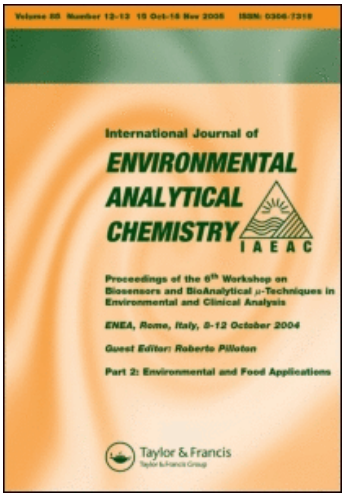

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Improvement of Photometric Determination of Trace Amounts of Nitrate and Nitrite in Water

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An improved rapid method of extraction-photometric determination of trace amounts of nitrate and nitrite in water has been developed. In this method, nitrate is quickly reduced to nitrite at pH 3.0 in 5 min with freshly prepared cadmium sponge, which is produced *in situ* by action of zinc powder in dilute solution of cadmium chloride in presence of ammonium chloride. At pH 2.0, nitrous acid diazotizes with *p*-amino-acetophenone, which is then coupled with N-(1-naphthyl)-ethylenediamine. The azo-dye formed is extracted into *n*-butanol at pH 2.0 in the presence of *β*-naphthyl sulfonic acid and aluminium nitrate. The absorbance is measured at 550 nm. The molar absorptivity of the extract is about $4.8 \times 10^4 \, l \cdot mol^{-1} \cdot cm^{-1}$. The ions normally present in water do not interfere when sodium metaphosphate is added as a masking agent. Water from several sources has been analyzed by this method, and results found are satisfactory.

KEY WORDS: Improvement; photometric determination; trace amount; nitrate; nitrite; water.

INTRODUCTION

Determination of nitrate and nitrite in trace amounts is required in environmental protection, some chemical processes, agricultural chemistry and hygiene. Colormetric methods have been reviewed.[1] Determination of nitrate at very low concentrations has been usually conducted by reducing nitrate to nitrite, followed by one of the

modifications of Griess–Ilosvay reactions. So far the most acceptable results have been obtained by using cadmium, and the optimal conditions for reduction have been systematically studied.[2]

A comparison of different forms of cadmium as reductant has been made.[3] Cadmium column is usually used, however, its pretreatment time is about 2 hours.[4] In this paper, a new rapid reduction procedure is reported, in which the nitrate is reduced quantitatively to nitrite in 5 minutes at pH 3.0 by cadmium sponge formed freshly by action of zinc powder in a dilute solution of cadmium chloride in the presence of ammonium chloride. An excess of ammonium chloride is added[5] in order to eliminate the tendency of nitrite to over-reduce to ammonium.

The procedure using the Griess–Ilosvay reaction seems to be a satisfactory one, but in order to enhance sensitivity, extraction has been proposed. It was reported[6] that nitrous acid diazotize *p*-aminoacetophenone, which is then coupled with *m*-phenylene-diamine; the 2,4-diamino-4′-acetyl-azobenzene formed is extracted into toluene at pH 9, and the absorbance is measured at 450 nm. The molar absorptivity is about $2.3 \times 10^4 \text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$. In the present paper, an improvement on this extraction system has been suggested. Nitrite at pH 2.0 diazotizes with *p*-aminophenone and is then coupled with N-(1-naphthyl)-ethylediamine. The azo dye is further associated with *β*-naphthyl sulfonic acid in acid medium and extracted into *n*-butanol in the presence of aluminium nitrate. Absorbance of the extract is measured at 550 nm in 1-cm cell. Molar absorptivity is about $4.8 \times 10^4 \text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$. Beer's law is obeyed in the range 0.1 to 2.0 μg $NO_2^- - N$ in 5 ml of extract.

EXPERIMENTAL

Reagents

Standard nitrate solution: Dissolve 0.722 g anhydrous potassium nitrate and dilute with water to 100 ml (1.00 mg nitrogen or 4.43 mg nitrate per ml). Prepare a working solution by suitable dilution and store in plastic bottles.

Standard nitrite solution: Dissolve 0.492 g anhydrous sodium nitrite having been dryed in desiccator for 4 h and dilute with water to 100 ml (1.00 mg nitrogen per ml). Prepare a working solution by

suitable dilution and store in a brown bottle under refrigeration. Standardize iodometrically before using.

p-Aminoacetophene hydrochloride solution: Prepare a 0.5% (w/v) solution in 1 + 9 hydrochloric acid, and store in a brown bottle.

