

FT-IR Investigation of Organic Discharge in Polluted Water

II. Monitoring of Cyclohexylamine and Morpholine

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Aliquots of waste water from power stations were analyzed by a FT-IR spectroscopic procedure and showed both qualitatively and quantitatively the presence of cyclohexylamine and morpholine. The detection limit and the sensitivity of the method were investigated and the validity of the Lambert—Beer law was checked. To maintain the selectivity of the method the pH must be maintained around 6.

The applicability of FT-IR method to air monitoring problems generally was recognized within past years [1]. Recently some works appeared trying to use this spectroscopic method to water monitoring [2]. Thus, FT-IR analysis of the biocides and detergents used industrially is often perturbed by the presence of different amines that may decrease the selectivity of the analytic method [2]. Among these amines there are cyclohexylamine, morpholine, and hydrazine.

Several methods were already developed for the analysis of primary and secondary aliphatic amines. Some of them require reaction of the amines being analyzed with different reactants to yield compounds suitable for subsequent spectrophotometric analysis [3] including fluorescence measurements [4] and atomic absorption spectrometry [5]. There is even an amperometric titration method reported in the literature for analysis of a morpholine derivative [6].

Both morpholine and cyclohexylamine molecules contain six-member saturated rings with two or none heteroatoms, respectively. Vibrational spectroscopic studies have previously assigned the main absorption peaks of these compounds to skeletal vibrations as well as to various methylene stretching and deformation modes [7—10]. Starting from these assignments this paper presents some results concerning the quantitative analysis of cyclohexylamine and morpholine in aqueous solutions by means of an FT-IR method. Calibration curves were obtained for the solutions containing one of these nitrogenous bases. An analytical procedure including quantitative features has been developed based on the relatively good solubility of bases in carbon tetrachloride allowing them to be extracted from aqueous solutions. The detection limit and sensitivity of the method for monitoring cyclohexylamine and morpholine were determined.

EXPERIMENTAL

IR spectra of the aqueous or carbon tetrachloride solutions were investigated by Fourier transform technique using a Nicolet Magna-IR™ 550 spectrometer under a spectral resolution of 4 cm⁻¹, using the lowest aperture and 256 scans. An IR cell with 30 mm path length (20 cm³ volume) and KRS5 windows was used: recordings with cells thinner than 30 mm were less useful due to need of a higher concentration in the studied substance.

Solvent extraction was performed using usual laboratory glass vessels. A Radiometer pH-meter was used to measure the pH.

Carbon tetrachloride (anal. grade, Merck) and commercially available cyclohexylamine were used. Other anal. grade reagents were purchased by Reactivul (Romania).

Sample Preparation

Several types of samples were submitted to analysis: *a*) solutions of pure cyclohexylamine in carbon tetrachloride, at various concentrations; *b*) solutions of amines extracted from water containing known concentration of cyclohexylamine and other nitrogenous bases as well as some nonionic surfactants; *c*) solutions of organic layer containing cyclohexylamine and morpholine extracted from different specimens of polluted water.

The *a*-type samples were obtained by diluting the pure cyclohexylamine in carbon tetrachloride in order to have concentration of 0.5 to 50 g dm⁻³. The solutions were resulted by gradually adding the corresponding amount of cyclohexylamine in the IR cell, filled with the solvent. Each time after a best addi-

