

COLORIMETRIC METHOD FOR THE DETERMINATION OF  
TRACE AMOUNTS OF CYANIDE IN WATER

by

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## INTRODUCTION AND REVIEW OF LITERATURE

There are found in the literature various methods for the determination of trace amounts of cyanide ion including colorimetric, titrimetric, polarographic and chromatographic methods. A review (1) of the literature indicates that colorimetric methods are superior to the others. The standard methods for industrial trade wastes and effluents (2,3,4,5) and waters (4,6) use as a basis either the colorimetric procedure developed by Aldridge (7,8) or that of Epstein (9), which both make use of the Konig reaction (10,11) for the synthesis of pyridine dyestuff. The Konig method uses the reaction of cyanogen bromide or chloride with pyridine and an aromatic bromide. The method of Aldridge involves the reaction of cyanogen bromide with a pyridine/benzidine mixture; Epstein uses the reaction of cyanogen chloride with pyridine/1-phenyl-3-methyl-5-pyrazolone and a small amount of bis-1-phenyl-3-methyl-5-pyrazolone. Other workers (12,13,14,15) have used variations of these procedures, notably substituting barbituric acid in place of benzidine (12).

A recent investigation (15) into these various methods point out that each has very serious drawbacks. The pyridine/pyrazolone color development requires the preparation of a relatively unstable reagent, while the benzidine method has the distinct disadvantage in that the aromatic amine is a well-known active carcinogen and the developed color only obeys Beer's law up to concentrations of the order of 1 mg/ml so that it can not be used directly for effluents containing more than 2 p.p.m. cyanide in the measured sample. The barbituric acid method requires a relatively long period of heat treatment (40 min at 40°C); furthermore, the reagent becomes discolored on standing for short periods.

Most of these methods are subject to interference from a number of common

substances and make use of an acidic distillation (4) to form hydrocyanic acid which is trapped by bubbling through a basic wash solution. This distillation is very effective but in the case of interfering ions which form strong cyanide complexes such as ferric and cobaltic ions, the period for quantitative recovery becomes rather long, running over thirty minutes.

From this review of the literature, there appears a need for a rapid method for the determination of trace amounts of cyanide which uses safe, stable reagents and does not require a preliminary distillation.

Metal-dye reagents have been shown (16) to be a convenient tool for the determination of certain anions by selective ion exchange. The released dye anion concentration, measured spectrophotometrically, is directly proportional to the concentration of the displacing ion. Studies of supported metal-dye reagents have been reported (16,17,18). These reagents were found to be sensitive and reasonably selective.

Lambert and co-workers have proposed several methods for the determination of fluoride (16,17,18) using this method of dye release. A thorium-Amaranth compound (18) supported on cellulose was used to determine fluoride in the range of 1 to 30 p.p.m. Recently, paper supported zirconium-trypan blue chelate (16) has been used for the colorimetric determination of fluoride. The absorbance of the released dye was measured spectrophotometrically as a function of fluoride ion concentration. Sensitivity as low as 2 p.p.m. was achieved.

One of the main problems in such methods is either to separate the ion to be determined, or to find a combination of dye-metal ion which reacts selectively with the ion in the presence of interfering ions.

The investigation was undertaken to find a method which used safe, stable reagents and which was free from interferences. Preliminary studies

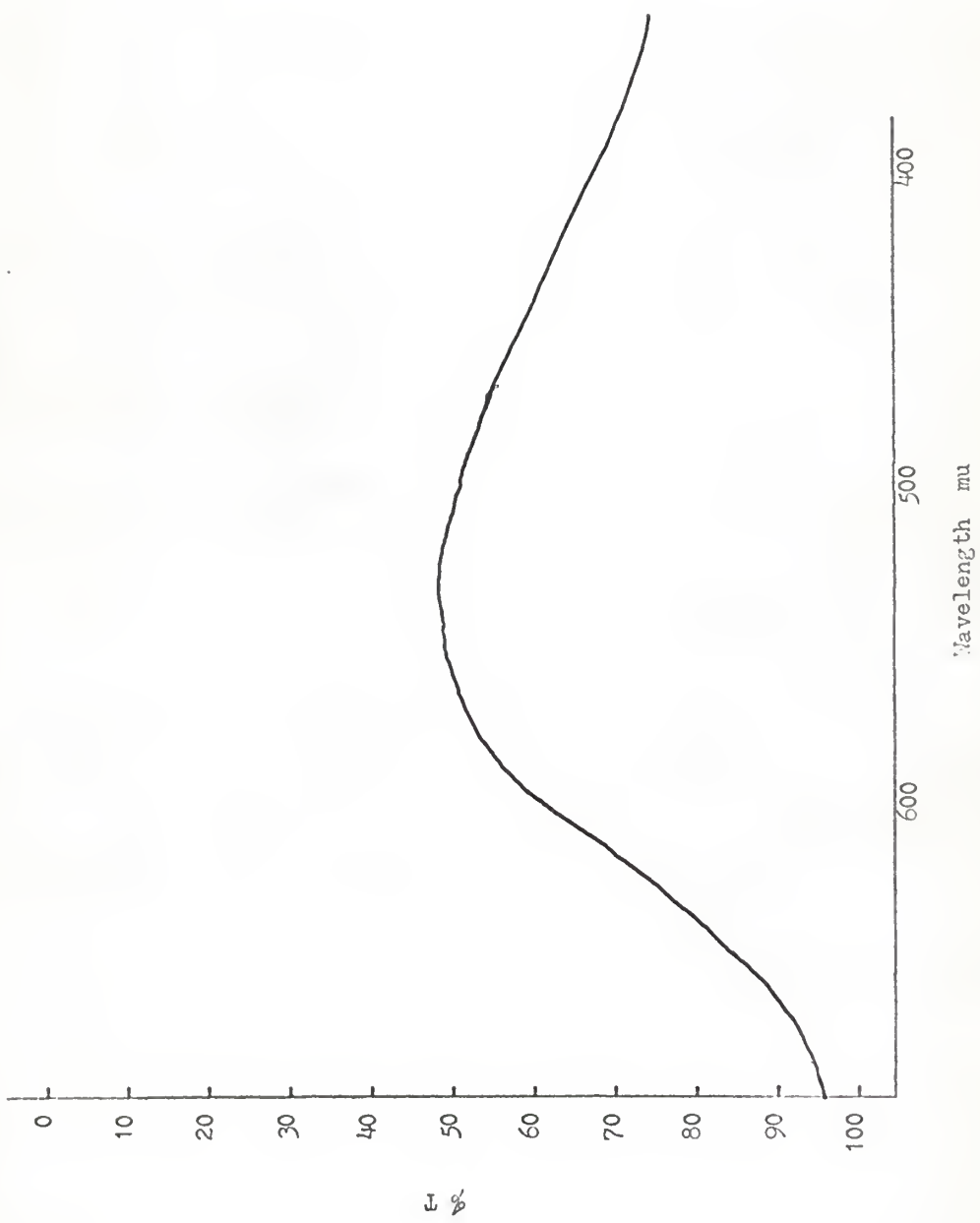
were made with metal-organic dye compounds supported on filter paper. First experiments were performed with Trypan Blue-metal compounds. Later, Trypan Blue, an active carcinogen, was replaced by Dianil Blue. (See Figure 1.) A paper supported Dianil Blue zirconayl reagent gave good response to cyanide ion in the range 1-25 p.p.m. but was subject to many interfering ions.

