Original articles

Construction and evaluation of a crystalline silver double-membrane tubular potentiometric detector for flow injection analysis. Application to chloride determination in wine

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Abstract. This paper describes the construction and assessment of the operating characteristics and analytical usefulness of a homogeneous crystalline silver double membrane tubular electrode with increased sensitivity. The constructed electrodes allowed Ag(I) determinations in the $3 \times 10^{-5} - 1 \times 10^{-1}$ M range with a calibration slope of 114 mV dec^{-1} and with good reproducibility (0.6 mV). The development and application of a flow injection analysis system manifold for chloride determinations in wine samples, in a wide concentration range ($10 - 800$ mg L^{-1}), with a titrant consumption of 90 μg determination^{-1} is also described. The results obtained from the analysis of 12 wine samples showed good agreement between the proposed method and the reference one, accomplishing $90 - 200$ samples h^{-1}.

Key words. Tubular electrode — increased sensitivity — chloride — wine — FIA.

Introduction

Potentiometry used as detection method offers many advantages [1]. Unfortunately, one of the most important problems in analytical potentiometry is its poor precision in the determination of sample concentration. A ± 0.5 mV error in the emf reading causes a 2% error in the concentration calculated for the electrode sensitive to single charge species. Also, there are some limitations due to the correct definition of titration end point, when potential variations are small close to the equivalence point. A determination error of some significance can be minimised if the determination noise level is reduced or the potentiometric measurement sensitivity is increased [2]. Some solutions to solve this limitation have been advanced, based in an increase of the

potentiometric measurement sensitivity [3-6] leading to a higher potential jump at the end point titration.

This paper reports the construction and evaluation of a double membrane tubular Ag$_2$S electrode with increased sensitivity and precision to be used in flow injection analysis systems. In order to evaluate the usefulness of the constructed potentiometric detector, chloride determination in wines was selected.

The presence of chloride in wines is basically endogenous, although sometimes it derives from technical procedures during wine production. Some of the factors responsible for chloride content are the proximity of the vineyards to the coast line, the use of anion exchange columns in the tartrate stabilisation, the application of additives containing chloride [7] and also its deceitful addition.

The wine chloride content is rather diverse. It can be over 1000 mg L^{-1}, expressed as sodium chloride, in wines from coast regions, although it is generally less than 50 mg L^{-1} [8].

Literature presents several automatic methodologies for the chloride determination in wines, namely atomic absorption spectrophotometry [9] in continuous flow or HPLC with UV/VIS spectrometric detection and conductimetry [10] and continuous flow technique (FIA) with potentiometric detection [11-13]. Potentiometry offers simplicity, economy and higher sampling rates over the former. A differential titration at zero current, with two identical electrodes coated with a silver salt [11], or a continuous flow system coupled to a second-kind silver tubular electrode [12], were used for chloride determination in wines. In the latter process, the potential was highly dependent on the matrix composition due to the type of electrode used. Using FIA systems with tubular potentiometric detectors prepared with homogeneous crystalline silver membranes [13], with increased selectivity, presented several advantages especially in complex matrices.

Materials and methods

Reagents and solutions

All solutions were prepared with deionised water (specific conductivity < 0.1 μS cm^{-1}) and analytical reagent grade chemicals without further purification. Chloride standard solutions were prepared by dilution of 0.1 M NaCl stock solution, obtained by carefully weighing the solid reagent previously dried at 110 °C in an oven. The silver (I) solutions were prepared from solid silver nitrate and standardised by conventional potentiometric titration against a chloride standard solution.

Apparatus and electrodes

The potential was measured with a 2002 Crison potentiometer (sensitivity of ± 0.1 mV) connected to a BD 111 Kipp & Zonen recorder.

An ORION 90-00-02 double junction electrode with a 10% KNO_3 solution was used in the outer compartment as reference electrode. A Ag_2S double membrane electrode was used as indicator and the potentials given out by each membrane were measured against the reference electrode and externally summed by means of an electronic device [14].

A Gilson Minipuls 2 peristaltic pump and Rheodyne 5020 injection valve were used. The connection of all components of the FIA system was done with PTFE tubing (0.8 mm i.d.). Auxiliary laboratory-made devices, namely joints, grounding electrode, tubular and reference electrode supports, were used and constructed as previously described [15]. A perspex mixing chamber, with internal variable volume, used in the manifold for the sample dispersion was constructed as described elsewhere [16]. An inner volume of 290 μL was selected.

