

Total cyanide determination by a segmented flow injection–on-line UV digestion–amperometric method

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Extensive species and concentration dependent cyanide recovery studies were carried out using a novel automated segmented flow injection–on-line UV digestion–amperometric (FI-UV) method for determination of total cyanide in water and wastewater samples. In addition, the response of the method to the presence of potential interferents was tested. The performance of the proposed method was compared with that of the standard method. The data obtained show that the FI-UV method has significant advantages over the EPA/ASTM approved procedures. Total cyanide levels and spike recoveries were determined for nine different industrial effluents. The precision and accuracy of the method, when applied to these effluents, expressed in terms of mean relative standard deviation and average percentage of spike recovery, were 1.5% and 101.0%, respectively. The technique developed eliminates the need for the time consuming, labor intensive distillation called for in the EPA/ASTM approved procedures. The method is rapid, selective and reproducible with a detection limit of 0.2 $\mu\text{g L}^{-1}$ and a throughput of 30 analyses per hour.

Introduction

The US Environmental Protection Agency (EPA) and the American Society for Testing and Materials (ASTM) approved methods for determination of total cyanide are based on the liberation of hydrogen cyanide from a sample acidified with sulfuric acid using a 1 h reflux distillation procedure. The HCN gas formed is trapped by the alkaline scrubbing solution. Cyanide in this solution is then quantified by a spectrophotometric or potentiometric procedure.^{1,2}

Serious problems associated with the approved method have been recognized.^{3–9} Most of them stem from the fact that the method utilizes harsh analytical conditions ($> 100\text{ }^{\circ}\text{C}$ and $\text{pH} < 0$). In addition, the chromogenic reaction in the spectrophotometric quantification procedure involves the addition of the strong oxidant (chloramine-T). These conditions along with the complexity of sample matrices often produce complicated reaction pathways that can result in the production of cyanide (real or as an artifact) during distillation and associated colorimetric procedures. All these factors result in low reproducibility and repeatability of the method, which in turn lead to a low quality of the cyanide concentration data obtained.

From the above-enumerated problems, it is apparent that alternative approaches to the determination of total cyanide in water and wastewater samples are needed. One such approach is the use of UV irradiation in combination with a gas-diffusion separation step and amperometric detection method as described here. It has been shown previously that cyanide can be liberated from certain metal–cyano complexes using UV and/or visible light irradiation.^{10–13} In order to minimize the photo-induced conversion of thiocyanate to cyanide, the use of a Pyrex glass instead of a quartz reactor was suggested.¹² Diffusion of HCN through a hydrophobic porous membrane has been successfully utilized for the removal of ionic interfering substances in cyanide determination methods.^{13–16} The advantage of amperometric detection, utilized in the proposed FI-UV procedure, is that the species of interest, the CN^{-} ion, is determined directly. This is in contrast to using indirect

complex chromogenic reaction schemes prescribed in the EPA/ASTM approved methods.

Experimental

Materials

Sodium cyanide, potassium hexacyanoferrate(II) trihydrate, potassium hexacyanoferrate(III), potassium hexacyanocobaltate(III), potassium hexacyanoplatinate(IV), potassium hexacyanonitrate(II), potassium tetracyanoplatinate(II), potassium tetracyanopalladate(II), mercury(II) cyanide, potassium thiocyanate, potassium nitrate, sodium thiosulfate, sodium carbonate, sodium nitrite, potassium cyanate, sodium sulfate, sodium sulfite, sodium sulfide nonahydrate, glucose, glycerol, acetaldehyde, sodium hypochlorite (Aldrich Chemical Company), potassium bromide, sodium chloride, potassium iodide, ammonium chloride (Fisher Scientific Company) potassium dicyanoargentate(I) and potassium dicyanoaurate(I) (Aesar/Johnson Matthey) were obtained as analytical-reagent grade chemicals and were used as received. Potassium tetracyanozincate(II), tetracyanocadmiate(II), tetracyanocuprate(I), tetracyanonickelate(II) and tetracyanomercurate(II) were synthesized and recrystallized by the reported procedures.¹⁷ Standard cyanide solutions, which were made in 0.01 M NaOH, were prepared daily by diluting aliquots of the stock solution (1.00 $\text{g L}^{-1} \text{CN}^{-}$) to the appropriate volume. Standard solutions of cyanide complexes, which were also made in 0.01 M NaOH, were prepared daily by diluting aliquots of the stock solutions (1.00 g L^{-1} in cyanide) to the appropriate volume. Stock solutions (10.0 g L^{-1}) of potential interfering species (for details, see Table 2) were prepared in reagent water and stored in a refrigerator at 4 $^{\circ}\text{C}$.

