

# A NEW PERTECHNETATE-SELECTIVE ELECTRODE BASED ON SUPRAMOLECULAR POLYMER COMPOSITION

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**DOI: 10.13140/RG.2.2.31744.07686 Abstract**

Basic electroanalytical parameters have been determined for an ion-selective electrode (ISE) with a supramolecular polymer membrane containing polyvinyl chloride (PVC), a plasticizer *o*-nitrophenyloctyl ether, ionophor tetradecylammonium teraphertehtetate (PTTDF) and a lipophilic dopant tetraphenylborate tetradecylmonium. The electrode function of these ISEs was shown to be linear in the concentration range  $(\text{TcO}_4)^- 2 \cdot 10^{-7} \div 10^{-2} \text{ mol / l}$ ; the slopes of the electrode function at 20 ° C are  $57.5 \pm 1.5 \text{ mV} / p_{\text{TcO}_4^-}$ . The potentiometric coefficients of selectivity to various anions are determined. It was established that a change in the pH of the analyzed solution from 0.5 to 13 does not affect the potential. The possibility of using the ISE to determine Tc in the products of reprocessing spent nuclear fuel (SNF) is shown.

## Introduction

Determination of technetium in the products of reprocessing of spent nuclear fuel is an important problem for the atomic industry. At the present time, radio-metric [1] and mass spectral [2,3] methods and X-ray fluorescence analysis [4] are mainly used for this purpose. However, the above methods require rather complicated sample preparation, for example, for the radiometric determination of technetium, it is necessary to separate it from other radioactive isotopes, and other methods additionally require expensive equipment. Therefore, all these methods do not allow for the rapid determination of technetium at the sites of spent nuclear fuel.

Potentiometric method using ISE is a good alternative to the above methods, because it does not require expensive equipment, it is quite easy to use and allows rapid analysis of spent nuclear fuel for technetium. However, this method has sufficient technetium detection limit (up to  $10^{-7} \text{ mol / l}$ ) and high selectivity. Now, the potentiometric method for determining technetium is rarely used due to the lack of reliable  $\text{TcO}_4^-$  selective electrodes. Still known two publications of using this electrodes. One of which describes liquid ISE specific to pertechnetate ions [5], are difficult to use because of structural features of the electrodes with liquid ion exchanger. Another described electrode with a polymer membrane can be used in a number of cases for fast SNF analysis for technetium content [7]. The proposed study is aimed at the development of an electrode membrane with improved electroanalytic characteristics for the determination of pertechnetate ions.

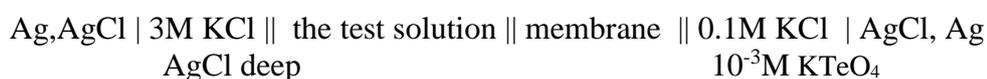
## Experimental

In the process of the studies were used reagents qualifications "hp", reagents firm "Fluka" - selectors: PVC – poly(vinyl chloride), high molecular weight, cyclohexanone as solvent.

Ionofor pertechnetate of dodecyltrimethylammonium was prepared by ion exchange extraction ion  $\text{TcO}_4^-$  from 0.01 M aqueous solution of bromide of tetradecylammonium in dichloromethane and subsequent recrystallization. In this case, 20 ml of 0.05 M tetradecylammonium bromide solution in  $\text{CH}_2\text{Cl}_2$  was contacted in a separating funnel with 25 ml of 0.05 M potassium pertechnetate solution. The organic phase was separated and distilled with 100ml. water. Studies have shown that one contact is enough for 100% replacement of bromide ions with anions  $\text{TcO}_4^-$  in the organic phase. The resulting organic phase was transferred to a Petri dish. After removal of methylene chloride at room temperature, a white powder  $[(\text{C}_{10}\text{H}_{21})_4\text{N}][\text{TcO}_4]$  was obtained, which was used in the manufacturing process of the membrane. The powder composition was confirmed by chemical analysis and IR spectra.

To obtain a lipophilic additive  $[(C_{10}H_{21})_4P][B(C_6H_5)_4]$ , 20 ml of 0.05 M solution of bromide tetradecylammonium in  $CH_2Cl_2$  was mixed with 20 ml of 0.05 M solution of tetraphenylborate sodium chloride in methylene chloride. NaBr precipitate was filtered out. A white substance (as a powder) of  $[(C_{10}H_{21})_4P][B(C_6H_5)_4]$  composition was isolated from the obtained solution by evaporation of methylene chloride. It was then used for preparation of membranes.