Potentiometric titration with conventional electrodes was used as reference procedure [17] for chloride determination. It was performed by using an automatic titrator. where the end-point detection was evaluated by a conventionally shaped silver electrode [13] combined with an Orion 90-00-02 double junction reference electrode.

Construction and evaluation of the double membrane electrodes

The sensor membrane used for the construction of the silver sensitive electrodes was prepared from the solid obtained from the precipitation reaction of 0.1 M Na_2S solution with an equal volume of 0.1 M $AgNO_3$ solution . The Ag_2S precipitate obtained was dried for 24 hours at 100 °C in an oven, grounded in an agate mortar and kept from light in an exsicator. The sensor membranes were obtained by applying a pressure of 19000 Kg cm^{-2} to 0.25 g of the precipitate.

The double membrane tubular electrodes were constructed (Fig. 1) according to [14] by using a rectangular shaped silver plate of about 2 × 4 mm that was soldered to the inner conductor of a shielded cable (A) and glued to the square membrane with a conductive silver epoxy resin. (B − C). After drying, both membranes were placed in the parallelepiped cavities of a perspex cylinder, 3 mm apart, and glued with a non-conductive epoxy resin (D). After hardening, the set was drilled through the centre of the membrane (0.8 mm i.d. channel) (E). This module was inserted in a perspex rectangular block (F) and firmly attached to the FIA manifold.

The response characteristics of the tubular detectors were assessed by using a low dispersion FIA system and a solution of 0.1 M potassium nitrate with 2 10^{-5} M silver nitrate both as carrier and ionic strength adjuster. The purpose of $AgNO_3$ was to contribute to the stabilisation of the baseline as well as to promote a quick return to the baseline during assays. Calibration curves were obtained by replicate injections of Ag (I) standard solutions in the 1 10^{-5} M − 1 10^{-1} M concentration range.

The FIA system parameters were optimised; different injection volumes (100 − 500 μL), flow rates (4 − 8 mL min^{-1}) and coil lengths between injection valve and detector (30 − 100 cm) were assayed. A 200 μL injection volume, a 8.0 mL min^{-1} flow rate and a length between injection valve and detector of about 35 cm were selected, providing reproducible analytical data, with a peak height of about 95% of the value of the stationary state, sampling rates of 120 to 200 samples h^{-1}, a detection limit of 3 10^{-5} M Ag(I) and a reproducible slope of 114.0
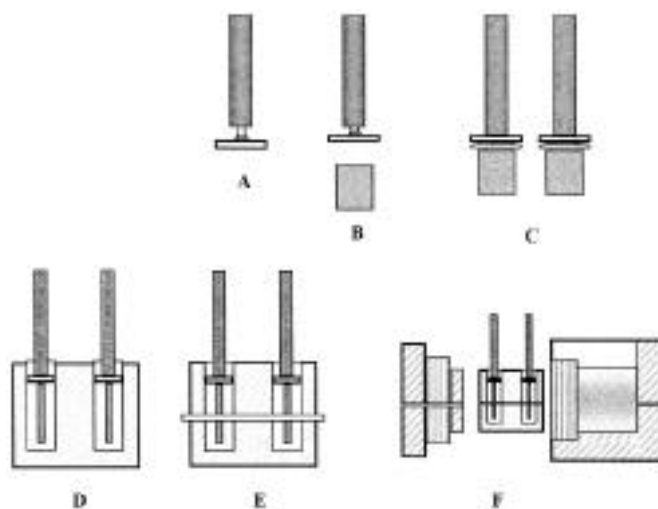

Fig. 1. Construction steps of the crystalline silver double membrane tubular potentiometric detector.

mV dec^{-1}. The reproducibility of the electrodes, assessed after 16 consecutive injections of standard solutions within the linear response range, presented potential variations less than ± 0.6 mV.

The pH influence on the response of the tubular detectors was assessed in a system similar to that previously described [18], for a concentration value of the main ion of $1 \cdot 10^{-3}$ M, and an operational range of $1.8 - 9.6$ was obtained.