For convenience the support was changed from the filter paper, which was difficult to store and had a tendency to fall apart in the solutions, to porcelain chips. The porcelain chips were obtained by grinding porous porcelain plates and then grinding and sieving to the desired size. For this research 30-60 mesh size was used.

It was found that the tris-1,10-phenanthrolineiron(II) cation formed an insoluble compound with the triiodide ion,  $I_3^-$ . This compound reacted with the cyanide ion to liberate the highly colored tris-1,10-phenanthrolineiron (II) cation (Plate 2). Preliminary studies were performed to ascertain if one of the higher iodide complexes, such as  $I_5^-$  or  $I_7^-$ , would prove to be better than the triiodide. Although there appeared a possibility of increased sensitivity, reagents prepared with these higher complexes proved too unstable to be considered as a reagent.

EXPLANATION OF PLATE 1.

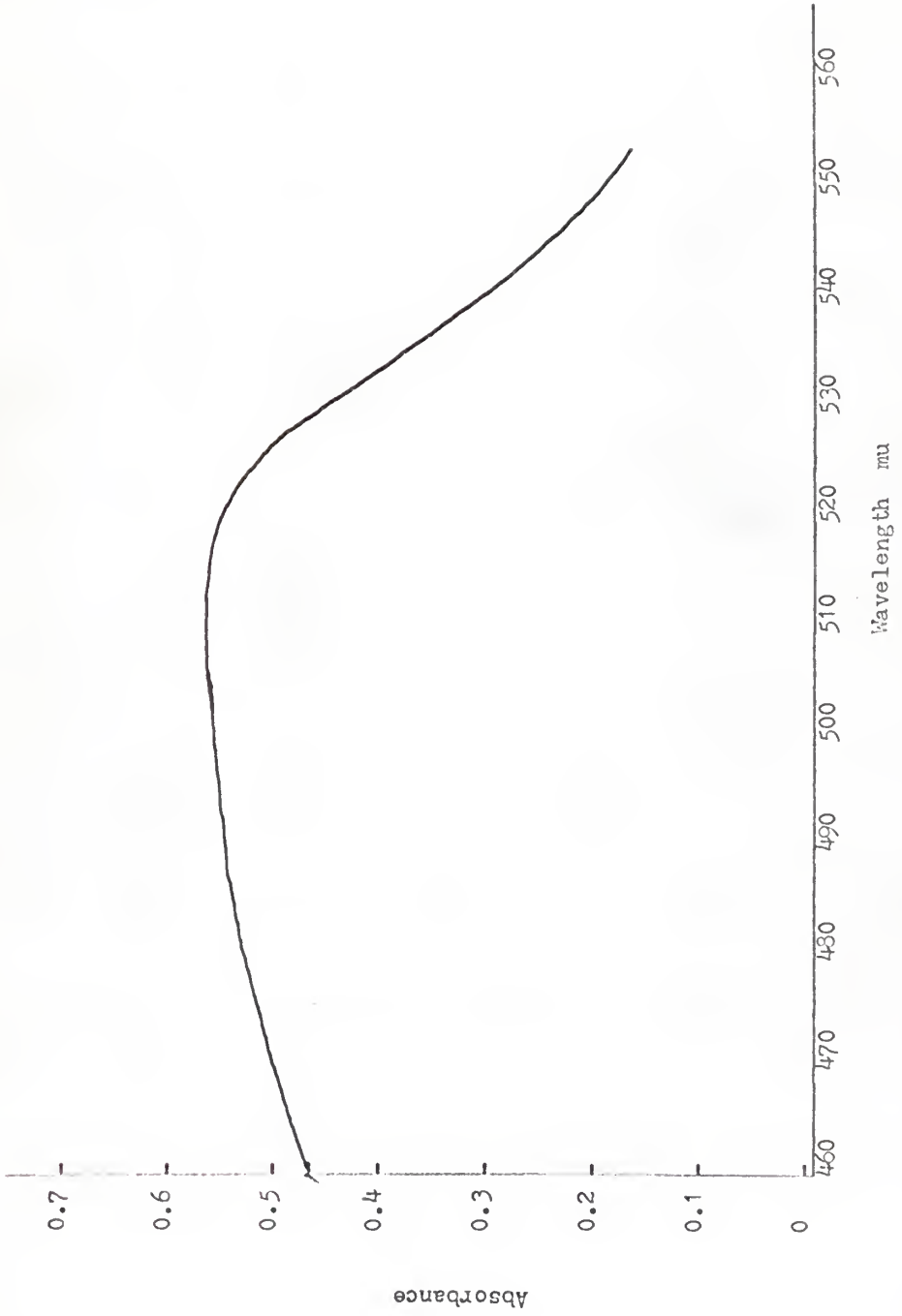
Visible Absorption Spectra of Dianil Blue  
Acid Solution



