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Overcoming the Schlieren Effect in Flow Injection Spectrophotometry by Introduction of Large Sample Volumes. Determination of Chloride in the Electrolyte of Lead-acid Batteries

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Um sistema de análise por injeção em fluxo com detecção espectrofotométrica é proposto para determinação de cloreto em eletrólito de bateria chumbo-ácido, utilizando a reação com tiocianato de mercúrio(II) em meio contendo ferro(III). A formação de gradientes de índice de refração no centro da zona de amostra foi evitada utilizando um elevado volume de amostra. Interferência devida a sulfato foi investigada e a correlação entre os equilíbrios químicos envolvidos e os sinais transientes gerados foi utilizada para desenvolver uma estratégia para a quantificação de cloreto. Amostras contendo de 2,2 a 3,7 mol L⁻¹ de ácido sulfúrico podem ser determinadas utilizando a mesma curva analítica, sem efeitos matriciais ou qualquer tratamento prévio. O limite de detecção e o desvio padrão relativo das medidas foram estimados em 0,37 mg Cl⁻ L⁻¹ (nível de confiança de 99,7 %) e 1,6% (n = 10), respectivamente. A frequência de amostragem foi 45 h⁻¹. Porcentagens de recuperação entre 95,9 e 108% foram obtidas para adições de cloreto (2,00 a 8,00 mg L⁻¹) nas amostras.

A flow injection spectrophotometric system is proposed for determining chloride in lead-acid battery electrolyte by using the displacement reaction between mercury(II) thiocyanate and chloride in a medium containing iron(III). The employment of a large sample volume was effective to avoid refractive index gradients in the central part of the sample zone. Sulfate interference was studied and the correlation between the chemical equilibria involved and the transient signals was used to develop a strategy for chloride quantification. Samples containing from 2.2 to 3.7 mol L⁻¹ of sulfuric acid can be determined by using the same analytical curve, without matrix interference or any previous treatment. The detection limit and the relative standard deviation were estimated in 0.37 mg Cl⁻ L⁻¹ (99.7% confidence level) and 1.6% (n = 10), respectively. The sampling rate was 45 h⁻¹. Recoveries between 95.9 and 108% were obtained for additions of chloride (2.00 to 8.00 mg L⁻¹) in the samples.

Keywords: *flow injection spectrophotometry, lead-acid batteries, chloride, refractive index effect*

Introduction

Flow injection analysis (FIA) is characterized by the formation of concentration gradients, caused by the dispersion of the sample in the carrier stream. When sample matrices contain high concentrations of concomitants, intense refractive index gradients can be established in the sample zone. This is called the Schlieren effect and can affect the measurements of transient signals in flow injection spectrophotometry^{1,2}. The usual way to overcome this

perturbation is to employ a carrier with physical and chemical characteristics as similar as possible to the samples. In some situations this is not a practical alternative and some experimental procedures need to be used to avoid or to correct for the Schlieren effect². The use of flow diagrams with high dispersion is the simplest alternative to avoid refractive index gradients, since in these systems the mixture between sample zone and carrier is improved³. However, sensitivity is negatively affected by the flow

conditions adopted. An instrumental method for Schlieren compensation based on measurements at two wavelengths was proposed by Zagatto *et al.*¹. In this procedure, measurements must be equally affected by the Schlieren effect at both wavelengths and the molecular absorption process must occur only for one of them. More recently, Yamane and Saito⁴ employed a flow diagram with injection of a large sample volume. Thus, the central part of the sample zone does not interact with the carrier and measurements can be made without perturbation. This is an ingenious way to overcome the Schlieren effect when there is no limitation in available sample volume and the sampling frequency is not a critical aspect. The employment of a large sample volume causes an additional advantage by improving sensitivity due to the lower dispersion.

