Food Chemistry 50 (1994) 423–428
© 1994 Elsevier Science Limited
Printed in Great Britain. All rights reserved
0308-8146/94/$7.00
Analytical Methods Section

Flow injection titration of chloride in food products with a silver tubular electrode based on an homogeneous crystalline membrane

Isabel M. P. L. V. O. Ferreira, José L. F. C. Lima*

Departamento de Química-Física, Faculdade de Farmácia, Universidade do Porto,
Rua Aníbal Cunha 164, 4000 Porto, Portugal

&

António O. S. S. Rangel

Escola Superior de Biotecnologia, Universidade Católica Portuguesa, Rua Dr.
António Bernardino de Almeida, 4200 Porto, Portugal

(Received 9 August 1993; accepted 8 November 1993)

A flow injection system for the pseudo-titration of chlorides in food products with potentiometric detection has been developed. For this purpose, a silver ion selective tubular electrode based on a homogeneous crystalline membrane, prepared by pressing silver sulphide at high pressure, was constructed. Its operational characteristics were evaluated and compared with the corresponding conventionally shaped electrodes obtained with the same sensor.

The results obtained for chloride determination in wine, milk, beer and vinegar by using the FIA methodology were in good agreement with those provided by reference procedures. The sampling rate achieved varied between 120 and 360 samples per hour.

INTRODUCTION

The determination of chloride in food products such as wine, milk, beer or vinegar is usually accomplished by potentiometric titration with silver (I) cations. The automation of these determinations by developing a flow injection analysis (FIA) pseudo-titration manifold is described in this paper. As a detection system for the flow titration, a silver ion selective electrode based on a homogeneous crystalline membrane with a tubular configuration was constructed.

In the so-called pseudo-titration FIA systems (Stewart, 1986), the sample is introduced into the titrant carrier stream, mixed in an exponential gradient device (typically a well-stirred mixing chamber), and the concentration of one of the reactants, or the product monitored with a suitable detector. Under these conditions, there is a linear relationship between the time interval (peak width at a preset signal level) and the logarithm of analyte concentration.

In the manifold described here for chloride determination in food products, the sample is injected into a carrier stream containing silver cations, and the decrease in the silver concentration is monitored by a silver tubular detector constructed in our laboratory.

The utilization of tubular electrodes as detectors for the chloride titration in some matrices in a flow injection system has already been described by some authors. Alegret *et al.* (1988) constructed a silver ion selective electrode based on a silver sulphide heterogeneous crystalline membrane for the titration of chloride in serum, and Lima and Rangel (1989) constructed a second kind of electrode of Ag_2S/Ag for the determination of chloride in wines. In this paper we describe the construction of a tubular silver (I) electrode based on a homogeneous crystalline membrane obtained by pressing silver sulphide powder at high pressure. As the quality of the tubular electrodes is strongly dependent upon the quality of the conventionally shaped electrodes, conventional units were also constructed and the operating characteristics compared. This type of electrode presents less dependence upon the matrix composition and a faster response over those using heterogeneous membranes (Alegret *et al.*, 1987*a*; Alegret *et al.*, 1989). Regarding the second kind of electrode, its potential is strongly affected by the sample matrix, so its use is rather limited, unless some previous matrix separation such as dialysis is performed before measurement.

---

* To whom correspondence should be addressed.

The reason for the construction of a tubular configuration for the electrode, rather than the incorporation of a conventionally shaped silver ion selective electrode, is due to the problems that arise when electrodes with a conventional configuration are inserted into a flow system. The main problem is the mechanical instability that arises from the difficulty of fixing the electrodes in a rigid way, causing electric noise and creating dead volumes that affect the reproducibility and time to return to the baseline. Additionally, the distortion of the hydrodynamic characteristics of the flow introduced usually does not allow the use of another detection system located after the electrode and so multiparametric determinations cannot be performed.

These difficulties can be overcome by constructing electrodes with a tubular configuration expressly dedicated for incorporation in the flow system (Ferreira & Lima, 1993). As the tubular flow-through electrodes present the same shape and approximate diameter of the tubing used, they can be incorporated in a rigid and robust way, backpressure is reduced and no significant distortion of the sample plug occurs.

