VOC analysis in water samples by headspace-GC-MS - optimization in several stages

Volatile organic compounds, in short VOC, belong to a group of organic compounds which, in addition to carbon and hydrogen atoms, contain often halogen atoms (fluorine, chlorine, bromine, iodine).
The use of these substances over decades, as well as the largely careless handling of VOC-containing waste and their landfilling results in their ubiquitous distribution in the compartments air, water and soil.
This poses a threat to the environment, in particular due to their sometimes extremely high persistence, accumulation in the biosphere, and mobility.
Due to this situation, most VOC in Germany are classified into the highest water hazard class 3.
By degradation processes in soil and groundwater formation of very critical secondary products takes place, such as vinyl chloride, which is a strong carcinogen. In addition to their carcinogenic effect, chronic exposure of these compounds can cause kidney dysfunction as well as disorders of the central nervous system (CNS).

„Classical Headspace“

The „classical“ way of analyzing VOC in water and soil samples is using the Headspace-GC-MS approach. The sample is placed in a headspace vial, which is then closed with gas-tight septum and then shaken or stirred.
This serves for the rapid adjustment of an equilibrium (equilibrium) between the VOC (analytes) to be analyzed in the liquid or solid sample phase and the vapor space (headspace) located above it in the vial.
In the past, many efforts have been made to optimize the parameters for this headspace determination method. Both the addition of salts to the measurement solutions ("salting-out effect") and the setting of an ideal pH lead in some cases to improvements in the detection sensitivity for some VOCs.
Ultimately, however, there are limits to this headspace technique, so that a significant improvement in terms of the detection limit for all, but especially for the very volatile components such as vinyl chloride, etc. is possible only through the use of an electric cold trap described here (Chromtech eTrap Plus).

„Splitless Headspace“

One of the great advantages of the electric cold trap is the possibility of splitless injection of the gaseous sample. In contrast to the "classical" headspace sample task, which is always operated in split mode (typical are split ratios of 1: 5 to 1:10), when using the eTrap Plus the entire sample volume (typically 1.0 - 2.5 mL) can be used instead, which further increases the detection sensitivity.
The following chromatogram shows an EPA-VOC standard, once with a split of 1:10 and once as a splitless task of 1000µL headspace volume using the Chromtech eTrapPlus:

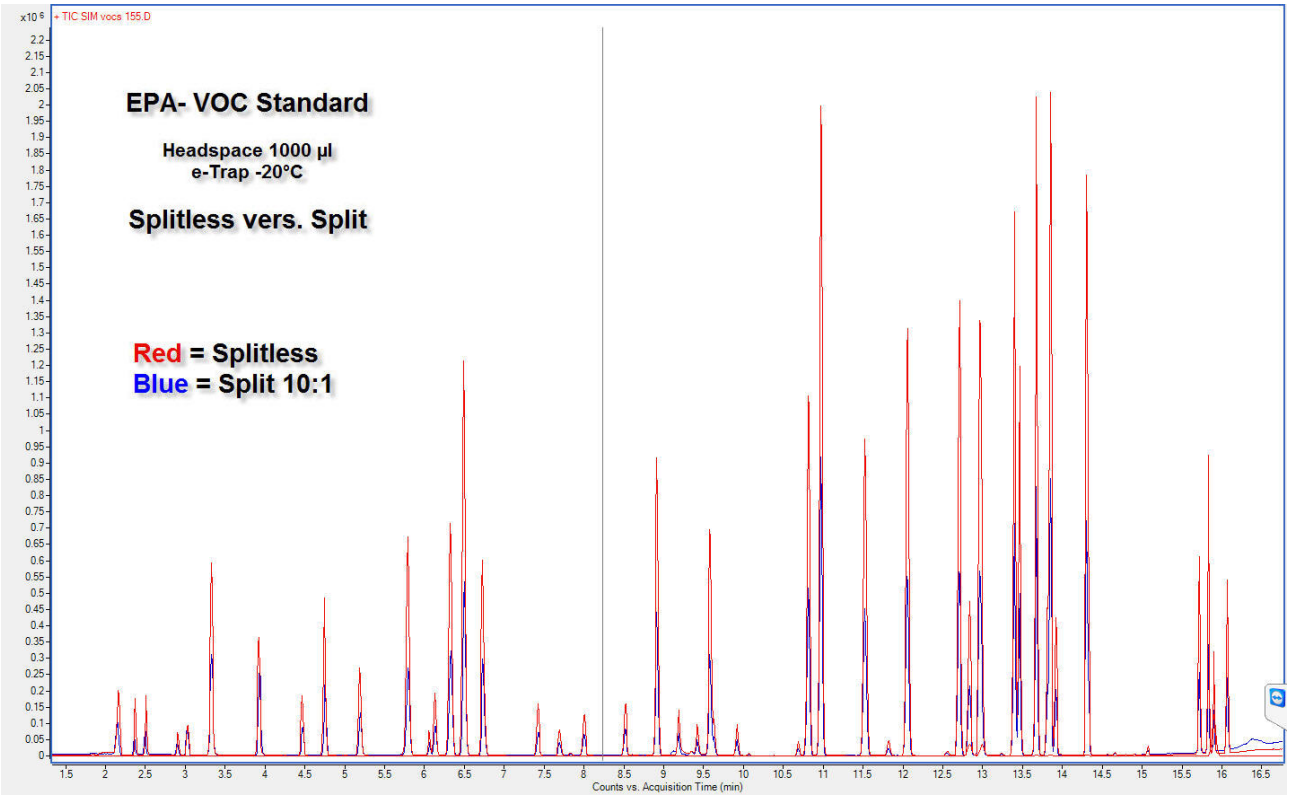


Figure 1: EPA-VOC standard, TIC, difference from split (1:10) to splitless injection of 1000µL headspace volume with Chromtech eTrapPLus (-20 ° C)

The following images illustrate the gain in sensitivity based on selected analytes with increasing headspace volume when using Chromtech eTrap Plus:

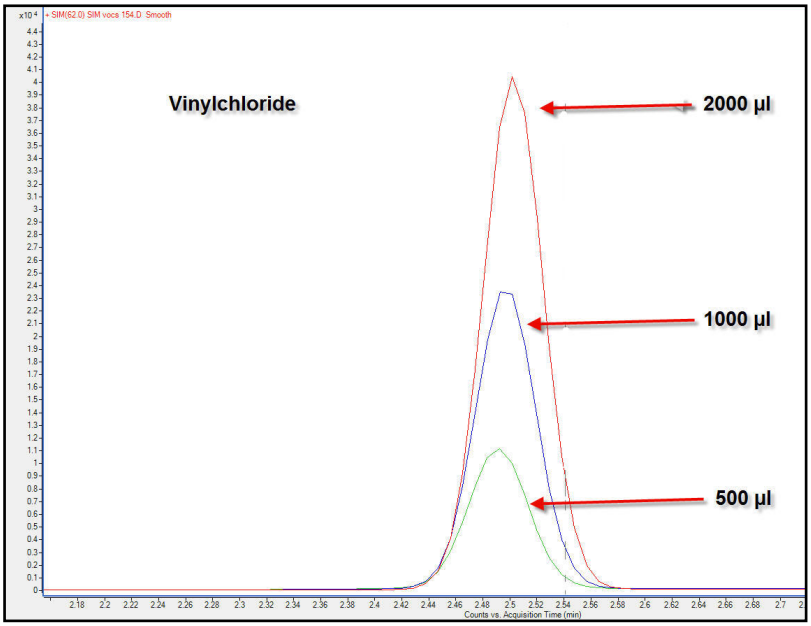


Figure 2: Vinyl chloride, m/z 62, comparison of different headspace sample volumes of 500µL, 1000µL and 2000µL.

