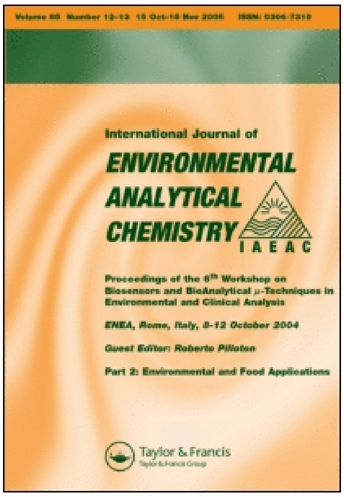

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FIA TUBULAR POTENTIOMETRIC DETECTORS BASED ON HOMOGENEOUS CRYSTALLINE MEMBRANES. THEIR USE IN THE DETERMINATION OF CHLORIDE AND SULPHIDE IONS IN WATER

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The construction techniques and behaviour of tubular potentiometric detectors based on homogeneous crystalline membranes to be used in flow injection manifolds are reported. Tubular detectors for chloride and sulphide anions were prepared using pressed membranes with silver salts. The results of the assessment of their behaviour against that of the conventional selective electrodes using the same membrane are reported. Data obtained with FIA manifolds with tubular detectors in the determination of chloride and sulphide anions in natural and waste waters are also presented.

KEY WORDS: Tubular potentiometric detectors, FIA, sulphide, chloride.

INTRODUCTION

The analytical determinations in environmental studies are frequently done routinely in a great number of similar samples. This fact has provided a great impetus in the use of automatic analytical methods, and flow injection analysis (FIA) proves no exception.

Potentiometry as a detection process in FIA[1] gained widespread support due to the simplicity and economy of the setups and also because it can be applied in large range of concentrations without complex sample preparations. Tubular and sandwich detectors based on mobile carrier sensors, with and without internal reference solutions,[2–6] proved to possess not only the above mentioned advantages, but their shape also allowed to solve some of the practical difficulties associated with the use of conventional electrodes. Namely, it becomes possible to incorporate sequentially the electrodes in FIA manifolds obviating the traditional use as end-line detectors.

The literature contains a great number of references concerning the use of crystalline membranes electrodes in FIA, but they are scarce on units of tubular configuration.[7–9] This number can be increased if the metallic silver tubular electrodes coated with some of its insoluble salts are considered,[10–14] although their use is obviously encumbered by the typical behaviour of second kind electrodes.

In this paper we report a simple and economic construction process for FIA tubular potentiometric detectors based on homogeneous crystalline membranes for chloride and sulphide anions.

EXPERIMENTAL

Apparatus

The evaluation of the conventional ion selective electrodes was done with standard equipment and techniques.

The FIA manifolds included a Gilson Minipuls peristaltic pump, a Rheodyne 5020 injection valve, teflon tubing (0.8 mm i.d.) for connections and some auxiliary home-made devices namely joints, pulse dampener, grounding electrode and reference electrode support, constructed as previous reported.[15]

Sensors and Membranes Preparation

The silver sulphide and its mixture with silver chloride for use in the membranes of the chloride and sulphide electrodes (both tubular and conventional) were prepared as previously reported.[16]

The membranes were made by pressing 0.4 g of the sensor in a 13 mm diameter anvil yielding 0.5 mm thick discs.

Conventional Electrodes

A shielded electrical cable was welded on one of the faces of a silver disk 5 mm in diameter; on the other face of the disk was then glued the sensor membranes with a silver based conductive epoxy (Figure 1).

The free extremity of the shielded cable was inserted in a perspex tube (10 mm external diameter) and the membrane fixed to the end of the perspex tube with non-conductive epoxy.

Through the open end of the tube was then poured the same non-conductive epoxy up to a height of 2 cm, to strengthen the membrane bond to the electrode body, and the protruding membrane was then shaved off.

Tubular Detectors

A rectangular piece of silver (2 × 4 mm) is welded to a shielded electrical cable and then to the silver plate is glued (Figure 2A) with a silver based conductive epoxy, a membrane, prepared as described above.

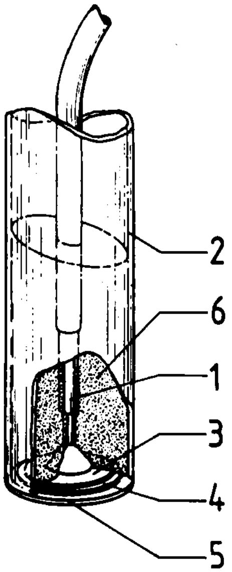

Figure 1 Conventional electrode: (1) Shielding cable; (2) Perspex tube; (3) Silver disk; (4) Conductive epoxy; (5) Sensor membrane; (6) Non-conductive epoxy.