N-(1-naphthyl)-ethylenediamine dihydrochloride solution: Dissolve 0.5 g N-(1-naphthyl)-ethylenediamine dihydrochloride in 100 ml of 1 + 99 hydrochloric acid.

Potassium chloride–hydrochloric acid buffer solution: Mix 50 ml of 0.2 M potassium chloride with 17 ml of 0.2 M hydrochloric acid dilute to 200 ml with water, and adjust pH to 1.8 with hydrochloric acid.

Ammonium chloride solution, 30% (w/v).

β-Naphthyl sulfonic acid 0.5% (w/v): Dissolve 0.5 g β-naphthyl sulfonic acid in 100 ml water. Adjust to pH 6.0 with sodium hydroxide solution.

Sodium metaphosphate solution, 5.0% (w/v).

Sodium acetate solution, 30% (w/v).

Cadmium chloride solution, 0.1% (w/v).

Zinc powder, 100–200 mesh: Before use, wash with 0.2 M hydrochloride acid, then rinse with water and dry.

Unless stated otherwise, all reagents used are of analytical pure grade, and all solutions are diluted with nitrite-free water, which is obtained by distilling alkaline permanganate-distilled water using an all-glass distillation apparatus.

Recommended procedure

Determination of nitrate: Transfer about 20 ml or less of the sample containing 0.5 to 10 μg nitrate-N to a 25 ml graduated flask. Add 1.0 ml of ammonium chloride, 1.0 ml of potassium chloride-hydrochloric acid buffer, 1.0 ml of cadmium chloride and 1.0 ml sodium metaphosphate, mix, adjust to pH 3.0, dilute to the mark with water and again mix thoroughly. After addition of 100 mg of zinc powder through a small glass funnel, mix the contents of the flask by inverting three times (each time swirling for 10 seconds) within 5 minutes, and let it stand 2 minutes for clarification. Pipette aliquots of the clear solution for determination of nitrite as follows.

Determination of nitrite by extraction-photometric method. Take about 30 ml or less of sample solution containing 0.1 to 2.0 μg

nitrite-N in a 60 ml separatory funnel. Add 1.0 ml of *p*-aminoacetophenone hydrochloride solution and adjust to pH 2.0 with either sodium acetate solution or hydrochloric acid. After 15 minutes standing at room temperature, add 1.0 ml of N-(1-naphthyl)-ethylenediamine dihydrochloride solution and swirl. Add 1.0 ml of *β*-naphthyl sulfonic acid and 3 g of powdered aluminium nitrate, mix thoroughly again and extract the azo compound into 5.0 ml of *n*-butanol by shaking mechanically for 3 minutes. After clarification, measure the absorbance of the *n*-butanol layer at 550 ml in 1-cm cell against a reagent blank.

RESULTS AND DISCUSSION

Absorption spectra

Absorption maximum of the azo compound formed by diazotization of nitrous acid with *p*-aminoacetophone and its coupling with N-(1-naphthyl)-ethylenediamine in aqueous solution, is at 543 nm, and that of *n*-butanol extract, 550 nm. All absorbance measurements of the extract are made at the latter wavelength.

Investigation of reduction conditions

Selection of reductant: In order to obtain theoretical reduction yield, it is desirable to study the reduction efficiency of the various reductants, such as sodium hydrosulphite, ferrous sulfate, granular zinc, iron powder, aluminium foil, magnesium ribbon, granular cadmium and zinc amalgam, of which only the latter two are promising. Further tests show that nitrate can be reduced quantitatively to nitrite, by zinc powder in the presence of a dilute solution of cadmium chloride. A black cadmium sponge is formed and settles rapidly during reduction. In the case where only zinc powder is used in the absence of cadmium chloride, reduction efficiency is low (10–80%).

Effect of variables: Effects of variables on the reduction of nitrate have been studied. Results are summarized in Table 1.

Time of reduction plays an important role in attaining full colour development. It is found that the absorbance became constant after

TABLE I

Effects of variable on reduction of nitrate

Conditions	Tested	Optimum value	Preferred
pH at beginning of reduction	2.8–8.0	2.8–5.0	3.0
Amount of ammonium chloride solution added, ml	0.25–1.5	0.5–1.5	1.0
Amount of cadmium chloride solution added, ml	0.1–2.0	0.25–2.0	1.0
Amount of zinc powder added, mg	10–250	50–250	100
Temperature, °C	5–50	15–35	20

shaking 10 to 40 seconds. It is preferred to shake three times within 5 minutes, and each time for 10 seconds.

