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Applicability of the Cyanide Electrode for Measuring Free and Total Cyanide

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by

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory-Cincinnati conducts research to:

- Develop and evaluate techniques to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.

- Investigate methods for the concentration, recovery, and identification of viruses, bacteria, and other microbiological organisms in water. Conduct studies to determine the responses of aquatic organisms to water quality.

- Conduct an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

There is an ever-increasing interest in the use of electrode methods to analyze water and waste samples, whether the resulting data are to be used for research, surveillance, compliance monitoring, or enforcement purposes. Accordinaly, the Environmental Monitoring and Support Laboratory has an ongoing methods research effort in the development, evaluation, and modification of electrode procedures. This particular report pertains to the evaluation of the cyanide electrode. The method has potential routine application for the analysis of free cyanide in surface waters and domestic and industrial wastes.

Dwight G. Ballinger
Director
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ABSTRACT

The Orion model 94-06 cyanide electrode was evaluated to determine its applicability to water and wastewaters. The calibration curve was Nernstian over the concentration range of 0.26 to 26 ppm, and the slope of the curve was 59 mv per decade change. This work consisted in studying the response of the cyanide electrode to cyanide when this ion was present in solution in both free and complex forms. The results show conclusively that the electrode responds only to free cyanide in solution and not at all to that complexed to metals.

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SECTION I
INTRODUCTION

The classical cyanide determination uses acid-hydrolysis to convert free and complexed cyanide into hydrogen cyanide, which is distilled from solution for subsequent determination. The result of this analysis thus gives the total amount of cyanide in solution (i.e. both free and complexed cyanide). It can be argued that for evaluation of environmental impact, in most cases, the free cyanide levels are of more significance than the total cyanide content. Cyanide complexed with ferrous or ferric iron, for example, is both kineticly and thermodynamicly inert, and thus, the complexed-cyanide has no business being classified with the free cyanide if the amount of chemically-active cyanide is being evaluated. The important distinction between free and total cyanide levels has not received sufficient attention by those doing cyanide analyses or by those evaluating the results of cyanide determinations. Though the classical hydrolysis-distillation cyanide determination was only amenable to determinations of the total cyanide levels, the recent development of the cyanide-selective electrode makes measurement of free cyanide potentially feasible. It is essential that the meaning of the cyanide concentrations measured with the cyanide electrode be carefully ascertained and their relationship to free and total cyanide determined. Though the responses of the cyanide electrode to cyanide levels in laboratory-prepared samples and its utility in the analysis of many natural products have been amply reported, the meaning of the results as free or total cyanide remains ambiguous. The purpose of this report is to clarify the meaning of the cyanide electrode responses. This study investigates the effect of metal-cyanide complexes on the ion selective electrode, the effects of metal-contaminats on the cyanide electrode response, and the conditions under which the electrode can be used to give evaluations of the free and total cyanide levels.

SECTION II
SUMMARY

The work presented here consisted of studying the response of the cyanide electrode to cyanide when this ion was present in solution in both free and complexed forms. The results show conclusively that the electrode responds only to free cyanide in solution and not at all to that complexed to metals. Nickel and copper are shown to form the most stable complexes, and ferrous and ferric iron, zinc, and lead form less stable complexes.

Attempts were made to use the cyanide electrode to measure total cyanide concentration (i.e. both free and complexed cyanide) by adding a strong complexing agent to decompose the cyanide complexes. Both hydroxide and ethylenediamine tetracetic acid (EDTA) were investigated, but the thermodynamic and kinetic stability of the cyanide complexes rendered determination of total cyanide with the cyanide electrode unfeasible.

Studies with the cyanide electrode in the hydrolysis-distillation procedure for determining total cyanide indicate that high metal ion concentrations can give low results. In light of this result and the demonstrated kinetic and thermodynamic stability of the metal-cyanide complexes, the environmental significance of determination of total cyanide levels is questioned. It is suggested that determination of free cyanide concentrations with the cyanide electrode might be more significant and meaningful.

Studies of the cyanide levels in natural water samples are found to be at the limit of Nernstian response of the cyanide electrode. Electrode responses seem to correlate with free cyanide levels even though the determinations contain larger errors.

The cyanide electrode is used to determine the cyanide levels in two fish and one crayfish that died in a large fish kill. Though an effluent containing cyanide was suspected, this study indicates normal cyanide levels.

