Short communication

Observation of sorptive losses of volatile sulfur compounds during natural gas sampling

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Abstract

The reason for the compound-dependent over-estimation of the recoveries of several volatile organic sulfur compounds when using a Silcosteel cylinder for sample storage as reported earlier was examined. From the different possible sources of errors that were taken into consideration, the silicone tubing, which was used to fill a standard Tedlar sample bag for calibration, was identified as the cause of the artefact. The comparison of different tubing materials showed that PTFE is the best choice since it causes only minor losses ($<10\%$) of propyl- and butylmercaptans. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Sampling artefacts; Sorptive losses; Natural gas; Volatile sulfur compounds

1. Introduction

The determination of volatile sulfur compounds (VSCs) is known to be complicated by their tendency to adsorb onto several kinds of materials, which are used for sampling and analysis [1]. In contrast to ambient air analysis, which includes several potential sources of analyte losses (e.g. adsorbent, dryer, ozone scrubber), grab sampling of mercaptans, which is usually performed in the analysis of natural gas, may be expected to be less critical, particularly because of the higher analyte concentrations. However, little is known about interactions between C_2–C_4 mercaptans and materials used for sampling, and particularly the sampling lines used for this purpose. This is rather surprising for two

reasons: on the one hand, C_2–C_4 mercaptans and sulfides are widely used for odorisation of natural gas in order to make gas leaks more easily detectable and to prevent accidents, and for this reason require regular monitoring of their concentrations. On the other hand, natural gas is usually sampled in Tedlar bags from pipelines, and a non-inert sample transfer line may cause considerable analyte losses, since this connection should have a certain length for convenient handling.

The existing literature only deals with losses of inorganic VSCs (COS, H_2S, etc.), methylmercaptan and dimethyl sulfide. Kuster and Goldan examined wall loss rates of several VSCs in emission flux chambers made of fluorinated ethylene propylene (FEP) PTFE, tetrafluoroethylene (TFE) PTFE, Pyrex glass and polycarbonate [2]. Under moist conditions, the FEP PTFE exhibited the smallest losses for all compounds investigated, only SO_2 and MeSH showed large wall losses on this material. Lodge also

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recommended PTFE as preferable to other polymers [3]. PTFE is also a widely accepted material for sample loops and chromatographic columns in the analysis of VSCs, although some authors observed adsorption and memory effects and consequently preferred stainless steel [4] or Pyrex glass [5].

In a recent publication [6] our group examined the stability of a gaseous multicomponent standard containing nine mercaptans and sulfides in three different types of sample containers (standard Tedlar sample bags, black and clear layered Tedlar bags and Silcosteel sample cylinders). Recoveries higher than 100% were observed for the Silcosteel cylinders (up to 160%, increasing with decreasing volatility of the analytes) compared to the Tedlar bag, which was used for calibration. Since this over-estimation was reproducible, it did not influence the relative concentration changes in the sample containers during the stability study. Nevertheless, the unexpected over-estimation of recoveries prompted us to carry out further studies. This was done by comparing sampling using standard Tedlar sample bags and Silcosteel cylinders with a third method (sampling directly from the gas cylinder using a syringe adapter).

2. Experimental

2.1. Materials

The gaseous multicomponent standard used in this work was purchased from Sapio (Monza, Italy). The components and their concentration are given in Table 1.

The 1-l Silcosteel sample cylinder was purchased from Restek (Bellefonte, PA, USA), the 12-l standard

Tedlar sample bag was obtained from SKC (Eighty Four, PA, USA). The PTFE tubing (tetrafluoro-ethylene PTFE, 5 mm O.D., 3 mm I.D.) was obtained through Burde (Vienna, Austria), the silicone tubing (6 mm O.D., 3 mm I.D., made from silicone SI, hardness 55, Shore A, temperature limits -60 and 180 °C, respectively) and the poly(vinyl chloride) (PVC) tubing (6 mm O.D., 3 mm I.D.) were obtained through Labor Becker (Vienna, Austria).

2.2. Sampling

The sample containers were purged three times with the calibration gas prior to sampling. The Silcosteel sample cylinders and the syringe adapter were connected directly to the pressure regulator on the gas bottle using a suitable Swagelok fitting. To fill the Tedlar bags, a silicone tubing (1.5 m length $\times 3$ mm I.D.) was connected to the pressure regulator using a tubing adapter and the 12-l bags were filled in approx. 30 s.

