METROLOGY for
HYDROGEN VEHICLES

REPORT:

A4.3.2: Literature review – state of art of sampling and storage of compounds selected in A4.3.1

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This report was written as part of activity A4.3.2 from the EMPIR Metrology for Hydrogen Vehicles (MetroHyVe) project. The three year European project commenced on 1st June 2017 and focused on providing solutions to four measurement challenges faced by the hydrogen industry (flow metering, quality assurance, quality control and sampling). For more details about this project please visit www.metrohyve.eu.

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Contents

1 - Introduction

Among the characteristics for the fuel specification that are listed in Table 1 of the standard ISO14687-2, three are total species: Total hydrocarbons (Methane basis), Total sulphur compound (H2S basis) and total halogenated compounds (Halogenate ion basis).

Determination of total species is a real analytical challenge from a metrological point of view. A total compounds family cover a large number of species with physical properties (molecular weight, polarity, boiling point…) which vary greatly within the family.

Quantification is mostly based on converting all compounds into one species. Due to large differences in physical properties, it is a real challenge to sample all the compounds of one family into one unique vessel. It then requires the conversion to be efficient for all compounds of the family. Interferences may also lead to biased results.

Moreover, only a few impurities of a total compounds family may actually be present in the hydrogen. Development of speciation methods would allow measuring what the actual impurities are in the real samples of hydrogen which in turn could enable the replacement of the total species characteristics with the actual impurities in the standard 14687-2 [1].

In activity A4.3.1, compounds belonging to the three “total” families (hydrocarbons, sulphur and halogenated) have been selected. These compounds are:

For hydrocarbons: Methane, Ethane, propane, butanes, acetone, methanol, ethanol, octane, decane.

For halogenated compounds: dichloromethane, tetrachloroethylene, tetrachlorohexafluorobutane, dichlorobenzene and eventually if proven possible during the current activity, chloroform.

For sulfur compounds: carbonyl sulphide (COS, if proven possible during the current activity), carbon disulphide (CS2, if proven possible during the current activity), tert-butyl mercaptan, tetrahydrothiophene and methylmercaptan.

In this report, we have reviewed literature discussing the performances of sorbents for trapping these compounds. The focus is on the trapping efficiency at different temperatures, the breakthrough volume and the detection limit (for a specified volume sampled). Three sorbents for each family have then been selected for the other activities of task 4.3 (Efficiency of sorbent tubes).

2 - General considerations about sorbents

Sorbent tubes are tubes made of different materials (glass, stainless steel or inert-coated metal) filled with an adsorbent. The sorbent(s) is/are maintained in the tube with sorbent retainers (or sorbent-retaining gauzes) having precise tolerances to ensure that they correctly fit the front groove of the tube. In some cases, quart wool is also used as retainer and springs are then needed to ensure that the plug of quartz wool remains positioned correctly. Two-piece caps are used to avoid contamination of the sorbent before and after sampling. These caps are made of different materials depending on the storage time.

