

## Extraction and separation of $^{141}\text{Ce}$ and $^{153}\text{Gd}$ with HDEHP

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Studies on liquid–liquid extraction of trace level cerium and gadolinium,  $^{141}\text{Ce}$  and  $^{153}\text{Gd}$ , from HCl and  $\text{HNO}_3$  media with liquid cation exchanger, HDEHP reveal that a quantitative separation of the elements from an admixture of the two radioisotopes can be achieved with 0.1% HDEHP and 0.01N HCl. The condition is also valid for separation of trace amount of  $^{153}\text{Gd}$  from bulk or macro quantity of cerium.

### Introduction

In the recent years the intrinsic properties of radioisotope lanthanides are used in various directions including technological and biomedical sciences. For example, microsphere labeled with  $^{141}\text{Ce}$  can be used for the measurement of cerebral blood flow.<sup>1</sup>  $^{141}\text{Ce}$  labeled microspheres are also used for sequential evaluation of glomerular blood flow distribution in rat.<sup>2</sup>  $^{153}\text{Gd}$  labeled compounds are used as a potential MRI contrast agents for liver and biliary tract.  $^{153}\text{Gd}$ -DTPA is used in animals to detect image contrast following coronary, renal and splenic artery ligations.<sup>3–5</sup> It has also been used in humans without known toxic effects for the detection of brain tumours.<sup>6,7</sup>

Though the purity requirement is one of the stringent criterion for such sophisticated applications, the inherent close chemical behavior of all the lanthanide elements limit the purity of any single radioisotope of lanthanide series. So the separation of any lanthanide element from another lanthanides specially in trace scale is always a challenging task for the radioanalytical chemists.

Earlier, attempts were made for the separation of cerium from mixtures of fission products or from mixtures of REE. The distribution of  $^{141}\text{Ce}$  between an aqueous solution of  $\text{HNO}_3$ ,  $\text{HClO}_4$  or HCl in the presence of  $\text{NaBrO}_3$  and dibutylphosphoric acid (HDBP) in  $\text{CCl}_4$  was studied.<sup>8</sup> PEPPARD et al.<sup>9</sup> and MCCOWN et al.<sup>10</sup> also reported the extraction of cerium by alkylphosphoric acids from  $\text{HNO}_3$  medium. The extraction of cerium(IV) using  $^{144}\text{Ce}$  tracer, from  $\text{H}_2\text{SO}_4$  medium by HDEHP dissolved in kerosene was studied by TEDESCO et al.<sup>11</sup> Extraction and separation of mixtures of carrier-free  $^{141}\text{Ce}$  and  $^{152,154}\text{Eu}$  was studied using TBP and HDEHP in n-alkane as extractants and  $\text{NaNO}_3$  as an aqueous phase by KOPUNEC et al.<sup>12</sup>

However, the trace level separation of cerium–gadolinium pair by liquid–liquid extraction (LLX) or chromatographic methods has yet not been reported. The present paper reports the separation of

$^{141}\text{Ce}$  and  $^{153}\text{Gd}$  by means of LLX using HDEHP as the liquid cationic extractant.

The excitation function calculation for compound nucleus formation (code Pace 2) indicates a moderate cross section for the production of carrier-free radioisotopes of gadolinium, e.g.,  $^{146}\text{Gd}$  from high energy heavy ion bombardment ( $^{12}\text{C}$ ) on the cerium target. Keeping this in mind, attempt has also been made for the separation of trace amount of  $^{153}\text{Gd}$  from a bulk or a macro quantity of cerium.

### Experimental

The trace scale separation of cerium and gadolinium was performed using  $^{141}\text{Ce}$  and  $^{153}\text{Gd}$  as the precursor of the elements. Both radioisotopes were procured in chloride form from BRIT, Mumbai, India. A HPGe detector of 1.71 keV resolution at 1.33 MeV in conjunction with PC based MCA, PCA3, and OxfordWIN-MCA software (all from OXFORD) were used for  $\gamma$ -spectroscopic studies. Nuclear characteristics of the isotopes used are shown in Table 1.

The liquid cation exchanger, HDEHP, was procured from Spectrochem Pvt. Ltd., India. The extractant solutions of desired concentration were prepared by adding calculated amount of HDEHP to cyclohexane.

In order to study the separation of cerium and gadolinium pair, about 5 ml of an HCl or  $\text{HNO}_3$  solution of particular strength containing measured activities due to  $^{141}\text{Ce}$  and  $^{153}\text{Gd}$  tracer was shaken vigorously with an equal volume of HDEHP solution of desired concentration for about 5 minutes. After disengagement of the liquid phase the radioactivity present in both phases were measured by  $\gamma$ -ray spectrometry.

