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Project Summary

EPA Method Study 12, Cyanide in Water

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EPA Method Study 12, Cyanide in Water, **reports the results of a study by EMSL-Cincinnati for the parameters *total cyanide and cyanides amenable to chlorination* which are present in water at microgram per liter levels. Four methods, pyridine-pyrazolone, pyridine-barbituric acid, electrode, and Roberts-Jackson were used by 60 laboratories in Federal and State agencies, municipalities, universities, and the private/industrial sector in the method validation study.**

Sample concentrates were prepared in pairs with similar concentrations at each of three levels. Analysts diluted the samples to volume with distilled and natural waters for analysis. Precision, accuracy, bias and the natural water interference were evaluated for each analytical method and comparisons were made between the four methods.

This Project Summary was developed by EPA's Environmental Monitoring and Support Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Cyanides are common constituents in a variety of industrial wastes such as quench waters from coke plants and blasts furnaces, and the rinse water from heat treating and metal finishing operations. In addition to these metal industries, other industrial operations, particularly chemical manufacturing, utilize and discharge cyanide compounds. Becuase of the extreme toxicity of the cyanide ion to aquatic life and to humans, rigorous treatment of wastewaters containing cyanide is required.

The measurement of cyanides in the analytical laboratory is complicated by the ease with which the cyanide ion complexes with other metal ions. Complexing occurs in several ways with metals. For example, cyanide combines with iron to form ferrous cyanide, $Fe(CN)_2$; ferric cyanide, $Fe(CN)_3$; ferrous ferrocyanide $Fe_3[Fe(CN)_6]_2$; ferric ferricyanide $Fe[Fe(CN)_6]$; ferrous ferroycyanide, $Fe_2[Fe(CN)_6]$ and ferriferrocyanide, $Fe[FE(CN)_6]_3$. Similarly, copper may form a series of copper-iron-cyanide complexes. Other metals such as cadmium, silver, tin, zinc and lead form simple cyanides ($Cd(CN)_2$, $Ag(CN)_2$, and so on, as well as the metal-iron-cyanide complexes.

At the normal pH's and temperatures of streams, the dissociated cyanide ion (CN^-) is toxic to most species of fish at a level of 0.1 mg/liter. Complexed cyanides are far less toxic and discharge of relatively large concentrations of these compounds to receiving streams is not immediately harmful. Consequently, it has been suggested that cyanide be complexed with metals such as iron, prior to discharge, to reduce toxicity. However, enforcement authorities are reluctant to authorize cyanide discharge, even complex cyanides, because such complexes may revert to simpler, more toxic forms under the influence of stream pH, temperature, and ultra-violet radiation.

Cyanide Measurements

Cyanide is usually measured as the following parameters: *free cyanide, cyanides amenable to chlorination and total cyanide.*

Free or *simple cyanide*, such as NaCN, KCN, or HCN, is directly measurable by volumetric titration or colorimetry.

Cyanides amenable to chlorination measures common metal cyanide compounds and most complexes except for the iron cyanides. The sample is divided

into two parts and total cyanide is determined before and after an alkaline chlorination step. Cyanides amenable to chlorination are the difference between th two total cyanide analyses. The method is equivalent to ASTM, Annual Book of ASTM Standards; 11.02 *Water*, D2036-82, Method B-Cyanide Amenable to Chlorination by Difference, p. 113, 1983.

Total cyanide is a measure of all cyanides including iron cyanide complexes after conversion to HCN by acidification, distillation and absorption in an NaOH scrubber. The cyanide is titrated as HCN against a silver nitrate solution or is converted to cyanogen chloride and read colorimetrically using a pyridine-pyrazolone or pyridine-barbituric acid reagent.

Analytical Methods for Cyanide

The methods for the measurement of cyanide have been a subject of debate and dissatisfaction among environmental chemists for many years. Unfortunately, the complexing properties of the cyanide radical which make it useful in metal plating operations are the same properties which make definition and measurement difficult. Current analytical methods can directly measure cyanide-metal complexes and cannot uniformly breakdown the complexes for measurement as simple cyanide.

The analytical methods attempt to isolate the cyanide as sodium cyanide, using a distillation or stripping action, with absorption of (HCN) as a basic solution followed by a colorimetric measurement. The methods of distillation stripping and the color forming reagents used vary. Cyanide ions may also be measured electrometrically using an ion selective electrode, but despite its speed and simplicity the method has not been widely accepted. So called *free cyanide*, such as sodium or potassium cyanide, is also frequently determined volumetrically by titration with silver nitrate, but the procedure is not useful for levels of cyanide below one (1) microgram found in may wastewaters. Cyanides amenable to chlorination also employs the usual colorimetric methods, but measures total cyanide before and after oxidation of the sample by chlorination with Chloramine-T.

