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Development of a potentiometric flow cell with a stainless steel electrode for pH measurements. Determination of acid mixtures using flow injection analysis

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Abstract

In this work a stainless steel electrode was prepared, characterised and used as indicator electrode in a potentiometric flow cell. Due to its versatility, it was possible to study different electrode geometries and flow cell arrangements. After optimising the system, mixtures of succinic and oxalic acids were determined by titration. Partial least squares (PLS) regression as multivariate calibration tool was applied for data treatment. The predicted results obtained in a test set showed a relative error of 4.3% for succinic acid and 5.5% for oxalic acid. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Potentiometric flow cell; pH measurements; Flow injection analysis

1. Introduction

Flow injection analysis (FIA) [1] is based on the injection of a liquid sample into a moving, non-segmented continuous carrier stream of a suitable liquid. The injected sample forms a zone, which is transported toward a detector. The detector continuously records the absorbance, electrode potential, or other physical parameter that changes continuously due to the passage of the sample material through the flow cell.

In the flow potentiometric system used for pH measurement, it is necessary to have an indicator electrode that gives a fast response to variation of the H^+ ion in a reproductive form. A time response, stability and reproducibly of the signal are limiting factors for the use of potentiometric detectors in a FIA system [2]. The metal–metal oxide can give appropriate time response for this kind of system. Beyond this, metal–metal oxide electrodes are more versatile to be adapted in the flow potentiometric cell and can be used in instead of glass microelectrodes as a low cost alternative. The response of the metal–metal oxide electrode in the flow system is controlled by its chemical properties and by the dispersion in the system. The electrode efficiency is influenced by: the nature of the electrode membrane surface, the way in which the electrode is coated, the condi-

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tioning of the electrode, the variation of the linear response with relation to pH and the time response and selectivity of the electrode [3,4]. The life-time and the stability of the electrode in flow injection analysis are also important factors, and can be a problem in experiments that demand more precision. However the re-calibration of the detection system does not present many problems because, in the FIA system, this procedure is normally simple and fast.

Stainless steel has been studied in some works to be used as an indicator electrode in water solution instead of the glass electrode [5–7]. This electrode has a fast response, low cost and can be adapted easily to building a potentiometric cell in a FIA system.

In the potentiometric FIA system, a gradient concentration is built, by injecting the base into a carrier stream of acid (sample). This gradient is produced by a dispersion chamber in the system and a zone dispersion concentration is obtained. In the dispersion profile, several acid/base concentration relationships are formed, which has one point where the acid is exactly neutralised by base. Normally the width peak is used as a method for calculating the concentration. The peak width is measured at different times between two points, one in the front of the zone of the dispersion and the other in the end of the dispersion zone, where the dispersion coefficient is the same.

The concentration determination of several different weak acids is necessary in the food industry, scientific research or in a clinical laboratory. But this task is not easily done by potentiometric titration when acid mixtures with close pK_a values need to be determined. Peak width only is not sufficient as an analytical signal for quantification of such acid mixtures.

More information from the FIA titration system can be obtained when the entire profile of the titration is used, instead only one point. This leads a multivariate approach, where it is possible to quantify acid mixtures even in cases of close pK_a values. This procedure was proposed for conventional titrations [8,9] using linear multivariate calibration modeling by partial least squares (PLS) [10–12], or using non-linear modelling by neural networks [13]. These multivariate approaches require the realisation of thousands of manual titrations and this work is boring and time consuming. If this step could be automated, the determination of weak acid mixtures using multivariate calibration methods would be facilitated greatly, and more applications could be formulated.

In this work a stainless steel electrode was evaluated as a pH sensor in a FIA system, and two different electrode geometries and three potentiometric flow cells were developed. A multivariate calibration model by PLS was used to process the signals from a flow injection potentiometric acid–base titration system involving a mixture of succinic and oxalic acids. This mixture is an example of a mixture of two acids with close pK_a values.

2. Experimental

A bar of stainless steel with composition 16–18% Cr, 10–14% Ni, 2–3% Mo, 0.08% C, 2% Mn, 1% Si, 0.045% P, 0.03% S and the Fe (SAE 316, Villares), equivalent described by Nomura and Ujihira [5], was used as substrate for preparation of the electrode.

Electrodes with two different geometries were constructed. In the first case, a planar electrode with dimensions of 30 × 10 × 3 mm was prepared. Another electrode was made with a tubular geometry, with 1 mm diameter and 3 mm of length. The surface of the stainless steel was roughened mechanically with sandpaper of different granulations and polishing with a commercial dolomite product.

