

Successful application of Thermal Desorption-Gas Chromatography/Olfactometry/Mass Spectrometry (TD-GC/O/MS) technique to the identification of main odorants in complex mixtures of volatile compounds

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A GC/MS system equipped with a thermal desorber and a sniffing port has been set up and used for identification of main odorants in complex mixtures of volatile compounds. Emissions were sampled from the soil in a former refinery plant in LaSpezia during remediation, and have been analyzed with TD-GC/O/MS technique; headspace samples of the soil have been tested in the same way. Samples had a strong disturbing odour but their chromatograms were covered by a great number of peaks of saturated, branched and cyclic hydrocarbons.

Aromagrams allowed to individuate as main odorants (garlic-like odour) small peaks of linear and cyclic olefins; their identification has been confirmed by peak disappearance after oxidation of the emission bubbling through a permanganate solution.

Other trace odorants were found analyzing the water after scrubbing of the emission through a Drechsel bottle; water was extracted using SBSE technique, and aromagram showed very small peaks identified as cyclic thioethers (broccoli-like odour): their presence was confirmed by peak disappearance after addition of hydrogen peroxide and oxidation to sulfoxide.

Aromagram allowed to individuate also a few aromatic hydrocarbons (grass-like, gasoline-like odour) as responsible of the whole odour of the emission.

1. Introduction

Identification of volatile compounds responsible of odour nuisance may be a very challenging task: often environmental malodours are due to small amounts of compounds with harsh disturbing odour and very low Threshold Odour Concentration (TOC), and chemical characterization of odorous sampled air may be quite difficult because of the great number of interfering substances usually present in ambient air. For solving this kind of environmental problems we have developed in our laboratory an analytical system dedicated to enrichment, separation, chemical and olfactory characterization of main odorants in complex gaseous mixtures; the system is based on a traditional GC/MS equipment, upgraded with a thermal desorber and an olfactory port. Adsorption of large volumes of sampled air on sorbents allows a high enrichment of interesting analytes, usually present at a very low level and easily lost during chromatogram evaluation. Chromatographic column effluent splitting to chemical and

sensorial detectors permits the simultaneous acquisition of the mass spectrum and the olfactory response of the main odorants, allowing their full characterization.

A disagreeable odour emission during remediation in a former refinery plant in La Spezia (Italy) was attributed at the first time to mercaptans, despite GC/MS analyses did not find these compounds. Air and soil samples were collected and analyzed using TD-GC/O/MS technique with the aim of identifying the compounds responsible of the nuisance.

2. Experimental

2.1 Sampling

Ambient air has been sampled near the excavation in 8-litres Nalophan bags using a vacuum pump, and stored at room temperature for less than 24 hours before analysis. Contaminated soil samples have been collected from the ground inside the excavation into sealed glass jars.

2.2 Sample preparation

Known volumes of air samples have been sucked and adsorbed into tubes filled with Tenax TA, and stored at 4°C before thermal desorption.

Known amounts of soil samples from the jars were put in 8-litres Nalophan bags filled with pure nitrogen; after an one hour equilibration time at room temperature different volumes of the headspace were sucked and adsorbed into tubes filled with Tenax TA and stored at 4°C before thermal desorption.

2.3 Stir Bar Sorptive Extraction (SBSE)

After an one hour equilibration time at room temperature, 8 litres of contaminated soil headspace were forced by a vacuum pump to bubble into a Drechsel bottle filled with 200 mL of deionised water at a rate of 0.1 L/min. A volume of 20 mL of scrubbing water was transferred into a 20-mL sealed vial, containing a Twister™ (a magnetic stir bar coated with a polydimethylsiloxane thick film), and stirred at room temperature for 30 min. After this extraction phase the Twister was put in an empty glass tube for thermal desorption and analyzed.

2.4 TD-GC/O/MS

The GC/MS system was a gas chromatograph model 6890N (Agilent Technologies, USA) coupled with a quadrupolar mass spectrometer model 5973N (Agilent Technologies, USA). The instrument was equipped with a temperature programmable injection port model CIS4 (Gerstel, Germany) cooled with liquid nitrogen, a thermal desorber model TDS2 (Gerstel, Germany) and an olfactory port model Phaser (Atas GL, Nederland). A fused silica capillary column (30m x 0.25mm I.D., 0.25 µm film thickness) coated with poly[5% phenyl]methylsiloxane was installed.

