

Automatic Determination of Ethylene Glycol in Anti-freeze Solutions with a Periodate-sensitive Flow-through Electrode

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The response of the perchlorate ion-selective electrode toward periodate is known.¹ A detailed study of this electrode as a periodate activity sensor and its capability of monitoring periodate reactions have been reported.² New schemes of kinetic^{3,4} and catalytic⁵⁻⁷ analysis

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have been developed based on the high reactivity of periodate toward certain classes of compounds in conjunction with the capability of the perchlorate electrode to follow periodate activity during the course of these reactions.

Recently, a new type of flow-through ion-selective electrode unit operating with liquid ion exchangers has been developed in our laboratory: This electrode unit can be filled with almost any type of liquid ion exchanger, resulting in an excellent in-flow monitor for the corresponding ion, suitable for use in conjunction with automated flow systems of analysis. This paper describes the use of a periodate flow-through electrode of the aforementioned type for the determination of ethylene glycol in aqueous solutions. The analysis is completely automated and samples can be analysed at a rate of forty per hour. Amounts of ethylene glycol in the range 75–750 μg (0.4 ml of 0.003–0.03 M solution) were determined in synthetic samples with an average error of 1.9% and a coefficient of variation of 0.7%. The method has been applied to the analysis of anti-freeze solutions obtained from the cooling system of military vehicles. Comparison with the Fleury - Lange iodimetric method⁸ gave satisfactory results.

Experimental

Equipment

The periodate flow-through electrode consists of a piece of porous glass (pore size 5–10 μm) with an equilateral triangular cross-section entrapped in a cylindrical time-cured plastic material (Epofyx resin, Struers Scientific Instruments, Copenhagen, Denmark). An axially drilled hole passing through the porous glass constitutes the pathway for the solution under measurement. Radially drilled holes reaching the porous glass serve as liquid ion-exchanger reservoirs. These holes are filled with small amounts (0.1–0.2 ml) of perchlorate liquid ion exchanger (Orion ClO_4^- ion exchanger, Cat. No. 92-81-01). This exchanger consists of an almost saturated solution of the complex $\text{Fe}(4,7\text{-diphenyl-1,10-phenanthroline})_3(\text{ClO}_4)_3$ in 2-nitro-*p*-cymene. The porous glass is always kept wet with the liquid ion exchanger, acting as a solid support for the liquid membrane. One of the radially drilled holes is filled with 0.1 M sodium chloride - 0.1 M sodium perchlorate internal reference solution into which a silver - silver chloride wire is dipped. A detailed description of the flow-through electrode unit will be published elsewhere.⁹

The periodate-sensitive flow-through electrode is used in conjunction with a Technicon AutoAnalyzer II system consisting of a sampler and a proportioning pump. The potential of the flow-through electrode is measured against a saturated calomel electrode, and a Sargent-Welch, Model XKR, recorder is used. A Corning, Model 12, Research pH meter, acting as a voltage follower, is inserted between the electrodes and the recorder to match the high output impedance of the electrodes with the relatively low input impedance of the recorder. Fig. 1 shows a schematic diagram of the automated analysis system.

Reagents

All solutions were prepared from analytical-reagent grade materials using de-ionised, distilled water.

Sodium periodate working solution, 0.0200 M. Dissolve 4.28 g of sodium periodate in water and dilute to 1 l. This solution should be kept in an amber-glass bottle.

Composite phosphate buffer - EDTA solution, pH 7.0. Dissolve 69.0 g of sodium dihydrogen orthophosphate monohydrate ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$) and 7.44 g of EDTA (disodium salt) in about 800 ml of water. Adjust the pH to 7.0 with saturated sodium hydroxide solution and dilute to 1 l with water. This solution is 0.50 and 0.020 M in phosphate and EDTA, respectively.

Ethylene glycol stock solution, 0.30 M. Dissolve 18.6 g of ethylene glycol in water and dilute to 1 l. The exact titre should be determined iodimetrically with the Fleury - Lange method.⁸ Standard ethylene glycol solutions of concentration 0.0030, 0.0100, 0.0200 and 0.0300 M are prepared from the stock solution by dilution.

