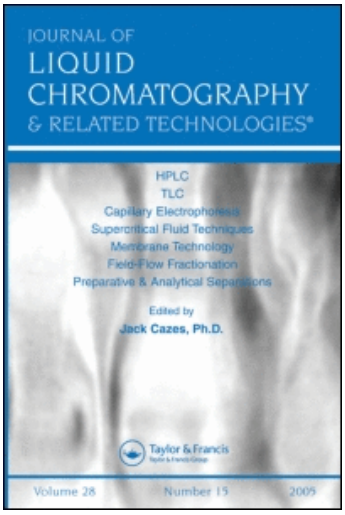

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DETERMINATION OF METHYL- AND DIMETHYLAMINE IN WASTE WATER BY HPLC

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ABSTRACT

Two liquid chromatographic methods have been developed for the selective determination of methyl and dimethylamine in waste water after derivatization. The derivatization was made in aqueius medium (pH = 11.2) by phenylizothiocyanate and p-toluenesulphochloride. Examples for the determination of methyl- and dimethylamine in waste waters are shown. The presented methods were proposed for the control of the performance of the purification plant.

INTRODUCTION

Recently greater attention is paid to the protection of environment. The used chemicals or the decomposition products of these, respectively, often have toxic influence on the mankind. The aliphatic amines are industrial chemicals with a wide variety of applications. They are used as raw materials or at an intermediate stage in the

production of other chemicals. Amines are sensitizers and irritants to the skin, and respiratory tract, some are precursors of N-nitrosamines, which are carcinogenic substances. Consequently, it would be useful to determine the unconverted amines in the waste water and human environment. Their contents in waste waters are frequently decreased by using of purification plants.

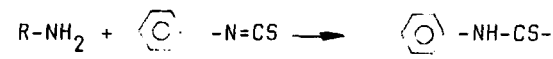
In the literature several possibilities of determination of aliphatic amines are described. The derivatization with fluoresceinamine was carried out by Ingles and Gallimore /1/. The methylamine determination in blood plasma as well as in urea by derivatization with trinitrobenzenesulphochloride was worked out by Wingender /2/. The trace analysis of amino acids by derivatization with orthophthalaldehyde with the following separation by the HPLC method was worked out by Griffin and Price /3/. The amino acids may be derivatized also with the phenylizothiocyanate in the aqueous medium /4/. The determination of aliphatic amines in the air was described by Simon and Lemancon /5/. These used the preconcentration column filled with silica gel and the desorption was made directly with the derivatization agent. The determination of aliphatic amines in sea foods was published by Wills et al./6/. The determination of amines by dansyl-derivatives was described by more authors /7,8/.

The aim of the presented work was to work out the method of methyl- and dimenthylamine determination in waste waters which will make possible to determine the effeciency of the purification plants of waste waters and to control the contents of aliphatic amines in the waste waters.

EXPERIMENTAL

The methylamine and dimethylamine standards were supplied in gas bombs (Fluka AG, Buchs SG Schweiz). The determination of their aqueous solutions was made by the 4.10^{-3} M titration by the solution of hydrochloric acid. The con-

centration of methylamine and dimethylamine in the aqueous solution was 0.439 g/liter and 0.153 g/liter, respectively. The derivatization was made in the aqueous medium (pH=11.2) in two ways by phenylizothiocyanate and p-toluenesulphochloride according to the reaction :



$$R\text{-}NH_2 + \text{C}_6\text{H}_4 \text{-N=CS} \longrightarrow \text{C}_6\text{H}_4 \text{-NH-CS-NHR}$$

$$R\text{-}NH_2 + \text{C}_6\text{H}_4 \text{-}SO_2Cl + 2\ NaOH \longrightarrow \text{C}_6\text{H}_4 \text{-}SO_2\text{-}RNa + NaCl + 2\ H_2O$$

In the same way also the derivatization of waste water samples was made the pH value of which was adjusted to 11.2. The derivatization with p-toluenesulphochloride was made by the Schotten-Baumann method.

