Hydrogen Purity Analysis: Suitability of Sorbent Tubes for Trapping Hydrocarbons, Halogenated Hydrocarbons and Sulphur Compounds

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Abstract: The ISO 14687-2 standard sets requirements for the purity of the hydrogen that is delivered at refuelling stations. These specifications cover a wide range of impurities and include challenging measurements, mainly due to the very low levels of the required detection limits and the need for “total” measurements (total hydrocarbons, total sulphur compounds, halogenated compounds). Most of the compounds belonging to the species are organic. Thermal desorption often coupled with gas chromatography is a common speciation method used to determine the content of organic impurities. However, no existing sorbent tubes are sufficiently universal to trap all possible impurities; depending on the sorbents and the sampling volume, some compounds may irreversibly adsorb or may break through. It is therefore necessary to evaluate sorbents for the compounds targeted at the level required. In this study, the suitability of sorbent tubes for trapping organic impurities in hydrogen was investigated. Suitable sorbents were selected based on a literature review of suitable sorbent materials. Short-term stability studies for compounds among hydrocarbons, halogenated compounds and sulphur compounds on the selected sorbents have then been performed for storage periods of two weeks since this is the period typically required to complete the collection, transport and analysis of hydrogen samples. The study clearly shows that the method is promising for total species, even through the results show that not all of the compounds belonging to the three total species to be analysed when performing hydrogen purity analysis can be quantified on one unique sorbent. A multibed sorbent consisting of Tenax TA (weak), Carboxen 1003 (medium), Carbograph 1 (strong) is shown to be a versatile sorbent suitable for the three “total species”; only a few compounds from each family would need to be analysed using other analytical methods. This method proposed here for total species will not only provide a sum of concentrations, but also an identification of which compound(s) is/are actually present in the hydrogen.

Keywords: hydrogen; fuel cells; hydrogen vehicle; sorbent; thermal desorption; hydrogen quality

1. Introduction

Hydrogen vehicles are currently commercially available from, or in development by, many manufacturers [1]. With regards to performance, fuelling time and range, these vehicles are nowadays comparable to conventional engines and have one major advantage: they only produce water in the exhaust. The implementation of these vehicles into the consumer market is necessary to help Europe meet the challenging targets for lowering carbon dioxide levels. However, the implementation of these vehicles requires the development of a sizable hydrogen fuelling infrastructure.
There are several methods currently used to produce hydrogen for use at fuelling stations. These methods include the electrolysis of water, the steam methane reforming (of natural gas or biogas) and the chloralkali process. Depending on the methods, different impurities that may be present in the final product have negative and sometimes irreversible effects on the vehicle’s fuel cell. Therefore, the industry has developed specifications to ensure that these impurities will not impair the operations; the ISO 14687-2:2012 [2] standard (currently under revision) and EN 17124:2018 [3]. These standards set requirements for purity of hydrogen provided by the refuelling stations; no laboratory can however currently perform all of these measurements under accreditation. The specifications in these standards cover a wide range of impurities (13 gaseous species and particles) and include challenging measurements, mainly due to the very low levels of the required detection limits and the need for “total” measurements (total hydrocarbons, total sulphur compounds, halogenated compounds). Furthermore, erroneous results can arise from the use of an inappropriate sampling method or from choosing the wrong sampling container. Currently, the methods used for sampling hydrogen gas and particulates from a refuelling station have not been verified to ensure that the sample is representative of the hydrogen at the station. Additionally, the sampling containers used for transporting the gas and particulate samples to the analytical laboratories must be tested to ensure that the sample remains stable during transport. For example, if impurities were to absorb onto the surfaces of the sampling vessels, a “dirty” hydrogen could appear to be sufficiently pure during quality assurance checks.

A total compounds family usually covers a large number of species having rather different physical properties and the identification of all species is almost impossible in routine analysis. Quantification is mainly done after conversion of the compounds into one species. Interferences or compounds that cannot be converted efficiently may lead to biased results. However, only a few impurities per family may actually be present in the hydrogen. Defining the compounds that are the most likely to be present must be done by a speciation method. As most of the compounds belonging to the species are organic, sorbent tubes could be used to sample hydrogen. By using the right sorbent and the adequate sampling volume, organic impurities belonging to hydrocarbons, halogenated compounds and sulphur compounds will be trapped and retained on the sorbent while the hydrogen will pass through. This will lead to an enrichment of the targeted compounds enabling challenging detection limits to be attained.

Recently, a review [4] of publicly available purity analyses of real samples of hydrogen was performed as part of the EMPIR project (European Metrology Programme for Innovation and Research), “MetroHyVe” [5]. Totally, 32 hydrogen purity reports [6–8] from more than 20 different stations were reviewed, focusing on “total” species. For hydrocarbons, methane, ethane, acetone were the most common impurities in the hydrogen (present in more than 10 samples). Ethanol, isopropyl alcohol and propane were also found in several samples (in more than 5 samples). Finally, heptane, cyclohexane, n-butane, isobutane, octane and decene were found in a few samples (between 1 to 5 samples). Very few halogenated compounds have so far been found in hydrogen samples. Only dichloromethane, tetrachloroethylene and tetrachlorohexafluorobutane have been reported so far. The most commonly identified sulphur compounds in hydrogen samples were hydrogen sulphide (H₂S), carbonyl sulphide (COS) and carbon disulphide (CS₂) whereas tert-butyl mercaptan (T-BM) and tetrahydrothiophene (THT) have been found in one sample.

Most of these compounds are organic. Different containers can be used for collecting gas samples. These include gas cylinders (of different materials, with or without internal passivation), sampling bags (of different materials), canisters [9], adsorbent tubes and impingers.

There are two principal ways to sample: sampling with or without enrichment. Sampling without enrichment can be performed in cylinders, canisters or bags. For sampling with enrichment, the compounds to be determined are either adsorbed onto a solid collection phase (using adsorbent tubes), or absorbed in a solution (using impingers). Due to the stringent thresholds to reach for hydrogen purity testing, methods allowing enrichment can be a good alternative.
Thermal desorption often coupled with gas chromatography is a common separation method that can be used for speciation used to determine the content of organic impurities. The analytical method has the advantage that it indirectly lowers the detection limits by a considerable factor. By means of pumped sampling, according to ISO 16017:2000 [10], organic impurities are trapped onto the sorbent, whereas the hydrogen matrix passes through without being retained. The analytes’ boiling point is the key factor when deciding which sorbent type to use. The amount preconcentrated onto the sorbent can be calculated by measuring the gas flow rate and sampling time during sampling on the sorbent tube.

