# Nanofiltration–Complexation: A New Method for Isotopic Separation of Heavy Metals

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(Received March 22, 2001; CL-010260)

Nanofiltration coupled with a selective complexation step was applied to separate isotopes of neodymium and gadolinium in aqueous solution.

Isotopic separation has been carried out for nearly 50 years by industry in which separation methods such as gaseous diffusion, electromagnetic methods and ultracentrifugation were employed. However these physical processes are expensive because they require a large number of separative stages and a high temperature to maintain elements in gas phase through the process. They are therefore only conceivable for applications in nuclear industry whose economical features are far different from other industrial and scientific areas.

Other processes are based on chemical methods, i.e., chemical exchange,[1] liquid–liquid extraction[2–4] or membrane-based.[5] Some of them gave efficient isotopic separation factors for light elements[6] ($^7$Li/$^6$Li, $^{24}$Na/$^{22}$Na, $^{44}$K/$^{40}$K, $^{48}$Ca/$^{40}$Ca), in accordance with the conventional Bigeleisen–Mayer approximation[7] based on the isotopic mass difference and the product of mass of two isotopes ratio. For elements with $Z > 40$, especially rare earth metals, less substantial isotopic enrichment factors were obtained not only because of the less pronouced nuclear mass effect but also because of the major contribution of the properties of nuclei as the nuclear size, shape and the nuclear spin.[8]

As an alternative to liquid–liquid extraction, nanofiltration–complexation (NF) has been developed by our laboratory since 1993.[9] It appeared to be an efficient and reliable method for separating traces of cesium from highly concentrated aqueous medium[10] and also for separating lanthanides in aqueous solution.[11,12] In fact nanofiltration can be combined with a selective complexation step in order to increase ionic separation. Retention of the target element is improved because the complex with the ligand, of larger size and mass than the target ion, prevents the ion from passing through the membrane (Figure 1). Based on the fact that nanofiltration–complexation gave high separation factors between lanthanides (La, Pr, Gd),[12] we applied this method to the isotopic separation of two lanthanides, neodymium and gadolinium.

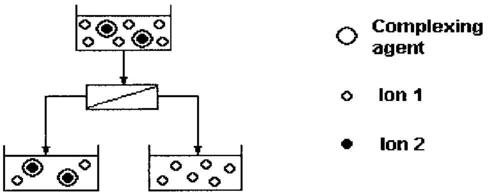


**Figure 1.** Principle of ion separation by nanofiltration combined with a complexation step.

Amounts of Nd and Gd were determined by ICP-AES spectrometry with Spectro D ICP Spectrometer. Isotopic compositions were measured with Finnigan-Mat Element ICP-MS spectrometer. To ensure that small isotopic separation effects were not due to standard deviation of the analytical system, the accountability of ICP-MS spectrometer was assessed by measurements of $^{160}$Gd/$^{155}$Gd ratio. The isotopic separation factor of the two isotopes A and B between two phases is defined as :

$$\alpha = ([A]_1/[A]_2) \times ([B]_2/[B]_1) = ([A]/[B])_1 \times ([B]/[A])_2$$

The natural $^{160}$Gd/$^{155}$Gd ratio was artificially modified by addition of known amounts of $^{160}$Dy. Natural dysprosium has a 160 isotope but no 155 isotope. Samples of Gd were successively “enriched” at 0.05%, 0.1%, 0.2%, 0.5% and 1% with $^{160}$Dy compared to $^{160}$Gd. The $^{160}$Gd/$^{155}$Gd ratio was then measured by ICP-MS. Figure 2 illustrated the measured $^{160}$Gd/$^{155}$Gd ratios as a function of theoretical $^{160}$Gd/$^{155}$Gd ratios. For each sample, several measurements were performed. Therefore results are figured by mean values (black points) with their corresponding standard deviation. The broken line indicates where experimental results should theoretically be found.

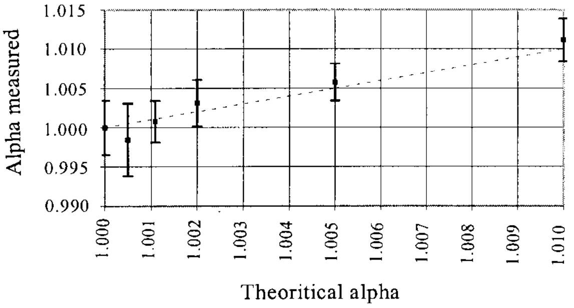


**Figure 2.** Experimental enrichment factor between $^{160}$Gd and $^{155}$Gd measured by ICP-MS as a function of theoretical enrichment factor.

This experiment showed that for $1 < \alpha < 1.001$, ICP-MS measurements could not be used. For $1.001 < \alpha < 1.002$, ICP-MS measurements could be applied (black points on the theoretical line), but the 0.2% standard deviation did not ensure a real isotopic enrichment. For $\alpha > 1.002$, ICP-MS measurements were accurate and standard deviation, even if not negligible, ensured with 95% probability to have a right tendency for isotopic enrichment. Therefore every measurement for $\alpha > 1.002$ was sufficiently high to be taken into account.

