ISSN 1066-3622, Radiochemistry, 2023, Vol. 65, No. 1, pp. 87–90. © Pleiades Publishing, Inc., 2023.
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Strontium-Selective Sensors with Di-*tert*-butyldicyclohexano-18-crown-6 Membranes

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Received October 27, 2022; revised November 3, 2022; accepted November 3, 2022

Abstract—Strontium-selective potentiometric sensors with polymeric membranes based on di-*tert*-butyldicyclohexano-18-crown-6 were developed to control the strontium content in technological solutions of radiochemical industries. The detection limit is shown to be 2×10^{-6} M, and the slope of the electrode function is 29 ± 1 mV/pSr. The selectivity coefficients of the strontium-selective sensor towards the main interfering ions were determined. It was established that the dose of ionizing radiation at the 10 kGy level does not significantly affect the performance of the developed strontium-selective sensors.

Keywords: strontium-selective sensor, crown ethers, limit of detection, selectivity, electrochemical cell, potentiometric determination, ionizing radiation

DOI: 10.1134/S1066362223010137

Potentiometric sensors are widely used in analytical practice, including radiochemical studies [1, 2], as an effective tool for express analysis of liquid media. A number of review papers devoted to various aspects of the production and use of chemical sensors are published annually in the scientific literature [3, 4]. Neutral carriers are among the most important membrane materials for chemical sensors. Their molecules have a spatial configuration consisting of polar groups, which allow retaining the potential-determining ion, and lipophilic groups, which provide good solubility in organic media. This class of membrane materials also includes such an extensive group of compounds as crown ethers. Currently, various potentiometric sensors based on a number of crown ethers are used in analytical practice, in particular, sensors for alkali and alkaline earth metal cations [5, 6].

Chemical sensors are known for the determination of strontium ions, where the strontium salt of methylphosphonic acid monoisooctyl ester is used as a sensitive substance (the content in the membrane is 2.5–20.5 wt %), and 1,2-dichloroethane was chosen as the solvent. The slope of the electrode function of the sensor is 28.0 ± 1 mV/pSr [7]. Strontium-selective sensors have also been proposed containing a sensitive membrane based on 5,11,17,23,29,35-hexacalix(1,1,3,3-tetramethylbutyl)-37,38,39,40,41,42-hexakis(carboxymethoxy)calix[6]-arene with a polyvinyl chloride membrane and plasticizer dibutyl adipate (DBA) [8]. Main performance characteristics: detection limit 1.9×10^{-5} M; response time 15 ms; selectivity to Na ions 2.5×10^{-2}, K 2.0×10^{-2}, Ca 3.5×10^{-2}. Matrices for selective membrane compositions can be not only classical plasticized membranes based on polyvinyl chloride (PVC), but also carbon nanotubes, graphene layers, and semiconductor structures [9, 10]. This study was aimed at developing the potentiometric sensor towards strontium ions, which can be successfully used in radiochemical practice.

EXPERIMENTAL

To fabricate a strontium-selective sensor, plasticized film membranes based on di-*tert*-butyldicyclohexano-18-crown-6 (DTBDCH18C6) crown ether were synthesized. During the synthesis of membranes,

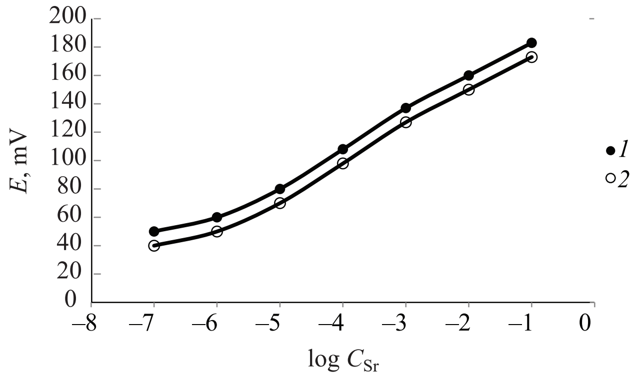

Fig. 1. Electrode function of a strontium-selective sensor with two types of membranes: (*1*) Macromembrane, (*2*) micromembrane.

