Report Nr. 8/75

THE IDENTIFICATION AND MEASUREMENT OF REFINERY ODOURS

prepared by

CONCAWE's Special Task Force on
ODOURS

Stichting CONCAWE
The Hague

December 1975

CONTENTS

MEMBERS OF CONCAWE's SPECIAL TASK FORCE ON ODOURS

Mr. J. Charlton (chairman)

Mr. J.H. Boddy

Mr. M. Brilland

Mr. E.D. Edwards

Mr. J. Goldbach

Dr. E. Jocke

Mr. C. Plantard

Mr. R. Sarteur

Mr. J.M. Sharkey

SUMMARY

This report, which quotes current European regulations on odours and systems adopted for receiving odour complaints from the general public, summarizes the types of compounds giving rise to odours from oil refineries and identifies the possible sources.

Instrumental and olfactory methods for the identification and measurement of odours are described, in particular chromatographic methods for the determination of hydrocarbons and sulphur compounds in the atmosphere. A novel method of presenting the data to highlight the compounds causing odour is given.

The selection and use of odour panels as a means of establishing good public relations and of monitoring public complaints are discussed.

1. INTRODUCTION

A primary consideration in refinery operations is to achieve safe working conditions within the plant and to avoid any toxic hazards. In most cases the steps taken for safe operation eliminate most odour problems which would affect the general public in the vicinity of the refinery. However, because some compounds can be detected at very low concentrations (e.g. 1 part in 10^9 or 10^{10}) there still remains some nuisance. The assessment of the degree of odour nuisance is difficult. Individual reaction to odour is highly subjective and threshold concentrations at which odours can be detected vary from person to person by a factor of as much as one hundred. The relationship between odour intensity and concentration is rarely linear, and the characteristic of odours may change at some critical concentration. Meteorological conditions, particularly wind direction and strength, have a profound effect on the degree of odour nuisance. For these reasons it is not possible to set definite conditions for an acceptable odour level which is universally applicable, and consequently there are few statutory levels set by governments, unlike the wide variety of toxic limits. To our knowledge the only Western European country that has specific legislation for odorous compounds is Germany, where immission values for hydrogen sulphide and methyl mercaptan around new installations have been introduced. However, in most countries the authorities can, and do, apply sanctions on companies through laws governing general nuisance when public opinion, which is becoming increasingly active in environmental matters, brings pressure to bear. It is essential, therefore, that companies have satisfactory means of identifying and measuring odours to pinpoint sources of emission.

In 1969 CONCAWE produced a report entitled "An Investigation into the Causes of Refinery Smells" (Doc. No. 3875) which summarized the results of questionnaires sent to 80 refineries to determine the frequency and causes of reported smells. A further survey of over 100 refineries is planned for 1975. Since the 1969 report, analytical techniques have been devised to identify and measure the concentration of odorous compounds, and this new report collects the knowledge and expertise available both from the literature and member companies in this field.

Particular mention should be made of the help given by Mr. Sarteur of ELF-ERAP. His wide practical experience proved invaluable in preparing this report.

2. ODOUR COMPLAINTS

There are several different systems for receiving and dealing with odour complaints. Probably the most sophisticated is the one operated by the Rijnmond Authority in Holland. This Authority covers the City of Rotterdam and the major industrial area to the west which includes several oil refineries as well as numerous other industries. The public reports complaints to the Authority on a special, well-publicized telephone number. Each complaint is logged by a central controller who then contacts one of the patrolling inspectors by radio. These inspectors investigate the complaint to validate it and also to attempt to identify possible sources. In the last three years the Authority received about 15,000 calls/annum of which approximately 80% were about odours originated from industrial installations of many types located in the area.

Several authorities in other industrial areas have similar, but less comprehensive, systems whilst isolated refineries tend to receive and deal with odour complaints directly. Certain refineries use the local newspaper to inform residents in the vicinity of the refinery when there is likely to be an odorous emission. This can be done during a planned shutdown when degassing and washing operations can cause odorous emissions even though every effort is made to minimize them. Plant mal-function or mal-operation can also generate odours, and these tend to be difficult to identify and quantify. However, recently developed analytical techniques, in particular chromatographic methods, have provided the tools for identifying and measuring most refinery odours, and some of these techniques will be discussed later in the paper.

3. COMPOUNDS CAUSING ODOURS IN REFINERIES

The nose is an extremely sensitive detector of odours and can be matched by only the most sensitive instrumental techniques. Many smells are identified by comparison with pure compounds diluted by odour-free air until they are near the odour threshold limit. However, the introduction of gas chromatography, coupled to mass spectrometry, has now made it possible to confirm the identity of many of the compounds giving rise to odours in refineries.

The main offenders have been shown to be sulphur compounds, such as H_2S, mercaptans and disulphides, which are known to be present in crude oil fractions and have been detected in refinery atmospheres (1), (2). Because of their offensive smell and low olfactory levels, these compounds give rise to the majority of complaints. Any olfactory level quoted in the literature must be treated with caution. Typical detectable limits for the most important sulphur compounds are:

		ppm v/v
Hydrogen sulphide	H_2S	0.001 - 0.014
Methyl mercaptan	CH_3SH	0.001 - 0.0085
Ethyl mercaptan	C_2H_5SH	0.001 - 0.0026
Dimethyl sulphide	$(CH_3)_2S$	0.002 - 0.0052

Hydrocarbons can give rise to offensive odours, but the olfactory level of detection is generally about a thousand times higher than for sulphur compounds. Most complaints are due to unsaturated C_5/C_6 and aromatic compounds which emanate from plants where these compounds are concentrated; the occasional mal-operation results in a detectable leak.

Other specific operations can give rise to identifiable odours such as the smell of methylene dichloride from wax recovery plants. A list of olfactory and threshold limit values is given in Table 1.

Complaints have been reported recently about odours from a few biological treatment plants for purifying refinery effluents. The complainants often quote a "sewer"-type smell which has been reported to be due to the presence of dimethyl sulphide, ethyl and amyl mercaptans (2). This is not a common occurrence, but in some places where a persistent problem has appeared, it has been overcome by steam-stripping the bio-filter feed.

TABLE 1

OLFACTORY AND THRESHOLD LIMIT VALUES

Substances	Odour threshold limits ppm vol/vol	Threshold**) limit values ppm vol/vol
n-Pentane	-	500
n-Octane	-	400
Benzene	5	25
Toluene	2	100
p-Xylene	0.5	100
Cyclopentadiene	-	75
Butadiene	-	1000
Hydrogen sulphide	0.004*)	10
Dimethyl sulphide	0.002*)	-
Carbon disulphide	0.21	20
Methyl mercaptan	0.0008*)	0.5
Ethyl mercaptan	0.0003*)	0.5
Methylene chloride	214	250
Methyl ethyl ketone	10	200
Ammonia	50	25
Phenol	0.05	5

*) WILBY, F.V.: Variation in Recognition Odor Threshold of a Panel. Journal of Air Pollution Control Association, Feb. 1969, Vol. 19, Nr. 2, Feb. 1969, p. 96-100

**) Threshold limit values refer to airborne concentrations of substances and represent conditions under which it is believed that nearly all workers may be repeatedly exposed day after day without adverse effect. In other words a time weighted average for an 8-hour day, 40-hour work week.

