



DEPARTMENT OF
ENERGY, MINES AND RESOURCES
MINES BRANCH
OTTAWA

*CONTINUOUS AUTOMATIC CYANIDE
TITRATION IN COPPER-BEARING
GOLD MILL LEACH LIQUORS*

J. C. INGLES

EXTRACTION METALLURGY DIVISION

DECEMBER 1969

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CONTINUOUS AUTOMATIC CYANIDE TITRATION IN COPPER-BEARING
GOLD MILL LEACH LIQUORS

by

J.C. Ingles*

ABSTRACT

This report describes the preparation and evaluation of a new silver-complex reagent formulation for the continuous titration of cyanide in cupriferous gold-leaching solutions. Some improvements in the design of the continuous automatic titrating apparatus are also described, and the significance of the "free" cyanide value in the control of the cyanide gold-leaching process is discussed.

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Direction des mines

Rapport de recherches R 212

LE TITRAGE AUTOMATIQUE CONTINU DU CYANURE DANS
LES SOLUTIONS CUPRIFÈRES PROVENANT DU
LESSIVAGE DES MINÉRAIS D'OR

par

J. C. Ingles*

RÉSUMÉ

Ce rapport décrit la préparation et l'évaluation d'une nouvelle formule de réactifs à argent, pour le titrage continu du cyanure dans les solutions cuprifères provenant du lessivage de certains minerais d'or. On y décrit aussi quelques améliorations dans le modèle de l'appareil pour le titrage automatique continu, et on y discute la signification du terme "cyanure libre" en rapport avec le contrôle du procédé de lessivage de l'or au cyanure.

* Chef de la Section de l'analyse chimique, Division de la métallurgie extractive, Direction des mines, ministère de l'Énergie, des Mines et des Ressources, Ottawa, Canada

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INTRODUCTION

Since the publication, in 1964, of the original report describing the continuous automatic cyanide titrator (1), the apparatus has been successfully employed to measure, record and control cyanide in a number of gold mills (2,3,4). As might be expected, interest has been particularly keen from operators dealing with ores that are high in soluble copper minerals. This interest is occasioned by, on the one hand, a desire to maintain cyanide levels within the narrow range required to minimize copper dissolution and maximize gold dissolution, and, on the other, the well-known difficulty that is encountered in accurately estimating the end-point of the familiar Liebig visual argentometric titration in such solutions. These two problems, taken together, are undoubtedly major factors in the wastage of cyanide and the leaching, precipitation and refining problems that are features of the treatment of such ores.

It will be recalled that the principal advantages of the automatic titration (in addition to the continuous permanent record, and adaptability to automatic control) are: (1) the reproducibility of the EMF/cyanide relationship, which is responsible for the long-term stability; and (2) the ability to measure and record cyanide concentrations considerably above and below a selected control value. The reproducibility is made

possible by use of a high concentration of argentocyanide ion, while the extended range (with maximum response at the control value) is due to the presence in the reagent solution of excess silver ions at a concentration stoichiometrically equivalent to that cyanide concentration in the mill solution about which interest centres.

This excess of silver, which ordinarily would react with the argentocyanide ion and lead to precipitation of silver argentocyanide, was prevented from doing so by the use of ammonia in the original formulation of the reagent. Unfortunately, ammonia is an even more effective complexing reagent for copper than it is for silver, and although the copper cyanide complexes are slightly more stable than the corresponding silver complexes, the net effect with the original reagent is a very considerable overestimation of the indicated "free" cyanide content at lower cyanide concentration levels, when the cuprocyanide concentration level is high.

A recent request from a mill processing an ore of high copper content, for a laboratory evaluation of a typical sample of mill solution to determine its amenability to analysis by the continuous titration method, provided the occasion for undertaking a search for a method of overcoming this difficulty. Indeed, analysis of the submitted solution indicated a copper content nearly twice that of the highest level previously encountered,

and preliminary tests with the silver-ammonia argentocyanide reagent demonstrated that it was virtually incapable of discriminating between differences in cyanide content at the levels existing in the solution as received.

An examination of stability-constant data for the silver complexes of a number of common ligands, along with some preliminary qualitative experiments, indicated that an improved reagent could be formulated, using sodium thiosulphate as the complexing agent, which would considerably mitigate this difficulty.

The present report describes the experiments done to demonstrate the superiority of the new reagent formulation for the indication of "free" cyanide concentration in solutions containing significant concentrations of cuprocyanide ion. It is also used as a vehicle to present several improvements in the construction and operation of the titrator which have been developed since the original report appeared.

OUTLINE OF EXPERIMENTS

As in the original report, two different techniques were employed in evaluating and comparing reagent formulations, one with the laboratory recording titrator and the other with the continuous automatic titrator.

1. Titration with the Laboratory Recording Potentiometric Titrator

The first technique employed a recording potentiometric titrator incorporating a micro-size syringe burette, in a manner similar to that described in the original report; that is, the reagent formulation under test, and a standard cupriferos cyanide solution of minimum cyanide content, were mixed in the 5:1 volume ratio which has been adopted for the operation of the continuous titrator. This mixture was then titrated with a standard cyanide solution the strength of which was high enough that the overall volume change during the course of the titration was negligible. The electrode system was the same as that employed in the continuous titrator. The two chief components were an indicating silver electrode dipping into the solution to be titrated, and a reference electrode (see Figure 1) consisting of an identical silver electrode dipping into a separate portion of the reagent formulation which was contained in a glass shell with a permeable tip to act as a bridge. Thus the recorder chart provided a continuous series of potential read-out indications identical with those to be expected from the continuous titrator itself. One such chart would give data for a particular system over a complete range of cyanide concentrations, data that would have required several days to obtain on the continuous titrator. The cyanide-EMF calibration relationship

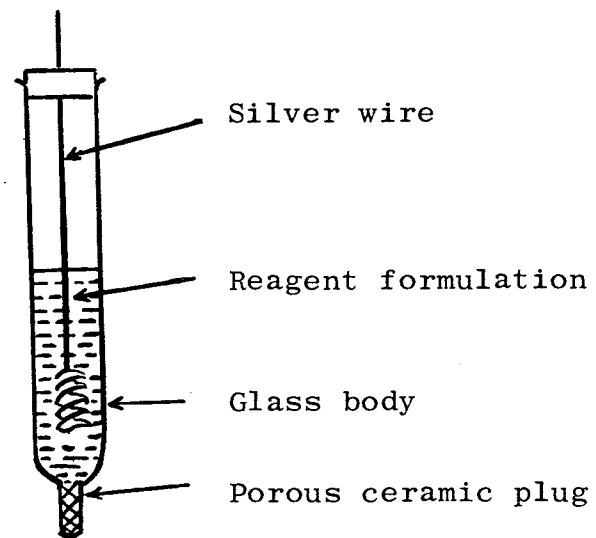


Figure 1. Detail of reference electrode construction.

for a particular reagent formulation was also quickly established by means of a similar titration, in which water was substituted for the cupriferos cyanide solution. Application of this calibration curve to the data from the cupriferos cyanide solution permitted construction of a graph of indicated cyanide content as a function of added cyanide (or as a function of total cyanide present, since the initial cyanide content of the cupriferos cyanide solution was known). In this way, the effectiveness of the reagent formulation over a wide range of cyanide concentrations levels, and for various specific copper contents, could be quickly evaluated.

2. Continuous Titrations Using the Continuous Automatic Titrator

Following the development work with the recording titrator, confirmatory experiments were carried out with the continuous automatic titrator, using freshly mixed synthetic solutions (see Figure 2).