SECTION III
CONCLUSIONS

This work has demonstrated four things:

1. that the cyanide electrode responds to free cyanide levels as opposed to the total cyanide concentration in aqueous solution;

2. that a simple procedure for determining total cyanide using the cyanide electrode is not feasible because of the great stability of metal-cyanide complexes;

3. that the classical acid hydrolysis-distillation procedure for determining total cyanide may not accurately yield true total cyanide levels in the presence of large metal ion concentrations;

4. that the concentrations of cyanide in natural surface water samples are at the limit of Nernstian response of the cyanide electrode and beyond.

The unusually great kinetic stability of metal-cyanide complexes, even the very labile nickel-cyanide complex, coupled with their great thermodynamic stability renders determination of total cyanide levels with the cyanide electrode extremely unlikely. Concomitantly, this exceedingly great stability brings to question the significance of determinations of total cyanide. This work indicates that evaluation of free cyanide, or perhaps cyanide freed by EDTA using the cyanide electrode, might be the more significant measurement of the cyanide content in water samples. Such measurements would more accurately reflect the level of chemically active cyanide present in samples.

SECTION IV
RECOMMENDATIONS

Several additional avenues of research on measurement of cyanide levels in water samples need to be explored:

1. the indication from this work that the acid hydrolysis-distillation procedure for total cyanide gives low cyanide results when metal ions are present in solution needs to be confirmed;

2. a procedure for concentrating cyanide in natural water samples must be developed so accurate determinations with the cyanide electrode can be made;

3. determination of the mechanism of decomposition of metal-cyanide complexes (if indeed any decomposition occurs) in natural and wastewaters should be investigated. If it can be shown that these complexes are nearly totally stable, or if their decomposition mechanism results in destruction of the cyanide (e.g. to methane and ammonia), then it can be convincingly argued that free cyanide and NOT total cyanide is the only environmentally meaningful measurement.

SECTION V
EXPERIMENTAL

Measurements

All readings in this report were collected using an Orion Model 801A Digital pH/mVolt meter, an Orion Model 90-02 double junction reference electrode and an Orion Model 94-06 cyanide electrode.

Solutions

All solutions were prepared from reagent grade potassium cyanide Hydroxide concentrations were established using standard solutic . pre-pared from Acculutes prepared by Anachemia Chemicals Ltd. and obtained from the Sargeant-Welch Company. Sodium nitrate was used to adjust the ionic strength of solutions to 0.10M although most readings were carried out in 0.10M NaOH (pH = 13) solutions. The outer chamber of the double junction reference electrode was filled with a 10% solution of sodium nitrate.

All other chemicals used were of reagent grade except the potassium tetracyanonickelate (II) which was prepared by the procedure given in Inorganic Synthesis, volume 1.

Distilled water was used to prepare all solutions. Checks of the cyanide level in the distilled water with the cyanide-electrode always indicated considerably less than 10^{-7}M concentration.

Stock and Standard Solutions

A 0.10M stock solution of potassium cyanide at a pH of 13 was prepared at least once a month for most of the succeeding readings. From this solution were prepared a series of standard solutions ranging in concentration from 1 x 10^{-3}M (26 ppm) to 1 x 10^{-7}M (2.6 ppb) cyanide. These standard solutions were prepared fresh at least once every two weeks. All solutions were stored in polyethylene bottles. No sign of decomposition was observed for any solution. A 1 x 10^{-5}M (.26 ppm) cyanide solution at a pH of 13 gave the same electrode response even after a four month storage period.

Operating Procedure

The instrumental techniques and general operating procedures used with the cyanide electrode and digital pH meter were those suggested by

the manufacturers of the equipment. In general, readings were taken while stirring and after a wait of one or two minutes for stabilization. Under certain conditions (e.g. dilute solutions, high pH studies, etc.) drifting and fluctuating results were observed requiring longer waiting periods.

Calibration curves of electrode potentials versus pCN (the negative logarithm of the cyanide molarity) were prepared on the average of once a week and were always made immediately prior to taking readings deemed important. The curves were always linear and Nernstian over the concentration range of 10^{-3} (26 ppm) to 10^{-5}M (.26 ppm) cyanide. The slopes of these plots ranged from 56 to 65 although usually they were close to 59, the theoretical value for 24°C. The range of values for the slope are partially a result of poor temperature control in the room this work was carried out in during the summer months. The temperature of the samples in the course of this study ranged from 23°C to 30°C although for most, the temperature was 24°C. No attempt was made to take thermostatted readings.

