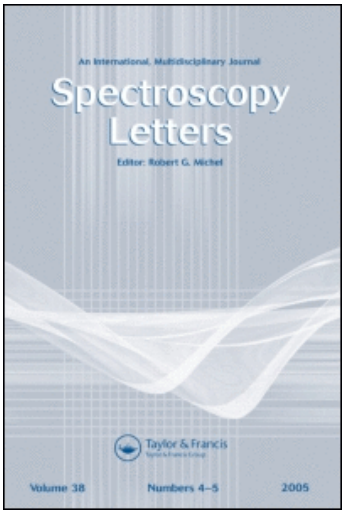

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Automated Flow Injection Method for Monitoring Total Cyanide Concentration in Petroleum Refinery Effluents Using Ninhydrin as Color Reagent

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To cite this Article Santelli, Ricardo Erthal , Micelli, Alexandre Santos and de Carvalho, Maria de Fátima Batista(2006) 'Automated Flow Injection Method for Monitoring Total Cyanide Concentration in Petroleum Refinery Effluents Using Ninhydrin as Color Reagent', Spectroscopy Letters, 39: 6, 605 — 618
To link to this Article: DOI: 10.1080/00387010600854238
URL: http://dx.doi.org/10.1080/00387010600854238

Spectroscopy Letters, 39: 605–618, 2006

ISSN 0038-7010 print/1532-2289 online
DOI: 10.1080/00387010600854238

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Abstract: An automated flow injection system was developed for monitoring cyanide concentration in effluents from petroleum refineries. The method takes advantage of the reaction of cyanide ions with ninhydrin in basic medium in a flow injection system. A linear range of 0.01 to 0.04 $\mu g\ mL^{-1}$ was obtained with a detection limit of 1.5 $ng\ mL^{-1}$ by using 500 μL sample injection, with an analytical throughput of 30 samples hr^{-1}, excluding sample pretreatment by distillation if required. Regarding interferences, cyanide can be determined in the presence of 100 $mg\ L^{-1}$ of thyocianate and sulfide, both species normally found in industrial effluents. For total cyanide determination, strong acid distillation is recommended due to the presence of cyano-metallic complexes in the refinery effluents. The method was validated by analyte addition and results compared with the standard methodology proposed by the American Public Health Association (APHA). The more significant advantage of the proposed method is the lack of use of carcinogenic

Received 25 March 2006, Accepted 12 June 2006

The authors were invited to contribute this paper to a special issue of the journal entitled "Spectroscopy and Automation". This special issue was organized by Miguel de la Guardia, Professor of Analytical Chemistry at Valencia University, Spain.

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reagent such as pyridine and psychotropic compound such as barbituric acid, both used in the recommended method by APHA. Thus, the proposed method is really a friendly analytical procedure.

Keywords: Cyanide determination, FIA, industrial effluents, ninhydrin, spectrophotometry

INTRODUCTION

Many industrial activities such as electroplating and metal and petroleum refining are responsible for the introduction of cyanide compounds in the environment through effluent disposal. This way, cyanide species can be delivered to water bodies (rivers, estuaries, lagoons, and bays) as inorganic or organic species. From the point of view of the petroleum industry, cyanide compounds are by-products of reactions that occur in the fluid catalytic cracking process (FCC) to produce petroleum derivatives, this is due to the presence of nitrogen in the original organic matter. Hydrogen cyanide formed inside the cracking reactor causes its corrosion, and metallo-cyanide complexes (mainly from Fe^{2+}) are produced. Due to the toxicity of cyanide species to biota, the aqueous refining effluents are subjected to both chemical and biological treatments to reduce cyanide concentrations (and other pollutants) below the maximum level allowed for disposal in water bodies. In this way, both free cyanides (HCN and CN^-) and cyano-metallic complexes [$Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, $Ni(CN)_4^{2-}$ and $Co(CN)_6^{3-}$] can be found in very low concentrations in these effluents. Cyano-metallic complexes are less toxic than free cyanides but they can be decomposed by UV light (sunlight) to generate free cyanides in the environment. Thus, federal regulations regarding maximum allowed concentration of cyanides in effluents refer to total cyanide concentration (free plus complexes). The Brazilian law (CONAMA Resolution 357/2005) states that the maximum permissible total concentration of cyanides in the effluents to be discharged is 0.2 mg L^{-1}.[1] This concentration level is considered by the U.S. EPA to be fatal to many fish species.[2] On the other hand, the EPA water quality criterion of total cyanides in water is 5 μg L^{-1}.[3]

