



DEPARTMENT OF
ENERGY, MINES AND RESOURCES
MINES BRANCH
OTTAWA

COMPLEX IONS OF COPPER AND CYANIDE

H.L. NOBLITT

MINERAL PROCESSING DIVISION

SEPTEMBER, 1973

© Crown Copyrights reserved

Available by mail from Information Canada, Ottawa,
and at the following Information Canada bookshops:

HALIFAX
1637 Barrington Street

MONTREAL
640 St. Catherine Street West

OTTAWA
171 Slater Street

TORONTO
221 Yonge Street

WINNIPEG
393 Portage Avenue

VANCOUVER
800 Granville Street

or through your bookseller

Price .75 cents Catalogue No. M38-1/268

Price subject to change without notice

Information Canada
Ottawa, 1973

Mines Branch Research Report R 268

COMPLEX IONS OF COPPER AND CYANIDE

by

H. L. Noblitt*

SUMMARY OF RESULTS

To define the role of cyanide and cupro-cyanide ions in flotation, a method for their identification and measurement is necessary. Absorption spectroscopy provides a non-destructive means of obtaining that information. Maximum cyanide ion consumption was determined in relation to cupric ions in solution. A method for monitoring cyanide ion concentration is suggested.

*Research Scientist, Metallic Minerals Research Laboratory, Mineral Processing Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.

Direction des Mines
Rapport de Recherches R 268

Complexes Ioniques de Cuivre et Cyanure

par

H.L. Noblitt*

- - -

RESUME

Pour définir le rôle du cyanure et des ions de cyanure de cuivre en flottation, il est nécessaire de se servir d'une méthode valable pour leur identification et leur valorisation. La spectroscopie par adsorption fournit la méthode nécessaire et assure une analyse nondestructive. L'on détermine la relation entre la consommation des ions de cyanure en fonction des ions cupriques et l'on propose un moyen de contrôle pour la concentration des ions de cyanure.

*Chercheur scientifique, Laboratoire de Recherche des minéraux métalliques, Division du traitement des minerais, Direction des Mines, Ministère de l'Énergie, des Mines et des Ressources, Ottawa, Canada.

CONTENTS

	<u>Page</u>
Summary of Results	i
French Résumé	ii
List of Tables.....	iv
Introduction	1
Historical	2
Theory	3
Experimental	8
Test 1	9
Test 2	11
Discussion of Results	15
Conclusions	18
References	19
Appendix 1	20
Appendix 2	21
Appendix 3	22

LIST OF TABLES

<u>No.</u>		<u>Page</u>
1	Ionic Concentrations in Cupric Nitrate Solutions.....	5
2	Ionic Concentrations from Absorbance Curve, 0.1.M. Cupric Chloride.....	6
3	Composition of Reaction Mixtures in Absorbance Tests.....	13
4	Ion Distributions for Solutions from Table 3.....	14
	Calculations of Ionic Concentrations, Test ii(e).....	1
	Calculations of Ionic Concentrations, Tests ii and iii....	1

INTRODUCTION

Concentration of Canadian base metal ores is, to a major extent, dependent upon the process of froth flotation. Recovery of the desirable minerals requires separation and rejection of undesirable species. Selective mineral depressants assist in this process. One of the reagents most commonly used to make separations between different valuable sulphide minerals and to reject undesirable ones is cyanide. It is reactive, extremely toxic, and, under certain conditions, it can release a lethal gas. Woodcock and Jones⁽¹⁾ in speaking of base metal concentrators, say "Flotation systems are dynamic, are not in equilibrium, and are subject to unpredictable changes. It is contended that in many plants it is unwise to measure or control only one parameter in solution. It is important to monitor and/or control several parameters, each of which has its part to play in flotation. Furthermore, it may be desirable to monitor and/or control certain parameters at several stages (e.g., in grinding as well as in flotation cells) so that an optimum chemical climate is maintained at all stages. Simple metering of reagents is seldom likely to be completely satisfactory". This can be done only when all of the parameters present are recognized and means become available for their determination.

The purposes of this paper are to elucidate the parameters present in mill solutions and to present a method of measuring some of them in one restricted area of the flotation process. In brief, it demonstrates how the concentrations of different cyanide ions, molecules, and complexes with copper may be determined without altering those concentrations. To this end, the cupric nitrate and cupric chloride solutions in water are examined and then the methods developed are applied to cyanide-copper complexes. The methods developed here may be applied profitably in other related areas.

Historical

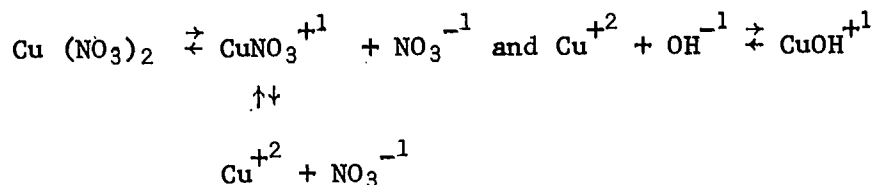
In 1901, Lock⁽¹⁾ mentioned that copper dissolved in cyanide solutions. In 1910, Clennell⁽³⁾ described a method for determining copper dissolved in cyanide solutions. Precipitation by nitric acid as cuprous cyanide gave no estimation of which cyanide-copper ions were present. In 1913, Julian and Smart⁽⁴⁾ mentioned $K_2Cu(CN)_4$ but gave no method of estimating its concentration. In 1915, Clennell⁽⁵⁾ mentioned $K_2Cu(CN)_3$, $K_2Cu_3(CN)_5$ and $K_3Cu(CN)_4$. No method of determining the concentration of each was given. In 1936, Dorr⁽⁶⁾ described $NaCu(CN)_2$ but gave no method of determination. In 1950, Dorr and Bosqui⁽⁷⁾ stated, "It is generally accepted that copper dissolved in cyanide solution exists in the form of complex ions such as $Cu(CN)_2^{-1}$ (thought to be the most common), $Cu(CN)_3^{-}$ and $Cu(CN)_4^{-}$." For copper determinations, the complexes had to be destroyed by strong acids. Also, in 1950, Willis and Woodcock⁽⁸⁾ used potentiometric titration with $AgNO_3$ to estimate the concentration of free cyanide ion and of some of the complex ions present. One of their observations was "It is to be noted that, even if a titration shows the presence of a particular complex ion in the solution at the end point, it does not necessarily imply that this complex was present in the original solution, which is the solution of interest". This may be amended to read it does not imply necessarily that this concentration of the complex was present in the original solution. They have developed a very usable method of estimating the concentrations of the ions present "at pH's that prevent hydrolysis of CN^{-1} to HCN ". In 1958, Simpson and Waind⁽⁹⁾ used ultra-violet absorption to estimate the apparent molar extinction coefficients of $Cu(CN)_2^{-1}$, $Cu(CN)_3^{-2}$, and $Cu(CN)_4^{-3}$ ions. In the 1960's, specific ion electrodes for the determination of cupric and cyanide ions became available but neither type responds to complex ions. In 1965, the Dupont 310 Curve

Resolver became available and resolution of the complex absorbance curves into individual Gaussian peaks became possible. With the assistance of these modern developments in instrumentation, it is expected that a much more coherent and complete picture of the nature of cupro-cyanide complexes can be presented.

THEORY

When light passes through a solution, containing ions having incomplete outer shells of other than 8 or 18 electrons, portions of the light having specific wave lengths are absorbed by the ions. One electron absorbs one photon of light and the energy received moves the electron from its basic orbit to an expanded one. The expanded orbit is unstable so the electron emits the same amount of energy and returns to its former orbit. The energy given up is radiated in all directions and the amount passing to the sensor along the original direction is greatly reduced. The same electron may absorb photons of several energies at different times but, if it does so, the expanded orbit for each will be different. Thus cupric ion absorbs at one wave length in the ultraviolet, one in the visible and one in the near infrared, at approximately 3630, 7580, and 11900 Å.

In a cupric nitrate solution, dissociation leads to the formation of cupric mono-nitrate and cupric mono-hydroxyl ions.



Cupric ion has 17 electrons in its M-shell and can absorb radiation of suitable wave lengths. The force necessary to remove an electron from the outer shell of Cu^{+2} in CuNO_3^{+1} is less than that needed for Cu^{+2} alone, therefore,

the wave length of the absorbed energy is longer. A method of calculating the wave length ratios is given in Appendix 1. In Figure 1, (a) and (b), the absorbance wave length curves are shown for 0.01 and 0.02-M solutions of copper nitrate in water.