HPLC separations were carried out using a Waters 910 pump, Reodyne 7125 injection valve, and Waters 484 variable wavelenght detector at 254 nm. The samples (10 ul) were separated using water - methanol (1:1) as the eluent with a flow rate of 0.5 ml/min on Separon C 18 columns (10 cmx4 mm i.d.) (Tessek, Prague).

The optimal separation system was estimated according to the R_{ij} values of two adjacent bands by the comparison of capacity ratios of the derivatives of amines and their derivative agents as well as by the comparison of the time of analysis. By using the Separon CN and Separon NH_2 column the overlapping of peaks of the methyl- and dimethylamine derivatives occurred.

RESULTS AND DISCUSSION

In order to achieve the correct result by the pre-column derivatization following criteria had to be fulfilled :

1. a reaction must produce a single well-defined product

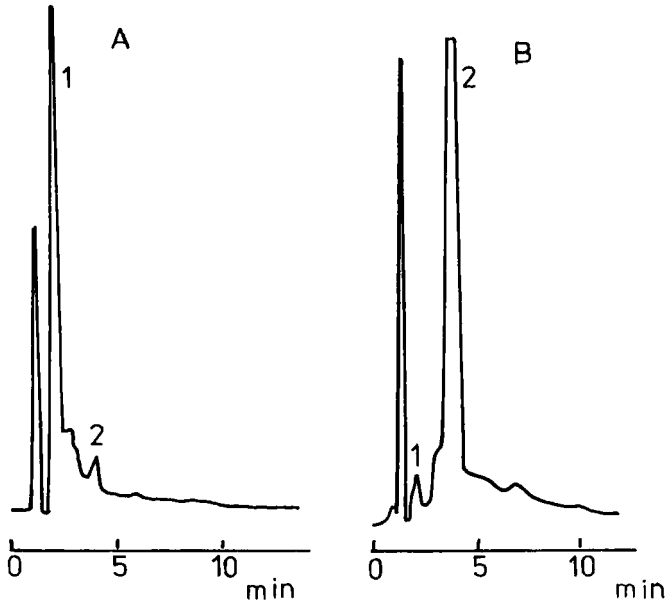


Figure 1. Chromatogram of 1 % methylamine aqueous solution after the derivatization with p-toluenesulphochloride after 2 minutes (A) and after 15 minutes (B), respectively. Column : Separon C 18, mobile phase : methanol-water (1:1). Flow rate : 0.5 ml/min; UV detection 254 nm.
1 - p-toluenesulphochloride; 2 - p-toluenesulphomethylamide.

2. single chemical mechanism
3. rapid fixation of equilibrium

From the available chemicals and on the basis of experiences from the organic analysis the use of two derivatization agents was investigated : phenylizothiocyanate and p-toluenesulphochloride. From the literature data it has followed that the presented derivatization agents may be used in the aqueous medium, too, which is very important in the determination of amines in waste waters.

The formation of derivatization products was observed by peak height or peak area of the derivatized product,

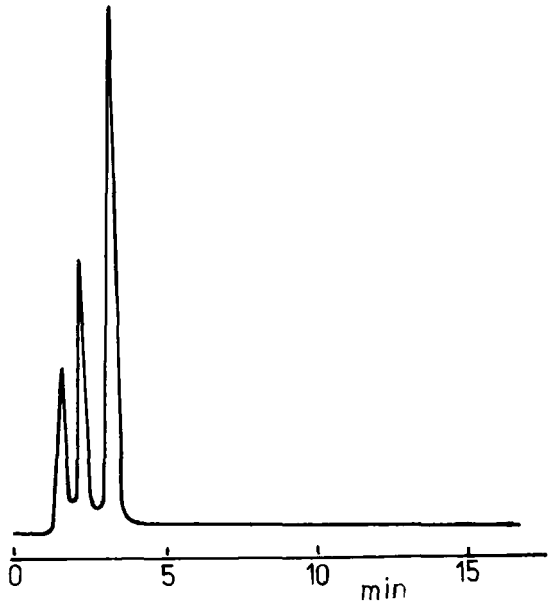


Figure 2. Chromatogram of waste water sample before the inlet into cleaner without derivatization.
Column : Separon C 18; mobile phase : methanol-water (1:1)
Flow rate : 0.5 ml/min; UV detection 254 nm.