'Real' samples from various industrial sources were obtained and the cyanide content was assessed. The samples were spiked with cyanide, metal–cyano complexes and/or thiocyanate and the cyanide spike recoveries were determined.

The comparison of the DPA and the FI-UV methods for the determination of total cyanide was carried out by analyzing nine samples obtained from a water treatment plant, a petroleum refinery and a precious metals metallurgical operation (before and after detoxification treatment). The tests for the presence of sulfide and oxidants were negative and the samples were preserved according to the standard procedure.¹

Instrumentation and analytical procedures

A Cyanide Solution® 3000 Analyzer (Alpkem®, A Division of O. I. Analytical, College Station, TX, USA) equipped with a gas-diffusion cell, an UV irradiation unit, an amperometric flow-through cell and random access autosampler was used (for details see the *Operation Manual*¹⁸). The UV irradiation unit consisted of two modules each containing 480 cm of PTFE tubing (0.8 mm id) coiled around an UV/Long 4 W, 312 nm lamp. The flow-through amperometric cell (P/N 37753, Dionex Corp., Sunnyvale, CA, USA) consisted of a silver working and stainless steel counter electrodes. The Ag/AgCl (1 M NaCl) reference electrode was separated from the flowing stream by an ion-exchange Nafion membrane. The analyzer was controlled using WinFLOW™ software. The manifold utilized is illustrated in Fig. 1.

Distillation of samples under the EPA protocol was carried out with a 10-sample, temperature controlled midi-distillation unit (EnviroPrep 1010, Alpkem®). Post-distillation quantification of cyanide in the absorbing NaOH solution was performed with an automated FI spectrophotometric Flow Solution™ 3000 Analyzer (Alpkem®) using the standard pyridine–barbituric acid chromogenic reaction.¹⁹

The manifold utilized for total cyanide determination by segmented flow injection–on-line UV digestion–amperometric (FI-UV) method is depicted in Fig. 1. The flow injection analytical cycle begins by introducing 200 µL of the sample into the water carrier line (C) which takes the sample plug to a confluence point with an acidic reagent stream (R). In order to prevent excessive dispersion of the sample, an air-segmenting line is connected after this confluence point. The mixing coil positioned downstream (MC) ensures thorough acidification of the sample. The acidified sample then enters the UV digestion module that facilitates dissociation of cyanide from the coordination sphere of certain metal complexes. The flow exiting the UV digester is mixed with the reagent (R₁) line. This reagent contains bismuth(III) nitrate that can remove on-line up to 50 mg L⁻¹ sulfide if necessary. The mixed stream then passes through a donor channel of the gas-diffusion unit and flows to waste. At the same time NaOH absorbing solution (A) is being pumped through the acceptor channel of the gas-diffusion unit. Hydrogen cyanide formed in the donor stream diffuses through the microporous hydrophobic membrane (0.45 µm, 25 mm

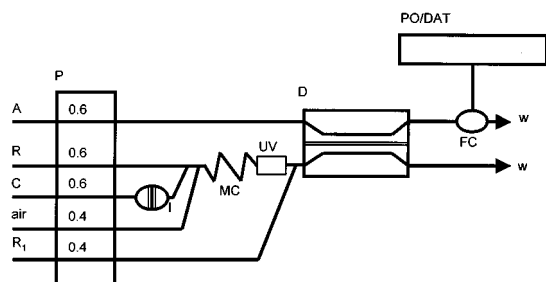


Fig. 1 The FI-UV manifold used for determination of total cyanide. C, carrier (H₂O); R, reagent (1.0 M H₂SO₄–0.19 M H₃PO₂); R₁, reagent [1.0 M H₂SO₄–0.19 M H₃PO₂–Bi(NO₃)₃]; A, acceptor solution (0.10 M NaOH); P, peristaltic pump; I, injection valve (200 µL sample loop); MC, mixing coil (50 cm × 0.8 mm id); D, diffusion cell; FC, amperometric flow-through cell; PO/DAT, potentiostat/data collection device; UV, on-line UV digester; w, waste. Flow rates are given in mL min⁻¹.

