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A RAPID COLORIMETRIC SOLVENT-EXTRACTION
PROCEDURE FOR THE DETERMINATION OF
CYANIDE IN GOLD-MILL EFFLUENTS
AND RECEIVING WATERS

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A RAPID COLORIMETRIC SOLVENT-EXTRACTION PROCEDURE FOR THE DETERMINATION OF CYANIDE IN GOLD-MILL EFFLUENTS AND RECEIVING WATERS

by

D. J. Barkley* and J. C. Ingles**

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ABSTRACT

A colorimetric procedure is described for the determination of the total cyanide content of effluents from gold cyanidation plants and of water from basins into which they discharge.

The method has several advantages over the official American Water Works Association Methods for routine mill use. First, the colour reagent is stable and easily prepared. Second, the initial colour development, which takes only 25 minutes, provides a visual indication as to whether the cyanide content exceeds 0.5 ppm and hence permits a quick screening-out of high-level samples. Determinations on samples with lower cyanide content can then be completed within an additional 45 minutes by a simple solvent extraction-spectrophotometric step. Actual working time is of the order of 20 minutes per sample and, since equipment requirements are minimal, a high throughput is possible.

The method determines cyanide present as hydrocyanic acid, cyanide ion, zincocyanide, cuprocyanide and nickelocyanide, but not cyanide present in the form of ferrocyanide or cobalticyanide. It is free from interference by thiocyanate or cyanate and other common constituents of gold-mill effluents. It is also unaffected by the products resulting from the decomposition of cyanide by hypochlorite; and, by means of an addition of sodium arsenite to the sample, the interfering effect of hypochlorite itself can be eliminated. It can therefore be used as a means of following the progress of the hypochlorite process for the destruction of cyanide.

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Direction des mines

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UN PROCÉDÉ COLORIMÉTRIQUE RAPIDE, À L'AIDE DE L'EXTRACTION PAR UN SOLVANT ORGANIQUE, POUR LE DOSAGE DU CYANURE DANS LES EFFLUENTS DES USINES POUR LE TRAITEMENT DES MINERALS D'OR, ET DANS LES EAUX DES BASSINS RECEPTEURS

par

D. J. Barkley* et J. C. Ingles**

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RÉSUMÉ

On décrit un procédé colorimétrique pour le dosage du cyanure total dans des effluents provenant des usines pour le traitement des minerais d'or, et des eaux provenant des bassins dans lesquels ces effluents se déversent.

Cette méthode possède plusieurs avantages sur les méthodes officielles de l'American Waterworks Association pour l'usage routinier à l'usine. Premièrement le réactif colorimétrique est stable et se prepare facilement. Deuxièmement, la formation au préalable du colorant ne prend que 25 minutes et forme un moyen d'estimer visuellement si le contenu en cyanure excède 0.5 ppm. Ainsi un triage rapide des échantillons d'une plus forte teneur peut se faire.

Cette méthode détermine le cyanure qui se trouve sous forme d'acide cyanhydrique, d'ion cyanure, de zincocyanure, de cuprocyanure et de nickelocyanure, mais ne détermine pas celui qui se trouve sous forme de ferrocyanure et de cobalticyanure. Ni le thiocyanate, ni le cyanate, ni les autres composés constitutifs habituels des effluents des usines pour le traitement des minerais d'or ne gênent. Les produits qui résultent de la décomposition du cyanure par le hypochlorite sont également sans effet, pendant que, par moyen de l'addition de l'arsenite du soude à l'échantillon, on peut éliminer l'effet gênant de l'hypochlorite lui-même. Alors cette méthode peut servir comme moyen de suivre le progrès du procédé au hypochlorite pour la décomposition du cyanure.

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INTRODUCTION

Increasing public concern over the subject of pollution has made it necessary for industrial operations of all types to monitor undesirable constituents in wastes being discharged to the environment. Cyanide-using industries, in particular, are falling under scrutiny because of the known toxic properties of this compound. Besides the constant surveillance of the wastes, the receiving waters must often be analyzed as well, since acceptable limits can be exceeded due to seasonal changes in such variables as stream flow rates and oxygen content of the water. In addition, if the cyanide content of the wastes is too high for direct discharge, some form of treatment will be needed and analyses will be required for the control of this process also.

Unfortunately, the official methods for the determination of cyanide [1,2] – which are lengthy, involve unstable reagents that must be freshly prepared, and require a bank of distillation equipment – are generally beyond the resources of the assay office at the typical small gold mill. A study was therefore undertaken to see whether a more simple alternative procedure could be found.

To satisfy the requirements of pollution control authorities, such a method must provide essentially the same results as the official methods. To do so, it must have (1) the ability to determine the total cyanide content, i.e. that

contained in complex cyanides in addition to that present as simple cyanides, and (2) sensitivity to the limits set by the International Standards for Drinking Water (0.01 ppm as CN) [3]. In addition, it must be simple, fast, and be free from interference by the common constituents of mill solutions, principally thiocyanate and cyanate.

The extensive review by Bark and Higson [4] greatly simplified the task of surveying the published literature on cyanide determination, and is recommended to those who wish to inform themselves of the various available procedures. If isolation of the cyanide by distillation is incorporated in the method, the relative absence of interferences permits a wide choice of methods for determining cyanide in the distillate. However, because the considerable length of time required for the distillation step is one of the objectionable features of the official method, a sensitive procedure which would be selective with respect to the impurities commonly found in gold-mill solutions (and hence would permit elimination of the distillation step) was desired. Unfortunately, the most sensitive colorimetric methods, e.g. those involving variations on the König synthesis [5,6] and that based on the formation and extraction of the dicyano-bis (1, 10-phenanthroline)-iron[II] complex [7], are as sensitive to thiocyanate (the concentration of which often far exceeds that of cyanide in gold-mill solutions)

as they are to cyanide. Most of the other well-known reactions
for cyanide suffer from similar defects in so far as these
solutions are concerned.

The picric-acid colorimetric method [8,9], however,
appeared to offer the desired simplicity and speed, if it could
be used for direct colour development. Preliminary tests showed
that neither thiocyanate nor cyanate interferes. It was found,
however, that although the method gave quantitative results
when the cyanide was present either as a simple cyanide or in
the zincocyanide complex, the recovery of cyanide from cuprocyanide
and nickelocyanide was incomplete. (While most of the cyanide
content of gold-mill effluents is present as the zincocyanide
complex, the cuprocyanide content can predominate in the case of
mills treating cupriferous ores - the nickelocyanide content is
always quite low.) Moreover, the sensitivity of the direct
method (that is, omitting the distillation step) at about 0.2 ppm
is insufficient.

This report describes the experimental studies carried
out to establish methods for releasing cyanide from the metal
complexes, and for increasing the sensitivity to a point approaching
that of the official methods. A large number of tests illustrating
the application of the method to both synthetic solutions and bona
fide samples are also presented to indicate the accuracy and re-
producibility of the procedure developed.

REAGENTS AND APPARATUS REQUIRED

Reagents:

Picric acid, 1% aqueous solution
Sodium carbonate, 0.5M solution
Ethylenediamine tetraacetic acid (EDTA),
    disodium salt, 0.1M solution
Stock cyanide solution: 1 ml = 1 mg CN,
    adjusted to pH 12
Standard cyanide solution (prepared by diluting
    stock solution): 1 ml = 0.005 mg CN, adjusted
    to pH 12
Potassium ferrocyanide
Potassium thiocyanate
Potassium cyanate
Sodium sulphide
Aliquat 336: a quaternary amine, available from
    General Mills, Kankakee, Ill.
Chloroform
Sodium sulphate, anhydrous

Apparatus:

Flasks, volumetric: 100-ml size
Flasks, Erlenmeyer: 250-ml size
                     50-ml size
Separatory funnels: 250-ml size
Boiling water bath: large enough to accommodate
    the required flasks, and about 4 in. deep
Spectrophotometer: Hitachi-Perkin Elmer Model 139
Spectrophotometer cells: 1-cm and 5-cm path length

TEST PROCEDURES

Transfer an aliquot containing the desired amount of
cyanide to a 100-ml volumetric flask. Dilute as indicated, add
the specified reagents, and heat in a boiling-water bath (at
100°C) for the specified length of time. Remove from the bath,
cool, dilute to volume, and read on a spectrophotometer, generally
in 1-cm cells, at the wavelength specified.