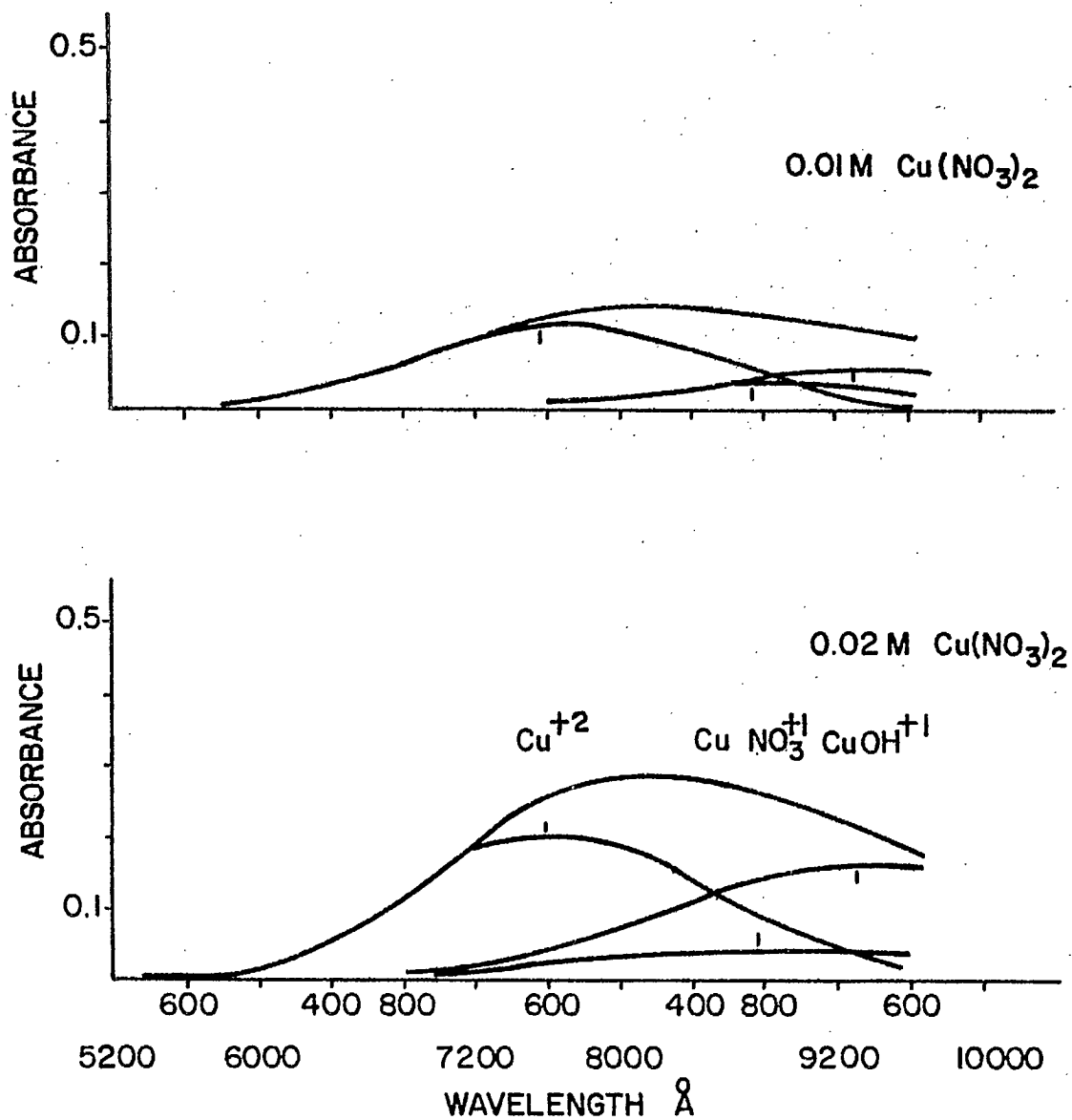


Figure 1 Absorbance Curves for Cupric Nitrate Solutions in Water.

Upon resolution, the absorbance of each ion become known and the concentrations of the ions are calculated in Table 1.

TABLE 1

Ionic Concentrations in Cupric Nitrate Solutions

(a) 0.01 M.

	Cu^{+2}		CuNO_3^{+1}		CuOH^{+1}	
Wave length, Å	7580		8750		9300	
Absorbance	0.122		0.040		0.060	
% transmitted	75.5		91.2		87.1	
% absorbed	24.5	+	8.8	+	12.9	= 46.2
% of copper	53.0		19.0		28.0	
[Ion] , M	0.0053		0.0019		0.0028	

(b) 0.02 M

Absorbance	0.204		0.040		0.158
[Ion] , M	0.0098		0.0023		0.0079

The manufacturer of the cupric nitrate standard solution used quoted concentrations of 0.0055 and 0.0096 M cupric ion in solutions of these strengths. With this excellent agreement the concentrations calculated for CuNO_3^{+1} and CuOH^{+1} may be accepted.

At concentrations of cupric chloride in water that give absorbance curves with absorbances sufficiently high for resolution, e. g., greater than 0.001 M, chloride ion interferes with the cupric-ion electrode so no comparison was possible for cupric chloride solutions⁽¹⁰⁾. In the tests on cyanide complexes it was thought best to use cupric chloride because

introduction of nitrate ion to a solution of a reducing ion such as cyanide might lead to unexpected complications. The absorbance curve for 0.1 M cupric chloride in water is shown in Figure 2, and the ionic concentrations calculated are given in Table 2.

TABLE 2

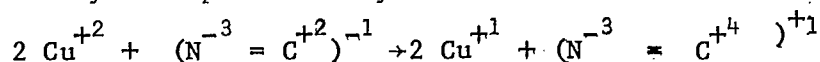
Ionic Concentrations from Absorbance Curve O.I.M. Cupric Chloride

Ion	Cu^{+2}	CuCl^{+1}	CuOH^{+1}	Cu^{+2}	CuCl^{+1}	CuOH^{+1}
Wave length, Å	7580	8220	9300	11900	12960	14800
Absorbance	0.600	0.500	1.080	0.180	0.155	0.230
Ion, M	0.0319	0.0291	0.0390	0.0322	0.0286	0.0392

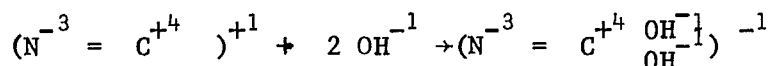
It is evident that absorption in the near infrared has the same distribution as in the visible portion of the spectrum.

Cupric-Cyanide Complexes:

It is known that the addition of a solution of cyanide in water to a solution of a cupric salt leads to precipitation of the green, flocculent cupric cyanide, $\text{Cu}(\text{CN})_2$. As cyanide is added in excess of that required for complete precipitation, the solid material turns white and eventually dissolves to a clear, colorless solution. Also the color change is accompanied by a change from cupric to cuprous ion. Cuprous ion, Cu^{+1} , has a complete outer shell of 18 electrons and as such does not absorb radiation in solution. Sodium cyanide has the formula: $\text{Na}^{+1} - \text{N}^{-3} = \text{C}^{+2}$. The reaction of cupric ion reduction may be represented by:



Hydroxyl is present in the solution so a further reaction is:



