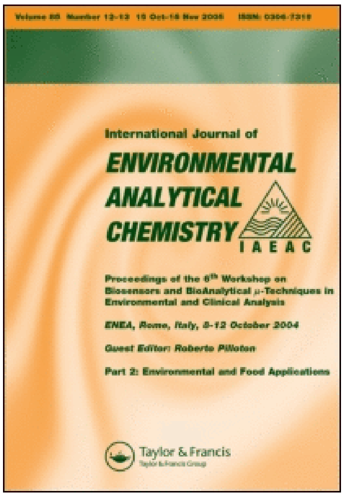

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Assessment of condensation of aromatic aldehydes with polyurethane foam for their determination in waters by diffuse reflectance spectroscopy and colorimetry

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The new reaction of polyurethane foam (PUF) with different aromatic aldehydes has been investigated. It proceeds with participation of terminal toluidine groups of PUF and yields coloured polymeric Shiff bases which can be used as convenient analytical forms for the determination of aromatic aldehydes by diffuse reflectance spectroscopy. The spectral characteristics of the products have been discussed. The optimal conditions of such interaction for different aromatic aldehydes have been found. It has been shown that a new approach based on using desktop scanner, digital camera and computer data processing can be used for evaluation of colour intensity of polymeric Schiff bases. The prospects for using PUF as a polymeric chromogenic reagent for determination of aromatic aldehydes have been considered. This approach seems to be promising for monitoring of aromatic aldehydes in environment.

Keywords: polyurethane foam; aromatic aldehydes; diffuse reflectance spectroscopy; colorimetry

1. Introduction

Carbonyl compounds are widely used in both industrial and non-industrial applications [1]. One of the important subclass of this chemical class is aromatic carbonyl compounds. These substances are frequently used in perfumery (benzaldehyde (BA), cinnamaldehyde) [2], food industry (vanillin, vanillal, curcumin) [3] and pharmacy (furfural, 5-nitrofurfural) [4]. Many of them are also applied in chemistry for derivatisation and as chromogenic reagents in spectrophotometry (4-nitrobenzaldehyde (4-NBA), 4-dimethylaminobenzaldehyde (DMABA), 4-dimethylaminocinnamaldehyde (DMACA)) [5–9].

The general techniques used for carbonyl compounds determination are spectrophotometry [10–12], chromatography [13,14], polarometry [15] and capillary electrophoresis [16]. The cheapest and most simple of them is spectrophotometric determination; however, the sensitivity of such techniques in most cases is low. In addition, these techniques cannot be used in case of muddy and colloidal solutions. It requires applying a laborious pretreatment. One of the possible ways to obviate these difficulties and to

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increase the sensitivity of the analyte determination is solid-phase preconcentration with direct determination in phase of the sorbent.

Terminal toluidine groups of polyurethane foam (PUF) were shown [17] to participate in different reactions like aromatic amines including the interaction with formaldehyde. This reaction yields yellow polymeric imine (Schiff base), which appears to be convenient for use in diffuse reflectance spectroscopy and for determination of formaldehyde.

The aim of this work was to investigate analytical potentialities of application of PUF as a polymeric chromogenic reagent for aromatic aldehydes determination by means of diffuse reflectance spectroscopy, desktop scanner, digital camera and computer data processing.

2. Experimental

2.1 *Reagents*

Polyether based PUF (trade mark 5–30) produced by 'Radikal' (Kiev, Ukraine) was used ($d = 20 \pm 3\,\mathrm{kg\,m^{-3}}$, isocyanate component: 2,4- and 2,6-diisocyanate, polyether component: ethylene/propylene glycol copolymer, catalyst: organotin compounds). PUF tablets (16 mm diameter, 5 mm thick) were cut from a commercially available polymer sheet. The mass of each PUF tablet was ~0.017 g. The tablets were washed with acetone, air-dried and stored in the dark. The work solutions of aromatic aldehydes were prepared by dissolving pure substances of analytical grade in water–ethanol mixtures. The content of ethanol was 20% for BA, 3-nitrobenzaldehyde (3-NBA); 40% for DMABA, DMACA; 60% for 4-NBA. Analytical grade hydrochloric acid was used.