For the tests involving the use of Aliquat 336, extract the entire 100 ml of solution after colour development in 250-ml separatory funnels with 20 ml of chloroform containing the specified amounts of Aliquat 336. Shake the funnels for 2 minutes, let the phases separate, and drain the contents into a 50-ml Erlenmeyer flask containing about 1 g of anhydrous sodium sulphate to remove water droplets. Transfer a portion of the dried extract to a 1-cm cell and measure the absorbance at the specified wavelength.

EXPERIMENTAL TESTS

1. <u>Direct Spectrophotometric Reading on the Aqueous Solution</u>

  (a) <u>Effect of Picric Acid Concentration</u>

  The effect of the picric acid concentration on colour intensity was investigated to establish the value giving the highest sensitivity. To 100-ml volumetric flasks, 0.10-mg portions of cyanide (as KCN) were added. The amount of picric acid added and the reaction volume were varied, while the amount of sodium carbonate was held constant at 5 ml of a 0.5M solution. The absorbance values of these solutions were measured after heating for 10 min, cooling to room temperature, and diluting to volume.

  The results (Table 1 and Figure 1) show that the colour intensity of the picric-cyanide compound increases with increasing picric acid concentration in the reaction volume which was heated.

TABLE 1

Effect of Picric Acid Concentration in the Reaction Volume That was Heated

Test	Ml 1% picric acid	Ml 0.5M sodium carbonate	Sample volume, ml	Reaction volume heated	Conc. sodium carbonate M*	Conc. picric acid, mg/ml*	Absorbance for 0.1 mg CN**
1	5	5	5	15	0.167	3.33	0.113
2	15	5	50	70	0.036	2.14	0.086
3	25	5	25	55	0.045	4.55	0.125
4	25	5	50	80	0.031	3.13	0.100
5	50	5	25	80	0.031	6.25	0.134

* Concentration in the reaction volume that was heated.
** All solutions diluted to 100 ml for reading.

For most of the remainder of the work, 25 ml of 1% picric acid and a reaction volume of 75 ml (diluted to 100 ml for reading) were used.

(b) Effect of Sodium Carbonate Concentration

Solutions containing 0.10 mg cyanide as CN were treated with 25 ml of 1% picric acid reagent and 2.5, 5.0, 10.0 and 20.0 ml of 0.5M sodium carbonate solution. The heating time was 10 min. The solutions were cooled, diluted, and the absorbance measured.

The optimum sodium carbonate concentration was found to be 0.025M in the final volume (after colour development).
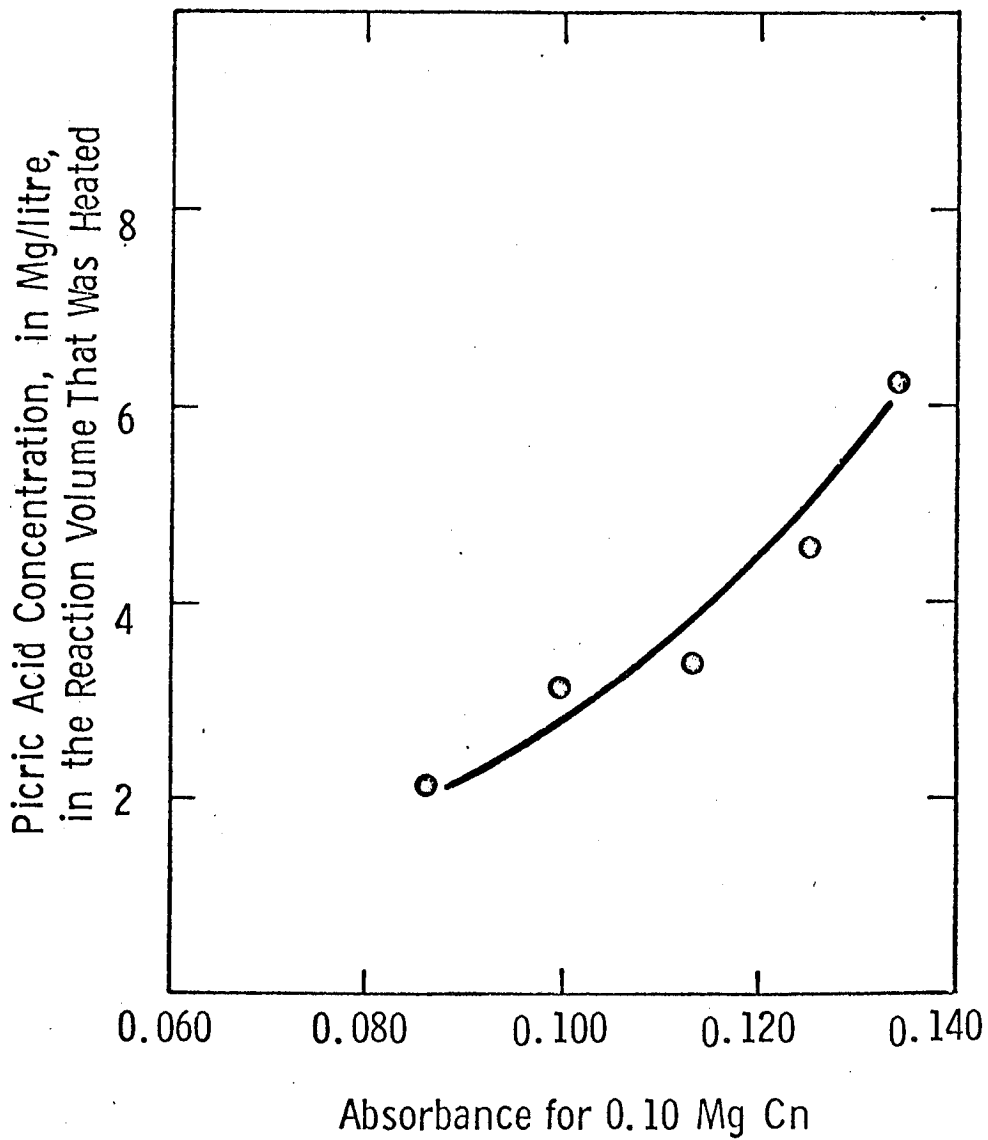
Figure 1. Effect of picric acid concentration –
Aqueous system.

This provided sufficient excess of carbonate to ensure a basic reaction, while higher concentrations caused a slight decrease in colour intensity.

(c) Effect of Heating Time

The solutions consisted of 5 sets, each of which contained 0.02, 0.10 and 0.30 mg cyanide as CN, 5 ml of 0.5M sodium carbonate, and 25 ml of 1% picric acid solution, in a total volume of 75 ml in 100-ml volumetric flasks. The sets were all placed in a water bath, and one set removed at intervals of 2, 5, 10, 20 and 30 minutes respectively. The flasks were cooled, diluted to volume, and the absorbance measured.

. The rate of colour development varied somewhat with cyanide concentration, but in all cases maximum intensity was achieved in 5 minutes. The heating time could be extended to 20 minutes without any harmful effect, and the exact reaction time was found not to be critical.

Interestingly, one method that was tried for increasing the sensitivity consisted of developing the colour in a litre of solution and then concentrating to 100 ml by evaporation. Satisfactory results were obtained with standards, but values on actual samples were high. The test illustrates vividly the excellent heat stability of the colour.

(d) Spectral Characteristics

A solution containing 0.15 mg cyanide as CN, and a
blank, were each treated with 25 ml of 1% picric acid and 5 ml
of 0.5M sodium carbonate in a volume of 75 ml in a 100-ml flask.
After a 5-min heating interval, the flasks were cooled, diluted
to volume, and the absorption measured over the wavelength
region 460 nm to 540 nm.