Therefore, the determination of cyanide species (free and total) in industrial waste effluents is a very important aspect in monitoring water pollution. Several methods for cyanide quantification in industrial effluents can be found in the literature employing analytical techniques such as atomic absorption spectrometry,[3,4] voltammetry,[5] capillary electrophoresis,[6] and spectrophotometry.[7–9] Barnes et al. reviewed the techniques that were most employed for the determination of cyanide compounds in gold extraction by cyanidation, which effluents contain metal cyanides as high as 100 mg L^{-1}.[10]

The usual spectrophotometric reaction for cyanide determination has advantages compared with the method proposed by Asmus and Garschagen[11]

that employed pyridine and barbituric acid as reagents. A well-established procedure for this task is recommended by APHA.[12] However, this method suffers from several interferences mainly due to the presence of sulfide and thiocyanate. To overcome this drawback and to ensure accurate cyanide determination in industrial effluents, a sample pretreatment involving distillation,[13] membrane diffusion,[14] and ion-exchange,[15] must be implemented.

Flow injection analysis (FIA) is today a well-known technique that can be used to analyze varieties of sample matrix using different analytical detectors. Because of its characteristics such as rapid response, good precision, high sample throughput, and feasibility to couple with separation techniques, FIA procedures have become widespread in chemical laboratories. Regarding cyanide determinations coupled to FIA procedures, Rios et al.[16] automatized spectrophotometric unsegmented flow methods using the reaction in which a dye is formed by using chloramine T, pyridine, and barbituric acid (recommended reaction by APHA). The authors showed three manifolds based on normal, reversed, and completely continuous FIA modes. Better sensitivity and lowest detection limit was attained by using normal FIA configuration useful in the range of 0.1 to 1.0 $\mu g\ mL^{-1}$. With these three manifolds, the interferences were severe [tolerance ratio interferent/analyte: $S^{2-} = 10$; $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, SCN^-, and $Fe^{3+} < 1$]. Although with these configurations it was possible to analyze 20 samples hr^{-1}, the authors only applied the method to simulate cyanide control in industrial waste. Ma and Liu[17] observed an unstable intermediate product in the reaction with pyridine–barbituric acid and they used its absorbance at 494 nm as a base to a fast FIA cyanide quantification in the range between 0.5 and 4 $\mu g\ mL^{-1}$ with a detection limit of 20 ng mL^{-1}. However, thiocyanate appears as a concern interferent (tolerance ratio: 1) and sulfide can be tolerated until 10 times cyanide concentration. The authors applied their work in wastewater (not specified) without sample pretreatment.

As a way to overcome interferences in the cyanide determination, Hangos-Mahr et al.[18] proposed an air segmented automatic system using membrane diffusion and isothermal distillation. The main interferences were overpassed but, unfortunately, volatile species such as sulfide and sulfite interfere in amounts of 5 and 10 times more than cyanide, respectively. In the isothermal distillation process, they could be tolerated after sample pretreatment by addition of Pb^{2+} (forming PbS) and $K_2Cr_2O_7$ (oxidizing sulfide and sulfite to sulfate). In these conditions, sulfide and sulfite can be tolerated until 1000 times more than cyanide, based on 0.05 mg CN L^{-1}. The analysis time can be very high such as 60 min. The authors did not show results using real samples. Gas diffusion was applied by several authors, both for cyanide preconcentration and interference removal in flowing systems.[19–21] Cyanide and thiocyanate can sequentially be determined using isonicotinate-barbiturate reagent according to the FIA method developed by Sweileh.[22] Following his procedure, both species were quantified together, and after that, cyanide complexation with nickel (II) thiocyanate was analyzed