REAGENTS

a. Silver-ammonia argentocyanide reagent (stock solution):

i. Ingredients -

10.0 g sodium cyanide (98%)

18.0 g silver nitrate

50 ml concentrated ammonium hydroxide

20 ml 50% sodium hydroxide solution

Distilled water

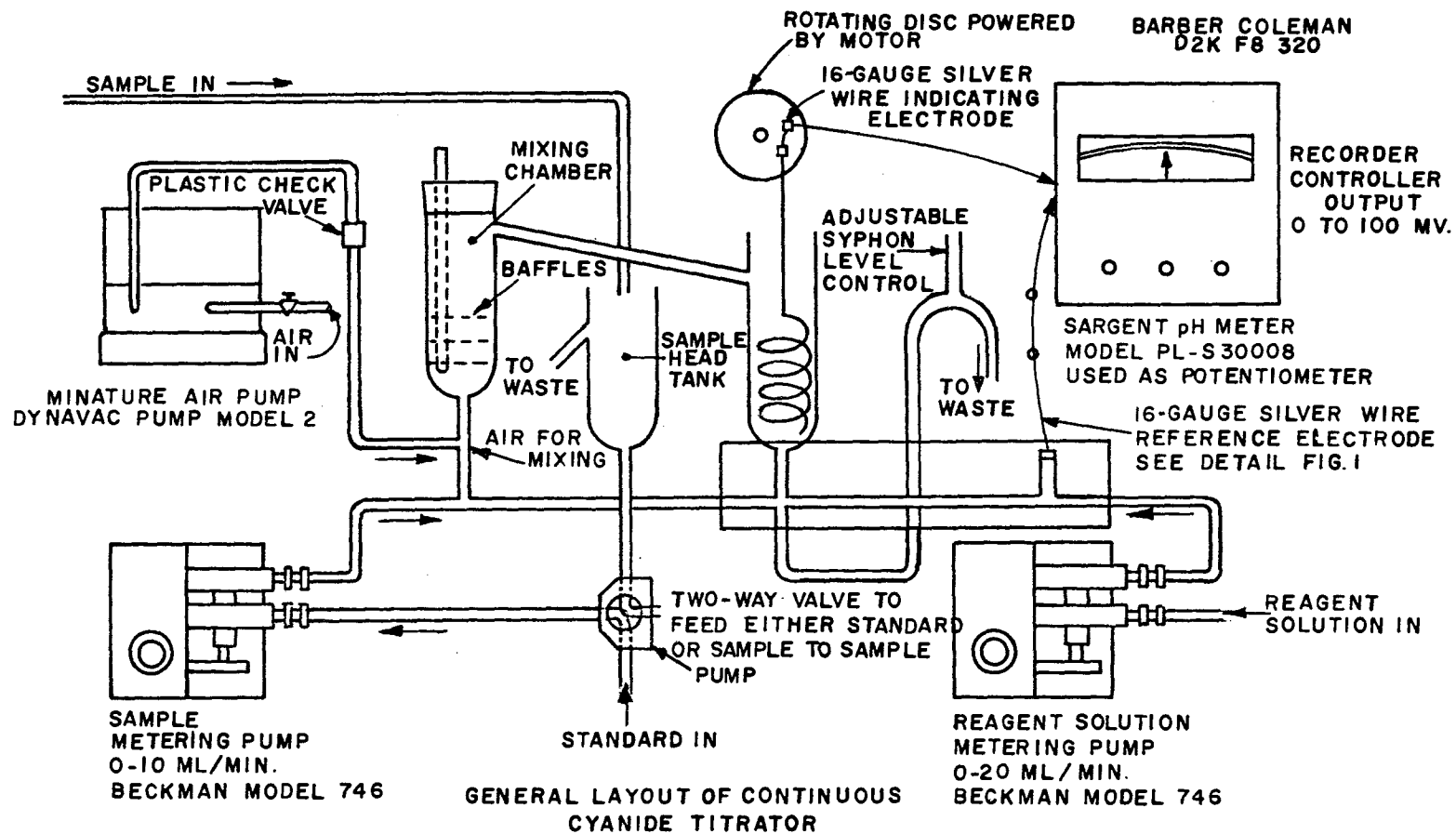


Figure 2. General layout of the automatic continuous cyanide titrator, illustrating installation of the modified reference electrode.

ii. Preparation -

Dissolve and dilute each of the ingredients in 200 ml of distilled water. To the dilute ammonium hydroxide, contained in a 1500-ml beaker, and stirred magnetically, slowly add the silver nitrate solution. Allow to stir a few minutes, then slowly add 250 ml of the sodium cyanide solution. Allow to stir till the white precipitate which forms has completely dissolved. Add the sodium hydroxide solution, transfer to a 1-litre volumetric flask, make to volume, and mix well. Dilute 10 times with distilled water for use.

This titrant solution, diluted for use, and employed at a ratio of 5 parts of titrant to 1 part of sample, was equivalent in free silver to 0.315 g per litre of sodium cyanide.

b. Silver-thiosulphate argentocyanide reagent (stock solution):

i. Ingredients -

10.0 grams sodium cyanide (98%)

18.0 grams silver nitrate

20.0 grams sodium thiosulphate, crystal $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$

20 ml 50% sodium hydroxide solution

Distilled water

ii. Preparation -

(Note: The sequence of operations and the rate of addition are both very important. Failure to observe them leads to the presence of a brown precipitate. Small amounts of this precipitate are not harmful but its presence is unnecessary if the reagent mixture is properly prepared.)

Dissolve the ingredients separately in 200-ml portions of distilled water. To the dilute silver nitrate solution, contained in a 1500-ml beaker and stirred magnetically, slowly add the dilute cyanide solution and allow to stir for about 5 minutes, washing down the sides of the beaker with a small amount of distilled water. A fairly voluminous, viscous, cream-coloured precipitate will remain. Slowly, and with constant stirring, add the sodium thiosulphate solution. Continue to stir until the precipitate has completely dissolved. Add the sodium hydroxide solution, transfer to a 1-litre volume flask, make to volume, and mix well. Dilute 10 times with distilled water for use.

This titrant solution, diluted for use and employed at a ratio of 5 parts of titrant to 1 part of sample, was equivalent in free silver to 0.336 g per litre of sodium cyanide.

c. Cupriferous gold-mill cyanide solution:

This was a sample of pregnant solution from a gold-leaching operation at a mill treating a copper-bearing flotation concentrate, and having the analysis given in Table 1.

TABLE 1

Analysis of Cupriferous Gold-Mill
Pregnant Cyanide Solution

<u>Constituent</u>		<u>Concentration</u>	
"Free" NaCN	-	0.31	g/l
Total NaCN	-	0.80	"
Free CaO	-	0.08	"
CNS	-	0.23	"
Fe(CN) ₆	-	<0.002	"
Cu	-	0.335	"
Zn	-	0.050	"
Ni	-	0.0005	"
Ag	-	0.004	oz/ton
Au	-	0.017	"
Conductivity	-	4.44 x 10 ⁻³ ohms ⁻¹ cm ⁻¹	

d. Synthetic cupriferous cyanide stock solution:

Dissolve 5.15 g cuprous cyanide and 0.90 g zinc cyanide in 100 ml of a solution containing 6.17 g of 98% sodium

cyanide and 5 ml of 50% sodium hydroxide solution. Dilute to 1 litre.

This stock solution, which contains 3.66 g Cu, 0.50 g Zn and 9.6 g total NaCN per litre, is diluted 10 times for use. (During the course of the work, the cyanide content, which was determined as required, decreased to 9.2 g total NaCN per litre.)

- e. Cyanide solution, 0.05M, for studies with the recording potentiometer:

Dissolve 5.0 g of sodium cyanide (98%) in 2 litres of distilled water containing 2 ml of 50% sodium hydroxide solution. Standardize potentiometrically against standard silver nitrate solution.

- f. Cyanide solution, 0.25 g/l NaCN, for standardizing the continuous cyanide titrator:

Dissolve 2.55 g of 98% sodium cyanide and 10 ml of 50% sodium hydroxide solution in 10 litres of water. Standardize against standard silver nitrate solution.

- g. Cyanide solution, 1 ml = 5.0 mg NaCN, for adjusting the free cyanide concentration of the synthetic cupriferous gold-mill solution, and for preparing standards for calibration of the continuous cyanide titrator:

Dissolve 5.10 g of 98% sodium cyanide, and 10 ml of 50% sodium hydroxide solution, and make to 1 litre.

Standardize against standard silver nitrate solution.

- h. Silver nitrate solution, 1 ml equivalent to 5.0 mg NaCN, for adjusting the free cyanide content of the synthetic cupriferous gold-mill solution:

Dissolve 8.668 g AgNO_3 in distilled water and dilute to 1 litre.

