

USE OF UV SPECTROPHOTOMETRY FOR DETERMINATION OF ORGANIC COMPOUNDS IN WATER

C. BOGATU*, D. BOTAU, E. BRINZEI, L. DUDA

*The National Research and Development Institute for Industrial Ecology (ECOIND), 2 Victoriei Street, Of. 1, P.O. Box 254, 1900 Timisoara, Romania
E-mail: tcapm@rectorat.utt.ro*

Abstract. Use of rapid liquid-liquid extraction for separation and concentration of organic compounds from prepared water solutions and their quantitative evaluation by UV spectrophotometry is proposed in this paper. The efficiency of the method was appreciated by using water solutions of acetosalicylic acid, triethylamine, phloroglucinol and ethyl ether, chloroform and petroleum ether for extraction. The recovery efficiencies with ethyl ether of the third compounds from solutions in concentrations 10 times smaller than those considered as minimum detectable by UV were 80.5, 87.5 and 89%, respectively. The proposed procedure may be used even in the field, for on-site analysis.

Keywords: group parameter, UV spectrophotometry, rapid liquid-liquid extraction, organic compounds.

AIMS AND BACKGROUND

There is a continuous need for new methods used for the determination of trace organics compounds in water¹. This need is more evident when it is necessary to solve analysis in the field.

Sometimes, group parameters like total organic carbon (TOC), total organic halogen (TOX), chemical oxygen demand (COD), are more accessible and often cheaper for characterisation of water organic content. Another group parameter that may be used for estimation of organic compounds from waters is the value of absorbance from ultraviolet spectrum. The choice of wavelength is many times arbitrary, e.g. 240 and 254 nm (Refs 2, 3). After Standard Methods, "UV absorption is a useful surrogate measure of selected organic constituents in fresh water, salt water and wastewater". This parameter is useful for monitoring both of natural water treated for drinking purposes and of industrial wastewater treatment. In many cases, the quantity of organic compounds in water may be too small to appear in ultraviolet spectrum. So, there is need for their separation and concentration.

A few procedures were proposed for this, like closed-loop-stripping, purge-and-trap, headspace analysis⁴⁻⁶. Because of the necessary analytical time for these

* For correspondence.

techniques, at times, a classical method is more useful for separation and concentration of organic compounds from water. One of this is the liquid-liquid extraction method⁷⁻¹⁰. This procedure has at least two advantages: use of equipment from water and wastewater laboratories and it produces precise and accurate results¹⁰. The use of liquid-liquid extraction process was intensively developed for separation of volatile organic compounds from water, especially of trihalomethanes. After author's name, there is Richard and Junk method, Henderson method and so on. The difference between them consists of the different ratios water:solvent and the volume of water sample used for analysis.

Taking into account that the principal steps in trace analysis are extraction, separation, concentration and detection-quantitation¹¹, the use of rapid liquid-liquid extraction of organic compounds from prepared water solutions and of UV spectrophotometry for estimate of their content is proposed in this paper. This method may be used even in the field for on-site analysis.

EXPERIMENTAL

The efficiency of the proposed method was appreciated by use of three organic compounds and four solvents. In the first step of the experiment, the dependences UV absorptions-concentrations were determined, and in the second step the recovery efficiencies for the three compounds from prepared water solutions, by use of rapid liquid-liquid extraction and ultraviolet spectrophotometry were estimated.

In order to determine the correlations between UV absorbance and concentrations, solutions of acetosalicylic acid (9.1-1.0 mg/l), triethylamine (11.5-1.2 mg/l) and phloroglucinol (2.0-0.28 mg/l) in distilled water were prepared. These dependences were also established for solutions of acetosalicylic acid in ethyl ether (12.5-0.4 mg/l) and chloroform (10-0.8 mg/l), phloroglucinol in ethyl ether (2.5-0.25 mg/l), triethylamine in ethyl ether (1.4-0.28 mg/l) and petroleum ether (2.3-0.35 mg/l). UV absorption spectra were recorded by use of an Jasco-500 UV-VIS spectrophotometer, Japanese 1998. The quality of reagents and solvents was p.a.

For rapid liquid-liquid extraction of organic compounds, diluted water solutions were prepared, thus their concentrations to be 5 and 10 times smaller than those considered as minimum detectable by UV spectrophotometry. Extraction process took place in 25 ml vials with stopper, in which 20 ml of sample was introduced. Volumic ratio water:solvent was the same in all experiments 10:1. Extraction was realised in two steps by use of 2 ml organic solvent in every step. Mixing time was 10 min and time for separation of solvent in funnel was 5 min. The two solvent samples were put together and concentrated up to 2 ml. The measurements of absorbance were made at the wavelengths presented in Table 1.

