

Matching Continuous Monitoring and Bag Olfactometric Sampling at the Source: a Case Study

Giorgio Innocente, Elisa Polvara, Marzio Invernizzi*, Selena Sironi

Politecnico di Milano, Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Piazza Leonardo da Vinci 32, 20133 Milano, Italy
marzio.invernizzi@polimi.it

The sampling of odorous emissions is a fundamental step in correctly quantifying odour concentration. Its importance was strongly emphasized in the recent Italian legislation (MASE, 2023), which describes strict constraints for conducting olfactometric sampling. In particular, for point sources, it is necessary to assess the variability of the source to evaluate any spikes in emissivity and then sample consistently with the trend of this emissivity. Therefore, this study aims to conduct a field sampling campaign that meets the criteria mentioned in the Italian recent directive, combining olfactometric sampling with continuous monitoring of the source using portable PID instrumentation. The results obtained during this preliminary monitoring campaign highlight that the variability in VOC emissions is not strictly correlated with potential variability in terms of odour concentration. Indeed, despite the variations observed in continuous measuring at the source, the odour concentration measurements remained stable throughout the monitoring period. Chemical speciation of samples identified high concentrations of propene, varying in accordance with PID reading, while the odour potential was primarily due to lower concentrations of octene and nonene, which remained relatively constant. These results indicate that continuous monitoring emission variability does not necessarily translate into odour concentration variability.

1. Introduction

The odorous substances emitted from anthropogenic activities can interfere negatively with the well-being of the human body since offensive odours cause undeniable and persistent discomfort, often becoming a source of conflict between citizens and productive activities (Bokowa et al., 2021).

Despite odour issues being one of the main sources of environmental complaints worldwide, odour legislation varies widely in most countries, with differences in regulatory approvals, assessment methodologies, impact criteria and detection standards (Brancher et al., 2017). Odour concentration is the most commonly used dimension for characterising odours for regulatory purposes. Determining odour concentration provides directly comparable data among odour sources. Additionally, odour concentration is used to calculate odour emission rates and provide input data for atmospheric dispersion models (Tagliaferri et al., 2024). Odour concentration is typically determined in a laboratory by dynamic olfactometry, which is an objective method for quantifying odour concentration based on a well-established methodology for execution and interpretation of results, standardised at the community level by the European Standard EN 13725:2022.

Odour measurements are therefore carried out directly at the sources, withdrawing an aliquot of the gaseous effluent and then bringing it to the laboratory (Capelli et al., 2013).

2. State of the art of point-source sampling

In a point source where odour is emitted from a single point, sampling involves collecting a fraction of the conveyed gaseous mixture.

If the gaseous substance to be sampled is under pressure, the collection can be done directly by inserting the Teflon tube, connected to the sampling bag, into the duct. Otherwise, the collection must be performed by creating a vacuum downstream of the bag. For this purpose, the bag must be placed in a container, inside which air is drawn through a pump (lung sampling system). Due to the vacuum created in this way, the gaseous

substance is indirectly drawn into the sampling bag, without coming into contact with either the pump or other materials that could alter its characteristics. The used container must be airtight. Before conducting the required sampling, it is possible to fill the bag with the gas to be sampled and then immediately empty it, aiming to condition the environment inside.

Annex 2 of Ministerial Directive No. 309 of June 28, 2023, regarding sampling (MASE, 2023), specifies that:

- to verify compliance with emission limits, sampling must be conducted with the plant in operation under conditions leading to the maximisation of odour emissions. In the case of plants with variable working conditions, sampling must be carried out for each condition that, based on experience, causes the highest odour emissions;
- for the use of olfactometric investigation results in assessing the olfactory impact of the plant, sampling must be conducted to obtain a representation of the plant's emissions under various operating conditions.

To ensure the representativeness of the sample, essential elements in the sampling phase include the choice of sampling duration and the number of samples, which must be evaluated based on the target of the olfactometric investigation and the use of the resulting data.

Regarding the duration of samplings, characteristics of the source must be considered in terms of evaluating fluctuations in odour flow. In general, the following situations can be considered:

- Emissions that can be considered characterised by reasonably constant emission levels, both in terms of flow (Nm^3/h) and chemical characteristics, and consequently, in terms of odour emissions.
- Emissions which are not reasonably constant and must be characterised by sampling multiple gaseous portions, each representative of a different emission condition of interest, possibly taken at the most critical moment from the perspective of odour emissions.

