



Measurement of very volatile organic compounds (VVOCs) in indoor air by sorbent-based active sampling: Identifying the gaps towards standardisation



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ABSTRACT

The ISO 16000-6 standard describes a method for the determination of volatile organic compounds (VOCs) in indoor and test chamber air by sorbent-based active sampling, thermal desorption and gas chromatography coupled with mass spectrometry (GC/MS). It also gives directions to adapt this methodology to very volatile organic compounds (VVOCs). Indeed, toxicologically based guideline values are being implemented for these compounds and it becomes necessary to measure them. But a comprehensive and robust measurement method is lacking. This work highlights the points that still need to be explored towards the standardisation of a suitable procedure: investigations on sorbent combinations, the suitability of chromatography columns and the use of gaseous standards are required. The biggest challenge remains in the fact that strong sorbents adsorb water together with VVOCs. Water may impair the analysis and the optimal approach to eliminate it is still to be found and integrated into the sampling strategy.

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1. Introduction

The acronym “VVOCs” refers to a group of compounds that are more volatile than the VOCs. This term is widely used in the field of indoor air chemistry but the definitions are multiple, resulting from the several ways to define VOCs [1]:

- via the boiling point: for the World Health Organization (WHO), VVOCs are organic components that have a boiling point (Bp) ranging from <0 °C to (50–100 °C) [2].
- analytically using their retention index (RI) on a non-polar GC column: the ISO 16000-6 standard [3] designates substances as VVOCs if they elute before n-hexane (RI < 600) on a non-polar GC column. EN 16516 [4] provides a more precise definition: VVOCs are organic components that elute on a 5% phenyl/95% methyl-polysiloxane column before n-hexane; the draft revision of the ISO 16000-6 provides the same definition [5].
- via the vapour pressure: VOCs are defined as organic compounds with a vapour pressure of > 10 Pa [6]. This represents the

limit between VOCs and semi-volatile organic compounds (SVOCs) but there is no upper limit representing a boundary between VOCs and VVOCs. Salthammer (2016) noted that VVOCs from the chromatographic definition usually have vapour pressures of >100 Pa or even > 1000 Pa [1]. Such a definition would be theoretically the most meaningful as emissions depend on vapour pressure but there are more uncertainties in vapour pressure measurements than in boiling point or retention index measurements [7]. Moreover, the vapour pressure is defined at a given temperature and contrary to the boiling point, which is measured at atmospheric pressure, there is no agreement about which exact temperature should be used for vapour pressure measurement.

These different definitions result in a boundary region between VVOCs and VOCs. According to Salthammer (2016), the second (chromatographic) definition is the most suitable [1]. Exemplary compounds are shown in Table 1. Some substances from the boundary region should also be considered in experimental investigations to show the complementarity of future VOC and VVOC methods. It is also worth mentioning that all those definitions only set a limit between VOCs and VVOCs, but no limit towards the highest volatilities has been defined for the VVOC group which will consequently include gases such as methane.

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Abbreviations		IUPAC	International Union of Pure and Applied Chemistry
AgBB	Ausschuss für gesundheitlichen Bewertung von Bauprodukten (Committee for the Health-related Evaluation of Construction Products)	LogP	Logarithm of the octanol-water partition coefficient
AIR	Ausschuss für Innenraumrichtwerte (Committee on Indoor Guide Values)	MS	Mass Spectrometry
Bp	Boiling Point	m/z	Mass-to-charge ratio
CMR	Carcinogenic, Mutagenic or toxic to Reproduction	NIK	Niedrigste Interessierende Konzentration (German LCI)
CMS	Carbon Molecular Sieve	PLOT	Porous Layer Open Tubular
DNPH	2,4-Dinitrophenylhydrazine	PTR-MS	Proton Transfer Reaction - MS
EU-LCI	European Lowest Concentration of Interest	RI	Retention Index
FID	Flame Ionisation Detector	RW	Guideline Value (German: Richtwert)
GC	Gas Chromatography	SIM	Selected Ion Monitoring
GCB	Graphitized Carbon Black	SVOC	Semi-Volatile Organic Compound
HPLC	High Performance Liquid Chromatography	TD	Thermal Desorption
		VOC	Volatile Organic Compound
		VVOC	Very Volatile Organic Compound
		WHO	World Health Organization

Table 1

VVOCs with existing guideline values; formaldehyde, acetic acid and formic acid were not included because robust methods exist for their analysis and they are difficult to determine with TD-GC/MS [28,30,31]. *measurable following ISO 16000–3 [28]; Bp: boiling point [32]; Pvp: vapour pressure at 25 °C [32]; RI: alkane retention index on a non-polar column applying a temperature programme or a ramp [33]; LogP: logarithm of the octanol-water partition coefficient [32]; - on the working or waiting list [26,27]; CMR: carcinogenic mutagenic or reprotoxic, according to CLP (EC 1272/2008) [34].