Helium (purity 99.999 %) was employed as carrier gas, with a constant flow of 1.0 ml/min. The injector was operated in the split mode (split ratio 15:1), at a constant temperature of 250°C. The GC oven temperature program was 40°C, hold 1 min., then it was increased to 250° with a gradient rate of 5°C/min. and hold at 250°C for 10 min. The mass range was scanned in the full scan mode from 35.0 to 350.0 m/z.

2.5 Dynamic dilution olfactometry

Odour concentration measurements have been performed through dynamic dilution olfactometry technique using an olfactometer model TO7 (ECOMA, Germany), installed in a clean room equipped with an active charcoal air filtration system, and a panel of eight candidates, according to EN 13725 (2003).

2.6 GC/O analysis by incremental dilution technique

Combination of gas chromatography and olfactometry (GC/O) consists of a simple modification of a traditional gas chromatograph, where a detector and a sniffing port are both connected to the end of a chromatographic column through a Y connector; this one allows the human nose to analyse the peaks at the same time they are revealed by the detector. The result of the analysis is a chromatogram indicating the smelling peaks, the so called "aromagram". The electric signal corresponding to perceived odours results in a series of square waves which represents the aromagram. During analysis the analyst describes with few words the perceived odours. Grosch (2001) applied GC/O to food analysis, determining the power of the main odorants using incremental dilution technique. In a similar way we analysed two different volumes of soil headspace, in order to distinguish the most powerful odorants (perceived also in more diluted samples).

3. Results and discussion

Air emissions and soil headspace samples showed a quite identical chromatographic profile: for this reason the full characterization of emission was performed on the soil headspace. GC/MS fingerprint's main components were found to be saturated, branched and cyclic hydrocarbons, such as methylcyclohexane, methylcyclopentane, isomeric dimethylcyclopentanes and dimethylcyclohexanes, as well isomeric methylhexanes, methyleptanes, methyloctanes (figure 1). Aromagrams showed about fifteen odour signals for concentrated samples, and five main odorants in diluted samples; odour descriptors were typically garlic-like, suffocating, rocket for the more volatile substances, and aromatic, parsley for heavier compounds. Corresponding peaks on the gas chromatogram have been identified as olefines, present in low concentration, such as isomeric methyl pentenes, and cycloolefines, such as methyl cyclopentenes and methyl cyclohexenes (figures 2a,2b,2c).

Due to the similarity of the mass spectra of olefines and cycloalcanes (both have molecular formula C_nH_{2n} and show the same fragments in the spectrum) it was indispensable to confirm peak attribution. For this purpose a chemical test has been set up: soil headspace was forced by a vacuum pump to bubble into a Drechsel bottle filled with 200 mL of potassium permanganate solution at a rate of 0.1 L/min. After oxidation the headspace was collected in a Nalophan bag and analyzed in comparison with the same headspace before oxidation: overlapped chromatograms showed the disappearance of olefins peaks (Figure 3).

