

Determination of Chemical Substances in Indoor Air as Cause of Discomfort and Annoyance - Sampling Strategy and Combined Chemical and Olfactometrical Analyses

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The indoor air of a room is highly important because it has a big impact on people's comfort. If the air is contaminated due to the materials installed within the room, the air can lead to annoyance reactions, discomfort, and even headaches and dizziness. However, until today, identifying the odorous sources remains difficult.

In this paper, a new approach for the determination of the odour sources of indoor air is described.

In the investigated room, sampling bags were placed on the various surfaces. The surface emission was thus captured in sample bags. An additional sample of the indoor air was taken. As a first step, the spectra in GC-IMS of the various surfaces and the room air were compared. From the similarities, the sample with the highest potential to be the odour source was chosen. From this sample, a GC-MS and a parallel GC-Sniffing analysis were performed.

The results were used to select two substances with a high odourous impact in the GC-Sniffing analysis but also have a matching odour description with the indoor air character. For these substances, no odour detection threshold (OTV) in literature was known. In a second step, an OTV was determined for these substances using the DIN EN 13725 (2003).

As a conclusion, the combination of molecular and olfactory analysis allows the identification of odorous sources in indoor air.

1. Initial Situation

A conference room was renovated years ago. The smell of the used compounds was strong at the beginning with decreasing intensity in the first period. However, a specific odour remained. This odour had led to user complaints. The reactions ranged from discomfort to headache.

It was assumed that a constant emission of volatile organic compounds (VOC) was the cause of the constant odour. Therefore, the VOC concentration was determined within 12 measurements over the last years (Gierden 2015). In all measurements 1-Nonanol, 6-Methyl-1-octanol and acetone were determined with concentrations higher than 5 µg/m³. In 9 measurements 2-Ethylhexanol and hexa acid were measured with concentration above 5 µg/m³.

From a pre-analysis of the used floor cover material, it was concluded that the probable source of the substances 1-Nonanol and 6-Methyl-1-octanol was the floor. However, the concentrations of these substances were not significant enough for the perceived odour. It could therefore not be concluded that the floor cover material was the sole source of the malodour.

A test design with an innovative sampling and evaluation approach was designed as a next step to find the source of the malodour. The odour emission of the floor, wall, and ceiling of the room were to be evaluated and compared with the odour in the room. The source with the highest correlation to the indoor air was determined. The identified source was tested for its odorous and molecular impact. For this, a combination of gas-chromatography and sniffing was used. From the most relevant odorous molecules, two substances were chosen for a determination of the specific odour threshold.

In the following paragraph, the procedures and methodologies are described. The focus is set on the odour determination and the relation to the chemical analysis.

2. Test Procedure and Methodologies

2.1 Test Procedure and Sampling

The conference room was ventilated before starting sampling. The sample bags were then fixed to the surfaces in question (see Figure 1): bags were attached to the wall, the ceiling and the floor. The floor was sampled at two positions. The bags were filled with air, that was purified using an active coal filter. The room was then locked for approximately 24 hours. After that period, the room was entered and two bags of room air were sampled. The room air quality was assessed (sensorically) by the odour expert (How?) and the bags were removed from the room. In parallel the room air was sampled for VOC content.

The samples were taken to the laboratory and were analysed the same day.

In a first step, trained odour assessors evaluated the samples for odour character, intensity and hedonic tone. Furthermore, they were asked to match samples with similar perceived characteristics. The results show that the sample taken from the floor matched the characteristics of the room air sample.

In a second step, the samples were analysed using Gas Chromatography - Ion Mobility Spectroscopy (GC-IMS). From the combined results (of what?) the sample of the suspected source for the perceived odour in the room was chosen. The sample was trapped on a Tenax TA/Carbograph tube (10 l Volume, flowrate 100 ml/min) for a gas-chromatographic (GC-ToF-MS) analysis combined with sniffing.

As a last step, the odour threshold of the two substances with the most odorous impact was determined.

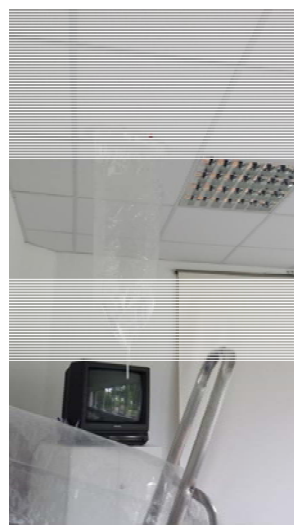


Figure 1: Sampling of floor (left), wall and ceiling (right) emission. Positioning of sample bags filled with cleaned air

2.2 GC-IMS

The study methodology was partly based on molecular spectra evaluation to deduce the source of substances in the room. The analysis was undertaken using Gas Chromatography - Ion Mobility Spectroscopy (GC-IMS) analysis. This analysis technique combines the separation of components within a mixture achieved through gas-chromatography with highly sensitive detection of the separated compounds achieved through ion mobility spectroscopy (IMS).

