A Comparative Study of AgX (X = Cl⁻, Br⁻, I⁻ and N₃⁻) Solid-Phase Reactors for Flow-Injection Determination of Cyanide in Electroplating Wastewater

Meissam NOROOZIFAR,^{*†} Mozhgan KHORASANI-MOTLAGH,^{**} Aboozar TAHERI,^{*} and Rohollah ZARE-DORABEI^{*}

^{*}Analytical Research Laboratory, Department of Chemistry, University of Sistan & Baluchestan, P. O. Box 98135-674, Zahedan, Iran

^{**}Inorganic Research Laboratory, Department of Chemistry, University of Sistan & Baluchestan, Zahedan, Iran

In this study, a rapid flow injection-flame atomic absorption spectrometry for cyanide detection was developed. Different AgX (where X is Cl⁻, Br⁻, I⁻ and N₃⁻) solid-phase reagents (SPR) were tested for indirect determination of cyanide. In a single-line FIA system, the cyanide was allowed to react with AgX SPR, which in turn changed Ag ions in AgX to silver cyanide complexes in a sodium hydroxide carrier stream. The eluent containing the analyte as silver cyanide complexes was measured by FAAS. The calibration curve was linear up to 30 mg l⁻¹ with a detection limit of 0.05 mg l⁻¹ for cyanides. The sampling rate and the relative standard deviation were <1.09% and >200 h⁻¹, respectively. The method was applied to the determination of cyanide in electroplating wastewater.

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Cyanides comprise a large class of inorganic and organic compounds which are produced by many industrial processes. Cyanide is a by-product resulting from industrial processes such as electroplating,¹ organic synthesis² and metal mining.³ However, there are also natural sources for cyanide release. Because of their content of cyanogenic glycosides, many medicinal and food plants are toxic for humans.⁴⁻⁶ Cyanide is known to be one of the most rapidly acting and powerful poisons; it inhibits cytochrome oxidase of the mitochondrial respiratory chain.⁷ Most of the CN⁻ in blood concentrates in the erythrocytes,⁸ presumably bound to methemoglobin,⁹ an oxidized form of hemoglobin, which acts as a "cyanide sink".⁸ Therefore, because of its extreme toxicity, a great deal of research has been done for cyanide determination using various techniques and methods, for example, its determination and evaluation by volumetric and gravimetric,¹⁰ high-performance liquid chromatography (HPLC),¹¹ ion chromatography (IC),¹² voltammetry,¹³ amperometry,¹⁴ polarography,¹⁵ potentiometry using solid-state membrane ion-selective electrodes,^{16,17} atomic absorption spectroscopy,¹⁸⁻²⁰ spectrophotometric²¹ and fluorometry.²² Also, there are many FI methods with different detection systems that have been reported for the determination of cyanide in water and wastewater samples.²³⁻²⁵ However, there are several disadvantages of in these methods, such as requiring a chromatography system for the separation of cyanide ions from other ions, low sample frequency, the application of complicated flow-injection systems and being expensive.

Solid-phase reagents (SPR) have been used for the determination of inorganic and organic compounds in our laboratory, previously.²⁶⁻²⁹ The use of solid-phase reactors in FIA assemblies has been demonstrated to be useful for the *in situ* preparation of unstable reagents,³⁰ or very dilute solutions³¹ due to the redox characteristics, or as in the present case, the

instability of silver ion solutions to room light. Other advantages of solid-phase reactors over their counterparts in homogeneous systems have been described.^{32,33}

In the present work, we used four solid-phase reagents AgX, where X is Cl⁻, Br⁻, I⁻ and N₃⁻ for the indirect determination of free cyanide ions. Our primary study showed that free cyanide can release Ag(I) ions from these reactors. Sample aliquots were inserted in a redistilled water or sodium hydroxide stream and led through a solid-phase reactor to the FAAS detector for the indirect determination of cyanide. The FAAS detection of Ag(I) is more useful than the usual cyanide-FIA detection.

Experimental

Reagents and solutions

All reagents were prepared from analytical reagent-grade chemicals, unless specified otherwise, and were supplied from Merck. All aqueous solutions were prepared with redistilled water. A standard solution of cyanide, 1.0 mg ml⁻¹ was prepared by dissolving an amount of 0.4710 g of sodium cyanide in water in a 250-ml standard flask, and the solution was standardized against the standard silver nitrate solution.

Insoluble silver salts (AgX, X = Cl⁻, Br⁻, I⁻ and N₃⁻) were prepared by adding 500 ml of 0.3 mol l⁻¹ NaCl, NaBr, NaI and NaN₃ solutions to 500 ml of 0.3 mol l⁻¹ silver nitrate solutions. The obtained precipitate was filtered and dried at 90°C for 10 h. The solid was kept in a closed container until being used. All of the experimental procedures were performed with the reagents protected from daylight.

