

Americium and Samarium Determination in Aqueous Solutions after Separation by Cation-Exchange

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ABSTRACT

The concentration of trivalent americium and samarium in aqueous samples has been determined by means of alpha-radiometry and UV-Vis photometry, respectively, after chemical separation and pre-concentration of the elements by cation-exchange using Chelex-100 resin. Method calibration was performed using americium (Am-241) and samarium standard solutions and resulted in a high chemical recovery for cation-exchange. Regarding, the effect of physicochemical parameters (e.g. pH, salinity, competitive cations and colloidal species) on the separation recovery of the trivalent elements from aqueous solutions by cation-exchange has also been investigated. The investigation was performed to evaluate the applicability of cation-exchange as separation and pre-concentration method prior to the quantitative analysis of trivalent f-elements in water samples, and has shown that the method could be successfully applied to waters with relatively low dissolved solid content.

Keywords: trivalent f-elements; determination; cation-exchange; composition; chemical recovery

1. INTRODUCTION

Analysis of man-made radionuclides in environmental samples is of particular interest with respect to radiation protection purposes and studies on the behaviour and transport of radionuclides in natural environment (e.g. air, water etc.). There is particular interest regarding actinides (e.g. U, Pu, Np, Am Cm), because of the amounts produced in fission reactors and their long-lived radionuclides, which are generally highly radiotoxic alpha radiation emitters. The trivalent state is one of the most common oxidation states of minor actinides (e.g., Am and Cm) in aqueous solutions under most environmental conditions. Additionally, the trivalent state is one of the four thermodynamically stable oxidations states of plutonium, which is a key radioelement in spent fuel and maybe the predominant oxidation state under reductive conditions [1].

Actinides and lanthanides show similar chemical behaviour in solid and aqueous phase, if present in the same oxidation state. This is attributed to the fact, that lanthanide elements and particularly Nd, Sm and Eu (112.3, 109.8 and 108.7 pm, respectively) have almost identical ionic radii with actinide elements such as Am and Cm (111.5 and 111 pm, respectively) in the M(III) oxidation state [2]. On the other hand, the aquatic chemistry of lanthanide ions is dominated by trivalent oxidation state under environmentally relevant conditions. Because of the direct similarities between the solid and aqueous phase chemistry of some of the actinides and lanthanides and the fact, that lanthanides are non-radioactive and can be handled in relatively higher amounts/concentrations without special safety precautions possess excellent spectroscopic properties, we have used besides americium (Am-241) samarium as analogue for Am(III) in this study [3].

Sample treatment for the radionuclide separation and pre-concentration is generally a

prerequisite prior analysis of alpha emitting radionuclides in environmental matrices. In this context, the pre-analytical procedures involved play a key role in the design and selection of a cost-effective technique. Chelex-100 as cation exchanger [4] and tributyl-phosphate (TBP) as complexing agent in liquid extraction [5-7] have been extensively investigated in the separation and pre-concentration of uranium, thorium and plutonium from aqueous solutions. Moreover Chelex-100 has been successfully applied in the separation of uranium from natural waters [8].

In this study, we have investigated the applicability of Chelex-100 in the separation and pre-concentration of americium and samarium from aqueous solutions prior analysis. Results obtained from experimental investigations regarding chemical recovery and the effect of physicochemical parameters such as pH, salinity, and the presence of competitive cations (e.g. Fe^{3+} and Ca^{2+}), humic acid and silica colloid concentration, on the separation of the trivalent actinide/lanthanide from aqueous solutions by Chelex-100 are presented and discussed. The investigation was performed to evaluate the applicability of cation exchange and as separation and pre-concentration procedure prior to the determination of americium in water samples.

2. MATERIALS AND METHODS

In all experiments analytical grade reagents and de-ionized water were used. For tracing the test solution with 100 mBq we used Am-241 standardized solution (North American Scientific Inc.) and the Sm(III) solutions were prepared from $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ salt obtained from Aldrich Co. The Chelex-100 resin (18-50 mesh, Merck) was used as received. HNO_3 solutions of various concentrations (e.g., 2 and 8M HNO_3) were prepared by diluting a concentrated solution (68% HNO_3 , Aldrich Co). 30% v/v $(\text{NH}_4)_2\text{SO}_4$ solutions were prepared by dissolving ammonium sulfate (99.999%, Aldrich Co.) in de-ionized water.