Electrodes varied less than ±0.7 mV throughout a working day and their lifetime, assessed by means of frequent calibrations, was over three years (Tab. I).

When the present tubular detectors showed some deterioration of their working characteristics, namely an increase in the lower limit of linear response (LLLR), a decrease of the response rate and of the calibration slope, they were polished with a cotton thread coated with aluminium oxide (Buehler, 3 micron, 40-6603-030-016) and conditioned in a solution of 1×10^{-3} M silver cation (I) for some hours. The electrodes were left in this solution during pauses between trials and kept from light when not in use for long periods of time.

Sample preparation

Different types of wine were analysed (Porto, Madeira, current white and red table wines). The wine samples were straight inserted into the proposed FIA system without prior treatment.

The samples analysed by the reference method did not undergo any prior treatment.

Reference method

The reference method [17] used for the determination of chloride in wine matrices consists in the potentiometric titration of wines in acid media with silver cation (I) using a AgCl/Ag indicator electrode. This work resorted alternatively to an electrode similar to that previously described [13].

Results and discussion

Taking advantage of FIA potentiometric detection this work attempted to develop a single FIA system that allowed more precise measurements, for the chloride titration in wine. For the chloride determination in wine, a FIA manifold was set up (Fig. 2), in which samples and standards were inserted through the carrier flow, composed of a silver nitrate (I) titrant, and flowed to a mixing chamber where high dispersion occurred. A homogeneous crystalline Ag_2S membrane tubular electrode with increased sensitivity was used to monitor the concentration level of the silver solution (I) and a linear relationship between peak width and the logarithm of concentration of the species to be determined was established.

Viscosity of solutions used in FIA titrations affects to some extent the size of the analytical peak height obtained, especially its width [19]. Therefore, particularly with wines, which present different levels of sugar and alcohol, this effect had to be eliminated. Prior studies carried out with gradient systems [20] showed that the matrix effect dimini-

Table I. Comparison between the working characteristics of the tubular detectors comprising one membrane (SMTE) and the double membrane detector system (DMDS).

Characteristic	SMTE	DMDS
Slope (mVdec^{-1})	57.3	114.0
LLLR (M)	$1.5 \cdot 10^{-5}$	$3 \cdot 10^{-5}$
pH range Ag$^+$ = 1×10^{-3} M	$2.5 - 8.4$	$1.8 - 9.6$
Precision (mV)	±0.2	±0.6
Sampling rate (samples h^{-1})	$160 - 300$	$120 - 200$
Response stability (mVday^{-1})	±1.0	±0.7

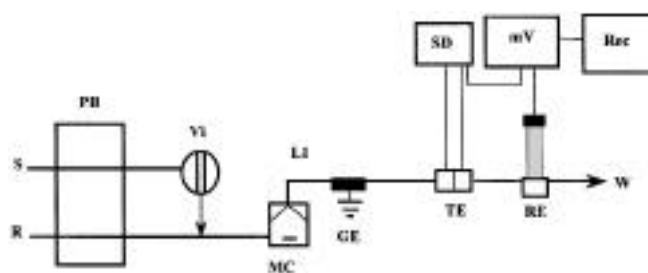LLLR - lower limit of linear response.

Fig. 2. Manifold used in the determination of chloride in wines, S - sample; C - carrier solution, R - titrant solution; Vi - Injection valve; PB - peristaltic pump; GE – "ground electrode"; TE - tubular electrode; RE - reference electrode; SD - summing device; mV - voltmeter; Rec - recorder; L1 - coil reactor; MC - mixing chamber.

shed when a mixing chamber was used to ensure a maximum dispersion. Once in this chamber, the solution undergoes a mechanic stirring and homogenisation perpendicularly to the flow what provides results much better than those obtained by using a coil or a single bead string reactor (SBSR) system with the same volume, and produces linear calibration curves (time interval vs. log concentration). This homogenisation procedure becomes of great importance when tubular electrodes are used since the measurements are made on the layer that is in contact with the membrane surface.

A wide gradient range of the sample plug concentration in the carrier solution can be achieved by varying the length and diameter of reactors as well as the reagent and sample flow rates. The concentrations obtained are reproducible and under control [20].

The FIA system was optimised considering the compromise between linearity of the concentration range, analytical sensitivity and sampling rate.