Table 1. Nuclear characteristics of the radioisotopes used

Radioisotopes	Half-life, d	Detected $\gamma$ -energies, keV
$^{141}\text{Ce}$	32.501	145.44
$^{153}\text{Gd}$	241.6	97.43, 103.18

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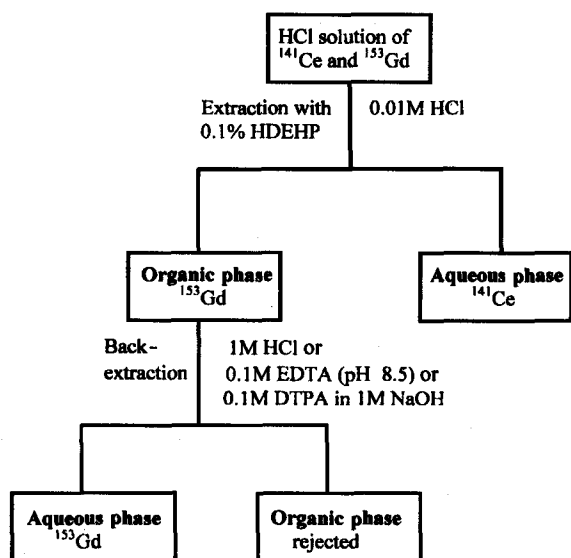


Fig. 1. A schematic diagram for the separation of  $^{141}\text{Ce}$  and  $^{153}\text{Gd}$  with HDEHP

At optimal condition gadolinium isotopes are transferred into the organic phase leaving cerium isotopes in the aqueous phase. The organic phase containing the gadolinium tracer can easily be back-extracted into an aqueous phase of 1M HCl. Considering the biomedical applications of  $^{153}\text{Gd}$ , its back extraction was also tried in diethylenetriaminepentaacetic acid (DTPA) and in EDTA.

The possibility of separation of  $^{153}\text{Gd}$  from macro quantity of cerium has also been studied. For this  $^{141}\text{Ce}$  was spiked with inactive cerium converted into chloride form. Different concentrations of cerium chloride solution were prepared by diluting the spiked cerium salt with 0.01M HCl. A trace amount of  $^{153}\text{Gd}$  was mixed with this macro quantity of cerium solution. Thereafter, the whole procedure was repeated as before to study the separation of trace amount of  $^{153}\text{Gd}$  from bulk cerium.

The scheme of the chemical procedure developed for the separation of  $^{153}\text{Gd}$  from  $^{141}\text{Ce}$  has been schematically given in Fig. 1.

### Results and discussions

LLX study of the tracer solution of  $^{141}\text{Ce}$  and  $^{153}\text{Gd}$  in HCl medium shows that at lower acidity, the extractibility of both  $^{141}\text{Ce}$  and  $^{153}\text{Gd}$  is sufficiently high and even quantitative which rapidly decreases to baseline with the increase of acidic strength (Fig. 2). Extractibility of these elements in lower acidity is attributed to the formation of cationic aquo-complexes like  $[\text{Ce}(\text{H}_2\text{O})_x]^{3+}$  and  $[\text{Gd}(\text{H}_2\text{O})_x]^{3+}$  which, in turn,

form complexes with the cationic extractant, HDEHP. It is also evident from Fig. 2 that the extraction of cerium isotopes is slightly lower than that of gadolinium isotopes. This may be due to the fact that the tendency for formation of cationic aquo-HDEHP complexes decrease with decreasing in atomic number of the lanthanide elements and as a result, the extraction of  $^{141}\text{Ce}$  isotopes reach the base line faster than that of gadolinium. Figure 3 represents the extraction behavior of  $^{141}\text{Ce}$ - $^{153}\text{Gd}$  pair with variation of the HDEHP concentration at a fixed acidity (0.01M HCl). Extraction of both elements increase with increasing HDEHP concentration. Again, the extraction of  $^{153}\text{Gd}$  is higher than that of  $^{141}\text{Ce}$ . The optimal condition has been obtained by combining these results. At 0.01M HCl concentration and 0.1% HDEHP concentration a considerable difference in extraction is obtained for the elements. At this stage about 83% of  $^{153}\text{Gd}$  can be extracted into the organic phase in a single run leaving  $^{141}\text{Ce}$  completely in the aqueous phase. Repeated extraction at this condition leads to the quantitative separation of trace amount of  $^{141}\text{Ce}$ - $^{153}\text{Gd}$  pair.