Figure 3 shows a schematic drawing of the nanofiltration loop used in our experiments. Nanofiltration was carried out with a Sepa MG-17 membrane (Osmonics) at 293 K, with a surface area of 0.015 m$^2$, designed for tangential filtration. This membrane has the following specifications : a high reten-

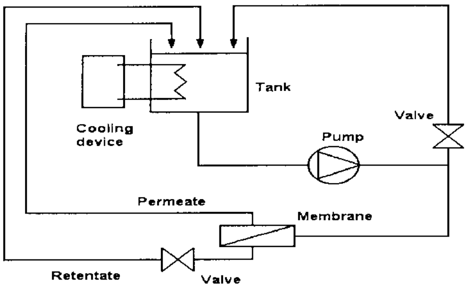
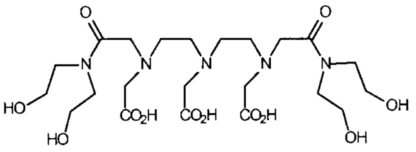


**Figure 3.** Scheme of the nanofiltration loop.

tion of neutral organic molecules with molecular weight above 500 g/mol and low retention of multivalent ions. Retention (%) of a substance i was calculated as follows : $R_i = 100(1 - C_{ip}/C_{ir})$, where $C_{ip}$ is the concentration of i in the permeate and $C_{ir}$ the concentration of i in the retentate.

Neodymium was chosen because of its natural isotope composition (142, 143, 144, 145, 146, 148, and 150, respectively in 27.13%, 12.18%, 23.80%, 8.30%, 17.19%, 5.76% and 5.64% ratios). Since nuclear mass effect will be significant on the isotopic separation, $^{142}$Nd and $^{150}$Nd isotopes were chosen to be measured because of their 5% relative mass difference. An aqueous solution of neodymium nitrate (5 mmol/L) was filtrated on a Sepa MG-17 NF membrane. Then, ligand **1**[12] (4.5 mmol/L) was added to the solution.

Retentate and permeate lines were recycled into the feeding tank, so that the feed remained at constant composition during the experiment. Samples of permeate and retentate were taken out of the loop, 2 h later. Retentate contained 613 mg/L of Nd and permeate 84 mg/L (i.e., an 86% Nd-retention). ICP-MS determination of the $^{150}$Nd/$^{142}$Nd ratio gave the following results : $0.22233 \pm 0.00034$ (permeate) and $0.22187 \pm 0.00040$ (retentate). The corresponding isotopic separation factor was $\alpha(^{150}\text{Nd}/^{142}\text{Nd}) = 1.0021 \pm 0.0016$.



Ligand **1** (Bis-diethanolamide-DTPA)

Gadolinium was chosen because of its natural isotope composition (152, 154, 155, 156, 157, 158 and 160, respectively in 0.20%, 2.18%, 14.80%, 20.47%, 15.65%, 24.84% and 21.86% ratios) and also because of the particular neutron capture behaviour of $^{155}$Gd and $^{157}$Gd. An aqueous solution (1000 mL) of gadolinium nitrate (10 mmol/L) with ligand **1** (9 mmol/L) were filtered on a Sepa MG-17 NF membrane. Permeate (700 mL) were taken out of the filtration loop (no recycling). Permeate and retentate were sampled at the end of the filtration experiment before analysis. Final retentate and permeate contained 1260 mg/L and 136 mg/L of Gd respectively (i.e., an 89%-Gd mean retention during the experiment). ICP-MS determination of the $^{160}$Gd/$^{155}$Gd ratio gave the following results : $1.5086 \pm 0.0016$ (retentate) and $1.5128 \pm 0.0011$ (permeate). The corresponding isotopic separation factor was $\alpha(^{160}\text{Gd}/^{155}\text{Gd}) = 1.0028 \pm 0.0014$.

Both NF experiments showed small but noticeable isotopic separation factors[13]. Greater separation factors could be obtained by optimising different physical and chemical factors such as metal concentration, ligand/metal ratio, pH, temperature, salinity or membrane electric charge. It can also be noticed that in both cases of gadolinium and neodymium, enrichment of heavier isotopes was observed in permeate and enrichment of lighter in retentate. These NF experiments showed without doubt that separating heavy isotope with an NF process combined with a selective complexation step is feasible. Further work concerning this subject is still needed. In fact, easy access to pure isotopes of elements such as transition metals and rare earths could lead to numerous applications in material science, electronics, optics, and in many other areas. Because this nanofiltration method only requires membrane separation of aqueous solutions, it can be performed with very smooth and probably cheaper conditions than with the other methods. As access to higher purified products usually leads to wider areas of applications, any improval concerning isotopic separation process is worth being taken into account.

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13 Obtained enrichment factors are accurate enough to be compared with those previously reported. For example, T. Fujii et al.[8c] study the influence of nuclear size and shape and nuclear spin chemical isotope effect of zirconium–crown complex with $\alpha$ ($^{92}$Zr/$^{90}$Zr) of 1.000648, 0.999593 or 0.99447 depending on the separation conditions, with an accuracy of measured isotope ratio of 0.11%. W. Dembinski et al.[4a,4d] described the cerium and europium isotope partition in $HNO_3$/TBP extraction system with $\alpha$ ($^{142}$Ce/$^{140}$Ce) of $1.00054 \pm 0.00012$ or $1.00037 \pm 0.00013$ or $1.00005 \pm 0.00015$ and $\alpha$ ($^{151}$Eu/$^{153}$Eu) of $1.0007 \pm 0.0002$. Finally, the isotope effect of zinc in a liquid–liquid extraction system using a crown-ether ligand was also reported by Nishizawa et al.[4c] with an $\alpha$ ($^{66}$Zn/$^{64}$Zn) of $1.026 \pm 0.02$.