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DETERMINATION OF ODOROUS VOLATILES IN AIR USING CHROMATOGRAPHIC PROFILES

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SUMMARY

Chromatographic profiles have shown that dimethyl sulphide, polysulphides, alkylated and acetylated thiophenes, alkylated pyrazines and indole are mainly responsible for the odour emission from a municipal sewage plant. Oxygen compounds, such as lower fatty aldehydes and free fatty acids, are essential for the characteristic odour. Malodorous air was sampled over activated carbon. After desorption with dichloromethane the odour can be assessed by an N and S odour profile obtained by glass capillary gas chromatography with N- and S-selective detectors.

It is shown that ammonia chemical-ionization mass spectrometry can also be used advantageously to establish an odour profile of a complex, mainly non-odorous hydrocarbon-containing, matrix. The proposed method for odour studies is highly selective and sensitive.

INTRODUCTION

The exact measurement of odour emissions from sewage plants, animal breeding stations, slaughter houses, etc., is still unsatisfactory. There are often arguments between the plant management and the neighbours about odour complaints without definite evidence on either side about odour quality, intensity and distribution.

The odorous compounds (osmogenes) are mainly aerobic and anaerobic decomposition products of carbohydrates and proteins. Recent investigations of the odour emission from municipal sewage plants¹⁻⁴ have shown that biogenic sulphur and nitrogen compounds such as sulphides, polysulphides, thiophenes and pyrazines are probably the principal osmogenes responsible for the odour complaints. Oxygen compounds such as lower fatty aldehydes and free fatty acids are essential for the characteristic odour observed.

In principle, there are two methods for the determination of odorous biogenic emissions: (1) via the sensory effect (the olfactometric method) and (2) via identification of the osmogenes (the physico-chemical method).

The human nose is probably the most sensitive detector able to perceive and identify odours in concentrations that are not detectable by physico-chemical detectors. However, the results obtained are highly dependent in a very unsatisfactory way

