy REEs, respectively. Figure 2 shows that in the presence of PTFE, the signal loss of the matrix (Ta) occurs at 500 °C, and Ta can be completely evaporated with an increase in ashing temperature. This indicates that the active fluorine radicals produced by the decomposition of the PTFE reacted with Ta to form TaF₅, which is highly volatile (b.pt. 230 °C) and can be removed quickly from the graphite furnace by the carrier gas. On the other hand, the ashing losses of the REEs do not appear until the ashing temperature rises to above 1600 °C. These facts indicate that the Ta matrix can be separated *in situ* from the REEs in the graphite furnace by selecting a suitable ashing temperature.

In addition, the results shown in Figure 3 show that the analytes' signal intensities do not decrease by prolonging the ashing time at the selected ashing temperature. On the contrary, the signal intensity of the matrix (Ta) decreases significantly owing to the formation of the highly volatile TaF₅. Based on the above experimental result, it appears possible to remove the matrix (Ta) by selecting an appropriate ashing temperature and time prior to vaporization of the analytes. In this work, an ashing temperature of 600 °C and an ashing time of 50 seconds were used for the following experiments. Under these conditions, the Ta matrix could be mostly removed, while the analyte still remained in the graphite tube without considerable loss.

Effect of Vaporization Temperature

The dependence of the signal intensities of the analytes on the vaporization temperature was investigated. It can be seen from Figure 4 that in the presence of PTFE, stronger signal intensities were detected, and reached a

Fig. 1. Typical signal profiles for Yb. (a) 3.0 ng mL⁻¹ of Yb with PTFE, (b) residual signal from a with PTFE, (c) 10 ng mL⁻¹ of Yb without PTFE, (d) residual signal from (c) with PTFE, and (e) signal from blank.

Fig. 2. Dependence of signal intensity on ashing temperature. With PTFE: La, Eu, Yb, and Ta, 3.0 ng mL⁻¹.

Fig. 3. Effect of ashing time on signal intensity. With PTFE: La, Eu, Yb and Ta, 3.0 ng mL⁻¹.

Fig. 4. Influence of vaporization temperature on signal intensity. With PTFE: La, Eu, and Yb, 3.0 ng mL⁻¹.

plateau above a proper vaporization temperature (about 2500 °C). This can be due to the formation of the easily volatile fluorides characterized by similar vaporization behavior. In this study, a vaporization temperature of 2500 °C was employed for the simultaneous multielement determinations.

Investigation of Matrix Effects

The effects of the matrix concentrations on the determination of the REEs were studied by measuring the signal intensities for the solutions with variable concentrations of Ta (from 10 to 200 µg mL⁻¹) and 3.0 ng mL⁻¹ of the analytes. The experimental results show that, with PTFE as the chemical modifier, there is no apparent matrix effect for the analytes with a Ta concentration of 200 µg mL⁻¹ at a pyrolysis temperature of 600 °C and a pyrolysis time of 50 seconds. Thus, the selective volatilization is beneficial for decreasing the effect of the matrix on the analytes. With respect to the mechanism of matrix effect, further research work needs to be carried out.

Influence of PTFE Amount

The effect of PTFE concentration was examined by varying the PTFE percentage (m/v) from 0.20% to 2.0%. The experimental results show that the signal intensities of the analytes increase with an increase in the PTFE concentration and reached a constant value at a PTFE concentration of about 1.0%. Taking into account that the PTFE could be consumed by the matrix in a real sample analysis, a suitably higher PTFE concentration of 1.5% was used in subsequent studies.

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 optimum conditions, the detection limits for La, Eu, and Yb were found to be 4.2, 1.9, and 3.5 ng g⁻¹, respectively. The precision for La, Eu, and Yb, expressed as relative standard deviations (RSDs), was 4.9, 2.7, and 4.1%, respectively (n=9, c=1.0 ng mL⁻¹). Calibration graphs of the analytes were linear over three orders of magnitude.

Sample Analysis

The proposed method was applied to the determination of La, Eu, and Yb in Ta₂O₅ by the calibration curve method and the standard addition method. The same sample was also analyzed by PN (pneumatic nebulizer)-ICP-MS after removal of the matrix by a solvent extraction procedure (1). The analytical results obtained and summarized in Table II show good agreement.

CONCLUSION

The formation of the volatile fluorides not only improves the vaporization and transportation efficiency of the analytes, but also enhances the difference in the volatilities between the analytes and the matrix components. This difference can then be exploited for separating *in situ* the matrix from the analytes by selective vaporization.

The proposed method for the determination of trace REE impurities in Ta₂O₅ offers the following advantages: (a) less sample pre-treatment, (b) small sample requirement, (c) simple and rapid

TABLE II
Analytical Results of the Rare Earth Impurities in Ta₂O₅ (n=5)

Element	Calibration Curve Method ($\mu\text{g g}^{-1}$)	Standard Addition Method ($\mu\text{g g}^{-1}$)	PN-ICP-MS ^a ($\mu\text{g g}^{-1}$)
La	3.8 ± 0.21	4.0 ± 0.37	3.5 ± 0.28
Eu	1.1 ± 0.09	1.2 ± 0.11	1.0 ± 0.06
Yb	0.67 ± 0.05	0.71 ± 0.12	0.72 ± 0.04

^a Analysis after matrix removal by solvent extraction.

operation, (d) reduction of sample contamination, and (e) no need for matrix matching. Therefore, this is likely to become an effective method for the determination of trace impurities in Ta-based powder samples.

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