

Expeditious Calibration Method for Quantification of Odorous Mixtures via GC

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An odour sample is generally a complex matrix consisting of numerous molecules (mostly volatile organic compounds, VOCs) chemically different from each other, and which can be perceived by the human nose. In order to chemically characterize this complex gaseous matrix, gas-chromatography (GC) is commonly used. By this analytical technique, it is possible to obtain the resolution of odour gaseous mixtures in order to qualify and quantify the compounds. However, the quantification is a tricky operation based on the comparison of the sample under examination with purpose-made gas mixtures containing a compound, chosen as a standard, at known concentration. Commonly, these mixtures are obtained from cylinders of compressed gases, the use of which involves problems relating to their management, thermodynamic equilibrium feasibility, considerable economic outlay and not-negligible procurement times.

This paper describes a method, proposed as a versatile and simple alternative to the use of such cylinders, for preparing gaseous calibration standards at known concentration. The method involves the continuous injection of VOC in liquid form, by means of a syringe pump, into a stream of neutral gas, such as air or nitrogen, which acts as diluent gas, controlled by a mass flow meter. Exploiting the volatility of the compounds used, it is possible to generate a continuous gas stream, exiting the system, containing the selected VOC at the desired concentration, which can be directly used as calibration standard.

1. Introduction

An odorous sample is generally a complex matrix consisting of many different molecules, characterized by specific chemical-physical properties and capable of being perceived by the human nose.

Although odour nuisance is linked to the sensory perception of a smell, generated often by volatile substances (VOCs) (EN ISO 5492, 2017), characterized mainly by high volatility and low molecular weight (Ruddigkeit et al., 2014), to identify and quantify the molecules responsible for this perception, it is necessary to conduct detailed chemical analysis of the odour sample under examination.

The complexity of the matrix under investigation implies the need to separate the different species present within the sample to allow a compound-specific chemical characterization. Among the analytical techniques capable of performing this operation, gas chromatography (GC) is commonly the most diffuse. The response of GC, however, is not absolute: the output of a GC analysis is a *chromatogram*, a graph characterized by peaks of different areas and heights, proportional to the concentration of the analytes (Sparkman et al., 2011). A general technique to obtain the molecules' quantification relies on the comparison of the unknown sample under examination with an external standard at known concentration (ASTM D7360, 2016; Dettmer-Wilde & Engewald, 2014).

In particular, this procedure is recommended for analysis of air mixtures sampled in polymer bags (mainly constituted by Tedlar™ or Nalophan™) and directly analyzed, as in the case of odour samples (EN 13725, 2022). In this case, bags containing mixtures at known concentrations are required to be used as external standards (Papurello, 2019).

Commonly, compressed gas cylinders are used as external standards (Fernandes et al., 2018; Liu et al., 2018). However, the use of gas cylinders involves critical issues, mainly due to the management and storage aspects of the cylinders themselves (EN ISO 144470, 2006).

Another problem inherent in the use of cylinders is their low versatility since they can provide a gaseous sample only at one concentration. This would involve large numbers of cylinders being purchased or being diluted, resulting in relative errors and, in the case of high-precision dilution instruments, in potentially expensive costs. Moreover, due to pressurization, there are limitations determined by the equilibrium conditions of the mixture. Therefore, this study aims to describe an expeditious and versatile system alternative to the gas cylinders, based on the vaporization of pure liquid VOCs, taking advantage of their high vapor pressure, to be applied in quantification analysis of odorous samples.

In particular, a *dynamic method for injection* was investigated (Barratt, 1981; EN ISO 6145-4, 2008; Platonov et al., 2018). This method is based on the introduction of a dosed liquid into a dilution gas flow, such as air or nitrogen, and it produces a continuous gas flow of gas mixture at known concentration.

2. Materials and methods

The implemented dynamic method under investigation requires the use of a syringe pump for the liquid flow and a mass flow meter for the gaseous flow (

Figure 1), to ensure controlled and constant, which are also easy to vary by the setting of the two instrument, to obtain quickly the desired concentrations.