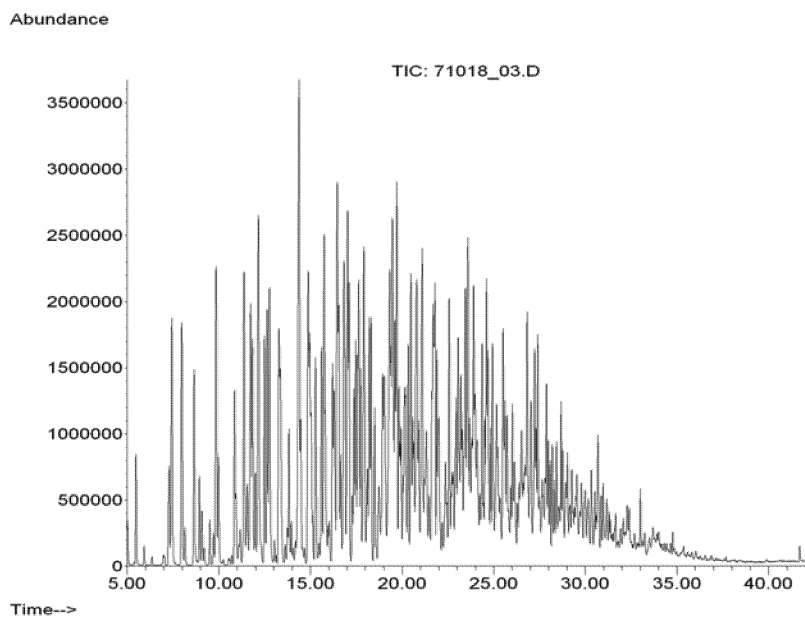


Figure 1. Soil headspace

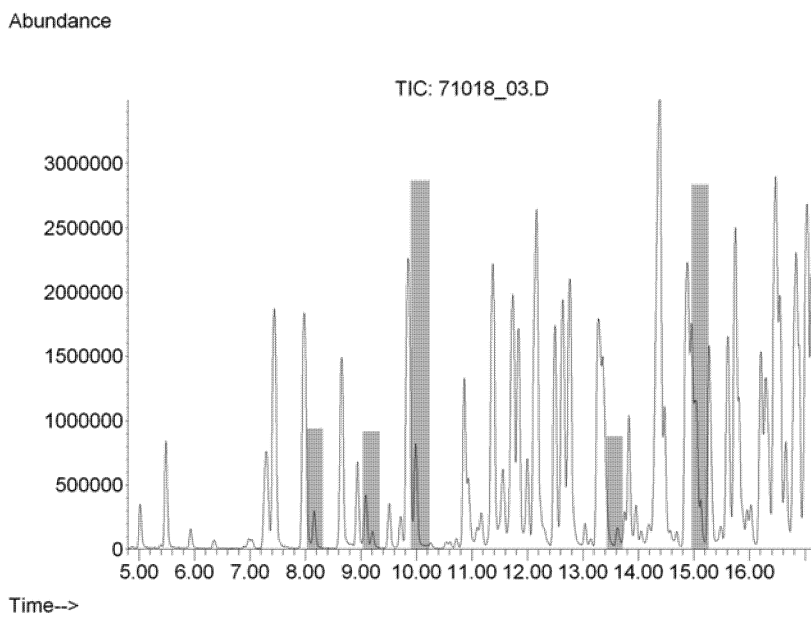


Figure 2a. Aromagram and gas chromatogram overimposed (RT: 5-17 min)

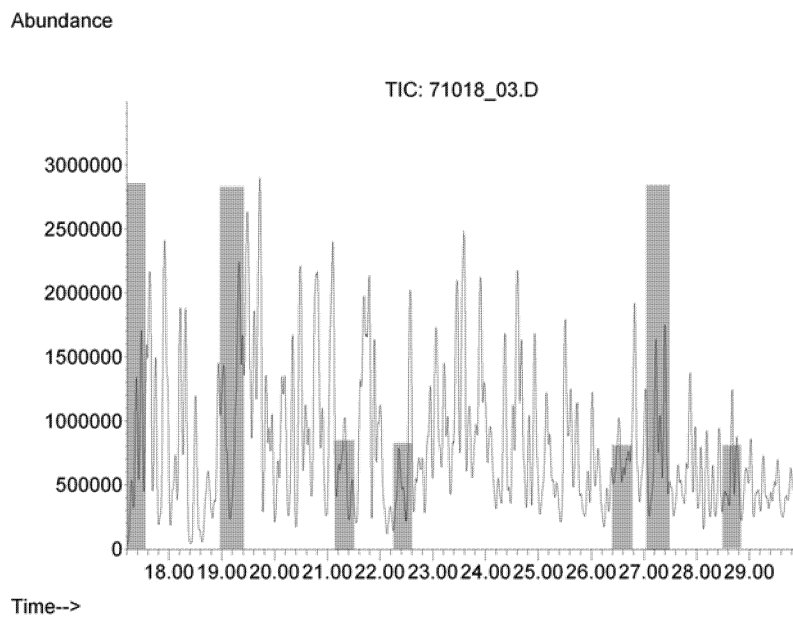


Figure 2b. Aromagram and gas chromatogram overlaid (RT: 17-30 min)