The absorption spectra of the cyanide coloration and
the blank are plotted in Figure 2. The wavelength of maximum
absorption for the coloured reaction product occurs at 490 nm,
but at this wavelength the absorption of the picrate reagent is
itself high, so that it would be necessary to maintain identical
concentrations of reagent in the sample and the blank in order
to prevent a relatively large error. A wavelength of 520 nm was
therefore chosen instead, since at this point the absorption of
the picric acid becomes negligible and hence the reagent blank
becomes unnecessary, the sample being read against a reference
cell filled with distilled water instead.

(e) Stability of the Developed Colour

Sets consisting of colours developed from solutions
containing 0.05, 0.1, 0.2, 0.3 and 0.5 mg of cyanide as CN
were allowed to stand for 0.25, 4 and 48 hours prior to absorbance
measurement.
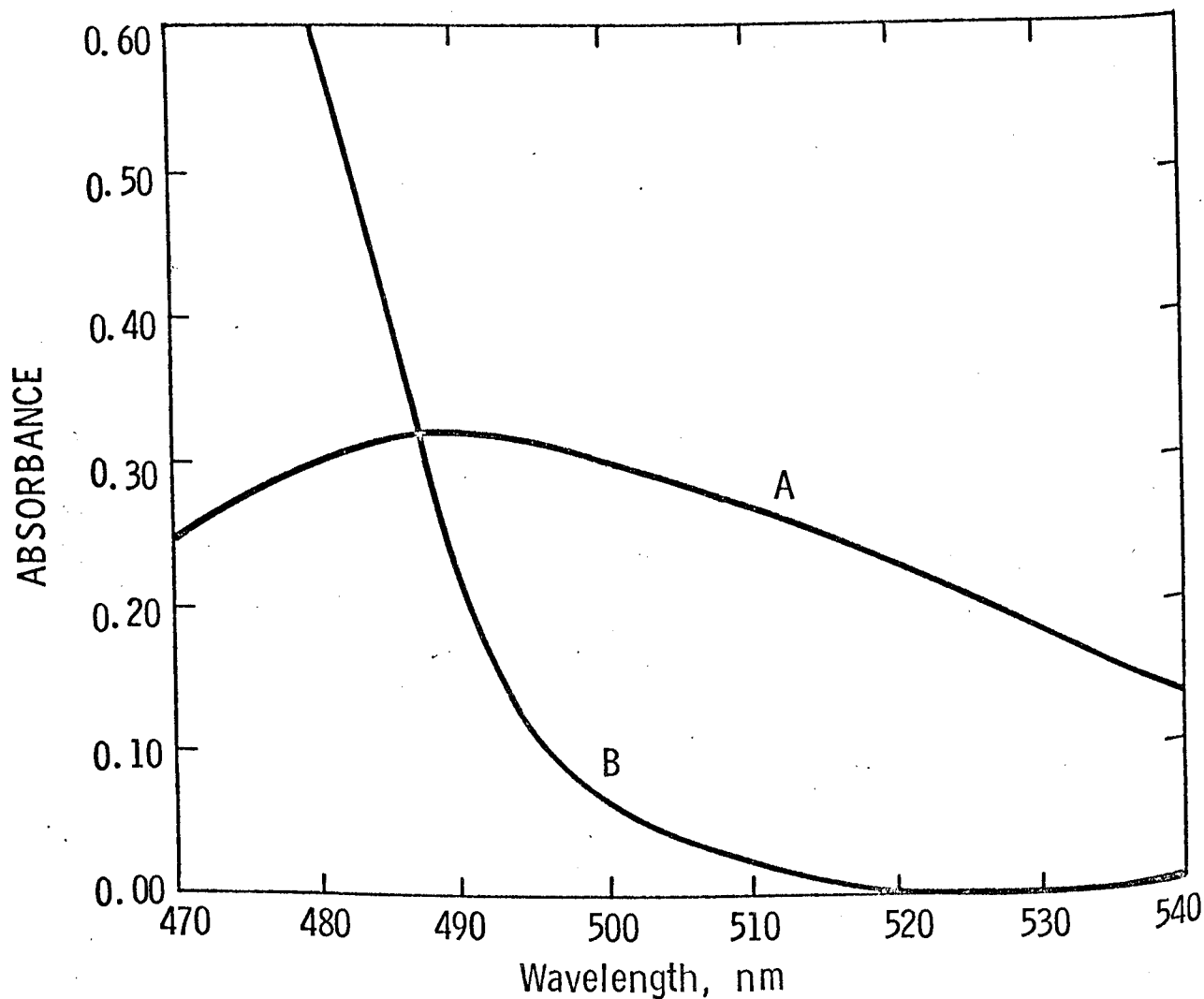
Figure 2. Absorption spectra of the cyanide-picrate colour, and of the picrate blank. Aqueous system.

25 ml 1% picric acid, 5 ml 0.5 M sodium carbonate, 0.15 mg cyanide in 100-ml volume; 1-cm cells

A. Cyanide-picrate colour, read against blank (B)
B. Picrate reagent blank

The absorbance values, given in Table 2, indicate that the colour undergoes negligible fading for at least 24 hours.

TABLE 2

Stability of the Cyanide-Picrate Colour

Time, hours	Absorbance of cyanide-picrate colour from				
	0.05 mg CN	0.1 mg CN	0.2 mg	0.3 mg	0.5 mg
0.25	0.055	0.113	0.240	0.355	0.584
4	0.054	0.113	0.240	0.355	0.582
48	0.054	0.113	0.235	0.342	0.566

(f)   Effect of Interfering Ions

Solutions containing respectively 1.3 mg $Fe(CN)_6$ in the form of potassium ferrocyanide, 50 mg of thiocyanate in the form of potassium thiocyanate, 50 mg of cyanate in the form of potassium cyanate, and 0.05, 0.1 and 0.2 mg of sulphide in the form of sodium sulphide, were carried through the outlined procedure.

The results of these tests are shown in Table 3 and demonstrate that thiocyanate and cyanate, in concentrations in considerable excess of those likely to be found in actual mill samples, have no interfering effect.

TABLE 3

Effect of Interfering Ions

Compound added	Concentration of foreign ion per 50-ml sample	Equivalent CN found, mg
$K_4Fe(CN)_6$	1.3 mg as $Fe(CN)_6$	0.00
KCNS	50 mg as CNS	0.00
KCNO	50 mg as CNO	0.00
Na_2S	0.05 mg as S	0.000
	0.1 mg as S	0.025
	0.2 mg as S	0.052

It has been stated [8] that certain reducing substances, such as sulphide, sulphite, aldehydes and ketones, may interfere by forming a coloured reaction product similar to that given by cyanide. Of these, sulphide is the most serious [10], and tests showed (Table 3) that its interference becomes significant at concentration levels above 1 mg per litre. However, sulphide ion is also a serious interference in the milling of gold ores by the cyanide process, so that operators normally make every effort to keep its concentration below 1 mg per litre in the leach liquor, usually by the addition of lead compounds.

The procedures that are used to reduce cyanide concentration for discharge (dilution or oxidation) must lower the cyanide concentration at least 100-fold to achieve a cyanide

concentration of 0.1 ppm, and in either of these processes an even greater proportional lowering of sulphide concentration would occur due to its much greater susceptibility to oxidation, so that it is extremely unlikely that interfering amounts would be present. In any case, precipitation with lead carbonate affords a simple means of reducing the sulphide concentration without disturbing that of the cyanide.

The other reducing agents (aldehydes and ketones), which must be present in large concentrations to interfere, are extremely unlikely constituents of the solutions in question.

(g) Use of EDTA to Release the Cyanide Contained in Metal Complexes

Solutions were made up in 100-ml volumetric flasks to contain the calculated amounts of nickel and cyanide, and copper and cyanide, to give the tetracyanatonickelate and the tricyanatocuprate, respectively. The nickel solutions contained 0.02 and 0.10 mg cyanide as CN, and the copper solutions contained 0.25 mg cyanide as CN, and three flasks of each solution were prepared. After addition of the carbonate and picric acid, one set of flasks was used as a control, the second set received 2 ml of 0.1M EDTA solution, and the third set received 5 ml of 0.1M EDTA solution. The colour was developed and read as before.