Procedure

The samples of anti-freeze solutions are filtered through a Whatman No. 41 filter to remove particulate matter and oil spills. The filtrate is diluted to adjust its ethylene glycol concentration to the range 0.003–0.030 M (typical dilutions are 1:520 to 1:500). Sample cups are

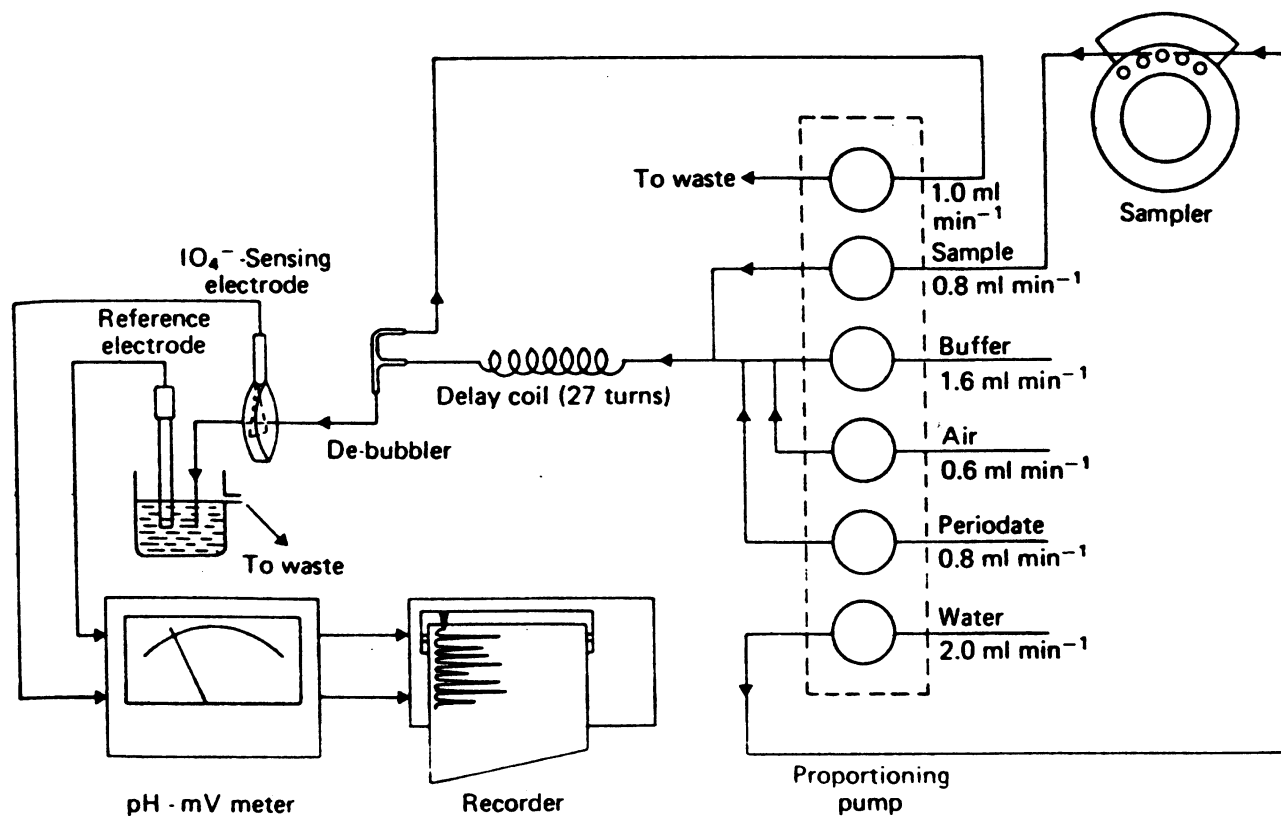


Fig. 1. Schematic diagram of automated analysis system.

filled with the samples and standard solutions. A cam is selected so as to run 40 samples per hour with a sample to wash ratio of 1:2. The instrument and the recorder are activated and the analysis proceeds automatically.