2.1 Analytes volability/sorbent´s strength

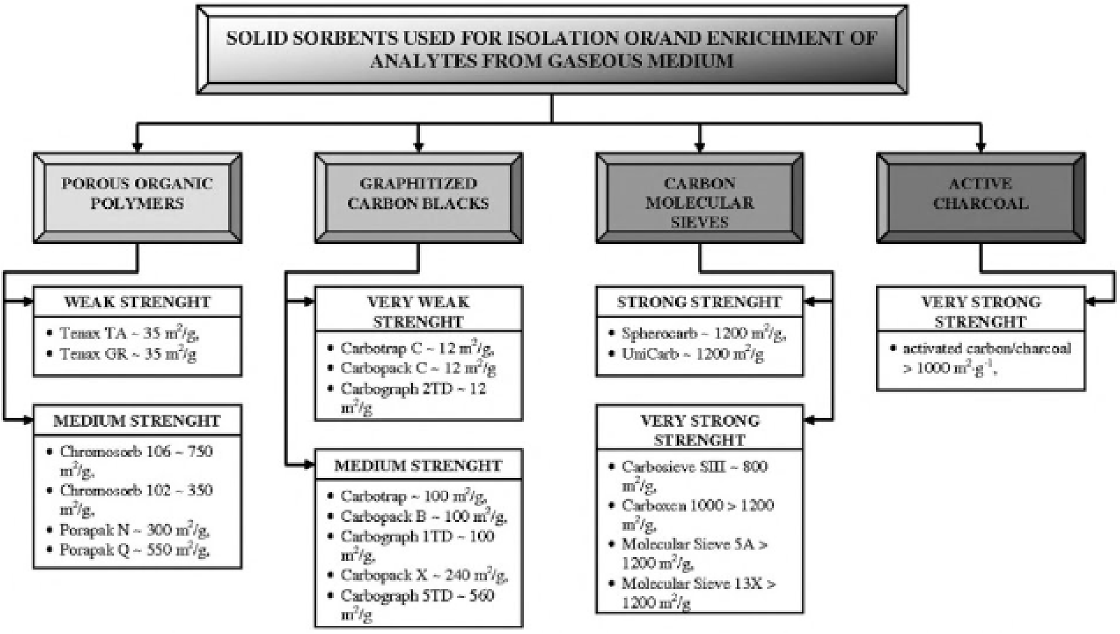
Many different sorbents with different properties exist. Analytes boiling point is the key factor when deciding on which sorbent type to use. Therefore, the sorbents are usually classified according to their strength. The sorbent selected must be sufficiently strong to retain the target analytes during sampling but weak enough to release them efficiently during the thermal desorption phase. Low-volatility analytes adsorb onto the weakest sorbent and high-volatility analytes adsorb onto the strongest sorbent.

A rule-of-thumb [2] when selected sorbent is:

- Use a weak sorbent when working with compounds boiling above 100°C
- Use a medium-strength sorbent for compounds boiling between 30°C and 100°C
- Use a strong sorbent for compounds boiling in the range -48°C to 30°C
- Compounds with boiling points below -48°C are typically too volatile for ambient-temperature sorbent sampling

If the targeted compounds are a mixture of low-volatility analytes and high-volatility analytes, the use of multi-bed sorbent tubes can be a good option. Another alternative is to use a train of different sorbent tubes. The last option offers more flexibility as each sorbent tube can then be desorbed using different temperatures/flow/desorption time. When using multi-bed sorbents and different sorbents in series, the weakest sorbent must always be first when sampling so that the less volatile compounds don´t irreversibly adsorb on the strongest sorbent. While desorption a multi-bed sorbent, the strongest sorbent must always be first. The classification of sorbents is described in the following figure [3].

Figure 1: Classification of sorbents according to their strength



*difference between Carbotrap C and Carbopack C is mainly the size of the sorbent particles (Carpotrap: 20/40 mesh, Carbopack: 40/60, 60/80, 80/100 and 100/120 mesh)

Porapak N: vinylpyrrolidine, Porapak Q: ethylvinylbenzene/divinylbenzene

Chromosorb 102: styrene/divinylbenzene, Chromosorb 106: polystyrene

‘

2.2 Compatibility sorbent/analyte

However, there are other properties than analytes´volability to consider when selecting sorbents, for example, compatibility of analytes and sorbent. Reactive species tend to require more inert sorbents (so graphitised carbon blacks should be avoided) while polar species are more compatible with porous polymer sorbents.

2.3 Sorbent surface area

Surface area provides a general idea of the sorbent strength. Generally, the higher the surface area value, the stringer the sorbent. However, other characteristics such as pore size, pore shape and porosity also play a role in the sorbent´s ability to retain and release different compounds. When the surface area is above 800 m^2/g, the size and shape of the pore becomes more important.

2.4 Desorption/conditioning temperatures

To release the compounds adsorbed, the sorbent is heated at an optimal so called recommended desorption temperature which is different from sorbents to sorbents. The desorption temperature should be kept below the conditioning temperature of the sorbent. Information about desorption flow rate, desorption temperature, conditioning flow rate and conditioning temperature are available for example in Annex D of the ISO standard 16017-1:2000 [4].