2.2 *Apparatus*

Diffuse reflectance spectra in the visible range and diffuse reflections were recorded by using a 'Spektroton' colorimeter (OKBA NPO 'Khimavtomatika', Chirchik, Uzbekistan).

The yield of polymeric Schiff bases was estimated by measuring the Kubelka–Munk function (F) at wavelength of maximum absorbance ($\lambda_{\max}$):

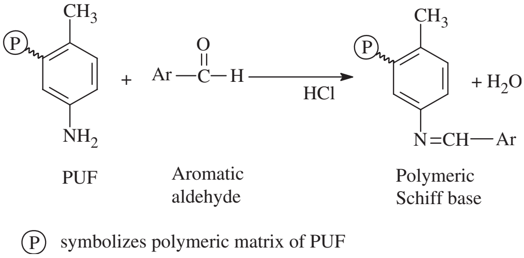
$$F(R) = \frac{(1-R)^2}{2R} = \frac{2.3\varepsilon}{S}c,$$

where R is the diffuse reflection, ε is the molar absorptivity of a sorbate ($\mathrm{M^{-1}\,cm^{-1}}$), c is the concentration (M) and S is the light scattering coefficient ($\mathrm{cm^{-1}}$). In some cases the $\Delta F = F_2 - F_1$ was calculated, where F_1 and F_2 are the Kubelka–Munk functions of PUF and polymeric Schiff base measured at the corresponding $\lambda_{\max}$.

Colour scales were scanned using Hewlett–Packard Scanjet 4400c scanner and photographed using a Canon PowerShot A610 digital camera. The separation of colours and the determination of RGB channel luminosities were performed using Adobe Photoshop 7.0 software. To do this, an oval zone was selected in a scanned image of the sample, the 'image histogram' menu command was run and an average value of the luminosity of each of the three channels was calculated. This procedure was repeated for every sample of the colour scale. The results were processed using Origin 6.0 software: the dependencies of the luminosity of R, G and B channels on the concentration were plotted and approximated.

2.3 *Condensation reaction*

The heterogeneous chemical reaction between PUF and aqueous solutions of aromatic aldehydes was performed by placing the PUF tablet in a closed vessel with 5 mL of the solution containing defined amount of the aromatic aldehyde in acidic medium, removing air bubbles by pressing with a glass rod, and effecting the vessel by ultrasound (US) at heating or shaking it mechanically to complete the reaction. The tablets were then removed and dried between the sheets of filter paper. Finally, the analytical response was measured by using a 'Spektroton' colorimeter, scanner or digital camera. The scheme of the reaction is given below:



3. Results and discussion

To examine possibility of reaction with PUF resulting in formation of coloured product and to investigate the influence of aromatic aldehyde structure/electronic properties on the reaction proceeding and properties of the product we chose BA, substituted BAs (3-NBA, 4-NBA and DMABA) and DMACA.

3.1 *Spectral characteristics*

Diffuse reflectance spectra of polymeric Schiff bases were investigated. In comparison with PUF that does not have pronounced absorbance band in the visible range, the diffuse reflectance spectra of the polymeric Schiff bases have absorbance bands of different intensity (Figure 1). The structures of used aromatic aldehydes and wavelengths of maximum absorbance of corresponding polymeric Schiff bases are given in Table 1. BA and NBAs give yellow Schiff bases which have the absorbance maximum at 380 nm (in investigated wavelength range) whereas dimethylaminobenzaldehyde and dimethylaminocinnamaldehyde result in products absorbing at 440 nm (lemon-yellow) and 530 nm (purple), respectively. This is evidently connected with electron donor effect of dimethylamino group that leads to bathochromic shift of the absorbance band. In the case of dimethylaminocinnamaldehyde this shift is also increased by additional conjugated double bond. The band at 380 nm in the spectrum of DMACA probably corresponds to sorbed aldehyde. This is confirmed by the fact that it disappears after washing samples with acetone.