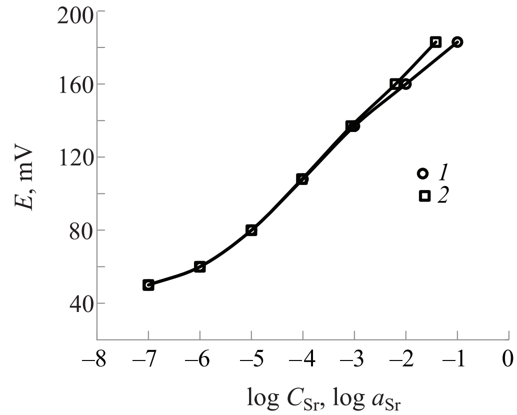

Fig. 2. Potential as a function of the logarithm of (*1*) concentration or (*2*) activity for a strontium-selective sensor with a macromembrane.

1350 mg of a plasticizer, 2-nitrophenyloctyl ether, 150 mg of DTBDCH18C6, and 100 mg of a lipophilic component—sodium tetraphenylborate, were added to a weighed portion (900 mg) of PVC powder. The prepared mixture was dissolved in 5.0–7.5 mL tetrahydrofuran (THF). After thorough mixing and partial evaporation of the solvent, the mixture of components was placed in a Petri dish and kept in a desiccator for 20–24 h. The film as-prepared had a thickness of 300–400 μm. Membrane 12 mm in diameter for macrosensors and 2 mm in diameter for microsensors were cut from the film, and the resulting membranes were glued with THF into the ends of PVC tubes. Thus, strontium-selective sensors with a membrane based on crown ether DTBDCH18C6 were fabricated.

The form of a potentiometric measuring cell is presented Table 1.

The studied solutions contained $Sr(NO_3)_2$ concentrations from 10^{-7} to 10^{-1} M, and mixed solutions of strontium nitrates (0.01 M) and sodium, potassium, calcium, and magnesium nitrates (0.1 M) were used to determine the selectivity coefficients of the strontium sensor. The cell potentials were measured using a high-resistance millivoltmeter ionometer (Mettler Toledo S20). Strontium nitrate was of chemically pure grade, and sodium, potassium, calcium and magnesium nitrates were of analytically pure grade.

RESULTS AND DISCUSSION

Testing of fabricated potentiometric sensors for strontium ions with film membranes based on crown ether DTBDCH18C6 was carried out in a measuring cell with a 50 mL volume. A silver chloride electrode with a 0.1 M KCl solution was used as a reference electrode. To measure the analytical characteristics of microsensors, we used a cell with a volume of 0.5 mL and a silver chloride capillary reference electrode. The first series of measurements was carried out in pure solutions of strontium nitrates. Figures 1 and 2 show the curves of the cell potentials vs.

Table 1. Potentiometric measuring cell

Ag, AgCl	KCl 0.1 M	$Sr(NO_3)_2 \times 10^{-7}$–$10^{-1}$ M	Crown ether membrane	0.1 M $SrCl_2$	Ag, AgCl
Reference electrode		Test solution	Strontium-selective sensor		

Table 2. Strontium sensor selectivity coefficient

Interfering ion	K^+	Na^+	Ca^{2+}	Mg^{2+}
Selectivity coefficient $K_{Sr/M}$	3.2×10^{-3}	$< 1.0 \times 10^{-3}$	1.2×10^{-2}	8.0×10^{-3}

logarithm of the concentration and activity of strontium ions. Figure 1 shows calibration curves for macro- and microsensors for strontium ions. It can be seen from the obtained data that membranes based on crown ether DT-BDCH18C6 exhibit high sensitivity to strontium ions (Fig. 1, curves *1, 2*). Figure 2 shows the electrode function in the E–log(a_{Sr}) coordinates for one of the strontium sensors containing a DTBDCG18C6-based membrane, with a slope close to the theoretical one (29 mV/pSr) and a detection limit of 2×10^{-6} M.

