



Analytical note

Direct determination of fluorine in niobium oxide using slurry sampling electrothermal high-resolution continuum source molecular absorption spectrometry



Mao Dong Huang^a, Helmut Becker-Ross^a, Michael Okruss^{a,*}, Sebastian Geisler^a, Stefan Florek^a, Silke Richter^b, Angela Meckelburg^b

^a Leibniz-Institut für Analytische Wissenschaften—ISAS—e.V., Department Berlin, Albert-Einstein-Str. 9, 12489 Berlin, Germany

^b BAM Federal Institute for Materials Research and Testing, Department of Analytical Chemistry, Reference Materials, Richard-Willstätter-Str. 11, 12489 Berlin, Germany

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ABSTRACT

Aiming for a round-robin test, a new method for the direct determination of fluorine in niobium oxide has been developed. It is based on the use of high-resolution molecular absorption spectra of calcium mono-fluoride (CaF) generated in the graphite tube, combined with the slurry sampling technique. The absorption measurement was performed at the 606.44 nm CaF rotational line. By using graphite tubes with zirconium carbide (ZrC) modified platform, the molecular absorption sensitivity of CaF has been improved by a factor of 20, and no additional chemical modifier was necessary. Generally, non-spectral interferences were observed in the presence of HCl, H₂SO₄, and H₃PO₄. For HCl, additional spectral interference occurred due to an overlap of the absorption spectra of CaF and CaCl. However, due to the absence of these mentioned substances in the current material, such interferences do not exist for this application. The characteristic mass found for the CaF 606.44 nm line was 0.1 ng; the limit of detection was 5 mg fluorine per kg solid sample (3 σ criterion). The results obtained by the method were within the range of certified values. Comparing to the classical method such as the pyrohydrolysis-photometric method, the developed new method showed clear advantages regarding sensitivity and specificity. The time requirement for one sample analysis was strongly shortened from several hours to only some minutes.

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1. Introduction

Niobium oxide (Nb₂O₅) is an indispensable material for various advanced technologies. It finds applications in optical glasses and in capacitors. Due to the high refractive index of 2.33 at 550 nm, thinner and lighter lenses can be made by using niobium oxide containing glass, which is already the case in many camera lenses and for eye-glasses. The high dielectric constant of 41 enables the development of capacitors with exceptionally high capacitance.

The purity requirements for niobium oxide depend on the specific applications. A purity level of 99.9% is sufficient for optical usage. A considerably higher degree is required for use as a source material for producing semiconductors, because impurity elements affect the properties of the electronic products. In this aspect, simple and sensitive analytical methods for the determination of impurity elements in niobium oxide are compulsory.

Fluorine is a common impurity in niobium oxide, because the manufacturing process of niobium oxide includes the use of fluorine-

containing chemicals, starting with the fluorination of the raw material and ending with the purification and separation steps of its fluoride complex [1]. The determination of fluorine in niobium oxide is therefore of particular importance and constitutes a difficult analytical task for several reasons. First, the general wet sample digestion procedure for the highly refractory niobium oxide material requires radical physical conditions such as high temperatures and/or the use of microwave power [2]. Second, the addition of hydrofluoric acid is mandatory. Although the digestion method can be used for the determination of many metallic impurities in niobium oxide [3,4], it is obvious that it cannot be applied to fluorine determination. A fusion method was used for the determination of the main component niobium in niobium oxide [5], but not for impurity elements like fluorine.

Owing to the mentioned problems, the pyrohydrolysis method [6] was recommended for fluorine determination in niobium oxide and other similar refractory materials. Here, the fluorine is liberated at a temperature of 1050 °C in an atmosphere of water vapor and oxygen. The gas mixture is then transferred into a solution of sodium hydroxide. Finally, the collected amount of fluorine is determined by a photometric method or by a fluorine ion selective electrode. These procedures are complicated and time consuming due to the special requirements for the heating and tubing system, and long time periods are needed for

* Corresponding author. Fax: +49 30 6392 3544.

E-mail address: michael.okruss@isas.de (M. Okruss).

sample treatment and measurement. Additional problems are the high contamination potential and the risk of incomplete fluorine recovery.

Digestion-free techniques have also been applied to the analysis of niobium oxide samples. For example, slurry sampling [7] and direct solid sampling [8] were used for the determination of 25 and 11 impurity elements, respectively. Laser ablation technique combined with the inductively coupled plasma mass spectrometry as elemental detector was used for the determination of 11 impurity elements in niobium oxide and tantalum oxide samples [9]. Fluorine, however, was not included in all these investigations.

Another major problem in fluorine determination is the lack of suitable detection techniques. Standard atomic absorption and emission spectrometers cannot access fluorine, because its resonance lines occur in the VUV spectral range below 100 nm. In the case of common inductively coupled argon plasmas (ICP), the plasma energy is too low to generate a significant population of excited fluorine atoms.

The situation has improved in recent years. The introduction of high-resolution continuum source absorption spectrometry (HR-CS MAS) provides a new way for the determination of non-metals including fluorine [10–13]. HR-CS MAS allows random and gapless access to any wavelength of analytical interest and enables the measurement of diatomic molecular absorption of non-metal compounds. The high resolution and the capability of effective and flexible background correction are responsible for the high reliability and accuracy of this technique [12,13]. Fluorine can be determined sensitively by measuring the diatomic GaF molecular absorption produced in the air–acetylene flame [10] or in a graphite tube [11]. In the latter case, a detection limit of about 10 pg F can be achieved, which makes the method the most sensitive one for fluorine determination. Recently, a similar method based on the CaF molecular absorption at 606.440 nm for the determination of fluorine in tea has been developed [14]. The achieved detection limit was 1.6 ng, which is relatively high but can be used very well for tea and other samples with higher fluorine contents.