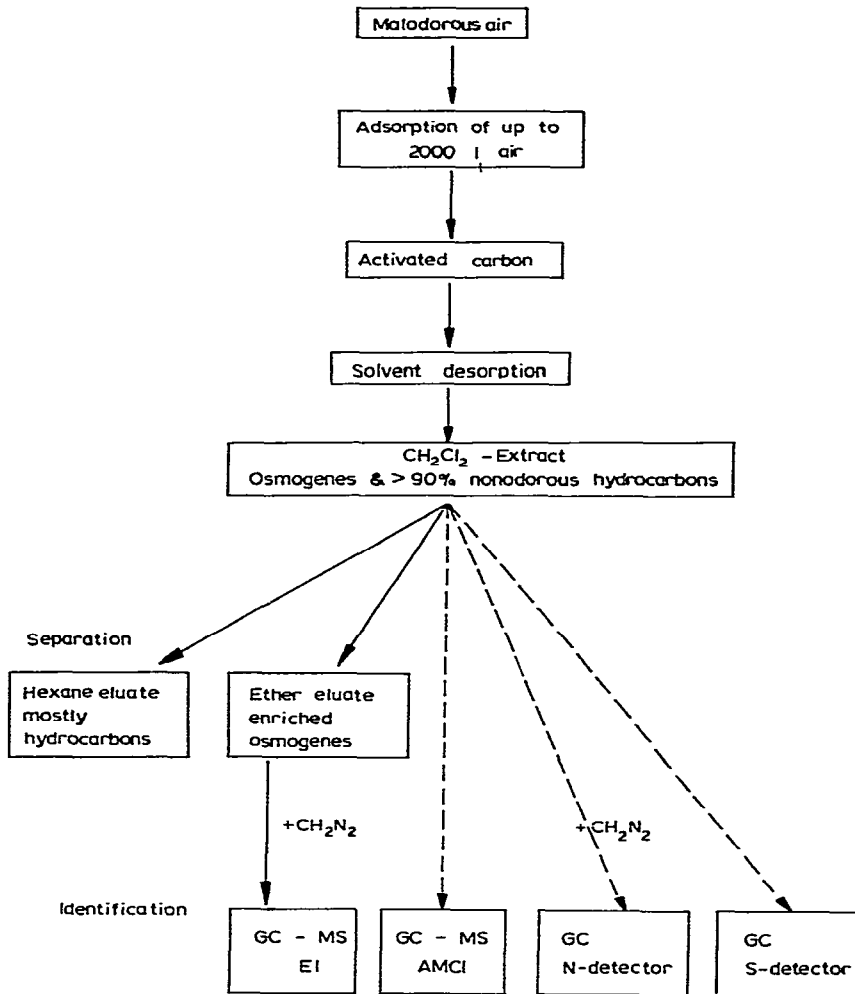


Fig. 1. Scheme of analysis.

on the choice of test persons, which makes this method unreliable. The identification and quantification of the osmogenes, for example, by computer-assisted high-resolution glass capillary gas chromatography combined with mass spectrometry (COM-GC-MS), open up new possibilities for the exact measurement of odour emissions. The principal question is whether there are key compounds correlating with the character and intensity of the odour observed.

Our investigations^{3,4} on the determination of key compounds in the emissions of a municipal sewage plant were carried out in the following way (see Fig. 1). To be able to identify the odorous compounds present at the 0.01–0.1 ppm level, it was necessary to remove the bulk of the masking non-odorous hydrocarbons (>90%) by column chromatography over silica, as described by Hangartner and Wanner¹. The enriched osmogenes in the ethereal eluate were then investigated, after methylation with diazomethane, by COM-GC-MS in the electron-impact mode. The results have

already been published^{3,4}. At present, it can be assumed that dimethyl sulphide, polysulphides, alkylated and acetylated thiophenes, alkylated pyrazines and indole are mainly responsible for the odour emission from a municipal sewage plant. Oxygen compounds, such as lower fatty aldehydes and free fatty acids, are essential for the characteristic odour observed. As expected, no thiophenes or pyrazines are present in the raw sludge odour emission, because these compounds are secondary products formed by the thermal treatment of the sludge's sulphur-containing amino acids and/or by Maillard reactions. It might therefore be possible to differentiate between both emission sources.

The greatest problem with the analysis of these and similar odour emissions is the high concentration of non-odorous hydrocarbons, which prevents the direct identification and quantification of the osmogenes present and, thus, the characterization of an odour situation by a GC odour profile. Even the extracted ion-current profiles (EICPs) of the osmogenes are not useful as an odour profile because of the high background of hydrocarbon ions. In quantitative work, removal of the hydrocarbons by column chromatography over silica is very difficult, because it is tedious and losses of volatile osmogenes easily occur.

With nitrogen- and sulphur-containing compounds the odour situation can be assessed, as shown later, by GC² with N- and S-selective detectors. The disadvantage of this method is that only by using pre-determined GC retention times can one be certain of measuring the characteristic osmogenes. A mass spectrometric method that allows selective detection, identification and quantification of the trace concentrations of osmogenes hidden in the bulk of hydrocarbons would be very welcome. The preliminary results reported in this paper show that by ammonia chemical-ionization mass spectrometry (AMCI-MS) this problem might be solved. In contrast to methane or isobutane CI-MS, the use of ammonia as a reagent gas allows the selective ionization of the basic components of a complex mixture. Aliphatic and aromatic hydrocarbons are not ionized. Whether odorous oxygen and sulphur compounds, such as aldehydes, alcohols, ketones, fatty acid methyl esters, phenols and thiophenes, are also preferentially ionized is not known in detail⁵.

EXPERIMENTAL

Sampling and preparation of an odour concentrate

Sampling was carried out in the thermal sludge treatment plant directly in the run-off of the sludge filtrate. The malodour observed was typical of the odour emission from this part of the sewage plant. Up to 2000 l of malodorous air was sampled over 200 mg of activated carbon (modified activated carbon from Bendix, Lewisburg, WV, U.S.A.; filter stainless-steel tube, 3 × 1/4 in.) using a Bendix BDX 44 air sampler with a flow-rate of 0.3 l min⁻¹. The sampling tubes were extracted for about 6 h by refluxing with 2–3 ml of dichloromethane. The extract was concentrated to 1 or 0.5 ml using a micro Kuderna–Danish concentrator.

