

Flow Injection Amperometric Determination of Acid-Available Cyanide: A Study of Sulfide and Thiocyanate Interferences

Joaquim A. Nóbrega* and Milton D. Capelato

Departamento de Química, Universidade Federal de São Carlos, Caixa Postal 676,
13560-970 São Carlos - SP, Brazil

Romualdo Gama

Instituto de Química de São Carlos, Universidade de São Paulo, Caixa Postal 369,
13560-970 São Carlos - SP, Brazil

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Desenvolveu-se um procedimento empregando sistema de injeção em fluxo para separação e pré-concentração de cianeto e posterior detecção amperométrica. Utilizou-se como eletrodo de trabalho um fio de prata polarizado em $-0,10$ V vs. Ag/AgCl, NaCl (0,1 M). O cianeto de hidrogênio foi coletado no canal receptor da câmara de difusão gasosa que atuou como uma alça de amostragem. Durante a etapa de separação e pré-concentração, a solução acidificada da amostra fluía continuamente através do canal doador e a solução alcalina permaneceu parada no canal receptor. Interferências causadas por sulfeto e tiocianato foram eliminadas empregando-se no canal doador uma solução de dicromato preparada em tampão acetato (pH 4,7). O desvio padrão relativo foi estimado como 1,33% ($n = 10$) para uma solução contendo $60 \mu\text{g CN}^- \text{L}^{-1}$. O limite de detecção foi de $1,2 \mu\text{g CN}^- \text{L}^{-1}$ ($3 s_{\text{branco}}$) quando a etapa de pré-concentração foi realizada em 60 s. Empregando-se esse tempo de pré-concentração, a velocidade analítica foi de 30 amostras h^{-1} .

A procedure for the separation and preconcentration of cyanide employing a flow injection system with amperometric detection was developed. A silver wire polarized at -0.10 V vs. Ag/AgCl, NaCl (0.1 M) was used as a working electrode. The acceptor stream of the gas diffusion chamber acted as a sample loop where the diffused hydrogen cyanide was collected. During the separation-preconcentration step, the acidified sample flowed continuously through the donor channel and the alkaline acceptor solution was stopped in the acceptor channel. Sulfide and thiocyanate interferences were eliminated by employing a dichromate-acetate oxidizing solution (pH 4.7) in the donor channel. For $60 \mu\text{g CN}^- \text{L}^{-1}$, the estimate of the relative standard deviation was 1.33% ($n = 10$). The detection limit was $1.2 \mu\text{g CN}^- \text{L}^{-1}$ ($3 s_{\text{blank}}$) when 60 s was employed in the preconcentration step. The throughput is 30 samples h^{-1} for a preconcentration time of 60 s.

Keywords: cyanide, flow injection amperometry, gas diffusion

Introduction

Flow injection is a useful tool for solution management and can also be used for the automation of separation procedures¹. Gas diffusion as a separation step in a flow injection system is suitable for the minimization of matrix interferences, primarily for less selective sensors. Frenzel² discussed about analytical characteristics of procedures involving gas diffusion, separation, and flow injection po-

tentiometry. It was clearly demonstrated that selectivity was significantly improved because the volatile analyte was removed from the sample matrix. However, procedures involving gas diffusion presented at least two disadvantages. First, the transfer efficiency seldom exceeds 50% and generally is less than 10%. In addition, interferences can also generate gaseous species which pass through the membrane and affect the analytical signal. The transfer efficiency could be improved by changing the relative flow

rates of the donor and acceptor streams. When the flow rate of the donor stream is maintained, the lower the flow rate of the acceptor stream the higher is the accumulation of the analyte³.

A flow injection manifold can be designed by making the gas diffusion unit an integrated part of the injection valve, with the acceptor channel being used as the injection loop. To the best of our knowledge, Meyerhoff & Martin⁴ and Meyerhoff & Chang⁵ were pioneers in the use of this design. Thus, after separation and preconcentration, these authors determined nitrogen oxides and salicylate using liquid-membrane electrodes.