The technique utilises the following principles:

1. The compounds within a sample are separated by the GC-column.
2. As the individual compounds exit the GC-column they are ionized and enter the drift region of the IMS.

3. The ions drift in a weak electrical field, against the direction of flow of a drift gas, towards a Faraday plate detector.
4. Depending on their charge, mass, and shape, the ions will interact with the drift gas in distinct ways and will reach different drift velocities, thus reaching the detector at staggered time points.
5. The relative concentration of compounds present is determined through the magnitude of current resulting from ions reaching the Faraday plate detector. Broadly speaking, the current can be used to determine the number of ions impacting the detector at any given time, hence the relative quantity of different components can be determined (each of which will have different GC retention and IMS drift times).

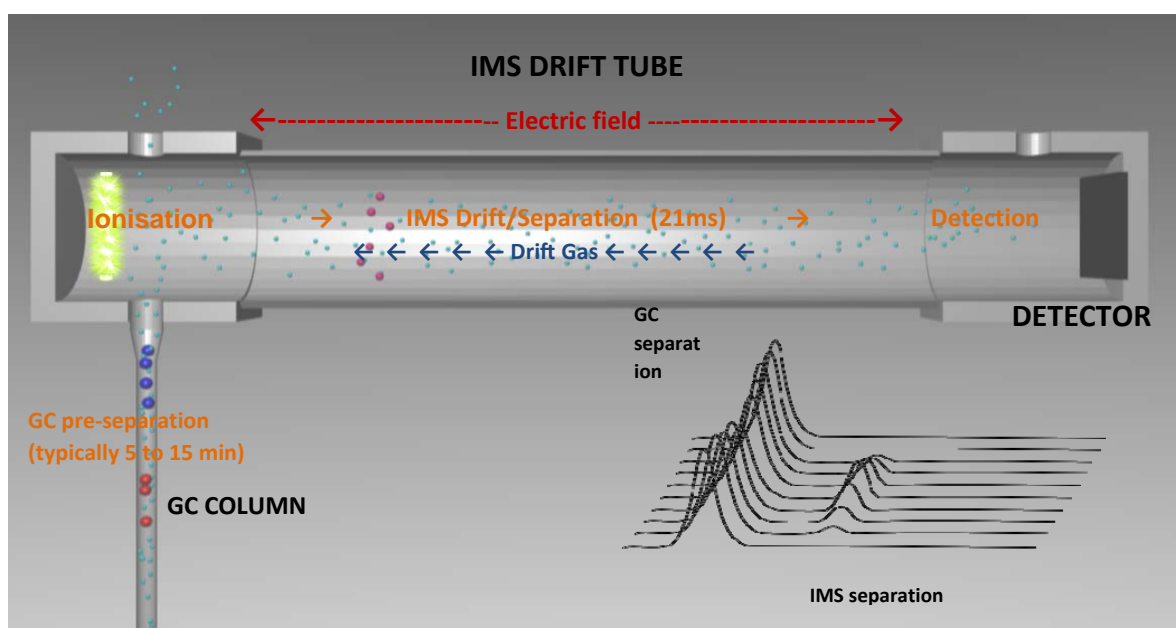


Figure 2: Functional scheme of the GC-IMS system

As the analysis results in both GC separation and IMS separation a 3 dimensional chromatogram is produced, see Figure 2. The visualisation tool used to represent the results is a 'heat map' 2D fingerprint. The y axis represents time associated with GC separation; the x axis represents IMS drift time. The detected signal as a z axis is converted in the heat map as coloured results. The higher the detector response (which is related to amount of compound detected) is, the more intense appears the heat spot. From the 2D fingerprint, components of interest can be identified and their relative presence compared between samples using LAV software (Laboratory Analytical Viewer) provided by G.A.S Dortmund.

2.3 GC-ToF-MS Sniffing

For the gas-chromatographic analysis a GC-ToF-MS was used. The analysis was performed at Odournet S.L.. The GC-ToF-MS is a standard method to derive the molecular composition of a sample. It can be combined with Sniffing, which is used to define at which retention time of the GC an odorous signal is retrieved. The intensity and the descriptor are reported. The sample air volume flow is split after passing the gas-chromatograph. One part is sent to the sniffing port and the other is analysed by the mass spectrometer. The method and validation scheme of the Sniffing is as follows.

The odour-active VOCs directed to the sniffing port is detected and characterized by two trained olfactory assessors. As soon as the assessor detects an odour, attribute, durability, and intensity values (from 1 to 5) are assigned (table 1). Meanwhile, the Mass Spectrometer is detecting the other chemical species in the sample for the posterior identification of chemical compounds, both odorous and odourless.

