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Direct determination of trace impurities in niobium pentaoxide solid powder with slurry sampling fluorination assisted electrothermal vaporization inductively coupled plasma mass spectrometry

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A method of fluorination assisted electrothermal vaporization inductively coupled plasma mass spectrometry (FETV-ICP-MS) was developed to directly determine the trace impurities in niobium pentaoxide solid powder in which a poly(tetrafluoroethylene) (PTFE) emulsion was used as fluorinating modifier to promote the vaporization of refractory elements from a graphite furnace and to avoid the formation of thermally stable carbides. The solid sample was introduced into the graphite furnace in the form of slurry without any chemical pretreatments. The electrothermal vaporizer device was connected to the ICP system by a laboratory-built interface, and the flow rates of sample carrier gas and auxiliary carrier gas were optimized experimentally. The potentially polyatomic interferences resulting from the pyrolysates of PTFE were evaluated. A new method by stepwise diluting the sample matrix is proposed for investigating the matrix effect and the results showed that no obvious matrix effect was observed with a sample matrix (Nb_2O_5) concentration of less than 200 mg L^{-1}. Under the optimal conditions, the absolute limits of detection for FETV-ICP-MS determination of Ta, Ti, Cr, W, Ni, Cu and Mn were in the range of 0.026–1.1 pg. For one analysis run, only 0.002 mg of Nb_2O_5 sample was required. The proposed method has been applied to determining the trace impurities in Nb_2O_5 powder, and both the results obtained from the external calibration method and the standard addition method were in a good agreement with those obtained by conventional nebulization ICP-MS.

Introduction

Niobium has many outstanding characteristics, such as high melting point, good resistance to corrosion, small thermal neutrons capture cross section and high thermal conductively. Niobium pentaoxide has increasing applications in optic materials, the fabrication of semiconductor components, production of various types of catalysts, and the microelectronics industry in the form of lithium niobate single crystals.[1] High-purity niobium pentaoxide is required for highly technical applications because the excessive impurities do influence the qualities of materials. Therefore, the development of a very effective method for accurate determination of impurities in high-purity niobium is widely demanded.

When conventional methods, ICP-AES[2–5] and ICP-MS,[5] are used for the quantification of impurities in a niobium matrix, a sample pretreatment involving hydrofluoric acid digestion and matrix separation is generally required prior to the analysis. However, it is hard to digest niobium pentaoxide and the decomposition process in open vessels is much more time-consuming. Although the microwave technique was used to accelerate it, the possibility of analyte loss and contamination was still present. Furthermore, when the analysis of niobium pentaoxide was performed with atomic spectrometric methods, such as ICP-AES, serious spectral interferences were expected from the niobium matrix which would need to be fully countered.[3] Successful separation of analyte from matrix prior to analysis was quite helpful in eliminating the interferences and improving the power of detection methods.[2,3] Anion-exchange separation with HF and HCl media was combined with ICP-AES to determine trace impurities in high-purity niobium, and a concentration of 4.4 μg g^{-1} for Ta was obtained.[2]

In recent years, solid sample introduction techniques, which may by-pass the defaults of complex procedures, time-consuming, analyte loss and contamination from acid digestion or fusion procedures, have received the greatest attention. Although laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has been applied to the direct analysis of niobium pentaoxide with somewhat lower LODs,[6] this method suffered from calibration problems because of the requirement for solid standards with the same components as samples, and the accuracy was influenced in some ways. When electrothermal atomic absorption spectrometry (ETAAS) was developed for the direct analysis of niobium pentaoxide, up to 15 mg of the niobium pentaoxide sample were loaded onto the platform vaporizer for determination of trace metals (Al, Co, Cr, Cu, Fe, Mn and Ni), and during the pyrolysis stage, the niobium pentaoxide matrix was converted into the thermally stable niobium carbide using a methane atmosphere, with the aim of avoiding the serious matrix-caused non-spectral interferences and background.[7] A similar method has also been used to determine silicon in high-purity niobium pentaoxide.[8]