Subsequently, Frenzel *et al.*⁶ also evaluated in-valve diffusive preconcentration of ammonia in flow injection systems. A preconcentration factor of 10, in comparison with a 30 μL sample injection, was achieved with a 10 min sampling time.

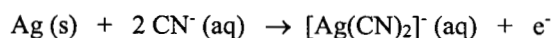
In the same year, Milosavljevic *et al.*⁷ developed a flow injection gas diffusion method for preconcentration and determination of sulfide. The analyte was accumulated through diffusion in a closed-loop of the acceptor stream. Thus, the flow diagram proposed contained a sample loop and an accumulation loop. This represents a slightly different strategy, but elevated sulfide preconcentration was attained. A flow-through amperometric cell was used for sulfide measurement.

More recently, Dasgupta *et al.*⁸, Gonzalo *et al.*⁹ and Kuban¹⁰ determined sulfide, phenols, and acid-available cyanide, respectively, using optical detection of these species after preconcentration in a membrane containing cell. All these authors employed the upper channel of the gas unit as an injection loop in an FI mode.

In the present paper, interferences caused by sulfide and thiocyanate were evaluated when acid-available cyanide was amperometrically measured after preconcentration in a gas separation unit. The flow diagram was designed with a time-controlled commutator device¹¹. The sample was time-base injected and the acceptor stream was stopped during the preconcentration step. Emphasis of the investigation was given to the elimination of positive interferences caused by sulfide and thiocyanate. Depending on the solution used for sample acidification, these anions can also generate gaseous species. It should be emphasized that wastewaters of petroleum refineries frequently contain a high concentration of sulfide. Carvalho *et al.*¹² investigated sulfide interferences in cyanide determination by anodic voltammetry and ion chromatography. Both techniques suffer deleterious effects caused by sulfide, and for the latter $\text{S}^{2-}/\text{CN}^-$ ratios higher than 300 are not tolerated. Worse effects were found using anodic voltammetry where 2 μg of CN^- can be accurately determined only if the sulfide concentration is less than 30 μg .

In the amperometric procedure proposed here, the anodic current related to cyanide concentration was obtained

by polarization of the silver wire working electrode and the transient current pulses were due to the main electrodic reaction:



Amperometric measurements are characterized by suitable sensitivity, but selectivity is poor and dependent on the applied potential. Use of a gas diffusion chamber will improve selectivity and with the flow diagram designed the analyte will also be preconcentrated.

Experimental Details

Materials

Propulsion of fluids was accomplished by a 12-channel peristaltic pump (MS Tecnologias - Brazil). The homemade flow-through amperometric cell is depicted in Fig. 1. During measurements, the polarization of the silver wire electrode was maintained at - 0.10 V vs. Ag/AgCl, NaCl (0.1 M). The potential was applied by an EG&G PAR model 173 potentiostat/galvanostat and current transients were measured through the same electrochemical equipment connected to a X-Y recorder (Houston - Omnigraphic 100). A stainless steel tube (i.d. 3 mm) was used as an auxiliary electrode.

The management of solutions was controlled by an electronically-temporized injector commutator (Micronal - model B352). The flow diagram was mounted by using 0.8 mm i.d. PTFE tubing; the pumping tubes were Tygon (Technicon). The gas separation unit was similar to those generally used in flow injection manifolds³, and a PTFE strip membrane was inserted between the donor and acceptor channels (length: 10 cm and thickness: 0.1 mm).

Reagents and solutions

All chemicals were of reagent grade, and distilled-deionized water was used throughout. All solutions containing sulfide were prepared with recently degassed water. Cyanide, sulfide and thiocyanate solutions were prepared with KCN, KSCN and $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$. Analytical solutions containing only cyanide, cyanide plus sulfide or thiocyanate or both, were prepared by appropriate dilutions of the

