

Formation of Thiocyanate During Removal of Sulfide as Lead Sulfide Prior to Cyanide Determination

The Analyst

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Most standard and other analytical procedures for the determination of cyanide suffer from sulfide interferences. As sulfide and cyanide co-exist in many 'real world' samples, this presents a significant problem. The standard procedure for removal of sulfide is its precipitation with a lead salt. However, lower cyanide recoveries are often obtained if this procedure is performed improperly. In this paper, the chemistry of the sulfide interferences in cyanide determination methods is explained and procedures are suggested for alleviating the problem.

Keywords: Cyanide determination; sulfide interferences; thiocyanate formation; flow injection; ion chromatography

Introduction

Cyanide in its various forms is a waste and/or a by-product of a variety of industrial operations, such as electroplating, electronics manufacturing, precious metals extraction, pharmaceutical production, blast furnaces, petroleum refineries and coke producing plants. Consequently, the safe and economical treatment of wastes containing various cyano species is currently a problem of great interest. In order to test the effectiveness of numerous detoxification methods, reliable analytical procedures are required. Unfortunately, the standard procedures for the determination of cyanide¹⁻⁵ suffer from various problems that have been discussed previously.⁶⁻¹⁰ The main problem with these procedures is the concentration-dependent cyanide recovery.¹⁰ In addition, the standard procedures and most other analytical procedures for the determination of cyanide manifest a serious sulfide interference. Drikas and Routley⁷ have examined the addition of lead salts for removing sulfide when using a 'total' cyanide determination method. They observed lower recoveries of cyanide when PbCO₃ was used for sulfide precipitation and suggested that some of the cyanide is lost by complexation or by occlusion on the precipitated PbS. In order to eliminate sulfide interference, a stoichiometric addition of lead acetate was proposed. To achieve this, a titration of the available sulfide with lead acetate using a redox electrode for end-point determination was utilized.

Our research group has recently described a novel flow injection-ligand exchange (FI-LE) method¹⁰ for 'free cyanide' determination that has significant advantages over the standard CATC¹⁻⁴ (cyanide amenable to chlorination) and WAD⁵ (weak and dissociable or weak acid dissociable cyanide) procedures. The sulfide ion was identified as the sole interferent in the FI-LE method. When carrying out the recommended treatment³

with PbCO₃, it was observed that the rapid loss of cyanide is due to the formation of thiocyanate and not to complexation and/or occlusion of cyanide as suggested earlier.⁷ Hence, it was decided to investigate in detail the reactions between sulfide and cyanide ions, in homogeneous and heterogeneous systems, as related to the development of reliable procedures for alleviating sulfide interferences in cyanide determination methods.

Experimental

Reagents and Materials

All chemicals were of analytical-reagent grade and de-ionized/distilled water was used throughout. A stock solution of 50.0 mmol dm⁻³ cyanide was made from >99.5% MicroSelect potassium cyanide (Fluka, Buchs, Switzerland). A stock solution of 50.0 mmol dm⁻³ sulfide was prepared daily from Na₂S·9H₂O (Fisher Scientific, Fair Lawn, NJ, USA). Standard cyanide and sulfide solutions, which were made to be 10.0 mmol dm⁻³ in NaOH, were prepared by diluting aliquots of the stock solution to the appropriate volume. Potassium thiocyanate 99+%, (Aldrich, Milwaukee, WI, USA), PbCO₃ ACS grade (Aldrich), CdCO₃ 98% (Aldrich) and PbS 99.9+%, (Aldrich) were used as received.

Instrumentation and Apparatus

Standard distillation analytical procedures used in the present work to determine the effects of sulfide on cyanide determination are described elsewhere.^{2,3,5} Most of the cyanide determinations were performed using a recently developed flow injection (FI) method.¹⁰

Thiocyanate levels were determined by ion chromatography (IC) with UV detection at 215 nm. A Dionex (Sunnyvale, CA, USA) Model 4000i ion chromatograph, equipped with Dionex OmniPac Pax100 guard and separator columns, a 0.1 cm³ sample loop and a Dionex variable-wavelength detector, was used to obtain chromatograms. The eluent was a 5.0 mmol dm⁻³ aqueous solution of NaClO₄ containing a 10% volume fraction of methanol and its flow rate was 1.1 cm³ min⁻¹. The output data were collected and analysed by a Hewlett-Packard (Avondale, PA, USA) Vectra QS/16 computer utilizing Dionex AI-450 chromatographic software. The limit of detection of this IC method is 5 µg dm⁻³ and the precision was better than a relative standard deviation of 1.8% at the 10.0 µg dm⁻³ level.

