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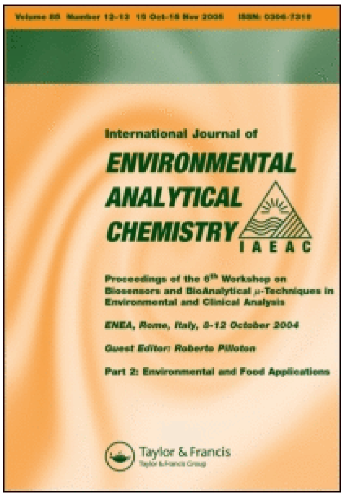

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Spectrophotometric Determination of Cyanide with Isonicotinic Acid and Barbituric Acid

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Spectrophotometric Determination of Cyanide with Isonicotinic Acid and Barbituric Acid

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A spectrophotometric method for the determination of cyanide in water with an isonicotinic acid-barbituric acid reagent having no offensive odor of pyridine is described. Cyanide reacts with chloramine-T, and then the reagent is added to form a soluble violet-blue product, which is measured at 600 nm. Maximum absorbance is achieved in 15 min at 25°C, and remains constant for about 30 min. This method is applicable to water samples containing 0 $-0.5\,\mu g\ CN^- ml^{-1}$. The reagent is stable for at least 4 weeks, if stored at about 10°C. The method is compared with a similar method using sodium isonicotinate and pyrazolone. Application of these methods to determination of cyanide in several plating wastewaters gave good results showing fair agreement with those obtained by the conventional pyridine-pyrazolone method.

KEY WORDS: Cyanide determination, water analysis, spectrophotometry, König reaction, isonicotinic acid-barbituric acid reagent.

INTRODUCTION

Of the methods for the spectrophotometric determination of cyanide based on the König reaction,[1] the pyridine-pyrazolone method[2] and the pyridine-barbituric acid method[3] have been generally used. Although these two methods are very sensitive, they have the following defects: the pyridine-pyrazolone reagent is unstable and must be prepared daily; in the pyridine-barbituric acid method the color fades rapidly after maximum absorbance is reached; and furthermore, pyridine, used in two methods, is offensive and noxious to analysts and surroundings.

Recently, three methods using odorless reagent without pyridine were reported.[4-6] The first method, the isonicotinic acid-pyrazolone method,[4] has low sensitivity and requires a long heating time (30 min at 40°C), because isonicotinic acid used in the reagent is difficult to dissolve in water. In the latter two methods,[5,6] sodium isonicotinate was used instead of isonicotinic acid; the sensitivity was enhanced and maximum absorbance was achieved in 30 min at 25°C. However, these two methods are somewhat troublesome in making their reagents, since it is necessary to prepare sodium salts in advance.

Therefore, in the present study, a reagent was prepared by dissolving isonicotinic acid and barbituric acid in a sodium hydroxide solution; and a phosphate solution was used for pH adjustment. By use of the reagent and the phosphate solution, maximum absorbance was achieved in 15 min at 25°C, and remained constant for about 30 min.

In order to compare the methods, an alkaline isonicotinic acid-pyrazolone reagent was prepared by a similar manner, but the developed color faded rapidly. Then, the sodium isonicotinate-pyrazolone method with some modifications was compared with the barbituric acid method.

The sensitivity of the barbituric acid method was higher than that of the pyrazolone method. The barbituric acid reagent was stable for at least 4 weeks, when stored at about 10°C. The effect of diverse ions differ in several ions between the two methods. These methods were applied to determination of cyanide in several plating wastewaters, and the results were in fair agreement with those obtained by the pyridine-pyrazolone method.[2]

EXPERIMENTAL

Apparatus and reagents

These were almost the same as those previously used,[6,7] except for the following reagents and solutions.

