Monitoring of Toxic Industrial Chemicals (TICs)

APPLICATION NOTE

Author:

Dr. C. Rosin, Scientist R&D / Applications
G.A.S. Dortmund, Germany

Rapid Monitoring of Dimethyl Sulfate ($DMSO_4$) in Chemical Plants using GC-IMS Technology

Introduction

Toxic industrial chemicals (TICs) or materials (TIMs) are substances that exhibit harmful effects on humans and are common in manufacturing facilities, chemical plants, maintenance areas or general storage areas. Exposure to those chemicals are seriously harmful especially after multiple low-level exposures. Dimethyl sulfate ($DMSO_4$) is commonly used as a reagent for the methylation of phenoles, amines, and thiols. In industry $DMSO_4$ is preferred, compared to other methylating agents, because of its low cost and high reactivity. It is known that $DMSO_4$ is carcinogenic, mutagenic, highly poisonous, corrosive, environmentally hazardous and volatile. The substance can be absorbed through skin, mucous membranes, and gastrointestinal tract.

With its GC-IMS device G.A.S. developed a highly selective and sensitive measuring system for rapid monitoring of dimethyl sulfate in chemical plants.

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Experimental Conditions

Table 1: GC Conditions	
Column	MCC-OV5
Temperature	60 °C
Flow rate	20 mL/min
Carrier gas	N_2

Table 2: IMS Conditions	
Radiation source	Tritium
Temperature	60 °C
Flow rate	150 mL/min
Carrier gas	N_2
Mode	negative

Table 3: Sampling Conditions	
Sample loop volume	1 mL
Temperature	55 °C
Purge rate (continuous)	~160 mL/min

In order to validate the GC-IMS performance regarding sensitivity and reproducibility a permeation oven was used.

Table 4: Calibration Conditions	
Calibrated concentrations	5, 25, 50, 75, 100, 120, 140 ppb
Permeation rate	164 ng/min
Method	Permeation oven
Oven temperature	70 °C

Results

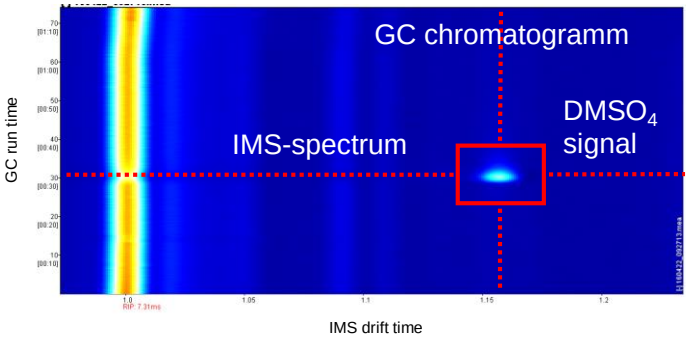

Figure 1: 2-dimensional representation of the $DMSO_4$ signal (red rectangle). GC-runtime: y-axis; IMS drift time: x-axis. Intensity is depicted in false colours: blue: low intensity; red: high intensity.

Under the applied GC and IMS conditions (Table 1) DMS elutes after 30 sec and exhibits a drift time of 8.46 ms (Figure 1).

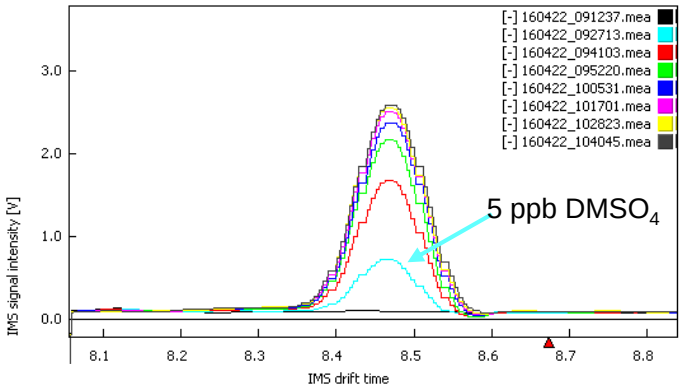

Figure 2: IMS spectra of $DMSO_4$ with increasing concentration (5 to 140 ppb).

The detected IMS-signals of $DMSO_4$ in the range of 5 to 140 ppb are depicted in Figure 2 and corresponding chromatograms in Figure 3.