With the variety of methods available and the lack of consensus among analysts regarding the most reliable method, it was agreed that a collaborative study was required to ascertain, if possible, which method should be adopted for general use. The following methods were subsequently chosen for collaborative testing:

1) Serfass distillation/pyridine-barbituric acid colorimetric method.
2) Serfass distillation/pyridine-pyrazolone colorimetric method.
3) Serfass distillation/ion-selective electrode.

Participants were requested to analyze for both total cyanide and cyanides amenable to chlorination, using Serfass distillation and their choice of detection method listed above. However, participants were encouraged to use the barbituric acid method if possible.

Upon receiving the invitation to participate in the study, a number of industrial labs indicated they would also like to provide data using the Roberts-Jackson method of measuring simple cyanides. This method uses the conventional colorimetric procedures, but modifies the distillation so that only simple cyanides are measured.

Description of Study

Design of Study

The study design is based on Youden's nonreplicate technique for the collaborative study of analytical methods. Using this design, sample pairs were developed with slightly different concentrations of the constituents, at each of several levels. The analyst is directed to do a single analysis and report *one* value for each sample, as in normal routine.

In this study, six samples were prepared as concentrates in sealed glass ampuls and presented to the analyst as unknowns. Three levels of cyanide concentration in three pairs of samples were tested at levels typical of those observed in wastewaters.

The analyst was directed to dilute a 5.0-mL aliquot of each concentrate to one-liter volume with distilled water and a second 5.0-mL aliquot to one-liter volume with a natural or effluent water. Natural or effluent water samples were analyzed with and without incremental aliquots and the recovery determined by difference. Each sample was analyzed only once. Analysis in distilled water evaluated the proficiency of the analyst in using the method on a sample free of interferences, while recovery of the increment from a natural or effluent water, such as river, lake, or an estuary, indicated whether the method was affected by interferences in these waters.

Data were recorded on standard forms and returned to EMSL-Cincinnati for statistical evaluation and preparation of the report.

Preparation of Samples

Sample concentrates were prepared by dissolving precisely weighed amounts of reagent grade chemicals in high purity water obtained by passing distilled water through a four cartridge Millipore Super-Q System, to produce accurate levels of simple and complex cyanides. Each sample contained simple and complex cyanides, present as potassium cyanide and potassium ferrocyanide, respectively. The concentrates were preserved with sodium hydroxide and checked by repeated analyses over a period of three months to confirm the calculated concentrations an the stability of the samples. Analyses of the samples by an outside laboratory confirmed the data of the Quality Assurance Branch, EMSL-Cincinnati.

When diluted to volume according to the instructions, the samples contained concentrations of cyanide as shown in Table 1.

Conduct of the Study

An invitational memorandum announced the study to the ten EPA Regions and to the ASTM D-19 committee members in October, 1974. A separate invitational letter was sent to industrial laboratories known to be routinely analyzing wastes for cyanides. Although it was estimated to require a minimum of one workweek of analytical effort, 112 laboratories from EPA, other Federal, State and local agencies, Canadian groups, universities and private industry agreed to participate.

Each participant received a set of six ampuls, instructions for sample preparation, duplicate report sheets, and a copy of the analytical procedures to be used. The participating laboratories were required to analyze samples using methods from EPA's *Methods of Chemical*

Table 1. *True Values for Cyanide Concentrations**

Sample	*Total Cyanide µg/L*	*Cyanide Amenable to Chlorination, µg/L*
1	*25*	*13*
2	*372*	*149*
3	*35*	*18*
4	*106*	*64*
5	*106*	*64*
6	*352*	*141*

**The concentrations were the actual levels calculated and added. Analyses were used for verification only.*

Analysis of Water and Wastes, 1974, EMSL-Cincinnati. However, a number of industrial laboratories participating in the study asked if it would be agreeable with EPA if they performed the cyanide analyses by a modified Roberts-Jackson method as well as by the pyridine methods. EPA agreed. Appendix B provides description of EPA methodologies, the original Roberts-Jackson paper, and the Woods River modification (Shell Oil Company) which the industrial laboratories used in this study. Participants were allowed 50 days to complete the analyses and report the data. Data reported later than the cut-off date were omitted. Fifty-six laboratories returned data in time to be included in this report.

