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Capillary microextraction combined with fluorinating assisted electrothermal vaporization inductively coupled plasma optical emission spectrometry for the determination of trace lanthanum, europium, dysprosium and yttrium in human hair

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ABSTRACT

In this work, a congo red modified single wall carbon nanotubes (CR-SWCNTs) coated fused-silica capillary was prepared and used for capillary microextraction (CME) of trace amounts of lanthanum (La), europium (Eu), dysprosium (Dy) and yttrium (Y) in human hair followed by fluorinating assisted electrothermal vaporization-inductively coupled plasma-optical emission spectrometry (FETV-ICP-OES) determination. The adsorption properties and stability of the prepared CR-SWCNTs coated capillary along with the various factors affecting the separation/preconcentration of La, Eu, Dy and Y by CME were investigated in detail. Under the optimized conditions, with a consumption of 2 mL sample solution, a theoretical enrichment factor of 50 and a detection limit (3σ) of 0.12 ng mL^{-1} for La, 0.03 ng mL^{-1} for Eu, 0.11 ng mL^{-1} for Dy and 0.03 ng mL^{-1} for Y were obtained, respectively. The preparation reproducibility of the CR-SWCNTs coated capillary was investigated and the relative standard deviations (RSDs) were ranging from 4.1% (Eu) to 4.4% (La) ($C_{La,\ Dy}$=1.4 ng mL^{-1}; $C_{Y,\ Eu}$=0.25 ng mL^{-1}, n=7) in one batch, and from 5.7% (Eu) to 6.1% (Y) ($C_{La,\ Dy}$=1.4 ng mL^{-1}; $C_{Y,\ Eu}$=0.25 ng mL^{-1}, n=5) among different batches. The proposed method was applied to the analysis of real-world human hair sample and the recoveries for the spiked sample were in the range of 93–105%. The method was also applied to the determination of La, Eu, Dy and Y in Certified Reference Material of GBW07601 human hair, and the determined values were in good agreement with the certified values.

1. Introduction

The widespread application of rare earth elements (REEs) in industrial and agricultural production accelerated the cycle of REEs in the natural food chain, and their accumulation in the human body was increased. Several deleterious effects due to occupational and environmental exposure to REEs have been reported [1], and some studies have demonstrated that trace of REEs has inhibitory as well as stimulatory effects on the crystallization of urinary stones [2]. Therefore, the topic of the safety of REEs intake has been becoming the subject of continual attention in analytical chemistry, and the determination of REEs in biological samples is becoming more and more important. Under a certain conditions, human hair is a good biological indicator, which has become a fundamental biological specimen, alternative to the usual samples blood and urine, for drug testing in the fields of forensic toxicology, clinical toxicology and clinical chemistry [3]. Moreover, hair-testing is now extensively used in workplace testing, as well as, on legal cases, historical research etc. Hair is an excretory organ of trace elements in body, which is easy to process non-destructive sampling, store and transport. Clinically, it is also often used as a biological specimen to evaluate heavy metals exposure and absorbance in different periods [4]. In order to achieve the judgement purpose whether there is any human body healthy risk of REEs by detecting the concentration of REEs in human hair, the simple, efficient, sensitive and accurate analytical method for analysis of trace/ultratrace REEs in human hair is highly demanded.

At present, the analytical methods for trace and ultra-trace REEs in human hair include inductively coupled plasma optical emission spectrometry (ICP-OES) [2,5], inductively coupled plasma mass spectrometry (ICP-MS) [6–10] and neutron activation analysis [11]. ICP-OES has been widely employed in the REEs analysis because of its advantages of affordable price, robust anti-interference capability and multi-element simultaneous determination capability. However, direct ICP-OES determination of trace REEs in biological samples sometimes is difficult due to the deficient detection limits and the

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matrix effects resulting from the major constituents such as organic compounds and inorganic salts. In order to achieve accurate and reliable analytical results, an efficient separation and preconcentration step prior to their determinations is required. The solid phase extraction (SPE) is one of the most commonly used sample pretreatment technologies for REEs analysis [5,9]. However, it suffered from the drawbacks of large volumes of toxic organic solvents required, tedious and time-consuming. Modern trends of sample pretreament techniques are toward the simplification, miniaturization and minimization of the reagents (especially organic solvents) and sample consumption. This has led to the development of some environmental friendly sample pretreatment techniques, such as liquid phase microextraction (LPME) [12,13], solid phase microextraction (SPME) [14,15] and capillary microextraction (CME) [16–19].