separately. Sulfide was responsible for severe interference in both cyanide and thiocyanate determination (5 $\mu g\ mL^{-1}$ compared with 0.5 and 3 $\mu g\ mL^{-1}$, respectively). This way, sulfide must be removed before sample analysis. Unfortunately, the proposed method was not applied to real sample analysis. This same reaction was exploited by Sun and Noller[23] using a stopped-flow system where cyanide ions were masked with formaldehyde. The samples must be in contact with the masking agent by overnight or heating it for 15 min at 60°C, which is not suitable for continuous detection. However, the method was not affected by sulfide concentrations until 50 $mg\ L^{-1}$. Samples from gold mining activities were analyzed by this procedure. Atomic absorption spectrometry was employed for industrial electroplating wastewater analysis using cadmium carbonate as a new solid-phase reactor. Linear range up to 15 $mg\ L^{-1}$ with detection limit of 0.2 $mg\ L^{-1}$ was obtained.[4]

Recently, Nagaraja et al.[9] and Drochioiu[24,25] proposed simultaneously a highly selective and sensitive method for cyanide determination. These authors have made efforts to elucidate the reaction mechanism between cyanide ions and ninhydrin. Nagaraja and co-workers[9] proposed that cyanide ions act as a specific base catalyst. On the other hand, Drochioiu[24] showed that a novel reaction might occur, not a catalytic one. Recently, Drochioiu et al.[26] demonstrate the mechanism of this reaction supported by isolation of the reaction products as well as spectroscopic data analyses (MS, IR, UV-Vis, and ^1H NMR). These authors showed that cyanide ions attack nucleophilically one of the C—O group of ninhydrin forming an intermediary compound that releases cyanate ion (CNO^-) generating a hydrindantin isomer (1,2-dihydroxy-3-keto 3H indene). This isomer turns into the 2H indene isomer, which is more stable. Then, cyanide ions react with hydrindantin to form 2-cyano-1,2,3-trihydroxy 2H indene, which at pH higher than 12 is present as a divalent ion (blue color). The complete schemes that contain all involved reactions were show by these authors.[26]

The aim of this work was to automate by a FIA procedure the reaction proposed by Nagaraja et al.[9] and Drochioiu[24,25] for cyanide determination using ninhydrin applied to effluents generated by the petroleum refining industry. This proposed method contributes to green analytical chemistry due to the use of less toxic reagent (ninhydrin) instead of carginogenic reagent (pyridine) and psychotropic reagent (barbituric acid), both frequently used when applying the APHA recommended method for cyanide determination.

MATERIALS AND METHODS

Apparatus

A flow injection system was built up using a peristaltic pump (Ismatec IPN 12; Ismatec, Glattbrugg, Switzerland) furnished with Tygon tubes; two Rheodyne

4051 four-way valves (Rheodyne, Cottati, CA, USA); PTFE tubing of 0.5 mm i.d.; thermostatic water bath (Quimis, São Paulo, Brazil); FEMTO 700 plus UV-Vis spectrophotometer (FEMTO, São Paulo, Brazil), and a Hellma 178-OS flow cell 80-μL inner volume (Hellma, Jamaica, NY, USA).

A glass sample pretreatment apparatus according to APHA was also used for sample strong acid distillation before cyanide determination by flow injection analysis.[12]

Reagents and Samples

All reagents were prepared using ultrapure water (Elix 5 and Symplicity; Millipore, Bedford, MA, USA) and analytical quality chemicals.

Safety procedures were carefully followed when manipulating cyanide-containing samples and reagents due to its toxicity. All experimental tests for developing this work were done in a fume hood, and personal protection equipment was always used to avoid skin contact or inhalation.