4. METHODS OF ANALYSIS

Three different approaches have been applied to refinery odour problems: instrumental measurements, olfactometry (dilution techniques) and odour panels. It is generally agreed that, where possible, a precise instrumental method is preferable to other methods because the instrument measures quantitatively and reproducibly, has a wider linear concentration range, and can usually be arranged to eliminate interference from other odours. However, if the compounds giving rise to the odour have not been identified, or an instrumental method cannot be devised, then one of the other methods must be used: the olfactometer for quantitative measurement, and odour panels to carry out "on the spot" investigations into public complaints.

A major problem with all methods of analysis is the transient nature of many odour problems. Very often the instrument or odour panellist cannot detect the smell even when the measurement is attempted a short time after the initial complaint.

4.1 Instrumental

Gas-liquid chromatography (GLC) is the method most generally used for the determination of air pollutants because of:

(a) the high separation efficiency of the chromatographic columns. Capillary columns are available which will separate most of the components present in gasoline.

(b) the sensitivity and specificity of the detectors (3).

A flame ionization detector (FID) will detect carbon compounds at the ppm level without preconcentration. The flame photometric detector (FPD) is specific for sulphur compounds, being twenty thousand times more sensitive to sulphur than to carbon. However, preconcentration by 10^3 or 10^4 is still necessary to accurately quantify sulphur compounds at the ppb range required for analysis of refinery odours (4), (5) and (6).

A recent invention is a microwave-plasma detector which can simultaneously detect Cl, S, N or O and C. The selectivity and sensitivity are not as good as, for example, those of the FPD, but will probably be adequate for many pollution problems. A unique attribute of this detector is that oxygenated compounds can be detected in the presence of hydrocarbons at the ppm level (7).

Two methods are described in detail because of their general applicability in refinery odour analysis, but it should be stated that many other column and trapping techniques can be employed satisfactorily:

The determination of hydrocarbons in air at the ppm level (Appendix I)
The determination of sulphur compounds in air (Appendix II)

4.2 Olfactometry

Olfactometry, or dilution techniques, involves quantitative dilution of odorous materials with odour-free air until the olfactory threshold limit is reached for a given observer. The strength of the odorous source can then be defined in terms of odour units, i.e. the number of dilutions necessary to reduce the odour to the threshold limit (8).
This technique is useful for:

(a) determining how far above the detectable limit a given odour is, and thus gauging the magnitude of the control problem;

(b) determining the relative efficiency of the various steps which may be taken to effect control;

(c) using pure substances as odorous materials, determining and identifying smells and olfactory levels.

Various commercial instruments are available for this type of work (9).

4.3 Odour Panels

Mention has already been made of the use of odour panels when instrumental methods are not available, but consideration should be given to the direct value of odour panels in the field of public relations. Most complaints from the general public are detected by the human nose and the public readily accepts the odour panel approach to investigating complaints. It must be stressed, however, that panels can assist only in the qualitative identification of odours and possibly in locating the source of an odour. A scheme that has been used for selecting and training an odour panel is outlined in Appendix III.

5. REPORTING OF RESULTS

Mr. Sarteur has devised a novel way of reporting results which highlights the compounds causing odour problems be producing an ODOUR SPECTRUM (1). The odour intensity of each component is determined from the formula:

$$\text{odour intensity } I = \left(\frac{\text{Measured Concentration}}{\text{Olfactory Threshold Limit}}\right)^{k}$$

$$\text{i.e. } \log I = k \log \frac{\text{Measured Concentration}}{\text{Olfactory Threshold Limit}}$$

k = The slope of the response curve for the component, i.e. a measure of the intensity of physiological response to the odour component (1).

The presentation of an odour spectrum is similar to that used for acoustic measurements. However, it should be remembered that odour measurement has not yet reached the precision of acoustics. The olfactory threshold limits quoted in the literature show considerable variation and it is not possible to add up intensities to give an overall intensity as odours can either intensify or suppress one another. However, the odour spectrum is a useful method for presenting results to illustrate which classes of compound are odour sources.

An odour spectrum relating to a point on an aromatic unit is given in Fig. 1. It can readily be seen that the aromatic hydrocarbon unsaturates and sulphur compounds give positive values, i.e. produce detectable smells, but the saturates and cyclic hydrocarbons give negative values and are undetectable.

Fig. 2 shows odour spectra for sulphur compounds from six points around a refinery, showing that the measured level was above the threshold limit.

FIG. 1

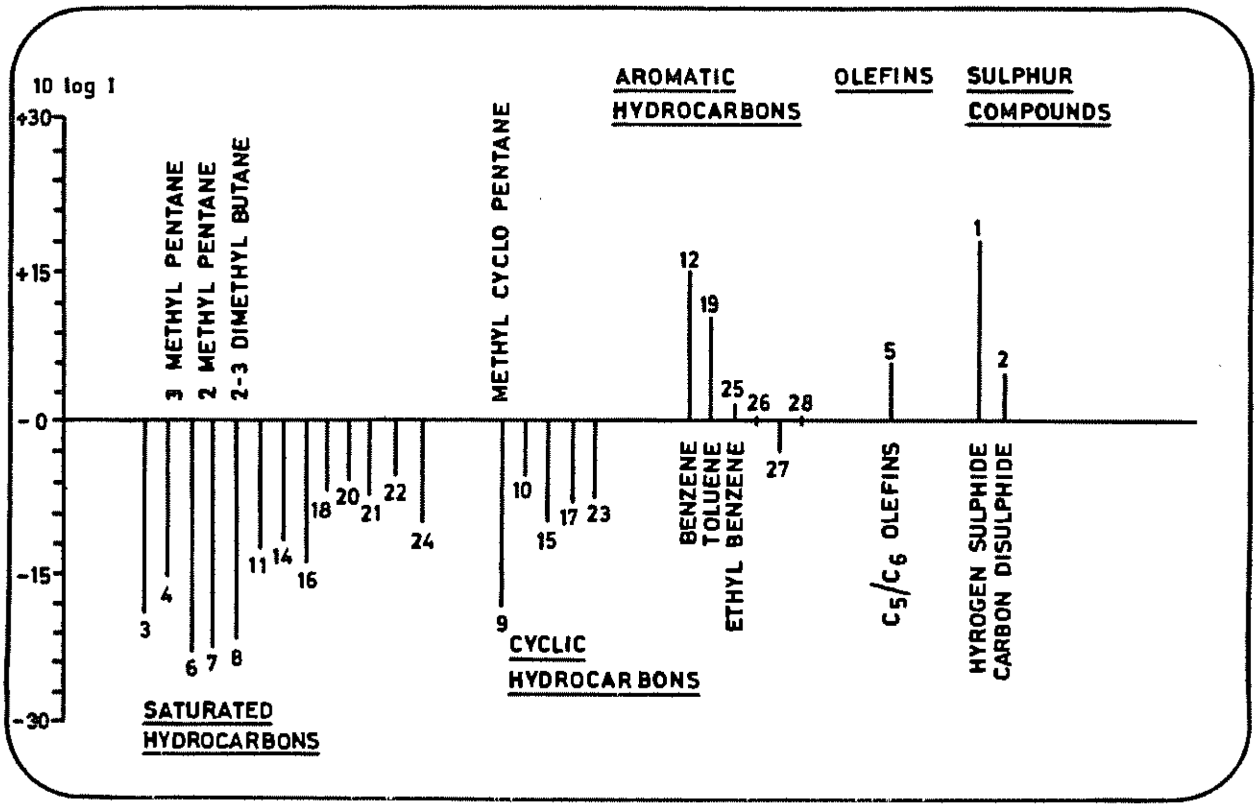
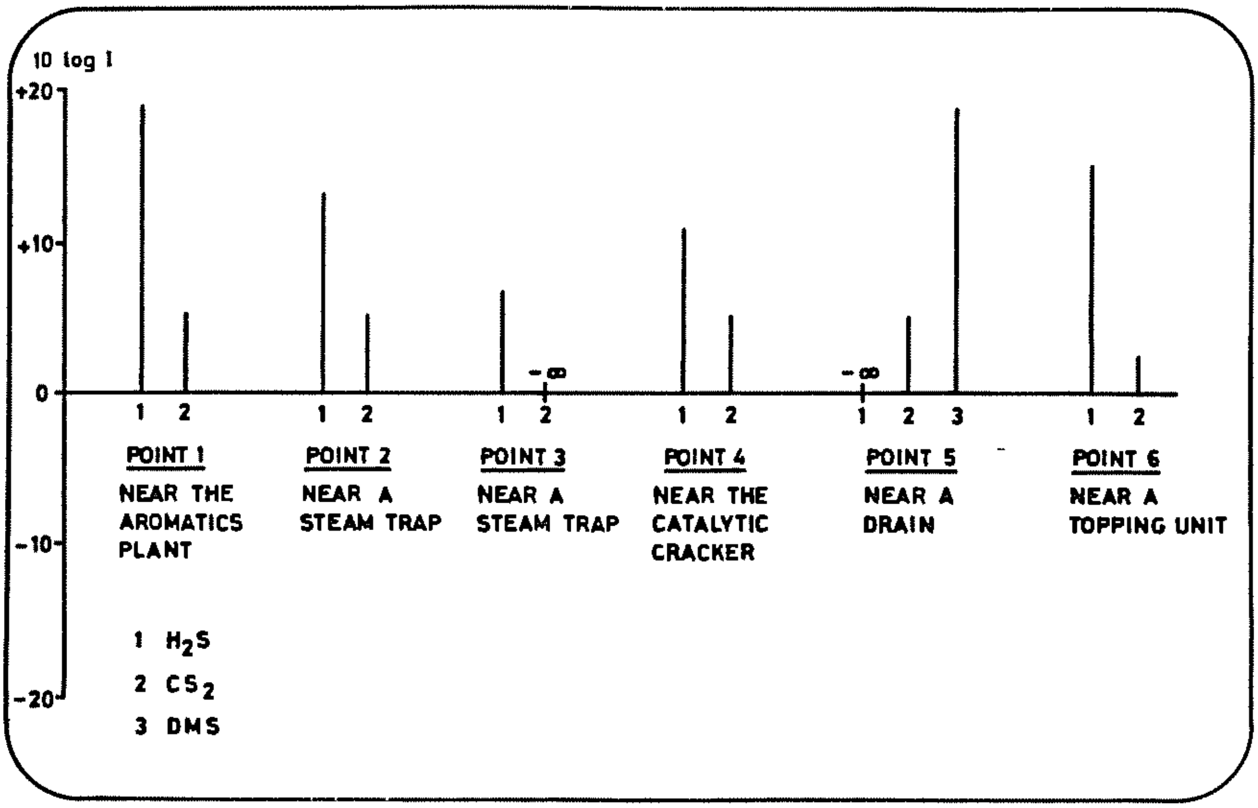

