

ANALYSIS, CHARACTERIZATION AND ESTIMATION OF ORGANIC COMPOUNDS IN WATERS BY USE OF ULTRAVIOLET ABSORPTION PARAMETERS

Corneliu Bogatu

National R&D Institute for Industrial Ecology, P-ta Victoriei nr.2 et.2. PO Box 254, Of.1. 1900 Timisoara Romania. Phone/fax: 0040 256 220369. e-mail: ecoind@rectorat.utt.ro

Abstract

The use of rapid liquid-liquid extraction and ultraviolet absorption spectrophotometry for analysis and estimation of organic content of both prepared water solutions, containing model compounds like acetosalicylic acid, triethylamine, phloroglucinol and wastewaters from surfactant and cosmetic industry was searched in this paper. Also, humic and fulvic compounds separated from a surface water, Bega river in Timisoara, were characterized by ultraviolet spectra analysis.

The recoveries of model compounds with ethyl ether from solutions in concentrations 10 times smaller than those considered as minimum detectable by ultraviolet spectra, were 80.5 %, 87.5% and 89.0% respectively. By use of ultraviolet absorption maxima of organic content in wastewater and their chemical oxygen demand or dried solids concentration, correlation coefficients greater than 0.963 were obtained; after computing the ratios of absorptions for 254 nm and 203 nm (A_{254} / A_{203}) it was concluded that the obtained values correspond with presence of substituted aromatic rings. Specific absorptions maxima were recorded for humic and fulvic compounds in water solutions and correlations of absorptions with concentrations were 0.980 and 0.920, respectively.

Introduction

There is a continuous need for new methods used for the determination of trace organics compounds in water. Sometimes, group parameters like total organic carbon (TOC), total organic halogen (TOX), chemical oxygen demand (COD), are more accessible and often cheaper for characterization of water organic content (1,2,3). 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 nm, and 254 nm (4).

It was established that for aromatic compounds, the ratio for absorptions of electron transfer bands (ET):benzenoid bands (Bz), i.e. (A_{ET} / A_{Bz}) depends on functional groups. E.g., for catechols and related phenolic compounds this ratio ranged between 0.25 - 0.35 and for aromatic rings containing carboxyl, carbonyl and ester groups the ratio A_{ET} / A_{Bz} may be greater than 0.40. Thus, this parameter may be an useful indicator to appreciate the presence of substituted aromatic rings in water (6).

Taking into account that the principal steps in trace analysis are, separation, concentration, detection and quantitation (5,7), the use of rapid liquid-liquid extraction of organic compounds from both prepared water solutions, wastewaters containing surfactants and cosmetics and of UV spectrophotometry for estimate of their content is proposed in this paper. Also, separation of humic and fulvic compounds from a surface water and their characterization with ultraviolet spectrophotometry is presented.

Methods

1. 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), chloroform (10-0.8mg/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).

The quality of reagents and solvents was p.a.

For the establishment of the efficiency of rapid liquid-liquid extraction of the above compounds with organic solvents, diluted water solutions of compounds were prepared, so their concentrations to be 10 times smaller than those considered as minimum detectable by UV spectrophotometry.

2.Characterization of wastewaters samples from two factories from Timisoara, one producing surfactants and the other cosmetic products, was made by determination of chemical oxygen demand (cod) and pH; the values of cod ranged from 1250 to 345 mg/L and 1050 to 468 mg/L, respectively; pH of samples was adjusted whatever was necessary, so all ultraviolet spectra to be recorded at the same value, pH=7. Correlations between maxima of absorption due to dissolved organic compounds from wastewaters and their chemical oxygen demand were undertaken. Also, the ratios of absorptions for electron transfer bands:benzenoid bands were computed, and the obtained values compared with those presented in the literature.

3.Every wastewater sample was evaporated by use of an vacuum-evaporator, in order to completely separate dried solids. The obtained solids were weighted and then ethyl ether and petroleum ether solutions were prepared. These solutions were prepared so, their concentrations in dried solids per liter to be 1:10 of initial wastewaters samples. After recording of uv spectra for solutions of organic solvents, an attempt for establishment of correlations between their absorption maxima and the corresponding quantities of dried solids was undertaken. These correlations were used for determination of organic content from diluted wastewaters samples, by extraction.

4.The concentrations of diluted wastewater was 1:10 of initial samples; organic compounds were separated and concentrated from these samples by rapid liquid-liquid extraction with ethyl ether or petroleum ether and then, their absorption maxima from ultraviolet spectra was measured. By use of these absorptions and correlations obtained at point 3, the recovery efficiencies were determined. For rapid liquid-liquid extraction volumic ratio water sample:organic solvent was 10:1, and time for mixing 10 minutes. All ultraviolet spectra were recorded with an Jasco V-530 instrument, 1998. Separation of dried solids from wastewaters was realized with an vacuum rotary evaporator type 351 Unipam, Poland.

