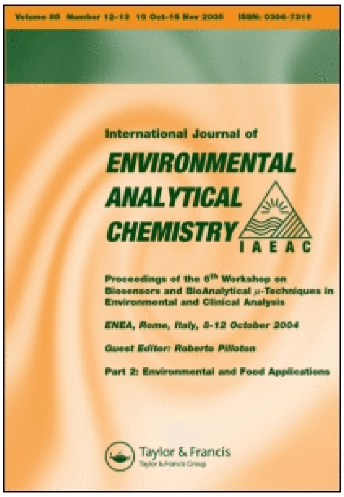

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Bhattacharjee, M. , Amlathe, S. and Gupta, V. K.(1991) 'An Extractive Spectrophotometric Method for the Determination of Pyridine in Air and Environmental Samples', International Journal of Environmental Analytical Chemistry, 45: 2, 127 — 134

To link to this Article: DOI: 10.1080/03067319108026982

URL: http://dx.doi.org/10.1080/03067319108026982

Intern. J. Environ. Anal. Chem., Vol. 45, pp. 127–134
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AN EXTRACTIVE SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF PYRIDINE IN AIR AND ENVIRONMENTAL SAMPLES

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(Received, 7 January 1991; in final form, 20 May 1991)

A new sensitive spectrophotometric method for determination of pyridine at ppm level is described. The method is based on the reaction of pyridine with cyanogen bromide to form glutaconic aldehyde, which is subsequently coupled with 4-aminosalicylic acid. The yellow polymethine dye formed, which is extractable in *iso*-amyl alcohol, shows an absorbance maxima at 400 nm. The reaction is very sensitive and follows Beer's law in the range of 0.025 to 0.2 ppm in the extractive system. The method has been successfully applied for the determination of pyridine in waste water, benzene, laboratory air and environmental samples.

KEY WORDS: Pyridine, spectrophotometry, air, waste water.

INTRODUCTION

Pyridine is a widely used organic solvent in many industrial processes. It finds use as intermediate in the preparation of pharmaceuticals, rubber, chemicals, bactericides, in dye industries, in manufacture of explosives, textiles and in paint industries. It is also used as a denaturant for alcohol[1,2].

Pyridine is readily absorbed through skin contact and by inhaling. Recently the threshold limit value for pyridine has been reduced from 10 ppm or 30 mg/m^3 to 5 ppm or 15 mg/m^3 by OSHA[3].

The popular spectrophotometric methods for the determination of pyridine are based on Konig reaction[4] which involves the reaction of pyridine with cyanogen bromide to form glutaconic aldehyde which is finally coupled with an aromatic amine or a compound containing an active methylene group to give a polymethine dye. Various compounds used as coupling reagents are aniline[5], benzidene[1], *p*-phenylene diamine[6], anthranilic acid[7], 4,4′-diaminostilbene 2,2′-disulphonate borate[8], sulphanilic acid[9], etc. But the sensitivity of methods using aniline is low and benzidine and *p*-phenylenediamine are carcinogenic[10] and banned in several countries.

In the present communication, pyridine is made to react with cyanogen bromide to form glutaconic aldehyde which is then condensed with a new reagent 4-aminosalicylic acid forming a yellow polymethine dye measured at 400 nm.

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The proposed method is much more sensitive than most of the reported methods[6,7,9] and the reagent used is cheap, non toxic, easily available and stable. The solvent extraction of the dye in *iso*-amyl alcohol has been done and by this step it has been possible to increase the sensitivity about 10 times, making it a promising reagent system for determination of traces of pyridine.

The method has been successfully applied for the determination of pyridine in waste water, benzene, laboratory air and environmental samples.

EXPERIMENTAL

Apparatus

A Carl Zeiss spectrophotometer with 1 cm matched silica cell was used for all spectral measurements.

Standard solutions

Pyridine solution. A 1 mg/ml solution of distilled pyridine was prepared in 1% glacial acetic acid. Appropriate dilution of the above solution gave a working standard solution of 10 μg/ml. The solutions were kept in amber coloured flasks.

Cyanide solution. A 500 μg/ml aqueous solution of cyanide was prepared from potassium cyanide.

Sodium arsenite solution. A 1.5% (w/v) solution of sodium arsenite was prepared in distilled water.

4-Aminosalicylic acid solution. A 1% (w/v) solution was prepared in distilled water.

Bromine solution. A saturated solution of bromine in distilled water was stored in an amber coloured bottle.

All chemicals used were of analytical reagent grade and solutions were prepared in distilled water.

Procedure

Calibration curve. Aliquots containing 0.25 to 2 ml of the standard pyridine solution were taken in a 10 ml volumetric flask. To this, 1 ml of cyanide solution and 0.5 ml of saturated solution of bromine were added, allowing the mixture to stand for 2 minutes for complete bromination. The excess of bromine was removed by the addition of a few drops of sodium arsenite solution followed by the addition of 2 ml of 4-aminosalicylic acid solution. The contents were allowed to stand for 10 minutes. The volume was made up to the mark and the yellow coloured polymethine dye, having an absorption maxima at 400 nm, was measured against distilled water.

