



Simultaneous determination of rare earth elements in ore and anti-corrosion coating samples using a portable capillary electrophoresis instrument with contactless conductivity detection



Thi Anh Huong Nguyen^a, Van Ri Nguyen^a, Duc Dung Le^a, Thi Thanh Binh Nguyen^{a,b}, Van Hoang Cao^b, Thi Kim Dung Nguyen^c, Jorge Sáiz^d, Peter C. Hauser^e, Thanh Duc Mai^{f,*}

^a Department of Analytical Chemistry, Faculty of Chemistry, Hanoi University of Science, Vietnam National University – 19 Le Thanh Tong, Hanoi, Vietnam

^b Faculty of Chemistry, University of Quy Nhon – 170 An Duong Vuong, Quy Nhon, Binh Dinh, Vietnam

^c Institute for Technology of Radioactive and Rare Elements, 48 Lang Ha, Hanoi, Vietnam

^d Institute of General Organic Chemistry (IQOG), Spanish National Research Council (CSIC), Calle Juan de la Cierva 3, 28006 Madrid, Spain

^e University of Basel, Department of Chemistry, Spitalstrasse 51, 4056 Basel, Switzerland

^f Centre for Environmental Technology and Sustainable Development (CETASD), Hanoi University of Science, Nguyen Trai Street 334, Hanoi, Vietnam[†]

ARTICLE INFO

Article history:

Received 15 April 2016

Received in revised form 8 June 2016

Accepted 15 June 2016

Available online 16 June 2016

Keywords:

In-houses-made instrument
Capacitively coupled contactless conductivity detection (C⁴D)
Capillary electrophoresis (CE)
Rare earth elements (REEs)
Ore samples
Vietnam

ABSTRACT

The employment of an in-house-made capillary electrophoresis (CE) instrument with capacitively coupled contactless conductivity detection (C⁴D) as a simple and inexpensive solution for simultaneous determination of many rare earth elements (REEs) in ore samples from Vietnam, as well as in anti-corrosion coating samples is reported. 14 REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) were determined using an electrolyte composed of 20 mM arginine and 10 mM α -hydroxyisobutyric acid adjusted to pH 4.2 with acetic acid. The best detection limit achieved was 0.24 mg/L using the developed CE-C⁴D method. Good agreement between results from CE-C⁴D and the confirmation method (ICP-MS) was achieved, with a coefficient of determination (r^2) for the two pairs of data of 0.998.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The rare earth elements (REEs), including the lanthanide series, scandium (Sc), and yttrium (Y), are playing an essential role in the scientific and technological advancement, especially in metallurgy, material science, microelectronics and medical diagnostics. They are used in numerous daily applications, notably in electronic components, superconductors, magnets, lasers, rechargeable hydride batteries, catalytic converters for cars, cell phones, fertilizers and medical devices [1–3]. In geology, REEs have been used as natural tracers for elucidation of igneous rock petrogenesis and interpretation of metasomatism, ore formation and rock alternation processes [4,5]. REEs have been mined mainly in the United States, Australia, Brazil, China, India, Malaysia, Russia, Thailand and

Vietnam. According to the U.S. Geological Survey in 2015, Vietnam is ranked at the 8th position worldwide among the countries having rare earth elements resources [6]. The rare earth elements in Vietnam, notably La, Ce, Pr, Nd and Sm, are often present in the form of fluoro-carbonate [7].

Due to the scientific and technological significance of REEs, there is a need for analytical methods. So far REEs have mostly been determined with costly instrumental methods, such as inductively coupled plasma-mass spectrometry (ICP-MS), ICP-optical emission spectrometry (ICP-OES), electrothermal atomic absorption spectrometry (ET-AAS), neutron activation analysis (NAA) and flame atomic absorption spectrometry [8–10]. However, these instrumental methods are not affordable for many geological centers in developing countries that are exploiting and exporting REEs. In Vietnam, REEs could to date only be determined at a few institutes that are equipped with one of the two types of ICP instruments, such as the Institute for Technology of Radioactive and Rare Elements (ITRRE) or the Vietnam Institute of Geosciences and Mineral Resources.

* Corresponding author.

E-mail address: maithanhduc83@gmail.com (T.D. Mai).

[†] www.CE-Vietnam.com.

There is therefore interest in the development of simpler and less expensive analytical techniques. In this context, capillary electrophoresis (CE) can be seen as a more economic alternative. This technique has been repeatedly employed for speciation of metallic ions in different sample matrices. Reviews on applications of CE for metal species determination in environmental and biological samples can be found in [11–15]. Indeed, the simplest format of the technique, namely capillary zone electrophoresis (CZE) has been reported for the determination of REEs in different matrices, using UV–vis (UV–vis) detection [16–23], laser induced fluorescence (LIF) detection [24,25], mass-spectrometric detection [26] or detection by ICP-MS [27,28]. Other modes of CE have also been used for this purpose, notably micellar electrokinetic chromatography (MEKC) [29–31], electrokinetic supercharging (ESK) [32] and isotachopheresis (ITP) [33]. Complexation with suitable UV/Vis or fluorescence absorbing ligands was needed to enable optical detection of the REEs.

Capacitively coupled contactless conductivity detection (C^4D) is an alternative universal detection method for CZE which does not require a chromophore. Attractive features are high versatility, ease in construction and operation, low power consumption and the possibility of miniaturization (see more details in the review [34] and references therein). These features also allow its use in compact portable CE instruments [35,36] for flexible mobile deployment, which can also be built in low cost versions [37,38]. Different portable and purpose-made CE- C^4D configurations have been developed, ranging from instruments with manual operations (see [39–41] for example), semi-automated systems [42] to fully automated single-channel versions (refer to references [43–46] for more details) and multi-channel configurations [47–50]. Although REEs in the native form of inorganic ions can be seen as suitable candidates for CE- C^4D , so far this methodology has to the best of our knowledge not been developed for this application.