Results and Discussion

Reaction of Cyanide With Sulfide in Homogeneous and Heterogeneous Systems

Our preliminary investigations, contrary to previous research,⁷ indicated that cyanide is relatively rapidly oxidized to thiocya-

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nate in the presence of sulfide and PbCO_3 . In order to study this process in detail, 0.100 dm³ (pH 12) of an equimolar mixture of cyanide and sulfide (50.0 $\mu\text{mol dm}^{-3}$) was shaken with 50 mg of PbCO_3 in a constant-temperature bath (25 °C) for 24 h. Samples were taken periodically and analysed for cyanide and thiocyanate utilizing FI and IC methods. The data obtained are summarized in Fig. 1.

As can be seen from Fig. 1, there is a rapid decrease in cyanide concentration as a function of time. Since the concentration profiles for cyanide reacted and thiocyanate formed almost coincide, it can safely be concluded that cyanide is quantitatively converted into thiocyanate. A control experiment containing the same cyanide and sulfide levels in a homogeneous solution (no PbCO_3 added) showed a very slow conversion of cyanide into thiocyanate. For example, after 24 h, less than 0.5% of cyanide was oxidized to thiocyanate.

The importance of rapid filtration of PbS formed when using the standard protocols for alleviating sulfide interference in cyanide determination methods is illustrated in Fig. 2. In this experiment, the molar ratio of sulfide to cyanide was 10 and again 50 mg of PbCO_3 were added. As can be seen, 90% of the initial cyanide is converted into thiocyanate after only 30 min.

In an attempt to characterize this reaction further, an experiment was run with PbS as the sole 'sulfur' source. The data obtained are shown in Fig. 3. Surprisingly, the cyanide was again converted into thiocyanate. The initial conversion rates

are slower when compared with the experiment depicted in Fig. 1; however, the per cent. conversions at the end of the experiment are higher. For example, in the experiment illustrated in Fig. 3A, the final thiocyanate concentration was 45.1 $\mu\text{mol dm}^{-3}$ (89.5% conversion) compared with the corresponding value of 33.5 $\mu\text{mol dm}^{-3}$ (66.5% conversion) for the experiment shown in Fig. 1.

The data presented so far indicate that PbS acts as both a catalyst and a reactive sulfur source in this reaction. This observation is supported by the fact that cyanide and sulfide in a homogeneous aqueous solution react very slowly to form thiocyanate (*vide infra*).

Reaction of Cyanide With Sulfide During Distillation Procedures

In standard total cyanide determination methods,^{2,3} the cyanide, as hydrocyanic acid (HCN), is released from the acidified sample (sulfuric acid) by means of a 1 h reflux distillation. The hydrogen cyanide gas liberated is absorbed in a scrubber containing NaOH solution. The cyanide in the absorbing solution is then quantified by colorimetric or potentiometric (ion-selective electrode) procedures. The protocols for standard cyanide determinations recommend the addition of 50 mg of PbCO_3 to the NaOH absorbing solution prior to distillation if compounds that may produce H_2S during the procedure are present in cyanide-containing samples. In order to quantify the conversion of cyanide into thiocyanate under distillation conditions, a series of samples of various composition were subjected to the distillation procedure. Identical samples were run in triplicate with and without the addition of precipitating reagents (PbCO_3 and CdCO_3) to the NaOH absorbing solution. After a prescribed 1 h distillation, the precipitate in the scrubber was filtered using a 1.2 μm syringe filter and the levels of cyanide and thiocyanate in the solution were determined using the previously described methods. The data obtained are summarized in Table 1 from which it can be seen that the