A liquid ionite was initially prepared for the membrane of the ion-selective electrode: it was solution with certain amount of ionophore and a lipophilic additive in an organic solvent – plasticizer (2-nitrophenyloctyl ether). To produce the polymer membrane with liquid ion exchanger were introduced into the PVC matrix. For this purpose, the certain amounts of 10% PVC solution in cyclohexanone and liquid ionite (EI) were mixed. The mixture was transferred to a Petri dish and dried at room temperature. After evaporation of the cyclohexanone was getting thin polymer film with a thickness of 0.3 – 0.5 mm from which were cut the disk with a diameter of 5 – 7 mm. This drive was used as a membrane. Membrane compositions are given in table.1. At the same time, the concentration of ionophore in THE  $10^{-2}$ -  $5 \cdot 10^{-4}$  M, and lipophilic additives  $10^{-2}$ - $10^{-3}$  M (table.1). During the study of the electroanalytical properties of the obtained membranes used standard housing Philips IS 561. The silver chloride electrode Radelkis OP – 0820 was used as the reference electrode. Measurements were carried out using the pH-ion analyzer Radelkis OP-300, using a galvanic circuit of the form:



Electroanalytical parameters of the ISE were measured according to the IUPAC recommendations (7) at pH 5 – 7. Selectivity coefficients were evaluated by the method bionic potentials.

The initial solution of  $10^{-2}M$  Tc (VII) was prepared by dissolving a sample of potassium pertechnetate in distilled water. Potassium pertechnetate was synthesized and identified in the laboratory of chemistry technetium IFHE RAS under the guidance of Professor K. E. German. Solutions with a lower concentration were prepared by successive dilution of the initial solution with distilled water.

### Results and discussion

The composition of membranes and their characteristics are given in table 1.

No electrodes	Content of components in the liquid ion exchanger in the membrane (at a ratio of: 30% PVC - 70% LI)		slope of the plot (mV)	Detection Limit
	$[(C_{10}H_{21})_4N][TcO_4]$ M	$[(C_{10}H_{21})_4P][B(C_6H_5)_4]$ M		
1	$10^{-2}$	$10^{-2}$	$56 \pm 1,0$	$2 \cdot 10^{-6}$
2	$10^{-2}$	$10^{-3}$	$56 \pm 1,0$	$2 \cdot 10^{-6}$
3	$10^{-3}$	$10^{-2}$	$58 \pm 1,5$	$2 \cdot 10^{-7}$
4	$10^{-3}$	$10^{-3}$	$55 \pm 1,0$	$8 \cdot 10^{-7}$
5*	$5 \cdot 10^{-4}$	$10^{-2}$	$49 \pm 2,0$	$(3-5) \cdot 10^{-7}$
6*	$5 \cdot 10^{-4}$	$10^{-3}$	$53 \pm 3,0$	$(2-5) \cdot 10^{-7}$

The solutions under study were stirred using a magnetic stirrer. Temperature during measurements was  $19 \pm 1$  °C. Electrode functions of the investigated ISE are shown in Fig.1. As follows from table 1, with the optimal composition of the membrane 3, the linearity of the electrode function is maintained in the range of the studied concentrations of pertechnetate from  $2 \cdot 10^{-7}$  to  $10^{-2}$  mol/l, with an slope of the electrode characteristic of  $58 \pm 1.5$  mV. The slope of the plot and detection limit changing the composition of the membrane there is a deterioration of electroanalytical characteristics. Membranes of composition 5.6 were poor reproducibility and stability of potential in time. The response time of the ISE was  $< 5$  s, the time to establish the equilibrium potential for dilute solutions ( $10^{-5}$  M and below) was 2-3

min., for more concentrated solutions – less than 0.5 min. For the electrode with the membrane composition 3, the effect of pH on the potential in solutions with a content of  $10^{-4}$  M  $\text{KTcO}_4$  was determined. The study was carried out in dilute HCl, neutral and alkaline solutions with a constant concentration of  $\text{Cl}^-$  ions equal to 1 mol / l (Fig. 2). One can see from the figure, the change in pH from 0.5 to 13 practically does not affect the value of the electrode potential.

