

Rapid Distillationless "Free Cyanide" Determination by a Flow Injection Ligand Exchange Method

EMIL B. MILOSAVLJEVIĆ,*
LJILJANA SOLUJIĆ, AND
JAMES L. HENDRIX

Department of Chemical and Metallurgical Engineering,
Mackay School of Mines, University of Nevada,
Reno, Nevada 89557

In the first part of this research, extensive species-dependent cyanide recoveries studies were performed using the approved standard methods available for determination of free cyanide. The data obtained show that serious problems are associated with both the CATC (cyanide amenable to chlorination) and WAD (weak and dissociable cyanide) methods. In the second part, a novel flow injection gas-diffusion method for the determination of free cyanide was developed. Complete cyanide recoveries even in the presence of a large excess of the free CN^- ion were found for the following species: $[\text{Zn}(\text{CN})_4]^{2-}$, $[\text{Cd}(\text{CN})_4]^{2-}$, $[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{Cu}(\text{CN})_4]^{3-}$, $[\text{Ag}(\text{CN})_2]^-$, $[\text{Hg}(\text{CN})_4]^{2-}$, and $\text{Hg}(\text{CN})_2$. No recoveries of CN^- were obtained from the species that are considered as non free cyanide producing ones, such as $[\text{Fe}(\text{CN})_6]^{3-/4-}$, $[\text{Co}(\text{CN})_6]^{3-}$, and $[\text{Au}(\text{CN})_2]^-$. The method developed is rapid, selective, reproducible, and easy to automate.

Introduction

Cyanide species in the environment originate mainly from a variety of industrial sources such as the electroplating industry, blast furnaces, coke-producing plants, gas works, etc. However, by far the greatest amount of cyanide-containing wastes are produced by precious metals milling operations. Consequently, the safe and economical treatment of milling wastes is a current problem of great interest. Presently available methods for removing and/or destroying cyanide have been summarized previously (1-3). In order to test the effectiveness and to compare different detoxification methods, reliable analytical procedures are required. The quality of the analytical results is very important since capital intensive business decisions related to detoxification and/or stabilization of cyanide-containing wastes must be made.

In a recent final rule (4) the U.S. Environmental Protection Agency (EPA) has promulgated maximum contaminant level goals (MCLGs) and/or maximum contaminant levels (MCLs) for five inorganic species among which was cyanide. The Agency accepted the view that a distinction should be made between free cyanides, which are readily bioavailable and extremely toxic, and total cyanides, which contain all cyanides including those low toxicity, inert species that do not dissociate CN^- ions. As a consequence, the EPA established that only free cyanides should be regulated since these are the species of health concern. Hence, the prescribed 0.2 mg/L MCLG/MCL applies to free cyanides as determined by a cyanide amenable to chlorination (CATC) method (5, 6). Of course, what the EPA classifies as free cyanide denotes the sum of the really free cyanide ion (CN^-), soluble hydrocyanic acid, and cyanides in the easily dissociable cyanide complexes. In the vast literature on the subject, one can find synonyms for the term free cyanide, such as simple cyanides, easily released, or easily dissociable cyanides, weak and dissociable cyanide, directly toxic cyanide, etc. In contrast, the sum of all potential CN^- groups in a sample, irrespective of origin, is universally called total cyanides.

The precious metals mining industry extensively uses an alternative procedure, the so-called weak acid dissociable (WAD) method for quantifying free cyanide (7) (the acronym WAD actually stands for *weak and dissociable*). The species-dependent cyanide recovery studies with the CATC and WAD procedures have identified some of the serious problems associated with these methods and stressed the need for more reliable analytical procedures for this analyte. The present paper reflects an effort to develop a novel flow injection (FI) ligand exchange (LE) method that avoids the pitfalls of the standard procedures.

The use of ligand exchange to displace cyanide from the coordination sphere of some metals is not a novel idea. Frant et al. described in 1972 a procedure for the analysis of free cyanide that makes use of EDTA (ethylenediaminetetraacetate) and an ion-selective electrode (8). Unfortunately, the method has a relatively high limit of detection, special calibration techniques had to be utilized, and EDTA does not release CN^- from mercury and silver cyano species.

* E-mail address: emilm@mines.unr.edu; Telephone: (702) 784-4213 or 784-6987; Fax: (702) 784-1766.

