

ISSUES IN VOC MONITORING AND REPORTING

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ABSTRACT

Volatile Organic Compounds (VOCs) present a particularly unique testing dilemma since there are a large number of different compounds defined as VOCs. The process of accurately and consistently measuring the quantity of total VOCs emitted is a matter of concern to policy makers and researchers.

Each method has advantages and disadvantages relative to the other methods. The choice of measurement and reporting techniques depends on the purpose that the data will serve. Due to differing analytical limitations for each of the VOC test methods, all sources may not be able to use the same method / procedures to monitor and report.

Because of the wide variety of compounds of interest coupled with the lack of standardized sampling and analysis procedures, determination of pollutants in ambient air is a complex task. Many toxic organics can be sampled and analyzed by several techniques, with different interferences and detection limitations. No uniform averaging period is defined for ambient VOC measurement.

1 INTRODUCTION

Volatile Organic Compounds (VOCs) are major class of pollutants causing concern. VOCs are part of the large hydrocarbon family, a vast array of aliphatic, aromatic hydrocarbons, their halogenated derivatives, alcohols, ketones and aldehydes. VOCs have a property of conversion into vapour or gas without any chemical change. They are highly reactive hydrocarbons and participate in atmospheric photochemical reactions. Some of them have negligible photochemical activity; however they play an important role as heat trapping gases in atmosphere.

Sources: Many VOCs are of natural origin while many owe their existence to anthropogenic activities. Natural sources of VOCs include forests, termites, oceans, wetlands, Tundras and volcanoes. Estimated global emission rate of biogenic VOCs is 1150 Tgyr-1 (Guenther et. al.1995)

The anthropogenic sources of VOCs consist of vehicular emissions, petroleum products, chemicals, manufacturing industries, painting operations, varnishes, coating operations, consumer products, petroleum handling, auto refinishing, cold clean degreasing, printing inks, dry-cleaning etc.

In presence of oxides of nitrogen and sunlight, VOCs form ozone and other products. Oxidation of VOCs by reaction with hydroxyl radicals is the main removal process. The oxidation of complex organic molecules leads to the fragmentation, production of a range of reactive free radicals and more stable smaller molecules such as aldehydes. VOCs are cause of concern firstly due to its role in formation of ground level ozone and smog and secondly due to some of them being carcinogenic, mutagenic and teratogenic in nature. Adverse effects

of ozone on human health, crop viability and yields are well documented. Wide range of VOCs, imply wide range of reaction rates, which means large range of transport distances. Many VOCs have low reactivity and thus long atmospheric life times and can be classified as Persistent Organic Pollutants (POPs). Some VOCs are Hazardous Air Pollutants (HAPs) by virtue of their toxicity.

International concerns regarding VOCs arise due to their ability of long range transport, distribution and accumulation in various components of environment, their toxic nature and significant contribution from natural sources.

1.1 Definitions of VOCs

Definitions of VOCs vary according to context. A general definition is "VOCs are organic substances which are volatile and are photochemically reactive". *Table 1* summarizes the definitions of VOCs used by various organizations.

Table 1. Definitions of VOCs.

UNECE Definition/ Environment Agency	USEPA Definition	LRTAP Definition	WHO Definition
VOC as any organic compound which is emitted from anthropogenic processes and has a photochemical ozone creation potential (POCP) excluding methane and naturally occurring VOCs.	VOC are compounds which contain carbon and has a vapour pressure of at least 0.01 kPa at 20°C. It defines a semi-VOC as an organic compound with a vapour pressure between 10-2 and 10-8 kPa and a non-VOC is any organic compound which has a vapour pressure less than 10-8 kPa excluding Methane, carbon monoxide, carbon dioxide and ions of carbon with oxygen.	VOCs as all anthropogenic organic compounds (except methane) that are capable of producing photochemical oxidants by reactions with nitrogen oxides in the presence of sunlight.	Based on B.P range VVOC < (0°C...50-100°C) VOC (50-100°C...240-260°C) SVOC (240-260°C...380-400°C) POM > 380°C

1.2. Challenges in monitoring VOCs

Volatile Organic Compounds (VOCs) present a particularly unique testing dilemma since there are a large number of different compounds defined as VOCs. The process of accurately and consistently measuring the quantity of total VOCs emitted is a concern to industry, researchers and regulatory agencies. Measurement of VOCs can be divided into two categories:

- Source Emissions
- Ambient Air

1.3. Source emission monitoring

There are three primary mechanisms for evaluating VOC emissions.