- i. Silver nitrate solution, 0.05M, for standardizing cyanide solutions and for cyanide determinations.

APPARATUS

Sargent Model D recording potentiometric titrator: with 10-ml microburette

Silver billet electrode, Beckman

or

Silver wire, 16 gauge

Reference electrode assembly (Figure 1):

Glass shell with porous ceramic plug, from Electronic Industries RJ 23 calomel reference electrode, filled with the titrating solution being used into which dips a 3-in. length of 16-gauge silver wire.

Automatic On-Stream Cyanide Analyzer:

Essentially the apparatus described in the previous paper (1), with a modified reference electrode section to replace the assembly described immediately above. This consists of a glass cross-shaped tube with a by-pass, through which passes a section of porous ceramic tubing with a silver wire insert. The porous ceramic tube is inserted into the reagent line so that the silver wire insert, which has an external electrical connection, functions as a reference electrode with a continuously renewed filling. The porous ceramic tubing provides solution contact with the reagent-sample mixture in the measuring section of the titrator via the by-pass which is connected into the overflow outlet from this section. Figure 2 has shown the general layout of the titrator with the modified electrode installed, while Figure 3 is an exploded drawing of the redesigned measuring section, with dimensions and other details of the components.

Another modification that simplifies the operation of the analyzer is the incorporation of a line-operated portable pH meter (Sargent PL-S3008) in the actual instrument cabinet, to provide current amplification of the EMF signal from the electrode system (rather than externally as in the previously described instrument). A convenience resulting from this arrangement is that the standardization control of the pH meter can be used to provide an output potential that is useful in setting the recorder span to the desired range.

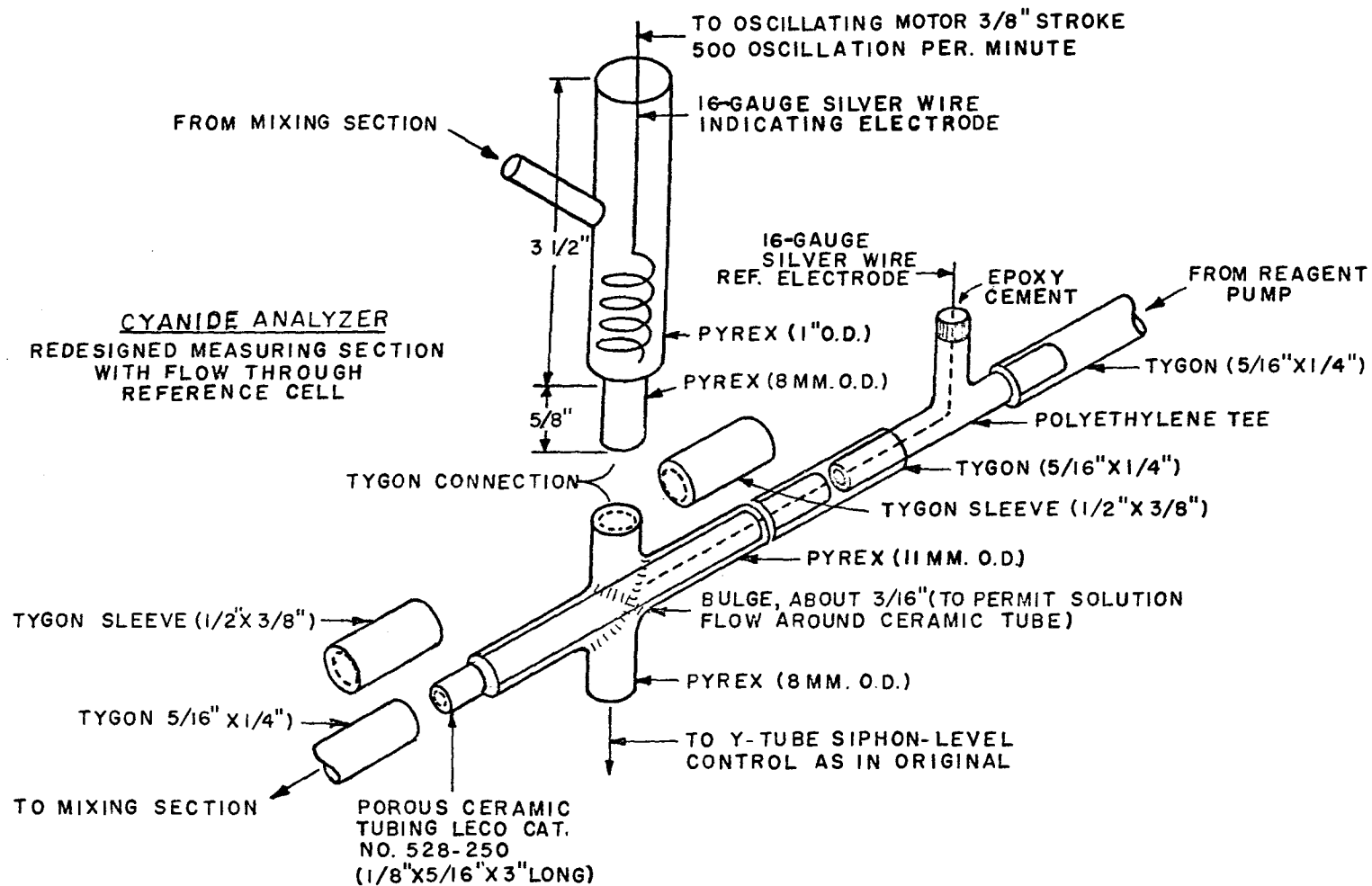


Figure 3. Exploded drawing of redesigned measuring section.

The only other modification of significance was the addition of a sample head-tank in the line leading to the two-way valve and the sample metering pump. This tank, which permits the addition of the occasional discrete sample without disconnecting the line from the reservoir of standard cyanide solution, is also illustrated in Figure 2.

PROCEDURE

1. Potentiometric Titrations with the Laboratory Potentiometric Titrator

Into a 150-ml beaker, pipette 25 ml of the diluted argentocyanide reagent under study, and 5 ml of the sample (or of water, for preparation of the cyanide calibration graph). This gives the same 5:1 reagent-to-sample ratio provided by the reagent and sample pumps of the continuous titrator. Place the beaker on the stirring platform, insert the silver electrode and the reference electrode, and, using the 10-ml microburette, titrate and record the resulting potential changes using 0.05 M sodium cyanide solution. A titration of 2.2 ml, corresponding to a final cyanide concentration of 0.021 M or 2.0 lb NaCN per ton, calculated on the 5-ml sample volume, covers the range of interest and requires no correction for volume change.

In the case of both the cupriferous gold-mill solution and its synthetic counterpart, it was desired to use samples in which the cyanide content had been depleted below normal levels,

since this is the condition which it is most important for the titrator to be able to detect and respond to. It is difficult to synthesize such a solution since the components simply will not dissolve, so the effect was simulated by adding stoichiometrically equivalent volumes of silver nitrate solution. There is no reason to believe that results obtained on samples whose cyanide content has been adjusted in this way will differ in any important particular from mill samples depleted in cyanide by the cyanicidic action of ore components. In the subsequent discussion, therefore, cyanide neutralized by the addition of silver ions will be considered as absent; that is, the effective cyanide content of the solutions will be regarded as the initial total cyanide, less the amount converted to argentocyanide by the added silver nitrate. This, of course, refers to cyanide converted prior to the titration and not that reacting with the free silver of the titrant solution itself. With respect to the test procedure, samples so treated were titrated as quickly as possible while all the constituents were still in solution, since lower cyanides of copper and zinc tended to be deposited if the solutions were allowed to stand more than 15 or 30 minutes.

Potentiometric titrations, using pure 0.05 M sodium cyanide solution as titrant according to the procedures described above, were carried out using each of the two reagents (the previously employed silver-ammonia argentocyanide reagent solution

and the proposed silver-thiosulphate argentocyanide solution).