Lead-acid batteries are inexpensive devices used to produce electrical energy from chemicals and are frequently employed to start engines, in communication devices and emergency power. In the 80's lead-acid batteries represented approximately 60% of the sales of all batteries in the world⁵. The analysis of the sulfuric acid electrolyte in this device is relevant because some constituents affect severely performance and lifetime. In this sense, chloride determination is important since this anion increases the sulfation rate and consequently reduces the lifetime. In addition, hydrochloric acid attacks both the sponge lead of the negative plate and the lead dioxide of the positive plate⁶. Chloride concentrations in of lead-acid battery electrolyte should be lower than 4 mg L⁻¹ to avoid these troubles⁷.

From an analytical point of view, this determination is not an easy task due to the high acidity of the medium that varies from 1.3 to 5.8 mol L⁻¹ of sulfuric acid depending on the application and charge state of the device⁵. Procedures proposed to determine chloride in these samples are not satisfactory due to the lack of precision and accuracy. Frequently, they are only used for semi-quantitative estimation⁸. In flow injection spectrophotometric systems the problem is further complicated due to the intense refractive index gradient that can be generated when this sample is injected in the carrier.

The majority of the flow injection procedures that have been proposed in the literature are related to the determination of chloride in waters, involving displacement spectrophotometric procedures⁹ and these cannot be easily adapted for high acidity samples. Lundell¹⁰ has previously mentioned, earlier in this century, that "there is no dearth of methods that are entirely satisfactory for the determination of elements when they occur alone", and it could be said that in the nineties there is no lack of methods for determining elements in water, but things change completely with respect to complex matrixes. Of course, procedures that have been developed for water analysis are useful. However, as efficient strategies for solution management, such as flow injection, are well established for less complex

samples it is required that they also be applied to analytes in more aggressive medium.

For determining chloride, a flow injection procedure based on a displacement reaction with mercury(II) thiocyanate in a medium containing iron(III) was used. This reaction was previously adapted for flow injection spectrophotometric determination of chloride in waters¹¹⁻¹³, blood serum¹⁴, ethanol¹⁵, plating baths¹⁶ and milk¹⁷. However, these procedures cannot be directly applied for chloride determination in lead-acid battery electrolyte due to the occurrence of the Schlieren effect, which depends on the flow diagram used, and the influence of sulfate on complex formation equilibria. To solve the former problem, a system with a large sample injection volume was investigated. The latter effect was not carefully evaluated in previous studies and it was focused by taking into account sulfate influence on complex formation equilibria.

Experimental

Apparatus

A peristaltic pump (Ismatec IPC-8) and Tygon tubes (Technicon) were used for fluid propulsion. Polyethylene tubing (0.8 mm i.d.) was used to set up the flow diagram. The absorbance was measured with a 432 Femto (São Paulo, Brazil) spectrophotometer equipped with a flow cell with 8.6 mm optical path (200 µL). A potentiometer recorder (Cole-Parmer) was used to register the transient signals. For injecting samples, a sliding bar commutator was used¹⁸.

Reagents and solutions

All solutions were prepared with distilled and deionized water, using analytical grade reagents. Sodium chloride was dried at 110 °C for 2 h and used to prepare a stock chloride solution, 1000 mg L⁻¹. Working standard solutions containing 0, 2.0, 4.0, 6.0, 8.0 and 10.0 mg Cl⁻ L⁻¹ were prepared in a medium containing 2.2 or 3.7 mol L⁻¹ H₂SO₄. Sulfuric acid solutions: 1.0, 2.0, 3.0, 4.0, and 4.5 mol L⁻¹ were prepared containing 2.0, 4.0, and 8.0 mg Cl⁻ L⁻¹. Chloride solutions of the same concentrations were also prepared without acid.

Chromogenic reagent was prepared containing 0.135% (m/v) Hg(SCN)₂, 3% (m/v) Fe(NO₃)₃·9H₂O, 0.2 mol L⁻¹ HNO₃, and 15% (v/v) ethanol. Distilled and deionized water was used as carrier in the flow system, except when the sulfuric acid effect on the absorbance signal was investigated. In this case, an acid solution with the same concentration as the reference solution was employed as carrier. Battery electrolyte samples were processed without any additional treatment.