GC-sniffing is performed by two expert panelists, at room temperature. During the analysis, each panelist takes on the GC-sniffing task for 15 minutes before handing over to the other panelist. Each sample is analyzed 4 times, which means each panelist covers the chromatographic runs twice to confirm those doubtful odours and /or try to find other additional odours not detected in the previous sniffing.

Table 1. Scale of values used to describe the odours perceived.

Value	Mean	Characteristic
1	Faintly perceived	Sometimes, difficulty to describe
2	Perceived	Noticeable
3	Strong	Very well perceived
4	Very strong	Nasal saturation
5	Extremely strong	Only extreme cases (Cause interruption of sniffing process)

All compounds detected by MS are chemically identified using TargetView software referencing to the NIST11 spectral library. Compounds above 80% of similarity are considered to be identified. Those compounds with concentration above odour threshold values are marked.

Odours detected by sniffing are confirmed after being detected at least twice out of the total of four analyses of the sample. Those odours identified just once are discarded.

Before assigning a chemical compound name (chemical structure) to each of the odours perceived, the results are cross checked with the MS results, using both public and internal databases.

After completing all checks listed above, a compound is confirmed.

2.4 Olfactometry and direct evaluation of odours

To create duplicate samples of the two identified substances of which the odour threshold was determined, the LiGaVa was used as the substances were a liquid. A defined amount of the liquid was injected in the heating block. The temperature of this device was set above the boiling point of the substance. A constant stream of neutral air was flowing through the heating block at a flow rate of 1.3 L/min. The produced sample volume was 10 L. The settings, "amount of liquid/substance" and "flow rate" were derived from a previous study. The equipment used is shown in figure 3.



Figure 3: LiGaVa system consisting of a heating block and a temperature and air flow control element.

For the odour threshold measurement, dynamic olfactometry was used. The olfactometry was performed according to EN 13725 (2003). Sample storage times were as short as possible.

The olfactometer was a standard TO-8. The panellists were well trained. To derive the odour threshold three samples of each substance were analysed (but I thought you created 2 samples per substance?). Each sample was analysed using a different panel, therefore nine different panellists were used ($3 * 4 = 12??$).

3. Project Implementation and Results

3.1 Results of GC-IMS

In figure 4, the heat maps of six samples is displayed. The samples are room air, floor sample A, floor sample B, wall, ceiling, and a second room air sample (from left to right). The figure represents the area in the spectra containing the most information. In the spectra of the room air relevant peaks (high intensity) were marked. The same was done for the floor sample A. These Marker-areas are picked out in all sample spectras. These intensity of the signal in the Marker area is shown in a comparison plot (Figure 5).

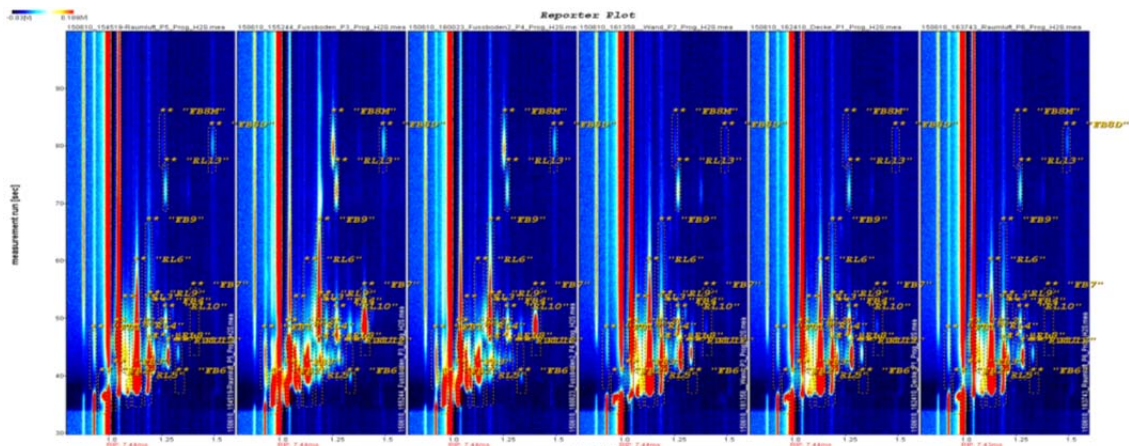


Figure 4: Detail of the Heat-Map plots of the samples, from left to right: room air, floor samples A, floor sample B, wall, ceiling, room air.

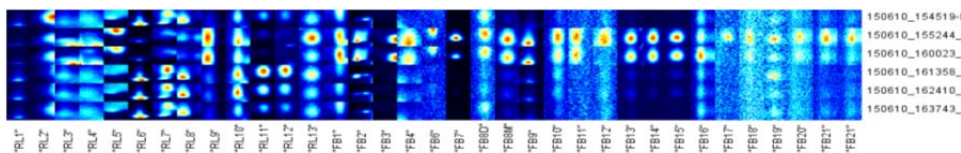


Figure 5: Comparison of the marked areas in the heat maps. From top to bottom: room air, floor samples A, floor sample B, wall, ceiling, room air. From left to right: 13 markers of room sample and 21 markers of floor samples.