	CAS	Compound	Bp (°C)	Pvap at 25 °C (kPa)	RI	LogP	EU-LCI (µg/m ³)	NIK (µg/m ³)	AIR (µg/m ³)	CMR Classification
C ₁	75-09-2	Dichloromethane	40.0	58.0	531	1.25			200/2000	Carc. 2
	67-56-1	Methanol	64.6	16.9	354	-0.77				
C ₂	75-07-0	Acetaldehyde*	20.1	120	381	0.34	1200	1200	100/1000	Carc. 1B, Muta. 2
	107-31-3	Methyl formate	31.7	78.1	401.1	0.03	-			
C ₃	64-17-5	Ethanol	78.3	7.91	459	-0.31				
	75-29-6	2-Chloropropane	35.0	68.7	477	1.9		(800)	800/8000	
	123-38-6	Propanal*	48.0	42.3	511	0.59	650	750		
	107-02-8	Acrolein	52.6	36.5	480	-0.01		14		
	67-64-1	Acetone*	56.1	30.8	500	-0.24	120,000	1200		
	79-20-9	Methyl acetate	56.8	28.8	515	0.18				
	67-63-0	Isopropanol	82.3	6.05	516	0.05				
C ₄	71-23-8	1-Propanol	97.2	2.8	568	0.25				
	106-99-0	1,3-Butadiene	-4.5	274	394	1.99				Carc. 1A, Muta. 1B
	108-05-4	Vinyl acetate	71.6	12	562	0.73				Carc. 2
	123-72-8	n-Butanal*	74.8	14.8	595	0.88	650	650	100/2000	
	78-93-3	2-Butanone	79.5	12.1	592	0.29	20,000	20,000		
	75-65-0	tert-Butanol	82.4	5.43	507.3	0.35	620	620		
C ₅	109-66-0	n-Pentane	36.1	68.5	500	3.39				
C ₆	96-14-0	3-Methylpentane	63.2	25.3	577	3.60				

The indoor VVOC sources are numerous. First, VVOCs may be present outdoors and enter buildings via windows or ventilation systems [8]. Then, they may arise from human activities indoors such as cooking [9], cleaning or sterilisation [10], environmental tobacco smoke [11], the use of scented products [12] or 3D printers [13]. Unintentional VVOCs can also emit from different materials such as wooden products [14–16], polyurethane foam sealant [17], mattresses [18] or photocatalytic paints [19]. VVOCs are also often reaction products [20], usually after exposure to ozone [21] or degradation products, e.g from flame retardants [22]. And lastly, they can also emanate from the humans themselves after exhalation [23].

Indoor air pollution is a serious health issue as it causes various pathologies often compiled as sick-building syndrome [24]. The German Committee on Indoor Guide Values (AIR) derives limit values (RWI and RWII) for indoor air concentrations based on current toxicological and epidemiological knowledge. They correspond to levels where no health impairment is expected, even after a life-long exposure [25]. AIR values already exist for some VVOCs such as dichloromethane or 2-chloropropane (see Table 1) and

allow to interpret measured indoor air concentrations. In Germany, the Committee for the Health-related Evaluation of Construction Products (AgBB) is working on regulations for the protection of a healthy indoor environment. In 2009, it decided to include the VVOCs in its evaluation scheme [26]. It implies that measured emissions of VVOCs from building materials should be compared to the corresponding lowest concentration of interest (EU-LCI or German NIK) values [26,27]. This is already in place since 2015 for VVOCs which can be analysed with the DNPH-method according to ISO 16000–3 [28] (formaldehyde, acetone, butanal and acetaldehyde). For further VVOCs, such as pentane, ethyl acetate, methanol, ethanol or 2-chloropropane, no suitable measurement methodology exists. For this reason, many of those compounds appear on the LCI waiting lists (see Table 1). The broadly used PTR-MS (Proton transfer reaction – MS) method allows the field detection of some of these compounds [29] but it does not enable the separation of the analytes. Moreover, the use of sorbent sampling is much more convenient for laboratories that regularly sample at different locations as the heavy analytical instrument does not need to be transported. A standardised sorbent-based VVOC measurement

procedure is still lacking for indoor air and emission testing laboratories. To tackle this issue, a detailed investigation of the current methods, the sorbents, the sample analysis and the water removal options is required and discussed in this manuscript.