Ingersoll et al. (9) studied in detail a previously proposed technique for determining free cyanide that was based on a 2-h room temperature aeration procedure carried out at a pH of 4.5 in the presence of EDTA. Complexes such as $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and $[\text{Co}(\text{CN})_6]^{3-}$ gave essentially no cyanide recoveries. This was not a problem since these species usually do not produce free cyanide. However, partial and irreproducible recoveries of cyanide from many of the remaining cyanide complexes severely limited the utility of this technique. The authors suggested that a slight increase in temperature not only would increase the stripping rate of the hydrocyanic acid from solution but would also increase the rate of cyanide displacement from the complexes. However, it was also pointed out that temperature change would increase the risk of decomposition of the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ species.

In a recent patent, Bilger and Wolf (10) also employed ligand exchange in combination with high temperature to develop a technique for continuous determination of cyanide in aqueous solution. The long-known colorimetric detection based on the red cyanide-picric acid color complex was utilized (11). In order to liberate cyanide from some of its complexes, the mixture had to be heated in a gas-tight manner for up to 60 min at up to 120 °C. The chelating agent used for CN^- release was either EDTA or DTPA (diethylenetriaminepentaacetic acid). By this technique, CN^- is released from cyano complexes of zinc, cadmium, copper, nickel, and silver. Unfortunately, incomplete CN^- release was obtained from $[\text{Au}(\text{CN})_2]^-$ and slight CN^- release was found for cyano complexes of iron and cobalt. There is no information on the behavior of the most problematic $\text{Hg}(\text{CN})_2$ and $[\text{Hg}(\text{CN})_4]^{2-}$ species. On the basis of the stabilities of these cyano compounds, one would expect that the release of CN^- from them would also be incomplete. The aforementioned problems with incomplete and/or slight release of cyanide from certain complexes put substantial limits on the applicability of the method for free cyanide determination.

Also, it should be noted here that the methods based on harsh experimental conditions (prolonged heating at temperatures around 100 °C) are prone to various interferences.

Experimental Section

Materials. Potassium cyanide, potassium hexacyanoferrate(II), potassium hexacyanoferrate(III), potassium hexacyanocobaltate(III), mercury(II) cyanide (Aldrich Chemical Company), potassium dicyanoaurate(I), and potassium dicyanoargentate(I) (AESAR/Johnson Matthey) were obtained as reagent-grade chemicals and were used as received. Potassium salts of tetracyanocuprate(I), tetracyanonickelate(II), tetracyanomercurate(II), tetracyanocadmiate(II), and tetracyanozincate(II) were synthesized and purified by the literature methods (12). A stock solution of 1 g/L (1000 ppm) was made from KCN and checked using the Liebig method (13). Standard cyanide solutions, which were made to be 0.01 M in NaOH, were prepared daily by diluting aliquots of the stock solution to the appropriate volume. Stock solutions of individual complexes were made to be 1 g/L (1000 ppm) in cyanide. Standard solutions of cyanide complexes, which were also made to be 0.01 M in NaOH, were prepared daily by diluting aliquots of the stock solution to the appropriate volume.

Instrumentation and Analytical Procedures. Analytical procedures utilized for the comparison of the standard

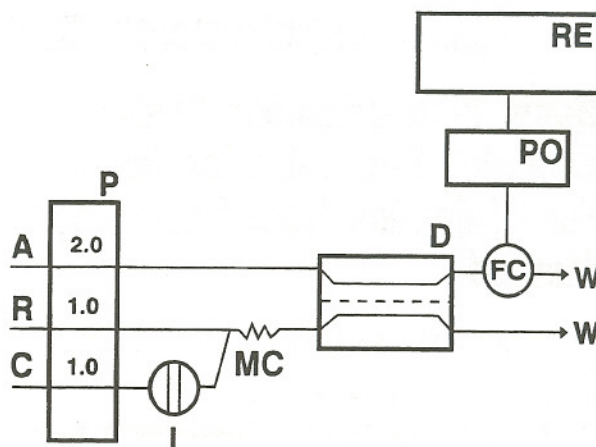


FIGURE 1. FI manifold used for quantification of cyanide in the pretreated sample. C, carrier (0.2 M HCl); R, reagent (0.2 M HCl); A, acceptor solution (0.01 M NaOH); P, peristaltic pump; I, injection valve (100 μL sample loop); MC, mixing coil (30 cm \times 0.5 mm i.d.); D, diffusion cell; FC, amperometric flow-through cell; PO, potentiostat; RE, recorder; W, waste. Flow rates are given in mL/min.