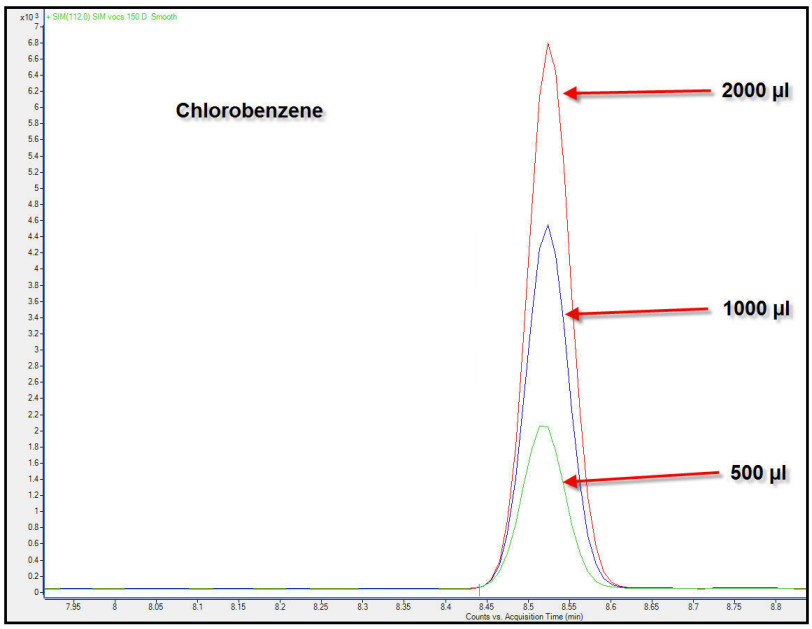


Figure 3: Chlorobenzene, m/z 112, comparison of different headspace sample volumes of 500µL, 1000µL and 2000 µL.

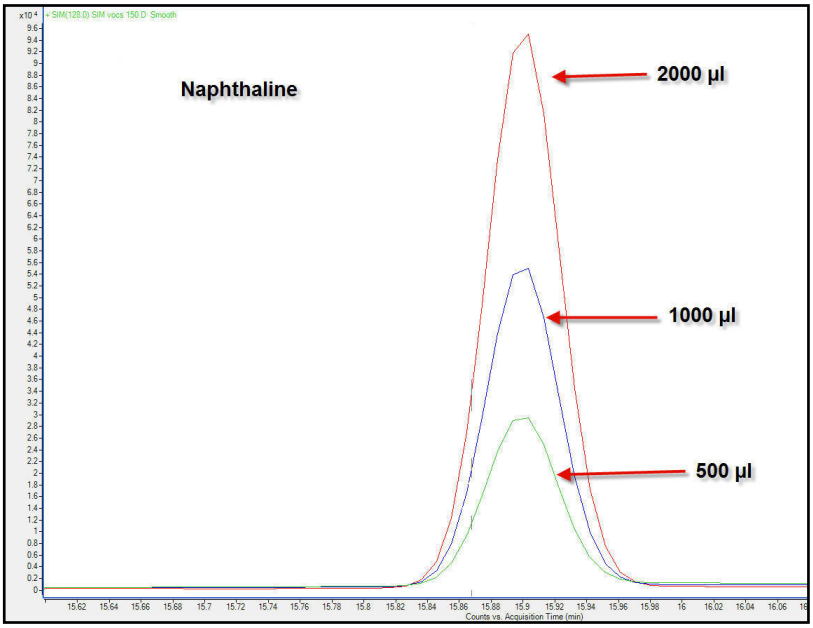


Figure 4: Naphthalene, m/z 128, comparison of different headspace sample volumes of 500µL, 1000µL and 2000µL

„Cryofocussing“

The installation of the electric cold trap ultimately causes cryofocusing of the very volatile components. The commonly used GC capillary columns with a thick film (eg DB-624, 1.4µm film) don’t achieve sufficient focusing of the extremely volatile substances, which is often noticeable in an unpleasant peak broadening, which makes quantification difficult and, above all has a negative influence on the detection sensitivity.
The following chromatogram (Figure 5) compares the "classic" headspace injection (injection volume 1000µL, split 10: 1) without any focusing with the cryofocusing by means of the Chromtech eTrapPlus. The gain in sensitivity is clearly visible.
The eTrap ensures extremely narrow peaks and thus an extreme sensitivity increase especially for the very volatile, early-eluting components.