When electrothermal vaporization (ETV) techniques were hyphenated to ICP-AES/MS for the purpose of direct analysis of solid samples, optimization of the ETV program could be used to alleviate and eliminate matrix interferences owing to the separation of the electrothermal vaporizer (where the analyte and matrix vaporization processes take place) and the ICP torch (where the analyte and matrix atomization/ionization process takes place). Otherwise, with the application of proper chemical modifier, such as trifluoromethane,[9] the analysis performance of refractory elements and carbide forming elements can be improved dramatically.[10,11] Fluorination assisted ETV-ICP-AES, using a polytetrafluoroethylene (PTFE) emulsion as chemical modifier, was applied with the thermochemical data to evaluate the fluorinating vaporization behavior of Nb and Ta in a graphite furnace.[12] It was also

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stated that the PTFE slurry modifier may present several advantages such as: (1) PTFE has a high fluorine content; (2) the F in PTFE pyrolysate has sufficient chemical activity to react with refractory materials; (3) PTFE has a suitably high decomposition temperature (about 415 °C); (4) PTFE contains many fewer inorganic impurities; and (5) PTFE emulsion is easy to use.[13,14]

In most of the literature on ETV-ICP-MS, the commercially available graphite furnace was employed as a vaporizer after some modification, where the transfer line between the ETV and ICP-MS was not longer than 80 cm.[15–20] In Verrept *et al.*'s work, a secondary flow of argon (at a rate about 0.7 L min^{-1}) was introduced to stabilize the plasma, leading to an improvement in the ETV-ICP-MS system; a part of the secondary flow was helpful in keeping the air out, and the sample boat was easily introduced into or removed from the graphite furnace without shutting down the plasma.[21] Such a flow of stabilization gas was similarly employed for ETV-ICP-MS determination of the trace metals in small atmospheric particles in Arctic air.[22] At the same time, Chen *et al.*[23] developed a new interface for connecting an ETV to an ICP-AES. It was reported that when a flow of auxiliary gas was introduced into ICP-AES through the interface, the plasma was quite stable during experiments and the transport efficiency could be promoted by decreasing the analyte losses in transfer line. When the transport losses of analytes in the individual segments of the ETV-ICP-AES system with various ETV-ICP connecting interfaces were investigated by Schaffer and Krivan, they also confirmed that an admixture of a cold gas to the carrier gas behind the vaporization cell would have a positive effect on the transport efficiency.[24]

The main purpose of this work was to interface the ETV sample introduction unit with the ICP-MS and to establish a new method for ETV-ICP-MS direct determination of trace impurities in a pure/high-purity refractory metallic oxide (niobium pentaoxide). For this purpose, an interface for connecting the ETV with the ICP was developed and the operating parameters were optimized; the chemical modification of poly(tetrafluoroethylene) (PTFE) in ETV-ICP-MS was investigated; the spectral and non-spectral interferences in both FETV-ICP-MS and conventional nebulization ICP-MS were comparatively studied; and, finally, the developed method was used to directly determine Ta, Ti, Cr, W, Ni, Cu and Mn in niobium pentaoxide powder. The method is characterized by high sensitivity, accuracy, rapidity, simplicity, a small sample amount requirement, and an absence of any chemical pretreatments.

Experimental

Instrumentation

An Agilent 7500a ICP-MS (Agilent, Japan), equipped with a modified commercially available WF-4C graphite furnace (Beijing Second Optics, China) as electrothermal vaporizer was used. The original silica windows at the two ends of the graphite furnace were removed and replaced by two PTFE cylinders, as has been detailed in previous work,[25] and one of them was connected to the injector tube of the plasma torch. The transfer line consisted of a laboratory-built connecting interface (detailed in Fig. 1) and a polyethylene tube (6 mm id) with total length of 70 cm. Optimization of the ICP-MS instrument (*i.e.*, lens settings, resolution, oxide and doubly charged ion formation) was performed with a conventional nebulization method (PN-ICP-MS) prior to connection to the ETV device. The operating conditions for ICP-MS and ETV are given in Table 1. Pyrolytic graphite coated graphite tubes were used throughout the work.

