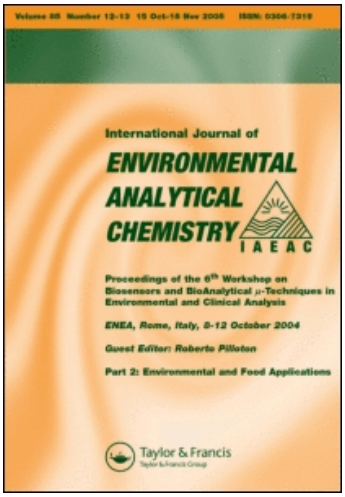


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# Sampling and Analysis of Odorous Compounds in Water Treatment Plants

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# Sampling and Analysis of Odorous Compounds in Water Treatment Plants†

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KEY WORDS: Odorous components, water treatment, capillary GC-MS, activated carbon sampling.



The following analytical method has been used to identify some odorous compounds in the air of the water treatment plant Werdhölzli, Zurich: sampling of contaminated air with the help of activated carbon, desorption by the solvents carbon disulphide and methylene chloride, separation of the carbon disulfide extract into a polar and a nonpolar fraction by adsorption column chromatography on silica. Hereafter gaschromatographic analysis of the polar fraction on glass capillary column (Ucon HB 5100); detection and identification were achieved by flame ionisation, thermoionic nitrogen selective detector and computerized mass spectrometry (Finnigan 3200 F, data system 6110).

The results show the presence of sulfur compounds: thiophenes, thiazoles; nitrogen compounds: pyrazines; oxygen compounds: phenols, alcohols and some unsatured hydrocarbons. The malodorous compounds were sulfur and nitrogen compounds in the range of 0.01–0.1 ppm.

## INTRODUCTION

In metropolitan areas, where land is markedly scarce, the problem of annoying odors in the vicinity of water treatment and wast composting plants has intensified sharply. These plants are sources of odor emissions and in recent years, the number of complaints about disagreeable odors has approached the total of all other air pollution complaints received by authorities.

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Feeling of annoyance impairs public well-being and—according to WHO definition—the health. The determination of odor nuisance is a very complex problem and there is still a lack of objective criteria.

Sensation of odor is an effect caused by odorants when they reach chemoreceptors in the nose. Thus, odor measurements may utilize two different approaches. The identity and the concentration of odorants in air can be established by appropriate analytical methods. The odor sensation, which is a physiological and psychological effect, can be evaluated using sensory methods which evaluate human responses to the odorous air. However, even if the components of the mixture are identified, conclusions of the odor properties are not yet possible because of synergism and antagonism of the odorants.

This study included:

—a method of sampling gaseous components in malodorous air
—analysis and identification of these organic components
—characterisation of the odorants relative to odor activity in the air of the water treatment plant Werdhölzli, Zurich, Switzerland.

## METHOD

Volatile, mostly organic compounds evoke an odor sensation. The most adequate approach involves scanning the composition for all possible odorants. This is approximated by gaschromatographic techniques. However, because of the necessity to measure very low concentrations, such analysis must be preceded by a preconcentration step. In this study it is performed by activated carbon adsorption and desorption by solvent.[1,2] During this enrichment process all components, mainly odorless hydrocarbons, are concentrated. These hydrocarbons overlap the odorous components to be determined in the gaschromatographic analysis. We assumed that odorous compounds have mostly functional groups in the molecule, which make them more polar than the hydrocarbons. The question then was: is it possible to preseparate the complex multicomponent mixture into a nonpolar and a polar fraction, in which the odorants are found?

Based on test experiments we developed the scheme of analysis presented in Figure 1. The results of these test experiments were as follows: first a preseparation step takes place through desorption by the solvents carbon disulphide and methylene chloride due to their different polarity. Then a second one through elution of the carbon disulphide extract with pentane, methylene chloride and ether on silica gel.