Isonicotinic acid-barbituric acid reagent. Dissolve 2.0 g of isonicotinic acid (4-pyridinecarboxylic acid) and 1.0 g of barbituric acid in 100 ml of sodium hydroxide solution (1.2 g NaOH/100 ml) at 60–70°C with stirring. After cooling, dilute the mixture to 100 ml with water. The reagent obtained was colorless and its pH was about 12.

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Sodium isonicotinate-pyrazolone reagent.† Dissolve 500 mg of 1-phenyl-3-methyl-5-pyrazolone in 20 ml of dimethyl-formamide, then add 100 ml of water and 2.0 g of sodium isonicotinate, and dissolve the salt. The reagent obtained was colorless and its pH was about 6.5. Sodium isonicotinate was prepared by the method described in the previous paper.[6]

Buffer solution (pH 7.3). Dissolve 6.8 g of potassium dihydrogenphosphate and 28.4 g of disodium hydrogenphosphate in water and dilute to 1 l.

Standard cyanide solutions were prepared by dissolving potassium cyanide in water, as made in the previous paper.[6,7]

Procedure for the isonicotinic acid-barbituric acid method

In a dried reaction tube, place 10.0 ml of sample solution (pH 5–8) containing less than 5 μg of cyanide, and free from sulfide and thiocyanate ions. Add 3.0 ml of potassium dihydrogenphosphate solution (1 M) and 0.2 ml of 1% (w/v) chloramine-T solution, stopper the tube and shake gently. After 1–2 min, add 5.0 ml of isonicotinic acid-barbituric acid reagent, stopper the tube again, mix, and keep the mixture at 25°C for 15 min. Measure the absorbance at 600 nm against a reagent blank.

Procedure for the sodium isonicotinate-pyrazolone method

In the above procedure, use buffer solution (pH 7.3) instead of potassium dihydrogenphosphate solution (1 M). After adding 5.0 ml of sodium isonicotinate-pyrazolone reagent, keep the mixture at 25°C for 20 min. Measure the absorbance at 638 nm against a reagent blank.

RESULTS AND DISCUSSION

Isonicotinic acid-barbituric acid reagent

Isonicotinic acid and barbituric acid are much easier to dissolve in alkaline water than in neutral water. But the excess alkaline is undesirable, because absorbance is higher and constant at pH 5.7 – 6.0 for the final reaction solution.[6] The reagent was thus prepared by dissolving these acids in a solution containing only a slightly more sodium hydroxide than that equivalent to the acids.

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†Watabe *et al.*,[5] used 250 mg of 1-phenyl-3-methyl-5-pyrazolone.

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Sodium isonicotinate-pyrazolone reagent

As mentioned before, alkaline isonicoytinic acid-pyrazolone reagent did not give good results. Sodium isonicotinate-pyrazolone reagent was thus prepared.

Color development with the reagents

Using the two reagents, the effects of temperature and time on color development were examined at 20, 25 and 30°C by varying the standing time after the addition of the reagents. As Figure 1 shows, at 25°C, maximum absorbance was achieved in 15 and 20 min, respectively; and the absorbance then remained constant for about 30 min. But, at 30°C, the absorbance decreased by about 4% after 30 min. At 20°C, maximum absorbance was reached in 20 and 30 min, respectively. These tests were made with 1.0 – 5.0 μg CN^-/10 ml. The reaction time was thus established as 15 and 20 min at 25°C, respectively.