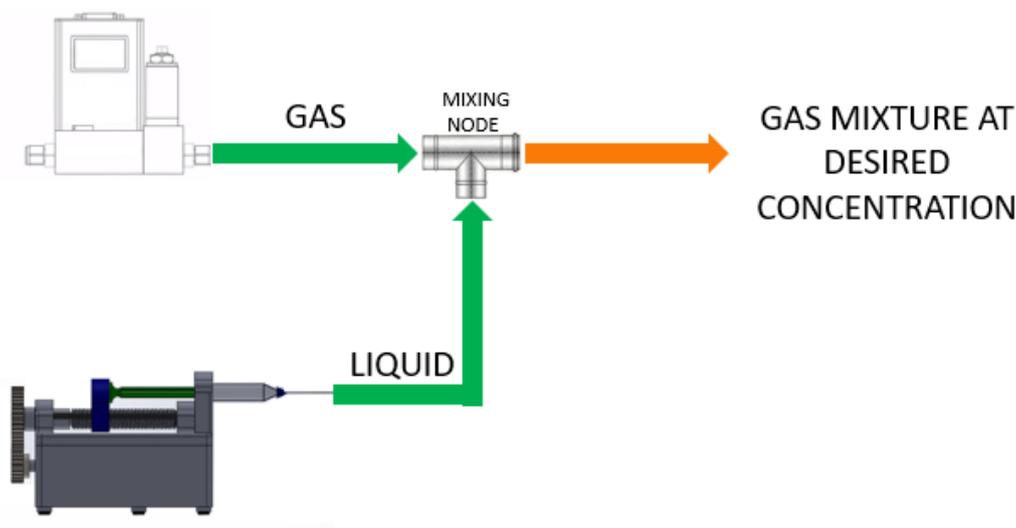


Figure 1. Simplified diagram of the system.

2.1 Equations

The concentration of VOCs, C_{VOC} [ppm], in the stream exiting the system can be determined by the Eq. 1:

$$C_{VOC} [\text{ppm}] = \frac{\text{Liquid molar flow rate} \left[\frac{\text{mol}}{\text{h}} \right]}{\text{Liquid molar flow rate} \left[\frac{\text{mol}}{\text{h}} \right] + \text{Inlet gas molar flow rate} \left[\frac{\text{mol}}{\text{h}} \right]} \cdot 10^6 \quad (1)$$

For this study, a flow rate of 1800 SL/h was set and kept constant throughout the tests.

2.2 Set-up materials

- Syringes: Hamilton™ 80384: glass liquid syringe with a capacity of 10 μL , to be installed on the syringe pump.
- Mass flow meter: Alicat™ Portable Calibration Unit Mass Flow Meters with a measurement range of 0.5 SCCM - 5,000 SLPM.
- Pump-syringe: NE-300 Just Infusion™ Syringe Pump.
- Nalophan™: constituent material of the bags used to sample the gaseous mixture flows (EN 13725, 2022).

2.3 Analysis

To evaluate the effectiveness of the method, a photoionization detector (PID) TIGER Ion Science® sensor, equipped with a 10.6 eV UV lamp, was used to assess the concentration of VOC present in the prepared single-component mixture. This detector measures the concentration expressed in ppm of isobutylene. The quantification of each compound has been based on a proper response factor, tabulated by the manufacturer of the instrument.

3. Results and discussion

3.1 Gross results

For each of the examined compounds, preliminary tests, performed in duplicate, were carried out by setting three different concentrations of the mixture exiting the system, equal to 5 ppm, 10 ppm and 15 ppm, and subsequently analyzed by PID. The results of these tests, in terms of the mean ratio between expected and measured concentration values for all the compounds, are shown in Figure 2. All the mixtures analyzed were prepared at the working temperature were $293 \text{ }^\circ\text{K} \pm 1 \text{ }^\circ\text{K}$.

