

Quaternary Alkylammonium and Alkylphosphonium Pertechnetates: Application to Pertechnetate Ion-Selective Electrodes

K. E. German,^{*,a} A. V. Dorokhov,^a A. V. Kopytin,^b Yu. Politov,^b E. N. Pyatova,^b A. V. Tarasov,^a V. E. Baulin,^a V. Peretroukhine,^a and A. Yu. Tsivadze^a

^aInstitute of Physical Chemistry RAS; Russia, Moscow

^bKurnakov Institute of General and Inorganic chemistry of RAS; Russia

Received: July 31, 2005; In Final Form: September 30, 2005

Pertechnetate ion-selective PVC membrane electrodes based on quaternary alkylammonium and phosphonium salts (bromides and pertechnetates) were examined. The most favorable ionophore was tetradecyltrimethylammonium bromide. The response function was linear within the concentration range 10^{-2} – 10^{-6} mol/L and the slope was 52 mV/pTcO₄. The detection limit remained at $5 \cdot 10^{-7}$ mol/L. The selectivity and response time of the electrodes was studied and it was found that the electrodes exhibited high selectivity to TcO₄⁻ anion against the main inorganic components of radioactive waste solutions and environmental waters (nitrate, sulfate, chloride and others). The electrodes response was stable over a wide pH range.

1. Introduction

Quaternary alkylammonium and phosphonium salts are widely used for preparation of the membranes giving a response to different ions. The selectivity of ion determination depends on hydration energy of ion and on the nature of membrane solvent.¹ With this approach to a creation of new ion-sensitive sensors some electrode membranes for different anions and acidocomplexes determination have been developed.²⁻⁵ But only one pertechnetate selective electrode was described earlier.⁶ However, this liquid membrane electrode has not enough high selectivity and contains concentrated radioactive solution (10^{-1} M KTcO₄). Thus, it can not be widely used in the analysis of the pertechnetate solutions.

The object of present work is a development and an investigation of new ion-selective electrodes for TcO₄⁻ determination.

2. Experimental

Tetradecyltrimethylammonium pertechnetate [CH₃(CH₂)₁₃N(CH₃)₃]TcO₄, tetradecylphosphonium pertechnetate [(C₁₀H₂₁)₄P]TcO₄, and ethyldiphenyldodecylphosphonium pertechnetate [(C₂H₅)P(Ph)₂(C₁₂H₂₅)]TcO₄ were synthesized by liquid-liquid extraction of Tc-99 from 0.1 mol/L aqueous solution of NaTcO₄ into solution of quaternary ammonium/phosphonium bromide in CH₂Cl₂. Properties of these compounds were studied by DTA, IR, Raman spectroscopy and X-ray diffraction.

Membranes preparation. The ionophore {[CH₃(CH₂)₁₃N(CH₃)₃]Br (I), [CH₃(CH₂)₁₃N(CH₃)₃]TcO₄ (II), [(C₂H₅)P(Ph)₂(C₁₂H₂₅)]Br (III), [(C₁₀H₂₁)₄P]TcO₄ (IV) or [(C₁₀H₂₁)₄P]Br (V)}, plasticizer (o-nitrophenyloctyl ether, Fluka) and high molecular weight polyvinylchloride (Aldrich) were dissolved in the appropriate volume of cyclohexanone and mechanically stirred. All membrane cocktails were cast in glass rings placed on glass plates. Solvent from PVC membrane was allowed to evaporate for a week at room temperature. The thickness of the resulting membranes was about 0.2–0.3 mm.

The electrochemical properties of the electrodes were investigated in the conventional configuration. Small disks were punched from the cast membranes and mounted in electrode

bodies. Electrode structure is shown in Figure 1. Table 1 summarizes the compositions of the membranes and the internal solutions of the pertechnetate-selective electrodes employed in this study.

The external reference electrode was a double-junction Ag/AgCl reference electrode OP-8020 P (Radelkis). The electrochemical potential was measured using pH/ion analyzer OP-300 (Radelkis, Hungary) and Ionix-Alpha ionometric combine.