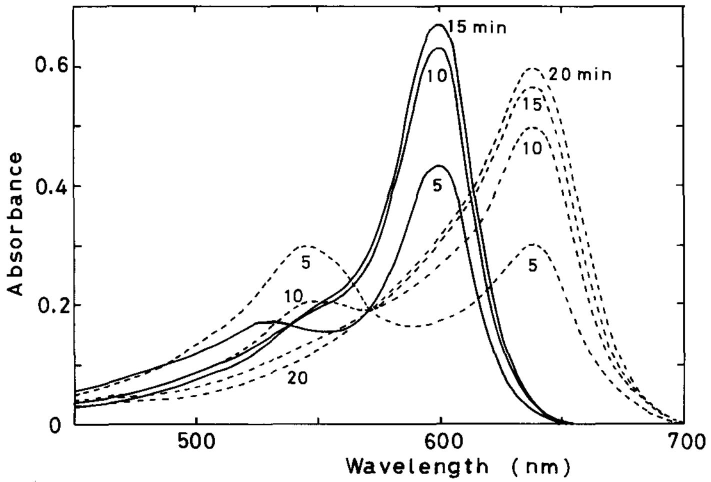

FIGURE 1 Variation of absorption spectra with time at 25°C. (—) Isonicotinic acid-barbituric acid reagent, (----) Sodium isonicotinate-pyrazolone reagent. CN^- taken: 3.0 μg/10 ml.

Effect of pH

In the barbituric acid method, the desired pH value is 5.7 – 6.0 as the final reaction solution.[6] The effect of varying the concentration of potassium dihydrogenphosphate solution (0.25 – 1 M) was thus tested, which showed the 1 M solution was the most effective. In the pyrazolone method, absorbance was found to be high and constant at pH 7.2–7.5 for the final reaction solution. Therefore, buffer solution was chosen as pH 7.3.‡

When pH of the sample solution is very distant from the desired values, there is a danger that pH adjustment with the phosphate solutions is unsuccessful. Thus, in the two methods, the effect of pH of sample solution was tested, which showed that constant absorbance was obtained in the pH range 5–8.

Stability of the reagents

Calibration curves obtained with an isonicotinic acid-barbituric acid reagent which had been stored for 4 weeks at about 10°C in a refrigerator agreed (within 2%) with curves prepared with fresh reagent. Almost the same results were obtained with a sodium isonicotinate-pyrazolone reagent stored for 2 weeks at about 10°C. But, when the two reagents were stored at room temperature (about 25°C), they gave reduction of calibration curves; it was about 4% after 2 weeks, about 8% after 3 weeks and about 14% after 4 weeks. The color of the pyrazolone reagent changed from colorless to yellow after 3–4 days.

Comparison of effect of diverse ions

In the two methods, the effect of diverse ions was examined by using solutions containing 2.0 μg CN^- and various ions. The results are shown in Table I. A large amount of sulfide caused a negative error; and 1 mg of sulfide did not develop color. In the pyrazolone method, sulfite and ferricyanide also led to a negative error.

Thiocyanate led to a significant positive error, and the error in the pyrazolone method was about half of that caused by the barbituric acid method. Similar results to the pyrazolone method had been obtained with pyridine-pyrazolone reagent by Epstein;[2] and similar results to the barbituric acid method had been obtained with pyridine-barbituric acid reagent by Asmus and Garschagen,[3] with pyridine-benzidine reagent by Aldridge[8] and with pyridine-p-phenylenediamine reagent by Bark and Higson.[9] And also in the present study, this was observed by using pyridine-pyrazolone reagent and pyridine-barbituric acid reagent. At any rate, when sulfide or thiocyanate ions are present in a sample solution, suitable pretreatment is necessary for the removal.

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‡Ishii *et al.*,[4] and Watabe *et al.*,[5] used pH 6.8 and pH 6.6 of phosphate buffer solution, respectively.

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TABLE I

Comparison of effect of diverse ions on the determination of 2.0 μg CN^-/10 ml by the two methods