Using the constructed flow-through detector, a flow injection system for the pseudo-titration of chlorides in wine, milk, beer and vinegar was developed and the results obtained with the FIA titration were compared with those obtained by the reference procedures.

MATERIALS AND METHODS

Reagents and solutions

All chemicals used were of analytical-reagent grade and deionized water with a specific conductivity less than 0·1 μS cm^{-1} was used throughout.

In the construction of the ion selective electrodes, the following epoxy resins were used: (a) conductive epoxyresin—1·5 g EPO-TEC 410 (component A) and 0·16 g EPO-TEC 410 (component B) from Epoxy Technology, USA; (b) non-conductive epoxy resin–1·0 g of Araldite M and 0·4 g of hardener HR from Ciba-Geigy.

The chloride stock solutions (1·00 and 10·0 g litre^{-1}) were prepared from solid sodium chloride previously dried at 100°C. The standard solutions used in the calibration curves were obtained by subsequent dilution of the stock solutions.

The silver solutions were prepared from solid silver nitrate. The solution that was used as titrant in the reference methods was standardized by potentiometric titration against a chloride standard solution.

The buffer solutions used in the calibration of the combined pH electrode were Tritisol (Merck), reference nos 9884 (pH = 4), 9887 (pH = 7) and 9889 (pH = 9).

Instrumentation and electrodes

A Crison Model 2002 digital voltmeter (±0·1 mV sensitivity) was used for the potentiometric measurements. In the FIA determinations this voltmeter was coupled to a Metrohm Model E586 chart recorder.

In the evaluation of the silver conventional and tubular-shaped electrodes, a double-junction AgCl/Ag Metrohm 6.0726.100 and a Russel Model 90-0029 reference electrode were used, respectively.

For tracing the Reilly diagrams in order to assess the influence of pH on the electrode potential, a Russel SWL/B14 combined glass electrode sensitive to protons was used.

The potentiometric titrations were performed in a set-up made up of a Crison Model Micro BUR 2031 burette controlled by a Hyundai Model Super 16 computer equipped with a Advantech Model PCL 720 board and connected to an Epson LX 800 printer. As indicator and reference electrodes a silver ion selective electrode (Lima & Rocha, 1990) and a double-junction AgCl/Ag Metrohm 6.0726.100 reference electrode, respectively, were used.

Flow injection system

An Ismatec Model S 820 peristaltic pump was used for propelling the solutions. The insertion of the solutions in the carrier stream was performed with a Rheodyne Type 5020 six-port rotary valve. Omnifit Teflon tubing (0·8 mm i.d.) with Gilson end-fittings and connectors was used for manifold conduits. For creating an exponential concentration gradient in the FIA titrations, a well-stirred mixing chamber with internal volume of 226 μl was used.

The support device for the tubular and reference electrodes as well as the ground electrode were constructed as described by Alegret *et al.* (1987*b*).

Construction of electrodes

Silver electrodes with a homogeneous crystalline membrane of silver sulphide, either with a tubular configuration for incorporation in FIA systems or with a conventional configuration, were constructed.

Preparation of the membrane

The sensor of the membrane was silver sulphide prepared by mixing equal volumes of equimolar (0·1 M) solutions of $AgNO_3$ and Na_2S in a similar way to that described by Lima and Rocha (1990). The solid obtained was filtered and dried in an oven for 24 h at 100°C. Finally it was ground and kept away from light in a silica-gel desiccator. The membrane discs were then prepared by pressing (at a pressure of 19 000 kg cm^{-2}) about 0·25 g of sensor thus enabling discs approximately 10 mm in diameter and 0·4 mm in thickness to be obtained.

Setting the membrane in the support for the tubular and conventional electrodes

The schematic tubular electrode construction is depicted in Fig. 1.

