Improved UV-Vis detection of lanthanides in synthetic standards by capillary electrophoresis: A new experimental evidence of the actual systematic odd-even pattern in sensitivities and detection limits

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Abstract

The systematic "odd-even" pattern of sensitivities and detection limits (LODs) of lanthanides, previously observed, in mass spectrometric and chromatographic measurements[1-5] was experimentally investigated.

Well-designed "geochemometric experiments" of capillary electrophoresis (CE) for determination of lanthanides in synthetic standards with equal amounts of lanthanides were carried out. An improved UV-Vis detection system based on indirect measurement at a wavelength of 214 nm, a voltage of +25 kV and a hydrostatic injection (100 mm for 20 s) were successfully used. A conventional fused-silica capillary (355 x 0.075 mm) was employed for all the lanthanide separations. Complete separation for all the lanthanides was efficiently achieved in ~2.8 min at a capillary temperature of 15ºC. The efficient separations show excellent resolutions (R) ranging from 1.324 to 5.741 and capillary efficiency values (N) in the interval 37289 to 939127.

The background electrolyte used consisted of 0.010 M UVCat-1 (Waters) with 0.004 M HIBA at a pH 4.4. A good reproducibility in migration times (< 2.7 %RSD), peak areas (< 3.8 %RSD) and peak heights (2.7 %RSD) were consistently found. Two types of calibration curves were derived from experimental CE data based on both peak area and peak height measurements versus lanthanide amount data, respectively. All calibration curves were based on seven replicates to transport the uncertainties of the measurements, and were prepared using the weighted linear regression (WLR) model. The statistical parameters of the WLR were used for estimating individual sensitivities and LODs for all lanthanides.

The calculated sensitivities were greater for lanthanides with an odd-atomic number (i.e., ^{57}La, ^{59}Pr, ^{63}Eu, ^{65}Tb, ^{67}Ho, ^{69}Tm, and ^{71}Lu) than for their corresponding neighboring element with an even-atomic number (i.e., ^{58}Ce, ^{60}Nd, ^{62}Sm, ^{64}Gd, ^{66}Dy, ^{68}Er, and ^{70}Yb).

Concerning the LODs, a clear zigzag pattern was systemically found where the odd atomic number elements have systematically lower LODs than the even atomic number neighbor elements (e.g., ^{57}La-^{58}Ce; ^{59}Pr-^{60}Nd; etc.). The systematic pattern of LODs can be explained by a simple relationship with physicochemical and environmental-geological factors. These CE results confirm the hypothesis of the existence of a systematic odd-even pattern as in sensitivities as in LODs.

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