The BAM Federal Institute for Materials Research and Testing is currently carrying out a certification campaign for a niobium oxide material in co-operation with the Chemists Committee of GDMB Society for Mining, Metallurgy, Resource and Environmental Technology. The objective of the campaign is the certification of the fractions of several trace elements, including fluorine content, in this material. The aim of the present research was the introduction of a simple and accurate method for the determination of fluorine at the 100 $\mu\text{g g}^{-1}$ level in niobium oxide materials. Due to the relatively high fluorine content, it was decided not to utilize the highly sensitive GaF molecule absorption; instead, CaF generated in a graphite tube was chosen for this application. Another issue of the study was the adaption of a direct sampling technique to avoid the laborious sample digestion procedure. Because the sample to be investigated was present in powder form with a mean particle size of 2.2 μm , the slurry sampling technique was chosen for sample introduction.

2. Experimental

2.1. Instrumentation

The molecular absorption measurements were made with a prototype of a high-resolution continuum source absorption spectrometer (ISAS Berlin, Germany) equipped with a 300 W xenon short-arc lamp (XBO 301, GLE, Berlin, Germany) as continuum source, a model AAS 6 Vario graphite furnace and an MPE 60 autosampler (Analytik Jena AG, Jena, Germany). The spectrometer (DEMON) consists of a high-resolution double monochromator, an echelle grating, and a linear CCD detector with 512 pixels, resulting in a narrow spectral bandwidth of $\lambda/50\,000$ (3 pixel criterion). It allows measurements at arbitrary wavelength within the spectral range between 190 nm and 900 nm. Further description of the spectrometer can be found in earlier publications [15,16].

The CaF molecular absorption line at 606.44 nm was used for the determination and quantification of fluorine. The corresponding spectral bandwidth per pixel was 5.4 pm. The optimized temperature program used for all measurements is given in Table 1. Pyrolytically coated graphite tubes with integrated platform (Analytik Jena, Part No. 407-A81.025) were used throughout the study. Prior to the analytical use, the platform of the graphite tube was modified with ZrC coating, which was accomplished by dosing 30 μL zirconyl chloride solution containing about 1% Zr and 20% ethanol onto the platform and performing a temperature program similar to the one listed in Table 1. The function of ethanol was to ensure a uniform spreading of the coating solution over the whole platform. The coating procedure was repeated twice.

The pretreatment of the sample slurries was carried out with a Sonorex RK100H ultrasonic bath (Bandelin Electronic, Berlin, Germany). For homogenization, a self-built magnetic stirring device with a stirring bar made of PVC material was used.

2.2. Standards, reagents and sample slurry preparation

All reagents were bought from Merck (Darmstadt, Germany). The fluorine standard was prepared by dissolving sodium fluoride (grade “pro analysi”) in de-ionized water. 1% Ca solution (nitrate or acetate) used for CaF generation was prepared by decomposing solid calcium carbonate (grade “Suprapur”) with nitric or acetic acid. The inorganic acids used, i.e., nitric (65%), hydrochloric (37%), sulfuric (98%) and phosphoric (85%) acids, were all of “pro analysi” quality. Argon for spectrometry (99.998% vol.) was supplied by Air Liquid (Berlin, Germany).

The niobium oxide powder sample (No. T-1-010) with a mean particle size of 2.2 μm was distributed by the BAM. The sample slurries were prepared in 15 mL polystyrene vessels by suspending 20–40 mg sample in 10 mL of water produced by Millipore system (containing 0.5% (v/v) HNO_3). The suspensions of the sample were pretreated for 20 min in an ultrasonic bath. During the final fluorine determination the slurries (in the vessels) were permanently homogenized by the stirring device. For the measurements 10 μL solution Ca (for the formation of CaF) and subsequent 10 μL sample slurry were taken up by the MPE 60 autosampler, then the complete 20 μL solution was dispensed onto the platform of the graphite tube. The temperature program shown in Table 1 was applied. Peak volume selected absorbance (PVSA), i.e., integrated absorbance summed over three pixels was used for signal evaluation. The calibration was performed using a standard addition method with an aqueous standard solution made from sodium fluoride salt. For this purpose, the sample slurry was first spiked with a predetermined quantity of fluorine standard solution and then homogenized by stirring. For the measurements, 10 μL solution Ca together with 10 μL spiked sample slurry was dispensed onto the platform of the graphite tube.

2.3. Pyrohydrolysis procedure (DIN 51084)

The ceramic sample boat was annealed in a muffle furnace at 1100 °C overnight. The sample boat loaded with about 500 mg niobium oxide sample was inserted into a furnace (I-05/RP-DIG, Ströhlein), preheated to 900 °C. Then the furnace temperature was raised to 1050 °C and held

Table 1
Temperature program used for fluorine determination via CaF molecular absorption in the graphite furnace.

Step	Temperature (°C)	Heating rate (°C s ⁻¹)	Holding time (s)
Drying 1	90	10	20
Drying 2	130	2	10
Pyrolysis	800	100	20
CaF vaporization	2300	2000	6
Cleaning out	2600	1000	3

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