Table 4 illustrates the effectiveness of the addition of EDTA in liberating complexed cyanides of these two metals. An

TABLE 4

Effect of the Addition of EDTA on the
Recovery of Complex Cyanides

Test solution, metal complex	Total CN present, mg	CN determined, mg		
		ml EDTA, 0.1M, added		
		0 ml	2 ml	5 ml
$K_2Ni(CN)_4$	0.020	0.007	0.019	0.018
	0.020	0.006	0.019	0.019
$K_2Ni(CN)_4$	0.10	0.051	0.095	0.097
	0.10	0.047	0.095	0.094
$K_2Cu(CN)_3$	0.10	0.015	0.11	0.11
	0.20	0.045	0.20	0.20
	0.25	0.095	0.26	0.26

addition of 2 ml of 0.1M EDTA per 50 ml of sample appears to be
adequate for the levels of complex cyanides normally found in
the waste discharge streams. However, most such streams contain
relatively large amounts of calcium salts, from the lime which
is added for pH control and to assist settling. This interferes
in two ways: 1) by using up some of the EDTA required for
decomposition of the metal complexes, and 2) by producing a
turbidity with the sodium carbonate. One ml of 0.1M EDTA complexes
4 mg of Ca, and a leach liquor can contain up to 1 g/l of Ca.
Assuming the leach liquor has undergone at least a tenfold

dilution, the EDTA requirement of a 100-ml sample would be 2.5 ml of a 0.1M solution. Accordingly, the addition of 0.1M EDTA was standardized for the test work at 5 ml (and subsequently modified in the final combined method, to 4 ml).

2. Spectrophotometric Reading after Concentration of the Colour by Extraction with an Immiscible Organic Solvent

(a) Effect of the Concentration of Aliquat 336 in the Chloroform used for Extraction

Colours were developed using 0.025 mg of cyanide as CN, 25 ml of 1% picric acid solution, 5 ml of 0.1M EDTA solution, and 5 ml of 0.5M sodium carbonate solution, in a 100-ml volume. A reagent blank free of cyanide was also prepared. The developed colours were extracted as described under "Test Procedure", using 20-ml portions of chloroform containing 0.6, 1.0 and 2.0 g of Aliquat 336. The absorbance spectra of the extracts were measured over the wavelength range 475 to 540 nm.

In preliminary experiments, it had been established that a minimum of 1.7 g of Aliquat 336 per gram of picric acid was required for visually complete extraction (i.e., 0.65 gram would be required for the 0.38 gram of picric acid used here), so that an excess of amine was present in all cases.

The absorption spectra of the extracts and of the reagent blank are shown in Figure 3, and illustrate that the absorbance of the extracted picrate blank increases considerably

Figure 3. Effect of concentration of Aliquat 336 on the absorption spectra of the cyanide-picrate colour and of the reagent blank, in the chloroform phase.

20 ml Aliquat 336 - chloroform solution, 0.25 g picric acid

A - cyanide (0.025 mg as CN) - picrate, vs picrate blank

B - picrate blank

A_1, B_1 - 3% w/v Aliquat 336

A_2, B_2 - 5% w/v Aliquat 336

A_3, B_3 - 10% w/v Aliquat 336

with increasing concentration of Aliquat 336, whereas that of the extracted cyanide-picrate colour (read against the blank) remains almost constant. Thus, from the standpoint of sensitivity the concentration of Aliquat 336 in the chloroform is relatively unimportant. For precision, however, it is desirable to have as low a blank as possible, and for this reason it is considered that the Aliquat 336 concentration should be kept to the minimum (3% w/v) consistent with complete extraction.

(b) Effect of Picric Acid Concentration

Colours were developed using 0.025 mg of cyanide as CN, 5 ml each of 0.5M sodium carbonate solution and 0.1M EDTA solution, and 10, 15 and 25 ml of 1% picric acid, in a 100-ml volume. A set of three reagent blanks was treated in the same way.

All were extracted as described above under "Test Procedure", using 20 ml of 3% w/v Aliquat 336 in chloroform. The absorption spectra are presented in Figure 4 and clearly demonstrate that, as was also noted for the unextracted, aqueous system, increasing picrate concentration increases the intensity of the extracted cyanide-picrate colour and hence the sensitivity of the method. There is, however, a concomitant increase in the extracted blank, and as noted above it is desirable to work with as low a blank as possible to minimize error. A picric acid addition of 0.25 gram per 100 ml of aqueous solution was therefore selected as optimum.

(c) Effect of Sodium Carbonate Concentration

Similar tests were carried out using 1 to 5 ml of 0.5M sodium carbonate solution. Variations over this range had no effect on the absorption spectra of the extracted cyanide-picrate colour or the extracted blank.

(d) Spectral Characteristics

The absorption spectra of the extracted cyanide picrate colour and of the extracted picrate blank under varying reagent conditions are presented in Figures 3 and 4. As with the aqueous system, maximum absorbance occurs around 490 nm but because of the high absorbance of the extracted picrate reagent blank in this region, reading errors, due to such factors as minor differences in volumes, cell path-lengths, reagent concentrations and phase distribution of reagents, could be excessive.

(e) Stability of the Extracted Colour

Colours were developed and extracted as described above and the absorbance spectra were measured after various time-intervals up to 2 hours.