From a segment of about 15 cm of a shielded cable,

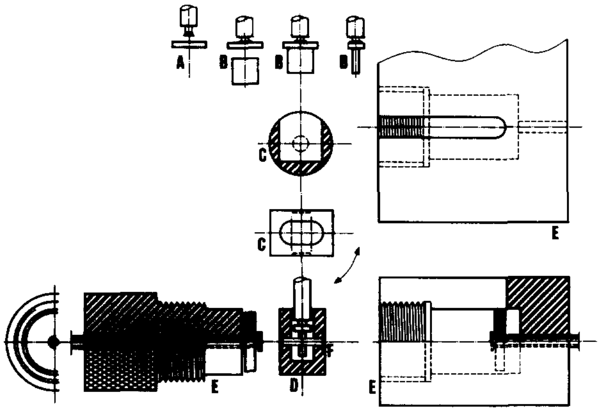

Fig. 1. Construction phases of the silver tubular electrodes. A: The inner conductor of a shielded electric cable is soldered to a rectangular silver plate; B: A fragment of the membrane is glued to the silver plate with a silver-based epoxy resin; C: The membrane is introduced in a perspex cylinder with a rectangular cavity filled with a non-conductive epoxy resin; D: A hole is drilled at the centre of the membrane; E: Rectangular block of perspex to house the tubular electrode; F: Circular depression with a diameter similar to that of the flow tubes flanges.

2 cm of external isolator and outer conductor were cut in one of the ends. Then, 1 cm of the inner conductor isolator was eliminated and the inner conductor covered with a solder film.

Over one previously polished small rectangular silver plate (2 mm × 4mm), a drop of solder was deposited and subsequently linked with the inner conductor already covered with a solder film (Fig. 1(A)). Then the outer insulator of the electric cable was moved until it almost reached the silver plate surface. A square-shaped sensor membrane (3 mm × 3 mm) was cut and glued with conductive epoxy resin through one of the minor edges to the surface of the silver plate (Fig. 1(B)), and left in an oven at 100°C for a few hours.

This set was then placed in a perspex cylinder (1 cm wide and 7 mm long) with a parallelepiped-shaped cavity of convenient dimensions (3 mm × 4 mm × 7·5 mm). The cavity was filled with non-conductive epoxy resin and then the silver plate with the membrane attached was dipped inside (Fig. 1(D)), taking care not to allow air bubbles to enter. This set was left to dry in an oven at 60°C overnight.

Finally, an axial hole (0·8 mm diameter) was drilled through the centre of the sensor membrane. This module was then inserted in a rectangular block of perspex (Fig. 1(E)), that allowed the intersection of the electrode into the flow injection manifold. This module had two flow conduits for connection to the manifold, and the quality of the joints between the tubes flanges and the sensor module was fixed by slotting it into a shallow circular depression (Fig. 1(F)) with a diameter similar to that of the flanges.

With this arrangement, 0·4 mm of the sensor surface of the tubular electrode can be in contact with the flowing solution, with the same diameter as the conduits of the flow injection system.

From time to time the sensor membrane was rejuvenated by polishing with a damp cotton cloth and aluminum powder (BDH, 3 μm).

Electrodes of a conventional shape and having the same sensor membrane were also prepared, in order to compare their functioning characteristics with the tubular ones. They were constructed in a similar way to that described by Ferreira *et al.* (1993).

Reference procedures

For the chloride determination in food products such as wine, milk, beer or vinegar, gravimetric or titrimetric methods using silver (I) solution as titrant (with visual or potentiometric detection with a AgCl/Ag second kind of electrode) are alternatively recommended (AOAC, 1984).

In this work, for comparison purposes, a potentiometric titration using a silver ion selective electrode (Lima & Rocha, 1990) as the detector was used.

RESULTS AND DISCUSSION

Behaviour of the tubular and conventional electrode

For assessing the behaviour of the tubular electrodes, a low dispersion flow injection manifold (Fig. 2) was assembled, in order to guarantee that the silver concentration in the sample plug reaching the detector is similar to that present at the moment of injection. In this way it is intended to establish experimental conditions in which the signal intensity obtained depends almost exclusively upon the tubular-electrode characteristics, thereby creating evaluation conditions similar to those used for assessing the conventionally shaped electrode characteristics, and allowing mutual comparison.