FIA system optimization

Carrier solution composition - This solution composed of a silver nitrate (I) and potassium nitrate solution was used as ionic strength adjuster and prepared in nitric acid to prevent the silver hydroxide and oxide precipitation. Different concentrations of the titrant ($1 \cdot 10^{-5} - 1 \cdot 10^{-3}$ M AgNO$_3$), were assayed in order to establish the sensitivity of the measurements and the detection limit of the analytical methodology.

Ag(I) concentration levels less than $1 \cdot 10^{-5}$ M originated highly sensitive calibrations (mV dec^{-1}) but at a low sampling rate, especially in the determination of samples with a high chloride content. Silver values over $1 \cdot 10^{-3}$ M led to the diminishing of the analytical sensitivity and chloride determination was compromised for values < 100 mg L^{-1}. Hence, a concentration of $1 \cdot 10^{-4}$ M AgNO$_3$ in 0.1 M KNO$_3$ and $1 \cdot 10^{-3}$ M HNO$_3$ was selected what enabled to obtain linear chloride concentrations from 10 to 800 mg L^{-1}.

Injection volume - After having established the titrant concentration, injection volumes of 25 to 100 μL were tested and it was found that a 50 μL volume allowed a good sensitivity without prejudice of the sampling rate. Lower volumes produced less reproducible signals whereas volumes over 50 μL led to a diminishing of the sampling rate.

Flow rate - This parameter was also assessed by being varied from 4 to 8 mL min^{-1} and it was found that a higher sensitivity was obtained with lower flow rates, although the sampling rate suffered a great decrease. A 8 mL min^{-1} flow rate was chosen since it allowed a high sampling rate and a good analytical reproducibility.

Mixing chamber - Different internal volumes of the mixing chamber were also studied and it was observed that they hardly affected the analytical signal. The lowest internal volume (290 μL) that did not affect the magnetic stirring operation was selected. The determination of the volume of the mixing chamber was evaluated by filling it up with a HCl solution with a known concentration which was then titrated with a NaOH solution of a known concentration, after having rinsed the chamber with deionized water for several times.

Coil length - The effect of the length between the mixing chamber and the detector (from 30 to 100 cm) was assessed too, and the shortest length was chosen so as to hinder a useless decrease of the sampling rate.

The height of the peak at which the width measurements were made affected the measurement sensitivity that was higher when the height values were the closest possible to the baseline. A 10 mV height above that of the baseline was selected for the measurements.

After optimisation, the system allowed sampling rates of 90 – 200 samples h^{-1} within a concentration range of 10 – 800 mg L^{-1} chloride. The results obtained were significantly better than previous ones [12].

Application to chloride determination in wines

The present system was used for the chloride determination in 12 samples of current red and white table wines and Porto and Madeira wines (Tab. II). Quality of the results given by the proposed FIA system (C_F) was assessed by comparison with the results provided by the reference method (C_R). There was a linear relationship expressed as follows: $C_F = -0.81 (\pm 0.8) +1.0 (\pm 5 \cdot 10^{-3}) C_R$ mg L^{-1} ($R = 0.9999$). The results show that there was a good agreement between both methodologies and a good precision of the results. The relative standard deviations for 10 replicate injections of 2 samples of 80.8 and 259.5 mg L^{-1} were less than 0.6%, which represents more accurate results when compared with those described in [12] with a precision of about 1%.

Table II. Results obtained from the chloride determination in wines by the proposed[a] and reference methods[a].

Sample	FIA (mg L^{-1})	REF (mg L^{-1})	RD%
1[#]	29.00 ±1.1	30.49 ±1.0	– 4.9
2[#]	308.5 ±4.9	310.4 ±4.5	– 0.6
3[#]	29.68 ±0.8	29.18 ±1.1	1.7
4[#]	26.84 ±1.5	26.66 ±1.6	0.7
5[##]	115.3 ±1.6	114.0 ±1.1	1.1
6[##]	86.57 ±2.4	84.87 ±2.1	2.0
7[###]	80.79 ±1.3	77.39 ±1.1	4.4
8[###]	61.23 ±2.1	60.94 ±2.2	0.5
9[##]	129.5 ±3.1	128.4 ±3.1	0.8
10[###]	229.6 ±2.2	228.9 ±2.3	0.3
11[###]	131.8 ±1.1	132.6 ±1.1	– 0.6
12[###]	259.48 ±2.7	257.63 ±2.9	0.7

[a]Average values corresponding to five determinations of the same sample.
[#] Porto and Madeira wines; [##] red wines; [###] white wines.