SECTION VI
DATA

The results of the applicability of the cyanide electrode for measuring free and total cyanide will be reported in three sections:

1. Does the cyanide electrode respond to free cyanide alone?

2. Can the cyanide electrode be used to directly determine total cyanide content?

3. Can the cyanide electrode be used with the hydrolysis-distillation procedure to determine total cyanide?

Does the Cyanide Electrode Respond to Free Cyanide Alone?

The data which follow indicate a definite "yes" as an answer to this question. The specifications supplied by the Orion Company with the cyanide electrode require work at pH values greater than 9.5 where all cyanide is in an ionic, unprotenated form. The electrode does not respond to cyanide when it is in the form of hydrogen cyanide in solution. The manufacturer makes no statement about the electrode response to solutions containing metal-cyanide complexes, however.

In considering potential metal-cyanide complexes for study, it was felt important to choose both stable, kineticly labile complexes, and stable, kineticly inert complexes. The tetracyanonickelate (II) complex, $Ni(CN)_4^{-2}$, was chosen as an example of a kinetic labile, thermodyanamically stable complex for this and subsequent studies. The ferrocyanide $Fe(CN)_6^{-4}$, and ferricyanide, $Fe(CN)_6^{-3}$, ions were chosen for their kinetic inertness a factor that needed careful consideration if the conclusions of this study were to be applied to complexes generally. The thermodynamic and kinetic characteristics of these and other cyanide complexes are given in Table 2. In this table the thermodynamic stability of the metal-cyanide complexes can be seen from their very large stability constants. The kinetic inertness of the iron-cyanide complexes and the kinetic lability of others is apparent from the rates of ligand exchange given.

TABLE 1. Stability equilibrium constants (Ks) and rates of ligand exchange for some typical metal-cyanide complexes

Complex	Ks	Exchange rate
$Ni(CN)_4^{-2}$	10^{30}	Very fast
$Mn(CN)_6^{-3}$	10^{27}	Measurable
$Fe(CN)_6^{-4}$	10^{37}	Very slow
$Fe(CN)_6^{-3}$	10^{44}	Very slow
$Hg(CN)_4^{-2}$	10^{42}	Very fast

The pH values of 12.7 (0.10M NaOH) and 9.8 (1.0×10^{-4}M NaOH and 0.10M $NaNO_3$), both uncorrected for sodium error, were chosen for subsequent measurements. The response of the cyanide electrode to 1.00×10^{-4}M (2.6 ppm) cyanide at these pH values were -157.5 millivolt at pH = 12.7 and -158.4 millivolt at pH = 9.8. The 9.8 value represents a near lower limit for the pH before protonation begins to appreciably reduce the syanide concentration. The good agreement of the millivolt readings experimentally verifies that essentially all cyanide is in the non-protenated form at these pH values.

The effect of the response of the cyanide electrode to the addition of various cyanide-metal complexes to a 1.00×10^{-4}M (2.6 ppm) cyanide solution was investigated. Specifically, reagent grade ferrocyanide, reagent grade ferricyanide and the tetracyanonickelate (II) ion (prepared according to the procedure in Inorganic Synthesis) were used. In Table 2 are some typical results.

TABLE 2. Response of the cyanide electrode to metal-cyanide complexes at different pH values

pH	Relative millivolts*
pH 9.8	
1.00×10^{-4} M KCN	-62.2
100 ml 1×10^{-4} M KCN + .1g $K_3Fe(CN)_6$	-57.2
100 ml 1×10^{-4} M KCN + .1g $K_4Fe(CN)_6$	-61.8
100 ml 1×10^{-4} M KCN + .1g $K_2Ni(CN)_4$	-62.0
pH 12.70	
1.00×10^{-4} M KCN	-62.0
100 ml 1×10^{-4} M KCN + .1g $K_3Fe(CN)_6$	-61.1
100 ml 1×10^{-4} M KCN + .1g $K_4Fe(CN)_6$	-61.3
100 ml 1×10^{-4} M KCN + .1g $K_2Ni(CN)_4$	-61.8

*In this table and most succeeding tables relative millivolt units are used since it is relative changes that are of interest.

In all cases addition of cyanide complexes to 10^{-4}M (2.6 ppm) CN^- solutions result in an increase in cyanide potential implying a decrease in the cyanide concentration as sensed by the cyanide electrode. While all decreases are very small and are nearly within experimental error, these decreases could be resulting from cyanide in solution complexing with uncomplexed metal impurities in the metal-cyanide complexes used. If the cyanide added in the above complexes were free, a cyanide molarity of about 2.5×10^{-2}M (650 ppm) would be realized. This is a 250-fold increase over the 1×10^{-4}M (2.6 ppm) cyanide present in the original solution. It thus appears that the cyanide electrode does not respond to complexed cyanide, but only the free and uncomplexed cyanide.