Capillary microextraction (CME, also termed as in-tube solid phase microextraction), developed from solid phase microextraction (SPME) [16], was first introduced by Bigham et al. [17] as a viable solvent-free extraction technique. CME utilizes an open tubular capillary column as extraction device, and a sorptive coating on the inner surface of capillary as the extraction medium in which the analyte in aqueous sample is directly extracted and concentrated. Similar to SPME, CME is also based on the distribution of analytes between the sample matrix and the extracting phase coated on the inner surface of a capillary. Utilizing a silica-fused capillary with stationary phase coating on the inner surface to perform extraction, CME overcomes the inherent shortcomings of fiber SPME such as fiber breakage and mechanical damage of the coating. As a simple, sensitive, time-effective, solvent-free, easy-to-automate and miniaturized sample preparation technique, CME has been widely used for analysis of trace organic and inorganic analytes by on-line coupling with different detection instrumentations such as gas chromatography (GC) [18], high-performance liquid chromatography (HPLC) [19], capillary electrophoresis (CE) [20], electrospray mass spectrometry (ES-MS) [21] and ICP-MS [22]. The recent development of CME in trace metals and their species analysis has been reviewed, and its future development is highly dependent on the exploration of new coatings with high selectivity and high extraction efficiency [23].

Carbon nanotubes (CNTs) is a special kind of carbon nanomaterials, which can be simply described as a nanometer-sized tube rolled into by a layer of graphite, including the hexagonal arrangement of carbon atoms rolled into a single-layer helical micro cartridge-single-walled carbon nanotubes (SWCNTs) and the hexagonal arrangement of carbon atoms rolled into a coaxial multi layer micro tube-multi-walled carbon nanotube (MWCNTs). The diameter of CNTs is generally from a few to tens of nanometers [24]. They have large specific surface area, high mechanical strength, good flexibility, excellent electrical conductivity, and spiral state of the graphite layer decides the semiconducting and metallic properties of carbon nanotubes; they can act with organic and inorganic analytes through different types of interactions, such as π–π interactions and Van der Waals interactions. These remarkable properties make CNTs such valuable materials to be widely applied in many fields, for example, as a gas or biological probes, electrochemical detection electrode and solid phase extraction materials [25,26]. CNTs are considered to be superior materials for adsorbing different analytes from samples because of their outstanding structural and chemical stabilities [25]. Some SPE methods using CNTs as adsorbents for preconcentration and separation of organic compounds and metal ions in real-world samples have been reported [27–30]. However, despite excellent properties, owing to their rigidity, chemical inertness and self-aggregation of CNTs with strong van der Waals forces, CNTs are difficult to dissolve or disperse in common organic solvents or polymeric matrices, which seriously limited the application potential of CNTs as the coating materials in different techniques. Great efforts have been focused on applying the methods of covalent or non-covalent functionalization to improve the solubilization of CNTs. Hu et al. [31] reported that a single or a small bundle of SWCNTs could be stripped from the original beam form of SWCNTs after their surface was modified with congo red (CR), and the solubility of CR modified SWCNTs in water medium could be up to 3.5 mg/mL. This means that the CR modified SWCNTs could be dispersed or dissolved well in water, which was beneficial for coating SWCNTs in the inner surface of the capillary.

The aim of this work was to prepare congo red modified SWCNTs coating capillary and to develop a new method of CR-SWCNTs coated capillary microextraction combined with fluorination assisted electrothermal vaporization (FETV)-ICP-OES for the determination of trace La, Eu, Dy and Y. Target REEs were extracted and preconcentrated by CR-SWCNTs coated capillary microextraction, and the obtained extracts were then introduced into ETV for subsequent ETV-ICP-OES determination. Experimental parameters affecting capillary microextraction of La, Eu, Dy and Y were studied in detail and the optimal experimental conditions were established. The developed method was applied to the analysis of trace La, Eu, Dy and Y in human hair with satisfactory results.

2. Experimental

2.1. Apparatus

The graphite furnace sample introduction device and ICP-OES instrument used in this work were identical with that reported

Table 1
FETV-ICP-OES operating conditions for determination of La, Eu, Dy and Y.