methods for free cyanide determination are described elsewhere (5–7). The only difference was that cyanide quantification in the absorbing NaOH solution was performed by the interference free ion chromatography method (14). If not otherwise specified and in order to allow the comparisons of the two methods, distillations and/or chlorinations were performed on a 100-mL aliquot of a given cyanide standard to which 400 mL of water was added. The volume of the NaOH absorbing solution was also 100 mL.

The FI manifold, which is illustrated in Figure 1, was constructed from a FIAstar 5020 analyzer (Tecator, Inc.), equipped with two peristaltic pumps and a Tecator Chemifold V gas diffusion cell. The membrane used was a PTFE one supplied with the Chemifold. A variable volume injector L-100-1 (Tecator, Inc.) equipped with a 100- μL sample loop was used. All connections were made with a 0.5 mm i.d. PTFE tubing.

The thin layer flow-through amperometric cell (Dionex Corp.) consisted of a silver working and platinum counterelectrode. The reference electrode was a Ag/AgCl (1 M NaCl), and it was separated from the flowing stream by an ion exchange Nafion membrane. The flow-through cell was potentiostated, and currents were measured by an pulsed amperometric detector (Dionex Corp.) operating in a single potential mode. The resulting transient FI signals were recorded on a strip chart Honeywell electronic 195 recorder.

Prior to the FI quantification finish, standards and samples were pretreated in the following manner: To a 100-mL cyanide standard or sample (pH \sim 12), two and one drop of ligand exchange reagents UNR/PEA LE-A (P/N 001-416) and LE-B (P/N 001-417) were added, respectively (UNR = University of Nevada, Reno; PEA = Perstorp Analytical Environmental, Wilsonville, OR).

Results and Discussion

Comparisons of Standard Methods. The cyanide species investigated in the present research are those that are likely to be found throughout the precious metals milling and/or leaching circuits as well as in the samples originating from other cyanide-containing wastes. Table 1 summarizes the species-dependent cyanide recoveries obtained with the

TABLE 1

Species-Dependent Cyanide Recoveries (%)
Obtained with the WAD and CATC Free Cyanides
Determination Methods^a

species	0.20 $\mu\text{g/mL CN}^-$		2.00 $\mu\text{g/mL CN}^-$	
	WAD	CATC	WAD	CATC
$[\text{Zn}(\text{CN})_4]^{2-}$	102.3 (1.9)	99.5 (0.5)	100.9 (0.3)	104.4 (2.6)
$[\text{Cd}(\text{CN})_4]^{2-}$	101.5 (1.5)	103.8 (1.3)	101.6 (1.8)	102.9 (1.7)
$[\text{Cu}(\text{CN})_4]^{3-}$	97.3 (1.1)	97.7 (1.9)	96.0 (1.5)	98.0 (1.2)
$[\text{Ag}(\text{CN})_2]^-$	97.8 (1.6)	97.8 (1.2)	99.0 (2.7)	54.8 (2.9)
$[\text{Ni}(\text{CN})_4]^{2-}$	105.8 (1.2)	104.2 (3.5)	97.3 (1.8)	72.0 (11)
$[\text{Hg}(\text{CN})_4]^{2-}$	71.3 (2.5)	95.8 (2.5)	58.9 (2.6)	97.6 (3.3)
$\text{Hg}(\text{CN})_2$	38.8 (9.0)	98.0 (5.9)	20.7 (7.1)	85.4 (3.8)
$[\text{Fe}(\text{CN})_6]^{4-}$	0.0	0.0	0.0	0.0
$[\text{Fe}(\text{CN})_6]^{3-}$	0.0	0.0	0.0	0.0
$[\text{Au}(\text{CN})_2]^-$	0.0	0.0	0.0	0.0
$[\text{Co}(\text{CN})_6]^{3-}$	0.0	0.0	1.9 ^b (2.9)	1.9 ^b (4.3)

^a % relative standard deviations ($n = 3$) are given in parentheses.