TefSep unlaminated Teflon, Micron Separation Inc., Westborough, MA, USA) and is converted to CN⁻ ion by the high pH solution in the acceptor channel. Cyanide in the acceptor solution is quantified amperometrically at the Ag working electrode at an applied potential of 0.0 V vs. Ag/AgCl reference electrode. The silver working electrode was stabilized by injecting a 10.0 ppm CN⁻ standard until the reproducibility of peak heights was better than 5% RSD (10 injections were usually sufficient). Even though silver is dissolved during cyanide quantification, owing to the very low currents generated by the amperometric systems a single electrode has been in use for over 2 years.

The residence time of each sample in the FI-UV manifold is ~6 min. However, since the baseline-to-baseline width of the FI signal is less than 2 min, and since the new WinFLOW™ software allows for multiple signal integration, it is possible to achieve a throughput of 30 analyses per hour. For samples with cyanide levels below 0.100 mg L⁻¹, the calibrations were conducted by injecting in triplicate a reagent blank and a series of five cyanide standards in the range 1.00 µg L⁻¹–0.100 mg L⁻¹. The slope and correlation coefficient were 702 ± 15 nA L mg⁻¹ and 0.9999, respectively (all the statistics were calculated for a 95% confidence level). For higher cyanide level samples, calibration runs were performed by injecting in triplicate a series of five cyanide standards from 0.100 to 5.00 mg L⁻¹. The corresponding slope and correlation coefficient were 686 ± 15 nA L mg⁻¹ and 0.9999, respectively. The response of the amperometric detector to the triplicate injections of three cyanide standards is illustrated in Fig. 2. The repeatability of the method at the 0.200 mg L⁻¹ cyanide level is better than 3% RSD (*n* = 3). The method detection limit (MDL) was determined by the prescribed procedure.²⁰

Results and discussion

The results of the comparative species and concentration dependent cyanide recovery studies using EPA Method 335.4¹⁹ and the FI-UV method are shown in Table 1. As may be seen, complete cyanide recoveries are obtained from all the species that belong to the group of WAD (weak and dissociable or weak acid dissociable) cyanides, or cyanides amenable to chlorination, *i.e.*, cyanide complexes of zinc, cadmium, copper, silver, nickel and mercury. In addition, essentially complete cyanide recoveries were obtained for stable iron(II) and -(III) cyano species. Incomplete or no cyanide recoveries were obtained by both methods for the cyano complexes of platinum, palladium, ruthenium, gold and cobalt.

Data obtained from the concentration dependent cyanide recovery study from the stable hexacyanoferrate(II) and -(III) species show that satisfactory cyanide recoveries (102–90%) were obtained in the interval 0.005–5.00 mg L⁻¹ for [Fe(CN)₆]⁴⁻ species. The RSDs of triplicate sample runs were 2.4 and 1.2% for 0.005 and 5.00 mg L⁻¹ cyanide standards, respectively. The corresponding recoveries from [Fe(CN)₆]³⁻ (100–75%) show a more pronounced concentration dependence that can be attributed to the slower hexacyanoferrate(III)

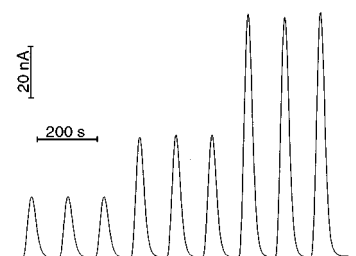


Fig. 2 Response of the amperometric detector to a triplicate injections of 0.050, 0.100 and 0.200 ppm CN⁻ standards.

decomposition compared with that of $[\text{Fe}(\text{CN})_6]^{4-}$ ion. Nevertheless, over 90% of cyanide can be recovered from $\text{Fe}(\text{III})$ -cyano species having cyanide levels up to 0.500 mg L^{-1} . The RSDs of triplicate sample runs for $[\text{Fe}(\text{CN})_6]^{3-}$ were 2.5 and 2.2% for 0.005 and 5.00 mg L^{-1} cyanide standards, respectively. The presence of hypophosphorous acid (H_3PO_2) in the system minimizes possible oxidation of cyanide by $[\text{Fe}(\text{CN})_6]^{3-}$. The combination of the photo-induced release of cyanide from metal-cyano complexes and the gas-diffusion separation step prior to amperometric quantification of cyanide renders the developed method nearly specific towards the analyte. Nevertheless, the species that do interfere in the classical total cyanide determination methods and also some other species were tested.