For sampling we utilized glass tubes of 8 cm length and 0.6 cm inner diameter, filled with 1.0–1.5 g of activated carbon. Before sampling the

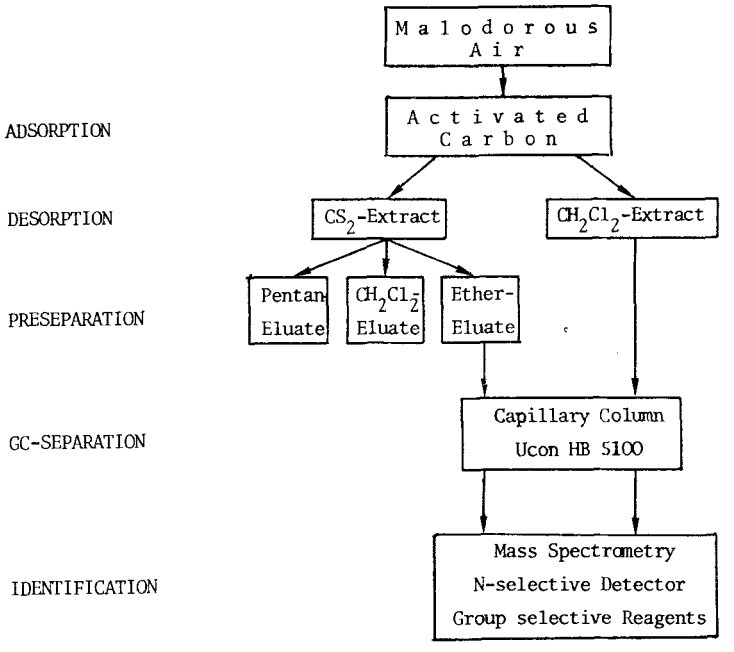



FIGURE 1 Scheme of analysis

charcoal tube was cleaned by extraction with methylene chloride and drying with nitrogen The charcoal tubes were connected to a pump equipped with a gasmeter. The air flow was not to exceed 4 l/min.

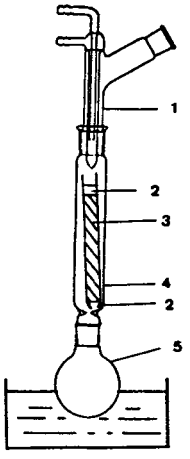
The desorption was achieved by extracting twice with 2.5 ml of carbon disulphide and thereafter with 2.5 ml of methylene chloride. Figure 2 shows the desorption device.

For preseparation the carbon disulphide extract was separated by adsorption column chromatography on silica gel into three fractions. The polar constituents eluted with ether were analysed by glass capillary column after evaporative concentration; the nonpolar eluates of pentane and methylene chloride were left out.

For GC-separation the methylene chloride extract and the ether eluate were expected to contain the odorous compounds.

The gaschromatographic conditions were:

| | |
|---|---|
| Gaschromatograph: | Carlo Erba GI 450 |
| Column: | Ucon HB 5100, 50 m $\phi_i$ 0.31 mm separation number 54 |
| Carrier gas: | Hydrogen 0.65 at |
| Heating: | T-progr. 80° (10 min); 4 /min to 170° |




1 Cooler
2 Glasswool
3 Activated Carbon
4 Intermediate Piece
5 Flask 5 ml

FIGURE 2 Apparatus for desorption

| | |
|---|---|
| FID: | Air 1.2 at; Hydrogen 0.35 at |
| N-selective detector: | Air 1.1 at; Hydrogen 0.7 at; Helium 50 ml/min |

For identification a Finnigan GC-MS combination (Model 3200 F) combined with an on-line computer (Model 6110) was used.[3] Further information was obtained with the help of a nitrogen selective detector and by vibration of samples with different group selective reagents.



## RESULTS

A 5 $m^3$ sample of malodorous air was taken in the sedimentation tank at the sewage treatment plant Werdhölzli, Zurich. Figure 3 shows a FID chromatogram of the methylene chloride extract and Figure 4 that of the ether eluate. The pentane and methylene chloride eluates were not analysed, they contain primarily aliphatic, respectively aromatic hydrocarbons.