ICP-OES operating parameters	
Wavelength (nm)	La 333.750; Eu 381.970; Dy 353.170; Y 371.030
Incident power(kW)	1.0
Carrier gas (L/min)	0.6
Coolant gas (L/min)	16
Plasma gas (L/min)	0.8
Observation height (mm)	12
Entrance slit-width (μm)	25
Exit slit-width (μm)	25
ETV parameters	
Drying temperature (°C)	120, ramp 15 s, hold 20 s
Ashing temperature (°C)	1200, ramp 15 s, hold 15 s
Vaporization temperature (°C)	2600, for 5 s
Introducing volume (μL)	50

previously [32]. An ICP spectrometric system (Beijing Broadcast Instrument Factory, Beijing, China) with 2-kW plasma generator was used with a conventional quartz torch. A WF-4C type heating device with a matching graphite furnace (Beijing Rayleigh Analytical Instruments Inc, Beijing, China) was used for analyte vaporization. The radiation from the plasma was focused as a 1:1 image on the entrance slit of a WDG 500-1A type monochromator (Beijing Second Optics) having a reciprocal linear dispersion of 1.6 nm mm^{-1}. The transient emission signals from plasma were detected with a R456 type photomultiplier tube (Hamamatsu, Japan) fitted with a laboratory-built direct current amplifier, and recorded by a U-135C recorder (Shimadzu, Japan). The used instrument operating conditions for ETV-ICP-OES are given in Table 1.

The pH values were controlled with a Mettler Toledo 320-S pH meter (Mettler Toledo Instruments Co. Ltd., Shanghai, China) supplied with a combined electrode. A WX-3000 microwave accelerated digestion system (EU Chemical Instruments Co. Ltd., Shanghai, China) was used for sample digestion. An HL-2 peristaltic pump (Shanghai Qingpu Instrument Factory, Shanghai, China) was used in separation and preconcentration process. Fused silica capillary (320 μm i.d. × 450 μm o.d.) was provided by Hebei Yongnian Optical Fiber Factory, Hebei, China. PTFE tubing with 0.5 mm i.d. was used for all connections. These connections were kept as short as possible to minimize the dead volume. The structure of CR-SWCNTs coating was characterized by 170SX FI-IR (NICOL ET, USA). The transmission electron micrograph (TEM) was obtained using a JEOL EM2010 electron microscope (Tokyo, Japan). Vacuum drying oven (DZG-6020, Shanghai Senxin Instrument Factory, Shanghai, China) was used to achieve the desired temperature. A SY 1200 type ultrasonic instrument (Shanghai Shengyuan Ultrasonic Instrument Equipment Corporation, Shanghai, China) was used for the preparation of CR modified SWCNTs.

2.2. Reagents and standard solutions

The La, Eu, Dy and Y standard stock solutions (1 g L^{-1}) were prepared by dissolving their SpecPure® oxides or nitrates (Merck, Darmstadt, Germany) in 1:1 (v/v) HNO_3. Analytical mixture standard solutions of La, Eu, Dy and Y with concentrations of 0.1 and 0.01 μg/mL were prepared by mixing and diluting the stock solutions with 1% (v/v) dilute HNO_3. 60% (m/v) PTFE suspension was purchased from Shanghai Institute of Organic Chemistry (Shanghai, China). Single-wall carbon nanotubes with purity > 90% were bought from Nano-era Company, Chengdu, China. Analytical grade congo red (CR) was obtained from Beijing Chemical Reagent Factory, Beijing China. All other chemicals were of analytical reagent grade at least. Milli-Q high purity water (18.20 MΩ cm, Millipore, Molsheim, France) was used throughout the experiments.

The Certified Reference Material of GBW07601 human hair was provided by National Standard Material Research Centre, Beijing, China. All laboratory-ware were made of polyethylene or polypropylene material and thoroughly cleaned by soaking in 10% (v/v) nitric acid for at least 24 h. Immediately prior to use, all acid-washed ware were rinsed with high-purity deionized water. High-purity deionized water and all containers were tested for blank analyte levels.

pH of solution was adjusted with the following corresponding buffer solution; pH = 1 with 0.1 mol/L nitric acid, pH 1–3 with 0.1 mol/L hydrochloric acid–glycine, pH 3–6 with 0.20 mol/L acetic acid–acetic acid sodium.

