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Sampling And Stability of Mercaptans: Comparison Between Bags, Canisters and Sorbent Tubes

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In this study the influence of sampling and storage of samples was studied focusing on a number of mercaptans. First the influence of the sampling material on the composition of the sampled gas was studied and secondly the stability of the mercaptans in the different sampling materials is followed over time.

Stainless steel, Teflon and deactivated stainless steel were tested as inlet material for a Nalofane bag. These were compared with sampling using both stainless steel or Silonite treated canisters. As a last sampling strategy, active sampling on sorbent tubes was considered.

The tests indicate the composition during sampling can be changed in presence of untreated stainless steel as this gives rise to the formation of disulfides. Furthermore, the stability over time of the mercaptans after sampling is very limited for the sorbent tubes with great loss of certain mercaptans over a very short period of time (>2 hours). Also in bags the stability is rather limited and the best stability can be obtained using canisters. So for sampling of mercaptans, Silonite or equivalent canisters are the most suitable way to transport the sample to the laboratory. In the lab, the samples should be analysed as quick as possible after sorbing them on tube or by an appropriate direct sampling system.

1. Introduction

The sampling of odour emissions and the stability of odour in different sampling bags has already been studied (e.g. van Harreveld, 2003; Zarra et al., 2012; McGinley et al., 2012) based on olfactometry. Also by chemical analysis different sampling materials, Nalophane, Tedlar and sorbent tubes, have been compared regarding the stability of different odorous compounds in the ppb level. The results indicate only minor differences between the studied bags and a better stability of the evaluated compounds on the sorbent tubes (Boeker et al., 2014). Kim et al. (2012) studied the storage stability of different odorous volatile organic compounds in two types of bag materials indicating some losses were found already after 3 days.

During waste handling, sewage collection and wastewater treatment often sulfur compounds are present in air. These sulfur compounds in air, even in low concentrations, give rise to unpleasant smells. In the surrounding of wastewater, waste management and agricultural practices, volatile organic sulfur compounds are an important component of the odorous emissions leading to annoyance to local populations. The analysis and sampling of these compounds can be troublesome. The sampling step is crucial for the quality of the results for all analysis and the knowledge of the quality of sampling is thus very important to obtain usefull results (Guillot, 2012).

Watson (2016) listed the advantages and disadvantages of tube sampling and canister sampling, indicating that they can offer complementary technology for sampling. So these sampling strategies will be compared in this study with the more common bags sampling used in odour sampling.

Within the sulfur compounds, mercaptans have very low odour threshold levels (see Table 1). Mercaptans tend to absorb onto the surface and may undergo partial oxidation. Some of these were already studied by Le et al. (2013) to find the influence of temperature on the stability of the volatile sulfur compounds in sampling bags. Previously Sulyok et al. (2001) compared the stability of some volatile sulfur compounds in two type of bag materials and a Silcosteel canister. Until now, the stability of volatile sulfur compounds was not investigated on sorbent tubes. In this study the stability of mercaptans will be studied in bags, canisters and sorbent tubes.

Table 1: Odour threshold level (OTV) of mercaptans

CAS no	Name	OTV(1) (µg/m³)
74-93-1	methyl mercaptan	0.1 – 2
75-08-1	ethyl mercaptan	0.03 – 3
107-03-9	1-propyl mercaptan	0.04 - 4
75-33-2	2-propyl mercaptan	0.02 – 1.1
513-44-0	2-methyl-1-propyl mercaptan	0.03 – 4
75-66-1	2-methyl-2-propyl mercaptan	0.03 – 1.3
109-79-5	1-butyl mercaptan	0.01 – 5
513-53-1	2-butyl mercaptan	0.1 – 0.7

(1) Devos et al. 1990 and Nagata et al. 2003

2. Materials and methods

2.1 Standard and sampling materials

A gas standard of 10 ppm of each of the mercaptans (methyl, ethyl, 1-propyl, 2-propyl, 2-methyl-1-propyl, 2-methyl-2-propyl, 1-butyl and 2-butyl mercaptan) (Air Products) was used as starting concentration. Dilutions were made using a CMK 5 calibration system model (MCZ Umwelttechnik).