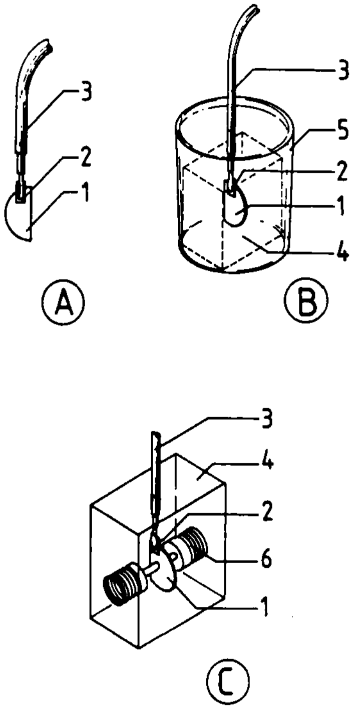

Figure 2 Construction phases for tubular detector: (1) Sensor membrane; (2) Silver plate; (3) Shielded cable; (4) Non-conductive epoxy; (5) Plastic cast; (6) Inlet/outlet threads.

Table 1 Performances of the conventional electrodes

	Chloride electrode	*Sulphide electrode*
Lower limit of linear response	2×10^{-4} M[a]	$< 10^{-5}$ M[b]
Lower limit of detection	5×10^{-5} M[a]	$< 10^{-5}$ M[b]
Slope	-58 ± 1 mV/dec.	-28 ± 1 mV/dec.
Stability of response	< 1 mV/day	1 mV/day
Response time (mixed solutions)	~ 15 sec.	~ 30 sec.
(separated solutions)	< 2 min.	~ 2 min.
Durability	> 1 year	> 1 year

Values obtained in:
[a]pure NaCl solutions;
[b]solutions with Sulphide Anti-Oxidant Buffer.

The membrane, the silver base and the tip of the cable are immersed in a plastic cast with non-conductive epoxy and left overnight in an oven at 60 °C to harden (Figure 2B). This block was cut to a rectangular shape and an 0.8 mm hole connecting to opposite faces was drilled. The extremities of the hole were then threaded (Figure 2C) to receive the PVC connectors of the FIA manifold.

RESULTS AND DISCUSSION

Behaviour of the Conventional Electrodes

The electrodes behaviour was assessed from the calibration curves for several different units. Their working characteristics (Table 1) were similar to those of other known electrodes with the same type of membranes, namely some commercially available (for example,[17]).

Since the goal of this work was the assessment the working properties of the membranes used in tubular detectors, some specific characteristics of their behaviour, namely the response to sulfide at very low concentrations, were not yet evaluated.

Behaviour of the Chloride Tubular Detector

The detector characteristics were evaluated in a low dispersion FIA manifold similar to those used before for tubular detectors with mobile carrier sensors.[2] The carrier was a solution (6 cm^3.min^{-1}) of KNO_3 (0.1 M) and of NaCl (10^{-5} M) in which it was injected a standard chloride solution (200 µl) with 0.1 M ionic strength adjusted with KNO_3.

Under this condition, the lower limit of detection was 5×10^{-5} M with a slope of -56 ± 1 mV/decade and a reproducibility better than 1 mV per hour.

The detector answer to changes in the carrier chloride concentration was very fast, allowing sampling rates better than 240 samples/hour.

Changing the injection volumes between 70 and 250 µl did not give variations in the signal amplitude larger than 10%.

When out of use for long periods of time, the electrodes were kept dry; before any new use they were conditioned for thirty minutes in a 0.1 M NaCl solution.

After about one month of use, the electrodes characteristics responses are lost occurring a reduction of slope and speed of answer. Their original behaviour could be obtained by renewing the membrane by polishing it with a wet cotton thread dipped in alumina powder.

Behaviour of the Sulphide Tubular Detector

The FIA manifold in this study was identical to the one described above, but with a solution of Sulphide Anti-Oxidant Buffer (SAOB; 1 M in sodium hydroxide and contained 20 g dm^{-3} of ascorbic acid), with a sulphide fixed concentration of 5×10^{-7} M, used as carrier. The standard sulphide solutions injected in the system had the same concentration in SAOB.

The calibration curves recorded in these conditions yielded a recorder output proportional to the logarithm of concentration up to 10^{-5} M, with a slope of -28 ± 1 mV/decade and a reproducibility better than 1 mV/hour. Under these conditions the sampling rate is about 80 samples/hour; although this number that can be increased for low sulphide concentrations.

After two months of use or conditioning in sulphide solutions with SAOB, the detectors calibration curves showed deviations from linearity between 10^{-4}–10^{-5} M, similar to those observed for conventional electrodes when used in the same medium. This effect can be attributed, as suggested by Gulens,[18] to the appearance of a metallic silver contact through the membrane.