EXPLANATION OF PLATE 2.

Visible Absorption Spectra of Tris-1,10-Phenanthrolineiron(II)





## EXPERIMENTAL - PART I

## Special Reagents and Apparatus

Care must be taken when working with cyanide ion, a poison. Acid solutions release hydrocyanic acid which is very poisonous. All work, especially distillations, should be done in a hood. All water used in the various steps was purified by passing distilled water through a Barnstead model BD-I deionizer equipped with a mixed bed column.

All readings were taken on a Spectronic 20 using curvette cells.

A convenient measure for the reagents was found to be an emptied 22 caliber long rifle shell. A fired shell was cleaned thoroughly using nitrobenzene, making sure to remove any residual waxes from the rim primer. A handle was attached to form a "scoop". In measuring the reagent chips the 22 caliber scoop was dipped into the chips and leveled. This was found to be a very reliable and convenient measure, being reproducible and delivering the right amount of reagent for the range 1-10 p.p.m. cyanide ion.

Preparation of Potassium Triiodide (19)

A saturated solution of 33 g of potassium iodide was prepared in 100 ml water at 80°C. 5.0 gm of iodine was added to the hot solution and stirred until all the solid dissolved. The solution was then allowed to cool to room temperature.

Preparation of Tris-1,10-Phenanthrolineiron(II) Cation

A saturated solution of  $(\text{NH}_4)_2 \text{Fe}(\text{SO}_4)_2 \cdot 6 \text{H}_2\text{O}$  was prepared. To 5 or 10 ml of this solution 1,10-phenanthroline was added in slight excess of what would dissolve. This solution was diluted with twice its original volume of water.

### Preparation of Reagent Chips

Porcelain chips (30-60 mesh) were soaked in tris-1,10-phenanthrolineiron (II) solution for 20 minutes. The solution was then filtered and the chips dried with suction on a Büchner funnel for approximately two hours. The chips were then allowed to air-dry for at least five hours and were then treated with the triiodide ion,  $I_3^-$  solution, for twenty minutes, and again air-dried for at least five hours. The chips were then again treated with tris-1,10-phenanthrolineiron(II) ion solution the same as before and again air-dried. After drying, the treated chips were washed several times with deionized water until the blank was reduced to a minimum. Continued washing did not seem to reduce the blank lower than about an absorbance of 0.05. Recent work has shown that this blank was due to fine dust particles which had not been cleaned from the porcelain chips. Firmer supports for the reagent will minimize the blanks. The treated and washed chips were allowed to dry over night and were then ready to be used in a determination.

### Analysis of Water Samples

Twenty (20) milliliters of the sample were added to a 125 ml evaporating dish containing a measured amount of the reagent chips. The solution was allowed to stand for twenty minutes with frequent but not continuous stirring. At the end of this period the solution was poured from the evaporating dish and the absorbance of the solution was read on the Spectronic 20 spectrometer at  $514 \text{ m}\mu$ . This absorbance was then compared to a standard curve and the concentration of cyanide was determined.

## DISCUSSION

The method given above using porcelain chip supported tris-1,10-phenanthrolineiron(II)-triiodide was found to be an accurate and sensitive means of determining cyanide ion in the 1-20 p.p.m. range, as shown in Plates 3 and 4 and Table 1. Many common ions (Tables 3 and 4) are found to give no interferences, within the experimental limits. It should be possible therefore to use this method on raw samples without any preliminary isolation or separation steps.

TABLE 1.

Tabulation of Results for a Typical Calibration Curve

Cyanide Concentration, p.p.m.	Average Absorbance*	Absorbance Range	Standard Deviation
0	0.052	0.005	.002
2.0	0.165	0.009	.005
4.0	0.245	0.021	.008
5.0	0.360	0.033	.013
8.0	0.541	0.039	.015

\* Average of five determinations

A determination of synthetic samples, using tap water in the preparation, showed good agreement with values obtained using deionized water. In cases where the sample is highly colored or contains suspended materials, the cyanide can easily be separated by an acid distillation (4). The sample is made strongly acid with sulfuric acid and placed in a distilling apparatus shown in Fig. 5. This mixture is then heated and the cyanide is released as hydrocyanic acid, which is passed into a basic scrubbing solution and converted

to the cyanide salt. The determination can then be made without any interfering ions present. Several determinations using the distillation method were performed with the results shown in Table 2.

TABLE 2.

