Matrix influence on the analysis of sulfur-containing compounds in hydrogen enriched natural gas and hydrogen with GC-SCD

Roel Beelen, Adriaan van der Veen, Annarita Baldan, Johan de Boed, Cas de Jong

VSL, Thijsseweg 11, 2629 JA Delft, the Netherlands (contact: rbeelen@vsl.nl)

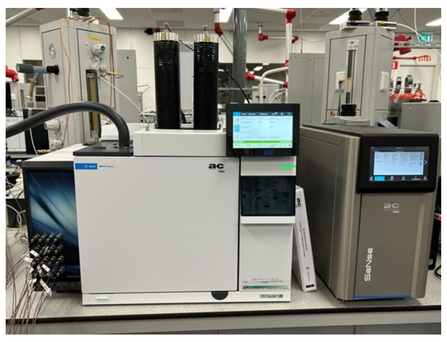
Introduction

The introduction of hydrogen in natural gas and pure hydrogen grids poses new challenges for the analysis of sulfur-containing compounds. Current gas chromatographic methods are fit-for-purpose for the analysis of sulfur-containing compounds in natural gas (e.g., hydrogen sulfide), but may suffer from matrix effects if samples of hydrogen-enriched natural gas or hydrogen are processed.

The matrix effects in sulfur analysis in natural gas, hydrogen-enriched natural gas and hydrogen are evaluated to assess the applicability of the standard ISO 19739 (Natural gas — Determination of sulfur compounds using gas chromatography) for µmol/mol-levels of sulfur-containing compounds in hydrogen-enriched natural gas and hydrogen.

Experimental equipment

Analytical system



The measurements were performed using a GC/SCD (Gas chromatography / Sulfur Chemiluminescence Detector), which is a highly-sensitive sulfur-selective detector for gas chromatography.

The system is also equipped with an FID (flame ionization detector) which was used for comparison. Gaseous mixtures are connected to the system via a multiposition valve and a sample shut-off valve.

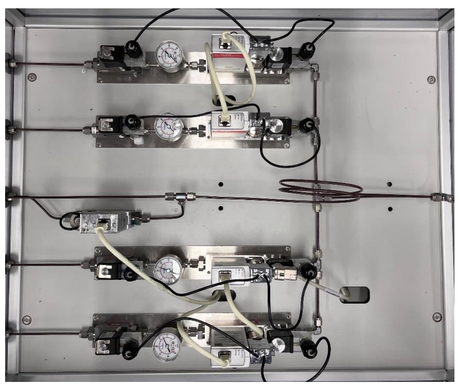
Agilent 8890	Column	Inlet type	Sample loop	Carrier	Column flow	Expanded Uncertainty (%)
FID channel	PDMS-1 60 m x 0.53 mm x 5 µm	-	250 µL	hydrogen	5 ml/min	1 %
SCD channel (SeNse)	PDMS-1 60 m x 0.53 mm x 5 µm	split/splitless	1 mL	hydrogen	10 ml/min	2 %

Matrix effects compared using Primary Standard Mixtures (ISO 6142-1)

Primary Standard gas mixtures (PSMs) are gravimetrically produced in high-pressure cylinders with a suitable passivation, in accordance with ISO 6142-1. Ethyl mercaptan (EtSH) and dimethyl sulfide (DMS) were introduced as liquid into the evacuated cylinder using the syringe method, the other sulfur components as gases.

Matrix effects compared using a dynamic dilution system (ISO 6145-7)

A dynamic dilution system is designed and passivated to generate standard gas mixtures or to dilute a primary standard gas mixture to a known amount of fraction with the desired matrix gases.



Equipped with 5 mass flow controllers (MFC's), 4 of which are dedicated for pure (matrix) gases (H_2, N_2, CH_4, CO_2) and 1 MFC for reactive gas mixtures. All MFCs are calibrated for the used gases using VSL's calibrated piston prover, giving an uncertainty of 0.5 % on a dynamically generated mixture.

Experiments

Matrix effects compared using Primary Standard Mixtures (ISO 6142-1)

VSL's hydrogen sulfide (H_2S) PSM's have been analysed to record several calibration curves of different amount fractions H_2S with the same matrix gas. H_2S PSM's with different matrices were compared using these calibration curves according to ISO 6143, to investigate the deviation from gravimetry.