As carrier stream, a AgNO$_3$ 2×10^{-5} M and KNO$_3$ 0·1 M solution was used. The presence of a low silver concentration in the carrier stream is necessary for baseline stabilization, guaranteeing constant conditioning of the electrode surface. The potassium nitrate is required to adjust the ionic strength and at the same time increase the solution conductivity. The calibration curves were obtained by injecting silver (I) standards with concentrations between $1{\cdot}00 \times 10^{-4}$ M and 1·5 ×

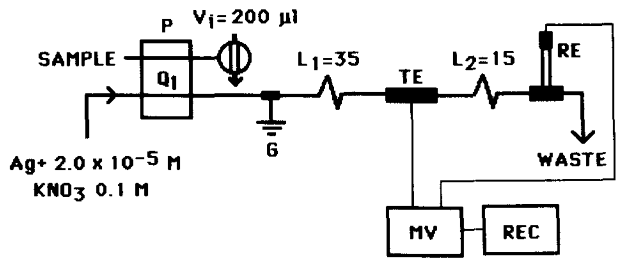

Fig. 2. Low-dispersion flow injection manifold used for the evaluation of the electrode characteristics. P: peristaltic pump; V_i: injection volume; G: ground electrode; TE: tubular electrode; RE: reference electrode; MV: voltmeter; REC: recorder; L_i: tube length (cm) (0·8 mm i.d.); Q_i: flow-rate = 8·1 ml min^{-1}.

10^{-2} M and ionic strength adjusted to 0·1 M with KNO_3. Some preliminary experiments were performed to establish the flow injection parameters to be set for evaluating the tubular electrode characteristics. This was performed by testing four injection volumes (150, 200, 350 and 500 μl) and three flow-rates (3·3, 5·7 and 8·1 ml min^{-1}).

For each injection volume it was found that the flow rate had a very low influence on the intensity signal, as is usually the case when potentiometric detection is used. However, the carrier flow rate had a marked influence on the time required for return to the baseline, i.e. the time elapsing from the signal appearance until the intensity signal drops to 5% of the peak height, on the tail of the peak. Therefore, the higher flow rate (8·1 ml min^{-1}) was chosen, which gave a return to the baseline in about half the time (13 s for an injection volume of 200 μl) of that observed when a flow-rate of 3·3 ml min^{-1} (27 s) was used.

The injection volume was set to 200 μl, allowing a signal corresponding to about 98% of the stationary state. Using a larger volume would produce an undesirable increase in the time to return to the baseline and only a slight increase in the signal intensity. These conditions were set for assessing the characteristics of the tubular electrode, thus providing experimental conditions similar to those used for the evaluation of the conventionally shaped electrodes.

With these preset experimental conditions, a more extense study of the electrode was carried out to assess the reproducibility of the calibration curve with time, daily stability and response time and also the effect of pH on the electrode's potential.

In order to assess the electrode's reproducibility, solutions with a silver concentration between $1{\cdot}0 \times 10^{-4}$ and $1{\cdot}5 \times 10^{-2}$ M were injected. For the same unit, two successive calibration curves repeated during a workday (7–9 h) were performed. It was found that the potential drift was no more than 1 mV per day and the slope drift was lower than 1 mV per concentration decade. The same electrode in a week's time presented a slope drift that did not exceed 1 mV. These characteristics indicate that when these detectors are incorporated in a flow injection system they can be used for a long time with no need for periodic calibrations or even multiple determinations.

For assessing the lower limit of linear response, calibration curves for the silver concentration interval from $1{\cdot}0 \times 10^{-5}$ M to $1{\cdot}0 \times 10^{-1}$ M, using a carrier solution of $AgNO_3$ $1{\cdot}0 \times 10^{-6}$ M and KNO_3 $1{\cdot}0 \times 10^{-1}$ M, were established. A value of 10^{-5} M was obtained.

The electrode's response time was taken as the elapsed time from the start of the ascending part of the peak to that corresponding to 95% of the steady-state signal. The response time was less than 4 s, thus presenting a sufficiently fast response for use in flow injection manifolds providing high sampling rates.

Regarding the influence of pH, the same FIA manifolds with some small alterations (Alegret *et al.*, 1984) were used. Operational pH intervals of 2·5–8·9 and 2·5–6·9, for silver concentrations of 10^{-3} M and 10^{-1} M, respectively, were obtained.

