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THE DETERMINATION OF CYANIDE
ION IN NATURAL WATERS WITH
A SELECTIVE ION ELECTRODE

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ABSTRACT

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The analysis of cyanide ion in natural water systems is complicated by the fact that natural waters contain certain metal ions which form extremely stable metal-cyano complexes. Current methods involve distillation techniques to separate cyanide from the sample in order to permit the analysis. However, certain metal-cyano complexes are so stable thermodynamically and release complexed cyanide so slowly that even those methods are not very satisfactory.

We have investigated an approach to secure the release of cyanide ion in the water sample so that a direct measurement with a selective ion electrode can be used. The proposed technique is based upon the addition of an organic ligand to the sample which will form a metal complex sufficiently stable to release a quantitative amount of cyanide from metal-cyano complexes.

We have shown that the complexing agents investigated will release 60-80% of complexed cyanide during simultaneous reflux and irradiation by a mercury lamp. Evidently this represents a state of equilibrium between complexed ligand and cyanide. The complexing agents, therefore, do not form metal complexes sufficiently stable to free enough cyanide ion to permit an analysis for the total cyanide ion concentration.

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INTRODUCTION

This project was designed to develop a method for the determination of the cyanide content of natural waters using the cyanide ion electrode. The method would permit the determination of both the free cyanide and the total cyanide content in natural waters. The principle obstacle to the direct determination of cyanide in aqueous solutions is the tendency for cyanide ions to form extremely stable complexes with the metal ions commonly found in natural water systems.

It has been found that the conventional hydrolysis-distillation analytical method for cyanide determination is unsatisfactory since that technique cannot completely separate complexed cyanide ion for direct chemical analysis. In order to use the cyanide ion-selective electrode for total analyses, all cyanide must be released from metal complexes since the electrode responds only to free ions in solution.

There have been a number of recent studies of the application of the cyanide ion electrode to the determination of cyanide in aqueous systems containing metal ions.^{3,4,5,7} Schleuter⁵ and Penland and Fischer⁴ have shown that the cyanide electrode yields better results for the analysis of cyanide than the usual titration and colorimetric methods. Schleuter⁵ and Higashiura³ have demonstrated that the metal-cyano complexes of Fe(II), Ni(II) and Cu(II) cannot be decomposed at high pH or in the presence of EDTA. However, EDTA has been shown to partially decompose the copper-cyano complex in aqueous solution.⁵

Schleuter⁵ has suggested that, as a result of the results with EDTA, other metal-complexing agents should be investigated for the release of cyanide from metal-cyano complexes.

Goulden, et. al.² reported a distillation method for analysis of complex cyanides in which sulfide ion is added to the solution to precipitate released metal ions in order to favor the release of cyanide ion. In their method, the sulfide-containing solution is irradiated during the distillation process with phosphoric acid being added to the solution to protect against cyanide oxidation. We attempted a series of reflux experiments of our systems to which sulfide and phosphoric acid were added.

The recent study by Schleuter⁵ demonstrated adequately that the cyanide electrode responds only to the activity of free cyanide ions in solution. Complexed cyanide has absolutely no effect on the potential of the cyanide electrode.¹ As we shall see later, the presence of organic ligands does not significantly affect the response of the cyanide ions in solution.

Our goal was to develop a method in which an organic complexing agent could be added to a sample of water containing metal-cyano complexes under conditions which would quantitatively free the complexed cyanide by formation of a metal-organic ligand and complex. The resulting solution would then be treated with an ionic strength-adjustment buffer, and the cyanide concentration would be determined by using a selective ion electrode. We did not intend to use any distillation or extraction methods as a simple and direct procedure was the object of this study.

The specific objectives of our project were:

1. To screen a series of metal complexing agents to find those with sufficiently large metal complex formation constants to quantitatively free complexed cyanide ions so that a direct non-distillation method for cyanide ion analysis could be developed.

3.

2. To investigate the effect of temperature and radiation on the exchange of cyanide for organic complexing agent in solution because the reaction rates for the formation or dissociation of some metal-cyano complexes are relatively slow.

MATERIALS AND METHODS

Table 1 lists relevant information about the ligands and metal-complex salts used in this investigation. These compounds were used without further purification. Measurements of pH and free cyanide ion concentration were carried out using a Beckman Research pH meter. Cyanide ion activity was measured using the Orion Cyanide Ion Electrode, Model No. 94-06A versus a saturated calomel electrode. Periodically, the surface of the cyanide electrode was polished with a commercial toothpaste preparation in order to prevent erratic response from surface coatings which developed after prolonged use of the electrode.

