Trace Level VOC Analysis in Different Sample Matrices

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In the routine analysis for VOC's (volatile organic compounds), the required system structure is composed of a sampler with special sample techniques followed by GC-MS analysis. The determination of the concentration of low- and medium-volatile organic compounds in drinking and surface water is especially important.

Easy-to-use and long time reliable handling systems are necessary and irreplaceable. Consequently, a unique 'in-vial' purge-and-trap system is presented, which is suitable for solid and liquid samples. The VSP4000 (Versatile Sample Preparator) purge and trap system can handle up to 80 samples in 20 ml standard vials. The sophisticated system is used in the Purge-and-Trap mode and also in the Thermal Desorption mode up to 280°C. The typical detection limit is in the lower ppt range, even for critical substances.

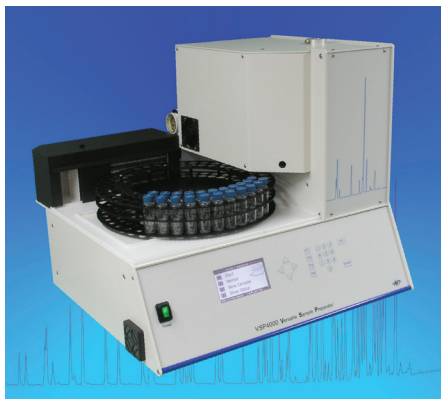

Figure 1. The VSP4000 (Versatile Sample Preparator)

The purge-and-trap technique is particularly suitable to get low detection limits and best performance. In principle there are two purge-and-trap techniques on the market: the standard method and the in-vial purging method. In the standard purge-and-trap method, the sample is pumped from the sample vial into a separate u-shaped purge vessel. To restrict contamination, the purge vessel and the tubing must be cleaned after each cycle. As a result of the u-shaped vessel principle, contaminations can not be avoided especially in the field of trace analysis. The in-vial-purging method uses the sample vial with a sample volume of 10 ml instead of an external purging vessel.

Functional Principle of the in-vial Purging of the VSP4000

The in-vial purging technique purges directly in the sample vial, where a long and a short needle is inserted into the septum. The long needle extends to the bottom of the sample vial through which the sample is sparged by the carrier gas and the volatile substances are completely blown out and enriched on the analytical trap. The purged water is retained on a Peltier water trap, and thus does not enter the analytical trap. All purged analytes are trapped on the analytical trap at a temperature of -35°C. After the purging process the analytical trap is desorbed thermally very fast and all concentrated analytes are transferred to the capillary column of the GC.

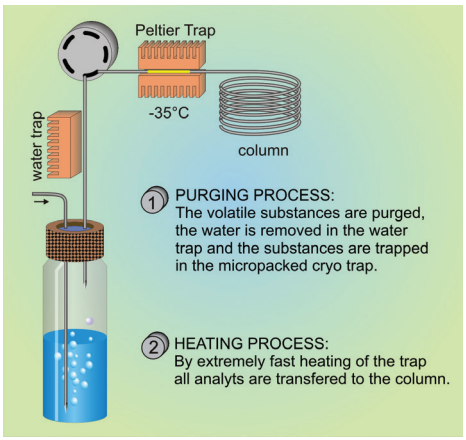

Figure 2. The schematic principle of the in-vial-purging

In contrast to the headspace technique, all light and medium volatile analytes are completely purged from the sample as the carrier gas purges the sample completely. With the headspace technique less than 100% of the analytes are available for the GC-MS analysis.

The in-vial purging technique of theVSP4000 works in principle splitless and allows the cryo-focussing of 100% of the purged analyts on the analytical trap. The classic purge vessel technique requires a split and therefore this principle has a lower performance.

Trap Enrichment at -35°C

During the purging process all purged analytes are frozen on a thermoelectrically cooled trap at a temperature of -35°C. This temperature is necessary for trapping all very volatile components e.g. dichlorodifluoromethane with a boiling point of -29.8°C. The trap is packed with Tenax, extremely miniaturised and is used for all analytes from the very volatile components up to the semi volatile components like hexachlorobutadiene. The durable trap allows up to 3000 analyses and is suitable for more than 100 different analytes with one method.

