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Membrane Extraction of Selected Nitrogen-Containing Compounds from Crude Industrial Waste Water

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APPLICATION SUMMARY

A procedure to analyze several semi-polar, nitrogen-containing compounds in untreated industrial waste water by means of membrane extraction is described. The selected analytes cover a broad range of volatility and can be extracted with either chloroform or diisopropyl ether. Recoveries are 40 – 110% for test solutions containing approximately 250 µg/L.

INTRODUCTION

The analysis of semi-polar, nitrogen-containing compounds in untreated industrial waste water is a challenging task. Firstly, liquid-liquid-extraction proves difficult for mid-polar compounds because of their poor extractability with solvents that are not water miscible. Secondly, waste water tends to form very stable emulsions which inhibit the phase separation. Thirdly, solid phase extraction as an alternative sample preparation is only suitable for selected compounds and may suffer from cartridge overload. Therefore, a liquid-liquid-extraction assisted by a third phase could be the method of choice.

In our study we combine two effects: A membrane prevents emulsion formation, and the addition of a salt enhances the extraction efficiency and allows the use of slightly water miscible extraction solvents such as diisopropyl ether (12 g/L at 20°C) or chloroform (8 g/L at 20°C).

INSTRUMENTATION

GC : HP 6890 Series Plus (Agilent)

MS : HP 5973 (Agilent)

Autosampler: CombiPAL (CTC)

Injector : KAS 4 (Gerstel)

Injection volume: 1 µL, split ratio 1:10

Injector temperature: 250°C

Temperature program GC: 40°C (0.2 min); 20°C/min; 250°C (5 min)

MS mode: full scan 29 – 250 amu

GC column: DB-5 ms, 30 m, 0.25 mm i.d., 1.0 µm df
30 µm polypropylene extraction membranes (Gerstel)

CHEMICALS

Methanol, chloroform, diisopropyl ether, heptane, hexane, cyclohexane and potassium carbonate in analytical grade quality.

Model analytes: Caprolactame (CAS-No. 105-60-2), aniline (CAS-No. 62-53-3), 2-methyl aniline (CAS-No. 95-53-4), N-methyl aniline (CAS-No. 100-61-8), 2-methyl pyridine (CAS-No. 109-06-8), N-methyl acetamide (CAS-No. 79-16-3), N,N-dimethyl acetamide (CAS-No. 127-19-5), N-methyl pyrrolidone (CAS-No. 872-50-4), and N,N-dibutyl formamide (CAS-No. 761-65-9).

Analyte standard solution: The model analytes were dissolved in methanol to a concentration of approx. 0.2 mg/mL each. The standard solution was used to spike aqueous samples to yield a final concentration of approx. 250 µg/L.

SAMPLE PREPARATION

Twelve g of potassium carbonate were weighed into a 20 mL headspace vial, subsequently 10 mL of the aqueous sample were added. The sample was either demineralized water spiked with the analyte standard solution or crude waste water. Subsequently, the membrane extraction insert was placed inside the vial and filled with 800 µL extraction solvent. The spike level for recovery experiments was in the 250 µg/L range. New membranes were used without preconditioning. The vial was closed with a crimp cap and placed in the CTC CombiPAL autosampler. After 30 min incubation at 55°C and 750 rpm agitation the vial was cooled to room temperature. The volume of the organic phase in the membrane extraction insert was measured with a syringe and the solvent was transferred into a 2 mL au-

tosampler vial. The extract was analyzed by GC-MS. For extraction recovery experiments chloroform was spiked directly with the analyte standard solution and injected into the GC-MS. The resulting peak areas served as a reference for the recovery calculation.

Note: The vials were placed on top of special inserts for 10 mL vials, which cause the top third of the vials to protrude from the oven. Thus, solvent vapors condensed on the cooler glass wall.

RESULTS AND DISCUSSION

To illustrate the effect of emulsion formation, Figure 1 shows a picture of a sample 24 h after liquid-liquid-extraction. Even after 24 h the upper (organic) phase is turbid, which indicates dispersed water. The residue in the bottom of the vial is potassium carbonate. Membrane extraction is one possibility to simply avoid emulsions.



Figure 1. Picture of a waste water sample 24 h after liquid-liquid-extraction. The (upper) organic phase is still turbid, which indicates an emulsion.

The initial membrane extraction experiments were carried out to select the appropriate solvent. Solvents tested were hexane, cyclohexane, heptane, diisopropyl ether and chloroform. Diisopropyl ether and chloroform were suited best regarding analyte recovery and recovered volume of the organic phase after the extraction process, respectively.

Figure 2 shows a chromatogram of the analyte standard solution diluted in chloroform to approx. 250 µg/L. The same solution was subsequently used to spike water, which was then membrane-extracted. The corresponding chromatogram is shown in Figure 3.

