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GLOBAL VOC STANDARDS TO ADDRESS A VOLATILE GLOBAL PROBLEM

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LGC Quality | ISO 9001 | ISO/IEC 17025
ISO 17034/ISO Guide 34

INTRODUCTION

With the potential to disperse over great distances, Volatile Organic Compounds (VOCs) have become a major contributor to global air pollution. Analytical testing around the world has to adapt to an evolving regulatory environment.



When VOCs are released into the air they can undergo a complex range of chemical reactions that form products irritating the eyes, nose and throat as well as aggravating asthma and other lung diseases. Even though VOCs, by definition, are volatile, a significant number are actually quite persistent in the environment. This persistence coupled with the fact that they are found in many household and industrial products, including fuels and paints, results in vast reservoirs of these pollutants in soils and wastewaters, with some VOCs causing long-term adverse health effects to our populations.

Additionally, the presence of VOCs in such a wide-ranging and far-reaching array of household and consumer products, such as indoor paint, cosmetics and cleaning supplies, has led to an increasing concern for indoor air quality. In Europe and North America, the average adult spends over 80% of their life indoors, whilst rooms are getting smaller and less well-ventilated – leading to higher risks to human health associated with VOCs.

As studies into the long-term effects of VOCs gain traction and concerns about the potential harm to both the environment and the world's population increase, global regulatory bodies are responding. There are an ever-growing number of emission controls, product specifications, monitoring and remediation plans associated with VOCs, and organisations such as the European Union (EU), Environmental Protection Agency (EPA) and Standardization Administration of China (SAC) have set out guidelines and criteria for residue monitoring, and established the range of substances to be tested.

To support this tightening regulation and control, and to monitor the impact of attempts to clean up the environment, reliable analytical testing using traceable reference standards is needed. In this paper, we will outline the VOC testing methods available to laboratories to meet both customer needs and regulatory requirements that vary around the globe.

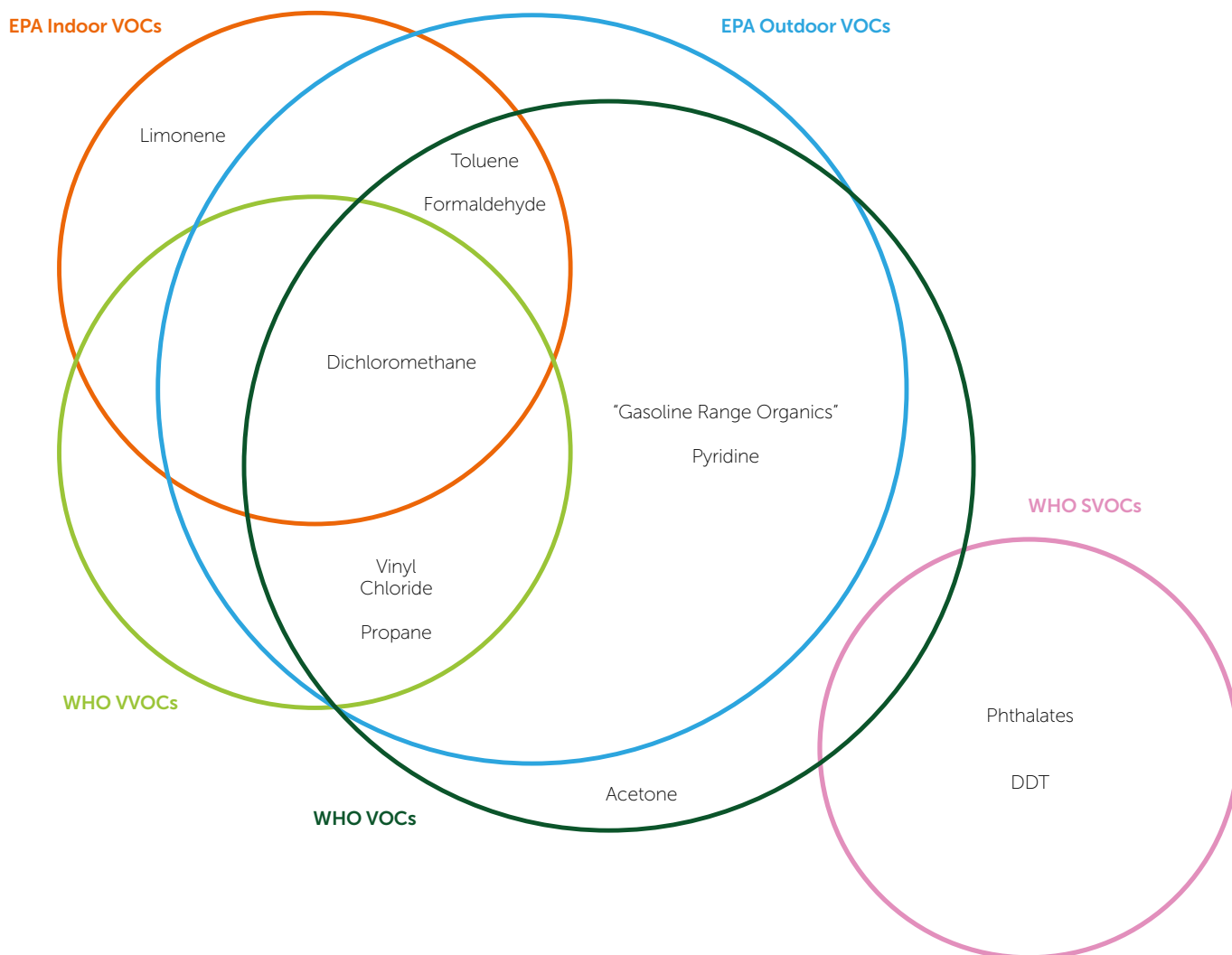
DIFFERING DEFINITIONS OF VOLATILE ORGANIC COMPOUNDS (VOCs)