Standard stock solutions of organic ligands were prepared at a concentration of 10^{-1} molar and pH 12 by weighing an appropriate amount of each ligand and dissolving in deionized water, using 10M NaOH to adjust to a final concentration of 10^{-3} molar NaOH. Desired solutions of ligands and metal-cyano complexes were prepared by volumetric dilution of the stock solution and pH adjustment using 10M NaH_2PO_4 .

Reflux was carried out in standard-taper glassware using a heating mantle. Solutions were degassed for 15 minutes by bubbling N_2 gas through the solution. During reflux, N_2 was slowly swept through the system above the solution surface in order to minimize air-oxidation of cyanide ion in solution.

The effect of photolysis on the exchange of ligand and cyanide in the metal complexes was evaluated. Solutions were irradiated with a 450 watt mercury lamp placed within 3 inches of the reflux vessel containing the solution. In all irradiation studies, the system was kept under an inert atmosphere of nitrogen.

Table 1: Metal complex salts and organic complexing agents used in this investigation.

<u>Metal complex salt</u>	<u>Source*</u>
$K_4Fe(CN)_6 \cdot 3H_2O$	1
$Na_2Fe(CN)_5(NO) \cdot 2H_2O$	1
$K_3Co(CN)_6$	2
$K_2Hg(CN)_4$	3
<u>Organic Complexing Agent</u>	<u>Source*</u>
EDTA, (Ethylenedinitrilo)-tetraacetic acid, disodium salt	1
DTPA, Diethylenetriamine pentaacetic acid	4
DCTA, 1,2 Diaminocyclohexane tetraacetic acid	4
EDDPA, Ethylenediaminedi (o-hydroxy-phenylacetic acid)	4
TTHA, Triethylenetetramine hexaacetic acid	4

*Sources of supply:

1. Matheson, Coleman and Bell Mfg. Chemists, Norwood, Ohio.
2. Apache Chemicals, Inc., Seward, Illinois.
3. Laboratory synthesized, Inorganic Syntheses.
4. K and K Laboratories, Plainview, N.Y.

Twenty solutions containing different combinations of a metal-cyano complex and organic ligand were prepared. The solution pH was adjusted to pH 11.5 and degassed with nitrogen. The solutions were then refluxed for varying periods of time under an atmosphere of nitrogen. In each case the molar concentration of metal-cyano complex was carefully adjusted to a concentration of 10^{-4} moles/liter. The effect of concentration of organic ligands on cyanide release was studied by carrying out two complete series of experiments where organic ligand concentration was 10^{-3} moles/liter and 10^{-2} moles/liter. (i.e. 10x and 100x the concentration of metal-cyano complex.) After the indicated period of solution reflux, the solution was allowed to cool to room temperature under the protection of the nitrogen atmosphere and free cyanide ion concentration was determined as described by Schleuter.¹ Solutions were prepared which were 10^{-4} molar in ferricyanide ion and 10^{-3} molar in organic complexing agent. Two control solutions of 5×10^{-4} molar CN^- , one containing EDTA at 10^{-3} molar were included to determine whether significant cyanide ion oxidation occurred during the radiation process. The solutions were subjected to radiation from a mercury lamp while under reflux for 5, 15, 30, and 60 minutes.

RESULTS

Results of this investigation will be presented in two sections, reflecting the 2 types of experiments.

Part I:

The first phase of this study involved determining the effect of time, concentration and ligand on the exchange of cyanide ion for different organic ligands in four different metal-cyano complexes. The results are summarized in Tables 2 and 3.

Stoichiometric release of cyanide by the various complexes would result in the free cyanide ion concentrations listed in Table 4.

An examination of Tables 2 and 3 shows that the metal-cyano complexes of Fe^{2+} , Fe^{3+} , Co^{3+} and Hg^{2+} are only partially substituted by the five organic ligands under consideration. It is well-known that exchange rates for cyanide removed from iron and cobalt are quite slow,¹ and this behavior is illustrated by the data shown. The amounts of CN^- released before reflux are very slight except in the case of Hg^{2+} where approximately half of the CN^- appears as free ions. On the other hand, iron and cobalt complexes require the higher temperature of reflux conditions to effect even a 10% release after a period of one hour.