Two hydroxyls on a single C^{+4} ion are unstable and one molecule of water is

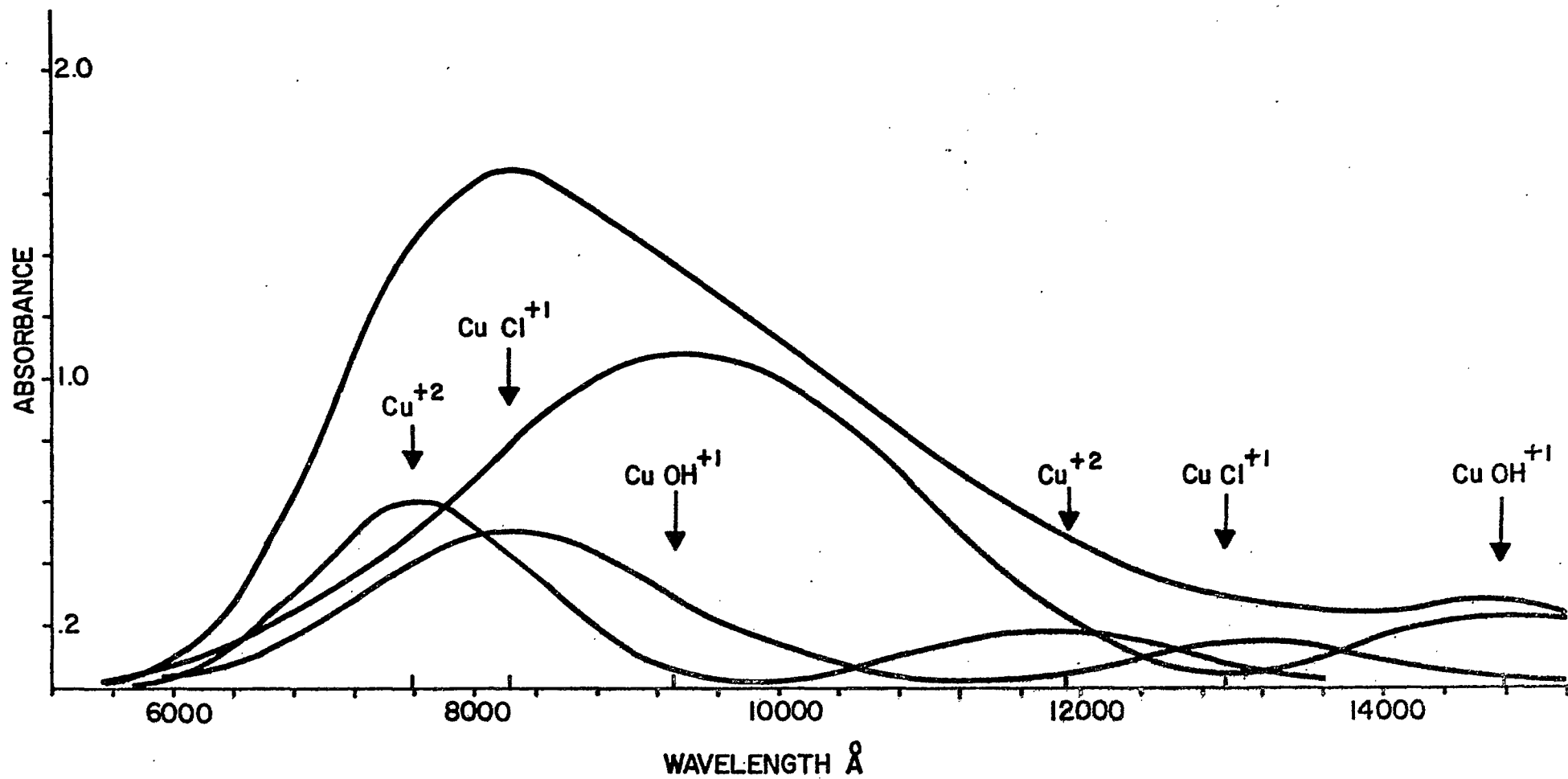
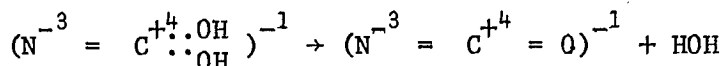


Figure 2. Absorbance, 0.1 M CuCl_2 in Water.

is split out (11).



The end products of the reaction are cuprous ion, cyanate ion, and water.

For each two cupric ions reduced, one cyanide ion is converted to cyanate.

Reduction of Cu^{+2} in $\text{Cu}(\text{CN})_2$ to Cu^{+1} produces the new ion, $\text{Cu}(\text{CN})_2^{-1}$, which is soluble, colorless, and capable of acquiring additional cyanide ions to form other colorless complexes.

When sodium cyanide dissolves in water, it hydrolyzes partially to HCN and NaOH. At a pH of 11, most of the cyanide is present as CN^{-1} but below this pH progressively more HCN is present until very little cyanide ion is found at pH 6. Because of the relatively high charges of N^{-3} and C^{+2} association of the cyanide ions leads to a measurable concentration of $(\text{CN})_2^{-2}$ in the solution.

It has been assumed generally that the final ion formed from cupric and cyanide solutions is $\text{Cu}(\text{CN})_4^{-3}$, but this has not been shown conclusively.

EXPERIMENTAL

The equipment used in the test work included; a Spectronic 20 Colorimeter, a Spectronic 600 spectrophotometer, a Beckman DK2A spectrophotometer, a Hewlett Packard two-pen Moseley Model 7100B strip chart recorder, a Moseley 17005A X-Y recorder, two 801 Orion pH Meters, a Corning pH Meter, Orion cupric and cyanide-specific ion electrodes and Fisher Scientific glass, calomel reference and double-junction reference electrodes.

Reagents used were Orion cupric nitrate standardizing solution and Shawinigan sodium cyanide; the first of reagent grade, the second not quite so pure.

Test 1

In this test, 200 ml of 0.025 M cupric chloride in distilled water was placed in a plastic reaction vessel provided with a magnetic stirrer. Making contact with the solution were glass, cupric, and cyanide electrodes and three reference electrodes. The glass electrode was paired with the calomel reference and the other two with double-junction electrodes that had a 10% sodium nitrate filling solution. The response of the glass electrode was sensed by the Corning pH meter. Cupric and cyanide electrodes were sensed by the two Orion pH meters. The outputs of these three meters were plotted by the strip chart recorders and are recorded in Figure 3 as sodium cyanide was added to the solution.

In Figure 3, the concentration of cupric ion is not noticeably reduced until a CN/Cu ratio of 0.3 is reached. After this, the concentration falls rapidly until none is found at a ratio of 2.5. At this point, precipitation of $\text{Cu}(\text{CN})_2$ is relatively complete and reduction has begun. No cupric ion is found at higher ratios. At ratio 3.0, the cyanide concentration becomes measurable and this increases to the end of the test at a ratio of 6. Up to ratio 2.5, precipitation and reduction progress at a very low cyanide concentration. However, when the reaction involves adding more cyanide to $\text{Cu}(\text{CN})_2^{-1}$ ion, an increasingly great concentration of cyanide ion must be present. At CN/Cu ratio 4.5, the cyanide concentration is 0.0041 M. At a ratio of 6 the cyanide curve becomes linear and the cyanide concentration is 0.0191 M. To achieve this, 60 ml of 0.5-M NaCN solution was added for a total of 0.03 moles. Cyanide remaining was 260 ml of 0.0191 M solution for a cyanide content of 0.00497 moles. At a pH of 9.6, the cyanide present as CN^{-1} is reported to be 0.755 of total free cyanide plus HCN. Then total remaining cyanide is $0.00497 / 0.755 = 0.00671$ moles. Cyanide consumed was 0.02329 moles. As this reacted

