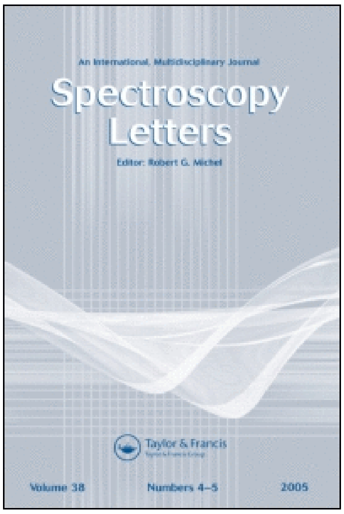

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FTIR investigation of organic discharge in polluted water: I. Renex monitoring study

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FTIR investigation of organic discharge in polluted water:
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Summary

Aliquots of waste water from power stations were analyzed by a special procedure in order to put in evidence the presence of renex, a nonionic detergent. The investigations were performed spectroscopically by FTIR technique. Qualitative and quantitative features of the procedure were established as specific peaks, detection limit and method sensibility. The validity of Lambert-Beer law was checked. Taking into account the selectivity of the method it results the necessity of separating renex from nitrogenous bases in the analyzed water.

1 Introduction

There is a growing interest in monitoring of the polluting exhaustions coming from different treatment plants of waste water; the most reliable methods to detect the toxic contents of polluted water are searched.

In the framework of one of the projects initiated under the United Nations Development Program environmental measurements were developed in our country using a mobile unit containing a FTIR spectrometer. Renex is a nonionic detergent used under specific conditions to inhibit the vegetative propagation on the internal system of pipes from power stations; being included on IRPTC (International Regulations for Potential Toxic Compounds) list the monitoring of this compound is impulsory. Polyoxyethylene (6) tridecyl ether is the main constitutive part of renex.

The present paper includes results regarding the mid-IR spectroscopic investigation on some surface waters polluted by renex. The renex good solubility in carbon tetrachloride allows to extract it from aqueous solutions. An analytical procedure including quantitative and qualitative features was elaborated. Detection limit and sensitivity of the method of renex monitoring were also established.

2 Materials and methods

2.1 Sample preparation

Carbon tetrachloride p.a. (Merck) and commercially available renex were used. Other p.a. chemicals where purchased by Reactivul (Romania).

Two types of samples were submitted to analysis:

a) samples of pure renex at various concentrations;

b) samples of renex extracted from different specimens of polluted water;

c) aqueous solutions of known concentration in renex and nitrogenous bases as hydrazine, cyclohexylamine and morfoline.

The a-type samples were obtained by diluting the pure renex in carbon tetrachloride in order to have solutions of 2.5÷50 mg per litre concentration. The solutions resulted by gradually adding the corresponding amount of renex in the IR cell, filled with solvent. The maximum error in concentration determination due to the volume non updating every time when adding a new amount of renex was ±0.005%.

Type b samples were obtained by extracting renex from a known amount of polluted water: solvent extracting technique is based as usually on phase distribution [1]. V_1 ml watery solutions were mixed with V_2 ml carbon tetrachloride, leading to an extraction ratio (V_1/V_2) up to 10.

The c-type samples were undertaken to the static extraction procedure with carbon tetrachloride. The extraction pH was between 0.5 and 3. The organic extract was dehydrated.

2.2 Apparatus

The presence of renex in our samples was investigated by FTIR technique using a Nicolet Magna - IR^{TM} 550 spectrometer under a spectral resolution of 4 cm^{-1}, a lowest aperture and 256 scans. An IR cell with 30 mm path length and KRS5 windows were used. Recordings using cells thinner than 30 mm were less conclusive than those with former path length. Extractions were performed using usual laboratory glass vessels. A Radiometer pH-meter was used to measure the pH.

3 Results and discussion

Mid IR spectrum of renex in the region where the solvent does not absorb is shown in Fig. 1. The intense peaks observed in the 2800-3000 cm^{-1} domain are due to the overlapping of the absorption peaks of symmetric and asymmetric stretching of CH_2 and CH_3 groups [2]. The main peak in this range is broadened due to the fact that renex is not a unitary substance. Peaks assigned to OH stretching appear at 3618 and 3710 cm^{-1}, showing that a hydrolysis process of the ether bonds took place [3].

Even though the peaks in the 2800-3000 cm^{-1} domain are characteristic to every substance containing hydrocarbon chains, we took them into consideration for further analysis of renex solutions due to the fact that they have high extinction coefficients. On the other hand they do not interfere with the solvent peaks.

Data recorded for the a-type samples served to draw the calibration curve. The fit of the experimental points used the least square method. Several calibrating curves were drawn taking into account either the height or the area of the peaks in the 2800 to 3000 cm^{-1} domain (Fig. 2). In this figure the straight line equations, as resulted by fitting, are also given. Curves 2-b, 2-c and 2-d were drawn by the corresponding peak heights; they show only small deviations from linear dependence. Due to the negative intercept these curves were not used in the following.

Therefore we have chosen the curve 2-a as the calibrating one. We assumed that the integrated absorption on 2800-3000 cm^{-1} domain indicates the presence of renex in the sample better than using peak heights. In addition, this curve has a rather high slope, this fact allowing a good reading accuracy.