The lack of an increase in cyanide in these solutions might be due to the kinetic inertness of these complexes. For example, while the tetracyanonickelate is very labile with an exchange half-life of only 30 seconds, the ferrocyanide, with considerable ligand field stabilization energy, has an exchange half-life of about 25 days. To better evaluate the response of the electrode to cyanide complexes without the complication of kinetic effects, additions of aqueous solutions of metal ions

into cyanide solutions and the response of the cyanide electrode to indicate formation of cyanide complexes was observed. The responses of the cyanide electrode to additions of 1.0×10^{-3}M (about 60 ppm for first transition series metals) aqueous metal ions to 100 ml of 1.00×10^{-4}M (2.6 ppm) cyanide were made at two pH values. The results are given in Table 3.

TABLE 3. Relative response in millivolts of the cyanide electrode to successive 1 ml additions of 1.0×10^{-3}M metal ions to 100.0 ml of a 1.0×10^{-4}M (2.6 ppm) cyanide solution

	1×10^{-4}M CN^- (100 ml)	+1 ml metal ion	+2 ml metal	+3 ml metal	+4 ml metal
			at pH = 9.8		
Fe^{+3}	-63.0	-60.5	-54.8	-44.4	-28.7
Fe^{+2}	-61.0	-56.2	-51.8	-46.0	-37.8
Ni^{+2}	-63.0	-52.3	-36.5	- 5.6	---
Cu^{+2}	-61.2	-53.4	-45.3	-34.1	-18.6
Ba^{+2}	-61.6	-60.8	-59.6	-58.8	-58.1
Sr^{+2}	-61.8	-61.0	-60.4	-59.8	-59.4
Zn^{+2}	-62.3	-58.9	-55.0	-51.9	---
Pb^{+2}	-61.5	-59.8	-57.6*	-55.0*	---
Mn^{+2}	-62.6	-61.2	-60.5	---	---
			at pH = 12.70		
Fe^{+3}	-61.2	-59.8	-58.3	-57.6	-56.9
Fe^{+2}	-60.7	-57.2	-56.2	-55.3	---
Ni^{+2}	-60.5	-56.1	-47.8	-35.5	-19.2
Cu^{+2}	-61.6	-58.5	-55.7	---	-46.7

*Precipitate forms

These data at pH 9.8 show that Ni^{+2} and Cu^{+2} quite strongly complex with cyanide removing it from solution as far as the cyanide electrode response is concerned. For a 3×10^{-5}M Ni^{+2} concentration (1.76 ppm), the free cyanide concentration has been reduced from 1.00×10^{-4}M (2.6 ppm) to 1.1×10^{-5}M (.29 ppm). This implies that each Ni^{+2} has complexed with 3 cyanide ions, or that three out of every four nickel ions exists as a tetracyano complex. Again, it is very clear that the cyanide electrode is NOT responding to complexed cyanide. Moreover, at a pH of 9.8 it appears that 1 ppm iron (II), and 2 ppm iron (III) complex with cyanide to a significant level, while zinc (II) and lead (II) show yet smaller effects. Barium and strontium ions which could not conceivably complex with cyanide show the slight positive shift in potential observed earlier for addition of metal complexes. This small positive shift is possibly due to ionic effects or the presence of metal ion impurities. Dilution cannot account for the magnitude of decrease observed.

At a pH of 12.70 the addition of nickel shows a significant reduction in the free cyanide level. Copper (II) shows a smaller, but definite effect, while Fe (II) and Fe (III) may exhibit a very small effect. Only by working at a pH value of 14 did the nickel-cyanide complex prove unstable:

1×10^{-4}M CN^- (100 ml)	+1 ml 10^{-3}M (Ni^{+2})	+2 ml	+3 ml	+4 ml
-143 millivolts	-146	-144	-142	-140

At this pH, however, the data had larger errors because of larger fluctuations in the digital readings.

These data demonstrate that the cyanide electrode does not respond to complexed cyanide, but only free cyanide ions. It must be kept in mind that the readings must be taken at pH values of about 10 and above and that caution must be taken in relating a free cyanide reading at a pH of 10 to that in the sample at pH of 7. As will be shown later in this report, however, the free cyanide concentration in natural water samples with its usual range of metal contaminents is probably nearly the same at pH = 10 as pH = 7.