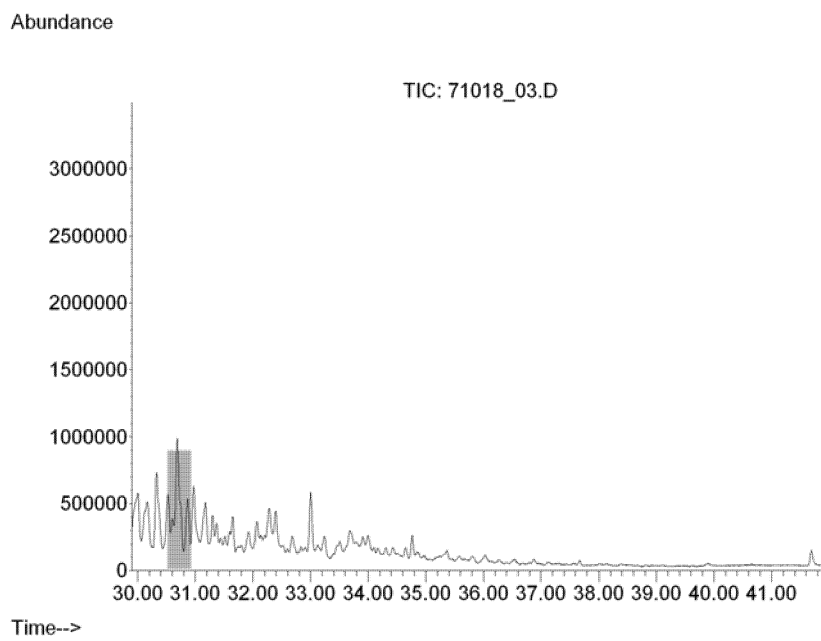


Figure 2c. Aromagram and gas chromatogram overlaid (RT: 30-42 min)

For evaluating odour removal efficiency of oxidation process, soil headspace was forced by a vacuum pump to bubble into a Drechsel bottle filled instead with 200 mL of deionised water at a rate of 0.1 L/min, and after water scrubbing the headspace was collected into a Nalophan bag and analyzed using dynamic dilution olfactometry for odour concentration determination in comparison with the same headspace after oxidation; results are reported in the following table:

N°	sample	odour concentration
1	soil headspace (no treatment)	14.000 OU/m ³
2	soil headspace (water scrubbing)	3.400 OU/m ³
3	soil headspace (oxidized)	1.500 OU/m ³

Because water scrubbing seemed very efficient in odour removal, water used for scrubbing was extracted using SBSE technique with a Twister, and analyzed with GC/MS. The more soluble fraction is rich in heavier compounds, such as aromatic hydrocarbons, methyl naphthalenes, methyl benzothiophenes, but also in sulphur compounds, that can be easily observed after main hydrocarbons removal.

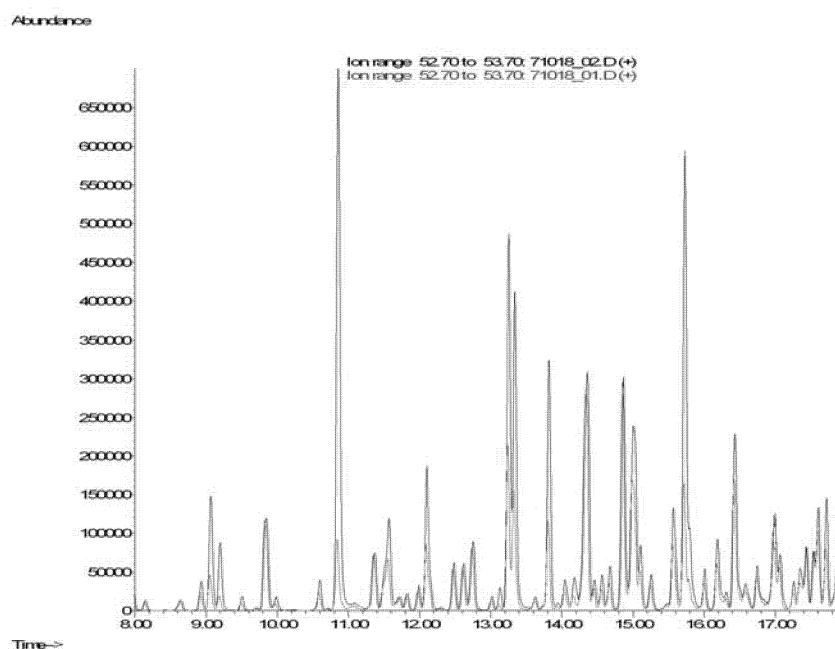


Figure 3. Disappearance of peaks of unsaturated hydrocarbons after KMnO_4 oxidation