Student t-test was also estimated and a theoretical value of 0.2189 was obtained for the chloride determination in wine, which is less than the fixed value (2.201) for a reliable interval of 95% [21]. The statistical comparison of the analytical results showed that there is no interference that might alter the quality of the analytical results obtained by the proposed method.

Conclusions

The crystalline silver double membrane tubular potentiometric detectors constructed and evaluated in a FIA system proved to be a valuable tool for analytical determinations. Electrodes were characterised by a high analytical sensitivity and good precision (0.6 mV). The good working characteristics of the detector and the solid attachment of the detectors to a flow injection manifold allowed to develop an inexpensive, robust and single FIA system for the determination of chloride in wines.

The developed system presents some advantages over others described in literature [12], since it provides a better analytical precision (RSD < 0.6%), a wide concentration range linearity and higher sampling rates. Other than these characteristics, the fact that the electrodes are easily prepared and preserved and particularly that they can be easily adapted to the FIA system should also be enhanced.

The system proposed is a robust manifold easily handled in routine laboratory work.

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analytically from all the other similar products on the market, thus protecting its authenticity. And a second reason, aiming at achieving the highest possible product quality in *Brandy de Jerez*, is that a useful way of analytically monitoring the brandy during its maturation process may be devised. It is during this process that variables such as humidity and temperature in the cellar, oxygenation and exposure to light, the characteristics of the oak casks, alcoholic content of the spirit and so on, exert their influence in various ways on the product's final composition.

Many papers have been published on acid determination in foods and beverages [1-3]. In wine, the analysis of organic acids is commonly carried out by reversed phase chromatography [4-7], ion-exchange chromatography [8], or ion exclusion chromatography [9], normally using refractive index or UV detection. The former detection system is characterised by its low sensitivity and so is generally only suitable for detecting the major compounds; while UV detection is very sensitive to many interferent compounds, which makes it necessary to employ inconvenient preparatory stages for sample preparation [10,11]. The levels of organic acids are relatively low and there are a significant number of interferent species such as phenolic compounds in "Brandy de Jerez". Given this situation, it may be useful to have an alternative means of detection with a greater degree of selectivity and sensitivity. Ion-exclusion chromatography with conductimetric detection has poor sensitivity for the detection of sugars and also, there is little interference with carboxylic acid determination [12,13]. However, it is difficult to apply this method since the necessary use of a mobile phase in ion-exclusion chromatography leads to a decreased response to the organic acids due to the inhibition of their dissociation. A way around the problem involves dissociation of the organic acids by buffering the effluent from the column [14].

In the present work, a suitable method for the analysis of organic acids in *Brandy de Jerez* has been optimized. It is based on chromatographic separation through an ion-exclusion column, using a dilute solution of trifluoracetic acid as the mobile phase, followed by conductimetric detection. In order to increase the sensitivity prior to the detection, a buffer of pH 6.5 is added to the mobile phase to ensure the ionization of the analytes.

Experimental

Reagents

All chemical species used, of analytical reactive quality, were obtained from Merck (Darmstadt, Germany). The water used was purified in a Milli-Q system (Millipore, Bedford, MA, USA). All the solvents used as elution phases, and all the samples, were filtered through 0.45 μm membranes.

Apparatus

The instrument arrangement comprised: two Model 2150 pumps and a Model 2155 oven for the columns, all from LKB (Pharmacia, Sweden); a Model Conductomonitor III, conductivity detector from Milton Roy (LDC, Florida, USA); a Model 717 automatic injector and a Millenium data treatment system, both from Waters (Milford, MA, USA).

Chromatographic conditions

The chromatographic separation was carried out with two ION-300, Ion-exclusion columns (Interaction Chromatography, S. José, CA, USA) installed in series (300 mm length, 4.6 mm ID). The oven temperature was set at a constant (60 ℃). The mobile phase used was a 2.5 mM solution of trifluoroacetic acid (TFA) with a flow rate of 0.4 mL/min. The sample volume injected was 20 μL. In order to increase the detection sensitivity, a solution consisting of 2.5 mM of TFA, 20 mM of bis-tris buffer and 100 mM of EDTA was added at the outlet of the column, by means of the second pump, at a flow rate of 0.4 mL/min.