2.5 –Volume sampled and Flow rate during sampling

The detection limit obtained when using thermal desorption is proportional to the volume sampled, the larger volume sampled is the lowest is the detection limit. However, for a given analyte, there is a maximum volume that can be sampled before the analyte passes out the back end of the sorbent bed (breakthrough).

For each sorbent there is an optimal range of flow rates but a typical range is between 10 and 250 ml/min. If the flow rate is too fast, the analytes don´t have enough time to interact with the sorbent material and if the flow rate is too slow, there is a risk of back-diffusion

2.6 - Relative humidity

Humidity can be a problem during sampling, water vapor can be retained by the sorbent. In that case, it can mask the available sites of the sorbent and in some cases, can displace the compounds. Sorbents are more or less hydrophobic, Tenax, Carbopack and Carbotrap are very hydrophobic while carbon molecular sieves which are alos classified as hydrophobic retained some water.

This is unlikely to be a problem with hydrogen as it is a dry gas.

2.7 – Tube material

Tubes for thermal desorption can be made of different materials: glass, stainless steel or inert-coated stainless steel. Glass can be more inert, the sorbents can be seen and a glass frit can be used in the inlet, however, tubes can break. Stainless present the advantages that the tubes will not break. To overcome possible problem of inertness, some providers propose inert coated stainless steel tubes (ex Markes) which are recommended for example for reactive sulfur species.

2.8 - Storage

Sampled sorbent tubes shall always be cautiously capped. Capped sampled tubes shall always be stored in as clean atmosphere. As an additional precaution sampled tubes can be wrapped in uncoated aluminium foil during transportation or extended storage.

It is not always necessary to store capped tubes (blanks or sampled) in refrigerated conditions - unless the sampled tubes contain more than one sorbent. In this case, refrigeration is recommended to minimise risk of middle volatility analytes migrating from weaker to stronger sorbents during storage and thus resulting in incomplete recovery during analysis. Refrigerated tubes must also be removed from the freezer/refrigerator and left to equilibrate with the laboratory temperature before the storage caps are removed for analysis. If the tubes are uncapped while they are still cold, humidity from the lab air can condense inside the cold tube causing subsequent analytical difficulties.

3 - Properties of the selected compounds

3.1 - Hydrocarbons including oxygenated organic species

Some of the properties of the compounds selected in A4.3.1 are reported on the following tables:

Table 1: Physical properties of selected hydrocarbons

Name	CAS number	Formula	MW (g/mol)	B.P. (°C)	Recommended sorbent´strength
Methane	74-82-8	CH_4	16.04	-162	-
Ethane	74-84-0	C_2H_6	30.07	-89	-
Propane	74-98-6	C_3H_8	44.10	-42	strong
Butane	106-97-8	C_4H_{10}	58.12	-1 to 1	strong
Isobutane	75-28-5	C_4H_{10}	58.12	-11.7	strong
Octane	111-65-9	C_8H_{18}	114.23	125	weak
Decane	124-18-5	$C_{10}H_{22}$	142.3	174	Weak
Methanol	67-56-1	CH_3OH	32.04	65	medium
Ethanol	64-17-5	C_2H_6O	46.07	78	medium
Acetone	67-64-1	C_3H_6O	58.08	56	medium

3.2 - Halogenated hydrocabons (organohalides)

Table 2: Physical properties of selected halogenated hydrocarbons

Name	CAS number	Formula	MW (g/mol)	B.P. (°C)	Recommended sorbent´strength
Chloroform	67-66-3	$CHCL_3$	119.4	61	Medium
Dichloromethane	75-09-2	CH_2CL_2	84.93	39.6	Medium
Tetrachloroethylene	127-18-4	C_2Cl_4	165.82	121	Weak
1,2-Dichlorobenzene	95-50-1	$C_6H_4Cl_2$	147.01	180	Weak
1,3-Dichlorobenzene	541-73-1	$C_6H_4Cl_2$	147.00	173	Weak
1,4-Dichlorobenzene	106-46-7	$C_6H_4Cl_2$	147.00	173	Weak
Tetrachlorohexafluorobutane	28107-59-7 375-34-8 375-45-1 423-38-1	$C_4Cl_4F_6$ 2,2,3,3 1,2,3,4 1,1,3,4	303.85	135	Weak