Tabulation of Results For Distillation Methods

Solvent	Concentration of Cyanide p. p. m.	Found Concentration p.p.m. *
Deionized Water	5	5
Tap Water	5	4.7
Tuttle Creek Lake Water	5	4.8
Kansas River Water	5	4.8

\* Concentration read from calibration curve, Plate I.

The distillation procedure may also be used as a means of concentrating samples of concentrations less than 1 p.p.m. A large volume of sample can be used for the distillation and the resulting hydrocyanic acid concentrated in a small volume of basic solution.

TABLE 3.

Effect of Possible Interferences in The Absence of Cyanide Ion

Ion	Substance	Concentration p.p.m.	Color
Na <sup>+</sup>	NaNO <sub>3</sub>	500	equals blank <sup>a</sup>
K <sup>+</sup>	KNO <sub>3</sub>	500	"
NH <sub>4</sub> <sup>+</sup>	NH <sub>4</sub> NO <sub>3</sub>	500	"
Ca <sup>++</sup>	Ca(NO <sub>3</sub> ) <sub>2</sub>	500	"
Fe <sup>+++</sup>	Fe(NO <sub>3</sub> ) <sub>2</sub> ·9 H <sub>2</sub> O	500	"
I <sup>-</sup>	KI	500	"
Cl <sup>-</sup>	NaCl	500	"
NO <sub>3</sub> <sup>-</sup>	NaNO <sub>3</sub>	500	"
CO <sub>3</sub> <sup>=</sup>	Na <sub>2</sub> CO <sub>3</sub>	500	"
SO <sub>4</sub> <sup>=</sup>	Na <sub>2</sub> SO <sub>4</sub>	500	"
F <sup>-</sup>	NaF	50	"
Tap Water	---	---	"

<sup>a</sup> Color equal in intensity to that obtained with distilled water by the regular procedure.

TABLE 4.

Effect of Possible Interferences in the Presence of Cyanide Ion

Ion	Substance	Concentration p.p.m.	Color
$\text{Na}^+$	$\text{NaNO}_3$	450	equals blank <sup>b</sup>
$\text{K}^+$	$\text{KNO}_3$	450	"
$\text{NH}_4^+$	$\text{NH}_4\text{NO}_3$	450	"
$\text{Ca}^{++}$	$\text{Ca}(\text{NO}_3)_2$	450	"
$\text{Fe}^{+++}$	$\text{Fe}(\text{NO}_3)_2 \cdot 9 \text{H}_2\text{O}$	10	interferes
$\text{I}^-$	$\text{KI}$	450	equals blank
$\text{Cl}^-$	$\text{NaCl}$	350	"
$\text{NO}_3^-$	$\text{NaNO}_3$	450	"
$\text{F}^-$	$\text{NaF}$	50	"
$\text{SO}_4^{=}$	$\text{Na}_2\text{SO}_4$	300	"
Tap Water	---	---	"

<sup>b</sup> Blank - Color equal in intensity to that obtained with  
5 p.p.m. cyanide by the regular procedure.

EXPLANATION OF PLATE 3.

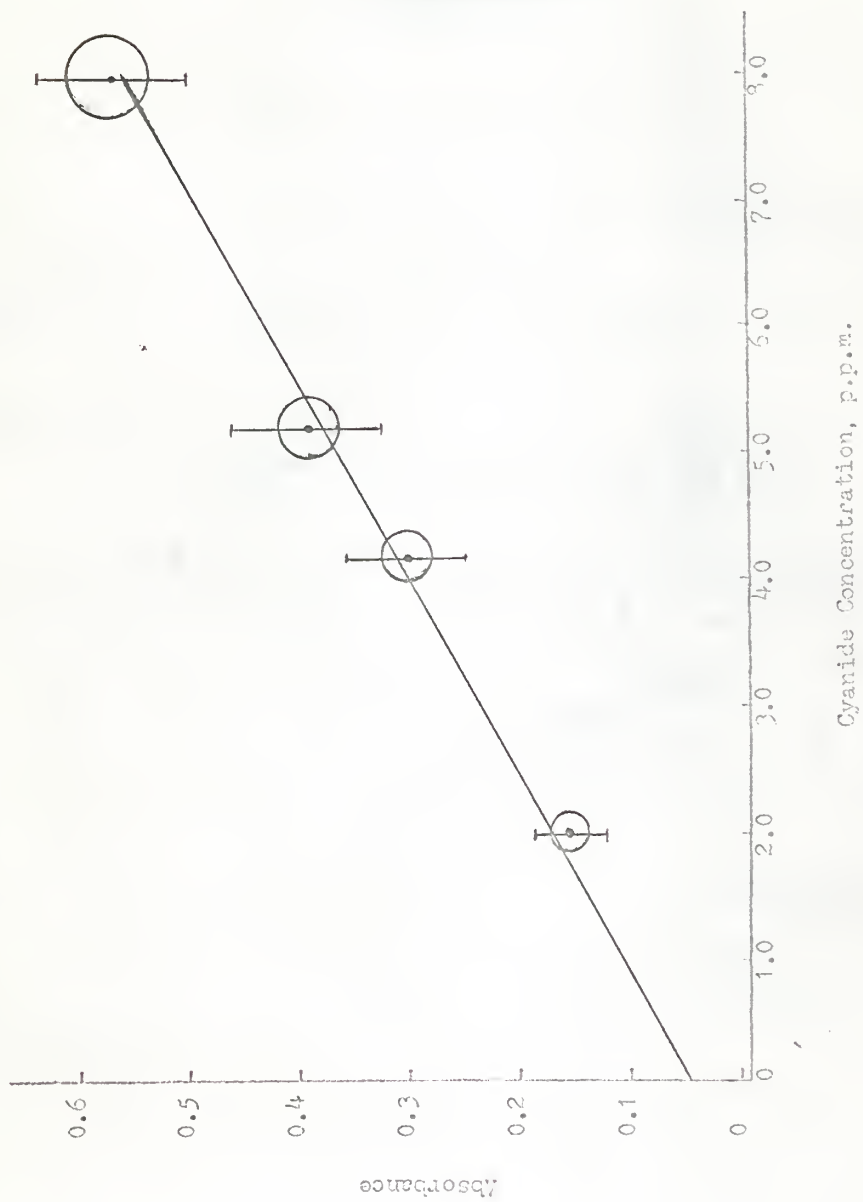
Typical Calibration Curve For Tris-1,10-Phenanthrolineiron(II) Reagent

