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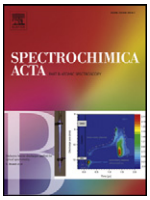

Analytical note

Accurate determination of ultra-trace impurities, including europium, in ultra-pure barium carbonate materials through inductively coupled plasma–tandem mass spectrometry

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ABSTRACT

Impurities, especially ultra-trace europium (Eu), in ultra-pure barium carbonate materials were accurately determined through inductively coupled plasma–tandem mass spectrometry (ICP-MS/MS). Two reaction modes, namely, mass shift (with O_2 as reaction gas) and on-mass modes(with NH_3/He and He as reaction gases), were extensively investigated using Eu^+ as target analyte. The use of $Eu^+ \rightarrow EuO_2^+$, instead of $Eu^+ \rightarrow EuO^+$, as ion pairs in mass shift mode eliminated polyatomic interferences based on Ba matrix ions ($^{135}Ba^{16}O_2^+$ on $^{151}Eu^{16}O^+$ and $^{137}Ba^{16}O_2^+$ on $^{153}Eu^{16}O^+$). This procedure exhibited enhanced sensitivity and selectivity. When the ICP-MS/MS was operated in NH_3 on-mass mode, Eu^+ can be determined in its original mass in interference-free conditions because NH_3 did not react with Eu^+ but with BaO^+ to form a neutral product (BaO). The two reaction modes, especially NH_3 on mass mode, were validated to be accurate because their resultant isotope ratios of $^{153}Eu/^{151}Eu$ matched well with that of the natural abundance ratio. The proposed ICP-MS/MS method is a sensitive technique with a limit of detection as low as 2.0 ng L^{-1} for $^{153}Eu^+$. Compared with conventional single-quadrupole (SQ) ICP-MS, both NH_3 on-mass mode and O_2 mass shift mode in ICP-MS/MS can be used to accurately determine Eu^+ in ultra-pure $BaCO_3$ materials. The detected concentration of Eu^+ was 4.0 ng L^{-1} to 15 ng L^{-1}, with spiked recoveries ranging from 100%–110%. ICP-MS/MS was also used to eliminate polyatomic interferences, particularly Ba-based interferences, prior to measurement of Gd and Sm. Impurities, including Na, Mg, Al, K, Mn, Fe, Cr, Sr, and Cs, in ultra-pure $BaCO_3$ materials were also determined using ICP-MS/MS in conventional SQ mode.

1. Introduction

$BaCO_3$ is a precursor material that undergoes solid-state reaction with TiO_2 to form $BaTiO_3$, which is one of the most widely used ferroelectric materials for multi-layered ceramic capacitors with high capacitance density [1,2]. The properties of $BaCO_3$ material, such as purity, particle size, and morphology, significantly influence the quality and function of $BaTiO_3$ products [3,4]. Preparation of high-purity or ultra-pure $BaCO_3$ products (with a purity exceeding 99.995%) has been the focus of many high-technology industries. $BaCO_3$ is commonly produced using ores (witherite and barite) as raw materials [5]. The presence of metal ions and rare earth elements (REEs) in these raw materials (witherite and barite) generates impurities during $BaCO_3$formation; such impurities consequently affect the quality of the final ultra-pure product and thus should be carefully controlled. Ultra-trace impurities in ultra-pure $BaCO_3$ products should be monitored for quality control of production processes in high-technology industries.

Numerous studies determined metal ions and REEs in the barium matrix by using different methodologies [6–8]. Inductively coupled plasma–mass spectrometry (ICP-MS) is a robust analytical tool that can achieve detection limits as low as parts per trillion (ppt) or sub-ppt range for most elements [9]. However, determination of some special REEs, e.g., Nd, Gd, Sm, and Eu, is limited when using quadrupole ICP-MS(ICP-QMS) because of significant spectral interferences from barium polyatomic ions, such as BaO^+ and $BaOH^+$. Some sample-pretreatment techniques, such as flow injection on-line solid phase extraction [10], ion exchange chromatography [6], and laser ablation ICP-MS [8], have been developed to separate Eu/Ba prior to ICP-MS detection. Satisfactory results were obtained. However, these methodologies require cumbersome pre-separation procedures and complex instrumental configurations.