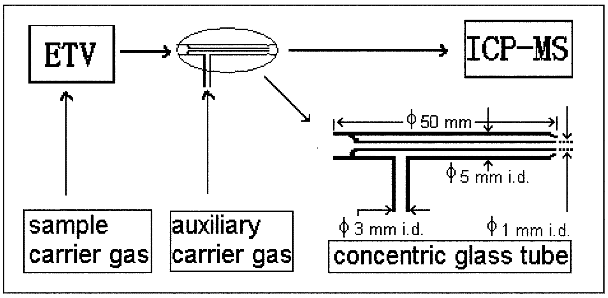

Fig. 1 Schematic diagram of the gas flow path from ETV to ICP and the ETV–ICP connecting interface.

Table 1 Equipment and operating parameters

ICP-MS plasma—	
Rf power	1250 W
Outer gas flow rate	15 L min^{-1}
Intermediate gas flow rate	0.9 L min^{-1}
Nebulizer gas flow rate	0.7 L min^{-1}
Sampling depth	7.0 mm
Sampler/skimmer diameter orifice	Nickel 1.0 mm/0.4 mm
Time-resolved data acquisition—	
Scanning mode	Peak-hopping
Dwell time	10∼20 ms
Integration mode	Peak area
Points per spectral peak	1
Electrothermal vaporizer—	
Sample volume	10 μL
Carrier gas flow rate	0.4 L min^{-1}
Drying step	100 °C ramp 15 s\hold 15 s
Pyrolysis step	420 °C ramp 5 s\hold 25 s
Vaporization step	2400 °C hold 4 s

Reagents

The stock standard solutions (1 g L^{-1}) for Ti, Cr, W, Ni, Cu and Mn were prepared from their specPure oxides using the conventional method. A Ta standard stock solution of 1 g L^{-1} was obtained with Ta_2O_5 (99.99% pure, Shanghai Yuelong Chemical Factory, China) by microwave digestion similar to Nb_2O_5 sample digestion (detailed later). A 60% m/v PTFE was purchased from Shanghai Institute of Organic Chemistry, China. All other chemicals used in this work were of specPure grade or analytical grade and the doubly distilled water was used throughout.

Sample preparation

Sample digestion. Solution of Nb was prepared from Nb_2O_5 (99.5% pure, Shanghai Yuelong Chemical Factory, China). After an appropriate quantity of oxide powder had been weighed into a PTFE vessel, HF and HNO_3 were added, the PTFE vessel was tightly sealed, and then the microwave digestion was performed with a home microwave oven. After the digestion had been completed, the PTFE vessel was naturally cooled down to room temperature, and the digests were diluted with 2% HNO_3 to volume and stored in a polypropylene vessel with a tightly closed cap. They were further diluted to the requited concentration step by step prior to use.

Slurry preparation. A 2.0 mg amount of Nb_2O_5 solid powder (with mean particle size of 105 μm) was accurately weighed into a 10 mL tube, 1.0 mL of 60% m/v PTFE emulsion was added, and then the mixture was diluted to volume with a 0.02% m/v agar solution as stabilizer. For calibration, the aqueous standard solutions containing 6% m/v PTFE as chemical modifier were used. All the slurry samples were dispersed with an ultrasonic vibrator for 20 min prior to analysis.

Procedure

After the ETV unit had been 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 of the temperature program, the dosing hole of the graphite furnace was kept open to remove water and other vapors. When the dosing hole was sealed with a graphite probe 10–15 s prior to the high temperature vaporization step, the vaporized analyte was swept into the plasma excitation source by a carrier gas of argon and the peak-hop transient mode of data acquisition was used to detect the ions selected.

Results and discussion

Connecting interface for ETV and ICP

ETV–ICP interface design was optimized for efficient sample transportation and the best analytical performance of ETV-ICP-MS. Design philosophies were influenced by the following needs, namely: (1) to minimize the analyte loss in the transfer line; (2) to keep the ICP stable during replacement of samples; (3) to maximize and maintain the ICP's atomization and ionization efficiency. Based on these criteria, an interface was designed to connect ETV with ICP-MS, which is shown in Fig. 1. The interface has a concentric structure (5 cm long, 1 mm id inner tube and 5 mm id outer tube with 1 mm interval between them) with two inlets, which offers two flows of gas introduced into the ICP torch. One is a sample carrier gas from the ETV to transport the vaporized sample into the ICP *via* the internal tube, and the other is a so-called auxiliary carrier gas to maintain the ICP channel *via* the outer tube of the concentric glass interface.