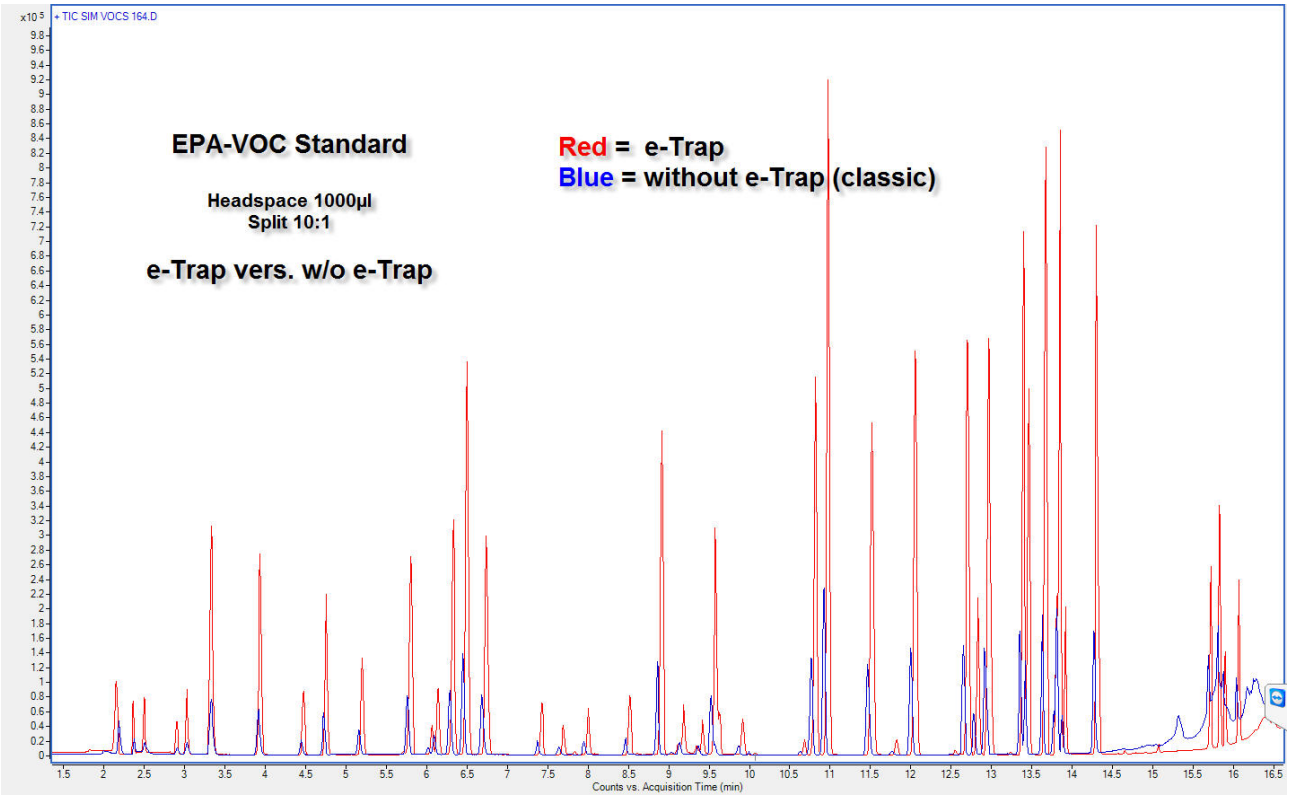
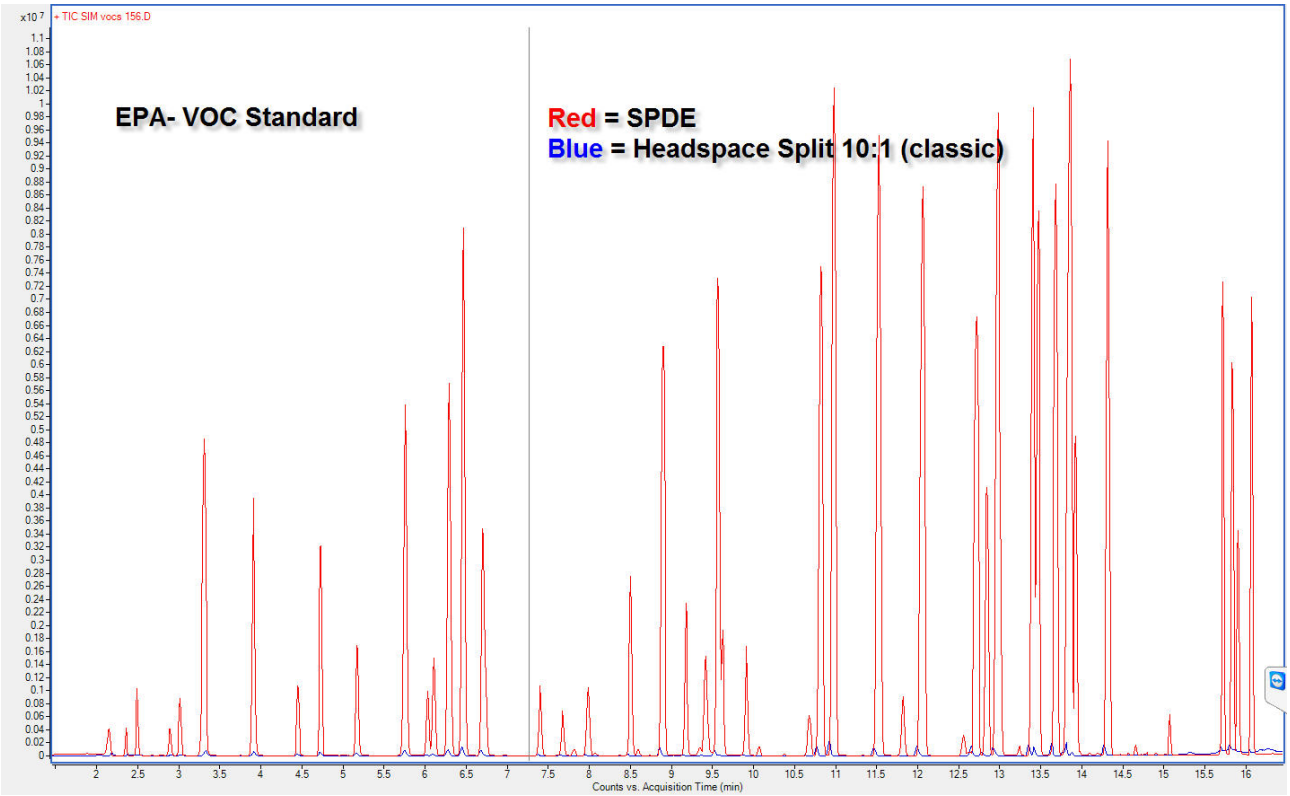