Solutions for carrier streams with different pH values were prepared by dilution of a Titrisol stock solution (0.1 mol l⁻¹ NaOH) with redistilled water.

Silica-gel beads (mesh 230 – 400, 0.04 – 0.063 mm) were treated for 3 h at 950°C for irreversible dehydration,³⁴ before mixing with solid-phase reagents. Titration of cyanide using a standard silver nitrate solution (Merck) and dithizone as an indicator was

[†] To whom correspondence should be addressed.
E-mail: mnoroozifar@chem.usb.ac.ir

Fig. 1 Schematic diagram of the single-line flow system used for the determination of cyanide. C.S., carrier stream; P, pump; S, sample; SPR, solid-phase reactor; FAAS, flame atomic absorption spectrometer detector; W, waste.

employed to validate the response of the FIA in the materials and determination of cyanide in standard solutions.¹⁰

Instrumentation

A schematic diagram of the single-line flow injection (FI) system is given in Fig. 1. A variable flow-rate peristaltic pump (Schlauchpumpe, Janke & Kunkel GmbH, Labortechnik, PA.B1) was used to pump carrier-streams and the sample through the manifold at a flow rate of 4.5 ml min⁻¹. Manifold lines consisted of 0.8 mm i.d. polyethylene tubing. A six-way injection valve (Rheodyne, Model 7125) allowed the sample to be directly loaded into a 220-μL loop, and subsequently injected into the carrier stream. After being placed in the carrier stream, the sample zone was pumped through the solid-phase reactor, and the products were channeled to a Philips flame atomic absorption spectrometer (Model PU 9100X) with an air-acetylene flame and a 5-cm optical path-length (burner). The light source was a silver hollow cathode lamp. The wavelength was set to 328.1 nm with a spectral slit-width of 0.5 nm and a 4-mA lamp current.

The solid-phase reactor

The solid-phase reactor was constructed from stainless tubing with i.d. and lengths of 7 and 100 mm, respectively, which were packed with silica-gel beads embedded by different AgX solid-phase reagents. The reactor was prepared by mixing powdered solid AgX with silica gel beads. This mixture was a homogenated using IR vibration mill (Shimadzu, Japan). Each packed reactor had to be conditioned for at least 30 min before use. Conditioning involved pumping redistilled water through the reactor for 15 min, followed by pumping a carrier stream, with different pH values, for another 15 min at a flow rate of 4.0 ml min⁻¹. The lifetime of the reactor was established by comparing the absorbance for the same standards from day to day. When the absorbance of the reactor decreased to 30% of the initial absorbance, the reactor usually had to be replaced. The total number of samples that could be processed with one column varied between 600 and 650, depending on the cyanide concentration.

Results and Discussion

Optimization of variables

The performance of the proposed single-line FI system depends on the efficiency of the reaction at the interface between the solid and liquid phases of the reactors, the pH of the carrier stream, the solid-phase reagents concentration in the reagent section and the loop volume.

The influences of the carrier flow rate were studied in the range 1.0 – 5.0 ml min⁻¹ for different reagents. The optimization is shown in Fig. 2. As can be seen, the optimum flow rates were 3.5 ml min⁻¹ for AgN₃, 4.0 ml min⁻¹ for AgCl and 4.5 ml min⁻¹ for

Fig. 2 Influence of the carrier flow rate on analytical signal: [AgX], 25% (m/m) (X: ◆ Cl⁻, ■ Br⁻, ▲ I⁻, ● N₃⁻); [CN⁻], 10.00 mg l⁻¹; T, 20°C; injection volume, 220 μL and carrier stream with pH 9 and 12 for AgN₃ and AgX (X are Cl⁻, Br⁻, I⁻), respectively.

AgBr and AgI. At lower flow rates from the optimum, the resulting signals were wide, because of increased longitudinal diffusion. Also, the results showed a decrease in the analytical signal with increasing flow rate. This means that the cyanide did not have enough time for interactions with the solid reagents. Based on this study, there is an increase in the absorbance with changing anions in the order of N₃⁻ > I⁻ > Br⁻ > Cl⁻.

The solubility of AgX varies with the pH or side reactions with the carrier, thus yielding different background values in the present system. The effect of the pH between 5.5 and 12.5 was evaluated. The analytical signals for the AgCl, AgBr and AgI reactors were increased with an increase in the pH between 5.5 and 12.5, but for AgN₃ the maximum absorbance was in the pH 9.0. At pH values down to 5.0, the solid reagents were soluble and the background absorbance was high. Thus, pH values of 11.0 and 9.0 were chosen as being optimum for AgX (X = Cl, Br and I) and AgN₃, respectively. Under the same condition, we obtained the highest absorbance for AgN₃ and AgI SPR.

