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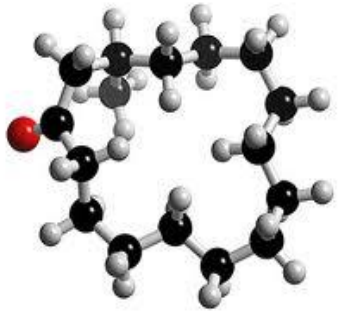
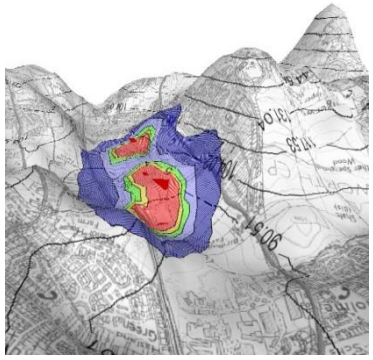
Sampling and analysis of mercaptans


Kurt Haerens

Emissions and Odours from Materials 2015
09/10/2015

Overview

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- Introduction

- Materials and methods

- Sampling of mercaptans
- Analysis of mercaptans
- Stability of mercaptans
- Analysis of sulphur compounds in complex matrices

- Conclusion

Introduction

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- Environmental consultancy around odours

- Chemical analysis of air by:
  - TD-GC-MS
  - TD-GC-MS/Sniffing
  - TD-GC-MS/FPD

Introduction

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Mercaptan or thiol:

R-SH

sulphur analogue of alcohol

strong odour

Odour threshold of mercaptans/thiols

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

Very reactive, not thermally stable and very volatile

1 Devos et al, 1990
2 Nagata et al, 2003

Materials and methods

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Analysis:

- Markes TD100 or Shimadzu TD20
- Shimadzu GC 2010
- Shimadzu MS GP2010 SE/Plus

Sampling:

- Stainless steel
- Deactivated stainless steel (deactivated or siltek treated)
- Teflon

Materials and methods

Deactivation of stainless steel:

- 15% BSTFA (N,O-Bis(trimethylsilyl)trifluoracetamide) in hexane*

Sorbent tubes:

- Tenax TA (Markes Ltd) stainless steel or inert coated
- Sulficarb (Markes Ltd) inert coated

* NCASI method rsc-02.0, 2007

Sampling of mercaptans

Bag inlet:

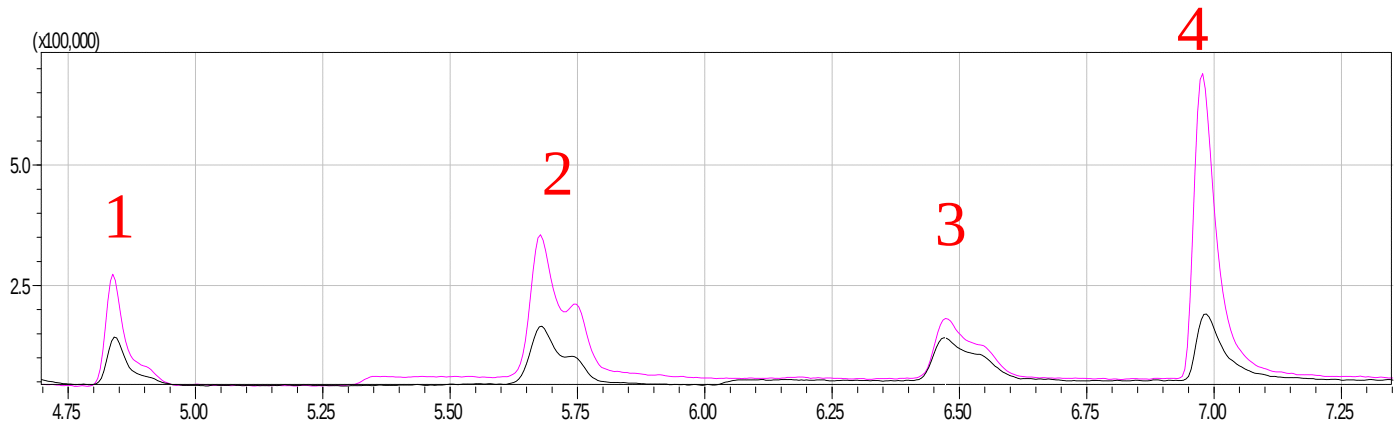
- Stainless steel
- Deactivated stainless steel
- Teflon