5.pH of surface waters was dropped to 1.9-1.7 with hydrochloric acid, for precipitation of humic fraction; after 24 hours, settled mass was dried and weighted and in liquid part remained fulvic fraction. Solid part was dissolved in distilled water: undissolved part was separated by filtration; it contains humates part, which are insoluble in water. UV spectra of both fractions at pH=7 were recorded and chemical oxidability (KMnO_4) was measured.

Results and Discussion

1.For triethylamine in water solutions absorption curves are placed between 190-225 nm. The values of absorptions taken into consideration in order to determine correlation with concentrations, were those for 192 nm. The computing of dependences between absorptions and concentrations for triethylamine in water (a), ethyl ether (b) and petroleum ether (c), led to the following equations:

$y = 0.020x + 0.033$, $r^2 = 0.955$ (a); $y = 0.232x - 0.014$, $r^2 = 0.969$ (b); $y = 0.128x + 0.100$, $r^2 = 0.945$ (c)

Minimum detectable concentrations were established so, 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 the above equations it is obvious that, for the same concentration of triethylamine in the three solvents, the values of absorptions are higher both in ethyl ether and petroleum ether than in water.

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.

2.UV absorption spectra of water samples containing surfactants covered all field of absorption, between 200-375 nm, fig. 1. Absorption maxima are situated at $\lambda_1 = 228$ nm, $A_1 = 2.1$ and $\lambda_2 = 275$ nm, $A_2 = 0.7$. It was established a correlation between the values of absorptions at 254 nm and the corresponding values of chemical oxygen demand and of dried solids of this type of wastewaters:

$y = 0.0008x - 0.187$ (1), $r^2 = 0.981$, $y = 0.0027x - 0.193$ (2), $r^2 = 0.998$, respectively.

In figure 2 are presented uv spectra of wastewater samples from cosmetic industry. Two absorption maxima may be identified: $\lambda_1 = 209$ nm, $A_1 = 2.3$ and $\lambda_2 = 298$ nm, $A_2 = 0.84$.

The correlation between absorptions measured at $\lambda = 254$ nm, chemical oxygen demand and dried solids are given by the following equations: $y = 0.0009x - 0.328$ (3), $r^2 = 0.963$; $y = 0.0044x - 0.411$ (4), $r^2 = 0.965$, respectively. In case of wastewater from surfactant industry A_{254} / A_{203} ratio ranged from 0.36 to 0.30; for samples 3 to 6 the ratio may be considered almost constant. For the other type of wastewaters the variability of ratio is greater, from 0.27 to 0.63. The obtained values for this ratio are typical for substituted aromatic rings with carbonyl, carboxyl and ester group.

3. The evolution of ultraviolet absorption spectra for ethyl ether solutions containing different quantities of dried solids separated from wastewaters with surfactants are presented in figure 3. These spectra are characterized by two maxima of absorption, corresponding to $\lambda_1 = 280$ nm and $\lambda_2 = 342$ nm. The correlation between concentrations of dried solids in mg/L and the corresponding values of absorptions measured at 280 nm is given by the following relation: $y = 0.0092x - 0.0499$ (5), $r^2 = 0.985$. In the case of solutions of dried solids from wastewaters with cosmetic products, the maxima of absorption taken into consideration was that corresponding to $\lambda = 254$ nm and linear correlation is: $y = 0.0235x - 0.145$ (6), $r^2 = 0.981$.

Table 1 The values of absorptions, cod and dried solids for wastewater from surfactant industry

sample	A_{203}^*	A_{228}	A_{254}	$A_{254} / 203$	cod, mg/L	dried solids, mg/L
1	2.1	1.9	0.75	0.36	1250	358
2	1.75	1.5	0.60	0.34	870	290
3	1.3	1.1	0.41	0.31	758	230
4	0.65	0.56	0.20	0.30	540	154
5	0.35	0.3	0.11	0.31	372	115
6	0.23	0.19	0.07	0.30	345	94

Table 2. The values of absorptions, cod and dried solids for wastewater from cosmetic industry

sample	A_{203}	A_{209}	A_{254}	A_{298}	$A_{254} / 203$	cod, mg/L	dried solids, mg/L
1	2.1	2.3	0.70	0.84	0.33	1050	240
2	1.25	1.45	0.35	0.36	0.28	850	188
3	0.74	0.84	0.20	0.12	0.27	724	151
4	0.30	0.40	0.15	0.11	0.50	530	132
5	0.19	0.20	0.12	0.05	0.63	468	105

