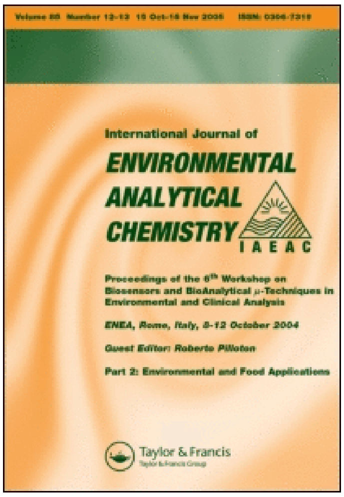

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Characterization of Malodorous Volatiles in Air Using Olfactometry and Computer Assisted Capillary-Gas Chromatography-Mass Spectrometry

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To cite this Article Termonia, M. , Guns, M. and Gillard, F.(1985) 'Characterization of Malodorous Volatiles in Air Using Olfactometry and Computer Assisted Capillary-Gas Chromatography-Mass Spectrometry', International Journal of Environmental Analytical Chemistry, 20: 1, 69 — 84

To link to this Article: DOI: 10.1080/03067318508077047

URL: http://dx.doi.org/10.1080/03067318508077047

Intern. J. Environ. Anal. Chem., 1985, Vol. 20, pp. 69–84
0306-7319/85/2002-0069 $18.50/0

Printed in Great Britain

Characterization of Malodorous Volatiles in Air Using Olfactometry and Computer Assisted Capillary-Gas Chromatography-Mass Spectrometry[†]

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(*Received November 23, 1984*)

Characterization of malodorous organic volatiles, arising from animal breeding stations and from the coke and steel industry was performed by means of dynamic headspace enrichment (active charcoal—CS_2 method) followed by capillary gas chromatography with olfactive and/or mass spectrometry detection. The results were associated to olfactive threshold values from the literature in order to present circular odour charts reflecting both the quality and the intensity of the odour sample. These charts, by visually indicating the respective contributions of specific chemical classes to the global odour, could help to elaborate the abatement techniques.

KEY WORDS: Olfactive pollution, gas chromatography, mass spectrometry olfactometry.

[†] Presented at the 14th annual symposium on the analytical chemistry of pollutants. Barcelona, November 21–23, 1984.

I. INTRODUCTION

In order to assess the contribution of volatile chemical compounds to the intensity and the nature of odours, it should be valuable to be able to objectively evaluate the odour perception. In principle, there are two methods for the determination of odours: via the sensory effect (the olfactometric method) and via the identification of the compounds responsible for the odours (the physico-chemical method).

Due to the complexity of the nerve-impulses transmitted to the brains during the sensory perception of the odours, it is difficult to directly deduce the intensity of these impulses from the physico-chemical composition of the odour.[1] However, results obtained by olfactometric methods cannot efficiently be used in abatement studies where the epuration yields to be determined are directly dependent on the chemical nature of the compounds present in the emissions.

Recently, analytical techniques have been introduced which offer detection limits that equal and even surpass the human olfactive sensitivity. The coupling of dynamic headspace analyses, involving the trappings of volatile compounds on suitable adsorbents, to capillary gas chromatography and computer-assisted mass spectrometry offers the selectivity, sensitivity and accuracy required for the qualitative and quantitative determination of trace amounts of compounds responsible for olfactive nuisances.

During the last decade, each of the steps of this high performance analytical scheme have been independently optimized by numerous research teams[2–5] involved in many fields such as agricultural chemistry, cosmetics, polymer chemistry, biomedical sciences or air pollution.

In this paper, results obtained by means of dynamic headspace enrichment and high resolution gas chromatography coupled to olfactometric and mass spectrometric detections are reported. They concern the chemical composition of malodorous emissions from agriculture and from the coke and steel industry. In the last case, they were associated to olfactive thresholds from the literature[6–8] in order to present circular odour charts[9] for the characterization of the contribution of 8 different chemical groups to the total odour sample.