2.3. Preparation of CR-SWCNTs coating capillary columns

Congo red modified single-wall carbon nanotubes (CR-SWCNTs) was provided by professor Shengshui Hu's group, Department of Chemistry, Wuhan University, Wuhan China. The preparation process was briefly described as follows: firstly, SWCNTs were purified by refluxing in 2.6 mol/L HNO_3 for 48 h and treating with 2.0 mol/L HCl for 12 h before use. The purified SWCNTs were mixed with CR at a mass ratio of 1/5 and ground sufficiently in agate mortar. After the mixture was dissolved in water by ultrasonication, it was centrifuged. The supernatant was collected and dried in the rotary evaporator. The dried product on the cellulose acetate millipore filtration membrane was washed with high purity water until the filtrate was colorless. The obtained CR-SWCNTs were directly dissolved and stored in water immediately after washing for future use [31]. And the concentration of CR-SWCNTs employed in our research work is 1.5 mg/mL (w/v, as SWCNTs).

The fused-silica capillary was activated at ambient temperature by rinsing sequentially with 1 mol/L sodium hydroxide for 2 h, water for 30 min, 1 mol/L hydrochloric acid for 2 h and water for 30 min. The capillary was dried at 160 °C while purged with nitrogen for 5 h.

CR-SWCNTs coating was prepared on the inner surface of a fused silica capillary (50 cm × 320 μm i.d.) by pumping the CR-SWCNTs solution with a constant flow pump through the fused-silica capillary. After the whole capillary was filled with the CR-SWCNTs solution, it was put in the vacuum oven and dried at 90 °C for 8 h, 100 °C for 6 h and finally aged at 120 °C for 5 h.

2.4. Experimental procedure

2.4.1. Capillary microextraction procedure

2 mL solutions containing 4 ng/mL La, Eu, Dy and Y were prepared and the pH value was adjusted to 3.0 with 0.1 mol/L hydrochloric acid–glycine. After the CR-SWCNTs coated capillary

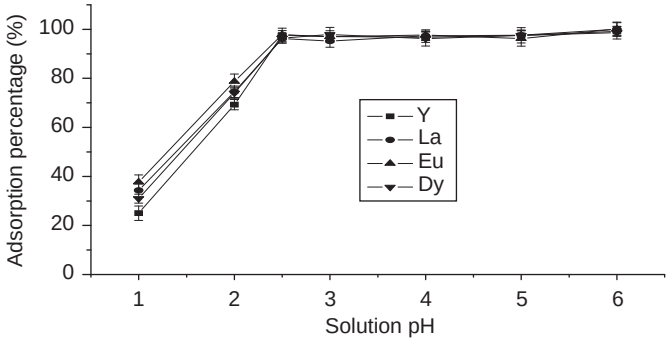

Fig. 1. Effect of pH (three replicates for each pH) on the adsorption percentage of La, Eu, Dy and Y with CR-SWCNTs coated capillary. Analyte concentration: 4 ng/mL; sample flow rate: 0.15 mL/min; sample volume: 2 mL.

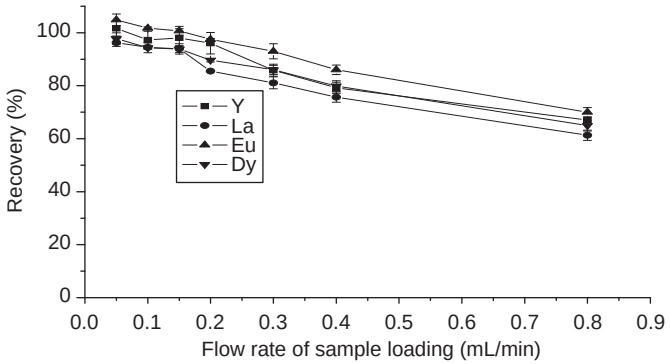

Fig. 2. Effect of sample loading flow rate (three replicates for each loading flow rate) on the recovery of La, Eu, Dy and Y. Analyte concentration: 4 ng/mL; pH: 3.0; sample volume: 2 mL.

column (320 μm × 50 cm) was equilibrated with pH 3.0 buffer solution, the sample solution was passed through the CR-SWCNTs coated capillary by using peristatltic pump at a flow rate of 0.15 mL/min, the target analytes retained in the capillary column were eluted with 40 μL of 0.8 mol/L HNO_3 solution at a flow rate of 0.1 mL/min and then determined by FETV-ICP-OES.