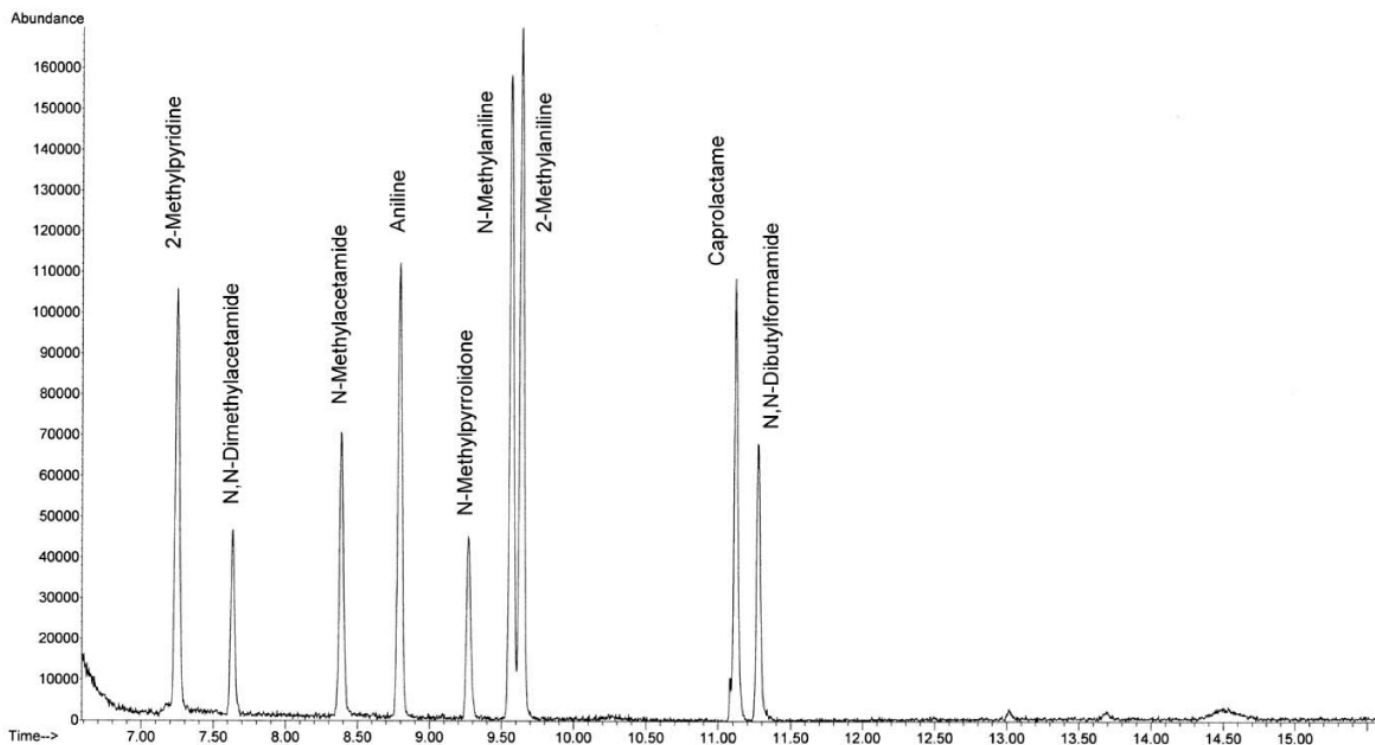


Figure 2. Chromatogram of the diluted analyte standard solution

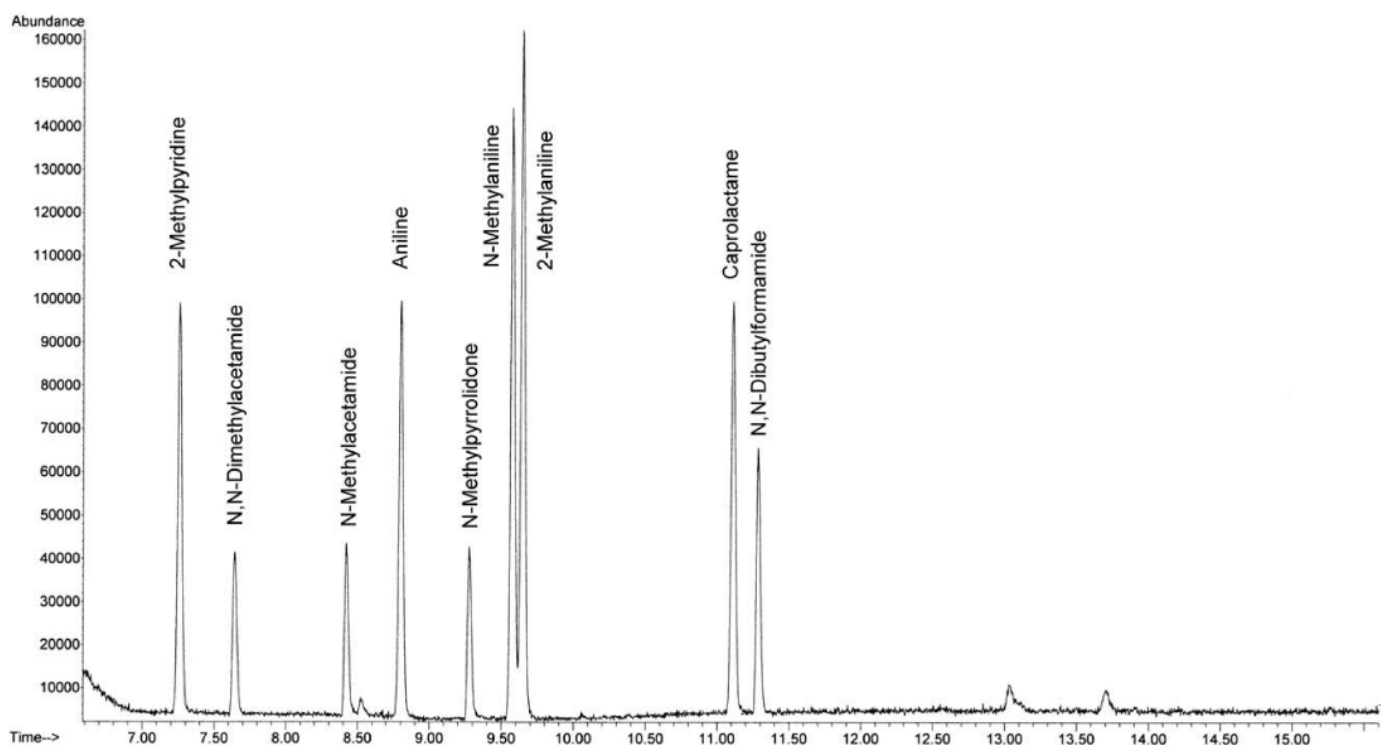


Figure 3. Chromatogram of a spiked aqueous sample after membrane extraction.

Of the 800 μL chloroform used for extraction only 650 μL can be recovered, the rest permeates the membrane and is dissolved in the aqueous phase. For assessing the recovery or any quantitation it is therefore necessary to correct for the loss of organic phase. The bar diagram

in Figure 4 shows the volume-corrected recovery of the model analytes. For most analytes the recovery is high (80-110%), except for N-methyl acetamide, which has a relatively poor recovery of approx 40%.