The radiometric analysis of Am-241 was performed using a high-resolution alpha-spectrometer (Alpha Analyst Integrated Alpha Spectrometer, Canberra) equipped with semiconductor detectors, after pre-concentration and separation of the radionuclide by cation exchange and (finally) its electrodeposition on stainless steel discs. On the other hand the quantitative analysis of samarium was performed by spectrophotometry using arsenazo-III [9]. The photometer was calibrated using a series of samarium standard solutions and from the slope of corresponding calibration curve the molar extinction coefficient ϵ of the Sm(III)-arsenazo at 650 nm was determined, $\epsilon = (27000 \pm 1000) \text{ (l mol}^{-1} \text{ cm}^{-1}\text{)}$. All measurements were repeated and the error bars in the graphs correspond to the standard deviation, which was calculated based on the repeated measurements.

For the evaluation of the pre-analytical procedure (e.g. the ion-exchange efficiency) the present method was applied to laboratory solutions of constant samarium concentration ($2 \times 10^{-6} \text{ mol/l}$) and variable composition (0.1, 0.3, 0.5, 0.7 and 1 M NaCl; 0.1, 0.3, 0.5, 0.7 and 1 M $\text{Ca}(\text{NO}_3)_2$; 0.05, 0.1, 0.5 and 1 mM FeCl_3 ; 5, 10, 50, 100 and 150 ppm SiO_2 ; 5, 10, 50, 100 and 150 ppm humic acid, sodium form). The solutions were prepared by dissolution of the appropriate amount of the corresponding salt (analytical grade, Aldrich) in de-ionized water and addition of a constant volume of the samarium standard solution.

3. RESULTS AND DISCUSSION

Effect of pH

A possible interaction between Am^{3+} and the iminodiacetic moiety is schematically given in Fig. 1 and could be described as a cation exchange reaction between the protons and the americium cations. Because proton concentration is a key factor governing both, the proton dissociation of the iminodiacetic moieties and Am(III) or trivalent lanthanide hydrolysis [10], the binding of the trivalent actinide/lanthanide by the resin is strongly pH dependent. According to experimental data shown in Fig. 2, the optimum pH for the separation efficiency of americium and samarium is given at pH 2.5. The similar pH-dependency of the separation efficiency for both metal ions proves the similar chemical behavior of the trivalent actinide and lanthanide in aqueous solutions. The significantly lower separation efficiency for americium below and above the optimum pH (pH= 2.5) is attributed to the orders of magnitude lower americium concentration (micro-mol range) compared to samarium concentration in solution (femto-mol range). On the other hand the effective binding of the metal ions even at relatively pH can be explained by the increased chemical affinity of M^{3+} for the iminodiacetic moieties of the Chelex-100 resin. Below and above pH 2 the affinity is decreasing because the concentration of the competing protons increases dramatically and because M(III) starts, forming hydroxo complexes species, which stabilize the metal ions in solution [10].

Effect of salinity and Competitive Cations

Because waters to be treated are complex containing dissolved species (e.g. ions and colloids), the effect of such species has been investigated as a function of their concentration in the test solution [11-13].

The effect of salinity on the chemical recovery of samarium is summarized graphically in Fig. 3. Increasing salinity (e.g. $[\text{NaCl}] > 0.1 \text{ M}$) results in a dramatic decrease of the chemical recovery ($< 10\%$) of the trivalent lanthanide, supporting basically the assumption that the binding of M^{3+} by the Chelex-100 resin at pH 2.5 is based on electrostatic interactions and a cation exchange mechanism. Hence, increasing salinity (e.g. $[\text{Na}^+]$) in solution results in decreasing the amount of resin-bound lanthanide, indicating that the method could be restricted only to low-salinity waters.

On the other hand, iron even at low concentration (10^{-4} mol/l) affects significantly the lanthanide recovery and leads to almost 45% separation recovery at $[\text{Fe}^{3+}] = 0.01 \text{ mol/l}$ (Fig. 4). The effect is attributed to the higher affinity of the resin for the Fe^{3+} cations under the given conditions (pH 2.5). Fe^{3+} cations present similar charge and hence increased tendency for complex formation competing effectively the trivalent actinide/lanthanide cations regarding binding by the resin through its iminodiacetic moieties, resulting in lower chemical recovery of the studied elements.