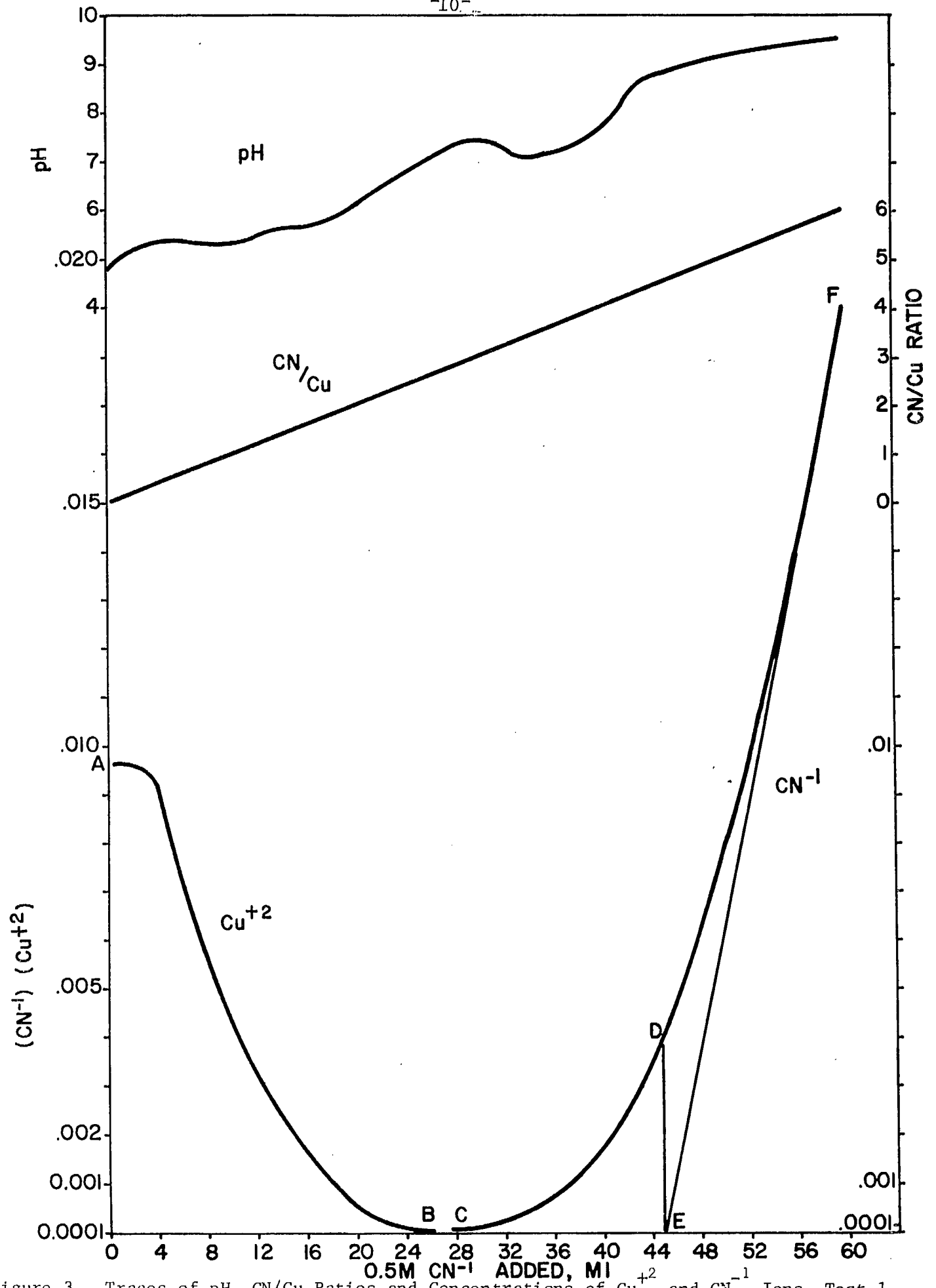


Figure 3. Traces of pH, CN/Cu Ratios and Concentrations of Cu⁺² and CN⁻¹ Ions, Test 1.

with 0.005 moles of cupric ion the ratio of consumed cyanide ion to cupric ion was 4.65:1. Within the limits of experimental error this is equivalent to $\frac{1}{2}$ CN to reduce one Cu^{+2} to Cu^{+1} and 4 CN to produce $\text{Cu}(\text{CN})_4^{-3}$. If a line be drawn from 45 ml 0.5 M NaCN added to F, it is approximately asymptotic to the curve at that point. Hence no complexes beyond $\text{Cu}(\text{CN})_4^{-3}$ are formed.

The reduction of cupric ion to cuprous ion removes hydroxyl, so it is to be expected that reduction will reduce the pH. This is indicated by a flattening of the pH curve between CN/Cu ratios 0.3 and 1.0 as precipitation takes place and again from ratio 3 to ratio 4 as the precipitate dissolves, freeing enclosed $\text{Cu}(\text{CN})_2$.

Test 2

This test investigates the behavior of mixtures of cupric chloride and sodium cyanide solutions in water at different concentrations and different CN/Cu ratios. Compositions are given in Table 3. The final volume in all tests was 200 ml. In the first sub-tests solid material was filtered out before the absorption curve was obtained. Total Cu and CN were unknown in these solutions.

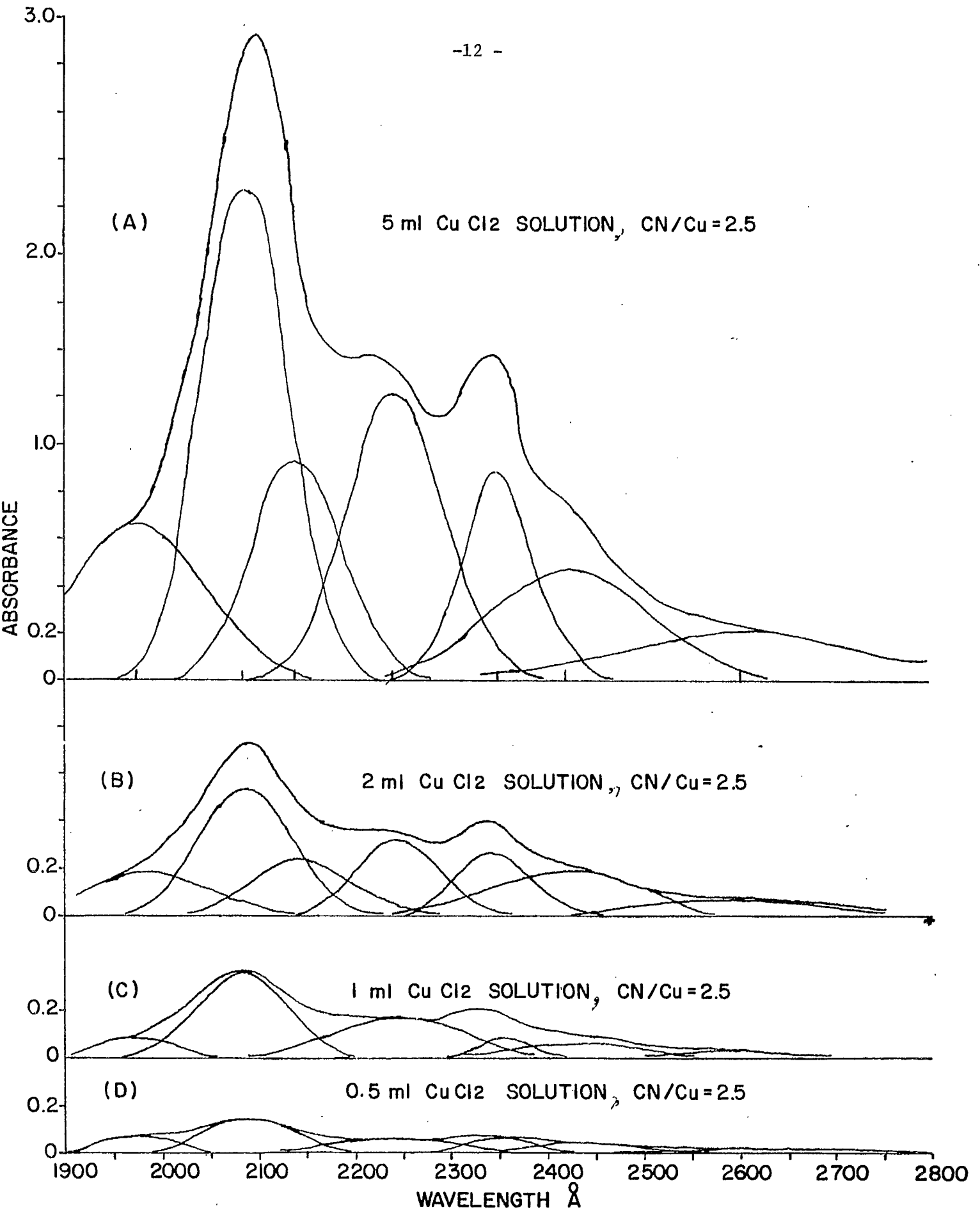


Figure 4, Test 1 (i) Absorbance of solutions having CN/Cu ratio = 2.5

TABLE 3

Composition of Reaction Mixtures in Absorption Tests

Test	Section	CuCl ₂ , ml	[CuCl ₂], M	NaCN, ml	[NaCN]	CN/Cu
(i)	(a)	5	0.005	12.5	0.005	2.5
	(b)	2	0.005	5.0	0.005	2.5
	(c)	1	0.005	2.5	0.005	2.5
	(d)	0.5	0.005	1.25	0.005	2.5
(ii)	(e)	0.5	0.05	1.75	0.05	3.5
	(f)	0.25	0.05	0.875	0.05	3.5
	(g)	0.1	0.05	0.35	0.05	3.5
	(h)	0.05	0.05	0.175	0.05	3.5
(iii)	(i)	0.768	0.005	0.461	0.05	6

The absorbance-wave length curves for Test (i) are plotted in Figure 4 with the results of curve resolution. In Figure 5, Curves (i) (b); (ii) (f); and (iii) (i) are plotted for comparison of ion distribution at different CN/Cu ratios.