2.4.2. Slurry sample preparation

5 microliters of 60% (m/v) PTFE emulsion was added to 40 μL elution solution (after CME), and diluted to 50 μL with high purity water. The aqueous standard solution series containing 6% (m/v) PTFE as chemical modifier was used for calibration. The resulting mixtures were dispersed with an ultrasonic probe for 15 min and the bottles shaken prior to sampling.

2.4.3. ETV-ICP-OES procedure

REEs are refractory elements. When they were determined by ETV-ICP-OES, an incomplete vaporization, much lower sensitivities and severe memory effects would be encountered [5,33]. Our previous research work has proved that PTFE emulsion is an effective fluorinating modifier for ETV-ICP-OES determination of REEs. In this work, PTFE was still used as the chemical modifier for ETV-ICP-OES determination of La, Eu, Dy and Y, and the ETV parameters used in this study were the same as in the previous work [33]. After the ETV unit had been connected to the ICP-OES and the system stabilized, a 25 μL volume of sample was injected into the graphite furnace. After drying step, stop the ETV heating program. Then another 25 μL volume of sample was injected into the graphite furnace, the ETV heating program was started again. During the drying and pyrolysis steps of the temperature program, the dosing hole of the graphite furnace was kept open to remove water and other vapor. When the dosing hole was sealed with a graphite probe 10–15 s prior to the high temperature vaporization step, the vaporized analyte was swept into the plasma using argon as carrier gas and the peak height was used for quantification.

The recommended procedure was used throughout the different tests that followed.

For determination of the procedure blank values, 2 mL buffer solution of 0.1 mol/L hydrochloric acid–glycine (pH = 3.0), chosen as the blank solution, was passed through the microextraction capillary. Then the microextraction capillary was eluted by 40 μL of 0.8 mol/L HNO_3 solution. The blank values of analytes were obtained by determining the elution. The same procedure was repeated seven times and the blank values were found to be constant when eluted with 40 μL of 0.8 mol/L HNO_3 solution.

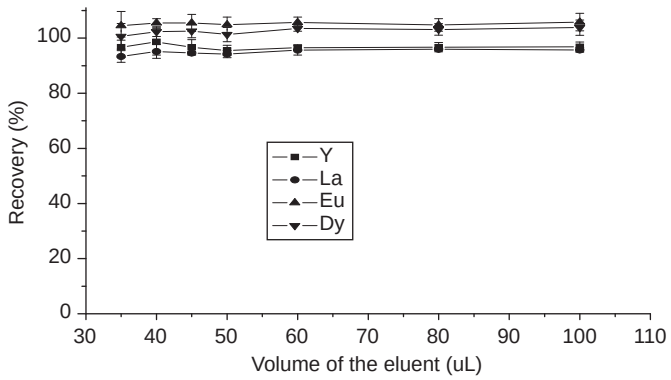

Fig. 3. Effect of eluent HNO_3 volume (three replicates for each eluent volume) on the recovery of La, Eu, Dy and Y. Analyte concentration: 4 ng/mL; pH: 3.0; sample flow rate: 0.15 mL/min.

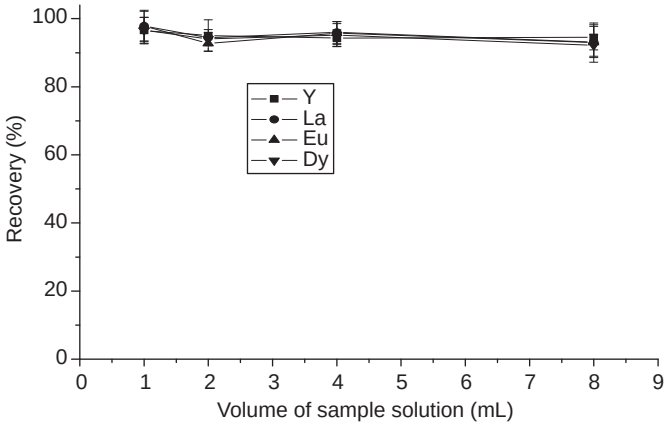

Fig. 4. Effect of sample solution volume (three replicates for each sample solution volume) on the recovery of La, Eu, Dy and Y. Analyte concentration: 4 ng/mL; pH: 3.0; sample flow rate: 0.15 mL/min.

2.5. Pretreatment of human hair samples

Human hair sample collected from local healthy person (Wuhan, China) was cut into about 5 mm long and was washed with non-ionic detergent solution. After vigorous rinsing with a large volume of high purity water, the hair rinsed with acetone and then air-dried prior to analysis.