10 log I
+30
+15
0
-15
-30
3 METHYL PENTANE
2 METHYL PENTANE
2-3 DIMETHYL BUTANE
METHYL CYCLO PENTANE
AROMATIC HYDROCARBONS
OLEFINS
SULPHUR COMPOUNDS
12
19
25
26
28
27
5
1
2
3
4
6
7
8
11
14
16
18
20
21
22
24
9
10
15
17
23
BENZENE
TOLUENE
ETHYL BENZENE
C5/C6 OLEFINS
HYROGEN SULPHIDE
CARBON DISULPHIDE
CYCLIC HYDROCARBONS
SATURATED HYDROCARBONS

FIG. 2


10 log I
+20
+10
0
-10
-20
-∞
-∞
1 2
1 2
1 2
1 2
1 2 3
1 2
POINT 1
NEAR THE AROMATICS PLANT
POINT 2
NEAR A STEAM TRAP
POINT 3
NEAR A STEAM TRAP
POINT 4
NEAR THE CATALYTIC CRACKER
POINT 5
NEAR A DRAIN
POINT 6
NEAR A TOPPING UNIT
1 H2S
2 CS2
3 DMS

6. SOURCES OF ODOUR IN REFINERIES

Refineries are not normally considered "bad smell" producing units and do not give off a continuous obnoxious odour. Most problems are due to leakages or other mal-operations which are intermittent in nature and which may usually be prevented by good housekeeping and maintenance.

The table below summarizes some typical refinery smells, their possible source and the most probable compounds contributing to the odour.

Type of Smell	Source	Odorous Compounds
Bad eggs	crude storage	H_2S + trace of disulphides
	distillation of gases	
	sulphur removal	
	flare stacks (extinguished)	
Sewer smell	effluent water	dimethyl sulphide, ethyl and amyl mercaptans
	biological treatment plants	
Burnt oil	catalytic cracking unit	unsaturated hydrocarbons
Gasoline	product storage API separators	hydrocarbons
Aromatics (Benzene)	aromatic plants	benzene, toluene

7. CONCLUSIONS

Oil refineries generally do not have a continuous odour problem. Most complaints are due to intermittent faults during plant operation.

Sulphur compounds, particularly H_2S and mercaptans, are the main source of odour from refineries. Unsaturated hydrocarbons and aromatics can cause odour problems, but less frequently.

Sulphur compounds can be determined down to 1 ppb using preconcentration techniques followed by GLC with a flame photometric detector. Hydrocarbons can be determined down to 1 ppm directly by GLC and down to 1 ppb if preconcentration is used.

Odour panels should be used where an instrumental method is not available or to assist in maintaining good public relations in the refinery area.

8. REFERENCES

1. SARTEUR, R and FAYARD, J.C.
Contribution à l'estimation quantitative d'une odeur par analyse spectrale.
Pollution Atmosphérique, October - December 1974, p. 398-404.

2. MATSUMURA.
A Method of Analysis of Trace Odour Components for Odour Pollution Control.
Sekiyu Gakkai-shi, Vol. 15, No. 7, p. 596-600. (1972) (in Japanese)

3. HARTMANN, C.H.
Gas Chromatography Detectors.
Analytical Chemistry, Vol 43, No. 2, Feb. 1971, 113A.

4. GOODE, K.A.
Gas Chromatographic Determination of Sulphur Compounds in North Sea Natural Gases by a Flame-Photometric Detector.
Journal of the Institute of Petroleum, Vol. 56, No. 547, Jan. 1970.

5. STEVENS, R.K. and O'KEEFFE, A.E.
Modern Aspects of Air Pollution Monitoring.
Analytical Chemistry, Vol. 42, No. 2, Feb. 1970, 143A.

6. PECSAR, R.E. and HARTMANN, C.H.
Automated Gas Chromatographic Analysis of Sulphur Pollutants.
Journal of Chromatographic Science, Vol 11, September 1973, p. 492-502.

7. MCLEAN, W.R.; STANTON, D.L. and PENKETH, G.E.
A Quantitative Tunable Element - Selective Detector for Gas Chromatography.
Analyst, June 1973, Vol. 98, p. 432-442.

8. CORMACK, D.; DORLING, T.A. and LYNCH, B.W.J.
Comparison of Techniques for Organoleptic Odour-Intensity Assessment.
Chemistry and Industry, 2nd November 1974, p. 857-861.

