



Enrichment of scandium by carbon nanotubes in the presence of calcium matrix

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ABSTRACT

The sorption behavior of Sc(III) on oxidized carbon nanotubes (CNTs) for the separation and preconcentration of trace amounts of scandium ions from aqueous solutions was investigated. The mechanism of separation and the effects of pH, flow rate, sample volume and interferences, with special focus on calcium, on the recovery of Sc were systematically studied and optimized. Generally, the sorption of scandium increases with increasing pH. For pH in the range of 2.5–5.5 the sorption of Sc(III) onto CNTs is quantitative, but its removal in the pH range of 1–3.5 is mainly attributed to sorption, while at pH > 4 there is overlap with the precipitation curve, indicating insignificant sorption. The adsorbed amount of Sc(III) at pH 2.0 was 42.0 mg g⁻¹. The procedure was applied to the enrichment of scandium with ICP-OES detection for natural water analysis with a preconcentration factor of 250 and a detection limit (3σ) of 0.05 μg L⁻¹.

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1. Introduction

Scandium, together with the lanthanides and yttrium, belongs to the rare earth elements, being similar in chemical properties and deposited in ores. This metal has attracted much interest because of its numerous and important applications in high-technology materials such as superconductors, laser crystals, supermagnetics, advanced materials, nuclear technology and alloys [1–3]. Since the use of scandium in industrial applications has been increasing, the possibility of its release into the environment has also increased. Sc has been detected in several runoff aquatic ecosystems as a consequence of industrial and agricultural practices [4–6].

Inductively coupled plasma optical emission spectroscopy (ICP OES) is currently recognized as one of the most efficient methods to detect scandium in environmental samples [7,8], especially since it is far less impacted by spectral interferences compared to its mass spectrometric (ICP MS) counterpart. However, ICP OES is not sensitive enough to detect low scandium levels and a preconcentration and separation step is often required to enhance the sensitivity and selectivity of Sc quantification [9,10].

It is now widely accepted that the application of the solid phase extraction (SPE) technique for the preconcentration and separation of trace analytes offers numerous advantages over liquid–liquid extraction, such as high enrichment factors, low consumption of organic solvents,

rapid phase separation and the possibility of easy coupling with spectroscopy techniques either in off-line or on-line modes [11]. The choice of appropriate sorbents is a key point in SPE procedures which will greatly benefit the improvement in analytical performance of SPE techniques. Various chelating agents have been immobilized on silica or polymeric supports including 1-(2-aminoethyl)-3-phenylurea [12], nalidixic acid [13], 4-(2-morinyldiazenyl)-N-(3-(trimethylsilyl)propyl)benzamide [14] and the bifunctional ionic liquid trioctylmethylammonium 1-phenyl-3-methyl-4-benzoyl-5-onate [15]. For the enrichment and determination of scandium concentrations, cellulose based silica nanocomposite [16], carbon-based sorbents [10,17] and ion imprinted polymers [18] have also been proposed.

Carbon nanotubes (CNTs) have been proposed as a novel sorbent for various inorganic and organic compounds due to their large specific surface area [19–21]. The sorption of ionic species, such as scandium ions, is mainly controlled by electrostatic forces, which are related to the various surface functional groups. Oxidation of carbon surfaces can offer not only a more hydrophilic surface structure, but also a larger number of oxygen-containing functional groups (–OH, –C=O and –COOH), increasing the ion-exchange capability of the carbon material.

The purpose of the present work is to develop a solid phase extraction approach using oxidized carbon nanotubes for separation and preconcentration of trace amounts of scandium ions from aqueous solutions. The effect of various experimental parameters on the recovery of Sc was systematically investigated and optimized. Particular attention was paid to the presence of calcium matrix. In environmental samples,

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Ca(II) ions occur in large excess to Sc(III) and may interfere with the extraction and determination of scandium. Moreover, ^{44}Sc , due to its favorable nuclear properties and amenable chemistry, has been recently recognized as a radiometal holding great potential for positron emission tomography (PET) applications [22]. It is usually produced using biomedical cyclotrons via the $^{44}\text{Ca}(p,n)^{44}\text{Sc}$ route; however, it must be separated from the irradiated calcium target [23]. Calcium is a non-toxic element and can be present in radiopharmaceutical preparations in quite large amounts; however, it could influence the yield of the radiolabelling process and thus must be removed to the greatest possible extent before radiopharmaceutical synthesis.

2. Experimental

2.1. Materials and reagents

Carboxylic acid functionalized multi-walled carbon nanotubes (CNTs-COOH, >8% carboxylic acid functionalized) with an average diameter of 9.5 nm and purity >95% were purchased from Aldrich (www.sigmaaldrich.com). The content of surface carboxylic functional groups evaluated using the Boehm titration method was 2.43 mmol g^{-1} . The applied chemicals were of analytical-reagent grade and all solutions were prepared with high-purity deionized water from the Milli-Q system (www.emdmillipore.com). Scandium solutions were prepared from 1000 mg L^{-1} stock solution from Merck (www.merckgroup.com).

2.2. Apparatus

A Thermo Scientific iCAP 6000 ICP OES spectrometer was used for Sc determination. The instrumental settings of the manufacturer were as follows: spectral line 361.384 nm, RF generator power 1.15 kW, auxiliary gas flow 0.5 L min^{-1} , nebulizer gas flow 0.40 L min^{-1} , coolant gas flow 12 L min^{-1} .