Ion	Added as	Amount added (μg/10 ml)	Isonicotinic acid-barbituric acid method: CN^- found (μg)	Isonicotinic acid-barbituric acid method: Error (μg)	Sodium isonicotinate-pyrazolone method: CN^- found (μg)	Sodium isonicotinate-pyrazolone method: Error (μg)
Cl^-	NaCl	1000	2.0	0.0	2.0	0.0
NO_2^-	$NaNO_2$	1000	1.9	−0.1	2.0	0.0
NO_3^-	KNO_3	1000	2.0	0.0	2.0	0.0
SO_3^{2-}	Na_2SO_3	100			1.9	−0.1
		1000	2.0	0.0	1.5	−0.5
SO_4^{2-}	Na_2SO_4	1000	2.0	0.0	2.0	0.0
CH_3COO^-	$CH_3COONa.3H_2O$	100	2.0	0.0	2.0	0.0
OCN^-	KOCN	1000	1.9	−0.1	1.8	−0.2
S^{2-}	$Na_2S \cdot 9H_2O$	1	2.0	0.0	2.0	0.0
		10	2.0	0.0	1.9	−0.1
		100	0.9	−1.1	turbidity	—
		1000	—	—	—	—
SCN^-	KSCN	2	2.9	+0.9	2.4	+0.4
		5	4.3	+2.3	3.2	+1.2
Fe^{3+}	$FeCl_3$	100	2.1	+0.1	2.0	0.0
$Fe(CN)_6^{4-}$	$K_4[Fe(CN)_6] \cdot 3H_2O$	100	2.0	0.0		
$Fe(CN)_6^{3-}$	$K_3[Fe(CN)_6]$	10			1.8	−0.2
		100	2.0	0.0	0.8	−1.2

Calibration curves

Thiocyanate caused a large positive error, which suggested that thiocyanate can be determined by the two methods. Figure 2 shows the calibration curves obtained for thiocyanate and cyanide solutions. They show a good linear relationship.

Cyanide determination in plating wastewaters

In order to confirm the certainty of the two methods, the present procedures were applied to the determination of "total cyanide" in several plating wastewater samples containing various amounts of cyanide. Distillation was made by the method of Kruse and Mellon[10] with phosphoric acid and an alkaline 10% ethylenediaminetetraacetic acid

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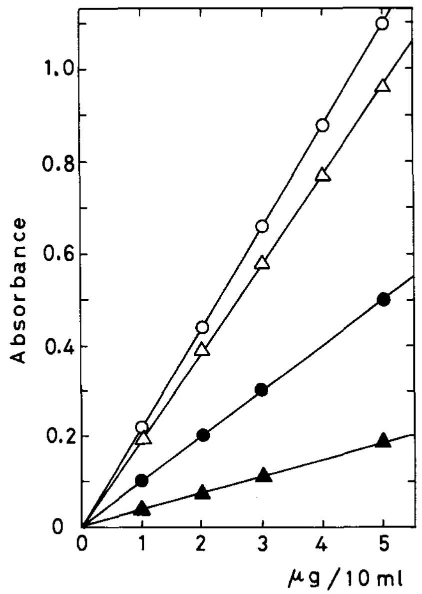

FIGURE 2 Calibration curves. Isonicotinic acid-barbituric acid method: (○) Cyanide, (●) thiocyanate. Sodium isonicotinate-pyrazolone method: (△) Cyanide, (▲) thiocyanate.

TABLE II

Determination of cyanide in plating wastewaters by the two methods and the pyridine-pyrazolone method in comparison

Sample	CN$^-$ concentration (mg l^{-1})					
	Isonicotinic acid-barbituric acid method		Sodium isonicotinate-pyrazolone method (Absorbent)		Pyridine-pyrazolne method	
	2% NaOH	2% CH_3COONa	2% NaOH	2% CH_3COONa	2% NaOH	2% CH_3COONa
I	0.04	0.04			0.03	0.04
II	0.11	0.12	0.11	0.12	0.10	0.12
III	0.19	0.18	0.18	0.18	0.19	0.18
IV	0.26		0.25		0.26	
V	0.35	0.34	0.34	0.34	0.34	0.35

(Versene) solution. Sodium hydroxide solution (2%) or sodium acetate solution (2%) were used as absorbent. For the sodium hydroxide solution (2%) absorbent, the receiving solution was neutralized with acetic acid. These receiving solutions were also analyzed by means of the conventional pyridine-pyrazolone method.[2] As Table II shows, good agreement was obtained.

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