9. DRAVNIECKS, A.
Measuring Industrial Odours.
Chemical Engineering, Deskbook Issue, October 21, 1974. p. 91-95.

APPENDIX I

DETERMINATION OF HYDROCARBONS IN AIR

1. OUTLINE OF METHOD

The method determines C_5 to C_{12} hydrocarbons in air down to 0.1 ppm by separation on an OV101 column temperature programmed from 0°C to 150°C using a flame ionization detector (FID).

2. APPARATUS

2.1 Gas Chromatograph

Any gas chromatograph capable of temperature programming from 0°C to 200°C, fitted with dual FID detectors.

2.2 Columns

Two 10 metres x 3 mm ID stainless steel columns packed with 2% OV101 on 80-100 mesh Chromosorb P support with 0.2% anti-tailing agent added, e.g. ADFET.

2.3 Integrator

An electronic integrator such as the Infotronics 204, Hewlett Packard 3370, the I.T.T. or their equivalent.

3. PROCEDURE

3.1 Setting up

The gas chromatograph is set up so that the two columns have approximately the same flow rate and the dual FID's with similar hydrogen and air rates. This eliminates changes in baseline due to the elution of the stationary phase during temperature programming.

3.2 Sampling

100 mls of sample are drawn through a stainless steel trap 100 mm x 3 mm ID packed with 2% OV101, which is cooled to -70°C with solid CO_2/acetone, using a hand pump of the Dräger or Gas Tec type. The trap maintained at -70°C, is then fitted on to the inlet of the chromatograph and carrier gas allowed to flow through the trap to remove residual air. The trap is then heated to 80°C with hot water and the hydrocarbons are desorbed on to the GLC column.

3.3 Separation and Integration

During the time taken to place the trap in the GC flow system and while any residual air is removed from the trap, the gas chromatograph is maintained at 0°C. As soon as the trap is heated to desorb the hydrocarbons, the temperature programme is started and the column heated from 0°C to 150°C at 3°C/min. Peaks are eluted in approximately the order of their boiling points.
Figure A shows a typical trace with some of the more important components named. A complete list of named peaks with retention times relative to toluene is given in Table A.

Each peak is integrated and the retention time and peak area recorded.

3.4 Calibration

Calibration mixtures containing 10 ppm v/v of hydrocarbon in air are prepared by injecting:

$$\left(\frac{0.1}{22\,400} \cdot \frac{273}{273 + X} \cdot \frac{Y}{760} \cdot \frac{\text{Molecular Wt of hydrocarbon}}{\text{Density of hydrocarbon}} \times 1\,000\right)$$

X = ambient temperature, °C
Y = atmospheric pressure mm Hg.

microlitres of liquid into a 10 litre flask containing a number of 0.5 mm glass beads. The flask is shaken well and the mixture allowed to stand for four hours. 100 mls of the calibration mixture is sampled and chromatographed as for the samples.

The area of each component is measured and the area equivalent for 1 ppm of each component determined. It is obviously not possible to determine responses for every component and it is reasonable to assume equal responses for all saturated compounds of the same carbon number. It is essential to calibrate for benzene, toluene, C_8 and C_9 aromatics as their responses are different from the saturates.

4. CALCULATION

$$\frac{\text{Measured area of component in sample}}{\text{Area response for 1 ppm from calibration}} = \text{ppm of component in sample}$$

Components are named by comparing relative retention times to toluene from those listed in Table A.