II. EXPERIMENTAL

1. Sampling of the odours

The odour emission samples were directly collected on activated carbon traps and in Tedlar® bags. The bags of approximately 16 liters volume were placed in metal cylinders which were evacuated in 10 minutes by means of a 12 V battery operated Austeen Capex MK II pump. Before analysis, the bags were placed in an oven at 60°C for 15 min. At this stage, a gas sample of 1 to 5 cc was taken with a gas syringe and directly submitted to mass spectrometric analysis for the determination of the inorganic compounds. The gases contained in the bags were then passed at a rate of 30 l/hour through a 5 mg activated carbon trap for enrichment of the organic odorous volatiles.

Direct sampling was performed during the same period as the bag collection, at the same place, with a sorbent trap (containing 25 mg of activated carbon) according to a method described by Grob.[10] Recovery of the adsorbed substances was performed by eluting the cartridge with 50 μl of carbon disulphide. The efficiencies of adsorption and elution of the traps were measured by analyzing the first and second CS_2 eluates of 2 traps placed in series, following the procedures described in reference 10. Carboxylic acids were specifically collected by pumping the malodorous air through a sampling train consisting of 3 air impingers placed in series, each containing 100 ml of a tetrabutylammonium hydroxyde aqueous solution (10^{-3} M). They were subsequently analyzed as their benzyl esters, according to a method described in reference 11.

2. Gas chromatography

The gas chromatograph (g.c.) used for this study was a Carlo Erba (Milano, Italy) model HR 4160 coupled to a Finnigan-MAT (Sunnyvale, U.S.A.) quadrupole mass spectrometer (m.s.) model 4500, assisted by an INCOS 2300 data system (d.s.) equipped with the July 1982 software version.

The g.c. columns used were made of borosilicate (DURAN 50) capillaries 40 m long and with an internal diameter of 0.3 mm.

The semi-polar stationary phase (OV1701) was chemically immobilized on the glass surface, with a film thickness of 0.8 μm,

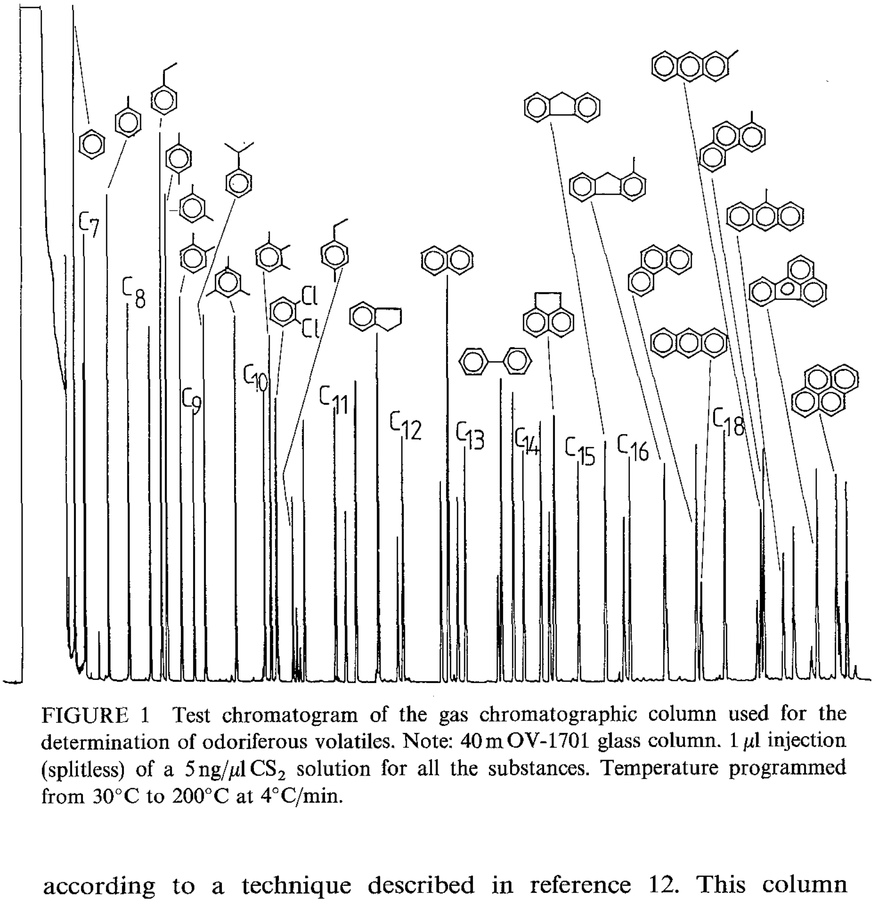

FIGURE 1 Test chromatogram of the gas chromatographic column used for the determination of odoriferous volatiles. Note: 40 m OV-1701 glass column. 1 μl injection (splitless) of a 5 ng/μl CS_2 solution for all the substances. Temperature programmed from 30°C to 200°C at 4°C/min.

according to a technique described in reference 12. This column allowed separation of test compounds ranging from benzene and n-heptane to eicosane and pyrene in less than one hour, as illustrated in Figure 1.

