

A NEW LIQUID-MEMBRANE ELECTRODE FOR SELECTIVE DETERMINATION OF PERCHLORATE

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Summary—A new liquid-membrane electrode which responds to perchlorate ion is described. It incorporates a $10^{-2}M$ solution of the nitron-perchlorate ion-pair complex, in nitrobenzene, as a liquid membrane. The electrode exhibits near-Nernstian response for 10^{-2} – $2 \times 10^{-5}M$ perchlorate with an anionic slope of 56 mV/pClO₄. The response time is 20–90 sec, the working pH 2.5–8.5, the lower limit of detection $8 \times 10^{-6}M$ perchlorate and the selectivity for perchlorate relative to 27 inorganic and organic anions of different nature is reasonably high. Periodate, permanganate and thiocyanate, however, interfere. Determination of 2–1000 µg/ml perchlorate in aqueous solutions shows an average recovery of 98.8% and a mean relative standard deviation of 1.9%. The electrode has been successfully used for direct potentiometric determination of the purity of perchlorate propellants and the solubility products of some sparingly soluble perchlorates.

Since the introduction of the first perchlorate ion-selective electrode in 1968 by Ross,^{1,2} many perchlorate membrane-electrode systems have been developed. These incorporate the perchlorate ion-association complexes of some metal chelates, long-chain quaternary ammonium ions and organic dyes, as electroactive species, dispersed in lipophilic solvents, polymeric membranes and hydrophobic porous matrices. The perchlorate complexes of tris-(phenanthroline)iron(II),¹⁻⁷ tricaprylmethylamine (Aliquat 336S),⁸⁻¹¹ tridodecylhexadecylamine,¹² triheptylhexadecylamine,¹³ tetrapropylamine,¹⁴ tetrabutylamine,¹⁴ benzylhexadecyldimethylamine,¹⁵ *N*-ethylbenzothiazole-2,2'-azine,¹⁶ the dimethyltetradecylamine derivative of Amberlite XAD-2 resin,¹⁷ the trioctylamine derivative of styrene-divinylbenzene copolymer,¹⁸ Ethyl Violet,¹⁹ Gentian Violet,²⁰ Brilliant Green,²¹ and Methylene Blue,²² have all been utilized as the electroactive materials. These complexes are either dissolved in organic solvents such as 1,2-dichloromethane,¹⁴ 1-decanol,^{8,9} nitrobenzene,^{4,18,22} tetrachloroethane,²⁰ chlorobenzene,²¹ and nitro-*p*-cymene,^{1,2} or dispersed in poly(vinyl chloride) matrix.^{5-7,10,12,13} Hydrophobic porous graphite rods,¹⁵ and fritted glass discs,^{4,20} have also been used to support the electroactive materials.

Many of these electrodes, however, are not sensitive enough to permit measurement of low levels of perchlorate, and/or display poor selectivity in the presence of various common contaminants. For most of these electrodes, selectivity data have been reported for only a few ions. The present work describes the preparation, characterization and some possible applications of a new perchlorate ion-

selective electrode based on the use of the nitron-perchlorate ion-pair complex, in nitrobenzene as solvent. The sensitivity and stability offered by this simple electrode configuration are high enough to allow accurate determination of low levels of perchlorate. The selectivity coefficients measured for many inorganic and organic anions of different nature are negligibly small.

EXPERIMENTAL

Apparatus

All emf measurements were made at $25 \pm 1^\circ$ (unless otherwise stated) with an Orion microprocessor "Ionalyzer" (Model 901), the nitron-perchlorate liquid-membrane electrode and an Orion double-junction Ag/AgCl electrode (Model 90-02), with its outer chamber filled with 10% sodium nitrate solution, as the reference electrode. An Orion glass-calomel combination electrode (Model 91-02) was used in pH adjustment.