A 1000 mg L^{-1} cyanide stock solution was prepared by adequate dissolution of KCN (Merck, Rio de Ganeiro, Brazil) in 0.05 mol L^{-1} NaOH (Merck). This solution was standardized by the argentimetric method.

Working cyanide solutions were daily prepared by dilutions from the stock solution. The 2% (m/v) ninhydrin solution was prepared by dissolving 2 g of the reagent (VETEC, Duque de Caxias, Brazil) in water and the volume filled up to 100 mL. This solution was stable at least for 2 weeks.

The 4% (m/v) sodium carbonate (Acros Organics, Morris Plains, NJ, USA) and 1 mol L^{-1} sodium hydroxide (Merck, Rio de Ganeiro, Brazil) were prepared by dissolving these chemicals in water.

The solutions needed for the sample pretreatment by distillation (133 g L^{-1} sulfamic acid; 25% (m/m) hydrochloric acid, and 51% (m/v) magnesium chloride) were prepared according to APHA[12] recommendations.

The solutions of sulfide, thiocyanate, hexacyanoferrate, ferricyanide, and iron (III) were prepared to contain 1000 mg L^{-1} for each concomitant and further diluted to the interference tests.

The effluents samples analyzed by the proposed method were collected in two different effluent tanks from a petroleum refinery in Brazil. At the sampling time, a small portion of zinc acetate was added to immobilize the sulfide as ZnS and the pH increased to 12 by sodium hydroxide addition (to avoid cyanide losses due to thiocyanate formation in presence of sulfide). Preserved samples were conditioned in amber glass flasks and delivered to the laboratory under refrigeration (ice bath). These samples were analyzed immediately as received by the laboratory. These procedures are according to the APHA recommendations for cyanide analysis in liquid effluent samples.[12]

Spectrophotometric Reaction and Flow System Design and Optimization

Before the flow injection system was built up, the reaction between cyanide ions and ninhydrin in alkaline medium was studied in a batch mode, according to Nagaraja.[9] In our laboratory tests, we verified a lack of sensitivity (and linearity) when using cyanide solutions from concentrations below 0.4 $\mu g\ mL^{-1}$. This drawback only was overcome with the addition of an extra (initial) well-known amount of cyanide ions to the calibration solutions. The linearity was obtained when the calibration solutions (and also the blank and samples) were previously prepared by addition of 0.04 $\mu g\ CN^{-}\ mL^{-1}$ in all solutions. This way, the linear calibration graphs were obtained in the range of 0.01 to 0.04 $\mu g\ mL^{-1}$; but the RSDs of the measurements were higher than 20%.

According to these preliminary tests, we decided to build up a flow injection system provided with two injection valves, one of them for injecting a cyanide solution of well-known constant concentration. This way, it was possible to maintain enough cyanide concentration inside the flow system to guarantee method linearity and sensitivity to measure low concentration of cyanide in effluent samples.

The flow injection system, in the sampling position, is depicted in Fig. 1. The flow system operates as follows. When the injection valves rest in the sampling positions, same volume of calibration solutions (or samples) and the cyanide solution of constant concentration were filled in the sample loops (500 μL), and the excess was adequately discharged (inside a flask containing sodium hydroxide solution from pH higher than 12). By switching simultaneously the valves, calibration solutions or samples (500 μL) and cyanide solution of constant concentration (500 μL of 0.5 $\mu g\ CN^{-}\ mL^{-1}$) were inserted each one into its carrier solution (4% m/v sodium carbonate; 1.26 $mL\ min^{-1}$) and merged forming a sample zone at the confluence point. Then, the ninhydrin solution (2% m/v; 0.66 $mL\ min^{-1}$) was added, and the intermediate compound formed inside the first reaction coil (RC 1; 300 cm). After that, the sodium hydroxide solution (1 $mol\ L^{-1}$; 0.30 $mL\ min^{-1}$) was added by the confluence point, and the chemical reaction to form the blue dye took place inside the following reaction coil (RC 2; 300 cm) and the absorbance was monitored at 590 nm as a transient signal. Peak height was proportional to the cyanide concentration in the sample.