However, no existing sorbent tubes are sufficiently universal as to trap all possible impurities, and therefore a selection process is required. In this study, the selection process was based on a literature review of the state-of-the-art regarding the suitability of different sorbents for the targeted compounds.

The suitability of sorbents for a given compound or group of compounds is often assessed by measuring the recovery yield and the storage stability for a given compound. The recovery yield is defined as the ratio of the measured and the spiked content and expressed as a percentage. In order to assess the fit for purpose of the analytical method for hydrogen purity testing, ISO 21087:2017 [11] states that, “the bias shall be small enough to have a relative combined standard uncertainty below 10% of the concentration”. If precision and trueness are considered to equally contribute to the uncertainty, a bias of up to around 7% will be acceptable. In the case of a total family, the overall bias includes the contribution of many compounds. To evaluate the different sorbents, the following criteria were then adopted: recoveries above 90% were considered as very good; recoveries between 85 to 90% were considered as good; recoveries from 50 to 84% were considered as low and finally, for recoveries below 50%, the sorbent material was considered as not suitable for the targeted compound.

The storage stability is defined as the change in content for a given compound as determined at the end of the storage time compared to that at the start of the stability test. In this paper, the results from short-term stability studies in different sorbents are presented for hydrocarbons (including oxygenated hydrocarbons), halogenated hydrocarbons and sulphur compounds. Storage periods of two weeks were evaluated since this is the period typically required to complete the collection, transport and analysis of hydrogen samples. To evaluate the different sorbents, the following criteria were selected: the storage stability was considered as very stable in the cases where the D14 concentration was found to be less (or more) than 10% lower than the initial concentration (D0); the storage stability was considered to be relatively stable in the cases where D14 (or D10 in some tests) was found to be less than 25% lower than the D0 concentration; the storage stability was considered as not stable in the cases where the D14 concentration (or D10 in some tests) was found to be more than 26% lower than the initial concentration.

2. Methods

2.1. Selection of Targeted Compounds

The choice of these compounds was mainly based on the outcome of the review of hydrogen purity reports [5] mentioned above. However, some compounds were added to cover a wide range of boiling points for each family.

For hydrocarbons: methane, ethane, propane, butane, isobutane, pentane, isopentane, acetone, methanol, ethanol, heptane, decane.

For halogenated compounds: dichloromethane, tetrachloroethylene, tetrachlorohexafluorobutane, dichlorobenzene and chloroform. Even chloromethane, vinyl chloride, ethane, 1,1,2-trichloro-1,2,2-trifluoro, 1,2-dichloroethylene, trichloroethylene, 1,2-dichloropropane, 1,1,2-trichloroethane were included in the study.

For sulphur compounds: hydrogen sulphide (H₂S), carbonyl sulphide (COS), carbon disulphide (CS₂), tert-butyl mercaptan (T-BM), tetrahydrothiophene (THT) and methyl mercaptan.
2.2. Selection of Sorbents

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.

Methane and ethane can only be trapped at very low temperatures (\(< -20 ^\circ C\)) on very strong sorbents; for example, carbon molecular sieves such as Carbosieve SIII. This cannot be done easily in the field \([12,13]\). Using sorbent with high strength may result in the irreversible adsorption of higher boiling point species. However, a weaker sorbent like Carboxen 569, and even lower temperatures (down to \(-80 ^\circ C\)), has been shown to trap both low- and medium-boiling-point hydrocarbons (nC\(_1\)-nC\(_4\)) \([14]\). Very volatile organic compounds between C\(_3\) to C\(_6\) of different volatility have been successfully detected using Carbograph STD (20/40 mesh) \([15]\). Carboxen 1016 has also been proven to be efficient since it is similar to Carboxen 569, but is not releasing sulphur dioxide (SO\(_2\)) during heating, which makes it a good candidate to trap low boiling point compounds. For the higher boiling point hydrocarbons such as decane and octane, Tenax TA is the most commonly used sorbent \([16]\). For the tests performed in this study regarding linear alkanes with 1 to 4 hydrocarbons, acetone, methanol and ethanol the following sorbents were selected; Tenax TA (Perkin Elmer, U.K.), 200 mg; a multibed sorbent consisting of Tenax TA (weak), Carboxen 1003 (medium), Carbograph 1 (strong) (Markes International Ltd., Llantrisant, UK) totally 200 mg, 1/3 of each sorbent material and two sorbents in series (medium/weak): Chromosorb 106 (Markes International Ltd., Llantrisant, UK + Tenax TA (Perkin Elmer, Llantrisant, UK) each containing 200 mg.

The trapping of the halogenated compounds selected in this study would require a medium sorbent (for chloroform and dichloromethane) and a weak sorbent (for tetrachloroethylene and dichlorobenzene). However, studies \([17,18]\) show that even strong sorbents and weak sorbents can efficiently trap chloroform and dichloromethane. For weak sorbents, small sampling volumes must be selected in order to avoid the loss of the more volatile compounds by breakthrough. If only strong sorbents are used, the risk that tetrachloroethylene and dichlorobenzene will be irreversibly adsorbed is high. In order to avoid this risk altogether, it is necessary to trap these compounds on a weaker sorbent first. Therefore, the same adsorbent materials than those selected for hydrocarbons were chosen for halogenated compounds. Tenax TA is probably the most popular sorbent used in thermal desorption. It presents the advantages to be a low bleeding material, exhibits a low level of impurities and is hydrophobic. Because methanol is only slightly retained, spiking Tenax TA with a liquid standard in methanol is a reliable option for calibration. A low volume should be sampled to avoid breakthrough of low volatile compounds. The multibed sorbent is expected to provide the optimal combination for trapping a large range of volatilities. Tenax TA was shown in the literature study to efficiently trap dichlorobenzenes and tetrachloroethylene while Carboxen has been shown to trap chloroform and dichloromethane efficiently. Finally, the train of two sorbents (medium/weak) 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) and if necessary, different desorption temperatures, desorption flows and desorption times can be used for each tube.

COS and CS\(_2\) are notoriously difficult to trap and require the trapping to be performed at low temperatures (at least \(-5 ^\circ C\)) on very strong sorbents for example carbon molecular sieves, such as Carbosieve SIII \([19–22]\). Some promising results have been obtained using Carbotrap 301 for COS. Tenax TA together with Carboxen 1000 has been shown \([23]\) to be a possible alternative for trapping methyl mercaptan, ethyl mercaptan, dimethyl sulphide, COS and CS\(_2\).

