Pergamon

0039-9140(93)E0016-7

Talanta, Vol. 41, No. 4, pp. 627–630, 1994
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0039-9140/94 $6.00 + 0.00

TRANSIENT SIGNALS WITH AN ANTIMONY(V) ION-SELECTIVE ELECTRODE: THE RELATIVE SIGNAL RETURN RATE AS A SELECTIVITY PARAMETER

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(*Received* 13 *July* 1993. *Revised* 29 *September* 1993. *Accepted* 25 *October* 1993)

Summary—The dynamic response of a Sb^{5+} ion-selective electrode based on 1,2,4,6-tetraphenylpyridinium hexachloroantimonate(V) to different ions, ClO_4^-, $HgCl_3^-$, $AuCl_4^-$, $TlCl_4^-$, $SbCl_6^-$ and tetraphenylborate, in a flow-injection analysis system using a flow-through cell, is studied. The transient signals obtained are different for every ion. A parameter called relative return rate, defined as the ratio of the return rate to peak height, was found to be characteristic for each ion. It was constant up to a concentration range of three decades for those ions with selectivity coefficients $K^{pot}_{sb,J} \ll 1$, thus providing a new source of analytical selectivity. Flow injection variables were studied in order to ascertain their influence on this new parameter.

In accordance with Mottola's advice[1] that there are "practical insights to be gained by acquiring basic kinetic information and understanding mechanistic considerations", the dynamic response of ion-selective electrodes (ISEs) was considered as a possible source for analytical information. Until now the characterization of this aspect of ion-selective electrodes has been of interest, firstly from a practical point of view, since the dynamic characteristics of the sensors or cells can drastically affect not only the attainable rate of analysis, but also the magnitude of the signal measured and thus the selectivity of the measurements in batch, continuous flow and flow injection analysis,[2] and secondly from a theoretical point of view since studies under dynamic conditions may provide information on the partial processes of the electrode response mechanism.

Different techniques, including the impedance, polarization and activity step methods, have been used in ISE dynamic studies. Several theories to interpret their dynamic behaviour have been proposed and reviewed.[3–5] An in depth description of the electrical relaxation processes contributing to the time response of ISEs has also been reported.[4]

A coated wire antimony(V) ion-selective electrode based on the ion-pair between 1,2,4,6-tetraphenylpyridinium and hexachloroantimonate(V) using a poly(vinyl)chloride membrane was developed[6] and later applied to the kinetic determination of iodide.[7] A more recent version using the internal filling solution has been used for the kinetic determination of copper.[8]

In this paper the dynamic response of the latter described sensor to different ions, ClO_4^-, $HgCl_3^-$, $AuCl_4^-$, $TlCl_4^-$, $SbCl_6^-$, and tetraphenylborate (TPB^-), to which the electrode responds with different sensitivity, is studied using a flow-through cell incorporated in a flow injection analysis system. The results obtained indicate that the dynamic response can provide a new source of analytical selectivity.

EXPERIMENTAL

Apparatus

A Gilson Minipuls 3 peristaltic pump, Omnifit injection valve, connecting tubing of 0.5-mm bore, PTFE tubing and various end fittings and connectors (Omnifit) were used.

Potentials were measured with an Orion Expandable ion Analyzer EA940. The recorder output of the ion Analyzer was connected to a personal computer via an analogic-to-digital converter DGH1121 module. An Orion 90-02 double junction silver-silver chloride reference electrode containing $0.10M$ potassium chloride in the outer compartment was used.

The construction of the antimony(V) ion-

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selective electrode has been described previously.[8] The ion exchanger of this electrode consists of the ion pair between hexachloroantimonate(V) and the 1,2,4,6-tetraphenylpyridinium dissolved at 3.3% in 2-nitrophenyl octyl ether (NPOE) and incorporated in a poly(vinyl chloride) (PVC) matrix (2:1 PVC to NPOE mass ratio).

Construction of the flow-through cell

The cell design is shown in Fig. 1. The body cell consists of two separate perspex blocks tightly pressed together by screws. A gasket, made with a twice folded (four sheet) parafilm paper, in the centre of which an 8.5-mm diameter circular hole had been with a cork borer, was placed between them. The upper block was drilled to fit the electrode body and secured by a screw. The lower block was drilled to accommodate the inlet and outlet PTFE tubes.

The flow-through cell with the electrode was incorporated in the flow injection system shown in Fig. 2.