In Tables I and II the proposed structures from the MS interpretation are listed. * means, the compound could be verified by injection of the corresponding pure substance and thereafter by comparison of the retention times. The verification was restricted to substances available on the market.

The results show the present of sulfur compounds (thiophenes, thiazoles); nitrogen compounds (pyrazines, amides); oxygen compounds (phenols, alcohols) and some unsaturated hydrocarbons. The concentrations ranged from 0.01 to 0.1 ppm.

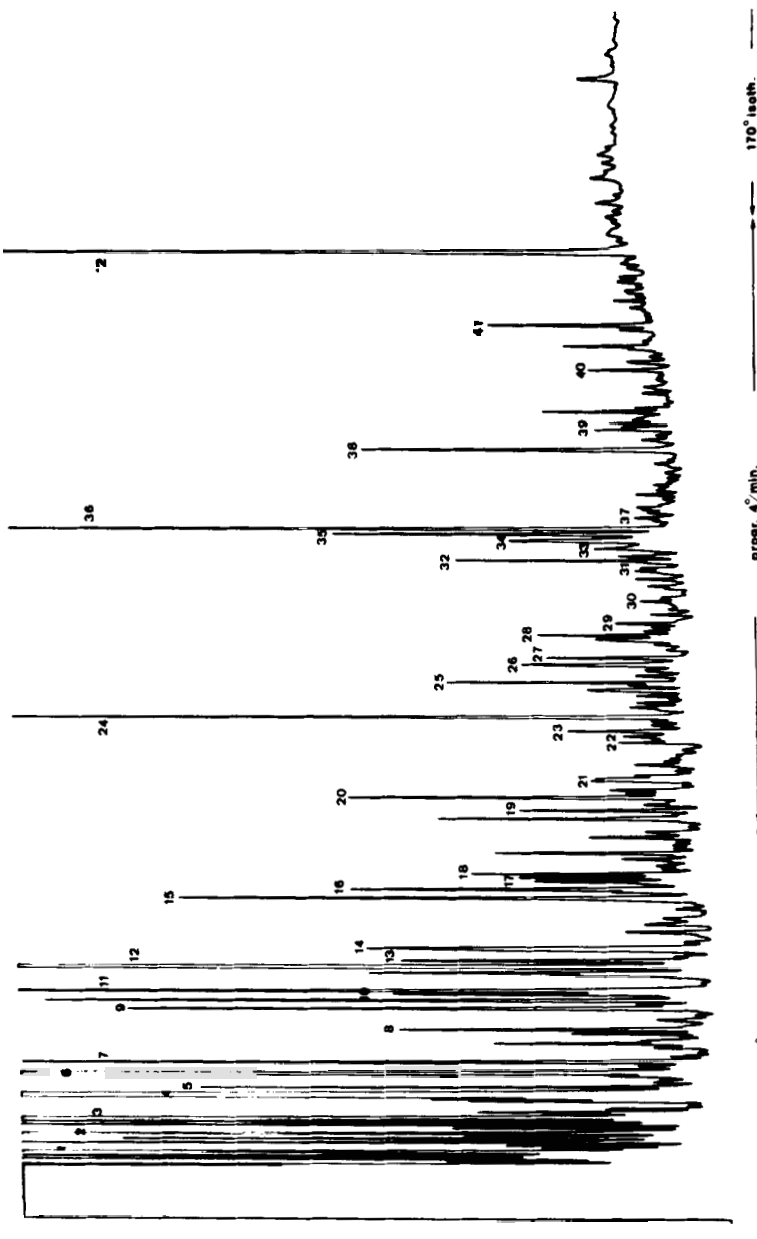



FIGURE 3 Methylene chloride extract of a sample in the sedimentation tank of Werdhölzli (FID). For peak identification see Table I.