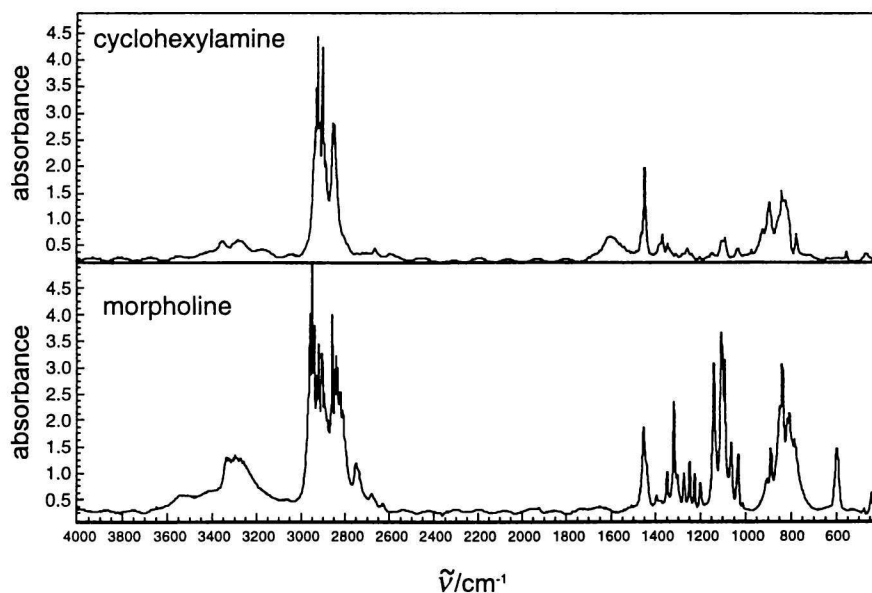


Fig. 1. IR spectrum of liquid cyclohexylamine (up) and morpholine (down). The cell path length is 0.025 mm.

tion the IR spectrum was recorded. Initially the cell had been filled with solvent (20 cm^3), and the amine doses added to draw the calibration curves were of 1 mm^3 . The concentration in the cell was always calculated by dividing the amine amount to 20 cm^3 of solution, without updating the volume due to amine adding. However, the maximum error in determination of amine concentration due to the volume nonupdating was 0.005 %.

Type *b* samples were obtained by extracting the organic part from a known amount of polluted water. Solvent extracting technique is based on the phase distribution [11]: V_1 volumes (usually 1 dm^3) of aqueous solutions were carefully mixed with a V_2 volume of carbon tetrachloride as solvent, leading to an extraction ratio (V_1/V_2) up to 10. The pH of the aqueous solutions was controlled.

The *c*-type solutions were undertaken to the extraction procedure with carbon tetrachloride as described for *b*-type samples.

In the former study concerning the renex monitoring [2], we showed that cyclohexylamine does not extract in the organic layer at pH less than 3. Thus the extraction pH was more than 6 in the present experiments. The organic extract was dehydrated before separating.

In general, a minimum of six separate samples was used individually to ensure the reproducibility of the measurements.

RESULTS AND DISCUSSION

Mid-IR spectra of cyclohexylamine and morpholine in the region where they do not interfere with the solvent are shown in Fig. 1. The intense peaks observed in the domain $2800\text{--}3000 \text{ cm}^{-1}$ are due to

the overlapping of the absorption peaks of symmetric and asymmetric stretching of CH bonds in the CH_2 groups [12]. The main peaks of the top curve (Fig. 1) are broadened. One of the reasons might be that cyclohexylamine used is not a unitary substance: in the presence of small amounts of HCl, a secondary reaction takes place leading to the formation of ammonium salts (like $>\text{NH}_2^+\text{Cl}^-$) easy to be identified by the absorption in the wavenumbers domain 1800 to 2000 cm^{-1} [13, 14]. In addition, overtones and combination bands of the scissors and wagging fundamentals lead to the IR bands with considerable intensity in the region $2850\text{--}3000 \text{ cm}^{-1}$ [9].

On the other hand, both these amines are strong hydrogen bond acceptors, forming dimers or polymers, depending on the base concentration [8]. Both can exist as two conformers, equatorial or axial with an inversion barrier of $\approx 130 \text{ kJ mol}^{-1}$ [15]. The mentioned broadening might be also due to the presence of axial conformers [16]. Stretching N—H mode for cyclohexylamine appears at 3283 cm^{-1} and 3357 cm^{-1} for the two conformers (with low intensity in the equatorial conformer). In the range $1350\text{--}1500 \text{ cm}^{-1}$ the deformation vibrations of the methylene groups [17] can be observed at 1455 cm^{-1} and $\approx 1425 \text{ cm}^{-1}$.

Morpholine spectrum (down curve, Fig. 1) has absorptions in similar positions with those of cyclohexylamine, having the same attributions. Morpholine presents some additional peaks at 1320 cm^{-1} , 1150 cm^{-1} , and 600 cm^{-1} related to its ether group. However, these peaks are weaker than the peaks corresponding to the stretching of the CH groups and therefore they will be not taken into consideration for further analysis.