3.3 - Sulfur compounds

Table 3: Physical properties of selected sulfur compounds

Name	CAS number	Formula	MW (g/mol)	B.P. (°C)	Recommended sorbent´strength
Carbonyl sulfide	463-58-1	COS	60	-50	strong*
Carbon disulfide	75-15-0	CS2	76.1	46	Medium
methyl mercaptan	74-93-1	CH_4S	48.11	6	Strong
tert-butyl mercaptan	75-66-1	$(CH_3)_3CSH$	90.18	62-65	Medium
Tetrahydrothiophene	110-01-0	C_4H_8S	88.17	119	weak

4 – Literature review of trapping efficiency for the selected compounds

4.1 – Supelco study

Supelco published a technical report entitled “a tool for selected an adsorbent for thermal desorption applications” [5]. In this study, 6 different sampling volumes were tested (0.2, 1, 5, 10, 20 and 200 liter of nitrogen) at a flow rate of 50 ml/min at room temperature. These volumes represent in this case concentrations of analytes of 100, 20, 4, 2, 1 and 0.2 ppb respectively. The targeted compounds were either hydrocarbons or halogenated compounds (no sulfur compounds were studied). In the ISO14687-2 standard, the acceptable limit for total hydrocarbons is 2 ppm. Hereby all the volumes tested in this study are relevant for the total hydrocarbons while 0.2 liter doesn´t allow to reach the acceptable limit stated in ISO14687-2 for halogenated compounds. Results are presented in the tables 4 and 5 with the following colour code:

- Green: safe to use: recovery is greater than 80%
- Yellow: Recovery is between 21 to 79%
- Red: Not recommended, recovery is less than 20%

The adsorbents were desorbed at their maximal desorption temperature.

Table 4: targeted compounds found in Supelco technical report for selecting sorbents

	Carbopack F	Carbopack C	Carbopack Y	Carpopack B	Carbopack X	Carboxen-563	Carboxen-564	Carboxen-569	Carboxen-1000	Carboxen-1001	Carboxen-1002	Carboxen-1003	Carboxen-1016	Carboxen-1018	Carbosieve S-III	Tenax TA	Tenax GR	Chromosorb 106	Porapak N	Hayesep D
Dichloromethane	🟥	🟥	🟥	🟥	🟩 a	🟩 a	🟩	🟩	🟩	🟩	🟩 a	🟩 a	🟩 d	🟩	🟩 a	🟩 e	🟩 e	🟩 e	🟩 d	🟩 d
Chloroform	🟥	🟥	🟥	🟩 a	🟨	🟩 a	🟩 c	🟩	🟩	🟩	🟩	🟩 a	🟩 a	🟩	🟨	🟩 d	🟩 d	🟩 d	🟩 c	🟩 c
Tetrachloroethylene	🟥	🟥	🟩 a	🟩	🟩	🟨 I	🟨	🟨	🟨 I	🟩 c	🟨	🟨	🟩	🟨	🟥	🟩 a	🟩 a	🟩 d	🟩 a	🟩
Dichlorobenzenes	🟩 b	🟩 a	🟩	🟩	🟩 c*	🟨 I	🟨 c	🟥	🟥 I	🟥 I	🟥 I	🟥 I	🟩 a	🟥 I	🟥 I	🟩	🟩	🟩 f	🟩	🟩

a: up to 20 liter, b: up to 10 liter, c: up to 5 liter, d: up to 1 liter, e: up to 0.2 liter, f: from 20 liter or more, I: potentially irreversibly adsorbed