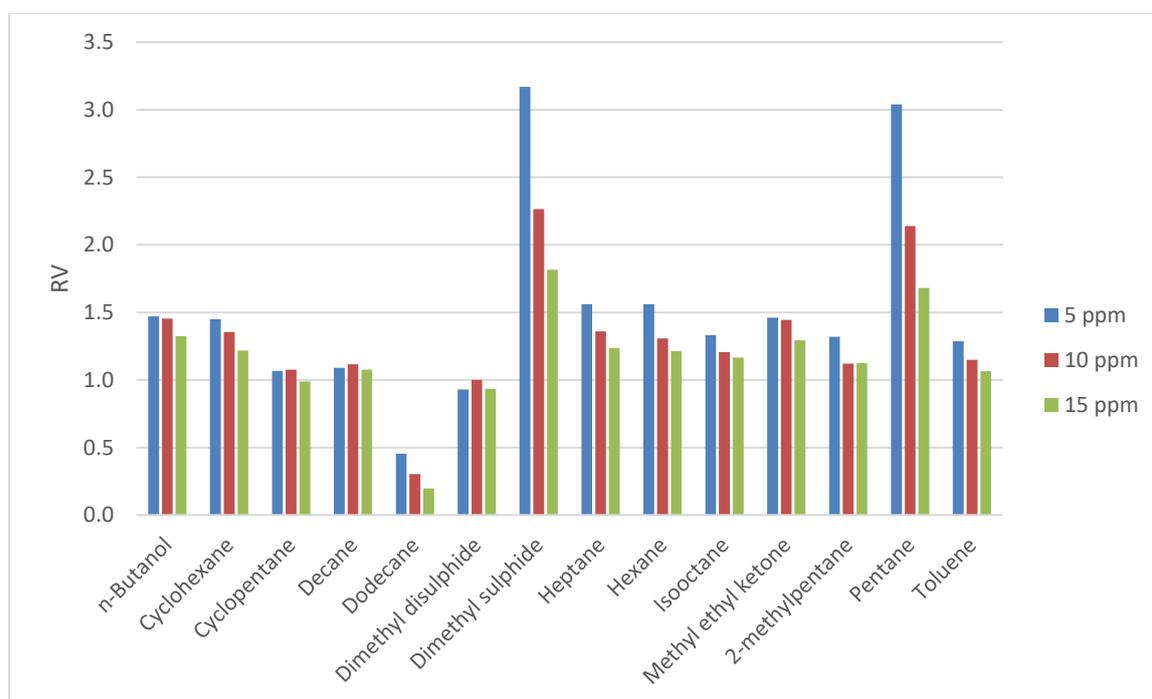


Figure 2. Ratio value (RV): measured values vs expected values

From the graph, the volatile compounds under examination show RVs close to the ideal value equal to 1, except for dodecane, characterized by ratios lower than 0.5, DMS and pentane, with ratios up to 3. These anomalous behaviors can be explained by examining the vapor pressure (reported in Table 1) of these VOCs at the working conditions, which are comprised between 0.1 kPa and 37 kPa for all the compound with the exception of dodecane (the least volatile), DMS and pentane (the two most volatile), are respectively 0.01 kPa, 53 kPa and 57 kPa.

Focusing also on direct experimental observation, in the case of dodecane it was observed that the liquid does not vaporize completely, and an accumulation of liquid drops was observed at the mixing point between the gas and the liquid streams, preventing the proper operation of the system. Otherwise, in the case of DMS and pentane, the main problem is related to a possible non-optimal seal of the liquid in the syringe (Grob, 2001), resulting in the spontaneous and uncontrolled evaporation of the liquid compounds from the syringe needle. In addition, for these two compounds, a clear decreasing trend in the ratio values increases can be observed as the concentration increases, this is the result of increasing the imparted thrust from the syringe pump, condition for which the thrust itself tends to become the driving force of the system, rather than the uncontrolled release due to poor sealing. For each compound, triplicate tests were carried out at the considered concentrations (5 - 10 - 15 ppm) and a standard deviation value of less than 10% was always estimated, demonstrating the method's

good reproducibility. Furthermore, this result is consistent with that reported in a similar study focused on the preparation of gaseous mixtures analyzed by PTR-MS, applied to toluene, 1,2,4-trimethylbenzene and α -Pinene (Faiola et al., 2012).