- Material Balance
- Emission Factors
- Emission Testing

All of above can be used for source emissions and reporting format depends on the compliance requirement. Any technique of measuring VOCs must consist of three major components namely,

- ★ the means of detection of the target analytes;
- ★ the means of extraction, and
- ★ the sampling and transport media

USEPA has promulgated number of methods for VOC measurement.

Table 2. Key promulgated USEPA methods for VOC monitoring.

Method number	Title/application
USEPA M18	VOCs by GC analysis, sampling and on-line systems
USEPA M21	VOC leaks (fugitive emissions).
USEPA M25a	Gaseous VOC concentration by Flame Ionisation Detector
USEPA M25b	Gaseous VOC concentration by infrared analyser
USEPA M25c	Non-methane organic carbon in landfill gases
USEPA M25d	VOC of waste samples
USEPA M25e	Vapour Phase organic concentration in waste samples
OSW M0010	Semi VOCs by GC after sampling with a modified Method 5 (MM5) train
OSW M0011	Aldehydes by sampling with a MM5 train and 2,4-DNPH. Analysis by GC-M5 or HPLCUV
OSW M0030.	Sampling with a 2-tube VOST and analysis by GC. For medium volatility VOCs
OSW M0031	Sampling with a 3-tube VOST, and analysis by GC. For medium to very high volatility organic compounds.
OSW M0040	Bag sampling for high volatility, high concentration compounds.
USEPA M106	Determination of Δ /CM (Vinyl Chloride Monomer)
USEPA M107	VCM of in-process waste water samples
USEPA M107a	VCM of solvents
USEPA M204A	VOCs in liquid input stream
USEPA M204B	VOCs in captured stream
USEPA M204C	VOCs in captured stream (dilution technique)
USEPA M204D	Fugitive VOCs from temporary total enclosure

Table 2. Key promulgated USEPA methods for VOC monitoring (Continued).

Method number	Title/application
USEPA M204E	Fugitive VOCs from building enclosure
USEPA M204F	VOCs in liquid input stream (distillation)
USEPA M305	Potential VOC in waste
USEPA M307	Emissions from solvent vapour emissions
USEPA M308	Sampling for methanol with a heated system. Analysis by GC-FID
USEPA M318	Extractive FTIR for measuring emissions from the mineral wool and wood Fibreglass industry.
USEPA M310A	Residual hexane
USEPA M310B	Residual solvent
USEPA M3201C	Residual n-hexane in EDPM rubber
USEPA M312A	Styrene in SBR latex (GC)
USEPA M312B	Styrene in SBR latex by capillary GC
USEPA M312C	Styrene in SBR latex produced by emulsion polymerisation
USEPA M320	Vapour-phase, organic and inorganic emissions by extractive FTIR

The correct determination of VOC emission rates is dependant on multiple factors. One factor is the ultimate purpose of the data. If testing is performed for regulatory purposes, then the regulating agency must define the pollutant and the reporting units. Usually regulating agencies require knowing total VOC emission, control efficiency of control equipments and concentration limits. Commonly used methods are M18, M25 and M25A. These methods suffer from limitations of detection technology and accept M18 other report TVOC as "Carbon" or "Methane". M18 uses FID & MS as a detector. M18 is excellent for speciating individual compounds, testing for Toxic Air Pollutants (TAPs) and Hazardous Air Pollutants (HAPs), for mass emission tests when there are only a few VOCs in the gas stream, and for characterizing a gas stream. Method 18 utilizes gas chromatography to separate the VOC compounds from each other and from other interferences in the gaseous stream. The detector used in this method is specifically calibrated for each VOC compound present using known standards to develop response factors and linear operating ranges for the method. This method is capable of providing true results in terms of individual VOC components which when totaled provide a total VOC concentration. The main advantage of this method is that results are reported "as VOC".