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Ardini et al. [11] investigated the behavior of REE ions in a dynamic reaction cell pressurized with oxygen by using ICP-MS prior to their determination at $m/z + 16$. The conversion of REEs into molecular monoxide ions (REEO$^+$) was quantitative (>96%) for most elements, except Tm, Eu, and Yb, and the conversion into EuO$^+$ is only approximately 10%. In addition, Eu in marine sediment samples must be measured using mathematical correction other than O-atom addition approach because the spectral interferences of Ba, a major element in sediments, cannot be effectively alleviated.

Although determination of Eu by directly using ICP-QMS or through analyte–matrix separation can be achieved in some cases, measurement of Eu remains challenging when using complex and high-matrix samples, such as ultra-pure ones based on Ba compounds as mentioned in this paper. Thus, these materials have not been reported yet. Therefore, a new and robust method must be developed for Eu determination.

An ICP tandem mass spectrometer (ICP-MS/MS) combining two quadrupole mass filters was proposed [12,13]. This robust technique exhibits high sensitivity in measuring several elements, such as sulfur and phosphorus in peptides and phosphopeptides [13], Ti in blood serum [14], sulfur in organic matrix [15], and ^{129}I in soil samples [16]. The proposed method was also utilized for isotopic determination of some radioactive elements, such as ^{134}Cs/^{137}Cs, ^{135}Cs/^{137}Cs, and ^{236}U/^{238}U [17–19].

In the present study, ultra-trace impurities, especially Eu, in ultra-pure BaCO$_3$ materials were accurately determined using an advanced ICP-MS/MS technique. Different reaction modes and possible reaction mechanisms were also explored in detail.

2. Experimental

2.1. Samples and reagents

Two ultra-pure BaCO$_3$ materials with a purity of 99.996% (sample no.1) and 99.997% (sample no.2) were obtained from a semi-conductor industry elsewhere. The samples were gently dissolved in electronic-grade HNO$_3$ (TAMA-Pure-AA-100, Kanagawa, Japan) and diluted to the required concentration (as Ba^{2+}). Water was purified using Milli-Q (Millipore, Molsheim, France) system to a specific resistivity of 18.2 MΩ cm.

The standard solutions of Eu used for optimization and calibration were prepared by diluting commercially available single-element standard solutions (1.0 g L^{-1}) with 0.14 mol L^{-1} HNO$_3$. Five standard solutions with concentrations ranging from 0 μg L^{-1} to 5.00 μg L^{-1}were prepared for external calibration.

2.2. Instrumentation

An ICP-MS/MS (Agilent 8800, Agilent Technologies Inc., Japan) was used in the current study. The standard instrumental configuration included Ni interface cones, standard ion lens, and sample introduction system consisting of a MicroMist glass concentric nebulizer, a Peltier-cooled (2 °C) quartz double-pass Scott-type spray chamber, and a quartz torch with 2.5 mm injector.

The ICP-MS/MS can be operated in two reaction modes by using MS/MS. These modes include “on-mass” mode with ammonia (10% NH$_3$in He) or He (100% He) as cell gas and “mass shift” mode using oxygen (O$_2$) as reaction gas. The schematic of the operating principle of the two MS/MS modes with Eu as model analyte is illustrated in SI-Fig. 1. The conventional single quadrupole (SQ) ICP-MS mode with He as collision gas was also used in the study to compare with MS/MS modes. For all cell modes, the ICP-MS/MS was operated with the plasma conditions preset as CeO$^+$/Ce$^+$ < 0.8% (in no gas mode). The operating parameters for MS/MS are shown in Table 1.

Table 1
ICP-MS/MS operating parameters.