Ion distributions used in Table 3 are given in Table 4.

TABLE 4

Ion Distribution for Solutions from Table 3

Wave length, Å	1975	2086	2140	2242	2353	2420	2602
				α	β		
Ion	HCN	CN^{-1}	$\text{Cu}(\text{CN})_4^{-3}$	$\text{Cu}(\text{CN})_3^{-2}$	$\text{Cu}(\text{CN})_3^{-2}$	$\text{Cu}(\text{CN})_2^{-1}$	$(\text{CN})_2^{-2}$
Abs C ⁺² Ions	1	1	2	3	3	2	2
(i)							
(a) Absorb.	0.672	2.086	0.935	1.225	0.895	0.480	0.208
% of Ions	23.48	29.60	13.19	9.35	8.69	10.00	5.69
(b) Absorb.	0.185	0.545	0.245	0.325	0.265	0.180	0.055
% of Ions	18.91	38.97	11.74	9.58	8.30	9.25	3.25
(c) Absorb.	0.095	0.366	- -	0.180	0.097	0.080	0.033
% of Ions	18.46	53.42	- -	10.58	6.25	7.87	3.42
(d) Absorb.	0.062	0.1315	0.0015	0.0620	0.0315	0.0272	0.018
% of Ions	25.84	50.70	0.40	8.62	4.53	5.93	3.98
(ii)							
(e) Absorb.	0.680	1.980	1.350	1.238	1.210	0.430	0.155
% of Ions	23.60	29.55	14.27	9.37	9.34	9.38	4.49
(f) Absorb.	0.165	1.040	0.535	0.648	0.590	0.220	0.100
% of Ions	14.74	42.41	16.53	6.37	5.88	9.27	4.80
(g) Absorb.	0.053	0.398	0.108	0.235	0.245	0.063	0.045
% of Ions	9.39	48.99	8.99	11.38	11.73	5.52	4.00
(h) Absorb.	0.031	0.188	0.048	0.100	0.095	0.043	0.015
% of Ions	10.28	52.33	7.82	10.23	9.79	7.01	2.54
(iii)							
(i) Absorb.	0.065	0.330	0.020	0.145	0.160	0.046	- -
% of Ions	14.77	56.50	2.39	10.06	10.91	5.37	- -

Absorption by cyanide is through the C^{+2} ion, (incomplete L-shell), and is proportional to absorbing C^{+2} content. HCN and CN^{-1} each have one C^{+2} ion; $Cu(CN)_4^{-3}$ has two that absorb at one wave length within the range of the spectrophotometer used. The other two absorb further into the ultra-violet. Both $Cu(CN)_3^{-2}$ ions have three C^{+2} ions that absorb at the same wave length. $Cu(CN)_2^{-1}$ and $(CN)_2^{-2}$ have two. The percentages of cyanide ion complexes must be reduced by these factors before a true picture of concentration emerges. This has been done for the cyanide complexes observed.

DISCUSSION OF RESULTS

The degree of agreement between concentrations of cupric ion calculated from absorption curves for cupric nitrate and manufacturer's reported concentrations for standards indicates that the method can give excellent results when properly applied. Also, the distribution of ionic concentration is the same from the visible and from the infrared absorptions of cupric chloride, so either will give accurate results.

Test 1 proves that the maximum consumption of cyanide possible by cupric ion is 4.5 moles of cyanide for each mole of cupric ion. Also, no measurable cyanide is present until the CN/Cu ratio is greater than 2.5. The reduction of cupric ion to cuprous ion is not reversible, i.e., cyanide consumed in this way is not recoverable. Dissociation of $Cu(CN)_4^{-3}$, $Cu(CN)_3^{-2}$ and $(CN)_2^{-1}$ on dilution leads to recovery for re-use of some cyanide. It is doubtful that $Cu(CN)_2^{-1}$ dissociates at usable concentrations.

In flotation plants, the effective depressant is cyanide ion. From an examination of Figures 4 and 5, it may be noted that cyanide ion absorbs at 2086 Å. In most cases, the only interference is from $Cu(CN)_4^{-3}$ at this wave length. Woodcock and Jones⁽¹⁾.

Woodcock and Jones⁽¹⁾ report that the ore treated at Mount Isa Copper Mines contains, "Chalcopyrite as the main copper mineral and pyrite in a silica-dolomite gangue. Some ore has been deep-leached underground; some has been heated to relatively high temperatures prior to or during mining and some has been partly oxidized. Rougher concentrate is cleaned in a three-stage circuit. Scavenger concentrate is reground and refloated to give a concentrate that goes to the cleaning circuit. 0.15 pounds of NaCN are added to the rodmill per ton of feed and 0.1 pounds are added to the cleaning circuit". Rougher flotation feed solution contains less than 2 ppm cyanide as NaCN; 6 ppm total cyanide as NaCN; and less than 4 ppm ferrocyanide and 31 ppm CNS⁻¹. Solution from the third cleaner tailing was not analysed. Absorption curves for these two solutions are included in their Figure 6 and are reproduced here as Figure 6. Curve 4, for the rod mill discharge, shows relatively high cyanide and probably high thiosulphate absorption but relatively low absorption by $\text{Cu}(\text{CN})_3^{-2}$ and $\text{Cu}(\text{CN})_2^{-1}$. Curve 2, for solution from the third cleaner tailing, shows the same high absorption in the 2050 to 2200-Å range with well-developed peaks at about 2240 and 2340 Å, corresponding to $\text{Cu}(\text{CN})_3^{-2}$ absorption, and enhanced absorption in the 2420 to 2460-Å range due to $\text{Cu}(\text{CN})_2^{-1}$. This suggests that plants milling simple copper ores from the Precambrian and unoxidized ores from later deposits in Canada might use the method developed above for cyanide control.

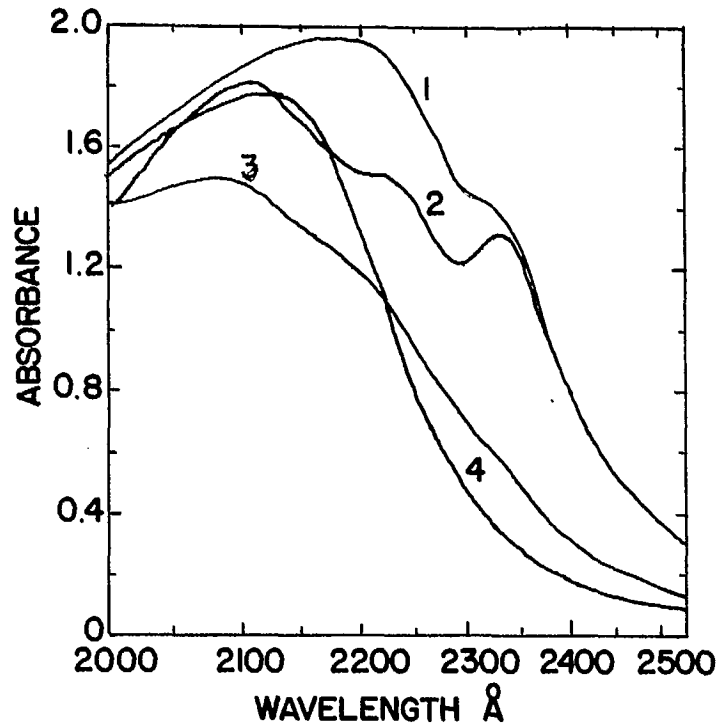


Figure 6. Spectral Curves for Selected Solutions. (1) Rod-mill discharge, Mount Isa lead-zinc plant; (2) third cleaner tail, Mount Isa copper plant; (3) zinc rougher tailing, Mount Isa lead-zinc plant; and (4) rod-mill discharge Mount Isa copper plant. From Woodcock, J. T., and Jones, M. H., "Oxygen concentrations, Redox Potentials, Xanthate Residuals, and other Parameters in Flotation Plant Pulps", Ninth Commonwealth Mining and Metallurgical Congress, 1969, Paper 4.