The small diameter of the trap ensures the lowest possible thermal capacity and therefore rapid desorption. All enriched analytes are abruptly transferred to the directly coupled column of the gas chromatograph resulting in narrow and high peaks.

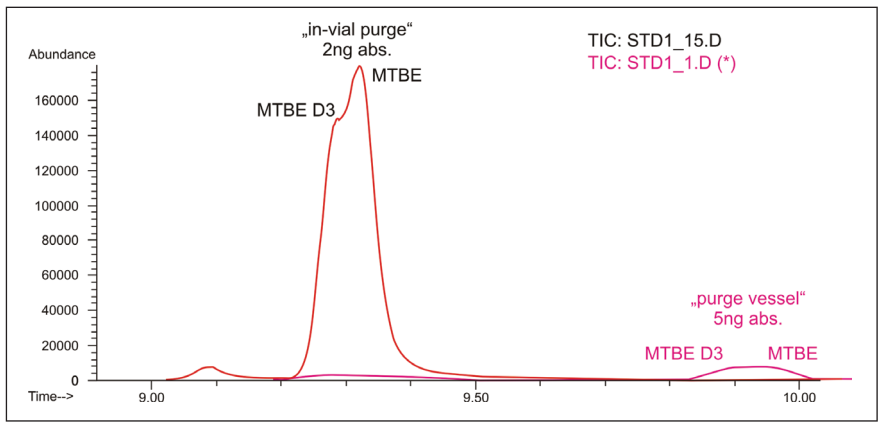

Figure 3. Chromatogram showing the difference between in-vial purging and the classic purge vessel technique

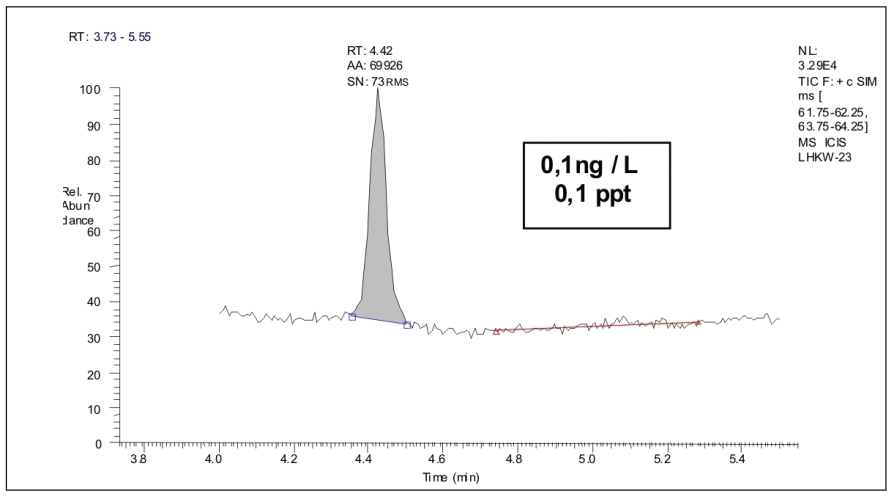

Figure 4. Chromatogram showing the performance for vinyl chloride

Advantages of the in-vial Purge Technique

The following essential advantages secure the in-vial purging technology unmatched analytical performance:

- Purging process in the sample vial with splitless injection technique
- Water removal before the trapping process and enrichment of analytes at a temperature of -35°C on a miniaturised trap
- One trap material and one method for more than 100 analytes
- Detection limits in the lower ppt range
- Automatical Internal Standard dosing
- Adjustable split up to 1:50
- Different options, such as, Thermal Desorption and use for IR-MS applications with LN2 cooling to -180°C

The VSP4000 allows the detection of the substances identified in the following EPA standards:
EPA 502.1, EPA 502.2 (Volatile Halogenated Organics);
EPA 524.2 Rev . 4.1 (Volatile Organics);
EPA 601 (Purgeable Hydrocarbons);
EPA 602 (Purgeable Aromatics);
EPA 603; EPA 624 (Purgeable Halocarbons).

Optional Extensions

Without changing the performance the VSP4000 allows with optional extensions the analysis of liquid, solid or gaseous samples.