The operating conditions for the g.c. were as follows. The carrier gas was Helium. 1 μl of the CS_2 solution was injected in the splitless mode (gas hold-up time: 35 sec) with the injection chamber at 200°C. The column temperature was programmed from 30°C to 200°C at a rate of 4°C/min. The column outlet was connected to an effluent splitter[13] by means of deactivated fused silica lines, conducting 1/5 of the flow to the m.s. and 4/5 to a sniffing port, allowing olfactive detection of the eluting g.c. peaks.

3. Mass spectrometry

The compounds eluting from the chromatographic system were submitted to electron impact ionization and analyzed according to their mass to charge ratio, by means of a quadrupole filter. Full spectra were acquired in the mass range 40 to 400 u.m.a. at a scanning frequency of 1 Hz, saved on hard disc and processed under the control of the INCOS data system. The operating conditions were as follows. Temperature settings of the g.c.–m.s. interface line, of the ion source and of the m.s. mantel were 250°C, 150°C and 85°C respectively. The cathode current was 25 mA, the electron energy 70 eV and the electron multiplier potential 1750 V. The residual pressure was approximately 5.10^{-6} Torr in the analyzing section. Compound identification was performed by comparison of the m.s. spectra of the unknowns with reference spectra and by co-chromatography of pure compounds in the same g.c.–m.s. conditions. Reference test mixtures containing the major substances found in the emissions were synthesized. They consist of 18 BTX (benzene, toluene, xylene derivatives), 10 alcanes, 25 PAH (polyaromatic hydrocarbons), 12 phenols, 4 nitrogen-compounds, 10 sulfur-compounds and 8 carboxylic acids.

The routine analysis of the odour samples was then performed by means of the Target Compound Analysis Software (TCA, Finnigan-MAT). During this procedure, each mass spectrum in a specified time window, centered on the expected g.c. retention time of a compound, was reverse-searched, using the library spectrum of a compound present in a test mixture.

III. RESULTS AND DISCUSSION

1. Odorous emissions from animal breeding stations

Recent investigations have shown that dimethylsulphide, polysulphides, carboxylic acids, phenols and indole are mainly responsible for the odour emissions from animal breeding stations.[14–15]

The chromatograms of Figures 2, 3 and 4 illustrate the results obtained for the analysis of odoriferous air in the neighbourhood of an intensive pig breeding station.

