

Contribution to selective strontium separation and its sorption behaviour study using ^{85}Sr as radioindicator

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SUMMARY

An optimization of extraction procedure for Sr^{2+} in model solutions containing many-fold abundance of interfering ions using a commercially available mixture of cis-syn-cis and cis-anti-cis isomers of DCH18C6 has been carried out. ^{85}Sr has been used as radioindicator, trichlormethane as organic solvent and picric acid as counter-ion. At the optimal extraction parameters including 2-fold molar abundance of the extraction reagent, 350-fold abundance of picric acid and pH value in range 3.6–3.8 a 500-fold abundance of Ca^{2+} and Mg^{2+} ions do not have significant interfering effect on extraction selectivity of strontium. At the same conditions a 2-fold abundance of Ba^{2+} ions measurable decreases the extraction efficiency of strontium and a 50-fold abundance of Ba^{2+} disables the realization of extraction. At low Sr^{2+} concentrations, not exceeding $10^{-6} \text{ mol dm}^{-3}$, lignite and natural clinoptilolite show high distribution ratios, while at higher concentrations the ones significantly decrease. Montmorillonite shows from the investigated sorbent samples the lowest distribution ratio. For lignite the influence of the time of foregoing contact with water is for strontium sorption not significant.

Keywords: strontium, DCH18C6, selective extraction, sorption, lignite, clinoptilolite.

INTRODUCTION

Strontium and barium rank 15th and 16th in order of element abundance in the Earth's crust with concentrations not exceeding 400 ppm. The abundance of strontium is far smaller in comparison with the most important alkaline metals (the concentration of Ca in Earth's crust reaches 41000 ppm and the one of Mg reaches 23000 ppm), nevertheless its abundance is 7-fold that of zinc and copper and 30-fold that of lead (Lide 2005). Sr has

no significant biological functions and the reason why its chemical and physical-chemical characteristics are frequent subjects of investigation is as the fact that in the fission process of the mostly used nuclear fuel, namely ^{235}U , its extremely radiotoxic isotope ^{90}Sr is produced with high yields reaching ~6%. As a result of nuclear activity of the mankind as well as the chemical and biochemical similarity of Ca and Sr, in human skeleton the strontium content averages approximately at 4 SU of ^{90}Sr ¹. Owing to its chemical similarity to calcium the contamination of the environment with ^{90}Sr – the consequence of whatever fission products effluences – leads to the possibility of its massive penetration to the food chain via agricultural production. The nuclear properties ^{90}Sr bring about detection problems, which are to solve by including a sample preparation step, namely the selective separation of strontium. The mentioned step represents by environmental samples, as a rule, a difficult task (*Horwitz et al.* 1991, *Andryushchenko et al.* 2003), which is to be handled using specific extraction reagents (*Koreňová et al.* 1990). Some derivatives of macrocyclic polyethers, namely DCH18C6 show for the relevant separation promising results. The extraordinary mobility of strontium in soils significantly influences the remediation potentiality of radiostrontium-contaminated ones (*Sysoeva et al.* 2005). This fact on one hand enables the application of wide scale of natural sorbents, however in the same time the rapid contamination of underground water collectors makes the remediation more difficult.

MATERIALS AND METHODS

Samples & Reagents: The radioindicator etalon for the strontium extraction selectivity investigation as well as for the strontium distribution ratios (D_c) determination, namely $^{85}\text{SrCl}_2$ solution of known specific activity (106.6 kBq g^{-1}) and of known chemical concentration (20 mg dm^{-3} diluted in 3 g dm^{-3} HCl) was obtained from the Czech Meteorology Institute (Czech Republic). All the chemicals used were of analytical reagent grade. The stock solution of the relevant crown ether in trichlormethane was prepared from DCH18C6 – a mixture of cis-syn-cis and cis-anti-cis isomers (Across Organics, Belgium). Aqueous solutions of picric acid were prepared using the relevant reagent (Merck, Germany). All aqueous solutions have been prepared using ultrapure deionized water ($0.054 \mu\text{S cm}^{-1}$). Solutions of interfering cations (Ca^{2+} , Mg^{2+} , Ba^{2+}) were prepared from their commercially available chlorides. Sodium citrate and hydrochloric acid of proper concentrations were used as buffer solutions.