^b Commercial product contains some free cyanide.

standard free cyanide determination methods. As may be seen from this table, complete cyanide recoveries were obtained from the relatively unstable complexes such as Cu, Cd, and Zn, and no recoveries were obtained from the stable Fe, Co, and Au cyano complexes. The problems obviously start with the complexes of medium stabilities such as the two Hg species and the cyano complexes of Ni and Ag. For example, the WAD method at 2.00 mg/L CN^- levels achieves complete cyanide quantification from Ni and Ag cyano species. For $[\text{Hg}(\text{CN})_4]^{2-}$, the recovery is about 60%, whereas only 20% of cyanide from $\text{Hg}(\text{CN})_2$ was recovered. On the other hand, the CATC method has higher recoveries for Hg complexes, but lower ones for Ni and Ag cyano species.

To be a viable method for determination of free cyanide, the accepted procedure should give complete recoveries of cyanide from the less stable cyanide complexes and no recoveries from the more stable species, such as $[\text{Fe}(\text{CN})_6]^{3-/4-}$, $[\text{Co}(\text{CN})_6]^{3-}$, and $[\text{Au}(\text{CN})_2]^-$. Unfortunately, neither the CATC nor the WAD procedure fulfills these criteria.

There is, however, an even more serious problem associated with these methods. Cyanide recoveries from certain species are also concentration dependent, which is illustrated in Figure 2 for a couple of cyano complexes (the concentrations presented on the abscissa are the actual concentrations of cyanide samples in the distillation and/or chlorination vessels). At very low cyanide concentrations, recoveries from $[\text{Ag}(\text{CN})_2]^-$ by the CATC methods were around 100%. However, at 5 mg/L levels they dip to below 35%. The situation is even worse for cyanide recoveries from $\text{Hg}(\text{CN})_2$ with the WAD method. For example, at 5 mg/L levels, they are below 4%.

This explains why many analysts involved in cyanide analyses are frustrated with the lack of reproducibility and repeatability of the free cyanide analyses methods. The results even depend on how a given sample is diluted prior to chlorination and/or distillation. The "good" analytical chemist can actually tailor the results while at the same time following the analytical protocols to a letter, which only require that cyanide concentration in the chlorination vessel and/or distillation flask does not exceed the 10 mg/L levels. The highest concentration tested in the present work was 5 mg/L. However, from the shape of these graphs, one can extrapolate to 10 mg/L levels.

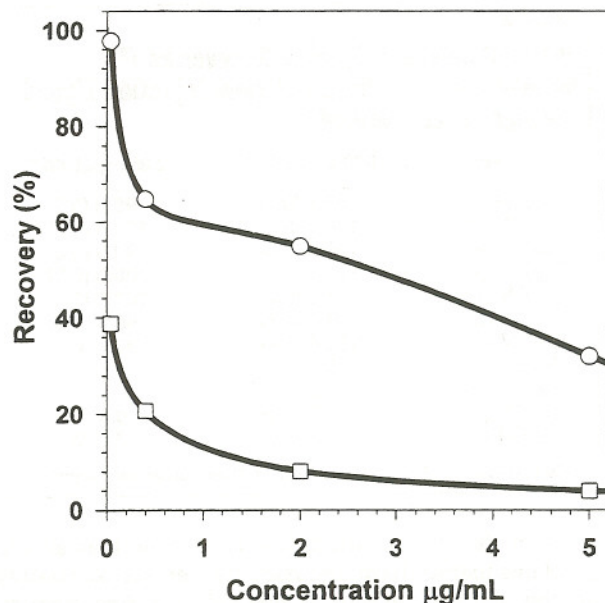


FIGURE 2. Concentration-dependent cyanide recoveries obtained by the CATC and WAD methods for $[\text{Ag}(\text{CN})_2]^-$ (○) and $\text{Hg}(\text{CN})_2$ (□), respectively.

To be succinct, we will enumerate just some additional problems associated with the standard procedures for free cyanide analysis. Further information is available in the literature (9, 15, 16).

One of the main problems associated with standard cyanide determination procedures is the analysis time. With the protocols prescribing hour-long distillations, chlorination also taking 1 h, and the two separate aliquots of a given sample having to be distilled and analyzed independently in order to determine the CATC levels, one can envision the bottlenecks in laboratories performing these assays. Also, since the chlorination and distillation are so protracted, it is advisable that both be carried out in the dark. Prolonged exposure to light might increase the free cyanide levels in certain samples which contain $[\text{Fe}(\text{CN})_6]^{3-}$ and/or $[\text{Fe}(\text{CN})_6]^{4-}$, although these complexes are considered non free cyanide producing ones. This increase is caused by the photoassisted dissociation of CN^- from the corresponding iron cyano species (17).