The flow injection system for cyanide determination shown in Fig. 1 was optimized by the univariate procedure.

Effluent Sample Pretreatment

Due to the inherent complex chemical composition of effluents from petroleum refinery plants, a sample pretreatment by strong acid distillation

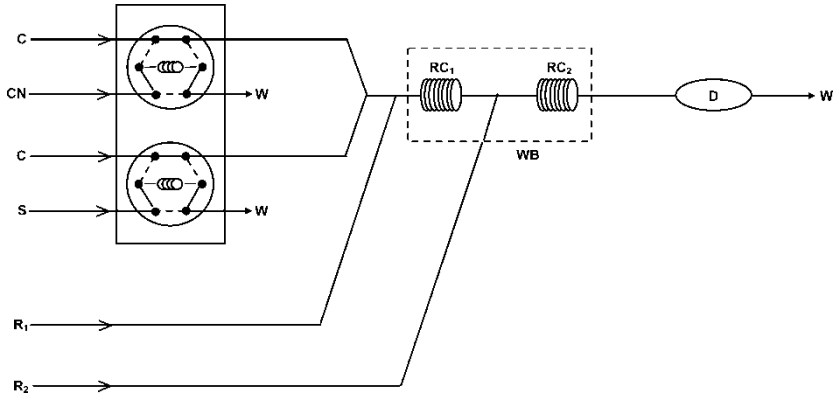

Figure 1. Flow injection system proposed by monitoring of cyanide ions in effluents from petroleum refinery samples. Sample loops in the filling positions. Peristaltic pump is not shown but arrows indicate pumping positions. C (carrier solution) = 5% (m/v) Na_2CO_3, 1.26 mL min^{-1}; CN (0.5 μg mL^{-1} CN solution), 500 μL; S (sample or calibration solution), 500 μL; R1 = 2% (m/v) ninhydrin, 0.66 mL min^{-1}; R2 = 1 mol L^{-1} NaOH, 0.30 mL min^{-1}; RC1 and RC2 = reaction coils, 300 cm, 0.5 mm i.d.; WB = water bath (70°C); D, detector (590 nm); W, waste.

was followed according to APHA[12] recommendations. Briefly, a sample portion of 125 mL was placed inside the distillation flask, the glass apparatus was mounted, and the absorber flask was filled up with 20 mL of 0.5 mol L^{-1} sodium hydroxide. The process occurred under vacuum, which was adjusted (air flow rate around one bubble per second), and 3.75 mL of 133 g L^{-1} sulfamic acid, 12.5 mL of 25% m/m hydrochloric acid, and 5 mL of 51% m/v magnesium chloride were added in sequence. A mixture of ice and water was placed in a cold finger condenser, and the distillation was carried out by 150 min under reflux. The solution from the absorber flask was diluted by 50 mL and analyzed in the flow system using the calibration graphs as reference.

Interference Study

Several species normally found in petroleum refinery effluents (considered as potential interferents) were studied with the aim to know their influence on the automated spectrophotometric method. The following ions were chosen as potential interferents: SCN^-, $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, S^{2-}, and Fe^{3+}. Several solutions containing CN^- 0.02 μg mL^{-1} were prepared to contain different concentrations of each one interferent species: SCN^- (50–150 μg mL^{-1}); $Fe(CN)_6^{4-}$ (4–40 μg mL^{-1}); $Fe(CN)_6^{3-}$ (5–30 μg mL^{-1}); S^{2-} (90–150 μg mL^{-1}), and Fe^{3+} (0.01–20 μg mL^{-1}), which were introduced in the

flow system. The analytical signal produced by an analytical solution containing CN^- at 0.02 μg mL^{-1} was also obtained for comparison.