2. Current methods

The ISO 16000–3 [28] standard method describes a procedure for the determination of carbonyl compounds in indoor and test chamber air via active sampling on cartridges coated with 2,4-dinitrophenylhydrazine (DNPH) and subsequent analysis by high performance liquid chromatography (HPLC) with detection by ultraviolet absorption. The VDI 4301 sheet 7 [30] is a method for the measurement of carboxylic acids in indoor air using silica gel cartridges and analysis with ion chromatography. Of note, formic acid and acetic acid present the rare properties of having a Bp over 100 °C but an RI below 600 on non-polar GC columns. These methods fit these compound groups but the most suitable analytical technique for most VVOCs would be alike for VOCs sorbent-based active sampling followed by thermal desorption and GC/MS. Several methods already describe the adaptation of VOC analysis to more volatile compounds.

Already in 1984, the use of carbon molecular sieve (CMS) sorbents instead of Tenax TA® for specific substances with Bp between –15 and 120 °C (e.g. vinyl chloride, acrylonitrile, dichloroethane, benzene) was presented in the TO-2 method of the United States Environmental Protection Agency (US EPA) [35]. It recommends the use of compressed gas bottles for standard mixtures and a dry purge of the adsorbents before the analysis for moisture removal.

At the end of the last century, the US EPA published in 1999 two new methods: the TO-15 for the determination of VOCs in air collected in canisters and analysed by GC/MS [36] and the TO-17 for the determination of VOCs in ambient air using active sampling onto sorbent tubes [37]. Both methods suggest the use of stronger sorbents for more volatile compounds but pointed out the resultant problem of water retention. The use and generation of gas standards and water removal approaches are also discussed.

The international standard ISO 16000–6 was first published in 2000. In the last final version of 2011 [3], indications for the determination of VVOCs are given in Appendix D. The use of gas standards is recommended and the different sorbent materials (graphitized carbon blacks (GCB), carbon molecular sieves (CMS), multi-sorbents) are examined. Unlike for VOCs, sorbent-filled or cooled liners and the use of a longer chromatographic column with a thicker film is suggested. In September 2020, a draft for a revision of ISO 16000–6 was published. In this new document, the indications for the analysis of VVOCs are in the normative part [5] but it remains very similar to the previous version: no clear experimental setups are recommended for this compound group.

In the European standard EN 16516 for emission measurements [4], Appendix C only indicates that the sorbents used, the sampling parameters and the analysis should be adapted for VVOCs. This document mainly refers to other sources, especially to ISO 16000–6.

These methods give insights for the measurement of VVOCs, but those compounds are often neglected because the adaptation of the procedure is elaborate. There is an urgent need for a reliable and standardised measurement method which will apply to a specified broad list of VVOCs. Indeed, dodging the analysis of VVOCs can lead to concerning health risks: many of them are CMR (Carcinogenic, mutagenic or toxic to reproduction, see examples in Table 1) or have the potential to induce irritations or other unwanted health consequences.

A method has to be developed and validated for the regulated VVOCs, it should be able to analyse as many VVOCs as possible and past research studies were limited to a maximum of 20–30 compounds. From the suggestions made in the VOC measurement methods, the point that need to be adapted can be identified: the sorbents, the thermal desorption parameters, the GC column, the use of gas standards and the water removal. Several research works have considered the influence of these parameters on VVOC analysis, as discussed in the following.

3. Sorbents for active sampling

Besides the mere analysis, the sampling media (adsorbents) and procedures are of crucial importance: it represents the first step of the measurement and it is necessary to trap the target substances on an appropriate medium before analysis. The tubes made of glass or stainless steel are used for VOC analysis and are therefore adapted to the sampling and analysis apparatus owned by the test laboratories. They can be filled with various adsorbents or combinations of them. The adsorbents used must be able to trap and desorb the desired analytes with low artefacts [38].

Three types of adsorbents are commonly used for volatile analytics and could be eligible for the analysis of VVOCs:

- Porous polymers (e.g. Tenax TA® for carbon number C₆ to C₂₆ [39]).
- Graphitized carbon blacks (GCB, e.g. Carbotrap, Carbograph, Carbopack for carbon number C₃ to C₃₀ [39]).
- Carbon molecular sieves (CMS, e.g. Carbosieve, Carboxen for carbon number C₁ to C₉ [39]).