The following sorbents were selected for sulphur compounds: (1) A double bed sorbent of Tenax/SulfiCarb (Markes International Ltd., Llantrisant), 50/50 w/w. SulfiCarb exhibits a greater retention volume for volatile species. However, there is a risk that compounds with higher boiling points could be irreversibly adsorbed onto this sorbent; (2) Carboxen 1003 (Markes International Ltd.) is another carbonized molecular sieve, this sorbent performs slightly better than Carbosieve SIII in
situations where water or humidity may be present in the sample; (3) the third sorbent material used is
Tenax TA (Markes International Ltd.). All sorbent tubes used for the short-term stability test of sulphur
compounds were treated with a SilcoTek® inert coating and packed with 200 mg sorbent each.

All tubes used in the study were conditioned prior spiking at the temperatures recommended for
each sorbent materials. Sampling was in all cases performed at room temperature. If lower sampling
temperature can practically be applied, the trapping can be improved.

2.3. Chemicals and Gas Mixtures

For the hydrocarbons and the halogenated hydrocarbons, the short-term stability tests were
carried out at RISE at concentrations between the “threshold in ISO 14687-2” times 2 and times 10 over
a period of 2 weeks. For the sulphur compounds, the short-term stability tests were carried out at
The Dutch Metrology Institute, VSL at concentrations 35 and 120 times higher than the challenging
threshold of 0.004 µmol/mol in order to ensure that the compounds would be detectable with the
analysis method used in this study.

2.3.1. Hydrocarbons

To a reference gas mixture containing hydrocarbons with 1 to 5 carbon atoms each at approximately
100 µmol/mol was added ethanol, acetone, methanol, heptane and decane (1 to 3 µL of each pure
substance). This gas mixture was then diluted 111 times in hydrogen to obtain a gas mixture containing
all the targeted compounds at a mole fraction of approximately 1 µmol/mol. The composition of the
end gas mixture is given in Table 1. The sum of hydrocarbons in the mixture is then 6.5 µmol/mol,
about 3 times the threshold in ISO 14687-2 [2], which is 2 µmol/mol for total hydrocarbons in hydrogen.

Table 1. Gas mixture used for the short-term stability tests on sorbents.

| Components   | Mole Fraction (µmol/mol) | Expanded Uncertainty (k = 2) (µmol/mol) |
|--------------|--------------------------|----------------------------------------|
| Methane      | 0.942                    | 0.019                                  |
| Ethane       | 0.899                    | 0.018                                  |
| Propane      | 0.688                    | 0.014                                  |
| Isobutane    | 0.855                    | 0.017                                  |
| Butane       | 0.915                    | 0.018                                  |
| Isopentane   | 0.913                    | 0.027                                  |
| Pentane      | 0.845                    | 0.025                                  |
| Acetone      | 0.169                    | 0.0051                                 |
| Ethanol      | 0.117                    | 0.0035                                 |
| Methanol     | 0.117                    | 0.0035                                 |
| Heptane      | 0.044                    | 0.0013                                 |
| Decane       | 0.031                    | 0.0009                                 |

A volume of 100 mL of this gas mixture has been transferred onto the sorbent tubes on the starting day (D0). All the
tubes were then stored in the fridge (+4 °C) prior to analysis.

2.3.2. Halogenated Hydrocarbons

The composition of the gas mixture used for the halogenated hydrocarbons is given in Table 2.
The gas mixture was then diluted 100 times in hydrogen to obtain a gas mixture containing all
the targeted compounds at mole fraction of approximately 50 nmol/mol. The composition of the final
gas mixture is also given in Table 2. The sum of halogenated hydrocarbons in the mixture is then 0.57
µmol/mol; i.e., approximately 10 times the threshold in ISO 14687-2 [2], which is 0.05 µmol/mol for
total halogenated hydrocarbons in hydrogen.
Table 2. Composition of the gas mixture used for halogenated hydrocarbons.

| Components                                      | Mole Fraction before Dilution (nmol/mol) | Mole Fraction after Dilution (nmol/mol) | Expanded Uncertainty (nmol/mol) (k = 2) |
|-------------------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|
| Chloromethane                                   | 5130                                    | 51.30                                   | 3.08                                    |
| Vinyl chloride                                  | 5009                                    | 50.09                                   | 3.51                                    |
| Ethane, 1,1,2-trichloro-1,2,2-trifluoro          | 4768                                    | 47.68                                   | 2.86                                    |
| Dichloromethane                                 | 5005                                    | 50.05                                   | 3.00                                    |
| 12-dichloroethylene                             | 5173                                    | 51.73                                   | 3.10                                    |
| Chloroform                                      | 5196                                    | 51.96                                   | 3.12                                    |
| Trichloroethylene                               | 5276                                    | 52.76                                   | 3.17                                    |
| 12-dichloropropene                              | 5261                                    | 52.61                                   | 3.16                                    |
| 112-trichloroethane                             | 6951                                    | 69.51                                   | 4.17                                    |
| Tetrachloroethylene                             | 5242                                    | 52.42                                   | 3.15                                    |
| Tetrachloroethylene                             | 5242                                    | 52.42                                   | 3.15                                    |
| Tetrahexafluorobutane                           | 3030                                    | 30.30                                   | 2.12                                    |
| Dichlorobenzene                                 | 1005                                    | 10.05                                   | 0.70                                    |

Subsequently, a volume of 240 mL of this gas mixture was transferred onto the sorbent tubes on the starting day (D0). All the tubes were then stored in the fridge (+4 °C) prior to analysis.

2.3.3. Sulphur Compounds

A static gas mixture was prepared in an aluminium cylinder containing all the sulphur compounds listed in Table 3. As an internal standard, n-hexane was added. For the preparation of the static gas mixture, a liquid mixture containing CS2, T-BM, THT and hexane (C6) was prepared using a Liquid Mixture Robot (LMR) developed at VSL. The LMR is equipped with a Multi-Purpose Sampler (MPS), a multifunctional autosampler and sample preparation robot (from Gerstel), an analytical balance (from Mettler), and a system for controlling the MPS and the balance. The LMR allows the automatic preparation of liquid mixtures containing up to 20 individual components. The individual components were added in decreasing order according to their boiling points. The liquid mixture obtained was injected with a syringe into an evacuated cylinder, treated with an Alphatech® H2S coating, then vaporized and diluted with nitrogen, to obtain a mother mixture. The mother mixture was further diluted and COS, H2S and CH4S were added to obtain the end mixture. The gas mixture preparation was performed by static gravimetry according to ISO 6142-1 [24]. The composition of the final mixture (VSL162904) used for the short-term stability tests is given in Table 3.