RESULTS AND DISCUSSION

Optimization of Flow Variables

For the optimization of the flow injection system, the variables selected were those mainly studied in flow system. These variables included ninhydrin, sodium carbonate, and sodium hydroxide concentrations; reaction coil length; reagent flow rates and sample loop volumes. This study was done by the univariate procedure. First of all, the chemical variables were studied as follows. Ninhydrin concentrations in the range from 0.25% to 2% (m/v) pumped at 0.66 mL min^{-1} were assayed, maintain the sodium carbonate (1.50 mL min^{-1}) and sodium hydroxide (0.50 mL min^{-1}) concentrations at 5% (m/v) and 1 mol L^{-1}, respectively. These experiments showed that as ninhydrin concentration increases, the absorbance signals also increase. Due to the low ninhydrin solubility in water, higher concentrations cannot be assayed, and, thus, a ninhydrin concentration of 2% (m/v) was chosen for future work.

For the sodium carbonate solutions, concentrations between 1% and 10% (m/v) were tested. It was verified that the signals increase up to a concentration of 5% (m/v) and remain constant until 10% (m/v). Then, 5% (m/v) sodium carbonate concentration was selected in the flow system. Sodium hydroxide solutions with concentrations from 0.5 to 3.5 mol L^{-1} were studied. It was observed that at the concentration of 1 mol L^{-1} best signals were obtained. Thus, this concentration was selected throughout.

The reaction coil (B_1 and B_2) lengths were studied in the range of 100 to 500 cm (from 785 to 3925 μL). Better signals were observed by using 300 cm (2355 μL) for length of both reaction coils. For lower reaction coil lengths, the signals were lower, and lengths higher than 300 cm led to more dispersion inside the system, lowering the absorbance signals. The sample loops were studied from 250 to 1000 μL. Both sample loops (one for sample introduction and another for the cyanide solution of constant concentration injection) were assayed simultaneously. Loop volumes higher than 500 μL do not incease significantly the signals, and for better analytical throughput 500 μL loops were chosen.

Reagent flow rates were also studied in the range of 0.88 to 1.5 mL min^{-1} for the carrier solution (sodium carbonate 5% m/v); 0.30 to 0.66 mL min^{-1} for ninhydrin (2% m/v), and from 0.30 to 0.55 mL min^{-1} for sodium hydroxide (1 mol L^{-1}). Best signals were observed by using 1.26 mL min^{-1}, 0.66 mL min^{-1}, and 0.30 mL min^{-1} for sodium carbonate (carrier solution), ninhydrin, and sodium hydroxide solutions, respectively.

As the reactions that take place inside the reactor coils are not very fast, a temperature study was done. With both the reactor coils B_1 and B_2 (300 cm)

inside a water bath, the temperature was varied between 40°C and 80°C. As the temperature increases, the signals also increase and 70°C was chosen to give rise to better sensitivity without bubbles formation.

Using the optimized conditions, a dispersion coefficient of 12.6 was achieved. The residence time of the sample zone inside the reactor coils (placed inside the water bath) was about 30 s and the transient signal was measured after 45 s elapsed before sample introduction.

Interference Study

It is well documented that spectrophotometric methods involving cyanide determination are susceptible to many interferences from concomitant species present in the real samples. In particular, in the petroleum industry, the physicochemical manufacturing processes involved in petroleum compound cracking are highly complex, dealing with fractionated distillation to separate hydrocarbon fractions and producing a variety of wastes. The nitrogen and sulfur compounds present in the organic matter are transformed in several compounds such as sulfides, polysulfides, mercaptans, single and complex cyanides, and so forth, which must be removed from the effluents before disposal in the environment.