Table 1. Values of wavelengths (nm) used for the absorbance measurement of acetosalicylic acid, phloroglucinol and triethylamine solutions in different solvents

Solvent	Acetosalicic acid	Phloroglucinol	Triethylamine
Water	220	202	192
Ethyl ether	230	228	232
Chloroform	278	-	-
Petroleum ether	-	-	268

Separation and concentration of acetosalicylic acid from distilled water solutions by liquid-liquid extraction was realised with ethyl ether and chloroform; for triethylamine ethyl ether and petroleum ether were used, and for phloroglucinol ethyl ether, only.

RESULTS AND DISCUSSION

UV absorption spectra of the third compounds in the mentioned solvents are presented in Figs 1-3. For triethylamine in water solutions absorption curves are placed between 190-225 nm. The values of absorption taken into consideration in order to determine correlation with concentration, were those for 192 nm (Fig. 1A). When ethyl ether was used as solvent, triethylamine spectra ranged from 225 to 300 nm and for petroleum ether ranged from 265 to 330 nm. The measurement of absorptions for the establishment of absorbance-concentration dependences took place for 232 and 278 nm, respectively. The computing of depen-

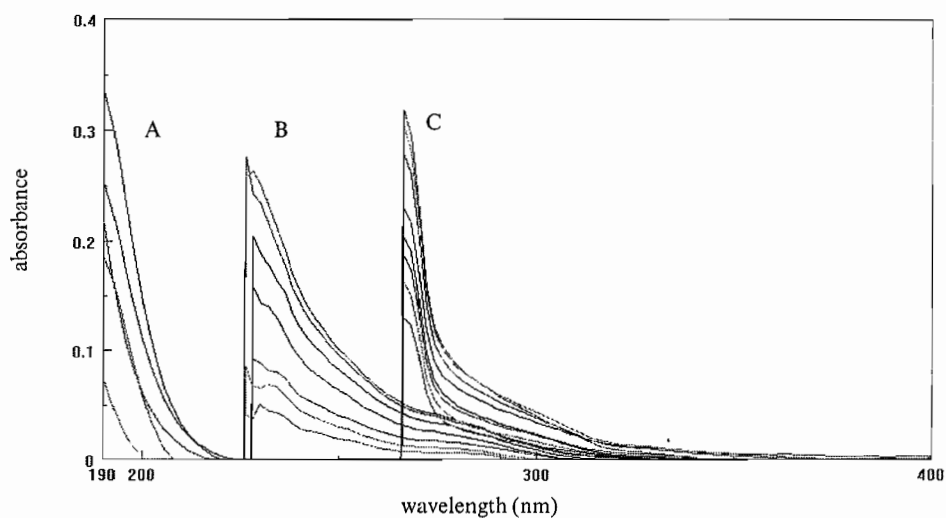


Fig. 1. UV absorption spectra for triethylamine in water (A), ethyl ether (B) and petroleum ether (C)

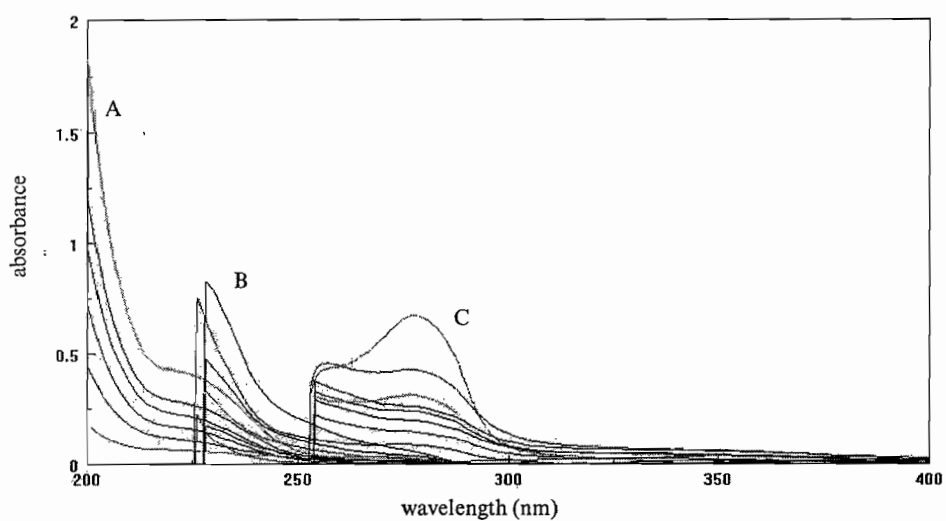


Fig. 2. UV absorption spectra for acetosalicylic acid in water (A), ethyl ether (B) and chloroform (C)

