

Short Communication

ANALYTICAL STUDY OF A NEW PICRATE-SELECTIVE MEMBRANE ELECTRODE

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Since the introduction of a liquid-membrane electrode selective for calcium in 1967 [1], many new electrodes of this type for different ions have become available. The use of liquid ion-exchangers has significantly extended the number of ions which can be determined. Salts of bulky quaternary ammonium ions with various anions have been widely used for constructing anion-selective liquid-membrane electrodes. Tetrahexylammonium picrate in methylene chloride has been used as the liquid ion-exchanger in an electrode which was used for several ions but not for picrate ions [2].

The communication reports the use of the water-insoluble tetrapentylammonium picrate, dissolved in 2-nitrotoluene, as the active electrode substance in a picrate-selective membrane electrode. This picrate-selective electrode has been used successfully in direct potentiometry and in the potentiometric titration of silver in the presence of thiourea with picrate.

Experimental

Apparatus. The picrate-selective electrode was used as the indicator electrode, with a double-junction silver—silver chloride electrode, Orion Model 90-02-00, as the reference electrode. The outer chamber of the reference electrode was filled weekly with a 10% (w/v) KNO_3 solution. The electrode potential was measured with an Orion Ionalyzer (Model 801A digital pH/pIon meter). The cell potential was recorded with a Heath-Schlumberger system, which consisted of a pH/pIon electrometer (EU-200-30) a potentiometric amplifier (EU-200-01), a d.c. offset module (EU-200-02) and a strip-chart recorder (EU-205-11). The titrant was added with a multi-speed constant-rate burette (Sargent-Welch Model S-111 20-12). pH values were measured with a Metrohm pH meter (Model E350B). Test solutions were placed in 50-ml cells thermostated at 25.0°C and stirred magnetically.

Reagents. All solutions were prepared with deionized twice-distilled water and reagent-grade substances, except where stated.

Sodium picrate (0.1000 M) was prepared by neutralizing a suitable picric acid solution with NaOH to a pH of about 6. More dilute standard solutions were prepared by serial dilution. All picrate solutions were stored in amber

bottles. The picric acid used (Fluka, purum) was standardized against sodium hydroxide solution.

Tetrapentylammonium bromide (Eastman Organic Chemical Co.) was used without purification.

Preparation of the liquid ion-exchanger. Tetrapentylammonium picrate was precipitated by mixing equimolar (0.1 M) aqueous solutions of tetrapentylammonium bromide and sodium picrate. The salt is readily soluble in 2-nitrotoluene, which was therefore used for its extraction; the nitrotoluene solution was washed twice with double-distilled water to remove any traces of the bromide salt (and NaBr). The organic phase was dried thoroughly with anhydrous sodium sulfate.

Construction of the electrode. The body of an Orion 92 electrode equipped with Orion 92 membranes (e.g. 92-81-04 perchlorate membrane) was used as the liquid membrane electrode. The electrode was assembled as described in the manufacturer's instructions, and the internal reference and liquid ion-exchanger solutions were injected into the appropriate ports in the electrode body. The internal reference solution was 0.01 M sodium picrate—0.1 M NaCl. The liquid-ion exchanger solution was a 0.01 M solution of tetrapentylammonium picrate in 2-nitrotoluene.

The measuring cell was:



The picrate electrode was conditioned by soaking in a 0.01 M sodium picrate solution for 48 h before use, and was also stored in this solution when not in use. The operative life of the electrode was about 40 days.

Results and discussion

The tetraalkylammonium salts tested for preparing the picrate ion-exchanger were: trimethylphenylammonium bromide, tetrahexylammonium bromide, tetrapentylammonium bromide, tetraheptylammonium bromide, tetrapropylammonium bromide, tetrabutylammonium bromide, dimethyldioctadecylammonium chloride, didodecyldimethylammonium bromide, and tetraphenylarsonium bromide. The solvents tested were: 2-nitrotoluene, dibenzyl ether, dichloroethane, 1-decanol, chlorobenzene, and phthalic dibutylester. The shorter the chain length, the greater the solubility of the picrate in water. The tetrapentylammonium picrate was the most suitable sensor and 2-nitrotoluene was the best solvent.