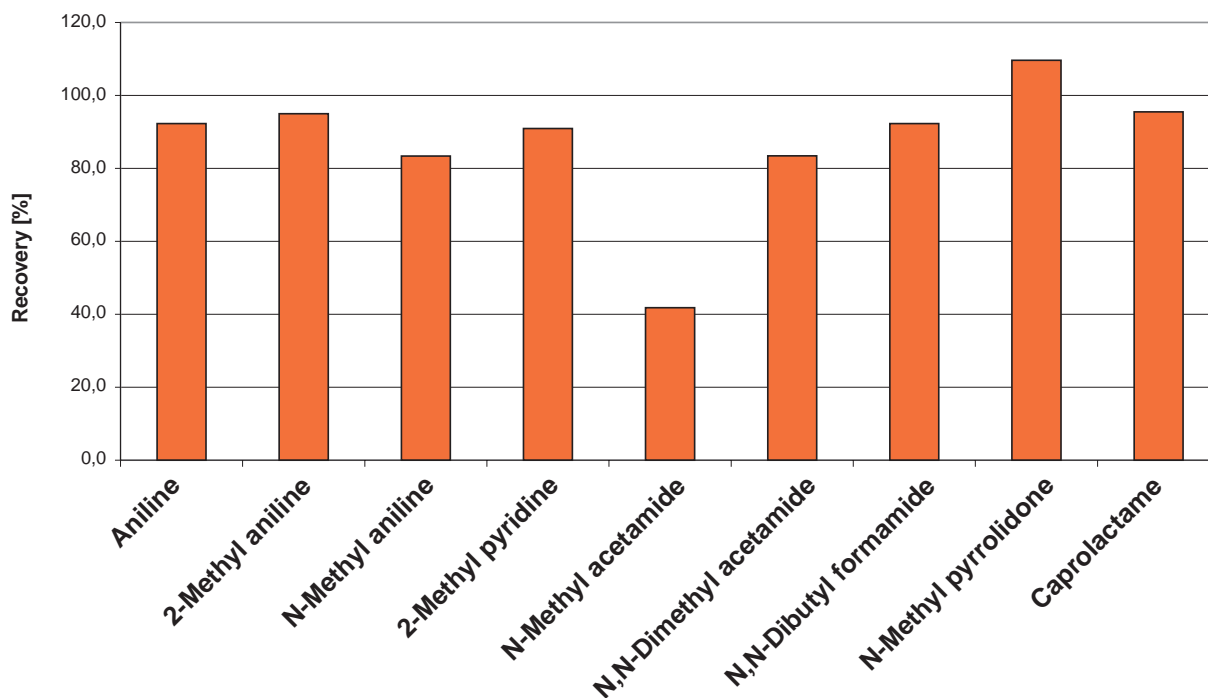


Figure 4. Recovery of the model analytes after membrane extraction.

To demonstrate the feasibility of the extraction technique untreated industrial waste water was analyzed using membrane extraction. Figure 5 shows the resulting chromatogram. Not all of the model compounds

are present in the sample, therefore the peaks for the acetamides, N,N-dibutyl formamide and 2-methyl pyridine are missing.

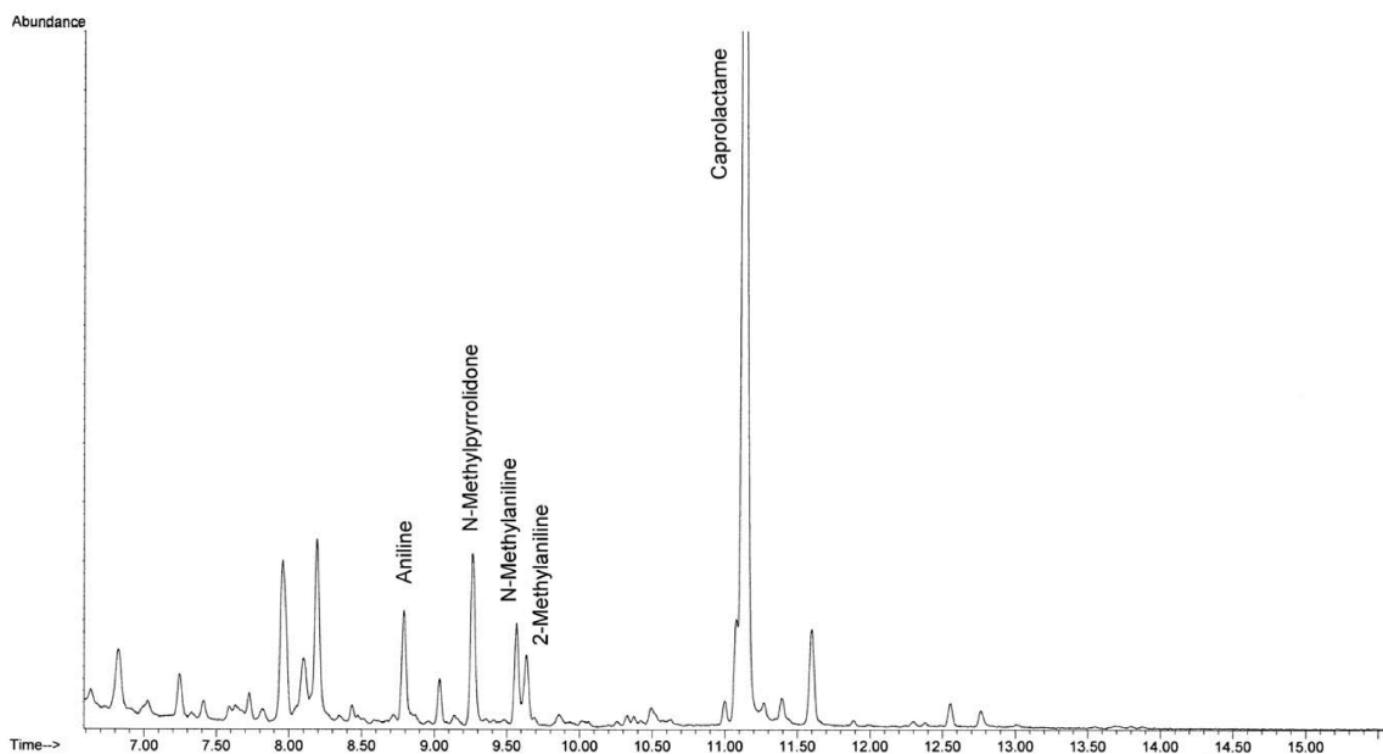


Figure 5. Chromatogram of a crude waste water sample after membrane extraction.

CONCLUSION

We demonstrated that membrane-assisted extraction is a suitable means of sample preparation for the analysis of semi-polar, nitrogen-containing compounds even in crude waste water. This technique requires minimal sample pre-treatment, avoids the formation of emulsions and can additionally be automated if required.



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