Conditioning of the electrode

The electrode was conditioned by pumping a freshly prepared $10^{-3}M$ $SbCl_6^-$ in $0.10M$ hydrochloric acid solution until the electrode gave a constant potential. The same procedure was then followed with a solution containing only hydrochloric acid of the same concentration. The electrode was stored in the cell filled with $0.10M$ hydrochloric acid solution and conditioned before use as described above.

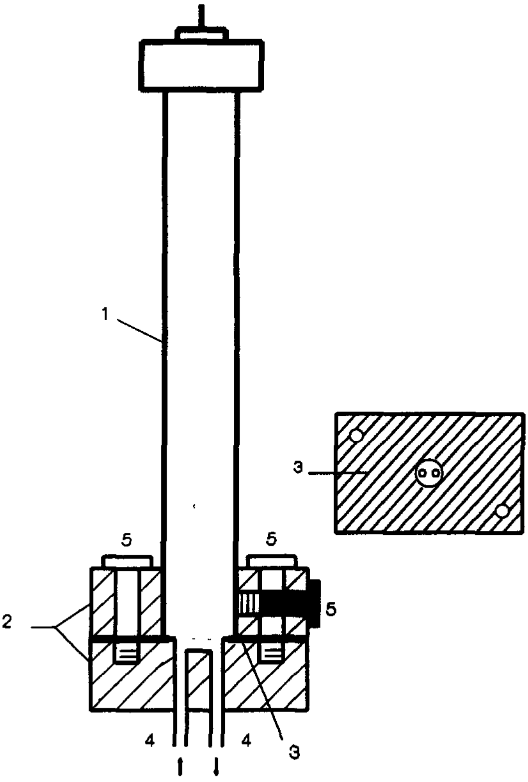

Fig. 1. Flow-through cell design: (1) ISE; (2) Perspex blocks; (3) Parafilm membrane; (4) PTFE tubes; (5) Screws.

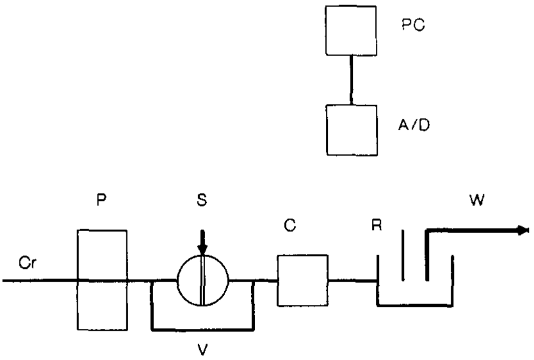

Fig. 2. FI system: (Cr) Carrier solution; (P) Pump; (V) Injection valve; (S) Sample; (C) Cell; (R) Reference electrode; (W) Waste; (A/D) Analogic-to-digital converter; (P/C) Personal computer.

Reagents

All solutions were prepared with doubly distilled water from analytical-reagent grade materials. 2-Nitrophenyl octyl ether (NPOE) and poly(vinyl chloride) (PVC) of high relative molecular mass were supplied from Fluka. Tetrahydrofuran (THF) was from Merck.

*1,2,4,6-Tetraphenylpyridinium acetate (TPPA) solution, 0.10*M. Prepared by the method of Chadwick.[9]

*Perchlorate standard solution, 0.010*M. Prepared by dissolving sodium perchlorate (Merck) in water and standardised gravimetrically.[9]

*Mercury(II) standard solution, 0.010*M. Prepared by dissolving mercury(II) nitrate (Merck) in $0.10M$ hydrochloric acid and standardized by titration with EDTA.[10]

*Gold(III) standard solution, 0.010*M. Prepared by dissolving tetrachloroauric acid (Merck) in $0.10M$ hydrochloric acid and standardized by iodometric titration with thiosulphate.[11]

*Thallium(III) standard solution, 0.010*M. Prepared by dissolving thallium chloride (Merck) in $0.10M$ hydrochloric acid and standardized by titration with EDTA.[12]

*Antimony(V) standard solution, 0.25*M. Prepared by dissolving antimony(V) chloride (Merck) in $12M$ hydrochloric acid.