Union:

- Stainless steel
- Siltek treated steel

Results sampling

Chromatogram of a deactivated metal connector (pink) and a normal metal connector (black)



1 - ethyl mercaptane (RT 4.85)

2 - 2-proyl mercaptane (RT 5.68)

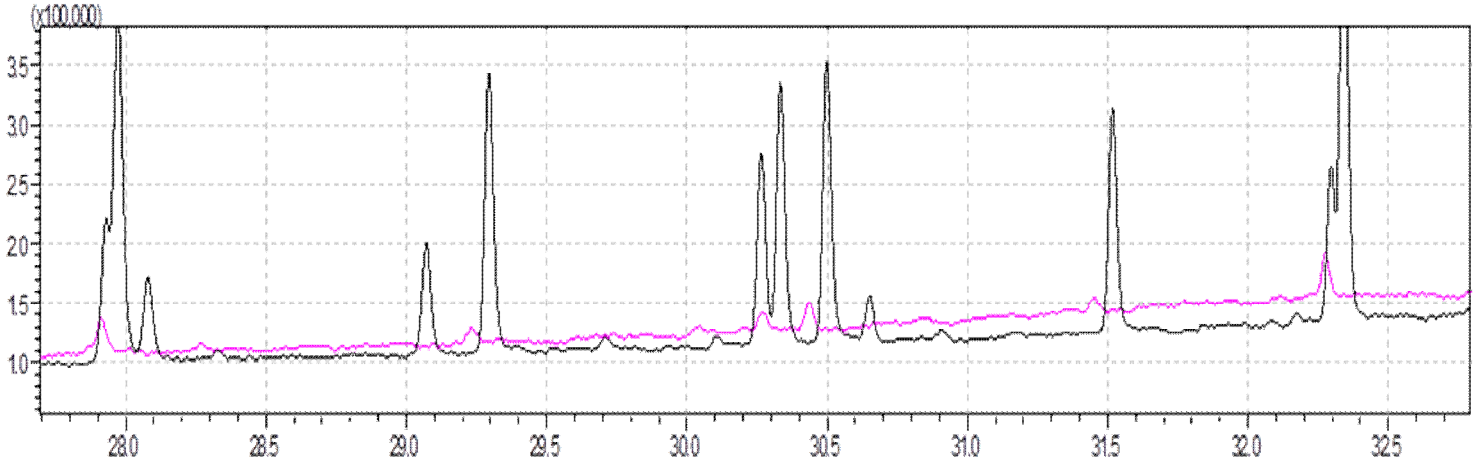
3 - 2-methyl-2-propyl mercaptane (RT 6.47)

4 - 1-proyl mercaptane (RT 6.98)

Results of teflon similar to deactivated metal

Results sampling

Chromatogram of a desactivated metal connector (pink) and a normal metal connector (black)



Disulfide peaks

Use of stainless steel union and Siltek steel gives similar results

Disulfides formed due to presence of metal

Analysis of mercaptans

TD conditions were altered

- Lower trap desorption temperatures
- Lower temperature of transfer line (as higher temperatures lead to formation of disulfides)

GC program: 33 to 220 ° C at 15° C/min

MS SIM ï target ions of the different mercaptans combined with SCAN (28.5-100)

Special calibration standard (10 ppm of 8 mercaptans) (Air Products)

