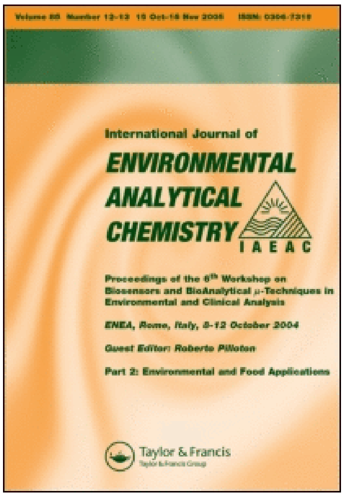

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Extractive Photometric Determination of Nitrite in Polluted Water in ppm Level Using *p* -Nitroaniline and Guaiacol

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Extractive Photometric Determination of Nitrite in Polluted Water in ppm Level Using *p*-Nitroaniline and Guaiacol

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Nitrite is diazotized with *p*-nitroaniline in hydrochloric acid medium and coupled with guaiacol in alkaline medium to give an orange red azo dye having λ_{max} at 505 nm and $\varepsilon_{max} = 4.8 \times 10^4\,\mathrm{l.mole^{-1}\,cm^{-1}}$. Extraction of the dye into isopentanol shifts the absorption maxima to 540 nm and having $\varepsilon_{max} = 6.2 \times 10^4\,\mathrm{l.mole^{-1}\,cm^{-1}}$. Beer's law is obeyed in the range of 0.12 to 0.8 ppm nitrite for aqueous system and 0.03 to 0.2 ppm for extractive system. The Sandell sensitivity for the aqueous and extractive systems were found to be $0.00095\,\mu\mathrm{g\,cm^{-2}}$ and $0.00074\,\mu\mathrm{g\,cm^{-2}}$ respectively. The method is applicable to polluted waters.

KEY WORDS: Nitrite, spectrophotometry, diazotization.

INTRODUCTION

Environmental samples containing traces of nitrite give an excellent indication of level of pollution and eutrophication. The recent

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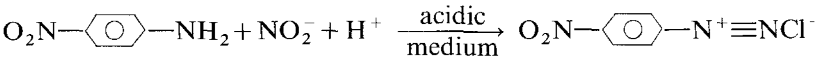
discovery that nitrite can induce methemoglobinemea and form carcinogenic nitroso amines has increased the importance of nitrite as a pollutant.[1,2] The nitroso amines can be formed in the body by the reaction of nitrite with secondary/tertiary amines and amides. The nitrites owe their occurrence in water to the biodegradation of nitrogenous waste. Effluents of several industries are also some of the major sources of nitrites in water. The maximum permissible limit specified by U.S. Public Health Service is 0.06 ppm.[3] Hence, to determine nitrite in environmental samples in traces is very important from industrial hygienic point of view. Methods involving diazotization and coupling, i.e. Griess reaction, are widely used for determination of nitrites in polluted water. Solvent extraction has been positively employed to increase the sensitivity of the reactions.[4-7] Guaiacol has been recommended by Nash[8] as an efficient absorbing medium for nitrogen dioxide of air and subsequent using sulphanilamide and NEDA for determination of nitrite formed.[9] However, guaiacol was not used as a coupling agent.

In this communication a new method for the determination of nitrite in polluted water is described. The method is based upon the diazotization of *p*-nitroaniline by the nitrite present in water and subsequent coupling with guaiacol in alkaline medium to give an orange red dye. The dye is extractable in isopentanol. The method is highly sensitive and having $\lambda_{max} = 505$ nm, $\varepsilon_{max} = 4.8 \times 10^4$ l. mole^{-1} cm^{-1} for the aqueous system and $\lambda_{max} = 540$ nm, $\varepsilon_{max} = 6.2 \times 10^4$ l. mole^{-1} cm^{-1} for the extractive system. The other parameters to optimise the reaction have been studied. Most of the common ions present in water do not interfere. The method is compared with the standard method recommended by APHA[9] for the analysis of nitrites in polluted water.