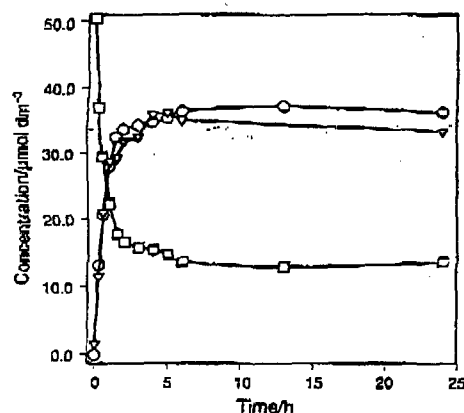


Fig. 1 Concentration profiles for CN^- (□), SCN^- (▽) and CN^- reacted (○) for a 24 h experiment. Initial conditions: $[\text{CN}^-] = [\text{S}^{2-}] = 50.0 \mu\text{mol dm}^{-3}$; $m(\text{PbCO}_3) = 50 \text{ mg}$; $V = 0.100 \text{ dm}^3$; pH 12; $T = 25^\circ\text{C}$.

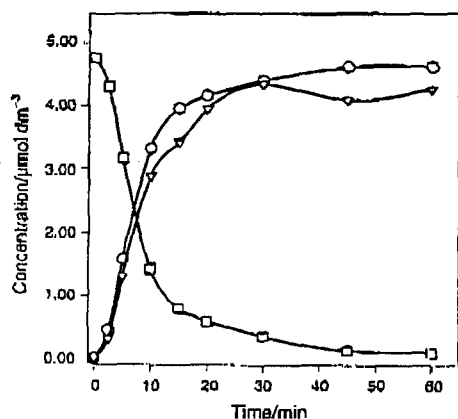


Fig. 2 Concentration profiles for CN^- (□), SCN^- (▽) and CN^- reacted (○) for a 60 min experiment. Initial conditions: $[\text{CN}^-] = 5.00 \mu\text{mol dm}^{-3}$, $[\text{S}^{2-}] = 50.0 \mu\text{mol dm}^{-3}$; $m(\text{PbCO}_3) = 250 \text{ mg}$; $V = 0.500 \text{ dm}^3$; pH 12; $T = 25^\circ\text{C}$.

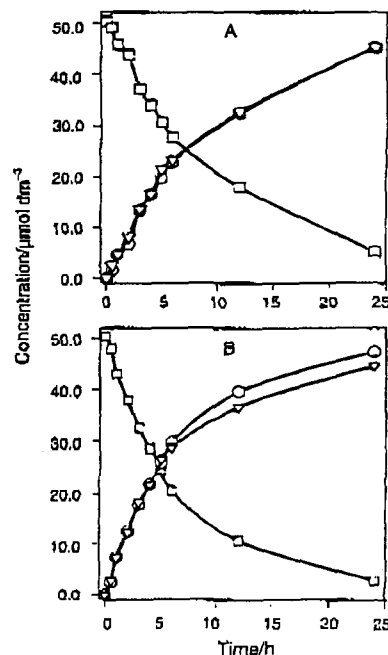


Fig. 3 Concentration profiles for CN^- (□), SCN^- (▽) and CN^- reacted (○) for a 24 h experiment. Initial conditions: $[\text{CN}^-] = 50.0 \mu\text{mol dm}^{-3}$; $V = 0.100 \text{ dm}^3$; pH 12; $T = 25^\circ\text{C}$; A, $m(\text{PbS}) = 45 \text{ mg}$; and B, $m(\text{PbS}) = 90 \text{ mg}$.

Table 1 Conversion of CN^- into SCN^- during distillation procedure prescribed for standard total cyanide determination*

Initial concentration/ $\mu\text{mol dm}^{-3}$		Ratio $\text{CN}^-:\text{S}^{2-}$	Precipitating agent	Concentration found in the NaOH scrubber/ $\mu\text{mol dm}^{-3\dagger}$		Conversion [‡] of CN^- into SCN^- (%)
CN^-	S^{2-}			CN^-	SCN^-	
50.0	50.0	1:1	None	51.5 ± 0.98	0.551 ± 0.036	1.10
50.0	5.0	10:1	None	51.6 ± 0.56	0.185 ± 0.022	0.37
5.00	50.0	1:10	None	4.40 ± 0.07	0.150 ± 0.016	3.00
50.0	50.0	1:1	PbCO_3	36.9 ± 1.45	12.1 ± 0.330	24.2
50.0	5.00	10:1	PbCO_3	49.0 ± 0.55	1.16 ± 0.040	2.32
5.00	50.0	1:10	PbCO_3	3.77 ± 0.49	2.34 ± 0.80	46.8
50.0	50.0	1:1	CdCO_3	51.2 ± 0.54	1.20 ± 0.63	2.40
50.0	5.00	10:1	CdCO_3	51.2 ± 0.41	0.465 ± 0.18	0.93
5.00	50.0	1:10	CdCO_3	†	1.30 ± 0.50	26.0