Table 3. Composition sulphur gas mixture VSL162904.

| Component | Mole Fraction (nmol/mol) | Expanded Uncertainty (nmol/mol) (k = 2) |
|-----------|--------------------------|----------------------------------------|
| H2S       | 392.66                   | 0.19                                   |
| CH4S      | 395.4                    | 0.4                                    |
| COS       | 392.19                   | 0.32                                   |
| C6 *      | 434.4                    | 0.5                                    |
| CS2       | 408.1                    | 0.5                                    |
| THT       | 427.0                    | 0.5                                    |
| T-BM      | 389.9                    | 0.6                                    |

* Internal standard.

According to ISO 14687-2 [2] the threshold for total sulphur compounds in hydrogen is 0.004 µmol/mol (4 nmol/mol). This value is based on requirements from the Proton Exchange Fuel cell producers and the detection limits of available instruments and test methods. To reach lower mole fraction, the static gas mixture was dynamically diluted with N2 using thermal mass-flow controllers according to ISO 6145-7 [25]. Dilutions from approximately 400 nmol/mol per sulphide in the static gas mixture to approximately 100 and 20 nmol/mol per sulphide in the dynamic gas mixture were produced for the short-test stability (Table 4).
The dynamically obtained gas mixtures were transferred onto sorbents using a specially designed sampling manifold. The manifold is equipped with mass-flow controllers (MFCs) and 3-way valves to allow the simultaneous sampling of 12 sorbent tubes. For the short-term stability study of sulphur compounds, the tubes (totally, 30 Tenax TA tubes, 30 Tenax TC/SulfiCarb tubes and 30 Carboxen 1003 tubes for each concentrations level) were sampled at a flow rate of 50 mL/min for 10 min; the total volume being 500 mL. The tubes were stored at room temperature (+20 °C) prior to analysis.

2.4. Analytical Methods

Different set-ups and instruments were used for the tests depending on the equipment at the test facility.

2.4.1. Hydrocarbons and Halogenated Hydrocarbons

The sorbent tubes were desorbed using a Markes TD100 thermal desorber with a two stages desorption; a primary tube desorption followed by a secondary trap desorption. Depending on the sorbents, different temperatures were used for the primary tube desorption (no inlet split): 275 °C for 7 min for the Tenax tubes, 320 °C for 7 min for the multi-sorbent tubes (Tenax TA/Carboxen 1003/Carbograph 1) and 250 °C for 7 min for the Chromosorb 106 tubes. The desorption gas flow rate was 60 mL/min. In the second stage, a cold trap packed with Tenax TA and Carbograph 1TD (50/50) (−10 °C) was heated quickly (1.3 °C/s) to 300 °C so the compounds were released and reached the gas chromatographic column where they were separated. The outlet split ratio was 6:1. The instrument used for the analyses was an Agilent technologies 6890N coupled with a flame ionization detector and a 5975C inert MSD Mass Spectrometer Detector (electron impact, EI, mode). The GC column was a BPX5 non-polar capillary column (5% phenyl polysilphenylene-siloxane, 50-m long, 0.32-mm internal diameter, 1-µm film thickness). The initial GC oven temperature was 35 °C (hold 4 min). The oven temperature was then raised with three ramp rates: to 100 °C at 3 °C/min, to 220 °C at 8 °C/min and finally to 300 °C at 15 °C/min. The temperature was then held at 300 °C for 10 min. For detection, one part of the effluent was sent to a flame ionization detector and the other part to the mass spectrometer. Compounds can be quantified using both detectors; the FID (Flame Ionisation Detector) or the MS. When quantifying with the MS, two modes can be used; the total ion chromatogram mode which represents the summed intensity across the entire range of masses being detected (m/z 29 to m/z 390) or an extracted-ion chromatogram mode where one m/z value characteristic for one compound are recovered from the entire data set. In this study, data were collected using the total ion chromatogram mode.

2.4.2. Sulphur Compounds

The sorbent tubes were desorbed using a Perkin Elmer hermal desorber ATD650 with a two stages desorption: a primary tube desorption followed by a secondary trap desorption. The temperature used for the primary tube desorption was 300 °C for 5 min. The desorption gas flow rate was 30 mL/min. In the second stage, a cold trap packed with carbonaceous sorbents was quickly heated (at least 1 °C/s) so the compounds were released and reach the gas chromatographic column where they are separated. The outlet split was 10 mL/min for entry and 6 mL/min for entry 2. The instrument used for the analyses was an Agilent technologies 7820A coupled with a 5977E inert MSD mass spectrometer (electron
The GC column was a Rxi 624Sil MS, 60-m long, 0.25-mm internal diameter, 1.4-µm film thickness. The initial GC oven temperature was 40 °C (hold 4 min). The oven temperature was then raised with two ramp rates: to 120 °C at 20 °C/min, to 220 °C at 25 °C/min. The temperature was then held at 220 °C for 2 min. For detection the compounds were quantified using MS, the range of masses detected was m/z 45 to m/z 100 and data were collected using the total ion chromatogram mode.

3. Results and Discussion

This study discussed the storage stability and recovery of a wide range of compounds that must be analysed in order to provide sufficient proof that the hydrogen provided by HRS will not damage or degrade the fuel cell system of the vehicles. There is currently limited information about how stable the impurities to be analysed are when transported in commercially available sampling vessels. Several different sorbent tubes were here tested for their suitability in capturing and desorbing these compounds and for their suitability in storing these compounds during the transportation time. Due to the large number of impurities to analyse at stringent detection limits, performing the whole set of analyses required for hydrogen purity testing (ISO 14687) is both technically challenging and time-consuming for any laboratory and will require a combination of several analytical techniques or instruments. Therefore, methods allowing the simultaneous analysis of several species are specially of interest for laboratories intending to implement hydrogen purity testing.

3.1. Required Sampling Volumes

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 high, the analytes will not have enough time to interact with the sorbent material and if the flow rate is too slow, there is a risk of back-diffusion.

Several factors affect the detection limit of a TC–GC–MS method; among others some of the parameters of the thermal desorption such as the inlet split ratio during the primary (tube) desorption and the outlet split ratio during the secondary (trap) desorption. Moreover, the total detection limit is also affected by the sensitivity of the detector. Another important factor affecting the limit of detection is the volume sampled; the larger the volume sampled the lower 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).

The sampling volumes required to ensure that the analytical method will meet the thresholds set in ISO 14687-2 [2] for hydrocarbons, sulphur compounds and halogenated compounds have been estimated here based on several assumptions. (1) The quantification limit (LOQ) for each family was calculated using the criterion stated in ISO/CD 21087 [10]: LOQ + uLOQ < thresholds set in ISO 14687-2; for the calculation, uLOQ was estimated to be 50%. Based on these assumptions, the method’s LOQs are 1 µmol/mol for total hydrocarbons, 0.002 µmol/mol for total sulphur compounds and 0.025 µmol/mol for total halogenated compounds; (2) In order to estimate what would then be the required LOQ for each individual compound, we used the method for missing data where it is common practice to replace every value below LOQ by a constant such as LOQ/2 or LOQ/√2. Here we chose LOQ/2. Based on this assumption, the method’s LOQs are 0.5 µmol/mol for each hydrocarbon, 0.001 µmol/mol for each sulphur compound and 0.0125 µmol/mol for each halogenated compound. (3) Finally, it was assumed that the LOQ for any compound with the analytical methods used in this study is 2 ng. This limit is fairly easy to obtain with most systems based on TD–GC–MS.

