

What is Headspace?

Headspace analysis is a sample preparation technique which can be used to extract volatile organic compounds (VOCs) from both solid and liquid sample matrices. Headspace is an extremely useful technique for analyzing VOCs with minimal sample preparation. Other extraction techniques may be needed for more complex sample matrices in which the EPA offers guidance.

EPA Method 5021A

Method 5021A: "Volatile organic compounds in various sample matrices using equilibrium headspace analysis" gives guidance on the preparation of volatile organic compounds (VOCs) for headspace sampling.¹ This method specifically discusses soil/sediment, solid waste, aqueous and water miscible samples preparation for static headspace sampling to be analyzed by gas chromatography (GC) or gas chromatography-mass spectroscopy (GC-MS).

Matrix modifier

With the sample types described in method 5021A, it is necessary to use a matrix modifier to be able to effectively analyze the sample matrices. The matrix modifier is a water soluble salt solution that is added to your samples which aids in increasing VOCs into the vial headspace prior to analysis.

This is beneficial because it will lead to a better response and reproducibility of the VOCs which would not go into the headspace otherwise from the aqueous phase. It also will decrease discrepancies between samples due to aqueous activity.

To prepare a matrix modifying solution select an appropriate water soluble salt such as sodium chloride and mix 180 g with 500 mL of water until all components dissolved as stated in Method 5021A. This matrix modifying solution should not affect sample pH to where analyte stability should be a concern. By adding the matrix modifying solution to the vial prior to adding the sample and sealing immediately will minimize the loss to VOCs and therefore give a better overview of the sample.

Chemical Preservatives

Some samples may need to be preserved by altering the pH with a chemical preservative such as hydrochloric acid solution, sodium bisulfate or trisodium phosphate. These preservatives should be added before sealing of the sample vial before analysis.

Choosing a chemical preservative will be dependent on the target VOCs and the sample matrix. Altering the sample pH can protect against degradation of certain VOCs such as hydrolysis

of esters. Preparing a chemical preservative for a 40 mL water sample if a basic preservative is required can be conducted by adding 100 mg of trisodium phosphate dodecahydrate. This will raise the pH above 10.

If an acidic preservative is required then add 2-3 drops of 6N hydrochloric acid to a 40 mL water sample. The HCl solution can be prepared by diluting concentrated HCl 1:1. For soil samples which require an acidic preservative, add 1 g sodium bisulfate to the 22 mL headspace vial.

Be aware that if the sample being analyzed contains fuel ethers such as methyl tert-butyl ether (MTBE) and has had sodium bisulfate or hydrochloric acid added as an acidic preservative then the pH of the sample must be adjusted to pH > 10 using trisodium phosphate dodecahydrate before analysis.

Sample Types

EPA method 5021A is directed for use with samples which contain low level of VOCs or aqueous dilutions but also includes guidance for solid samples which contain high concentrations of VOCs or oily materials in which the method for low level VOCs analysis would be unsuitable.

At the time of taking a water sample, a 40 mL volatile organic analyte vial should be filled so no headspace remains. Chemical preservatives can be added at the point of sampling. Before analysis the water sample must be sub-sampled into a headspace vial and any matrix modifying solution, internal standards or surrogates being used must be added.

For low concentration soil samples, 2 g of soil should be collected at point of sampling using a coring tool and added to a crimp seal or screw top glass headspace vial of a known mass. If the sample requires chemical preservation and/ or matrix modifying solution then these should be added at point of sampling before the vial is sealed. Internal standards and surrogates can be added at point of sampling or just before analysis.

For high concentration soil or other solid samples, sample using a coring tool and add to a pre-weighed glass vial and seal. The soil sample can be preserved by adding an extraction solvent such as methanol prior to sealing at point of sampling or at arrival to laboratory. The methanol extract is then diluted with the same matrix used for the calibration standards and analyzed as an aqueous sample. Depending on the scope of the analysis surrogate compounds can be spiked into the solution at point of extraction or into the solution just prior to analysis.

References

1. EPA, <https://www.epa.gov/sites/default/files/2015-12/documents/5021a.pdf>, (date accessed 21 Jul 25).