Figures 2A and B show the analysis of the carboxylic acids

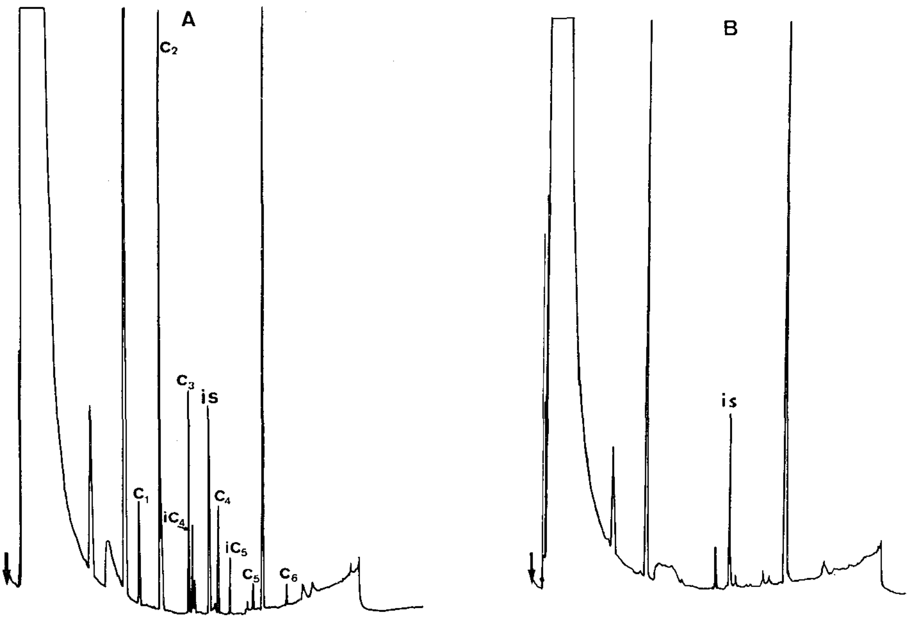

FIGURE 2 Analysis of C_1–C_6 fatty acids present in emissions from animal breeding stations. Note: A and B: acids collected in the first and second impingers respectively. Analytical details: see text.

sampled in the first and second impingers, respectively. The total acid content of the 1000 l air sample was 80 μg, expressed for acetic acid. When anaerobic fermentation of the animal wastes took place, enhancement of the concentration of the polysulphides occurred. An example of this situation is presented by the chromatogram of Figure 3 where the concentration for the detected sulphides was about 100 $\mu g/m^3$ expressed for dimethylsulphide. This observation is in agreement with the results obtained by König *et al.*[16] and by Zeman[17] for municipal sewage plants.

Figure 4 illustrates the presence of phenol, p-cresol, indole and skatole at the 1 $\mu g/m^3$ level.

2. Odorous emissions from the Coke and Steel Industry

Between October 82 and December 83, 10 different sources were investigated for 2 coke oven plants and 3 for a blast furnace. They are listed in Table I.

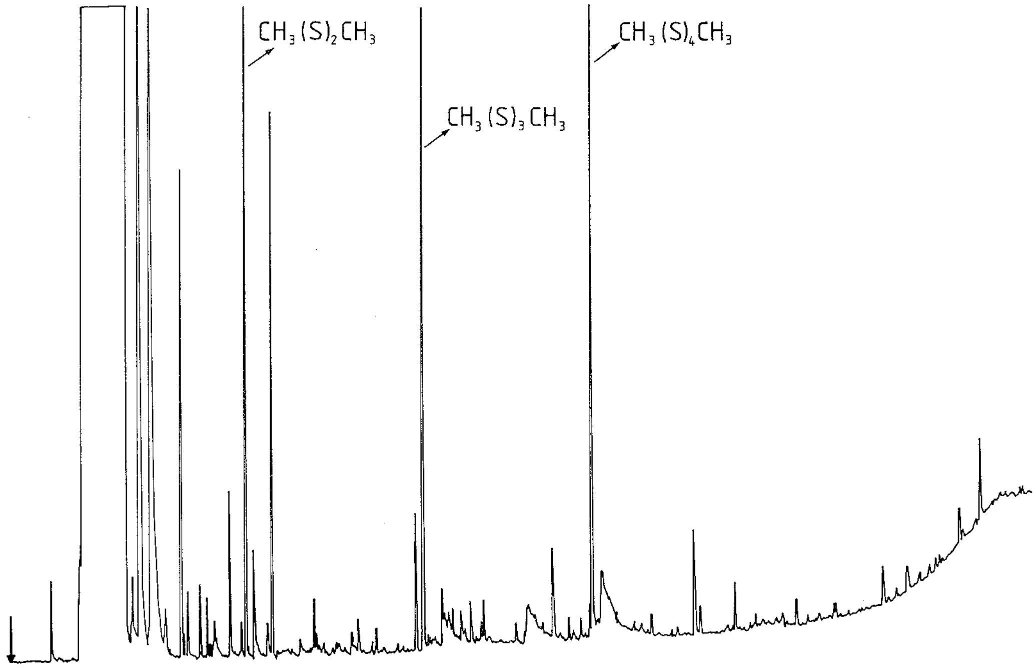

FIGURE 3 Chromatogram of polysulphides present in emissions from animal breeding stations. Chromatographic conditions: see text and Figure 1.