*not for 1,4-dichlorobenzene (yellow)

Table 5: Compounds studied in Supelco technical report that have chemical formulas and relatively close boiling point interval compared to targeted compounds not studied in this report

		Carbopack F	Carbopack C	Carbopack Y	Carpopack B	Carbopack X	Carboxen-563	Carboxen-564	Carboxen-569	Carboxen-1000	Carboxen-1001	Carboxen-1002	Carboxen-1003	Carboxen-1016	Carboxen-1018	Carbosieve S-III	Tenax TA	Tenax GR	Chromosorb 1006	Porapak N	Hayesep D
Butadiene (BP = -5°C)	Butane (BP = -1 to 1°C)	🟥	🟥	🟥	🟩 e	🟩 a	🟥	🟥	🟨	🟨	🟨	🟨	🟨	🟩 c	🟨	🟥	🟥	🟥	🟥	🟥	🟩 e
Trimethylbenzene (BP = 166°C)	Decane (BP = 174°C)	🟩 b	🟩 a	🟩	🟩	🟨	🟨	🟨 c	🟥	🟥 I	🟨 d-I	🟥 I	🟥 I	🟩 c	🟥	🟥	🟩	🟩	🟩 f	🟩	🟩

a: up to 20 liter, b: up to 10 liter, c: up to 5 liter, d: up to 1 liter, e: up to 0.2 liter, f: from 20 liter or more, , I: potentially irreversibly adsorbed

4.2 Sisweb

Scientific Instrument Services inc. (SIS) provides exhaustive information about thermal desorption on their website [6], inclusive an adsorbent resins guide and so called breakthrough volume data by resin for a large number of compounds.

The term breakthrough volume is defined as the volume of carrier gas that will purge an analyte through one gram of sorbent in a desorption tube at a specific temperature. In other words, this is the volume of carrier gas per gram sorbent which causes the analytes to migrate from the front to the back of the sorbent bed. To assure that no analyte is lost during the sample collection process, an acceptable sampled volume is typically the breakthrough volume divided by 2. Moreover, sorbent tubes are usually packed with less than one gram sorbent (typically 200-300 mg), so we can assume that reliable sampling volumes can be obtained by dividing the breakthrough volume by totally 10.

Breakthrough volumes of more than 10 liters/gram of sorbent are considered to be the generally usable ranges of the trapping of the analytes. This corresponds to 1 liter or more for the sampling volume. For most of the compounds, the detection limit reachable (data from RISE using a TD/GC/FID) when sampling 1 liter of gas is about 5 ppb/compound which is an acceptable limit for hydrocarbons and for halogenated but not for sulfur compounds. Breakthrough volumes of less than 10 l/g of sorbent would generally not be acceptable temperatures for the efficient trapping of analytes unless the gas volume samples were kept small (which is acceptable for hydrocarbons up down to at least breakthrough volumes of 1 l/g sorbent).

Release (during analysis)

To assure that no analytes remain trapped during the desorption/release, an acceptable volume of carrier gas used during desorption could be the breakthrough volume multiplied by 10. The release of the compounds from the tube is usually performed at flow rate around 30-60 ml/min during a 5-7 minutes period (totally 0.15 to 0.4 l of gas). Breakthrough volumes below 0.01 l/g sorbent are usually acceptable temperatures for the efficient release of analytes. Breakthrough volumes well above this limit imply that an excessive volume of gas is needed to efficiently release the analytes from the sorbent.

