Use of *In situ* Matrix Removal for the Determination of the Volatile Elements Pb, Cd, and Zn in High Purity Tantalum Pentaoxide by ETV-ICP-MS

Shizhong Chen*, Shengping Zhu, and Dengbo Lu

College of Chemical and Environmental Engineering, Wuhan Polytechnic University,
68 Xuefu South Road Changqing Garden, Wuhan 430023, P.R. China

INTRODUCTION

Tantalum pentaoxide (Ta_2O_5) is an interesting basic substance for the production of advanced materials used in various technological fields owing to its excellent physical, chemical, and electrical characteristics (1-3). Several investigations have shown that any trace impurities in the advanced materials strongly influence the quality of products (4-7). Accordingly, there is a need for methods allowing precise and accurate determination of a large number of impurity elements in Ta_2O_5 powders.

Due to its high sensitivity, wide linear range, rapid multielement detection capability and limited interferences (compared to the line-rich spectrum interferences encountered in ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS) has become a very effective tool for the analysis of trace impurities in advanced materials (8-12). However, it is often difficult to directly determine trace impurity elements in high purity materials by conventional ICP-MS because of very low analyte concentrations and a complex sample matrix. To increase analyte concentration and eliminate matrix interference, an effective separation and preconcentration step is often required prior to their determination (13-19). It is worth noting that a lengthy and tedious sample pretreatment could lead to a long analysis time, risk of contamination and loss of analytes, and discharge of pollutants from sample pretreat-

ABSTRACT

In this work, a novel method was developed for the determination of the volatile elements Cd, Pb, and Zn in high purity tantalum pentaoxide (Ta_2O_5) by *in situ* matrix removal and electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS). A polytetrafluoroethylene slurry (PTFE) was used as a chemical modifier in ETV for converting both the matrix (Ta) and the volatile elements into their fluorides. This strategy greatly enhanced the difference in the volatility between the analytes and the matrix. As a result, the Ta matrix was removed *in situ* as a more volatile TaF_5 without signal loss of the analytes due to the formation of their fluorides with good thermal stability. Under the optimum operating conditions, the detection limits (DLs) for Cd, Pb, and Zn were 1.4, 3.2, and 6.8 ng g⁻¹ with relative standard deviations (RSDs) less than 6.0%, respectively. This method was applied to the determination of the trace volatile elements Cd, Pb, and Zn in high purity Ta_2O_5 , and the results were in good agreement with those obtained by conventional pneumatic nebulization (PN) ICP-MS after the separation of the matrix with a solvent extraction procedure.

ment. Therefore, the development of a novel sample introduction technique with less sample pretreatment is desired.

Electrothermal vaporization (ETV) as a sample introduction device for ICP-MS can offer many advantages, such as high introduc-

tion efficiency, small sample requirement, low absolute detection limit, and partial or complete removal of organic/inorganic matrix (20-26). However, conventional ETV inherits the disadvantages with respect to the very low sensitivity and severe memory effects for the refractory elements such as Zr, Ta, V, Ti, and the rare earth elements. On the other hand, ashing loss may occur in ETV for easily volatilized elements such as Cd, Zn, and Pb which results in an obvious decrease of analytical signals. Fortunately, the application of a chemical modifier in ETV to change the volatility of refractory and volatile elements is an alternate way to solve these problems. The representative chemical modifiers are halogenating reagents, metal salts, and chelating reagents (27-33). In our previous work, polytetrafluoroethylene (PTFE) was applied as a classical and effective chemical modifier for the determination of the refractory elements La, Eu, Yb, and Cr as well as the medium volatile elements Cu and Mn in Ta_2O_5 (34, 35). However, the use of PTFE as the chemical modifier for the determination of the volatile elements Cd, Zn, and Pb in Ta_2O_5 has received little attention by ETV-ICP-MS.