Sample bags were made from Nalofane^{TM} and the bag inlet either of Teflon, stainless steel or deactivated stainless steel. Deactivation of the stainless steel inlet was done with 15% BSTFA (N,O-Bis(trimethylsilyl)trifluoroacetamide) in hexane (NCASI, 2007).

For the connection of the bag to the sorbent tube either a stainless steel or Siltek treated steel union (Swagelok) was used.

Two types of canisters were used, stainless steel canisters (Analytical Industries Inc) and Silonite canisters (Entech Instruments Inc).

2.2 Analysis

SulfiCarb adsorption tubes (Markes Ltd) were used for adsorption of the gases. Analysis of the mercaptans was done by TD-GC-MS (Markes TD100, Shimadzu GC 2010-plus and Shimadzu MS GP2010 SE). The thermal desorption program was modified to reduce possible reaction of mercaptans to disulfides based on TDTS 32 (Markes, 2012). In the Markes TD100 all parts are inert (sulfinert parts) to avoid formation of disulfides, the trap is filled with the same sorbent as the tubes (SulfiCarb). The temperature of the valve, cold trap heat and interface were set at a lower temperature (120°C), this results in a better respons for the mercaptans and a lower concentration of disulfides. No disulfides were observed during the experiments which can originate from the thermal desorption process.

2.3 Performed tests

Initially the difference between treated and untreated steel was tested both for the use of bag inlet and union. Also the use of Teflon inlet was compared with the other inlets.

Stability over time was tested for all bag types during 48 h. For the canisters, stability was evaluated up to 16 days. Also the adsorption tubes stability was first evaluated over 16 days and then also on a shorter time period. Stability was tested for different concentrations (10 ppm, 1 ppm and 50 ppb).

3. Results and discussion

3.1 Use of stainless steel, deactivated/Siltek steel or Teflon as inlet or union

It can be clearly seen in Figure 1 and Figure 2 that the concentration of mercaptans are reduced (and the concentration of disulfides is increased) due to the presence of stainless steel in the inlet.

This shows the mercaptans are oxidized to disulfides in the presence of stainless steel which can be explained by the heavy metal oxides at the surface of the stainless steel (Oae, 1991) . One-electron oxidants such as Fe(III) and Mn(III) which are present in the surface of the stainless steel are known to catalyse the auto oxidation of thiols (Sheldon et al., 1981). The results of the Teflon inlet were similar to the results of the deactivated steel inlet. So for sampling mercaptan containing gases, the use of stainless steel in contact with the sample should be avoided. Here the reduction of mercaptans is measured chemically indicating reduction will take place and thus sampling and analysis of these gases should be performed without contact with stainless steel.

The results of the stainless steel union and the Siltek treated union also showed a reduction of the mercaptans when using the stainless steel union while almost no disulfides were detected when the Siltek treated union was used.