Effect of Colloids

The effect of colloidal species on the chemical recovery of samarium from aqueous solution by Chelex-100 has been investigated using silica and humic acid colloids, representing the inorganic and organic colloids, respectively. Silica colloids were chosen because these species are omnipresent and present even at low pH negatively charged surface ($\text{pzc} \sim 2$), which attracts positively charged metal ions. On the other hand humic acids are also naturally occurring colloids affecting strongly the chemical behavior and migration of pollutants in the geosphere [14].

The effect of colloidal species (e.g. silica and humic acid colloids) present in solution on the chemical recovery of trivalent actinides/lanthanides by Chelex-100 from

aqueous solutions is shown in Fig. 5. The data in Fig. 5 clearly show that increasing both silica and humic acid concentration results in small reduction of the chemical recovery of the trivalent metal ions. The effect is more pronounced for the organic colloids indicating on the higher affinity of humic acid for trivalent lanthanides and actinides. The binding of the trivalent lanthanides/actinides is based on the interaction of the M(III) cations with the hydroxy groups of the metal oxide and the carboxylic groups of the humic acid colloids [15, 16]. However, this interaction is significantly smaller than the corresponding interaction of thorium resulting in the formation of very stable thorium pseudocolloids [14], which stabilize far effective thorium in solution.

Conclusions

The results obtained from this study lead to following conclusions:

- The maximum separation efficiency of Chelex-100 for trivalent lanthanides/actinides is given at pH 2.5 and differs significantly (about 2 pH units) from the corresponding separation efficiency for uranium (pH 4.5), indicating that a pH-adjusted selectivity of Chelex-100 for these two actinides could be possible.
- Increasing salinity (e.g. $[\text{Na}^+]$ and $[\text{Ca}^{2+}]$), iron ($[\text{Fe}^{3+}] > 10^{-4}$ mol/l) and colloid concentration in solution results generally in decreasing chemical recovery. Nevertheless, the method could be successfully applied for americium determination in waters of low-salinity and metal-ion contamination.

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Figure Captions

Fig. 1: Schematic illustration of the Am^{3+} binding by the iminodiacetic moieties of the Chelex-100 resin

Fig. 2: Relative chemical recovery of americium and samarium by cation exchange using Chelex-100 as a function of pH

Fig. 3: Separation recovery of samarium as a function of the Na^+ ion concentration in solution

Fig. 4: Separation recovery of samarium as a function of the Fe^{3+} ion concentration in solution

Fig. 5: Separation recovery of samarium as a function of the humic acid and silica colloid concentration in solution

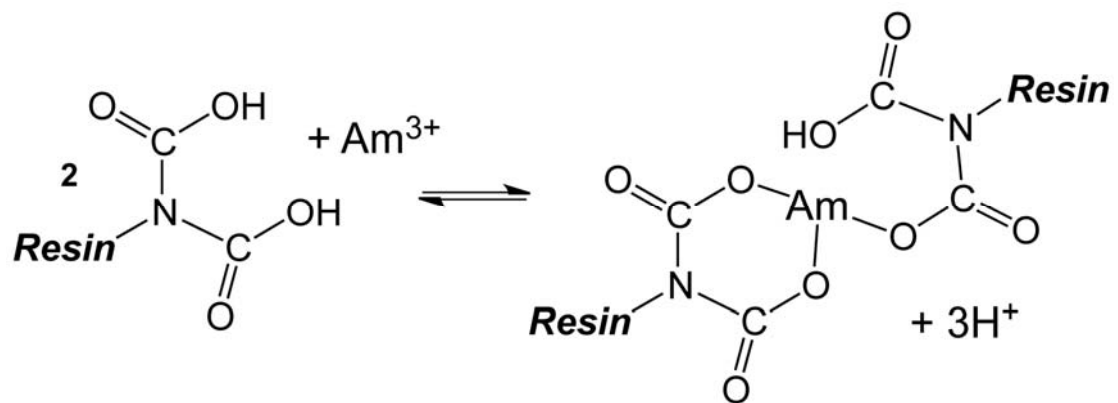


Fig. 1: Schematic illustration of a possible binding of Am(III) by the iminodiacetic moieties of the Chelex-100 resin