It was shown that this interface would not only be able to keep the ICP stable during analysis and obtain high sensitivity for signal intensity by optimizing the flow rates of the sample carrier gas and the auxiliary carrier gas, but also be beneficial when performing multi-element analysis with an ETV-ICP-MS due to the somewhat prolonged transportation time of vaporized sample from ETV to ICP. Additionally, as described in ref. 22, when the furnace was open during the drying step, the auxiliary gas would help the sample carrier gas to remove the water and other vapors *via* the dosing hole. Therefore, the plasma would be protected from overloading.

Optimization of sample/auxiliary carrier gas

Under the different flow rates of sample carrier gas, the effect of auxiliary carrier gas on signal intensity of analyte (Ta for example) was studied and the results are shown in Fig. 2. It can be seen that: (1) too fast or too slow a flow rate of the auxiliary carrier gas were not favorable to achieve better signal intensity; (2) the best signal intensity could be obtained with lower sample carrier gas and higher auxiliary carrier gas flow rates; and (3) the highest signal intensity of analyte depended on the total carrier gas flow rate of the two parts of carrier gas. From Fig. 2, it can be also found that the optimal total flow rate was in the range of 1.1–1.2 L min^{-1}, which was similar to the optimal flow rate of nebulizer carrier gas for conventional ICP-MS. In this work, a flow rate of the sample carrier gas of 0.4 L min^{-1} and of the auxiliary carrier gas of 0.7 L min^{-1}, which gave a total flow rate of 1.1 L min^{-1}, was selected. At this level, it can maintain the ICP channel, make the plasma stable, minimize dilution of the vapor and improve the transport efficiency.

Fluorination assisted electrothermal vaporization

Optimization of ETV parameters. Both ETV-ICP-AES and ETV-ICP-MS can be used to investigate the vaporization behavior of the analyte (Ta). It was reported in fluorination assisted ETV-ICP-AES that the occurrence of analyte (Ta) losses happened with pyrolysis temperatures higher than 415 °C and the maximum signal intensity was achieved at a PTFE concentration of 6% m/v.[12] Thus, a pyrolysis temperature of 420 °C was chosen in this work and a 2400 °C was chosen as the compromise vaporization temperature for the purpose of multi-element analysis of Ta, Ti, Cr, W, Ni, Cu and Mn.

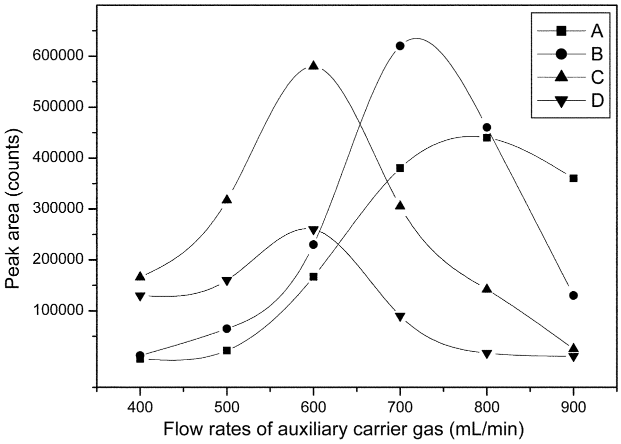

Fig. 2 Effect of flow rate of carrier gas and the auxiliary carrier gas on the signal intensity of Ta (100 pg). With flow rates of carrier gas at A, B, C and D of 300 mL min^{-1}, 400 mL min^{-1}, 500 mL min^{-1} and 600 mL min^{-1}, respectively.