In order to properly regulate a chemical class, it must be clearly defined. The difficulty of this regulation can be seen in the fact that global VOC definitions are not consistent. For example, the World Health Organisation (WHO) classifies VOCs by approximate boiling point, whereas the US Environmental Protection Agency (EPA) considers outdoor and indoor VOCs to be two different

classes, requiring different regulation and testing. While the EPA definitions are the most widely adopted in an environmental context, they are also not straightforward, as considerable overlap exists between the different classes of EPA VOCs, particularly in the case of solvents (**Figure 1**).

Examples of VOC definitions:	International Definitions
WHO Definitions	Indoor VOC An organic chemical compound whose composition makes it possible to evaporate under normal indoor atmospheric temperature and pressure (Indoor Air Quality, US EPA)
WVOCs (Very Volatile Organic Compounds) Boiling point below the range of 50-100 °C	Outdoor VOC Organic compounds that participate in atmospheric photochemical reactions, including non-methane hydrocarbons, oxygenated, chlorine-containing, nitrogen-containing and sulphur-containing organic compounds (China ; other national definitions such as US EPA are similar but not identical)
VOCs (Volatile Organic Compounds) Boiling point from 50-100 ° to 240-260 °C	
SVOCs (Semi Volatile Organic Compounds) Boiling point from 240-260 ° to 380-400 °C	