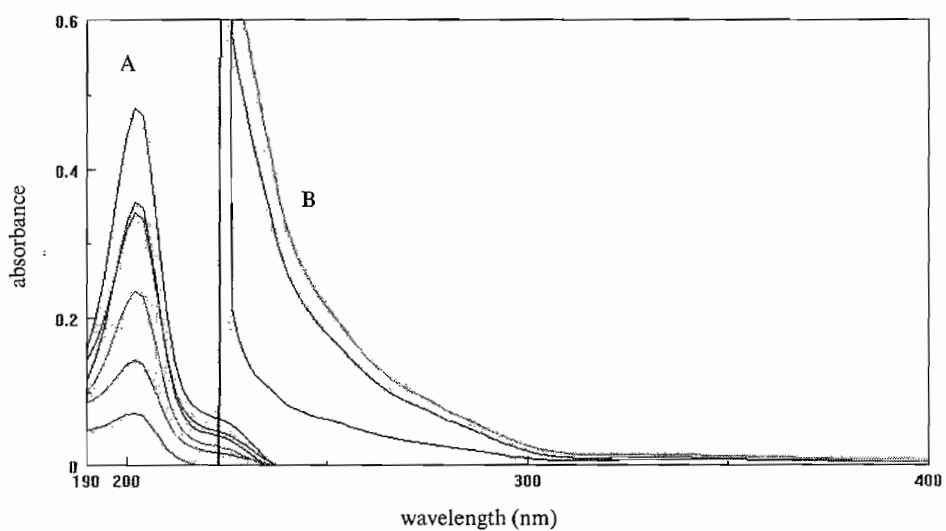


Fig. 3. UV absorption spectra for phloroglucinol in water (A) and ethyl ether (B)

dences between absorption and concentration for triethylamine in water (1), ethyl ether (2) and petroleum ether (3), led to the following equations:

$$y = 0.020x + 0.033, \quad (1)$$

$$y = 0.232x - 0.014, \quad (2)$$

$$y = 0.128x + 0.100. \quad (3)$$

Correlation coefficients for these dependences have the values: 0.955 (1); 0.969 (2); 0.945 (3) (Fig. 4). Minimum detectable concentrations were established so that the values of the corresponding absorbance to be at least 0.1. Taking into account this criterion, the following concentrations were considered as minimum detectable: 3.5 mg/l for triethylamine in water solutions, 0.5 mg/l in ethyl ether, and 0.78 mg/l in petroleum ether. From spectra presented in Fig.1 and the above equations it is obvious that for the same concentration of triethylamine in the third solvents the values of absorptions are higher both in ethyl ether and petroleum ether than in water.

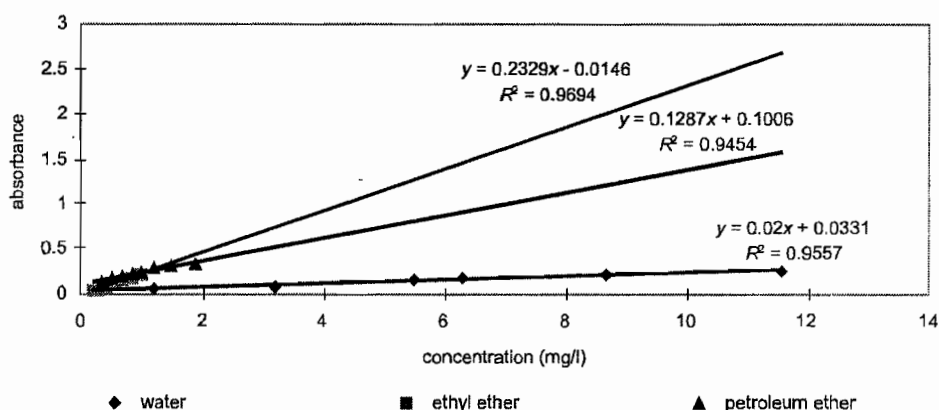


Fig. 4. Dependence of UV absorbance versus concentration for triethylamine in water, ethyl ether and petroleum ether solutions

UV absorption spectra for solutions of acetosalicylic acid in distilled water (A), ethyl ether (B) and chloroform (C) for the mentioned concentrations are presented in Fig. 2. Spectra in distilled water consists of broaden bands in the field of 200-280 nm, with an inflexion at 220 nm. The intensity of this inflexion is depended of solution concentration: the more concentrated a solution, the more distinct is absorption maximum. When ethyl ether is used as solvent, the shape of spectra is different: now it is situated between 225-280 nm, like that for triethylamine in the same solvent. In the case of chloroform, the dependence of spectra shape versus sample concentration is more evident (Fig. 2C). The differences between absorptions for solutions of acetosalicylic acid in the third solvents are small for the same concentration.