The absorbance of the extracted colour remained constant for up to 45 minutes. After this time, the absorbance of the lower intensity colours increased.
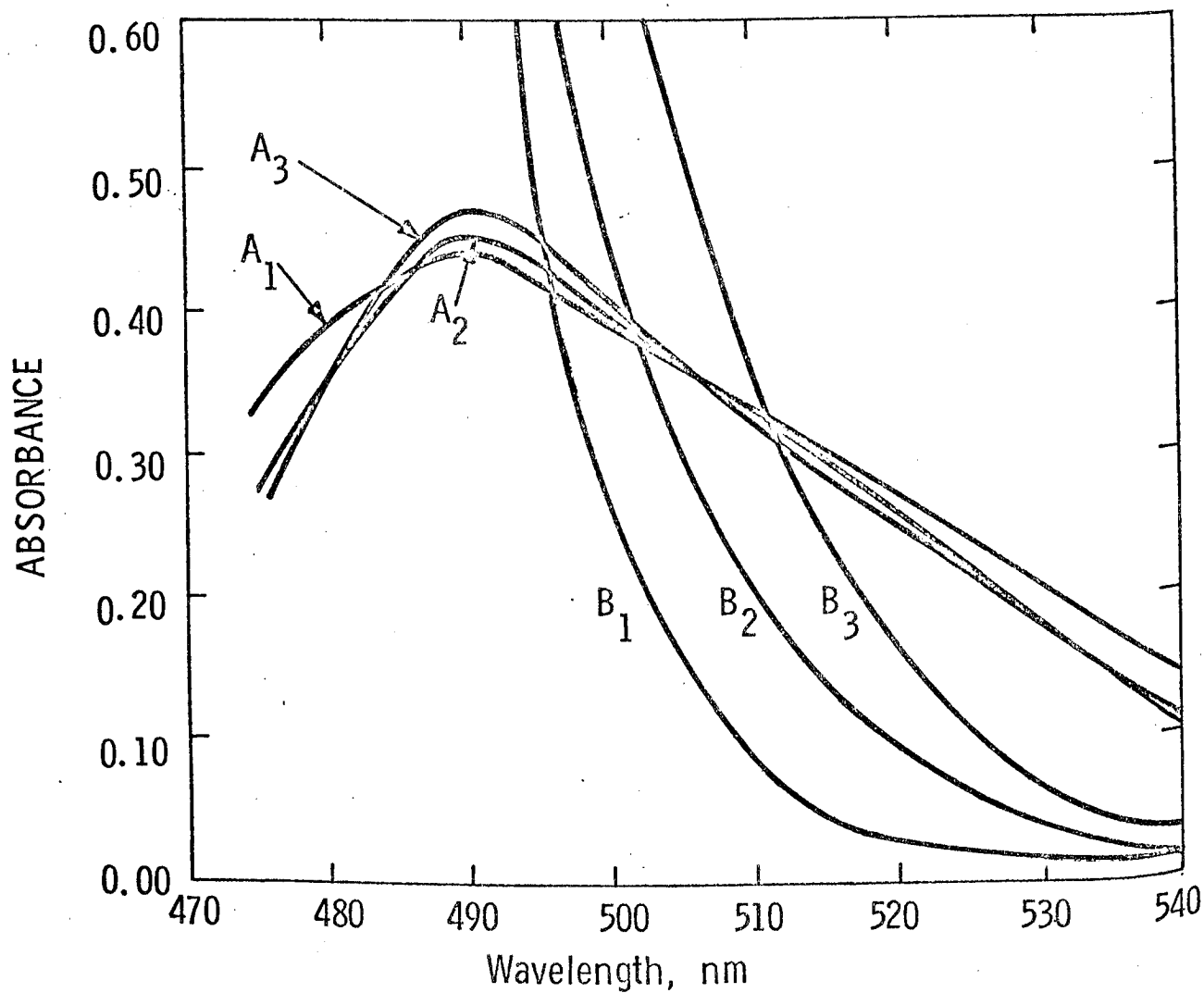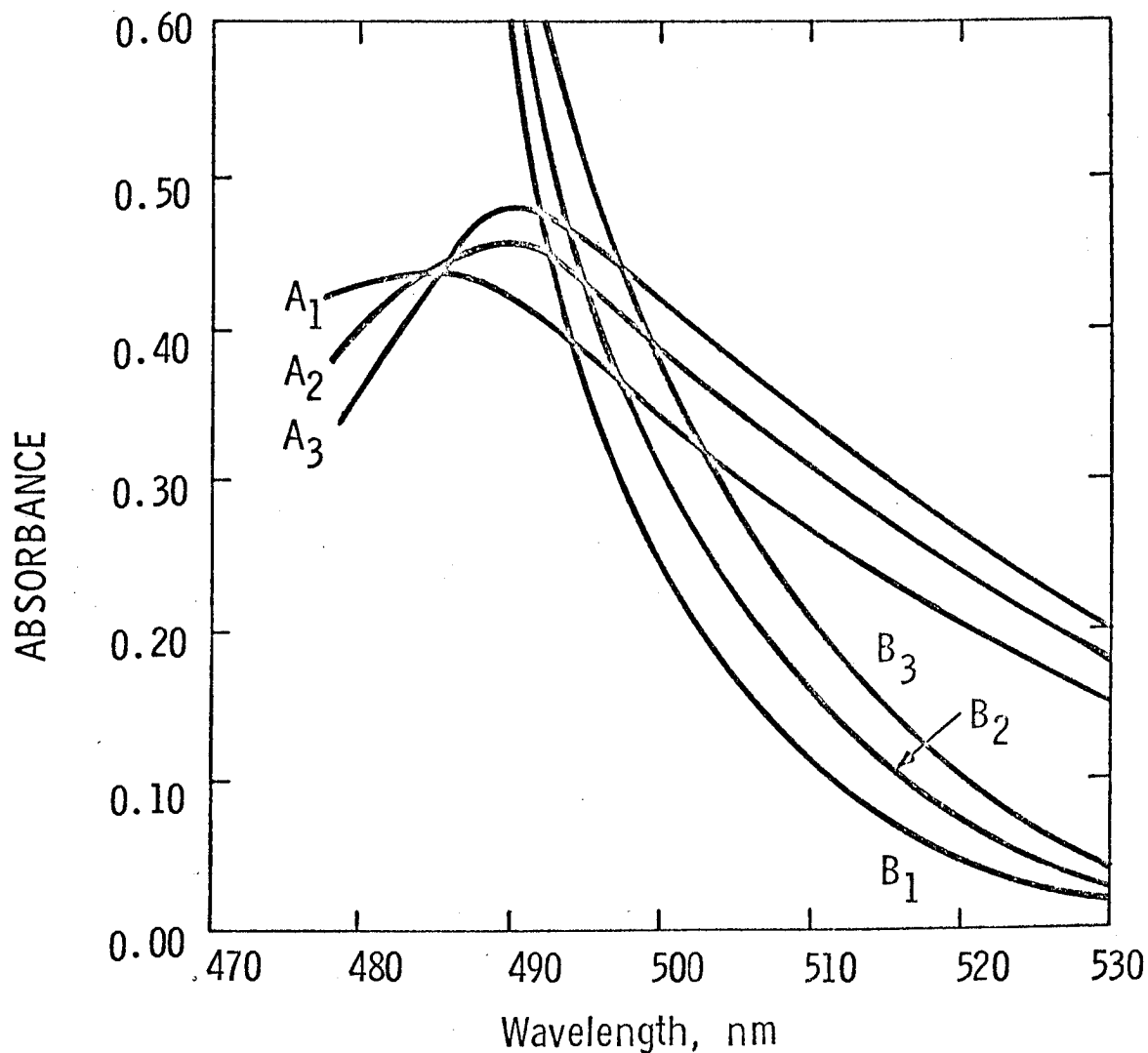
Figure 4. Effect of picrate concentration on the
absorption spectra of the cyanide-picrate
colour and of the picrate reagent blank,
in the chloroform phase.

A - cyanide (0.025 mg as CN) - picrate against
picrate blank
B - picrate blank against chloroform

A_1, B_1 - 0.10 g picric acid

A_2, B_2 - 0.15 g picric acid

A_3, B_3 - 0.25 g picric acid

RECOMMENDED METHOD

In the recommended procedure the optimum quantities of solid reagents indicated by the preceding work were combined into a powdered mixture which is added directly to an aliquot of the sample to permit the use of a larger aliquot and hence provide greater sensitivity.

Apparatus

Flasks, volumetric: 100-ml size.

Flasks, Erlenmeyer: 250-ml size,
50-ml size.

Plastic stoppers: Nalgene, to fit 50-ml Erlenmeyer flasks.

Boiling water bath: Large enough to accommodate the required number of 250-ml flasks, and about 4 in. deep.

Colorimetric apparatus:

For visual comparison:
100-ml volume Nessler tubes, with rubber stoppers, and support stand.

For spectrophotometric comparison:
Spectrophotometer with 1-cm and 5-cm cells.

Reagents

Picric acid, crystal, 10% water: e.g. Baker's Analyzed (the 50% water slurry sold by some suppliers is inconvenient to use).

Sodium carbonate, anhydrous, reagent-grade.

Ethylenediamine tetraacetic acid (EDTA): disodium salt.

Reagent mixture: Mix together thoroughly: 10.4 g of sodium carbonate (anhydrous powder) and 3.0 g of EDTA. Add and mix thoroughly 2.7 g of picric acid (do not grind in a mortar). Store in a stoppered bottle or weighing dish (this is enough reagent for 20 determinations). 0.80 g of the mixture is required for one determination.

Amine-chloroform solution: 3% w/v Aliquat 336 in reagent-grade chloroform. Weigh out 30.0 g of Aliquat 336 in a 100-ml beaker. Transfer to a one-litre flask with chloroform. Dilute to the mark with chloroform. (Aliquat 336 is a quaternary amine, and is a product of General Mills, Kankakee, Ill.)

Sodium sulphate, anhydrous.

Stock cyanide solution: Dissolve 1.90 g of sodium cyanide (or 2.5 g of potassium cyanide) in distilled water in a 1-litre volumetric flask. Add 2 drops of 50% sodium hydroxide solution, and dilute to volume. 1 ml = 1 mg CN. Standardize before use by the silver nitrate method.

Standard cyanide solution: Transfer 1 ml of the stock cyanide solution to a 200-ml volumetric flask. Add 1 drop of 50% sodium hydroxide solution, and dilute to volume. Prepare fresh as needed. 1 ml = 0.005 mg CN (or as calculated from the strength of the stock solution).

