

Introduction

BaCO₃ is a precursor material that undergoes solid-state reaction with TiO₂ to form BaTiO₃, which is one of the most widely used ferroelectric materials for multi-layered ceramic capacitors with high capacitance density. The presence of metal ions and rare earth elements (REEs) in these raw materials (witherite and barite) would affect the quality of the final product. Numerous studies concerning impurities analysis in the barium matrix by using different methods were reported. Inductively coupled plasma-mass spectrometry (ICP-MS) is a robust analytical tool that can achieve detection limits at ppt or sub-ppt level for most elements. However, measurement of some REEs, e.g., Nd, Gd, Sm, and Eu, is limited when using single quadrupole ICP-MS(ICP-QMS) because of serious polyatomic interferences from barium matrix, such as BaO⁺ and BaOH⁺. Several sample-pretreatment techniques, such as flow injection on-line solid phase extraction, and ion exchange chromatography, have been developed to separate Eu/Ba matrix prior to ICP-MS detection. Although satisfactory results could be achieved by these sample preparation techniques, these approaches require cumbersome pre-separation procedures.

ICP triple quadrupole mass spectrometer (ICP-QQQ) combining two quadrupole mass filters was newly developed for removing serious polyatomic interference. In the present study, impurities, especially Eu, in ultra-pure BaCO₃ materials were accurately determined using an advanced ICP-MS/MS technique without matrix separation process.



Experimental

ICP-QQQ Agilent 8800 series ICP-QQQ was used in this paper, with a standard configuration, including oxygen, helium, hydrogen and ammonia cell gas. Two kinds of ultra-pure barium carbonate samples were applied for the analysis.

Sample preparation Standards were prepared in 2% (v/v) electronic-grade nitric acid (TAMA-Pure-AA-100, Kanagawa, Japan). Weigh the samples to the nearest 0.100g, and add 2% (v/v) HNO₃ solution, 20ml. Prepare the mixture with ultrasonic technique for 20 min continuously and then allow to stand for 5 min. Keep the final volume of this solution at 100 ml for ICP-MS/MS analysis.

Three modes were used in this study, for investigating the interference removal capability.

ICP-MS Operating Parameters

Agilent 8800 Triple Quadrupole ICP-MS #100 with 2.5 mm injector torch. RF = 1550W, SD = 8.0mm, CRGS = 0.8L/min, MUGS = 0.4L/min, Spray Chamber Temp. = 2 °C

Results and Discussion

Measurement of Eu in ultra-pure BaCO₃

Different kinds of cell gas were applied for studying interference removal capacity. The results of 1 µg/kg Eu spike recovery was evaluated for the method verification.

Table 1. Results of Eu spike recovery test with different modes

	Mode		Found*	Found after spiked*	Recovery (%)
151 Eu	He-SQ	µg/kg	68.21±0.75	70.26±0.75	205
151 -> 151 Eu	He-MSMS	µg/kg	10.04±0.59	11.34±0.76	130
151 -> 151 Eu	NH ₃ -MSMS	ng/kg	14.58±1.19	1.038±0.19	102
151 -> 183 EuOO	O ₂ -MSMS	ng/kg	13.69±0.75	1.015±0.15	101
153 Eu	He-SQ	µg/kg	174.32±4.18	178.68±4.18	436
153 -> 153 Eu	He-MSMS	µg/kg	23.49±2.45	24.80±1.23	131
153 -> 153 Eu	NH ₃ -MSMS	ng/kg	14.25±0.73	1.042±0.73	102
153 -> 185 EuOO	O ₂ -MSMS	ng/kg	15.37±0.75	1.039±0.75	103

*mean±SD (n=3)

In order to evaluate the method, three different cell gas, SQ (single-quad) and MS/MS modes, are tested. The results are shown in table 1. Intense barium oxide interference presented in the SQ mode, in which Eu at 151 and 153 are overlapped respectively by polyatomic ions due to serious interference from Ba. With MS/MS reaction modes, the concentration of Eu have good agreement at both m/z 151 and 153, using O₂ and NH₃ as reaction gas. In addition, great spike recovery was also achieved in both O₂ and NH₃ modes. BaO⁺ can be effectively removed in MS/MS mode, due to two independent mass filters.

To verify the interference removal capability, the isotope ratio of 153/151 was studied. With both O₂ and NH₃ modes, excellent agreement between test results and natural isotope ratio could be obtained.

