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Odour Detection Threshold Values for Fifty-Two Selected Pure Compounds

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This paper provides updated odour detection threshold values (ODTV) for fifty-two (52) pure compounds. In 2014, the first updated odour threshold data (Bokowa, 2014) was presented for twenty-four (24) pure compounds. Over the past eight (8) years, more studies were performed, and another twenty-eight (28) compounds were chosen for odour threshold studies. There have only been a few publications with odour detection threshold values for pure chemicals, and most of these publications have not been updated and are therefore not current.
Between 1960 and 1990, different methodologies for determining odour thresholds were used. In the 1960 and the 1970s, the common approach for defining ODTV was to determine the odour threshold value by smelling a syringe filled with different chemical concentrations. This, of course, was highly inaccurate and did not rely on scientific analysis, but rather on estimation. In the late 1970s when dynamic olfactometry was introduced, new ODTVs were developed based on the dynamic olfactometry method. However, at this time, it was unknown that the flows from the sniffing ports play an important role in the evaluation process, and, therefore, in the final results. In the late 1980s, flows at the sniffing ports of the olfactometer were too low, and actual samples were diluted with ambient air during evaluations resulting in much higher odour detection threshold values (actual lower results). In 2003 with a newly developed European Standard, and armed with the knowledge that sniffing flows during evaluations should be around 20 L/min in order not to dilute the sample during analysis, there was a need to update the ODTV. This study is based on the evaluation of fifty-two compounds for odour detection threshold values. These values were compared with those previously developed for those chemicals or any other available resources. Odour offensiveness and complaint threshold values are also determined for these compounds.
Keywords: Odour, odour detection threshold value, olfactometry, odour evaluation, odour offensiveness threshold value, odour complaint threshold value, panelist, pure compounds

1. Introduction

The most common odour threshold value is the odour detection threshold value. There are other threshold values that have been developed (Bokowa, 2008) such as the offensiveness threshold value and the complaint threshold value. These values represent a point where 50 % of the population can determine that the already detected odour is offensive or they will complain about the odour, respectively.
Originally the ODTVs for pure compounds were studied and developed in the late 1960s. However, the odour threshold data previously available had shown wide variations reflecting the diversity of procedures and techniques used. In 1967, Leonardos, Kendall and Barnard presented data for odour detection threshold values (Leonardos et al., 1967) for 53 pure compounds. The technique used by these three researchers was based on injecting liquids of pure compounds into the test room using gas-tight syringes. The technique used by these researchers was very simple and contained many errors from today's perspective of odour evaluations. Another well-known researcher: Andrew Dravnieks 1980 published threshold values for pure compounds (Dravnieks, 1980). At this time, he studied the dynamic olfactometry method versus the syringe method. In 1983, two other researchers, Amoore, and Hautala, developed odour threshold values for 214 chemicals (Amoore, Hautala, 1983). The American Industrial Hygiene Association (AIHA) published odour thresholds for 102 compounds in

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1989. (AHIA, 1989). The AHIA reference did not incorporate any odour threshold data that were more recent than the 1980s, even though it was last published in 1997, and a lot of the data they relied on was much older. However, since then, there have been many changes in the odour evaluation process, moving from the rudimentary syringe method to a more complex dynamic olfactometry method. Changes in the flow rate presented at the sniffing ports during dynamic olfactometry evaluation, and changes in the criteria selection for panelists resulted in the urgency to update real odour detection threshold values for pure chemicals. In 2003, the European Standard EN 13725 (EN 13725:2003) set some parameters for odour evaluations, such as using 20 L/min flow-rates at each sniffing port, which had been carefully studied by European researchers. They determined that the flow at these sniffing ports was critical for obtaining relatively error-free final results. Flows lower than 20 L/min greatly impacted the results due to the flow registering below the average sniffing rate of an average person. This resulted in dilution of the sample with ambient air during evaluations and therefore lowered the overall results (I.E., higher numbers).