CONCLUSIONS

- (1) The addition of either cupric or cyanide ion to a solution of the other inevitably leads to the formation of solid copper-cyanide compounds or to cupro-cyanide complexes.
- (2) No complex richer in cyanide than $\text{Cu}(\text{CN})_4^{-3}$ is formed.
- (3) No significant concentration of cyanide ion can be obtained until all cupric ion is complexed.
- (4) Unless excessive interference is present it is feasible to monitor or control, or both, the cyanide ion concentration by the use of a monochromator set at 2086 Å.
- (5) The method provides a non-destructive means of estimating the concentrations of all the cyanide forms and copper-cyanide complexes in a flotation solution.
- (6) In flotation work, one mole of cupric ion can consume no more than 4.5 moles of cyanide ion.

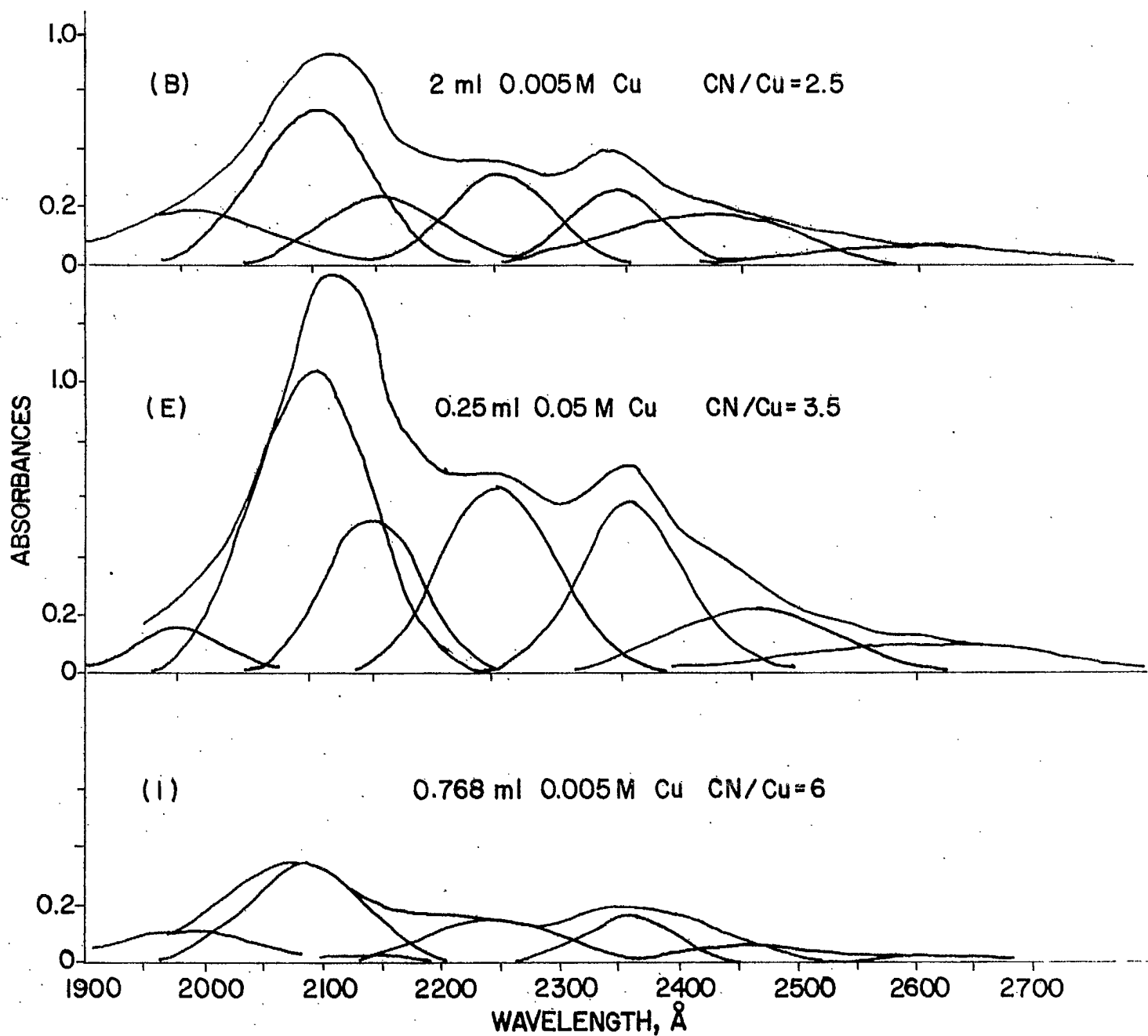


Figure 5 Absorbances at different CN/Cu Ratios.

REFERENCES

- (1) Woodcock, J. T., and Jones, M. H., "Oxygen Concentrations, Redox Potentials, Xanthate Residuals, and other Parameters in Flotation Plant Pulp", Ninth Commonwealth Mining and Metallurgical Congress, 1969, Paper 4.
- (2) Lock, C. E., Wainford, E & F. N., Spon Ltd., 1901.
- (3) Clennell, J. E., "The Chemistry of Cyanide Solutions", McGraw-Hill, 1910.
- (4) Julian, H. F., Smart, E., "Cyaniding Gold and Silver Ores", Griffin, 1913.
- (5) Clennell, J. E., "The Cyanide Handbook", McGraw-Hill, 1915.
- (6) Dorr, J. V. N., Bosqui, F. L., "Cyanidation and Concentration of Gold and Silver Ores", McGraw-Hill, First Edition, 1936.
- (7) Dorr, J. V. N., Bosqui, F. L., "Cyanidation and Concentration of Gold Ores", 2nd Ed., McGraw-Hill, 1950.
- (8) Willis, G. M., Woodcock, J. T., "Chemistry of Cyanidation" Proceedings Aust. I. M. M. (INC), 1950.
- (9) Simpson, E. A., Waind, G. M., "The Ultraviolet Spectra and Stability Constants of Cuprous Cyanide Complexes", J. Chem. Soc., 1958, 1746-9.
- (10) Instruction Manual, Cupric Ion Electrode, Orion Research Inc., Cambridge, Mass.
- (11) Richter, G. H., "Textbook of Organic Chemistry", 2nd Ed., Wiley, 1946, p 71.

APPENDIX 1

Calculation of Absorption Wave Lengths

These calculations are based on the assumption that the wave length absorbed by a simple ion having an incomplete outer shell in a complex ion is inversely proportional to the net charge at the nucleus of the absorbing ion.

(1) Cu⁺² ion

Very dilute solutions of CuCl₂ show an absorption peak at 7580 Å.

This is a second-order absorption, first and third-order absorptions are found at 3630 and 11,900 Å.

(2) CuCl⁺¹ ion

The ionic radius of Cu⁺² is 0.72 Å, that of Cl⁻¹ is 1.815 Å. So the centre of Cl⁻¹ is at a distance of 2.535 Å from the nucleus of Cu⁺². The effect of Cl⁻¹ is then $-1/2.535^2 = -0.1556$ units of charge. The net charge is $2 - 0.1556 = 1.8444$ units, and the absorption wave length of Cu⁺² in CuCl⁺¹ is $7580 \times 2/1.8444 = 8219.5$ or 8220 Å. See Figure i, (a).

(3) CuOH⁺¹ ion

The ionic radius of O⁻² is 1.40 Å (+ to -). H⁺¹ ion is found at a distance of 0.12 Å from the surface of O⁻². O⁻² is centred at 2.12 Å and H⁺¹ at 3.64 Å from the nucleus of Cu⁺². Net effect at that point is $2.0000 - 0.4450 + 0.0755 = 1.6305$ units. Wave length of absorption is $7580 \times 2/1.6305 = 9298$ or 9300 Å. See Figure i (b). The ion is linear.

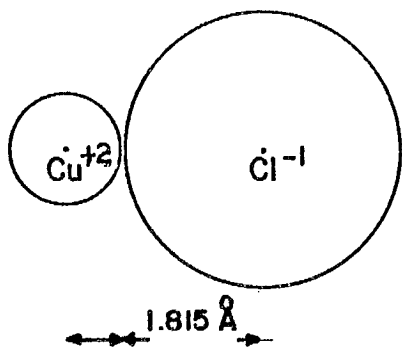
(4) CuCN⁺¹

The ionic radius of N⁻³ is 1.68 Å and of C⁺² is 0.31 Å. The ion is linear. Then the net force at the centre of Cu⁺² is $2,000 - 3/2.40^2 + 2/4.39^2 = 1.5830$ units of charge. Wave length = $7580 \times 2/1.5830 = 9577$ or 9580 Å.