Herein a CE- C^4D method for the determination of REEs using an in-house-made compact instrument is reported. The method developed was applied for the screening of REEs in ore and anti-corrosion coating samples in Vietnam. The significance of this study is threefold, including i) development of a new analytical methodology for REEs determination, ii) new arrangement of the portable CE- C^4D instrument for better operation and adaptation to the local infrastructure, and iii) combination of the developed CE- C^4D methodology and portable instrumentation as a straightforward and cost-effective option for determination of REEs in ore and anti-corrosion coating samples.

2. Experimental

2.1. Chemicals and materials

All chemicals used in this study were of analytical reagent grade. La, Ce, Pr, Nd, Sm, Eu, Gd, Tm, Dy, Ho, Er, Tb, Yb, Lu in the oxide forms, as well as other inorganic salts were purchased from (Merck, Darmstadt, Germany). L-histidine (His), ascorbic acid (Asc), arginine (Arg), acetic acid (Ace), sodium hydroxide (NaOH), hydrochloric acid (HCl), hydrofluoric acid (HF), sodium carbonate (Na_2CO_3), perchloric acid ($HClO_4$), 4-methyl 2-pentanol and α -hydroxyisobutyric acid (HIBA) were purchased either from Merck or Fluka (Buchs, Switzerland). Stock solutions of REEs (10 mM) were prepared by dissolving precise amounts of respective oxides with HCl in a volumetric flask of 25 mL which was then filled up to the defined volume with deionized water. HIBA solutions were prepared by dissolution in deionized water.

Polyimide coated fused silica capillaries of 50 μ m I.D. and 365 μ m O.D. (from Polymicro, Phoenix, AZ, USA) with total (L) and effective (L_{eff}) lengths of 60 cm and 53 cm respectively were used

for separations. Before use, the capillaries were preconditioned with 1 M NaOH for 10 min and deionised water for 10 min prior to flushing with buffer. Deionised water purified using a system from Water Pro (Labconco, Kansas City, MO, USA) was used for the preparation of all solutions and for sample dilution if required. Background electrolyte (BGE) solutions were prepared by addition of the pre-selected acid (Ace or Asc) into a basic solution containing either His or Arg (at a pre-defined concentration) until it reached the desired pH value. pH values of solutions were controlled with an HI 2215 Hanna Instruments pH meter (Woonsocket, RI, USA).

2.2. Instrumentation

All experiments were performed on a portable CE instrument which employs siphoning for sample injection. A miniature Spellman unit (UM20*4, 12 V 200 μ A, Pulborough, UK) was used which provides a maximum of 20 kV. The high voltage (HV) end of the capillary was isolated in a safety cage equipped with a microswitch to interrupt the HV when the lid was opened. Detection was carried out with a miniaturized C^4D cell built in-house [50,51]. The resulting signals were recorded with an ADC-20 data acquisition system (Pico Technology, St. Neots, UK) which was connected to the USB-port of a personal computer. For powering the CE- C^4D system, a lithium battery pack of 14.8 V (capacity of 6.6 Ah, CGR 18650CG 4S3P, Contrel, Hünenberg, Switzerland) and a separate pair of smaller Li-ion batteries (capacity of 2.8 Ah each, CGR 18659CG 4S1P, Contrel) were fitted with suitable voltage regulators to provide +12 V and \pm 12 V outputs for CE and C^4D respectively. Alternatively, mains power can be utilized when available.

2.3. Procedures

The concentrated ore samples in which total rare earth oxides account for approximately 30% w/w were provided by the Institute for Technology of Radioactive and Rare Elements (ITRRE, Vietnam). The procedure for sample treatment, which was adapted from that used for ICP-MS was also provided by IRTTE. About 50 mg of homogenous powder sample was weighed in a platinum crucible, wetted by some drops of deionized water. 1 mL of 57% $HClO_4$ was then added. The mixture was heated on the hot plate to 200–300 °C until the appearance of a white fume. 2 mL of 47% HF was then added and this mixture was heated until complete evaporation. 1 mL of 37% v/v HCl was then added into the crucible to dissolve completely the dried residue. The water-diluted solution was filtered through a 0.45 μ m ash-free filter paper. The filtrate containing dissolved REEs in the form of chloride salts was noted as solution 1. The residue on the filter paper was re-treated by ashing the filter paper at about 650 °C, followed by fusing the ash with sodium carbonate (using a Na_2CO_3 /ash ratio (w/w) of 6:1) at 950 °C for 5–10 min. The melted mass was cooled down, then dissolved with 50 mL water and filtered through a 0.45 μ m filter paper. 2 mL of 37% HCl was added into the filter paper to completely dissolve the precipitate. This solution was mixed with the solution 1 noted above, evaporated at 200–300 °C and finally diluted to 25 mL in a volumetric flask. The solution obtained was further diluted with deionized water if needed prior to CE- C^4D analyses. Note that the sample after dilution with water was still under acidic conditions (pH around 1–2); therefore no hydrolysis of rare earth metal ions is expected. For each ore sample, two replicates were prepared in parallel using this procedure. For determination of REEs in anti-corrosion coatings, the steel plates painted with these anti-corrosion coatings were immersed in 100 mL HCl (1 M) and heated at 90 °C (for about 1 h) until the coating layers were removed from the plates. The obtained solution was subsequently evaporated and filled up to 25 mL with deionized water prior to CE- C^4D analyses.

Download English Version:

<https://daneshyari.com/en/article/1198671>

Download Persian Version:

<https://daneshyari.com/article/1198671>

[Daneshyari.com](https://daneshyari.com)