Method 25 measures TGNMO (total gaseous non-methane organic) by first separating the VOC components from methane, carbon monoxide and carbon dioxide. The remaining VOC compounds are chemically converted to methane molecules, which are quantitatively measured by a FID (flame ionization detector). This method provides a measurement of the VOC composition in terms of its carbon content. This method normalizes the response factor for individual VOC components since the carbon in each component is converted to methane before performing the quantification. This method has detection limit of about 50 ppm carbon cannot be used on many outlets where the concentration is often considerably less than that. This method reports VOC "as Carbon".

This procedure involves two errors: response factors and total VOC molecular weight. For eg without an average MW, the data is often reported on a mass basis 'as carbon' or in terms of another surrogate.

$$\text{gms/hr (as Carbon)} = K * \text{ppm} * 12.01 * \text{Flow rate}$$

$$\text{gms/hr (as VOC)} = K * \text{ppm} * \text{Flow rate} * (\text{MW VOC} / \text{no.C})$$

Method 25A is an instrumental method in which the VOC is introduced into a FID chamber without first separating the VOC components. The FID is calibrated with a standard gas such as methane or propane and the method results are often reported in terms of the calibration gas used (e.g., "as propane"). The main problem with this method is the variation of the FID response to VOC components other than hydrocarbon compounds. VOC compounds containing oxygen or halogen atoms may differ as much as two-fold in FID response from similar hydrocarbon compounds. This method is sensitive to low concentrations, relatively easy to use, low cost and may be converted to "as VOC" results for simple gas streams where the composition is known.

1.4 Ambient Air Monitoring

Measurement of VOCs in ambient air is often difficult, because of the variety of VOCs of potential concern, the variety of potential techniques for sampling and analysis, and the lack of standardized and documented methods. Measuring TVOC concentrations does not provide reliable indication of potential health impacts of air pollution. In case of ambient air monitoring of VOC is aimed to control /avoid adverse impacts on humans and ecology must result in knowledge of

- Types of VOCs
- Concentrations of VOCs
- Their dispersion routes
- Their fate in environment
- Category of VOCs in terms of photochemical ozone creating potential

VOCs that are of important due to their toxicity are listed in *Table 3*.

Table 3. List of VOCs Identified to be of Importance due to their Toxicity.

Compound	Category
acrylamide	cat.2 carcinogen and mutagen
acrylonitrile	cat.2 carcinogen
aziphos-methyl	very toxic
benzene	cat.1 carcinogen
benzo(a)anthracene	cat.2 carcinogen
benzo(b)fluoranthene	cat.2 carcinogen
benzo(k)fluoranthene	cat.2 carcinogen
benzo(j)fluoranthene	cat.2 carcinogen
benzo(a)pyrene	cat.2 carcinogen, mutagen and teratogen
butadiene	cat.2 carcinogen
carbon disulphide	cat.2 teratogen
1-chloro-2,3-epoxypropane	cat.2 carcinogen
chloroethene (vinyl chloride)	cat.1 carcinogen
dibenzo(a,h)anthracene	cat.2 carcinogen
1,2-dichlorethane	cat.2 carcinogen
dichlorvos	very toxic
dieldrin	very toxic
diethyl sulphate	cat.2 carcinogen and mutagen
dimethyl sulphate	cat.2 carcinogen
dnoseb	cat.2 teratogen
endosulfan	very toxic
endrin	very toxic
1,2-epoxypropane	cat.2 carcinogen
2-ethoxyethanol	cat.2 teratogen
2-ethoxyethyl acetate	cat.2 teratogen
4,4'-methylenebis(2-chloroaniline)	cat.2 carcinogen
4,4'-methylenediphenyl diisocyanate	very toxic (inhalation)
nitrobenzene	very toxic
2-nitropropane	cat.2 carcinogen
phenol	very toxic (inhalation)
phorate	very toxic
phosgene	very toxic
polychlorinated biphenyls	IARC group 2A
2-propen-1-ol	very toxic (inhalation)
pyrene	very toxic
1,1,2,2-tetrachloroethane	very toxic