The different adsorbents have their own advantages and disadvantages. Most VVOCs break through porous polymers (i.e. they are not adsorbed quantitatively while flowing through the sorbent). While GCB make it possible to expand the analyte range, the CMS can sorb even smaller and more polar molecules. In 2000, indications for the sorbent selection were given in ISO 16017–1 [40] but no difference was made between VOCs and VVOCs. ISO 16000–6:2011 applies these recommendations towards analysis of VVOCs and SVOCs in appendix D: it indicates that GCB are hydrophobic and suitable for substances with vapour pressure under those that are characteristic of C₄-hydrocarbons, such as 1,3-butadiene [3]. In comparison, it also states that CMS are suitable for substances with higher vapour pressure such as vinyl chloride, but are not completely hydrophobic, and sometimes even hydrophilic. This was demonstrated by Helmig and Vierling (1995) [41] and adsorbed water can impair the analysis. For the analysis of a wide range of analytes, multi-sorbents can be used with up to three beds. Combinations could also theoretically be applicable for the analysis of a wider range of compounds (e.g. glass wool, Tenax TA®, GCB for the SVOC-VOC-VVOC area), provided that the analysis is also adapted to this wide range. The new draft of 2020 does not give any crucial additional information for sorbent choice.

Most previous studies compared sorbents directly with one another [31,42,43]. This is a good approach to obtain the best possible result, but it does not give any information on the actual recovery. Indeed, the key objective should be to sample 100% of the target compound present in the air sample to make sure that small traces are being detected: this is important for example for carcinogenic compounds which can be harmful even at low concentrations. According to the International Union of Pure and Applied Chemistry (IUPAC), recovery is “the proportion of the amount of analyte, present in or added to the analytical portion of the test material, which is extracted and presented for measurement.” [44]. The analyte recovery from a sorbent will then be the proportion of

the amount of analyte flown through the adsorbent, which is desorbed for measurement.

In the new draft of the ISO 16000–6 [5], a method to assess the desorption recovery by repeating the calibration procedure with liquid injections is proposed: however this only refers to the desorption, which can also be assessed by analysing the tube twice, and not the adsorption. In practice, the analyte recovery from a sorbent can also be measured by comparing the adsorbed amount of compound with a direct injection of the compound in the analytical instrument [45–47]. Considering six studies where actual recoveries were reported (even when no experimental details on recovery calculation were provided), Fig. 1 shows the polarity (LogP) and volatility (Bp) ranges where the adsorbents depicted a recovery between 80 and 120%. LogP and Bp are important analyte properties for sorption. For the volatility, the boiling point was preferred to the vapour pressure because the measurement values are less uncertain [7].

Fig. 1a shows that most adsorbents are likely to be suitable for a wider range of polarities. Fig. 1b reveals that the combination of different adsorbents (e.g. Tenax GR/Carboxen/Carbosieve SIII) is necessary in order to be able to cover the wide range of volatility of VVOCs. On-going sorbent research has not yet found better modern materials, with carbon nanotubes leading for example to poorer recovery than Tenax TA® for VOCs [51]. Traditional sorbents seem suitable, but the optimal combination is still to be found for a given list of VVOCs which are relevant for both indoor air and human health. The conditioning and desorption temperature should not then exceed the maximum temperature limit of the individual adsorbents. Moreover, ISO 16000–6:2011 states that adsorbents should be placed in order of increasing strength in the multibed and that the tubes should be refrigerated when stored, to avoid irreversible adsorption of less volatile compounds on stronger sorbents [3]: even at high temperature, high-boiling compounds could stay trapped on strong sorbents like molecular sieves.