Table 1. Evaluation of the electrode's functioning characteristics with a conventional and a tubular configuration

Characteristic	Conventional	Tubular
Slope (mV $decade^{-1}$)[a]	58·7[b]	57·7[c]
LLLR (M)[a]	$4{\cdot}2 \times 10^{-6}$	$1{\cdot}5 \times 10^{-5}$
PDL (M)[a]	$9{\cdot}0 \times 10^{-7}$	—
Standard potential (mV)	801[b]	794[c]
Response time[a]	<20 s	<4 s
Response stability (mV day^{-1})[a]	± 0·6	± 1
pH range: $\mid Ag+ \mid = 10^{-3}$ M	2·0–9·3	2·5–8·4
$\mid Ag+ \mid = 10^{-1}$ M	2·2–7·1	2·5–6·9

[a] Values obtained in a solution with the ionic strength adjusted to 0·1 M; LLLR, lower limit of linear reponse; PDL, practical detection limit.

[b] Average values obtained with four electrodes tested twice, one time per month during 9 months (72 experimental values).

[c] Average values obtained with two tubular detectors tested eight times in two different days (32 experimental values).

For comparison purposes, the evaluation of conventionally shaped silver electrodes constructed with the same sensor membrane as the tubular electrodes, was carried out using standard procedures. The parameters evaluated for both the tubular and the conventionally shaped electrodes are summarized in Table 1.

From inspection of the results presented in Table 1, it becomes clear that the operating characteristics of the tubular and conventional electrodes are very similar. The main differences refer to the lower limit of linear response and pH operational range. Regarding the first parameter, this is probably due to the fact that in FIA, there is a certain amount of silver in the carrier stream to stabilize the baseline, and also the fact that some dispersion, although very small, occurs. The narrower pH ranges for the tubular electrodes can be explained by the larger mobility of the proton and hydroxide anion than the silver cation. This result is similar to that obtained with other tubular electrodes (Alegret *et. al.*, 1985; Alegret *et al.*, 1989; Ferreira *et al.*, 1993).

FIA titrations

Once the silver tubular ion selective electrode was constructed and the operational characteristics assessed, a flow injection system incorporating the above detector for the titration of chloride in some food products was developed and subsequently used for the determinations in wine, milk, beer and vinegar.

Manifold development

For the titration of chloride, a single-channel flow injection system was devised (Fig. 3).

For creating the exponential concentration gradient necessary in flow injection titrations, a well-stirred mixing chamber was used. This choice was justified by previous experience in FIA titrations where this device

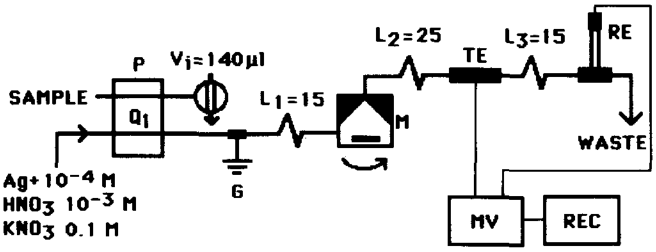

Fig. 3. Flow injection titration system. P: peristaltic pump; V_i: injection volume; G: ground electrode; TE: tubular electrode; RE: reference electrode; MV: voltmeter; REC: recorder; L_i: tube length (cm) (0·8 mm i.d.); Q_1: flow-rate = 8·1 ml min^{-1}; M: well-stirred mixing chamber.

allowed good linear calibration plots (time interval *versus* logarithm of concentration). Additionally, the forced mixing imposed by the magnetic bar has proved to be very efficient in minimizing the influence of the sample's physical properties (namely viscosity) on the shape of the analytical signal (Lima & Rangel, 1989). This could be particularly important in this work as the food products to be analysed (wine, milk, beer and vinegar) present matrices with different physical characteristics. Even within the same food product, such as wine, many matrix differences could be expected from different types, which would require matching the composition of standards and samples. By using a well-stirred mixing chamber, these problems can be minimized.

Therefore, the standards and samples were injected in the silver (I) carrier stream and directed to the well-stirred mixing chamber where the exponential concentration gradient is created. The decrease in the silver concentration in the carrier stream was subsequently monitored by the silver tubular flow-through electrode. The carrier stream also contains potassium nitrate to adjust the ionic strength and to increase the solution conductivity and nitric acid to prevent silver oxides and hydroxides precipitating.

With this manifold, parameters such as injection volume, flow rate and silver (I) concentration were optimized in order to allow chloride determination in each food product with no previous sample treatment. The first goal was to obtain a linear dependency between the peak width (time interval measured at some fixed value of the intensity signal) and the logarithm of chloride concentration in the expected concentration intervals for each product. Additionally a good sensitivity and sampling rate were sought.

