A NEW TETRAFLUOROBORATE LIQUID MEMBRANE ELECTRODE FOR SELECTIVE DETERMINATION OF BORON

By

SAAD S. M. HASSAN

Department of Chemistry, Faculty of Science,

Qatar University, Doha, Qatar

ABSTRACT

The construction and performance characteristics of a new liquid membrane electrode selective for BF_4^- ion are herein described. The electrode incorporates nitron–tetrafluoroborate ion pair complex in nitrobenzene as a liquid membrane. The electrode shows a rapid Nernstian response for BF_4^- ion over the concentration range of 10^{-1} to 10^{-5} M and the potential is almost independent of the pH over the range of 3 – 9. The selectivity coefficient values obtained for 21 different anions and cations show no significant interference. The electrode is satisfactorily used for the determination of 0.5 – 500 μg / ml of boron after conversion to BF_4^- ion. The average recovery is 98.8 % and the mean standard deviation being 2.1 %. The electrode is also used for determination of boron in borosilicate glasses.

INTRODUCTION

Determination of low levels of boron is becoming increasingly important in glass, semiconductor, nuclear and pharmaceutical industries. The analysis of almost all boron-containing compounds requires a preliminary treatment which ultimately results in an aqueous boric acid solution. The most successful and commonly used methods for selective determination of boron are based on a prior conversion of boric acid to tetrafluoroborate ion (BF_4^-). Ion pair complexation of BF_4^- ion with methylene blue (Lanza and Buldini 1974), tetrabutylammonium salt (Grallath *et al.,* 1980) and tris (1,10 – phenanthroline) Cd (Liu *et al.,* 1985), followed by extraction and measurement of the colour, boron content and cadmium content of these complexes by spectrophotometry, atomic emission spectrometry with plasma excitation and atomic absorption spectrometry, respectively, have been suggested. Tetrafluoroborate has also been determined gravimetrically by precipitation as nitron derivative (Lucchesi and DeFord, 1957).

The recent advances in the ion selective electrodes (Ma and Hassan, 1982, Lakshminarayanaiah, 1976) made it possible to determine low levels of BF_4^- ion directly without further treatment. The membranes of most of the described BF_4^- electrodes consist of quaternary ammonium (Chang, *et al.,* 1980), basic dyes (Fogg *et al.,* 1974) and metal phenanthroline (Lakshminarayanaiah, 1976) as counter ions. These types of membranes, however, suffer from substantial interferences by many common ions. In the present work we describe a new liquid membrane electrode based on the use of nitron–tetrafluoroborate ion pair as a novel electroactive material. The electrode is highly selective and sensitive for BF_4^- ion and offers many advantages over many of those previously described.

MATERIALS AND METHODS

Apparatus. All potentiometric measurements were made at $25 \pm 2\,^{\circ}C$ with an Orion (Model 901) microprocessor ionalyzer using nitron–tetrafluoroborate liquid membrane electrode in conjunction with an Orion double junction Ag / AgCl reference electrode (Model 90–02) with 0.1M NH_4F in the outer compartment. Adjustment of the pH was conducted with an Orion combined glass–calomel electrode (Model 91–02). Pipettes and volumetric flasks made of polypropylene were used. The spectrophotometric measurements were carried out with a Unicam SP 1800 spectrometer using 1.00 cm quartz cuvettes.

Reagents. All the reagents used were of analytical reagent grade unless otherwise stated. Deionized twice distilled water and distilled organic solvents were used throughout. Stock aqueous boric acid solution (0.1 M) was prepared and standardized by titration with standard sodium carbonate–free sodium hydroxide in the presence of mannitol to a phenolphthalein end point. Nitron reagent was prepared by dissolving 4 g of pure nitron in a 25 ml aliquot of 5 % (v / v) acetic acid and stored in a brown bottle. National Bureau of Standards Borosilicate Glasses Nos. 92 and 93 as well as borosilicate Rasching rings from Corning Glass Works were used.