The solutions titrated included the following:

- a) Water, to provide the EMF-cyanide concentration calibration curve.
- b) A 5-ml portion of the cupriferous gold-mill cyanide solution.
- c) A 5-ml portion of the same gold-mill solution, with the addition of standard silver nitrate solution to reduce the "free" cyanide content by 0.30 g NaCN per litre.
- d) A 5-ml portion of the synthetic cupriferous cyanide solution.
- e) A 5-ml portion of the same synthetic solution, with the addition of standard silver nitrate solution to reduce the "free" cyanide content by 0.30 g NaCN per litre.
- f) Aliquot portions of 0.1, 0.2, 0.3, 0.5, 0.8 and 1.0 ml of the stock synthetic cupriferous cyanide solution, diluted to 5 ml in each case (to provide a range of cuprocyanide contents).

2. Titration with the Continuous Automatic Titrator

In view of the close correlation between the various recording titrator curves and those obtained with the continuous titrator, it was considered unnecessary to duplicate the tests with the silver ammonium argentocyanide on the continuous titrator.

The work described below is therefore confined to tests carried out using the silver thiosulphate argentocyanide reagent.

a) Preparation of the calibration curve for pump flow-ratio settings -

This curve is required to establish the optimum operating pump flow-rate setting of the sample pump for control at the desired effective cyanide concentration level of 0.25 g NaCN per litre, with respect to the cyanide equivalence of the reagent, and at the selected reagent pump setting. It is also an operational convenience, simplifying the calculation of pump settings to accommodate specific control requirements. It was obtained by operating the instrument on the standard solution, 0.25 g sodium cyanide per litre, in place of a sample, using a fixed reagent pump flow-rate setting of 10.0 ml/min and varying the flow-rate setting on the sample pump. A graph of the resulting EMF readings is then plotted against the flow-rate setting of the sample pump. If it is desired to select some other value of cyanide concentration as the control point (i.e., to adjust the instrument so that this cyanide concentration gives an EMF exactly in the middle of the instrument's range), this is done by first calculating an approximate sample pump setting which will provide the same absolute

amount of cyanide per minute, using the expression:

new sample pump setting =

$$\frac{\text{previous sample pump setting} \times \text{previous standard cyanide conc'n, g/l}}{\text{new standard cyanide conc'n, g/l}}$$

Using this calculated sample pump setting, the instrument is then operated using the new standard cyanide solution and the measured EMF is recorded. The optimum sample pump setting can then be found by means of the pump-flow ratio calibration graph, using the expression:

$$\frac{\text{calibration curve pump setting for desired EMF (from graph)}}{\text{calibration curve pump setting for measured EMF (from graph)}} \times \text{actual pump setting}$$

Such adjustments may be needed to accommodate alterations in the cyanide concentration of the standard cyanide solution, differences in the cyanide equivalence of successive batches of reagent solution, or drift in the pump calibration.

b) Preparation of the calibration curves for cyanide concentration vs EMF, at a constant pump-rate ratio -

With the sample pump adjusted to the optimum value (2.75 ml per minute), potential measurements were made by adding standard cyanide solutions to the head tank and allowing the apparatus to run until there was no further change in the EMF reading. The standards used were prepared by diluting the 5.0 g/l standard sodium cyanide solution with distilled water to give solutions covering

the range of 0.0 to 0.8 g sodium cyanide per litre and having a pH in the range 11-12. A graph of the resulting EMF-cyanide concentration curve was then plotted.

c) Continuous automatic titration of cupriferous gold mill cyanide solutions -

These titrations were carried out using discrete samples of the synthetic cupriferous gold-mill cyanide solutions which were prepared by adding the desired increments of standard sodium cyanide solution or standard silver nitrate solution to a 10-ml aliquot of the stock synthetic solution, adding sodium hydroxide to give a final pH of 11-12, and diluting to 100 ml. The diluted solutions were added to the titrator via the sample head tank, as in the previous section. The resulting EMF response was recorded and the data plotted.

RESULTS

1. Potentiometric Titrations with the Laboratory Recording Potentiometric Titrator

The results of the calibration titrations (a) are plotted in Figures 4a and 4b. These calibration curves were then used in plotting the results of the subsequent titrations,

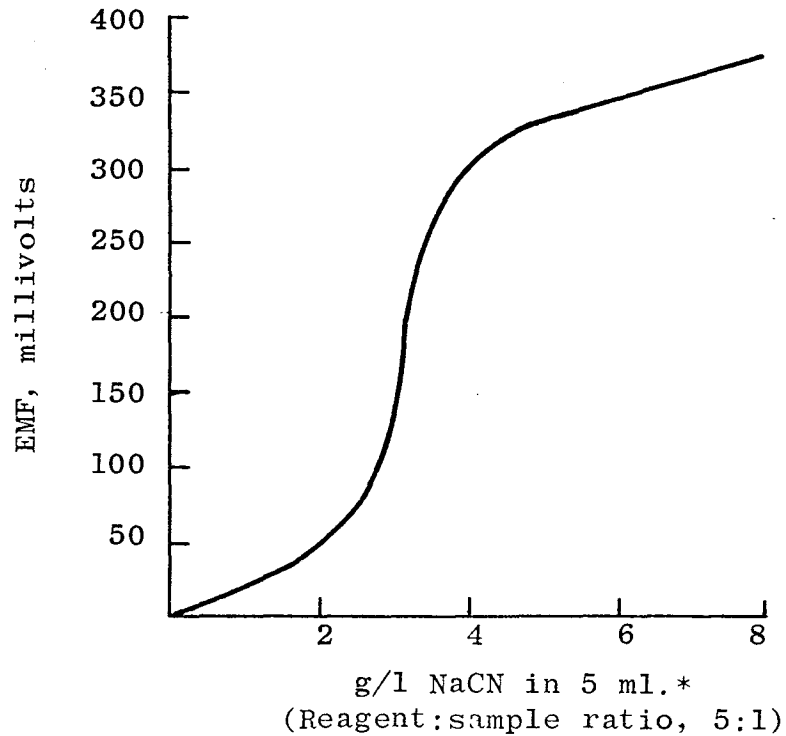


Figure 4a. Calibration titration curve - silver ammonium argentocyanide reagent.
(Laboratory recording titrator)

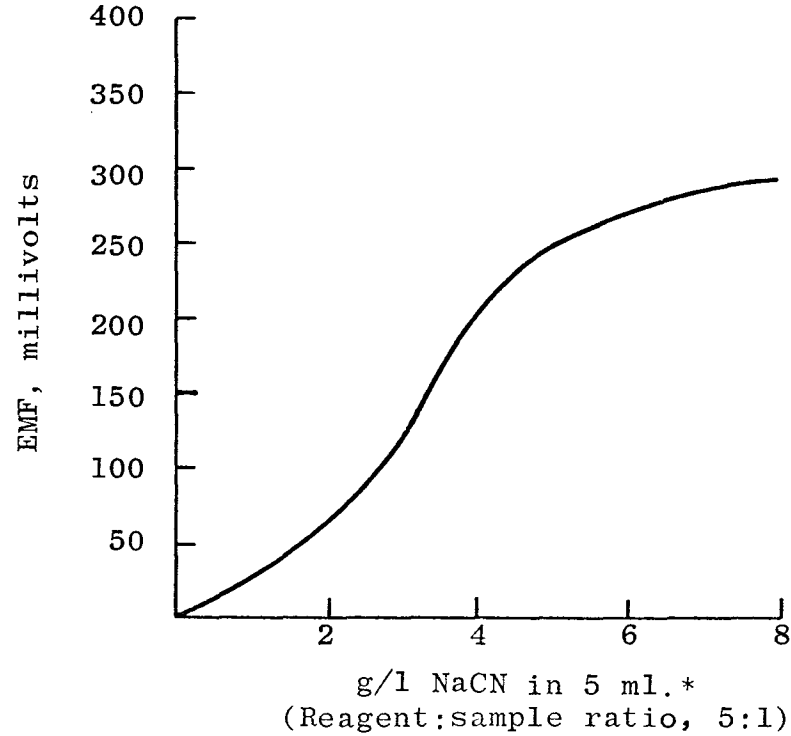


Figure 4b. Calibration titration curve - silver thiosulphate argentocyanide reagent.
(Laboratory recording titrator)

(*See footnote on page 22)

as a means of converting potential readings to "Indicated cyanide concentration as g/l NaCN in 5 ml".* The values so converted are plotted as a function of added cyanide, in the subsequent Figures 5 to 7, for this series of tests. Thus, Figures 5a and 5b illustrate the results of titrations 1b and 1c ("Experimental") (on the cupriferous gold-mill cyanide solution) using, respectively, the silver ammonia argentocyanide reagent and the silver-thiosulphate argentocyanide reagent. Figures 6a and 6b provide the same comparison for the synthetic cupriferous cyanide solution (titrations d and e). In Figures 7a and 7b, the results of the series of titrations in which the copper content was varied are plotted for each of the reagent systems.