In addition, it should be stressed here that hour-long macro-distillation procedures have inherently low reproducibility. In order to alleviate this problem, some companies have put on the market micro- or midi-distillation apparatus. However, even with these systems the reproducibility is far from satisfactory. For example, the company's own quality-check data for one of the midi-distillation system gave the following recoveries for a relatively high 0.50 mg/L cyanide standard: 80% (0.40 mg/L); 106 (0.53); 86 (0.43); 92 (0.46); and 104 (0.52). Also, high distillation temperatures can create a safety hazard, and macro methods require large amounts of samples and special distillation equipment to capture HCN generated by the distillation.

Both the CATC and WAD methods suffer from various interferences. The CATC method suffers from serious interferences even from some ubiquitous species such as NH_4^+ , NO_2^- , SCN^- , etc. For example, when the ammonium cation is present in a sample at a 100:1 ratio at 0.2 ppm CN^- levels, recoveries of only 57% were obtained (9).

TABLE 2

Species-Dependent Cyanide Recoveries (%)
Obtained with the Proposed Flow Injection Ligand
Exchange (FI/LE) Method^a

species	0.20 $\mu\text{g/mL CN}^-$	2.00 $\mu\text{g/mL CN}^-$
$[\text{Zn}(\text{CN})_4]^{2-}$	97.4 (0.7)	98.5 (0.7)
$[\text{Cd}(\text{CN})_4]^{2-}$	100.0 (0.8)	100.0 (0.2)
$[\text{Cu}(\text{CN})_4]^{3-}$	100.9 (1.3)	99.0 (0.6)
$[\text{Ag}(\text{CN})_2]^-$	101.8 (0.9)	100.0 (0.5)
$[\text{Ni}(\text{CN})_4]^{2-}$	104.3 (0.2)	103.0 (0.5)
$[\text{Hg}(\text{CN})_4]^{2-}$	100.0 (0.6)	99.0 (0.3)
$\text{Hg}(\text{CN})_2$	103.4 (0.4)	98.0 (0.3)
$[\text{Fe}(\text{CN})_6]^{4-}$	0.0	0.0
$[\text{Fe}(\text{CN})_6]^{3-}$	0.0	0.0
$[\text{Au}(\text{CN})_2]^-$	1.3 (0.0)	0.0
$[\text{Co}(\text{CN})_6]^{3-}$	2.9 (0.0)	2.0 (0.0)

^a % relative standard deviations ($n = 3$) are given in parentheses.

From the aforementioned, it is obvious that all the problems that we have discussed put serious constraints on the standard approved methods for free cyanide determination and that better analytical procedures are needed to obtain more reliable analytical data for regulatory and other purposes.

Flow Injection Ligand Exchange (FI/LE) Method. The analytical procedure employed for determination of free cyanide may be divided into two steps: (1) sample pretreatment and (2) cyanide quantification finish. In the pretreatment step, a sequestering reagent (a mixture of ligand exchange reagents UNR/PEA A and B) is added at room temperature to a cyanide-containing sample. The sequestering (releasing) agents form thermodynamically very stable complexes with various transition metal ions, resulting in the release of the CN^- ion from the coordination sphere. The sequestering reagents used release the CN^- ion from all of the corresponding metal complexes with the exception of $[\text{Fe}(\text{CN})_6]^{3-/4-}$, $[\text{Co}(\text{CN})_6]^{3-}$, and $[\text{Au}(\text{CN})_2]^-$, the species that do not dissociate CN^- ions under the commonly used methods for free cyanide determination. The treated sample then undergoes an assaying (finishing) step in order to determine the free cyanide concentrations.