Reagent

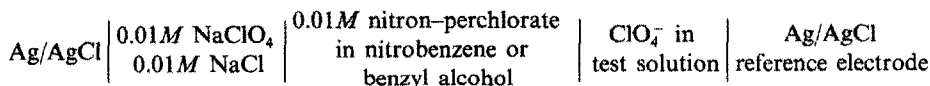
All solutions were prepared with demineralized doubly distilled water and all chemicals were of analytical reagent grade unless otherwise stated. A 0.1M stock perchloric acid solution was prepared in 0.1M sodium chloride and standardized by potentiometric titration with standard sodium carbonate solution (glass-calomel electrode system). A 0.1M stock sodium perchlorate solution was also prepared in demineralized doubly distilled water. Standard perchlorate solutions (10^{-2} – $10^{-6}M$) were freshly prepared by accurate dilutions of the stock perchloric acid and sodium perchlorate solutions with 0.1M sodium chloride and demineralized doubly distilled water, respectively.

Procedures

Membrane preparation. Nitron-perchlorate was prepared by mixing 30 ml of aqueous 0.01M perchloric acid with 30 ml of 0.01M nitron solution in 10% acetic acid. The mixture was cooled in ice-water and the precipitate was filtered off by suction, washed with demineralized doubly distilled water, dried at about 110° for 20 min and ground. The liquid ion-exchanger was prepared by making a 0.01M solution of nitron-perchlorate in nitrobenzene.

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Electrode preparation. An Orion liquid-membrane electrode barrel (Model 92) was used for electrode assembly with a porous membrane (Orion 92-06-04). The internal reference solution was 0.01M sodium chloride/0.01M sodium perchlorate. After assembly of the electrode, the internal reference solution and the liquid ion-exchanger were injected into the appropriate ports. The electrode was conditioned by soaking in 0.01M sodium perchlorate for 2 days. When not in use, the electrode was kept immersed in the same solution.



Electrode calibration. Portions (25 ml) of 10⁻²–10⁻⁶M perchloric acid or sodium perchlorate standard solutions were transferred to 50-ml beakers, and adjusted to pH 3–7 by addition of dilute sodium hydroxide solution. The nitron-perchlorate liquid-membrane electrode, in conjunction with a double-junction Ag/AgCl reference electrode, was immersed in the stirred solutions. The potentials were displayed on a chart recorder and the stable values were plotted as functions of pClO₄, to give a calibration graph.

Electrode selectivity. The selectivity coefficients were evaluated by the mixed solution method of Srinivasan and Rechnitz²³ from potential measurements on solutions containing 10⁻³M sodium perchlorate and various concentrations (10⁻²–10⁻⁵M) of the interfering anion. Equation (1) was used for the calculation, where Δ*E* is the change in potential in the presence of a second anion, *j*^{z-}, *S* is the slope of the calibration graph for perchlorate and *a*₁ and *a*₂ are the concentrations of perchlorate and the second anion, respectively.

$$K_{ij}^{\text{pot}} = (10^{\Delta E/S} - 1)a_1/(a_2)^{1/z} \quad (1)$$

Determination of perchlorate in propellants. A quantity of the powder equivalent to 0.2–10 mg of perchlorate ion was weighed out, transferred to a 50-ml beaker and dissolved in 25 ml of 0.1M sodium chloride. The pH was adjusted to 3–7 and the potential was recorded as for the calibration standards and the perchlorate concentration read off the calibration graph.

Solubility of sparingly soluble perchlorates. A 1-g portion of the sparingly soluble perchlorate was suspended in 50 ml of demineralized doubly distilled water in an airtight Erlenmeyer flask. The mixture was shaken vigorously for 3 hr in a thermostat adjusted to 35 ± 1° and allowed to stand for an hour at the same temperature before potential measurement as previously described. The perchlorate concentration was read from the calibration graph prepared with aqueous standard sodium perchlorate solutions. The solubility (*M*) and solubility product (*K_{sp}*) were then calculated.

RESULTS AND DISCUSSION

Nature and composition of the membrane

The strong organic base 4,5-dihydro-1,4-diphenyl-3,5-phenylimino-1,2,4-triazole (nitron) forms a fairly insoluble crystalline nitrate and perchlorate.²⁴ In this study a nitron-perchlorate precipitate was prepared and examined as a novel electroactive material in a liquid-membrane responsive to the perchlorate ion. Elemental analysis of the product agreed with the composition C₂₀H₁₆N₄·HClO₄. The most significant absorption bands in the infrared spectrum of the precipitate, at 3320 and 1100 cm⁻¹, are assigned to stretching vibrations of the secondary amino and perchlorate groups, respectively.