2. Titration with the Continuous Automatic Titrator

As mentioned in the experimental section above, the results presented here are those obtained using the silver thiosulphate argentocyanide reagent only, since further comparisons with the silver ammonium argentocyanide reagent appeared to be superfluous.

* "g/l NaCN in 5 ml.": The sample is presented to the electrode system after dilution of 1 part of the sample with 5 parts of the reagent. The potential reading obtained is converted to cyanide concentration by comparison with standard cyanide solutions that have been similarly treated. Provided that the ratio is maintained, the final volume (and hence the size of the sample aliquot taken) is immaterial. For purposes of illustration and comparison, therefore, all values are expressed in terms of a 5-ml sample aliquot to which 25 ml of reagent solution has been added.

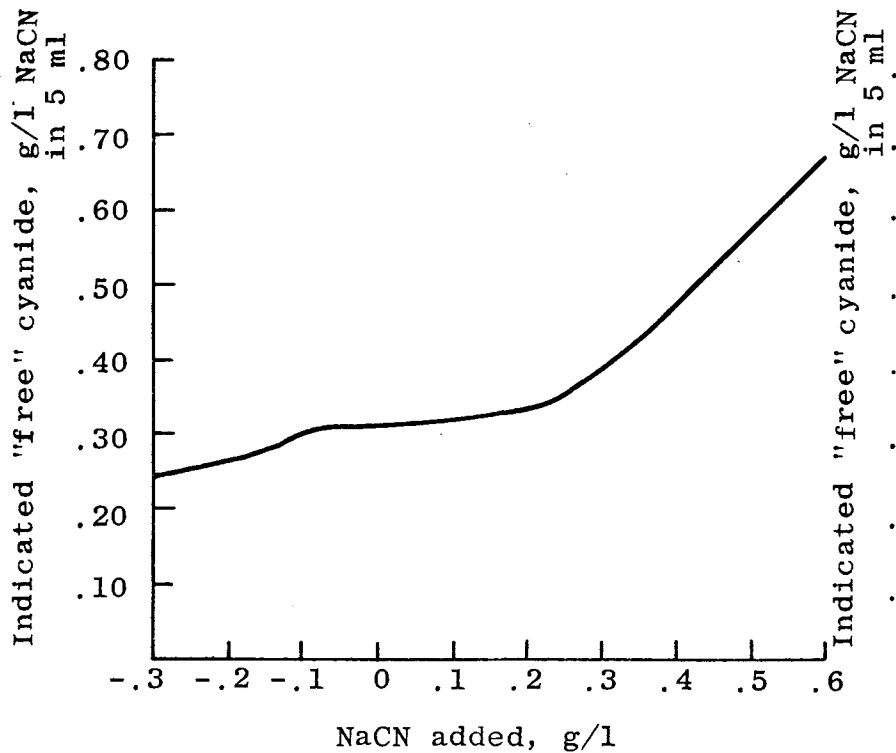


Figure 5a. Titration of cupriferous gold-mill cyanide solution - silver ammonium argentocyanide reagent. (Laboratory recording titrator)

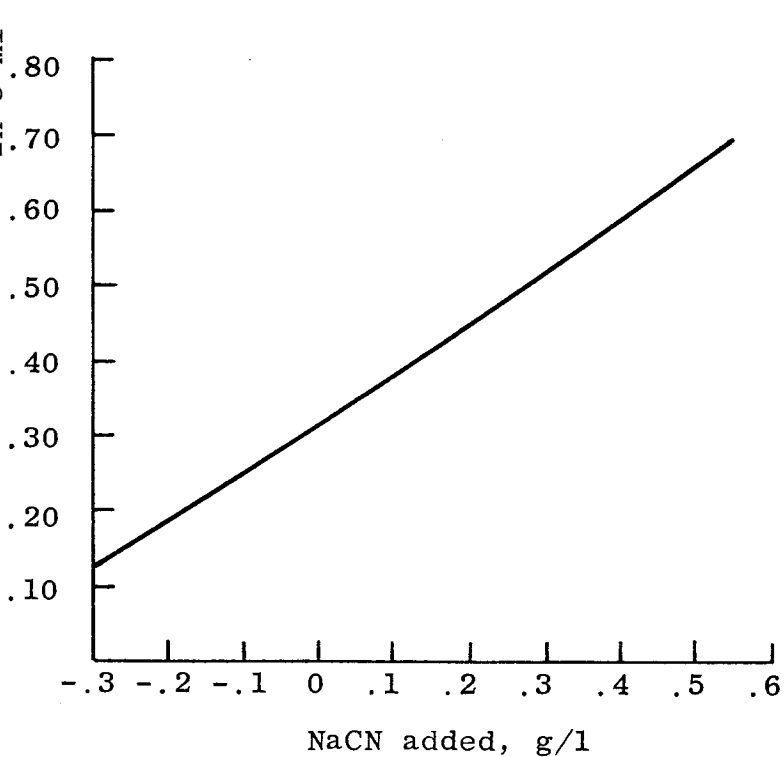


Figure 5b. Titration of cupriferous gold-mill cyanide solution - silver thiosulphate argentocyanide reagent. (Laboratory recording titrator)

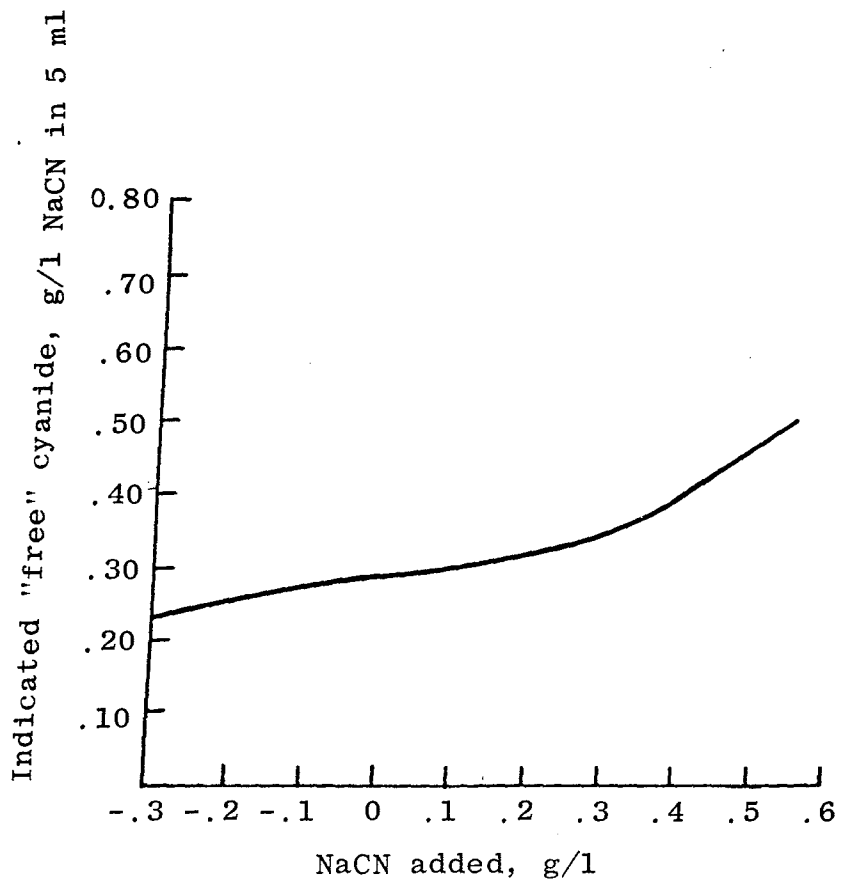


Figure 6a. Titration of synthetic cupriferos cyanide solution with silver ammonium argentocyanide reagent. (Laboratory recording titrator)