The results show that:

- The wall and ceiling emission show similar areas in the heat maps compared to the room air.
- The structure of the heat maps of the two floor samples is very complex and a high number of substances are emitted.
- The markers FB 16 to 21 (not readable in the figure) can be related to trace amounts? which can be found in the room air as well.

From these results and the descriptions of the panelists in the direct assessment of the samples, the choice was made for the floor sample to be analyzed with GC-Sniffing.

3.2 Results of GC-Sniffing

In GC-ToF-MS 118 VOC components were detected. The parallel sniffing resulted in 49 descriptions of odours (at 49 retention times). From these, 18 could be identified chemically.

The intensity of the odour was between level 2 and 4 (see table 1) which corresponds from perceived to very strong. Seven substances were perceived with a very strong impression. These substances were: 2,3-Butanedione (CAS-No. 431-03-8), 6-pentyl-2H-Pyran-2-one, (CAS-No. 27593-23-3), Benzaldehyd (CAS-No. 100-52-7), Octanal (CAS-No. 124-13-0), Acetophenon (CAS-No. 98-86-2), 1-Nonanol (CAS-No 143-08-8) and Decanal (CAS-No. 112-31-2).

Reliable odour thresholds for 1-Nonanol (Nagata Y, 2003) as well as Octanal and Decanal (Bundesgesundheitsblatt, 2014) are published. However, concentrations found with GC-MS in the current and previous studies in both the room air and floor sample were below these published odour thresholds. Therefore these substances were excluded from further analysis.

Of the remaining four substances with an intensive odour impression, Acetophenon and Benzaldehyd were chosen for the determination of odour thresholds. These two suspicious compounds were identified in the previous study in 11 of the 12 VOC measurements with concentrations above 1 µg/m³. Furthermore, the descriptions given in the GC-Sniffing are in the list of characters given by the panelists when assessing the samples from the room air and floor. In addition, in comparable studies of room air quality these substances were detected as well, e.g. Bundesgesundheitsblatt (2008, Ostendorp (2009).

3.3 Determination of the odour threshold

Acetophenon and Benzaldehyd were provided by Sigma Aldrich as chemical analytical standard for the odour threshold evaluation. The concentration of the substance used for the sample preparation, derived from the GC-ToF-MS results. For Benzaldehyd the concentration was $52.8 \mu\text{g}/\text{m}^3$; for Acetophenon $25.2 \mu\text{g}/\text{m}^3$.

The samples for the olfactometric measurement were prepared shortly before analysis. Each sample was analyzed in triplicate, using three different panels. This resulted in 9 individual odour concentrations for the samples.

For Benzaldehyd the odour concentration varied between $2,170 \text{OU}_E/\text{m}^3$ and $3,649 \text{OU}_E/\text{m}^3$ with a geometrical mean value of $2,860 \text{OU}_E/\text{m}^3$. The odour threshold can thus be calculated at $18.5 \mu\text{g}/\text{m}^3$ with a range from $15.9 \mu\text{g}/\text{m}^3$ to $20.9 \mu\text{g}/\text{m}^3$.

For Acetophenon, the odour concentration varied between $5,468 \text{OU}_E/\text{m}^3$ and $23,170 \text{OU}_E/\text{m}^3$ with a geometrical mean value of $10,450 \text{OU}_E/\text{m}^3$. The determined odour threshold is thus $2.4 \mu\text{g}/\text{m}^3$ with a range from $1.6 \mu\text{g}/\text{m}^3$ to $3.8 \mu\text{g}/\text{m}^3$. The range of the odour concentration and the variability in the panelists responses leads to the impression that reception of Acetophenon is highly variable.

4. Conclusions

The aim of this study was to combine chemical analyses and odour measurements to gain knowledge on chemical impacts on indoor air quality. Air samples were analyzed using classical methods like GC-MS and new approaches like GC-IMS to determine the source of the odour contamination of a conference room. These analytical methods were combined with human sensory observations.

The GC-IMS results can help to find emission sources for indoor air contamination. This is a fast method to select the source.

The GC-Sniffing can give more insight in the odour impact of single components of a sample. It can relate descriptions of an odour to a specific substance. In combination with the knowledge of the odour threshold of the substance and the present concentration in the room air, the relevance of the impact of the substance can be assessed.

As a conclusion, the molecular methodologies are very helpful to identify the odourous sources. Nevertheless, to understand indoor odour complaints, the combination of both molecular and odour measurements are essential.

Acknowledgement

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