

Influence of digestion procedures on the determination of rare earth elements in peat and plant samples by USN-ICP-MS

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Analytical procedures for the determination of rare earth elements (REE) in 250 mg aliquots of difficult-to-digest peat and plant matrices by ICP-MS were developed. Three different pressurised digestion approaches were tested for this purpose, namely (i) closed vessel acid digestion on a hot-plate at 180 °C, (ii) digestion in a microwave high pressure autoclave at a temperature of 240 °C and (iii) high pressure ashing (HPA) at a temperature of 320 °C. Acid mixtures for digestion contained concentrated nitric acid (3–5 ml) alone or additions of hydrofluoric acid (HF) or tetrafluoroboric acid (HBF₄) at volumes of 0.05–1.0 ml. The selection of appropriate volumes of HF or HBF₄ was identified as a critical step in obtaining accurate results. For several reasons, HBF₄ is preferred in comparison with the normally used addition of HF for the destruction of siliceous matter in the samples investigated. The optimum acid mixture consisted of 3 ml of HNO₃ and 0.1 ml of HBF₄. High sample throughput (40 samples simultaneously in about 2 h) favours the microwave autoclave over the other two digestion systems. An ultrasonic nebuliser (USN) with membrane desolvation used for sample introduction reduced the spectral interferences originating from oxide formation of lighter REE and Ba to a negligible extent. Internal standardisation with Rh and Re proved to be essential for obtaining correct results. In this way, all REE could be reliably quantified by USN-ICP-MS without applying any mathematical correction equations. The accuracy of the optimised procedures was assessed by the determination of REE in digests of the certified reference material GBW 07602 Bush Branches and Leaves and of the candidate reference material CRM 670 Aquatic Plant. The developed analytical procedures were applied to the determination of REE in two different peat matrices. Results for these peat samples obtained by USN-ICP-MS showed good agreement with INAA values. Strong fractionation of REE caused by the addition of HF or HBF₄ in excess, known as lanthanide contraction, could be experimentally established, except for europium, which revealed a different behaviour.

Introduction

In recent years, the quantitative determination of rare earth elements (REE) has gained in importance.^{1–13} Besides a variety of industrial applications, REE are of increasing relevance to geological, geochemical and environmental studies. Among the most commonly utilised approaches for REE determinations are neutron activation analysis (NAA), X-ray fluorescence (XRF) spectrometry, isotope dilution mass spectrometry, ICP-AES and ICP-MS.^{1–13}

ICP-MS is nowadays by far the most frequently employed analytical technique to quantify REE from $\mu\text{g g}^{-1}$ levels in steel¹⁰ to ultratrace levels in aqueous samples.¹¹ However, two latent problems may hamper the reliable quantification of REE by ICP-MS, especially in geochemical and environmental matrices: (i) the dissolution of siliceous material; and (ii) the occurrence of spectral interferences in the mass spectrum.

Solid material is commonly dissolved by heating with acids in either open or closed vessels. Disadvantages of open vessel digestion systems include the greater risk of loss of volatile elements. Therefore, closed vessel digestion systems are preferred in cases where subsequent trace element analyses are planned.^{14,15} Digestion of silicate containing material is normally achieved by adding hydrofluoric acid to the digestion mixture which attacks silicates and quartz particles and liberates silicon as the volatile SiF₄. The amount of HF needed in the digestion will depend on the mass of silicates present in the sample.¹⁴ Especially critical in this respect is “excess” of HF that is not consumed during digestion, *i.e.* not

used for the destruction of silicates. Many elements such as Ca and REE form insoluble fluorides that will precipitate in digestion solutions containing excess of fluoride, resulting in too low recoveries of these elements.¹⁶ Therefore, several researchers have proposed the addition of a saturated solution of boric acid (H₃BO₃) to the resulting solution after digestion to overcome this problem.^{2,10} Precipitated fluorides will thus be redissolved and excess of HF will be complexed as BF₄⁻. This addition of H₃BO₃, however, has two severe drawbacks. First, a heavy matrix load is introduced into the ICP-MS. Second, and perhaps more important, H₃BO₃ contains relevant amounts of elemental impurities which will lead to elevated detection limits for the elements investigated.²

In addition to the dissolution of the REE themselves, the occurrence of severe spectral and non-spectral interferences may hamper their reliable determination by ICP-MS. Separation of REE from the matrix by cation exchange chromatography,⁴ solvent extraction⁶ or by using a flow injection on-line filterless precipitation–dissolution system⁹ or a chelating resin⁵ efficiently helps to reduce those interferences. These procedures can also be used to preconcentrate REE, which leads to further improvements in method detection limits. However, it is desirable to develop a more straightforward approach which would be both faster, as well as less prone to analyte loss and/or contamination. Normally, pneumatic nebulisation of the digestion solution requires extensive mathematical correction of ICP-MS signals if the ratio of light REE to heavy REE is high to take into account the oxide formation of potential interfering elements on REE.¹