Very little guidance is available for the determination of toxic organic compounds in ambient air. As a result, while monitoring VOCs as air pollutant one is required to develop his own monitoring strategies, including selection of monitoring methods, sampling plan design, and specific procedures for sampling, analysis, logistics, calibration and quality control and averaging time. USEPA has compiled compendium of methods to monitor VOCs and toxics in ambient air (Table 4). It gives description of technical aspects of the available methods. However none of these methods recommend any averaging period. Literature shows that concentration of VOCs have been reported as ppmv/ ppbv and also microgram per meter cube for samples collected as grab sample or for time periods varying from few seconds to hours.

Table 4. List of USEPA Compendium of Methods for VOC / Toxic Air Pollutant Monitoring.

Compendium Method No	Type of Compounds	Determined Sample Collection Device	Analytical Methodology
TO-12	Volatile organic compounds	Tenax® solid sorbent	GC/MS
TO-22	Volatile organic compounds	Molecular sieve sorbent	GC/MS
TO-32	Volatile organic compounds	Cryotrap	GC/FID
TO-4A	Pesticides/PCBs	Polyurethane foam	GC/MD
TO-52	Aldehydes/Ketones	Impinger	HPLC
TO-62	Phosgene	Impinger	HPLC
TO-72	Anilines	Adsorbent	GC/MS
TO-82	Phenols	Impinger	HPLC
TO-9A	Dioxins	Polyurethane foam	HRGC/HRMS
TO-10A	Pesticides/PCBs	Polyurethane foam	GC/MD
TO-11A	Aldehydes/ketones	Adsorbent	HPLC
TO-122	NMOC	Canister or on-line	FID
TO-13A	Polycyclic aromatic	Polyurethane foam	GC/MS
TO-14A	Volatile organic compounds (nonpolar)	Specially-treated canister	GC/MS and GC/MD
TO-15	Volatile organic compounds (polar/nonpolar)	Specially-treated canister	GC/MS
TO-16	Volatile organic compounds	Open path monitoring	FTIR
TO-17	Volatile organic compounds	Single/multi-bed adsorbent	GC/MS, FID, etc.

2 CONCLUSIONS

In order have uniformity in data reported for VOC concentrations in ambient air, indoor air and source emissions it is essential to develop a common methodology for sampling, analysis and reporting.

REFERENCES

1. The Categorisation of Volatile Organic Compounds (DOE/HMIP/RR/95/009). HMIP (1996).
2. Directive 96/61/EC. A European Community System for Integrated Pollution Prevention and Control (IPPC). Official Journal No. L257, 10.10.1996.
3. Directive 1999/13/EC. On the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations. Official Journal L85/1, 29.3.1999.
4. 2000/76/EC. Directive on the incineration of waste. Official Journal L332/91, 28.12.2000.
5. International Standards Organisation, ISO. www.iso.ch
6. United States Environmental Protection Agency, USEPA. www.epa.gov/ttn/emc .

- 8 BS EN 12619 (1999) - Stationary source emissions - Determination of the mass concentration of total organic carbon at low concentrations in flue gases – continuous Flame ionization detector method.
9. BS EN 13526 (2001) - Stationary source emissions - Determination of the mass concentration of total gaseous organic carbon at high concentrations in flue gases - Continuous flame ionization detector method.
10. BS EN 13649 (2002) – Stationary source emissions – Determination of the mass concentration of individual gaseous organic compounds – Activated carbon and solvent desorption method.
11. Technical Guidance Note M1, Sampling and safety requirements for monitoring stack releases to atmosphere, Environment Agency, 2002.
12. Technical Guidance Note M2, Monitoring stack emissions to air, Environment Agency, 2004.
13. BS EN 14181 (2000) – Stationary source emissions -Quality assurance of automated measuring systems.
14. BS EN ISO 14956 (2002) - Air quality - Evaluation of the suitability of a measurement procedure by comparison with a required measurement uncertainty.