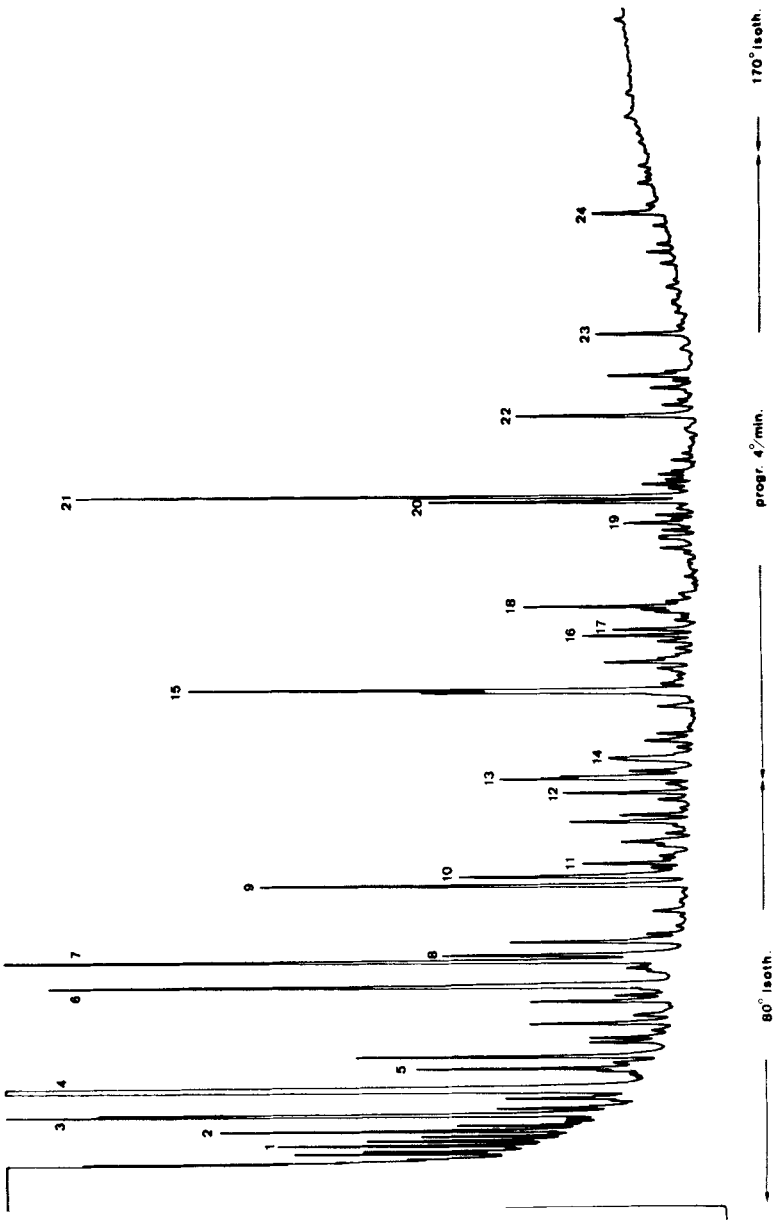



FIGURE 4 Ether eluate of a sample in the sedimentation tank of Werdhölzli (FID). For peak identification see Table II.

## CHARACTERISATION OF THE IDENTIFIED ODORANTS

The odorants available on the market were judged by simple sensory testing (see Table III).

The odor in the sedimentation tank is intense and burning. If one mixes all components mentioned above together, a different odor sensation from the air of the sedimentation tank is noticed. The pyrazines and benzothiazole come closest to the original odor sample. This means, that a number of further odorous components must be present.

## CONCLUSION

The odorous components in a sample of malodorous air are in a much lower concentration than the hydrocarbons present in general ambient air. The separation efficiency of capillary chromatography is rather small to detect the odorants besides the hydrocarbons. As the results in Tables I and II show, it is possible to solve this separation problem by a simple

TABLE I

List of proposed structures for the odorants found in the methylene chloride extract of a sample taken from the sedimentation tank, Werdhölzli (see also Figure 3).