Chloride was spiked in samples of lead-acid battery electrolyte in concentrations between 2.00 and 8.00 mg L⁻¹.

Flow diagram and procedure

The schematic flow diagram used to investigate sulfuric acid influence on complex formation equilibria and to determine chloride in batterie electrolytes is shown in Fig. 1. The sample volumes used were 0.5 and 2.0 mL, respectively. In the former case, a sulfuric acid solution of similar concentration was employed as carrier with samples. In the later, water was used as carrier. To investigate the effect of the sample volume on the signal pattern, the flow diagram (Fig. 1) was employed with sample volumes that varied from 0.025 to 3.0 mL.

The sample was injected by sliding the central part of the commutator and the chromogenic reagent was introduced by confluence. Absorbance measurements were made at 480 nm.

Results and Discussion

As mentioned above, the usual way to circumvent the Schlieren effect in flow injection systems is to use samples and carrier with same matrix characteristics. However, if the samples present different media or very aggressive media the matrix matching strategy cannot be easily employed. Both problems are found with battery electrolyte samples, since the concentration varies depending on the application and the charge state of the device⁵.

The use of water as carrier for electrolyte samples causes the Schlieren effect in flow systems with limited or medium dispersion. A practical alternative to solve this problem is the injection of a large sample volume to avoid intense gradients in the center of the sample zone. Thus, measurements of the transient signals could be done in this region without perturbation of measurements due to the Schlieren effect. In this sense, the sample volume was varied to attain a condition in which the Schlieren effect at the front and tail portions of the sample zone do not affect the measurements in the central part of the sample zone. The results obtained are shown in Fig. 2. A minimum sample volume of 1.2 mL is necessary to permit the separation of the portions affected by the Schlieren effect. When

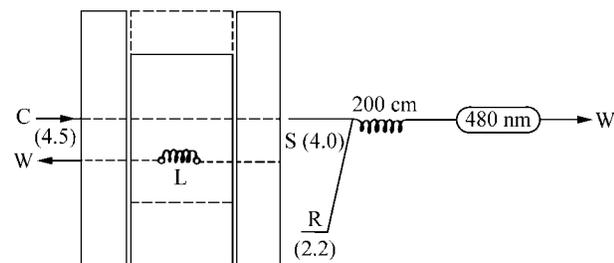


Figure 1. Flow diagram used to determine chloride in batterie electrolyte samples. L = sampling loop; S = sample or reference solution; R = chromogenic reagent; W = waste; C = carrier (sulfuric acid solution or water). Numbers between brackets indicate flow rates in mL min⁻¹. For details see text.

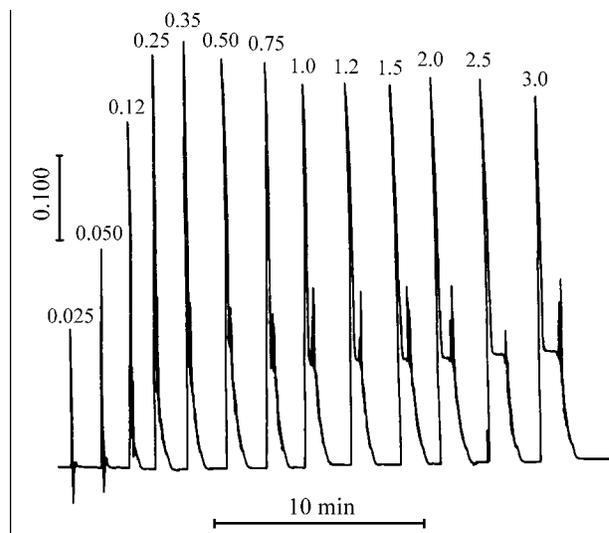


Figure 2. Effect of sample volume on the transient signal shape to a solution containing 8 mg L⁻¹ chloride in 3.7 mol L⁻¹ sulfuric acid. Numbers indicate the sample volume (mL) injected into the carrier.

the sample volume is greater, a plateau can be observed in the central part of the transient signals and this point can be employed for analyte quantification. To assure that measurements would not be affected by refractive index gradients, a 2 mL sample volume was used. Although this volume is greater than that frequently employed in flow systems, this is not a critical aspect due to the availability of the electrolyte samples.