The indicator electrode was prepared by imersing the stainless steel in a solution of 2.5 mol l^{-1} $K_2Cr_2O_7$ and 5.0 mol l^{-1} H_2SO_4 at a temperature of 70°C for different periods of time (between 10 min and 3 h) with agitation. After that, the electrodes were taken out of the oxidant solution and washed with water.

For evaluation of the electrode response, several buffer solutions were prepared, with pH in the range of 2.0–12.0, from mixtures of citric and boric acids and sodium phosphate. All buffers values were checked using a potentiometer (Corning-pH/ion analyser 350) and a glass electrode.

Three flow potentiometric cells were developed while two different FIA manifolds were studied. Fig. 1 shows one FIA manifold, where the reference electrode was placed together with the indicator electrode in the flow cell. In a second system, the reference electrode was placed inside a beaker with 3.0 mol l^{-1} KCl solution.

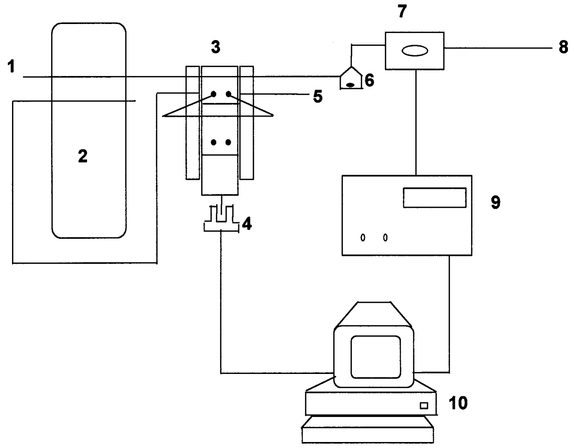

Fig. 1. FIA system used for evaluation of the cell models. (1) Carrier stream; (2) peristaltic pump; (3) injector; (4) opto switch; (5) sample; (6) dispersion chamber; (7) potentiometric cell; (8) waste; (9) potentiometer; (10) microcomputer.

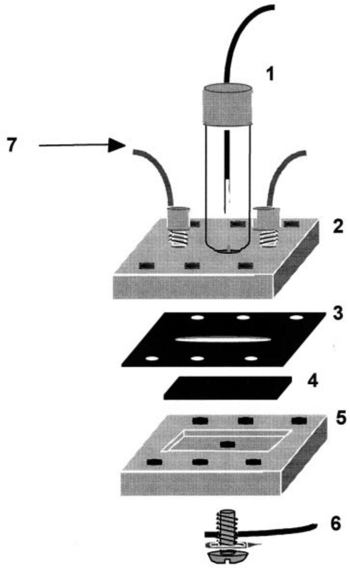

Fig. 2. Potentiometric flow cell studied. (1) Reference electrode; (2) acrylic block; (3) rubber gasket; (4) planar electrode; (5) acrylic block; (6) electric contact; (7) flow direction.

For the potential measurements a Corning pH/ion analyser 350 potentiometer was employed. Data acquisition was accomplished using a Pentium 150 MHz microcomputer with 32 Mb RAM memory, and an Advantech PCL-711S interface, with an A/D converter of 12 bits. The program for acquisition and control of the system was written in Visual Basic 3.0.

The injector had an opto switch to synchronise the injection of the reagent with the data acquisition.

2.1. Potentiometric flow cells

Fig. 2 presents one of the potentiometric flow cells developed. It has a planar electrode, and a rubber gasket with a central cut (1 mm of thickness, 20 mm of length and 4 mm of width), resulting in a cell volume of 80 µl. The planar indicator electrode and the reference electrode (Ag/AgCl) were placed together to the same cell. The sample was carried through this cell, staying simultaneously in contact with both electrodes.

The second model has one difference: the reference electrode was placed in a solution 3.0 mol l^{-1} KCl outside of the measurement cell.

A third cell model with the indicator electrode having a tubular geometry was also developed. The stainless steel plate was drilled resulting in an internal cell volume of 15 µl and the solution was passed through this hole.

2.2. Acid mixtures and experimental set up for multivariate calibration

Twenty-three mixtures of oxalic and succinic acids were prepared in the range from 5.0×10^{-3} to 8.0×10^{-3} mol l^{-1} for succinic acid and from 5.0×10^{-3} to 1.0×10^{-2} mol l^{-1} for oxalic acid. The carrier was pumped at 0.5 ml min^{-1} and 250 µl of 0.1 mol l^{-1} NaOH was injected into the system, where a dispersion chamber of the 500 µl was adapted. The data was obtained over a period of 420 s.

