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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 ( $3\sigma$ ) of  $0.12 \text{ ng mL}^{-1}$  for La,  $0.03 \text{ ng mL}^{-1}$  for Eu,  $0.11 \text{ ng mL}^{-1}$  for Dy and  $0.03 \text{ ng mL}^{-1}$  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) ( $C_{\text{La}}, C_{\text{Dy}} = 1.4 \text{ ng mL}^{-1}$ ;  $C_{\text{Y}}, C_{\text{Eu}} = 0.25 \text{ ng mL}^{-1}$ ,  $n = 7$ ) in one batch, and from 5.7% (Eu) to 6.1% (Y) ( $C_{\text{La}}, C_{\text{Dy}} = 1.4 \text{ ng mL}^{-1}$ ;  $C_{\text{Y}}, C_{\text{Eu}} = 0.25 \text{ ng mL}^{-1}$ ,  $n = 5$ ) 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.

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## 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/ultra-trace 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 pretreatment 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  $\pi$ - $\pi$  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 ( $\mu$ m)	25
Exit slit-width ( $\mu$ m)	25
ETV parameters	
Drying temperature ( $^{\circ}$ C)	120, ramp 15 s, hold 20 s
Ashing temperature ( $^{\circ}$ C)	1200, ramp 15 s, hold 15 s
Vaporization temperature ( $^{\circ}$ C)	2600, for 5 s
Introducing volume ( $\mu$ L)	50

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