3.2 *Optimisation of the condensation reaction conditions*

3.2.1 *Influence of ultrasound and heating*

Using US and heating is known to be the most widespread approach to acceleration of chemical reaction. The influence of these two factors on the condensation reaction of

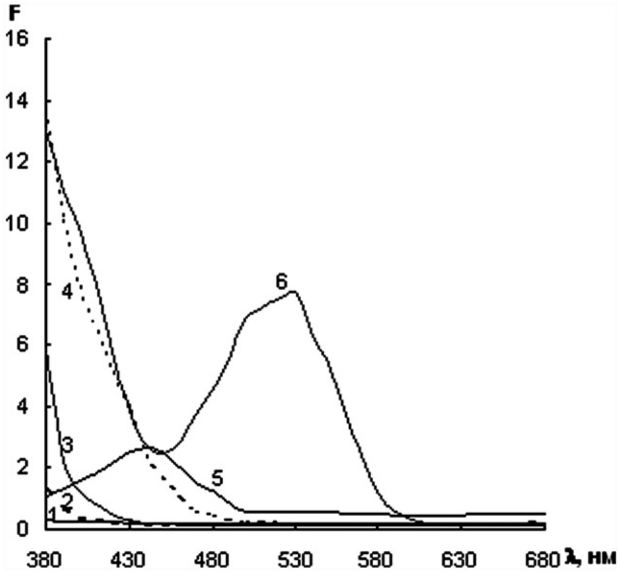
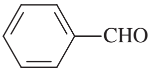
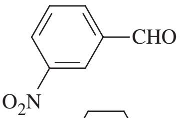
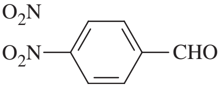
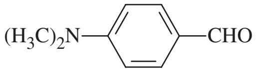
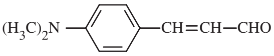


Figure 1. Diffuse reflectance spectra of PUF (1) and the products of its reaction with benzaldehyde (2), 3-NBA (3), 4-NBA (4), DMABA (5) and DMACA (6). Conditions of the reaction: $c_{\text{aldehyde}} = 0.2\,\text{mg}\,\text{mL}^{-1}$, $c_{\text{HCl}} = 0.1\,\text{M}$, $t = 30\,\text{min}$, shaking at 25°C.

Table 1. Wavelengths of maximum absorbance for corresponding polymeric Schiff bases obtained after the reaction of PUF and different aromatic aldehydes (data taken from Figure 1).

Aromatic aldehyde	Structure	Abbreviation	$\lambda_{\max}$, nm
Benzaldehyde		BA	380
3-Nitrobenzaldehyde		3-NBA	380
4-Nitrobenzaldehyde		4-NBA	380
4-Dimethylaminobenzaldehyde		DMABA	440
4-Dimethylaminocinnamaldehyde		DMACA	530

aromatic aldehydes with PUF was investigated. As it is shown in Figure 2, the joint action of these two factors results in increasing yield of the polymeric Schiff base. It is very remarkable in the case of DMABA and DMACA that may be explained by more intense action of US on charged protonated molecules due to cavitation phenomenon. For 4-NBA