In general, all of the solutions show a decrease in CN^- concentration at 5 hours of reflux compared to one hour. The cause of this phenomenon becomes apparent when we examine the data for control solutions in Tables 2 and 3 where solutions of 6×10^{-4} molar CN^- are refluxed in the presence of the various ligands. In all cases the control solutions show a decrease of CN^- concentration as time of reflux increases. This indicates that carrying out the reflux procedure under a nitrogen atmosphere does not prevent the oxidation of CN^- to the cyanate ion, CNO^- .

Table 2.

Effect of reflux time on exchange of cyanide ion in metal complexes by various organic ligands. In each case, metal complex concentration is 10^{-4} M and ligand concentration is 10^{-3} M.

Metal Salt	Ligand	Before Reflux	Free Cyanide Conc., moles/liter		5 hr. reflux
			1 hr. reflux	∞	
$K_4Fe(CN)_6 \cdot 3H_2O$	EDTA	5.73×10^{-7}	1.24×10^{-5}	1.07×10^{-5}	
	DTPA	1.44×10^{-7}	1.85×10^{-5}	4.01×10^{-5}	
	DCTA	2.18×10^{-7}	2.04×10^{-5}	4.81×10^{-5}	
	EDDPA	4.21×10^{-7}	2.05×10^{-5}	4.40×10^{-5}	
	TTHA	5.25×10^{-7}	1.22×10^{-5}	1.09×10^{-5}	
$Na_2Fe(CN)_5(NO) \cdot 2H_2O$	EDTA	8.79×10^{-7}	3.31×10^{-5}	3.49×10^{-5}	
	DTPA	1.76×10^{-7}	2.65×10^{-5}	3.17×10^{-5}	
	DCTA	8.99×10^{-7}	3.34×10^{-5}	3.96×10^{-5}	
	EDDPA	1.84×10^{-6}	4.65×10^{-5}	3.34×10^{-5}	
	TTHA	2.13×10^{-6}	3.57×10^{-5}	3.97×10^{-5}	
$K_3Co(CN)_6$	EDTA	3.46×10^{-5}	2.43×10^{-6}	7.55×10^{-7}	
	DTPA	3.55×10^{-5}	2.48×10^{-5}	5.06×10^{-6}	
	DCTA	4.80×10^{-5}	2.50×10^{-5}	4.73×10^{-6}	
	EDDPA	3.08×10^{-5}	4.08×10^{-5}	5.48×10^{-6}	
	TTHA	5.78×10^{-5}	2.08×10^{-5}	1.44×10^{-6}	
$K_2Hg(CN)_4$	EDTA	2.03×10^{-4}	7.53×10^{-5}	1.35×10^{-6}	
	DTPA	2.05×10^{-4}	1.62×10^{-4}	1.20×10^{-5}	
	DCTA	1.46×10^{-4}	1.30×10^{-4}	2.87×10^{-5}	
	EDDPA	1.75×10^{-4}	2.40×10^{-4}	2.38×10^{-5}	
	TTHA	2.03×10^{-4}	6.08×10^{-4}	1.55×10^{-5}	

Table 2. (cont'd)

<u>Metal Salt</u>	<u>Ligand</u>	Free Cyanide Conc., moles/liter		
		<u>Before Reflux</u>	<u>1 hr. reflux</u>	<u>5 hr. reflux</u>
Control [CN ⁻] = 6 x 10 ⁻⁴	EDTA	6.30 x 10 ⁻⁴	2.00 x 10 ⁻⁴	2.23 x 10 ⁻⁶
	DTPA	6.33 x 10 ⁻⁴	4.10 x 10 ⁻⁴	1.17 x 10 ⁻⁴
	DCTA	6.67 x 10 ⁻⁴	5.59 x 10 ⁻⁴	1.99 x 10 ⁻⁴
	EDDPA	6.89 x 10 ⁻⁴	4.58 x 10 ⁻⁴	1.75 x 10 ⁻⁵
	TTHA	6.36 x 10 ⁻⁴	4.52 x 10 ⁻⁴	1.65 x 10 ⁻⁴

Table 3.

Effect of reflux time on exchange of cyanide ion in metal complexes by various organic ligands.