Signal profiles. Typical signal profiles of analyte (Ta) in ETV-ICP-MS with PTFE chemical modifier and without chemical modifier are shown in Fig. 3. It can be seen that in the absence of PTFE the signal intensity of Ta was very weak (Fig. 3A) and the residue signal with the same ETV parameters was much more intense (Fig. 3A′), which indicated incomplete vaporization of Ta and a serious memory effect. The reason for this is that Ta is a refractory and carbide forming element, and the boiling points for Ta and TaC are 5400 °C and 5500 °C, respectively, so tantalum has also been used for the treatment of graphite cups[26] in order to promote electrothermal vaporization. However, dramatic changes of signal profiles of Ta occurred in the presence of PTFE modifier. A sharper, symmetrical and much more intense peak (Fig. 3B) was obtained, and no obvious memory effect was observed (Fig. 3B′). The possible reasons for this are that, on one hand,

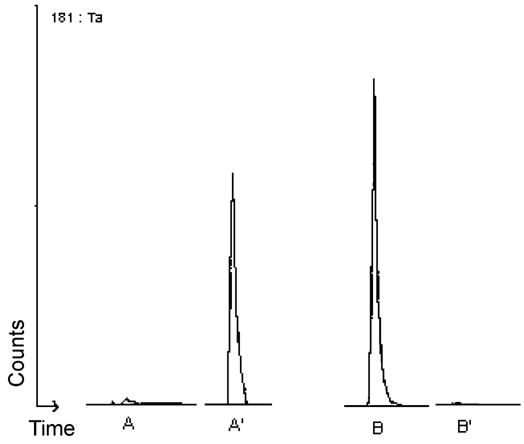

Fig. 3 Typical signal profiles of Ta vaporization in ETV-ICP-MS for: A, 2 ng Ta without PTFE; A′, residue signal profile of A with 6% m/v PTFE as chemical modifier; B, 20 pg Ta with PTFE; B′, residue signal profile of B with 6% m/v PTFE as chemical modifier. The ETV temperature of the vaporization step was 2400 °C for 4 s and the sample volume was 10 µL.

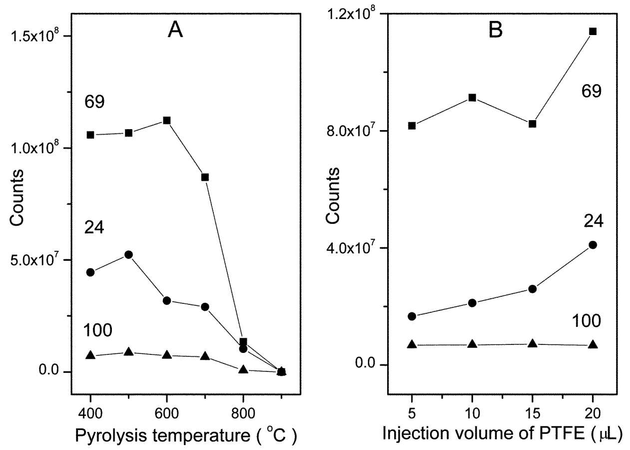

Fig. 4 Pyrolysate signals of 6% m/v PTFE changing with different pyrolysis temperature (A) and injection volume (B) in ETV-ICP-MS.

fluorine can combine very strongly with the refractory element Ta and the fluorinating reaction between Ta and PTFE is the main reaction taking place in the graphite furnace at high temperature; on the other hand, the fluoride produced can be easily vaporized from the graphite furnace because the boiling point of tantalum fluoride is 230 °C, which is much lower than those of its carbide and metal Ta.