During the operational sampling phases, the new Italian guideline introduced the necessity to verify the emission variability in the field, by conducting direct and continuous measurements with continuous instrumentation. A unique tool is not prescribed, but the possibility of a Flame Ionization Detector, FID, or a Photoionization Detector, PID are explicitly quoted. With this solution, the new guideline would ensure a representative sampling of emission conditions intended to be characterised.

In detail, MASE (2023), specifies that:

- in the case of constant emissions, in both terms of flow and chemical characteristics, and so presumably in terms of odour emissions, each portion of the sample gas to be analysed must be obtained over the day, by at least 3 individual samplings in a representative time interval of at least 30 minutes;
- In the case of constant-flow emission, but variable in terms of chemicals, and so presumably variable in terms of odour potential, a single sampling may be conducted, attempting to identify the most critical emission moment. This approach would be used in case, of course, only the extreme condition is of interest. If emission variability is also to be assessed, multiple individual samplings should be carried out, with a sufficient number of individually analysed bags, to adequately characterise different emission levels.

For emissions characterized by well-defined production phases associated with distinct emission characteristics, the sampling methods described above must be implemented for each of the phases of interest. In cases where only the maximum emission levels generated by a specific activity are to be highlighted, albeit associated with short periods, the sampling activity can be focused on the phase considered most critical, while ensuring the need to identify it with sufficient reliability based on available information.

The present paper aims to present the experimental results obtained in a field sampling campaign, conducted to meet the criteria mentioned in the recent MASE (2023) matching the olfactometric sampling with the continuous monitoring of the source.

3. Materials And Methods

This monitoring case study was carried out on the emission from a stack that collects air extracted from fume hoods, within a metal heat treatment plant.

The continuous monitoring at the source was carried out using a portable PID detector (Tiger VOC detector 10.6 eV, Ion Science Ltd, Fowlmere Royston UK). For details on the instrument please refer to (Sartore et al., 2022). This portable instrument was used for continuous monitoring of emissions at the source, allowing us to assess the trend of emissions of Volatile Organic Compounds (VOCs).

During the continuous monitoring at the source, four Nalophan sampling bags were withdrawn, in order to obtain different aliquots of the gaseous effluent and measure them separately. These bags were, first of all, analysed via dynamic olfactometry, aiming to obtain the odour concentration (Cod) of the different phases of the emission.

The analyses were conducted via the “Yes/No” method using an Ecoma olfactometer TO8 with 4 testing stations. The same bags, after the Cod measurement, were sent to a determination of TVOC (Total Volatile Organic Carbon) according to standard (EN 12619:2013, 2013). The instrument used was a Ratfish RS 55-T (Tagliaferri, et al., 2024).

Finally, a specific chemical analysis of VOCs was conducted, using a chromatograph (GC) coupled to three detectors (single quadrupole mass spectrometry detector, MS; FID; Pulsed Flame Photometric Detector, PFPD). For the details of the instrumentation and the settings, please refer to (Polvara et al., 2022).

4. Results And Discussion

Figure 1 depicts the continuous monitoring at the source via PID. Moreover, the sampling instants of the four different bags are highlighted with red circles. As mentioned, due to the aim of characterising the different odour emission potentials, among the different phases, multiple individual samplings were carried out in moments with different real-time readings at the source.

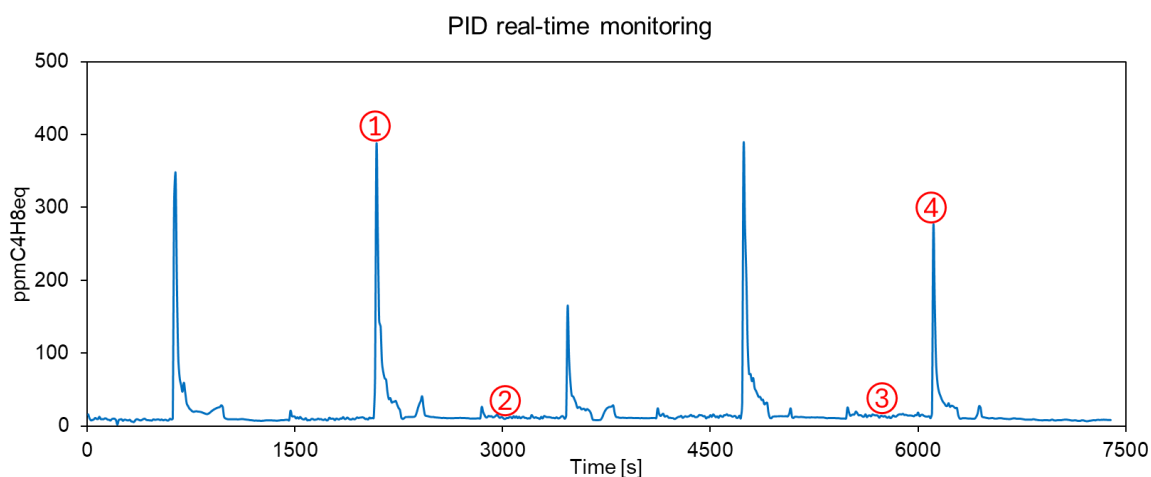


Figure 1. Continuous PID reading throughout the monitoring period, with highlighted bag samplings