Three portions (0.4000 g) of human hair or Certified Reference Material GBW07601 human hair were accurately weighed and transferred into three PTFE vessels, and 6 mL of concentrated HNO_3 and 2 mL hydrogen peroxide were added to each vessel, respectively. The vessels were kept open for about 1 h at room temperature to ventilate the gas generated from the vigorous reactions. The vessels were then closed and placed in a re-programmed microwave oven for digestion. The microwave digestion was performed according to the following heating programs: 3 atm for 1 min, 8 atm for 2 min and then 10 atm for 3 min until clear solution was obtained. The digest was then heated on a hot plate until near dryness to remove the superfluous acid, the residue was dissolved in 5 mL of high purity deionized water. After the pH of the sample solution was adjusted to 3.0 prior to dilution to 10 mL with high purity water, it was subjected to the subsequent CME-FETV-ICP-OES determination. The blank sample with the same amount of acid but without analytes was prepared using the same procedure described above.

3. Results and discussion

3.1. Characterization of CR-SWCNTs

The FT-IR spectra of SWNTs, CR and CR-SWNTs were obtained and compared, which can be referred to Ref. [31]. The obtained spectra show that the purified SWNTs exhibit three peaks in the range of 600–2000 cm^{-1}. The appearance of the peak situated at 1729 cm^{-1} indicates the existence of carboxyl groups, and the peaks located at 1577 and 1215 cm^{-1} are assigned to the C=C stretch of carbon nanotube backbones and the C–O stretch of the acid groups, respectively. In the case of CR-SWNTs, the main characteristic peaks of SWNTs and CR coexist and no new peaks appear, reflected by the presence of the peak at 1729 cm^{-1} associated with SWNTs and the peaks at 1042, 834 and 764 cm^{-1} related to CR. These results suggest that the interaction between adsorbed CR and SWNTs might be noncovalent.

The TEM of SWNTs and CR-SWNTs was shown in Ref. [34]. The experimental results indicated that the strongly bundled nanotube

Table 2
Analytical performance of CR-SWCNTs-CME-FETV-ICP-OES.

Elements	RSD[a] (%)	RSD[b] (%)	Linear equation	LOD (ng/mL)
La	4.4	5.9	$y=10.26x+4.41$	0.115
Eu	4.1	5.7	$y=38.44x+9.16$	0.032
Dy	4.3	5.8	$y=9.55x+6.14$	0.110
Y	4.3	6.1	$y=36.59x+8.31$	0.028

[a] within batch ($C_{La,\ Dy}=1.4$ ng/mL, $C_{Y,\ Eu}=0.25$ ng/mL, $n=7$).
[b] among different batches ($C_{La,\ Dy}=1.4$ ng/mL, $C_{Y,\ Eu}=0.25$ ng/mL, $n=5$).

ropes (presented in SWNTs) are effectively exfoliated into small bundles or individual nanotubes (presented in CR-SWNTs), ensuring the formation of more subtle film structure, which is attributed to the highly selective and strong π-stacking interactions between CR and carbon nanotubes.

3.2. Optimization of CME operation conditions

3.2.1. Influence of sample solution pH

Medium pH plays an important role in the adsorption of target analyte in the CR-SWCNTs coated capillary column. To investigate the influence of sample solution pH on CME, the adsorption behaviors of La, Eu, Dy and Y on the self-prepared CR-SWCNTs coated capillary were studied with pH varying in the range of 1–6, three replicates for each pH value were processed and the results are shown in Fig. 1. As can be seen, a quantitative adsorption for all studied metals could be obtained in a relatively wide pH range of 2.5–6.0. For further experiments, sample solution adjusted to pH 3.0 was employed.

3.2.2. Effect of sample flow rate

The flow rate of sample solution has great influence on the extraction of metal ions by CME. Therefore, the effect of sample flow rate on CME was evaluated by passing 2.0 mL of sample solution through the capillary with the flow rate varying in the range of 0.05–0.8 mL/min. The experimental results in Fig. 2 demonstrate that target ions could be quantitatively adsorbed on the CR-SWCNTs coated capillary with a flow rate less than 0.15 mL/min, while the adsorption percentages of target ions were decreased with further increasing of the flow rate, possibly due to decreased adsorption kinetics at high flow rate. Accordingly, a sample flow rate of 0.15 mL/min was employed in subsequent experiments.