Acetone, technical: For cleaning glassware.

Calibration (Spectrophotometric Procedure)

If Nessler tubes are to be used for comparison, proceed directly to the section headed "PROCEDURE".

Pipette aliquots of the standard cyanide solution containing 0.005, 0.01, 0.02 and 0.05 mg of CN into 250-ml Erlenmeyer flasks. Include a blank flask as well. Dilute to 100 ml with distilled water. Add 0.80 g of solid reagent mixture and swirl to dissolve. Heat the flasks in a boiling-water bath (100°C) for 20 minutes. Remove the flasks from the bath and cool them to room temperature in cold water. Transfer the contents to 100-ml volumetric flasks, dilute to the mark, and mix well.

If desired, the developed colour may be read directly at this point, using 1-cm cells and a wavelength setting of 520 nm, and employing the reagent blank as a reference. The values obtained are then plotted to give a calibration graph for cyanide concentrations in the range 0.1 ppm and up.

Where maximum sensitivity is required, transfer the contents of the flasks to 250-ml separatory funnels. By pipette, using a rubber bulb, add 20 ml of the amine-chloroform solution to each funnel, and shake the funnel 2 minutes. Let the phases separate for 10 minutes and drain the chloroform layer into a 50-ml Erlenmeyer flask containing about 1 g of anhydrous sodium sulphate. Stopper the flasks and swirl the contents until the organic solution is clear and free from bubbles of water. Transfer a portion to a 1-cm cell, stopper the cell to prevent evaporation of chloroform, and measure the absorbance at 510 nm against the reagent blank. Record the values and plot a calibration graph of absorbance vs mg CN in a 100-ml sample. (Figure 5 presents an example of a typical calibration graph.)

Procedure

1. Colour Development Step

Transfer 100-ml aliquots of the samples, containing 0.001 to 0.5 mg CN, to a 250-ml Erlenmeyer flask (for higher concentrations, take a smaller aliquot and dilute to 100 ml with distilled water). Measure 100 ml of distilled water into a similar flask for the reagent blank. If the sample solution is coloured, see Note 1. To the samples and to the reagent blank, add 0.80 g of the solid reagent mixture. Swirl the flasks to dissolve the reagents, and place them in a boiling-water bath (100°C) for 20 minutes. Remove the flasks from the bath and cool them to room temperature in cold water.
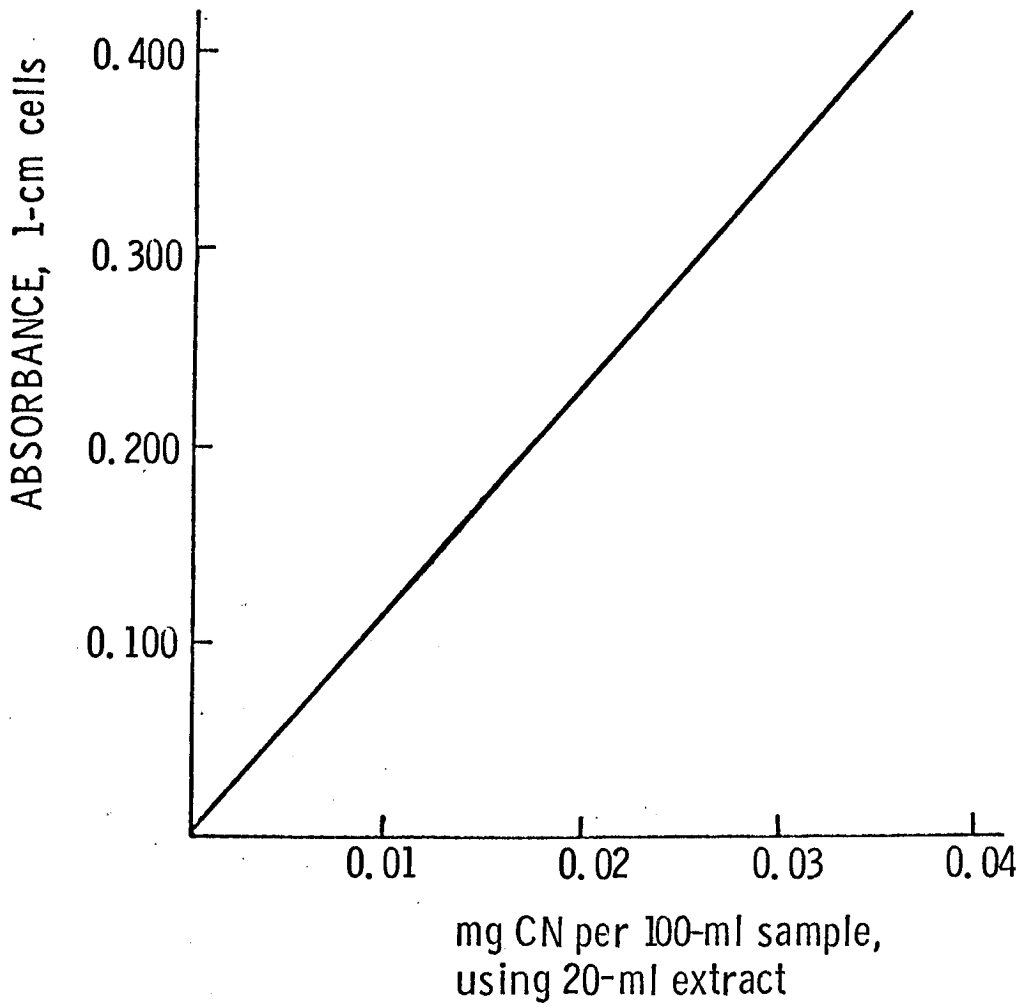
Figure 5. Typical calibration graph: picric acid-solvent extraction method for cyanide.

If the solvent-extraction step is to be used, i.e. if by visual comparison there is no perceptible colour difference between the reagent blank and the sample, proceed directly to section 3 below. If, however, the cyanide content is sufficiently high (0.2 ppm or over), the colour can be read directly on the aqueous solution at this point, using a spectrophotometer if one is available, or by means of Nessler tubes.

2. Colour Comparison of Aqueous Solutions

a) Spectrophotometric comparison

Read and record the absorbance of the samples against the reagent blank as reference at 520 nm. Determine the CN concentration of the samples by reference to the appropriate "Calibration Graph".

b) Nessler tube comparison

If no spectrophotometer is available, compare the colour of the samples with those of appropriate standards carried through the procedure, using Nessler tubes. A set of standards can be kept for at least three days if the Nessler tubes are stoppered when not in use. Visual standards which are stable for several weeks can be prepared by diluting potassium dichromate solution to match the colour of the standards prepared above. Estimate the cyanide contents by visual interpolation between the two closest standards, and calculate the cyanide content of the original sample on the basis of the size of aliquot taken.

3. Solvent Extraction Step

If maximum sensitivity is required, transfer the solutions to 250-ml separatory funnels. By pipette, using a rubber bulb, add 20 ml of the amine-chloroform solution to each funnel and shake the funnels for 2 minutes each. Let the phases separate for 10 minutes and draw the chloroform layers into 50-ml Erlenmeyer flasks containing about 1 g of anhydrous sodium sulphate. Stopper the flasks and swirl the contents until the organic solutions are clear and free of water droplets. Transfer a

portion to either 1-cm or 5-cm cells, depending on the range, stopper the cells, and measure the absorbances at 510 nm against the chloroform extract from the reagent blank.

Rinse the cells with chloroform, and drain, before filling with the next chloroform extracts. The chloroform extracts should be read within 45 minutes after extraction.

Record the values, and determine the CN concentration of the original samples by reference to the Calibration Graph. If a spectrophotometer is not available, compare the colours of the extracts visually against standards carried through the procedure using Nessler tubes, as described above.