The breakthrough volumes for 5 different sorbents are presented on tables 6, 7, 8, 9 and 10. The following colour codes are used:

Red: BV < 0.01 (for release)

Green: BV > 10 (for trapping)

Blue 1 < BV < 10 (for trapping, low volumes)

Table 6: Breakthrough volumes on Tenax TA

	0	20	40	60	80	100	120	140	160	180	200	220	240	220	240	260	280	300
methane		🟥	🟥	🟥														
Ethane			🟥	🟥	🟥	🟥												
Propane					🟥	🟥	🟥	🟥										

Butane	🟦						🟥	🟥	🟥	🟥								
Octane	🟩	🟩	🟩	🟩	🟦						🟥	🟥	🟥					
Decane	🟩	🟩	🟩	🟩	🟩	🟦	🟦					🟥	🟥	🟥	🟥			
Methanol	🟦						🟥	🟥	🟥	🟥								
Ethanol	🟦	🟦						🟥	🟥	🟥	🟥							
Acetone	🟩	🟦	🟦					🟥	🟥	🟥	🟥							
Dichloromethane	🟩	🟦	🟦						🟥	🟥	🟥							
Chloroform	🟩	🟩	🟦	🟦						🟥	🟥	🟥	🟥					
Tetrachloroethylene	🟩	🟩	🟩	🟩							🟥	🟥	🟥	🟥				
Dichlorobenzene	🟩	🟩	🟩	🟩	🟩	🟦	🟦						🟥	🟥	🟥	🟥		

Table 7: Breakthrough volumes on Tenax GR

	0	20	40	60	80	100	120	140	160	180	200	220	240	220	240	260	280	300
methane	🟥	🟥	🟥	🟥														
Ethane			🟥	🟥	🟥	🟥												
Propane					🟥	🟥	🟥	🟥										
Butane	🟦					🟥	🟥	🟥	🟥									
Octane	🟩	🟩	🟩	🟦	🟦					🟥	🟥	🟥						
Decane	🟩	🟩	🟩	🟩	🟩	🟦	🟦					🟥	🟥	🟥				
Methanol						🟥	🟥	🟥	🟥	🟥								
Ethanol	🟦						🟥	🟥	🟥	🟥	🟥							
Acetone	🟩	🟦	🟦					🟥	🟥	🟥	🟥							
Dichloromethane	🟦	🟦						🟥	🟥	🟥	🟥							
Chloroform	🟩	🟩	🟦	🟦						🟥	🟥	🟥	🟥					
Tetrachloroethylene	🟩	🟩	🟩	🟦	🟦						🟥	🟥	🟥	🟥				
Dichlorobenzene	🟩	🟩	🟩	🟩	🟩	🟦	🟦						🟥	🟥	🟥	🟥		

Table 8: Breakthrough volumes on Carbotrap (kolla om C)

	0	20	40	60	80	100	120	140	160	180	200	220	240	220	240	260	280	300
methane	🟥	🟥	🟥	🟥	🟥													
Ethane	🟥	🟥	🟥	🟥	🟥	🟥												
Propane	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥										
Butane					🟥	🟥	🟥											
Octane	🟩	🟩	🟩	🟦	🟦					🟥	🟥	🟥						
Decane	🟩	🟩	🟩	🟩	🟩	🟦	🟦					🟥	🟥	🟥				
Methanol						🟥	🟥	🟥	🟥	🟥								
Ethanol	🟦							🟥	🟥	🟥	🟥							
Acetone	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Dichloromethane							🟥	🟥	🟥	🟥	🟥							
Chloroform	🟦	🟦							🟥	🟥	🟥	🟥	🟥					
Tetrachloroethylene	🟩	🟩	🟩	🟦	🟦	🟦										🟥	🟥	🟥
Dichlorobenzene	🟩	🟩	🟩	🟩	🟩	🟦	🟦	🟦	🟦							🟥	🟥	🟥

Table 9: Breakthrough volumes on Carboxen 569

	0	20	40	60	80	100	120	140	160	180	200	220	240	220	240	260	280	300
methane						🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥

Ethane											🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥
Propane	🟦	🟦	🟦										🟥	🟥	🟥	🟥	🟥	🟥
Butane	🟩	🟩	🟩	🟦	🟦	🟦									🟥	🟥	🟥	🟥
Octane	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟦	🟦	🟦	🟦	🟦	🟦	🟦				
Decane	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Methanol	🟦	🟦															🟥	🟥
Ethanol	🟦	🟦	🟦	🟦														🟥
Acetone	🟩	🟦	🟦	🟦	🟦												🟥	🟥
Dichloromethane	🟩	🟩	🟩	🟩	🟦	🟦	🟦											🟥 320
Chloroform	🟩	🟩	🟩	🟩	🟩	🟩	🟦	🟦	🟦									🟥 340
Tetrachloroethylene	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Dichlorobenzene	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Table 10: Breakthrough volumes on Carbosieve SIII