Can the Cyanide Electrode Be Used to Directly Determine the Total Cyanide Content?

In the previous section the cyanide electrode was shown to respond to free cyanide only. Since the classical hydrolysis-distillation procedure for determination of total cyanide is a time consuming (at least one hour of distillation) one, it was considered profitable to investigate the possible use of the electrode for determining the total cyanide content of solutions directly without prior distillation of hydrogen cyanide from solution. To measure total cyanide a complexing agent capable of decomposing the metal-cyanide complexes would be necessary. The two agents

investigated in this study were hydroxide and ethylenediaminetetraacetic acid (EDTA). The pH dependence of the formation of the metal-cyanide complexes is clearly evident in the previous discussion. The question here is not one of the formation of the complexes, but rather, one of their decomposition. Their demonstrated thermodynamic instability at pH = 13 (except nickel) does not necessarily require their kinetic instability. The stability of the ferrocyanide and ferricyanide as a function of pH is shown in Table 4.

TABLE 4. Relative millivolt readings

pH	After mixing	1 day later	After heating 1 hour
2×10^{-5} M $Fe(CN)_6^{-3}$ at:			
pH 7	250	205	210
pH 10	156	198	181
pH 11	131	139	120
pH 12	136	133	106
pH 13	134	131	109
2×10^{-5} M $Fe(CN)_6^{-4}$ at:			
pH 10	177	---	118
pH 12	206	---	61
pH 13	227	132	---

If all of the cyanide had been released to the solution as free cyanide a relative millivolt reading of -10 millivolts would have been realized. These data demonstrate the tremendous kinetic stability of the iron-cyanide complexes. After two days at room temperature and one hour under reflux, less than 1% of the ferrocyanide-cyanide was released and less than 10% of the ferrocyanide-cyanide. These results imply that distillation times of 24 hours or longer would be required to obtain near quantitative release of cyanide from iron-cyanide complexes. A procedure requiring distillation times of this magnitude obviously represents no improvement over the classical acid-hydrolysis-distillation procedure. Further investigation of hydroxide-decomposition of metal-cyanide was dropped at this point although additional

work ought to be carried out to find conditions or catalyst to facilitate this decomposition.

EDTA, an excellent chelating agent for most metals, was next investigated as a potential general agent for decomposing metal-cyanide complexes and freeing all cyanide. It was anticipated that the EDTA would complex with metal ions in solution, preventing metal-cyanide complex formation and thus giving cyanide readings corresponding to the total cyanide concentration in the solution. In order to evaluate whether EDTA formed metal complexes more stable than the metal-cyanide complexes, addition of 1.0 ml portions of 1.0×10^{-3}M (58 ppm) Ni^{+2} to 100 ml of 1.00×10^{-4}M (2.6 ppm) cyanide containing 1.00 ml of 1.10M disodium EDTA were made at pH = 13. The results are given in Table 5.

TABLE 5. Relative response in millivolts of the cyanide electrode to the addition of nickel (II) and copper (II) to solutions containing both EDTA and cyanide (pH 13)

ml 10^{-3}M Ni^{+2} added	10^{-4}M CN^- without EDTA	10^{-4}M CN^- with EDTA	ml 10^{-3}M Cu^{+2} added	10^{-4}M CN^- without EDTA	10^{-4}M CN^- with EDTA
0.0 ml	-60.5 mVolt	-58.0 mVolt	0.0	-61.6	-59.0
1.0	-56.1	-55.0	1.0	-58.5	-56.0
2.0	-47.8	-54.0	2.0	-55.7	-54.0
3.0	-35.5	-52.0	3.0	---	-52.0
4.0	-19.2	-51.0	4.0	-46.7	-51.0

These results show that EDTA appears to have some effect, although by no means complete, in blocking the interferences of both copper and nickel, the two metals found to form the cyanide complexes most stable in strongly basic solutions. This implies that the metal-EDTA complexes are slightly more stable than the metal-cyanide complexes and that EDTA, thus, might dissociate the metal-cyanide complexes to allow the cyanide electrode to measure total cyanide in solutions.

Again the reverse experiment is the relevent one. While the above data demonstrate the EDTA-metal complexes to be more stable, the important question is whether EDTA will kinetically decompose the metal-cyanide complexes to release complexed cyanide. To answer this question the following experiments were run with ferrocyanide and tetracyanonickelate (II): to 100 ml of 1.00×10^{-4}M (2.6 ppm) cyanide were added successive 1.00 ml increments of 1.0×10^{-3}M (about 60 ppm) metal ions. Reduction of the free cyanide concentration was observed as metal-cyanide complexes formed as reported earlier in the first section. After waiting until metal-cyanide complex formation was complete, 1.00 ml of

0.10M disodium EDTA was added and the response of the cyanide electrode to cyanide as the metal-complexes decomposed was observed. Data for nickel are given in Table 6.