Determination of Chloride and Sulphide in Waters

The determination of these two species was made with the FIA manifold depicted in Figure 3 and includes two channels. Through one flows the sample till a joint where is added, through the other chanel, a solution that adjusts the conditions for the measurement. After this joint is placed a mixing coil (60 cm in length) where the two solutions are more intimately homogenized before reaching the detector.

The flow rates in both channels were adjusted such that the sample plug reaches the detector with a composition similar to those used in the studies of detectors behaviour in the single channel manifold.

In the chloride determination the added solution at the joint was 0.4 M in potassium nitrate and 6×10^{-5} M in sodium chloride; for the sulfide this solution was SAOB at 50%, with the composition suggested by Midgley,[19] and 3.2×10^{-6} M in sodium sulphide. In both cases the presence of the primary ion in the carrier stream is convenient for a good stabilization of the base line.

The manifolds with potentiometric detectors were tested in the analysis of chlorides in waste waters from different provenances, and in the analysis of sulphide concentrations in waste waters from one tannery.

For chloride concentrations obtained by FIA, the control procedure was A.S.T.M. norm D 512-67 (method B; titration with visual detection). For sulphide

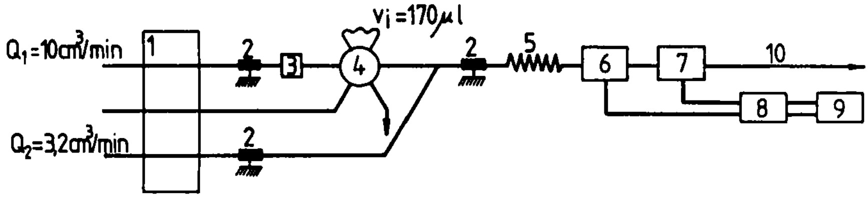

Figure 3 Flow injection manifold used in the determination of chloride and sulphide ions in waters: (1) Peristaltic pump; (2) Grounding electrodes; (3) Pulse dampener; (4) Injection valve; (5) Dilution coil (60 cm in length); (6) Tubular electrode; (7) Reference electrode; (8) pH meter; (9) Recorder; (10) Waste

it was used direct potentiometry.[19] The results of this control are presented in Table 2 and a fairly good agreement between them can be claimed.

The experimental conditions used and the tubular detectors characteristics allowed a sample rate of about 120 samples/hour for the chloride determinations and of 80/hour for the sulphide's.

CONCLUSION

The constructed tubular detectors show good working characteristics and when incorporated in FIA manifolds for water analysis yielded results identical to the conventional procedures.

Table 2 Results for the water samples[a]

Sample	*Chloride content* ($\times 10^{-3}$ *M*)		*Sample*	*Sulphide content* ($\times 10^{-4}$ *M*)	
	FIA	*ASTM* (*D* 512-67)		*FIA*	*Direct Potentiometry*
1	0.780	0.785	A	2.55	2.57
2	0.830	0.858	B	1.47	1.45
3	2.48	2.52	C	3.20	3.20
4	1.74	1.77	D	2.03	1.80
5	1.32	1.51	E	1.75	1.85
6	0.950	0.930	F	5.20	4.95
7	2.20	2.31	G	5.35	5.40
8	1.32	1.31	H	5.40	5.75
9	1.21	1.32	I	35.0	36.0
10	1.60	1.91	J	20.5	20.8
11	1.15	1.32	K	3.50	3.80
12	0.320	0.303	L	1.30	1.40
Slope[b]	0.94			0.97	
Intercept[b]	1.5×10^{-5}			5.2×10^{-6}	
Correlation Coefficient[b]	0.994			0.999	

[a] Average of 3 determinations are given.

[b] Linear regression analysis of the results obtained by the two methods.

The potentiometric tubular electrodes when incorporated in FIA manifolds present great advantages over the conventional configuration electrodes because they do not disturb the hydrodynamic flow characteristics and they can be placed on-line in complex flow systems to allow sequential determinations. This possibility has been outstanding in previous work about tubular electrodes with PVC membranes supporting mobile carrier sensors.[3]

Additionally, these detectors configuration allows assemblages with better mechanic stability then the cascade arrangement and are particularly convenient when used with unstable solutions, as for sulphide.

Wider applications for these FIA detectors can be foresighted, namely for determinations in other matrices where the conventional electrodes with this type of membrane have provided useful analytical results.

The construction technique described is very easy to perform, economic and effective and can be extended to the manufacturing of other tubular detectors for which it is possible to prepare crystalline membranes with good behaviour, as for bromide and iodide anions and for lead (II), cadmium (II) and copper (II) cations. This observation is supported by preliminary results from our laboratory.

Acknowledgements

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