Transient signals of solutions containing different chloride concentrations were obtained by using the flow system shown in Fig. 1 and a sample volume of 2 mL. By observing the results (Fig. 3), it can be seen that negative signals were

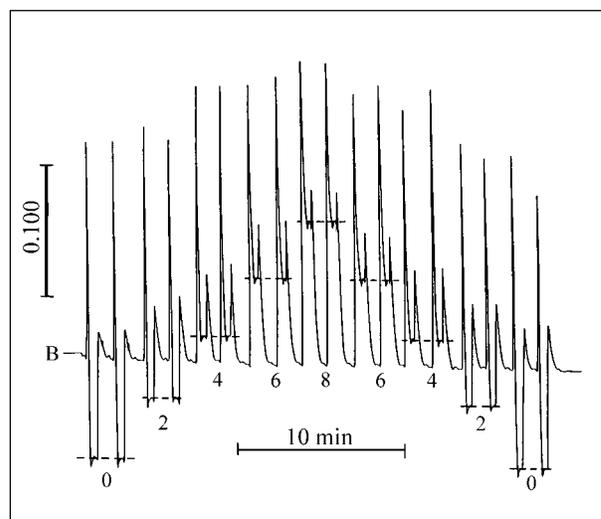
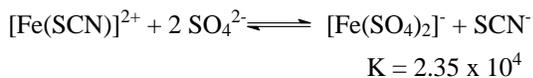


Figure 3. Transient signals obtained for chloride solutions in a sulfuric acid medium (3.7 mol L⁻¹). Analytical signals were measured as the distance between dashed lines in the center of the "brank" signal and dashed lines to the other reference solutions. Numbers indicate chloride concentrations in mg L⁻¹.

obtained for some chloride concentrations. Despite its unusual pattern, the reproducibility was good and the effect of chloride concentration was noted. In order to understand these results, some experiments were made to evaluate the effect of sulfuric acid on absorbance. As previously described, these experiments were conducted by using samples and carrier with same acidity. The results obtained are shown in Fig. 4 (a-c). Comparing signals obtained in water with those obtained in 1.0 mol L⁻¹ H₂SO₄ a strong negative interference can be observed. However, for higher concentrations of sulfuric acid the absorbance is practically constant. At this point, it was not clear if the effect on absorbance was caused by acidity or by sulfate concentration. In a previous work¹⁹, it was observed that nitric and perchloric acids produced a slight effect on the displacement reaction with mercury(II) thiocyanate and formation of iron(III)-thiocyanate complex. However, sulfuric acid caused a pronounced effect. These results can be explained by considering that the sulfate anion was the interfering species. This hypothesis can be confirmed by observing the variation of equilibrium sulfate concentration in sulfuric acid media (Fig. 4d). It can be seen that the variation of absorbance is closely related to the variation of sulfate concentration. While the equilibrium sulfate concentration increases (until about 1.0 mol L⁻¹ sulfuric acid), the absorbance signal decreases. For higher concentrations of sulfuric acid the absorbance change is less because the sulfate equilibrium concentration is constant.

The negative signals observed (Fig. 3) can be explained taking into account the chemical equilibria involved in formation of thiocyanate complexes of iron(III). The indirect spectrophotometric method for chloride determination involves the displacement of thiocyanate from mercury(II) thiocyanate and the complexation of iron(III) by the displaced anion. The chromogenic reagent contains iron(III) and mercury(II) thiocyanate. Thus, the iron(III) thiocyanate complexes are formed due to the equilibria established. In a medium containing high concentrations of sulfate an interference will occur as this anion is a stronger complexant than thiocyanate for iron(III):