Nitron–tetrafluoroborate. A 60 ml aliquot of an aqueous 0.1M boric acid solution and a 20 ml aliquot of the nitron reagent were placed in a 250–ml polyethylene beaker followed by 4 ml of concentrated HF (29 M). The mixture was allowed to stand at room temperature for 2 hours and the precipitate was filtered with a G–3

sintered glass crucible, washed with deionized twice distilled water and dried at $105\,^{\circ}C$ for one hour.
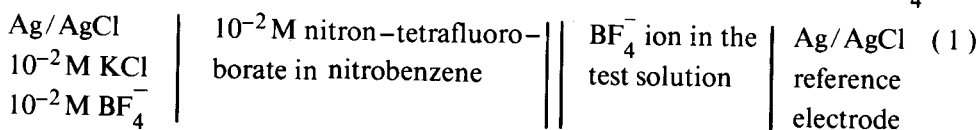
Nitron–tetrafluoroborate liquid membrane electrode. An Orion liquid membrane electrode barrel (Model 92) was used with an Orion 92 – 05 – 04 porous membrane to separate the organic phase from the test solution. The organic phase was a 10^{-2} M solution of nitron–tetrafluoroborate in nitrobenzene. The internal filling reference solution was a mixture of an equal volume of 10^{-2} M KCl and BF_4^-. The electrode was conditioned by soaking in 10^{-2} M BF_4^- solution for 3 days before use and stored in the same solution when not in use.

Calibration of the electrode and determination of boron. 25–ml aliquots of 10^{-1} to 10^{-4} M aqueous boric acid solution were transferred to 100–ml polyethylene beakers and mixed with 6 ml aliquots of concentrated HF (29 M). The solutions were allowed to stand for 10 – 15 min at room temperature (20 – 25 $^{\circ}C$). The pH of the solutions was adjusted to 5 – 7 with concentrated aqueous ammonia solution (14.5 M), using a combined glass–calomel electrode system, then transferred to 250 – ml polypropylene volumetric flasks and completed to the volume with deionized twice distilled water. After shaking, 25 ml aliquot of each solution was transferred to a 100 – ml polyethylene beaker and the nitron–tetrafluoroborate liquid membrane electrode in conjuction with a double junction Ag / AgCl reference electrode was immersed into the solution. The potentials of the stirred solutions were recorded when becoming stable and plotted as a function of logarithm of boron concentration. The calibration plot was used for subsequent determination of boron in unknown solutions. A blank experiment was carried out under identical conditions.

Determination of boron in borosilicate glasses. The borosilicate glasses were first dried at $105\,^{\circ}C$ for 24 hours and a weighed sample ($\sim$200 mg) was placed in a 250 – ml polyethylene Erlenmeyer flask. A 5 – ml aliquot of deionized bidistilled water was added to form a slurry followed by 10 ml of concentrated HF (48 %). The flask was covered with a plastic stopper and swirl under a stream of cold tap water. After 10 – 15 min, complete dissolution of the glass and formation of tetrafluoroborate were achieved. The pH of the solution was adjusted to 5 – 7 with concentrated aqueous ammonia and the solution was quantitatively transferred to a 500 – ml volumetric flask. Deionized bidistilled water was added to bring the volume to the mark. After shaking, a 25 ml aliquot of the formed tetrafluoroborate solution was transferred to 100 – ml polyethylene beaker and measured as previously described.

RESULTS AND DISCUSSION

Nature and composition of the membrane. Nitron–tetrafluoroborate was prepared by the reaction of nitron with tetrafluoroboric acid, characterized and examined as an electroactive material. A 10^{-2} M solution of nitron–tetrafluoroborate in nitrobenzene was tested as a liquid membrane responding for BF_4^- ion. The electrochemical cell represented by equation 1 was used for direct potentiometric determination of boron after conversion to BF_4^- ion.

Ag/AgCl	10^{-2} M nitron–tetrafluoro–	BF_4^- ion in the	Ag/AgCl	(1)
10^{-2} M KCl	borate in nitrobenzene	test solution	reference	
10^{-2} M BF_4^-			electrode	

The emf was measured at 25 °C as a function of logarithm BF_4^- ion concentration. Least squares analysis of the data obtained shows that the electrode displays a linear response for BF_4^- ion over the concentration range of 10^{-1}–10^{-5} M with an anionic slope of 59 mV / concentration decade. The lower limit of detection is 8×10^{-6} M (equivalent to 88 ng boron/ml).