Range I

Mean Value •

Average Deviation ○





EXPLANATION OF PLATE 4.

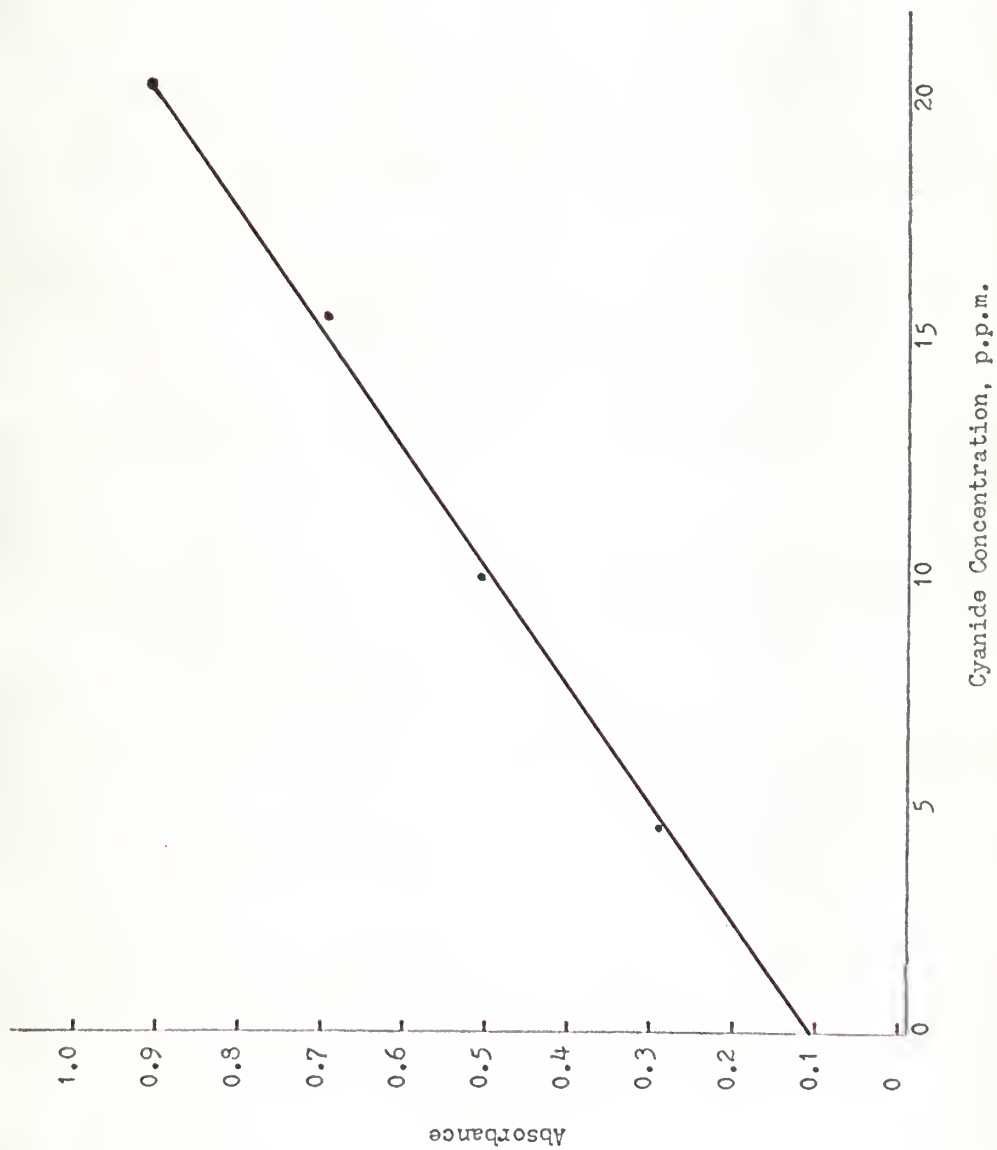
Typical Calibration Curve For Iris-1, 10-Phenanthrolineiron(II) Reagent