APPENDIX I-4

FIG. A

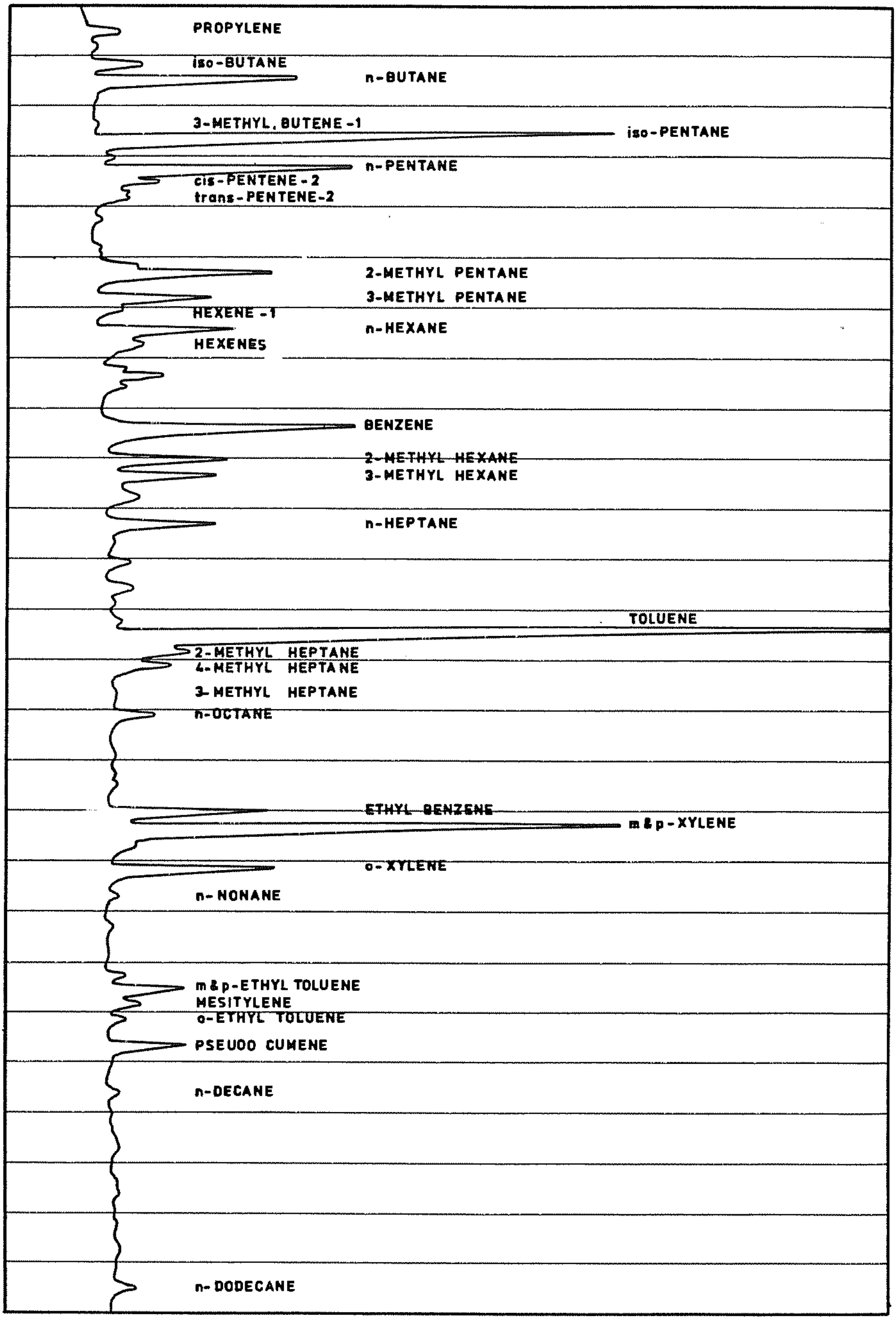


TABLE A

ELUTION ORDER AND RELATIVE RETENTION TIMES OF HYDROCARBONS ON OV101 COLUMN PACKING

ISO-C_5	0.289	TOLUENE	1.000
PENTENE-1	0.316	2 Me HEPTANE	1.023
n-C_5	0.331	3 Me HEPTANE	1.041
TRANS PENTENE-2	0.346	n-C_8	1.113
CIS PENTENE-2	0.353	ETHYL BENZENE	1.248
2 Me BUTENE-2	0.365	m & p XYLENE	1.271
Me PENTENES	0.399	Me OCTANE	1.297
CYCLOPENTANE	0.436	o-XYLENE	1.331
2.3 Di Me BUTENE	0.466	n-C_9	1.365
2 Me PENTANE	0.474	ISO-PROPYL BENZENE	1.406
3 Me PENTANE	0.511	n PROPYL BENZENE	1.477
HEXENE-1	0.526	p-ETHYL TOLUENE	1.496
n-C_6	0.556	MESITYLENE	1.519
Me CYCLOPENTANE/2.2 Di Me PENTANE	0.624	o-ETHYL TOLUENE	1.541
2.4 Di Me PENTANE	0.639	PSEUDO CUMENE	1.571
BENZENE	0.699	p-CYMENE	1.714
CYCLOHEXANE	0.714	n-C_{12}	2.038
2 Me HEXANE	0.744		
3 Me HEXANE	0.767		
n-C_7	0.835		
Me CYCLOHEXANE	0.895		

APPENDIX II

DETERMINATION OF SULPHUR COMPOUNDS IN AIR

APPENDIX II

1. OUTLINE OF METHOD

The method will determine H_2S, SO_2, CH_3SH, CS_2 and $(CH_3)_2S$ down to 1 ppb v/v by trapping these components from a known volume of air on a Porasil D trap at -80°C, desorbing at 40-100°C directly into a polyphenyl ether/phosphoric acid column at 40°C and detecting the eluted components with a flame photometric detector.

2. APPARATUS

2.1 Gas Chromatograph

Any gas chromatograph fitted with a flame photometric detector (Fig. B).

2.2 Detector Conditions

Hydrogen flow 70-80 mls/min, Oxygen flow 20 mls/min and N_2 flow 70-80 mls/min. Temperature 100°C and bias voltage 750 Volts.

2.3 Trap

A U-tube 160 mm long x 3 mm ID packed with Porasil D. To avoid adsorption or reaction the tube must be made of glass with stop valves in passivated INOX steel or made completely in polytetrafluoroethylene (PTFE).

2.4 Chromatographic Column

A metre x 3 mm ID glass column packed with 5% polyphenyl ether and 0.2% H_3PO_4 on 100-150 mesh Porasil D.

3. PROCEDURE

3.1 Sampling

Air is drawn through the trap which is cooled to -70°C with solid CO_2/acetone by a battery operated pump. The residual air being then pumped into a polythene bag so that the actual volume passed through the trap can be measured.

A schematic diagram of the apparatus is shown in Fig. C.

Samples can be taken in the field and then analysed in the laboratory. Tests have shown that the reproducibility of trapping is between 5-10% at the ppb range, if the samples are analysed immediately. On keeping the samples the concentration of H_2S and mercaptans decreases due to oxidation, and it is, therefore, recommended that samples are analysed within three hours of taking to avoid oxidation problems.

3.2 Analysis

The trap is attached to the chromatographic column heated to 40°C and the GLC column carrier gas switched through the trap to desorb the sulphur compounds. The components are eluted in the order, H_2S, SO_2, CH_3SH, CS_2 and $(CH_3)_2S$. Fig. D shows a typical trace. The concentration of each component is determined by measuring the peak area and reading off from a previously prepared calibration graph the equivalent in micrograms (μg).

3.3 Calibration

The chromatograph is calibrated for each component to be measured, using permeation tubes to produce gases of known concentration. An excellent description of the technique is given by Pecsar and Hartmann (Ref. 6), but the essentials are that clean nitrogen at a constant rate is passed into a thermostatted chamber holding PTFE tubes containing a known weight of the component. Diffusion at a constant rate occurs from the PTFE tube depending on the temperature of the chamber. The actual rate of diffusion is measured by weighing the tubes at fixed time intervals on a microbalance. Hence, knowing the nitrogen flow, the concentration of component in the gas can be calculated. Three or more different concentration levels are produced to give a concentration versus peak area curve.

3.4 Calculation of results

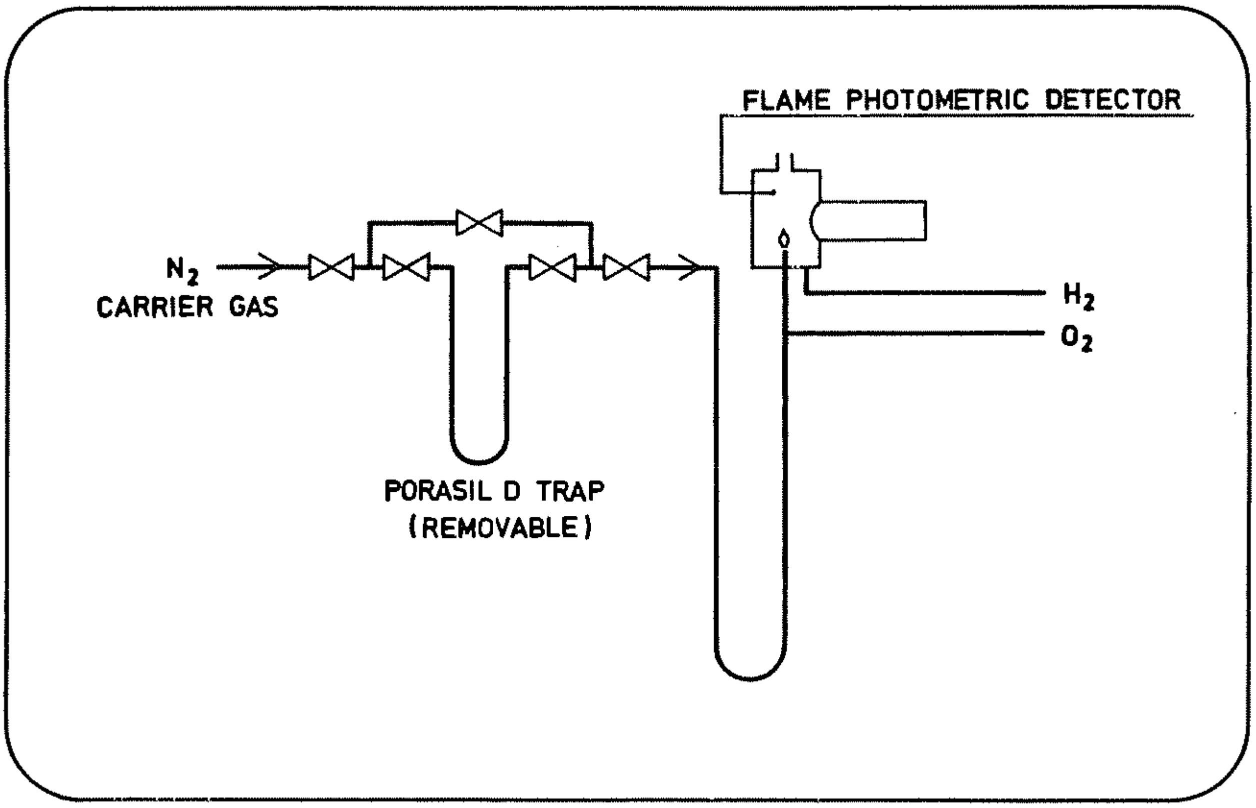
$$\frac{\text{micrograms of component found}}{\text{volume of air taken in litres}} \times 1000 = \mu g/m^3$$

The limits of detection are as follows:

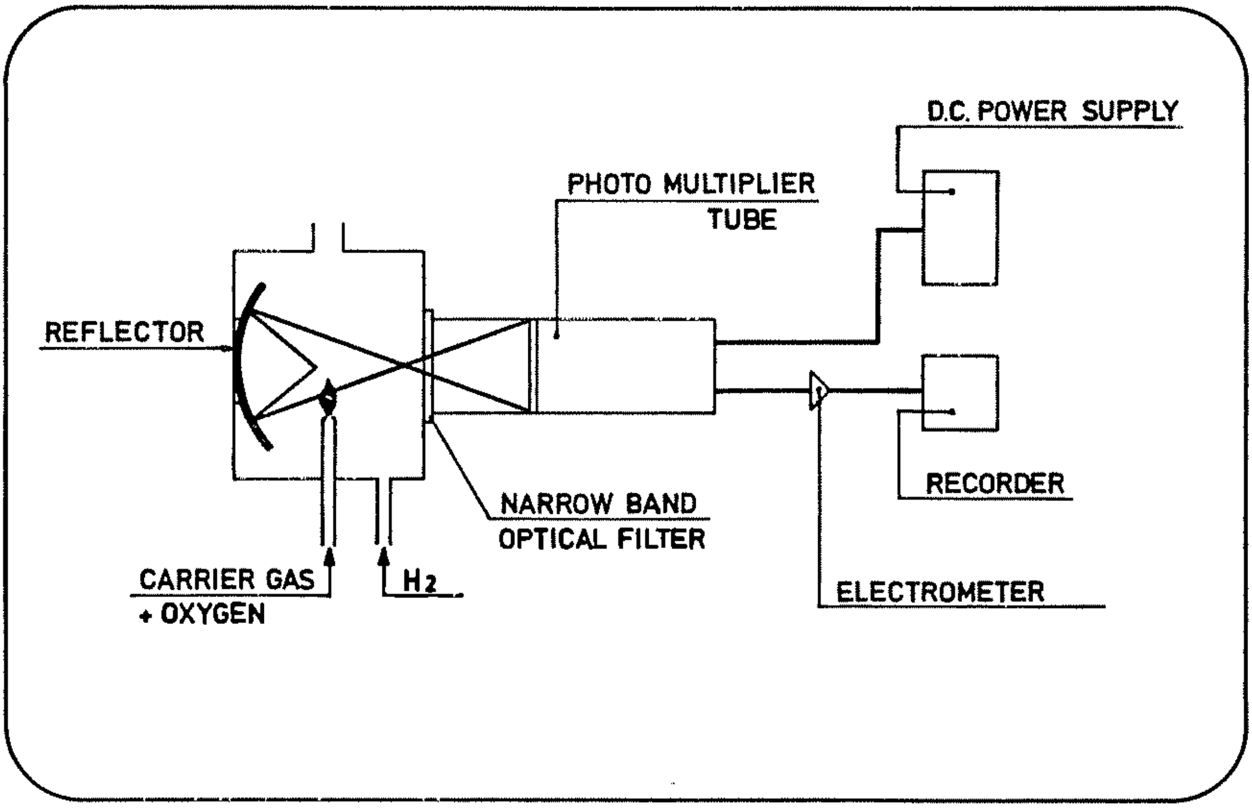
Component	Volume of Air taken	Limit of Detection
H_2S	100 mls	3.5 $\mu g/m^3$
SO_2	3000 mls	0.1 $\mu g/m^3$
CH_3SH	3000 mls	0.1 $\mu g/m^3$

If more than 100 mls of air are taken, then the trap cannot adsorb all the H_2S and break-through occurs.