The solubility of nitron-perchlorate in some lipophilic solvents such as nitrobenzene, 1-octanol, 1-decanol and benzyl alcohol was tested. Nitron-perchlorate has high solubility in both nitrobenzene and benzyl alcohol. Hence, solutions of nitron-perchlorate in both solvents were prepared and examined as liquid-membranes for potentiometric determination of perchlorate by use of the electrochemical cell.

The emf may be expressed as a function of perchlorate activity according to the equation

$$E = E_0 - S \log[a_1 + K_{ij}^{\text{pot}}(a_2)^{1/z}] \quad (2)$$

where *E*₀ is the conditional standard potential of the electrode under the conditions used in the cell, *S* is the slope of the calibration graph, *K_{ij}^{pot}* is the selectivity coefficient, *a*₁ and *a*₂ are the activities of the perchlorate ion and of a foreign ion of charge *z*, in the test solution, respectively. A similar equation can be used to relate the emf to concentration.

Performance characteristics of the membrane

The response characteristics of an electrode incorporating 0.01M nitron-perchlorate in nitrobenzene were evaluated at 25 ± 1°. The potential-response to perchlorate was linear for aqueous solutions over at least 3 orders of magnitude of activity or concentration, with near-Nernstian slope (Fig. 1). The activity coefficient for perchlorate in 0.1M sodium chlo-

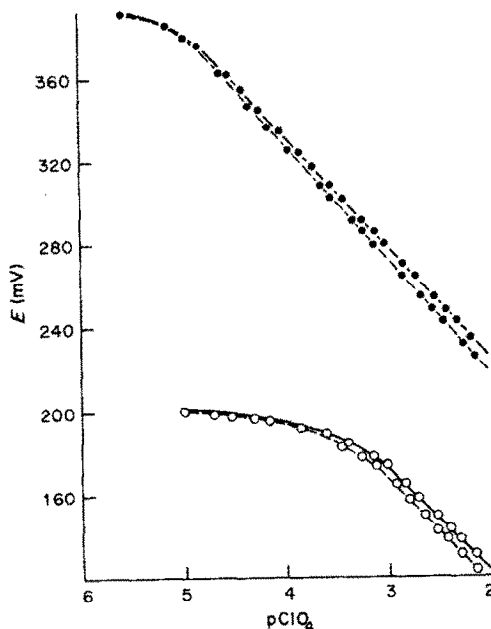


Fig. 1. Potential-response curves for nitron-perchlorate liquid-membrane electrodes with nitrobenzene (●) and benzyl alcohol (○) as membrane solvent as functions of activity (—) and concentration (---).

ride, as calculated from an extended Debye-Hückel relation, is 0.76.

Least-squares analysis of the data showed that the calibration plot was linear from 10^{-2} to $2 \times 10^{-5} M$ with a slope of 56 mV/pClO_4 . The standard deviation of a measurement was 0.8 mV . The lower limit of detection, defined as the concentration of perchlorate corresponding to the intersection of the extrapolated linear segments of the calibration graph, was $8 \times 10^{-6} M$. This limit is lower than those obtained with many other previously described electrodes.^{5,8,10,25} With benzyl alcohol as the solvent, however, the electrode response was poor, probably because benzyl alcohol is more viscous and more soluble in water, and has a lower dielectric constant than nitrobenzene.

Potential stability and response time

The results obtained from 5 different perchlorate electrodes, all with nitrobenzene as the membrane solvent but prepared over a period of 6 months, showed that the reproducibility of the potential readings on the same day for the same perchlorate solutions was within $\pm 1.2 \text{ mV}$. The variation in potential reading for a given pClO_4 during 6 weeks of normal use was within $\pm 3 \text{ mV}$. Electrode age up to 6 weeks had no significant effect on the slope of the calibration plot, which remained within 1.8 mV/pClO_4 of its original value. The liquid membrane was usable for 6 weeks before renewal.

