In situ Matrix Removal Studies and Determination of Trace Mn, Cr, and Cu in High Purity Tantalum Pentaoxide by Electrothermal Vaporization-Inductively Coupled Plasma Mass Spectrometry

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INTRODUCTION

Due to its unique physical and chemical characteristics, tantalum pentaoxide (Ta_2O_5) has become an important material in the electrical, mechanical, steel, optical, aviation, and semiconductor industries (1,2). It should be pointed out that the growing application of advanced materials in high-tech fields enhances the demand for strictly controlled properties which are often directly correlated to the concentrations of trace impurities (3-6). Therefore, a powerful, rapid, and reliable analytical method is required for the elemental characterization of impurities at trace and ultra-trace levels in Ta_2O_5 .

It is well known that the most common methods for analysis of high purity materials include atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS) (7-12). However, the conventional methods for the analysis of trace impurities in high purity Ta_2O_5 may suffer from insufficient sensitivity, matrix effects, and spectral interferences (13-15). In order to solve these problems, sample pretreatment methods involving matrix (Ta) separation are generally required prior to the analysis (1,16-19). Unfortunately, this could lead to a long analysis time, risk of contamination and loss of analytes, and discharge

ABSTRACT

Based on converting both the matrix (Ta) and the analytes (Mn, Cr, and Cu) into different volatile fluorides at high temperature in a graphite furnace, an *in situ* matrix removal method was developed for the determination of trace amounts of Mn, Cr, and Cu in high purity tantalum pentaoxide (Ta_2O_5) by electrothermal vaporization-inductively coupled plasma mass spectrometry (ETV-ICP-MS) with a polytetrafluoroethylene slurry (PTFE) as the chemical modifier. The experimental results showed that the more volatile TaF_5 was removed *in situ* during the pyrolysis stage prior to the determination of the analytes. As a result, the matrix effect was effectively suppressed. Under optimum operating conditions, the detection limits (DLs) for Mn, Cr, and Cu were found to be 7.3, 4.8, and 10 ng g^{-1} with relative standard deviations (RSDs) of less than 4.5%. The recommended method was successfully applied to the determination of trace amounts of Mn, Cr, and Cu in Ta_2O_5 . The results obtained from external calibrations and the method of standard additions were in good agreement with those obtained by conventional pneumatic nebulization (PN) ICP-MS after separation of the matrix with a solvent extraction procedure.

of pollutants from sample pretreatment.

In recent years, electrothermal vaporization (ETV) as a sample introduction device for ICP-MS has received considerable attention owing to some very attractive features, including small sample requirement, high transport efficiency, low absolute detection limits, and direct sample analysis (20-24). The application of various chemical modifiers in ETV not only enhances the analytical sensitivity for refractory and carbide-forming elements, but it also enables the separation of the matrix constituents from the analytes by suitable selection of the furnace temperature programs. The representative chemical modifiers are halogenating reagents, metal salts, and chelating reagents (25-31). Among them, polytetrafluoroethylene as a classical and effective chemical modifier has been used in ETV-ICP-AES because of its attractive features: high fluorine content, sufficient activity, suitable decomposition temperature (about 415 °C), fewer inorganic impurities, and convenient use (32-34). To the best of our knowledge, however, polytetrafluoroethylene as a chemical modifier for ETV-ICP-MS determination of trace impurities in Ta_2O_5 has received little attention so far (35).

The present work is aimed at converting both the matrix (Ta) and the analytes (Cu, Mn, and Cr) in Ta_2O_5 into corresponding fluorides with different volatilities at high temperatures in a graphite furnace, using polytetrafluoroethylene as a chemical modifier. Prior to the

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transportation of the analytes to plasma, the more easily volatile tantalum fluoride (boiling point: 230 °C) can be vaporized and separated *in situ* from the fluorides of the analytes (boiling points: higher than 1200 °C) in the pyrolysis step. Based on the facts mentioned above, a novel method was developed for the analysis of trace impurities (Mn, Cr, and Cu) in Ta₂O₅ by ETV-ICP-MS via *in situ* separation of the matrix from the analytes 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 listed in Table I. A Model Ethos T microwave system (Milestone, Italy) was used for sample digestion.

Standard Solutions and Reagents

The standard solutions (1.0 mg mL⁻¹) of Mn, Cr, and Cu were prepared by dissolving their oxides in dilute HNO₃, and making up to a certain volume with doubly-distilled water. A 60% (m/v) polytetrafluoroethylene emulsion (d<1 µm, viscosity 7×10⁻³–15×10⁻³ Pa s) was purchased from 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 water purification system (Millipore Corporation, USA), was used throughout this work.