* The distillations were performed on a 0.100 dm^3 aliquot of a given sample to which 0.400 dm^3 of water was added; the volume of the NaOH absorbing solution was also 0.100 dm^3 . † Mean \pm standard deviation ($n = 3$). ‡ Based on the levels of SCN^- found in the scrubber solution. § Colloidal CdS formed could not be filtered adequately.

addition of PbCO_3 to the absorbing solution enhances the oxidation of cyanide to thiocyanate.

Cadmium carbonate performs better; however, it is obvious that the best cyanide recoveries (lowest conversion of cyanide into thiocyanate) were obtained when no precipitating agents were added to the NaOH solution. It can also be seen from Table 1 that the thiocyanate values found in the absorbing solution in the presence of a precipitant are imprecise, especially at lower cyanide:sulfide ratios. The probable reason for this phenomenon is the irreproducibility of thiocyanate formation in the heterogeneous absorbing solution. This conclusion is indirectly supported by the fact that the IC method utilized for thiocyanate determination has high precision (see under Experimental) and that the highest relative standard deviation in the absence of a precipitant was 12% even though the levels of thiocyanate determined were very low.

Conclusion

The conversion of cyanide into thiocyanate in the presence of the sulfide ion in homogeneous solutions, even at elevated temperatures, occurs slowly. However, in the presence of PbS , the reaction is significantly accelerated. Hence, it is not advisable to add PbCO_3 to the absorbing solution prior to the distillation procedure. If potential sources of H_2S are present in a cyanide sample, it is better to perform the distillation without the addition of precipitating reagents to the scrubber. After the completion of the distillation, PbCO_3 can be added and the supernatant-containing cyanide should be filtered immediately in order to avoid loss of cyanide due to the formation of thiocyanate. If cyanide samples suspected of containing sulfide are to be preserved in the field for longer storage times, addition of PbCO_3 and rapid filtration should be performed.

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References

- 1 US Environmental Protection Agency, *Methods for Chemical Analysis of Water and Wastes*, Environmental Monitoring and Support Laboratory, Cincinnati, OH, 1983, Method 335.1.
- 2 US Environmental Protection Agency, *Methods for Chemical Analysis of Water and Wastes*, Environmental Monitoring and Support Laboratory, Cincinnati, OH, 1983, Method 335.2.
- 3 American Public Health Association, American Water Works Association, Water Pollution Control Federation, *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, Washington, DC, 17th edn., 1989, pp. 4-28-4-32.
- 4 American Public Health Association, American Water Works Association, Water Pollution Control Federation, *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, Washington, DC, 17th edn., 1989, pp. 4-34-4-35.
- 5 American Public Health Association, American Water Works Association, Water Pollution Control Federation, *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, Washington, DC, 17th edn., 1989, pp. 4-38-4-39.
- 6 Ingersoll, D., Harris, W. R., Bomberger, D. C., and Coulson, D. M., *Development and Evaluation of Procedures for the Analysis of Simple Cyanides, Total Cyanide, and Thiocyanate in Water and Waste Water*, EPA-600/4-83-054, US Environmental Protection Agency, Washington, DC, 1983.
- 7 Drikas, M., and Routley, B. I., *Analyst*, 1988, 113, 1273.
- 8 Milosavljevic, E. B., and Hendrix, J. L., in *Proceedings of Managing the Mine Environment, Randol at MINEexpo '92, Las Vegas, NV, 1992*, pp. 169-174.
- 9 Goldberg, M. M., Clayton, A. C., and Potter, B. B., in *Proceedings of the Seventeenth Annual EPA Conference on the Analysis of Pollutants in the Environment, Norfolk, VA, 1994*, EPA 821-R-95-008, 1995, pp. 395-427.
- 10 Milosavljevic, E. B., Solujic, Lj., and Hendrix, J. L., *Environ. Sci. Technol.*, 1995, 29, 426.

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