PTFE pyrolysates and spectral interferences

The decomposition of PTFE starts at a temperature about 415 °C. The pyrolysates of PTFE would interact with the analyte or with the matrix in a graphite furnace and, as a result, alter its volatility and alleviate the matrix interferences. On the other hand, the plentiful molecules from pyrolysis would also act as physical carriers to promote the vaporization/transport efficiency. Therefore, it is necessary to investigate the pyrolysates of PTFE in a graphite furnace to better understand the role of chemical modifiers and to forecast the potent polyatomic interferences. For this purpose, the molecules of $^{12}C_2$ (*m*/*z* 24), $^{12}C^{19}F_3$ (*m*/*z* 69) and $^{12}C_2{}^{19}F_4$ (*m*/*z* 100) which result from the decomposition of PTFE by electrical heating in a graphite furnace were selected, and the dependence of ion counts of the above particles on the pyrolysis temperature and injection volume of 6% PTFE was studied. It can be seen from Fig. 4: (1) the ion counts of $^{12}C^{19}F_3$ are much higher than those of $^{12}C_2$ and $^{12}C_2{}^{19}F_4$, which indicates a good fluorinating atmosphere in the graphite furnace; and (2) the ion counts for all three particles observed change similarly with the change of pyrolysis temperature and injection volume of 6% PTFE, their ion counts decreasing with the increase of the pyrolysis temperature (Fig. 4A) and increasing with the increase of the 6% PTFE injection volume (Fig. 4B). When the pyrolysis temperature was higher than 800 °C, the ion counts for three particles decreased remarkably, which indicated that the PTFE had entirely decomposed and that the decomposed species had been removed from graphite furnace at a temperature of 800 °C for 30 s. However, the abundant pyrolysates containing C and F may be result in serious interferences directly or indirectly. Table 2 gives the potentially polyatomic interferences induced by the decomposition of PTFE in ETV-ICP-MS. It should be noted that the spectroscopic interferences induced by the decomposition of PTFE could be decreased by the use of higher pyrolysis temperature or prolonging the pyrolysis time. In our experiment, a pyrolysis temperature of 420 °C with a pyrolysis time of 30 s was chosen with the aim of avoiding the analyte losses and performing multi-element analysis.

Table 2 Isotopes of interest and potentially polyatomic interferences in FETV-ICP-MS

Isotope	Potentially interfering species
^{47}Ti	^{28}Si^{19}F, ^{35}Cl^{12}C, ^{31}P^{16}O
^{49}Ti	^{30}Si^{19}F, ^{37}Cl^{12}C, ^{36}Ar^{13}C
^{53}Cr	^{40}Ar^{13}C, ^{37}Cl^{16}O
^{55}Mn	^{36}Ar^{19}F, ^{40}Ar^{15}N, ^{39}K^{16}O
^{60}Ni	^{41}K^{19}F, ^{36}Ar^{12}C$_2$, ^{44}Ca^{16}O
^{63}Cu	^{44}Ca^{19}F, ^{40}Ar^{23}Na
^{181}Ta	^{12}C$_4{}^{19}$F$_7$
^{184}W	—

Matrix effect

When ETV-ICP-MS is used to determine trace impurities in niobium pentaoxide, a serious matrix effect may be present due to excessive matrix (Nb) transported from graphite tube into ICP. In order to investigate the matrix effect, a new method that does not require high purity of Nb_2O_5 as matrix was proposed. For this purpose, the following experiment was designed. A series of samples with different sample matrix concentrations were prepared by diluting the digested sample solution stepwise, and the signal intensities of the analytes were plotted against the concentration of sample matrix. Under the optimal experimental conditions, if there is a good relationship between the signal intensity of the analyte and the concentration of the sample matrix, it can be assumed that there is no obvious matrix effect. Otherwise, it must be said that there is a matrix effect. It should be pointed out that the interferences in ICP-MS could be divided into spectroscopic interferences, which will result in the increase of signal intensity of analyte, and non-spectroscopic interferences (matrix effect), which generally will lead to the suppression of analyte signal. The above criterion is valid on the condition that there is no spectroscopic interference induced by the matrix, and is based on the fact that the matrix effect in ICP-MS depends on the absolute mass introduced into ICP rather than the molar ratio of matrix element to analyte.[27] The dependence of signal intensity of analyte on the sample matrix concentration for FETV-ICP-MS and PN-ICP-MS was investigated and a linear relationship between the signal intensity of Ta and the matrix (Nb) concentration was obtained for both FETV-ICP-MS and PN-ICP-MS, with the matrix concentration ranging from 10 to 200 mg L^{-1}. The regression coefficients (*r*) obtained in this work ranged from 0.9901 (Ni) to 0.9973 (Ta) for FETV-ICP-MS and from 0.9920 (Ni) to 0.9999 (Cr) for PN-ICP-MS. Because there are no spectroscopic interferences induced by matrix Nb with Ta, it can safely be said that there is no apparent matrix effect when the matrix concentration is less than 200 mg L^{-1} for both FETV-ICP-MS and PN-ICP-MS. With respect to the mechanism of matrix effect, some further research work should be carried out.