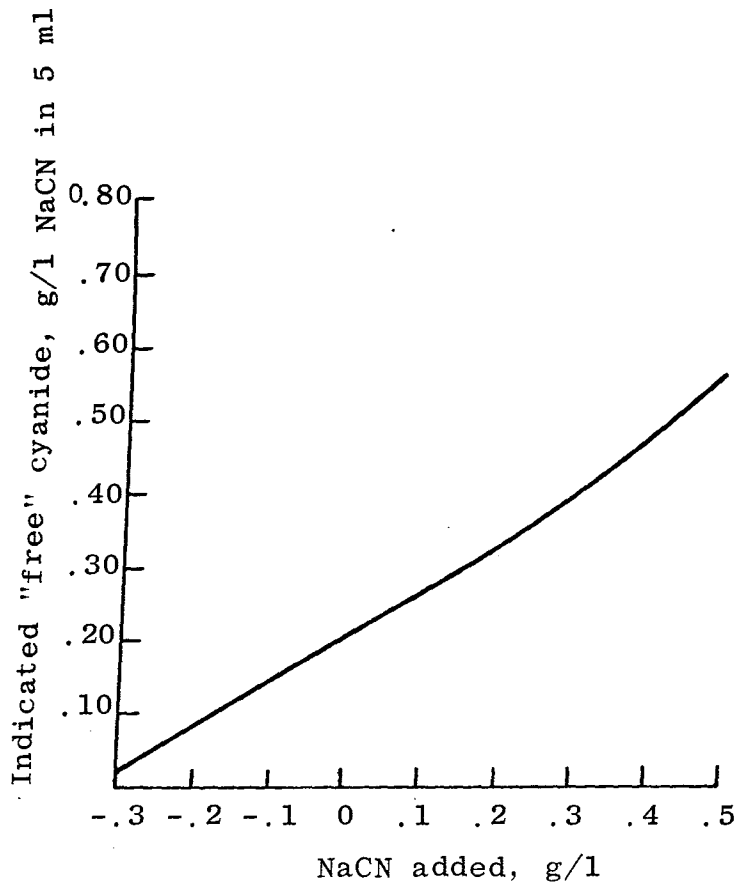


Figure 6b. Titration of synthetic cupriferos cyanide solution with silver thiosulphate argentocyanide reagent. (Laboratory recording titrator)

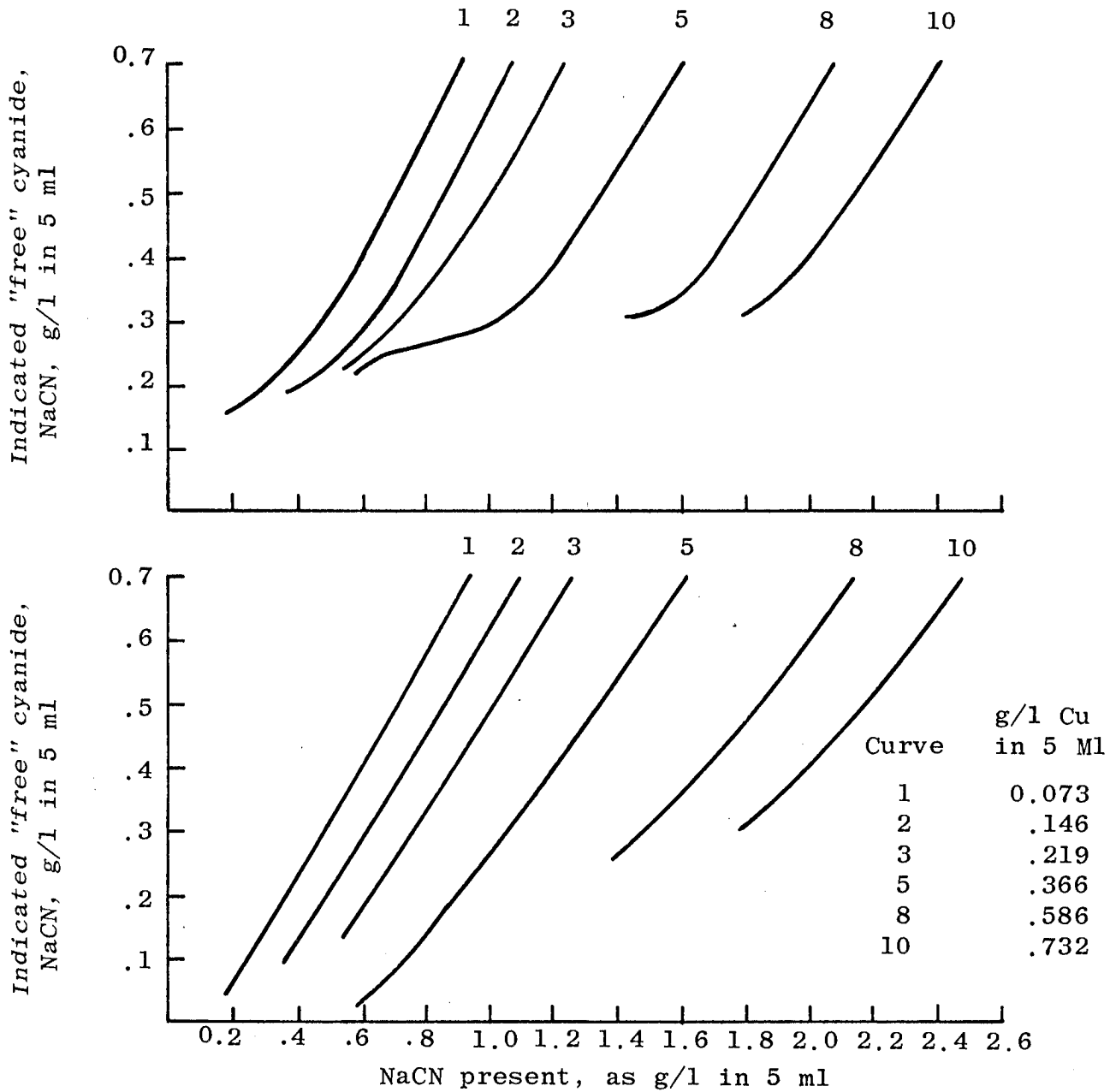


Figure 7a. Effect of varying copper content on the cyanide indication - silver ammonium argentocyanide reagent.

Figure 7b. Effect of varying copper content on the cyanide indication - silver thiosulphate argentocyanide reagent.

The calibration curve for pump-ratio settings is plotted in Figure 8. It established the optimum sample pump flow-rate setting, for the reagent used in the present study and a reagent pump flow rate of 10.0 ml per minute, to be 2.75 ml per minute (for control at 0.25 g/l NaCN).

The calibration curve for the relationship between the indicated EMF and the cyanide concentration (at a constant pump-rate ratio) is presented in Figure 9.

Finally, in Figure 10, indicated "free" cyanide values, obtained for the series of discrete samples of the synthetic cupriferous gold-mill solutions, are plotted against the concentration of added sodium cyanide (and, where silver nitrate was added to eliminate "free" cyanide, the amount of sodium cyanide so neutralized).