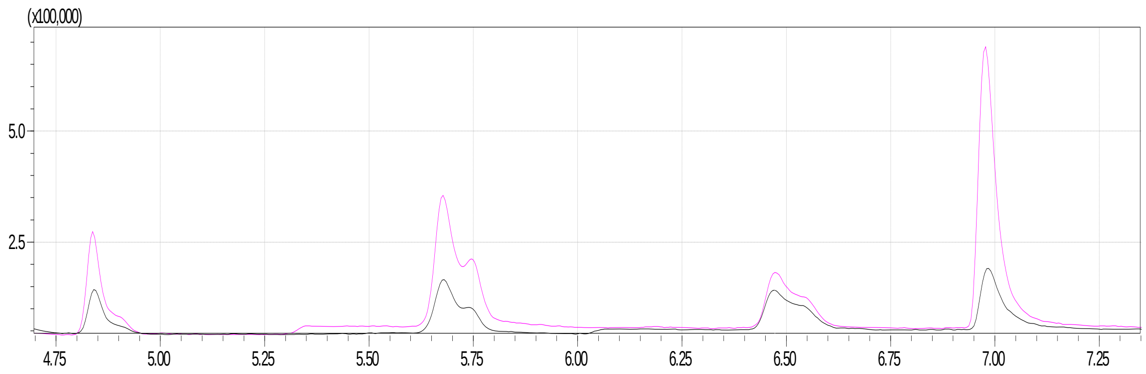

Figure 1: Chromatogram of a deactivated metal inlet (pink/light grey) and a normal metal inlet (black) for ethyl mercaptan (RT 4.85), 2-propyl mercaptan (RT 5.68), 2-methyl-2-propyl mercaptan (RT 6.47) and 1-propyl mercaptan (RT 6.98)

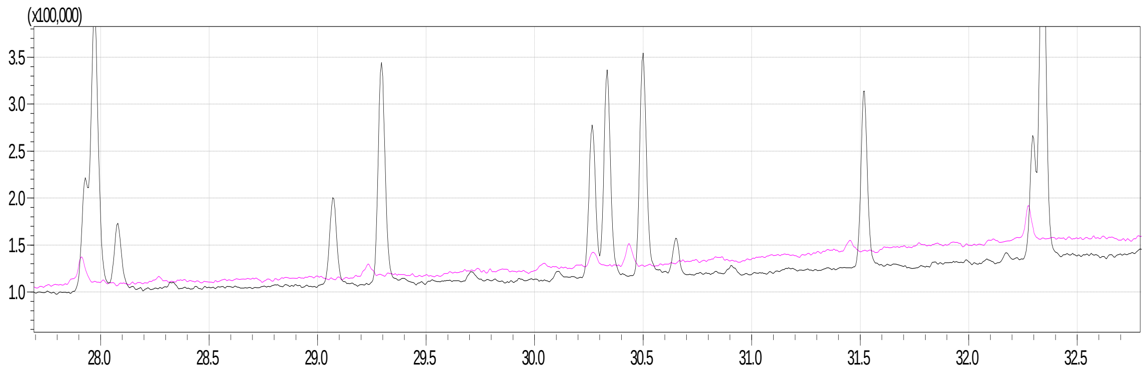

Figure 2: Chromatogram of a deactivated metal inlet (pink) and a normal metal inlet (black) showing some disulfide peaks

3.2 Stability of mercaptans in different sampling bag inlets

The results for a deactivated inlet are shown in Table 2.

Table 2: Recovery (%) of mercaptans during 24 hours in a Nalofane sampling bag for 10 ppm

	1h	2h	3h	4h	5h	8h	24h
Methyl mercaptan	93	78	80	59	49	51	48
Ethyl mercaptan	100	98	100	84	85	91	98
2-propyl mercaptan	101	101	105	92	95	101	105
2-methyl-2-propyl mercaptan	101	97	105	89	91	99	102
1-propyl mercaptan	100	102	104	92	96	100	107
2-butyl mercaptan	101	102	105	95	98	103	105
2-methyl-1-propyl mercaptan	102	101	105	95	98	103	107
1-butyl mercaptan	101	100	103	92	96	100	100

The concentration of methyl mercaptan decreases after 4 hours, all other compounds are more or less stable within 24 hours. These results are in line with those found by Le et al. (2013) where after 24 hours the of methyl mercaptan only showed a recovery of around 75% at 30°C. Also Sulyok et al. (2001) found a decrease of this compound already after a short period of time after storage in a bag (< 24 h).

The results of the other concentrations and the other inlets showed similar results, indicating the use of stainless steel inlets doesn’t influence the stability over time. So the disulfides are only formed during sampling and by passing through the inlet, during storage no changes can be seen between the different inlets.

3.3 Stability of mercaptans in different canisters

The results of the stability of the Silonite canister can be found in Table 3. The concentrations of methyl mercaptan are not reported as the time between sampling and analysis was not constant and leaded to unstable measurements for this compound.