Analysis of mercaptans

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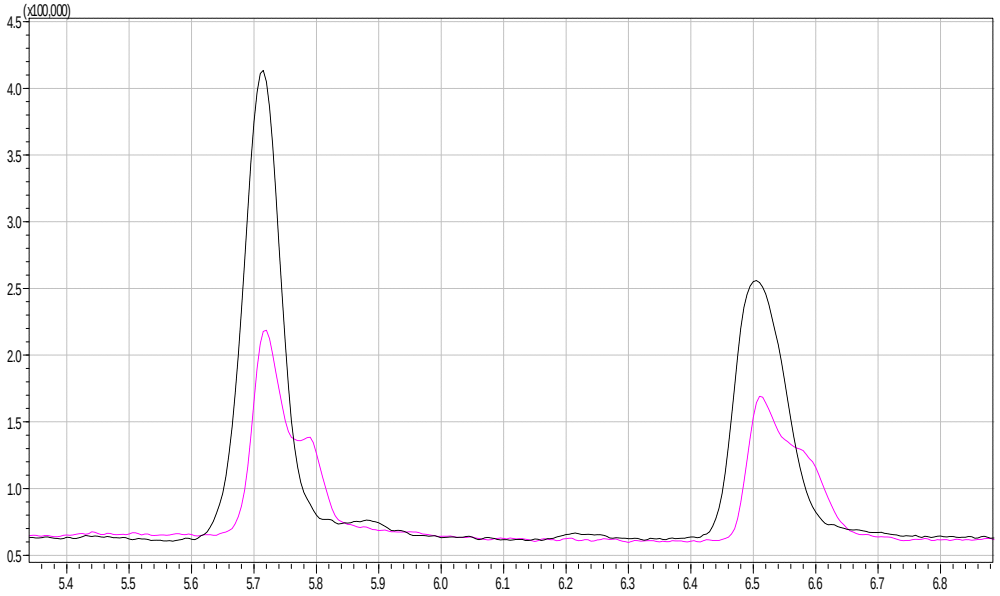
Selection of sorbent:

- Breaktrough for Tenax TA (100 ml) < SulfiCarb (200 ml)
- Sometimes strange peak shape when using SulfiCarb



Chromatogram of ethyl mercaptan and 2-propyl mercaptan for Tenax TA (black) and SulfiCarb (pink)

Analysis of mercaptans

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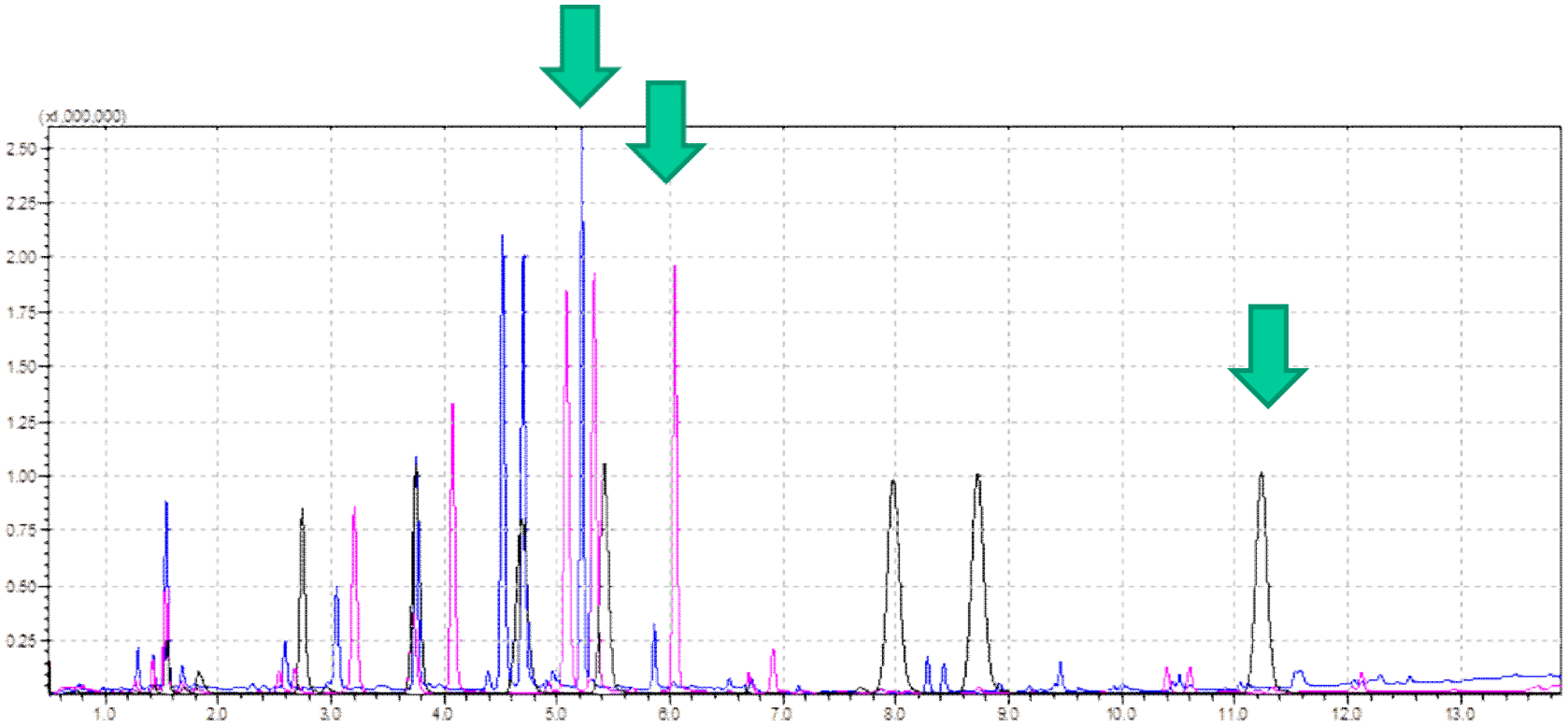
Influence of temperature program of GC



