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Oil Product Development/J Viljanen

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THRESHOLD ODOUR NUMBER FOR MTBE

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SUMMARY

Odour threshold value was determined for methyl tertiary butyl ether (MTBE). The measurement was carried out as a sensory panel test according to the ASTM Standard Method D 1391-78. The panel consisted of eight members. Odorous samples in order of increasing concentration and blank air samples were presented to the panelists by means of glass syringes. The panel-averaged odour detection threshold was 1.1 mg/m^3. All the individual threshold values were in the range of 0.37 to 1.9 mg/m^3. The estimated maximum concentration of MTBE emissions in the process area is of the same magnitude as the threshold odour number measured in this study. A fairly low odour threshold number indicates that excessive MTBE emissions are readily detected because of easily perceptible odour.

1. INTRODUCTION

A chemical's odour threshold can be defined as the minimum concentration of the compound that is definitely perceived by a tester. However, at present there are no known physical or chemical properties of odorous materials that reliably correspond with their odour. The only accepted method of measuring odours uses a panel of human observers. Consequently, no absolute values can be obtained because the detection limits vary among individuals and with time and perception conditions. Even with these deficiencies, average odour threshold values are useful parameters for environmental and safety assessments. One can use the threshold odour number to predict:

* Will a particular chemical cause smell in the vicinity of processing and handling equipment ?

* How easily dangerous concentrations (occupational health and flammability hazards) can be identified by means of odour ?

In an extensive literature search, no threshold value was found for the MTBE odour in air. Instead, a review of published data for gasoline components /1/ presents a threshold value of 0.7 mg/l for the odour of MTBE in water. Because more accurate knowledge of the odour behaviour of MTBE is needed for the design of MTBE plants, we decided to determine the threshold odour number experimentally at research laboratories of Neste.

Different methods and different experimental conditions yield wide scattering of threshold values. For some components published data have varied in the range of several order of magnitudes; for example the range for 24 published odour threshold values for benzene was from 0.05 to 495 mg/m^3 /1/. In order to get a reliable result, our measurement system was arranged to meet at least the three main criteria set as minimum requirements for a valid odour threshold determination procedure /1/:

* Odorants presented to panelists in an ascending concentration series.

* A maximum of 2- to 3-fold concentration interval separating stimuli in the series.

* Panel size of greater than five judges.

2. EXPERIMENTAL TECHNIQUE

2.1 Summary of the Method

A standard test method ASTM D 1391-78 /2/ was used to determine the threshold odour number for MTBE. This method is based on the use of a human sensory panel. Samples of the substance whose odour threshold is to be measured are tested beginning with a dilution beyond the point at which odour can be detected. Increasing concentrations in air are examined until a point is reached at which the odour is consistently detected, each step in the concentration increase consisting of doubling the proceeding concentration.

2.2 Panel

The total number of panel members in the study was eight, divided into two groups of four. Most of the panelists were aged between 30 and 40. Both sexes were represented (5 female, 3 male). All panel members were experienced in sensory testing (both odour and taste). All precaution conditions required in the standard test were fulfilled: none of the panelists had used perfume preparations prior the test nor had smoked tobacco or eaten for at least one hour before the test.

2.3 Samples

A sample of commercial MTBE product with purity of 99.0 WT% was used to prepare gaseous MTBE/air mixtures, which were used as stock materials in the preparation of the diluted samples for evaluation by the panel.

Three stock samples (see Table 1) were prepared into plastic bags made of TEDLAR^{R} and equipped with a metallic valve. These bags were flushed with pure nitrogen and evacuated with a vacuum pump several times before use. Each bag was then filled with an air volume of 20 litres, which was measured with a dry-operated displacement type dosimeter pump. A measured amount of liquid MTBE was injected with a microsyringe through the connecting hose wall into the air stream inside the valve space of the bag. This procedure ensures that all MTBE added will be evaporated in the gas phase. The similar equipment and technique are used to prepare low concentration calibration samples for environmental control analyses at Neste.

Table 1. Stock samples of MTBE in air

Code	Mixing ratio of ingredients	MTBE concentration mg/m^3
A	20 l MTBE / 20 l air	745
B	1 l MTBE / 20 l air	37.25
C	50 ml of A / 19.95 l air	1.8625

Both odorous and blank samples were presented to the panelists in 100 ml Luer-type hypodermic glass syringes (manufactured by Becton-Dickinson & Co., Rutherford, N.J., U.S.A.). These syringes have a ground glass plunger and barrel without any O-ring seal, which could give rise to interfering odours. All syringes were rinsed in ethanol and distilled water and dried in an oven before use.

In filling of the presentation syringes, a transfer needle described in the ASTM method was not used because the desired volume of sample gas could easily be taken directly into the syringe from the sampling bag. The series of MTBE concentrations used in testing was prepared by diluting the measured sample gas volumes with odour-free air in the manner described in Table 2.