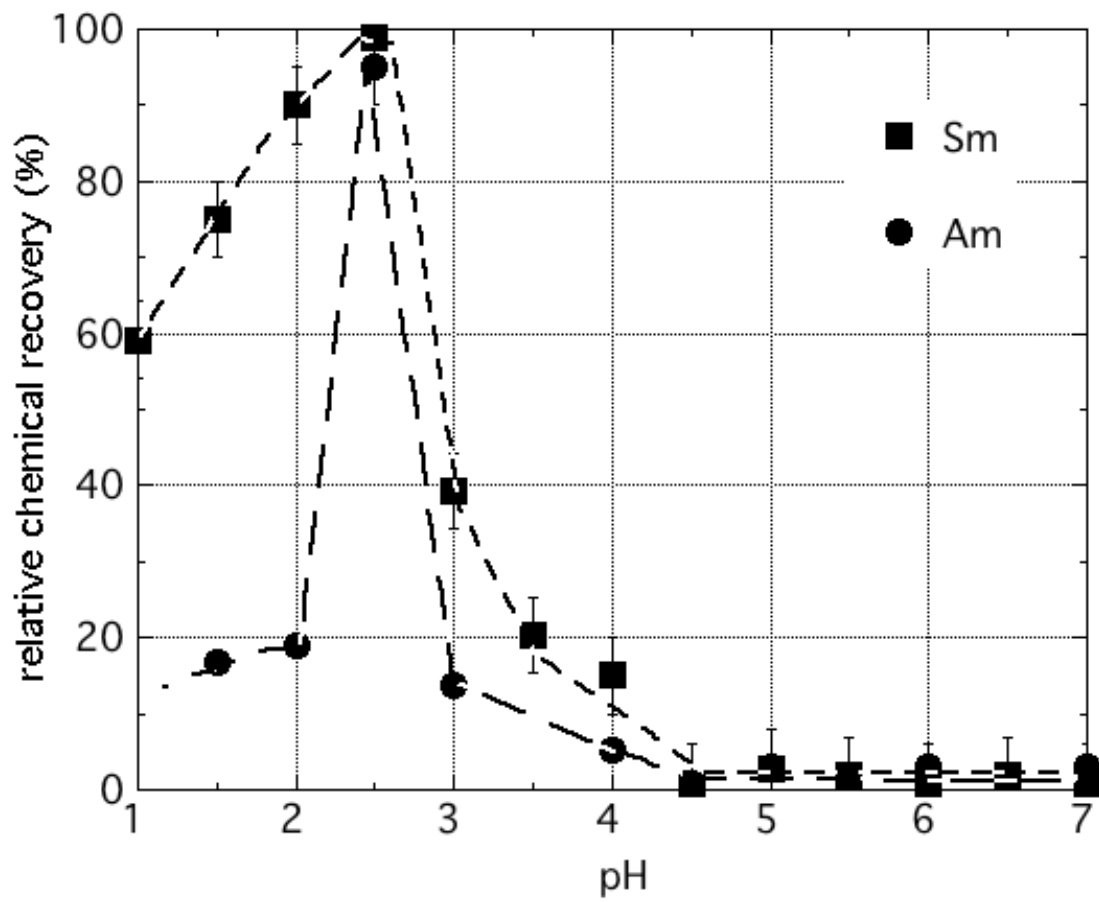


Fig. 2: Relative chemical recovery of americium and samarium by cation exchange using Chelex-100 as a function of pH