Using the three assumptions, the minimum volume of hydrogen that should be sampled on sorbent tubes to reach the thresholds set in ISO 14687-2 is presented in Table 5. The minimum volume of hydrogen sampled also depends on the amount of the sorbent in sorption tubes; in this case, 200 mg in each tube.

The minimum sampling volume required for hydrocarbons and halogenated hydrocarbons with the method used in this study is very low for sorbent tubes (typical sampling volumes range from
0.5 L up to at least 10 L). However, due to the stringent threshold set for sulphur compounds, this minimum volume is higher for this family.

**Table 5.** Calculation of the minimum volume of hydrogen that should be sampled on sorbent tubes to reach the thresholds set in ISO 14687-2.

| LOQ nmol/mol | Minimum Volume of Hydrogen to Sample (mL) |
|--------------|----------------------------------------|
| Methane      | 500                                    |
| Ethane       | 250                                    |
| Propane      | 160                                    |
| Butanes      | 125                                    |
| Acetone      | 160                                    |
| Methanol     | 500                                    |
| Ethanol      | 250                                    |
| Heptane      | 70                                     |
| Decane       | 50                                     |
| Dichloromethane | 15                               |
| Tetrachloroethylene | 15                                |
| Tetrachlorohexafluorobutane | 15                               |
| Dichlorobenzene | 15                                |
| Carbonyl sulphide | 1.5                             |
| Carbon disulphide | 1.5                             |
| Tert-butyl mercaptan | 1.5                             |
| Tetrahydrothiophene | 1.5                             |
| Methyl-mercaptan | 1.5                              |

### 3.2. Suitability of Sorbent Materials

The suitability of the sorbent tubes was assessed by measuring the recovery yield (for hydrocarbons and halogenated hydrocarbons: ratio of the measured and the spiked content at day 0 (D0) expressed as a percentage, for the sulphur compounds: control of the breakthrough using two tubes in series) and the storage stability over a period of maximum 14 days. The storage stability is defined as the change in content for a given compound as determined on the different storage days compared to at the start of the stability test. Each data presented below is the average of 2 or 3 measurements; except at D0 where 4 to 6 replicates have been analysed.

As expected, some of the targeted compounds with very low boiling points (BP); methane (BP $-162^\circ C$), ethane (BP $-88^\circ C$) and hydrogen sulphide (BP $-61^\circ C$) were not recovered in the conditions used in this study. These compounds can only be trapped at low temperatures (not practical to implement onsite) and on very strong sorbents. Even methanol (BP $64^\circ C$) and methyl-mercaptan (BP $6^\circ C$) were not recovered. Other analytical methods should therefore be used for these compounds when performing hydrogen purity analysis. Fortunately, there are already well-established methods for these compounds (e.g., optical methods or other GC methods) that allow their quantification at the level required in ISO 14687-2.

#### 3.2.1. Hydrocarbons

The results from the short-term stability studies for hydrocarbons are presented in Table 6 (recovery yield) and in Figures 1–3 (storage stability).
Table 6. Recovery yield obtained for hydrocarbons on 3 different sorbent tube.

|                  | Chromosorb 106 | TCC       | Tenax TA   |
|------------------|----------------|-----------|------------|
|                  | Recovery (%)   | Rel. Std. Deviation | Recovery (%) | Rel. Std. Deviation | Recovery (%) | Rel. Std. Deviation |
| Propane          | 91.3           | 2.1       | 95.0       | 1.0               | 9.9          | 49.9                 |
| Isobutane        | 96.5           | 0.7       | 88.3       | 1.9               | 20.4         | 15.0                 |
| Butane           | 97.5           | 0.4       | 96.3       | 1.4               | 61.3         | 24.6                 |
| Ethanol          | 102.1          | 7.2       | 145.9      | 36.6              | 81.0         | 1.3                  |
| Isopentane       | 95.9           | 0.4       | 85.4       | 0.8               | 54.0         | 8.6                  |
| Acetone          | 91.9           | 5.0       | 51.4       | 6.9               | 55.3         | 6.1                  |
| Pentane          | 95.1           | 0.7       | 93.1       | 1.4               | 87.9         | 3.3                  |
| Heptane          | 97.6           | 5.4       | 97.7       | 3.6               | 91.9         | 6.3                  |
| Decane           | 92.8           | 2.5       | 98.4       | 4.1               | 91.5         | 4.2                  |

As it can be shown in Table 6, the relative standard deviations obtained from 4 to 6 replicates were found to be lower than 5% for most compounds or slightly above 5% for ethanol and heptane on Chromosorb 106, for acetone on TCC and for heptane, acetone and isopentane on Tenax TA. High relative standard deviation (>15%) were obtained for ethanol on TCC and for propane, isobutane and butane on Tenax TA. Unpredictable losses tend to indicate that the sorbent material is not suitable for the targeted compounds.

Recovery yields above 90% were observed for most compounds on Chromosorb 106 and on TCC (through just under 90% for isobutane and isopentane on TCC) for most of the targeted compounds. However, on TCC, low recovery yields were observed for acetone (51.4%). For most of the compounds, the recovery yields on Tenax TA were under 80% with the exception of pentane (88%), heptane (92%) and decane (91.5%). As Tenax TA is a weak sorbent, compounds with low boiling points (<50 °C) are logically not well retained on this sorbent. However, with the low volume used in this study at the concentration tested, a measurable amount of isobutane (20%) and butane (60%) are retained on Tenax TA. When using two sorbents in series (for instance Tenax TA and Chromosorb 106), it would therefore be necessary to sum up the amount recovered on both sorbents.

Figure 1. Storage stability of hydrocarbons on Chromosorb 106. (a) for butane, propane, isobutane, decane, ethanol; (b) for pentane, isopentane, acetone and heptane.

![Figure 1](image1.png)

Figure 2. Storage stability of hydrocarbons on TCC. (a) for butane, acetone, isobutane, decane, pentane; (b) for propane, isopentane, ethanol and heptane.