In addition, a study performed in 2006 (Bokowa, 2006) showed that any flow-sets below 14 L/min at the sniffing port of a dynamic olfactometer used for odour evaluations would significantly lower the results (and result in a greater ODTV). For example, the flow of 3 L/min, which in the 1980s was commonly used at the dynamic olfactometer for odour evaluations, produced up to 10 times lower results when compared to results obtained when 20 L/min flow was used for evaluations. Therefore, all data developed before 2003 are considered irrelevant and need to be updated. There is an urgency to update the odour detection threshold values (ODTV) for pure compounds due to these values being very often used by regulators to set guidelines.

In 1991, Nagy undertook work sponsored by the Air Resources Board of the Ontario Ministry for the Environment (Nagy, 1991). The odour detection threshold values were developed for 86 pure compounds. However, this research was done with a low flow-rate. Van Gemert (1999) is a compilation reference based on literature values of odour threshold concentrations incorporating studies since 1977 (Gemet, 1999). The most recent study incorporated prior to this review was Devos et al,1990. This latest reference is essentially an update of the earlier compilations. No attempt was made to critically evaluate the data, but data were given chronologically for each compound with the original data source identified. More than 1100 compounds with one or more odour threshold references were reported. However, there has been no published data for detection threshold values since 2003, and thus there is a need to determine the real detection threshold values, which will be based on the 20 L/min flow rate at the sniffing port, representing the most accurate threshold values.

2. Methodology

Originally, when the project started in 2014, the purpose of this paper was to develop odour threshold values for only 24 pure compounds. However, over the past eight years, more studies have been performed, resulting in the development of odour threshold values for 52 pure compounds. Therefore, this study was divided into three rounds: the first two rounds of the study were performed up to 2014. During the first round only fourteen pure compounds were selected for an extensive study, where the tests were repeated three times. For round two of the study, where only one set of evaluations was presented the remaining ten compounds were selected. The third round of the study was performed between 2014 and 2020, and an additional twenty-eight more compounds were studied.

The following fourteen pure compounds were selected for Round 1 (extensive study):

Acetone; Acetic Acid; Butyric Acid; Butyraldehyde; Carbon Disulfide; Dimethylamine; Ethanol (Ethyl Alcohol); Ethyl Benzene; Hexane; Hydrogen Sulphide; 2-Propanol (Propyl Alcohol); Sulphur Dioxide; Toluene; Valeric Acid.

The following ten compounds were selected for Round 2 (limited study):

Ammonia; Acrylic Acid; Dimethyl Disulphide; Dimethyl Sulphide; Formaldehyde; Methyl Mercaptan: Ozone; Phenol; Tetrahydrofuran; Trimethylamine.

The following twenty-eight compounds were selected for the third round of the study:

Acetaldehyde; Acetylene; Biphenyl; Benzyl Sulphide; Benzene; Carbon Tetrachloride; Chlorobenzene; Dimethyl Ether; Diphenylamine; Ethyl Acetate; Ethyl Isobutyrate; Ethyl Acrylate; Ethyl Mercaptan; 2-Ethyl- 1 Hexanol; Furfural; Heptane; Heptanol; Isobutyl Isobutyrate; Isopropyl Acetate; Methyl Acrylate; Methyl Amyl Ketone; Methyl Ethyl Ketone; Methacrylic Acid ; Naphthalene; Oleic Acid; Propionic Acid; Pyridine; Styrene.

Samples of the odorant were prepared in clean sample bags. Each bag was filled with a known amount of nitrogen. For the first and third rounds of the study, each pure compound was determined three times and three odorant sample bags were prepared the same way. For the limited study (Round 2), only one sample bag was prepared in the same way. A small amount of the pure compound was injected into the bag. The injected amount of pure compounds was determined based on the strength of the compound. For example, 100 uL of Hexane was injected into 20L of nitrogen, whereas only 10uL of Toluene was injected into the same amount of nitrogen.

Before injection, the syringe was purged three times with the compound. After injection, the sample bag was left for 30 minutes so that the compound was well mixed in the bag.