Potassium pertechnetate solutions in 1 mol/L Li₂SO₄ were used for the electrode response function determination. The selectivity coefficients were determined by the separate solution method (SSM) using 0.01 mol/L potassium or sodium salts

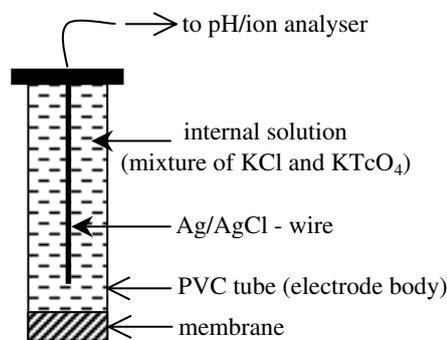


Figure 1. Electrode structure.

TABLE 1: ISEs Composition

No of electrode	Active component (ionophore)	Internal solution composition	
		KCL, M	KTcO ₄ , M
1	I	10^{-5}	10^{-6}
2	I	10^{-4}	10^{-5}
3	I	10^{-3}	10^{-4}
4	I	10^{-2}	10^{-3}
5	III	10^{-3}	10^{-5}
6	IV	10^{-3}	10^{-3}
7	IV	10^{-3}	10^{-5}
8	V	10^{-3}	10^{-3}
9	V	10^{-3}	10^{-5}

*Corresponding author. E-mail: guerman@ipc.rssi.ru. FAX: +7-495-335-1778.

of the anions in accordance with the equation

$$\lg K_{\text{TcO}_4^-/\text{anion}}^{\text{pot}} = (E_A - E_{\text{TcO}_4^-})/S + (1 - Z_A/Z_{\text{TcO}_4^-}) \cdot \lg[A] \quad [7],$$

where $K_{\text{TcO}_4^-/\text{anion}}^{\text{pot}}$ is the selectivity coefficient, $E_{\text{TcO}_4^-}$ is the potential measured in 0.01 mol/L solution of KTcO_4 , E_A is the potential measured in 0.01 mol/L solution of the interfering anion, S is the slope of the response function, $Z_{\text{TcO}_4^-}$ and Z_A are the charges of the pertechnetate anion and the interfering anion respectively, $[A]$ is the concentration of the interfering anion.

The influence of pH on the electrode response was examined by adjusting the pH of the measured solution with 1 mol/L sodium hydroxide and hydrochloric acid. Potassium chloride aqueous solution (1 mol/L) was used as a background electrolyte.

3. Results and Discussion

The only pertechnetate selective electrode was described earlier.⁷ It is the liquid membrane electrode based on **IV**. However, this electrode has not enough high selectivity and contains concentrated radioactive solution (10^{-1} M KTcO_4). Therefore, it can not be widely used in the analysis of the pertechnetate solutions.

We have developed new TcO_4^- ISEs based on quaternary ammonia and phosphonia ionites with low radioactive internal solution. The response functions for electrodes based on **I** with different solution composition are shown in Figure 2. For all these electrodes response function is linear in the range 10^{-6} – 10^{-2} mol/L KTcO_4 with the slope equal to 59 ± 2 mV/pTc at 25 °C. The concentration of KTcO_4 in the internal solution has no marked influence on response function as well as on selectivity [Figure 2 (electrodes No 1–4); Figure 3 (electrodes No 1, 2)] but addition of pertechnetate into the internal solution is necessary in order that TcO_4^- -ISEs work stable. Thus, low radioactive diluted pertechnetate solutions (10^{-5} – 10^{-6} mol/L) can be used in the TcO_4^- ISEs.

The electrodes **1–4** are workable in the wide range of pH – from 0.5 to 13 (see Figure 4). The electrodes response time is 3–5 min for diluted pertechnetate solutions and less than 1 min for concentrated solutions. Almost the same results have been obtained with tetradecyltrimethylammonium pertechnetate (**II**) and, therefore, it is possible to apply non-radioactive membranes in the TcO_4^- -ISEs.