Table 3: Recovery (%) of mercaptans during 16 days in a Silonite canister for 1 ppm

Compound/Time	1	2	4	8	16
Ethyl mercaptan	79	92	85	100	71
2-propyl mercaptan	98	93	96	101	92
2-methyl-2-propyl mercaptan	105	100	104	105	107
1-propyl mercaptan	92	91	92	100	86
2-butyl mercaptan	99	96	100	103	94
2-methyl-1-propyl mercaptan	97	96	99	102	97
1-butyl mercaptan	97	95	95	101	91

Even after 16 days the recoveries are still quiet high, only for ethyl mercaptan a substantial decrease is seen in the results. But this could possibly be explained by the difference in time between sampling and analysis (as this was not constant during the testing period). Also a comparable Silcosteel canister showed good recoveries for ethyl mercaptan (Sulyok et al., 2001).

The stainless steel canister was only tested for 6 days but shows similar results, so for the canisters the contact with stainless steel does not result in a reduction of the mercaptans over time (see Table 4).

Table 4: Recovery (%) of mercaptans during 16 days in a stainless steel canister for 1 ppm

Compound/Time	1	2	3	6
Ethyl mercaptan	90	97	101	95
2-propyl mercaptan	86	86	106	94
2-methyl-2-propyl mercaptan	93	91	113	97
1-propyl mercaptan	82	87	104	94
2-butyl mercaptan	89	86	103	96
2-methyl-1-propyl mercaptan	88	86	102	92
1-butyl mercaptanl	86	86	95	89

So during storage the concentration is not effected but the concentration found in the Silonite canister at the start was 1.02 ppm while the concentration in the stainless steel canister was only 0.85 ppm

3.4 Stability of mercaptans on adsorbent tubes

Except from SulfiCarb adsorption tubes, also some other type of tubes (Carbopack, Carbograph) were used. But as these tubes were not deactivated or Silco/Silonite treated, large peaks of disulfides could be found in the resulting analyses. These lead to wrong results for the mercaptans and thus these tubes were not further investigated.

Two concentrations of mercaptans (1 ppm and 50 ppb) were loaded on all tubes at the same time. Tubes were stored at room temperature and analysed at different time intervals (0, 1, 2, 4, 8 and 16 days). The recoveries are shown in Table 5.

It is clear concentration of methyl and ethyl mercaptan has decreased a lot even after 1 day. Also for 1-propyl and 2-propyl mercaptan show a strong decrease (>10 %) already after 2 days. Based on this test, also the stability over a shorter period (30 h) was checked, the results are shown in Table 6. During the test, the samples were stored in the TD100 before analysis.

Table 5: Recovery (%) of mercaptans during 16 days on a tube for 1 ppm

Compound/Days	1	2	4	8	16
Methyl mercaptan	40	31	30	28	11
Ethyl mercaptan	48	18	9	3	3
2-propyl mercaptan	90	81	66	35	11
2-methyl-2-propyl mercaptan	95	90	89	66	48
1-propyl mercaptan	88	76	77	53	19
2-butyl mercaptan	98	102	109	100	75
2-methyl-1-propyl mercaptan	95	100	104	97	73
1-butyl mercaptan	93	94	98	89	62

Table 6: Recovery (%) of mercaptans during 28 h on a tube for 1 ppm

Compound/Time	0u30	1u	1u30	2u	3u	4u	6u30	9u	11u15	13u30	18u	22u45	27u45
Methyl mercaptan	99	120	78	59	39	34	34	26	32	22	18	19	18
Ethyl mercaptan	101	103	100	92	72	63	58	40	41	27	17	14	11
2-propyl mercaptan	106	104	108	106	109	102	101	99	90	89	78	67	62
2-methyl-2-propyl mercaptan	109	111	115	114	120	111	115	114	106	109	101	91	96
1-propyl mercaptan	106	106	106	105	102	97	97	86	86	78	64	61	46
2-butyl mercaptan	105	105	108	107	112	107	108	107	103	107	107	105	101
2-methyl-1-propyl mercaptan	107	105	105	108	114	105	108	107	104	108	108	104	99
1-butyl mercaptan	105	105	105	107	109	104	104	100	100	97	95	93	82

For methyl mercaptan the decrease of mercaptans starts already after one and a half hour. The decrease after 24 hours is even bigger in this stability test compared to the test over 1 day, this can probably be attributed to the storage of the tubes before analysis. For the last test, the tubes were stored inside the TD100 while for the other test the tubes were stored in the lab at room temperature. Storage on sorbent tubes is thus not possible when mercaptans are of interest in the analyses, in that case the use of Silonite or equivalent canisters is recommended. Indicating as already stated by Watson et al. that canisters and sorbent tubes provide complementary sampling technology.