Each prepared sample was evaluated within two hours after preparation by the dynamic dilution olfactometer at Environmental Odour Consulting's laboratory, based on the European Standard EN 13725:2003 (EN 13725, 2003) and the Ontario Ministry of the Environment Method ON-6 "Determination of Odour Emission from Stationary Sources (ON-6, 2010). The binary choice mode was chosen for odour evaluations. The panelists' responses were recorded by computer software and were processed to determine the ODTV for each sample. The ODTV is a dilution factor and therefore has no units. For convenience, however, the ODTV may be expressed in odour units (ou). In addition, the offensiveness threshold value and complaint threshold value were determined for each sample. The point where 50 percent of the panel determined that the odour is offensive was recorded as the offensiveness threshold value (OFTV), and the point where 50 percent of the population would complain about the odour was recorded as the complaint threshold value (OCTV). A screened odour panel was used for all evaluations. They were tested for odour sensitivity and were considered to be within the normal range according to the European Standard EN 13725:2003 (now 2022). Each sample was evaluated once according to the Ontario Ministry of Environment Method ON-6 guideline.

The results for extensive study for odour detection threshold values, offensiveness threshold values and complaint threshold values for 14 compounds are presented in Table 1.

Table 1: Odour Detection Threshold Values, Offensiveness Threshold Values and Complaint Threshold Values for Selected Pure Compounds: Round 1

Compound	ODTV ppm	OFTV ppm	OCTV ppm
Acetone	3.96-5.39	5.25-7.50	7.09-8.37
Acetic Acid	0.48-0.55	0.66-0.80	0.78-1.00
Butyric Acid	0.004-0.005	0.005-0.006	0.005-0.006
Butyraldehyde	0.013-0.015	0.016-0.019	0.016-0.019
Carbon Disulfide	0.026-0.038	0.029-0.041	0.033-0.046
Dimethylamine	0.081-0.104	0.097-0.126	0.115-0.154
Ethanol	4.76-7.48	6.25-12.32	7.62-16.76
Ethylbenzene	0.014-0.018	0.023-0.028	0.028-0.036
Hexane	1.31-2.07	1.90-2.58	2.45-3.32
Hydrogen Sulphide	0.000047-0.000072	0.00009-0.0001	0.00009-0.0001
2-Propanol	2.16-2.41	3.36-4.15	3.88-4.86
Toluene	0.089-0.117	0.153-0.195	0.180-0.261
Sulphur Dioxide	0.11-0.12	0.11-0.12	0.11-0.12
Valeric Acid	0.0014-0.0016	0.0019-0.0022	0.0022-0.0025

The results for the limited study for odour detection threshold values, offensiveness threshold values and complaint threshold values for 10 compounds are presented in Table 2.

Table 2 Odour Detection, Offensiveness and Complaint Threshold Values for Selected 10 Pure Compounds- Round 2

Compound	ODTV ppm	OFTV ppm	OCTV ppm
Ammonia	0.7	0.9	1.1
Acrylic Acid	0.0088	0.0092	0.0092
Dimethyl Disulphide	0.0019	0.0022	0.0026
Dimethyl Sulphide	0.0028	0.0032	0.0036
Formaldehyde	0.070	0.090	0.10
Methyl Mercaptan	0.00015	0.00018	0.00018
Ozone	0.001	0.0020	0.0040
Phenol	0.011	0.013	0.014
Tetrahydrofuran	0.4	0.6	0.8
Trimethylamine	0.00011	0.00013	0.00013

Table 3 Odour Detection, Offensiveness and Complaint Threshold Values for Selected 28 Pure Compounds-Round 3