TABLE 6. Relative response in millivolts of the cyanide electrode to the dissociation of the nickel-cyanide complex by EDTA at pH 13

Solution	Relative millivolt reading
100.0 ml 1.00 x 10^{-4}M CN^-	0.0
+1.00 ml 1.0 x 10^{-3}M Ni^{+2}	3.6
+2.00 ml Ni^{+2}	6.7
+3.00 ml Ni^{+2}	10.8
+4.00 ml Ni^{+2}	17.3
+5.00 ml Ni^{+2}	24.0
Above solution after 20 minutes	29.5
Above solution after 1 hour	45.2
Above solution after 1 1/2 hours	50.0
Solution + 1.00 ml 0.10M EDTA	47.5
Above solution after 1/2 hour	45.0
Above solution after 21 hours	33.0
Above solution after 26 hours	33.0
After 47 hours and 1 hour reflux	3.3

Since the electrode gives nearly the same response at the end of the experiment as at the beginning, these data show that EDTA will give virtually quantitative decomposition of the nickel-cyanide. Refluxing, however, is necessary to effect this decomposition. The unexpected kinetic stability of the very labile nickel-cyanide complex renders EDTA decomposition of inert iron-complexes an unlikely prospect. A similar study to the above, using iron (II) is place of nickel (II) seemed to confirm the very slow iron (II)-cyanide complex decomposition,

but since the iron (II)-cyanide stability is less than that for nickel the magnitute of the changes were much smaller and thus more difficult from which to draw conclusions.

At this point, neither hydroxide nor EDTA have proven to be effective in quickly decomposing metal-cyanides to enable direct electrode measurement of total cyanide in solution. While these experiments demonstrate the electrodes inability to simply measure total cyanide, they also dramatically show that the free-cyanide response of the cyanide electrode is to a large degree, pH independent. If the free-cyanide level in a natural water sample at a pH of 7 is needed, adjusting the pH to 10 will have little change in the free-cyanide level. The cyanide electrode, thus, represents a means of accurately assessing the free cyanide concentration in natural water samples. The high thermodynamic stability of nickel and copper cyanide complexes renders them stable at this pH whereas the kinetic stability of the iron-cyanide complexes prevents their dissociation in the time required to make a reading.

Can the Cyanide Electrode Be Used with the Hydrolysis-Distillation Procedure to Determine Total Cyanide?

The inability to find a chemical agent for decomposition of metal-cyanide complexes led to studies of the classical hydrolysis-distillation procedure for total cyanide determination. It was felt that the cyanide electrode would at least supply a faster and simpler method for analysis of cyanide after distillation than the spectrophotometric or titration procedures usually employed. Moreover, the remarkable stability of the metal-cyanide complexes observed to this point led to questions of their stability in acid solutions. Specifically of interest was the question of whether these complexes were completely decomposed in the acid-hydrolysis-distillation procedure used in cyanide determinations (Methods for Chemical Analysis of Water and Wastes, 1971, Environmental Protection Agency, pages 41-52).

The reliability of the method was first checked using potassium cyanide solutions. In the procedure used, 50.0 ml of a cyanide solution was nydrolyzed and pulled by aspirator vacuum through a sintered glass bubbler into 50.0 mi of a 0.1 M NaOH solution. The cyanide concentrations of the solutions before and after hydrolysis thus should be the same if the apparatus is working correctly. Verification of this is seen in Table 7.

TABLE 7. Response of the cyanide electrode to the cyanide concentrations in solutions resulting from acid hydrolysis-distillation of solutions of KCN and metal-cyanide complexes

Determination number	Acid hydrolysis-distillation of KCN solutions 1	2	3
Cyanide millivoltage before distillation	-253.0	-214.0	-281.0
Cyanide millivoltage after distillation	-250.0	-217.0	-270.0
CN^- conc.	$1x10^{-4}$ M (2.6 ppm)	$3x10^{-5}$ M (.78 ppm)	$2.5x10^{-4}$ M (6.5 ppm)

When solutions of accurately weighed cyanide complexes were treated by acid hydrolysis to investigate their stability under acidic conditions, the results were not consistent, however. Typical results can be seen in Table 8.