Linear response range. A typical calibration graph for the electrode in stirred sodium picrate solutions (Fig. 1) shows that the response is linear in the 10^{-2} – 10^{-5} M range; the graph has a slope of 58 mV/decade change in activity at 25°C. All concentrations were converted to activities by the expression: $\log f = -0.511 [\mu^{1/2}/(1 + \mu^{1/2})]$, where f is the activity coefficient ($z_{\text{pic}} = -1$). After 8 days there was a decrease in the calibration graph slope in the 10^{-4} – 10^{-5} M range.

Effect of pH. To check the pH-dependence of the potential of the picrate-selective electrode, potential—pH curves at various picrate concentrations were constructed. The pH of the initial solution was altered by addition of very small volumes (less than 0.1 ml per 20 ml of test solution) of NaOH or H₂SO₄ solutions. The plots (Fig. 2) show that between pH 3 and 10 the potential is practically independent of pH. At higher pH the potential increases slowly, probably because of complex formation between picrate and hydroxide ions [3]. During the operative life of the electrode, no discernible change in the potential—pH behavior was observed.

Dynamic response of the electrode. The dynamic response was tested for 10⁻²–10⁻⁵ M sodium picrate solutions; the sequence of measurements was from low concentrations to high concentrations and back. The response times were quite short (less than 4 s, including the mixing and recorder time) and depended on the concentration change, the stirring rate and efficiency of solution mixing. It should therefore be possible to employ the picrate electrode in titrations with continuous addition of titrant and for the continuous monitoring of changing systems.

Potentiometric selectivity coefficients. The interference of various anions was studied by the graphical mixed solution method [4]. The concentration of the tested anion was kept constant, while the picrate concentration was varied in the range 10⁻²–10⁻⁵ M. Selectivity coefficients are presented in Table 1. The electrode has a very high selectivity for picrate compared to the following ions: Cl⁻, F⁻, NO₃⁻, HCO₃⁻, CH₃COO⁻, IO₃⁻. At constant ionic strength, variations in the concentrations of these anions did not affect the electrode potential.