Samples

For the final preparation of the chromatographic elution and the subsequent construction of the corresponding calibration curves, model solutions were used; these were composed of a 35% (v/v) ethanol in water medium in which citric, tartaric, malic, fumaric, succinic, lactic, formic and acetic acid, in concentrations ranging between 5.8 and 806 mg/L, were dissolved.

The samples of "Brandy de Jerez" analyzed, all of which were from commercial products, were supplied by the Regulatory Commission for the Specific Denomination of "Brandy de Jerez".

In all cases, the samples were filtered through 0.45 μm membranes before injection.

Results and discussion

When the conductimetric detection method is used to detect ionizable species, it is influenced by the pH of the mobile phase in which they are eluted. In the present study which takes as its starting point the experimental conditions described by Hayashy [14], the variables (composition of the mobile phase, temperature at which the chromatographic separation is performed, and composition of the post-buffering phase) were optimized in order to determine the organic acids present in Brandy de Jerez.

Firstly, the composition of the mobile phase was optimized, which enabled the best resolution of the peaks corresponding to the eight organic acids present in the Brandy de Jerez by trials with p-toluenesulfonic acid, trifluoroacetic acid, sulfuric acid and phosphoric acid. The best option proved to be trifluoroacetic acid (TFA) at a concentration of 2.5 mM; this produced a good resolution and an acceptable background in the detector.

With regard to the temperature at which the chromatographic separation was performed, it was determined that the optimum corresponded to 60 ℃.

For the post-buffering stage, the same phase as before (TFA 2.5 mM) was added by means of a T connector at the outlet of the column. In addition, a buffer of low conductivity, bis-[2-hydroxyethyl]-iminotris-[hydroxymethyl]-methane, (BIS-TRIS), was incorporated. This was proved to present an adequate buffering capacity, since the pH of the effluent at the system outlet was 6.5. Also EDTA at a concentration of 100 μM was added to this phase, to prevent the formation of coordination complexes between the citric acid and the possible metallic traces present. And to prevent

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Table I. Effect of post-column buffering on the sensitivity of the method.

Compound	t_R (min)	RSD (%)	Without buffering		With buffering		B/A
			Area (µV s) (A)	RSD (%)	Area (µV s) (B)	RSD (%)	
Citric Acid	19.77	0.08	6787	0.68	14158	1.88	2.09
Tartaric Acid	20.95	0.05	7772	0.63	10048	3.22	1.29
Malic Acid	24.74	0.05	3170	1.03	8124	3.15	2.56
Succinic Acid	31.68	0.07	1093	6.70	9037	3.23	8.27
Fumaric. Acid	32.85	0.02	6871	2.09	8489	0.58	1.23
Lactic Acid	34.11	0.03	790	8.83	3138	5.69	3.97
Formic Acid	36.29	0.07	1320	8.52	3839	9.22	2.90
Acetic Acid	40.67	0.07	172	30.47	2645	13.65	15.37

Table IIa. Characteristics of the calibration curves.

Compound	Explored Range (mg/L)	Regression coefficient	Slope (µVs L/mg)	Intercept (µVs)
Citric Acid	10.60 − 213.20	0.9991	126.7506	− 384.1767
Tartaric Acid	15.04 − 300.80	0.9997	122.6523	− 977.3872
Malic Acid	13.36 − 336.72	0.9978	148.8978	− 2 148.4302
Fumaric Acid	5.80 − 115.52	0.9994	246.8204	− 335.4398
Lactic Acid	11.60 − 388.99	0.9999	55.6390	− 348.8357
Succinic Acid	11.76 − 130.88	1.0000	208.4457	− 320.7854
Formic Acid	9.88 − 98.80	0.9999	194.8948	− 363.9608
Acetic Acid	6.01 − 806.61	0.9989	127.9628	− 2 041.3522

Table IIb. Performance characteristics of the analytical method.