The response function for the electrodes based on quater-

nary alkylphosphonium salts is also linear in the range 10^{-6} – 10^{-2} mol/L KTcO_4^- , with the slope equal to 63 ± 2 mV/pTc at 25 °C (Figure 5). Electrodes electroanalytical characteristics remain stable in the range of pH from 1 to 13 (Figure 6). The electrodes response time is almost the same as for alkylammonium based ISEs.

High potentiometric selectivity to TcO_4^- of the new ISEs against several important anions was found for all the ISEs developed (selectivity coefficients are in the range 10^{-4} – 10^{-7} (see Figure 3). It means that TcO_4^- can be determined in the presence of interfering anions with the concentrations of 10^4 – 10^7 times higher than one of TcO_4^-). The ISEs have the highest selectivity of Tc-determination in the phosphates, sulfates and chlorides solutions. These results are of importance: phosphates are the main component of solutions proposed to Tc-stripping from anion-exchange resins used in REPA process. Sulfates are the salt base of Tc-electrodeposition solutions for Tc-electroplating. And large amount of chlorides is contained in the radioactive wastes of pyrochemical reprocessing of spent

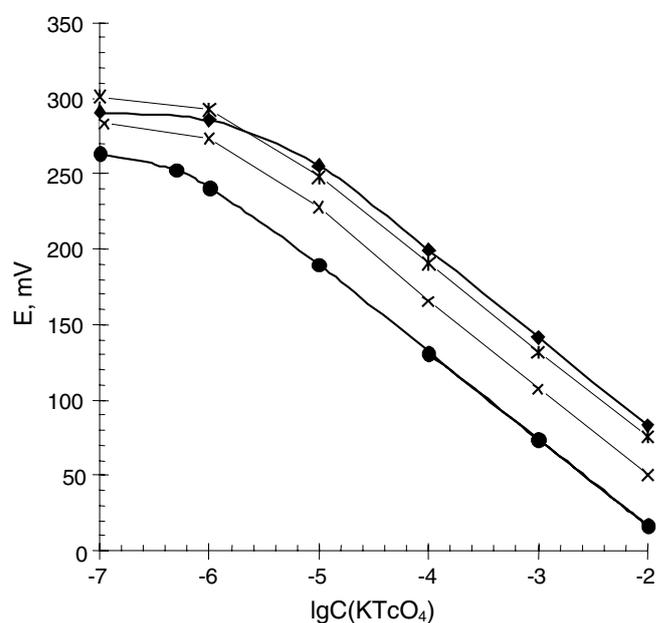


Figure 2. Electrode response function for ISEs **1–4**. ●–**1**; ×–**2**; *–**3**; ◆–**4**. The numbers of electrodes follow the corresponding numbers in table 1.