Detection limits, precision and linearity

According to the IUPAC definition, the limit of detection was calculated as the concentration or absolute mass of analyte yielding a signal equivalent to tree times the standard derivation of the blank value ($n = 5$). The relative and absolute limits of detection are listed in Table 3. For comparison, Table 3 also gives the limits of detection of PN-ICP-MS (analysis performed with a Babington nebulizer and with a sample volume of 0.4 mL). Compared with PN-ICP-MS, the absolute limits of detection of FETV-ICP-MS were improved by 1–2 orders of magnitude. For analysis of 0.002 mg of sample (Nb_2O_5), the limits of detection were 0.028 μg g^{-1} (Ta), 0.091 μg g^{-1} (Ti), 0.49 μg g^{-1} (Cr), 0.013 μg g^{-1} (W), 0.22 μg g^{-1} (Ni), 0.55 μg g^{-1} (Cu) and 0.055 μg g^{-1} for Mn, respectively, in the original solid powder. The relative standard deviations (RSDs)

Table 3 Limits of detection obtained in the direct analysis of Nb_2O_5 slurry

	Ta	Ti	Cr	W	Ni	Cu	Mn
Pneumatic nebulizer (PN)-ICP-MS/ng mL^{-1}	0.0056	0.14	0.24	0.28	0.021	0.053	0.018
pg[a]	2.2	56	96	11	8.4	21	7.6
Fluorination assisted (F)ETV-ICP-MS/ng mL^{-1}	0.0056	0.018	0.099	0.0026	0.045	0.11	0.011
pg	0.056	0.18	0.99	0.026	0.45	1.1	0.11
ETAAS[13]/pg			30		30	15	7.5
FETV-ICP-MS (for solid sample)/μg g^{-1}	0.028	0.091	0.49	0.013	0.22	0.55	0.055

[a] Obtained with sample volume of 0.4 mL. [b] Noted the results of FETV-ICP-MS were obtained on the optimal conditions of Ta.

Table 4 Percentage concentrations of impurities obtained in Nb_2O_5 solid powder (% m/m)

	PN-ICP-MS	ETV-ICP-MS		Reference
	A1[a]	A2[a]	B[b]	C[c]
Ta	0.0725 ± 0.0030	0.0741 ± 0.0041	0.0734 ± 0.0035	⩽0.1
Ti	0.0152 ± 0.0011	0.0171 ± 0.0020	0.0156 ± 0.0012	⩽0.025
Cr	0.0011 ± 0.0001	0.0014 ± 0.0001	0.0017 ± 0.0002	⩽0.005
W	0.0038 ± 0.0002	0.0032 ± 0.0003	0.0031 ± 0.0003	⩽0.01
Ni	0.0020 ± 0.0001	0.0015 ± 0.0002	0.0016 ± 0.0002	⩽0.005
Cu	0.0028 ± 0.0001	0.0028 ± 0.0003	0.0031 ± 0.0003	⩽0.005
Mn	0.0013 ± 0.0001	0.0010 ± 0.0001	0.0012 ± 0.0001	⩽0.01

[a] A1, A2 calculated from calibration against aqueous standards (mean ± *s*, $n = 3$). [b] B calculated from calibration against standard additions (mean ± *s*, $n = 3$). [c] C the tolerant percentage concentrations of impurities given by the reagent factory.

were 4.7% for solution samples and 11% for slurry samples ($n = 3$), respectively. The calibration was linear for 3–4 orders of magnitude (Ta, for example, showed good linearity with concentrations ranging from 0.1 ng mL^{-1} to 500 ng mL^{-1}).

Sample analysis

Slurry sampling FETV-ICP-MS was applied to direct determination of the trace metals in Nb_2O_5 powder. The concentration of Nb_2O_5 in slurry was 200 mg L^{-1} and the sample volume was 10 μL, thus only 0.002 mg of original sample was introduced into the graphite furnace. The results obtained from the external calibration method and the standard addition method for Ta, Ti, Cr, W, Ni, Cu and Mn in Nb_2O_5 are given in Table 4. Table 4 also lists the analytical results obtained by PN-ICP-MS and reference values (the tolerant concentrations) supplied by the reagent factory. As could be seen, a fairly good agreement among these values was obtained.