Response time and stability. The time required for nitron–tetrafluoroborate liquid membrane electrode to reach a value of ± 1 mV from the final equilibrium potential after successive immersion in various BF_4^- solutions each having a 10 – fold difference in concentration is measured. The time required to achieve ± 1 mV of the steady potential by rapid 10 – fold increase of BF_4^- concentration to the same solution was also monitored. Both results indicate that the electrode provides stable and fast potential readings. The average response time for 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4} and 10^{-5} M BF_4^- are 15, 30, 60, 90 and 120 seconds, respectively. The electrode exhibits a day–to–day reproducibility within ± 2 mV and the life span of the electrode is at least 2 months.

Effect of pH. To check the pH dependence of the electrode potential, potential–pH curves for 10^{-1}–10^{-5} M BF_4^- solutions were constructed. The pH values of the initial BF_4^- solutions were altered over the range of 2 – 12 by addition of small volumes of 0.1 M NaOH or HCl. The results show that the potential values are almost independent of the pH in the range of 3 – 9. The potential difference does not exceed ± 3 mV within the entire range of pH.

Membrane selectivity. The response of nitron–tetrafluoroborate liquid membrane

electrode was examined in the presence of some interfering anions and cations and the corresponding selectivity coefficients ($K_{i,j}^{pot}$) were calculated using the mixed solution method (Ma and Hassan, 1982). The potentials displayed by solutions each containing 10^{-2} M of the foreign substance with variable BF_4^- concentrations in the range of $10^{-2} - 10^{-5}$ M were measured and equation 2 applied.

$$K_{i,j}^{pot} = (10^{\Delta E/S} - 1) a_i /(a_j)^{1/z} \tag{2}$$

Where S is the slope of the calibration curve of BF_4^-, z is the charge of the foreign ion, ΔE is the change in the potential due to the presence of the interfering substance j, a_i and a_j are the concentrations of BF_4^- and the interfering substance, respectively. The results obtained (Table 1) show no significant interference by many anions and cations commonly associated with boron. The electrode shows better selectivity for BF_4^- over many anions compared with those commercially available (Orion Research Inc., 1977) or previously described (Chang et al., 1980, Fogg et al., 1974) electrodes. The presence of IO_4^-, CNS^- and I^-, however, interfere; the $K_{i,j}^{pot}$ values are 1.21, 1.09 and 1.16, respectively. The effect of these interfering ions is tolerated by addition of glycerol, iron (III) and sodium nitrite solutions and heating before converting boron to BF_4^-, respectively.

Formation and stability of BF_4^-. Quantitative transformation of the boron into BF_4^- is a prerequisite for the determination of boron with the nitron–tetrafluoroborate liquid membrane electrode. BF_4^- is formed by the reaction of HF with boric acid (equation 3).

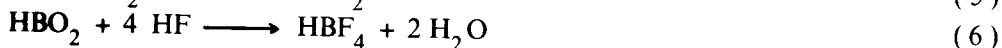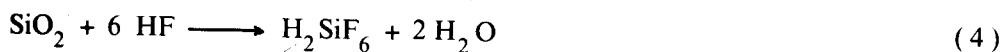$$H_3 BO_3 + 4 F^- \longrightarrow BF_4^- + 3 OH^- \tag{3}$$

The rate of this acid catalysed reaction is enhanced by the presence of strong acid, excess HF and heat (Gulens and Leeson, 1980). An investigation of the effect of both the HF concentration over the range of 0.2 – 10 M and the temperature over the range of 20 – 60 °C on the rate of BF_4^- formation indicates that 10^{-1} to 10^{-5}M $H_3 BO_3$ solutions are quantitatively converted at 20 – 25 °C to BF_4^- within 10 – 15 min in the presence of 4 – 5 M HF. Since the electrode response is affected by the excess acid and not influenced by the F^- ion concentrations over the pH range of 3 – 9, 5M HF is used for converting $H_3 BO_3$ to BF_4^- and aqueous ammonia solution is added after complete reaction to neutralize the excess acid. It is worth mentioning

that BF_4^- ion is hydrolyzed at high or low pH values to the species $BF_3(OH)^-$, $BF_2(OH)_2^-$ and $BF(OH)_3^-$ which are not sensed by the electrode, Thus, the pH of the test BF_4^- solutions should be adjusted to $5-7$. Neutral BF_4^- solutions are relatively stable for a long period of time.