Table 1. Sample compositions can be analysed with the VSP4000

Liquid	Solid	Gaseous
Water	Paper, cardboard	Air
Mineral water	Foils, packing material	Exhaust gas
Fruit juice (orange juice)	Plastic granules	Cigarette smoke
Alcoholic beverages	Spices	
Milk	Coffee, cocoa, chocolate	
Honey	Cosmetics	
Cooking oil	Tenax - sample tubes, Sorb-Star®	
	Carpet, textiles	
	Soil samples	

In addition to the standard purge-and-trap mode, simple modifications allow the following operation modes:

a) Thermal desorption TD to 280°C (Tenax sampling tubes or other substances)
b) Dynamic headspace technique
c) Tedlar Bag or Canister Sampling (VOC's in gases)
d) Application in isotope analysis, LN2 cooling to -180°C

a) Thermal Desorption
The conversion to the TD mode can be done by replacing the trap and the removal of the water trap. Instead of the glass sample vial a stainless steel vial is inserted with an axial bore for receiving the sample tube. The stainless sample tube is purged with the carrier gas from the bottom upwards and the purged analytes are transferred by the axial needle to the trap. This new sampling technique is patented under Pat. No. DE 102 006 025 932.

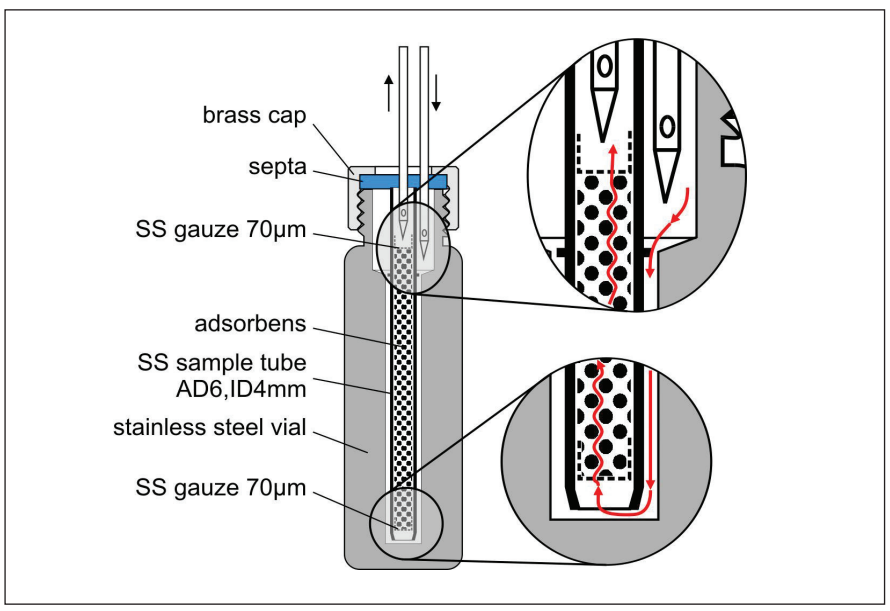

Figure 5. The stainless steel sample vial with a sample tube filled with an adsorbent and the gas path of the carrier gas

b) Dynamic Headspace
By installing a needle block with two short needles the enrichment of the analytes from the headspace of the sample can be realised. This less sensitive option enables the analysis of samples with higher concentration and thus expands the measurement range of the system.

c) Tedlar-Bag-Sampling of VOC's in air samples
By the installation of a vertical mounting plate up to 14 Tedlar bags with a single volume of 5 l can be analysed automatically. The Tedlar bags are processed cyclically by a multi-port valve. By this simple option the possibility of VOC analysis in gas samples can be realised with the full analytical performance of the VSP4000.

d) Analysis of Stable Isotopes
The isotope analysis is indispensable in hydrogeology, determining the authenticity of food and other fields. By an expansion of the cooling method, the trap can be cooled to a temperature of -180°C and also isotope analysis of methane and ethane can be realised. The adjustable trap cooling is done with liquid nitrogen, which is provided in a 50 l Dewar. In addition, the VSP4000 is also used for GC-IRMS determination of the stable isotopes of hydrogen (2H / 1H), carbon (13C / 12C), nitrogen (15N / 14N), oxygen (18O / 16O) and chlorine (37Cl / 35Cl).

