Flow Injection Titration of Chloride in Electroplating Baths with a Silver Tubular Electrode as a Detector

Mª Begoña Etxebarria*, José L. F. C. Lima**, Mª Conceição B. S. M. Montenegro** and Ricardo Pérez-Olmos*†

*Departamento de Química Analítica, Escuela Universitaria de Ingeniería Técnica Industrial, Plaza de la Casilla 3, 48012 Bilbao, España
**CEQUP–Departamento de Química-Física, Faculdade de Farmácia, Rua Antal Cunha 164, 4050 Porto, Portugal

A flow injection system has been constructed for the “pseudo-titration” of chloride in electroplating baths with potentiometric detection. A silver ion-selective tubular electrode based on a homogeneous crystalline membrane was used. The FIA manifold has been developed and optimized in order to analyze samples with a chloride concentration range of 6.0 × 10⁻² M to 2.5 M. The proposed method is precise (relative standard deviation about 5%) and the results obtained by a simultaneous application of the FIA method and an automatic precipitation titration method, adopted as a reference technique, are in good agreement (r=0.996). The sampling rate for the FIA manifold is 78 samples per hour.

Keywords Flow injection analysis, chloride, ion-selective electrode, electroplating bath

Chloride is commonly used in the electroplating industry as a mean to increase the conductivity of electroplating baths and to improve their throwing power. Many metal chlorides are sufficiently soluble, and baths prepared with chloride contain those for plating nickel, iron and zinc. Chloride is also used in small amounts in a nickel sulfate bath to prevent passivity of the anodes. Moreover, the tensile stress increases along with the chloride content, which explains the high levels of this anion in electroplating baths.¹

The analytical methods recommended for determining chloride in electroplating baths are commonly carried out using gravimetric or volumetric methods employing silver nitrate as an analytical reagent.²³ Potentiometry with conventionally-shaped ion-selective electrodes has the advantage of allowing the analysis of samples with a heterogeneous composition, such as electroplating baths.⁴ In addition to their selectivity, the electrodes are characterized by a high range of linear response. Despite these advantages, the potentiometric method with conventional electrodes is yet too low when considering the necessity of industrial control to analyze a large number of samples per hour.

Flow injection analysis (FIA) is a well-established analytical method that, in association with potentiometric detection, is an advantageous alternative to direct potentiometry with conventionally-shaped selective electrodes. Therefore, an FIA manifold has been developed for determining chloride in electroplating baths using a silver tubular detector without an inner reference solution. The silver tubular electrode is based on a homogeneous crystalline membrane obtained by a high-pressing silver sulfide powder.⁶

In the FIA manifold samples are injected, without any previous treatment, into a titrant carrier stream containing silver cation, and mixed with the plug in an exponential gradient device. In this “pseudo-titration” technique, the decrease in the silver concentration is monitored by the variation in the potential between the silver tubular electrode and the reference electrode.

Experimental

Reagents and solutions
All of the chemicals used were of analytical-reagent grade; further deionized water with a specific conductivity of less than 0.1 µS/cm was used throughout.

A stock solution of sodium chloride (2.6 M) was prepared after careful weighing of a solid reagent previously dried at 100°C in an oven.

The silver solutions were prepared from solid silver nitrate. The solution used as the titrant (0.1 M) in the reference methods was standardized by potentiometric titration against a chloride standard solution.

The different electroplating baths analyzed were prepared following the recommendations given in the literature¹ from the corresponding solid analytical-grade
reagents in order to achieve the final concentrations presented in Table 1.

**Apparatus and electrodes**

The potentiometric measurements were performed with a digital potentiometer (sensitivity of ±0.1 mV) using a double-junction reference electrode with its external compartment filled with a potassium nitrate 1.0 M solution.

The silver tubular electrodes with a homogeneous crystalline membrane, used as indicator electrode in the "pseudo-titration" by FIA, were constructed as described in a previous study.6

Potentiometric titrations with conventional electrodes were performed using an automatic titrator. This procedure is similar to the Mohr method recommended in the literature3, changing the visual indicator for the conventionally-shaped chloride electrode in end-point detection.