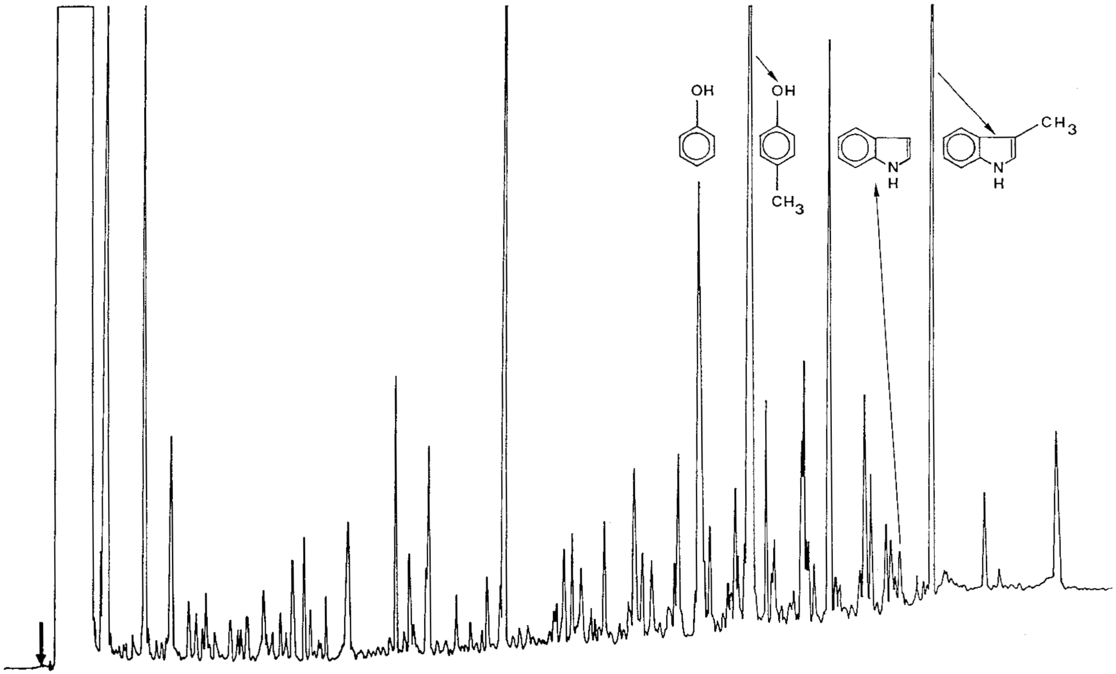

FIGURE 4 Chromatogram of trace-level odoriferous volatiles present in emissions from animal breeding stations. Chromatographic conditions: see text and Figure 1.

TABLE I
Investigated sources

Coke ovens	Blast furnace
Door leakage	slag granulation stack
Coal charging area	drainage sump
Coal charger cabin	sumps filling
Pumphouse	
Tar tank	
Tar purge-pots (primary condensation)	
Benzole plant	
Naphthalene crystallizers	
Tank of warm debenzolated oil	
Residual tar collector	

Sampling was performed at the work places under the direct influence of the odour emissions.

Figure 5 shows a typical gas chromatogram obtained for the g.c.–m.s. analysis of emissions due to coke oven door leakage, collected in a Tedlar® bag. In this case, 73 odorous compounds were identified. By means of the olfactive detection of the g.c. eluting peaks, it was possible during this run to confirm the odorous character of indene and naphthalene which were present in concentrations of 13 and 6 $\mu g/m^3$ respectively.

A total of 38 analyses for the coke oven emissions and 11 for the blast furnace were performed in a similar manner. They present little differences in the qualitative composition of the samples, but a high variability of the measured concentrations, especially for the PAH and BTX groups.

In order to characterize the odours discharged from the thirteen studied sources, a graphic presentation similar to that proposed by Hoshika *et al.*[9] was used, which relates the olfactive threshold and the measured concentration of the odorous chemicals identified in the gaseous emissions of these sources.