*Tetraphenylborate, 0.010*M. Prepared by dissolving sodium tetraphenylborate (Merck) in water and standardized according to Vytras.[13]

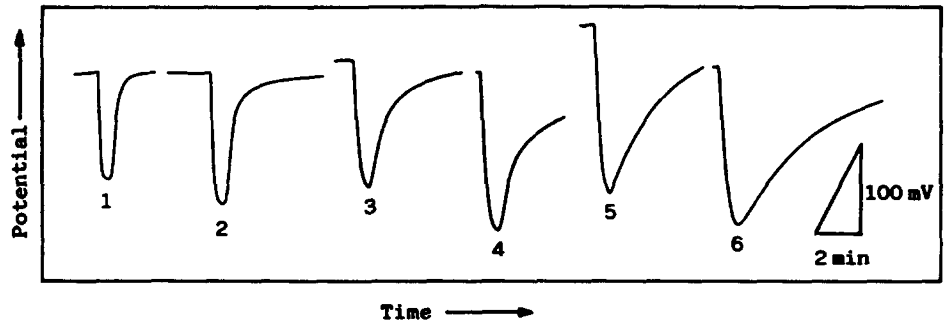

Fig. 3. Transient signals obtained with: (1) $10^{-2}M$ ClO_4^-; (2) $10^{-2}M$ Hg^{2+}; (3) $10^{-5}M$ Tl^{3+}; (4) $10^{-5}M$ Au^{3+}; (5) $10^{-5}M$ Sb^{5+}; (6) $10^{-5}M$ TPB^-.

Working solutions were prepared by diluting and adjusting the final hydrochloric acid concentration to 0.10*M*. Antimony(V) dilutions had to be freshly prepared as such solution hydrolyze[6] slowly.

RESULTS AND DISCUSSION

Preliminary studies

First, the shapes of the FI peaks are obtained by injecting several ions ClO_4^-, $HgCl_3^-$, $AuCl_4^-$, $TlCl_4^-$, $SbCl_6^-$, and tetraphenylborate (TPB^-), to which the Sb^{5+} selective electrode responded with different sensitivity. The ions were injected into a 0.10*M* hydrochloric acid carrier solution, at such concentrations as to present similar peak heights, *i.e.*, the higher the selectivity coefficient, the lower the concentration. The flow rate was 0.87 ml/min, the injected sample volume was 430 μl and the distance between the valve and cell was kept low (20 cm) to minimize dispersion. The different transient signals obtained for each of the ions are shown in Fig. 3 and it can be seen that the higher selectivity coefficients[6] produced wider peaks, the width being decided by the different return times to the base line. This provides a new source of analytical selectivity. It was decided to characterize the return rate by the maximum slope (inflection point) observed in the second part of the peak.

Influence of the concentration

The influence of the concentration of the different ions on the transients signals was studied by injecting increasing concentration decades, ranging from 10^{-5} to $10^{-2}M$ for ClO_4^- and Hg^{2+} and from 10^{-6} to 10^{-3} for Au^{3+}, Tl^{3+}, Sb^{5+} and TPB^-. The FI conditions used were those described above. A new concept, the relative return rate, can be defined as the ratio between return rate and peak height. The relative return rate values obtained for the ions assayed at the different concentrations are shown in Table 1. As can be seen this parameter is characteristic and constant for ClO_4^-, $HgCl_3^-$, $TlCl_4^-$ and $AuCl_4^-$ in the 3-decade concentration range studied, all of which present a selectivity coefficient much less than 1. This new parameter decreases with increases in the selectivity coefficient. For $SbCl_6^-$ and TPB^- ions, which present selectivity coefficient of unity and higher respectively, the relative return rates are not constant over the whole range.

Apparently an inverse relationship between the relative return rate and anion size can be observed. It could be due to the greater ability of bigger anions to form ion-pairs with the pyridinium cation of the membrane. These ions should have greater difficulty (lower rate) to leave the membrane.

Influence of the flow rate

The influence of the flow rate on the relative return rate was studied by fixing the sample volume injected at 430 μl and varying the flow rate between 0.43 and 1.27 ml/min. For each flow rate, a complete set of concentrations of each ion ClO_4^-, $HgCl_3^-$, $TlCl_4^-$ and $AuCl_4^-$ was injected, as described above. For each ion the relative rates were calculated, plotted against peak heights and fitted to a first order equation. The slopes (relative return rates) and correlation

Table 1. Influence of the concentration on the relative return rate, sec^{-1}

Ion/ Concentration	$10^{-2}M$	$10^{-3}M$	$10^{-4}M$	$10^{-5}M$	$10^{-6}M$
ClO_4^-	0.040	0.039	0.040	0.042	—
$HgCl_3^-$	0.026	0.026	0.025	0.025	—
$TlCl_4^-$		0.014	0.014	0.014	0.018
$AuCl_4^-$		0.013	0.013	0.014	0.018
$SbCl_6^-$		0.0094	0.0062	0.0054	0.014
TPB^-		0.0051	0.0035	0.0041	0.0044

Table 2. Influence of the flow rate and sample volume on the relative return rate, sec^{-1}