The average response time, defined as the time required for the electrode to reach a potential within $\pm 1 \text{ mV}$ of the final equilibrium value after transfer between perchlorate solutions differing in concentration by a factor of 10, or after rapid 10-fold increase in concentration by addition of sodium perchlorate, was 20 sec for concentrations $\geq 10^{-3} M$ and 90 sec for concentrations $\leq 10^{-4} M$.

Effect of pH on the membrane response

Figure 2 shows that the electrode potential is independent of pH in the range 2.5–8.5 (the electrode

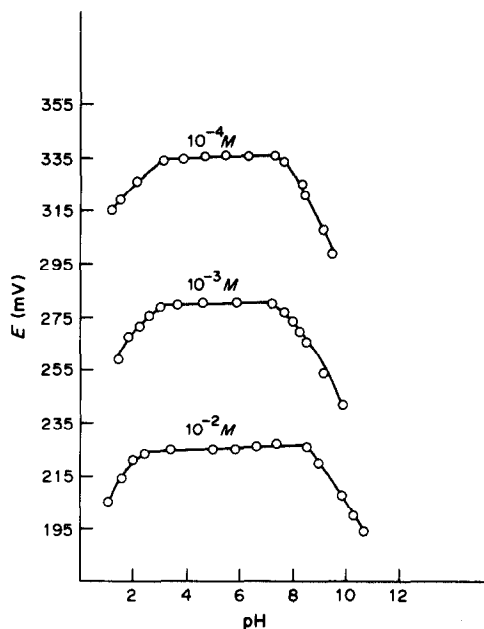


Fig. 2. Effect of pH on the potential response of nitron-perchlorate liquid-membrane electrode at different concentrations of ClO_4^- .

potential did not vary by more than $\pm 2 \text{ mV}$ for any perchlorate concentration in the range of 10^{-2} – $10^{-4} M$). Above pH 9, however, there was a substantial decrease in the electrode potential, probably owing to gradual dissociation or decomposition of nitron-perchlorate at the membrane surface.

Effect of other anions

The performance of the electrode in the presence of 30 different inorganic and organic anions was assessed by measuring the selectivity coefficient values ($K_{i,j}^{\text{pot}}$) by the mixed solution method.^{23,26} The results obtained (Table 1) show that the electrode displays high selectivity for perchlorate.

Table 1. Selectivity coefficients for some common anions with the nitron-perchlorate liquid-membrane electrode

Interfering ion (j)	$K_{i,j}^{\text{pot}}$	Interfering ion (j)	$K_{i,j}^{\text{pot}}$
F^-	4.1×10^{-3}	$\text{Fe}(\text{CN})_2^{2-}$	1.3×10^{-4}
Cl^-	7.2×10^{-4}	$\text{Fe}(\text{CN})_6^{4-}$	8.2×10^{-5}
ClO_3^-	4.3×10^{-3}	MnO_4^-	2.6
Br^-	2.7×10^{-3}	CrO_4^{2-}	6.2×10^{-4}
BrO_3^-	1.3×10^{-3}	H_2PO_4^-	5.3×10^{-3}
I^-	8.3×10^{-2}	CO_3^{2-}	2.7×10^{-4}
IO_3^-	1.1×10^{-3}	VO_3^-	1.3×10^{-4}
IO_4^-	3.6	MoO_4^{2-}	3.1×10^{-4}
NO_2^-	3.2×10^{-3}	WO_4^{2-}	3.5×10^{-4}
NO_3^-	1.1×10^{-3}	Acetate ⁻	4.2×10^{-3}
SO_3^{2-}	3.2×10^{-4}	Oxalate ²⁻	3.0×10^{-4}
SO_4^{2-}	3.8×10^{-4}	Tartrate ²⁻	3.2×10^{-4}
$\text{S}_2\text{O}_3^{2-}$	2.8×10^{-4}	Succinate ²⁻	2.8×10^{-4}
$\text{S}_2\text{O}_8^{2-}$	7.7×10^{-4}	Citrate ³⁻	1.2×10^{-4}
CNS^-	1.8	Benzoate ⁻	4.3×10^{-3}