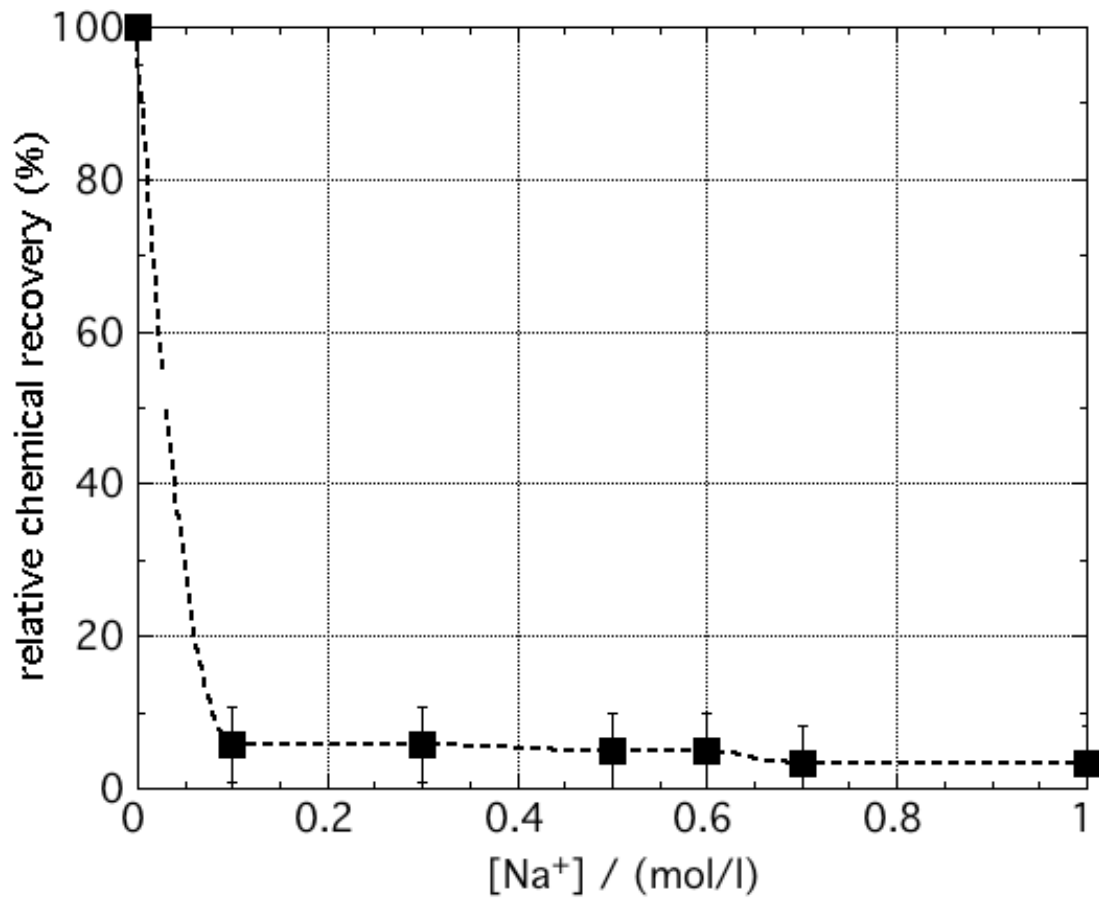


Fig. 3: Separation recovery of samarium as a function of the Na⁺ ion concentration in solution