Chromatographic conditions

S profile. The column was a 50 m × 0.25 mm I.D. glass capillary coated with OV-101 (WGA. Griesheim, G.F.R.); the temperature was held for 5 min at 50°C, then increased to 200°C at 10°C min⁻¹; the carrier gas was helium at a flow-rate of 1 ml min⁻¹; a Carlo Erba Model 250 S-selective detector was used.

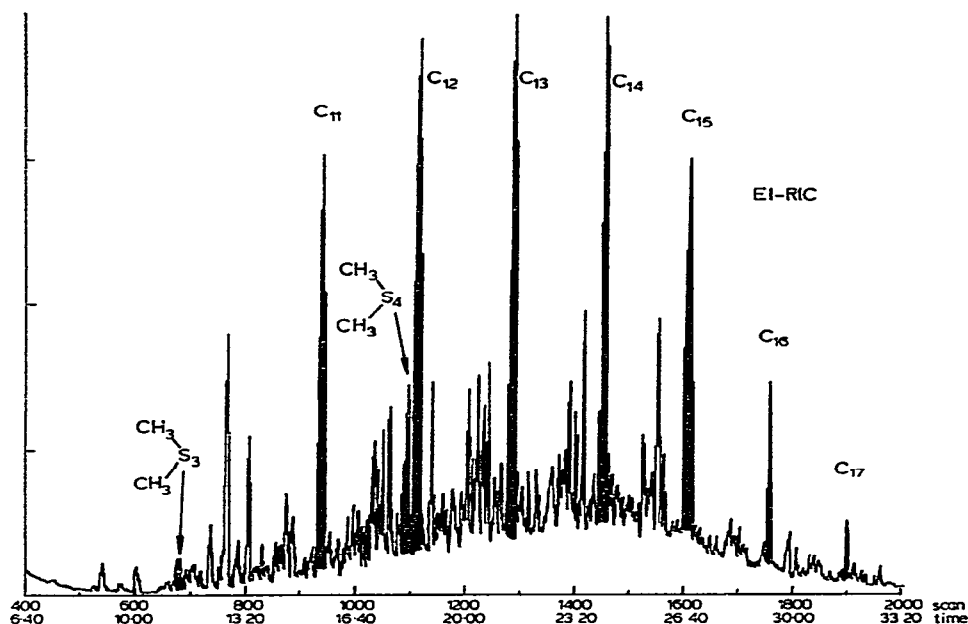


Fig. 2. Reconstructed ion chromatogram (EI-RIC) of the dichloromethane extract of a malodorous air sample from a thermal sludge treatment plant.

N profile. The column was a 50 m × 0.25 mm I.D. glass capillary with UCON HB 5100 (WGA); the temperature was held for 10 min at 50°C, then increased at 10°C min⁻¹ to 80°C and at 5°C min⁻¹ to 200°C; the carrier gas was helium at a flow-rate of 1.2 ml min⁻¹; a Carlo Erba Model 793 N,P-selective detector was used.

GC. The column was a 50 m × 0.25 mm I.D. glass capillary coated with OV-1 (Jaeggi, Trogen, Switzerland); the temperature was held for 5 min at 40°C, then increased rapidly to 80°C and at 5°C min⁻¹ to 250°C; the carrier gas was helium at a flow-rate of 1 ml min⁻¹.

GC-MS. The GC capillary was combined directly with the ion source of a Finnigan 4000 quadrupole EI/CI mass spectrometer. Positive CI mass spectra were recorded continually with an Incos data system, using ammonia as reagent gas. The ammonia flow-rate was adjusted to an ion source pressure of 0.30 torr; the ion source temperature was 250°C and the ionization energy 70 eV.