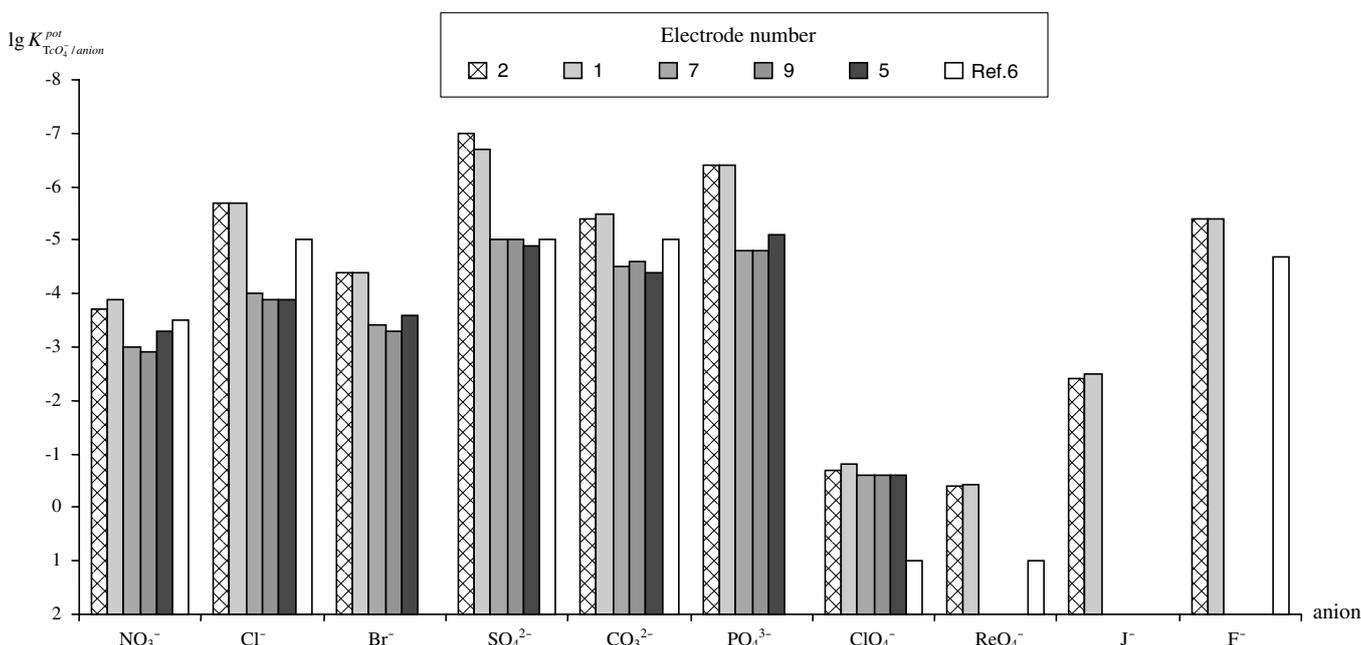


Figure 3. Potentiometric selectivity coefficients for some of TcO_4^- -ISEs developed to compare with the electrode described in [7].

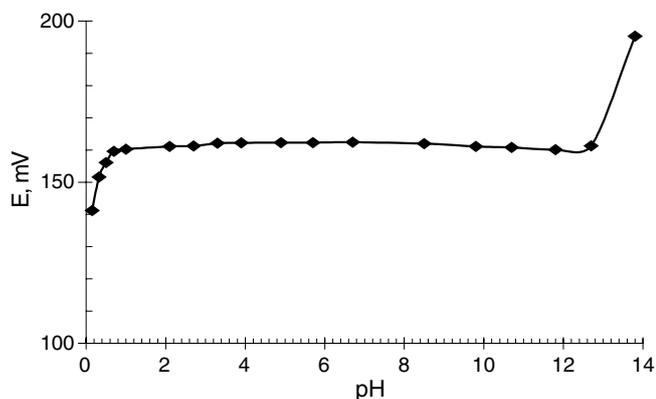


Figure 4. Influence of pH on the electrode response function (ISE No 1). (10^{-4} mol/L KTcO_4 in $\text{HCl}/\text{KCl}/\text{KOH}$ solutions, background electrolyte – 1 mol/L KCl).

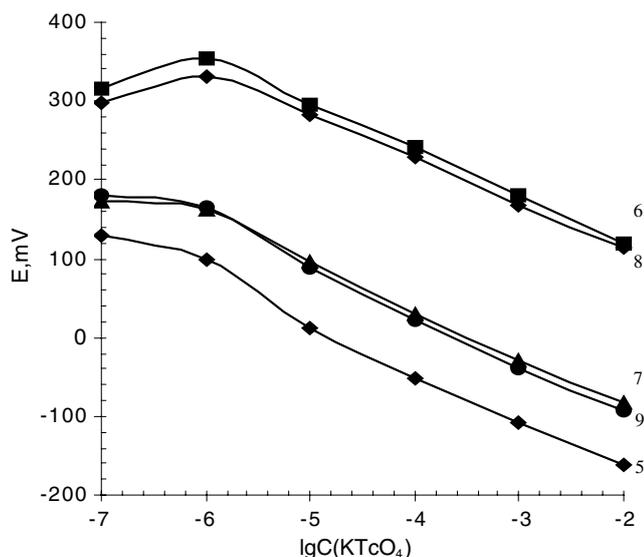


Figure 5. Electrode response function for ISEs 5–9.

nuclear fuel. The ISEs selectivity against NO_3^- anions is lower but with the electrodes 1 and 2 it is possible to determine Tc in some back extraction and wasting nitric acid solutions of improved PUREX.