• Average of Three (3) Determinations

Range I

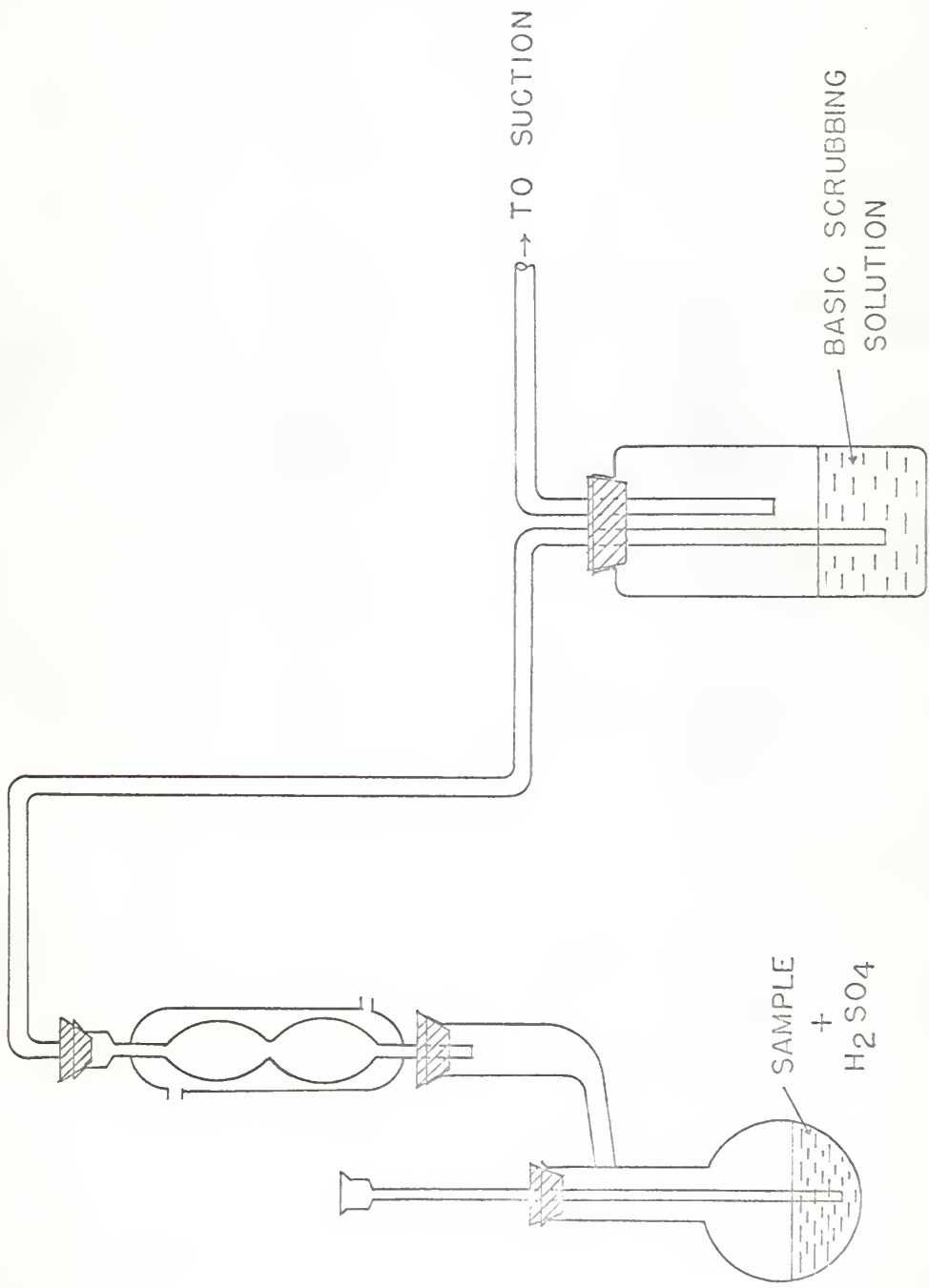
Mean Value •

Average Deviation ○



EXPLANATION OF PLATE 5.

Apparatus for Distillation of Hydrocyanic Acid



The stability of the reagent was investigated by making determinations six weeks apart with the same reagent batch. During the period between the determinations no special precautions were taken, the reagent was stored in a tightly sealed clear glass sample bottle on an open shelf in diffuse daylight. The readings obtained in the two sets of determination were reproducible within experimental error. The fact that the reagent is stable would allow the preparation of batch quantities of reagent, which then could be stored conveniently without any special precautions.

There was some difficulty with reproducibility among different batches of reagent. Although the preparation of reagent was straightforward and involved few steps, there are some variables which must be considered in order to insure reproducible reagents. The support medium, the porcelain chips, must be prepared as reproducible as possible each time. Different sizes of the particles will result in a change in response, since the surface area, and thus the amount of reagent available, will be different. The porcelain chips should be ground, sieved and cleaned in exactly the same manner each time they are prepared. In treating the chips with the reagent solution care should be taken to keep the exposure time the same for each preparation. This does not seem to be too critical as the uptake of reagent reaches a maximum very rapidly. However, care must be taken to insure that the chips are uniformly treated with the reagent. Often the chips form lumps which must be broken up and stirred to allow the reagent solution to contact all the particles. One of the more critical steps in the preparation is the washing. After several washings the absorbance of the solution reaches a level which changes only very slowly. However, while the blank remains nearly the same with repeated washings, the response of the reagent chips to cyanide ion concentration decreases quite markedly. Therefore, the washing procedures must be standard-

ized. With attention paid to the above considerations, it did not prove too difficult to have good reproducibility between different batches of reagent chips.

The precision of this method, although fairly good, could most likely be improved. The method of stirring the solutions in this research was simple swirling (by hand) of the beaker containing the solution and reagent. Thus there could have been greater latitude in both rate and duration. A mechanical stirring method would no doubt give an improvement in the precision of the method and could increase the sensitivity, since continuous, instead of occasional, stirring would enhance the release of tris-1,10-phenanthrolineiron(II) cation.