Investigation of extraction conditions

Selection of extraction system. In an acidic solution, nitrite reacts with a primary aromatic amine to produce diazonium salt, which in turn couples with an aromatic amine or phenol to form a coloured azo dye. In the original Griess reaction, sulfanilic acid was used and diazotized, but the azo compound formed cannot be extracted quantitatively, because of the hydrophilic nature of the sulfonic group. By using *p*-aminoacetophenone in place of sulfanilic acid,[6] the hydrophobic ability of the azo compound is enhanced, favouring extraction into organic solvents. The azo dye obtained by coupling with N-(1-naphthyl)-ethylenediamine, is not directly extracted into an immiscible solvent, because it is protonated in the acidic media. By using a large anion, the dye cation can be extracted as an ion association complex with a polar solvent. Hexoic acid, benzene sulfonic acid and naphthyl sulfonic acid were investigated as large anions and *n*-butanol, methyl isobutyl ketone, iso-amyl alcohol, amyl acetate, cyclohexamone, hexanol, 1,2-dichloroethane and chloroform as solvents. It was found experimentally that β-naphthyl sulfonic acid and *n*-butanol are preferable for obtaining efficient extract.

Effect of pH: A study of effect of pH or the relevant diazotization and coupling reaction disclosed that diazotization of *p*-aminoaceto-

phenone should be carried out in acidic solution; a constant and maximum absorbance is obtained at pH 0–3. In the coupling of the diazonium cation with N-(1-naphthyl)-ethylenediamine, the coloured compound has a constant absorbance in the pH range of 1.0–3.0. Accordingly, nitrite can be determined when the diazotization and coupling reaction are carried out successively at pH between 1.0 and 3.0 without adjusting that of the solution. In practice, when 1 ml of *p*-aminoacetophenone hydrochloride solution is added to a sample, the pH becomes about 2.0 and remains almost the same even when N-(1-naphthyl)-ethylenediamine is added. In order to minimize the effect of foreign ions, a pH of 2.0 is preferred.

It is already known that diazotization and coupling reactions should be carried out at 0–5°C. However, reactions in this case proceed quantitatively at 10–30°C. Therefore the reactions may be carried out at room temperature.

A complete diazotization requires at least 5 minutes, and the coupling reaction 15 minutes or more. The azo compound formed in aqueous phase is stable at least for 2 hours, and in the *n*-butanol phase for 24 hours.

Effect of other factors on extraction of azo dye are shown in Table II.

Effect of diverse ions: The effect of diverse ions on reduction of nitrate and extraction of the azo dye was examined. No interference was found with the following ions (when present the amount in mg

TABLE II

Effect of other factors on extraction of azo dye

Variable	Tested	Optimum	Preferred
Amount of acetophone, ml	0.1–2.0	0.8–2.0	1.0
Amount of N-'1-naphthyl)-ethylenediamine, ml	0.1–2.0	0.2–2.0	1.0
Amount of β-naphthyl sulfonic acid, ml	0.05–2.0	0.1–2.0	1.0
Amount of aluminium nitrate, g	0.5–4.0	1.0–4.0	2.0
Volume ratio of aqueous to organic phase	1:1–10:1	1:1–7:1	5:1
Shaking time, min	1.0–4.0	2.0–4.0	3.0

as listed in parentheses). Na^+(200); K^+(200); NH_4^+(200); Be^{2+}(5); Ca^{2+}(5); Mg^{2+}(5); Ba^{2+}(2); Sr^{2+}(2); Mn^{2+}(2); Cd^{2+}(2); Zn^{2+}(1); Cu^{2+}(1); Pb^{2+}(1); Hg^{2+}(0.5); Co^{2+}(0.1); Al^{3+}(2000); Ga^{3+}(1); Cr^{3+}(1); Sm^{4+}(1); Sb^{5+}(1); As^{3+}(0.1); Cl^-(500); F^-(40); OAc^-(30); BO_3^-(14); Br^-(8); I^-(1); MoO_4^{2-}(0.1); Citrate(30); Tartrate(30). Interference by large amounts of Fe^{3+} can be masked by addition of sodium metaphosphate.

Samples analysed

The method has been applied to the determination of nitrate and nitrite in tap water, river water, sea water, industrial wastewater, saliva and macerated extracts of soil, sludge and vegetable.

Our results obtain with the discussed method are in agreement with the conventional method.[4]

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