respectively. The constant peak height in the dependence on reaction time indicated the end of derivatization. The phenylizothiocyanate reacted with the aliphatic amines relatively rapidly - in 2 minutes the height of peak has been already constant. The p-toluenesulphochloride reacted in the aqueous solution more slowly which is documented by the chromatographic records in Figure 1. After 15 minutes the height of p-toluenesulphomethylamide peak has not changed anymore.

The prepared derivatives of amines as well as the derivatization agents have been investigated also from the point of view their stability. The derivatives of the ali-

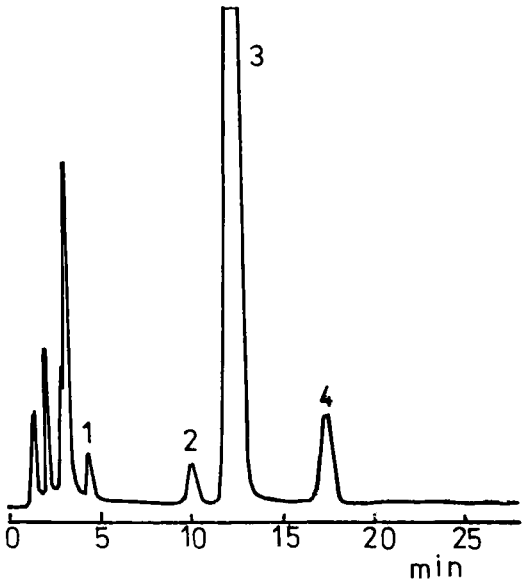


Figure 3. Chromatogram of waste waters sample before the inlet in cleaner after derivatization with phenylizothiocyanate.
Column : Separon C 18; mobile phase : methanol-water (1:1).
Flow rate : 0.5 ml/min; UV detection 254 nm.
1 - methylamine derivative;
2 - dimethylamine derivative;
3 - phenylizothiocyanate;
4 - unidentified amine derivative.

phatic amines were in the aqueous solutions stable and their concentration has not changed during 24 hours.

In the case of phenylizothiocyanate no concentration changes or the formation of decomposition products have been observed during 24 hours. In the aqueous solution of the p-toluenesulphochloride products of decomposition were formed during 24 hours. This effect may be probably explained on the basis of the reaction of p-toluenesulphochloride with water.

TABLE 1

Determination of amines after derivatization with phenylizothiocyanate in waste waters before inlet (A) and after outlet (B) from the purification plant

Methylamine

Sample number	A mg/liter	B mg/liter	effectivity of purification plant /%/
1	0.65	0.41	36.9
2	0.48	0.29	39.6
3	0.60	0.38	36.7
4	0.54	0.33	38.9
5	0.60	0.36	40.0

relative standard deviation was ± 4.8 % in 3 measurements

Dimethylamine

Sample number	A mg/liter	B mg/liter	effectivity of purification plant /%/
1	0.38	0.20	47.4
2	0.28	0.16	42.9
3	0.31	0.17	45.2
4	0.26	0.14	46.2
5	0.28	0.16	42.9

relative standard deviation was ± 6.3 % in 3 measurements

The samples were taken from waste waters before the inlet into the cleaner of waste waters as well as during their outlet so that it might be possible to control the performance of the purification plant for methyl- and dimethylamine, respectively. During the derivatization with phenylizothiocyanate in the waste water both methylamine and dimethylamine could be determined since the interference with further peaks of unknown substances did not occur. Figure 2 presents the chromatogram of waste water be-