The influence of the concomitant on the 0.02 $\mu g\ mL^{-1}$ CN^- signal until 10% was not considered as interference. In Table 1 the obtained results can be seen. From the results shown in Table 1, it could be concluded that Fe^{3+} is the species that show more effect on the spectrophotometric reaction. However, according to our laboratory experience in effluents analysis from several Brazilian petroleum refineries, this species is scarcely present in more than 0.1 $\mu g\ mL^{-1}$ of the final effluent after chemical and biological treatments and before its disposal. The cyano-complexes of iron (II) and (III) could be tolerated until 15 and 20 $\mu g\ mL^{-1}$, respectively. From these species, mainly $Fe(CN)_6^{4-}$ could be found in these effluents but only in very low concentrations, as a result of stainless steel reactor corrosion due to the presence of HCN in vapor phase. In this work, we found interference from $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ with tolerance ratios of 750 and 1000, respectively, but Nagaraja et al.[9] found tolerance levels lower than 330 for both species. Drochioiu[25] has asserted that these metallic cyano complexes did not interfere.

It is well-known that petroleum refinery effluents may contain thiocyanate and sulfide. According to the authors that introduced this reaction, their methods are relatively free of interferences. However, Drochioiu[25] has mentioned that thiocyanate ion interferes at stoichiometric conditions. In our automated method, this concomitant can be tolerated until 100 $\mu g\ mL^{-1}$ (interferent:analyte ratio of 500 when tested in relation to 0.02 $\mu g\ CN^-\ mL^{-1}$). This result is in agreement with Nagaraja et al.[9] who found a tolerance limit of 120 $\mu g\ mL^{-1}$ for thiocyanate based on 0.12 $\mu g\ CN^-\ mL^{-1}$ (interferent:analyte ratio of 1000). For sulfide, the maximum

Table 1. Relative signals obtained in the presence of interfering species when compared with a cyanide solution containing 0.02 μg mL^{-1}

Interferent concentration (μg mL^{-1})	Relative signal in presence of interferent				
	SCN^-	$Fe(CN)_6^{4-}$	$Fe(CN)_6^{3-}$	S^{2-}	Fe^{3+}
0.1	—	—	—	—	1.06
0.5	—	—	—	—	1.11
1.0	—	—	—	—	1.19
4.0	—	1.01	—	—	1.54
5.0	—	1.05	1.00	—	—
10	—	1.06	1.08	—	—
15	—	—	1.09	—	—
20	—	1.09	1.15	—	—
30	—	1.09	1.15	—	—
40	—	1.10	—	—	—
50	1.00	—	—	—	—
60	1.03	—	—	—	—
75	1.08	—	—	—	—
90	—	—	—	1.00	—
100	1.09	—	—	1.11	—
110	1.12	—	—	1.11	—
120	1.13	—	—	1.13	—
130	—	—	—	—	—
140	—	—	—	—	—
150	1.20	—	—	1.13	—

concentration allowed in FIA method was 100 μg mL^{-1} (tolerance ratio of 500) also in agreement with Nagaraja et al.[9], who did not find interference until 120 μg mL^{-1} (tolerance ratio of 1000). Drochioiu[25] also found the same level of interference.

From the interference tests, it can be seen that the proposed automated method is almost free from interferences from sulfide and thiocyanate (interferent:analyte ratio of 5000 times for both species).

Analytical Features

The optimized flow system (Fig. 1) was able to measure cyanide concentrations in a linear range of 0.01 to 0.04 (maximum tested) μg mL^{-1} with typical linear regression values such as Abs = 3.97 [CN^- (μg mL^{-1})] – 0.006. The relative standard deviation (RSD) was very good (5.13, 2.56, 1.69, and 1.26) for the calibration solutions from 0.01 to 0.04 μg mL^{-1} CN^- (n = 8). The detection limit estimated as 3σ/slope was 1.5 ng mL^{-1} and the quantification limit (10 σ) was 5 ng mL^{-1}.