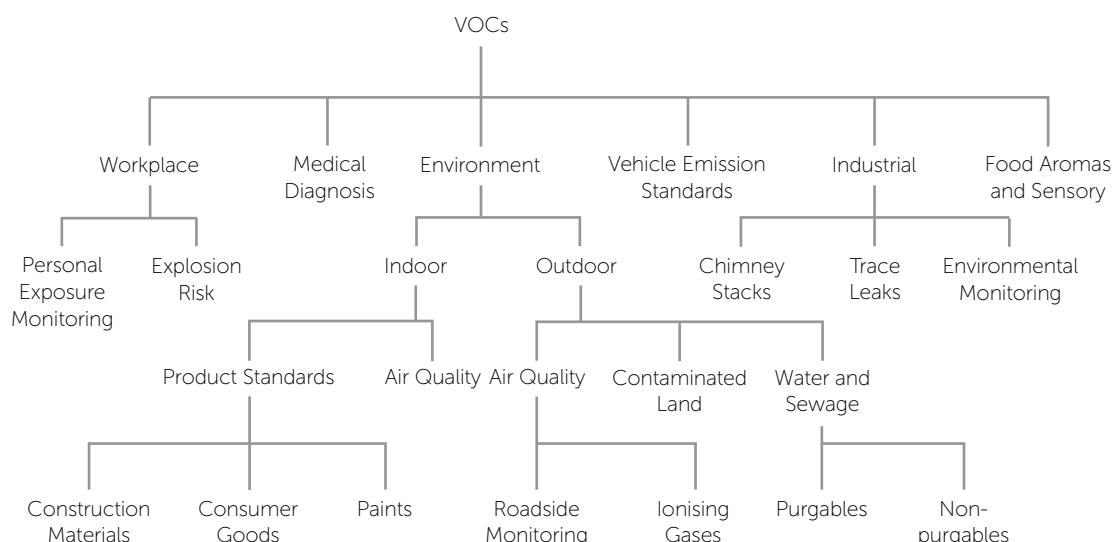
Figure 1: WHO vs EPA VOC definitions



To further complicate the matter, it is necessary to provide testing guidelines for VOCs in myriad areas, which results in different methods to measure VOC concentration even

within one specific area, as authorities sometimes require VOCs to be measured in subtly different ways (**Figure 2**).

Figure 2: Areas in which VOCs are regulated



An example of such a requirement is that in the indoor construction materials sector in Germany, VOCs must be measured as toluene equivalents by the sum of peaks between n-hexane and n-hexadecane on a 5% phenyl GC column, plus nominated individual VOCs must be quantified vs their own reference standards rather than vs toluene¹. In the UK, VOCs evolved from indoor paints must be measured solely as toluene equivalents (TVOC) and the maximum VOC concentrations for different types of paint are set in law: some paint brands use a “low-VOC” label for anything below the legal minimum, many use a “low-VOC” benchmark of < 50g/L TVOC, and the public sector requirement is < 8g/L (UK government procurement specifications).

SOURCES OF VOCs

VOCs are found everywhere, with some even desirable, such as food flavours. Unfortunately, many are pollutants that ultimately originate from petrochemicals and pervade the entire post-industrial ecosystem. VOCs can be viewed as a subset within many other classifications and so can be found throughout the spectrum of organic pollutants (**Figure 3**).

Due to their varied definitions, sources and methods of analysis, controlling VOCs requires a high volume and wide range of individual regulations and specifications for many different chemicals, products and processes. Two examples of this range are controls on vinyl chloride (**VOC Highlight 1**) and on dichloromethane in paint strippers (**VOC Highlight 2**).

Figure 3: Human Activity as a Source of VOCs

This figure shows how prevalent VOCs are across the multiple outputs of human activities.

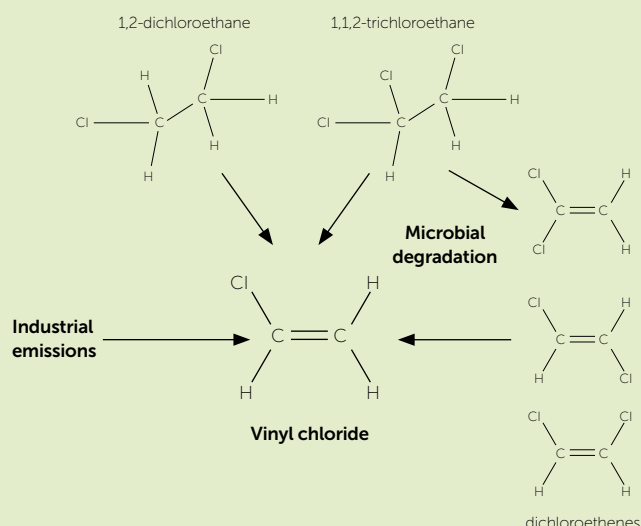
	Petrochemical Industry & Mining	Industry	Transport	Waste	War	Health & Household	Construction	Accidents
VOCs	Light hydrocarbons	Solvents	Light hydrocarbons	Monomers	BTEX	Scents	Monomers	BTEX
								Light hydrocarbons
Organic contaminants including some VOCs	Hydrocarbon oils	Reaction by-products	Hydrocarbon oils	Hydrocarbon oils		Solvents	Hydrocarbon oils	
		Unreacted feedstock	PAHs					
Non-VOC contaminants	PAHs	Dyes	Organometallics	Flame retardants	PAHs	Pharmaceutical Residues		PAHs
				Dioxins / Furans	Dioxins / Furans			
				PCBs	Organometallics	Detergents		Dioxins / Furans