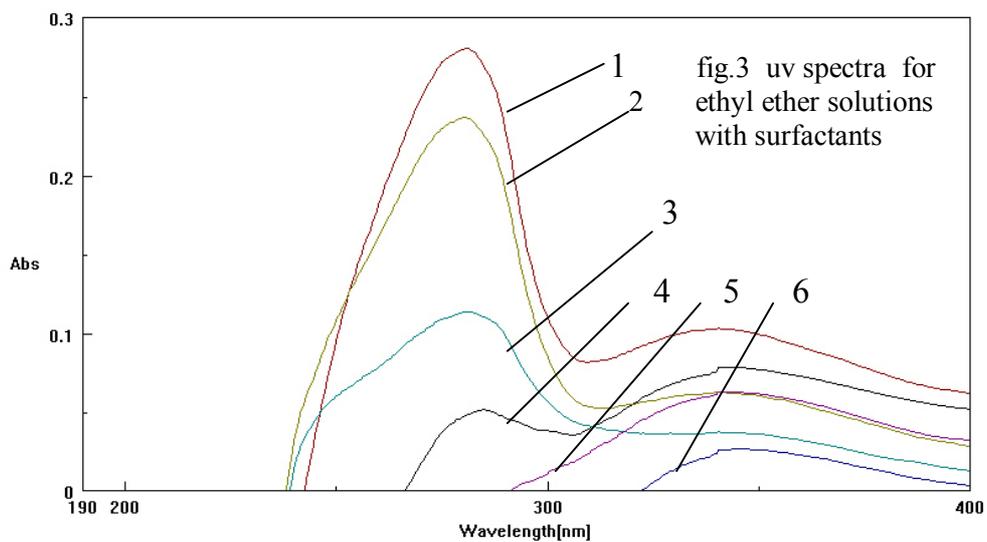
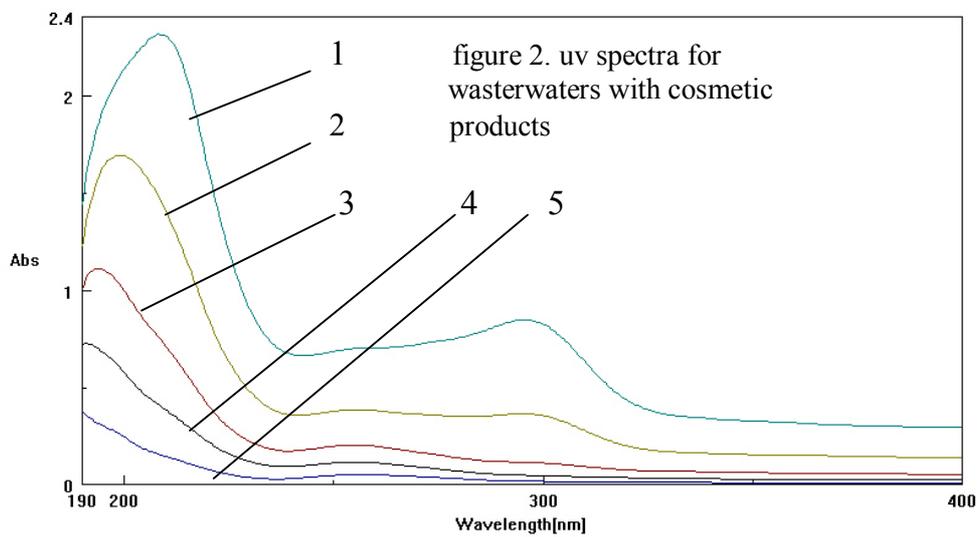
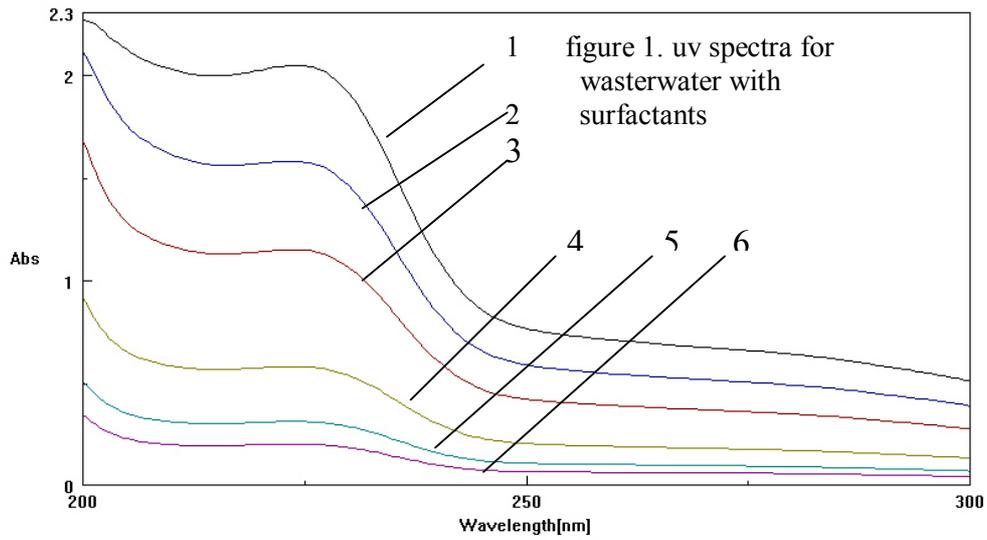
* A_λ = absorption for λ (nm)