| No. | Component | No. | Component |
|---|---|---|---|
| 1 | iso-Butanol | 23 | ? |
| 2 | n-Butanol* | 24 | 2-Ethylhexanol |
| 3 | Pyrazine* | 25 | Octadien |
| 4 | 2-Metyl-l-butanol | 26 | ? |
| 5 | Methylthiazole | 27 | ? |
| 6 | 2-Methylpyrazine | 28 | ? |
| 7 | ? | 29 | ? |
| 8 | ? | 30 | ? |
| 9 | 2,5-Dimethylpyrazine* | 31 | N,N-Dimethylacetamide |
| 10 | ? | 32 | ? |
| 11 | 2-Ethylpyrazine | 33 | Acetamide* |
| 12 | Diacetonealcohol* | 34 | ? |
| 13 | 2-Methylhexadien | 35 | 2-Acetylthiophene* |
| 14 | Dimethyltrisulfide | 36 | 3-Acetylthiophene |
| 15 | Ethylmethylpyrazine | 37 | ? |
| 16 | Ethylmethylpyrazine | 38 | Dimethylethylthiophene |
| 17 | Ethylmethylpyrazine | 39 | ? |
| 18 | Trimethylpyrazine | 40 | Decanol |
| 19 | 2-Nonanone | 41 | Phenol* |
| 20 | ? | 42 | p-Cresol* |
| 21 | ? | | |
| 22 | Octen | | |

TABLE II

List of proposed molecular structures for the odorants found in the ether eluate of a sample taken from the sedimentation tank Werdhölzli (see also Figure 4).

| No. | Component | No. | Component |
|---|---|---|---|
| 1 | iso-Butanol | 13 | Dimethylethylpyrazine |
| 2 | n-Butanol* | 14 | Dimethylethylpyrazine |
| 3 | 2-Hexanone* | 15 | 2-Ethylhexanol |
| 4 | Methylbutanol | 16 | ? |
| 5 | Methylcyanopyrrole | 17 | 2-Octanol |
| 6 | Ethylpyrazine | 18 | Acetophenone* |
| 7 | Diacetonealcohol* | 19 | Dimethyloctanol |
| 8 | 4-Methylpentanol-(2) | 20 | 2-Acetylthiophene* |
| 9 | Ethylmethylpyrazine | 21 | 3-Acetylthiophene |
| 10 | Ethylmethylpyrazine | 22 | Methylpropylthiophene |
| 11 | Ethylmethylpyrazine | 23 | t-Butylthiophene |
| 12 | Dimethylethylpyrazine | 24 | Benzothiazole* |

TABLE III

Characterisation of the identified components with respect to their odor and intensity

| Odorant | Description | Intensity | Odor threshold ppm (1, 4, 5) |
|---|---|---|---|
| Pyrazine | bitter, burning | × | — |
| 2-Methylpyrazine | bitter, burn. | × | — |
| 2,5-Dimethylpyrazine | bitter, burn. | × × | — |
| Acetamide | oily, burn. | × × | — |
| 2-Acethylthiophene | aromatic, spicy | × | — |
| Benzothiazole | burn. rubber | × × × | — |
| Diacetone alcohol | sweet, etherical | × | $2.8.10^{-1}$ |
| Acetophenone | spicy | × | $1.7.10^{-1}$ |
| n-Butanol | etherical | × | 11 |
| 2-Hexanone | sweet | × | 8 |
| Phenol | medicinlike | × × | $6.5.10^{-1}$ |
| p-Cresol | tarlike, sharp | × × × | $4.7.10^{-4}$ |

× × × : maximum × : minimum



preseparation step on silica gel into a polar and a nonpolar fraction. The disadvantage is a further analytical step, which makes a subsequent quantification more difficult.

In this way of odor analysis, a list of odorous compounds is obtained, which has no claim to completeness. Furthermore only an intelligent guess

can be made of the entire odor sensation, and only this "entire odor sensation" is of hygienic relevance. But the list of odorants gives the base for the choice of leed components, whose concentration correlate with the sensation of panelists. It is also useful for process control, e.g. design of air purification systems.

The method of sampling air passed the test in practice. The necessary equipment (charcoal tubes, air pump, gasmeter) can easily be handled. The expenses of analysing odorous air are considerable, but once the major compounds of interest are known, routine analysis can be done.

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