In each case, metal complex concentration is $10^{-4}M$ and ligand concentration is $10^{-2}M$.

<u>Metal Salt</u>	<u>Ligand</u>	Free Cyanide Concentration, moles/l		
		<u>Before reflux</u>	<u>1 hr. reflux</u>	<u>5 hr. reflux</u>
$K_4Fe(CN)_6 \cdot 3H_2O$	EDTA	9.16×10^{-7}	2.13×10^{-5}	1.38×10^{-5}
	DTPA	1.66×10^{-6}	1.82×10^{-5}	2.27×10^{-5}
	DCTA	9.16×10^{-7}	2.74×10^{-5}	3.37×10^{-5}
	EDDPA	1.80×10^{-6}	1.31×10^{-5}	2.96×10^{-5}
	TTHA	2.42×10^{-6}	1.73×10^{-5}	1.23×10^{-6}
$Na_2Fe(CN)_5(NO) \cdot 2H_2O$	EDTA	3.48×10^{-6}	3.35×10^{-5}	3.24×10^{-5}
	DTPA	5.05×10^{-6}	3.33×10^{-5}	3.38×10^{-5}
	DCTA	2.93×10^{-6}	4.37×10^{-5}	3.80×10^{-5}
	EDDPA	3.85×10^{-5}	8.57×10^{-5}	5.85×10^{-5}
	TTHA	5.00×10^{-6}	5.43×10^{-5}	5.35×10^{-5}
$K_3Co(CN)_6$	EDTA	2.80×10^{-5}	5.93×10^{-5}	1.69×10^{-5}
	DTPA	3.01×10^{-5}	1.50×10^{-5}	5.52×10^{-6}
	DCTA	2.49×10^{-5}	1.69×10^{-5}	4.29×10^{-6}
	EDDPA	7.79×10^{-5}	2.96×10^{-5}	1.60×10^{-5}
	TTHA	6.26×10^{-5}	1.63×10^{-5}	6.44×10^{-6}
$K_2Hg(CN)_4$	EDTA	2.90×10^{-4}	2.40×10^{-4}	4.33×10^{-5}
	DTPA	3.09×10^{-4}	2.20×10^{-4}	7.94×10^{-5}
	DCTA	3.15×10^{-4}	2.27×10^{-4}	1.03×10^{-4}
	EDDPA	2.54×10^{-4}	3.01×10^{-4}	9.14×10^{-5}
	TTHA	2.83×10^{-4}	2.87×10^{-4}	1.32×10^{-5}

Table 3. (cont'd.)

<u>Metal Salt</u>	<u>Ligand</u>	Free Cyanide Concentration, moles/l		
		<u>Before reflux</u>	<u>1 hr. reflux</u>	<u>5 hr. reflux</u>
Control [CN] = 6×10^{-4}	EDTA	4.22×10^{-4}	1.39×10^{-4}	3.45×10^{-6}
	DTPA	4.76×10^{-4}	3.32×10^{-4}	1.08×10^{-4}
	DCTA	4.08×10^{-4}	3.33×10^{-4}	1.34×10^{-4}
	EDDPA	4.03×10^{-4}	1.48×10^{-4}	6.23×10^{-6}
	TTHA	3.40×10^{-4}	2.60×10^{-4}	9.50×10^{-5}

Table 4: Total CN^- concentration in moles per liter resulting from stoichiometric release from metal cyano complexes at 10^{-4} molar.

<u>Salt</u>	<u>Stoichiometric CN^-, moles/liter</u>
$\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$	6×10^{-4}
$\text{Na}_2\text{Fe}(\text{CN})_5(\text{NO}) \cdot 2\text{H}_2\text{O}$	5×10^{-4}
$\text{K}_3\text{Co}(\text{CN})_6$	6×10^{-4}
$\text{K}_2\text{Hg}(\text{CN})_4$	4×10^{-4}

The conclusion to be drawn from this series, then, is that the organic ligands do not form sufficiently stable metal complexes to result in the release of quantitative amounts of CN^- in solutions of the metal-cyano complexes. Furthermore, for the complexes which undergo slow exchange, the elevated reflux temperatures of the solution are such that significant amounts of cyanide are oxidized to a form which cannot be sensed by the cyanide ion electrode.