Another area of possible improvement would be the support. The porcelain chips used were prepared rather carefully, but thought should be given to other support media, such as the inert solids used in gas chromatography columns, filter paper, or others. A commercially obtainable support would be more convenient and perhaps more uniform than the prepared chips.

The range of cyanide ion concentration that this method is applicable to is limited by the amount of reagent used, the amount of stirring, and the contact time between sample solution and reagent. Using the experimental conditions of this research, a period of 20 minutes and a "22 long rifle" measure of reagent (approximately 0.3 gm), the determination is good for a range of from one to ten p.p.m. cyanide. The limiting factor seems to be the amount of reagent available. If the amount of reagent is doubled from one to two measures and the time shortened to ten minutes, the range is extended to from 1 to 20 p.p.m. The limiting factor here is the absorbance of 20 p.p.m. is over 0.90, and higher concentration could thus not be measured with any degree of precision.

Several adjustments could be made to raise the upper limit of this range. The period of time could be shortened thus keeping the absorbance readings down to where the higher concentrations could be discerned. Preliminary studies indicate that if the reagent chips are prepared with the order of soakings reversed, the response decreases giving good readings in the 25 through 60 p.p.m. range.

To increase the sensitivity to below 1 p.p.m. seems to be unfeasible with the present reagent. The blank is sufficiently high to indicate that 1 p.p.m. should be the lower limit; however, increasing the period of time should enhance the response of the range of 1 p.p.m. and just above. Preliminary work on the  $I_5^-$  complex reagent indicated that very good response could be obtained in lower than 1 p.p.m. concentrations of cyanide but the instability of the  $I_5^-$  complex makes reproducible results difficult to obtain.



## EXPERIMENTAL - PART II

## Determination of Cyanide Using Paper Supported Zirconyl - Dianil Blue Chelate

## Special Reagents and Apparatus

Zirconyl Nitrate, purified, was obtained from the Fisher Chemical Company.

All water used was purified by passing distilled water through a Barnstead model BD-1 deionizer equipped with a mixed bed column.

All absorbance measurements were made using a Beckman model DV spectrophotometer and 1.0 cm silica cells.

Dianil Blue dye, acid form (16). Dissolve 3.63 grams of benzidine in 75 ml of 3 N HCl with heating as necessary in a 250 ml flask, and cool rapidly with stirring to 0°C in an ice bath. Add 10 grams of ice and then add immediately 2.80 grams of sodium nitrate, reagent grade, dissolved in the minimum amount of cold water. Stir about 15 minutes, and then add 16.0 grams of chromotropic acid disodium salt dissolved in the minimum amount of cold water. Transfer the solution to a 1 liter beaker and add solid sodium carbonate carefully with enough water so that the mixture can be stirred. When there is no longer any foaming action on addition of the sodium carbonate, add 10 grams excess and heat to about 80°C for at least 1 hour. Cool to room temperature and add 6 N HCl carefully with stirring until foaming ceases; then add 200 ml excess and filter. Wash several times with 100 ml portions of 3 N HCl and dry in air at 50-60°C for at least a day.

Preparation of Reagent Paper

Whatman 54 paper was soaked in Dianil Blue solution (0.5%) for 5 minutes, blotted and hung up to dry for 5 hours. The dyed paper was then placed in a bath of 100 ml of zirconyl nitrate solution and stirred frequently for 10 min.

utes. The paper was then washed with 100 ml of deionized water for 1 minute. The washing was repeated 5 times. The paper was then hung up and allowed to dry overnight. After drying the circle of prepared paper was cut into quarters for use.

In preparing the paper care should be taken to avoid touching the paper with the hand at any time, since skin oils transferred to the paper interfere with uniform wetting. Not more than 5 pieces of the paper should be soaked in a single 100 ml portion of the dye or zirconyl solution. The prepared paper should be kept in a desiccator until ready for use.

#### Analysis of Water Sample

Twenty (20) milliliters of the sample were added to a 9 mm Petri dish. A quarter circle piece of reagent paper is placed in the solution and allowed to stand, with occasional swirling, for 15 minutes. At the end of this period the solution is swirled gently for 15 seconds and the paper removed from the solution. The absorbance was then read on the Beckman DU at 584 mu.

## DISCUSSION

The method using Zirconyl-Dianil Blue on paper support gave good accuracy and response in the range 1-10 p.p.m. cyanide ion, as shown in Plate 6 and Table 5. However, the presence of other ions was found to interfere and give greatly varying results. If a distillation was used, and the cyanide separated from other ions present, this method is accurate and sensitive down to 1 p.p.m.

TABLE 5.

Tabulation of Results For a Typical Calibration Curve  
Using Dianil Blue (Zirconyl) on Paper Support

Cyanide Concentration p.p.m.	Average Absorbance <sup>a</sup>	Range	Standard Deviation
0	0.073	0.021	0.008
2.5	0.236	0.040	0.017
5	0.363	0.049	0.018
8	0.578	0.030	0.011

<sup>a</sup> Average of three (3) determinations

The range of this method could be widened by differing the amount of reagent paper used. To increase its range much below 1 p.p.m. would prove somewhat difficult, since the blank increases with increasing amount of reagent paper used.

The stability of this reagent proved to be about one month if the paper was stored in a desiccator. Paper left in the open showed wide variance in sensitivity, and was noted to give low results on particularly humid days.

If the washing of the reagent paper during this preparation is incomplete, response will decrease due to unchelated zirconyl ion remaining in the paper which can react with cyanide ion, but releases no dye in doing so.

EXPLANATION OF PLATE 6.

