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Sorption/Photometric Determination of 1-Naphthylamine Using Polyurethane Foams and 4-Nitrophenyldiazonium Tetrafluoroborate

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Abstract—The sorption of 1-naphthylamine (NA) as 4-nitrobenzeneazonaphthylamine was studied as function of phase contact time, aqueous acidity, 4-nitrophenyldiazonium tetrafluoroborate (NPD) concentration, and NA concentration. A highly efficient method for the sorption/photometric determination of NA was developed.

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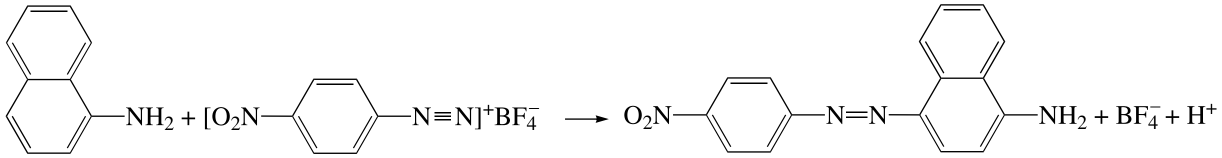
1-Naphthylamine (hereafter, NA) is used as a diazo and azo component in azo dye synthesis; it also serves as a precursor for the production of aminonaphthalenesulfonic acids, 1-naphthol, some herbicides, and pigments [1]. Violations of process flowsheets in the textile industry or chemical engineering or insufficient sewage purification lead to environmental pollution with NA. Another source of NA is the metabolism of agricultural pesticides, e.g., naphthalam; as a result, NA piles up in soils, from which it enters either water or air due to soil erosion by wind. In addition, NA is contained in emissions from vehicles and metallurgical facilities. The current provisional safe levels for NA are 0.003 mg/m^3 in the atmosphere of residential areas and 0.002 mg/L in potable water [2].

Spectrophotometric [3] and chromatographic [4–6] methods are most frequently used for NA determination. Trace analysis of NA in environmental objects is possible only after NA preconcentrating. To improve the selectivity and efficiency of preconcentration, aromatic compounds are frequently converted to more hydrophobic derivatives, in particular, azo compounds [7]. This approach with the use of polyurethane foams (PUF) was employed to the sorption/photometric determination of phenols [8] and 1-naphthol [9] in the form of azo derivatives.

This work is intended to study the sorption of NA as 4-nitrobenzeneazonaphthylamine with the use of PUF and to develop a technique for the sorption/photometric determination of NA.

EXPERIMENTAL

Solutions and reagents. Analytical grade 1-naphthylamine was used. The stock solution (1 mg/mL) was prepared from an exact NA weight dissolved in 0.1 M HCl. Solutions with lower concentrations (10 μg/mL) were prepared from the stock solution by diluting it with distilled water immediately before measurement. 4-Nitrophenyldiazonium tetrafluoroborate (NPD) was synthesized and purified as in work [8]. An aqueous solution of NPD (2.5×10^{-3} mol/L) was prepared from an exact weight immediately before use. Acetone (chemically pure grade) and hydrochloric acid (high purity grade) were used.



Scheme 1.

The sorbent used was PUF based on ethylene oxide and propylene (type 5–30, from Radical). Polyurethane foam pellets (16 mm in diameter, 0.025(5) g in weight) were punched out of a commercial polymer sheet 5 mm thick with a metallic punch. The pellets were shaken with acetone twice for 10 min on an electromechanical vibromixer in order to free them from impurities; then, they were dried to an air-dry state. The pellets were stored away from light.