Notes

1) To compensate for coloration present in the water:

If the sample solution is judged to exhibit sufficient colour to interfere with the estimate of the cyanide content of the sample, this can be overcome in the following manner:

Prepare a second identical aliquot of the sample as a "sample blank", to compensate for any coloration present in the water. Add 0.52 g of sodium carbonate and 0.15 g of EDTA, i.e. omit the picric acid. Carry this reagent blank through the procedure along with the sample and reagent blank.

For the direct spectrophotometric comparison, read and record the absorbance of the samples against the reagent blank as reference. Then read the absorbance of the "sample blanks" against distilled water, and correct for the original colour of the water by subtracting these readings from those of the corresponding samples which were treated with the complete reagent mixture. Determine the CN concentration of the samples by reference to the appropriate "Calibration Graph", using the corrected absorbance values.

If the concentration of CN^- is low, i.e. below 0.2 ppm, the picrate-cyanide solutions will have to be extracted in any case, and any interference from the original colour of the water samples will be eliminated.

2) In the case of samples containing a high concentration of calcium, the calcium may react with the sodium carbonate of the reagent mixture to give a precipitate of calcium carbonate. In this case, add 2 ml of 0.1M EDTA solution to the sample aliquot before adding the solid reagent, so as to complex the calcium and provide a clear solution.

3) The glassware used for the solvent-extraction procedure can be cleaned with acetone and rinsed with distilled water.

4) Picric acid is an explosive and all residues should be flushed away with water.

5) The reagent stains the hands. This can be avoided by wearing gloves.

ANALYSES OF TYPICAL MILL SOLUTIONS AND EFFLUENTS BY THE RECOMMENDED METHOD

To confirm the reliability of the method over as wide a range of compositions as possible, typical gold-mill solutions and effluents from a number of mills in Northern Ontario and Northern Quebec, and synthetic solutions, whose cyanide content was established independently, were analyzed by the "Recommended Procedure", either by direct measurement of the colour of the aqueous solution or using the solvent-extraction step, depending on the cyanide content of the aliquot taken.

Table 5 shows the values obtained for the mill-process solutions. Suitable aliquots were diluted to 100 ml with distilled water for the colorimetric procedure. The results are compared with values obtained by the standard AWWA distillation titration (Serfass) method [2].

TABLE 5

Comparison of the Recommended Procedure with AWWA
Method [2] for Typical Mill Solutions

Sample		Cyanide as CN	
Mill	Type	AWWA methods: – distillation – titration	Recommended procedure (aqueous reading)
A	Pregnant liquor	0.43 g/l	0.45 g/l
B	Pregnant liquor	0.11 g/l	0.11 g/l
C	Pregnant liquor	0.43 g/l	0.40 g/l
D	Overflow	0.42 g/l	0.44 g/l
B	Barren	0.11 g/l	0.09 g/l
B	Tailings effluent	41 ppm	53 ppm
E	Disposal tails	7.8 ppm	7.8 ppm

The agreement obtained is generally quite adequate.

Table 6 illustrates the quantitative recovery of
cyanide added to two of the mill solutions whose analysis is
given in Table 5, and diluted with distilled water into a range
typical of effluents.

These results confirm that good recovery can be
obtained for relatively low amounts of cyanide, and considered
along with the results of Table 5, confirm that there are no
serious interferences present in the mill solution themselves.

TABLE 6

Recovery of Cyanide from Typical Mill Solutions
Diluted and Spiked with Cyanide

(100-ml aliquot; aqueous reading)

Mill	Type of solution	Present initially, mg	Added, mg	Cyanide as CN, total present		Recovered, mg
				ppm	mg	
A	Overflow	0.13	0.10	2.3	0.23	0.23
A	Pregnant	0.13	0.10	2.3	0.23	0.23

The results in Table 7 were obtained on synthetic
metal cyanide solutions similar to those described on page 13,
and confirm that the use of EDTA to release the metal cyanides
is without deleterious effect on the solvent-extraction step.
They also illustrate the reproducibility at the 0.05-ppm level.

Samples of typical tailings dam effluents provided
by different gold mills were analyzed for total cyanide by the
recommended procedure. Known amounts of cyanide (in the form
of cuprocyanide) were added to each, and the cyanide content
of the spiked samples were determined. The results (each
value the average of two determinations) are shown in Table 8.

In Table 9, a sample of mill tailings effluent of
relatively high cyanide content (41 ppm, determined by the
AWWA distillation-titration method) was used to spike a tailings
from another mill, which had been found to be free of cyanide.
Two levels of spiking were employed.

TABLE 7

Recovery of Cyanide from Synthetic Metallocyanide Solutions - Solvent Extraction Procedure

Test solution	Cyanide present		Recovered,
	ppm	μg in 100 ml	μg in 100 ml
$K_2Ni(CN)_4$	0.05	5.0	5.3
	0.05	5.0	5.6
	0.05	5.0	5.4
	0.25	25.0	24.3
$K_2Cu(CN)_3$	0.05	5.0	5.2
	0.05	5.0	5.1
	0.25	25.0	23.2
	0.25	25.0	25.2

TABLE 8

Recovery of Added Cyanide from Samples of Typical Tailings Dam Effluents: 100-ml Aliquots - Solvent Extraction Procedure

(Cyanide addition in the form of $K_2Cu(CN)_3$)

Mill and samples	Cyanide as CN		
	Added (ppm)	Found (ppm)	Recovery (ppm)
D Tailings dam effluent	--	0.01	--
	0.05	0.06	0.05
F Tailings dam effluents	--	<0.01	--
	0.05	0.05	0.05
H Tailings dam effluents	--	0.07	--
	0.05	0.12	0.05
K Tailings dam effluents	--	0.03	--
	0.05	0.08	0.05

TABLE 9

Recovery of Cyanide from a Low-Cyanide Mill
Effluent Spiked with a High-Cyanide Mill
Effluent - Solvent Extraction Procedure

Low-cyanide effluent: Mill F, <0.01 ppm (Table 8)
High-cyanide effluent: Mill B, 41 ppm (Table 5)

Test	Cyanide as CN			
	Added (ppm)	Absorbance	Recovered	
			ppm	
1	0.20	0.172	0.0165	(Avg.,
		0.205	0.020	0.18)
		0.175	0.0170	
2	0.041	0.020	0.002	(Avg.,
		0.022	0.002	0.025)
		0.028	0.003	

The results of these two sets of tests clearly
indicate that, in so far as these particular samples are
concerned, there is no interference from other constituents
present in the effluents.

As an indication of the reproducibility of the
extraction modification of the method, a sample of a mill
effluent that had been analyzed both by the AWWA procedure
and by the picrate-aqueous method, was diluted into the
0.2-ppm range and the cyanide content determined.

These results are given in Table 10 and show that
satisfactory reproducibility can be obtained at the 0.2-ppm
level, and, even at the 0.07-ppm level, precision and accuracy
are sufficient to demonstrate that an adequate indication of
0.02 or 0.03 ppm would be possible.

TABLE 10

Comparison of the Direct Picrate-Aqueous Procedure,
the Picrate-Solvent Extraction Procedure, and the
AWWA Distillation Titration Procedure, on a
Typical Effluent   (Mill F)

Method	Aliquot, ml	Absorbance	Cyanide as CN, ppm			
			of original sample		after dilution	
			Individual	Avg.	Present	Found
AWWA titration	–	–	6.7			
			6.8			
			6.8	6.8		
Picrate direct	20	0.166	7.4		1.4	1.5
	40	0.325	7.2	7.3	2.7	2.9
Picrate extraction	1	0.130	10		0.07	0.10
		0.102	8			0.08
		0.095	7	8		0.07
	3	0.296	8.1		0.21	0.24
		0.290	8.0	8		0.24

As further confirmation of the reliability of the method, arrangements were made to have samples collected and shipped to this laboratory, and to another laboratory experienced in cyanide analysis, within a two-day period. The samples were collected from two different tailings streams on two different days. Both laboratories analyzed the two samples by the AWWA distillation-titration method and by the picrate procedure-aqueous modification. These results are given in Table 11 and show reasonable agreement, both between laboratories and between methods.