The determination of D_c for strontium has been realized for five different sorbents, as follows: a) representative lignite sample obtained by grinding, quartering, sieving (fraction under 1.2 mm) and air-drying of relevant young coal collected from coal-mining site Záhorie (South-West Slovakia), b) and c) the above mentioned sample after 5 minutes and

¹ SU (Strontium unit) represents a unique specific activity unit of ^{90}Sr referring to calcium content in skeleton, which quantitatively equals to $3.7 \cdot 10^{-2} \text{ Bq g}^{-1}$ (1 pCi g^{-1}) (*Takizawa et al.* 2000).

20 hours of agitation with deionised water and air drying, d) representative clinoptilolite sample gained by quartering and sieving of grinded (fraction under 0.5 mm) natural zeolite from the mining site Nižný Hrabovec (East Slovakia), e) montmorillonit K10 with surface area 220–270 m² g⁻¹ (Aldrich, Swiss).

Extraction procedure: For solvent extraction experiments 20 cm³ glass vessels have been applied. As for aqueous and organic phases, an equal volume, 2.5 cm³ have been chosen. The extraction mixtures were horizontally shaken (agitation intensity 2 rps) at 25 °C. Immediately after the separation of phases 1 cm³ of both aqueous and organic phases was taken and the counting rate in all of the resulting solutions has been measured using a gamma spectrometric detection assembly. All analytical procedures have been carried out in three replicate experiments.

Distribution ratios: The experiments targeted the strontium distribution ratios have been carried out using 10 cm³ centrifuge tubes containing 0.05 g of the relevant sorbent and 5 cm³ of radioactively labelled Sr²⁺ solutions of different initial concentrations (from thousandth to tens of mmols). In order to reach quasi-equilibrium state an equal agitation process – 20 h of horizontal shaking by 2 rps – has been chosen. After centrifugation (5 minutes, 3,500 rpm, centrifuge arm length 5.5 cm) the specific counting rates of supernatants have been measured using a gamma spectrometric detection assembly and the particulate distribution ratios have been calculated according the relation, that used by *Wenning et al.* (2000).

Radiometric analysis: For radiometric determinations of ⁸⁵Sr in water, as well as in organic phases a gamma spectrometric detection assembly consisted of the gamma spectrometric scintillation detector 54BP54/2-X, the well type scintillation crystal NaI(Tl) (Scionix, Netherlands) and the data processing software Scintivision32 (Ortec, USA) were used. The counting time 400 s was sufficient for obtaining data with the relative detection error < 2%.

RESULTS AND DISCUSSION

The choice of expected interfering cations was carried out considering the presumptive concentrations in the sample matrixes and the related size correlation with DCH18C6. Our experiments show (*Figure 1*) that the presence of Ca²⁺ and Mg²⁺ has only a negligible influence on the strontium extraction even at 500-fold abundance. However, in markedly lower abundance, Ba²⁺ influences the extraction of Sr²⁺ significantly (*Figure 2*).

The interference effects of Ba²⁺ ions are more evident in comparison with the Ca²⁺ and Mg²⁺ ones. This feature is obviously due to the stronger impact of the favourable ionic radius of Ba²⁺ to the cavity structure of the DCH18C6 than the adequate coincidence of Ca²⁺ and/or Mg²⁺ with the one. The relevant complexation size compatibility plays apparently a critical role. The effect of phase contact time on the extraction efficiency of strontium in the presence of interfering cations at the described conditions we investigated as well. The results show only negligible extraction efficiency changes for time interval 2–120 minutes.

Figure 1. The effect of presence Ca^{2+} and Mg^{2+} on the extraction of strontium
 ($c_{\text{Sr}^{2+}} = 1.25 \cdot 10^{-4} \text{ M}$, $c_{\text{DCH18C6}} = 2.5 \cdot 10^{-4} \text{ M}$, $c_{\text{C6H3N3O7}} = 4.36 \cdot 10^{-2} \text{ M}$)