Determination of CN^- by the FI-UV method in the presence of possible interferents was performed with solutions containing 0.200 mg L^{-1} cyanide {added as NaCN or $\text{K}_4[\text{Fe}(\text{CN})_6]$ } and potential interferent at concentrations 100 and 1000 times greater than the CN^- level. Each interferent was added to the cyanide solutions and, after pH adjustment with sodium hydroxide, the samples were allowed to stand for approximately 12 h (overnight) at 4°C before analysis. Samples containing S^{2-} , OCl^- , CH_3CHO or NO_2^- were prepared in duplicate. One set of samples was prepared as described above in order to allow

the determination of CN^- in the presence of untreated interferences. The other set was treated with the recommended interference removal procedures^{1,2} immediately upon the addition of the interferent to the sample. All treated samples were also left to stand for 12 h at 4°C before analysis. The results obtained are summarized in Tables 2 and 3.

At the 20.0 mg L^{-1} interferent level, for NaCN containing solutions, essentially complete cyanide recoveries were obtained from all untreated samples except for the sample containing the hypochlorite ion, where no CN^- was found. When this sample was treated with ascorbic acid, the CN^- recovery was 59%. It should be noted that the presence of sulfide (20.0 mg L^{-1}) does not interfere in the FI-UV determination of cyanide. This is due to the fact that $\text{Bi}(\text{NO}_3)_3$ present in reagent R_1 allows for the on-line removal of S^{2-} up to the 50 mg L^{-1} level. Therefore, pre-treatment of cyanide samples containing S^{2-} with PbCO_3 is only necessary when the sulfide levels are greater than 50 mg L^{-1} .

When potential interferents are present at the 200 mg L^{-1} level in NaCN samples, incomplete cyanide recoveries were obtained for samples containing sulfite (87.5%) and acetaldehyde (22%) owing to the oxidation of cyanide and formation of cyanohydrin, respectively. The recovery of cyanide in the presence of acetaldehyde can be improved with

Table 1 Species dependent cyanide recoveries (%) obtained with the EPA/ASTM and FI-UV total cyanide determination methods

Species	$0.200 \text{ mg L}^{-1} \text{CN}^-$		$2.00 \text{ mg L}^{-1} \text{CN}^-$	
	EPA/ASTM	FI-UV	EPA/ASTM	FI-UV
$[\text{Zn}(\text{CN})_4]^{2-}$	99.5 (0.5) ^a	97.2 (1.8) ^a	104.4 (2.6) ^a	99.6 (1.9) ^a
$[\text{Cd}(\text{CN})_4]^{2-}$	103.8 (1.3)	104.3 (0.9)	102.9 (0.7)	100.9 (2.2)
$[\text{Cu}(\text{CN})_4]^{3-}$	97.7 (1.9)	100.0 (1.0)	98.0 (1.2)	100.3 (1.4)
$[\text{Ag}(\text{CN})_2]^-$	97.8 (2.3)	104.3 (1.2)	100.2 (2.6)	99.2 (1.6)
$[\text{Ni}(\text{CN})_4]^{2-}$	104.2 (3.5)	98.3 (2.5)	97.1 (0.3)	100.0 (0.4)
$[\text{Hg}(\text{CN})_4]^{2-}$	95.8 (2.5)	96.7 (2.3)	97.6 (3.3)	99.6 (2.4)
$\text{Hg}(\text{CN})_2$	98.0 (5.9)	96.1 (1.6)	97.3 (0.9)	102.5 (0.8)
$[\text{Fe}(\text{CN})_6]^{4-}$	100.8 (5.5)	101.0 (0.5)	99.6 (2.0)	99.5 (1.0)
$[\text{Fe}(\text{CN})_6]^{3-}$	104.0 (1.3)	95.0 (1.6)	99.5 (2.8)	83.5 (1.8)
$[\text{Pd}(\text{CN})_4]^{2-}$	69.1 (2.5)	17.7 (2.6)	66.5 (1.9)	21.9 (1.6)
$[\text{Au}(\text{CN})_2]^-$	56.6 (2.0)	49.5 (1.3)	58.4 (1.9)	42.8 (1.0)
$[\text{Ru}(\text{CN})_6]^{4-}$	50.1 (1.7)	0.50 (1.9)	51.0 (1.1)	0.50 (2.0)
$[\text{Co}(\text{CN})_6]^{3-}$	N/D ^b	13.8 (2.6)	2.5 (1.2)	14.6 (2.3)
$[\text{Pt}(\text{CN})_4]^{2-}$	N/D	0.54 (2.3)	N/D	0.44 (1.5)
$[\text{Pt}(\text{CN})_6]^{2-}$	N/D	N/D	N/D	N/D

^a RSDs (%) ($n = 3$) are given in parentheses. ^b Not detected.

