

New Chloramine T and Picrate Ion-selective Electrodes

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Chloramine T Electrode

The electro-active material of the chloramine T (CAT) electrode is the [(bathophenanthroline)₃-Ni^{II}]-chloramine T salt dissolved in 2-nitro-*p*-cymene. This sensor was obtained by converting the liquid ion exchanger of the Orion nitrate-selective electrode into the CAT form. The CAT electrode exhibits Nernstian response to chloramine T ion activity for concentrations of from 10⁻¹ to 10⁻⁴ M, which is unaffected by pH in the range 5 to 9. The dynamic response times tested for the linear response range of the electrode were <2 s for a 6-fold increase or 20% decrease in CAT concentration. The operative lifetime of the electrode was about 1 month. Various ions have been tested for their interference with the CAT electrode and potentiometric selectivity coefficients have been evaluated.¹ $K_{\text{CAT},j}^{\text{pot}}$ values for various *j* ions are: for IO₄⁻ and ClO₄⁻, ~10; for benzoate and NO₃⁻, ~10⁻²; for phthalate, H₂BO₃⁻, HCO₃⁻, HPO₄²⁻ and CH₃COCOO⁻, ~10⁻³; and for malonate, tartrate, citrate, F⁻, CrO₄²⁻, MoO₄²⁻ and SO₄²⁻, ~10⁻⁴.

Applications

The CAT electrode has been used for indirect potentiometric determination of arsenic(III), ascorbic acid, hydrazine, isonicotinic acid hydrazide (isoniazid), S^{2-} and $S_2O_3^{2-}$. The reductants react stoichiometrically with a known excess of chloramine T and the unconsumed excess of chloramine T is measured with the CAT electrode. Aqueous samples of the aforementioned reductants were analysed with an average accuracy and precision of about 1–2% (Table I). The method was applied successfully to the determination of ascorbic acid and isoniazid in pharmaceutical preparations.

TABLE I

RESULTS FOR INDIRECT POTENTIOMETRIC DETERMINATION OF REDUCTANTS WITH THE CHLORAMINE T ION-SELECTIVE ELECTRODE

Reductant	Range/mg	Error, %	Relative standard deviation, %
Arsenic(III)	0.5–1.7	2.4	0.9
Ascorbic acid	0.7–40	1.8	1.2
Hydrazine	0.06–3	1.4	0.6
Isoniazid	0.3–14	2.0	1.4
Sulphide	0.01–1.6	2.6	0.8
Thiosulphate	0.06–5.6	2.6	1.2

The CAT electrode has been used for the semi-automatic potentiometric titration of ascorbic acid and chloramine T, with continuous addition of titrant, in the ranges 4–40 and 7–70 μg , respectively, with accuracy and precision of 1%.

The CAT electrode has also been used as a monitor in a kinetic potentiometric method for the micro-determination of iodide and osmium(VIII), based on their catalytic effect on the CAT - As(III) reaction. The time required for this reaction to consume a fixed amount of chloramine T, and therefore for the potential to increase by a pre-selected amount (25 mV), is measured automatically with a solid-state "double switching" network and related directly to the catalyst concentration. Commercial equipment and an auxiliary relay system are easily combined and provide automatic results shortly after the start of the reaction. Trace amounts of iodide in the range 1.5–30 μg and of osmium in the range 10–150 μg were determined with relative errors and coefficients of variation of 1–2%.² Iodide has also been determined on the basis of its catalytic effect on the CAT - H_2O_2 reaction.

Measurements made with a combination of glass and CAT electrodes in acidified chloramine T solutions of various ionic strengths have been used to determine the dissociation constant of chloramine T acid. The value obtained for K_a for this acid at 25 ± 0.2 °C and at zero ionic strength was 2.5×10^{-5} , which is in close agreement with reported values.

Picrate Electrode

The water-insoluble salt of tetrapentylammonium picrate, dissolved in 2-nitrotoluene, is the active electrode substance of the picrate ion-selective membrane electrode. Nernstian behaviour is obtained in the p(picrate) range 2–5; potentials are established rapidly (dynamic response time < 4 s) and are unaffected by pH in the range 3–10. Common ions (Cl^- , F^- , NO_3^- , HCO_3^- , CH_3COO^-) do not interfere. The potentiometric selectivity coefficients for 2-nitrophenol, 2,4-dinitrophenol, phthalate, benzoate, IO_4^- and ClO_4^- were about 0.01.³

Applications

A method has been developed for the semi-automatic potentiometric titration of thiourea with silver nitrate and of silver ions with thiourea; in the presence of picrate ions, using as indicator electrode the picrate ion-selective electrode. The method is based on the formation of insoluble complexes of silver, thiourea and picrate. Micro-amounts of thiourea and silver in the ranges 15–1 500 and 200–1 800 μg , respectively, were determined with relative errors and relative standard deviations of about 1%.⁴

The rapid response of the picrate electrode to changes in picrate concentration makes it a valuable sensor for following the rate of picrate reactions. A kinetic potentiometric method

was developed for the determination of creatinine in urine, based on the reaction that takes place between creatinine and sodium picrate in alkaline medium (Jaffé reaction). Under controlled conditions a linear relation exists between the increase in electrode potential within a fixed period of time (90 s) and the amount of creatinine present. Recovery and comparison experiments gave satisfactory results.⁵

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