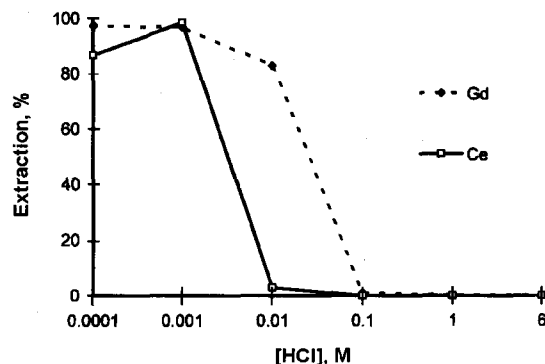


Fig. 2. Extraction profile for  $^{141}\text{Ce}$  and  $^{153}\text{Gd}$  with varying concentration of HCl at 0.1% HDEHP concentration

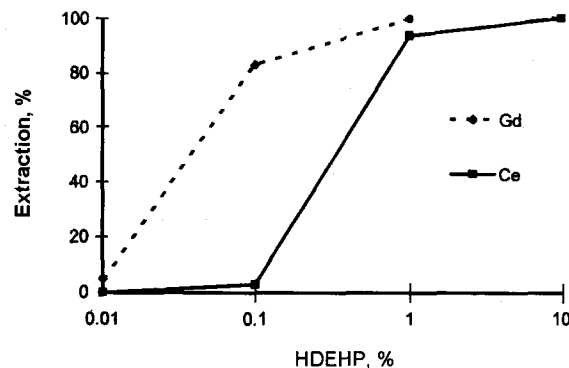


Fig. 3. Extraction profile for  $^{141}\text{Ce}$  and  $^{153}\text{Gd}$  with varying concentration of HDEHP keeping HCl concentration fixed at 0.01M

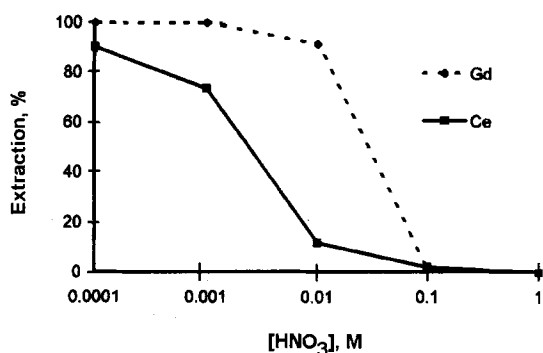


Fig. 4. Extraction profile for  $^{141}\text{Ce}$  and  $^{153}\text{Gd}$  with varying concentration of  $\text{HNO}_3$  at 0.1% HDEHP concentration

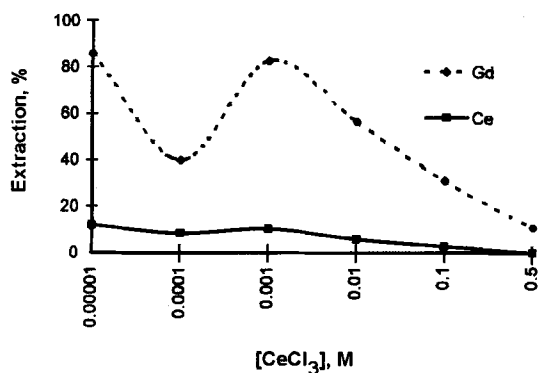


Fig. 5. Extraction profile for bulk cerium spiked with  $^{141}\text{Ce}$  and trace amount of  $^{153}\text{Gd}$  with varying concentration of  $\text{CeCl}_3$  at 0.01M HCl and 0.1% HDEHP concentration

Similar extraction pattern has been observed for  $^{141}\text{Ce}$ – $^{153}\text{Gd}$  pair in  $\text{HNO}_3$  medium (Fig. 4). The optimal conditions for separation of trace scale cerium and gadolinium from the admixture of two isotopes are shown tabulated in Table 2.

Table 2. Distribution ratios ( $D$ ) of cerium and gadolinium at optimal conditions

Condition	$D_{\text{Ce}}$	$D_{\text{Gd}}$	$S$
0.01M HCl, 0.1% HDEHP	0.0315	4.89	154.8
0.01M $\text{HNO}_3$ , 0.1% HDEHP	0.135	10.72	79.4

$S$  – Separation factor ( $D_{\text{Gd}}/D_{\text{Ce}}$ ).

It has been observed that the complete back-extraction of  $^{153}\text{Gd}$  from the organic phase is possible by an aqueous solution of 1M HCl. Back-extraction of  $^{153}\text{Gd}$  has also been studied by DTPA and EDTA, so that the element can be directly applied to in-vivo application without further processing. The quantitative back-extraction is possible both with 0.1M EDTA at pH 8.5 and with 0.1M DTPA in 1M NaOH.

In order to study the separation of  $^{153}\text{Gd}$  from macro amounts of cerium, stock solutions of different concentrations of cerium chloride solution were prepared spiked with  $^{141}\text{Ce}$ . Trace amount of  $^{153}\text{Gd}$  was mixed with this stock solution. It has been observed that the extraction of cerium is almost constant and negligible over a wide concentration range of cerium (Fig. 5). A decrease in the extraction of  $^{153}\text{Gd}$  has been observed at higher cerium concentration. However, the difference of the extracted amount is appreciable over a wide range of cerium concentration and the isolation of trace amount of  $^{153}\text{Gd}$  is possible from bulk amount of cerium upto its 0.01M concentration.

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