The selectivity of alkylammonium ISEs is slightly better than those of alkylphosphonium but all the new Tc-ISEs have better characteristics compared to earlier proposed ISE with liquid membrane⁶ (see Figure 3). Studies of some new Tc-ISE are in progress.

4. Conclusion

The electrodes proposed do not contain high radioactive solutions and possess high selectivity to TcO_4^- against to the

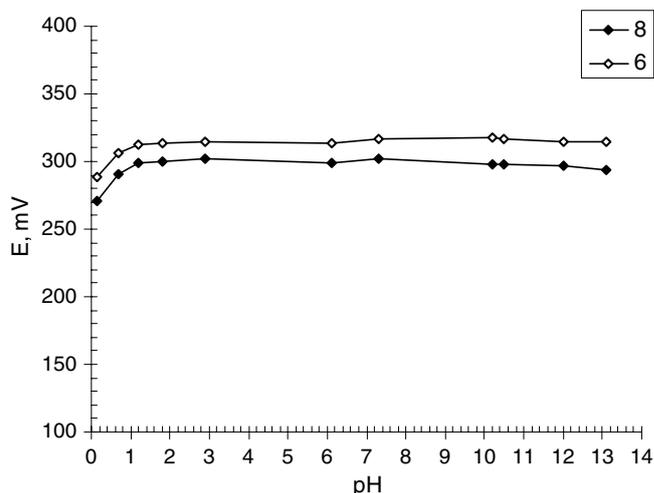


Figure 6. Influence of pH on the electrode response function (ISE No 6, 8). (10^{-4} mol/L KTcO_4 in $\text{HCl}/\text{KCl}/\text{KOH}$ solutions, background electrolyte – 1 mol/L KCl).

main inorganic components of radioactive waste solutions and environmental waters (nitrate, sulfate, chloride and others) and, therefore, they can be applied to the analyses of Tc in some kinds of technological solutions formed in the reprocessing of the spent nuclear fuel.

Acknowledgements. The authors are much thankful to the RFBR, the RFASIE and “Ionix-Alfa” assistance for the supplied ionometric equipment.

References

- (1) N. Lakshminarayanaiah, Membrane electrodes. Academic Press. New York, San Francisco, London 1976.-360 p.
- (2) B. Fu, E. Bakker, J. H. Yun, V. C. Yang, and M. E. Meyerhoff, Analytical Chem. **66**, 2550 (1994).
- (3) T. Ito, H. Radecka, M. Kataoka, K. Tohda, E. Kimura, K. Odasima, and Y. Umezawa, J. Am. Chem. Soc. **120**, No13, 3049 (1998).
- (4) A. Schwake, K. Cammann, A. L. Smirnova, S. S. Levitchev, V. L. Khitrova, A. L. Grekov, and Yu. G. Vlasov, Anal. Chim. Acta **393**, 19 (1999).
- (5) E. M. Rakhimenko, I. Prilutskaya, T. M. Yakimenko, and O. V. Yakimenko, Proceedings of the National Academy of Sciences of Belarus. Series of Chemical sciences, No1 (2000), 18-23.
- (6) G. A. Akopov, M. K. Abdulhatov, and A. P. Krinitsyn, Radiochem. **28**, No 3, 434 (1986).
- (7) G. G. Guilbault, R. A. Drust, M. S. Frant, H. Freiser, E. H. Hansen, T. S. Light, E. Pungner, G. Rechnitz, N. M. Rice, T. J. Rohm, W. Simon, and J. D. R. Thomas, Pure Appl. Chem. **48**, 127 (1976).