Sample Preparation

An appropriate amount of Ta₂O₅ powder was accurately weighed into Teflon® microwave digestion vessels, to which 1.0 mL of concentrated HNO₃ and 3.0 mL 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 was completed, the vessels were cooled to room temperature and vented carefully. The resulting solutions were transferred into PTFE beakers and heated to near dryness for removal of HF. The residues were dissolved with 2% HNO₃, then 0.05 mL of 60% (w/v) polytetrafluoroethylene slurry was added and finally diluted to 2.0 mL with deionized water. The resultant mixture was dispersed with an ultrasonic vibrator for 15 minutes before use. Aqueous standard solutions containing 1.5% (w/v) polytetrafluoroethylene slurry 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. 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 at about 10 seconds before the high temperature vaporization step, and 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 Plasma	
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	0.93 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	⁵⁵ Mn, ⁵² Cr, ⁶⁵ Cu, and ¹⁸¹ Ta
ETV	
Sample volume	10 µL
Carrier gas flow rate	0.46 L min ⁻¹
Drying temperature	100 °C, ramp 10 s, hold 20 s
Pyrolysis step	600 °C, ramp 10 s, hold 40 s
Vaporization step	2200 °C, hold 4 s

RESULTS AND DISCUSSION

In Situ Removal of Tantalum Matrix

In order to characterize the removal of the Ta matrix in ETV prior to ICP-MS determination, the volatile characteristics of the matrix (Ta) and the analytes (Mn, Cr, and Cu) were investigated with polytetrafluoroethylene slurry as the chemical modifier. As noted earlier, tantalum fluoride is the most volatile among the fluorides. Therefore, a rational selection of pyrolysis temperature and time would be the key to the possibility of *in situ* separation of the matrix from the analytes in the graphite furnace. For this reason, the effect of pyrolysis temperature and pyrolysis time on the signal intensities of the analytes was investigated; the results are presented in Figures 1 and 2, respectively. Figure 1 shows that in the presence of polytetrafluoroethylene slurry, the signal loss of the matrix (Ta) occurs at 500 °C, but for the analytes at above 1200 °C. Furthermore, the results in Figure 2 indicate that the signal intensities of the analytes do not decrease by prolonging the pyrolysis time at the

selected pyrolysis temperature. On the contrary, the signal intensity of the matrix (Ta) decreases significantly owing to the formation of the highly volatile TaF_5 . Based on the above experimental results, it appears then possible to remove the matrix (Ta) by selecting an appropriate pyrolysis temperature and pyrolysis time prior to the vaporization of the analytes. Taking their complementary effects into account, a pyrolysis temperature of 600 °C and a pyrolysis time of 40 seconds were used for the following experiments in this work.

Comparison of Vaporization Behavior

As a kind of classically refractory and carbide-forming element, Cr was selected as a representative element from the analytes to investigate their vaporization behaviors in ETV-ICP-MS with and without polytetrafluoroethylene slurry as the chemical modifier.

Figure 3 shows the typical signal profiles of Cr with and without polytetrafluoroethylene slurry. It can be seen that a sharper, symmetrical, and much more intense signal

of Cr was detected (a), and no obvious memory effect was observed (b). The results mentioned above can be explained by the fact that the decomposition products of polytetrafluoroethylene can strongly react with Cr to form the corresponding fluoride whose boiling point (1200 °C) is lower than for Cr, its oxide and carbide, thus leading to an improved vaporization and transport efficiency.

However, dramatic changes to the Cr signal profiles occurred in the absence of a chemical modifier. The signal intensity of Cr was very weak (c) and the residue signal was much more intense in the presence of the chemical modifier (d), indicating incomplete vaporization of Cr and a serious memory effect. The reason for this is that Cr is a refractory element and difficult to vaporize and determine directly by conventional ETV-ICP-MS, even at a high temperature, because the boiling points of both the carbide and oxide for Cr are 3800 °C and 4000 °C, respectively, which are much higher than 2800 °C provided commonly by conventional ETV. Similar results were obtained for Ta and

Fig. 1. Dependence of signal intensity on pyrolysis temperature in the presence of a chemical modifier. Mn, Cr, Cu, and Ta: 5.0 ng mL⁻¹.

Fig. 2. Effect of pyrolysis time on signal intensity in the presence of a chemical modifier. Mn, Cr, Cu, and Ta: 5.0 ng mL⁻¹.

the other analytes. In addition, Figure 3 provides the signal of the blank solution with the same operating parameters (e).