TABLE 11

Interlaboratory Comparison Using the AWWA Distillation-
Titration Procedure and the Picrate-Aqueous Procedure on
Three Typical Mill Effluent Samples

Mill	Laboratory	Method	Cyanide as CN, ppm
G	OWRC	Picrate	52
		AWWA	47
	This laboratory	Picrate	44
		AWWA	41
L	OWRC	Picrate	27
		AWWA	27
	This laboratory	Picrate	23
		AWWA	22
F*	OWRC	Picrate	7.8
		AWWA	9.7
	This laboratory	Picrate	7.3
		AWWA	6.8

*See also Table 10.

Since cyanide is often used in the flotation process as well (to improve selectively by acting as a depressant for various minerals), it was of interest to know whether the picrate procedure could be applied to a flotation liquor. A sample of such a liquor (from mill M) was analyzed, both by the AWWA procedure and by the picrate procedure. The results, along with a partial analysis of the solution, are shown in Table 12.

Finally, since it is assumed that some mill effluents will have to undergo chemical oxidation to reduce the cyanide level prior to discharge, tests were carried out to see whether

TABLE 12

Determination of Total Cyanide in a Typical
Flotation Liquor (Mill M)

Partial analysis:	
Constituent	Concentration
Au	0.003 oz/ton
Zn	0.0003 g/l
Cu	0.05 g/l
CNS	0.038 g/l
Pb	<0.0005 g/l
Xanthate	<0.1 ppm

Method	Total cyanide found, g/l as CN
AWWA distillation	0.042
Picrate-aqueous	0.049

residual hypochlorite or reaction products from the commonly-used
hypochlorite oxidation process would affect the results. Two
portions of the effluent from mill F (Table 10, 6.8 ppm CN)
were each treated with the equivalent of 2 ml of commercial
hypochlorite bleach solution (58.6 g/l available chlorine) per
litre of sample, after adjusting the pH to 10. After standing 1
hour and 18 hours respectively, both samples were analyzed by
the two methods - the AWWA distillation-titration method and
the picrate-aqueous method. The results are given in Table 13.

If an attempt was made to determine the cyanide by
the picrate-aqueous method within a few minutes after adding
the hypochlorite solution, visible colour fading occurred. In

TABLE 13

Determination of Cyanide in an Effluent
(Mill F, 6.8 ppm CN) Treated with Hypochlorite
Solution (2 ml of 58.6 g/l available chlorine per litre)

Test	Time after hypochlorite addition, hours	Residual cyanide, ppm	
		by AWWA method	by picrate-aqueous method
1	1	3.5	4.3
2	18	3.4	3.8

the official method [1], the addition of sodium arsenite is recommended for overcoming the interference of hypochlorite. Tests were therefore carried out to determine whether arsenite addition would be equally effective in eliminating hypochlorite interference with the picrate method.

To two sets of reaction flasks were added 95 ml of water, 1 drop of 50% sodium hydroxide solution, and 0.2 ml of sodium hypochlorite solution (58.6 g available chlorine per litre). Sodium arsenite (0.1 g) was added to the solutions in one set of the flasks. To both sets of flasks, standard cyanide solution equivalent to 0.10 mg CN, followed by 0.80 g of the solid reagent mixture, was then added, and the colour was developed and read as usual. The results are given in Table 14.

TABLE 14

Use of Sodium Arsenite to Eliminate
Hypochlorite Interference in the Picrate Method

(95-ml sample)

Test	Cyanide added, mg as CN	Sodium arsenite present, g	Absorbance	Cyanide recovered, mg as CN
1	0.10	Nil	0.080	0.07
2	0.10	Nil	0.045	0.04
3	0.10	0.1	0.138	0.10
4	0.10	0.1	0.135	0.10

DISCUSSION: BASIS FOR THE SELECTION OF THE CONDITIONS
DESCRIBED IN "RECOMMENDED METHOD"

On the basis of the results of the experimental studies,
reagent and volume conditions were selected to provide a single
set of optimum conditions, regardless of whether the cyanide
content of the sample is high enough that the cyanide-picrate
colour can be read directly in the aqueous phase, or is so low
that it can only be satisfactorily measured after extraction.
These are the conditions detailed in "Recommended Method". The
choice, naturally, represents a compromise with respect to the
conditions that would have been chosen for either alternative
used separately. The experimental studies were performed using
the reagents in solution, but it occurred to us that by adding

the reagents in solid form, with the sample itself as the
solvent, the maximum sensitivity of which the picrate cyanide
reaction is capable could be achieved. This turned out to be
both feasible and operationally more-simple. The proportions
of the components in the dry reagent mixture were chosen to
provide the same concentrations that had been indicated as
desirable in the tests with the components added as solutions.

The amount of picric acid was set at 0.15 g per 100 ml
of sample (at some sacrifice to sensitivity), to ensure complete
extraction of picrate and the picrate-cyanide colour. The EDTA
addition was set at 0.15 g per 100 ml of sample (0.004 M) to
ensure an adequate excess even in samples having high calcium
concentration. The sodium carbonate addition was increased to
0.52 g per 100 ml of sample (0.05 M) to accommodate the hydrogen-
ion released from EDTA during the complexing of calcium in such
samples. A wavelength of 520 nm was selected for reading the
absorbance in the aqueous system, to improve precision, while
a wavelength of 510 nm was selected for reading the absorbance
of the organic extract, to provide the best sensitivity.

The method does not include any of the cyanide present
as cobalticyanide or as ferrocyanide. Cobalticyanide is not
normally present in detectable amounts in gold-mill effluents,
and is not included in the total cyanide as determined by the
standard methods [1][2]. Ferrocyanide represents a more serious

problem, since the proportion present in effluents from some

areas can be quite high. Where this is known to be the case,

an indication of its concentration can usually be obtained

fairly rapidly by means of a colorimetric iron determination

(using, for example, the 1,10-phenanthroline method) after

removing uncomplexed iron by sodium hydroxide precipitation.

This procedure, however, would not permit the determination

of amounts of cyanide (present in the form of ferrocyanide) of

less than 0.5 ppm, using a 100-ml sample. It should be pointed

out that in our opinion any ferrocyanide present in the samples

will probably have been present in the original effluent

discharge and is not likely to have been formed as the result

of interactions that have occurred after leaving the mill.

This is because the cyanide in the effluents is usually present

at quite low activity (as metal complexes) and is thus incapable

of interacting with either the solid tailings or the stream-borne

iron.

Thiocyanates and cyanates in concentrations up to

50 mg per litre do not interfere. Sulphide ion causes the most

interference, 0.1 mg of S^- being equivalent to 0.025 mg of CN^-.

However, the relative concentrations of the two ions in gold-mill

solutions, and the ease with which sulphide ion is oxidized by

air, make it unlikely that amounts of this ion sufficient to

affect the analysis would be present.

For samples containing more than 0.1 ppm CN, the extraction step can be omitted and a determination completed in 25 minutes. The solvent extraction step increases the over-all time to just over an hour (20 minutes of which is actual working time) and permits the determination of as little as 0.02 ppm. The steps are simple and a very large throughput is possible.

No trouble has been experienced in obtaining satisfactory results on any solution analyzed so far. Elimination of the distillation step for the isolation of the cyanide, while essential for obtaining the speed and simplicity required, results in the possibility that some as yet unknown interference could lead to erroneous results, so that, until the method has proved itself in use in a particular area, some form of cross-checking will be necessary. However, at least as far as samples from the gold-mining areas of northern Ontario and northern Quebec are concerned, the results demonstrate that considerable confidence can be had in the method.

Picric acid is also known as trinitrophenol, and is explosive. It is not readily detonated and is not particularly hazardous to use, but all spills should be wiped up and solutions should be disposed of by washing down a sink with copious amounts of water. Aqueous and organic solutions (particularly the latter) act

as dyes and stain many materials, including the skin. Most of
the stain can be removed from working surfaces and glassware by
means of acetone, but the hands should be protected with rubber
gloves.

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