As a refractory element, Ta is difficult to vaporize even at a high temperature by conventional ETV because its boiling point is about 5425 °C. However, Cd, Zn, and Pb are classically easily volatilized elements which have a low ashing loss temperature in ETV (36). In this work, PTFE was used as the chemical modifier to convert the refractory element Ta (matrix) and the volatile elements Cd, Zn, and Pb

*Corresponding author.
E-mail: chenshizhong62@163.com
Fax: +86 27 83956442

(analytes) into the more volatile TaF_5 and the less volatile CdF_2 , ZnF_2 , and PbF_2 , respectively. In other words, the formation of fluorides greatly enhances the difference in volatility between the analytes and the matrix. This difference may be used for the separation of the matrix (Ta) from the volatile analytes Cd, Zn, and Pb in ETV by selective vaporization. Based on the facts mentioned above, an *in situ* matrix separation method was developed for the determination of the trace volatile elements Cd, Zn, and Pb in high purity Ta_2O_5 by ETV-ICP-MS. The experimental results show that this method provided very attractive features such as convenience, speed, and less 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.

Standard Solutions and Reagents

The standard solutions (1.0 mg mL^{-1}) of Cd, Zn, and Pb were prepared by dissolving their oxides in dilute HNO_3 and brought to a certain volume with doubly distilled water. A 60% (m/v) polytetrafluoroethylene emulsion ($d < 1 \text{ }\mu\text{m}$, viscosity $7 \times 10^{-3} - 15 \times 10^{-3} \text{ Pa s}$) was purchased from Shanghai Organic Chemistry Institute (Shanghai, P.R. China). All other reagents were of analytical grade or better. High

purity deionized water ($18.2 \text{ M}\Omega$), obtained from a Milli-Q® A10 system (Millipore Corporation, USA), was used throughout this work.

Sample Preparation

An appropriate quantity of Ta_2O_5 powder was accurately weighed into Teflon® microwave digestion vessels to which 1.0 mL of concentrated HNO_3 and 3.0 mL HF were added. The samples were heated in a microwave oven at $200 \text{ }^\circ\text{C}$ (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% HNO_3 , 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 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.

RESULTS AND DISCUSSION

It is well known that Cd, Pb, and Zn are classically volatile elements.

TABLE I
Instrumental Operating Parameters for ETV-ICP-MS

ICP-MS	Thermo Elemental X-7 ICP-MS
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	0.90 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	^{113}Cd , ^{208}Pb , ^{66}Zn , and ^{181}Ta
ETV	
Sample Volume	10 μL
Carrier Gas Flow Rate	0.43 L min^{-1}
Drying Temperature	$100 \text{ }^\circ\text{C}$, ramp, 10 s, hold, 20 s
Pyrolysis Step	$600 \text{ }^\circ\text{C}$, ramp 10 s, hold 40 s
Vaporization Step	$2200 \text{ }^\circ\text{C}$, hold 4 s

In order to carry out *in situ* separation of the analytes from the matrix in ETV prior to ICP-MS determination, the volatile characteristics of the analytes (Cd, Pb, and Zn) were investigated with and without PTFE as the chemical modifier. Figure 1 shows that the signal loss of the analytes occurs at 400 °C without PTFE. However, in the presence of PTFE, the signal loss of the analytes occurs at above 1200 °C, and for the matrix (Ta) at 500 °C (Figure 2). The reason for this is that the decomposition products of PTFE can strongly react with the analytes to form the corresponding fluoride with lower volatility. Thus, it is possible to remove the matrix (Ta) by selecting an appropriate pyrolysis temperature prior to vaporization of the analytes.

In addition, the effect of pyrolysis time on the signal intensity of the analytes was investigated with PTFE. The results in Figure 3 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 TaF₅. 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.

Comparison of Signal Profiles for Analytes

Figure 4 shows the typical signal profiles of the easily volatile element Cd with and without PTFE. It can be seen that a sharper, symmetrical, and much more intense signal of Cd was detected (a and c) and no obvious memory effect was observed (b and d), no matter if the PTFE was used in the experiments or not. Similar results were obtained for Pb and Zn. These facts indicate that the addition of PTFE greatly enhanced the thermal stability of the volatile elements Cd, Pb, and Zn, but has not negative impact on their signal intensity.

In addition, Figure 4 provides the signal of the blank solution with the same operating parameters (e).

Optimization of Vaporization Temperature

At the pyrolysis temperature of 600 °C, the effect of vaporization temperature on the signal intensity of the elements of interest was investigated. The results in Figure 5 demonstrate that the analytical signal intensity of these elements is enhanced with increasing temperature and reached their plateau at about 2000 °C. This can be due to the fluorides of the analytes 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 multielement determination.