Table 2 FI-UV determination of $0.200 \text{ mg L}^{-1} \text{CN}^-$ (added as NaCN) in the presence of possible interferents (20.0 or 200 mg L^{-1})

Species	Ratio ^a	CN^- found/ mg L^{-1}		Ratio ^a	CN^- found/ mg L^{-1}	
		Untreated samples	Treated samples		Untreated samples	Treated samples
Cl^-	73	0.202 (1.4) ^b		730	0.201 (0.3) ^b	
Br^-	33	0.198 (0.5)		330	0.197 (1.8)	
I^-	20	0.204 (0.8)		200	0.203 (3.0)	
SO_4^{2-}	27	0.199 (1.3)		270	0.202 (1.2)	
SO_3^{2-}	32	0.199 (0.5)		320	0.175 (1.3)	
NO_3^-	42	0.201 (1.0)		420	0.201 (2.5)	
NO_2^-	56	0.199 (0.5)	0.198 (1.2) ^b	560	0.199 (2.5)	0.200 (1.4) ^b
CO_3^{2-}	43	0.200 (1.6)		430	0.200 (0.5)	
OCN^-	62	0.197 (1.3)		620	0.201 (1.2)	
OCl^-	50	N/D ^c	0.118 (3.0)	500	N/D	N/D
NH_4^+	144	0.202 (1.8)		1440	0.201 (1.2)	
CH_3CHO	59	0.188 (2.0)	0.193 (1.2)	590	0.044 (1.3)	0.168 (2.1)
$\text{C}_3\text{H}_8\text{O}_3$	28	0.199 (2.5)		280	0.200 (1.6)	
$\text{C}_6\text{H}_{12}\text{O}_6$	14	0.202 (1.2)		140	0.185 (0.9)	
$\text{C}_6\text{H}_8\text{O}_6$	15	0.199 (0.8)		150	0.188 (2.0)	
S^{2-}	81	0.198 (1.0)	0.189 (1.7)	810		0.153 (1.3)
SCN^-	45	0.208 (1.4)		450	0.211 (2.4)	
$\text{S}_2\text{O}_3^{2-}$	23	0.196 (1.1)		230	0.218 (2.9)	

^a Molar concentration ratio: species/ CN^- . ^b RSDs (%) ($n = 3$) are given in parentheses. ^c Not detected.

ethylenediamine treatment (84%). Of course, this treatment cannot recover the already reacted cyanide, it can only prevent further cyanohydrin formation. No cyanide was found in the treated or untreated solutions containing OCl^- owing to instantaneous oxidation of cyanide.²¹

When the sulfide levels exceed 50 mg L^{-1} , the sulfide interferent treatment is required since acidification of these samples produces H_2S that diffuses through the gas-diffusion membrane and is detected at the silver working electrode. Hence the cyanide standard containing 200 mg L^{-1} sulfide was treated with lead carbonate. The lower recovery observed (76.5%) is due to the formation of thiocyanate during the interferent removal procedure.²⁶

In order to compare the performance of the FI-UV method with that of the approved method for total cyanide determination, concentrations of CN^- in NaCN samples containing interfering species were also determined by EPA Method 335.4.¹⁹ The results obtained are given in Table 4.

From the data presented in Table 2 and 4, the following conclusions can be drawn. Hypochlorite and acetaldehyde should not be considered as method interferences. They cause the removal of cyanide prior to the quantification procedures owing to the oxidation of cyanide and the formation of cyanohydrin, respectively. When the samples with hypochlorite and acetaldehyde (at 20.0 mg L^{-1} levels) were treated with ascorbic acid and ethylenediamine, respectively, both methods determined the CN^- remaining in the solutions.