Three injection volumes were tested (115, 140 and 165 µl), these producing the best reproducibility with the 140 µl loop. The silver (I) concentration in the carrier stream presented a decisive influence in the sensitivity and detection limit of this methodology. A silver concentration of 10^{-4} M was chosen as a compromise between sensitivity and sampling rate. In fact, a concentration of 10^{-5} M produced a higher calibration curve slope (sensitivity), but the sampling rate was significantly low because the peak width was larger. On the other hand, a 10^{-3} M concentration did not allow the determination of low levels of chloride.

The carrier flow rate was set to 8·1 ml min^{-1}. Lower flow rates produced an increase in the sensitivity but a significant decrease in the sampling rate.

Determination of chlorides in food products

In the FIA titrations, the wine, milk and vinegar samples were injected without any previous treatment. As already mentioned, this became possible by using a well-stirred mixing chamber as a gradient device. Only the beer samples had to be previously degassed in an ultrasonic bath in order to obtain reproducible results.

In every set of determinations, the standards were firstly injected to establish the calibration curve (peak width *versus* logarithm of concentration) and then the samples (Fig. 4). The peak width, that corresponds to a time interval Δt, was measured at a fixed peak height (potential, E) above the baseline: 10 mV for determinations in wine, 25 mV in milk and 40 mV in beer and vinegar samples. Under these conditions it was possible to make determinations in a linear range between 10 and 500 mg litre^{-1} for wine, between 100 and 1800 mg litre^{-1} for milk, and between 40 and 500 mg litre^{-1} for beer and vinegar, under conditions of linear dependency between the peak width and the logarithm of concentration. The sampling rate achieved varied between 120 and 360 h^{-1} for samples with a concentration of 1800 and 10 mg litre^{-1}, respectively. This large dependance of the sampling rate upon concentration is due to the fact that we tried to obtain a broad linear concentration range that could contain the usual chloride levels in the food products.

In order to assess the quality of the results obtained with the developed methodology, determinations for a

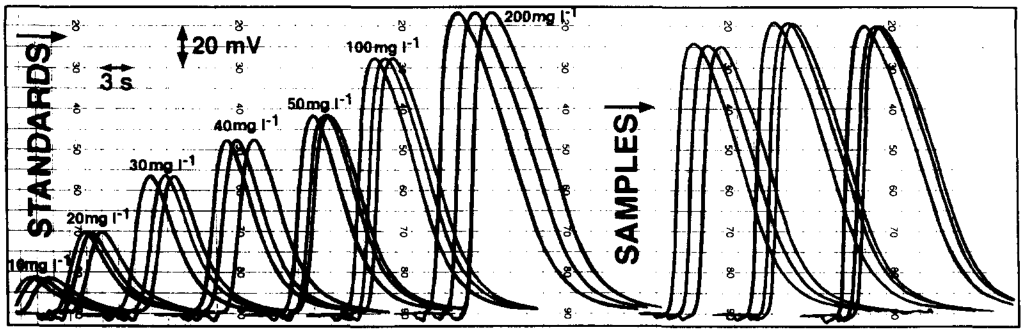

Fig. 4. Flow injection titration recorded signals corresponding to the injection of a set of standards and samples.

Table 2. Parameters of the equation $C_f = C_0 + S\ C_r$ for comparing the results (mg litre^{-1}) obtained by FIA (C_f) and by the reference procedures (C_r)

	No. of samples	Equation parameters		
		C_0 (mg litre^{-1})	S	R^a
Wine	11	-6×10^{-4}	1·00	0·999 8
Milk	9	152	0·856	0·998
Beer	7	6·45	0·977	0·999 0
Vinegar	7	0·33	0·995	0·999 8

[a] Correlation coefficient.

set of samples were carried out by FIA (C_f) and by the reference procedures (C_r). A relation of the type $C_f = C_0 + SC_r$ was established for each food product determinations, with the results obtained presented in Table 2.