In our studies, we have employed FI gas diffusion with amperometric detection for quantification of CN^- . The manifold utilized is depicted in Figure 1. The details of the experimental setup, apparatus, and procedure used have been described previously (18–20). The flow injection analytical cycle begins by introducing 100 μL of the pretreated sample into the acidified carrier line which takes the sample plug to a confluence point with an acid stream. The mixing coil positioned downstream ensures thorough acidification of the sample. The acidified sample then passes through a donor channel of the gas-diffusion unit and flows to waste. At the same time, NaOH trapping solution 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 and is converted to the sodium salt in the acceptor channel. Cyanide in the acceptor solution is quantified by the amperometric flow-through detector equipped with the silver working electrode.

Species-dependent cyanide recoveries at two cyanide concentration levels obtained with the new FI/LE method are shown in Table 2. As may be seen from this table, complete CN^- recoveries were found for $[\text{Zn}(\text{CN})_4]^{2-}$,

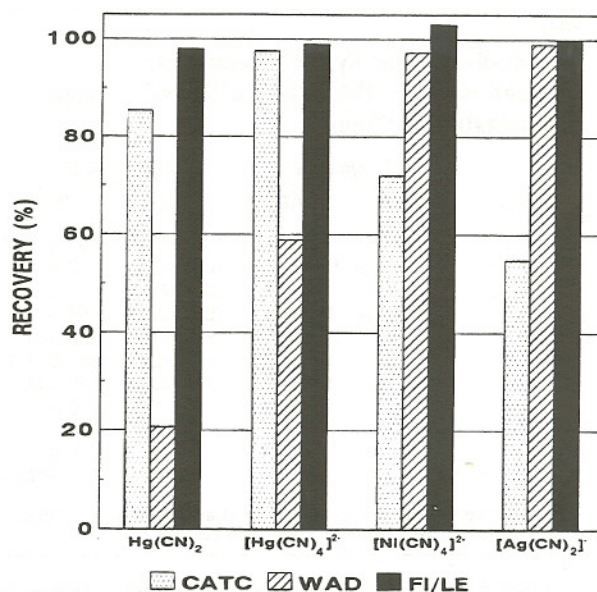


FIGURE 3. Species-dependent cyanide recoveries (at 2.00 $\mu\text{g/mL CN}^-$ levels) obtained by the FI/LE, CATC, and WAD methods for the moderately stable cyano complexes.

$[\text{Cd}(\text{CN})_4]^{2-}$, $[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{Cu}(\text{CN})_4]^{3-}$, $[\text{Ag}(\text{CN})_2]^-$, $[\text{Hg}(\text{CN})_4]^{2-}$, and $\text{Hg}(\text{CN})_2$. Essentially no recoveries of CN^- were obtained from the species which are considered non free cyanide producing, such as $[\text{Fe}(\text{CN})_6]^{3-/4-}$, $[\text{Co}(\text{CN})_6]^{3-}$, and $[\text{Au}(\text{CN})_2]^-$.

Figure 3 shows the comparison of cyanide recoveries from the four moderately stable cyano complexes obtained by the proposed method and the standard methods available for free cyanide determination. The comparison shows that the newly developed method is far superior to either the CATC or the WAD methods.

The analysis time per sample with the novel FI method, without the automation of the pretreatment step, is in the range of 2–3 min, compared to ~2.5 h for the CATC method. Repeatability of the method at MCL levels (0.20 $\mu\text{g/mL}$) is better than 2% relative standard deviation ($n = 3$) for all species shown in Table 2. The limit of detection (LOD) was found to be ~1 $\mu\text{g/L}$ (ppb). Use of the FI gas-diffusion preconcentration manifold, similar to those described previously (18, 21, 22), should lower the LOD values to the submicrogram per liter range.

The combination of room temperature ligand exchange induced release of CN^- from the corresponding cyano complexes, and the gas-diffusion separation step prior to amperometric quantification of CN^- renders the developed method nearly specific toward the analyte. Nevertheless, the ions that do interfere in the classical free cyanides determination methods as well as some other anions were tested. The results obtained are summarized in Table 3.