It is interesting that the nitrite ion does not interfere with the determination of free cyanide with the FI-UV method. However, when cyanide was added as $[\text{Fe}(\text{CN})_6]^{4-}$, significantly

lower recoveries were obtained for the untreated samples. The possible explanation for this phenomenon may be that nitrite ion absorbs some of the UV energy that would otherwise effect the photo-dissociation of the CN^- ion from the coordination sphere of iron. As can be seen from Table 3, the problem of incomplete cyanide recoveries from $[\text{Fe}(\text{CN})_6]^{4-}$ in the presence of NO_2^- can be obviated by the standard sulfamic acid pre-treatment method.

One of the primary problems with the standard methods for total cyanide determination is the interferences, for which there are no reliable interference recognition tests ('spot tests'). That is the case, for example, with the SCN^- , SO_3^{2-} and $\text{S}_2\text{O}_3^{2-}$ ions. These are the species that are often found in the cyanide containing samples. From the results obtained (Table 4), it is obvious that the sulfuric acid distillation procedure creates conditions that may result in the reaction of cyanide with either the reaction products of these species with acid or with the species themselves.

In the case of sulfite, recoveries of cyanide with the distillation procedure from 0.200 mg L^{-1} CN^- solutions containing 20.0 and 200 mg L^{-1} SO_3^{2-} are 40 and 0% , respectively. The concentrations of CN^- in the absorbing solutions found after distillation were determined with both colorimetric and amperometric detection methods. Since comparable results were obtained, it is clear that the low recoveries are caused by the oxidation of cyanide with sulfite and not because of the reaction of SO_3^{2-} with chloramine-T in the colorimetric quantification step. On the other hand, the corresponding recoveries obtained with the FI-UV method are 100 and 88% . Low recoveries of cyanide in the presence of

Table 3 FI-UV determination of 0.200 mg L^{-1} CN^- {added as $[\text{Fe}(\text{CN})_6]^{4-}$ } in the presence of possible interferents (20.0 or 200 mg L^{-1})

Species	Ratio ^a	CN^- found/ mg L^{-1}		Ratio ^a	CN^- found/ mg L^{-1}	
		Untreated samples	Treated samples		Untreated samples	Treated samples
Cl^-	73	0.197 (2.1) ^b		730	0.202 (1.7) ^b	
Br^-	33	0.201 (2.3)		330	0.198 (0.8)	
I^-	20	0.170 (1.2)		200	0.173 (1.2)	
SO_4^{2-}	27	0.194 (0.5)		270	0.197 (0.9)	
SO_3^{2-}	32	0.199 (1.3)		320	0.201 (0.3)	
NO_3^-	42	0.202 (2.3)		420	0.198 (2.8)	
NO_2^-	56	0.137 (0.7)	0.198 (0.8) ^b	560	0.068 (4.2)	0.200 (0.5) ^b
CO_3^{2-}	43	0.202 (0.6)		430	0.202 (0.5)	
OCN^-	62	0.198 (1.6)		620	0.199 (2.6)	
OCl^-	50	0.191 (0.6)	0.199 (1.5)	500	0.176 (1.7)	0.200 (0.9)
NH_4^+	144	0.200 (2.8)		1440	0.203 (0.9)	
CH_3CHO	59	0.198 (1.8)	0.198 (1.3)	590	0.198 (2.2)	0.198 (1.7)
$\text{C}_3\text{H}_8\text{O}_3$	28	0.199 (1.3)		280	0.199 (0.3)	
$\text{C}_6\text{H}_{12}\text{O}_6$	14	0.200 (0.3)		140	0.196 (0.3)	
$\text{C}_6\text{H}_8\text{O}_6$	15	0.198 (1.3)		150	0.196 (0.3)	
S^{2-}	81	0.189 (0.8)	0.186 (1.1)	810		0.148 (1.8)
SCN^-	45	0.199 (0.5)		450	0.204 (0.8)	
$\text{S}_2\text{O}_3^{2-}$	23	0.197 (1.3)		230	0.199 (1.0)	

^a Molar concentration ratio: species/ CN^- . ^b RSDs (%) ($n = 3$) are given in parentheses.