TABLE 8. Acid hydrolysis-distillation of metal-cyanide complexes

$K_3Fe(CN)_6$		$K_4Fe(CN)_6 3H_2O$		$K_2Ni(CN)_4 2H_2O$	
CN^- exp. found	CN^- calc.	CN^- exp. found	CN^- calc.	CN^- exp. found	CN^- calc.
$2.51x10^{-4}$ M	$.99x10^{-4}$ M	$.89x10^{-4}$	$1.36x10^{-4}$	$0.8x10^{-4}$ M	$1.21x10^{-4}$ M
$1.26x10^{-4}$ M	$1.16x10^{-4}$ M	---	---	$0.75x10^{-4}$ M	$1.44x10^{-4}$ M
$0.95x10^{-4}$ M	$1.46x10^{-4}$ M	---	---	$0.31x10^{-4}$ M	$1.44x10^{-4}$ M
$1.55x10^{-4}$ M	$1.15x10^{-4}$ M	---	---	---	---
$1.01x10^{-4}$ M	$1.15x10^{-4}$ M	---	---	---	---

Generally the tetracyanonickelate complex gave results consistently lower in cyanide than it should have. The ferricyanide results were spurious once giving 2.5 times as much as experimentally calculated, and once only 75%. The difficulty in making accurate measurements of this type lies in the fact that a shift in pCN from 4.0 to 4.1 means a change from 1.0×10^{-4} to 0.8×10^{-4}. Thus, a 2.5% error in the potential

reading in this case is reflected as a 20% error in cyanide concentration. The daily shift in the working millivolt versus pCN curve is frequently greater than 2.5% introducing significant errors. The lack of consistent air conditioning during the summer months has also introduced errors by greater than desired temperature fluctuations. Nonetheless, there is some evidence that the presence of nickel will cause low cyanide results in acid hydrolysis determinations.

To reduce experimental error and observe the interference of metal ions in the acid hydrolysis determination of cyanide the following determinations were made. The cyanide electrode response to a known solution containing cyanide was measured, additions of metal ions to the solution were made, and the solution immediately acid hydrolysed and distilled to release the cyanide into an identical volume of 0.10M NaOH. The response of the cyanide electrode to this final solution was then made. Since the initial and final solution volumes are kept the same, and since the readings are made close in time to each other, the interference of the metal ions should be reflected with minimum experimental error. Results of these determinations with 0.1 g samples of nickel (II), copper (II) and iron (II) nitrates added are shown in Table 9.

TABLE 9. Effect of metal ion on the recovery of cyanide with acid hydrolysis-distillation

Item	Run #1	Run #2	Run #3	Run #4	Run #5
Millivolt before adding metals	-165	-165	-100	-253	-271
Millivolts after adding metals & distilling	-155	-153	- 83	-235	-260
CN^- Molarity	$1x10^{-4}$ (2.6 ppm)	$1x10^{-4}$ (2.6 ppm)	$1x10^{-5}$ (.26 ppm)	$1x10^{-4}$ (2.6 ppm)	$2.5x10^{-4}$ (6.5 ppm)

These data clearly show that metal ions will cause low results in the acid hydrolysis-distillation determination of cyanide. The results nearly always are 40% to 50% low. Extended distillation times on several samples failed to release significantly larger cyanide concentrations.

At this point it appears that metal ions cause low cyanide results even when the acid-hydrolysis-distillation procedure is used. While it is true that the 250 ppm metal ion concentration used in the last sequence of determinations is very high, the data demonstrate an effect that is very important and needs further study. At this point it appears that even the classical acid-hydrolysis, distillation procedure does not always

yield the total cyanide levels in samples with large metal-ion concentration.

One of the principle purposes of this work was to check the response of the cyanide electrode with natural water samples as well as laboratory-prepared samples. The original intention was to use samples collected by the Miami Conservancy District and arrangements for this had been made. Unfortunately, due to cut-backs in financial support, the Miami Conservancy District reduced their sample collection from daily to monthly. While they would have supplied us with samples, their sampling schedule did not agree with our needs. Samples were obtained instead from the Springfield Water Pollution Control. They supplied us with three water samples: one from the Mad River above Springfield, one from the Mad River below Springfield, and one from Buck Creek in Springfield. They also supplied us with three frozen fish which died in a large fish kill in the Mad River in Springfield. An industry using pickling solutions with high cyanide as well as nickel and copper ion concentrations was the principle suspect in the kill. We were asked to determine cyanide levels in the fish using our cyanide electrode.