COLOUR REACTION

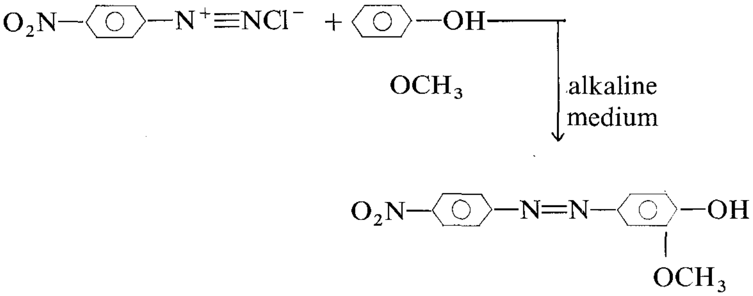
Two steps are involved in the colour reaction. In the first step *p*-nitroaniline reacts with nitrite in acidic medium to form diazonium ion (I) and in the second step this diazonium ion is coupled with guaiacol in alkaline medium to give orange red coloured azo dye (II). The relation is as follows:

First step:



(I)

Second step:



(II)

EXPERIMENTAL

Apparatus

Spectrophotometric determinations were carried out in Carl Zeiss spekol with 1 cm matched silica cells and an ECIL spectrophotometer model GS 865. Calibrated glasswares were used for volumetric measurements.

Reagents

Standard sodium nitrite solution A stock solution of sodium nitrite containing 1 mg NO_2^-/ml was prepared. A little chloroform was added as a stabilizer.[10] 1 μg NO_2^-/ml was prepared by appropriate dilution of the stock.

p-*Nirtoaniline solution* (*PNA*) A 1×10^{-3} M solution of recrystallised PNA was prepared in 2 M hydrochloric acid.

Guaiacol solution 0.2% v/v solution of guaiacol was prepared in demineralized water containing 1 ml of 2 M sodium hydroxide.

Solution of diverse ions Solutions of diverse ions were prepared by the method of West[11] mostly taking chlorides or nitrates of the concerned metal.

All chemicals used were of Analytical Reagent grade and demineralized and deareated water was used for preparing the solutions.

Procedure for aqueous system

An aliquot of sample containing 3 to 20 μg of nitrite (0.12 to 0.8 ppm) was taken in a 25 ml volumetric flask. To this 1 ml of PNA was added and acidity was adjusted to ~1 M with hydrochloric acid. 1 ml of EDTA solution was added for making the metal ions. The solution was kept for 5 min for complete diazotization. After this 1 ml of guaiacol was added and solution was shaken. The colour was developed by making the solution alkaline by the addition of excess of sodium hydroxide. The orange red coloured dye was measured after 2 min at 505 nm using distilled water as reference.

Procedure for solvent extraction

A 100 ml of sample containing 3 to 20 μg of nitrite (0.03 to 0.2 ppm) solution was taken in a 250 ml separatory funnel with 2 ml of *p*-nitroaniline reagent, and the acidity was adjusted to ~1 M with hydrochloric acid. After 5 min 1 ml of EDTA solution (masking agent) and 1 ml of guaiacol were added and developed the colour in alkaline medium as described earlier. The orange red dye was extracted with two 5 ml portions of isopentanol. The extract was dried over anhydrous sodium sulphate and then diluted to 25 ml in a volumetric flask with isopentanol. The absorbance was measured at 540 nm, against isopentanol as reference. Samples of higher concentrations were diluted appropriately before reaction.

RESULTS AND DISCUSSION

The absorption spectra of the coloured dye shows maximum absorption at 505 nm and 540 nm for the aqueous and extractive systems respectively.