Surprisingly, the electrode displays only a weak response to nitrate ($K_{ij}^{pot} = 1.1 \times 10^{-3}$) although nitron reacts quantitatively with both perchlorate and nitrate under the same conditions. To understand this phenomenon, the partition of perchlorate and nitrate between water and a solution of $10^{-2}M$ nitron in nitrobenzene was tested by measuring the concentrations of both ions in the aqueous phase after the extraction. The results showed that nitrobenzene extracted the perchlorate and retained the nitron-perchlorate almost quantitatively. The degree of extraction of nitrate was only about a hundredth of that of perchlorate, probably owing to the difference in the hydration energies of the two ions. It is known that the perchlorate ion is more hydrophobic and larger than the nitrate ion. The hydration enthalpies (ΔH_{aq}°) are -57.1 and -74.5 kcal/mol and the ionic radii are 2.45 and 1.96 Å for the perchlorate and nitrate ions, respectively.²⁷ The larger, more hydrophobic, anion has the smaller hydration enthalpy.²⁷ Competition between the perchlorate ion and the smaller and more strongly hydrated nitrate ion thus favours preferential extraction of the former by the membrane phase, causing the higher selectivity of the electrode for perchlorate. The effect of relative anion hydration energies has similarly been used to explain the solvent extraction behaviour of some anions^{28,29} and the selectivity of some anion-exchange resins.³⁰

Compared with some of the commercially available perchlorate ion-selective electrodes,^{31,32} the nitron-perchlorate liquid-membrane electrode is notably tolerant of Br^- , NO_2^- , NO_3^- , ClO_3^- and carboxylate anions and is less affected by many other inorganic anions (Table 1). It has been reported that NO_3^- , NO_2^- , Br^- , ClO_3^- , CN^- and I^- ions cause serious errors with some perchlorate membrane electrodes, as evidenced by the 5–25% error produced when there are equal quantities of these ions and perchlorate.^{31,32} The use of the nitron-perchlorate liquid-membrane electrode for the determination of perchlorate in the presence of these ions, however, is without complications. Mixtures containing 10–100 $\mu\text{g/ml}$ perchlorate and ten times that concentration of any of these ions can be determined with the present electrode by the calibration graph method, with an average recovery of 97–102% and mean standard deviation of 2.3%.

The nitron-perchlorate liquid-membrane electrode responds, however, to CNS^- , IO_4^- and MnO_4^- ions. Most of the commercially available perchlorate ion-selective electrodes are also known to respond to MnO_4^- , IO_4^- and $Cr_2O_7^{2-}$ ions.³² Fortunately, the interference of a 10-fold ratio of IO_4^- or MnO_4^- to ClO_4^- is completely circumvented by prior heating of the test solution at 60–80° for 10 min with glycerol and oxalic acid, respectively. On the other hand, the responses of the electrode to CNS^- , IO_4^- and MnO_4^- were linear over the concentration range 10^{-2} – $10^{-4}M$ with slopes of 40, 52 and 65 mV/decade, respectively.

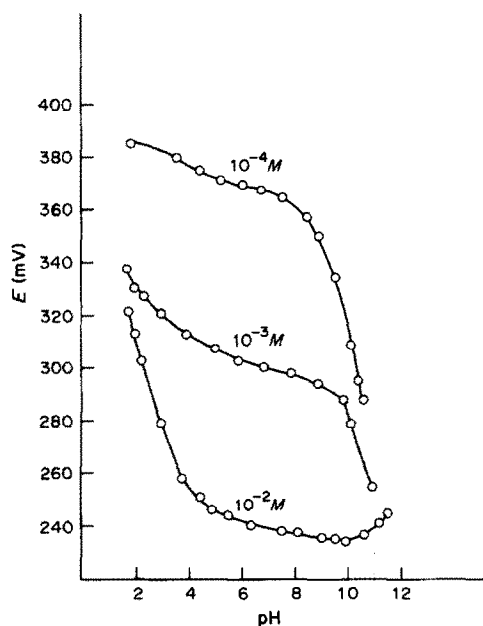


Fig. 3. Effect of pH on the potential response of the nitron-perchlorate liquid-membrane electrode at different concentrations of MnO_4^- .

