DETERMINATION OF NANOGRAM LEVELS OF LANTHANOIDS IN A MARINE MACRO-ALGA BY NEUTRON ACTIVATION ANALYSIS COMBINED WITH SEPARATION BY SELECTIVE PRECIPITATION

Y. IWATA,* H. IMURA, N. SUZUKI

Department of Chemistry, Faculty of Science, Tohoku University, Aoba-ku, Aramaki, Sendai 980 (Japan)

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Preseparation of lanthanoids by substoichiometric precipitation of calcium oxalate and simple radiochemical separation of lanthanoids by lanthanum oxalate have been developed. They were combined with neutron activation analysis of a marine macro-alga (Laminaria religiosa, brown alga) sample. Quantitative recovery of lanthanoids throughout the procedure was examined by radiotracer technique. Eleven lanthanoids, La, Ce, Pr, Nd, Sm, Gd, Tb, Er, Yb and Lu, at 0.7–140 ng g⁻¹ were determined with a relative standard deviation of 1–7% (n = 3). Concentrations of lanthanoids in the marine macro-alga were compared with land plant and sea water.

Many determinations of elements in various marine organisms were carried out and these analytical data were summarized in some books.¹,² However, there have been few systematic research works on analytical methods and determination of series of major, minor and trace elements in marine macro-alga, and this circumstance obstructs a fruitful discussion on the elemental abundance and/or the elemental enrichment of marine macro-algae.

We have developed some novel radioanalytical methods for major, minor and trace elements in marine macro-algae such as photon activation analysis,³ α-particle activation analysis after solvent extraction and polystyrene foam collection,⁴ PIXE analysis after solvent extraction and polystyrene film collection⁵ and substoichiometric isotope-dilution analysis.⁶⁻¹⁰ By these previous studies, it has been known that abundances of alkali metals and halogens are very high, on the other hand, abundances of first transition metals are very low in marine macro-algae. For example, elemental concentrations are Na, 3%; K, 14%; Cl, 12%; Br, 1000 μg · g⁻¹; Mn, 6 μg · g⁻¹ and Cu, 1 μg · g⁻¹ in a dry sample of Laminaria religiosa (brown alga).

Lanthanoids are very interesting and important elements in biogeochemistry and environmental studies, but determination of lanthanoids in these natural samples are not so easy mainly due to their very low concentrations. Neutron activation analysis (NAA) has excellent sensitivity for lanthanoids, but non-destructive γ-ray spectrometry cannot

*Author to whom correspondence should be addressed.

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Akadémiai Kiadó, Budapest
be performed for marine macro-alga samples, because of the extremely low concentration levels of lanthanoids, and the high background radioactivity induced from high concentrations of alkali metals and halogens such as $^{24}\text{Na}$, $^{38}\text{Cl}$, $^{80}\text{Br}$ and $^{82}\text{Br}$. Non-destructive NAA has been applied for marine organisms, but only a few lanthanoids were determined.\textsuperscript{11-13} For the biogeochemistry study, reliable data for series of lanthanoids are necessary.

Radionuclides produced from some lanthanoids have short half-lives such as $^{165}\text{Dy}$ (2.33 h) and $^{171}\text{Er}$ (7.52 h). A long cooling time is required to avoid high background radioactivity mainly caused by $^{24}\text{Na}$ (15 h) and dissolution of biological samples and radiochemical separation are often time-consuming. To obtain reliable results for series of lanthanoids at very low concentrations, appropriate preseparation techniques are required. Complicated radiochemical separation is not suitable for the determination of series of lanthanoids.

In a previous paper, we reported the distribution equilibrium of lanthanoids with calcium oxalate in detail.\textsuperscript{14} Using this knowledge, we proposed a new type of selective separation of lanthanoids by substoichiometric precipitation of calcium oxalate, and it has been applied to the NAA of NIST SRM Citrus Leaves and eleven lanthanoids and scandium were determined.\textsuperscript{15,16} In this paper, the selectivity of the preseparation technique has been improved and eleven lanthanoids in marine macro-alga samples could be determined by combination of NAA with the simple radiochemical separation.

**Experimental**

*Reagents.* Oxalic acid dihydrate and chloroacetic acid were of guaranteed reagent grade and were purified by repeated recrystallization from water. Nitric acid of high purity reagent grade was doubly distilled by sub-boiling system. Aqueous ammonia was a high purity reagent (Wako). Standard solutions of lanthanoids were prepared in the same way as in the previous paper.\textsuperscript{14} Lanthanoid oxides ($> 99.9\%$ purity) were heated at 800 °C for 3h and were dissolved in 6M nitric acid. In the case of Ce, heated CeO$_2$ was dissolved in 6M nitric acid containing 5\% of hydrogen peroxide. Water purified in a Mill–Q apparatus (Millipore) was used throughout.

*Radioisotopes.* $^{46}\text{Sc}$, $^{140}\text{La}$, $^{153}\text{Sm}$, $^{160}\text{Tb}$, $^{177}\text{Lu}$ and $^{47}\text{Ca}$ were produced by neutron irradiation of the corresponding nitrate and CaCO$_3$ in a nuclear reactor (JRR–4, $\Phi = 5.5 \cdot 10^{13}$ n cm$^{-2}$ s$^{-1}$) of the Japan Atomic Energy Research Institute. $^{22}\text{Na}$ was produced from Na$_2$CO$_3$ (99.97\%) by photo nuclear reaction $^{22}\text{Na}(\gamma \text{n})^{22}\text{Na}$. This target was irradiated by 30 MeV bremsstrahlung for 12 hours in a linear electron accelerator of Tohoku University.