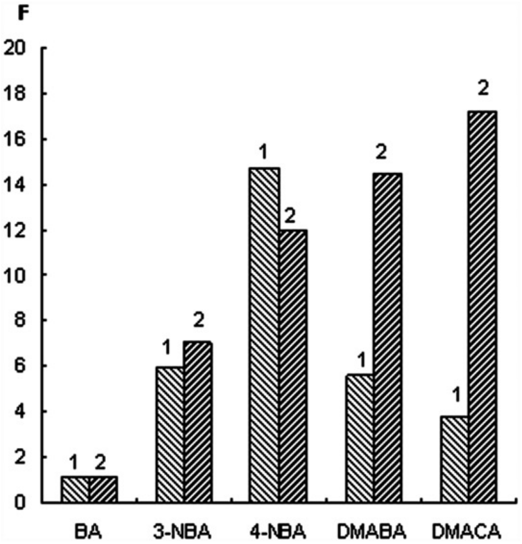


Figure 2. The Kubelka–Munk function meanings of polymeric Schiff bases when the reaction is carried out on shaker (1; 30 min, 25°C) and on us bath (2; 30 min, 50°C). c_{aldehyde}: 0.1 mg mL^{-1} (DMACA), 0.2 mg mL^{-1} (BA, 3-NBA, 4-NBA), 0.4 mg mL^{-1} (DMABA).

one can see decrease of yield of corresponding Schiff base when heating and acting US. It may be connected with decreasing the equilibrium constant. Only in case of this aldehyde the equilibrium has time to become settled because of its very high carbonyl activity due to nitro-group which is an electron acceptor. The yield of polymeric Schiff base for BA does not depend on heating and US action.

3.2.2 *Influence of HCl concentration*

The influence of the concentration of hydrochloric acid on the reaction between the PUF and the aromatic aldehydes was investigated. The data obtained are represented in Figure 3. It can be seen that maximal yield of each polymeric Schiff bases is achieved in 0.1–0.2 M solution of HCl. The decrease of the yield at lower concentrations may be explained by decreasing concentration of reactive protonated form of the aromatic aldehyde. The decrease at higher concentrations seems to be connected with proceeding competitive processes such as protonation of the terminal toluidine groups of PUF and hydrolysis of polymeric Schiff base.

3.2.3 *Influence of phase contact time*

The influence of the phase contact time on the yield of the polymeric Schiff bases was investigated. The dependences of the Kubelka–Munk function on time are represented in Figure 4. One can see that the time required to reach the equilibrium depends on electron-seeking activity of the aromatic aldehyde. It results in the lowest rate of the reaction between PUF and aromatic aldehydes containing electron-donor dimethyl-amino group (the time required is 60 min). For 4-NBA which is the most active electron-seeking reagent, the equilibrium is reached in 30 min at room temperature.

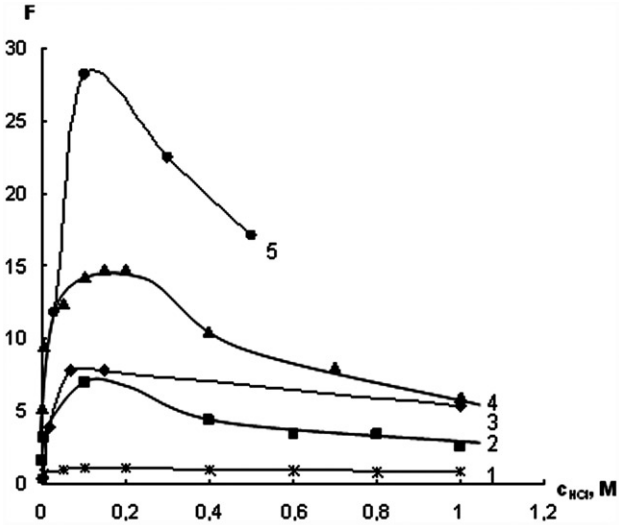


Figure 3. The dependences of the Kubelka–Munk function of polymeric Schiff bases on the concentration of HCl. The aromatic aldehyde: (1) BA: US, 50°C; (2) 3-NBA, (3) DMABA: US, 50°C; (4) 4-NBA: shaker, 25°C; (5) DMACA: US, 50°C. $c_{\text{aldehyde}} = 0.2\,\text{mg}\,\text{mL}^{-1}$, $t = 30\,\text{min}$.