RESULTS

Fig. 2 shows the reconstructed ion chromatogram (EI-RIC) of the dichloromethane extract of a malodorous air sample from a municipal sewage plant. *n*-Alkanes are marked C₁₁–C₁₇ for clarity. This RIC is very similar to analogous chromatograms of non-odorous air samples, except for the peaks identified as dimethyl trisulphide and tetrasulphide. The other peaks are mainly the usual aliphatic and aromatic hydrocarbons and chlorinated hydrocarbons found in polluted air plus phthalates and antioxidants. With the EICP method, only a few 2-alkanones can be

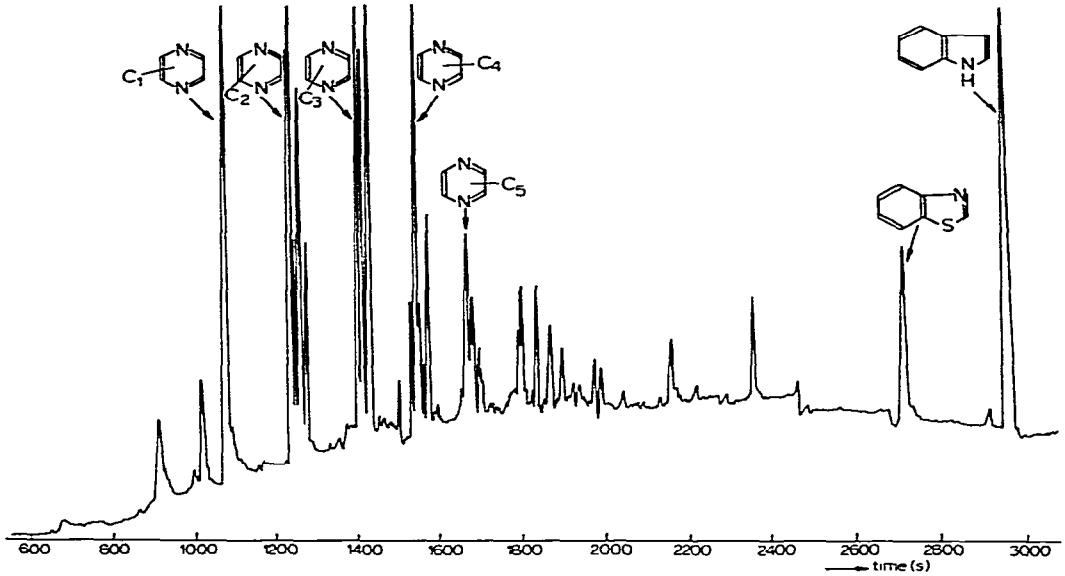


Fig. 3. Nitrogen odour profile of the dichloromethane extract of a malodorous air sample from a thermal sludge treatment plant.

identified and the other osmogenes^{3,4} are not detectable. Figs. 3 and 4 show that by establishing N and S odour profiles an odour situation in a sewage plant can be characterized because the interfering hydrocarbons are not detected.

A clear disadvantage is that the oxygen-containing osmogenes, which con-

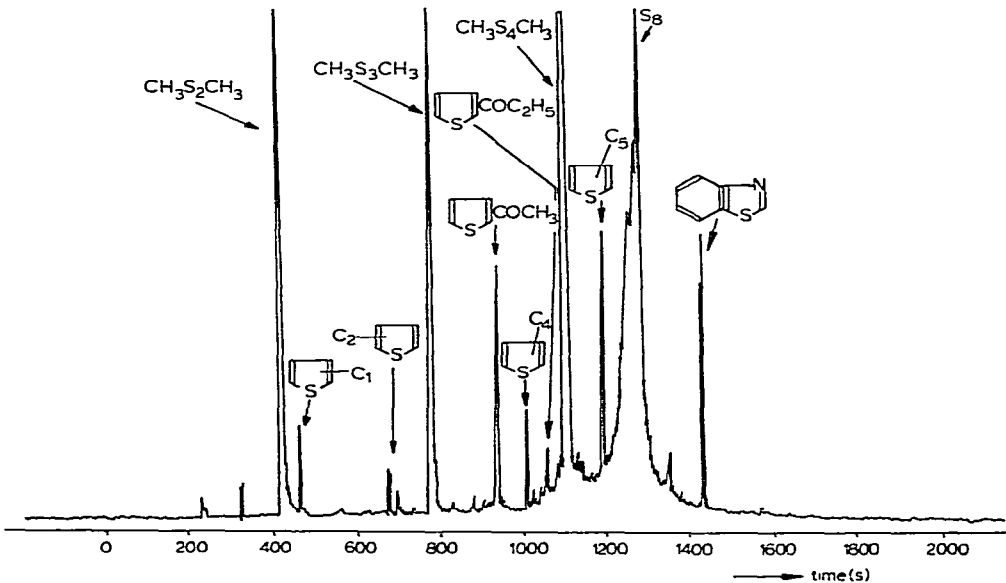


Fig. 4. Sulphur odour profile of the dichloromethane extract of a malodorous air sample from a thermal sludge treatment plant.