Table 2. MTBE concentrations in air presented to the panel

Sample no.	Odorous stock sample measured ml	Diluting air ml	MTBE concentration mg/m^3
1	10 of C	90	0.18625
2	20 of C	80	0.3725
3	50 of C	50	0.93125
4	100 of C	0	1.8625
5	10 of B	90	3.725
6	20 of B	80	7.45
7	40 of B	60	14.9
8	80 of B	20	29.8
9	10 of A	90	74.5

2.4 Procedure

The sensory test was carried out in an odour-free room, where the panelists were partitioned off each other. The syringes were filled in an odour-free preparation room out of sight of the panel. All syringes and sample bags were kept at least for two hours before the test in the preparation room in order to reach a temperature equilibrium.

Beginning at the lowest concentration, a pair of similar capped syringes containing both a diluted sample and a blank was presented on a tray to each panelist. Both the test assistants and the panelists wore cotton gloves to avoid any misinterpretations due to smell of fingers. Each panel member ejected a stream from one syringe at a time in front of his/her nose and tried by sniffing to identify which of the syringes contained the odorous sample. A forced-choice technique was applied, i.e. each panelist had to select the syringe he/she thought would contain the odorous substance. In addition, panel members were allowed to mark on the questionnaire whether the selection was made purely on the ground of guessing.

The syringe pairs were circulated from one panelist to another in the consecutive rounds so that the syringe codes were different from those of the previous choice situation. The blank sample syringes were never used for dilution samples.

When a panelist has chosen correctly at one odour level and at two subsequent levels, the concentration at which the panelist first made a correct choice is taken as his/her odour threshold for that substance.

3. RESULTS

When the lowest concentration was presented, none of the panelists was firmly able to distinguish between the odorous and the blank sample: they all guessed. At the following concentration level, two panel members were convinced that they had identified the odorous sample, but out of these two only one had chosen the correct alternative. The distribution of the right and the wrong answers was half and half at each of the two lowest concentrations.

Beginning at the concentration of 1.86 mg/m^3 (the fourth sample), all panelists were able to make the correct choices. Each panel member also expressed that they could identify the odorous sample syringe without any hesitation from the fifth sample onwards at the latest.

As presented in Table 3, the individual threshold values of the panelists ranged from 0.37 to 1.86 mg/m^3. As the geometric average of the panelists' thresholds, the measured threshold odour number for MTBE is 1.1 mg/m^3 (0.3 vol-ppm).

Table 3. The results of the odour threshold determination

Panelist	Individual threshold value	
	MTBE conc. C mg/m^3	log C
A	0.93125	- 0.031
B	1.8625	0.270
C	0.93125	- 0.031
D	0.93125	- 0.031
E	1.8625	0.270
F	0.3725	- 0.429
G	0.93125	- 0.031
H	1.8625	0.270
Average		0.0321
Panel-averaged detection threshold		1.08 mg/m^3

4. DISCUSSION

Odour detection threshold values for some gasoline components and other chemicals are given in Table 4. An adequate comparison with MTBE is difficult because of large variations in published values. In general, it can be stated that typical problematic odorous substances such as methyl mercaptan and H_2S can be detected at much lower concentration than MTBE. The odour detection thresholds for major aromatic compounds found in gasoline are fairly close to that of MTBE.

Table 4. A comparison of threshold odour numbers

Compound	Odour detection limit in air, mg/m³ Accepted by API/1/	Other data	Range of published data, mg/m³	Reference
Benzene	123		0.05 - 420	/1/
Toluene	12		0.39 - 170	/1/
m-Xylene	2		0.35 - 5.2	/1/
p-Xylene	8		0.6 - 8	/1/
Cumene	0.5		0.025 - 0.5	/1/
Naphthalene	0.1		0.053 - 0.48	/1/
n-Hexane			230 - 875	/1/
Methanol	7800		4 - 260,000	/1/
Ethanol	93		8 - 76,000	/1/
Isopropanol		8.8	3 - 1,500	/1,3/
Acetone		5.4	0.20 - 1,085	/3,4/
Diethyl ether		2.9	1 - 300	/3,4/
MTBE		1.1		This study
Hydrogen sulphide		0.006		/3/
Methyl mercaptan		0.0008		/3/

Typical MTBE emission levels of approximately 1 vol-ppm or below have been found in the process area of major U.S. MTBE plants /5/. This means that the odour of MTBE can possibly be perceived only in the immediate vicinity of fugitive emission sources. Larger leakages are yet readily revealed to the process personnel in the area due to the fairly low odour detection threshold. The odour of MTBE thus helps to notice leakages much earlier than dangerous (e.g. flammable) concentrations are formed.

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