	Flow rate, *ml/min*			Sample volume, *μl*		
Ion	0.43	0.87	1.27	270	430	1400
ClO_4^-	0.028	0.039	0.043	0.047	0.039	0.033
$HgCl_3^-$	0.022	0.026	0.037	0.040	0.026	0.026
$TlCl_4^-$	0.013	0.013	0.016	0.025	0.013	0.014
$AuCl_4^-$	0.012	0.012	0.015	0.020	0.012	0.013

coefficients were obtained for each case. At all the flow rates assayed, a good linearity was found for the four ions. The correlation coefficients for the four ions studied, 0.9999, 0.9998, 0.9981 and 0.9951, respectively were somewhat better for the intermediate flow rate of 0.87 ml/min.

The results for the relative return rates are shown in Table 2. A tendency to increase the relative return rate when the flow rate is increased, is observed.

Influence of the sample volume

The influence of the sample volume was studied by fixing the flow rate at 0.87 ml/min and varying the injected sample volume between 270 and 1400 μl. For each volume a set of concentrations of each ion was injected and the relative return rates were calculated as described in the previous paragraph. Good linearity in the plots of the return rates versus peak heights was obtained for all the ions, except at the lower sample volume. The best correlation coefficients corresponded to the intermediate volume assayed, 430 μl. The relative return rates obtained versus sample volume are shown in Table 2. As can be seen the sample volume has little effect on the relative return rate for samples volumes $\geqslant 430$ μl.

CONCLUSIONS

The transient potentials obtained for ClO_4^-, $HgCl_3^-$, $AuCl_4^-$, $TlCl_4^-$, $SbCl_6^-$ and TPB^-, with an ion-selective electrode containing 1,2,4,6-tetraphenylpyridinium hexachloroantimonate(V) as electroactive material, incorporated in a flow injection system with a flow-through cell, are different. A new parameter called relative return rate defined as the relative return to peak height was found to be characteristic for each ion and constant over about 3 decades of concentration for those ions with selectivity coefficients $\ll 1$ (ClO_4^-, $HgCl_3^-$, $AuCl_4^-$ and $TlCl_4^-$. The relative return rate increases as the selectivity coefficients decrease. Thus, transient signals with the ISE described provide a new source of analytical selectivity.

The possibility of applying this technique to other ISEs is being studied. At present a similar tendency has been found with the use of a calcium ISE (Phillips IS 561). The relative return rate obtained for Sr^{2+} (selectivity coefficient 0.01) was 0.040 sec^{-1}, and was found constant in the range 10^{-4}–$10^{-2}M$. A lower average value, 0.020 sec^{-1} was obtained for Ca^{2+}. Further theoretical and experimental work will be useful to elucidate the observed behavior.

Acknowledgements—The authors are grateful to the Spanish Dirección General de Investigación Científica y Técnica (DGICYT) (Project 87-0053) for financial support.

REFERENCES

1. H. A. Mottola, *Kinetic Aspects of Analytical Chemistry*, p. 259. Wiley, New York, 1988.
2. E. Lindner, K. Tóth and E. Pungor, *Dynamic Characteristics of Ion-Selective Electrodes*, p. 121. CRC Press, Boca Raton, 1988.
3. W. E. Morf, *The Principles of Ion-Selective Electrodes and of Membrane Transport*, p. 375–400. Elsevier, Amsterdam, 1981.
4. R. P. Buck, *Crit. Rev. Anal. Chem.*, 1975, **5**, 323.
5. A. Shatkay, *Anal. Chem.*, 1976, **48**, 1039.
6. C. Sánchez-Pedreño, J. A. Ortuño and J. Alvarez, *Anal. Chem.*, 1991, **63**, 764.
7. C. Sánchez-Pedreño, J. A. Ortuño and A. L. Ros, *Analyst*, 1992, **117**, 1619.
8. C. Sánchez-Pedreño, J. A. Ortuño and J. Martinez-Ródenas, *J. Anal. Chem.*, 1992, **344**, 100.
9. T. C. Chadwick, *Anal. Chem.*, 1976, **48**, 1201.
10. G. Schwarzenbach and H. Flaschka, *Complexometric Titrations*, Methuen, London, 2nd Ed., p. 271. 1969.
11. F. E. Beamish, *The Analytical Chemistry of the Noble Metals*, *p.* 350. Pergamon Press, Oxford, 1966.
12. J. Kinnunen and B. Wennerstrand, *Chemist Analyst* 1957, **46**, 92.
13. K. Vytras, *Internat. Lab.*, 1979, **9(2)**, 35.