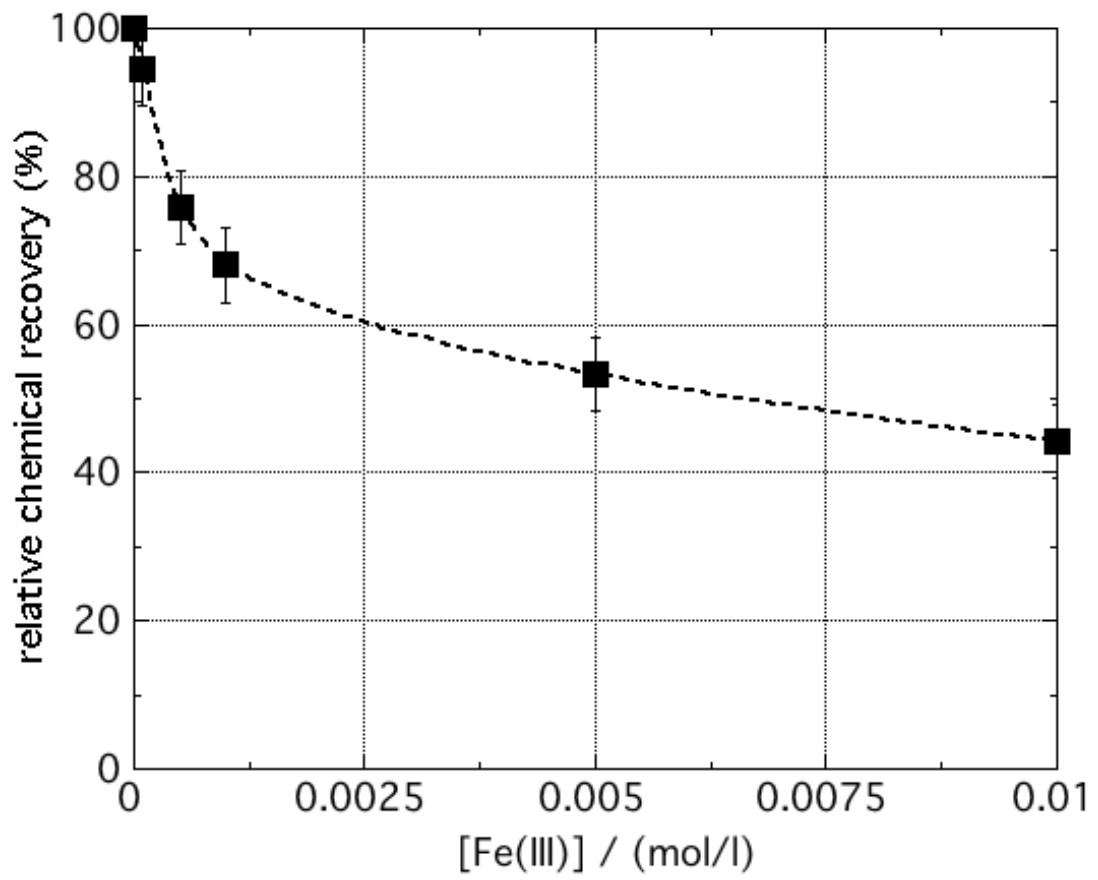


Fig. 4: Separation recovery of thorium as a function of the Fe^{3+} ion concentration in solution

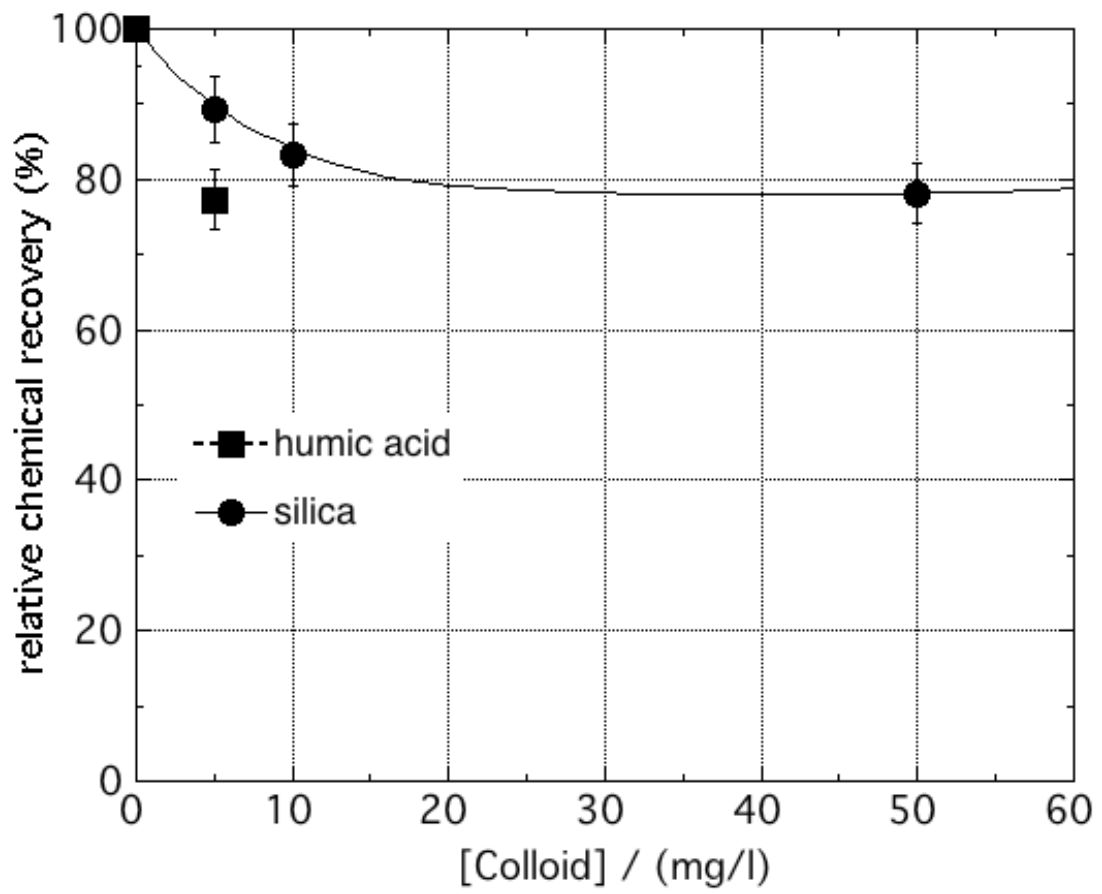


Fig. 5: Separation recovery of samarium as a function of the humic acid and silica colloid concentration in solution