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## Simultaneous measurement of fifteen rare earth elements using diffusive gradients in thin films

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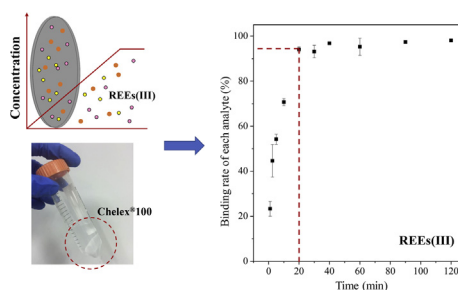
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### HIGHLIGHTS

- DGT is a feasible technique for simultaneous measurement of REEs in soils.
- REE elution efficiencies ranged from 86.5% to 93.8% using 2 M HCl.
- DGT uptake was independent of solution pH (3–9) and ionic strength (3 mM–100 mM).
- Chelex<sup>®</sup>100 DGT had capacities of 5.39–6.75  $\mu\text{g cm}^{-2}$  for measurement of mixed REEs.

### GRAPHICAL ABSTRACT



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### ABSTRACT

A new method for simultaneous measurement of fifteen rare earth elements (REEs) [La (III), Ce (III), Pr (III), Nd (III), Sm (III), Eu (III), Gd (III), Tb (III), Dy (III), Ho (III), Er (III), Tm (III), Yb (III), Lu (III), and Y (III)] was established in this study using the diffusive gradients in thin films (DGT) technique with Chelex<sup>®</sup>100 binding gel. Five different types of ion exchange resins (Chelex<sup>®</sup>100, D418, D001-cc, 001  $\times$  7, and HSTY<sup>®</sup>-SS) were selected for the initial investigation of their adsorption performance for REEs. The Chelex<sup>®</sup>100 binding gel had the greatest uptake efficiencies of >95% for the fifteen REE ions, which was used for all subsequent experiments. The binding gel exhibited rapid binding dynamics to REEs in mixed solution of the fifteen REE ions. Elution efficiencies ranging from 86.5% to 93.8% for these REEs were obtained based on extraction using 2.0 M HCl. The Chelex<sup>®</sup>100 DGT uptake of the fifteen REE ions increased linearly with the deployment time and found to be independent of pH (3–9) and ionic strength (3 mM–100 mM). The capacities of Chelex<sup>®</sup>100 DGT for measurement of the mixed elements were determined at a range of 5.39–6.75  $\mu\text{g cm}^{-2}$ . Application of the DGT for soil analysis showed that Chelex<sup>®</sup>100 DGT was a useful tool in simultaneous measurement of the fifteen REE ions, even in a soil with high concentrations of REEs. This study demonstrated the advantage of Chelex<sup>®</sup>100 DGT in simultaneous measurement of the fifteen REE ions due to high uptake efficiencies and a wide tolerance to environmental interference.

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## 1. Introduction

Rare earth elements (REEs), including the lanthanide group (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) and yttrium (Y), are generally regarded as a group of trace metals with similar chemical features [1–3]. Practical application of REEs have been dramatically increasing especially with their usages in a large number of common commodities in our daily life since recent years [4]. Because of the unique physical and chemical properties of REEs, they become indispensable chemicals in modern industry such as new energy, new materials, environmental protection, aerospace, and electronic information industries [5–9]. Due to the growing demands for REEs and the excessive exploitation of rare earth minerals [10], more and more REEs enter the environment through anthropogenic inputs [11]. Recently, considerable concerns have been raised about the toxicological effects and related environmental risks of REEs, especially when they are accumulated in the environment [12–14]. The mining, processing and improper waste disposal are important pathways for exogenous REEs entering soil, water and air, causing increasing death rates of aquatic and terrestrial organisms [15,16]. Occupational exposure to dust containing REEs may cause pneumoconiosis according to previous studies [17,18]. It has been reported even at low levels in the environmental REEs may cause the generation of genetic toxicity in bone marrow cells and changes in the bone for long-term exposure [19–21]. Furthermore, long-term consumption of food contaminated with REEs can decrease the intelligence quotient of children and hinder the conduction of adult nervous system [22]. Due to the natural co-existence of REEs [1,23,24] and their potential environmental risks [25–27], simultaneous measurement of these REE ions in a single assay will greatly favor the evaluation of their environmental behavior.