Table 4 EPA Method 335.4 determination of 0.200 mg L^{-1} CN^- (added as NaCN) in the presence of possible interferents (20.0 or 200 mg L^{-1})

Species	Ratio ^a	CN^- found/ mg L^{-1}		Ratio ^a	CN^- found/ mg L^{-1}	
		Untreated samples	Treated samples		Untreated samples	Treated samples
NO_2^-	56	0.155 (3.4) ^b	0.203 (1.0) ^b	560	0.133 (4.4) ^b	0.204 (2.0) ^b
SO_3^{2-}	32	0.080 (10.0)		320	N/D ^c	
OCl^-	50	N/D	0.120 (6.2)	500	N/D	N/D
CH_3CHO	59	0.168 (6.0)	0.184 (4.8)	590	N/D	0.028 (2.1)
SCN^-	45	0.174 (8.0)		450	0.054 (1.0)	
$\text{S}_2\text{O}_3^{2-}$	23	0.124 (4.3)		230	0.040 (3.2)	
S^{2-}	81		0.120 (2.5)	810		N/D

^a Molar concentration ratio: species/ CN^- . ^b RSDs (%) ($n = 3$) are given in parentheses. ^c Not detected.

sulfite obtained with the distillation procedure are probably due to the temperature enhanced sulfite oxidation of cyanide to cyanate.

As can be seen from Table 4, incomplete cyanide recoveries were also obtained in the presence of thiocyanate with EPA Method 335.4. It has been established previously that decomposition of thiocyanate at elevated temperatures in acidic solutions and in the absence of oxidants produces elemental sulfur, sulfur(IV) oxide and carbonyl sulfide, which is converted into sulfide upon adsorption in alkaline solution.^{22,23} Under similar conditions the thiosulfate ion may be converted into sulfur, sulfur(IV) oxide, hydrogen sulfide and polysulfide.²⁴ The high temperature distillation of cyanide containing samples in the presence of thiocyanate and/or thiosulfate creates conditions conducive to the conversion of cyanide to other species, which in turn causes a decrease in cyanide recoveries. Hence it is not surprising that the recoveries of cyanide in the presence of 20.0 and 200 mg L⁻¹ SCN⁻ obtained by EPA Method 335.4 are 87% and 27%, respectively. The corresponding recoveries in the presence of S₂O₃²⁻ are 62% and 20%. In contrast, complete cyanide recoveries in the presence of the SCN⁻ and S₂O₃²⁻ are obtained with the proposed FI-UV method (for details see Tables 2 and 4). It should be noted that the standard distillation Method 4500-CN²⁵ recommends the addition of lead carbonate to the NaOH absorption solution prior to the distillation of the cyanide samples that may also contain various sulfur species. Our experiments, and also the results obtained previously,³ show that the treatment is not effective in removing SO₃²⁻, SCN⁻ and S₂O₃²⁻ interferences, and may in fact be problematic.

It is interesting that the SCN⁻ ion may also cause a positive interference in the determination of cyanide under the distillation protocols. At high acidity and in the presence of strong oxidants (e.g., NO₃⁻), the sulfur in the thiocyanate is oxidized with concomitant liberation of hydrogen cyanide.⁸ Under the experimental conditions that exist during the FI-UV determination of cyanide, no production of HCN from SCN⁻ in the presence of nitrate occurs. For example, cyanide recovery from the sample containing 0.200 mg L⁻¹ CN⁻, 500 mg L⁻¹ NO₃⁻ and 100 mg L⁻¹ SCN⁻ was 102%. The corresponding recovery with the distillation procedure was over 5000%. Hence the cyanide levels in the samples that also contain thiocyanate and nitrate can be determined reliably with this method.

The FI-UV determination of cyanide in the [Fe(CN)₆]⁴⁻ samples with an interferent concentration of 20.0 mg L⁻¹ produced incomplete recoveries only in the presence of I⁻ (85%) and NO₂⁻ (68.5%). The iodide ion, which absorbs in the UV region, probably causes lower recoveries for the same reason as the NO₂⁻ species (see above). At interferent levels of 200 mg L⁻¹, incomplete cyanide recoveries were obtained in the presence of hypochlorite (88%), iodide (86.5%) and nitrite (34%). The pre-treatment with sulfamic and ascorbic acid

completely eliminates the NO₂⁻ and OCl⁻ interferences, respectively (see Table 3 for details).