Table 2. Isotope ratio of 153/151 with different modes

Mode	¹⁵¹ Eu	¹⁵³ Eu	Ratio (¹⁵³ Eu/ ¹⁵¹ Eu)
Natural abundance	47.81%	52.19%	1.09
NH ₃ -MS/MS	46.80±0.20%	53.20±0.20%	1.14±0.02*
O ₂ -MS/MS	48.60±0.10%	51.40±0.13%	1.06±0.02
He-SQ	29.80±0.21%	70.20±0.19%	2.33±0.04

Note: 1000 mg/kg BaCO₃ matrix spike Eu with the concentration of 1.0 µg/kg

*Uncertainty (n=3)

The isotope ratio of 153Eu/151Eu achieved by NH₃ on-mass mode and O₂ mass shift mode is consistent with the natural abundance of 1.09 (with 4.59% and -2.75% relative error to the natural abundance in on-mass mode and mass shift mode, respectively). However, for further consideration, the experimentally obtained 153Eu/151Eu ratio would be overestimated in relation to the natural theoretical ratio by 4%–6%, as a mass bias correction factor of around 2%–3% negative obtained. Therefore, using NH₃/He as reaction gas in MSMS mode, presented more accurate in isotope ratios measurement, which demonstrated the MS/MS mode could completely remove the polyatomic interference.

Results and Discussion

Ba undergoes chemical reaction with O₂ as follows:

- 1) Ba⁺ + O₂ → BaO⁺ + O
- 2) BaO⁺ + O₂ → BaOO⁺ + O
- 3) BaOO⁺ + O₂ → no reaction or slow rate

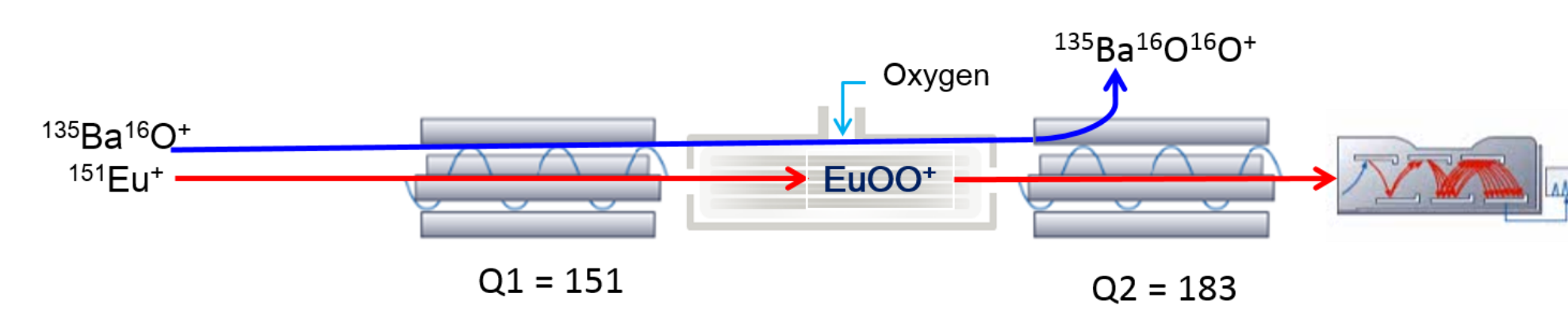


Fig.1 Mechanism of MS/MS mass-shift, using O₂ for the detection of Eu

O₂ mass-shift method was applied to Eu measurement; O₂ flow rate = 0.15 ml/min, Eu reacts with O₂ molecule and forms product ion, thereby Eu is detected as EuOO⁺.

In this study, several tests were carried out to track the product ion between barium and oxygen in the collision/reaction cell (Data are not shown here). The dioxide product of the BaO⁺→BaO₂ reaction is dominant in the cell after reacted with O₂, whereas the formation of trioxide product (BaO₃⁺) presented negative reaction.

Table 3. Results of Sm spike recovery test with different modes (µg/kg)

Mode	¹⁴⁷ Sm		¹⁴⁹ Sm	
	Found	Recovery(%)	Found	Recovery(%)
He(SQ)	8.62	99.2	9.52	98.5
NH ₃ (MS/M S)	0.048	99.0	0.030	101
O ₂ (MS/MS)	0.024	99.1	0.021	99.8

Table 1 and table 2 indicated that the MS/MS mode with reaction gas could completely remove barium oxide interference. Meanwhile, the BaOH⁺ was also taken into consideration as the main polyatomic interference in this study. In table 3, although excellent spike recovery at 1 µg/kg level of Sm were achieved in the both SQ and MS/MS mode, only NH₃ and O₂ in MS/MS mode could provide great agreement results at the two isotopes, 147 and 149.

Conclusions

As can be seen, MS/MS mode presents more effective and powerful than single-quad (SQ) mode for both oxide and hydroxide interference removal. In compared to conventional ICP-MS (Single-Quad MS), The detected concentration of Eu⁺ was 4.0 ng/kg to 15 ng/kg, and the concentration of Sm⁺ was 20-40 ng/kg, with spiked recoveries ranging from 100%–110%. It is more than two or three orders of magnitude lower interferences obtained by ICP-QQQ. For the high-purity samples, 8800 ICP-QQQ can easily to meet the requirements of ppt or sub-ppt level impurities analysis.