VOC Highlight 1: Vinyl Chloride (monochloroethane), a carcinogen

Vinyl chloride is an important intermediate in the manufacture of many chemicals and plastics and has been produced in large quantities since the 1950s. As well as being acutely toxic, vinyl chloride is a carcinogen.

It is now an omnipresent environmental contaminant in air, water and land. Contamination has originated from industrial spills and emissions, but also from the microbial degradation of polychlorinated ethanes and ethenes in landfill sites. Older polyvinyl chloride (PVC) products also contain unreacted vinyl chloride monomer, which has slowly leached out of PVC waste. The only environmental remediation route is a slow process: further microbial degradation to ethene, which can then safely volatilise.

Vinyl chloride is used in the manufacture of PVC, which is used in the construction of buildings. Workplace exposure to vinyl chloride was regulated in the 1970s, after reported fatalities in the US. Global environmental release standards were tightened in the early 1990s² as the scale of the issue became apparent. Vinyl chloride is now a staple inclusion in multi-VOC testing methods.



VOC Highlight 2: Dichloromethane in paint strippers



It has been reported that at least two deaths in 2018 can be attributed to inhalation of the toxic VOC paint stripper ingredient, dichloromethane. In reaction, the EPA proposed enacting a ban for inclusion of dichloromethane in private household paint strippers but exempting professional use. Activists, however, are claiming that this is not sufficient to protect citizens, as at least one of the reported incidents occurred in a professional setting.

As such, they are threatening to sue the government for not fully implementing a 2017 proposal to completely ban the use of dichloromethane all paint strippers.

In the EU, it has been banned, whether for public or professional use, with some exemptions for industrial use.

VOC TESTING METHODS

Reliable analytical testing is needed to underpin these tightening regulations and controls, to monitor the level of VOCs pollution, and to measure the impact of attempts to clean up the environment. Because VOCs are so chemically diverse it is unreasonable to assume a single test method will cover them all. As a result all methods involve compromises.