Compound	Analytical Sensitivity	Detection Limit (LOD, mg/L)	Quantitation Limit (LOQ, mg/L)	Linearity (LOL %)	Recovery (%)
Citric Acid	3.3288	9.415	31.384	98.460	96.21
Tartaric Acid	4.1642	10.819	36.063	98.638	112.10
Malic Acid	6.2998	16.367	54.558	96.168	86.96
Fumaric Acid	1.7411	4.523	15.078	98.016	88.58
Lactic Acid	2.9252	7.600	25.333	99.052	100.43
Succinic Acid	0.2817	0.732	2.440	99.708	99.22
Formic Acid	0.4087	1.062	3.539	99.408	96.43
Acetic Acid	16.0454	43.054	143.514	97.705	103.06

Fig. 1. Profile of the organic acids content of the three classes of Brandy de Jerez. A) Brandy "Solera", B) Brandy "Solera Reserva", C) Brandy "Solera Gran Reserva".

the pulse produced by the second pump from affecting the detection, a restrictor was inserted between the pump and the *T* connector to dampen this pulse.

Table I shows the results obtained from the study of the influence of the post-column buffering. The peak areas for standard solutions of carboxylic acids obtained by direct electric conductivity detection were compared with those obtained with post-buffering prior to detection. As can be seen, this technique enabled the signal to be multiplied significantly, by a factor of 15.37 in case of acetic acid, without producing any significant changes in the repeatability of the method. In direct detection, sensitivity is influenced by
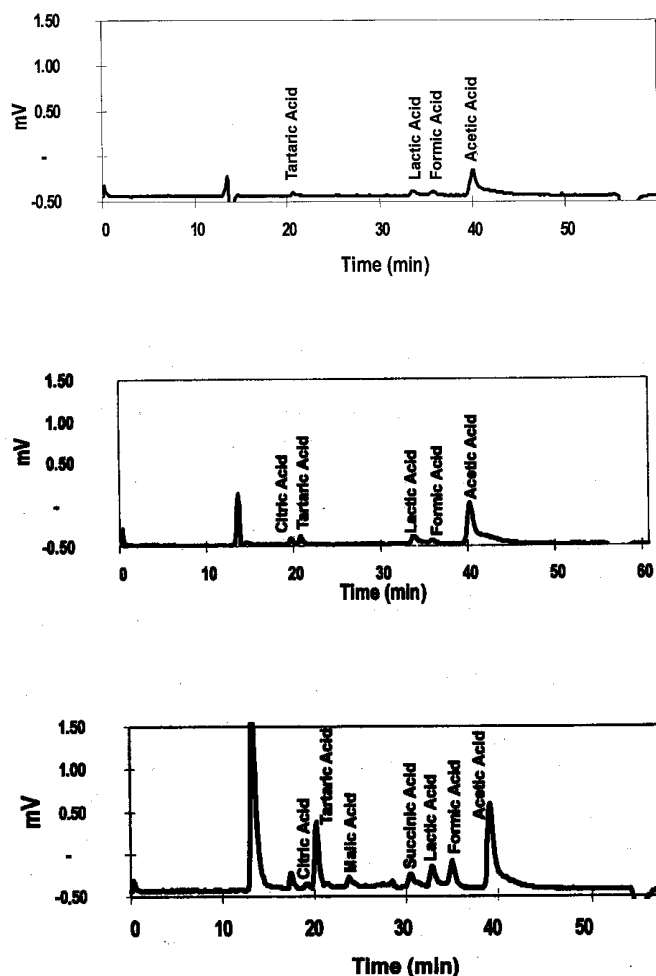
the concentration of the mobile phase acid while in post-buffering method, sensitivity can be kept almost constant by adjusting the concentration of the buffer solution according to the acidity of the mobile phase.

In order to validate this method, a series of calibration curves were constructed using the organic acids anticipated to be present in *Brandy de Jerez*; the calibration ranges were based on the expected concentrations of these acids. Repeatability of both retention times and peak areas was studied on the basis of 12 injections, and the values obtained are shown in table IIa.

Another series of parameters related to the performance of the analytical method was calculated from the calibration curves previously constructed using the ALAMIN computer program [15].

As can be seen, the method appears linear for the ranges of concentrations and the acids studied; and the limits of detection achieved are lower than those obtained using the refractive index detection system.

In order to check the accuracy of the method, the technique of standard additions was used. A sample of representative commercial brandy was taken as the matrix sample. Then known quantities of analytes were added at 5