Table 1 Effect of air flow rate on absorption efficiency of pyridine (Sampling time = 15 min).

Amount of pyridine (µg)	*Flow rate (l/min)*							
	0.10		*0.25*		*0.75*		*1.00*	
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*
5	4.5	90.0	4.95	99.0	4.85	97.0	4.15	83.0
10	9.2	92.0	9.91	99.1	9.82	98.2	8.20	82.0
20	18.5	92.5	19.80	99.0	19.05	95.25	16.05	80.25

a = amount of pyridine found (µg);
b = % absorbed.

Water analysis. Aliquots of water samples (~100 ml) containing 0.025 to 0.2 µg/ml of pyridine were taken in a separatory funnel. The yellow coloured dye was obtained by the above procedure and then extracted in 10 ml of *iso*-amyl alcohol by taking two 5 ml portions, after making the solution acidic with 5 ml of 6 M HCl. The extract was dried over anhydrous sodium sulphate and the absorbance was measured at 400 nm against *iso*-amyl alcohol.

Air analysis. A modification of Wilson's procedure[11,13,14] was used for investigating the collection efficiency of the absorbing solution for pyridine. Since the standard air samples of pyridine were not available, known concentrations of pyridine vapours were obtained by dropping a dilute solution of pyridine from a microburette into a preheated closed chamber connected to an air sampling train[11].

Air containing pyridine vapours was drawn at a flow rate of 0.25 l/min for 15 minutes through two midget impingers, connected in series, each containing 10 ml of 4.4% glacial acetic acid[12]. After sampling, aliquots of this solution were analysed by the proposed method. It was found that ~100% absorption takes place in the first impinger itself.

The effects of the flow rate and time on the absorption efficiency are given in Tables 1 and 2.

Table 2 Effect of air sampling time on absorption efficiency of pyridine (Flow rate = 0.25 l/min)

Amount of pyridine (µg)	*Sampling time (in minutes)*							
	10		*15*		*20*		*35*	
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*
5	3.50	70.0	4.98	99.6	4.25	85.0	4.18	83.6
10	6.68	66.8	9.93	99.3	8.85	88.5	4.80	84.0
20	14.98	74.9	19.81	99.05	17.85	89.25	17.50	87.5

a = amount of pyridine found (µg);
b = % absorbed.

RESULTS AND DISCUSSION

The yellow dye showed a maximum absorbance at 400 nm in aqueous as well as in *iso*-amyl alcohol, whereas the reagents showed negligible absorbance in this range. The effects of the following variables on the spectral characteristics were investigated.

Time and temperature. The colour of the dye appeared after 1 minute but reached the maximum of absorbance after 10 minutes. Afterwards, the dye was found to be stable for at least 15 min.

The optimum temperature range for the complete colour reaction was found to be between 15–40°C. At higher or lower temperatures, the absorbance values as well as the stability of the dye decreased.

pH. The maximum absorbance and stability of the polymethine dye formed was found to be at pH 7–8. At pH lower and higher than these, the absorbance values decreased.

Reagent concentration. The effect of various reagents on the colour reaction were studied. It was found that 1–2 ml of 500 μg/ml of cyanide was sufficient to produce appropriate quantity of cyanogen bromide with 0.5 ml of bromine water. An excess of bromine water caused no change in the absorbance as it was removed with a few drops of sodium arsenite solution. However, the absorbance value decreased if an excess of sodium arsenite was used. Finally, it was found that 2–4 ml of 4-aminosalicylic acid gave the maximum absorbance.

Foreign species. The effect of various foreign species likely to co-exist with pyridine in industrial effluents were studied by adding known amounts of different organic

Table 3 Effect of foreign species in water (Concentration of pyridine = 2 μg/ml).

Foreign species	*Tolerance limit* (μg/ml^{-1})*
Phenol	1000
p-cresol	800
Benzene, Thiophene	2000
Formaldehyde	9000
Acetophenone	10000
Aniline	800
Acetone	1000
Ethanol, Methanol	1200
Acetonitrile	900
Cu^{2+}	350
Ni^{2+}	250
Fe^{2+}, Fe^{3+}	275
Na^{+}, K^{+}	500
SO_4^{2-}, CH_3COO^{-}, Cl^{-}	500

* Amount of foreign species that causes a ±2% change in absorbance.

pollutants and inorganic ions to the test solution containing a total amount of 10 μg of pyridine per 10 ml of final volume.

As shown in Table 3, no interferences were found for phenol, *p*-cresol, benzene, formaldehyde, aniline, acetophenone, etc.