This suggests possible use of the electrode as a potentiometric sensor for determination of these ions. Direct potentiometric determination of 50–1000 $\mu\text{g/ml}$ CNS^- , IO_4^- and MnO_4^- concentrations at pH 6–7 by use of calibration graphs prepared with standard solutions of these ions showed an average recovery of 97% and a mean standard deviation of 3.1%. The effect of pH on the electrode responses for CNS^- and IO_4^- was rather similar to that for ClO_4^- itself, with a working range of pH 3–7, but the MnO_4^- response was more seriously affected, as shown by Fig. 3.

Table 2. Direct potentiometric determination of the perchlorate ion with the nitron-perchlorate liquid-membrane electrode

[ClO_4^-]		Relative standard deviation, † %
Taken, $\mu\text{g/ml}$	Recovery, * %	
2.0	97.1	2.8
5.0	98.4	2.5
10.0	99.5	1.8
19.9	98.9	1.9
29.8	99.1	1.7
39.8	98.9	2.0
79.6	99.4	1.8
99.5	100.0	1.7
199.0	98.5	2.1
298.5	98.0	1.8
398	99.3	1.8
597	97.9	1.7
796	98.5	1.5
995	99.5	1.3

*Average of 3 measurements.

†Range method.

Table 3. Direct potentiometric determination of perchlorate in propellants

Compound*	[ClO ₄ ⁻], %		Relative standard deviation, %
	Theory	Recovery†	
Ammonium perchlorate	84.68	98.2	1.7
Urea perchlorate	61.99	99.1	1.9
Hydrazine perchlorate	75.09	98.5	2.1
Ethylamine perchlorate	68.38	97.9	1.8
Ethylenediamine perchlorate	61.99	99.2	1.7

*Concentration used 10–200 µg/ml.

†Average of 5 measurements.

Table 4. Direct potentiometric determination of the solubility products of some sparingly soluble perchlorates

Compound	K _{sp}		
	Present method at 35°	Potentiometric method ²⁵ at 35°	Gravimetric method at 25°
Potassium perchlorate	1.6 × 10 ⁻²	1.6 × 10 ⁻²	8.9 × 10 ^{-2*}
Hexa-amminecobalt(III) perchlorate	9.2 × 10 ⁻⁶	9.4 × 10 ⁻⁶	6.3 × 10 ^{-6†}
Tetrakis(pyridine)copper(II) perchlorate	5.2 × 10 ⁻⁵	5.4 × 10 ⁻⁵	—
Nitron perchlorate	2.9 × 10 ⁻⁸	—	3.8 × 10 ^{-8§}

*Nordmann.³³†Taylor *et al.*³⁴§Vogel.²⁴

Determination of perchlorates

The use of the nitron–perchlorate liquid-membrane electrode for direct potentiometric determination of perchlorate was first examined with 2.5–1225 µg/ml sodium perchlorate (equivalent to approximately 2–1000 µg/ml perchlorate), in triplicate. The average recovery was 98.8% and mean standard deviation 1.9% (Table 2). The purity of some perchlorate compounds commonly used as propellants was also determined by preparing the sample solution in 0.1M sodium chloride (to control the ionic strength), adjusting the pH to 3–7 if necessary, and measuring the potential; a sodium perchlorate calibration graph was used. The average recovery was 98.6% and mean standard deviation 1.8% (Table 3).

The solubilities of some sparingly soluble perchlorates were also determined. The equilibrium potentials of saturated solutions of potassium, hexa-amminecobalt(III), tetrakis(pyridine)copper(II) and nitron perchlorates were directly measured at 35 ± 1°. The solubility products computed and given in Table 4 compare favourably with values previously recorded by other measurement techniques.^{24,25,33,34}

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