Selection of Vaporization Temperature

Figure 4 shows the variation in the signal intensities of the analytes with polytetrafluoroethylene slurry as the chemical modifier at the different vaporization temperatures. The vaporization curves were obtained using a drying step at 100 °C (ramp: 10 seconds, hold: 20 seconds), pyrolysis at 600 °C (ramp: 10 seconds, hold: 40 seconds), and then direct vaporization in the range from 800 °C to 2400 °C (ramp: 0 seconds, hold: 4 seconds). It can be seen from Figure 4 that the signal intensity proportionally increased with an increase in vaporization temperature, reaching a plateau above 2000 °C. This can be due to the formation of the easily volatile fluorides with similar vaporization characteristics. In this study, a vaporization temperature of 2200 °C was employed for vaporization.

Influence of Chemical Modifier Amount

The effect of polytetrafluoroethylene amount 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 when increasing the chemical modifier amount and reached a constant value at about 1.0%. Taking into account that the chemical modifier could be consumed by the matrix in a real sample analysis, a suitably higher polytetrafluoroethylene concentration of 1.5% was used for subsequent studies.

Investigation of Matrix Effects

Matrix effects were studied by measuring the signal intensities of the analytes with variable concentrations of Ta (from 0 to 200 $\mu\text{g mL}^{-1}$) and 5.0 ng mL^{-1} of the analytes. The matrix effect was defined as the difference between the signal intensities from spiked and unspiked Ta solutions. According to the literature (13,14), the obvious matrix effect was observed when the con-

centration of the matrix (Ta) is higher than 20 $\mu\text{g mL}^{-1}$. However, these experimental results show that there is no apparent effect of the matrix on the analytes with a Ta concentration of 200 $\mu\text{g mL}^{-1}$ in the presence of polytetrafluoroethylene as the chemical modifier at a pyrolysis temperature of 600 °C and a pyrolysis time of 40 seconds.

The reasons for the reduced matrix effect observed with polytetrafluoroethylene as the chemical modifier can be explained by the difference in the vaporization behavior of the analyte (Cr) and the matrix (Ta). The results in Figure 5 show that the Ta peak (a) appears before the Cr peak (b). In other words, selective volatilization between the matrix (Ta) and the analyte (Cr) took place in the vaporization process. This selective volatilization behavior is beneficial for decreasing the matrix effect of the analytes.

Fig. 3. Typical signal profiles for Cr. (a) 5.0 ng mL^{-1} of Cr with chemical modifier; (b) residual signal from "a" with chemical modifier; (c) 10 ng mL^{-1} of Cr without chemical modifier; (d) residual signal from "c" with chemical modifier; (e) signal from blank.

Fig. 4. Influence of vaporization temperature on signal intensity in the presence of chemical modifier. Mn, Cr, and Cu: 5.0 ng mL^{-1} .

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 Mn, Cr, and Cu were found to be 7.3, 4.8, and 10 ng g⁻¹, respectively. The precisions for Mn, Cr, and Cu, expressed as the relative standard deviations (RSDs), were 4.2, 2.1, and 3.6%, respectively (n=11, c=1.0 ng mL⁻¹). The calibration graphs of the analytes were linear over three orders of magnitude.

Sample Analysis

The proposed method was applied to the determination of Mn, Cr, and Cu in Ta₂O₅ using the external calibration and standard addition method. The same sample was also analyzed by PN-ICP-MS after removal of the matrix by a solvent extraction procedure (15). The analytical results obtained and summarized in Table II show good agreement between all three analytical schemes.

CONCLUSION

In the presence of polytetrafluoroethylene as the chemical modifier, the formation of the volatile fluorides in ETV 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 *in situ* separation of the matrix from the analytes by selective pyrolysis temperatures. The proposed method for the determination of trace impurities (Mn, Cr, and Cu) in Ta₂O₅ offers the following advantages: decrease in sample pre-treatment, avoidance of the discharge of pollutants from sample pre-treatment, reduction of sample contamination, no need of matrix matching for calibration, and simple and rapid operation. Therefore, this procedure is likely to become an effective method for the determination of trace impurities in high purity materials.

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Fig. 5. Analytical signals versus vaporization time in the presence of chemical modifier.
(a) Ta: 20 ng mL⁻¹; (b) Cr: 10 ng mL⁻¹.

TABLE II
Analytical Results of Trace Impurities in Ta₂O₅ (n=5)

Element	Calibration Curve Method (μg g ⁻¹)	Standard Addition Method (μg g ⁻¹)	Pneumatic Nebulization PN-ICP-MS ^a (μg g ⁻¹)
Mn	5.6 ± 0.51	5.2 ± 0.45	5.8 ± 0.39
Cr	2.1 ± 0.19	1.9 ± 0.16	1.7 ± 0.14
Cu	7.5 ± 0.65	7.9 ± 0.53	8.1 ± 0.59

^a Analysis after matrix removal by solvent extraction.

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