FIG. B

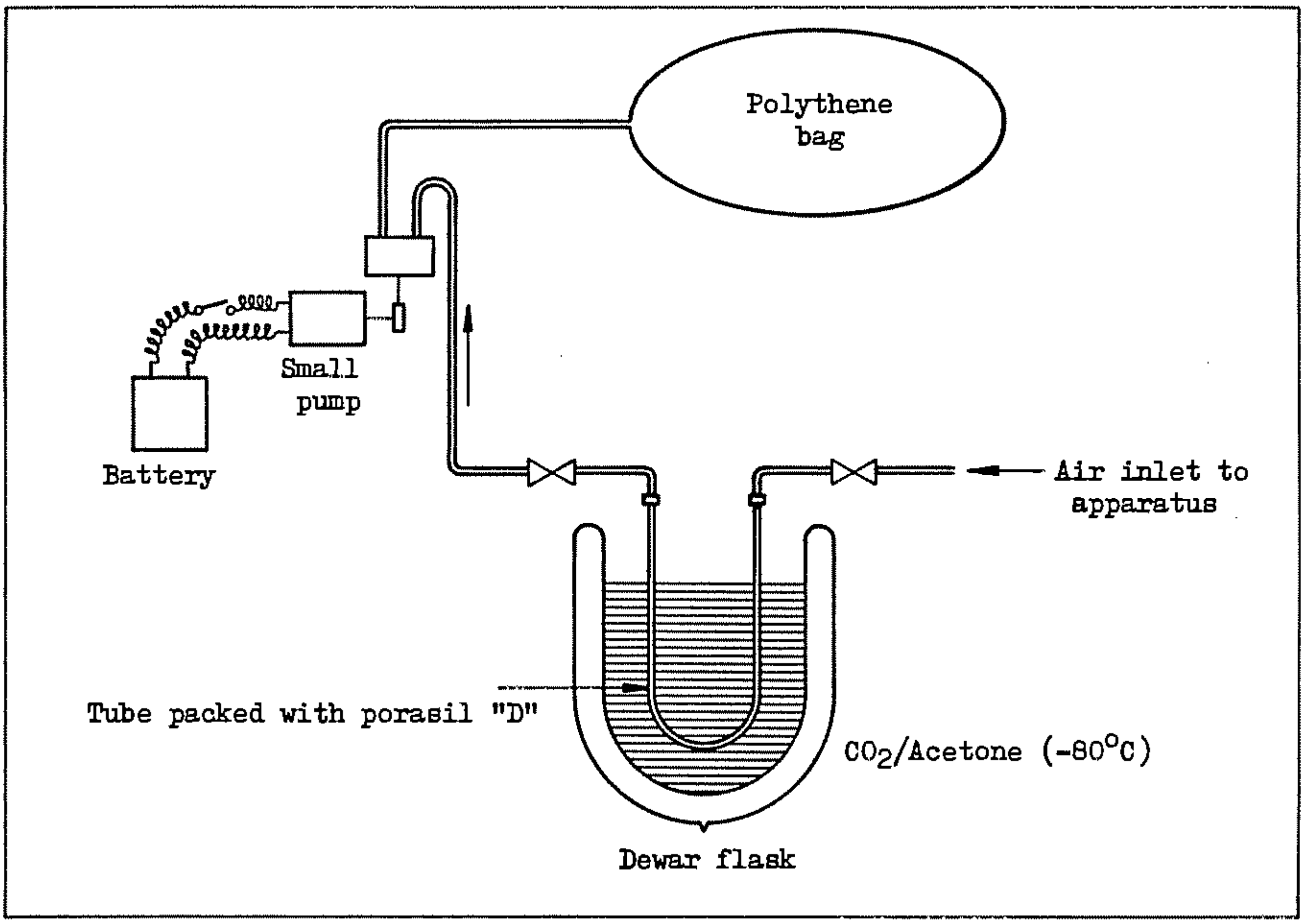


GLC FLOW DIAGRAM FOR ANALYSIS OF SULPHUR COMPOUNDS IN AIR

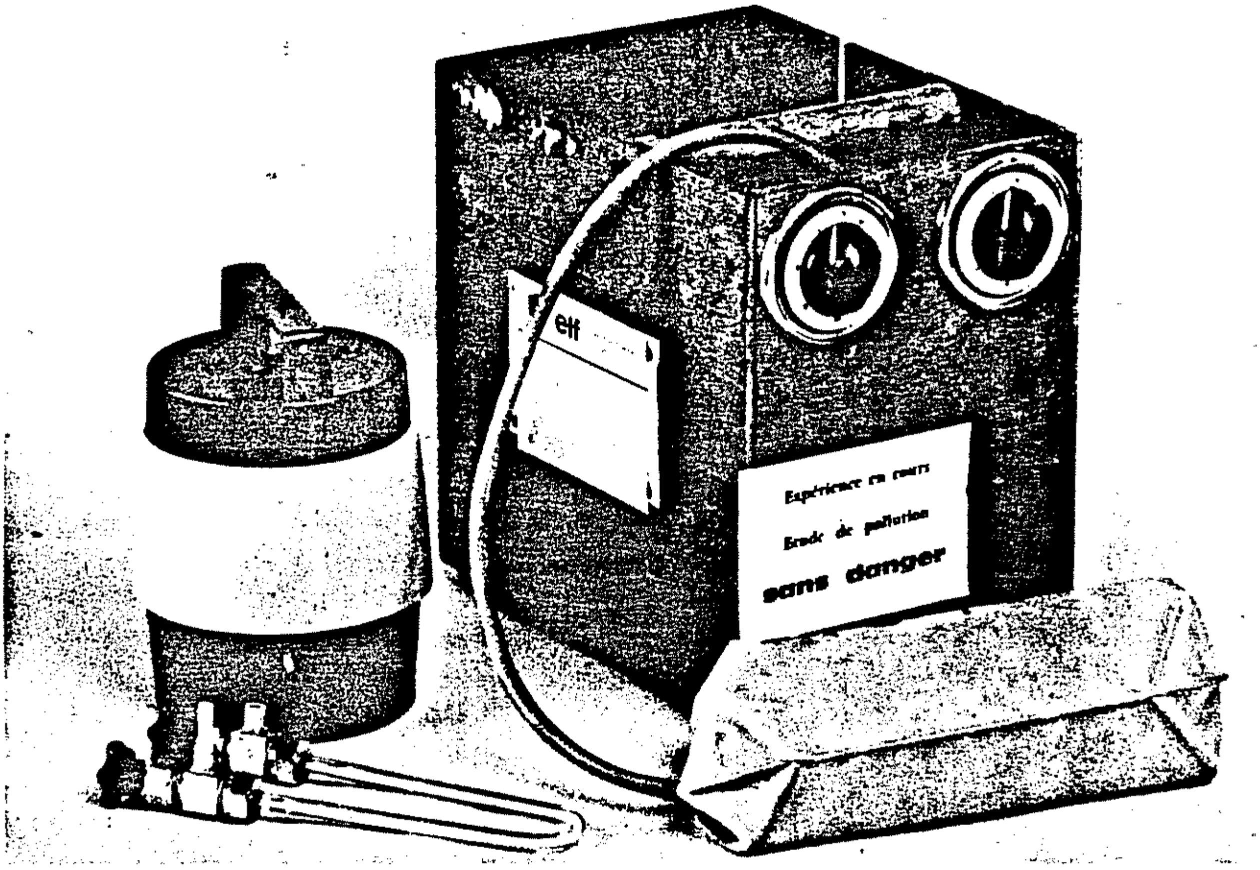


FLAME PHOTOMETRIC DETECTOR (Schematic)

FIG. C

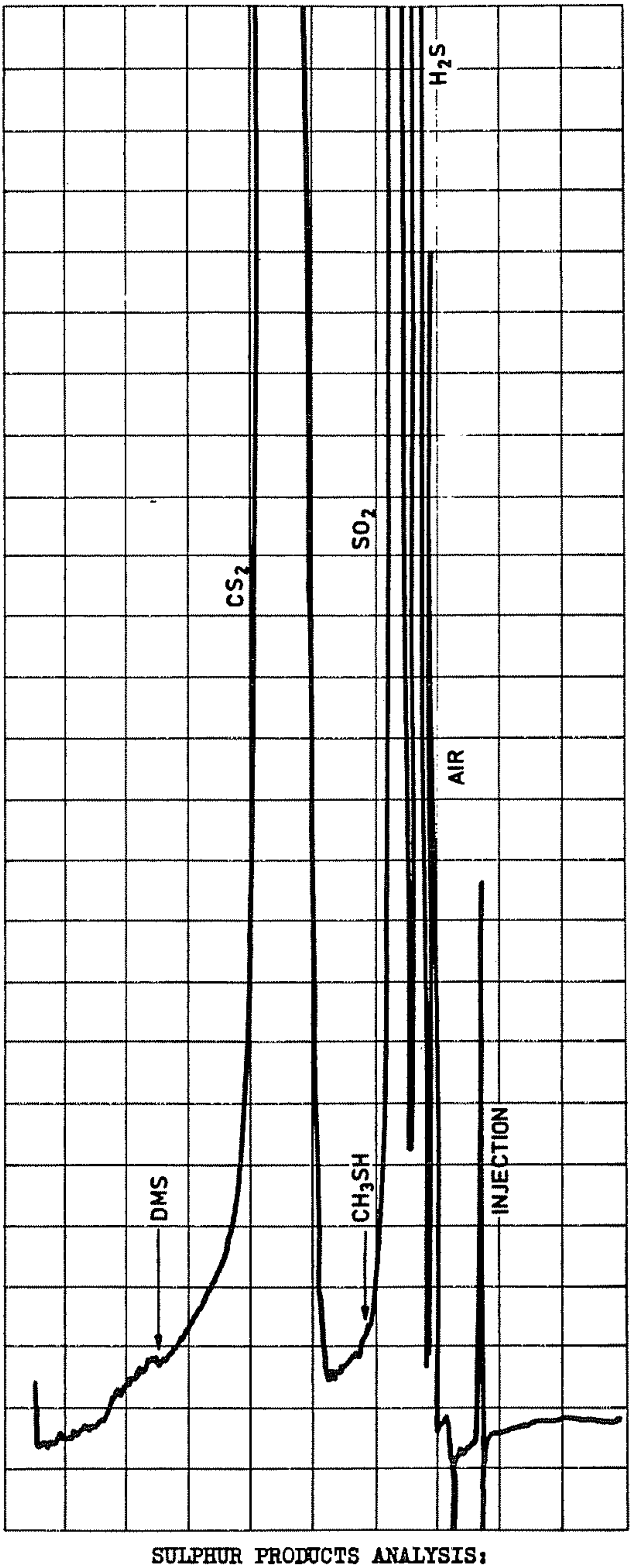


SAMPLING SYSTEM FOR SULPHUR COMPOUNDS (Schematic diagram)



THE APPARATUS

FIG. D



SULPHUR PRODUCTS ANALYSIS:
Chromatogram of trapped sulphur products

APPENDIX III

SELECTION AND TRAINING OF AN ODOUR PANEL

1. SELECTION OF A PANEL

The qualities essential for a panellist depend on the use or uses envisaged for the panel. For this scheme the panellists were required to have the following qualities:

- Sensitivity - able to detect low concentrations of odourants
- Reliability - able to reproduce consistently accurate results
- Honesty - always say exactly what he (or she) perceives
- Good odour memory - able to recall some 50 different odours associated with factory operations and differentiate between similar odours.