DISCUSSION

1. Comparison of Silver Ammonium Argentocyanide and Silver Thiosulphate Argentocyanide as Cyanide Titrants

As was noted in the previous report, ammonia was selected as the complexing agent for maintaining excess silver in solution, mainly because its use was already familiar (from its application in Dénigès' modification of the Liebig method for cyanide). The difficulties attending its use with cyanide solutions containing moderately high amounts of cuprocyanide have

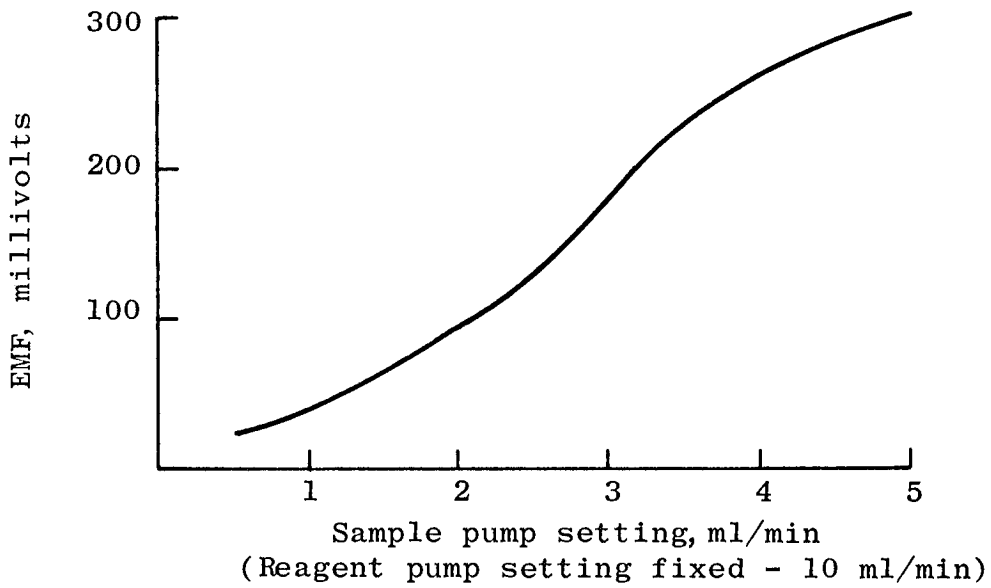


Figure 8. Continuous Automatic Titrator - calibration curve for pump flow-ratio settings.

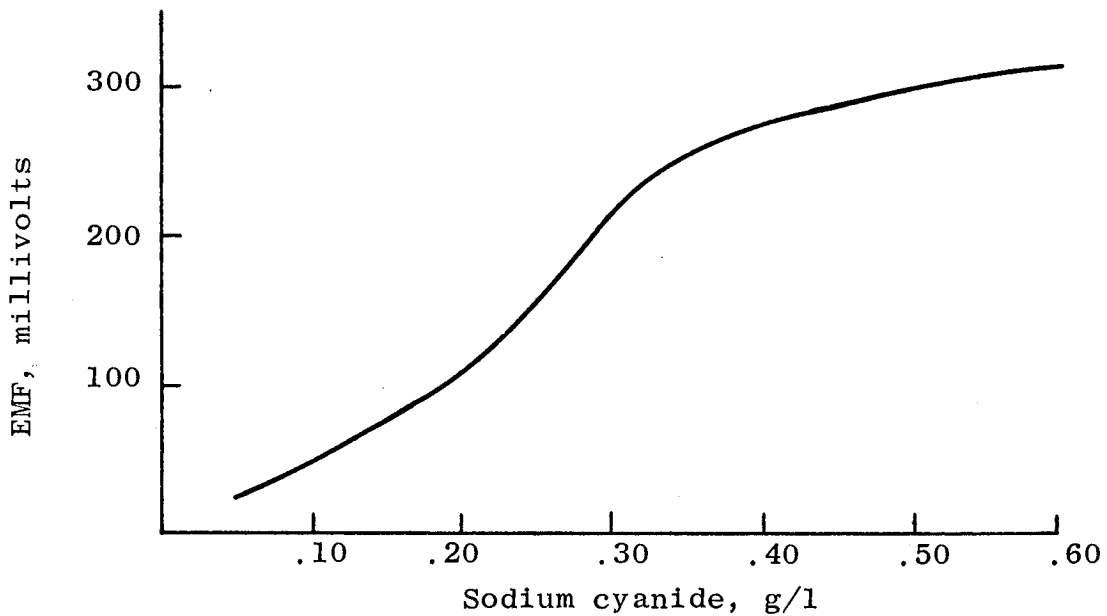


Figure 9. Continuous Automatic Titrator - calibration curve for cyanide concentration - EMF relationship.

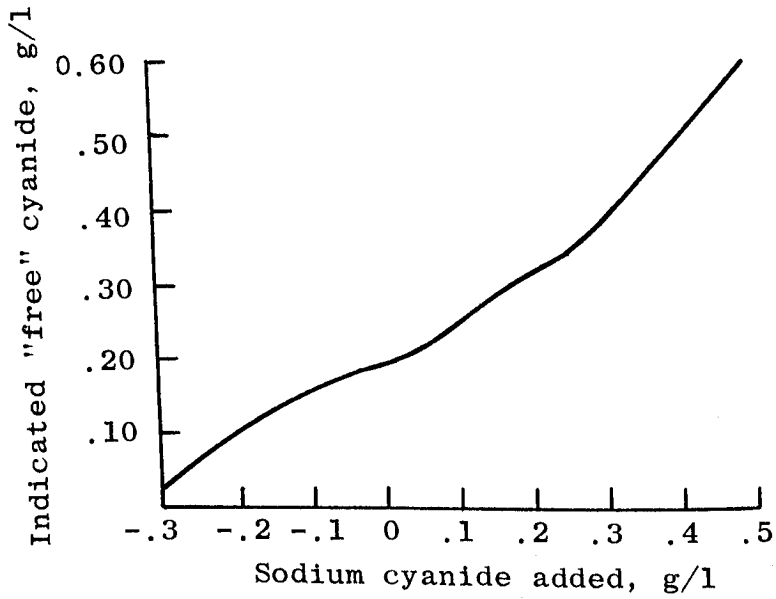


Figure 10. Continuous Automatic Titrator - titration of synthetic cupriferos cyanide solutions.

already been described in the Introduction. Accordingly, a search was undertaken for a complexing agent that would be capable of maintaining excess silver in solution (but still at a considerably higher activity than the silver in the argentocyanide ion) while having a minimum tendency to abstract cuprous copper from cuprocyanide ion. That is, the desired ligand should have, first, a stability constant for its silver complex which demonstrates a favourable ratio to the solubility product of $\text{Ag}_2(\text{CN})_2$ but which is substantially less than that for argentocyanide, and, secondly, a stability constant for its cuprous complex which is as low as possible and, in any case, less than that of the corresponding silver complex. Although literature data for cuprous copper are sparse, stability constants were found for the thiocyanate, sulphite and thiosulphate complexes of silver and cuprous copper, and these, along with the corresponding values for cyanide and for ammonia (all taken from reference 5), are given in Table 2.

TABLE 2

Stability Constants of Silver and Copper Complexes with Cyanide, Ammonia, Thiocyanate, Sulphite and Thiosulphate (5)

Ligand	Silver (Ag^+)			Copper (Cu^+)			
	K_1	β_2	β_3	K_1	β_2	β_3	β_4
Cyanide	-	21.1	22.0	-	24.0	28.6	30.3
Ammonia	3.2	7.1	-	5.9	10.9	-	-
Thiocyanate	-	8.2	9.3	-	12.1	17.3	-
Sulphite	6.0	8.3	9.0	7.8	8.6	9.2	-
Thiosulphate	8.9	13.5	-	10.4	12.3	13.7	-

It is apparent that thiosulphate, while still far from ideal, most closely meets the above criteria.

A comparison of the calibration curves for the reagents prepared with the use of these two ligands (Figures 4a and 4b) would, at first glance, suggest that the reagent containing thiosulphate is actually less desirable than that containing ammonia, since the EMF span for the latter is some 20% greater. The most probable explanation for this is the lower silver-ion activity in the mixture of sample and reagent solutions, due to the greater complexing ability of thiosulphate as compared to ammonia, particularly on the low cyanide side where excess silver is present. This slightly compressed EMF span is not a drawback from the operational point of view, since it is readily expanded electrically. On the other hand, the significantly flatter curve of the thiosulphate reagent is a distinct advantage in this application, since it provides a pseudo-linearity over a much greater portion of the EMF-cyanide activity scale and hence facilitates the reading of the indicated cyanide concentration over a wide range about the control point.