Effect of Matrix Concentration

The effects of matrix concentration on the signal intensity of the analytes was investigated by changing the Ta concentration from 0 to 300 µg mL⁻¹ and keeping the concentration 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 Ta solutions. In the literature (37), the obvious

Fig. 1. Dependence of signal intensity on pyrolysis temperature without PTFE. Cd, Pb, and Zn: 5.0 ng mL⁻¹.

Fig. 2. Influence of pyrolysis temperature on signal intensity with PTFE. Cd, Pb, Zn, and Ta: 5.0 ng mL⁻¹.

matrix effect was observed when the concentration of the matrix (Ta) is higher than $20 \mu\text{g mL}^{-1}$. However, the results of this study show that there is no apparent effect of the matrix on the analytes with a Ta concentration of $300 \mu\text{g mL}^{-1}$ with PTFE as the chemical modifier at a pyrolysis temperature

of 600°C and a pyrolysis time of 40 seconds. This low-level matrix effect observed in the presence of PTFE can be attributed to the removal of most of the matrix at the ashing stage owing to the formation of TaF_5 with a lower boiling point (230°C).

Influence of Chemical Modifier Amount

The effect of PTFE 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 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 IUPAC definition, 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 Cd, Pb, and Zn were 1.4, 3.2, and 6.8 ng g^{-1} , respectively. The precision for Cd, Pb, and Zn, expressed as the relative standard deviations (RSDs), was 5.8, 4.7, and 5.2%, respectively ($n=11$, $c=1.0 \text{ ng mL}^{-1}$). The calibration graphs of the analytes were linear over three orders of magnitude.

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

Fig. 4. Typical signal profiles for Cd. (a) 5.0 ng mL^{-1} of Cd with PTFE; (b) residual signal from "a"; (c) 5.0 ng mL^{-1} of Cd without PTFE; (d) residual signal from "c"; and (e) signal from blank.

Fig. 5. Influence of vaporization temperature on signal intensity in the presence of PTFE. Cd, Pb, and Zn: 5.0 ng mL^{-1} .

Application of the Method

This method was applied to the determination of the easily volatile elements Cd, Pb, and Zn in Ta₂O₅ 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 (13). The analytical results obtained, summarized in Table II, show good agreement between all three analytical schemes. Compared with PN, however, this method does not require a lengthy and tedious sample pretreatment (solvent extraction) for removal of the matrix.

CONCLUSION

With polytetrafluoroethylene as the chemical modifier, the formation of the fluorides for the matrix and the analytes in ETV greatly enhances the difference in the volatility between the analytes and the matrix components. This difference can be applied for *in situ* separation of the easily volatile analytes from the matrix by selective pyrolysis temperature without the loss of their signal intensity. In addition, the addition of PTFE greatly enhanced the thermal stability of the volatile elements Cd, Pb, and Zn, but has no negative impact on their signal intensity. This method was used for the determination of the volatile impurity elements Cd, Pb, and Zn in Ta₂O₅ with the advantages such as convenience, speed, small sample requirement, and without use of chemical pretreatment for removal of the matrix (i.e., solvent extraction in PN). Therefore, this procedure is likely to become an effective method for the determination of trace impurities in high purity materials.

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

Element	Calibration Curve (μg g ⁻¹)	Standard Addition (μg g ⁻¹)	PN-ICP-MS ^a (μg g ⁻¹)
Cd	0.9 ± 0.11	1.2 ± 0.09	1.3 ± 0.12
Pb	2.7 ± 0.15	2.8 ± 0.19	3.0 ± 0.20
Zn	2.0 ± 0.21	1.9 ± 0.15	2.2 ± 0.18

^a Analysis after matrix removal by solvent extraction.