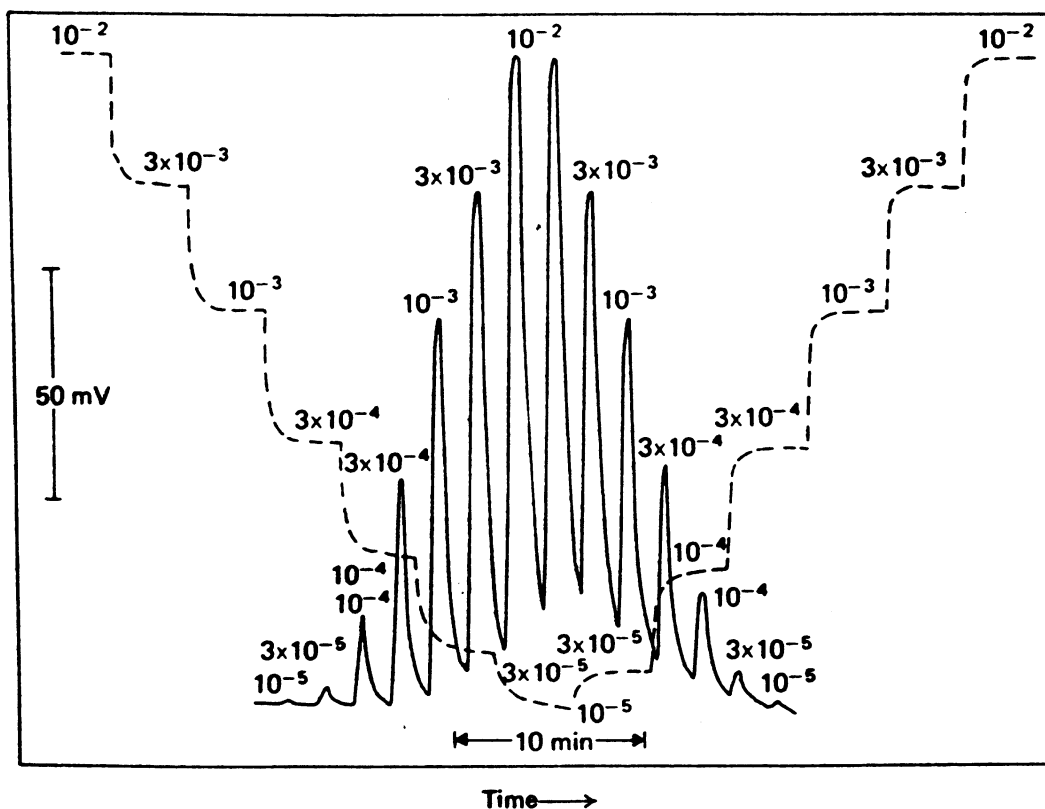


Fig. 2. Dynamic response (solid lines) and steady-state response (dashed lines) of the periodate sensitive flow-through electrode. Concentrations, in moles per litre, are shown at the corresponding peaks and plateaux.

Results and Discussion

Electrode Response

Fig. 2 shows the recorded signal (solid lines) obtained when the periodate solution of the manifold shown in Fig. 1 was replaced with water and various sodium periodate solutions were sampled (dynamic response). It should be noted that because of the dilution factor the final periodate concentration is one quarter of the initial concentration. Therefore, it is concluded from Fig. 2 that the electrode can detect periodate at concentrations of about 2.5×10^{-6} M. Fig. 2 also shows the recorded signal (broken lines) when the sampler is set permanently in the "wash" position and various sodium periodate solutions are pumped through the periodate channel (steady-state response).

The electrode steady-state potential is directly proportional to the logarithm of periodate activity at periodate concentrations down to 3×10^{-5} M, which is about the same as for the Orion 92-18 liquid membrane perchlorate electrode.² Steady-state potential values are equal to the dynamic peak potential values. The peak values show excellent reproducibility for initial periodate concentrations higher than 10^{-3} M.

The electrode response is stable provided that one drop of perchlorate liquid ion exchanger is added every 2-3 working days.

Calibration Graph

Calibration graphs are prepared by plotting peak-height values in millivolts against the ethylene glycol concentrations in the standard solutions. Linearity and reproducibility are improved at higher periodate concentrations, but the sensitivity is reduced. A 0.020 M initial sodium periodate concentration was chosen as a compromise.