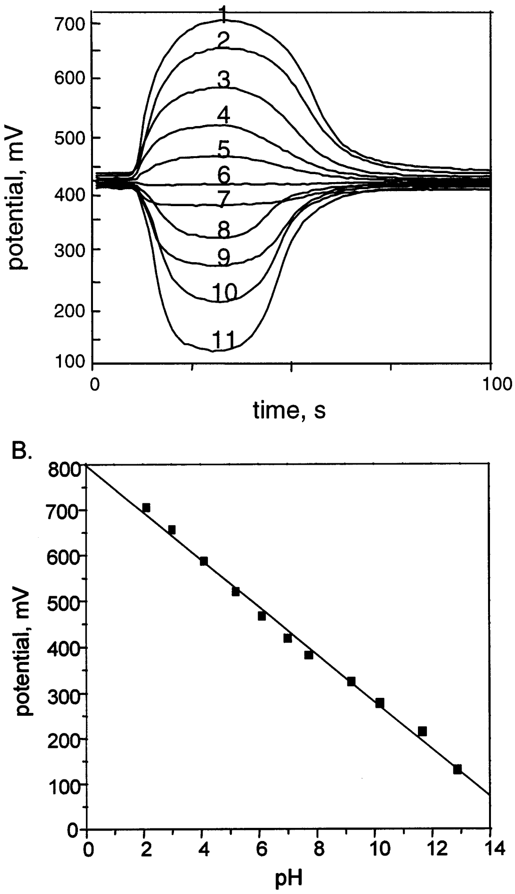

Fig. 3. (A) Response electrode for different buffer solutions injected: (1) pH 2.1; (2) pH 3.0; (3) pH 3.9; (4) pH 5.0; (5) pH 6.0; (6) pH 6.8; (7) pH 8.6; (8) pH 9.6; (9) pH 10.4; (10) pH 11.4; (11) pH 12.6. The volume injected was 500 µl of the carrier buffer solution with pH 6.0, flow rate of 1 ml min^{-1}. (B) Calibration curve of the electrode. The curve equation is potential $= -51.84$ pH $+ 798.48$; and the correlation coefficient is 0.9973.

The experiment was carried out in a reverse FIA system, Fig. 2, where the reactant (base) was injected into carrier containing the sample (acid mixture) and the stream merged to a mixture chamber for base dispersion.

2.3. Partial least squares

PLS is a mathematical model built from the linear combination of instrumental measurements x and the concentration results y. Scores and loadings are obtained from the X and Y matrix.

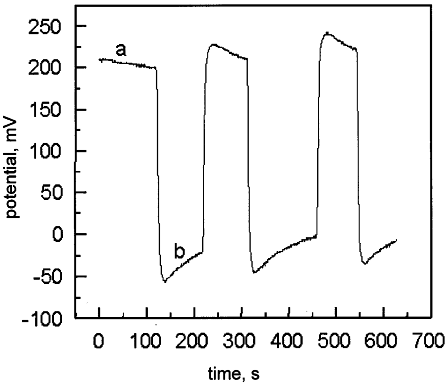

Fig. 4. Electrode response when the carrier buffer is changed from pH 4(a) to 9 (b).

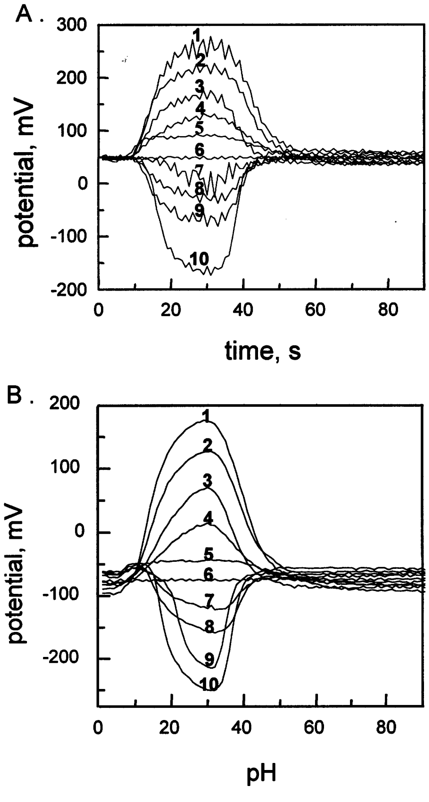

Fig. 5. (A) Electrode response of the flow cell when indicator and reference electrodes are separated. (B) Electrode response when the stainless steel tube is used. (1) pH 2.1; (2) pH 3.0; (3) pH 3.9; (4) pH 5.0; (5) pH 6.0; (6) 6.8; (7) pH 8.6; (8) pH 10.4; (9) pH 11.4; (10) pH 12.6.