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REFERENCES

- O.N. Grebneva, I.V. Kubrakova, T.F. Kudinova, and N.M. Kuz'min, *Spectrochim. Acta Part B* 52, 1151 (1997).
- B. Jiang, Q. Huang, D. Zheng, S. Quan, and Q. Zeng, *J. Nanch. Univ.* 30(2), 120 (2008).
- S. Chen, S. Zhu, and D. Lu, *At. Spectrosc.* 35(3), 103 (2014).
- M. Lucic and V. Krivan, *Fresenius J. Anal. Chem.* 363, 145 (1999).
- J.A.C. Broekaert and G. Tog, *Microchim. Acta [Wien]* II 173 (1990).
- S.B. Deb, B.K. Nagar, M.K. Saxena, and K.L. Ramakuma, *At. Spectrosc.* 31(4), 122 (2010).
- A.L. de Souza, M.E.B. Cotrim, and M.A.F. Pires, *Microchem. J.* 106, 194 (2013).
- S.K. Thulasidas, S.K. Gupta, and V. Natarajan, *At. Spectrosc.* 35(4), 177 (2014).
- H. Matsumiya, T. Kato, and M. Hiraide, *Talanta* 119, 505 (2014).
- S. Kozono, S. Takahashi, and H. Haraguchi, *Analyst* 127, 930 (2002).
- M.A. Reddy, R. Shekhar, and S.J. Kumar, *At. Spectrosc.* 34(4), 119 (2013).
- V.K. Karandashev, K.V. Zhernokleeva, V. B. Karpov, and Y.A. Karpov, *Inorg. Mater.* 49(14), 1249 (2013).
- V. Krivan, R. Hausbeck, P. Wilhartitz, R. Krismer, and H.M. Ortner, *Fresenius J. Anal. Chem.* 341, 550 (1991).
- A.C. Sahayam, S. Thangavel, and S.C. Chaurasia, *At. Spectrosc.* 24(1), 11 (2003).
- O.N. Grebneva, N.I. Shchitmina, I.V. Kubrakova, T.F. Kudinova, G.V. Myasoedova, and N.M. Kuzmin, *J. Anal. Chem.* 53(1), 79 (1998).
- S. Li, F. Ren, L. Chen, and Q. Hu, *J. Cent. South Univ. Technol.* 31(3), 242 (2000).
- G. Venkateswarlu, A.C. Sahayam, and S.C. Chaurasia, *At. Spectrosc.* 31(6), 187 (2010).
- S. Thangavel, K. Dash, S.M. Dhavile, and A.C. Sahayam, *Anal. Meth.* 5(20), 5799 (2013).
- V.K. Panday, J.S. Becker, and H. Dietze, *Anal. Chim. Acta* 329(1-2), 153 (1996).
- T.D.S. Pierre, R.C.C. Rocha, and C.B. Duyck, *Microchem. J.* 109, 41 (2013).
- S. Chen, S. Zhu, and D. Lu, *At. Spectrosc.* 35(1), 1 (2014).
- M. Lin and S. Jiang, *Food. Chem.* 141(3), 2158 (2013).
- D.L.G. Borges, B. Welz, and A.J. Curtius, *Microchim. Acta* 159, 19 (2007).

24. S. Chen and L. Dengbo, *At. Spectrosc.* 33(1), 9 (2012).
25. S. Chen, X. Cheng, Y. He, S. Zhu, and D. Lu, *Microchim. Acta* 180, 1479 (2013).
26. S. Huang and S. Jiang, *Anal. Meth.* 2(9), 1310 (2010).
27. S. Huang and S. Jiang, *Anal. Meth.* 2(9), 1310 (2010).
28. M.A Reddy, R. Shekhar, and S.J. Kumar, *At. Spectrosc.* 34(4), 1 (2013).
29. A.B. Volynsky and M.T.C. de Loos-Vollebregt, *Spectrochim. Acta Part B* 60(11), 1432 (2005).
30. J. Hassler, P. Barth, S. Richter, and R. Matschat, *J. Anal. At. Spectrom.* 26(12), 2404 (2011).
31. S. Chen, D. Lu, Z. Hu, and B. Wu, *Spectrochim. Acta Part B* 60(4), 537 (2005).
32. S. Chen, S. Zhu, and D. Lu, *Microchem. J.* 97(2), 196 (2011).
33. Y. Yi, S. Jiang, and A.C. Sahayam, *J. Anal. At. Spectrom.* 27(3), 426 (2012).
34. S. Chen, S. Zhu, and D. Lu, *At. Spectrosc.* 34(1), 1 (2013).
35. S. Chen, S. Zhu, and D. Lu, *At. Spectrosc.* 35(3), 103 (2014).
36. Y. Li and S. Jiang, *Anal. Chim. Acta* 359, 205 (1998).
37. G. Peng, *Chinese J. Anal. Lab.* 27(3), 106 (2008).