Samples were taken with a 1-ml gas-tight syringe (Hamilton, Reno, NV, USA) with a PTFE Luer Lock needle type, which was also purged three times prior to sampling. In order to prevent leakages in the septum of the sampling port of the bags, they were not pierced with the syringe for sampling. Instead, the valve of the fitting of the bags was opened, the connected silicone tubing was purged with a flow of at least 20 ml/min and samples were taken from this purged gas line very close to the sampling port. In contrast to this, the manifold used for filling the Silcosteel sample cylinders allows direct sampling, since a valve separates the sampling port, which is closed by a septum, from the sample cylinder. The final pressure in the sample cylinders was 57 p.s.i. (1 p.s.i.$=6894.76$ Pa). Sampling from the syringe adap-

Table 1
Composition of the gaseous multicomponent standard

Substance	ppm (v/v)	mg S/m^3	mg compound/m^3
Methylmercaptan (MeSH)	3.7	4.9	7.4
Ethylmercaptan (EtSH)	2.4	3.2	6.2
Dimethyl sulfide (DMS)	2.3	3.1	6.9
2-Propylmercaptan (2-PrSH)	2.4	3.2	7.6
1-Propylmercaptan (1-PrSH)	2.5	3.3	7.9
2-Butylmercaptan (2-BuSH)	2.4	3.2	9.0
1-Butylmercaptan (1-BuSH)	2.4	3.2	9.0

ter was also performed by piercing its septum while the main valve of the gas bottle was open.

2.3. Sample introduction, separation and detection

Samples were injected into a laboratory-built, highly inert thermodesorption/cryofocusing unit [7], which was coupled directly to the analytical column. GC–atomic emission detection (AED) analysis was carried out using an HP 5890 II gas chromatograph coupled to an HP 5921A atomic emission detector (Hewlett-Packard, Palo Alto, CA, USA). The parameters for sample introduction as well as the separation and detection parameters are given in Table 2.

2.4. Quantification

In our previous work [6], a freshly filled 12-l standard Tedlar sample bag had been taken as reference point for the determination of the recoveries. In the course of this stability study, it appeared that a problem with this reference had been accounted (see Results and discussion). Therefore, sampling from the syringe adapter was taken as the reference point for the calculation of the recovery in contrast to our previous publication [6].

Every calibration and the measurement of every data point were carried out threefold, performing the different sampling methods alternately. The standard deviation of the recovery of one data point was calculated from the standard deviations of the peak areas of the calibration and of the data point itself by the law of the propagation of errors.

3. Results and discussion

We would like to point out first that for reasons of availability, the concentrations of the VSCs of the gaseous standard used in this study are higher than the concentrations in the standard used for our previous work [6]. Nevertheless, the same differences in recovery between the Tedlar bags and the Silcosteel cylinders were observed.

The following potential sources of error were taken into consideration to explain the discrepancy of the recoveries from the Silcosteel cylinders and from the standard Tedlar sample bags observed when the stability of selected VSCs in different sample containers was studied [6]: (1) enrichment of the analytes in the Silcosteel sample cylinder; (2) enrichment or losses in the gas-tight syringe used for sampling; (3) analyte losses due to retrieving sample aliquots from the Tedlar bags through the attached tubing instead of piercing the septum; and (4) losses of analytes in the tubing used for filling the bags.

Table 2
Parameters of sample introduction, separation and detection

Cryofocusing time	20 min
Carrier gas flow through thermodesorption/cryofocusing unit	20 ml He/min
Cyrofocusing temperature	−196 °C
Desorption temperature	100 °C
Coupling of thermodesorption unit	On column
Analytical column	GS-Q PLOT (J&W Scientific, Folsom, CA, USA) 25 m×0.32 mm I.D.
Column flow	3 ml/min helium (>99.9996%)
Temperature program	60 °C for 2 min, with 5 °C/min to 130 °C, with 30 °C/min to 240 °C, 2.5 min hold
AED total He flow	20 ml/min
AED reagent gases	2.1 bar O_2 (>99.998%), 0.7 bar H_2 (>99.999%)
Detection wavelengths	181 nm (sulfur), 193 nm (carbon)
Data acquisition rate	5 Hz
Transfer line temperature	290 °C
Cavity temperature	300 °C

A partial enrichment of the analytes on the inner surface of the Silcosteel sample cylinders during purging under higher pressure and later release could be excluded, since the recoveries did not deviate significantly from 100% compared to sampling using the syringe adapter. Enrichment of the analytes on the PTFE parts inside the syringe, when pressurized sample from the Silcosteel cylinders or the syringe adapter was drawn in order to purge the syringe before sampling, is another possible cause of error. A replacement of the PTFE Luer Lock syringe by a removable needle syringe, which has less parts made from PTFE and thus a smaller potentially active surface exposed to the sample inside the glass body, did not result in any significant change in the recoveries. In addition, no significant dependence of the recoveries on the sample pressure could be observed, which would be expected if the air–PTFE partitioning of the analytes was a relevant factor. As a consequence, the syringe can be ruled out as a source of error.