The only potential interference in the FI/LE determination of cyanide is the S^{2-} ion. However, this is not a serious problem since sulfide, if present in a given sample, should immediately upon sampling be precipitated with Pb^{2+} . The standard method protocols advise this procedure be carried out in order to avoid the reaction of S^{2-} with CN^- . Our experiments have shown that if PbCO_3 is used for sulfide precipitation, the supernatant-containing cyanide should be filtered immediately. This procedure is necessary since rapid loss of CN^- due to the formation of SCN^- is otherwise observed. For example, when 100 mL of a solution

TABLE 3

Determination of CN^- in the Presence of Possible Interferents^{a,b}

ion	ratio ^c	CN^- found ($\mu\text{g/mL}$)	ratio ^c	CN^- found ($\mu\text{g/mL}$)
NH_4^+	144	0.200 (1.3)	1440	0.202 (0.0)
OCN^-	62	0.200 (1.3)	620	0.202 (1.3)
SCN^-	45	0.200 (1.3)	450	0.204 (0.7)
SO_4^{2-}	27	0.203 (1.3)	270	0.199 (1.2)
$\text{S}_2\text{O}_3^{2-}$	23	0.205 (1.3)	230	0.204 (1.2)
Cl^-	73	0.201 (0.0)	730	0.200 (0.7)
Br^-	33	0.197 (0.0)	330	0.202 (0.8)
I^-	20	0.205 (0.0)	200	0.203 (1.4)
CO_3^{2-}	43	0.198 (1.3)	430	0.197 (1.1)
NO_2^-	56	0.200 (1.3)	560	0.202 (1.1)
NO_3^-	42	0.197 (1.3)	420	0.202 (1.2)

^a All samples contained 0.200 $\mu\text{g/mL}$ CN^- and 20 or 200 $\mu\text{g/mL}$ of the potentially interfering ion. ^b % relative standard deviations ($n = 3$) are given in parentheses. ^c Molar concentration ratio ion/ CN^- .

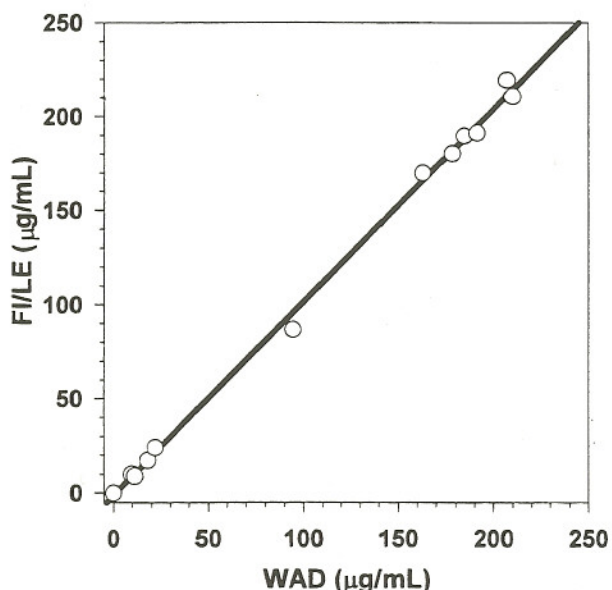


FIGURE 4. Comparison of the cyanide values found by the FI/LE and WAD methods for a series of real-world samples.

containing 2.00 $\mu\text{g/mL}$ of S^{2-} and CN^- was treated with 50.0 mg of PbCO_3 and filtered immediately, 99.5% of CN^- was recovered. However, when the same solution was filtered after 30 min, only 66.5% of cyanide was recovered.

A series of real-world samples obtained from various precious metals milling operations (process streams, pilot plants, and wastes) were analyzed by the new and WAD cyanide methods. As may be seen from Figure 4, linear correlation was found for the wide interval of cyanide concentrations (12 $\mu\text{g/L}$ –210 $\mu\text{g/mL}$). Slope and correlation coefficient of 1.02 and 0.9990 were obtained, respectively.

Conclusion

From the above discussion, it is obvious that the proposed method has significant advantages over the standard approved methods available for determining the free cyanides levels. Some characteristics and/or advantages of the FI/LE method are summarized below:

- (1) Complete cyanide recoveries from all metal cyano complexes that produce free cyanides.
- (2) Cyanide recoveries are not concentration dependent throughout the dynamic range of the method (1 $\mu\text{g/L}$ –5 $\mu\text{g/mL}$).

(3) No cyanide recoveries from stable metal cyano species that are considered nontoxic.

(4) Total analysis time 2–3 min, compared to ~2.5 h for the CATC method.

(5) Limit of detection ~ 1 $\mu\text{g/L}$ (ppb).

(6) No known interferants.

(7) Less than 1 mL of sample required for triplicate analysis even at concentration near the limit of detection, compared to ~ 1.5 L for WAD and CATC methods.