**Flow injection manifolds**

In constructing the FIA manifold (Fig. 1) a four-channel peristaltic pump was used to ensure the flow of different solutions. A six-port rotary injection valve was used to inject samples and standards. PTFE tubing with an internal diameter of 0.8 mm was used in the connections. To create an exponential concentration gradient in the FIA "pseudo-titrations", according to the different composition of the samples analyzed, a long coil or a well-stirred mixing chamber was used.

**Reference procedure**

With the purpose of establishing a comparison, a potentiometric titration based on the Mohr method, recommended in the literature1, was used, replacing the visual indicator by a silver electrode with a homogeneous crystalline membrane and a conventional configuration.4

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**Results and Discussion**

For titrating chloride in electroplating baths a single-channel flow injection manifold of high dispersion was developed. The standards and sample solution were directly injected in the silver nitrate carrier stream (1.5 X 10^-3 M), which also contained potassium nitrate (1 M) so as to increase the solution conductivity and to adjust the ionic strength; nitric acid (2.5 X 10^-1 M) was used to prevent the precipitation of silver oxides and hydroxides.

Initially, in order to create the exponential concentration gradient necessary in FIA "pseudo-titrations", a well-stirred mixing chamber was used. This choice was justified by previous experience in which this device allowed good linear calibration plots. Unfortunately, it has proved not to be efficient enough for mixing the carrier stream and sample due to the high chloride concentration in the electroplating baths; thus, a long coiled tube was used (Fig. 1). Experience gained by using this coil showed a good reproducibility of the signals.

To optimize the FIA manifold, different injection volumes, coil lengths and flow rates were assayed. The best results were obtained by injecting 16 µl of chloride standards into the carrier stream with a silver nitrate concentration of 1.5 x 10^-3 M through a coil having a length of 390 cm. The optimum flow rate to assure good sensitivity suitable for an adequate sampling rate was 3.6 cm^3 min^-1.

Before injecting samples, a calibration curve with standard solutions of different chloride concentrations was made (Fig. 2). Under these conditions it was possible to perform chloride determinations within a linear range between 0.30 and 2.60 M with a correlation coefficient of 0.9997, thus obtaining a sampling rate of 73 samples per hour. Reproducibility experiments were carried out by performing eleven injections of the same sample; the average relative standard deviation obtained was 4.9%.
A chloride-sulfamate electroplating bath, with the lowest chloride concentration, could not be analyzed using the aforementioned FIA manifold. Thus, a change in the manifold design was introduced. In this case, a well-stirred mixing chamber proved to be efficient to assure a good carrier stream plus sample homogenization; the same parameters studied in the former manifold were evaluated. The composition of the carrier stream was: silver nitrate (1 X 10.4 M), potassium nitrate (1 M) and nitric acid (1 X 10-3 M). The optimized parameters of this FIA manifold were: an injection volume of 80 µl, a silver nitrate concentration of 1.0 X 10.4 M, a volume mixing chamber of 226 µl and a flow rate of 8.0 cm3 min'. A linear response was obtained by injecting chloride standard solutions with concentrations of between 1.4X 10-3 and 1.3 X 10-1 M. The correlation coefficient was 0.9996 with a sampling rate of 83 samples per hour. The relative standard deviation obtained by eleven replicate injections of this electroplating bath sample was 4.7%.

In order to assess the quality of the results obtained by the proposed methodology, determinations of the electroplating baths of different compositions and different concentrations were carried out by FIA and by the reference procedure (Table 1). A relation of the type \( C_f = C_0 + S C \) was established between the results obtained by FIA "pseudo-titration" \( (C_f) \) and those obtained by the reference method \( (C) \). Values of \(-6.50 \times 10^{-2} \) M for \( C_0 \), 1.13 for \( S \) and 0.996 for the correlation coefficient were obtained, showing a fairly good agreement between both methods. The precision of the results obtained in both cases was also compared by performing an F test. The precision of the two methods is similar; what can be proved by the calculated F value does not exceed the theoretical one, with the exception of the chloride/sulfamate electroplating bath.

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References