	O$_2$(MS/MS)	NH$_3$(MS/MS)	He(MS/MS)	He (SQ) [a]
RF Power (w)	1550	1550	1550	1550
Plasma gas (L/min)	15	15	15	15
Auxiliary gas (L/min)	1.0	1.0	1.0	1.0
Carrier gas (L/min)	0.50	0.50	0.50	0.50
Dilution gas (L/min)	0.60	0.60	0.60	0.60
Sampling depth (mm)	9.0	9.0	9.0	9.0
Cell gas	O$_2$	NH$_3$	He	He
Gas flow rate (mL min^{-1})	0.15	9.5	5.0	5.0
KED (V)	−15.0	−15.0	3	3
Octopole bias (V)	−10.0	−10.0	−18.0	−18.0
Cell entrance (V)	−50	−50	−50	−50
Cell exit (V)	−60	−120	−60	−60
Deflect lens (V)	−3.0	8.0	−3.0	−3.0
Plate lens (V)	−70	−130	−70	−70

[a] Single quadrupole MS.

3. Results and discussion

3.1. Optimization of the reaction gas flow rate

The optimal flow rate of reactive gas was investigated by studying the calculated background equivalent concentration (BEC) versus the flow rate. BEC represents the capability for interference removal, which is achieved with BaCO$_3$ matrix and BaCO$_3$ matrix-spiked Eu standard solution (1.0 μg L^{-1}). The gas flow rate in the Agilent Masshunter software was set at.%. Under the “fully open (100%)” condition, the flow rate for the NH$_3$/He (10% NH$_3$/90% He) mixture and O$_2$ is 10 mL min^{-1} and 1.0 mL min^{-1}, respectively. The relationship between the BEC and the actual gas flow rate is shown in SI-Fig. 2 and 3. Minimal BEC can be obtained at the cell flow rate of 9.0 mL min^{-1} (cell gas flow rate is 90%) and 0.2 mL min^{-1} (cell gas flow rate is 20%) for NH$_3$ and O$_2$, respectively. Therefore, 9.0 mL min^{-1} for NH$_3$ and 0.2 mL min^{-1} for O$_2$ was selected as the optimal flow rate for the entire analysis.

3.2. Determination of Eu with NH$_3$ on mass mode

As a highly reactive gas, NH$_3$ is commonly used as cell gas in SQ ICP-MS to eliminate spectral interference, e.g., dealing with Ar-based interference by charge transfer reactions [12]. However, for some clustering reactions, high reactivity of NH$_3$ is considered a nuisance because of the formation of some unwanted adducts, which lead to complex reaction behavior. These limitations can be easily resolved using the reported ICP-MS/MS, e.g., interference-free determination of Ti by converting Ti into Ti(NH$_3$)$_6^+$ ions under different Q1and Q2 settings [14].

In this experiment, NH$_3$ was used in on-mass mode to eliminate the interfering effect of Ba polyatomic ions (BaO$^+$ and BaOH$^+$) on Eu. Preliminarily, Ba solution, with concentrations (for Ba^{2+}) of 5.0 and 1000 mg L^{-1}, was introduced into the ICP-MS/MS with m/z of Q1 and Q2 both set at the mass of 151 (for^{135}Ba^{16}O$^+$ and ^{134}Ba^{16}O^{1}H), respectively. The MS/MS was operated under optimal conditions as described above. No signals were found (0 cps for 5.0 mg L^{-1}and 0.15 cps for 1000 mg L^{-1} Ba^{2+}) for these two analytes. For further investigation, the spiked solution with a concentration of 5.0 mg L^{-1}for both Eu$^+$ and Ba^{2+} was subsequently introduced into the MS/MS operated under the same parameters mentioned above. The signal obtained was 1.22×10^6 cps, which was obviously produced by ^{151}Eu$^+$, whereas the Ba polyatomic ions (^{135}Ba^{16}O$^+$ or ^{134}Ba^{16}O^{1}H$^+$) cannot emit any signal. These phenomena were observed because a charge transfer reaction between BaO and NH$_3$ occurred in ORS^3, and a stable neutral product BaO was formed, which was rejected by Q2. Using the productions scan mode, we fixed Q1 at 151, and no signal was found at 135 (for ^{135}Ba) or 16 (for ^{16}O), indicating that BaO is a stable product ion and did not dissociate into its constituting atoms. The charge transfer