TABLE I
AMCI-MS OF COMMON NITROGEN COMPOUND OSMOGENES AT THE 1 ng/ μ l LEVEL

<i>Compound</i>	<i>Ions observed (m/z)</i>	<i>Relative intensity (%)</i>	<i>Relative peak area (methyl dodecanoate = 1.00)</i>
C ₂ -Pyrazine: ethylpyrazine	109 (M + H ⁺)	100	4.09
C ₃ -Pyrazine: 2,3,5-trimethylpyrazine	123 (M + H ⁺)	100	5.95
C ₃ -Pyrazine: 2-ethyl-3-methylpyrazine	123 (M + H ⁺)	100	7.81
C ₄ -Pyrazine: 3-ethyl-2,5-dimethylpyrazine	137 (M + H ⁺)	100	4.30
C ₅ -Pyrazine: 2,3-diethyl-5-methylpyrazine	151 (M + H ⁺)	100	7.38
Indole	118 (M + H ⁺)	100	4.37
2-Methylindole	131 (M + H ⁺)	100	6.27

tribute considerably to the odour, are lost. The problem of measuring the typical key odour compounds by relying on GC retention times only has already been mentioned.

Reports on the AMCI-MS of different classes of organic compounds in the literature are scarce. A well known example is the selective ionization of nitrogen compounds such as nucleosides which are sufficiently good Brønsted bases to accept proton transfer from NH₄⁺. As a result of this finding, Wilson *et al.*⁶ suggested that as the high proton affinity for NH₄⁺ and other reagent ions from ammonia preclude proton transfer to most non-nitrogen-containing compounds, ammonia might serve as a highly selective reagent gas for preferentially ionizing nitrogen-containing compounds.

TABLE II
AMCI-MS OF COMMON SULPHUR COMPOUND OSMOGENES AT THE 1 ng/ μ l LEVEL

<i>Compound</i>	<i>Ions observed (m/z)</i>	<i>Relative intensities (%)</i>	<i>Relative peak area (methyl dodecanoate = 1.00)</i>
C ₂ -Thiophene: 2,5-dimethylthiophene	113 (M + H ⁺); 130 (M + NH ₄ ⁺)	72; 100	1.63
C ₃ -Thiophene: 2-methyl-5-ethylthiophene	127 (M + H ⁺); 144 (M + NH ₄ ⁺)	82; 100	1.50
2-Acetylthiophene	127 (M + H ⁺); 144 (M + NH ₄ ⁺)	86; 100	1.85
C ₄ -Thiophene: 2-methyl-5-propylthiophene	141 (M + H ⁺); 158 (M + NH ₄ ⁺)	100; 94	1.96
C ₆ -Thiophene: 2-butyl-5-ethylthiophene	169 (M + H ⁺); 186 (M + NH ₄ ⁺)	100; 91	1.91
Dimethyl disulphide	94 (M ⁺)	100	2.16
Dimethyl trisulphide	126 (M ⁺); 94 (M - 32 ⁺)	100; 65	2.71