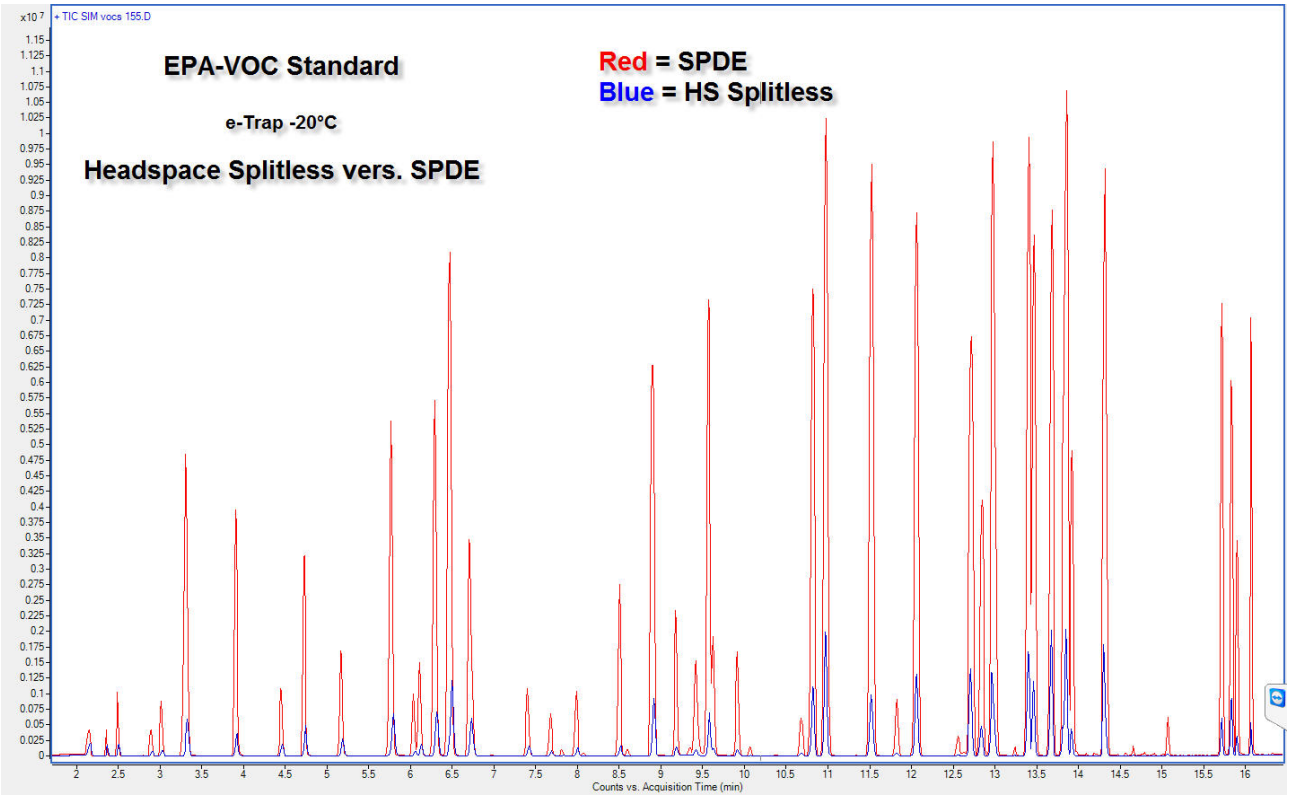
Figure 5: EPA-VOC standard, TIC, 1000µL headspace volume, without eTrap Plus (blue trace), with Chromtech eTrapPlus (red trace)