For each source, a pOU number was calculated for the characterization of VIII odorant classes (hydrogen sulphide, sulphur-compounds, ammonia, nitrogen-compounds, alcanes, BTX, PAH and

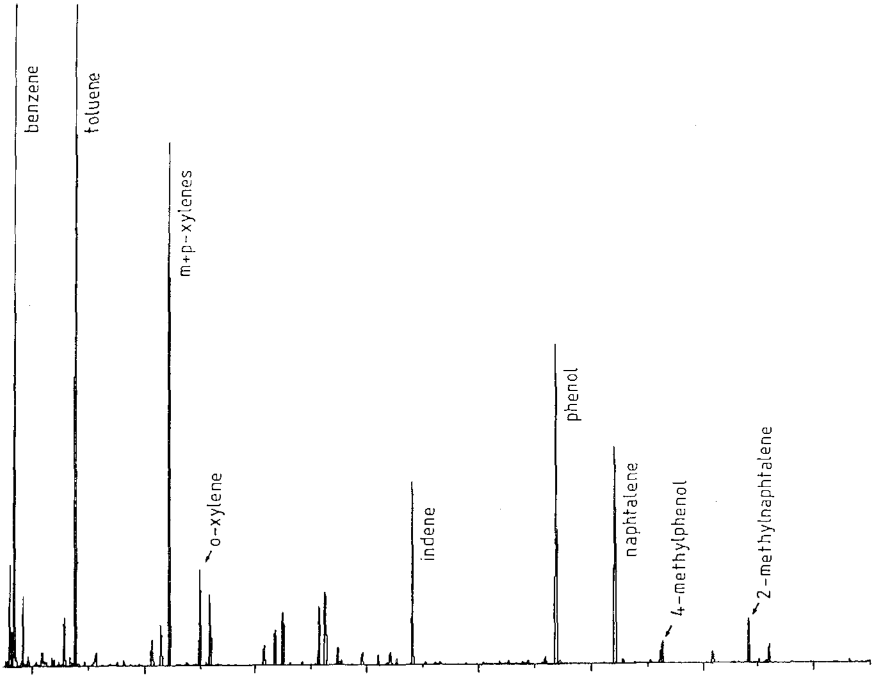

FIGURE 5 Chromatogram obtained for the gc–ms analysis of odoriferous emissions arising from a coke oven door leakage. Chromatographic conditions: see text and Figure 1.

phenols) according to the following equation:

$$(\mathrm{pOU})m = \log(C_1/d_1) + \log(C_2/d_2) + \cdots + \log(C_n/d_n)$$

where: $-m$ is class I to class VIII

$-C_1, C_2, \ldots, C_n$ are the measured odorant concentrations (in μg/m^3)

$-d_1, d_2, \ldots, d_n$ are the olfactive threshold values (in μg/m^3).

By consulting the literature[6–8] it was possible to collect consistent values for 34 of the 73 compounds which were detected by g.c.–m.s.

analysis. Fortunately, olfactive thresholds were available for the most odoriferous and abundant compounds detected.

The names of the 34 compounds taken into account for the graphic presentations are listed in Table II, together with their olfactive threshold values used for calculation of the pOU values.

As an example for a door leakage of a coke oven, Table III presents the detected compounds, their measured concentration (C in $\mu g/m^3$), their olfactive threshold (d in $\mu g/m^3$) if known, and the calculated pOU value. When the log of the C/d ratio of all the measured odorants in the same class are negative, the pOU value for this class is defined as zero.

The calculated pOU values of the eight odorant classes from eleven odour sources (listed in Table I) were plotted in the circular odour charts given in Figures 6 and 7.

Examination of the charts from Figures 6 and 7 leads to the following observations. The shape and size of the charts are characteristic for the considered source, as they represent the quality and the intensity of the perceived odours.

In the case of the emissions arising from the coke oven itself (Sources I, II and III), the contribution of the odorant Classes VI (BTX) and VII (PAH) is predominant. These compounds produce the more intense olfactive nuisance reported in this work. The PAH class is also the most important family to take into account at the naphthalene crystallizers and in the proximity of the tar tanks.

Odour emissions from the blast furnace, as shown in Figure 7, are practically only due to hydrogen sulphide, especially in the case of the slag granulation stack.