The pressure drop across the reactor was diminished by using AgX-silica. The effect of the AgX:silica (or natural alumina) ratio on the absorbance between 5 and 30 was evaluated. At the end, 25% AgCl, AgBr and AgI and 20% AgN₃ mixtures were chosen to ensure a longer reactor lifetime and better sensitivity. Also, the experimental results showed that mentioned the absorbance for a natural alumina support was lower than silica support in the above optimum conditions.

The loop volume has a significant effect on absorbance, range of linearity and sensitivity, as one would expect. The response of the system was studied for various sample volumes injected (loop volume): 80, 120, 220, 300, 500 and 1000 μL. The peak height increased with an increase in the volume. Larger volumes resulted in higher, yet broader peaks. Consequently, the sampling frequency and the peak capacity sharply decreased. The loop volume of 220 μL was chosen as the optimum.

Finally, the effect of the reactor temperature at between 15 and 80°C was evaluated. The analytical signals for AgCl, AgBr and AgI were increased at between 15 and 30°C and then decreased with increasing in temperature. However, for AgN₃, the absorbance increased between 15 and 20°C, and then decreased with increasing temperature. A temperature of 20°C was chosen as the optimum.

Sample matrix interference

An investigation of anion interferences was carried out for the CN⁻; AgX reaction, by adding the interfering element to a CN⁻ standard solution. Anions were added as sodium or potassium salt. Tolerance is defined as the maximum weight ratio of

foreign compounds to CN^- producing an error of $\pm 5\%$ in the determination of $10.00 \text{ mg l}^{-1} \text{CN}^-$. The results are given in Table 1. The results revealed that most of the common ions have no interfering effect on the proposed method for the determination of cyanide using AgN_3 SPR. However, the anions such as NO_3^- , SO_3^{2-} as well as heavy metal, such as Hg^{2+} were interfered in the determination of cyanide using AgX SPR. Based on this study, AgN_3 is the best SPR for the determination

of cyanide in real samples.

Evaluation of the method

Using the experimental conditions described above, the calibration graphs were studied for three solid-phase reagents in the proposed system. Analytical figures of merits for four solid-phase reagents are given in Table 2.

The results showed that the AgN_3 and AgI solid-phase reagents are better than other proposed solid-phase reagents. The figures of merit, such as the samples rate, dynamic range, limit of quantitation (LOQ) and relative standard deviation (RSD %) of the proposed method with other published method using solid-phase reagents,^{19,20,36,37} are compared in Table 3. The figures of merit of the proposed method seem to be favorable compared with other published procedures for the determination of cyanide.

Under the same optimum conditions, the slope for calibration curves for all SPR suspended on natural alumina beads increased by a factor of approximately 2, and the sensitivity for determination of cyanide decreased.

Precision and recovery tests of proposed method

The precision of the method was determined by seven repetitive analyses of different standard solutions under the optimum conditions. The results indicate that the relative standard deviation (RSD) could be better than 1.09%. The method was also applied to a recovery test of five electroplating wastewater samples containing cyanide, and the test for each sample was carried out in triplicate using AgN_3 SPR. The recoveries were between 98.8 and 102.4.

Application to industrial samples

The proposed method was applied to the determination of cyanide in different kinds industrial effluents from different kinds electroplating industrials using AgN_3 SPR. The obtained results were compared with the provided by the recommended

Table 1 Influence of foreign compounds

Species	Tolerance ^a for different solid-reagents			
	AgCl (pH 11)	AgBr (pH 11)	AgI (pH 11)	AgN_3 (pH 9)
NO_3^-	1	5	8	90
S^{2-}	50	50	50	30
SO_3^{2-}	20	10	10	90
$\text{S}_2\text{O}_4^{2-}$	10	10	10	150
$\text{S}_2\text{O}_5^{2-}$	25	20	20	160
$\text{S}_2\text{O}_8^{2-}$	5	5	5	180
SO_4^{2-}	50	50	50	50
SCN^-	20	30	30	20
H_2PO_4^-	40	50	50	65
CO_3^{2-}	100	80	110	70
$\text{C}_2\text{O}_4^{2-}$	25	25	30	90
CH_3COO^-	50	70	50	65
F^-	40	40	40	30
Br^-	70	70	80	35
Cl^-	50	40	40	35
I^-	60	60	50	35
$\text{B}_4\text{O}_7^{2-}$	120	120	150	130
N_3^-	80	90	90	130

a. Maximum weight ratio of foreign ion to cyanide ion (10.0 mg l^{-1}) giving an error of $<5\%$.