Even though the peaks in the $2800\text{--}3000 \text{ cm}^{-1}$ domain are characteristic of every substance contain-

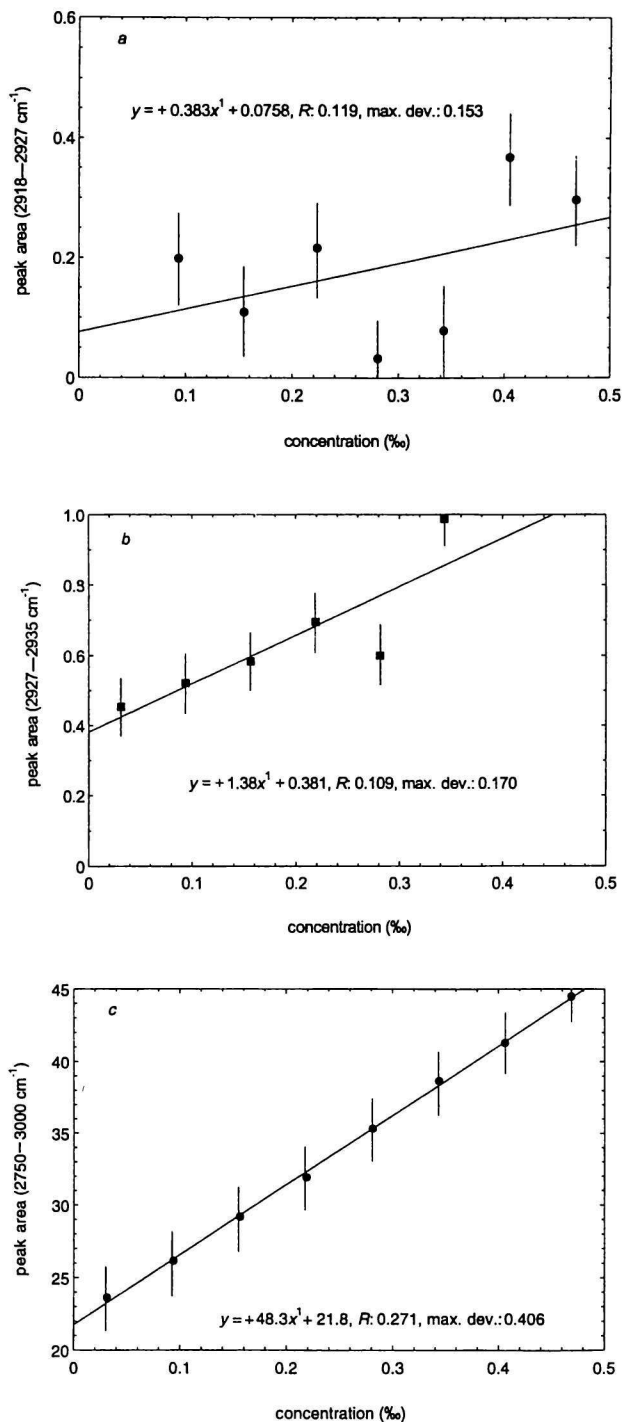


Fig. 2. Calibration curves for cyclohexylamine in carbon tetrachloride. The equations describe the linear fit.

ing hydrocarbon chains, we consider them for further analysis of amine solutions since these peaks have high extinction coefficients; on the other hand, they do not interfere with the solvent peaks.

Data recorded for the *a*-type of cyclohexylamine samples served to draw the calibration curve. The fit of the experimental points used the least-squares method. Several calibrating curves were drawn taking into account the domain of stretching vibrations

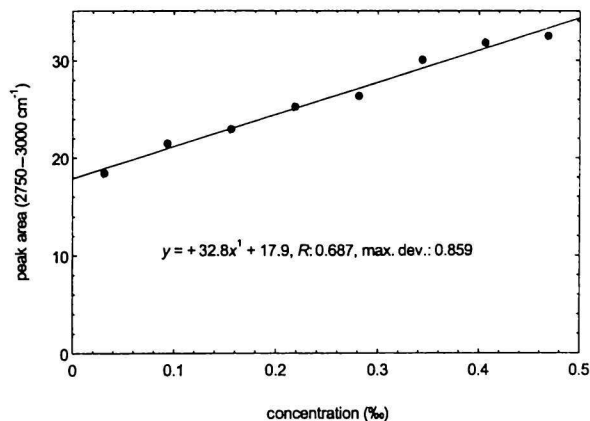


Fig. 3. Calibration curve for morpholine in carbon tetrachloride. The equation describes the linear fit.

of CH₂ groups (Fig. 2); the straight line equations, as resulted by fitting, are also given. Curves with negative ordinate intercept were not considered in the subsequent analysis.