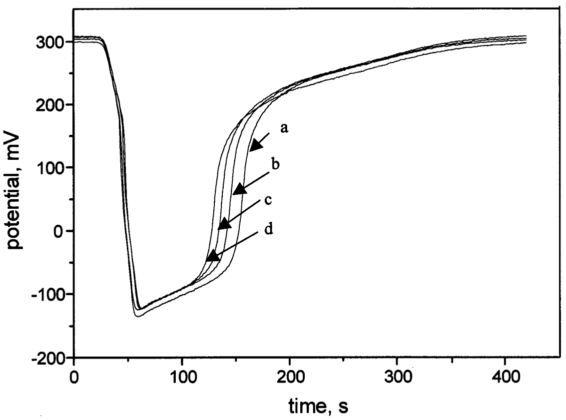

Fig. 6. Titration curves obtained for the 4 mixtures of weak acids: (a) 6.0×10^{-3} mol l^{-1} succinic acid and 5.0×10^{-3} mol l^{-1} oxalic acid; (b) 7.0×10^{-3} mol l^{-1} succinic acid and 5.0×10^{-3} mol l^{-1} oxalic acid; (c) 8.0×10^{-3} mol l^{-1} succinic acid and 5.0×10^{-3} mol l^{-1} oxalic acid; (d) 9×0.10^{-3} mol l^{-1} succinic acid and 5×0.10^{-3} mol l^{-1} oxalic acid.

$$X = TP' + E \tag{1}$$

$$Y = UQ' + F \tag{2}$$

where T and U are the scores matrix of X and Y; P and Q are the loadings matrix of X and Y; and E and F are the residues. The relationship between two blocks X and Y is obtained by linear regression coefficient.

$$U = bT \tag{3}$$

where b is a vector of the coefficient of regression between the matrix scores U of Y and the matrix scores T of X.

3. Results and discussion

The electrodes showed different colours after oxide film formation, such as yellow, red, green, blue or violet, depending on the time, temperature, and stirring during treatment.

Fig. 3 presents the response of an electrode prepared by chemical treatment and stirring during 1 h. This stainless steel electrode showed a green colour and a smooth and brilliant surface, with a potential versus pH curve inclination of -52.0 mV pH^{-1} (sub-nernstian response). In this study, the FIA system of Fig. 1 was used with the flow potentiometric cell shown in Fig. 2.

In a second calibration, using the same electrode described above after 5 days of uninterrupted use, a new inclination curve with -43.7 mV pH^{-1}, was obtained remaining near to this value when further calibrations were performed. The calibration curves for ten different electrodes showed a medium inclination value of -45.0 mV pH^{-1}.

The electrode response time is very good, on the order of 5 s, as is shown in Fig. 4, when the carrier buffer solution was changed from pH 4 to 9, using a reduced FIA manifold without large connecting tubes to avoid sample dispersion. This response time is fast enough to permit its use as a detector in a FIA system.

The time life of the electrodes was also studied during 1 month. The response and sensitivity, given by the curve inclination, was stable during all the time monitored. However, it was observed that with the use of a solution with a pH <3 or

Table 1
Predicted and real values for succinic and oxalic acid mixtures obtained with PLS

Mixture	Succinic acid (mol l^{-1})			Oxalic acid (mol l^{-1})		
	Real	Predicted	Relative error	Real	Predicted	Relative error
1	0.00600	0.00595	−0.6	0.00600	0.00587	−2.1
2	0.00700	0.00711	1.5	0.00600	0.00545	−9.0
3	0.00500	0.00511	2.3	0.00700	0.00702	0.3
4	0.00800	0.00808	1.0	0.00700	0.00706	0.8
5	0.00600	0.00617	2.8	0.00800	0.00782	−2.1
6	0.00800	0.00789	−1.3	0.00900	0.00922	2.4
RMSEP			1.6			2.8

in the presence of Cl^- ions, the time life decreases to only 1 week [5].

From several electrodes prepared, the selection of the best electrode to be used during the FIA measurements was based on its time response and on its reproducibility.