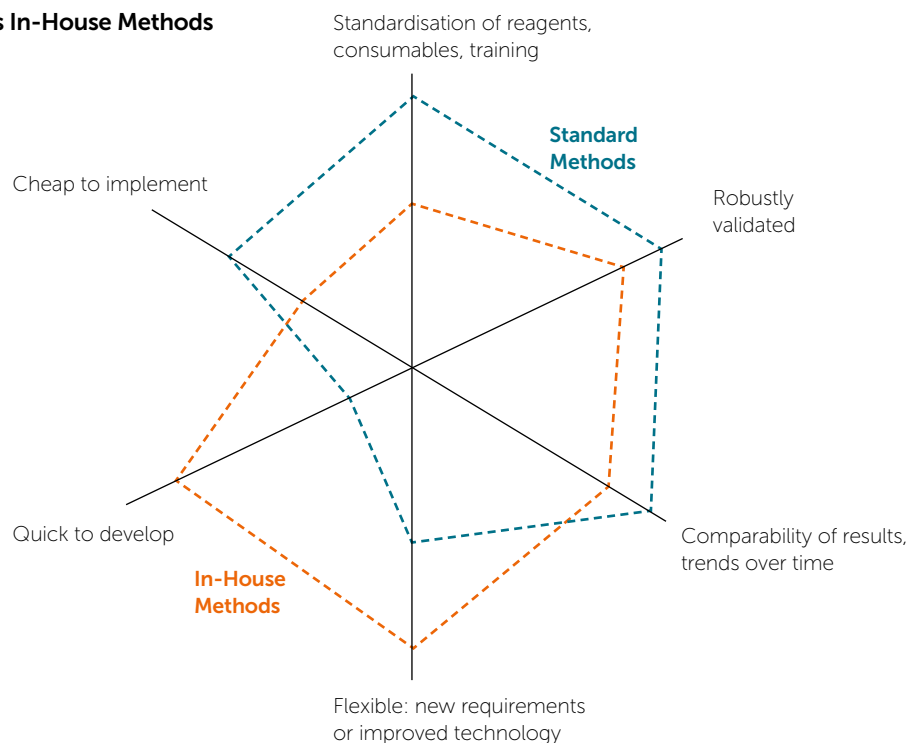
It is critical that testing laboratories develop a clear understanding with their customers as to the purpose of the analysis and the VOC definition they are using. This will determine the analytes to be measured, the reference standards to be used and the expression of results. It may also dictate the test method to be used. This need for a clear understanding has been made explicit in the 2017 revision of ISO/IEC 17025³, with clauses mandating the communication and agreement of requirements before a laboratory starts work.

Standard vs in-house methods

Some legislators, most notably in the US and increasingly in China, require the use of official standardised methods for environmental testing. These have been inter-laboratory validated - a robust process, but potentially expensive and slow (**Figure 4**). Laboratories must still verify that standard methods perform in their hands, but verification is a relatively quick process.

In the EU, legislators rarely reference standard methods, preferring to leave the choice of method open, provided it meets the minimum performance characteristics given in the relevant industry regulations, best-practice guidance or law. This does not preclude local regulators or licensing authorities sometimes stipulating standard methods, usually EPA methods.

Figure 4: Standard vs In-House Methods



Many of the more established EPA environmental testing methods are designed to be modular, so that laboratories can couple an extraction method with a chromatographic

detection method. Newer methods cover the whole process. Some examples are in **Table 1**.

Table 1: Examples of EPA Environmental Testing Methods

Example	Testing Method
Incinerator Stack Sampling	EPA 0040 ⁴ : using Tedlar® bags
Air Sampling	EPA TO-15 ⁵ : using stainless steel canisters (with GC-MS)
Effluent, Liquid, Soil Sampling	EPA 624 ⁶ : purge-and-trap (624-1 with GC-MS) EPA 5021 ⁷ : static headspace
Detection and Measurement	EPA 8015 ⁸ : GC-FID EPA 8260 ⁹ : purge-and-trap, GC-MS

Similar standard methods are published by the Chinese Ministry of Environmental Protection; for example, HJ-642-2013⁴⁰ (Headspace GC-MS).

Some of the more recent EPA methods, such as 642.1 (**VOC Highlight 3**) give much more analytical flexibility and discretion

than the more established methods. In their detail, they are converging with the European performance characteristic approach. In practice, too many laboratories default to the recommended conditions without challenging whether they could be optimised.

VOC Highlight 3: EPA method 624.1 Purge-and-trap, with GC-MS

Although a standard method, operating conditions are given only as examples. Laboratories have scope to vary most conditions to meet their own needs (provided they can demonstrate equivalent performance characteristics). This includes:

- The purging temperature
- The sample size
- The trap sorbent(s)
- GC column stationary phase
- GC injection and oven conditions
- MS type and operating conditions

The procedure for daily calibration and performance checks is more rigidly defined. Reference standards may be mixtures (e.g. DRE-GA09000903ME) or prepared in-house from neat materials (e.g. DRE-CA17738300) but must be traceable to national or international standards. The method defines criteria such as minimum injection carry-over, retention time drift and response drift, injection repeatability and ion ratios.