	0	20	40	60	80	100	120	140	160	180	200	220	240	220	240	260	280	300
methane							🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥
Ethane	🟦 0.8											🟥	🟥	🟥	🟥	🟥	🟥	🟥
Propane	🟩	🟦	🟦	🟦	🟦	🟦												🟥 320
Butane	🟩	🟩	🟩	🟩	🟩	🟩												>320
Octane	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Decane	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Methanol	🟩	🟦	🟦	🟦	🟦											🟥	🟥	🟥
Ethanol	🟩	🟩	🟩	🟩	🟦	🟦	🟦	🟦										🟥 340

4.3 Studies for sulfur compounds

Recently a review [7] was performed regarding the sampling of gaseous sulfur containing compounds. Among the articles reviewed, there is a series of articles [8,9,10], Devai et al. who tested 14 different sorbents for the trapping of H2S, COS and MM (methyl mercaptan) respectively. The sulfur containing gas (here are only reported results regarding dry gas, N2 and air) was either injected through a tube or directly into the desorption apparatus. The immediate recovery was determined by comparing the two results. The results for the multi-bed sorbents show that only one of the sorbent was actually trapping the targeted compounds. Stability tests (36 hours) performed for MM on silica gel and Molecular Sieves show no loss during the storage period.

The results are presented in the Table 11.

Table 11: Recovery on 14 sorbents for H2S, COS, MM

Sorbents	Composition[a]	Recovery (%) H2S*	Recovery (%) COS**	Recovery (%) MM***
Silica Gel	-	🟦 80	🟩 >90	🟩 >90
Silica gel + Molecular sieves	-	🟦 80	🟩 >90	🟩 >90
Molecular sieves	-	🟨 40	🟦 75	🟦 86
Molecular sieves + silica gel	-	🟨 40	🟦 70	🟦 83
Carbosieve SIII	-	🟥 <10	🟦 70	🟥 15
Tenax TA	-	🟥 <1	🟥 <1	🟦 75
Molecular sieves + Tenax TA	-	🟨 40	🟦 70	🟦 80
Carbotrap 100	Carpotrap B	🟥 <1	🟥 <1	🟥 <10

Carbotrap 150	Glass beads/Carbotrap C	<1	<1	<10
Carbotrap 200	Glass beads/Carbotrap B/Carbosieve SIII	<10	65	<20
Carbotrap 300	Carbotrap C/carbotrap B/ Carbosieve SIII	<10	55	<20
Carbotrap 301	Carbopack C, Carbopack B, Carboxen 1000	<10	>90	<20
Carboxen 569	-	[b]	[b]	[b]
Carbotrap 400	Carbotrap F, Carbotrap C, Carbotrap B, Carboxen 1000	[b]	[b]	[b]

*40-50 ppm but diluted with air, 0.4 ml onto the tubes, 3 replicates, desorption: 310°C@2min, 20 ml/min

** 9.9 ng S but diluted with air, 3 replicates, desorption: 310°C@2min, 20 ml/min

***6.6 ng S, 3-5 replicates, desorption: 310°C@2min, 20 ml/min

[a] mesh of sorbents and 100% of each sorbent for multi-bed tubes are specified in the articles

[b] large artefacts of SO2 already when analysing blank tubes

Red < 39% recovery, yellow: 40% < recovery < 69%, blue: 70% < recovery < 89%, green > 90% recovery

Lestremau et al. [11] show that methyl mercaptan (in an air matrice) is partially converted to dimethyl sulfide on Tenax TA and on molecular sieve 5A.