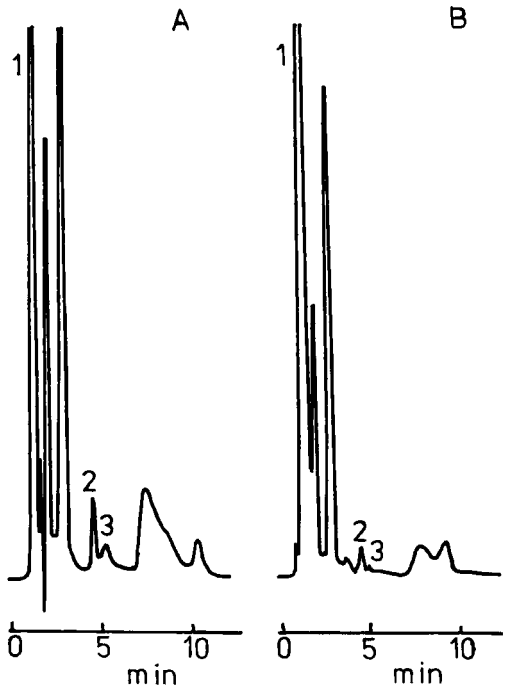


Figure 4. Chromatogram of waste water sample before the inlet (A) and after the outlet (B) from the purification plant after derivatization with p-toluenesulphochloride.
Column : Separon C 18; mobile phase : methanol-water (1:1)
Flow rate : 0.5 ml/min; UV detection 254 nm
1 - p-toluenesulphochloride
2 - the derivative of methylamine
3 - the derivative of dimethylamine.

fore the inlet purification plant without derivatization and Figure 3 presents the chromatogram of the same sample after the derivatization. By the comparison of these chromatograms it is obvious that besides methylamine and dimethylamine also other, up till now unidentified amines with different concentration occur in the sample of the waste water which may be assumed on the basis of the se-

TABLE 2

Determination of amines after derivatization with p-toluenesulphochloride in waste waters before inlet (A) and after outlet (B) from the purification plant

Methylamine

Sample number	A mg/liter	B mg/liter	effectivity of purification plant /%/
1	0.61	0.42	31.1
2	0.44	0.27	38.6
3	0.61	0.36	41.0
4	0.50	0.31	38.0
5	0.56	0.34	39.3

relative standard deviation was $\pm$ 5.1 % in 3 measurements

Dimethylamine

Sample number	A mg/liter	B mg/liter	effectivity of purification plant /%/
1	0.36	0.18	50.0
2	0.27	0.14	48.1
3	0.28	0.15	46.4
4	0.25	0.12	52.0
5	0.27	0.15	44.4

relative standard deviation was $\pm$ 6.9 % in 3 measurements.

lective reaction of phenylizothiocyanate with the primary and secondary amines. The presented chromatograms document the connection of selectivity of the derivatization reaction with that of the chromatographic system. Similar chromatograms were obtained during the analysis of waste water which was taken during the outlet from the purification plant of waste water.

The quantitative evaluation was made on the basis of the regression analysis where the dependence between the

areas of peaks of reference substances and the quantity determined. The preparation of reference solutions of the methylamine and dimethylamine derivative was made in the same way as the derivatization of the sample of waste waters. The concentration range was from 0.4 mg/l to 1.8 mg/l. The value of the correlation coefficient was 0.976 by which the linearity of the dependence is proven. The obtained results of dimethylamine determinations after the derivatization with the phenylizothiocyanate before the inlet and after the outlet from the purification plant, respectively, are presented in Table 1.

Similarly we determined methylamine and dimethylamine, respectively, with p-toluenesulphochloride. Figure 4 presents chromatographic records of waste water before the inlet and after the outlet from the purification plant after the derivatization from which the performance of purification plant is obvious. Table 2 summarizes the results of methyl- and dimethylamine determinations.

By the comparison of results presented in Table 1 and Table 2, respectively, good accordance is evident although in the case of derivatization with the p-toluenesulphochloride lower results are achieved. F-test has shown that the results obtained by both methods are identical to the 95 % probability.

The performance of purification plant is somewhat higher in the case of dimethylamine which may be caused by lower conntents of this amine compared with the methylamine.

The presented methods of the determination of amines were proposed for the control of the waste waters purification. Their advantage is also in the possibility of determination further aliphatic amines.

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