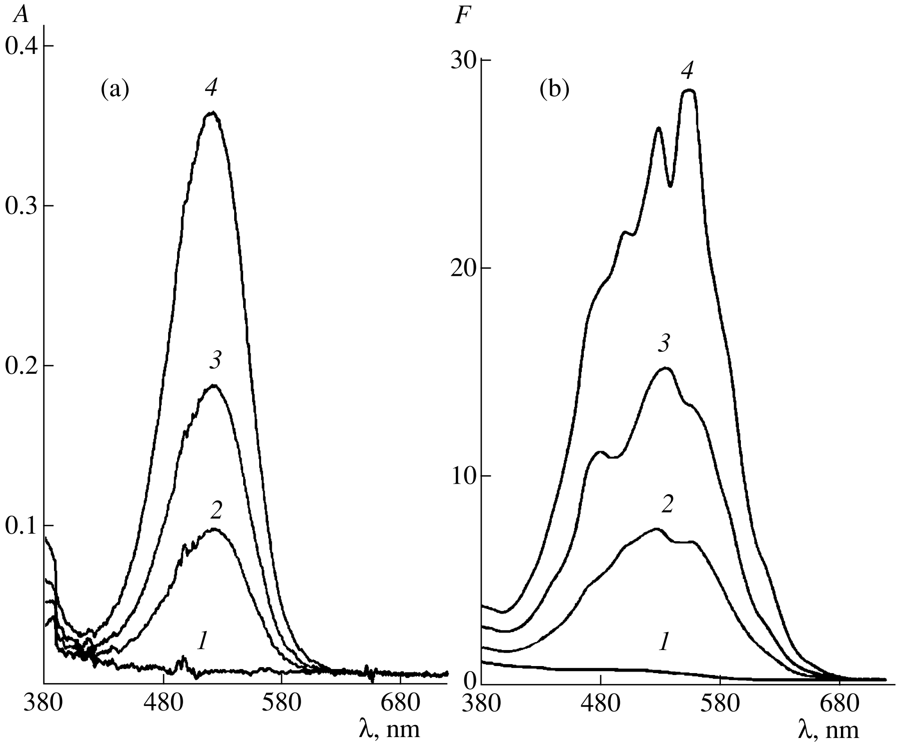


Fig. 1. Panel (a): absorption spectra of 4-nitrobenzeneazonaphthylamine. Panel (b) : diffuse reflectance spectra of 4-nitrobenzeneazonaphthylamine sorbed on PUF 5-30. $c_{HCl} = 5 \times 10^{-3}$ mol/L, $c_{NPD} = 1 \times 10^{-4}$ mol/L, $l = 2$ cm (a), $t = 60$ min (b), and c_{NA} (μg/mL) = (*1*) 0, (*2*) 0.25, (*3*) 0.5, and (*4*) 1.0.

Procedure. Sorption experiments were carried out in a batch mode. A test solution (25 mL) was poured to a vessel with a ground stopper; then, a PUF pellet was pressed with a glass rod to remove air bubbles, and the vessel was shaken on an electromechanical vibromixer until sorption equilibrium was acquired. The pellet was removed and squeezed between two paper filters. Then, the diffuse reflectance was measured. The NA concentration in the aqueous phase after sorption was determined spectrophotometrically.

Diffuse reflectance spectra and diffuse reflectance were measured on a Spectroton colorimeter using fluoroplastic cells. Absorption spectra and optical densities of solutions were measured on an SF 103 spectrophotometer (Akvilon) and a KFK 2 photoelectrocolorimeter. Solution pH was measured on an Expert 001 ionometer.

RESULTS AND DISCUSSION

Spectral characteristics of 4-nitrobenzeneazonaphthylamine. 4-Nitrobenzeneazonaphthylamine, red-lilac in color, was prepared by the azo coupling of NA with 4-nitrophenyldiazonium tetrafluoroborate (scheme). Preliminary experiments intended to study the formation conditions for 4-nitrobenzeneazonaphthylamine showed that the product yield is affected by the pH of azo coupling and the 4-nitrophenyldiazonium tetrafluoroborate concentration. 1-Naphthylamine enters azo coupling in acid solutions; at higher pHs, the reaction produces a low-soluble compound.

Figure 1a displays absorption spectra for 4-nitrobenzeneazonaphthylamine. With increasing NA concentration to 1.0 μg/mL, the optical density increases, which signifies an increase in the amount of the azo product. The position of the absorption peak in the spectrum remains unchanged, lying at 520 nm. Figure 1b displays diffuse reflectance spectra for 4-nitrobenzeneazonaphthylamine sorbed on PUF. The sorption of 4-nitrobenzeneazonaphthylamine induces a small bathochromic shift of the diffuse reflectance peak relative to the absorption spectra: in the diffuse reflectance spectra, $\lambda_{max} = 530$ nm.

Choice of optimal parameters of 4-nitrobenzeneazonaphthylamine sorption. The effect of the phase contact time on the extraction of 4-nitrobenzeneazonaphthylamine was studied (Fig. 2a). One can see from Fig. 2a that sorption equilibrium is acquired after 60 min (ensuring 95% extraction). In all subsequent experiments, the phase contact time was 60 min.

The effect of 4-nitrophenyldoazonium tetrafluoroborate concentration on the sorption of 4-nitrobenzeneazonaphthylamine was studied. One can see from Fig. 2b that the sorption increases with increasing 4-nitrophenyldiazonium tetrafluoroborate concentration to 1×10^{-4} mol/L; then, it does not respond to increasing