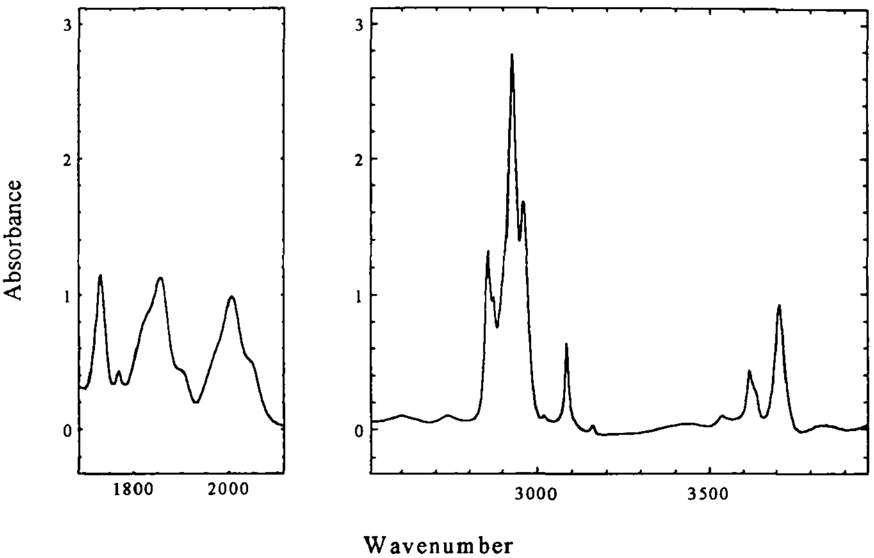

Figure 1
IR spectrum of renex

Attention was always payed to the solvent contribution at the peak features, especially when the cell of long path length was used. The best method to eliminate this influence in our case was to consider the solvent during the background recording.

The peak features in the spectra of b-type samples lead to the concentration of the corresponding extract using the calibrating curve, then to the concentration of polluted water.

The presence of other chemicals having CH functional group is quite possible in aqueous solutions: polyoxyethylene (6) tridecyl ether is often associated with nitrogenous bases like hydrazine, cyclohexylamine or morfoline.

Hydrazine does not give absorption in the spectral domain of interest. We expect then to do not influence the renex peaks in the 2800-3000 cm^{-1} domain (Table 1). One can see the area remain practically the same even by gradually adding hydrazine up to an amount equivalent to the renex content in the later solution. However the other two bases clearly interfere due to the CH

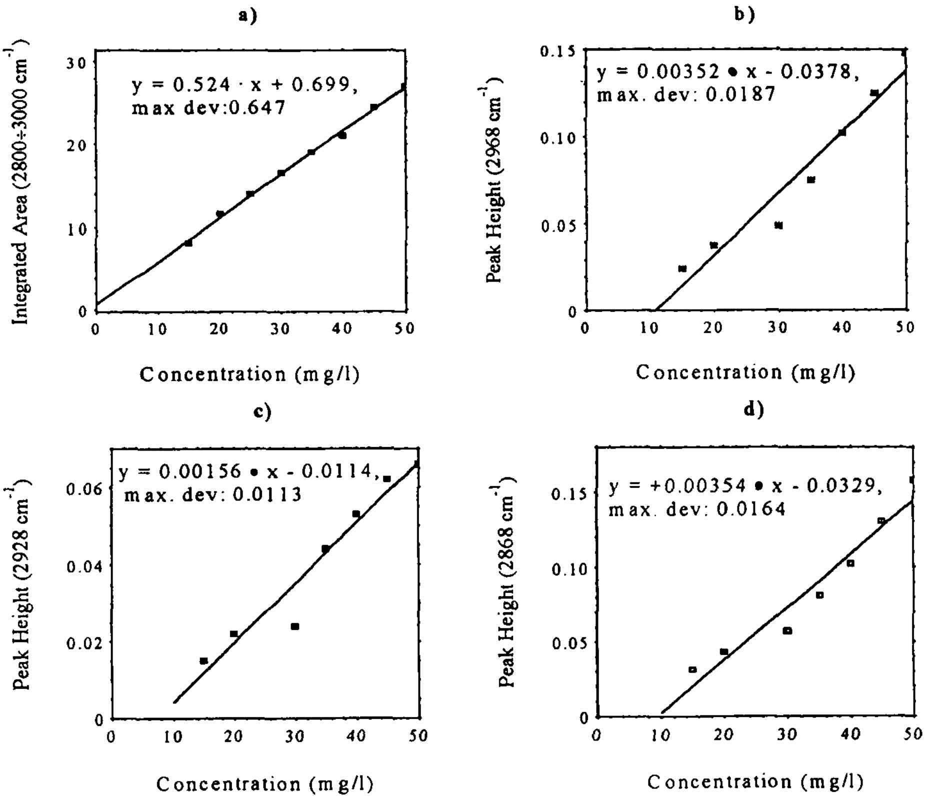

Figure 2
Different plots of calibration curve

Table 1
Hydrazine influence on the renex spectrum

Hydrazine concentration (mg/l)*	0.0	7.5	11.25	15	18.75
Integrated Area	96.058	95.81	96.32	95.81	95.98

*in the renex solution

groups. Therefore it was necessary to eliminate them. Considering the basic properties of cyclohexylamine and morfoline we had to use low pH conditions when extracting renex from watery solutions.

We found that an extraction pH lower than 2.5 is sufficient to take off the disturbing nitrogenous bases at a molar ratio bases/renex up to 4.

On the other hand all the renex solutions showed a good stability in time: unchanged spectral characteristics were kept after 78 hours. This property recommends the method as a highly reliable one.

We considered the detection limit being the lowest concentration of renex for which the highest characteristic peak in the 2800-3000 cm^{-1} domain can be distinguished from the noise. This limit was 2.5 mg (carbon tetrachloride solution), meaning 0.25 mg renex per litre of aqueous solution when an extraction ratio of 10 was used. Traces of renex smaller than this amount could be detected by concentrating the carbon tetrachloride solutions but further studies are necessary to establish the impurity influence on the method accuracy.

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