Typical Calibration Curve Zirconyl-Dianil Blue

Range

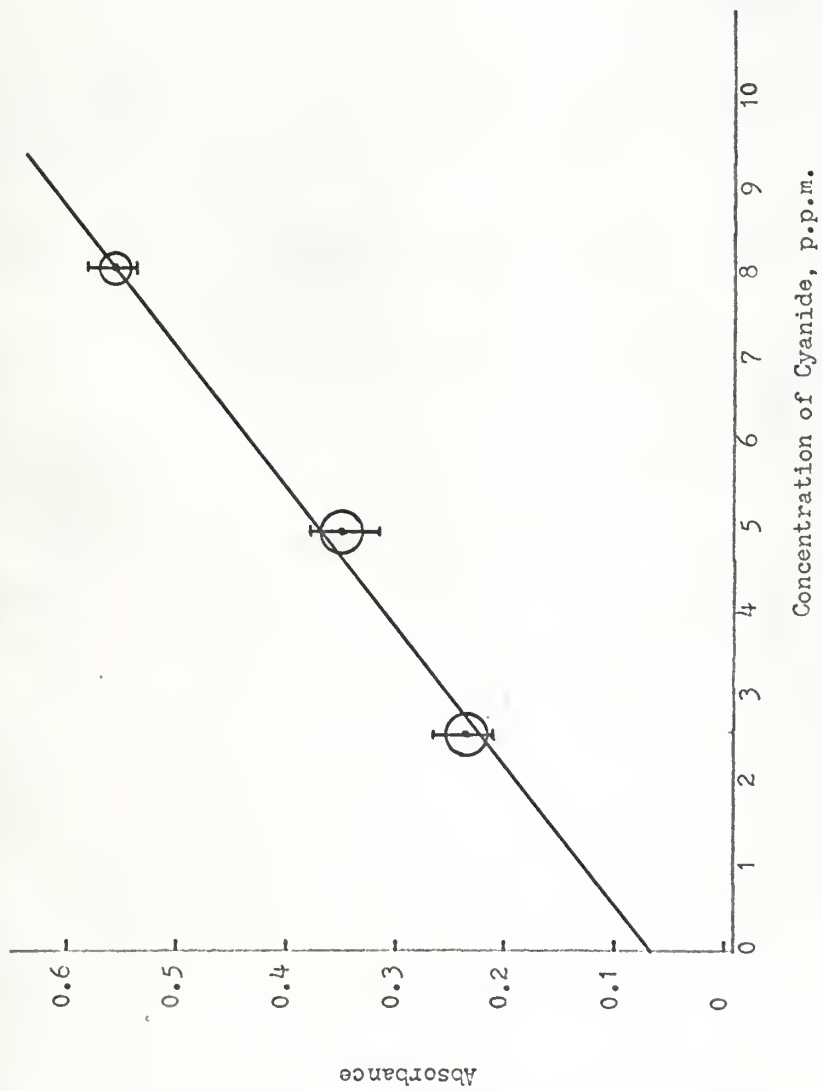
I

Mean Value

.

Average Deviation

O



## CONCLUSIONS

The methods developed in this research using chip - and paper-supported reagents can offer advantages in speed and safety over other methods, and are comparable in sensitivity.

The chip-supported tris-1,10-phenanthrolineiron(II) triiodide reagent offers a method which is indifferent to the presence of other ions present and thus could do away with preliminary separation and isolation steps in many cases. It is rapid, taking little operator time, and sensitive to 1 p.p.m. cyanide ion. The reagent is easily prepared and quite stable, thus enough reagent can be prepared for several weeks work, making it ideal for routine determinations.

The Dianil Blue-Zirconyl paper supported reagent was found to be a good method for the range of 1-25 p.p.m. cyanide when no interfering ions were present. Thus, it could be considered for determinations where distillation method was used. This method was not fully explored in this research, since it was desirable not to use a distillation and the tris-1,10-phenanthroline-iron(II) method was superior in regards interference by other ions. However, its precision and sensitivity to cyanide were good and further study, particularly on different supports, could develop this into a useful method.

A possible extension of this research could be a colorimetric determination for water. If ICM was used in place of  $I_2$  in the Karl Fischer reagent and cyanide was released, it would react with the tris-1,10-phenanthrolineiron (II) reagent, allowing a colorimetric determination for water.

Some of the existing dye release methods used now could be done using the porcelain chips as support instead of the paper or cellulose originally used. The porcelain chips show promise as a support and could prove valuable once a method of preparation has been standardized.

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## VITA

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AN ABSTRACT OF A MASTER'S THESIS

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KANSAS STATE UNIVERSITY  
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Two methods for the determination of trace amounts of cyanide ion in water have been developed in the course of this research. In both methods, cyanide ion is reacted with a solid supported reagent releasing a species which may be determined by a colorimetric procedure.

The first method involves the use of tris-1,10-phenanthrolineiron(II) triiodide supported on porcelain chipd. On reaction with cyanide ion, this reagent releases the highly colored tris-1,10-phenanthrolineiron(II) cation. The absorbance is measured at 514 mu. This method is applicable in the range of 1-20 p.p.m. and with modifications this range could be extended. Several ions were tested and shown to give no interference with the determination.

In the second method, a chelate of zirconium with Dianil Blue dye supported on Whatman No. 54 filter paper. A portion of the treated filter paper is placed in a 20 ml. sample containing cyanide ion. Dianil Blue is released and after 20 minutes the paper is removed and the absorption measured at 584 mu. This method has a range of 1-25 p.p.m. There is considerable variance in response when other ions are present and this will probably restrict its use to those samples from which most other ionic materials have been removed.