As illustrated by the comparison of the circular charts presented in Figure 8, results obtained with the 2 sampling techniques described, i.e. bag sampling followed by activated carbon enrichment and direct activated carbon trapping, indicate that odour sampling with Tedlar® bags is a suitable technique for evaluating the contribution of odoriferous compounds to a global odour. This is confirmed by the observations made by Leonardos *et al.* for the sampling of odours in the stack of a paint bake oven.[18]

CONCLUSIONS

Odoriferous emissions from animal breeding stations and from the

TABLE II

Names and olfactive threshold values of the compounds taken into account for characterization of the odoriferous sources

Class	Compound	$d(\mu g/m^3)$	Reference
I	hydrogen sulphide	1.9	6
II	thiophene	9.4	6
III	ammonia	1825	7
IV	indole	0.6	8
	quinoline	30	8
	pyridine	83	6
V	n-octane	4700	6
	n-nonane	8670	6
	n-decane	11300	8
	n-undecane	2921	8
	n-dodecane	5390	6
	n-tridecane	6110	6
	n-tetradecane	3580	6
VI	benzene	4700	6
	toluene	3750	6
	ethylbenzene	67	8
	$m+p$-xylene	735	7
	o-xylene	926	8
	isopropylbenzene	47	8
	1, 3, 5-trimethylbenzene	661	6
	1, 2, 4-trimethylbenzene	232	8
	styrene	406	6
	methylstyrene	1563	8
VII	indene	5.1	8
	naphthalene	675	7
	biphenyl	60	8
	phenanthrene	58	8
VIII	phenol	12350	7
	2-methylphenol	201	7
	4-methylphenol	25	8
	2, 6-dimethylphenol	100	8
	2, 3-dimethylphenol	250	8
	3, 4-dimethylphenol	1500	8

TABLE III

Measured concentration (C in μg/m^3), olfactive threshold values (d in μg/m^3) and pOU values for emissions arising from a door leakage of a coke oven

Class	Compound	Measured conc., C (μg/m^3)	Olfactive threshold, d (μg/m^3)	pOU
I	hydrogen sulphide	114	1.9	1.78
II	benzo(b)thiophene	301	—	0
III	ammonia	39278	1825	1.33
IV	N-compounds	—	—	0
V	n-octane	8954	4700	0.32
	n-nonane	4506	8670	
	n-decane	32	11300	
VI	benzene	104630	4700	6.35
	toluene	23251	3750	
	ethylbenzene	2218	67	
	$m+p$-xylene	787	735	
	o-xylene	1469	926	
	iso-propylbenzene	133	47	
	1, 3, 5-trimethylbenzene	3919	661	
	styrene	8917	406	
VII	indane	1396	—	4.35
	indene	13143	5.1	
	naphthalene	5716	675	
	2-methylnaphthalene	228	—	
	1-methylnaphthalene	538	—	
	benzofuran	1140	—	
	dibenzofuran	9	—	

steel industry were investigated by dynamic headspace enrichment coupled to high resolution gas chromatography and computer-assisted mass spectrometry combined with olfactometry. From the results, it is deduced that these techniques can be helpful for the characterization of various olfactive pollution situations. In particular, when the results are graphically presented in charts which take into account the concentration of the chemical species in combin-