Analyte losses could also occur during sampling from the Tedlar bags. Due to the small sample flow through the valve of the bag, analytes might be adsorbed by the plastic valve. Therefore, calibration by direct sampling of the bag (piercing of the septum with the syringe) was also studied. No significant difference to sampling from an attached tubing could be observed.

Another potential source of error is the silicone tubing, which was used to fill the Tedlar bags. Shortening of the tubing to 5 cm for filling the calibration bag resulted in a drastically reduced difference between the recoveries from the Silcosteel sample cylinder and the standard Tedlar sample bag (Fig. 1). Obviously, the tubing causes analyte losses during filling of the Tedlar bags for calibration, which resulted in the over-estimation of the recoveries of mercaptans from the Silcosteel sample cylinders during the storage experiments reported previously [6]. For this reason, we decided to change the data presentation for the present study and defined sampling using the syringe adapter as 100%. Thereby the term ''over-estimation of the recoveries'' is avoided in the following, since it is misleading. Recoveries higher than 100% usually point to contamination problems, which were not encountered here.
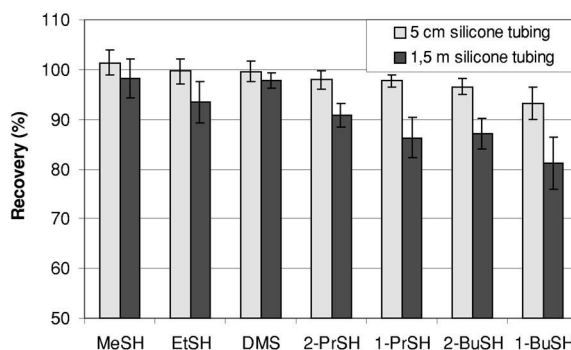

Fig. 1. Dependence of the analyte losses in the standard Tedlar sample bag on the length of silicone tubing used to fill the bag.

Silicone apparently is an effective adsorbent for higher mercaptans, since the extent of the losses is remarkable, taking into consideration the high concentration of the standard used in this work and also the low contact time between analytes and the tubing due to the high gas flow during filling of the bags. This agrees well with the results of the study of Baltussen et al., who used polydimethylsiloxane (PDMS) particles as adsorbent for higher mercaptans, thioethers, -esters and mercaptoalcohols [8]. Although the breakthrough volumes were lower compared to Carbotrap and Tenax, the authors concluded that PDMS is a suitable adsorbent, especially in terms of inertness. However, one has to take into consideration that the absolute amounts of the analytes in the work of Baltussen et al. are several orders of magnitude lower compared to those in our studies. It was therefore not expected that significant losses occur at the high concentrations and at the high flow rates used for filling the bags.

As a consequence, we evaluated other tubing materials using the same tubing dimensions. Fig. 2 shows that PTFE is a better choice than PVC and silicone, although there are still minor losses of higher mercaptans.

4. Conclusion

The procedure for sampling natural gas from pipelines often requires a flexible connection with a certain length of tubing. Particular consideration has thus to be given to the choice of the tubing material.
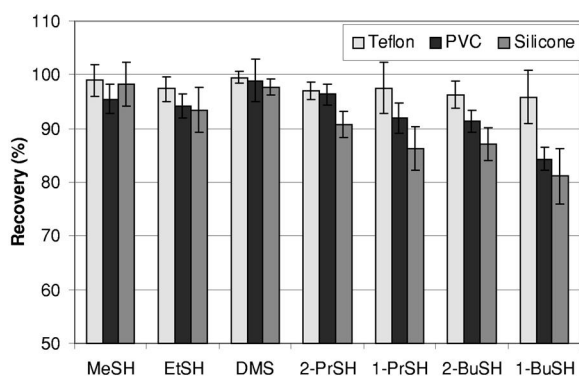
Fig. 2. Dependence of the analyte losses in the standard Tedlar sample bag on the tubing material used for filling the bag (tubing length 1.5 m×3 mm I.D.).

PTFE should be preferred to PVC or silicone, because the latter two cause significant losses of higher ($>C_1$) mercaptans, even if only a tubing length of a few centimetres is used.

The conclusions of the stability study of the VSCs in different sample containers published earlier [6] are still valid, as only the relative changes in the recovery from the different containers were followed in the course of the storage period to evaluate the performance of the different containers. These relative changes were not influenced by the constant systematic error caused by the problems with the calibration system whose source has been disclosed herewith.

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