The results show good agreement between the values obtained by the developed FIA methodology and by the reference procedures, as can be perceived by slopes and correlation coefficients close to unity. The high C_0 value obtained for the milk correlation is irrelevant because at the high chloride concentration levels measured the deviation from the desired relationship ($C_0 = 0$ and $S = 1$) is very small. In fact, the maximum relative deviations observed were 6% for wine and milk analysis, 0·3% for beer and 1% for vinegar.

CONCLUSIONS

The flow injection system developed for the chloride pseudo-titration in several food products is a good alternative to the reference procedures as it provides comparable results with large sampling rates (between 120 and 360 determinations per hour), with no need for previous sample treatment of wine, milk or vinegar samples, only beer has to be degassed before the analysis.

The evaluation in a low-dispersion FIA manifold of the constructed silver tubular detectors, based on silver sulphide membranes obtained by high pressure, shows that they possess good functional characteristics, similar to the conventionally shaped electrodes with the same membrane.

The results obtained with the food products tested allow us to foresee that the developed methodology could be extended to the determination of chloride in other food products whose evaluation is currently performed by potentiometric titration with silver (I).

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support from Junta Nacional de Investigação Científica e Tecnológica (JNICT) and FEDER through Project STRDA/C/CEN/554/92. One of the authors (I. M. P. L. V. O. F.) acknowledges support from JNICT (BD832/90-IF).

REFERENCES

Alegret, S., Alonso, J., Bartroli, J., Paulis, J. M., Lima, J. L. F. C. & Machado, A. A. S. C. (1984). Flow-through tubular PVC matrix membrane electrode without inner reference solution for flow injection analysis. *Anal. Chim. Acta*, **164**, 147–52.

Alegret, S., Alonso, J., Bartroli, J., Lima, J. L. F. C., Machado, A. A. S. C. & Paulis, J. M. (1985). Flow-through sandwich PVC matrix membrane electrode for flow injection analysis. *Anal. Lett.*, **18**, 2291–303.

Alegret, S., Lima, J. L. F. C., Machado, A. A. S. C., Martinez-Fàbregas, E. & Paulis, J. M. (1987*a*). A new procedure for construction of mouldable shape membrane ion-selective electrodes accommodating crystalline sensors dispersed in epoxy resin. *Quim. Anal.*, **6**, 176–91.

Alegret, S., Alonso, J., Bartroli, J., Machado, A. A. S. C., Lima, J. L. F. C. & Paulis, J. M. (1987*b*). Construction of equipment for potentiometric determinations in flow injection analysis. *Quim. Anal.*, **6**, 278–92.

Alegret, S., Alonso, J., Bartroli, J., García-Raurich, J. & Martinez-Fàbregas, E. (1988). Chloride determination in serum by a flow injection analysis precipitation pseudotitration technique using a flow-through all-solid-state silver electrode. *J. Pharm. Biomed. Anal.*, **6**, 749–55.

Alegret, S., Florido, A., Lima, J. L. F. C. & Machado, A. A. S. C. (1989). Flow-through tubular iodide and bromide selective electrodes based on epoxy resin heterogeneous membranes. *Talanta*, **36**, 825–9.

AOAC (1984). *Official Methods of Analysis*, 14th edn. Association of Official Analytical Chemists Inc., Arlington.

Ferreira, I. M. P. L. V. O. & Lima, J. L. F. C. (1993). Tubular electrodes and other devices for potentiometric detection in FIA. *J. Flow Injection Anal.*, **10**, 17–32.

Ferreira, I. M. P. L. V. O., Lima, J. L. F. C. & Rocha, L. S. M. (1993). Construction and evaluation of tubular potentiometric detectors sensitive to chloride, bromide, and iodide and based on homogeneous crystalline membranes. *Fresenius Z. Anal. Chem.*, **347**, 314–19.

Lima, J. L. F. C. & Rangel, A. O. S. S. (1989). Chloride pseudotitration in wine by FIA using a Ag_2S/Ag tubular electrode as detector. *J. Food Comp. Anal.*, **2**, 356–63.

Lima, J. L. F. C. & Rocha, L. S. M. (1990). FIA tubular potentiometric detectors based on homogeneous crystalline membranes. Their use in the determinations of chloride and sulphide ions in water. *Int. J. Environ. Anal. Chem.*, **38**, 127–33.

Stewart, K. K. (1986). Time-based flow injection analysis. *Anal. Chim. Acta*, **179**, 59–68.