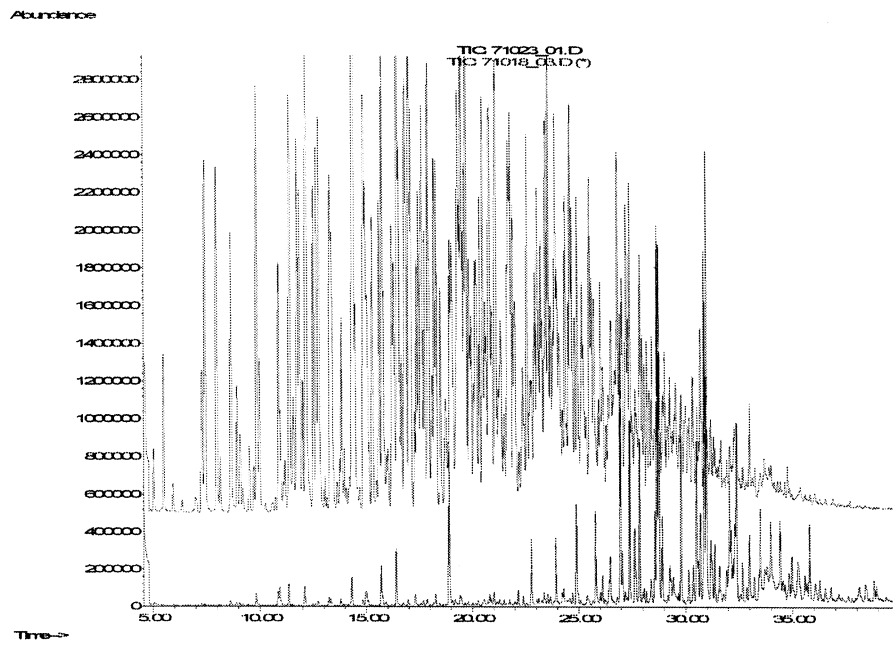


Figure 4. Headspace before water scrubbing and water soluble fraction

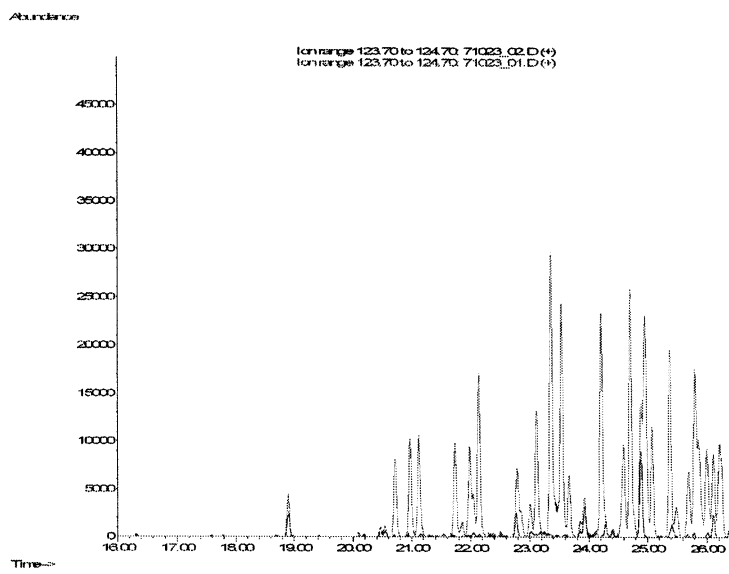


Figure 5. Disappearance of peaks of thioethers after H_2O_2 oxidation

Such sulphur compounds have been identified as t-butyl alkyl sulphides and cyclothioethers like isomeric methyl thians (six atom ring) and dimethyl thiolans (five atom ring); confirmation of this attribution has been done by addition of hydrogen peroxide to the scrubbing solution: sulphides have been oxidized to sulphoxides, and peak disappearance confirmed chemical class identification (figure 5).

According to the resulting attributions, the following table has been obtained:

peak	low concentration	high concentration	assigned analyte
1	-	suffocating	methyl pentene
2	-	suffocating	methyl pentene
3	suffocating	garlic-like	dimethyl cyclopentene
4	-	garlic-like	methyl cyclohexene
5	-	sulphurous	not identified
6	geranium	garlic-like	trimethyl cyclopentene
7	garlic-like	garlic-like	trimethyl pentene
8	rocket	garlic-like	t-butyl ethyl sulphide
9	-	garlic-like	trimethyl pentene
10	-	garlic-like	t-butyl isopropyl sulphide
11	-	rocket	t-butyl propyl sulphide
12	parsley	aromatic	diethylbenzene
13	-	hydrocarbon	tetramethylbenzene
14	-	aromatic	methyl indane

4. Conclusions

The strong suffocating, garlic-like odour perceived during site remediation was caused mainly by olefins and cycloolefins, but traces of thioethers also contributed; the aromatic, grassy note was provoked by small amounts of aromatic hydrocarbons. TD-GC/O/MS technique was very effective in evaluating main odorants in presence of many interfering compounds; because heavy contamination by hydrocarbons is very common in environmental remediation, this approach will be easily applied.

References

- EN 13725, 2003, European Norm, Air quality - Determination of odour concentration by dynamic olfactometry
 Grosch, W., 2001, Chem Senses, 26, 533