Table 2 Analytical figures of merits for four solid-phase reagents

	AgCl	AgBr	AgI	AgN_3
Linear range/ mg l^{-1}	25	25	30	20
Calibration curve	$A^a = 0.012 + 0.017[\text{CN}^-]$ $r^b = 0.996$ $n^c = 12$	$A^a = 0.015 + 0.023[\text{CN}^-]$ $r^b = 0.994$ $n^c = 12$	$A^a = 0.018 + 0.025[\text{CN}^-]$ $r^b = 0.998$ $n^c = 12$	$A^a = 0.024 + 0.031[\text{CN}^-]$ $r^b = 0.999$ $n^c = 12$
Detection limit ^d / mg l^{-1}	0.17	0.14	0.08	0.05
Sampling rate/ h^{-1}	200	200	225	144

a. Absorbance. b. Correlation coefficient. c. Number of determinations. d. The detection limit (DL) was calculated using the equation $\text{DL} = 3S_{\text{bk}}/m$, where S_{bk} is the relative standard deviation of blank signal and m is the slope of the calibration graph.

Table 3 Analytical features of some FIA-FAAS systems used for cyanide determination

Solid-phase reagent	Sample	Sampling rate/ sample h^{-1}	Linear range/ mg l^{-1}	LOQ ^a / mg l^{-1}	RSD, %	Ref.
CuS	nd ^b	40 – 50	2.6 – 52	nd ^b	2	36
AgI entrapped in polymeric resin beads	Pharmaceutical	193	0.2 – 6.0	0.33	2.2 – 3.1	37
CdCO_3 suspended on silica gel beads	Industrial waste waters	72	Up to 15	0.60	1.22	19
ZnCO_3 suspended on silica gel beads	Industrial waste waters	65	Up to 25	0.40	1.41	20
AgCl suspended on silica gel beads	Industrial waste waters	200	Up to 25	0.59		
AgBr suspended on silica gel beads	Industrial waste waters	200	Up to 25	0.43		
AgI suspended on silica gel beads	Industrial waste waters	225	Up to 30	0.40	< 1.09	This work
AgN_3 suspended on silica gel beads	Industrial waste waters	144	Up to 20	0.30		

a. LOQ: Limit of quantitation. The LOQ was calculated using the equation $y = y_b + 10S_b$, where S_b is the relative standard deviation of blank signal and the calculated intercept in calibration curve was used as an estimate of y_b .⁵⁷ b. No data.

Table 4 Analysis of samples from different industrial electroplating wastewater samples^a

Sample	Proposed method/mg l ⁻¹	Standard method/mg l ⁻¹
1 ^b	6.14	6.27
2 ^b	5.31	5.36
3 ^c	1.67	1.70
4 ^d	1.39	1.30
5 ^d	0.78	0.80

a. Average of 10 replicates.

b. Gold industrial electrolyte bath solution.

c. Brass industrial electrolyte bath solution.

d. Copper industrial electrolyte bath solution.

method based on titration with silver nitrate. Table 4 lists the results obtained upon application of the proposed method. The obtained results were compared with those provided by the recommended method based on titration with silver nitrate by the paired *t*-test.³⁸ The paired *t*-test equation applied in statistics is: $t = \bar{d}\sqrt{n}/s_d$, where $\bar{d}$ and s_d are the mean and standard deviation, respectively, of *d* (the difference between paired values). For the pairs of values in Table 4, $\bar{d}$ is 0.028 and s_d is 0.079. The calculated *t* was found to be 0.793. The critical value of *t* (tabulated *t*) for *n* – 1 degrees of freedom (in this work 4) is 2.78 (*P* = 0.05). Since the calculated value of *t* is less than this, the null hypothesis is not rejected; the methods do not give significantly different results for cyanide concentration. These results indicate that the proposed method could be readily implemented on a very simple and stable FIA system.

Four solid-phase reactors in a single-line FI procedure were proposed for the indirect determination of cyanide in industrial effluent. The manifold is provided with a solid-phase reactor containing immobilized AgX, (X is Cl⁻, Br⁻, I⁻ and N₃⁻). The sample is forced through the reactor and the liberated silver ions, complexed by the cyanide in the sample solution, are monitored by a flame atomic-absorption spectrometer. The procedure resulted in a selectivity that fits well with the real samples tested. Based on the results given in Table 2, AgI and AgN₃ solid-phase reagents are the best reagents among the four reagents and the detection limit for AgN₃ is smaller than the other AgX. The proposed method is very simple, rapid and sensitive for the determination of cyanide. The dynamic range, detection limit, samples rate and RSD% of this method are acceptable relative to many of the previously reported methods for the determination of cyanide. The AgX reagents used are cheap, stable and readily available in every laboratory. The recovery for the proposed FIA system is close to 100%.

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