

Rapid and Accurate Determination of Rare Earth Elements Contents in Barium-rich Samples by ICP-MS

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The rare earth elements (REEs) are called “fingerprints elements”, which have been extensively applied in geochemistry field for tracing material provenances. Hence, the accurate determination of REEs contents, especially the contents of Ce and Eu, are critical and necessary, and are the prerequisite for the application of REEs in various geological perspectives. The inductively coupled plasma-mass spectrometry (ICP-MS) has been commonly used for precise determination of REEs contents in geological samples due to its advantages of low detection limit, multi-element analysis and relatively simple sample preparation. However, the oxides and hydroxides ions would be formed at high temperature in the plasma during ICP-MS analysis, resulting in relevant spectral interferences (e.g. $^{135}\text{Ba}^{16}\text{O}$ on ^{151}Eu or $^{130}\text{BaOH}$ on ^{147}Sm , etc.). Barium (Ba) is a major element in many geological samples (e.g. barite/witherite-rich samples) usually accompanied with a high Ba/Eu ratio (e.g. >50000) especially in Ba-rich samples, which would introduce serious oxide and hydroxide interferences on REEs during the ICP-MS analysis. Hence, eliminating Ba interference is an indispensable procedure for accurate ICP-MS analysis of REEs. Though ion-exchange chromatography is widely used for REEs purification, the tediousness, time-consuming and high cost limit the application of this purification method.

In this study, we developed a rapid and reliable separation method to eliminate Ba from geological samples for precise measurement of REEs by ICP-MS. The new method is established based on the different solubility between Ba and REEs in concentrated nitric acid, as barium nitrate ($\text{Ba}(\text{NO}_3)_2$) is almost insoluble, contrasting to REEs. The whole separation procedure could be achieved in less than two hours and only consumes 1.5 mL 15 M nitric acid. The protocol results in acceptable recovery of REEs (above 96%), low Ba content (0.37 ± 0.14 $\mu\text{g/mL}$, 2SD, $n=50$) and significant reduction of Ba/REEs mass ratio (i.e. Ba/Eu from 500000 to 180) in final purified solution. The method was successfully applied to four natural barite-rich samples with BaSO_4 ranging from 18.87 wt% to 42.41 wt%. Overall, this accurate and rapid method shows great potential for the precise determination of REEs contents in Ba-rich samples by ICP-MS.