Figure 1 points out that this emission appears to show a discontinuous chemical behaviour, suggesting that there may also be an important discontinuity in terms of odour potential. The reading of the PID, which can be roughly assimilated to a qualitative reading of the VOCs present in the effluent, spans over different orders of magnitude, with a baseline around 10 ppm_{C4H8eq} and peaks reaching 400 ppm_{C4H8eq}.

Table 1 summarises the measurements conducted on the four sampled bags: as expected, a wide range of TVOC is detected, confirming the data detected by portable PID. Cod, conversely, is confined to a much narrower range: taking into account the uncertainty due to the resolution of dynamic olfactometry (factor 2), these data can be considered largely overlapping. The same data are graphed in Figure 2, where it is clear the linearity present between the PID reading and the TVOC, and a total absence of correlation between the continuous field reading and the Cod value, which remains essentially constant.

Table 1: PID reading, C_{od} and TVOC values recorded at the various samples.

Sample	PID reading [ppm _{C4H8eq}]	TVOC [mgc/Nm ³]	Cod [ouE/m ³]
1	380	320	1200
2	11	39	1100
3	13	41	1000
4	270	200	1300

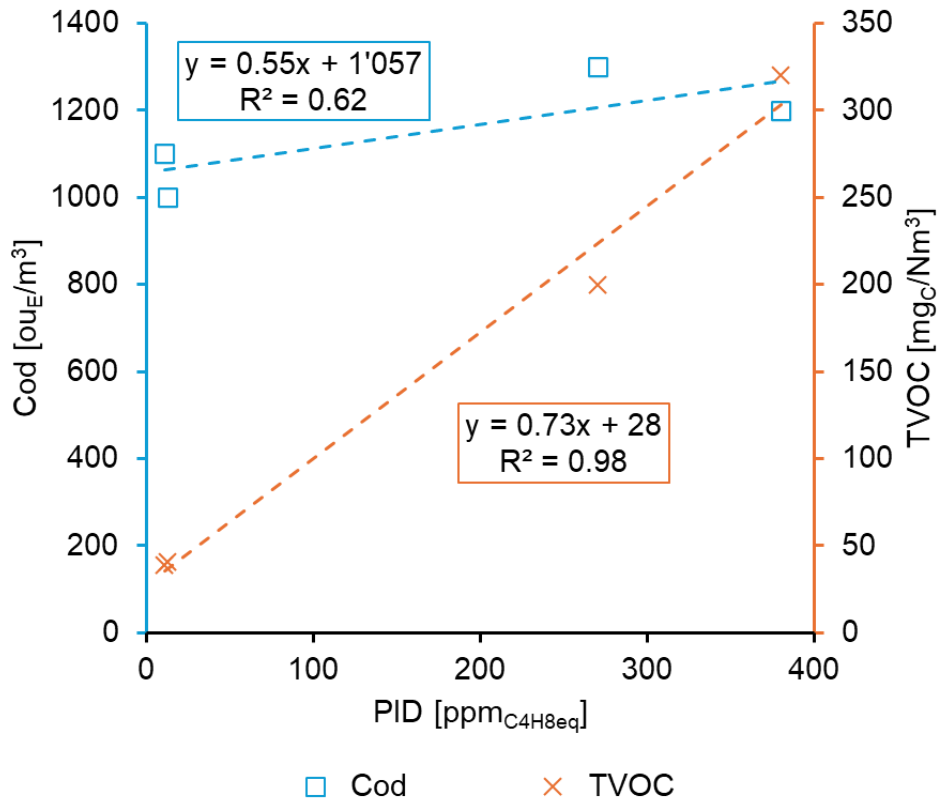


Figure 2. Cod trend and TVOC value related to emission output sampling.

Based on the results obtained, a first conclusion was the absence of prevailing concentrations of methane: this molecule is indeed detectable by FID and thus quantified in TVOC, but not by PID due to its high ionisation energy (12.5 eV). This is one of the main reasons why PID is usually preferred for this type of monitoring. Despite the robustness of FID technology, methane is essentially an interfering gas in this case: it is odourless, and its reading can mask the presence of other potentially odorous VOCs.