3.2.3. Effect of eluent concentration

As can be seen from Fig. 1, the adsorption percentage of La, Eu, Dy and Y was obviously decreased when the pH of sample solution was less than 2.5, indicating a feasibility of desorption with high acidity solution. Therefore, HNO_3 was chosen as the eluent and the effect of HNO_3 concentrations in the range of 0.2–2.0 mol/L on the recovery of La, Eu, Dy and Y was investigated. It was found that four target ions could be quantitatively recovered when the concentration of HNO_3 was above 0.4 mol/L. For a complete elution, 0.8 mol L^{-1} HNO_3 was employed as the eluent in the following experiments.

3.2.4. Effect of eluent volume

The effect of eluent volume on the recovery of La, Eu, Dy and Y was studied in the range of 35–100 μL with 0.8 mol/L HNO_3 as eluent and the obtained results were shown in Fig. 3. It was found that all of the target analytes can be quantitatively recovered in the whole tested volume range. In order to obtain higher enrichment factor, 40 μL of 0.8 mol/L HNO_3 was selected as the eluent.

3.2.5. Effect of eluent flow rate

The effect of eluent flow rate on the recovery of La, Eu, Dy and Y was studied by fixing the eluent volume at 40 μL with flow rate varying in the range of 0.05–0.3 mL/min. The experimental results show that all of the target analyte can be quantitatively recovered (more than 90%) in the flow rate range (0.05–0.2 mL/min). In this paper, 0.1 mL/min flow rate of elution was chosen.

3.2.6. Effect of sample volume

In order to ensure the quantitative recovery and increase enrichment factors as much as possible, the effect of sample solution volume on the recovery of La, Eu, Dy and Y was studied by passing 1, 2, 4 and 8 mL of sample solution containing 8 ng of La, Eu, Dy and Y through the CR-SWCNTs coated capillary under the optimized conditions. As shown in Fig. 4, the quantitative recovery of La, Eu, Dy and Y could be obtained in the whole tested sample solution volume range. To trade off enrichment factor and the analytical speed, 2 mL sample solution volume was selected in this study. Considering that 40 μL 0.8 mol/L HNO_3 was selected as the eluent solution, an enrichment factor of 50 was obtained.

3.2.7. The interference of the coexisting ions

To investigate the effect of common coexisting ions on the separation/precoencetration and determination of La, Eu, Dy and Y, different concentrations of K^+, Na^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{3+}, Mn^{2+}, Cu^{2+} and Zn^{2+} were added in 1 ng/mL of La, Eu, Dy and Y solution, respectively. The obtained sample solutions were subjected to the general procedure. The tolerance limit was defined as the largest amount of coexisting ions making the recovery of the target elements maintaining in the range of 90–110%. The experimental results show that the tolerance amount of coexistence ions are: Na^+, K^+ (1.0 mg/mL); Mg^{2+}, Ca^{2+} (0.5 mg/mL); Mn^{2+} and Zn^{2+} (0.1 mg/mL); Cu^{2+} (0.05 mg/mL); Al^{3+} and Fe^{3+} (0.01 mg/mL), indicating that the prepared CR-SWCNTs coated capillary has an excellent selectivity for the target elements under the optimal conditions.

3.3. Capillary stability and adsorption capacity

The lifespan of the prepared CR-SWCNTs coated capillary was studied, and the experimental results show that the CR-SWCNTs coated capillary could be reused for more than 100 times with the recovery for the target analytes still keeping above 90%.

In order to study the adsorption capacity of CR-SWCNTs coated capillary, a sample solution containing 20 ng/mL of La, Eu, Dy and Y was continuously pumped through the CR-SWCNTs coated capillary, each 1 mL effluent fraction was collected and the concentration of the target analytes was determined by FETV-ICP-OES. The maximum adsorption capacities of the CR-SWCNTs coated capillary evaluated from the breakthrough curve were 0.8, 0.7, 0.7 and 0.7 μg/m for La, Eu, Dy and Y, respectively.

3.4. Analytical performance

Under the optimal experimental conditions, the analytical performance of the developed method was evaluated and the results are listed in Table 2. The linear range was in the range of 0.35–30 ng/mL for La and Dy and 0.1–10 ng/mL for Eu and Y. The theoretical enrichment factor is 50-fold. According to the definition of IUPAC [35], the limit of detection, expressed as the concentration (or the quantity), is derived from the smallest measure that can be detected with reasonable certainty for a given analytical procedure. Based on 3 times standard deviation of the blank signal, the limits of detection of La, Eu, Dy and Y were calculated to be in the range of 0.03 (Y)–0.12 (La) ng/mL.