TABLE III
AMCI-MS OF COMMON OXYGEN COMPOUND OSMOGENES AT THE 1 ng/ μ l LEVEL

<i>Compound</i>	<i>Ions observed (m/z)</i>	<i>Relative intensities (%)</i>	<i>Relative peak area (methyl dodecanoate = 1.00)</i>
2-Octanone	129 (M + H ⁺); 146 (M + NH ₄ ⁺)	11; 100	1.89
5-Nonanone	143 (M + H ⁺); 160 (M + NH ₄ ⁺)	13; 100	1.55
2-Methyl-decanone	171 (M + H ⁺); 188 (M + NH ₄ ⁺)	14; 100	2.00
Methyl pentanoate	134 (M + NH ₄ ⁺)	100	1.00
Methyl hexanoate	148 (M + NH ₄ ⁺)	100	1.02
Methyl nonanoate	190 (M + NH ₄ ⁺)	100	1.01
Methyl decanoate	204 (M + NH ₄ ⁺)	100	1.03
Methyl dodecanoate	232 (M + NH ₄ ⁺)	100	1.00
Hexanal	100 (M ⁺); 102 (M + 2H ⁺); 118 (M + NH ₄ ⁺)	100; 92; 33	2.89
Heptanal	114 (M ⁺); 116 (M + 2H ⁺); 132 (M + NH ₄ ⁺)	100; 95; 27	3.02

Although this suggestion is generally valid, there are some non-nitrogen-containing compounds that have unusually high proton affinities, such as conjugated ketones, and thus they readily form [M + H⁺] ions⁷. The fact that characteristic osmogenes are also preferentially ionized in contrast to hydrocarbons in AMCI-MS is shown in Tables I–III, which give some preliminary results. Mixtures of the more common osmogenes were investigated at the 1 ng/ μ l level. In the mass spectra of most compounds very intense M + H⁺ ions are observed, and occasionally also additional collision-induced M + NH₄⁺ ions. There is almost no fragmentation of the molecules.

These results show that not only the basic nitrogen compounds are ionized, but also in lower yields the common polar oxygen and sulphur compounds. Aliphatic and aromatic hydrocarbons are not ionized. Thus it was possible to detect without difficulty 1 ng of typical pyrazines in *ca.* 10 μ g of a complex hydrocarbon matrix (aviation turbine fuel). The selective ionization of the characteristic osmogenes of a sewage plant odour emission directly in the dichloromethane extract of the malodorous air sample (see Fig. 1) should therefore be possible (AMCI odour profile).

Fig. 5 shows the AMCI-RIC of the malodorous air sample corresponding to Fig. 2. This RIC is nearly identical with the EI-RIC of an ether eluate (not shown) from silica column chromatography (see Fig. 1). This is evidence for the preferential ionization of the most important osmogenes in the dichloromethane extract. In this particular odour sample no fatty acids were present. The concentration of the aldehydes and alcohols was too low to be detected by our preliminary AMCI-MS technique.

Fig. 5 is obviously a new and unique way of characterizing a special odour situation by an AMCI odour profile. Fig. 6 and Tables I–III show that by means of