Diffusive gradients in the films (DGT) is a dynamic passive sampling technique that has been developed for the measurement of labile chemicals, which was initially developed by Davison and co-workers in the early 1990s [28]. This technique is established based on a diffusion flux through a well-characterized diffusion layer, in which the concentration of a solute ( $C_{DGT}$ ) at the outside surface of the diffusion layer over a span of time can be quantified according to Fick's First Law [29–31]. The traditional methods for evaluating REE bioavailability in soils include single-step chemical extractions such as neutral salts ( $\text{CaCl}_2$ ) [32] and chelating agents such as ethylene-diamine-tetra-acetic acid (EDTA) [33] and sequential extraction methods [34]. In comparison, metals collected by DGT can mimic their uptake from soil to plants by lowering the concentration locally and inducing diffusive supply and release from the solid phase [35–38]. Previous studies have shown that the DGT measured metals in soils correlated strongly with their concentrations accumulated within plants [39,40]. DGT offers the advantage over traditional chemical extraction methods with the ability for oxidic materials to re-supply metals to soil solution [41]. Moreover, this technique has been applied in a wide range of research areas, such as water quality monitoring, chemical speciation in solution, sediment geochemistry, dynamic processes in waters and soils and bioavailability in waters and soils [42–47].

The first and most frequently used binding agent is an iminodiacetate chelating resin (Chelex<sup>®</sup>100), which has been developed for measurement of a large number of metal ions, e. g. Cu, Ni, Zn, Cd, Mn [28,29,48,49]. A similar layer using suspended particulate reagent-iminodiacetate (SPR-IDA) has been reported for measurement of trace metals (Co, Ni, Cu, Zn, Cd, Pb) with analysis using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) [50]. Li et al. [51] developed a solution phase poly (4-styrenesulfonate) (PSS) binding layer for measurement of Cu and Cd in synthetic water. Specific measurement of some cationic metals have been made using other binding agents [52–54].

Recently, due to the great DGT capacities, strong tolerance to competitive ions, and chemical stability, the Chelex<sup>®</sup> 100 gel has received increasing attention as a binding agent in DGT measurement [55–59].

To date, the sampling device for simultaneous measurement of fifteen REE ions using DGT is scarce. Studies related to the extraction of REE ions generally use various ion exchange resins such as strong acidic cation exchanger-sulfonic acid functionality ( $001 \times 7$ , D001-CC) [60–62] and chelate ion exchanger (D418) [63,64]. Wang et al. [65] studied the separation of heavy rare earths with extraction resin containing Cyanex272 and HEOPPA. Gupta et al. [66] investigated the adsorption of light REEs on Cyanex 923 from hydrochloric acid solutions. These extraction resins can be potentially used as binding agents for DGT measurement of REEs.

The aim of this study was to develop DGT for the simultaneous measurement of the fifteen REEs. Five different types of ion exchange resins (Chelex<sup>®</sup>100, D418, D001-cc,  $001 \times 7$ , and HSTY<sup>®</sup>-SS) were selected for the initial investigation of their adsorption performance for REEs, based on which the binding agent Chelex<sup>®</sup> 100 was chosen for DGT use. A series of validation experiments, including the binding kinetics of each element in mixed solutions and the tolerance of ionic strength and solution pH, were conducted to examine the DGT responses under laboratory conditions. In the meantime, the DGT capacities were measured and field application in soils were tested.

## 2. Experimental

### 2.1. Materials and solutions

Strong acidic cation exchanger-sulfonic acid functionality (D001-cc,  $001 \times 7$ ) and Chelate ion exchanger (D418) were purchased from Chemical Plant of NanKai University, China. Cell<sup>®</sup>/HSTY<sup>®</sup> Metal Scavenger Toolkit was purchased from XinAo Science and Technology Co., Ltd. Acrylamide (ultrapure grade), *N,N*-methylenebisacrylamide (ultrapure grade), ammonium persulfate (ACS grade), *N,N,N,N*'-tetramethylethylenediamine (TEMED, ACS grade) were purchased from AMRESCO for the preparation of the binding gel [55]. Agarose (low electroosmosis) and Chelex<sup>®</sup> 100 (200–400 mesh, sodium form) were obtained from Bio-Rad [55]. A new dual-mode DGT holder with a 10 mm depth and 20 mm diameter exposure window was provided by EasySensor Ltd [67]. The REE ion solutions were prepared by dissolving  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{Dy}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{Ho}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{Tm}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{Lu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and  $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in deionized water (18.2 M $\Omega$  cm Milli-Q water, Millipore). The concentration of stock solution for each REE was 100  $\mu\text{g mL}^{-1}$ . The test solutions used for subsequent experiments were composed of the fifteen REE ions, diluted from the stock solution. The pH values of the solutions were adjusted within 4.5–5.5 to avoid competition and precipitation reactions among multiple elements. Standard solutions of each element were supplied from the National Standard Materials Network, China. Plastic containers and DGT subassemblies were acid-cleaned in 10% (v/v)  $\text{HNO}_3$  for more than 24 h and then rinsed thoroughly with deionized water prior to use [31,55]. For the experiment on ionic strength effects, NaCl was added to each solution at 0.01 mol  $\text{L}^{-1}$  to minimize adsorptive losses from solution [31,55].

### 2.2. Gel preparation, DGT deployment and retrieval

Agarose diffusive gel containing 1.5% agarose was prepared by dissolving agarose in an approximate volume of deionized water at

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