A series of tests was devised to select suitable candidates for further training and, because it was felt that chemists would be more conversant with the names of the various compounds, it was decided to ask for volunteers from laboratory personnel.

a. Screening Test 1A - people were asked to indicate what odours they thought they could recognize from a list of 40 chemicals, fragrances and flavours.

Screening Test 1B - samples of 15 of these 40 substances and five other flavours and fragrances were submitted for identification.

This test indicated whether people really could identify a substance from its odour, and also how many odours they thought they knew.

The results showed that less than 12 people could identify more than 90% of the odours they thought they knew.

b. Screening Test 2 - diluted aqueous solutions of a chemical, including unknown "blanks", were used to assess the sensitivity of the volunteers who were asked to indicate whether they could detect an odour.

By repeating the test several times at weekly intervals, it was possible to determine the candidates who were sensitive and honest by their reporting exactly what they perceived and their ability to detect consistently the "blanks".

A similar series of tests was carried out in the vapour phase, diluting a known volume of air containing a known concentration of odorant with known volumes of odour-free air (obtained by passing the air over freshly activated charcoal beds).

Only eight people (from 40) were found to be both highly sensitive and consistently able to detect the "nil" odour of the blanks.

c. Screening Test 3 - a series of "triangle" tests in which the "odd-man-out" of a group of two indentical samples of the same substance and one of a contaminated sample of the same substance, which ranged from markedly different to very similar, was used to determine whether people could hold the memory of an odour and compare it with another, albeit very similar odour.

From all these initial screening tests it was found that there were eight people worth further training.

1.1 Training the Panel

Samples of the odours of the various raw materials, "intermediates", final products and effluents, which were odorous, were obtained from each plant and the panel was allowed to familiarize themselves with the odours during short training sessions held several times each week for some months.

Regular tests were carried out to assess their ability and consistency to identify the odours. A minimum 90% reliability was required.

Routine tours around the various plants, the perimeter and at a distance from the factory were carried out so that the panel could associate certain odours not only with certain plants, but with particular parts of those plants. The tours around the factory and at distance from the factory helped the panel to experience the effect of dilution of an odour under ambient conditions and to determine which odours were persistent. Panellists operated in pairs, but a compound was only deemed to have been identified if both recognized it independently.

It was most necessary during the training period, which lasted many months, and during the subsequent various investigations and routine refresher tests to have a high degree of availability of the panel members. Because of this, the Billingham panel finally comprised six members.

1.2 Advantages of the Use of an Odour Panel

i. An odour can be recognized almost instantaneously "in the field" by a trained panellist, thus obviating the need to obtain a sample, then return to a laboratory and attempt to transfer the sample to an instrument for identification.

ii. The panellist is mobile and can "follow the odour". He can also track the odour back to its source.

iii. An assessment can be made of the character of the odour, i.e. whether it would result in public complaints.

iv. Mal-odours which result in complaints from the general public are detected by human noses. This was why the use of an Odour Panel is accepted by the general public.

1.3 Disadvantages of an Odour Panel

i. It can only be used in short spells, otherwise olfactory fatigue would affect the panellists.

ii. Like an instrument, other odours can affect the panellist, e.g. diesel engine exhaust fumes.

iii. It is not possible to operate for very long in cold weather.

iv. A head-cold or any restriction of the nostrils will seriously reduce the effectiveness of a panellist.

v. A panellist must not wear any odorous material, e.g. perfume, powder, after-shave lotion, which might interfere with the perception of other odours.

vi. The effectiveness of female panellists is seriously reduced during menstruation.

2. DESCRIPTION OF SCREENING TESTS

2.1 Screening Test 1A

Could you please tick any of the following odours which you think you would recognize.

Name: ______________________

Acetone	29 *)	Iso butyl acetate	3
Acetic Acid	29	Lauryl mercaptan	9
Almond	26	Lemon	28
Alphanol	7	Lime	22
Alkyl Amine	16	Methylene chloride	7
Ammonia	30	Mothballs	27
Amyl Acetate	18	Nutmeg	17
Amyl Alcohol	8	Orange	29
Camphor	21	Peppermint	29
Carbon tetrachloride	26	Phthalic Anhydride	16
Chloroform	24	Phenol	22
Cyclohexane	12	Pyridine	23
Dettol	24	Rose	20
Diphenyl Oxide	15	Spearmint	27
Ethanol	24	Sodium Hypochlorite	26
Ether	26	Styrene	12
Ethyl Acrylate	3	TCP	20
Isobutanol	13	Terbutol	8
Isopropanol	16	Toluene	23
Isooctanol	9	White Spirit	19

*) Thirty volunteers participated and the figures by each substance show how many thought they could recognize the odour.

2.2 Screening Test 1B

Name: ______________________________

Samples of 20 different odours are presented to you for this test. The odours are of several types:

i. Specific chemicals, e.g. methanol

ii. Fragrances and flavours, e.g. rose, nutmeg

iii. Common commercial products, e.g. Dettol, "Chloros".

Volunteers should smell all the bottles (numbered 1 to 20) and write down what they think each odour is. If you cannot give a specific name to each odour try and give a description of the odour, e.g. rubber, sweet, leather, beans.

1. Almonds
2. Carbon Tetrachloride
3. Lemon
4. Chloroform
5. White Spirits
6. Spearmint
7. Orange
8. Acetone
9. Iso Propanol
10. Iso Butanol
11. Peppermint
12. Rose
13. Sodium Hypochlorite
14. T.C.P.

------ Additional Odours ------

15. Oil of Wintergreen
16. Cinnamon
17. Coconut
18. Caramel
19. Oil of Cloves
20. Caraway

2.3 Screening Test 2

Name: ____________________________

In this test 10 bottles are presented to you. The bottles marked numbers 1 to 9 contain water which MAY or MAY NOT contain a chemical. The tenth bottle is marked "WATER" and is a sample of uncontaminated water used to make up the solutions in the bottles marked 1 to 9. Volunteers should smell each bottle in sequence and indicate below whether they can or cannot detect an odour. Reference can be made to the bottle marked "WATER" at any time in the test. For the other bottles no repeat sampling is allowed, e.g. after smelling say Bottle 6 a candidate cannot re-smell Bottle 4. You are not required to identify the odour. All you are required to do is to indicate whether you can or cannot detect an odour.

All candidates must wear a clean pair of disposable gloves before handling the bottles.

Tick as Applicable

	Yes	Probably Yes	Possibly	Possibly Not	No
Bottle 1					
Bottle 2					
Bottle 3					
Bottle 4					
Bottle 5					
Bottle 6					
Bottle 7					
Bottle 8					
Bottle 9					

2.4 Screening Test 3

Name: ______________________________

The object of this test is to distinguish differences between food flavours or fragrances that are very weak in intensity. There are eight sets of samples. Each set consists of three samples, e.g. Set 5 consists of three samples numbered 5A, 5B and 5C. In each set two samples are the same, and one of the three samples is different from the other two. Your task is to pick out the different or odd one. You do not have to identify the odour, just pick the "odd-man-out". Enter on the score sheet the code number of the sample which you choose as the odd one.

Candidates should wear a pair of disposable gloves before handling the bottles. Alternatively, candidates should wash their hands thoroughly before taking the test.

Set 1. ....

Set 2. ....

Set 3. ....

Set 4. ....

Set 5. ....

Set 6. ....

Set 7. ....

Set 8. ....