Table 1. Compounds and vapor pressure values at 273 °K

Compound	CAS	Vapor pressure [Pa]
n-Butanol	71-36-3	625
Cyclohexane	110-82-7	10 384
Cyclopentane	287-92-3	36 660
Decane	124-18-5	127
Dodecane	112-40-3	12
Dimethyl disulphide	624-92-0	3 000
Dimethyl sulphide	75-18-3	65 000
Heptane	142-82-5	4 703
Hexane	110-54-3	16 000
Isooctane	540-84-1	5 300
Methyl ethyl ketone	78-93-3	9 867
2-methylpentane	107-83-5	22 700
Pentane	109-66-0	57 000
Toluene	108-88-3	2 900

3.2 Comparison with known concentration gas cylinders

In order to compare the dynamic method described with gas cylinders, toluene was chosen as reference compound, due to its frequent presence in odorous compounds and its volatility's properties (i.e. value of vapor pressure in the middle of the selected range). In Figure 3, the comparison among the mixtures obtained at 3 ppm, 6 ppm and 13 ppm both with the dynamic method and a compressed gas cylinder diluted to the three concentrations of interest, are shown.

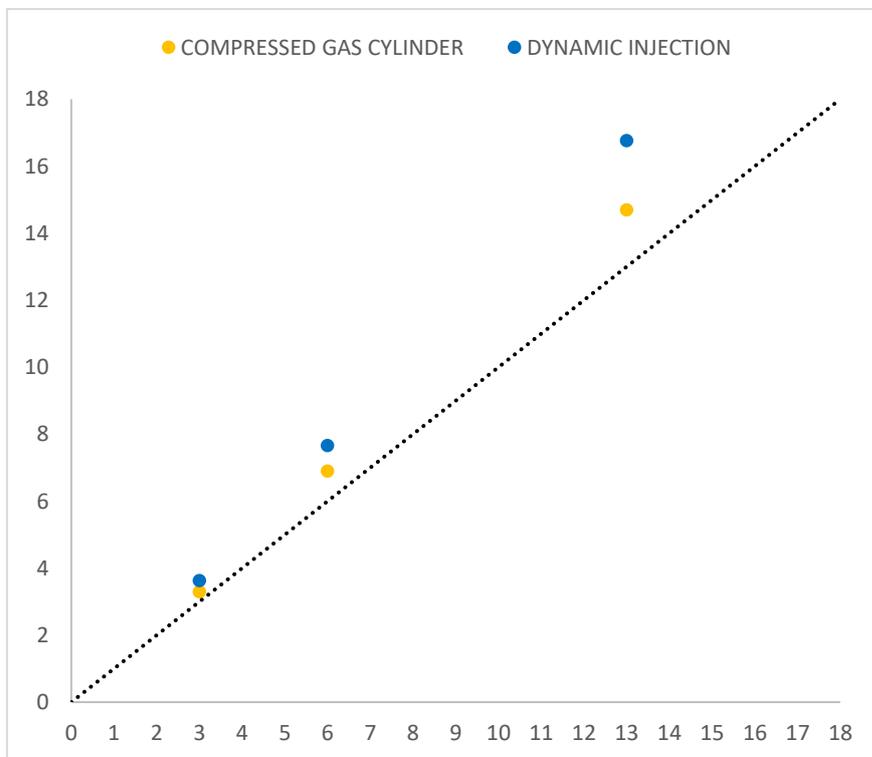


Figure 3. Dynamic injection vs known concentration gas cylinder at medium concentration - toluene

In **Errore. L'origine riferimento non è stata trovata.** the RSD% value of the dynamic method and its relative error with respect to the certified gas cylinder at known concentration are shown. (U.S. Environmental Protection Agency (EPA), 1999).

Table 2. RSD % and relative error (%) with respect to gas cylinder

RSD %	Relative error %
<5%	<14%

3.3 Limits of dynamic method – low concentration

Considering toluene as reference, whose functioning seems to be optimal, it was tried to verify the behavior of the method at lower concentrations.