4. Conclusion

When sampling odorous gases which contain mercaptans, the contact of the sample with stainless steel should be avoided to minimize the reduction of mercaptans to disulfides. This reduction may lead to different odour concentrations as the odour threshold levels of mercaptans differ from disulfides.

During storage no influence of the inlet material or the type of canister is seen on the concentration of the mercaptans due to contact with stainless steel, indicating the reaction takes place immediately and the active sites on the metal get deactivated ones the mercaptans have passed.

The stability of mercaptans on sorbent tubes is very short (< 2 h), so samples should be analysed immediately after adsorption on tube or should be adsorbed directly onto the trap out of the canister. For appropriate sampling and storage a Silonite or equivalent canister is thus recommended to avoid oxidation of mercaptans during sampling and loss of mercaptans during storage.

References

Boeker P., Leppert J., Shulze Lammers P., 2014, Comparison of odorant losses at the ppb-level from sampling bags of NalophaneTM and TedlarTM and from adsorption tubes, Chemical engineering transactions, 40, 157-162

Devos M., Patte F., Rouault J., Laffort P., Gemert L. J., 1990, Standardized human olfactory thresholds, IRL Press Oxford, UK

Guillot J.M., 2012, Odour measurement: focus on main remaining limits due to sampling, Chemical engineering transactions, 30, 295-300

Le H., Sivret E.C., Parcsi G., Stuetz R.M., 2013, Stability of volatile sulfur compounds (VSCs) in sampling bags – impact of temperature, Water science & technology, 68 (8), 1880-1887

Kim Y.-H., Kim K.-H., Jo S.-H., Jeon E.-C., Sohn J.R., Parker D.B., 2012, Comparison of storage stability of odorous VOCs in polyester aluminium and polyvinyl fluoride Tedlar bags, Analytica Chimica Acta, 712, 162-167

Markes Ltd, Application note TDTS 32 The analysis of sulfur compounds using on-line and off-line TD-GC-MS, 2012

McGinley C., Henningsen S., Tuday M., McGinley C., McGinley M., 2012, Chemical and odor evaluation of various potential replacement films for sampling bags, Specialty conference: Odors and air pollutants 2012, Louisville, KY

Nagata Y, 2003, Measurement of odor threshold by triangle odor bag method. Odor Measurement Review, 118-127, Japan Ministry of the Environment

Oae S., Doi J., 1991, Organic Sulfur Chemistry, Volume 1: Structure and Mechanism, CRC Press, Boca Raton

Sheldon R.A., Kochi J.K., 1981, Metal catalysed oxidation of organic compounds, Academic press, New York

Sulyok M., Haberhauer-Troyer C., Rosenberg E., Grasserbauer M., 2001, Investigation of the storage stability of selected volatile sulfur compounds in different sampling containers, Journal of chromatography A, 917, 1-2, 367-374

van Harreveld A.Ph.T., 2003, Odor concentration decay and gas stability in gas sampling bags, journal of the air & waste management association, 53(1), 51-60

Watson N.M., Cooper D., Tube sampling versus canister sampling – the pros and cons of each approach, http://events.awma.org/education/Posters/Final/Cooper_Poster.pdf accessed 07.03.2016

Zarra T., Reiser M., Naddeo V., Belgiorno V., Kranert M., 2012, A comparative and critical evaluation of different sampling materials in the measurement of odour concentration by dynamic olfactometry, Chemical engineering transactions, 30, 307-312