Some good recovery (98-99%) was obtained by Mochalski et al. [12] when using a dual bed tube containing Tenax TA and Carboxen 1000 for a mixture of methyl mercaptan, ethyl mercaptan, dimetyl sulfide, carbonyl sulfide and carbon disulfide. However, it required an immediate analysis of the tubes otherwise significant losses were observed after a short period of storage (24 hours).

Tangeman [13]developed a method for trapping compounds as H2S, COS, CS2, thiols, sulphides and disulphides at ppt levels in air using Tenax TA at -196°C (glass tubes). At this temperature, the breakthrough volume is largely above 40 l/ 200 mg sorbent. The compounds are subsequently desorbed from the tube at 200C and directly injected into the GC system.

5 – Discussions and selection of sorbents

5.1 – Hydrocarbons, ketones and alcohols

Methane and ethane is notoriously difficult to trap on sorbents without sub-ambient temperatures (<-5, -20> ˚C) and very strong sorbents like carbon molecular sieves (CMS), like Carbosieve SIII (Table 10). This is not accomplishable in laboratory or in field unless it is a preconcentration unit on a gas chromatograph [14][15]. With sorbent strength come complications of injection of higher boiling point species, like propane and butane. But a weaker sorbent like Carboxen 569 (Table 9) and even lower temperatures <-20, -80>˚C can trap both lower and medium boiling point hydrocarbons (nC_1-nC_4) on a preconcentration unit [17]. Also Carboxen 1016 has proven efficient since it is similar to Carboxen 569, but is not releasing SO_2 during heating (Table 11), which makes it a good candidate to trap sulfur compounds together with silica gel in future work.

For trapping nC1-nC4, acetone, methanol and ethanol it is encouraging to try the following sorbents in combination or alone on a preconcentrator with ability to manipulate temperature under ambient temperature. Any SO_2 release will be noted down as for other compounds on blank injects.

- Carboxen 569
- Carboxen 1016
- Carbosieve S-III

For the higher boiling point hydrocarbons like decane and octane, Tenax TA is recommended (Table 6) [18]. It might be possible to trap acetone, methanol, ethanol and perhaps butanes by include a second stronger adsorbent, like Carbopack B (Table 4).

5.2 – Halogenated compounds

The trapping of compounds selected in this study according to table 2 of this report would require a medium (for chloroform and dichloromethane) and a weak sorbent (for tetrachloroethylene and dichlorobenzene). However the literature study shows that even strong sorbents and weak sorbents can efficiently trapped chloroform and dichloromethane. For weak sorbents, it is then required to use small sampling volumes in order to avoid loss of the more volatile compounds by breakthrough. Using only strong sorbents will imply irreversible adsorption of tetrachloroethylene and dichlorobenzene) and then require the use of another sorbent for these compounds placed before the strong sorbents during sampling.

Taking into account the information gathered in this report, the following sorbents have been selected:

Tenax TA is probably the most popular sorbent used in thermal desorption. It presents the advantages to be a low bleeding material and exhibits a low level of impurities. As methanol is not retained, spiking this sorbent with liquid standard is a reliable option for calibration. Precautions to be taken: low volume to avoid breakthrough of low volatile compounds, possibly low temperature during sampling.

Multi-bed sorbents: Tenax TA (weak), Carboxen 1003 (medium), Carbograph 1 (strong): this combination of sorbents in one tube is expected to provide an optimal combination to trap a large range of volatilities. Tenax TA has been shown in the literature study to efficiently trap dichlorobenzenes and tetrachloroethylene while Carboxen has been shown to efficiently trap chloroform and dkíchloromethane (Table 4).

Train of 2 sorbents (medium/weak): Chromosorb + Tenax TA: using two sorbents in series allows in some aspects, more flexibility. Larger volumes can be sampled (as there is more sorbent in one tube than in a multi-bed tube, the breakthrough volume being dependent upon the weight of the sorbent). Different desorption temperatures/flow/time can be applied for each tube.

5.3 – Sulfur compounds

6 – References

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