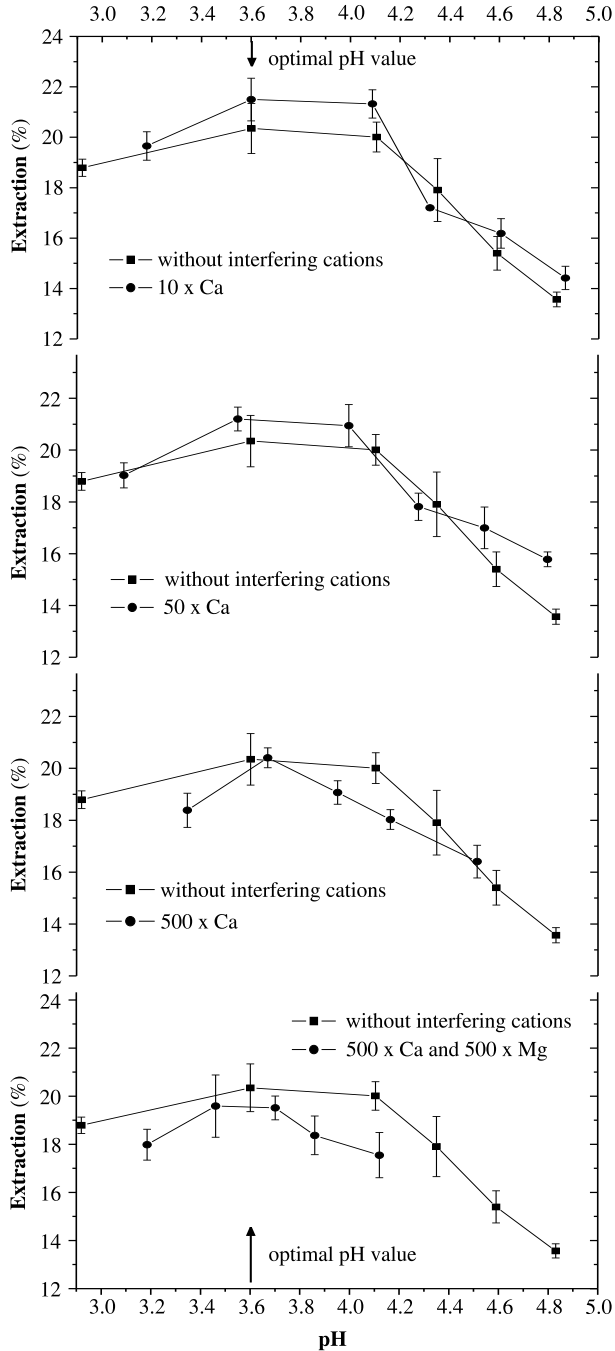
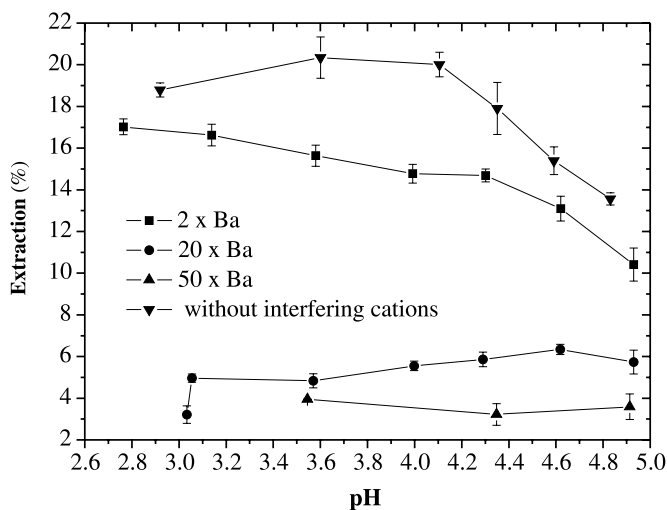
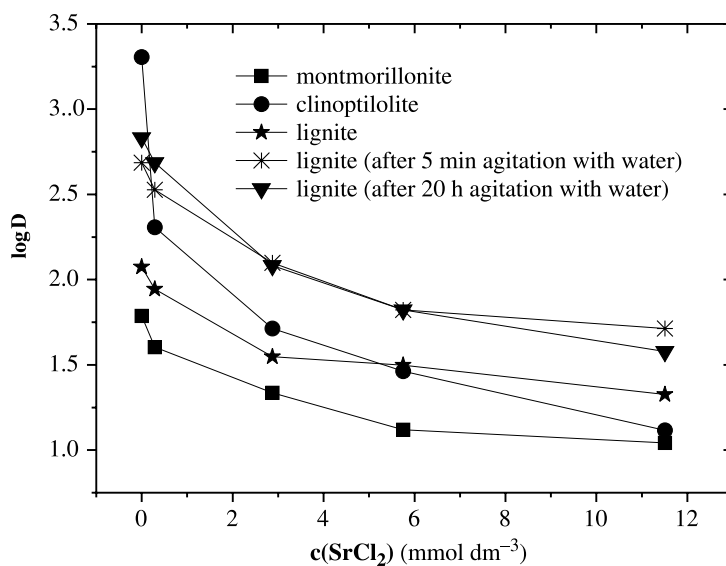