Petroleum Refinery Effluent Analysis

Six effluents from a Brazilian petroleum refinery were analyzed using the developed method. Although the developed procedure was relatively free of interferences normally found in the effluent samples selected for its application, due to the sample complexity and following APHA[12] recommendations for total cyanide analysis without interferences, a sample pretreatment by strong acid distillation was performed for each sample. In order to verify in our laboratory the feasibility of the distillation process, several analytical solutions containing from 0.01 to 0.05 $\mu g\ mL^{-1}$; CN^- were submitted to the pretreatment as recommended by APHA[12] and further analyzed by the developed procedure. In Table 2 the obtained results are shown. From the recovery tests presented in Table 2, it could be concluded that very good recoveries were obtained for cyanide solutions containing more than 0.02 $\mu g\ mL^{-1}$. For solutions of 0.01 $\mu g\ mL^{-1}$, the obtained absorbance signal was of the same order of magnitude as the blank. This way, only cyanide concentrations higher than 0.02 $\mu g\ mL^{-1}$ can be quantitatively distilled using the APHA method.[12]

There are no reference materials dealing with cyanide species in effluents. In order to validate the developed method, analyte spiking and sample analysis by using the recommended method from APHA[12] was performed to ensure accuracy. Table 3 shows the results obtained, and it can be concluded that the effluents did not contain measurable quantities of cyanides.

CONCLUSIONS

The automation by flow injection analysis of the method for determination of cyanide by using ninhydrin as color reagent has several advantages when compared with the batch methods proposed by Nagaraja et al.[9] and

Table 2. Recovery obtained by using strong acid distillation pretreatment as recommended by APHA[12] using analytical solutions of CN^- from 0.01 to 0.05 $\mu g\ mL^{-1}$

CN^- concentration ($\mu g\ mL^{-1}$)	Recovery (%)
0.01	—[a]
0.02	97 ± 2
0.03	99 ± 2
0.05	98 ± 2

[a]Obtained signal as the same as the blank solution.

Table 3. Results obtained for the analysis of refinery effluent samples and analyte addition test

Sample	CN^- found ($\mu g\ mL^{-1}$)	Recovery from analyte spiking ($\mu g\ mL^{-1}$)	
		Added 0.020 ($\mu g\ mL^{-1}$)	Added 0.030 ($\mu g\ mL^{-1}$)
Ba-68324a	<0.020	0.019 ± 0.002	—
Ba-68324b	<0.020	0.020 ± 0.001	—
Ba-68324c	<0.020	—	—
Ba-68339a	<0.020	—	0.030 ± 0.001
Ba-68339b	<0.020	—	—
Ba-68339c	<0.020	—	0.029 ± 0.002

Drochioiu.[24,25] First of all, the automated method developed in this work presents advantage of the inherent sample throughput of FIA procedures. With the developed methodology, each sample can be analyzed in only 120 s, faster than the batch procedures that according to Nagaraja et al.[9] and Drochioiu[25] need 30 and 15 min for color development for blue (590 nm) and purple (510 nm) dyes, respectively. It worth mentioning that the time needed for sample pretreatment by steam distillation is about 1 hr and the sample throughput of 120 s can only be obtained for samples that do not need any pretreatment.

Regarding detection limits, the FIA procedure presents 1.5 ng mL^{-1} (3σ/slope), whereas 18 ng mL^{-1}[9] and 3 ng mL^{-1}[24] were found in batch mode. Linear regression graphs were obtained between the range of 0.01 to 0.04 (maximum tested) $\mu g\ mL^{-1}$ by FIA procedure, in comparison with 0.04 to 0.24 $\mu g\ mL^{-1}$[9] and 0.01 to 1 $\mu g\ mL^{-1}$[24,25] for batch methodologies.

The sensitivity of the proposed flow analysis method is greater than that of other spectrophotometric ones,[16,17] and the procedure is very simple and fast.

On the other hand, the utilization of friendly reagents in chemical analysis is of concern. Our methodology could be used as an alternative APHA[12] procedure, without the use of carcinogenic (pyridine) or psychotropic (barbituric acid) compounds, while the sensitivity is better than that required to be used for environmental water bodies protection analysis.

ACKNOWLEDGMENTS

The authors are grateful to Conselho Nacional de Desenvolvimento Científico e Tecnológico-CNPq and Fundação Carlos Chagas Filho de Amparo a Pesquisa do Estado do Rio de Janeiro–FAPERJ for grants and fellowships.

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