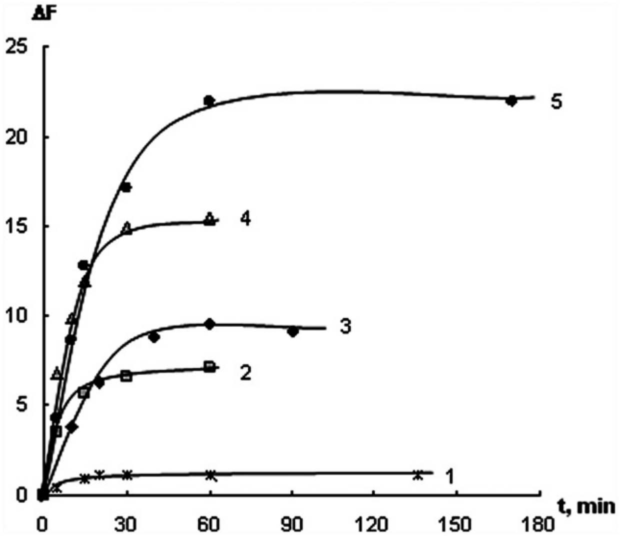


Figure 4. The dependences of the Kubelka–Munk function of polymeric Schiff bases on the phase contact time. The aromatic aldehyde: (1) BA: $c = 0.2\,\text{mg}\,\text{mL}^{-1}$, US, 50°C; (2) 3-NBA, (3) DMABA: $c = 0.2\,\text{mg}\,\text{mL}^{-1}$, US, 50°C; (4) 4-NBA: $c = 0.2\,\text{mg}\,\text{mL}^{-1}$, shaker, 25°C; (5) DMACA: $c = 0.1\,\text{mg}\,\text{mL}^{-1}$, US, 50°C. $c_{\text{HCl}} = 0.1\text{M}$.

3.3 *Prospects for the determination of aromatic aldehydes*

3.3.1 *Determination using diffuse reflectance spectroscopy*

The Kubelka–Munk function is linear in certain range of concentration of the aromatic aldehydes. It gives an opportunity for determination of them using diffuse

Table 2. Metrological characteristics of the aromatic aldehydes determination using PUF and diffuse reflectance spectroscopy.

Aromatic aldehyde	Optimal conditions of the reaction with PUF	λ_{max}, nm	Calibration curve equation ($\Delta F = k \cdot c^a$; c, mg mL^{-1})	Linearity range, μg mL^{-1}	c_{min}, μg mL^{-1}
BA	0.1 M HCl, 25°C, 30 min	380	$\Delta F = 4.36c$, $r = 0.9967$	30–700	10
3-NBA	0.1 M HCl, 50°C, 30 min	380	$\Delta F = 33.36c$, $r = 0.9971$	6–700	2
4-NBA	0.1 M HCl, 25°C, 30 min	380	$\Delta F = 72.58c$, $r = 0.9951$	2–200	0.7
DMABA	0.1 M HCl, 50°C, 60 min	440	$\Delta F = 40.20c$, $r = 0.9953$	3–400	1
DMACA	0.1 M HCl, 50°C, 60 min	530	$\Delta F = 218.34c$, $r = 0.9996$	0.6–100	0.2

Note: $^a k = 2.3\varepsilon/S$, where ε is the molar absorptivity of a sorbate (M^{-1} cm^{-1}), S is the light scattering coefficient (cm^{-1}).

Table 3. Accuracy verification of the aromatic aldehydes determination by analysing distilled water spiked with aromatic aldehyde ($n = 3$, $p = 0.95^a$).

Aromatic aldehyde	Added, mg mL^{-1}	Found, mg mL^{-1}	RSD
BA	0.20	0.21 ± 0.02	0.04
3-NBA	0.20	0.19 ± 0.03	0.07
4-NBA	0.20	0.19 ± 0.01	0.02
DMABA	0.40	0.38 ± 0.05	0.05
DMACA	0.10	0.09 ± 0.02	0.08

Note: $^a n$ is number of experiments; p is confidence probability.

reflectance spectrometer. The optimal conditions and metrological characteristics of the aromatic aldehydes determination are listed in Table 2. Limit of detection was estimated as: $c_{min} = 3s_0/S$, where s_0 is SD of blank experiment, S is slope of the calibration curve. One can see that the limit of detection depends on the nature of aldehyde. The lowest limits of detection are reached at the longest system of conjugated double bonds in the aldehyde molecule. Besides, the possibility of involving different substituents in the conjugation remarkably influences on the sensitivity of the determination. The accuracy was verified by analysing distilled water spiked with several amount of the aromatic aldehyde (Table 3).