Powerful Combination with the Atomic Emission Detector EPED

For various applications the combination of the VSP4000 and the new GC detector EPED (Echelle Plasma Emission Detector) allows advantages in the detection and quantification of the following elements: sulphur, chlorine, fluorine, bromine and iodine. This atomic emission detector was developed for the simultaneous and quantitative multi-element analysis and is based on the excitation of atoms in a helium micro plasma at atmospheric pressure. The emission lines of the target atoms are continuously recorded by an Echelle polychromator which is directly adapted to the plasma cell. The detector EPED is equimolar and this advantage allows the calibration with only one element/molecule and thus the quantitative determination of unknown molecules. Customers use this advantage e.g. to determine fluorinated substances in sports wear in combination with the splitless thermal desorption mode of the VSP4000. The detector EPED is installed directly on top of the GC and the durable quartz plasma cell allows detection limit of 10 pg/s for all elements.

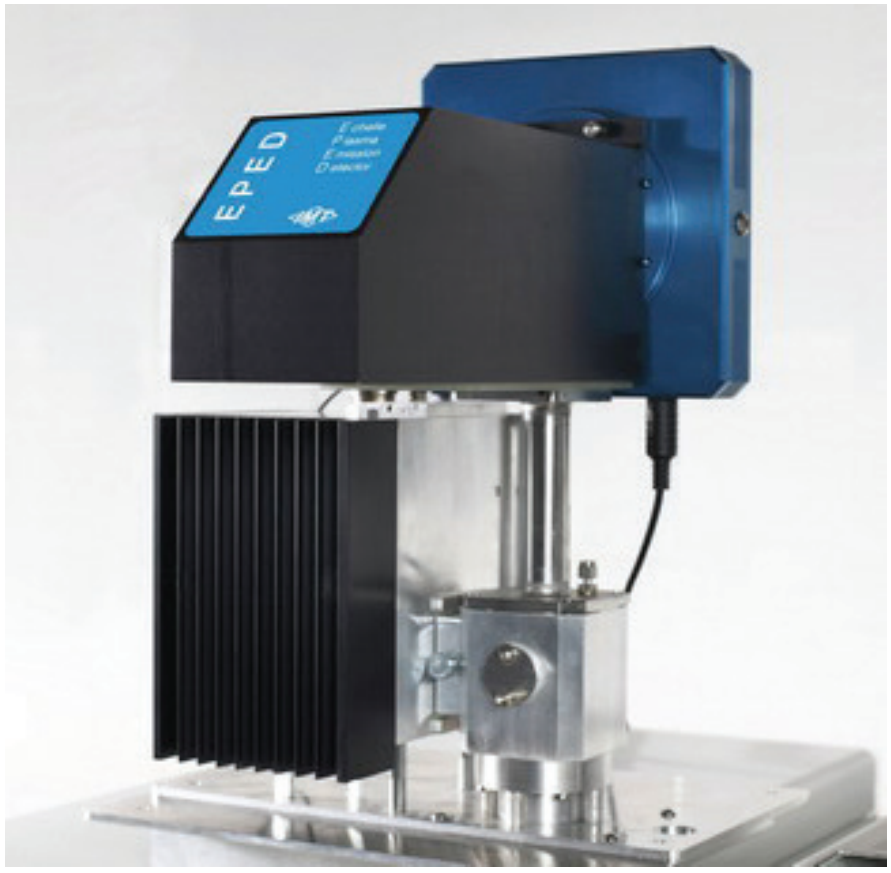

Figure 6. The detector EPED

Summary

The in-vial purge technique is one of the most powerful methods in the analysis of VOC's in drinking and surface water. The various options of the VSP4000 enable the use of almost any sample matrix up to a temperature of 280°C. Even with solid and gaseous sample matrix detection limits in the lower ppt range and standard deviations in the range of 5% are typical. When using the optimal and the best possible analysis technique in routine analysis of VOC's, it is advantageous not only to meet the current standards and requirements, but also get better sensitivity and overall performance with the VSP4000 in-vial purging method.