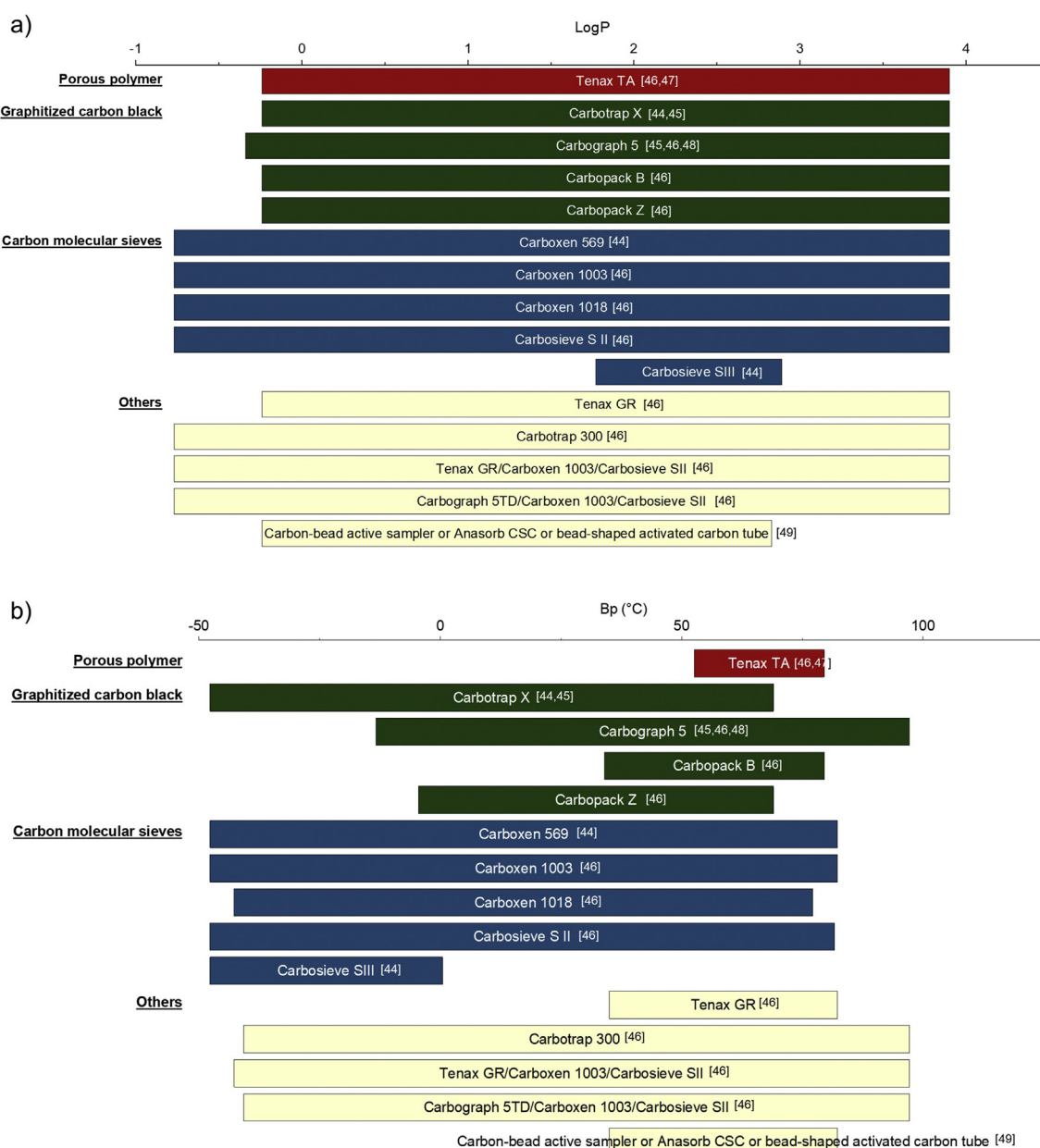


Fig. 1. Adsorbents with analyte recovery rates between 80 and 120% for VVOCs from the displayed LogP (a) and Bp (b) regions; results from six past studies [45–50].

Optimal tube storage conditions represent another point that needs to be investigated once a suitable sorbent is chosen for the target compound list.

Adsorbing at lower temperature could appear like a solution to increase sorbent strength [52] but the water from humidified air found in real samples would freeze and may block the flow path, it is also less practicable for field measurements.

Another important parameter for sorbent choice is the study of sorbent artefacts. Sorbents can already contain compounds in blanks and the adsorbed analytes can either react with one another, react with the sorbent or degrade. It is necessary to recognize those mechanisms and take them into account. Some sorbents present blank values of certain analytes, this is the case for benzene on Tenax TA® due to thermal treatment or SO₂ on carboxen type sorbents [47]. If this does not concern target analytes, this would not cause any problem and if it does, the blank values should be subtracted to the measured ones. Some VVOCs such as aldehydes or chlorofluorocarbons are highly reactive. Schieweck et al. (2018) detected the apparition of 2-butenal and methyl acetate on different sorbents but it was unclear if the reactions took already place in the methanol solutions or on the sorbents [31]. Recoveries above 120% can also be a sign for reactivity, it has been observed for propene and propane on Carbosieve SII and butane on Carbotrap 300 [47]. The mechanisms behind these artefacts are often unknown but it is not necessary to elucidate them: it is crucial to carry out investigations to identify them in order to avoid quantification mistakes.

4. Sample analysis via TD-GC/MS

The thermal desorption temperature must be adapted to desorb all analytes without degrading the sorbent or the analytes themselves. According to TO-15 [36], it is also advisable to dispense the compounds to the GC column with a smaller volume of carrier gas after focusing on a secondary trap to avoid peak broadening and co-elution for compounds such as chloromethane and vinyl chloride. ISO 16000-6:2011 also recommends cryofocusing at lower cooling temperatures than for VOCs (−150 °C) [3]. Another approach would be to focus the analytes on a sorbent trap if cryofocusing is not available: in this case, a reverse flow would be necessary for desorption if a multi-bed sorbent is used as trap to prevent irreversible adsorption of less volatile compounds [53]. Fig. 2 gives a schematic representation of the two injection systems.