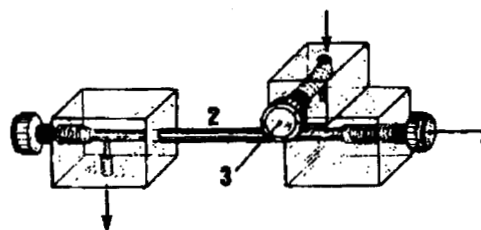


Figure 1. Flow-through amperometric cell. 1 - silver wire working electrode (length: 5 cm and diameter: 1.0 mm); 2 - stainless steel auxiliary electrode; 3 - reference electrode. Arrows indicate flow direction.

stock solutions containing 1000 mg L^{-1} of the corresponding anion. On-line acidification of the cyanide containing solution was made by addition of a confluent solution containing: (I) 1.0 M sulfuric acid; (II) 0.12 M potassium dichromate in 1.0 M sulfuric acid; or (III) 0.25 M potassium dichromate in 1.0 M acetate buffer (pH 4.7). A 0.1 M sodium hydroxide solution was used to collect the diffused hydrogen cyanide.

Interference effects caused by sulfide and thiocyanate were evaluated by using the following solutions: (1) 0.050 mg CN^{-1} (solution 1); (2) 0.050 mg CN^{-1} plus 0.050 ; 0.50 ; 5.0 ; 10.0 or $50.0 \text{ mg S}^{2-}\text{L}^{-1}$ (solutions 2 to 6); (3) 0.050 mg CN^{-1} plus 0.050 ; 0.50 ; 5.0 ; 10.0 or 50.0 mg SCN^{-1} (solutions 7 to 11); and finally (4) 0.050 mg CN^{-1} plus $10.0 \text{ mg S}^{2-}\text{L}^{-1}$ plus 10.0 mg SCN^{-1} (solution 12).

Procedure

The flow diagram is depicted in Fig. 2. The flow rate of the cyanide containing solution and of the acid confluent stream were fixed at 1.2 and 0.4 mL min^{-1} , respectively. The sodium hydroxide solution flowed at 1.0 mL min^{-1} following the preconcentration step. In the commutator position shown in Fig. 2, the sample was time-base injected and the acceptor stream remained stopped during the separation and preconcentration steps. The preconcentration time was adjusted in accordance with the desired concentration factor. After commutation, the acceptor stream containing the accumulated cyanide was carried to the flow-through amperometric cell and the sample was changed or re-circulated. The commutation resting time in this position was adjusted to permit suitable signal measurement and to avoid carry over.

Results and Discussion

The effect of preconcentration time was investigated by the introduction of a $100 \mu\text{g CN}^{-1}$ solution. As expected, the peak current intensity increased when higher precon-

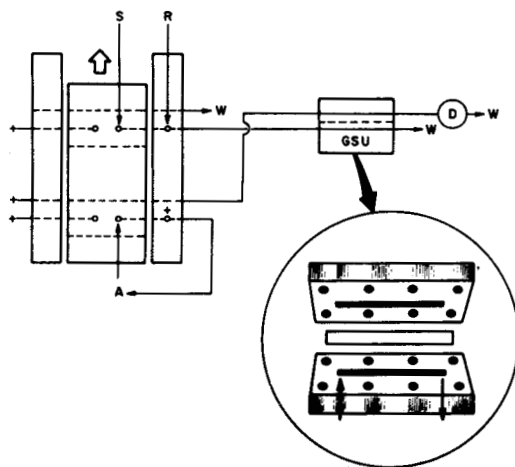


Figure 2. Flow diagram. A - acceptor solution; S - sample; R - acid solution; GSU - gas separation unit; D - amperometric cell; W - waste.