Table 3
Comparison of analytical performance of the proposed method with other method for the determination of REEs.

Sample pretreatment technique	Coatings/adsorbent	Enrichment factor	LODs (ng/mL)	Extraction time (min)	sample	Detection technique	Ref
CME	CR-SWCNTs	50 (> 200 is available)	0.03–0.12	Appr. 14	hair	ICP-OES	This work
PAME	Polymer monolith	12.5–15.1	0.83–1.47	Appr. 6	tea	MPT-AES	[36]
SPE	carbon-ferrite magnetic nanocomposite	141–246	0.5–10	15	soil	ICP-OES	[37]
SPE	C18-cartridge modified with l-(2-pyridylazo) 2-naphtol	275–382	0.011–0.069	20	natural water samples	ICP-OES	[38]
SPE	tribromoarsenazo–cetylpyridinium bromide–naphthalene	1–200	1.3–8.6	10	bush branches and leaves, and citrus leaves	ICP-OES	[39]

MPT-AES, microwave plasma torch-atomic emission spectrometry.

Table 4
Analytical results and recoveries of analytes in real sample of human hair.

Elements	Added (μg/g)	Found[a] (μg/g)	Recovery (%)
La	0	0.048 ± 0.009	105
	0.06	0.111 ± 0.012	
Eu	0	0.005 ± 0.001	95
	0.004	0.0088 ± 0.0004	
Y	0	0.064 ± 0.005	93
	0.05	0.110 ± 0.005	
Dy	0	0.0159 ± 0.0012	106
	0.01	0.0265 ± 0.003	

[a] Mean value ± standard deviation, $n=3$.

Table 5
Analytical results of analytes in standard material of human hair (GBW07601).

Elements	Found[a](μg/g)	Certified (μg/g)	*T*-test[b]
La	0.045 ± 0.012	0.049 ± 0.008	0.58
Eu	0.005 ± 0.001	(0.006)[b]	1.73
Y	0.090 ± 0.004	0.084 ± 0.016	2.60
Dy	0.015 ± 0.001	(0.017)[b]	3.46

$t_{0.02,\ 3}=4.54$.
[a] Mean value ± standard deviation, $n=3$.
[b] recommended values.

The preparation reproducibility of the CR-SWCNTs coated capillary was evaluated. Seven capillaries prepared in the same batch and five capillaries prepared in five batches were tested for the extraction of four target elements from an aqueous solution ($C_{La,\ Dy}=1.4$ ng/mL; $C_{Y,\ Eu}=0.25$ ng/mL). The experimental data listed in Table 2 reveals that satisfactory reproducibility was achieved in the preparation of CR-SWCNTs coated capillary. The relative standard deviations (RSDs) were 4.1–4.4% ($n=7$) within one batch and 5.7–6.1% ($n=5$) among the different batches.

Table 3 lists the comparison of the analytical performance of the proposed method with other methods involving solid phase extraction or solid phase microextraction techniques for the determination of REEs in various samples. As can be seen, the proposed CR-SWCNTs coating CME-FETV-ICP-OES is obviously featured with high enrichment factor, fast extraction dynamics, simple operation, and good selectivity, with the application potential for the analysis of complicated samples.

3.5. Sample analysis

The developed method was applied for the determination of La, Eu, Dy and Y in human hairs, and the analytical results along with the recovery for the spiked samples are given in Table 3. As can be seen, the recoveries of the target elements for the spiked human hair samples are in the range of 93–106%.

To validate the accuracy of the method, a Certified Reference Material of GBW07601 human hair was analyzed and the analytical results are shown in Table 4. As can be seen, the determined values are in good agreement with the certified or recommended values. Table 5

4. Conclusions

A stable homogeneous CR-SWCNTs coated capillary was prepared and a new method of CME-FETV-ICP-OES for the determination of trace La, Eu, Dy and Y in human hair was successfully established. The developed method has the advantages of simplicity, high sensitivity, less sample and reagents consumption, and is suitable for the analysis of trace and ultratrace rare earth elements in environmental and biological samples with complicated matrix.

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