For the subsequent series of experiments, we chose membranes with the best characteristics towards the strontium ion and measured their selectivity with respect to sodium, potassium, calcium, and magnesium ions in mixed solutions. Based on the obtained data, the selectivity coefficients for the sensor towards strontium were calculated (Table 2).

An important parameter affecting the use of chemical sensors in analytical practice is the dependence of the potentials of strontium-selective membranes on the pH of measured solutions. Our experiments on the study of the pH effect on the stability of electrode potentials showed that for sensors with membranes based on crown ether DTBDSG18C6 in solutions with a content of 10^{-1}–10^{-3} M $Sr(NO_3)_2$, the most stable region is the pH range from 2.0 to 6.5. Samples of strontium-selective sensors were periodically tested (interval 3–7 days) in strontium nitrate solutions (10^{-7}–10^{-1} M). It was found that during 6–8 months the slope of the electrode function remained within 28 ± 2 mV/pSr, and the limit of detection was in the range of 2×10^{-6}–4×10^{-6} M. Error in determining the concentration by a strontium-selective sensor is 3–4% in the concentration range 1×10^{-5}–1×10^{-1} M and 8–10% in the concentration range 2×10^{-6}–1×10^{-5} M.

Since strontium potentiometric sensors were developed for use in radiochemical technologies, their performance was studied both before and after exposure to various doses of ionizing radiation. We used a ^{60}Co γ-radiation source (experimental setup K-120000) with an intensity of 20 kGy/h. Two series of sensor samples (4 samples each) received the following doses of ionizing radiation as a result of the experiment: the first, 10 kGy (irradiation for 0.5 h), the second, 150 kGy (irradiation for 7.5 h). After irradiation, two sensor calibrations were conducted in 10^{-6}–10^{-1} M strontium nitrate solutions at pH 2.

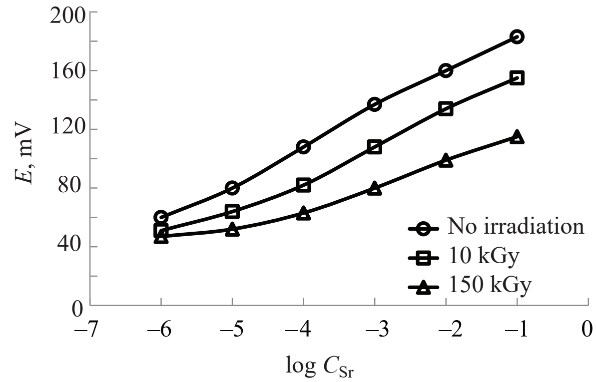

Fig. 3. Electrode functions of the strontium-selective sensor before irradiation and after irradiation to doses of 10 and 150 kGy.

Figure 3 shows the electrode functions of strontium-selective sensors before irradiation and after irradiation depending on dose. Based on the data obtained, it can be concluded that the sensors practically retain their performance at received radiation doses of ≤10 kGy. At higher radiation doses (~150 kGy), the electrode function of strontium-selective sensors deteriorates significantly.

CONCLUSIONS

Potentiometric strontium-selective sensors based on crown ether di-*tert*-butyldicyclohexano-18-crown-6 (DTBDCH18H6) with PVC film membranes were produced. It was shown that a sensor with a membrane containing crown ether DTBDCH18C6 has an almost theoretical function with a slope of 29 mV/pSr and a detection limit of 2×10^{-6} M. The selectivity coefficients ($K_{Sr/X}$) of the sensor to sodium ($<1.0 \times 10^{-3}$), potassium (3.2×10^{-3}), calcium (1.2×10^{-2}), and magnesium (8.0×10^{-3}) ions were measured. The operating range of the sensors was determined: pH 2.0–6.5. Thus, the developed strontium-selective sensor has characteristics that exceed those previously known [7, 8]. It is shown that the sensors retain their performance after exposure to ionizing radiation (10 kGy) and can be used to determine strontium in analytical and radiochemical laboratories.

FUNDING

This work was supported in part by a grant from the Russian Science Foundation (project no. 20-13-00143).

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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