Part II:

Because reaction times were quite lengthy, we undertook a study to determine whether ultraviolet radiation would activate the complexes sufficiently to increase the ligand exchange rates. Since this study was begun near the end of the project, we restricted our measurements to the ferricyanide ion, $\text{Fe}(\text{CN})_6^{3-}$. We chose this ion because of the ubiquitous distribution of the ferric ion in natural waters and because of the slow exchange rate of the ferricyanide ion. The results of this portion of the study are shown in Table 5.

The first set of experiments which were conducted in this part of the study involved attempts at cyanide exchange by the various organic ligands without deoxygenation and protection of the solution with an inert atmosphere. Those preliminary experiments showed a dramatic effect due to the oxidation of free cyanide ions in solution. As seen above, if the solutions are irradiated during reflux, exchange rates are increased sufficiently that only minor oxidation of released cyanide ion occurs.

Table 5 indicates that the control solutions were not oxidized to any significant degree during the course of the experiment showing that for the periods of time chosen, the free cyanide ions in solution were probably not

Table 5.

Effect of time on exchange of CN^- by organic ligands from $\text{Fe}(\text{CN})_6^{3-}$ complex during reflux and U.V. irradiation. Metal complex concentration is 10^{-4}M , ligand concentration is 10^{-3}M .

Samples	Free CN^- concentration after reflux under U.V. Radiation for:			
	5 min.	15 min.	30 min.	60 min.
Std., $5 \times 10^{-4}\text{MCN}^-$ in H_2O	3.68×10^{-4}	4.75×10^{-4}	4.21×10^{-4}	4.24×10^{-4}
Std., $5 \times 10^{-4}\text{MCN}^-$ in EDTA solution	4.22×10^{-4}	5.16×10^{-4}	4.24×10^{-4}	4.04×10^{-4}
<u>$10^{-4}\text{M Fe}(\text{CN})_6^{3-}$ in:</u>				
1. EDTA	2.07×10^{-4}	1.58×10^{-4}	2.78×10^{-4}	3.47×10^{-4}
2. DTPA	2.80×10^{-4}	3.31×10^{-4}	3.23×10^{-4}	3.53×10^{-4}
3. DCTA	1.78×10^{-4}	2.44×10^{-4}	3.13×10^{-4}	4.15×10^{-4}
4. TTHA	2.71×10^{-4}	2.78×10^{-4}	3.18×10^{-4}	3.01×10^{-4}

affected. For those solutions containing ferricyanide ion and organic ligands, approximately 60-80% of the complexed cyanide ion is released within 30 minutes.

This shows that although the exchange rate of the metal complexes is increased by radiation, and although the inert nitrogen atmosphere provides adequate protection from oxidation, the equilibrium states of these systems are not favorable to the release of free cyanide ion into solution for the determination of the total cyanide content by the method proposed here.

SUMMARY AND CONCLUSIONS

In attempting to develop a simple, direct method for the quantitative determination of total cyanide in natural waters we have investigated a series of organic complexing agents known to form extremely stable complexes with metal ions commonly found in those natural systems. These complexes displace cyanide ions in metal-cyano complexes formed by metal ions and cyanide ions in water samples. The object of the study was to identify organic complexing agents which would form metal complexes of sufficient stability to effect a quantitative release of complexed cyanide ions permitting in situ analysis of total cyanide ion with a selective ion electrode.

The results of this investigation show that, in the case of the five complexing agents investigated, an equilibrium was established under which some 60-80% of complexed cyanide was released. The release was accomplished by refluxing a solution containing metal-cyano complex and organic complexing agent under a protective atmosphere of nitrogen. Prolonged reflux resulted in some oxidation of free cyanide ion. In order to increase the rate of organic ligand-cyanide exchange, we irradiated the reflux vessel with a mercury lamp. The exchange rate was increased sufficiently that equilibrium was reached before appreciable oxidation occurred.

Although none of the organic ligands are suitable for the direct analytical determination of cyanide, this technique shows promise for an alternate method of analysis. If the solutions were irradiated while a distillation is carried out, the cyanide ions would be volatilized as HCN and rapidly removed from the solution. This technique would be an alternative to the technique of Goulden, et. al.¹ in which sulfide ion is added to the

sample to precipitate metal ions from complexes. This technique would allow the rapid separation of cyanide ions even from cobalt and iron complexes which are exceptionally stable. Further studies on this system will involve the application of our results to a distillation technique for cyanide analysis.

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