Effect of varying reaction conditions

The effect of acidity on diazotization reaction was studied in the range of 0–3 M hydrochloric acid. At least 0.1 M hydrochloric acid is necessary for complete diazotization. For 0.1 to 1 M acid, constant absorbances were obtained. Times for diazotization and coupling, the pH for full colour development and effect of varying molar ratios of *p*-nitroaniline and guaiacol were also studied. For *p*-nitroaniline and nitrite, the absorbance was constant at molar ratios of 1:1. A 2 to 20 M excess of *p*-nitroaniline had no significant effect on the final absorbance and a 10 M excess of guaiacol was sufficient for full colour development. However, large excess of guaiacol caused errors not greater than ±2% in the absorbance. Constant absorbance values were obtained for a diazotisation reaction time of 2–60 min and the maximum time required for the coupling reaction was found to be 2 min. There was no effect of temperature on diazotization and coupling reaction in the range of 15–40°C. It was also found that the colour started appearing at pH 9 and full colour development was obtained only above pH 11.

Beer's law, molar absorptivity, sensitivity and reproducibility

Beer's law is obeyed in the range of 0.12 to 0.8 ppm nitrite for the aqueous system and 0.03 to 0.2 ppm of nitrite for the extractive system. The molar absorptivity and the Sandell's sensitivity[12] for the aqueous and extractive systems were found to be $4.8 \times 10^4\,\mathrm{l.mole^{-1}\,cm^{-1}}$, $0.00095\,\mu\mathrm{g\,cm^{-2}}$ and $6.2 \times 10^4\,\mathrm{l.mole^{-1}\,cm^{-1}}$, $0.00074\,\mu\mathrm{g\,cm^{-2}}$ respectively. The standard deviation and relative standard deviation for 8 μg of nitrite per 100 ml over a period of 7 days were found to be ±0.0015 and ±0.28% respectively.

Effect of foreign ions

Since the system has been developed for the analysis of polluted waters, the interferences from foreign ions commonly present in water were studied, by adding known amounts of foreign ions to the solution containing 10 μg of nitrite per 100 ml of water. The tolerance limits for foreign ions are shown in Table I, which shows that most of the cations and anions do not interfere. The interference

TABLE I
Effects of foreign ions.
(Concentration of nitrite 10 μg/100 ml).

Tolerance limit[a] (ppm)	Foreign ions
800	SO_4^{2-}, NO_3^-, Cl^-
200	Al^{3+}, Co^{2+}, Ca^{2+}, Ba^{2+}, PO_4^{3-}, Sr^{2+}
100	Be^{2-}, $Cr6^+$, F^-, Ni^{2+}, Pb^{2+}, Zn^{2+}, Mn^{2+}, Bi^{3+}, Mg^{2+}, B^{3+}, Cu^{2+}, Fe^{2+}
80	Hg^{2+}, Mo^{6+}, Sb^{3+}
40	Sn^{2+}, I^-, Phenol

[a] The tolerance limit is the amount of interferent that cause an error of $\pm 2\%$ or less.

from sulphites can be masked by adding 1 ml of 10% tetrachloromercurate solution. Cu(II) which normally interferes with other reagents reported for nitrite, does not interfere with this method up to 100 ppm.

Analysis of polluted river water

Samples were collected by the recommended procedure[9] from upstream and downstream from the source of industrial effluents and preserved by the addition of mercuric chloride (4 mg/100 ml). The samples were stored at 0°C and filtered if necessary. The preserved samples were analysed by the recommended method as well as the standard method, using Sulphanilamide–NEDA method, having $\lambda_{max} = 540$ nm, $\varepsilon_{max} = 4.6 \times 10^4$ l. mole^{-1} cm^{-1}. The data is given in Table II which shows that the method is comparable to the standard method. The correlation coefficient of the two methods were found to be 0.999.

Hence the accuracy of the proposed method is satisfactory. The method is also found to be more sensitive than the standard method and other methods reported recently for determination of nitrites[4–7] in polluted water. Non-interference of Cu^{2+} is an added advantage of the proposed method.

TABLE II

Determination of nitrite in river water. Water from the River Kharoon (near Raipur) was sampled. The first five samples are from upstream and the remaining five from downstream of the effluent source. The values are the mean of five replicate determinations.

Concentration of nitrite, ppm	
Proposed method	Standard method
0.33	0.32
0.35	0.35
0.48	0.46
0.53	0.52
0.73	0.73
0.51	0.53
0.67	0.67
0.79	0.79
0.81	0.81
0.82	0.82

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