Determination of boron. Ten water samples prepared in triplicates to contain boron at levels ranging from 0.50 to 500 $\mu g/ml$ are analysed using the nitron–tetrafluoroborate liquid membrane electrode and the standard calibration graph method (Ma and Hassan, 1982). The results are shown in Table 2. The average recovery is 98.8 % and the mean standard deviation is 2.1 %. Similar results are obtained in the presence of $100-$fold excess of some common ions such as NO_3^-, SO_4^{2-}, PO_4^{3-}, CO_3^{2-}, F^-, Cl^-, Br^-, Co^{2+}, Zn^{2+} and Ni^{2+}. These data are compared with those obtained by the most commonly used spectrophotometric procedure which involve a reaction of BF_4^- with methylene blue, extraction of the coloured complex with dichloroethane, washing and absorbance measurement at 660 nm (Lanza and Buldini, 1974). This method shows an average recovery of 98.8 % and a mean standard deviation of 5.1 %. The simpler procedure offered by using the electrode makes the accuracy of the results higher and the precision better. Furthermore, the nitron–tetrafluoroborate liquid membrane electrode is free from many interferences that plague the other methods.

Some borosilicate glasses are also determined by the electrode method after dissolution in HF and formation of BF_4^- ion (Eq. $4-6$).

$$SiO_2 + 6\ HF \longrightarrow H_2SiF_6 + 2\ H_2O \tag{4}$$
$$B_2O_3 + H_2O \longrightarrow 2\ HBO_2 \tag{5}$$
$$HBO_2 + 4\ HF \longrightarrow HBF_4 + 2\ H_2O \tag{6}$$

Since 200 mg of the glass samples containing $0.7-23$ % B_2O_3 are used in each experiment and the total volume of the solution is 500 ml, then the boron content in the final test solution is in the range of 8×10^{-5} to 2.6×10^{-4} M boron. This range is within the linear response range of the electrode. The results obtained for the analysis of some standard borosilicate glasses using the calibration graph method show an average recovery of 99.8 % of the certified values and a mean standard deviation of 1.9 % (Table 3).

Table 1

Selectivity coefficients for the nitron–tetrafluoroborate liquid membrane electrode

Interfering ion, (j)	$K_{i,j}^{pot}$	Interfering ion, (j)	$K_{i,j}^{pot}$
F^-	1.1×10^{-3}	$[Fe(CN)_6]^{3-}$	7.8×10^{-4}
Cl^-	1.4×10^{-3}	$[Fe(CN)_6]^{4-}$	3.9×10^{-4}
Br^-	1.8×10^{-3}	$(Formate)^-$	1.2×10^{-2}
SO_4^{2-}	8.2×10^{-4}	$(Acetate)^-$	1.3×10^{-3}
NO_3^-	1.4×10^{-3}	$(Oxalate)^{2-}$	5.6×10^{-4}
		Co^{2+}	7.1×10^{-4}
HPO_4^{2-}	2.2×10^{-3}	Ni^{2+}	6.9×10^{-4}
$S_2O_3^{2-}$	1.5×10^{-3}	Pb^{2+}	5.8×10^{-4}
CO_3^{2-}	7.2×10^{-4}	Cd^{2+}	6.8×10^{-4}
BrO_3^-	2.4×10^{-4}	Zn^{2+}	5.6×10^{-3}
		Cu^{2+}	2.8×10^{-3}
VO_4^{3-}	2.3×10^{-3}		

Table 2

Determination of boron in aqueous solutions after conversion to $\overline{BF_4}$ using the nitron–tetrafluoroborate liquid membrane electrode and the methylene blue–spectrophotometric methods

Boron added, ug / ml	Electrode method		Spectrophotometric method*	
	Recovery**, %	St. dev. %	Recovery**, %	St. dev., %
0.50	98.2	2.1	97.4	4.1
0.75	98.3	3.0	101.5	5.2
1.00	98.2	1.8	102.0	3.1
10.00	99.5	1.7	97.3	2.8
35.00	98.9	1.9	98.2	6.2
75.00	99.1	1.8	98.0	7.4
125.00	99.7	2.2	98.0	6.2
200.00	98.8	2.1	101.0	4.2
300.00	98.7	2.3	97.1	5.2
500.00	98.6	2.1	97.0	6.0

* The method of Lanza and Buldini, 1974.
** Average of 3 measurements.