The major advantage of the proposed reagent, however, is illustrated in Figures 7a and 7b. These graphs demonstrate the difference in the instrumentally indicated cyanide content as the copper concentration increases (one of the curves, that for 0.366 g/l copper, has been extrapolated in each case on the

basis of the data of Figures 6a and 6b). It is quite evident that the thiosulphate reagent provides a usable indication of "free" cyanide levels down to 0.1 lb per ton (as NaCN). Extrapolation of the straight-line portion of these curves shows that the titrator provides a reasonably linear indication of all cyanide in excess of $\text{Cu}(\text{CN})_2^-$, i.e., the cyanide which has gone to form $\text{Cu}(\text{CN})_3^-$ and higher copper complexes from $\text{Cu}(\text{CN})_2^-$, as well as the cyanide present as zincocyanide and as cyanide ion.

2. Significance of the Indicated "Free" Cyanide Reading

The "free" cyanide value recorded by the continuous titrator includes, as just noted, all cyanide present in a mixed cuprocyanide-zincocyanide excess cyanide solution, except for an amount equivalent to that retained by the copper as $\text{Cu}(\text{CN})_2^-$. In other words, all the cyanide present as excess cyanide, as zincocyanide, and as the amount required to form the higher complexes of copper from $\text{Cu}(\text{CN})_2^-$, is included as free cyanide. However, the parameter which controls the rate of reaction between cyanide and metals is not this "free" cyanide content but, rather, the cyanide ion activity, and it is the magnitude of the latter which is the important factor, both in the leaching process and in the zinc-precipitation recovery process.

With regard to the leaching process, the limiting value for cyanide-ion activity in the leaching of pure gold with pure cyanide solution (i.e., that value above which no further improvement in the leaching rate can be expected) is still the subject of controversy. However, some recent values for air-saturated solutions have been 0.0013M (7), 0.038M (8) and 0.0041M (9), or a range of from 0.13 to 3.72 lb NaCN/ton. As for the zinc precipitation process, calculations based on a formula presented by Esdaile (10) indicate that the cyanide-ion activity level of a pregnant leach liquor (at, say, pH 11.5) below which difficulty could be anticipated during the precipitation process (due to the formation of a coating of zinc hydroxide on the zinc-dust particles) ranges from 0.0036M (0.35 lb NaCN/ton) in the case of a solution free of zincocyanide to 0.012M (1.18 lb NaCN/ton) in a solution 0.005M in zincocyanide.

Unfortunately, there is no simple way to establish the cyanide-ion activity level, even approximately, from the "free" cyanide titration data in solutions of complex metal cyanides. Figure 11, which gives the calculated distribution of cyanide-ion activity and metal cyanide complexes (as a function of total cyanide content) in the synthetic cyanide solution that was used in evaluating the reagent, demonstrates this clearly. Point A on the graph, which corresponds to a zero "free" cyanide content (i.e. the point where the total cyanide content is stoichiometrically

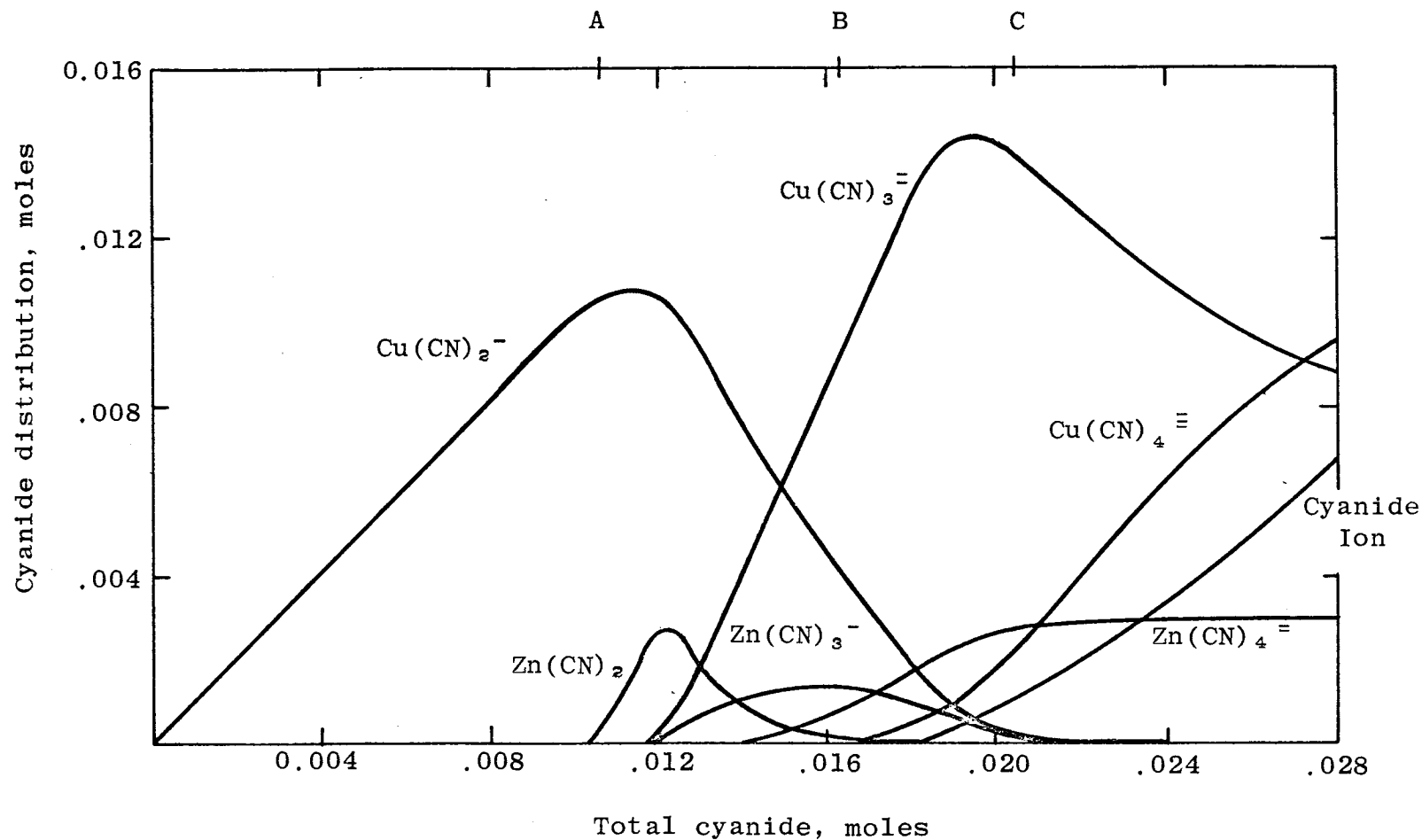


Figure 11. Distribution of cyanide among the various complex cyanide species, as a function of total cyanide content, in the synthetic cupriferos cyanide solution.

equivalent to $\text{Cu}(\text{CN})_2^-$, occurs at 0.0107 mole of total cyanide. At point B (0.0163 mole of total cyanide), where three moles of cyanide for each mole of copper and four moles of cyanide for each mole of zinc are present, the cyanide-ion activity is still only $5 \times 10^{-5}\text{M}$. A level of cyanide-ion activity of 0.001M (i.e. the lowest level capable, in theory, of being at all effective) is only reached at a point C, where the total cyanide content is 0.0204M and where the indicated "free" cyanide level would be about 0.96 lb NaCN per ton.

Thus, with the continuous titrator as with the manual titration, a knowledge of the metal content (particularly copper, nickel and zinc) would be necessary to arrive at the process-related variable of cyanide-ion activity. In the absence of this information, the "free" cyanide value is only a datum point, whose significance depends entirely on the operating experience of the particular mill and the immediate history of the solution.

Nevertheless, the "free" cyanide titration has been, and continues to be, the preferred method for the control of cyanide concentration in gold cyanidation. Many years of successful operation attest to the ability of experienced mill operators to interpret the values obtained so as to maintain suitable solution conditions. The reagent formulation described makes possible the application of the automatic cyanide titrator to cyanidation

liquors of high copper content, and hence extends the benefits of continuous data presentation, and of accurate values for "free" cyanide concentration, to the milling of ores of high copper content.

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