Pollutant Type: Gaseous Pollutants
Pollutant Name: Volatile Organic Compounds (VOCs)
Measurement Technology: Automated Sampling / Gas Chromatography / Detector

Volatile organic compounds (VOCs) are, based on the definition of the WHO, organic compounds with a high vapor pressure. This high vapor pressure results from a low boiling point ranging from 60 °C to 250 °C. VOCs are ubiquitous in the atmosphere and comprise numerous substances including e.g. aliphatic and aromatic hydrocarbons, terpenes, aldehydes or halogenated hydrocarbons. VOCs are naturally occurring (e.g. emitted by plants and soils) and also man made substances. Typical sources for manmade VOCs are traffic emissions, paints or protective coatings. VOC can be dangerous for human health and play an important role as precursor compounds for ozone and secondary organic aerosol formation.

Description of the method

**Online detection of VOCs using gas chromatography (GC) technology**
The online detection method for the quantification of different VOCs in ambient air comprises three units:
- sampling/pre-concentration (e.g. canisters or adsorptive tubes),
- separation of the compounds by gas chromatography column(s),
- quantification of the separated compounds.

GC technology in combination with different detectors is the most used technique for monitoring VOCs in ambient air (Santos & Galceran 2002).

The first unit is the sampling/enrichment stage. The method of automated sampling with a pump is described e.g. in ISO 16017-1 2000. For the enrichment the VOC of the sample are collected by adsorption onto appropriate adsorbents. Then they are released more concentrated by thermal desorption or extraction and the sample is transferred to the GC. An overview about the different sampling techniques is given e.g. by Wang & Austin 2006.

In the GC the different VOCs are separated. The sample together with a carrier gas (mobile phase) is moved through a column filled with the stationary phase. The motion of the molecules is inhibited by the adsorption to the stationary phase. The various VOC substances pass through the column filling at different rates depending on their different chemical and physical properties. Thus each substance exits the column at a different time, the specific retention time, and the mixture of substances is separated. To increase the separation effect more than one GC column can be used (Arsene et al. 2011). The separation of VOCs by GC is reported e.g. by Veillerot et al. 1998.

The third unit is the detection stage. At the outlet of the column the time at which each component exits and the amount of the component is monitored with an appropriate detector. The substances are qualitatively identified by their retention time. For the quantification different methods/detectors are utilized, Flame Ionization Detectors (FID), Photoionization Detectors (PID), Mass Spectrometry (MS), Ion Mobility Spectrometer (IMS), Pulsed Discharge Helium ionisation Detector (PDHID) and different sensors.
FID
The Flame Ionization Detector (FID) is the most widely used detector quantifying VOCs in combination with a GC for online ambient air measurements. It measures the total amount of organic carbon in a sample. Generally it has to be taken into account that FIDs are not suitable to measure concentrations of individual components in a mixture. As at the exit of a GC column only single components have to be quantified flame ionization detection is an adequate technology (McWilliam & Dewar 1958). The measurement principle of FIDs uses the phenomenon that the burning of organic carbon compounds produces ions. The amount of ions correlates with the amount of the organic component. When the air sample exiting from the GC column is entering the FID it is mixed with hydrogen (carrier gas) and clean, dry air. After mixing, the sample is burnt and the organic molecules are ionized in the flame. As each carbon atom in a molecule produces a signal calibration can be performed using the carbon-response method. The produced ions change the conductivity of the volumetric flow. This gives a recordable signal (Holm 1999) which is measured using a collecting electrode after the flame. The FID is a destructive detector, the sample is burnt and cannot be analyzed afterwards. The sensitivity for VOCs is in the ppt-range (e.g. Broadway & Tipler 2009). Numerous proceedings report the use of FID as detector in combination with GC to monitor ambient air quality, e.g. Badol et al. 2004, Farmer et al. 1994, Oliver et al. 1996.

PID:
In a photoionization detector a UV lamp produces high-energy photons. The photons break the molecules of the substance which concentration should be determined into positively charged ions. The ions produce an electric current, which is measured. Only molecules with conjugated double bonds can be detected. The concentration of the component corresponds with the value of the electric current. The PID is a non-destructive detector as the ions recombine after passing the detector. The sensitivity for VOCs is in the subppb-range (Jian et al. 2012, Lewis et al. 2010). Kelessis et al. 2006 report the use of PID as detector in combination with GC to monitor ambient air quality in Thessaloniki, Greece.

MS:
In a mass spectrometer chemical compounds are ionized and charged molecules or charged fragments of molecules are produced. For ionization a variety of methods is available, e.g. electron or chemical ionization. Then the ions are separated according to their mass-to-charge ratio in a mass analyzer. There exists a variety of mass analyzers using different methods, e.g. quadrupole mass analyzer or time-of-flight (TOF) analyzer. The last step is the detection and quantification of the ions. Again different detectors are available, e.g. photomultipliers or Faraday cups. The mass spectrometer is a destructive detector. Its sensitivity is in the ppt-range (Wedel et al. 2011). A MS detector is more expensive than an FID detector. A comparison between MS and FID detectors and the possibilities using them in combination are described by de Blas et al. 2011. The use of GC-MS technology for ambient air monitoring is reported e.g. by de Blas et al. 2011, Wedel et al. 1998.

IMS:
In an Ionization Mobility Spectrometer the substances of the sample are ionized (e.g. by a radioactive source or corona discharge). Then the ions enter into the so-called drift tube where an electric field is applied and the ions are accelerated depending on their electric mobility. The time-of-flight passing the tube is determined and the recorded ion mobility spectra provide the identification of the substances and their concentrations. The advantage of an IMS is that it operates at atmospheric pressure conditions. Thus no vacuum pump is needed and therefore the IMS dimensions are relatively small. The sensitivity of IMS is in the low ppb-range (Ho et al. 2001, Baumbach et al. 2000).
PDHID:
The Pulsed Discharge Helium Ionisation Detector as detector in combination with a GC was developed by Wentworth et al. 1992. It is appropriate for the permanent detection of VOCs, even for those ones which give little response with the FID (Forsyth 2004). In a PDHID helium is transformed in a pulsed high voltage discharge between platinum electrodes to high-energy photons. The photons ionize the respective VOC which is entering the PDHID. The resulting electrons change the measured current. The changes represent the detector response. The PDHID is a non-destructive detector. Its sensitivity for VOCs is in the ppt-range (Wentworth et al. 1994). Hopkins et al. 2003 and Hunter et al. 1998 report the application of GC-PDHID for the measuring of ambient VOCs.

Sensors:
Ho et al. 2001 gave an overview about the classification, function, costs and application of the different sensor types (electrochemical sensors, mass sensors, optical sensors) for the in-situ measuring of subsurface VOCs. The suitability of the sensors for gas phase monitoring is partially discussed. Sanchez et al. 2006 report the development of a portable chemical semi-conductor gas sensor for the monitoring of complex atmosphere on the example of measuring BTX with a sensitivity in the sub-ppm-range.

References


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