Compound	ODTV ppm	OFTV ppm	OCTV ppm
Acetaldehyde	0.0010-0.0014	0.0015-0.0021	0.0015-0.0021
Acetylene	78-82	118-124	178-187
Biphenyl	0.000051-0.00007	0.000077-0.00011	0.000077-0.00011
Benzyl Sulphide	0.00018-0.00024	0.00027-0.00036	0.00040-0.00054
Benzene	1.8-2.4	2.7-3.62	2.7-3.62
Carbon Tetrachloride	8.2-9.4	12.3-14.19	12.3-14.19
Chlorobenzene	0.09-0.11	0.136-0.166	0.136-0.166
Dimethyl Ether	20.26-22-14	30.59-33.43	46.19-50.48
Diphenylamine	0.0118-0.0164	0.0178-0.0248	0.0178-0.0248
Ethyl Acetate	1.2-1.6	1.81-2.41	4.12-5.50
Ethyl Acrylate	0.00010-0.00012	0.00015-0.00018	0.00023-0.00027
Ethyl Isobutyrate	0.000028-0.000032	0.000042-0.000048	0.000063-0.000073
Ethyl Mercaptan	0.0000052-0.0000064	0.0000079-0.0000097	0.0000079-0.0000097
2-Ethyl, 1 Hexanol	0.024-0.036	0.036-0.054	0.054-0.082
Furfural	0.036-0.042	0.054-0.063	0.082-0.095
Heptane	3.8-4.6	5.7-6.9	8.6-10.5
Heptanol	0.064-0.082	0.097-0.124	0.146-0.187
Isobutyl Isobutyrate	0.030-0.042	0.045-0.063	0.068-0.096
Isopropyl Acetate	0.14-0.16	0.21-0.24	0.32-0.36
Methyl Acrylate	0.0017-0.0020	0.0026-0.003	0.0039-0.0046
Methyl Amyl Ketone	0.0065-0.0082	0.0098-0.0124	0.0098-0.0124
Methyl Ethyl Ketone	0.32-0.40	0.48-0.60	0.72-0.91
Methacrylic Acid	0.042-0.050	0.063-0.076	0.095-0.115
Naphtalene	0.0028-0.0036	0.0042-0.0054	0.0063-0.0082
Oleic Acid	0.48-0.54	0.72-0.82	1.08-1.24
Propionic Acid	0.0059-0.0066	0.0134-0.0150	0.0202-0.0227
Pyridine	0.042-0.051	0.063-0.077	0.063-0.077
Styrene	0.029-0.042	0.044-0.063	0.044-0.063

Table 4 presents ODTV comparison between ODTV obtained by this study with common ODTV available in the literature (Amoore/Hatula, Nagy Leonardos/Kendall and Nagata data).

Table 4 Comparison of ODTV with Available Literature

Compound	ODTV ppm Bokowa-present Study	ODTV ppm Amoore/ Hautala	ODTV ppm Nagy	ODTV ppm Leonardos /Kendall	ODTV ppm Nagata
Acetone	3.96-5.39	13	16.9	100	NA
Acetic Acid	0.48-0.55	0.48	0.15	1	NA
Acetaldehyde	0.0010-0.0014	0.05	0.05	0.21	0.0015
Acetylene	78-82	620	478	NA	NA
Biphenyl	0.000051-0.00007	0.00083	0.00052	NA	NA
Benzyl Sulphide	0.00018-0.00024	NA	NA	0.0021	NA
Benzene	1.8-2.4	12	NA	4.68	2.7
Carbon Tetrachloride	8.2-9.4	96	NA	100	NA
Butyric Acid	0.004-0.005	NA	NA	0.001	0.00019