The measurements of absorbances in order to determine correlations with concentrations in distilled water, ethyl ether and chloroform were made at the following wavelengths: 220, 230 and 278 nm, respectively (Fig. 5). Linear depen-

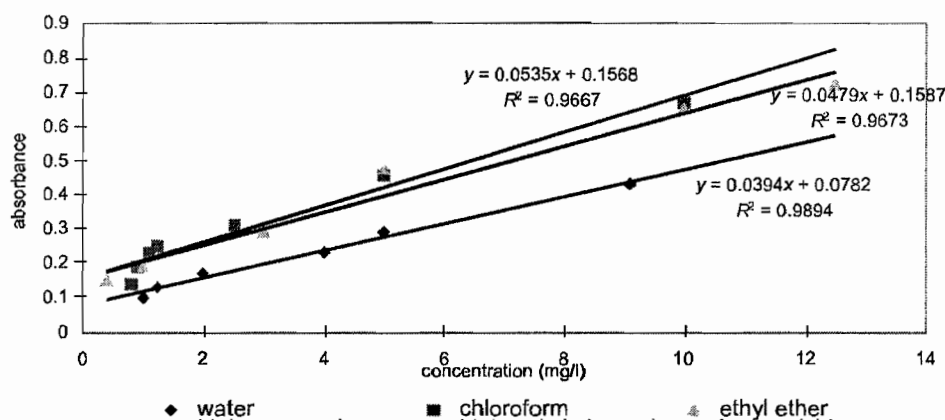


Fig. 5. Dependence of UV absorbance versus concentration for acetosalicylic acid in water, chloroform and ethyl ether solutions

dences obtained are given by the following equations:

$$y = 0.0390x + 0.0782, \quad (4)$$

$$y = 0.0479x + 0.1587, \quad (5)$$

$$y = 0.0535x + 0.1568 \quad (6)$$

and correlation coefficients are: 0.989 (4) and 0.967 (5) and 0.966 (6). Taking into account the mentioned criterion, minimum detectable values are: 2.0 mg/l in water, 1.0 mg/l in ethyl ether and 1.0 mg/l in chloroform.

In the case of phloroglucinol, solutions in distilled water (A) and ethyl ether (B) were prepared. One part of the recorded spectra is presented in Fig. 3. The absorption values for phloroglucinol in water solutions are measured at 202 nm and absorption curves are places between 190-235 nm. Absorption spectra of phloroglucinol in ethyl ether are very closed to those of acetosalicylic acid and triethylamine, and the measurements of absorbance took place at 230 nm (Fig. 6). The obtained correlations are given by equations:

$$y = 0.234x + 0.0408, \quad (7)$$

$$y = 0.2548x + 0.1158 \quad (8)$$

with correlation coefficient, $r^2 = 0.983$ (7) in water and $r^2 = 0.948$ (8) in ethyl ether. The minimum detectable concentrations considered are 1.0 mg/l in water and 0.33 mg/l in ethyl ether (Table 2).

For estimation of the recovery efficiency for the third compounds from diluted solutions by use of liquid-liquid extraction, water samples in concentrations of 5 and 10 times smaller than those considered as minimum detectable by ultraviolet spectrophotometry were prepared. Extraction of triethylamine was

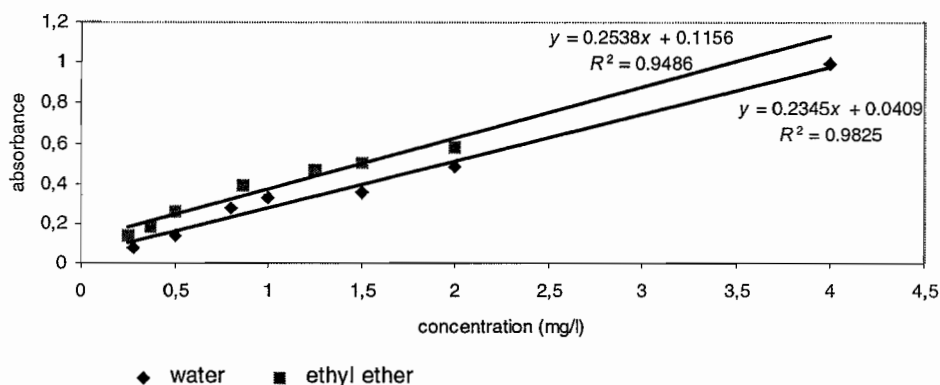


Fig. 6. Dependence of UV absorbance versus concentration for phloroglucinol in water and ethyl ether solutions