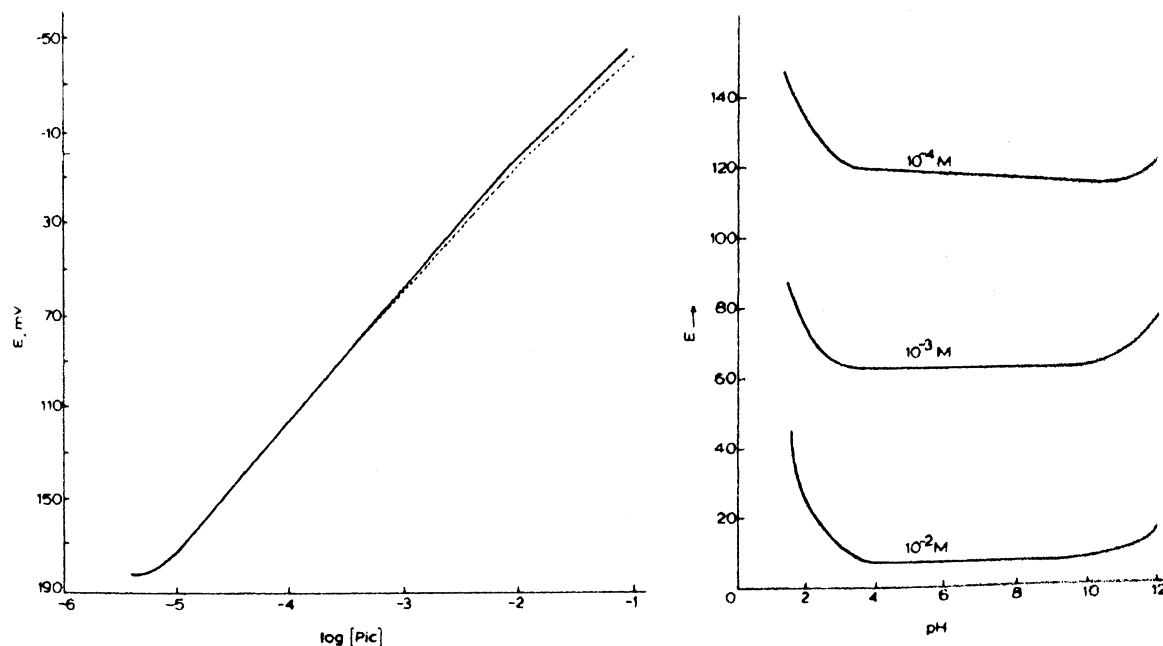


Fig. 1. Calibration curve for the picrate-selective membrane electrode. — Activity. ----- Concentration.

Fig. 2. Effect of pH on the potential of picrate-selective electrode at the different concentrations of sodium picrate marked.

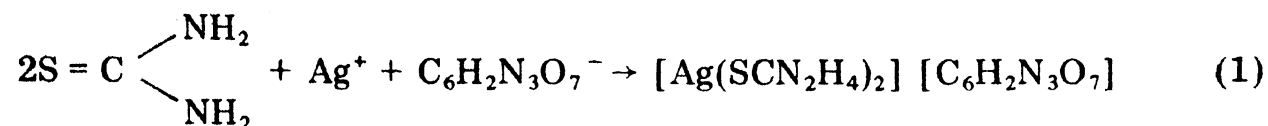
TABLE 1

Potentiometric selectivity coefficients for interfering univalent anions

Interferent, j	$[j]$	K_{picj}^{pot}
2-Nitrophenol	1.0×10^{-2}	1.5×10^{-2}
2,4-Dinitrophenol	1.0×10^{-2}	6.5×10^{-2}
Phthalate	1.0×10^{-2}	3.3×10^{-3}
Benzoate	2.5×10^{-2}	1.4×10^{-3}
Iodate	1.0×10^{-2}	3.7×10^{-2}
Perchlorate	2.0×10^{-2}	3.0×10^{-2}

Analytical application

The picrate-selective electrode can be used practically for the determination of picrate either by direct potentiometry, or by potentiometric titration. The electrode can also be used as an indicator electrode in potentiometric precipitation titrations of cations forming insoluble picrates. As an example, titration of silver(I) was examined, based on the formation of the insoluble picrate of the silver—thiourea complex [5, 6]



For the titration, a 20.00-ml aliquot of the sample and 5 ml of 0.2 M thiourea solution were pipetted into a 50-ml beaker and the mixture was titrated with standard 0.0250 M sodium picrate solution. The sharp potential change (ca. 80 mV) near the equivalence point allows precise location of the end-point.

Silver in aqueous solutions of known concentrations (2.2–18.4 mg) was determined with an average error of 1.1%; the absolute error varied from –1.9% at the 2-mg level to +1.2% at the 18-mg level. The relative standard deviation was 1.1% for a sample containing 12 mg of silver ($n = 6$). There was no interference from the following ions when present in amounts 10 times that of silver: Pb^{2+} , Zn^{2+} , Ni^{2+} , Co^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Mg^{2+} , and Cd^{2+} . Hg(I), Hg(II) and Cu(II) ions interfered seriously.

Work in progress indicates that thiourea can be determined by potentiometric precipitation titration with standard silver nitrate solution on the basis of reaction(1) with the picrate-selective electrode. It has also been found that creatinine can be determined by a kinetic method based on the Jaffé reaction [3]. This work and other analytical possibilities of the picrate-selective electrode will be reported later.

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