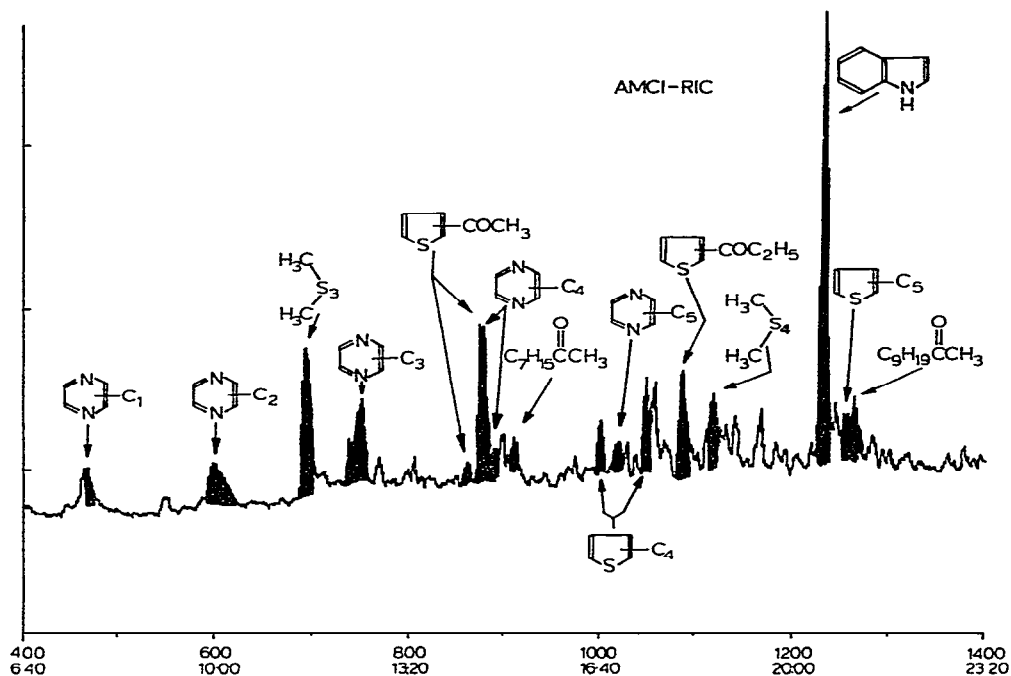


Fig. 5. Ammonia chemical ionization reconstructed ion chromatogram (AMCI-RIC).

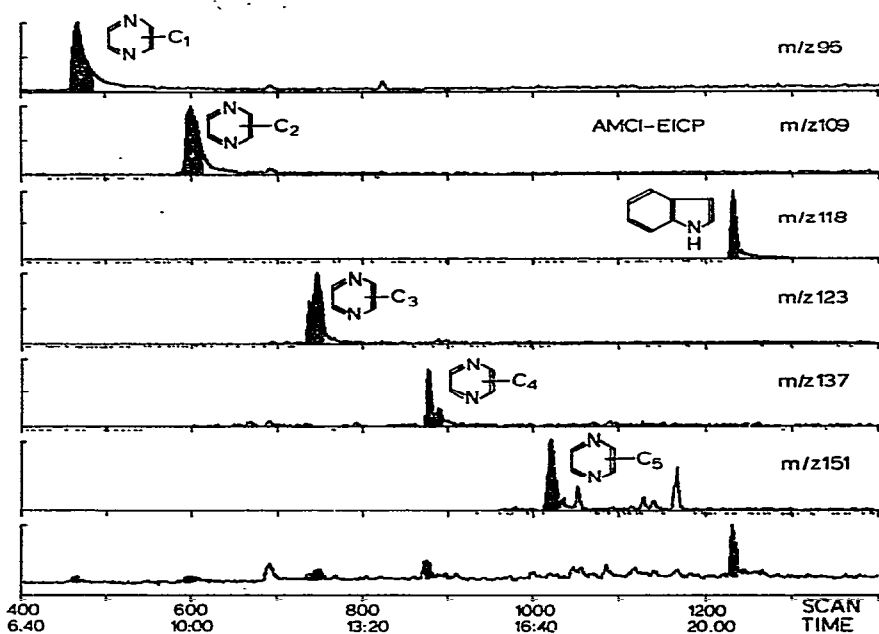


Fig. 6. Ammonia chemical ionization extracted ion current profile (AMCI-EICP) for alkylated pyrazines and indole.

EICPs the characteristic key compounds can be identified and quantified using their $M + H^+$ and/or $M + NH_4^+$ ions.

In conclusion, it has been shown that AMCI-MS of a complex hydrocarbon-containing malodour sample from a sewage plant is a highly selective and sensitive method for characterizing an odour situation. Qualitative and quantitative measurements are possible in principle. Field studies to test the method are in progress.

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REFERENCES

- 1 M. Hangartner and H. U. Wanner, *Wasser, Energie, Luft*, 70 (1978) 87.
- 2 P. Bartl, A. Schaaff and A. Zeman, *Wasser Abwasser*, 120 (1979) 269.
- 3 A. Zeman and H. Hagenguth, *JAPCA 73rd Annual Meeting, Montreal, Canada, June 1980*, Paper 80-40.7.
- 4 H. Hagenguth, H. Teichmann and A. Zeman, *Wasser Abwasser*, 120 (1981) 263.
- 5 D. F. Hunt, *Advan. Mass Spectrom.*, 6 (1974) 517.
- 6 M. S. Wilson, I. Dzidic and J. A. McCloskey, *Biochim. Biophys. Acta*, 240 (1971) 623.
- 7 I. Dzidic and J. A. McCloskey, *Org. Mass. Spectrom.*, 6 (1972) 939.