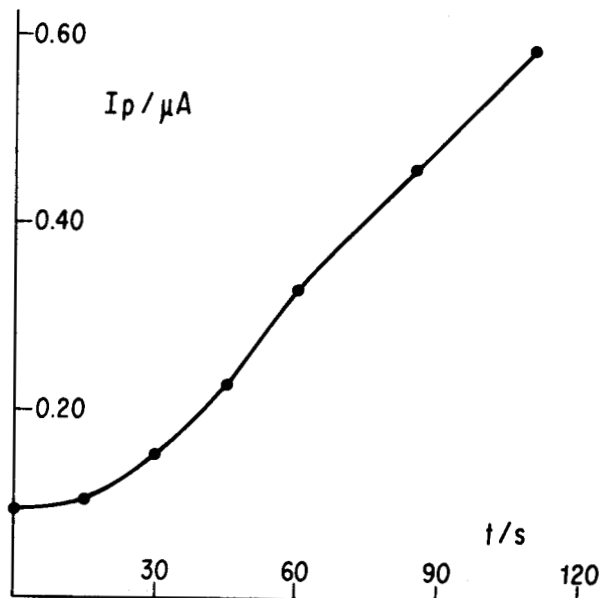


Figure 3. Effect of preconcentration time. Signal for $t=0 \text{ s}$ obtained by using a flow diagram without preconcentration.

centration times were used (Fig. 3). All signals were higher than those obtained with a system without the preconcentration step. Thus, the analyst should pre-set the preconcentration time considering the expected cyanide concentration in the sample. After commutation, the time was fixed at 60 s to promote cyanide transportation and signal measurement, and to avoid carry over effects.

Adopting 60 s for the preconcentration and residence cycles, ten consecutive signals were measured for a $60 \mu\text{g CN}^{-1}$ solution. The estimate of the relative standard deviation was 1.33% (Fig. 4). The baseline stability was observed and 36 signals were obtained per hour. All these results were obtained by using a 1.0 M sulfuric acid solution for acidification of the cyanide solution, and a 0.1 M sodium hydroxide solution for collecting the diffused hydrogen cyanide.

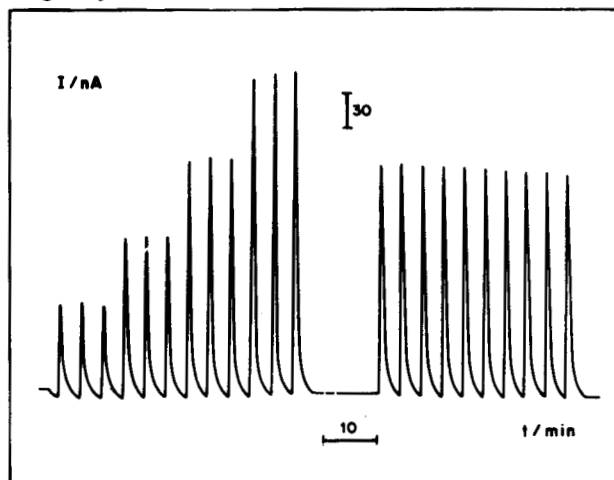


Figure 4. Triplicate signals for analytical solutions containing 20 , 40 , 60 , and $80 \mu\text{g CN}^{-1}$, and ten signals for a $60 \mu\text{g CN}^{-1}$ solution.

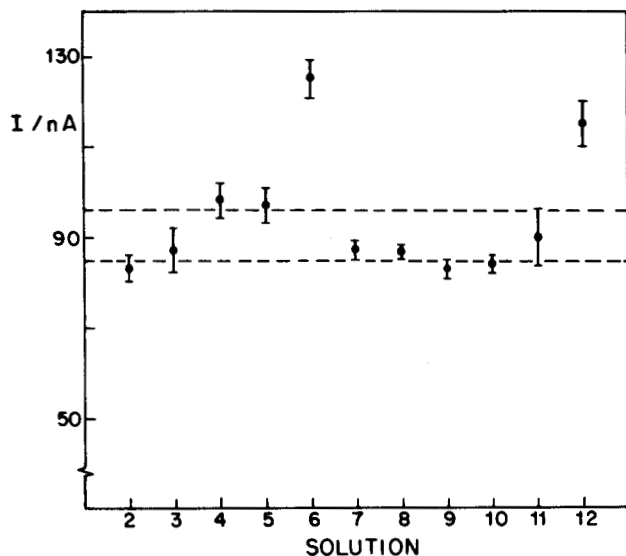


Figure 5. Interferences caused by sulfide and thiocyanate. Donor stream: dichromate in acetate buffer. Acceptable results are inside the traced lines. Numbers correspond to the solutions containing increasing sulfide or thiocyanate concentrations (see *Reagents and solutions* section).