![Figure 2](image2.png)
As it can be seen in Figures 1–3, most of the hydrocarbons evaluated in this study were determined to be very stable (D10 concentrations less than 10% below the initial concentrations) on Chromosorb 106 (except acetone), on TCC (except ethanol) and on Tenax TA (except propane and acetone). Surprisingly, the concentration of acetone increased during the storage time (25–30% higher than the initial concentration) both on Chromosorb 106 and on Tenax TA.

As already observed at D0 (recovery yields), the behaviour of ethanol on TCC was unpredictable (Figure 2b - D0: 0.17 nmol/mol, D2: 0.29 nmol/mol, D5: 0.33 nmol/mol, D8: 0.23 nmol/mol). The same behaviour was also observed for propane, acetone, decane and heptane.

3.2.2. Halogenated Hydrocarbons

The results from the short-term stability studies for hydrocarbons are presented in Table 7 (recovery yield) and on Figures 4–6 (storage stability).

As it can be seen in Table 6, the relative standard deviations obtained from 4 to 6 replicates were found to be lower than 5% for most compounds or slightly above 5% for ethanol and heptane on Chromosorb 106, for acetone on TCC and for heptane, acetone and isopentane on Tenax TA. High relative standard deviation (>15%) were obtained for ethanol on TCC and for propane, isobutane and butane on Tenax TA. Unpredictable losses tend to indicate that the sorbent material is not suitable for the targeted compounds.

Recovery yields above 90% were observed for most compounds on Chromosorb 106 and on TCC (through just under 90% for isobutane and isopentane on TCC) for most of the targeted compounds. However, on TCC, low recovery yields were observed for acetone (51.4%). For most of the compounds, the recovery yields on Tenax TA were under 80% with the exception of pentane (88%), heptane (92%) and decane (91.5%). As Tenax TA is a weak sorbent, compounds with low boiling points (<50 °C) are logically not well retained on this sorbent. However, with the low volume used in this study at the concentration tested, a measurable amount of isobutane (20%) and butane (60%) are retained on Tenax TA. When using two sorbents in series (for instance Tenax TA and Chromosorb 106), it would therefore be necessary to sum up the amount recovered on both sorbents.

As it can be seen in Figures 1–3, most of the hydrocarbons evaluated in this study were determined to be very stable (D10 concentrations less than 10% below the initial concentrations) on Chromosorb 106 (except acetone), on TCC (except ethanol) and on Tenax TA (except propane and acetone). Surprisingly, the concentration of acetone increased during the storage time (25–30% higher than the initial concentration) both on Chromosorb 106 and on Tenax TA.

As already observed at D0 (recovery yields), the behaviour of ethanol on TCC was unpredictable (Figure 2b - D0: 0.17 nmol/mol, D2: 0.29 nmol/mol, D5: 0.33 nmol/mol, D8: 0.23 nmol/mol). The same behaviour was also observed for propane and acetone on Tenax TA (Figure 3b).
recovery on all sorbents (72% on Chromosorb 106, 68% on TCC and 67% on Tenax TA). All other compounds were recovered at more than 90% on all sorbents with the exception of trichloroethylene (87% on Chromosorb 106), dichloromethane and 1,2-dichloroethylene on Tenax TA (both 89%).

Table 7. Recovery yield obtained for halogenated hydrocarbons on three different sorbent tubes.

| Compound                  | Chromosorb 106 | TCC   | Tenax TA |
|---------------------------|----------------|-------|----------|
|                           | Recovery (%)   | Rel. Standard Deviation | Recovery (%) | Rel. Standard Deviation | Recovery (%) | Rel. Standard Deviation |
| Chloromethane             | <5            | -     | 57.1     | 9.0       | <5            | -                     |
| Vinyl chloride            | 129.5         | 31.3  | 127.5    | 16.4      | 52.2          | 13.5                |
| Freon 113                 | 106.3         | 7.1   | 102.1    | 2.8       | 39.6          | 7.8                  |
| Dichloromethane           | 99.4          | 0.2   | 95.4     | 0.6       | 88.6          | 3.6                  |
| 1,2-Dichloroethylene      | 98.6          | 0.0   | 95.5     | 3.9       | 88.9          | 2.8                  |
| Chloroform                | 72.1          | 7.4   | 68.1     | 1.0       | 67.1          | 9.6                  |
| Trichloroethylene         | 87.1          | 4.7   | 100.3    | 4.4       | 90.9          | 2.5                  |
| 1,2-Dichlorobenzene       | 99.9          | 1.2   | 93.8     | 4.4       | 93.7          | 2.0                  |
| 1,1,2-Trichloroethane     | 113.2         | 2.9   | 106.4    | 3.1       | 98.7          | 3.7                  |
| Tetrachloroethylene       | 100.6         | 3.0   | 98.1     | 2.1       | 90.5          | 4.4                  |
| Tetrachlorohexafluorobutane | n.d.                | n.d.  | 99.3     | 5.2       | 94.6          | 4.3                  |
| 1,2-Dichlorobenzene       | n.d.          | n.d.  | 95.2     | 3.1       | 102.9         | 2.8                  |

n.d. not determined.

Figure 4. Storage stability of halogenated hydrocarbons on Chromosorb 106. (a) for 1,1,2-trichloroethane, chloroform, 1,2-dichloroethylene, vinylchloride; (b) for Freon 113, tetrachloroethylene, chloromethane,dichloromethane. (c) for 1,2-dichloropropane, trichloroethylene.

As it can be seen on Figures 4 and 6, most of the halogenated hydrocarbons were found to be very stable (D14 concentrations less than 10% below the initial concentrations) on Chromosorb 106 and on Tenax TA (except chloromethane which could not be recovered in detectable concentration already on D0 on both sorbents). However, high variations of concentrations at D4, D5, D8 are observed for some compounds (freon 113, dichloromethane, tetrachloroethylene and 1,2-dichloropropane) on Chromosorb 106. Surprisingly, trichloroethylene concentration increased during the storage time on Chromosorb 106 (Figure 4c). As already observed on D0 (recovery yields), the behaviour of vinyl chloride on TCC was unpredictable (D0: 64 nmol/mol, D12: 37 nmol/mol, D14: 43 nmol/mol). Most of the halogenated hydrocarbons showed a slow decrease with time when stored on TCC (Figure 5) leading to a D14 concentration 15 to 25% lower than the initial concentrations with the exception of 1,2-dichlorobenzene and trichloroethylene which were both observed to be very stable. The decrease was even more pronounced for chloromethane (almost 30% lower concentration at D14 compared to D0) and with chloroform (slightly more than 30% lower concentration at D12 compared to D0). It is possible that once the tube was capped, part of the compounds may have been released from the weaker first sorbent bed and then preferentially migrated to the stronger beds, where they might have been (partially) irreversibly adsorbed resulting in incomplete recovery during analysis.
Figure 5. Storage stability of halogenated hydrocarbons on TCC. (a) for 1,2-dichlorobenzene, 1,2-dichloropropane, 1,1,2-trichloroethane, chloroform; (b) for 1,2-dichloroethylene, vinylchloride, for chloromethane, dichloromethane. (c) for tetrachlorohexabutane, trichloroethylene, tetrachloroethylene, freon 113.