While the meaning and significance of the following results of natural samples are not always clear, they are presented to initiate a realistic evaluation of some of the limitations of the cyanide electrode in measuring cyanide concentrations. Readings were made on water samples with the cyanide electrode in two ways. With the first method, the solution was adjusted to a pH of 13 and a reading taken immediately with the cyanide electrode. According to the preceding arguments, this reading should give some measure of the free-cyanide content of the water. Some evaluation of the total cyanide was obtained in the second approach using the hydrolysis-distillation method and subsequent measurement of the cyanide concentration in the solution obtained. In addition, direct measurements with EDTA addition were made even though previous investigations indicate the problems with this approach. Results for the Buck Creek water sample and downstream Mad River samples are given in Tables 10, 11, and 12.

TABLE 10. Response of the cyanide electrode to the cyanide concentration in several natural samples using various analysis methods

Sample	Cyanide Molarity		
	Direct elect. determination	Direct det. EDTA addition	Hydrol. dist. determination
Buck Creek	4.2×10^{-7} M (11 ppb)	1.5×10^{-6} M (39 ppb)	1.58×10^{-7} M (4.1 ppb)
Downstream Mad River	5.6×10^{-7} (14 ppb)	1.5×10^{-6} (39 ppb)	6.3×10^{-6} (163 ppb)

TABLE 11. Electrode response to solutions spiked with additional cyanide (increased by 5×10^{-5}M)

Sample	Cyanide Molarity		
	Direct electrode response	Direct electrode response with EDTA	Electrode response to cyanide solution obtained after hydrolysis-distillation
Buck Creek	2.2×10^{-5} M (.57 ppm)	2.2×10^{-5} M (.57 ppm)	3.2×10^{-5} M (.83 ppm)
Mad River	3.2×10^{-5} (.83 ppm)	3.2×10^{-5} (.83 ppm)	3.5×10^{-5} (.91 ppm)

TABLE 12. Analysis of fish from fish kill

Types of fish	CN^-M obtained	ppm CN^- in fish
Small fish	1.1×10^{-4} M	2.4
Large fish	1.2×10^{-5} M	0.30
Crayfish	7.94×10^{-6} M	0.15

The upstream Mad River sample gave cyanide concentrations even less than the figures in Table 10. Because these readings were well beyond the region of Nernstian behavior of the electrode and because considerable drifting occurred before a reading could be taken their validity is very questionable. Even the results in the table are at the extreme limit of application of the cyanide electrode and contain greater errors than previous readings. The data do indicate, however, that addition of EDTA and heating does release additional cyanide. The result of the hydrolysis-distillation determination of cyanide in Buck Creek is suspicious since it is less than that found by direct electrode measurement of the original sample. Only large errors in these readings can explain this inconsistency.

To measure the recovery of cyanide from these natural water samples the Buck Creek and downstream Mad River samples were spiked with cyanide to increase the cyanide concentration by 5×10^{-5} M (1.3 ppm). The spiked solutions were then analyzed for cyanide by direct electrode measurement and by the hydrolysis-distillation procedure, followed by electrode measurement. The results are given in Table 11. In no case was all the added cyanide recovered, although the hydrolysis-distillation procedure gave 64% and 70% recovery. Again, it seems as if the classical cyanide procedure gives low results when contaminents are present. The reason for the low results by direct electrode response can be rationalized as a result of aqueous metal-ions in the samples complexing with the cyanide added. The low results for the hydrolysis-distillation while not easily explained are consistent with previous determinations made in this study. It is very clear from the data for the spiked solutions that the known addition method of analysis is entirely unapplicable to cyanide determinations.

The fact that the direct electrode measurements give lower cyanide concentrations is consistent with the earlier argument that these readings are measuring free and not total cyanide.

In the final study using the cyanide-electrode the cyanide content of two fish and one crayfish which died in a large fish kill in Springfield was determined. Each fish was liquified using a Waring blender. No attempt was made to measure the cyanide level in the resulting solution since it contained enormous concentrations of organic contaminants. Rather, the solution was subjected to the acid hydrolysis-distillation procedure and the cyanide concentration of the solution obtained determined with the cyanide electrode. The results are given in Table 12. The small size of the one fish precluded confirmation of the high cyanide concentration. The cyanide concentrations in the crayfish and large fish and reasonable copper and nickel ion concentrations in the fish as determined by atomic absorption led the Springfield Water Pollution Control to doubt a pickling solution to be the cause of the fish kill.