Beer's law, Sandell's sensitivity, Molar absorptivity

The colour system was found to obey Beer's law at 400 nm in the range of 0.25 to 2 μg/ml of pyridine in the measuring solution.

Molar absorptivity and Sandell's sensitivity were calculated and were found to be 34×10^3 litre mol^{-1} cm^{-1} (± 100) and 0.0023 μg cm^{-2}, respectively.

The reproducibility of the colour reaction was checked by replicate analysis over a period of seven days. The standard deviation and relative standard deviation were found to be ± 0.008 and 1.92%, respectively, for 10 μg of pyridine in 10 ml of final volume.

Applications of the method

In air. The vapours of pyridine in air obtained by evaporating a few millilitres of pyridine solution in a preheated chamber, in a fuming cupboard, were drawn through the absorbing solution (4.4% glacial acetic acid) placed in an impinger attached to the sampling train kept outside the fuming cupboard. The absorbing solution was then analysed by the proposed procedure.

The results obtained under a large variety of conditions have been already reported in Tables 1 and 2.

Table 4 Determination of pyridine in various samples of benzene and waste water (mean of three repetitive analysis).

Sample (2 ml)	*Pyridine* originally found (µg)*		*Pyridine* added (µg)*	*Total pyridine* found (µg)*		*Recovery %*	
	(A)	*(B)*		*(A)*	*(B)*	*(A)*	*(B)*
Benzene	4.35	4.25	5	9.42	9.31	100.7	100.6
	4.50	4.45	10	14.55	14.49	100.3	100.2
	4.30	4.28	20	24.45	24.30	100.6	100.1
Benzene	3.00	2.90	5	8.15	8.00	101.80	101.2
	2.50	2.42	10	12.67	12.46	101.30	100.3
	3.05	3.00	20	23.10	23.02	100.10	100.1
Waste water	3.20	3.00	5	8.32	8.10	100.4	100.1
	3.40	3.20	10	13.44	13.22	100.2	100.1
	2.90	2.85	20	22.95	22.87	100.2	100.1

(A) Proposed method;
(B) Reference method[7].

Table 5 Comparison of some spectrophotometric methods for determination of Pyridine.

Reagents (Ref.)	*max (nm)*	*Colour*	*pH*	*Time for full colour development*	*Lowest determination limit (ppm)*	*Remarks*
Benzidine[1]	520	Red	6.8–8	210 minutes	0.005	Carcinogenic
p-Phenylenediamine[6]	480	Intense orange	5	30 minutes	10	Carcinogenic
Barbituric acid[9]	578	Violet	5	50 minutes	2	Requires longer time for colour development
Sulphanilic acid[9]	465	Yellow	7.5	50–90 minutes	0.4	Longer time for colour development
Anthranilic acid[7]	470	Yellow	7.5	10 minutes	0.4	Less sensitive
4,4′-diaminostilbene 2,2′-disulphonate borate[8]	490	Orange	8.5	30 seconds	0.01	Kinetic method though more sensitive, reagent unstable and not easily available.
4-aminosalicylic acid (Proposed method)	400	Yellow	7–8	10 minutes	0.025	Sensitive, fast and reagent easily available.

In benzene. Pyridine is found to be present in the crude coal tar distillate along with benzene. Therefore, for determining the amounts of pyridine present in benzene, aliquots of C.P. benzene samples were extracted with 10 ml of 1 M dilute hydrochloric acid in two portions of 5 ml each. The extract was neutralized with dilute sodium hydroxide solution (1 M) and then analysed by the above method as well as by the earlier reported method[7]. The results are reported in Table 4.

In waste water. The present method has been applied for the analysis of pyridine present in waste waters collected from river Kharoon which receives effluents from the Bhilai Steel Plant. Aliquots of waste waters analysed by the present and a previously reported method[7] were in fair agreement, as indicated in Table 4.

In biological samples (urine). Known amounts of pyridine were added to a urine sample which was then deproteinated with trichloroacetic acid. The mixture was then analysed by the recommended procedure and the earlier reported method[7], providing recovery values in the order of 95%.

In alcohol. To check the recovery of pyridine from alcohol samples, known amounts of pyridine were added to pyridine free alcohol samples. The mixtures were then analysed by the recommended procedure and the recoveries were found to be ~94%,

Comparison of the present method with other spectrophotometric methods

The method has been found to be more sensitive and faster than most of the spectrophotometric methods (Table 5). The reagent used is stable and easily available.

A kinetic method[8] using 4,4′-diaminostilbene and 2,2′-disulphonate borate, though more sensitive suffers from the disadvantage that, it uses a reagant which is unstable and not easily available.

Acknowledgement

The authors are grateful to the Head of the Department of Chemistry, for providing laboratory facilities. One of the authors S.A. is thankful to C.S.I.R. for the award of S.R.F.

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