Concerning the chromatography, TO-15 [36] states that for a better resolution, the temperature in the column oven can be reduced to below the ambient temperature (e.g. −50 °C) at the beginning of the gas chromatographic run. This is unfortunately not possible with modern GC instruments commonly used for VOC measurements. In ISO 16000-6:2011 [3], the adaptation of the VOC method with the use of a longer dimethylpolysiloxane column (>60 m) and/or a thicker film (>0.5 μm) is suggested while in the new draft of 2020 [5] it is just indicated that more care is required with respect to column selection. In most previous studies on VVOCs, other various phases are usually used. Fig. 3 compares the different columns with phases and dimensions based on the analyte properties volatility and polarity.

Fig. 3a shows that most column phases are suitable for a wide polarity spectrum. In Fig. 3b, we observe that PLOT columns (Porous Layer Open Tubular) seem to be the most suitable for measuring substances with boiling point below −40 °C. The “624” phases (cyanopropylmethyl phenylmethyl polysiloxane) are also used for wide volatility and polarity ranges: according to the literature, these two types of phases are best suited for VVOC analysis. Examples of chromatograms of VVOCs on DB-624 (acetaldehyde to

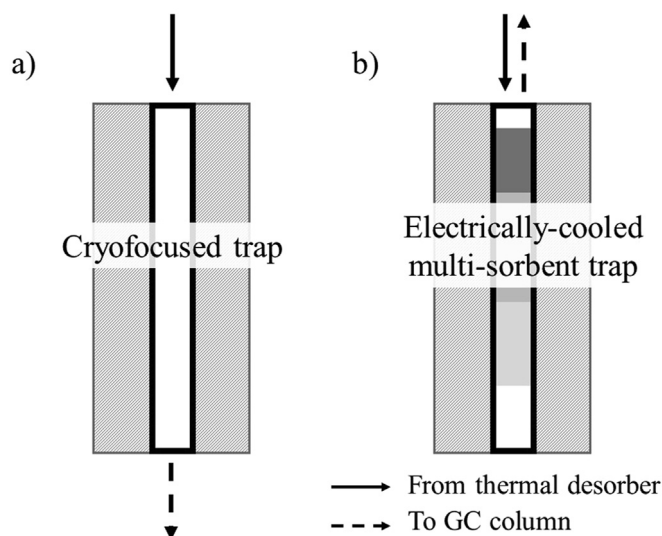


Fig. 2. Two types of injection system with a) forward flow and cryofocused trap and b) reverse flow and electrically cooled multi-sorbent trap.

trimethylsilanol) [31] and Porabond Q PLOT (ethane to pentanal) [47] columns are presented in published works.

However, a more systematic investigation should be carried out for the selection of an appropriate column for a standardised method. The measurement of a stable standard mixture would allow direct column comparison. Then, the appropriate length, film thickness should be selected [61], and the oven temperature program and pressure optimised. Important parameters for such a comparison include retention indices, peak width or column efficiency, peak symmetry, number of overlapped peak and total run time.

Concerning the mass spectrometry method, ISO 16000-6 states that quantification should be performed with extracted mass-to-charge ratio (m/z) that shall not be present in the neighbouring peaks and that are major fragments of the compound in question [3]. It is important to note that with small molecules like VVOCs, the probability to have substances with similar electron impact fragments (e.g. m/z 29, 43, 44, 56, 57) becomes higher. High resolution MS would allow a more accurate identification of the compounds, but laboratories would often need to invest in new instruments to comply with such a standardisation. Indeed, laboratories interested in VVOC measurement methods via TD-GC are already performing VOC measurements according to ISO 16000-6 with an FID or a single quadrupole MS. Tandem MS is not adapted to VVOCs of very low molar mass. For these small VVOCs (e.g. methanol, main fragment m/z 31), it will also be necessary to start scanning at $m/z < 50$: in this case, interferences with O₂ or N₂ may occur [5]. As the method should be used for a large number of compounds, it would be useful to develop an appropriate Selected Ion Monitoring (SIM) method to differentiate between target compounds with similar retention times. The use of a SIM method is however only applicable for a defined list of compounds and other substances will not be detected: for unknown samples, it is preferable to use a combination of MS scan and SIM.