Butyraldehyde	0.013-0.015	NA	NA	NA	NA
Carbon Disulfide	0.026-0.038	0.11	0.395	0.21	0.21
Chlorobenzene	0.09-0.11	0.05	0.977	NA	NA
Dimethylamine	0.081-0.104	0.13	NA	0.047	0.033
Dimethyl Ether	20.26-22-14	NA	228	NA	NA
Diphenylamine	0.0118-0.0164	NA	0.188	NA	NA
Ethanol	4.76-7.48	84	19.1	10	0.52
Ethyl Benzene	0.014-0.018	2.3	0.44	NA	0.17
Ethyl Acetate	1.2-1.6	3.9	7.77	NA	NA
Ethyl Acrylate	0.00010-0.00012	0.0012	0.00317	0.00047	NA
Ethyl Isobutyrate	0.000028-0.000032	NA	NA	NA	0.000022
Ethyl Mercaptan	0.0000052-0.0000064	0.00076	NA	0.001	0.0000087
Hexane	1.31-2.07	130	NA	NA	1.5
Heptane	3.8-4.6	150	26.84	NA	NA
Heptanol	0.064-0.082	NA	0.335	NA	NA
2-Ethyl, 1 Hexanol	0.024-0.036	NA	0.150	NA	NA
Furfural	0.036-0.042	0.078	0.712	NA	NA
Hydrogen Sulphide	0.000047-0.000072	0.0081	0.0039	0.00047	0.00041
Isobutyl Isobutyrate	0.030-0.042	NA	0.49	NA	0.035
Isopropyl Acetate	0.14-0.16	2.7	2.25	NA	0.16
n-butanol *	**0.02-0.08**	**0.2**	**0.195**	**NA**	**0.038**
Methyl Acrylate	0.0017-0.0020	0.0048	0.017	NA	0.0035
Methyl Amyl Ketone	0.0065-0.0082	0.35	0.257	NA	0.0068
Methyl Ethyl Ketone	0.32-0.40	5.4	1.63	10	0.44
Methacrylic Acid	0.042-0.050	NA	0.54	NA	NA
Naphthalene	0.0028-0.0036	0.021	0.086	NA	NA
Oleic Acid	0.48-0.54	NA	3.81	NA	NA
2-Propanol	2.16-2.41	2.6	NA	NA	NA
Propionic Acid	0.0059-0.0066	0.16	0.396	NA	0.0057
Pyridine	0.042-0.051	0.17	0.386	0.021	0.063
Styrene	0.029-0.042	0.32	0.305	0.1	0.035
Toluene	0.089-0.117	2.9	3.19	2.14-4.68	0.33
Sulphur Dioxide	0.11-0.12	1.1	NA	0.47	0.87
Valeric Acid	0.0014-0.0016	NA	NA	NA	0.000037
Ammonia	0.70	5.2	5.32	46.8	1.5
Acrylic Acid	0.0088-0.0092	0.094	NA	NA	NA
Dimethyl Disulphide	0.0019	NA	0.017	NA	0.0022
Dimethyl Sulphide	0.0028	NA	0.020	0.001	0.003
Formaldehyde	0.070	0.83	0.56	1.0	0.5
Methyl Mercaptan	0.00015	0.0016	0.0012	0.0021	0.00007
Ozone	0.001	0.045	NA	NA	0.0032
Phenol	0.011	0.04	0.13	0.047	0.0056
Tetrahydrofuran	0.40	2	6.1	NA	NA
Trimethylamine	0.00011	0.00044	0.0024	0.00021	0.000032

*- n butanol was used as screening compound

3. Conclusions

Based on evaluations of fifty-two pure compounds for odour detection threshold values (ODTV) with forty-two pure compounds being studied extensively, the results showed significant differences in odour detection threshold values when compared with previous studies such as Amoore/Hautala, Leonardos/Kendall and Nagy data. This is probably attributed to the fact that in the past, different methods were used for ODTV determinations, such as the syringe method or dynamic olfactometry with very low volumetric flow rates at the sniffing ports at the beginning of 1970- 0.5 l/min; 3l/min in 1980 (Amoore/ Hautala;) or 8 l/min in 1990 (Nagy results). In the past, when ODTV determinations were performed using dynamic olfactometry with low flow rates, the samples were diluted with ambient air, during evaluations, therefore, lowering the results (a higher value for ODTV). Since 2003, when mandatory flow rates of 20l/min were set at the sniffing ports in order to prevent any dilutions during the evaluations, no new data for ODTV for pure compounds were available.

This study showed that the factor between the recently developed ODTV for selected compounds compared to the past ODTV results (Nagy 1990) is in the range of four to even more than 34. This factor would be greater when comparing recent ODTVs with ODTVs developed in 1969 by Leonardos and Kendall due to the fact that the flow rate at the sniffing ports was in the range of 0.5 l/min (1969) to 8 l/min (1990).

The ODTVs for most of the studied compounds are in line with Nagata data obtained by Triangle Odor Bag Method. OFTV and OCTV were also established for this study and showed the results either at the same level as ODTV or approximately one-third lower (a higher value) than ODTV, which corresponds to the fact that at first, people detected the odour, and later the odour become offensive, and people started complaining. Please note that for determination of the OCTV other factors might be significant such as frequency and duration of the detectable odour.

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