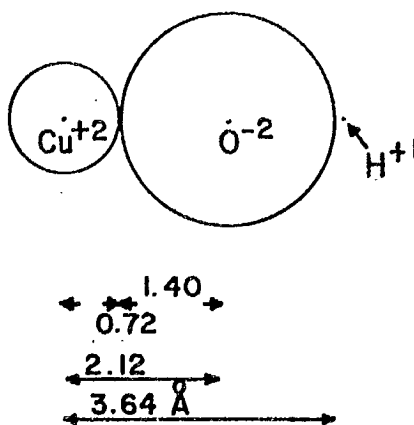
See Figure i (c).

(5) CuNO₃⁺¹

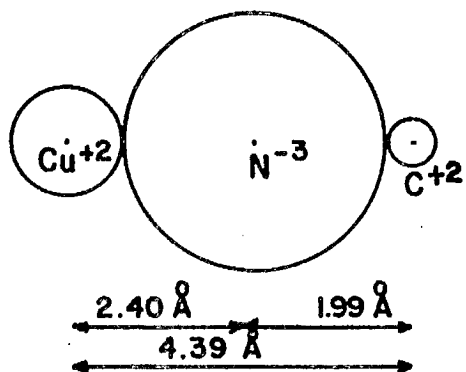
N⁺⁵ is at the centre of the three mutually touching O⁻² ions. They



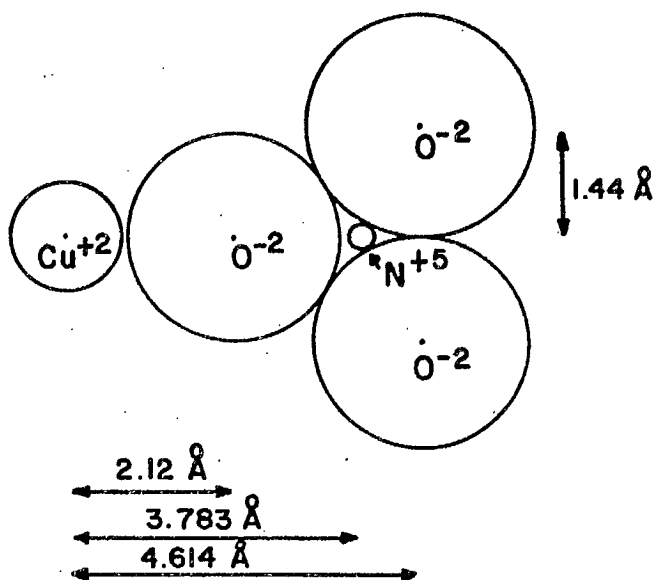
(A) - Cu Cl⁺¹



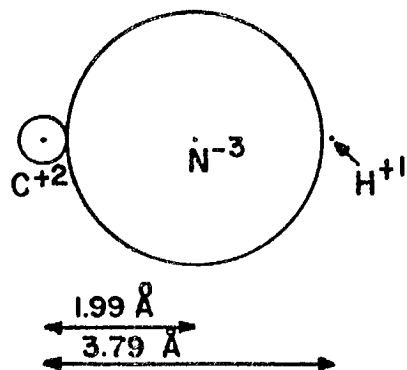
(B) - Cu OH⁺¹



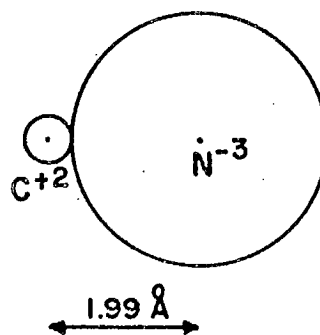
(C) - Cu CN⁺¹



(D) - Cu NO₃⁺¹



(E) - HCN



(F) - CN⁻¹

Figure 1 Structure of Simple Cupric and Cyanide Ions

are all negative so the radii with respect to one another is 3% greater or 1.44 Å. The net force is $2.000 - 2/2.12^2 + 5/3.783^2 - 2 \times 2/(4.614^2 + 1.44^2)$ = 1.7332 units. Wave length is $7580 \times 2/1.7332 = 8747$ or 8750 Å. See Figure i (d).

(6) HCN

C^{+2} is the absorbing ion. N^{-3} is centred at a distance of 1.99 Å from its centre. H^{+1} is 3.79 Å distant. Net force is $2.000 - 0.7575 + 0.0696 = 1.3121$ units. HCN absorbs at 1975 Å. See Figure i (e).

(7) CN⁻¹

Net force is $2.0000 - 0.7575 = 1.2425$ units. Wave length is $1975 \times 1.3121/1.2425 = 2086$ Å. See Figure i (f).

(8) CuCN⁺¹

Net force at centre of C^{+2} is $2.0000 - 3/1.99^2 + 2/4.39^2 = 1.3463$ units. Wave length is $1975 \times 1.3121/1.3463 = 1925$ Å. This is outside the range of the spectrophotometer that was used and appears only in the solutions that have a very low cyanide concentration. Then $CuCN^{+1}$ absorbs at 9580 and 1925 Å by two unlike simple ions. See Figure 1 (c).

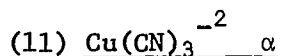
(9) (CN)₂⁻²

This complex ion forms in solution due to the relatively high charges on the component ions. Net force on either C^{+2} ion is $2.0000 - 2 \times 3/1.99^2 + 2/1.966^2 = 1.0024$ units. Wave length is $1975 \times 1.3121/1.0024 = 2585$ Å. See Figure ii (g).

(10) Cu(CN)₂⁻¹

In all subsequent complex ions copper is in the cuprous form and having a complete outer shell of 18 electrons, does not absorb radiation within the wave length range of the tests. Its radius is 0.96 Å. The net force is (from (9)) $1.0024 + 1/(4.37^2 + 0.983^2) = 1.0522$ units. Wave length is 1975

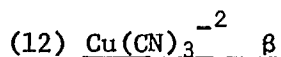
$\times 1.3121/1.0522 = 2463 \text{ \AA}$. See Figure ii (h).



In this ion, the three N^{-3} ions are in contact, their centres being at the corners of an equilateral triangle with side of 3.46 \AA . Cu^{+1} touches all three N^{-3} ions. Each C^{+2} ion is in contact with two N^{-3} and θ is 70° . With origin at O, X-axis perpendicular to the paper through O, Y-axis (positive) to the right and Z-axis (positive) up through O the co-ordinates of the centres of the ions are:

	X	Y	Z
C^{+2}_1	0	-1.33	0.92
C^{+2}_2	-1.15	0.665	0.92
C^{+2}_3	1.15	0.665	0.92
Cu^{+1}	0	0	-1.723
N^{-3}_1	-1.73	-1	0
N^{-3}_2	1.73	-1	0
N^{-3}_3	0	2	0

The net force on C^{+2}_1 , C^{+2}_2 or C^{+2}_3 is $2.0000 + 2(2/2.3036^2) + 1(1.33^2 + (1.723 + 0.92)^2) - 2 \times 3/(1.99^2) - 3/(3.33^2 + 0.92^2) = 2.0000 + 0.7538 + 0.1142 - 1.5150 - 0.2514 = 1.1016$ units. Wave length is $1975 \times 1.3121/1.1016 = 2352 \text{ \AA}$. See Figure ii (i).



The net force on C^{+2}_1 , C^{+2}_2 , or C^{+2}_3 is $2.0000 + 1/(3.99^2 + 1.723^2) + 2 \times 2/(3.99 \times 1.5)/0.86603^2 - 3/1.99^2 - 2 \times 3/(4.99^2 - 1.73^2) = 1.1641$ units.

The wave length is $1975 \times 1.3121/1.1641 = 2226 \text{ \AA}$. See Figure ii (j).