Figure 6. Storage stability of halogenated hydrocarbons on Tenax TA. (a) for 1,2-dichlorobenzene, 1,2-dichloropropane, 1,1,2-trichloroethane, chloroform; (b) for 1,2-dichloroethylene, vinylchloride, for chloromethane, dichloromethane. (c) for tetrachlorohexabutane, trichloroethylene, tetrachloroethylene, freon 113.

3.2.3. Sulphur Compounds

The gas mixture VSL162904 (concentration around 400 nmol/mol for each sulphur compound) was first analysed with GC/MS to verify the composition of the static gas mixture (Figure 7a). The compounds were detected by the mass spectrometer, even though hydrogen sulphide coelutes with carbon dioxide. When analysing the diluted gas mixtures after transfer onto sorbent tubes, hydrogen sulphide and methyl mercaptan could not be detected on either of the three selected sorbent materials (Figure 7b). Furthermore, sulphur dioxide which was not present in the gas mixture was identified; mostly on Carboxen 1003 (much smaller amounts were detected on Tenax TA and Tenax TA/SulfiCarb). A possible explanation for the presence of sulphur dioxide is that sulphur compounds partly react with oxygen when stored on the sorbent materials.
may have been released from the weaker first sorbent bed and then preferentially migrated to the stronger beds, where they might have been (partially) irreversibly adsorbed resulting in incomplete recovery during analysis.

### 3.2.3. Sulphur Compounds

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![Figure 7a](image1)

**Figure 7.** (a) Chromatogram analysis of VSL162904 containing approximately 400 nmol/mol per sulphur component (CO2: carbon dioxide, H2S: hydrogen sulphide, COS: carbonyl sulphide, CH4S: methyl-mercaptan, C6: Hexane, T-BM: tert-butyl-mercaptan, THT: tetrahydrothiophene). (b) Chromatogram analysis of the sulphur compounds (at ~100 nmol/mol) on Carboxen 1003.

The recovery yields were estimated by calculating the breakthrough of sulphur compounds for all three sorbent materials. To determine this, two tubes were connected in series during loading and both tubes were desorbed and analysed. If the recovery is complete, the first tube should contain the compounds while the second tube should remain clean. The second tube, when using either Tenax TA/SulfiCarb or Carboxen 1003 sorbent materials was observed to be clean (all compounds below detection limit). However, the Tenax TA tubes contained 5% of the total CS2 and 37% of the total T-BM.
To prevent breakthrough shorter loading times could be used however, loading times less than 10 min are not recommended because they lead to less accurate results.

The desorption efficiency at 275 °C was determined by analysing the tubes twice, to determine if there were traces of components left on the tubes after the first analysis. As the response for COS relative to C6 was very low it was difficult to determine the desorption efficiency for this compound. Only hexane was found on the Carboxen 1003 tubes in the second analysis. Therefore, the desorption temperature was then performed at 300 °C. During a second control of the desorption efficiency, no hexane was found.

Five tubes for each sorbent material, and 1 or 2 blanks were analysed on 6 different days during a period of 14 days to determine the short-term stability. During these 14 days, the sorbent tubes were stored in the laboratory at 20 °C. The peak area of each compound on the 5 tubes was averaged and the relative response factor (RRF) against the internal standard, C6, was determined according to Equation (1).

$$ RRF = \frac{A_i}{m_i} \frac{A_{C6}}{m_{C6}} $$ (1)

In which:

RRF = Relative Response Factor
$A_i$ = Average peak area compound $i$
$m_i$ = Mass compound $i$
$A_{C6}$ = Average peak area of the internal standard C6
$m_{C6}$ = Mass internal standard C6

The results from the short-term stability studies for sulphur compounds are presented in Figures 8–10 for the 100 nmol/mol gas mixture and in Figures 11–13 for the 20 nmol/mol gas mixture.

![Figure 8. Storage stability of sulphur compounds (~100 nmol/mol) on Tenax TA.](image-url)
Figure 9. Storage stability of sulphur compounds (~100 nmol/mol) on Tenax TA/SulfiCarb.

Figure 10. Storage stability of sulphur compounds (~100 nmol/mol) on Carboxen 1003.
Figure 11. Storage stability of sulphur compounds (~20 nmol/mol) on Tenax TA.

Figure 12. Storage stability of sulphur compounds (~20 nmol/mol) on Tenax TA/SulfiCarb.
The uncertainty of the RRF was determined by taking into account different sources of uncertainty; the uncertainties due to the gas mixture preparation, the uncertainties due to the sampling procedure, and the standard deviation for the peak area obtained when analysing five sorbent tubes.

The targeted compounds behaved differently depending on the tested sorbent materials. Under the conditions for the experiments, H₂S and CH₄S could not be recovered from any of the three selected sorbent materials.

The measurements performed on the 100 nmol/mol gas mixture showed that the COS response relative to C₆ decreased with time on Tenax TA. The amount of COS recovered sampling from this sorbent material after D7 was below the detection limit (Figure 8). Instabilities were observed for CS₂ and T-BM on the double bed sorbent material Tenax TA/SulfiCarb.

The results for the short-term stability with the 20 nmol/mol gas mixture were comparable to the results obtained with the 100 nmol/mol gas mixture. The uncertainties for the RRF were larger due to higher standard deviations for the measurement at these low concentration levels. The only noticeable difference was that T-BM at 20 nmol/mol could not be detected after D4 on the Carboxen 1003 sorbent material.

In summary, Tenax TA was observed to be a good sorbent material for the higher boiling sulphur compounds e.g., THT, CS₂ and T-BM even though some breakthrough occurred for T-BM. The issue could be resolved by lowering the sampling volume. THT and COS can be stored for 2 weeks on the Tenax TA/SulfiCarb sorbent material while CS₂ and T-BM showed decreasing recovery over time. Carboxen 1003 is a suitable sorbent material for COS. The other sulphur compounds showed instability. Tests should be performed to prevent the formation of SO₂ by the reaction of the sulphur compounds with oxygen.

The suitability of sorbents for the targeted compounds are summarized in Table 8. Some compounds with low boiling points (COS BP −50 °C), propane (BP −42 °C), isobutane (BP −11 °C), chloromethane (BP −24 °C) and vinyl chloride (BP −14 °C) were detected with more or less good stability using sorbents such as Carboxen 1003 (COS), Chromosorb 106 or even TCC. Even if recoveries were not always optimal using Tenax TA, most of the compounds exhibited good storage stability for a period of 10–14 days.

