



## GC-IMS INDUSTRIAL

### INTRODUCTION

Generally, a catalyst poison is a substance that reduces the effectiveness of a catalyst in a chemical reaction. Most reactions are irreversible and accumulation of poisonous compounds continuously reduce the facility's output.

The deactivation of heterogeneous catalysts in industrial processes causes a damage of billions of dollars per year caused by catalyst replacement and process shutdown.<sup>1</sup> Besides the loss of costly catalysts, the deactivation has a great impact on the final product's quality, hence the prevention of deactivation mechanisms and regeneration of catalysts plays an important role in today's industry.

Because new catalysts are expensive, causing high disposal costs and underlying stringent environmental regulations, regeneration often is the better choice. The world market of catalyst regeneration reached ~84 million US\$ in 2019 and is expected to grow significantly in the following years.<sup>3</sup>

Common compounds, which act as catalyst poisons, are carbon monoxide, halides, cyanides, sulfides, sulfites, phosphites. Likewise, organic molecules such as nitriles, nitro compounds, oximes and nitrogen-containing heterocycles may have a poisonous effect on catalyst materials too. Sulfur species are catalyst poisons especially for processes involving reduced metals when applied as active phase. Due to its strong metal-S bond, even at very low concentrations sulfur may cause a significant deactivation of the catalyst active sites.<sup>2</sup>

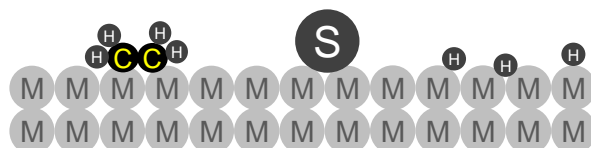


Figure 1: Schematic drawing of sulfur poisoning in ethene ( $\text{CH}_4$ ) hydrogenation process. A sulfur atom (S) strongly binds to the catalyst (M) metal surface, reducing the catalytic activity by the following exemplary effects:<sup>1</sup>

- Sterically blocking adsorption/reaction sites of the catalyst (also inhibiting lateral diffusion)
  - Electronically modification of catalyst surface
- Taken from [4]. Copyright 2006, Wiley-Interscience.

Since poisoning is generally caused by trace contaminants in the feed, reactants or products, the responsible compounds should be removed to levels that will ensure the catalysts' activity, which are typically located in the low or sub-ppb range. For this reason sensitive online-monitoring of compounds, which exhibit a poisonous effect on the catalyst, is needed.

The combination of gas chromatography and ion mobility spectrometry (GC-IMS) enables highest separation efficiency (2-dimensional separation), which is orthogonal and advantageous to separate matrix from analyte signals. Due to the high scanning rate (typically 20-30 ms) of the detector, fast GC runs are possible while providing high resolution. Furthermore the intrinsic sensitivity qualifies IMS as an appropriate tool for the detection of compounds in the low or sub-ppb range.

[1] Argyle, M.D.; Bartholomew, C.H. Heterogeneous Catalyst Deactivation and Regeneration: A Review. *Catalysts* 2015, 5, 145-269.

[2] Global Catalyst Regeneration Market Report 2019 - Industry Research Report by Manufactures, Types, Applications and Market Dynamics, Mar 27, 2019, [Link](#)

[3] Dunleavy, J. K., Sulfur as a Catalyst Poison, *Platinum Metals Rev.*, 2006, 50, (2), 110

[4] Nelson, A.E. (2007), *Fundamentals of Industrial Catalytic Processes*, 2nd Edition. C. H. Bartholomew and Robert J. Farrauto John Wiley and Sons, Hoboken, NJ, 966 pp., 2006. *Can. J. Chem. Eng.*, 85: 127-128.

## EXEMPLARY GC-IMS DATA OF COMMON CATALYST POISONS

Sulfur containing species can act as catalytic poisons whenever reduced metals are used as the primary active site in catalytic processes. Exemplary measurements of common sulfur containing compounds are shown and described in the following.