Fig. 3 shows recorded tracings for a typical calibration sequence. It can also be seen that the final value for the 0.0010 M ethylene glycol peak is approximately equal to 93% of the steady-state value obtained under continuous sample flow conditions.

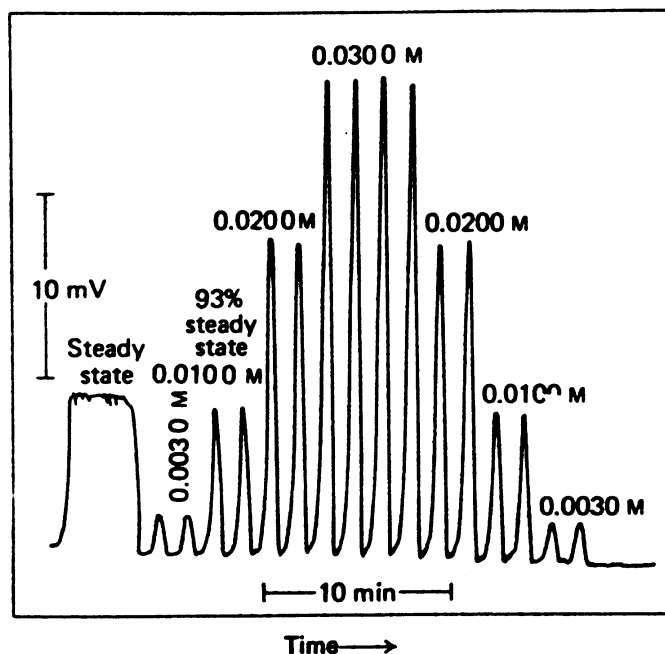


Fig. 3. Recorded tracings for a typical calibration sequence.

Effect of pH and Delay Time

pH has a moderate effect on the rate of the periodate - ethylene glycol reaction in the pH range 4-7.³ A pH of 7.0 was chosen because at this pH higher sensitivity and better precision were observed. EDTA was added to the buffer solution to prevent reactions of periodate with other reducing substances, frequently catalysed by uncomplexed metal ions, and also the accumulation of insoluble salts in the sensing porous glass membrane of the flow-through electrode.

A delay coil with 27 turns was found to be suitable for achieving acceptable sensitivity and linear calibration graphs. The peak-height potential values obtained correspond to periodate concentrations that indicate that about 50% of the ethylene glycol is oxidised until the peak value is obtained.

Interfering Substances

Any substance that reacts with periodate would interfere and should be eliminated prior to the measurements. Peak heights relative to ethylene glycol for several interfering polyhydroxy compounds are given in Table I.

TABLE I
PEAK-POTENTIAL HEIGHTS RELATIVE TO ETHYLENE GLYCOL FOR VARIOUS INTERFERING COMPOUNDS

Compound	Peak height ratio*
Propylene glycol	1.6
Butylene glycol†	1.6
Potassium sodium tartrate.. .. .	1.8
Glycerine	2.6
Glucose	5.9
Mannitol	7.3

* Ratio of peak height of interfering compound to that of ethylene glycol; all concentrations 0.0100 M.

† Mixture of *meso* and racemic form.

Precision and Accuracy

Fourteen replicate determinations were made with 0.0050 and 0.0020 M ethylene glycol solutions. The coefficients of variation were 0.78 and 0.71%, respectively. The accuracy of the method was checked with measurements on 18 samples of known ethylene glycol concentrations. The average error was 1.9%.

Analytical Application

Twenty samples of anti-freeze solution obtained from the cooling system of military vehicles were analysed according to the proposed method and also by the Fleury - Lange iodimetric method.⁸ The correlation graph of both methods was linear, passing almost through the origin, with the equation $y = 1.004x + 0.27$, $r_{yx} = 0.998$ and $n = 20$ (concentration range of the samples = 0-50% m/V). There was satisfactory agreement between the results obtained with the two methods, the average relative difference of the results obtained being 1.9%.

Conclusion

The proposed method for the determination of ethylene glycol is a typical application of an ion-selective electrode in the field of automated analysis. The periodate-sensitive flow-through electrode provides an inexpensive, sensitive and reliable sensor with many possible applications in automated analytical schemes. The possible application of this electrode to the determination of other reducing substances and catalytically active species is under investigation.

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