As mentioned previously, S²⁻ (up to 50 mg L⁻¹) does not interfere with cyanide determination by the FI-UV method. For example a 98% cyanide recovery was obtained for the sample that contained 10.0 µg L⁻¹ CN⁻ and 20.0 mg L⁻¹ S²⁻. When higher concentrations of sulfide were present, the samples were treated with PbCO₃ and the PbS formed was filtered immediately. It has been shown previously that the effect of sulfide on the recovery of cyanide, due to the formation of thiocyanate, can be minimized by timely filtration of the PbS.²⁶ The effect of contact time between cyanide and PbS is illustrated by CN⁻ recoveries obtained with the FI-UV method and EPA Method 335.4 for PbCO₃ treated sulfide (200 mg L⁻¹) containing samples (for details see Tables 2 and 4). Of course, much smaller sample volumes are needed for the FI-UV method than EPA Method 335.4. Hence in the former case a rapid syringe filtration is possible.

To demonstrate the applicability of the automated FI-UV cyanide determination method, a series of nine samples of different industrial categories were analyzed for their cyanide content. The samples were then spiked with known amounts of cyanide, metal-cyano complexes and/or thiocyanate. The range of the spike concentrations tested encompassed the dynamic range of the method. The metal-cyano complexes of Fe(II), Fe(III), Ag(I), Hg(II) and Ni(II) were chosen in order to illustrate the ability of the proposed method to recover cyanide from complexes of different thermodynamic stability. The results obtained are summarized in Table 5. As can be seen, excellent cyanide recoveries, irrespective of the sample matrix and spike type, were obtained for all the samples tested. In addition, a study was performed to compare EPA Method 335.4 and the FI-UV method for the determination of total cyanide. The results presented in Table 6 show that the concentrations of cyanide determined by the two methods are in agreement for six of the

Table 6 Comparison of the cyanide values found by the FI-UV method and EPA Method 335.4 for a series of real samples

Sample No.	CN ⁻ found/mg L ⁻¹	
	EPA 335.4	FI-UV
1	978 (1.6) ^a	970 (0.5) ^a
2	108.1 (2.1)	109.5 (0.9)
3	26.0 (1.6)	29.1 (0.7)
4	14.5 (2.3)	14.4 (1.0)
5	12.5 (1.4)	12.4 (1.0)
6	0.270 (2.6)	0.155 (1.0)
7	0.045 (13)	0.341 (0.4)
8	0.0258 (5.1)	0.0096 (2.8)
9	0.005 (3.5)	0.0050 (1.2)

^a RSDs (%) (*n* = 3) are given in parentheses.

Table 5 Results of the FI-UV determination of total cyanide in various industrial samples

Sample ^a	CN ⁻ found in the original sample/ mg L ⁻¹	Type and concentration of spike/mg L ⁻¹	CN ⁻ found in the spiked sample/ mg L ⁻¹	Spike recovery (%)
1	0.045 (2.0) ^b	2.00 as [Fe(CN) ₆] ⁴⁻	2.060 (1.2) ^b	100.7
2	0.004 (1.2)	0.100 as [Fe(CN) ₆] ³⁻	0.100 (0.3)	96.0
3	0.380 (1.9)	2.00 as [Ag(CN) ₂] ⁻ + 2.00 as [Ni(CN) ₄] ²⁻	4.40 (1.8)	100.5
4	3.45 (2.1)	1.00 as [Hg(CN) ₄] ²⁻	4.47 (1.1)	102.0
5	N/D ^c	0.020 as [Fe(CN) ₆] ⁴⁻	0.020 (1.1)	100.0
6	0.004 (3.6)	0.010 as [Fe(CN) ₆] ³⁻	0.0145 (2.2)	105.0
7	0.030 (1.1)	0.020 as [Fe(CN) ₆] ⁴⁻	0.052 (2.8)	110.0
8	0.033 (2.1)	1.00 as [Fe(CN) ₆] ⁴⁻ + 20.0 SCN ⁻	1.030 (1.3)	99.7
9	0.007 (3.2)	0.010 as CN ⁻	0.0165 (1.4)	95.0

^a Sample source: 1, drum handling facility (filter effluent); 2, POTW (secondary effluent); 3, petroleum refinery (secondary effluent); 4, coke plant (secondary effluent); 5, rolling mill (filter effluent); 6, metals forming plant (primary effluent); 7, die casting plant (secondary effluent); 8, precious metal operation (reclaim water); 9, water treatment plant (filter effluent). ^b RSDs (%) (*n* = 3) are given in parentheses. ^c Not detected.

nine samples analyzed. The discrepancy in cyanide values found for the other three samples was probably caused by the interference problems inherent in the distillation procedures.

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