Black: 33° C → 42° C (1° C/min) → 50° C (2° C/min)

Pink: 33° C → 220° C (10° C/min)

Blue: 33° C → 220° C (15° C/min)

Analysis of mercaptans

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Limit of Detection for different mercaptans

CAS no	Name	OTV[1,2] (µg/m³)	LOD (µg/m³)
74-93-1	methyl mercaptan	0.1 ï 2	1.5
75-08-1	ethyl mercaptan	0.03 ï 3	0.4
107-03-9	1-propyl mercaptan	0.04 - 4	0.5
75-33-2	2-propyl mercaptan	0.02 ï 1.1	0.5
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75-66-1	2-methyl-2-propyl mercaptan	0.03 ï 1.3	0.9
109-79-5	1-butyl mercaptan	0.01 ï 5	0.5
513-53-1	2-butyl mercaptan	0.1 ï 0.7	0.6

Stability of mercaptans in bag

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Concentration 10 ppm in Nalofane bag

Recovery (%)

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

Stability of mercaptans

Also on sorbent tube after 1 day decrease in recovery:

- Methyl mercaptan: 57%
- Ethyl mercaptan: 54%
- 2-propyl mercaptan: 87%

No recollection possible

What with lower concentrations?

Alternative sampling using canisters for longer sample stability?

Analysis of sulphur compounds in complex matrices

Example:

- Headspace of crude oil analysed by TD-GCMS

=> almost no sulphur compounds detected

Analysis of sulphur compounds in complex matrices

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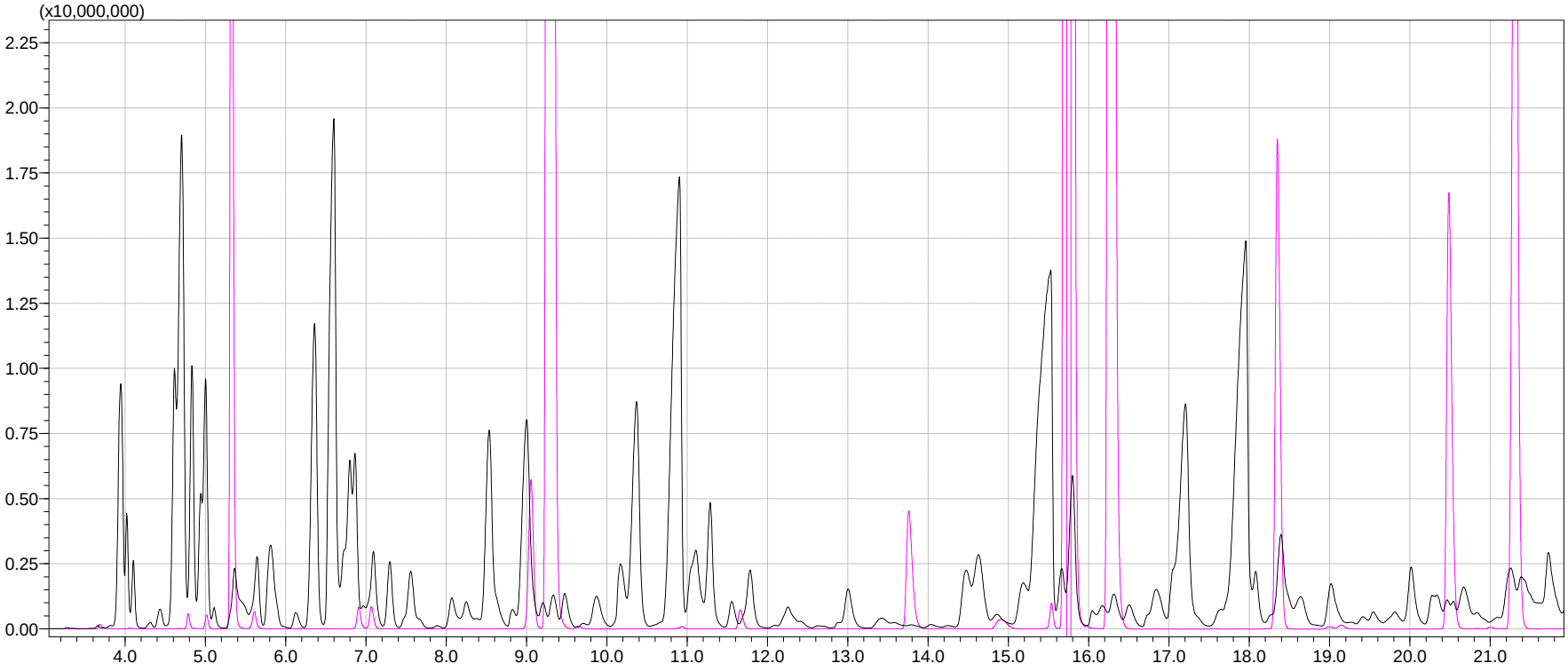
Use of GC-MS/FPD

MS-chromatogram (black) and FPD-chromatogram (pink)



Analysis of sulphur compounds in complex matrices

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Now database based on RT and target ions for identification

6	RT (min)	CODE (S,M,T,A)	Component	Ion 1	Ion 2	Ion 3	ION	Area (fragment)	Concentratie µg/m³
7	4.839	M	ethaanthiol	62	29	47	62	89256	51.8
8	5.057	S	dimethylsulfide	62	47	45	62	56895	22.4
9	5.375	S	carbondisulfide	76	44	-	44	21456	19.7
10	5.673	M	2-propaanthiol	76	43	61	43	36987	13.7
11	6.238	S	ethyleensulfide	45	60	59	45	105896	33.9
12	6.971	M	1-propaanthiol	76	41	47	76	47856	28.6
13	9.385	T	thiofeen	84	58	45	58	58468	19.4
14	13.901	S	dimethyldisulfide	94	45	79	94	89752	21.4
15	15.856	T	2-methylthiofeen	97	98	45	98	200458	60.9
16	16.423	S	methylethyldisulfide	108	80	29	108	68754	40.8

Usefull analysis to detect sulphur compounds in complex matrices

Conclusions mercaptans

Sampling:

- Use of stainless steel => formation of disulfides
- Teflon, deactivated SS or Silco treated steel should be used

Detection limit is close to the odour threshold of the mercaptans

Stability:

- For high concentrations only 1 hour in bag and up to 1 day on sorbent tube
- To be tested for lower concentrations (ppb-level)
- Use of canisters for sampling for better stability?

Thank you for your attention!

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