„SPDE“

Another significant improvement is possible through the use of SPDE (Solid Phase Dynamic Extraction) technology, where the "classic" headspace injection is replaced by a solvent-free microextraction process, in which an enrichment of the analytes takes place on an internally coated syringe cannula. This is followed by thermal desorption in the hot S/SL injector and sample transfer to the analytical GC separation column.
By exchanging the headspace syringe for a Chromtech SPDE syringe, which has a syringe cannula coated inside with a separating film, a true accumulation of the VOC analytes is given. In contrast to static headspace analysis, the SPDE technique is a dynamic extraction method in which an aliquot of the vapor space is always drawn through the syringe cannula by continuous, automatic pumping movement of the syringe plunger.
Similar to the related SPME technique, solution processes of the analytes in the SPDE phase are accompanied by an accumulation of these components.
Due to the fact that the SPDE syringe cannula is made of sturdy stainless steel, it can be used in a further expansion step with the SPDE Extraction Cooler,
a Peltier device, cooling down the syringe cannula down to -20 ° C.
This additional form of immobilization by the low temperature ultimately leads to the extreme improvement of the detection limit for especially the volatile VOC such as vinyl chloride, Dichlorfluorethen, etc.
In the following chromatograms, the influence of both the eTrap Plus in the first stage and subsequently the extraction by means of a SPDE cannula is shown:



Picture 6: EPA-VOC standard, TIC, comparison of "classic" headspace injection, split 1:10 (blue trace) with SPDE injection (red trace)



Picture 7: EPA-VOC standard, TIC, comparison of "classic" headspace injection, splitless (blue trace) with SPDE injection (red trace)

CONCLUSION

These examples clearly demonstrate that by the usage of the Chromtech eTrap Plus, as well as changing from „classic" headspace analysis to the SPDE technique, ideally complemented by the SPDE Extraction Cooler, there is an tremendous increase in sensitivity , especially for the very volatile substances in the context of VOC analysis.
The installation of the eTrap Plus does not require any changes to the existing headspace method, however, the advantage of the significantly increased sensitivity and improvement of the peak shape for the extremely volatile components is immediately available.
By changing from the headspace injection to the SPDE technology and the associated possibility of the cooled SPDE syringe cannula, the range of applications is extended and the sensitivity is further increased.

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