Calcium was determined with a Perkin Elmer FAAS 3110 apparatus under conditions recommended by the manufacturer.

The pH values were measured with a pH-meter model 827 (Metrohm Ltd., Switzerland), supplied with a glass-combined electrode.

2.3. Batch sorption experiments

The sample solution (10 mL) containing 5 mg L^{-1} of Sc(III) was taken in a glass stopped bottle after adjusting its pH to the required value using the appropriate buffers. 50 mg of CNTs-COOH were added to the bottle and the mixture was gently shaken for 4 h at room temperature. The supernatant was then decanted and the amount of retained metal ions was calculated as the difference between the initial and final concentration at equilibrium. The sorption efficiency was calculated as the ratio of the amount of Sc in the solution to the initial amount of Sc. The results are based on at least three replicated experiments for each pH value.

2.4. The column procedure

Microcolumns made from pipette tips of 1 mL, packed with 50 mg of CNTs-COOH, with glass wool stoppers at the ends, were used (Fig. 1S). The sample was loaded and eluted with an ISM833 Ismatec peristaltic pump (Fig. 2S). In the preconcentration step the aqueous solution containing scandium at pH 2 was passed through the microcolumn. The column was then rinsed with 0.01 mol L^{-1} HCl. Elution of scandium was done using 2 mL of 2 mol L^{-1} HNO_3 at a flow rate of 1 mL min^{-1} .

3. Results and discussion

3.1. The effect of pH and sample flow rate

The sorption of scandium ions depends on the pH condition of the sample as it affects the surface charge of the CNTs, the degree of ionization and the metal species present in the acid-base media. In the present work, uptake studies of Sc(III) were carried out under batch conditions at a concentration of 5 mg L^{-1} in the pH range 1–8. The results obtained are presented as sorption efficiency in Fig. 1. Significant rises in the removal of scandium occurred as the pH of the solution was increased up to 3, after which quantitative removal was achieved. The low metal uptake observed at low pH may have been due to the higher concentration and mobility of H^+ ions, which have a greater tendency to be sorbed in comparison to Sc(III) ions. However, precipitation also plays a significant role in the removal of heavy metal ions from aqueous solutions [24].

To check the possibility of scandium removal by precipitation, experiments were conducted to measure the pH-dependence of the percentage removal of Sc(III) without CNTs. The standard Sc solution was added to 10 mL of the appropriate buffer solution (in a pH range of 1–8) to obtain a concentration of 5 mg L^{-1} and all samples were shaken for 4 h. They were then passed through a $0.2 \mu\text{m}$ filter (Whatmann) to trap a possible precipitate. Subsequently, scandium from the filter was eluted by 5 mL of 2 M HNO_3 and determined by ICP OES. The percentage removal curves of Sc(III) vs. initial sample pH in the presence and absence of CNTs are presented in Fig. 1. For pH values up to 3 there was a little or no precipitation; significant increase of Sc removal by precipitation (without CNTs) was observed in the pH range of 3–5. Comparison of both curves indicates that removal of Sc(III) in the pH range of 1–3.5 could be mainly attributed to its sorption on carbon nanotubes. The curve in the presence of CNTs at $\text{pH} > 4$ overlaps with the precipitation curve, indicating insignificant sorption.

The hydrated Sc^{3+} ion predominates only at $\text{pH} < 4$, whereas the predominance fields for $\text{Sc}(\text{OH})^{2+}$ and $\text{Sc}(\text{OH})_2^+$ are very narrow [25]. Thus, the observed quantitative sorption of Sc(III) on activated carbon at pH 7.0 without any chelating agent [17] was probably mainly due to the precipitation of scandium hydroxide. The impact of the formation of insoluble scandium compounds on the sorption efficiency was also not tested experimentally in other works using the SPE technique [15, 16]. It can be seen from Fig. 1 that the difference between both curves is greatest at pH 3. However, taking into account the possibility of calcium ion retention, a pH of 2.0 was selected for further experiments.

The influence of sample loading flow rate on scandium recovery was examined under dynamic conditions. 5 mL of the test solutions at

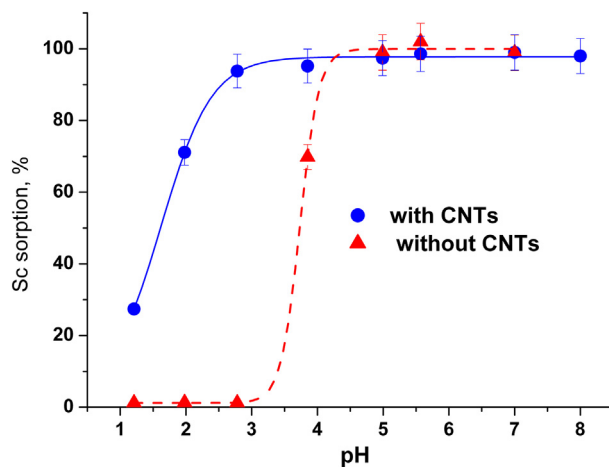


Fig. 1. The comparison of pH and precipitation on Sc(III) removal with [27] and without CNTs. Conditions: Initial metal concentration: 5 mg L^{-1} , solution volume 10 mL; mass of sorbent 50 mg; shaking time: 4 h.

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