Sampling and analysis of volatile organic compounds (VOC) relevant for the formation of photochemical oxidants

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Abstract

The paper presents a strategy for sampling and analysis of VOC, i.e. sampling sites, period and frequency, sampling systems and the various analytical methods as well as the preparation of VOCs standard mixtures. Moreover, in this work we report on a new system for the analysis of VOC in air. The device consists of a gas chromatograph equipped with a sampling loop (50 to 200 ml) and a liquid nitrogen cooled microtrap, placed in the chromatographic oven, connected via a valve with the sampling loop. The system allows 24-hour sampling and analysis of a large number of VOC (up to 25 individual hydrocarbons) ranging from C_2 to C_9. Thanks to the special geometry of the trap a minimum consumption of liquid nitrogen (150-300 ml) for each analytical run is required. In-field measurements in urban and remote areas have demonstrated the ability of the system to work under different environmental conditions and to respond to concentrations for individual hydrocarbons down to pptv level.

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1. Introduction

Volatile organic compounds (VOC) are known to play an important role in photochemical oxidant formation. Until now only few data on measurements of volatile hydrocarbons exist, mostly expressed as the sum of non-methane hydrocarbons, which have been used in photochemical models.

Because of the different reactivity, ozone forming potential and abundance of the VOC in the atmosphere, it seems reasonable to quantify the individual volatile compounds, which may serve as photooxidant precursors. [1-6]

In particular the need to develop ozone measurement and abatement strategies within the ;Member States of the EEC is closely connected with the measurement of individual VOCs in order:

- to check models
- to check the influence of VOC emission reduction programmes on VOC levels in ambient air and
- to see the influence of new legislation (like the use of unleaded petrol) on VOC emission and concentration patterns.

The Environment Institute of the JRC-Ispra has been requested by DG XI to organise and coordinate a working group of European experts on VOC measurement techniques. The main tasks of this working group are:

- to prepare a list of VOC which should be measured with priority;
- to prepare a common agreement on sampling, calibration and analysis methods to be used to identify and quantify VOC;
- to give recommendations and propositions on how to carry out a measurement campaign of VOC relevant for the formation of photochemical oxidants.

2. Selected compounds

A preliminary list of 33 VOC, that should be measured with highest priority, was established (s. table 1).

Main criteria for the selection of the listed compounds are:

- their reactivity
- their estimated emission rates and their measured abundances in urban atmospheres as well as in the free troposphere.

Table 1: Proposed VOC to be measured with priority

Methane	1-Pentene
Ethane	2-Pentene
Ethylene	Isoprene
Acetylene	n-Hexane
Propane	l-Hexene
Propene	n-Heptane
n-Butane	n-Octane
i-Butane	i-Octane
trans-2-Butene	Benzene
1-Butene	Toluene
cis-2-Butene	m+p-Xylene
1,3-butediene	o-Xylene
n-Pentane	Ethylbenzene
i-Pentane	1, 2, 4-Trimethylbenzene
	1, 2, 3-Trimethylbenzene
	1, 2, 5-Trimethylbenzene
	Formaldehyde as well as CO

3.1. Sampling sites

Two types of sampling sites appear relevant:

- near to anthropogenic VOC sources (urban areas) to assess the influence of VOC emissions in the urban atmosphere in order
  - to estimate the global level of VOC and the VOC trends in a city
  - to estimate VOC contribution by traffic and
  - to estimate the contribution/composition by industrial plants.
- In areas with no significant local sources (rural areas) which appear better suited for surveillance of long term changes and for validation of large scale models:
  - to estimate a representative general trend of VOC
  - to validate the chemical reaction schemes in the models
  - validate calculated concentrations in large scale models.

3.2. Selection of sampling sites

The selection criteria for the sampling sites as they are specified by the working group can be grouped as follows:

In an urban area

- cities with more than 300.000 inhabitants
- average distance to border of build-up area more than 3 km
- distance to streets (> 3000 vehicles/day) more than 35 km
- distance to busy streets (> 30.000 vehicles/day) more than 100 m
- distances to petrol stations more than 200 m
- measurement height 1.5 - 4m.

Traffic contribution

- sites with > 10.000 vehicles/day
- distance to road: < 10 m
- more sites: selection of average speed (13 - 22 - 44 km/h)
- distance to petrol stations / parking garage > 200 m
- distance to busstation > 100 m
- clear definition of street type, constant over at least 100 m
- distances to obstacles / buildings at least 1 m, preferably 5 m.

Industrial area

- two measurement sites: > 45 degree and > 1 km distances:

In a rural area

- distances to villages / forests, etc. more than 5 km.

In addition airplane measurements are recommended to evaluate the distribution of VOC in the free troposphere. This is of particular interest in relation to the background ozone level in the free troposphere which in turn influences also the ground level ozone concentrations.

VOC measurements should be combined with NO_x and O_3 measurements. Therefore, sampling sites should be selected taking into account the places where other atmospheric pollutants are measured.

4.1. Sampling period and frequency

To estimate global levels of VOC in a city 24 h-sampling every (4) days would be suitable. Alternatively 24 h-sampling every day for one week five times yearly could help in estimating VOC trends. For estimating the VOC impact by traffic, measurements twice/week with 2 h-sampling during high traffic frequency (rush hour) between 8-10.00 and 17-19.00 h would be suitable. Sampling period and frequency in industrial areas are very dependent on local situation.