realised with ethyl ether and petroleum ether, of acetosalicylic acid with ethyl ether and chloroform, and of phloroglucinol with ethyl ether. Applied extraction process was similar with those proposed in the literature for separation and concentration of volatile organic compounds from water samples. Obtained results are presented in Tables 3, 4 and 5. For five times smaller concentrations than those considered as minimum detectable by UV spectrophotometry, the recovery efficiencies by ethyl ether extraction were 82.5% for acetosalicylic acid, 88.0% for triethylamine, and 91.5% in the case of phloroglucinol (Table 4). When 10 times smaller concentrations were used, the obtained recovery are 80.5, 87.5 and 89.0%, respectively.

Table 2. Minimum detectable concentrations (mg/l) for acetosalicylic acid, phloroglucinol and triethylamine in different solvents by UV spectrophotometry

Solvent	Acetosalic acid	Phloroglucinol	Triethylamine
Water	2 (0.16)*	1.0 (0.27)	3.5 (0.1)
Ethyl ether	1.0 (0.21)	0.33 (0.2)	0.5 (0.1)
Chloroform	1.0 (0.2)	-	-
Petroleum ether	-	-	0.78 (0.2)

* Absorbance values.

Recovery of acetosalicylic acid from water solutions by extraction with chloroform was 75.0% for initial concentration of 0.2 mg/l and 81% for 0.4 mg/l. Attempts for recovery of triethylamine with petroleum ether conducted at poorer results, about 65% (Table 5).

Table 3. The recovery efficiencies for determination of acetosalicylic acid (0.4 mg/l), triethylamine (0.7 mg/l) and phloroglucinol (0.2 mg/l) by extraction with ethyl ether from water solutions and identification by UV spectrophotometry

No sample	Acetosalicic acid	Triethylamine	Phloroglucinol
1	78.2	86.4	93.7
2	81.5	89.0	88.3
3	84.0	92.7	90.5
4	86.8	85.0	88.0
5	83.0	86.9	97.0
Mean	82.7	88.0	91.5

Table 4. The recovery efficiencies for the determination of acetosalicylic acid (0.2 mg/l), triethylamine (0.35 mg/l) and phloroglucinol (0.1 mg/l) from water solutions by extraction with ethyl ether and identification with UV spectrophotometry

No sample	Acetosalicic acid	Triethylamine	Phloroglucinol
1	77.0	90.5	85.7
2	83.4	86.0	88.4
3	81.5	89.4	91.0
4	79.1	91.2	92.5
5	81.5	80.9	89.9
Mean	80.5	86.6	89.5

Table 5. The recovery efficiencies for the determination of acetosalicylic acid (0.2 mg/l and 0.4 mg/l) and triethylamine (0.7 mg/l) from water solutions by extraction with chloroform and petroleum ether respectively, and identification with UV spectrophotometry

No sample	Acetosalicic acid		Triethylamine
	0.2 mg/l	0.4 mg/l	0.7 mg/l
1	72.4	84.3	67.0
2	76.8	78.6	63.5
3	80.5	79.0	62.4
4	74.0	83.5	68.6
5	75.3	79.6	64.6
Mean	75.8	81.0	65.18

CONCLUSIONS

The dependence of absorbance against concentration obeys the Lambert–Beer law for studied concentrations of the mentioned organic compounds and solvents. The minimum detectable concentrations by UV spectrophotometry were thus considered, that the corresponding absorbance to be at least 0.1.

The recovery efficiencies after rapid liquid-liquid extraction with ethyl ether of acetosalicylic acid, triethylamine and phloroglucinol from prepared water

solutions, in concentrations 10 times smaller than those considered as minimum detectable by UV spectrophotometry, were 80.5, 87.5 and 89.0%, respectively.

The proposed procedure, rapid liquid-liquid extraction followed by measurement of the UV absorption value for estimation of organic content from water may be used even in the field, for on-site analysis.

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