Table 3

Direct potentiometric determination of boron in borosilicate glasses using the nitron–tetrafluoroborate liquid membrane electrode

sample	B_2O_3, %		Recovery %	St. dev. %
	Certified	Found *		
NBS, No 92	0.70	0.69	98.6	2.1
NBS, No. 93	12.76	12.69	99.5	1.9
Corning ML 2139	9.54	9.70	101.7	1.8
Corning ML 2143	15.59	15.35	98.5	1.8
Corning ML 2144	22.32	22.50	100.8	2.0

* Average of 3 measurements

REFERENCES

Chang, K. X., Fu, H. C., Chen, W. X., Wang, H. C., & Yuan, Q. 1980. Tetrafluoroborate – ion – selective electrode based on dodecyltriheptylammonium tetrafluoroborate–poly (vinyl chloride) matrix membrane. Hua Hsueh Hsueh Pao 38 : 223 – 230.

Fogg, A. G., Pathan, A. S. & Burns, D. T. 1974. A liquid–state tetrafluoroborate ion–selective electrode based on brilliant green tetrafluoroborate. Anal. Lett. 7 : 545 – 551.

Grallath, E., Tschopel, P., Kolblin, G., Stix, U. & Tölg, G. 1980. Zur spektralphotometrie und emission spektrometrie mit plasmenanregung (CMP, ICP) von bor–spuren in metallen, silicium und quarz nach HF–aufschlub und abtrennung durch BF_6–destillation bzs ausschutteln von BF_4^-–ionen–assoziaten. Fres. Z. Anal. Chem. 302 : 40 – 51.

Gulens, J., & Leeson, P. K. 1980. Direct ion–selective electrode determination of micromolar boron as tetrafluoroborate. Anal. Chem. 52 : 2235 – 2237.

Orion Research Inc. 1977. Instruction manual of fluoroborate electrode model 93 – 05. Cambridge, Ma.

Lakshminarayanaiah, N. 1976. Membrane Electrodes. Academic Press, New York, pp 268 – 269.

Lanza, P. & Buldini, P. L. 1974. Spectrophotometric determination of tetrafluoroborate. Anal. Chim. Acta 70 : 341 – 350.

Liu, C. Y., Chen. P.Y., Lin, H. M. & Yang, M. H. 1985. Determination of boron in high–purity silicon and trichlorosilane indirectly by measurement of cadmium in tris (1,10–phenanthroline) cadmium tetrafluoroborate. Fres. Z Anal. Chem. 320 : 22 – 28.

Lucchesi, C. A. & DeFord, D. D. 1957. Gravimetric determination of boron, precipitation as nitron tetrafluoroborate. Anal. Cham. 29 : 1169 – 1171.

Ma, T. S. & Hassan, S. S. M. 1982. Organic Analysis Using Ion Selective Electrodes, Vol. I. Academic Press, London.

قطب جديد ذو غشاء سائل لرابع فلورو البورات وإستخدامه للتقدير الإختياري لعنصر البورون

سعد السيد محمد حسن

إستحدث قطب جديد ذو غشاء سائل مكون من محلول رابع فلورو بورات النيترون في النيتروبنزين ، ويظهر هذا القطب إستجابة تتطابق مع معادلة نرنست في محاليل ذات تركيزات تتراوح بين 10^{-1} إلى 10^{-5} مولاري ، ولا يعتمد الجهد المقاس على قيمة الأس الأيدروجيني في المدى ٣ – ٩ .

ولقد أظهرت قياسات المعاملات الإختيارية لهذا القطب تجاه ٢١ أيوناً مختلفاً عدم وجود تداخلات من شأنها التأثير على إستجابة القطب ، ولقد إستخدم القطب في تقدير كميات من عنصر البورون يتراوح تركيزها بين ٠,٥ و ٥٠٠ ميكروجرام / سم^{3} وذلك بعد تحويل هذا العنصر إلى مشتق رابع فلورو البورات بمعالجته بحمض الأيدروفلوريك .

وبلغت دقة النتائج ٩٨,٨ ٪ بمعدل حيود قياسي قدره ٢,١ ٪ ، وأمكن إستخدام هذا القطب في تقدير عنصر البورون في بعض أنواع الزجاج .