Figure 2. The effect of presence Ba^{2+} on the extraction of strontium ($c_{Sr^{2+}} = 1.25 \cdot 10^{-4} M$, $c_{DCH18C6} = 2.5 \cdot 10^{-4} M$, $c_{C6H3N3O7} = 4.36 \cdot 10^{-2} M$)



From the measurements concerning the distribution ratios of strontium for investigated sorbents the following rising order of sorption ability is apparent: montmorillonite < natural clinoptilolite < lignite. Using initial Sr^{2+} concentrations below $10^{-6} \text{ mol dm}^{-3}$, natural clinoptilolite reaches – beside lignite – an extremely high distribution ratio value as well.

Figure 3. Dependence of strontium distribution ratio on initial Sr^{2+} concentration for the investigated sorbents



As the initial strontium concentration rises, the distribution ratios for studied sorbents distinctly decrease. While the lignite samples after agitation with deionized water show sorption increase, the contact time with water do not play in time interval from 5 minutes to 20 hours any significant role (*Figure 3*). The obtained results show good correlation with the recent literature data and in the same time they enable a more objective assessment of applicability of the investigated natural sorbents for strontium immobilization.

CONCLUSIONS

The investigated extraction reagent, namely the mixture of cis-syn-cis and cis-anti-cis isomers of DCH18C6 in trichlormethane ($c_{\text{DCH18C6}} = 2.5 \cdot 10^{-4}$ M) using picric acid as counter ion ($c_{\text{C}_6\text{H}_3\text{N}_3\text{O}_7} = 4.36 \cdot 10^{-2}$ M) at pH 3.6–3.8 is suitable for selective strontium separation ($c_{\text{Sr}^{2+}} = 1.25 \cdot 10^{-4}$) in as much as 500-fold molar abundance of Ca^{2+} and Mg^{2+} ions reaching 19% extraction efficiency. The interference of Ba^{2+} ions, however, causes severe decrease of strontium separation efficiency at much lower abundance not exceeding 2-fold molar concentration that of strontium. At Sr^{2+} concentrations $< 10^{-6}$ M lignite and natural clinoptilolite demonstrate relatively high distribution ratios reaching for wit water treated lignite $D \cong 700 \text{ cm}^3 \text{ g}^{-1}$ and for clinoptilolite even $D \cong 2000 \text{ cm}^3 \text{ g}^{-1}$. At higher Sr^{2+} concentrations the relevant distribution ratios fall down and at 10^{-3} M concentration do not exceed $100 \text{ cm}^3 \text{ g}^{-1}$.

Stroncium szelektív szeparációjához és szorpciós tulajdonságainak vizsgálatához való ^{85}Sr radioindikátoros hozzájárulás

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ÖSSZEFOGLALÁS

Sr^{2+} zavaró hatású ionok sokszoros többletének jelenlétében való extrakciós szeparációjának optimalizálását valósítottuk meg. Extrakciós reagensként DCH18C6 cis-syn-cis és cis-anti-cis izomerjeinek elegyét, radioindikátorként ^{85}Sr -ot, szerves oldószerként triklórmetánt és ellen-ionként pikrinsavat alkalmaztunk. A meghatározott paraméterek mellett – beleértve az optimalizált 3,6–3,8 pH-értéket, az extrakciós reagens 2-szeres és a pikrinsav 350-szeres többletét – 500-szoros Ca^{2+} és Mg^{2+} többletének nem volt jelentősebb hatása a

stroncium szelektív extrakciójára. Ezzel ellentétben a Ba^{2+} ionok 2-szeres többlete viszont jelentősen csökkentette a stroncium extrakciójának hatásfokát és 50-szeres Ba^{2+} többlet mellett az extrakciót már nem lehet megvalósítani.

Alacsony, mikromoláris koncentrációkat nem meghaladó Sr^{2+} koncentrációknál a lignit és a természetes klinoptilolit részére magas értékű elosztási együtthatókat határoztunk meg, magasabb koncentrációknál viszont az illető együtthatók erősen csökkennek. A vizsgált szorbensek közül a legalacsonyabb elosztási együtthatókkal a montmorillonit rendelkezik. A lignit részére a stroncium szorpcióját illetően a szorpciót megelőző vízzel való kontaktus ideje nem jár jelentősebb befolyással.

Kulcsszavak: stroncium, DCH18C6, szelektív extrakció, szorpció, lignit, klinoptilolit.

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