Results and Discussion

Basic statistical results were computed for each combination of sample method and water matrix using the Collaborative Study (COLST) computer system developed by the USEPA. Final relationships for recovery from the natural water matrix are given below.

Summary for Total Cyanide in Natural Waters

The mean recoveries ($\overline{X}$), overall standard deviations (S), and single analyst standard deviations (S_r) for natural water analyses by each of the methods within the concentration range 25-400 μg/liter, are as follows.

Method	$\overline{X}$	S	S_r
P-B*	0.916 (conc.) - 2.0	0.259 $\overline{X}$ + 9.0	0.104 $\overline{X}$ + 9.2
P-P**	0.965 (conc.) - 3.6	0.107 $\overline{X}$ + 16.3	0.018 $\overline{X}$ + 12.3
Electrode	1.00 (conc.) - 0.8	0.213 $\overline{X}$ + 40.6	0.246 X + 0.2

At the extremes of the applicable range, these equations lead to the following statistical estimates in μg/liter.

	25 μg/liter Level			400 μg/liter Level		
Method	$\overline{X}$	S	S_r	$\overline{X}$	S	S_r
P-B*	20.9	15.5	11.8	364.4	112.6	50.8
P-P**	20.5	19.0	14.3	382.4	59.1	44.7
Electrode	24.2	45.9	6.3	399.2	125.8	98.6

* Pyridine-barbituric Acid
** Pyridine-pyrazolone

These tables make the larger variability of the electrode method obvious and, although fortuitous averaging makes its mean recovery look better, recall that its mean recoveries were much more variable. Between the colorimetric methods, the apparent statistical advantage of the pyridine-pyrazolone method is also quite clear.

Summary for CATC in Natural Waters

The mean recovery ($\overline{X}$), overall standard deviation (S), and single-analyst standard deviation (S_r) results for natural water analyses by each of the methods, within the concentration range 13-150 μg/liter, are as follows.

Method	$\overline{X}$	S	S_r
P-B*	1.19 (conc.) - 10.0	0.540 $\overline{X}$ + 15.5	0.232 $\overline{X}$ + 16.1
P-P**	1.61 (conc.) - 15.0	0.686 $\overline{X}$ - 0.5	0.225 $\overline{X}$ - 4.0
Electrode	1.35 (conc.) - 11.9	0.852 $\overline{X}$ + 33.2	0.352 $\overline{X}$ + 22.1

At the extremes of the applicable range, these equations lead to the following statistical estimate in μg/liter.

	At 13 μg/liter			At 150 μg/liter		
Method	$\overline{X}$	S	S_r	$\overline{X}$	S	S_r
P-B*	5.47	22.5	19.1	168.5	96.5	50.9
P-P**	5.93	9.4	-1.1[a]	226.5	103.4	29.8
Electrode	5.65	44.3	26.7	190.6	161.0	74.9

* Pyridine-barbituric acid
** Pyridine-pyrazolone
[a] The variance-estimating equations for this method are not valid at this low concentration.

Although these tables show slightly better statistics for the pyridine-barbituric acid method, the cyanides amenable to chlorination statistics for all methods look very unsatisfactory. This suggests an inherent problem within the cyanides amenable to chlorination definition rather than a problem with measurement technique applied.

Conclusions

Total Cyanide

For the total cyanide parameter, statistics for the pyridine-barbituric acid and pyridine-pyrazolone methods were very similar. The electrode method showed significantly greater data variability. However, all three methods seem capable of producing valid data in the hands of a skilled analyst.

Cyanides Amenable to Chlorination

Although the pyridine-barbituric acid method showed the least bias and the smallest standard deviation, none of the three methods tested provided satisfactory data for the cyanides amenable to chlorination parameter. As a corollary, cyanides amenable to chlorination did not provide a reliable means for distinguishing between free and complexed cyanides.

Roberts-Jackson

The generation of data by the Roberts-Jackson method was encouraged, but only three labs submitted results and one of these sets was incomplete.

On the basis of the limited data obtained in this study, the Roberts-Jackson method shows promise of improved accuracy and precision, while providing greater safety by avoiding the open generation of toxic cyanogen chloride. However, because of limited data this study did not establish its real value.

General Conclusion

The compelling reason for preferring the pyridine-barbituric acid method over the pyridine-pyrazolone method is convenience rather than statistical improvement in the data produced.

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The complete report, entitled "EPA Method Study 12, Cyanide in Water," (Order No. PB 84-196 674; Cost: $13.00, subject to change) will be available only from:

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