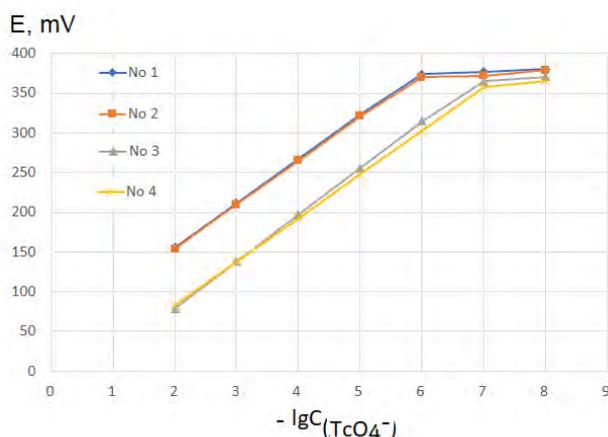


Fig.1. Electrode characteristics of membranes of different composition (table 1).

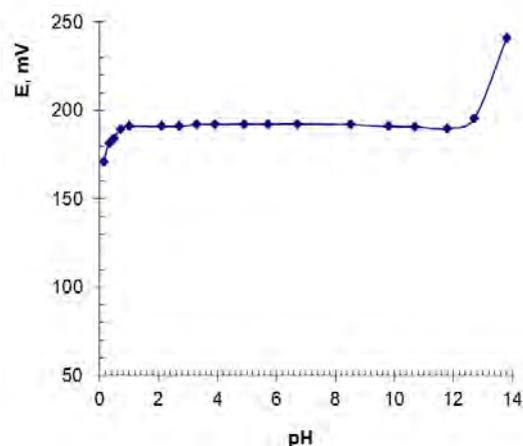


Fig.2. The dependence of the potential of the electrode with the membrane composition No. 3 of pH.

Selectivity coefficients were determined by the method of separate solutions (MPR) and by the method of mixed solutions (MSR) [10-12]. In the first case, the electrode potentials were measured in a solution of  $\text{KTcO}_4$  ( $10^{-2}$  M) and in a solution of interfering ion ( $10^{-2}$  M). Selectivity coefficients were determined by the formula:

$$\lg k^{\text{pot}}_{\text{TeO}_4^- / X} = (E_X - E_{\text{TeO}_4^-}) / S + (1 - z_{\text{TeO}_4^-} / z_X) \cdot \lg[X], \quad [7]$$

where  $\lg k^{\text{pot}}_{\text{TeO}_4^- / X}$  logarithm of the potentiometric selectivity coefficient,  $E_X$ ,  $E_{\text{TeO}_4^-}$  - potentials in the solution of the interfering ion and the solution of  $\text{KTcO}_4$ ,  $S$  –  $S$  the slope of the plot,  $z_{\text{TeO}_4^-}$ ,  $z_X$  – ion charges.

The potentials of binary solutions containing a constant concentration of the interfering ion (0.1 mol/l) and a variable concentration of pertechnetate ions were measured in the mixed solution method. The selectivity coefficients were determined by the graphical method recommended by IUPAC [9].

Table 2. Potentiometric selectivity coefficients.

ion	$\lg k^{\text{pot}}_{\text{TeO}_4^- / X}$		
	MPR	MSR	For ISE [5]
$\text{NO}_3^-$	-3.7	-3,9	-3.5
$\text{F}^-$	-5.4	-5,8	-4.7
$\text{Cl}^-$	-5.7	-6,0	-5
$\text{Br}^-$	-4.4	-4,7	-
$\text{J}^-$	-2.4	-4,8	-
$\text{ReO}_4^-$	-0.4	-0,7	1
$\text{ClO}_4^-$	-0.7	-0,9	1
$\text{SO}_4^{2-}$	<-6	<-6,0	-5

Comparison of the obtained values of selectivity coefficients with the data [5] (see table. 2) it is shown that the selectivity of the developed electrode is not inferior, and in some cases superior liquid selectivity of the electrode based on tetradecylphosphonic. Thus, the results showed the

possibility of using an electrode with the proposed composition of the membrane 3 to determine Tc(VII) in the form of  $TcO_4^-$  in solutions of complex salt composition.

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