Example: a laboratory monitoring a factory where pyridine (boiling point 115 °C) is used on site, but very volatile solvents are not used, could investigate increasing the purge temperature even above the default maximum of 80 °C.

Product specification testing – Industry protocols and methods

Product specification testing is required for a huge variety of sample types, including:

- Paints
- Cleaning products
- Building materials
- Car seats
- Toys
- Adhesives
- Computers
- Propellants

There is a correspondingly wide range of extraction protocols (**VOC Highlight 4**) (notwithstanding international standardisation in limited fields, such as the ISO 12219 series for VOCs in automobile interiors or the ASTM series of petroleum industry methods).



VOC Highlight 4: VOC measurement protocol examples

Two protocols for measuring total VOCs in paint illustrate the need to appreciate subtle differences between different specifications.

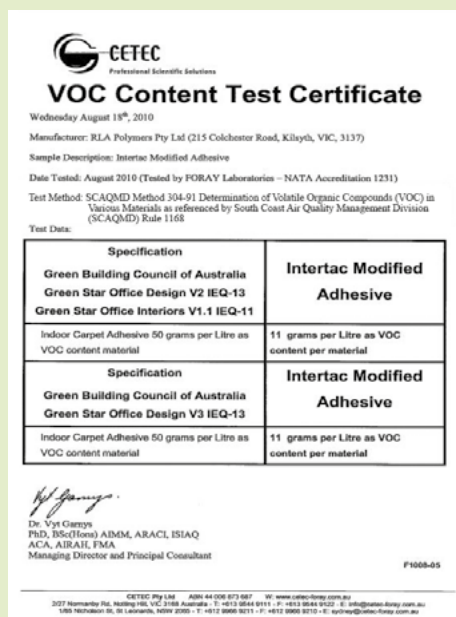
ISO 11890-1¹¹



Weight loss on drying, no correction for water content

SQ AQMD¹²

(adopted widely in the US, and in many other countries)



Weight loss on drying, corrected for water content

CONSIDERATIONS FOR VOC TESTING PROCEDURES

Cross-contamination

There is a high risk that VOCs from external sources will give a false result. VOCs are ubiquitous and highly mobile, and the sorbents used for sample extraction are also ideal for mopping up unwanted VOC cross-contaminants. Analysts must be diligent about risk management, including:

- Specifications for pipes, joints, lubricants, plastic consumables: must be leach-free from volatile small molecules
- Wash and dry all vessels before use where practical
- Use inert seals (e.g. PTFE) for vessels, septa and screw threads
- Control solvents used for other methods elsewhere in the laboratory

Stability of both samples and reference materials

It is critical that both samples and reference materials must not be compromised during their preparation, transport or storage.

Environmental sampling

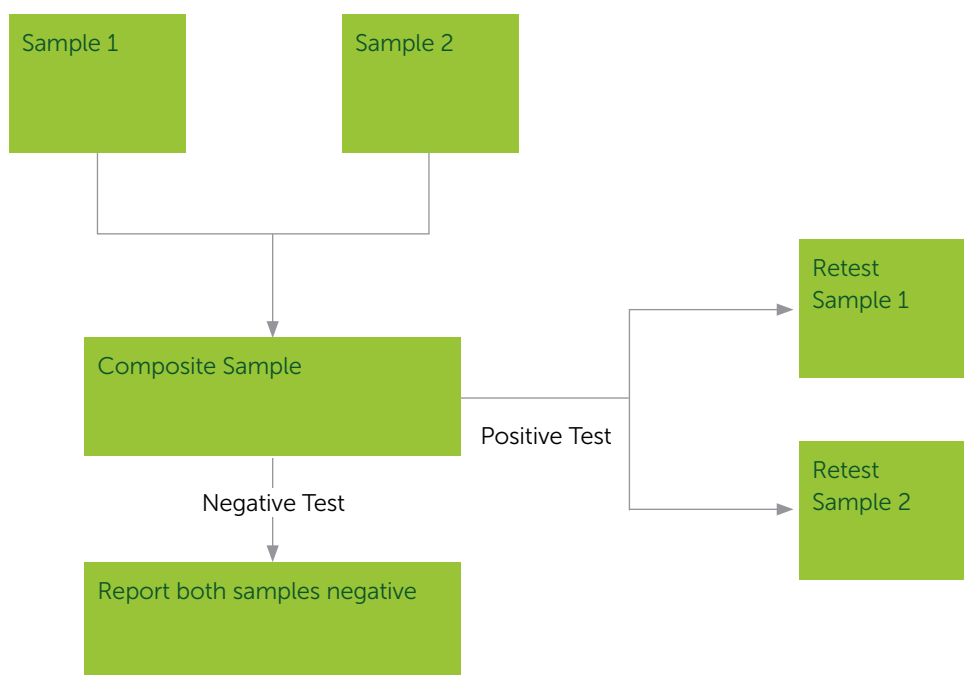
Environmental VOCs can be:

- Tested on site (fixed sensors)
- Extracted on site (adsorbed air samples, on-site purge-and-trap)
- Sampled for laboratory extraction (air grab-samples, liquid or solid samples)

Once at the laboratory, there can be economic benefit in testing sample composites (**Figure 5**), but there are limitations:

- A positive sample must not be diluted below detectability by mixing it with negative samples
- If there is a high incidence of positives, then the number of re-tests will outweigh the economic benefit of compositing

Figure 5: Composite Sample Screening



US EPA guidance¹³ is that up to four samples can be composited. This compositing must be after samples are received at the laboratory, not at the point of sampling.

There are many laboratories that have never considered this approach and would benefit from agreeing a composite sample protocol with their customers.



Extraction of laboratory samples

Most extraction techniques for liquid samples are common to both environmental samples and product specification testing. Solid samples must first be dissolved or dispersed in a liquid (usually aqueous) before extraction.

Solid Phase Extraction (SPE) is rarely used, as VOC analytes evaporate from the SPE cartridge before they can be eluted. SPE, however, is used for multi-residue testing of higher-boiling VOCs in combination with other classes of organic contaminants, and also for 1,4-dioxane (to improve detection limits).

Purge-and-trap	Headspace
<ul style="list-style-type: none"> EPA-driven industry standard for environmental testing Automated with GC Critical considerations: choice of sorbent, control of adsorption/desorption 	<ul style="list-style-type: none"> Static or dynamic Static used for VVOCs (as they are difficult to trap) Automated with GC Stability improved by co-sampling with adsorbent microfibre (Solid Phase Microextraction, SPME)
Liquid-Liquid Extraction	Modern Miniaturised Variants
<ul style="list-style-type: none"> Simple concept Labour-intensive High reagent and disposal costs Risk of emulsions Risk of loss of VVOCs For some regulators, the benchmark against which new SVOC methods must be validated 	<ul style="list-style-type: none"> e.g. Dispersive Liquid-Liquid Microextraction (DLLME) Many publications for SVOCs in oil industry, recent publications for VOCs⁴⁴ but not widely adopted Quick, simple, cheap Reliant on operator skill Lack of acceptance by some regulators

Chromatography

Chromatographic systems are common to both environmental and product specification testing. These are exclusively capillary gas chromatography (GC). GC is ideally suited to separating volatiles and can resolve the hundreds of required components.

Some methods hit a sensitivity limit dictated by the relatively small injection volume, even with the most sensitive choice of detector. This can be addressed by several approaches:

- Increasing the column loading
- Splitless injection (usually used by default)

- Programmable temperature vapour (PTV) injection
- Using focussing traps to concentrate samples prior to injection

Column stationary phases should be selected from the non-polar end of the available spectrum, to mirror the nature of the analytes:

- EPA methods and EN 16516 (TVOC) stipulate or suggest 5% phenyl columns
- ISO 16000 (indoor air) stipulates 100% methylpolysiloxane

For GCMS almost all laboratories use a low-bleed column to allow the column to be heated between injections to bake off co-extractives. Column manufacturers are continually developing new stationary phase supports and interior construction variations.