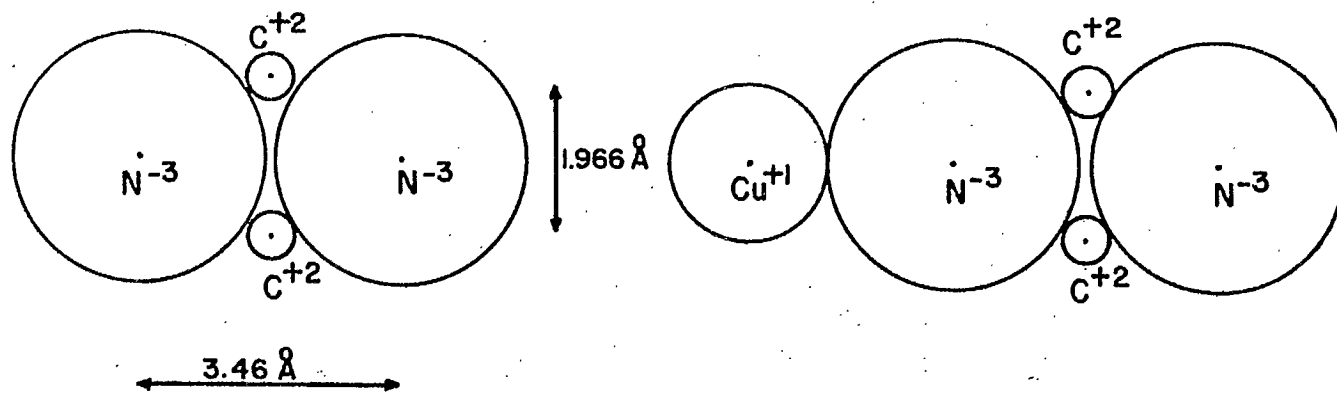
(13) $\text{Cu}(\text{CN})_4^{-3}$

With the same axes as in (12) the co-ordinates of the centres of the ions are:

	X	Y	Z
C^{+2}_1	0	0	0.983
C^{+2}_2	0	0	-0.983
C^{+2}_3	0	2.737	1.716
C^{+2}_4	0	2.737	-1.716
N^{-3}_1	0	-1.73	0
N^{-3}_2	0	1.73	0
N^{-3}_3	1.73	4.726	0
N^{-3}_4	-1.73	4.726	0
Cu^{+1}	0	-4.37	0

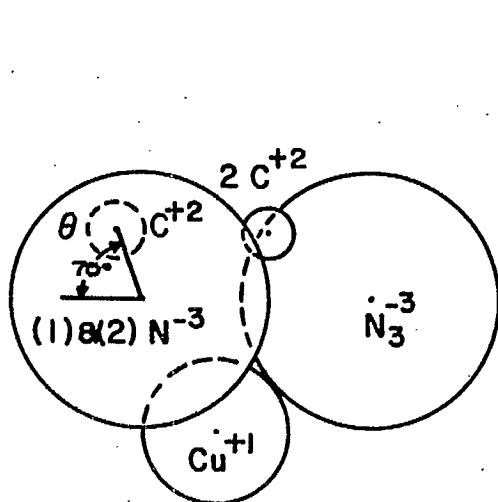
The net force at C^{+2}_1 or C^{+2}_2 is $2.0000 + 2 \times 2(0.983^2 + 2.737^2 + 1.716^2) - 2 \times 3/1.99^2 - 2 \times 3/(0.983^2 + 4.726^2 + 1.73^2) + 1/(0.983^2 + 4.37^2 + 2/1.966^2) = 1.1748$. The wave length is $1975 \times 1.3121/1.1748 = 2206 \text{ \AA}$. See Figure

ii (k).

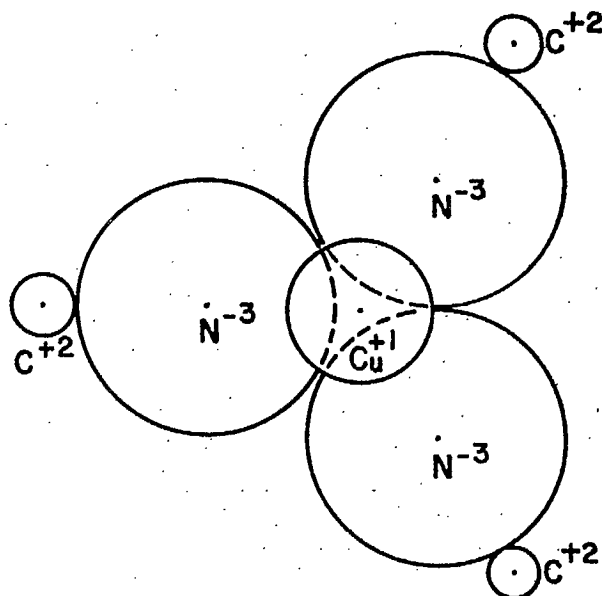


(G) - $(\text{CN})_2^{-2}$

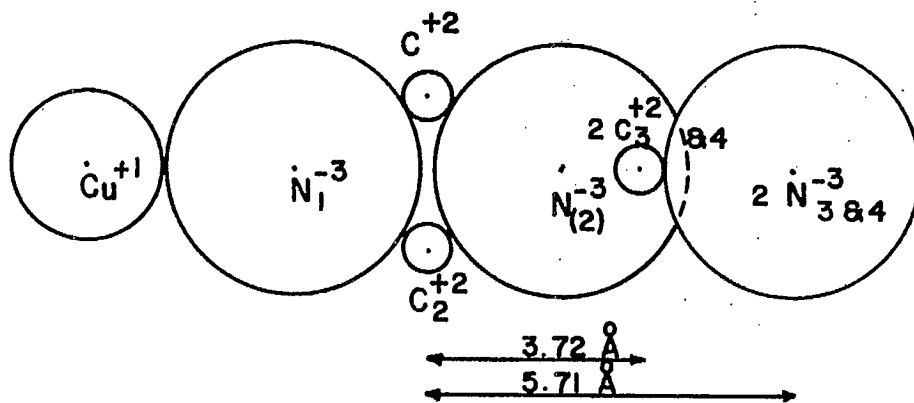
(H) - $\text{Cu}(\text{CN})_2^{-1}$



(I) - $\text{Cu}(\text{CN})_3^{-2} (\alpha)$



(J) - $\text{Cu}(\text{CN})_3^{-2} (\beta)$



(K) - $\text{Cu}(\text{CN})_4^{-3}$

Figure 11 Complex Cyanide and Cupro-Cyanide Ions

APPENDIX 2

Calculations of Ionic Concentrations, Test ii(e)

Wave length Å	1975	2086	2140	2242	2353	2420	2602
Ion	HCN	CN ⁻¹	Cu(CN) ₄ ⁻³	Cu(CN) ₃ ⁻² α	Cu(CN) ₃ ⁻² β	Cu(CN) ₂ ⁻¹	(CN) ₂ ⁻²
No. of Absorbing C ⁺² Ions	1	1	2	3	3	2	2
Absorbance	0.680	1.980	1.350	1.238	1.210	0.430	0.155
% Transmitted	20.9	1.0	4.4	5.8	6.2	37.2	70.0
% Absorbed	79.1	99.0	95.6	94.2	93.8	62.8	30.0
% of Absorbing CN	14.26	17.85	17.24	16.99	16.92	11.33	5.41
Corrected	14.26	17.85	8.62	5.66	5.64	5.67	2.71
% of Ions	23.60	29.55	14.27	9.37	9.34	9.38	4.49

APPENDIX 3

Calculations of Ionic Concentration For Tests (ii) (iii)

(ii)

(e)

Ion	HCN	CN^{-1}	$\text{Cu}(\text{CN})_4^{-3}$	$\text{Cu}(\text{CN})_3^{-2} \alpha$	$\text{Cu}(\text{CN})_3^{-2} \beta$	$\text{Cu}(\text{CN})_2^{-1}$	$(\text{CN})_2^{-2}$
% of Ions	23.60	29.55	14.27	9.37	9.34	9.38	4.49
% CN Ions	23.60	29.55	57.08	28.11	28.02	19.76	8.98
% CN	12.10	15.15	29.25	14.41	14.36	10.13	4.60
Moles CN = 0.0004375							
Moles CN $\times 10^6$	52.9	66.3	128.0	63.0	62.8	44.3	20.1
$[\text{Ion}] \times 10^6$	52.9	66.3	32.0	21.0	20.9	22.1	10.0
Mol wt	27.03	26.02	167.62	141.6	141.6	115.58	52.04
$\text{g/l} \times 10^3$	1.43	1.73	5.36	2.97	2.96	2.55	0.53
ppm	1.43	1.73	5.36	2.97	2.96	2.55	0.53
(f)							
ppm	0.46	1.29	3.22	1.05	0.96	1.25	0.29
(g)							
ppm	0.12	0.61	0.72	0.77	0.795	0.31	0.10
(h)							
ppm	0.07	0.34	0.33	0.37	0.35	0.21	0.034
(iii)	0.30	1.10	2.99	1.06	1.15	0.46	-----