In rural areas 24 h-sampling every four (49 days or 24 h-sampling every day for one week five times yearly has been suggested for estimating trends.

Alternatively, VOC measurements with a frequency of two samples per week (1 h sampling, centred at 12 noon GMT) over a period of several years would be suitable for revealing long term trends (as proposed by EMEP). [7]

In addition, more frequent VOC measurements could be carried out during ozone episodes. Activities aiming at the study of ozone episodes should be planned by a collaboration between modellers and analytical chemists.

4.2. Sampling of VOC

Sample collection systems for organic air contaminants have been reviewed and evaluated. The basic methods mostly used are:

Trapping in a sampling tube packed with porous adsorbent such as Porapack Q, Tenax-TA, activated charcoal or carbosieve S. Adsorption can also be combined with deep-freezing of the trapping tube (improvement of the trapping efficiency). The main problems encountered in adopting this last technique relates to the presence of water vapour, which rapidly condenses prior to the cold trap, altering the characteristics of the overall sampling operation. Thus, the use of appropriate dessicants (which should not absorb the organics to be analysed) prior to the sampling tube reduces this problem. Following adsorption, samples collected in sampling tubes are desorbed either by extraction with an organic solvent (hexane, dichloromethane, CS_2) or by rapid thermal desorption.

- **Solvent extraction:** Only a small portion of the extract can be injected into the GC column.
  Main advantage: Enrichment during sampling. Sample is available for further analysis.
  Main disadvantage: Dilution of the sampled compounds in the solvent (low sensitivity).

- **Thermal desorption:** The adsorbed compounds are rapidly eluted at high temperature (180-350°C) by means of a carrier gas (helium) and re-concentrated using liquid nitrogen (cryofocussing) in a cryotrap on-line connected with the analytical column. Finally flash heating of the cryotrap provides a rapid injection of all the VOC collected into the GC column.

Main advantage: Enrichment during sampling. The total amount of the VOC collected is available for the analysis at one (high sensitivity).
Main disadvantage: Sample is no more available for further analysis.

Pre-evacuated stainless steel canisters which allow capture of a certain volume of ambient air. By this method a great number of non-polar VOC are collected and can be subsequently analysed after a procedure of cryogenic trapping. The suitability of the method has to be checked for higher aromatics. Typically, 6L, 4L, 1.6L and 0.8L especially pre-treated (electropolished) canisters have been used for the collection of whole -air samples.

5. Analysis of VOC

Among the great number of modern analytical methods, the techniques of gas chromatography (capillary columns) with flame ionisation detector (GC-FID) or mass selective detector (GC-MSD)appear to have the widest applicability to the analysis of the listed compounds. Using fused silica $Al_2 O_3$ / KCI capillary columns analysis of almost,ost all the proposed compounds (formaldehyde and CO excluded) in one run is possible: Automated method (on-site) are available to carry out analysis of VOC. These methods allow greater sampling frequency and real time measurements, but are currently costly. For formaldehyde and other carbonyls formed as secondary pollutants high performance liquid chromatography (HPLC) with UV or diode array detector is often applied. By this method the carbonyls to be analysed are converted with appropriate reagents (e.g. dinitrophenylhydrazine) to non-volatile products (hydrazones) which can be further separated and characterised by HPLC. For CO a certain number of analysers with high sensitivity are commercially available.

6. Preparation of standard mixtures

Mixtures of the hydrocarbons under investigation can be prepared for calibration purposes by the static injection techniques: small aliquots of the pure hydrocarbons are injected in a known volume of pure air, under accurate temperature and pressure control. Gas mixtures prepared by this technique are primary calibration standards and can be stored over longer periods (1 year) with great stability (should be checked for aromatics) in special stainless steel canisters for calibration and intercomparison purposes.

Gravimetric (gas weighing) techniques can also be used for preparing accurate standards of VOC.

Standard mixtures at higher concentrations (≥ 100 ppm) are also commercially available. These mixtures can be diluted to the desired concentration by using the dynamic dilution technique. Recent developments in this technique allow the preparation of secondary calibration standards with a high degree of accuracy. This easy to handle technique is most commonly used for routine calibration purposes in the laboratory.

7. Intercomparison

Comparison of data obtained using different sampling and analytical techniques is of great importance. Therefore, before starting extended VOC measurements a preliminary work is needed for the harmonisation of the different methods.
This work should be carried out as an intercalibration exercise where identical, gravimetrically prepared standard VOC mixtures are analysed by various laboratories in, if possible, all of the EEC countries.

8. Final remarks

In order to face photochemical pollution, modelling studies have shown that substantial reduction of the precursor emission (VOC, NO_x) would be necessary.

For an accurate evaluation of emission reduction programmes as well as for the validation of models measurements of individual hydrocarbons (s. table 1) in urban and rural areas should be frequently carried out. Seasonal and annual variations of VOC should be considered.

Therefore, the working group on VOC measurement techniques proposes the following step-by-step procedure to meet the scientific objective:

- nomination of analytical laboratories, which should have the scientific and technical background for the measurement of specific VOC;
- intercomparison studies for sampling and analysis of VOC;
- in-field measurements of individual compounds in selected urban and rural areas, collection and evaluation of the data, model work.

Finally, a close cooperation with other international organisations which started/start similar activities (ECE-Geneva, EMEP) is suggested, in particular in the field of intercomparison studies on sampling and analysis procedures.

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