First a potentiometric cell where the reference electrode Ag/AgCl was separated from the indicator electrode was evaluated. A silver wire covered with AgCl was immersed in a beaker with a solution of 3.0 mol l^{-1} KCl that received the flow from the potentiometric cell. A volume of the 1000-ml of KCl solution was used to reduce the dilution effects during the data recording time. This study employed as carrier a buffer solution of pH 6.9 with flow rate of 1 ml min^{-1}. Other buffer solutions of pH in the range of 2.0 to 12.0 were injected into the FIA system. For all curves, as shown in Fig. 5A, a large noise is observed with maximal amplitude near 50 mV. This noise can be due to peristaltic pump pulsation, or interference of the 60 Hz from the electric circuit of the laboratory. In this case the distance between the indicator electrode and reference electrode was 16 cm. When the distance between the indicator electrode and the reference electrode was greater than 32 cm, a significant increase in the noise was observed with amplitudes above of 100 mV. As suggested by Alegret [14] for noise reduction, a tubular stainless steel was placed in the system and connected to ground. The carrier solution transporting the sample towards potentiometric cell was forced to pass through this metal tube. The level of the noise presented a significant improvement with amplitude of only 6 mV, as shown in Fig. 5B.

The next potentiometric cell evaluated was that shown in Fig. 3, where the indicator and reference electrodes are placed together. The response of this potentiometric cell presented little noise with an amplitude of 2 mV, and it is not necessary to place a stainless steel tube in the conducting tube to reduce the noise. For a lower level noise in the measurements it is necessary to use a cell that has both reference and indicator electrodes. However, one disadvantage of this kind of flow cell is the possibility of formation of small air bubbles on the surface of the electrode. These air bubbles are a serious drawback in electrochemical systems where the detector is in direct contact with the solution, and serious problems in data acquisition can thus appear (noise, distortion, lost of reproducibility, etc.).

Finally the tubular electrode was observed where the noise effect and loss of reproducibility were also estimated. This system presents less problems with air bubbles, but its response was not satisfactory. A loss in sensitivity was observed and also a long time to return to base line. The presence of the noise is associated with the distance between the electrodes because, in this configuration, it was not possible to place both electrodes into the same cell. The loss in sensitivity is due to the difficulty in obtaining an homogeneous oxide film with good quality on the internal surface of the tubular electrode because of its small dimension.

For the titrations experiments a cell configuration was adopted where the reference and indicator electrodes are placed together (Fig. 2) and the FIA system used was that shown in Fig. 1. This configuration guarantees a lower level of noise in the measurements with higher sensitivity, as well as a shorter response time.

3.1. Potentiometric titration of succinic and oxalic acid mixtures

The succinic and oxalic acids mixtures were titrated in triplicate, with the injection of 250 μl of a 0.5 mol l^{-1} NaOH solution. The potential was recorded immediately after the injection of base, and a time of 420 s was needed to monitor the whole of the titration. This volume of NaOH was selected to guarantee a reagent excess in the dispersion zone and to make a concentration gradient of the base within the system. This mixture disperses into the chamber, being pumped continuously in the direction of the detector, where a profile of the potential variation with the time is recorded. After that the potential value returns slowly to initial value, due to cleaning of the dispersion chamber and potentiometric cell.

In Fig. 6 the titration curves obtained for four mixtures of the weak acids described before is shown. The estimate of the median standard deviation for each triplicate set was 4 mV.

From the 23 mixtures prepared, 17 were used to build the calibration model and six were used to validate it. Before this, the data set was pre-processed, inverting the curve potential versus time, resulting in an array with 38 time values for each mV of potential. This treatment was important because by using time as the independent variable, more information can be obtained from the variations of the titration process.

PLS was used to establish the relationship between the titration data and acid concentrations. The number of latent variables to be used was determined by cross-validation [10], and the best model had four latent variables. The relative error in the validation set was 4.3% for succinic acid and 5.5% for oxalic acid. In Table 1 the real and predicted values are shown, and also the relative errors and root mean squares error of prediction (RMSEP).

The RMSEP is obtained by:

$$\mathrm{RMSEP} = \sqrt{\frac{\sum (xp - xr)^2}{n}}$$

where xp is the predicted value and xr is the real value and n is the number of samples in the validation set.

4. Conclusion

The preparation of a chromic oxide film on the surface of the electrode is the most important step for formation of a stable, reproducible and sensitivity electrode. The stainless steel electrode presents a fast time response and is suitable to be used in a FIA system. Also good response reproducibly for different injections of the buffer solution was observed. The usual FIA potentiometric titration has the reference and indicator electrodes separated, but it was demonstrated that if both electrodes are placed together an enhancement in the signal/noise relationship is obtained. Potentiometric titration of a mixture of weak acids using multivariate calibration presented good results for validation samples, opening future applications in pharmaceutical or food samples.

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