Conclusion

A simple method, slurry sampling fluorination assisted ETV-ICP-MS, has been developed for the direct analysis of refractory metallic oxide (Nb_2O_5) powder. The experimental results show that the vaporization behavior of refractory elements could be improved by the use of PTFE as a chemical modifier, and therefore the detection limits could be improved. In order to investigate the matrix effect, a new method without the use of higher purity of matrix was developed. The method of FETV-ICP-MS is characterized with high sensitivity (fg to pg level), rapidity, simplicity, low interference level, small size of sample requirement and no chemical pretreatment.

Acknowledgements

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References

1 J. S. Feng, *Rare Met. Mater. Eng. (Chinese)*, 1994, **23**(23), 8.
2 T. Imakita, N. Fudagawa and M. Kubota, *Analyst*, 1990, **115**, 1185.
3 O. N. Grebneva, I. V. Kubrakova, T. F. Kudinova and N. M. Kuzmin, *Spectrochim. Acta, Part B*, 1997, **52**, 1151.
4 J. Stummeyer, S. Kittel and G. Wunsch, *Anal. Chim. Acta*, 1992, **258**, 329.
5 J. Stummeyer and G. Wunsch, *Fresenius' J. Anal. Chem.*, 1991, **340**, 269.
6 S. J. G. Anderson, R. V. D. Robert and H. N. Farrer, *J. Anal. At. Spectrom.*, 1992, **7**, 1195.
7 M. D. Huang and V. Krivan, *Fresenius' J. Anal. Chem.*, 2000, **368**, 227.
8 M. D. Huang and V. Krivan, *Spectrochim. Acta, Part B*, 2001, **56**, 1645.
9 J. S. Alvarado and M. O. Erickson, *J. Anal. At. Spectrom.*, 1996, **11**, 923.
10 R. E. Sturgeon and J. W. Lam, *J. Anal. At. Spectrom.*, 1999, **14**, 785.
11 M. A. Belarra, M. Resano, F. Vanhaecke and L. Moens, *Trends Anal. Chem.*, 2002, **21**, 828.
12 B. Hu, Z. C. Jiang and Y. E. Zeng, *Rock Miner. Anal. (Chinese)*, 1993, **12**, 183.
13 B. Hu, Z. C. Jiang, Y. C. Qin and Y. E. Zeng, *Anal. Chim. Acta*, 1996, **319**, 255.
14 Z. C. Jiang, B. Hu, Y. C. Qin and Y. E. Zeng, *Microchem. J.*, 1996, **53**, 326.
15 J. D. Venable, D. Langer and J. A. Holcombe, *Anal. Chem.*, 2002, **74**, 3744.
16 F. Vanhaecke, M. Resano, M. P. Lopez and L. Moens, *Anal. Chem.*, 2002, **74**, 6040.
17 W. C. Wei, P. H. Chi and M. H. Yang, *J. Anal. At. Spectrom.*, 2000, **15**, 1466.
18 J. P. Snell, E. Bjorn and W. Frech, *J. Anal. At. Spectrom.*, 2000, **15**, 397.
19 Z. Arslan and A. J. Paulson, *Anal. Chim. Acta*, 2003, **476**, 1.
20 C. Y. Ho and S. J. Jiang, *Spectrochim. Acta, Part B*, 2003, **58**, 63.
21 P. Verrept, R. Dams and U. Kurfurst, *Fresenius' J. Anal. Chem.*, 1993, **346**, 1035.
22 C. Ludke, E. Hoffmann, J. Skole and M. Kriews, *J. Anal. At. Spectrom.*, 1999, **14**, 1685.
23 S. Z. Chen, T. Y. Peng, Z. C. Jiang, Z. H. Liao and B. Hu, *J. Anal. At. Spectrom.*, 1999, **14**, 1723.
24 U. Schaffer and V. Krivan, *Anal. Chem.*, 1998, **70**, 482.
25 B. Hu, Z. C. Jiang, T. Y. Peng and Y. C. Qin, *Talanta*, 1999, **49**, 357.
26 K. C. Ng and J. A. Caruso, *Anal. Chim. Acta*, 1982, **143**, 209.
27 E. H. Evans and J. J. Giglio, *J. Anal. At. Spectrom.*, 1993, **8**, 1.