Figure 13. Storage stability of sulphur compounds (~20 nmol/mol) on Carboxen 1003.
Table 8. Suitability of sorbents for the targeted compounds.

| Compound               | Chromosorb 106 | TCC | Tenax TA | Carboxen 1003 | Tenax TA/SulfiCarb |
|------------------------|----------------|-----|----------|---------------|--------------------|
|                        | Recovery Yield | Storage Stability | Recovery Yield | Storage Stability | Recovery Yield | Storage Stability | Recovery Yield | Storage Stability | Recovery Yield | Storage Stability | Recovery Yield | Storage Stability |
| Propane                | –42            | Very good | Very stable | Very good | Very stable | Not suitable | Unstable | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Isobutane              | –11            | Very good | Very stable | Good | Very stable | Not suitable | Very stable | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Butane                 | 0              | Very good | Very stable | Very good | Very stable | Low | Relatively Stable | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Ethanol                | 78             | Very good | Very stable | Not suitable | Unstable | Low | Relatively Stable | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Isopentane             | 28             | Very good | Very stable | Good | Very stable | Low | Relatively Stable | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Acetone                | 56             | Very good | Unstable | Low | Very stable | Low | Unstable | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Pentane                | 36             | Very good | Very stable | Very good | Very stable | Good | Very stable | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Heptane                | 98             | Very good | Very stable | Very good | Very stable | Very good | Very stable | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Decane                 | 174            | Very good | Very stable | Very good | Very stable | Very good | Very stable | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Chloromethane          | –26            | Not suitable | n.d. | Low | Relatively Stable | Not suitable | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Vinyl chloride         | –14            | Not suitable | Very stable | Not suitable | Unstable | Low | Very Stable | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Freon 113 (trichloroethane) | 47         | Very good | Very stable | Very good | Relatively Stable | Not suitable | Very Stable | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Dichloromethane        | 40             | Very good | Very stable | Very good | Unstable | Good | Very Stable | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 1,2-Dichloroethylene   | 55             | Very good | Very stable | Very good | Relatively Stable | Good | Very Stable | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Chloroform             | 61             | Very good | Very stable | Very good | Relatively Stable | Very good | Very Stable | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Trichloroethylene      | 87             | Good | Unstable | Very good | Very stable | Very good | Very Stable | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 1,2-Dichloropropane    | 97             | Very good | Very stable | Very good | Relatively Stable | Very good | Very Stable | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 1,1,2-Trichloroethane  | 114            | Good | Very stable | Very good | Relatively Stable | Very good | Very Stable | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Tetracloroethylene     | 121            | Very good | Very stable | Very good | Relatively Stable | Very good | Very Stable | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Tetrachloroethane      | 135            | n.d. | n.d. | Very good | Relatively Stable | Very good | Very Stable | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 1,2-Dichlorobenzene    | 180            | n.d. | n.d. | n.d. | Very good | Very stable | Very good | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Carbonyl sulphide      | –50            | n.d. | n.d. | n.d. | n.d. | Very good | Not stable | Very good | Very stable | Very good | Not stable |
| Carbon disulphide      | 46             | n.d. | n.d. | n.d. | n.d. | Very good | Very stable | Very good | Not stable | Very good | Not stable |
| tert-butyl mercaptan (T-BM) | 64           | n.d. | n.d. | n.d. | n.d. | Low recovery | Very stable | Very good | Not stable | Very good | Not stable |
| Tetrahydrothiophene (THT) | 119         | n.d. | n.d. | n.d. | n.d. | Very good | Very stable | Very good | Not stable | Very good | Very stable |

For recovery: Very good: recovery >90%; Good: recovery from 85 to 90%; Low recovery from 50 to 84%; Not suitable: <50%. For storage stability: Very stable: D10 or D14 concentrations less (or more) than 10% lower than the initial concentration; Relatively stable: D10 or D14 concentrations less than 25% lower than the initial concentration but more than 10% lower than the initial concentration; Not stable: Fluctuations of results or D10 or D14 concentrations more than 25% below the initial concentration.
4. Conclusions

Currently, vessels used to sample hydrogen from a refuelling station have not fully been tested to demonstrate that the concentration of gaseous impurities listed in ISO 14687 remain stable during sampling and transport, which is a requirement to ensure that the sample analysed is representative of the fuel delivered at the station. The results obtained during the short-term stability studies described in this paper show that a method based on thermal desorption—gas chromatography–mass spectrometry is promising for total species even though not all of the compounds belonging to the three “total species” listed in ISO 14687 can be quantitatively retained on one unique sorbent. This technique will not only provide a sum of concentrations but also an identification of which compound(s) is/are actually present in the hydrogen. The most suitable sorbent appears to be TCC, a three-bed sorbent, containing a weak (Tenax TA), a medium (Carbograph 1TD) and a strong sorbent (Carboxen 1003). Even through experiments have not been performed for sulphur compounds with TCC, two of the sorbents present in the three-bed sorbent have been tested (Carboxen 1003 and Tenax TA) and the results tend to indicate that this sorbent could also be a good alternative for sulphur compounds. Therefore, TTC is a versatile sorbent suitable for the three “total species”. It may, however, be necessary to sample different volumes on several tubes. Low sampling volumes reduce the risk of volatile components breaking through the sorbent bed during sampling but the enrichment may not be enough to reach the limit of detection required in ISO 14687, especially for sulphur compounds. A combination of small (less than 100 mL) and larger (more than 500 mL) sample volumes overcomes these issues.

Additionally, this study shows that compounds retained on the sorbent materials can be analysed several days after sampling without significant alteration of their concentration. Most of the compounds, with the exception of vinyl chloride, chloroform and ethanol, were found to be at least “relatively stable” (D10 or D14 concentrations less than 25% below the initial concentration) on TCC.

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Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

| Acronym | Description |
|---------|-------------|
| LOQ     | limit of quantification |
| TCC     | Tenax TA, Carboxen 1003, Carbograph 1 |
| T-BM    | Tert-butyl mercaptan |
| THT     | Tetrahydrothiophene |
| LMR     | Liquid Mixture Robot |
| MPS     | Multi-Purpose Sampler |
| GC      | Gas Chromatography |
| EI      | Electron Impact |
| FID     | Flame Ionization detector |
| MS      | Mass Spectrometer |
| BP      | Boiling Point |
| RRF     | Relative Response Factor |
| RISE    | Research Institutes of Sweden |
| VSL     | Dutch Metrology Institute |
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