3.3.2 *Determination using scanner, digital camera and computer data processing*

In previous works [18–20] we suggested a new approach to the determination of different substances sorbed on PUF. It is based on the use of a desktop office scanner for measuring the colorimetric characteristics (luminosities of RGB channels) of coloured PUF samples. The main idea of this approach includes the statement that colour of the object can be regarded as a sum of three basic colours – red (R), green (G) and blue (B). Value of luminosity for each of these three colour channels varies from 0 to 255. The combination {0, 0, 0} corresponds to black colour and {255, 255, 255} to white colour. It was established [18–20] that when the concentration of the analyte in the solution is increased, one can observe the decrease in RGB channel luminosities as a result of a decrease of the

Table 4. Comparison of metrological characteristics of DMACA determination using diffuse reflectance spectroscopy, scanner and digital camera.

Device	Determination range, $\mu g\,mL^{-1}$	$c_{\min}$, $\mu g\,mL^{-1}$
Diffuse reflectance spectrometer	0.6–100	0.2
Scanner	4–40	1
Digital camera	5–40	2

sample reflection power. This dependence was shown [18–20] in most cases to be described by first-order exponential function:

$$y = y_0 + Ae^{-c/t},$$

where y_0, A and t are parameters of the regression setting location and shape of the curve; y is the luminosity (from 0 to 255); and c is the concentration of analyte.

This work examines the possibility of using of a scanner, digital camera and computer data processing for aromatic aldehydes determination using the condensation reaction with PUF by the example of DMACA. The dependence of RGB characteristics on the concentration of the compound was determined. It was established that the equation which describes the dependence of RGB components on concentration of DMACA is similar to that suggested previously [18–20]. The comparison of the equation mentioned above with polynomial one was performed. It revealed that only four-parameter polynomial equation describes satisfactorily all experimental data whereas the exponential one contains three parameters. This proves good approximating ability of the exponential equation. The dependences were linearised as $\ln(A/(y-y_0)) = c/t$ and the metrological characteristics of the determination of DMACA using scanner and digital camera were calculated and compared with those for diffuse reflectance spectroscopy. The results are shown in Table 4. Limits of detection were calculated using formula: $c_{\min} = 3s_0/S$, where s_0 is SD for ln $(A/(y-y_0))$ in the blank experiment, $S = 1/t$. It can be seen from Table 4 that in case of the determination of DMACA scanner and digital camera have lower sensitivity and smaller range of determination. However, it seems they have certain advantages such as availability, simplicity in the use, compactness and low cost.

4. Conclusions

On the basis of experiments performed we conclude that there is a possibility of using PUF for aromatic aldehydes determination by means of diffuse reflectance spectroscopy as well as a scanner, digital camera and computer data processing. It has been found that structure of the aromatic aldehyde as well as electronic properties of the substituents remarkably influence on spectral characteristics of the product. The influence of US and heating, acidity, phase contact time has been investigated. The optimal conditions of the interaction have been found. The linear dependence of Kubelka–Munk function on concentration of the aromatic aldehyde gives an opportunity to determine it using diffuse reflectance spectroscopy. It has been shown that scanner, digital camera and computer data processing can be used for evaluation of colour intensity of polymeric Schiff bases. The use of PUF as a solid polymeric chromogenic reagent in condensation reaction seems to have a number of advantages over aromatic amines. The coloured product can be easily separated from other substances appearing in the reaction mixture. The PUF tablet is insoluble and non-volatile which makes this new type of analytical reagent more attractive in respect of environmental safety.

Acknowledgements

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