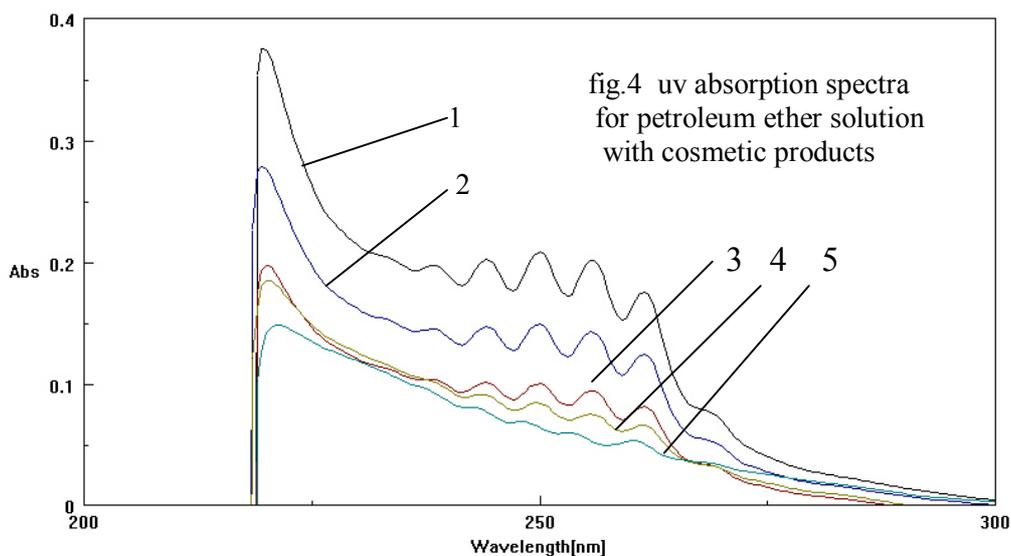
When petroleum ether was used as solvent, the uv absorption spectra are different. The field of absorption is between 220-300 nm, fig.4. For every sample, four maxima of absorption may be easily identified at: $\lambda_1 = 244$ nm; $\lambda_2 = 250$ nm; $\lambda_3 = 256$; $\lambda_4 = 262$ nm. The correlations between concentrations and absorptions are given by the following equations, for solutions with surfactants and cosmetics: $y = 0.0113x - 0.0534$, $r^2 = 0.956$ (7); $y = 0.0112x - 0.0571$, $r^2 = 0.995$ (8).

4. The efficiencies of rapid liquid-liquid extraction with ethyl ether and petroleum ether of organic content from diluted wastewater was measured by determination of absorptions of these solvents after extractions, and by use of the above equations.

The best results for recoveries were obtained with ethyl ether, 84.8% in the case of wastewater containing surfactants and 72% for those produced by cosmetic industry. When petroleum ether was used, poorer results were obtained..

5. Separation of humic and fulvic fractions from surface water was made by use of their pH solubility dependence. Both fractions revealed specific absorption maxima in ultraviolet field: 195 nm and 275 nm for humic part, and 195 nm for fulvic part. pH influence on peaks is more specific in alkaline medium, when both a bathochromic and hyperchromic moving was recorded. Correlation of absorption with concentration was more satisfactory for humic fraction, 0.980 than for fulvic fraction 0.839.





Conclusions

1. The use of rapid-rapid extraction with ethyl ether for recovery of three organic compounds from prepared water solutions led to the efficiencies of 80.5-89.0 %
2. By use of ultraviolet absorption maxima of wastewater with surfactants and cosmetic products and their chemical oxygen demand or dried solids concentrations, correlation coefficients greater than 0.963 were obtained. Also, good correlation coefficients between dried solids separated from wastewaters and maxima of absorption for their diluted solutions in ethyl ether and petroleum ether were obtained.
3. By comparison of absorption spectra of wastewater samples with corresponding spectra of ethyl ether and petroleum ether solutions, it was established that both their bands and maxima of absorption are more distinct in these solvents than in water. Although, in ethyl ether and petroleum ether ultraviolet absorption spectra are moved to longer wavelengths, maxima of absorption may be also attributed to substituted aromatic rings.
4. Recovery of organic content from diluted wastewaters by rapid liquid-liquid extraction was more efficient by use of ethyl ether, about 72-84.8%.
5. Correlation of absorption with concentration was more satisfactory for humic fraction, 0.980, than for fulvic fraction 0.839.

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