5. Quantification issues

In previous works, but also in practice, analytes for calibration and method development are often dissolved in solvents (mainly methanol). Desorption tubes are then spiked with these solutions

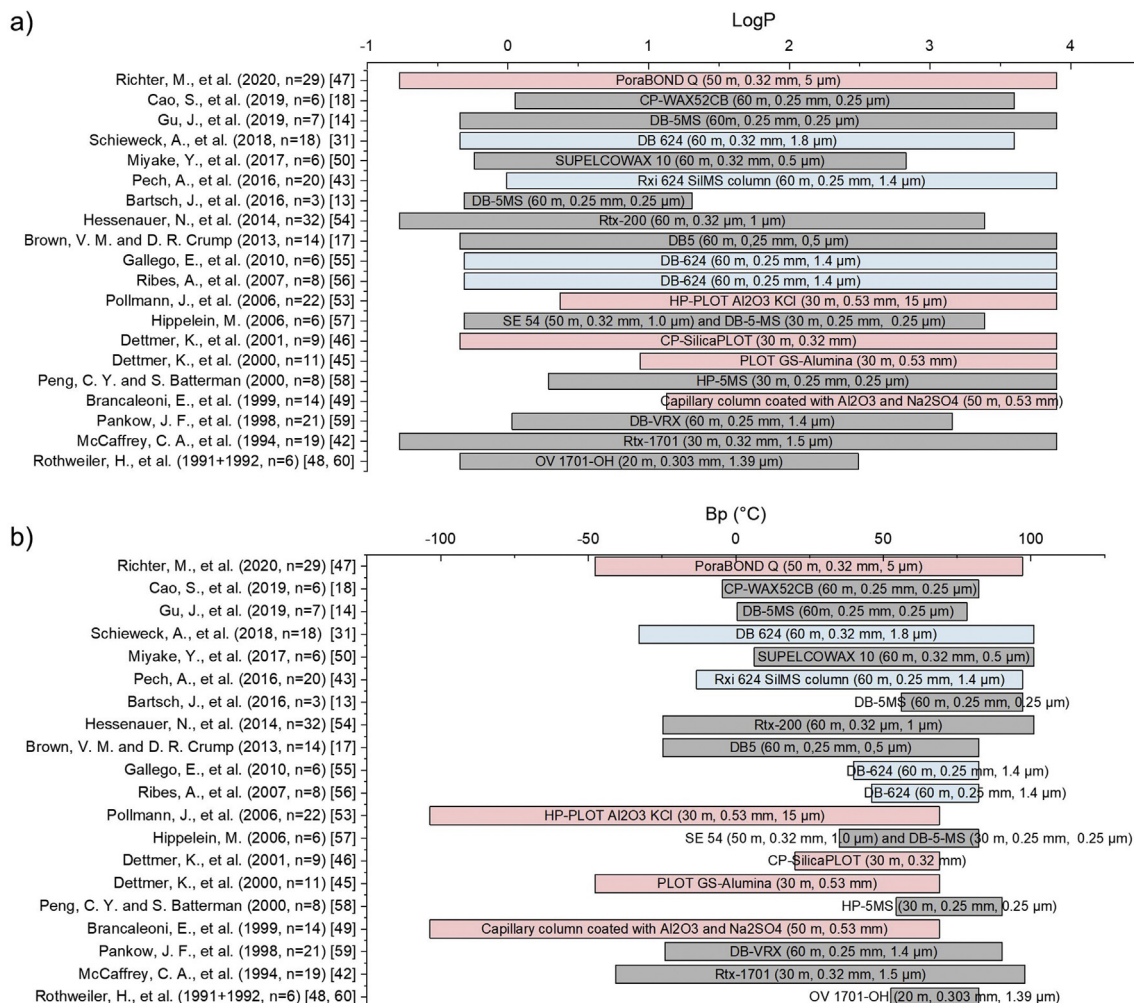


Fig. 3. Chromatography phases and dimensions used for VVOCs (n: number of VVOCs, chromatographic definition) from the displayed Log P (a) and Bp (b) regions in past studies [12,13,17,18,31,42,43,45–50,53–60]; red: PLOT columns, blue: “624” phases, grey: others.

following the procedure for VOCs described in ISO 16000–6 [3]. However, the solvents used are often VVOCs themselves and will engender the following problems [3,36,37]:

- Since stronger adsorbents are used, the solvent can no longer be flushed before the analysis: this creates a competition with the target analytes on the sorbent.
- The solvent must be masked during detection and can therefore no longer be an analyte itself. In the hidden area, analytes cannot be identified and quantified with m/z which are fragments of the solvent itself. Often, the corresponding retention time range is completely masked and no analytes with similar retention times can be considered [31].
- Handling during the solution preparation is very difficult for components that have a lower Bp (generally below room temperature).

For these reasons, the use of gas mixtures appears to be the only feasible solution for reliable VVOC calibration. Those mixtures can either be purchased or self-made. Paragraph 9 of the test method TO-15 [36] presents a detailed catalogue of methods for the generation of standard gas atmospheres. The series of standards ISO 6145 [62] describes the production of calibration gas mixtures using dynamic methods.

Commercial certified gas standards from compressed gas cylinders are often used in the literature. They can be dynamically diluted with humidified air using mass flow controllers and a calibration distributor [36,62,63].