Considering that the odor threshold value (OTV) for toluene is 0.3 ppm (Nagata, 2003), tests were conducted at concentrations in a range comprised between 0.1 ppm and 0.8 ppm, in order to include its OTV.

Mixtures containing toluene at 0.2 ppm, 0.4 ppm and 0.8 ppm were prepared via dynamic injection method, and compared to a compressed gas cylinder, containing nitrogen and toluene, diluted at the same concentration. The analyses were carried out using PID sensor and the results are shown in Figure 4.

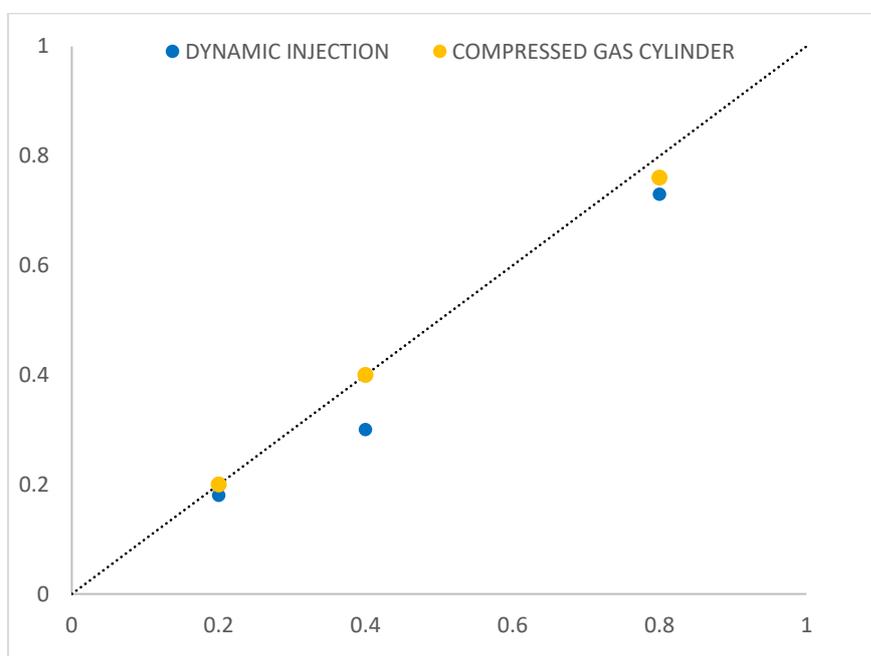


Figure 4. Dynamic injection vs known concentration gas cylinder at low concentration - toluene

Results confirm that, at considered concentrations (0.2 - 0.8 ppm), the injection-prepared mixtures show good accuracy with respect to the expected value with a measured error, compared to cylinder mixture, that is always less than 5%. In the present investigation, 0.2 ppm has also been identified as the minimum concentration achievable by this method: indeed, tests conducted at a concentration of 0.1 ppm, showed a generated mixtures with no detectable presence of toluene.

Below this concentration, by the present investigation, it appears that there are operational limits due to the low pump-syringe injection speed and/or to the highest gas flow rate to be supplied.

4. Conclusion

In this study, a method for the quick and flexible preparation of gaseous VOC standards at known concentration was proposed and tested on 13 different compounds. From the obtained results, the method shows limitations related mainly to the volatility of the compound used. In particular, among the considered compounds, for the assessed method pentane and DMS were characterized by a too high volatility. On the other hand, dodecane shows a too low volatility. These difference lead, in the first case, to an uncontrolled vaporisation of the liquid

caused by a non-optimal syringe seal, mainly clear at low concentration; in the second case, to an accumulation of liquid which does not vaporise.

Comparing the operation of the method with cylinders of known concentration, it shows a relative error less than 15% and analysing the lower limits of applicability, the method is reliable and accurate up to concentrations of 0.2 ppm, (taking toluene as a reference).

To conclude, this method can be considered a low-impact alternative to compressed gas cylinders, much more versatile and expeditious, and it allows to overcome all the limitations associated with the use of compressed gas bottles.

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