The chromatograms of the baseline separated signals of H<sub>2</sub>S and COS (Figure 2), Methane- and Ethanethiole (MeSH, EtSH) of a GC-IMS analyzer optimized with respect to run time (Figure 2). GC-IMS method for quantification of H<sub>2</sub>S and COS takes <100 sec, only. In case of the C1 and C2 thiols the measurement cycle time is < 150 sec.

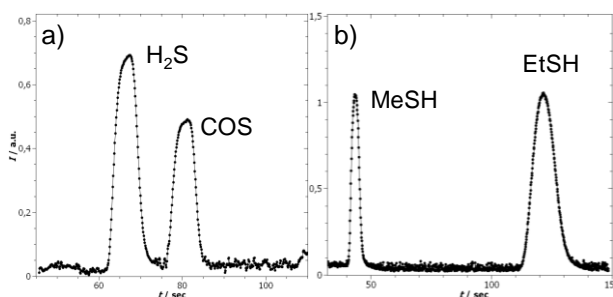


Figure 2: Chromatogram of 50 ppb H<sub>2</sub>S/COS (a) and 50 ppb MeSH/EtSH (b).

Analyte	LOD *1	σ *2
H <sub>2</sub> S	< 10 ppb	3.5 %
COS	< 10 ppb	2.1 %
MeSH	< 10 ppb	2.5 %
EtSH	< 10 ppb	2.8 %

\*1 Limit of detection was determined in an application relevant setup.

\*2 Standard deviation, σ, of signal intensity at a concentration of 50 ppb (n = 50).

Calibration measurements of SO<sub>2</sub> (Figure 3) in the range of 0-100 ppb. Standard deviation was calculated to 1.5 % @ 50 ppb (n=10). The limit of detection for SO<sub>2</sub> lies in the sub-ppb range.

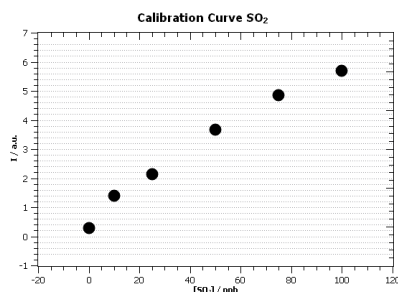


Figure 3: Calibration of SO<sub>2</sub> in the range of 0-100 ppb.

Alcohols, such as Methanol (MeOH) can also exhibit negative impact onto catalysts' performance.

Representative calibration measurements of Methanol in the range of 0-50 ppb are shown in figure 4. The standard deviation was calculated to 1.5 % @ 50 ppb (n=10). Depending on the setup the limit of detection for MeOH lies in the ppt-range.

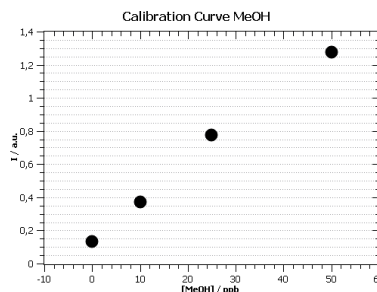


Figure 4: Calibration of MeOH in the range of 0-50 ppb

Organic silicon based compounds are also discussed as catalyst poisons. Figure 5 shows IMS spectra of linear (L3, L4) and cyclic (D3-D5) siloxanes pre-separated by an appropriate column. The detection limits for the mentioned siloxane species are typically in the one digit ppb-range.

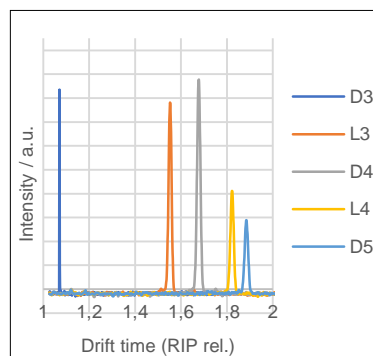


Figure 5: IMS spectra of exemplary linear and cyclic siloxane species varying in number of Si atoms.

## FURTHER COMPOUNDS

Further information about compounds, such as Benzene, Nitric oxide (NO), Dimethyl sulfide/disulfide, C<sub>3</sub>-C<sub>n</sub> mercaptanes or halogenated substances, which may be discussed in the course of catalyst poisonousness, can be downloaded on the G.A.S. website [gas-dortmund.de](http://gas-dortmund.de).