Calibration Curve PSM's	Matrix effect PSM's	Matrix effect PSM's
0.3 – 2.5 µmol/mol H_2S in H_2	1 & 1 µmol/mol H_2S in N_2	1 & 1.8 µmol/mol H_2S in CH_4
5 – 30 µmol/mol H_2S in N_2	10 µmol/mol H_2S in H_2	10 & 20 & 30 µmol/mol H_2S in CH_4

Matrix effects compared using a dynamic dilution system (ISO 6145-7)

The dynamic dilution system was used to dilute sulfur-containing PSM's to an amount of fraction of 5 or 50 µmol/mol.

The dilutions were performed for several matrices and the amount of fraction were calculated according to ISO 6145-7. By keeping the reactive MFC at the same setting and changing the matrix gas the effect of the gas matrices on the SCD could be observed. By measuring both detector channels a sample introduction effect could be eliminated.

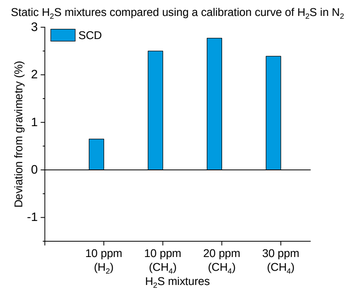
Amount fraction PSM	Amount fraction dilution	Matrix gas 1	Matrix gas 2	Matrix gas 3	Matrix gas 4
100 µmol/mol DMS in N_2	5 µmol/mol	N_2	H_2*	CH_4*	20 % H_2, balance CH_4*
100 µmol/mol DMS in N_2	5 µmol/mol	N_2	H_2*	CH_4*	20 % H_2, balance CH_4*
928 µmol/mol DMS in N_2	50 µmol/mol	N_2	H_2*	CH_4*	-
100 µmol/mol H_2S, COS, MeSH and EtSH in CH_4	5 µmol/mol	CH_4	20 % H_2, balance CH_4	H_2*	N_2*

*Contains also 5 % of the matrix gas of the original PSM

Using a single point calibration in accordance with ISO 12963 the difference between the calculated amount of fraction and the value from analysis were calculated, using the nitrogen result as reference.

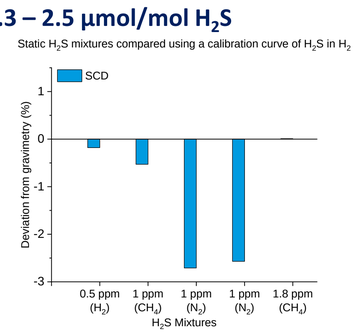
Matrix effects comparing static mixtures

5 – 30 µmol/mol H_2S



The measurement indicate a positive deviation from the gravimetry (≥ 2 %) for all three H_2S in CH_4 PSM's when verified against H_2S standards in N_2. For the H_2S in H_2 standard no significant matrix effect is observed.

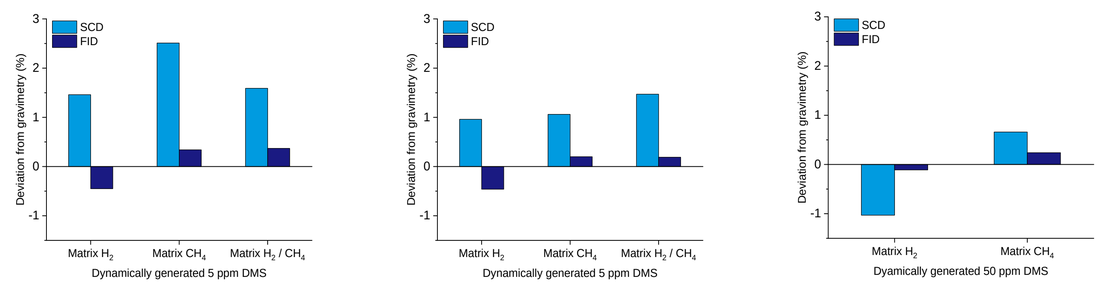
0.3 – 2.5 µmol/mol H_2S



The measurement indicate a negative deviation from gravimetry (≥ 2 %) for both H_2S in N_2 PSMs when verified against H_2S standards in H_2. For both H_2S in CH_4 standards no significant matrix effect is observed.