Consequently, to investigate this particular behaviour, which could appear to be absolutely counterintuitive, the speciation of individual chemical compounds was used.

Approximately 30 compounds were detected in the sample bags. All were revealed by FID and none by PFPD: no organic sulphur compounds were detected in the effluent. The identification of the individual species was carried out by MS. The general composition of all the samples consisted of a prevailing contribution, in terms of quantity and mass concentrations, of alkanes and alkenes, spread over C₃ to C₉. Aromatic and naphthenic organic compounds were detected only in traces (i.e. < 1 mg/m³).

For each compound in each sample, the value of Odour Activity Value (OAV_i) was calculated according to Equation (1):

$$OAV_i = \frac{C_i}{OTV_i} \quad (1)$$

Where OTV_i is the Odour Threshold Value of each single identified compound I (Nagata et al., 2003), and C_i is its concentration value. This value represents a measure of the importance of a specific compound to the odour potential of the sample (Rincón et al., 2019).

Based on the obtained elaborated data, for the sake of brevity, the data here presented relates only to a few of the detected species: propene due to its abundance in terms of mass concentration, and octene and nonene due to their contribution in terms of OAV. The OTV of these species are, respectively, 22.4 mg/m³, 4.6 µg/m³ and 2.8 µg/m³. Due to their very low OTV, the contribution of these two latter compounds is greater than 90% over the whole sample in all the bags.

Table 2. Concentration and OAV for most mentioned compounds.

Sample	C ₃ H ₆ [mg/m ³]	C ₈ H ₁₆ [mg/m ³]	C ₉ H ₁₈ [mg/m ³]	OAV C ₃ H ₆ [-]	OAV C ₈ H ₁₆ [-]	OAV C ₉ H ₁₈ [-]
1	66.3	0.61	0.50	3	133	179
2	6.6	0.35	0.36	0.3	76	129
3	4.8	0.38	0.21	0.2	83	75
4	37.0	0.94	0.77	2	204	275

Data obtained by chemical speciation show that, in quantitative terms, the most abundant compound is not significant from an odorous point of view (e.g. propene). This compound is anyway responsible for the variability of the trend recorded by PID continuous measurement and TVOC. On the other hand, the molecules which result to represent the most important contribution to the odour potential, octene and nonene, are present at largely lower concentrations. Moreover, these molecules show a much more constant trend, remaining within the same order of magnitude for all bags sampled in the different work phases.

These outcomes justify the different observed behaviours: the high concentration propene shows even higher variability in concentration among the different phases. These variations are well depicted by the trend of PID and TVOC. Nevertheless, the odour potential of the effluent is not due to this molecule, even if it had the highest concentration, but is due to the ones with the highest OAV: octene and nonene in this case. These molecules are present at far lower concentrations, being masked in the reading of general VOC analysers by the most concentrated ones, but are crucial in odour potential, due to their low OTV. Moreover, their trend is much narrower, leading to a nearly constant Cod trend at the emission.

5. Conclusions

The recent Ministerial Directive of Environment and Energy Security No. 309 of June 28, 2023, introduced a new approach for sampling point sources. According to this approach, continuous monitoring should be conducted at the source, to assess if the source can be considered constant, in terms of odour potential, or not. In the case where it is not, a deeper analysis to eventually characterise the different emissive conditions is favoured. The present work reports the experimental data obtained in a field case study, where the quoted approach was followed. The portable instrumentation (PID) had shown great variability in terms of emission potential at the investigated source. Different bags were collected to investigate the different phases. TVOC readings on the bags had shown a trend strictly comparable with PID. On the other hand, odour concentration remained essentially constant during the monitoring period. To shed light on this misleading outcome, chemical speciation was conducted on the olfactometric samples. These analyses had shown the presence of propene at high concentrations, variable coherently with PID and TVOC measurements. In parallel, the odour potential had been ascribed to octene and nonene, present at far lower concentrations. Their trend was more constant with respect to propene, leading to a generally constant odour concentration. This case study has shown that continuous monitoring at the source may furnish information about the different working phases of an emission, but, even if a non-constant trend is obtained, it cannot be taken for granted that this trend translates into a variability of odour concentration.

Future developments of this work may enlarge the experimental dataset, to compare different industrial sectors and emission typologies, with the aim of optimising the olfactometric sampling campaigns and eventually considering long-lasting continuous monitoring campaigns.

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