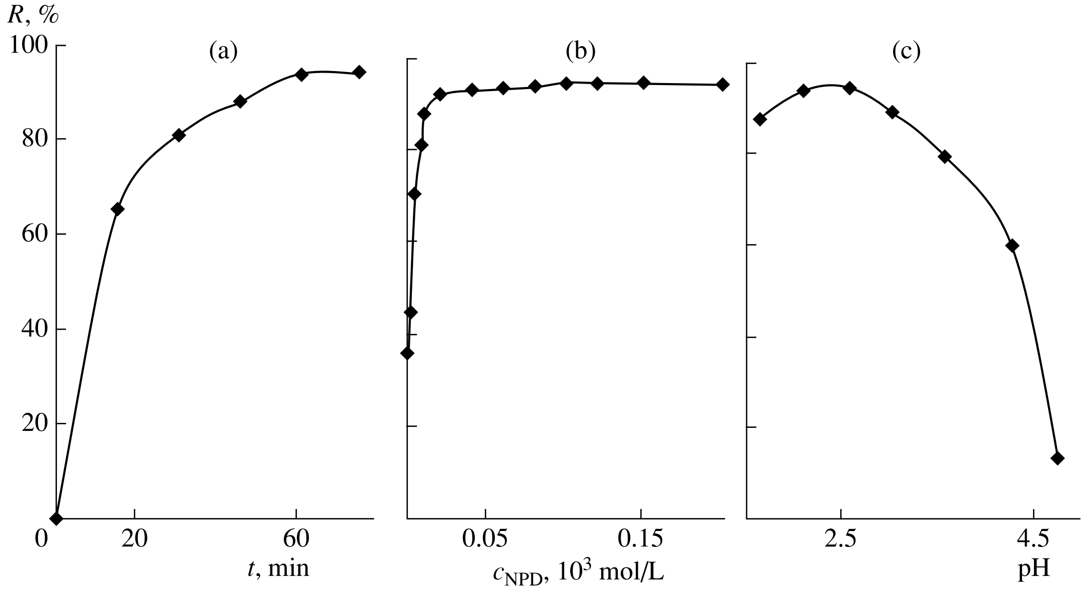


Fig. 2. Extraction of 4-nitrobenzeneazonaphthylamine on PUF 5–30 vs. (a) phase contact time, (b) 4-nitrophenyldiazonium tetrafluoroborate concentration, and (c) aqueous pH. c_{NA} = 1.0 μg/mL (a–c), $c_{HCl} = 5 \times 10^{-3}$ mol/L (a, b), $c_{NPD} = 1 \times 10^{-4}$ mol/L (a, c), t = 60 min (b, c), V = 25 mL, and m_{PUF} ~ 0.025 g.

reagent concentration. In all subsequent experiments, the reagent concentration was 1×10^{-4} mol/L.

The effect of the solution acidity in the range from 2 M HCl to pH 4 on the sorption of 4-nitrobenzeneazonaphthylamine was studied. The extraction increases with rising pH (Fig. 2c). In the range of pH 2.0–2.5, a plateau appears on the curve. In all subsequent experiments, the HCl concentration was 5×10^{-3} mol/L (pH 2.3).

Table 1. Metrological characteristics of the NA determination technique

Analyte sample volume, mL	Equation of the calibration curve	Concentration range of determination, μg/mL	c_{min}, μg/mL
25	$\Delta F = 17.4c$	0.007–0.750	0.0024
50	$\Delta F = 30.9c$	0.004–0.400	0.0014
100	$\Delta F = 47.5c$	0.003–0.300	0.0009
250	$\Delta F = 56.3c$	0.002–0.25	0.0007

Table 2. Added/found verification of NA determination ($n = 3$, $P = 0.95$)

Analyte	Added, μg/mL	Found, μg/mL	s_r
Distilled water	0.25	0.25 ± 0.02	0.03
Tap water	0.25	0.22 ± 0.04	0.07
River water (from River Volga)	0.25	0.26 ± 0.03	0.05

The Kubelka–Munk function is linearly related to the NA concentration in the aqueous solution, which indicates the feasibility of using diffuse reflectance spectroscopy for NA determinations.

1-Naphtylamine determination. Calibration curves were plotted as follows. 1-Naphthylamine samples (0–40 μg) were transferred to vessels with ground stoppers; then, 0.05 M HCl (2.5 mL), 4-nitrophenyldiazonium tetrafluoroborate (1 mL), and water (to bring the volume to 25 mL) were consecutively added. Polyurethane foam 5–30 pellets ($m \approx 0.025$ g) were placed into the solutions, pressed with a glass rod to remove air bubbles, and shaken for 60 min on a mechanical vibromixer. Then, the pellets were removed and squeezed between two paper filters. Diffuse reflectance R was measured at 530 nm on a Spectroton colorimeter. The calibration curve was plotted in the F–c coordinates, where c is the NA concentration in the solution, μg/mL; and $F = (1 - R)^2/2R$ is the Kubelka–Munk function.

Some characteristics of our developed technique are displayed in Table 1. The detection limit decreases with increasing analyte solution volume. When the solution volume changes from 25 to 250 mL, the detection limit decreases from 2 to 0.7 ng/mL.

We studied the determination selectivity. 1000-Fold amounts of phenol, 20-fold amounts of resorcinol or 2-naphthol, and 10-fold amounts of aniline or 1-naphthol (which form colored azo derivatives in alkaline solutions) do not interfere with the determination of 0.25 μg/mL NA. The following inorganic ions also do not interfere with the determination: hydrocarbonate ions in 1000-fold amounts; sulfate ions in 500-fold amounts; chloride, calcium, magnesium, potassium, and sodium ions in 200-fold amounts; copper ions in 100-fold amounts; and zinc and iron(III) ions in 10-fold amounts.

The validity and reproducibility of the results were verified using the added/found technique in the analysis of distilled, tap, and river (R. Volga) water. The results of verification are displayed in Table 2.

Comparing the characteristics of the sorption/photometric technique developed for NA determination with the characteristics of photometric determination (which is based on the formation of an analogous azo derivative [3]), we found that the detection limit of the new technique is five times that of the state-of-the-art technique with at least equal selectivity. Moreover, the new technique is simple and has a relative low cost, and the sorbent used is available.

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