Even within the constraints of a standard method, it is worthwhile regularly reviewing and re-optimising your column design and sample loading.

Detectors

Quadrupole Mass Spectrometry (MS)	Flame Ionisation Detector (FID)
<ul style="list-style-type: none"> Detection method of choice Sensitive, selective, near-universal coverage The detector response differs by analyte and tuning conditions – less suitable for summing all peaks vs one reference standard (e.g. total hydrocarbons) 	<ul style="list-style-type: none"> Uniform response to hydrocarbons – good for measuring sum-definitions Narrower analyte scope than MS Simple and robust
Photoionisation Detector (PID)	Electron Capture Detector (ECD)
<ul style="list-style-type: none"> Scope of coverage matches the effect-based definition of atmospheric VOCs Frequently used in series with FID 	<ul style="list-style-type: none"> Very sensitive for halogenated compounds Susceptible to interference Has been superseded by MS



Calibration and quality control

It is important that appropriate negative and positive controls are run to verify the performance of the method on each day. A traceable reference standard of each VOC being measured (or of toluene, in the case of TVOC) is essential for quantitative methods.

Reference standards are available in different formats to suit specific needs of testing laboratories. For VOC analysis, mixtures, rather than neats or single solutions, are an attractive option (**Table 2**).

Table 2: Mixtures vs neats or single solutions

Mixtures	Preparing mixtures from neats or single solutions
Ideal for standard methods: standardised analyte lists and concentrations	Flexibility to vary the analyte list and relative analyte concentrations
Single expiry date pre-defined for whole mixture: can split the suite into short shelf-life and long shelf-life mixtures	Ability to customise shelf-life of mixture
Allows even spread of cashflow and minimises waste – only buy what you need, when you need it	Cheaper in the long term (if no waste)

CONCLUSION

VOCs are a global problem and action to tackle them is being taken by regulators and industry bodies around the world. These emission controls, product specifications, monitoring and environmental remediation plans will only be effective if supported by laboratories who appreciate exactly what they are trying to measure, why they are measuring it, and the best method to achieve this.

Testing for VOCs has become routine in many settings, and it can be easy to forget that at a fundamental level it remains technically challenging.

Now is the time for laboratories to review their own approaches. Have you used standard methods by default rather than necessity?

Do you understand the context of your results?
Is there scope for improvement?

This internal scrutiny applies equally to regulated and non-regulated arenas, to method redesign and to incremental optimisation. In such a disparate field, take a deep-dive into your customers' needs and your own technical detail in order to provide a service that is truly fit for purpose.

Collaboration with customers, regulators, industry bodies and providers of quality assurance and measurement tools such as Dr. Ehrenstorfer will help to ensure your analytical testing for VOCs maintains pace with changing demands as well as the effective application of evolving methods.

ABOUT US

Since 1975, Dr. Ehrenstorfer™ has led the way in producing pesticide reference standards. Today, our portfolio has expanded to adapt to changing regulations and technology as we support your needs for high quality reference materials for food and environmental analysis.



ABOUT THE AUTHOR

John Points is a UK-based independent consultant, offering advice on chemical risks and testing strategies to industry, regulators and laboratories in the food, environment and pharmaceuticals sectors.

FOOTNOTES

1. German building regulations, laminate flooring, TVOCSPEZ
2. Example: Canada - Vinyl Chloride Release Regulations, 1992 SOR/92-631
3. ISO/IEC 17025 Third Edition 2017-11, General requirements for the competence of testing and calibration laboratories
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6. Method 624.1: Purgeables by GC/MS, December 2016
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8. Method 8015c Nonhalogenated Organics By Gas Chromatography, Revision 3 February 2007
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14. Example: Application of dispersive liquid-liquid microextraction and gas chromatography with mass spectrometry for the determination of oxygenated volatile organic compounds in effluents from the production of petroleum bitumen, Grzegorz Boczkaj, Patrycja Makoś, Andrzej Przyjazny, Separation Science, 39 (2016) 2604



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