Matrix effects comparing dynamic mixtures

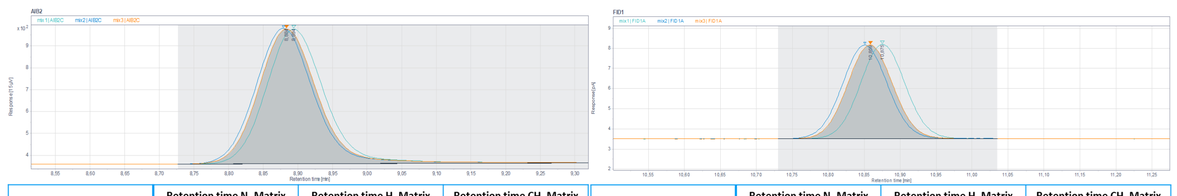
Dynamically generated 5 and 50 µmol/mol DMS mixtures in different gas matrices



The deviations between DMS in H_2, CH_4 and H_2-enriched CH_4 gas matrices are consistent on the SCD within the measurement uncertainty, there is a positive deviation of (≥ 1 %) compared to DMS in N_2.

The FID results show smaller deviations, which makes an injection effect less likely. Within the measurement uncertainty no matrix effect can be observed, although the DMS in H_2 is showing a negative trend.

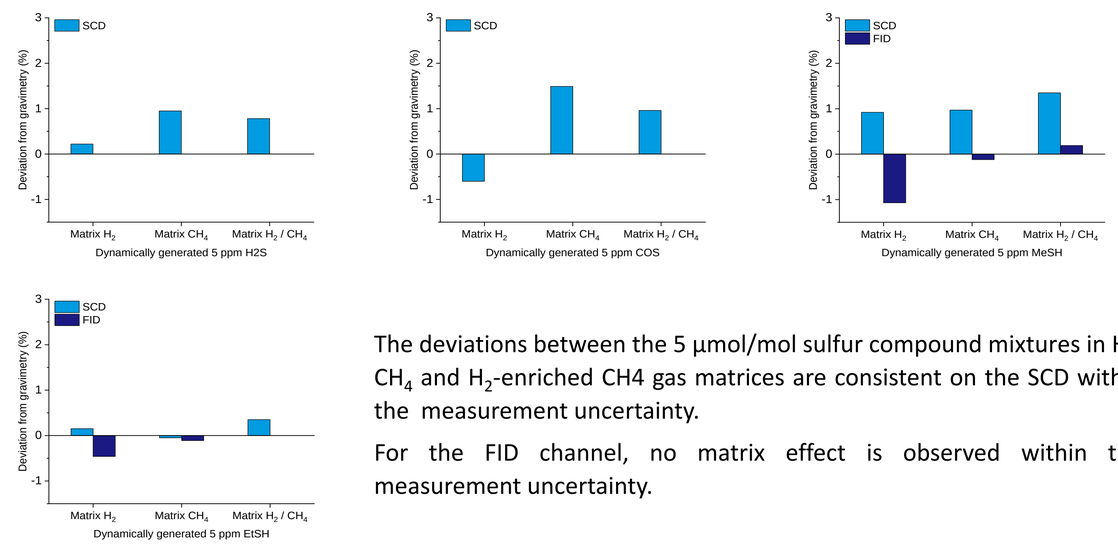
Chromatogram dynamically generated 5 µmol/mol DMS mixtures in different gas matrices



Detector	Retention time N_2 Matrix (minute)	Retention time H_2 Matrix (minute)	Retention time CH_4 Matrix (minute)	Detector	Retention time N_2 Matrix (minute)	Retention time H_2 Matrix (minute)	Retention time CH_4 Matrix (minute)
SCD	8.894	8.879	8.884	FID	10.875	10.851	10.859

The matrix gas has an effect on the retention time of the analyte, the effect is occurring on both channels.

Dynamically generated 5 µmol/mol H_2S, COS, MeSH and EtSH mixtures in different gas matrices



The deviations between the 5 µmol/mol sulfur compound mixtures in H_2, CH_4 and H_2-enriched CH4 gas matrices are consistent on the SCD within the measurement uncertainty.

For the FID channel, no matrix effect is observed within the measurement uncertainty.

Conclusions

- For the comparison of sulfur containing Primary Standard Mixtures there are matrix effects, but for most of the measurement practices in the field these differences will not be significant
- The matrix effects between sulfur compounds in H_2, CH_4 and H_2-enriched CH_4 are not significant within the measurement uncertainty of the SCD
- The SCD is more prone to matrix effects than the FID
- There are methods available to prepare and verify sulfur containing mixtures in different type of gas matrices

Funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or EURAMET. Neither the European Union nor the granting authority can be held responsible for them.

The project has received funding from the European Partnership on Metrology, co-financed from the European Union's Horizon Europe Research and Innovation Programme and by the Participating States.