When sulfuric acid was used for acidification, severe interferences were caused by sulfide and thiocyanate. The worst effects were due to sulfide because this anion formed an insoluble silver sulfide film on the electrode surface, causing a continuous elevation of the baseline. Positive errors on cyanide determination were also observed in the presence of sulfide. The interference caused by thiocyanate was less severe. To avoid these effects the solution employed in the donor channel was changed.

Sulfide positive interferences were partially eliminated by employing an oxidative acid solution ($K_2Cr_2O_7$ plus H_2SO_4). In this medium, sulfide was oxidized to sulfur and the hydrogen sulfide formation was decreased. A 100-cm tubular reactor was introduced prior to the donor channel of the gas separation unit to increase the time for sulfide oxidation. Severe positive interference (+40%) was still observed when the sulfide concentration was 1000-fold higher than the cyanide concentration. However, the worst effect caused by the dichromate-sulfuric acid solution was the oxidation of thiocyanate to cyanide. Thus, this solution was unsuitable in the presence of matrices containing thiocyanate.

Subsequently, the use of a dichromate solution prepared in acetate buffer was also evaluated. This less oxidative solution was efficient for promoting sulfide oxidation and

non-measurable oxidation of thiocyanate. Then, sulfide and thiocyanate interferences were practically eliminated by using a 0.25 M potassium dichromate solution prepared in 1.0 M acetate buffer. Figure 5 shows that positive interferences occurred when the sulfide or sulfide plus thiocyanate concentrations were higher than 50 or 20 $mg L^{-1}$. The region inside the traced lines was established by considering the mean current signal and the estimate of the standard deviation ($n = 5$) for a solution containing only cyanide.

A recovery test was performed by using dichromate-acetate solution. With a solution containing 15.0 $\mu g CN L^{-1}$ and 3.0 $mg S^{2-} L^{-1}$, a series of solutions was prepared by continuously increasing the cyanide concentration. The data in Table 1 were calculated by using an analytical curve obtained for reference solutions containing 10 to 50 $\mu g CN L^{-1}$ and 3.0 $mg S^{2-} L^{-1}$. The equation obtained for peak current intensity ($I_p; \mu A$) vs. cyanide concentration ($C; \mu g / L$) was:

$$I_p = 0.0019 C + 0.0026 \quad (r = 0.9986)$$

As can be seen, the added analyte was quantitatively recovered. During three months of measurements, mainly with pure cyanide solutions, no performance degradation was observed for the PTFE membrane.

Considering that sulfide and thiocyanate interferences were practically eliminated using a dichromate-acetate donor stream, and that the sensitivity attained by employing the flow diagram with a preconcentration step was good, the proposed procedure could be applied to the determination of acid-available cyanide in the wastewaters of petroleum refineries, as previously mentioned. This procedure could also be employed to determine the concentration of acid-available cyanide in electrodeposition baths. The bath composition can be adjusted in real time, so that better performance can be obtained. Also, the acid-available cyanide concentration can be determined in residual electrolytes before their discard.

Conclusions

The feasibility of the application of a non-selective amperometric detector to acid-available cyanide determination was demonstrated. The designed diagram made possible the simultaneous separation and preconcentration of cyanide. The sulfide interference was eliminated by oxidation to sulfur with a dichromate-acetate solution. It

Table 1. Addition and recovery of cyanide in solutions prepared in sulfide medium (3.0 $mg L^{-1}$)

$C(\mu g CN L^{-1})$	$C_{added}(\mu g L^{-1})$	$C_{found}(\mu g L^{-1})$	% recovery
15	0	14.9	99.7
15	5.0	20.2	101.1
15	10.0	24.2	97.7
15	15.0	28.6	95.4

was demonstrated that the peak current intensity was proportional to the preconcentration time. The sensitivity can be adjusted by considering the expected cyanide concentration in the sample. It should also be mentioned that the sample throughput is decreased when the preconcentration time is increased. Of course, the analytical conditions should be established considering sample characteristics.

Acknowledgments

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