The baseline absorbance is determined by the concentration of the iron thiocyanate complex that results when the chromogenic reagent is mixed with the aqueous carrier. The dispersion of the sulfuric acid solution injected into the carrier produces concentration gradients of sulfate in the sample zone. In the absence of chloride the baseline absorbance is decreased because the sulfate present in the sample zone reduces the concentration of the iron thiocyanate complex. In the presence of chloride, the previous process occurs simultaneously to the displacement of thiocyanate

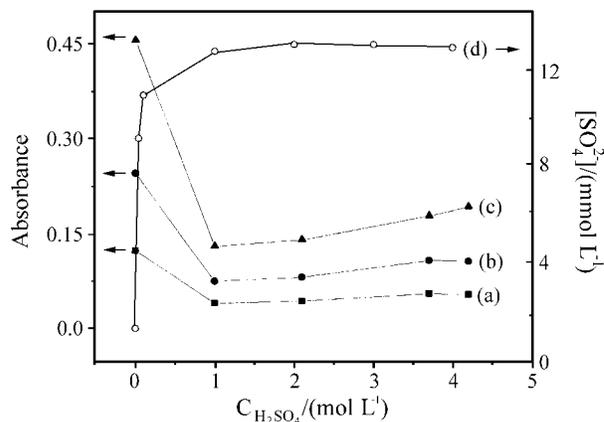


Figure 4. Sulfuric acid effect on the absorbance signal to: (a) 2.0, (b) 4.0 and (c) 8.0 mg Cl⁻ L⁻¹ and (d) equilibrium sulfate analytical concentration in sulfuric acid solutions. Arrows indicate the axis for the curves.

from mercury(II) thiocyanate by chloride and causes an increase in the blank absorbance, *i.e.* the absorbance signal obtained in absence of analyte. Depending on the chloride and sulfate concentrations, a negative or a positive signal will be observed and chloride can be quantified by measuring the difference between signal plateaus in the absence and in the presence of chloride. All signal interpretations are based on the formation of the first complex between iron(III) and thiocyanate. Other complexes were not considered because under the experimental conditions adopted iron(III) was present in large excess in comparison with the complexing anion.

Adopting this strategy for signal treatment, analytical curves obtained for samples containing 2.2 or 3.7 mol L⁻¹ H₂SO₄ presented slopes of 0.0233 and 0.0238 and correlation coefficients of 0.9998 and 0.9996, respectively. The slope ratio, practically equal to unity, is an indication that chloride could be determined in samples with different acidity by using only one analytical curve. A unity slope ratio was also obtained with curves generated from spiked samples or from standard solutions prepared in sulfuric acid by dilution of an analytical grade reagent. Data obtained from addition-recovery experiments are shown in Table 1. Recoveries varied from 95.9 to 108% and this indicates that matrix effects are not significant on the determination of chloride in battery electrolyte. A better evaluation of accuracy was not possible because standard reference materials or standard reference methods were not available. The relative standard deviation was 1.6% (n = 10) for a 3.7 mol L⁻¹ H₂SO₄ solution containing 8 mg Cl⁻ L⁻¹. The detection limit was estimated as 0.37 mg L⁻¹ and the sensitivity is adequate for the determination of chloride in lead-acid battery electrolyte, here up to 4 mg L⁻¹ is tolerable⁷. The sampling rate was 45 h⁻¹ and 2 mL of sample was consumed in each determination.

Table 1. Addition-recovery of chloride in lead-acid battery electrolyte.

Sample	Chloride / (mg L ⁻¹)		Recovery (%)
	Added	Found	
1	2.00	2.02	101
2	4.00	3.84	95.9
3	5.00	5.35	107
4	6.00	6.12	102
5	2.00	1.98	99.1
	4.00	3.92	98.1
	6.00	6.00	100
6	2.00	2.00	100
	4.00	4.04	101
	6.00	6.29	105
7	2.00	2.10	105
	6.00	6.47	108

The main feature of the proposed procedure is the flow injection chloride determination in relatively concentrated sulfuric acid without any preliminary sample preparation and without perturbations from the Schlieren effect on signal measurements.

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