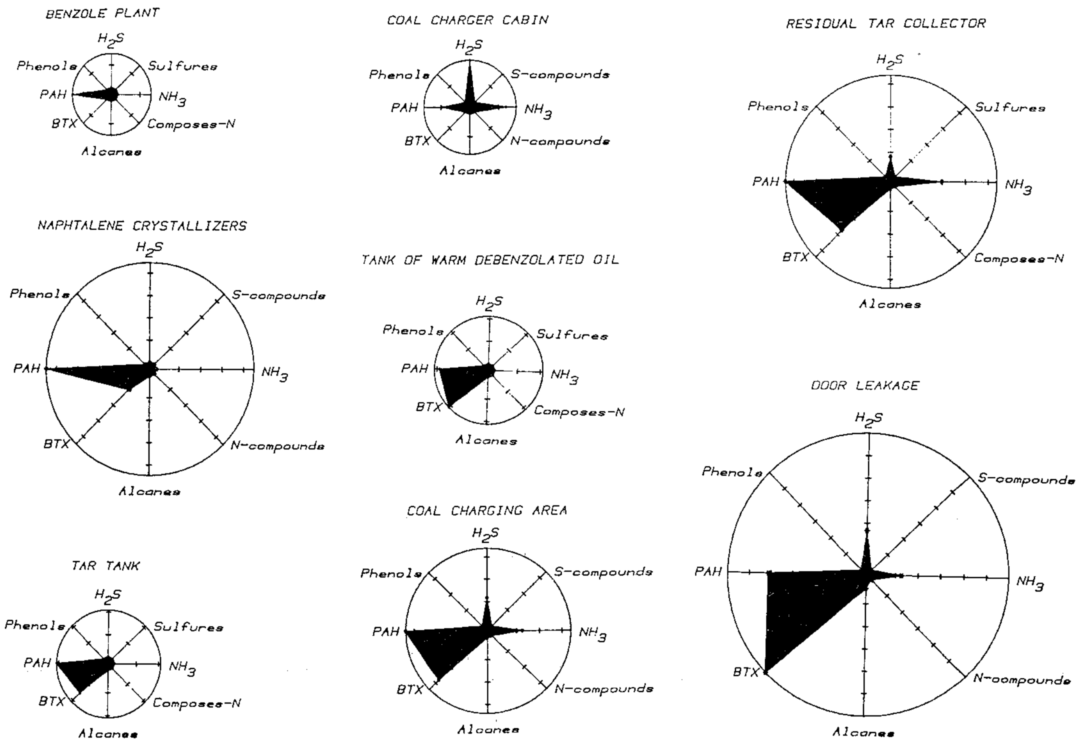

FIGURE 6 Odour charts characterizing emission sources from coke oven plants. The maximum pOU values for the 9 sources are given in increasing order of magnitude. Benzole plant: pOU = 1.5(PAH). Coal charger cabin: 1.8(H_2S). Tar tank: 2.1(PAH). Tank of warm debenzolated oil: 2.1(BTX). Coal charging area: 3.4(PAH). Residual tar collector: 4.4(PAH). Naphthalene crystallizers: 4.5(PAH). Door leakage: 6.3(BTX).

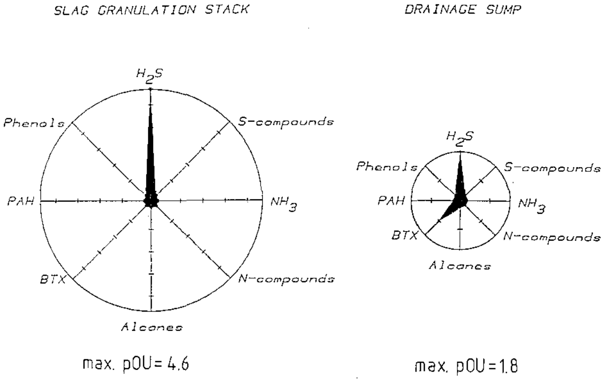

FIGURE 7 Odour charts characterizing 2 emission sources from a blast furnace. The maximum pOU values are: Slag granulation stack: 4.7(H_2S). Drainage sump: 1.9(H_2S).

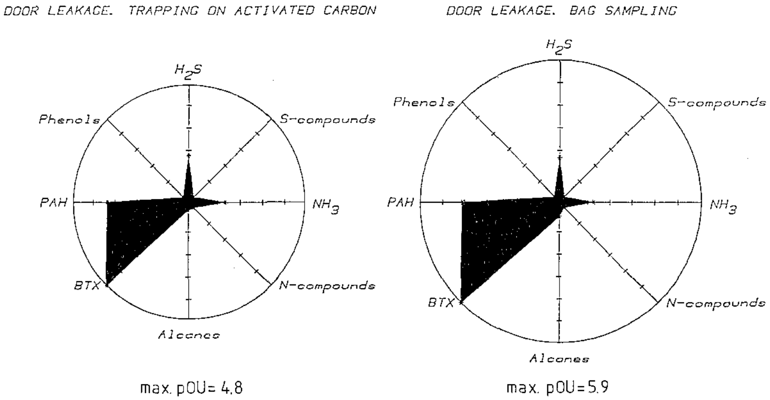

FIGURE 8 Odour charts obtained for the emissions due to a coke oven door leakage, with 2 different sampling techniques.

ation with its olfactive threshold, it is believed that the described method can help in elaborating the abatement techniques by indicating visually which chemical class is the most important to be epurated.

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