(8) Since no distillation is required, the method is easy to use in the field as well as to automate.

Acknowledgments

The authors acknowledge financial support of Perstorp Analytical Environmental from Wilsonville, OR.

Literature Cited

- (1) Scott, S. In *Proceedings of Conference on Cyanide and the Environment*; Tucson, AZ, 1984; Colorado State University: Fort Collins, CO, 1985; pp 307–325.
- (2) Knorre, H.; Griffiths, A. In *Proceedings of Conference on Cyanide and the Environment*; Tucson, AZ, 1984; Colorado State University: Fort Collins, CO, 1985; pp 519–529.
- (3) Devuyrst, E. A.; Conard, B. R.; Hudson, W. In *Proceedings of Conference on Cyanide and the Environment*; Tucson, AZ, 1984; Colorado State University: Fort Collins, CO, 1985; pp 469–486.
- (4) U.S. Environmental Protection Agency. *Fed. Regist.* **1992**, 57 (138), 31776–31849.
- (5) U.S. Environmental Protection Agency. *Methods for Chemical Analysis of Water and Wastes*; Environmental Monitoring and Support Laboratory: Cincinnati, OH, 1983; Method 335.1.
- (6) *Standard Methods for the Examination of Water and Wastewater*, 17th ed.; Clesceri, L. S., Greenberg, A. E., Trussell, R. R., Eds.; American Public Health Association: Washington, DC, 1989; pp 4-34–4-35.
- (7) *Standard Methods for the Examination of Water and Wastewater*, 17th ed.; Clesceri, L. S., Greenberg, A. E., Trussell, R. R., Eds.; American Public Health Association: Washington, DC, 1989; pp 4-38–4-39.
- (8) Frant, M. S.; Ross, J. W., Jr.; Riseman, J. H. *Anal. Chem.* **1972**, 44, 2227–2230.
- (9) Ingersoll, D.; Harris, W. R.; Bomberger, D. C.; Coulson, D. M. *Development and Evaluation of Procedures for the Analysis of Simple Cyanides, Total Cyanides, and Thiocyanate in Water and Waste Water*; EPA-600/4-83-054; U.S. EPA: Washington, DC, 1983.
- (10) Bilger, H. E.; Wolf, H. H. U.S. Patent 4,871,681, 1989.
- (11) Fisher, F. B.; Brown, J. S. *Anal. Chem.* **1952**, 24, 1440–1444.
- (12) Brauer, G. *Handbook of Preparative Inorganic Chemistry*, 2nd ed.; Academic Press: New York, 1963; pp 1087–1559.
- (13) Vogel, A. I. *A Textbook of Quantitative Inorganic Analysis*, 3rd ed.; Longman: London, 1961; pp 271–272.
- (14) Rocklin, R. D.; Johnson, E. L. *Anal. Chem.* **1983**, 55, 4–7.
- (15) Milosavljević, E. B. In *Proceedings of Conference on Successful Mine Reclamation—What Works*; Sparks, NV, 1992; pp 285–303.
- (16) Milosavljević, E. B.; Hendrix, J. L. In *Proceedings of Managing the Mine Environment*; Randol at MINExpo '92, Las Vegas, NV, 1992; pp 169–174.
- (17) Rader, W. S.; Solujić, L.; Milosavljević, E. B.; Hendrix, J. L.; Nelson, J. H. *Environ. Sci. Technol.* **1993**, 27, 1875–1879.
- (18) Milosavljević, E. B.; Solujić, L.; Hendrix, J. L.; Nelson, J. H. *Anal. Chem.* **1988**, 6, 2791–2796.
- (19) Utley, D. *Analyst* **1990**, 115, 1239–1242.
- (20) Pollema, C. H.; Hendrix, J. L.; Milosavljević, E. B.; Solujić, L.; Nelson, J. H. *J. Photochem. Photobiol. A: Chem.* **1992**, 66, 235–244.
- (21) Zhu, Z.; Fang, Z. *Anal. Chim. Acta* **1987**, 198, 25–36.
- (22) Kubán, V. *Anal. Chim. Acta* **1992**, 259, 45–52.

Received for review May 9, 1994. Revised manuscript received October 17, 1994. Accepted October 24, 1994.*

ES940294M

* Abstract published in *Advance ACS Abstracts*, December 1, 1994.