The generation of gas standards from liquid pure substances is an economical option if applicable. It was already mentioned in TO-1 [64] and is described in more details in TO-15 [36]: the pure components are doped in a 2 L glass bottle at 60 °C and evaporated. Gas samples are then taken from the bottle through the septum. Similar methods were performed by spiking teddlar bags [42], a mixing chamber [45] or a glass collecting tube [47]. In the two last studies, the analytes were dissolved in one another before spiking, it enables higher doping amounts and therefore more precision: the reactivity should then be studied in the solution where the analytes are in close proximity.

It is also crucial to ensure the shelf life of gas standards; particular attention should be paid to their possible reactivity. Typical indoor reactivity usually due to ozone or photo reactivity does not occur but the mixture components can degrade, react with one another or adsorb onto surfaces of the bottles and bags. Investigations are necessary to ensure standard stability, for example regular analysis of the mixture with an internal standard. It is also important to humidify the mixtures to a desired humidity rate; this is typically achieved by mixing dry air and wet air with an appropriate valve.

6. Water removal

As stated in part 3, water can adsorb on stronger sorbents like carbon molecular sieves and impair the analysis. Indeed, the presence of water on sorbent tubes is problematic: water competes with analytes on sorbents, it can freeze in the analytical system during cryofocusing, leading to pressure irregularities or reduce life of analytical components such as the column. As real air samples from test chamber or indoor environments are humid and the use of carbon molecular sieves seems inevitable to trap the most volatile and polar VVOCs, water removal is crucial. There are different methods to remove water after and before sorbent sampling:

- ISO 16000–6 and TO-2 advise to apply a purge before tube desorption [3,35], this will surely be helpful for moisture removal but could also lead to analyte loss. To prevent losses, TO-17 suggests to dry purge both the sampling tube and the focusing trap [37]. Drying the focusing trap is only possible if an injection system with reversed flow and sorbent trap is used (Fig. 2). Alternatively, TO-15 and TO-17 also recommend splitting the sample to overcome water issues [36,37] but this would induce a loss in sensitivity. In the study of Pollmann, Helmig et al., sample drying was achieved by a regenerable Peltier-cooled water trap which is inserted into the sample flow path before the actual analyte trap and has a higher temperature (e.g. $-10\text{ }^{\circ}\text{C}$ instead of $-20\text{ }^{\circ}\text{C}$) [53]; this may however also lead to analyte loss.
- Protection before sampling with an appropriate membrane or drying agent presents the advantage that water will not compete with the analyte on the sorbent anymore. Nafion membranes would be useful for non-polar compounds but retain polar analytes together with water [38]. Drying pre-tube filled with calcium chloride (CaCl_2) and diatomaceous earth led to full recovery for 1,3-butadiene and satisfying results for pentane and hexane as well as improvements in chromatogram baseline [65,66]. Investigations are still needed to find an agent that adsorbs water and lets the target analytes through; this seems to be the biggest challenge towards the development of a reliable measurement method for VVOCs. If water removal is achieved before sorbent sampling, it would also be suitable to use electrical cooling to enhance adsorption strength without risking water freezing.

Additionally, water could also have a positive effect of increasing recovery from the sorbent for polar compounds such as methanol or ethyl acetate [47] but this only concerns a minority of target VVOCs.

7. Conclusions and perspectives

Analysis of VVOCs by TD-GC/MS by analogy to VOC measurements following ISO 16000–6 is feasible but requires many adaptations. These adjustments need to be investigated and validated towards standardisation. Multi-sorbent selection, a suitable chromatography column, cost-effective and stable gaseous standards as well as methods for water removal are required.

It seems utopic, regarding the high variety of compounds, to think that a single method will be able to analyse perfectly the whole range of VVOCs: we believe that the solution resides in a method that would be able to quantitate reliably a long given list of VVOCs, including the regulated ones. It would also be possible to make a distinction between a method for less volatile VVOCs (e.g. 1,3-butadiene to *n*-hexane) for which the use of CMS and water management is not necessary and a more comprehensive method. The overall procedure should be validated by an inter-laboratory

comparison before standardisation. The concept of a TVVOC (total VVOC concentration) analogue to TVOC from the AgBB [26] is attainable if a lower limit for VVOCs (e.g. C_2) is defined. Moreover, VVOCs may be regulated in other fields (occupational, automobile components, outdoor air) where a suitable validated measurement method would also be useful.

Finally, the dream of a combined method which would be able to analyse the wide range of VVOC-VOC-SVOC (semi-volatile organic compounds) seems unattainable, at least on a single GC column. The PTR-MS method, which does not enable the separation of the analytes but has a better sensitivity, could be used complementarily.

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Sample Credit author statement

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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