Calibration curve obtained for morpholine solutions is given in Fig. 3. When comparing the calibration curves of the two amines under discussion, one observes a different slope, due to different number of methylene groups in these two molecules.

We checked the correctness of our results by estimating the integrated absorption coefficient of one methylene group: the values obtained in the case of cyclohexylamine and morpholine agree fairly well, meaning that the influence of the two heteroatoms on the methylene absorption coefficient is rather minimum. Moreover, our values for this integrated absorption coefficient are in the range 6600–8300 cm mmol⁻¹ depending on the concentration as found by *Snyder et al.* using FTIR methods [10].

Attention was always paid 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. It is possible that the hydrocarbon content of the solvent is the reason for the negative intercept of the above fitting curves.

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

The presence of other organic chemicals having CH₂ functional groups is quite possible in aqueous solutions: polyoxyethylene[6] tridecyl ether is often mixed with the nitrogenous bases. The bases and the polyether might be separated by using an appropriate pH of the solutions [2].

All the amine solutions showed a good stability in time: unchanged spectral characteristics were kept

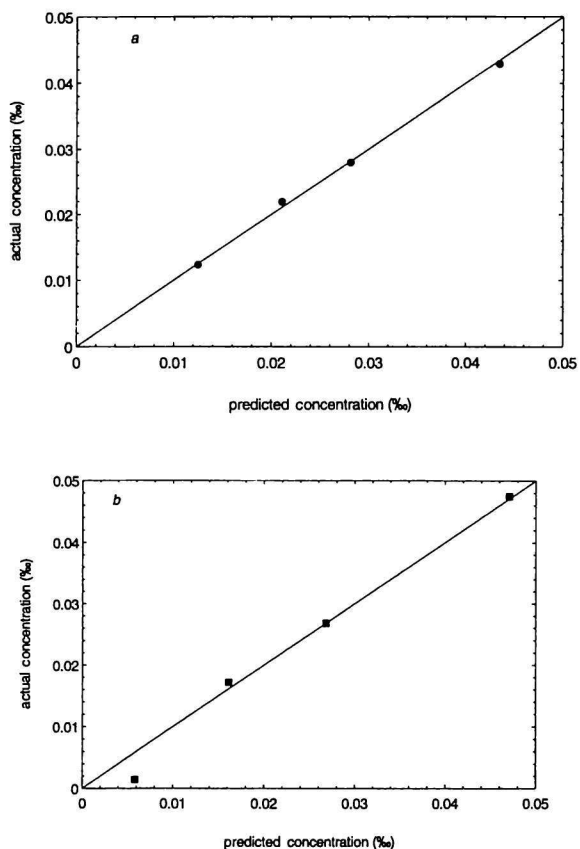


Fig. 4. The actual vs. predicted concentrations diagram; the concentration values correspond to *c*-type samples containing: a) cyclohexylamine, b) morpholine.

after 78 h. This property recommends the method as a highly reliable one.

We considered the detection limit being the lowest concentration of investigated amines for which the highest characteristic peak in the 2800–3000 cm^{-1} domain can be distinguished from the noise. Measuring absorbance as low as 1×10^{-4} units [18] cannot be expected in our system due to the long path cell. However, the obtained detection limit is low enough. This limit was 2.5 mg dm^{-3} in carbon tetrachloride solution, meaning 0.25 mg dm^{-3} of aqueous solution when an extraction ratio of 10 was used. This limit is lower than that found by the spectrochemical method of a coupling product [3]. Traces of cyclohexylamine smaller than this amount might be detected by concentrating the carbon tetrachloride solutions but further studies are necessary to establish the impurity influence on the method accuracy. Morpholine might be detected starting with 4 mg dm^{-3} under the conditions mentioned for cyclohexylamine, namely when an extraction ratio water : carbon tetrachloride of 10 was used.

Some samples of waste water, namely those coming from a nuclear powerplant, were analyzed using the method developed above. The actual composition

of the samples *c* was offered by the powerplant owner. The actual concentration values vs. the predicted ones were represented graphically in Fig. 4: one should take into consideration that the range is now 10 times lower than that in Fig. 2 or 3 due to the extraction ratio of 10. One can observe that there is a straight linearity between the two types of data. Other tests were performed using samples made by ourselves starting from known amount of the investigated bases, leading to the same good agreement between the actual and predicted values.

Therefore the method proposed by us for cyclohexylamine and morpholine analysis is reliable.

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