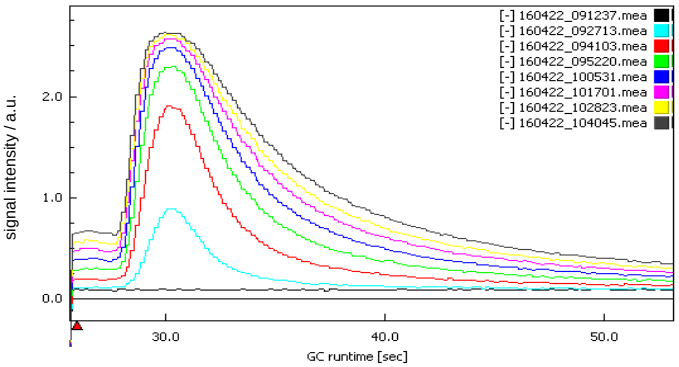

Figure 3: Chromatograms of $DMSO_4$ with increasing concentration (5 to 140 ppb).

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Based on the highly reproducible $DMSO_4$ specific signals the GC-IMS measurement system was calibrated in the range of 5 to 140 ppb by calculation of the maximum peak value in each IMS spectrum. As it can be derived from the signal height, the measured concentration of 5 ppb does not represent the limit of detection under these parameters. Extrapolation of the data yields to a detection limit of approx. 200 ppt.

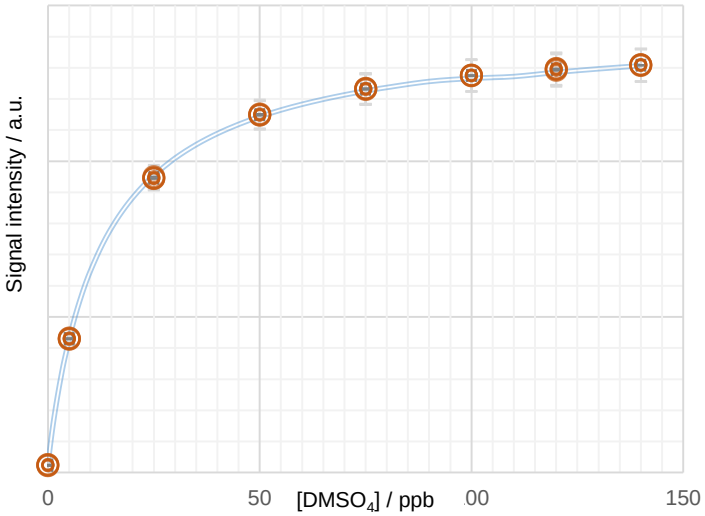

Figure 3: Calibration curve of $DMSO_4$ in the range of 5 to 140 ppb.

In order to prevent undiscovered system failures or false-negative measurement results the system comes with comprehensive self-monitoring check-up features. An integrated hardware watchdog monitors hardware failures, a sample flow controller assures sample specifity.
Further to that, the status, same as important parameters such as correct temperatures, pressures, carrier and drift gas flows, are continuously monitored.

Furthermore the whole measurement system at-site can be checked by a test substance to verify the accurate readiness and by that the reliability of the measurements results.
False-positive results, based on potentially interferring compounds, which might be present on chemical plants (anti-freezing agents, e.g.), are reduced to a minimum due to the 2-dimensional GC- and IMS-separation. For a complete list of compounds checked for cross-sensitivity click here. Despite the separation a full measurement run time only takes 2 min. This includes the GC- and IMS-separation/detection and also a cleaning period at the end of the measurement to avoid carry-over effects.

CONCLUSIONS

The developed method uses the GC-IMS made by G.A.S. with outstanding field performance. The instrument continuously samples the ambient air, which shall be monitored. The run time could be decreased to a value of 2 min, including a cleaning step of the instrument's gas touching parts in order to avoid carry-over. The calibration curve for $DMSO_4$ was established exhibiting a high reproducibility in the range of 5 to 140 ppb. The calculated detection limit (extrapolated) of the instrument is approx. 200 ppt. The standard deviation at 5 ppb is ± 2 % (n=100).

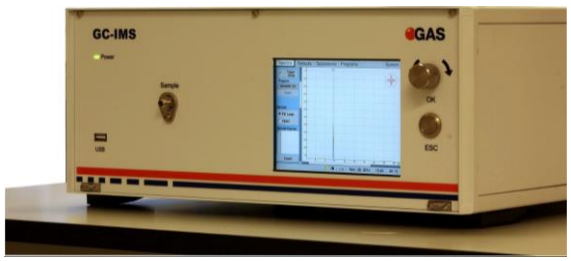

Figure 4: GC-IMS instrument for monitoring of TICs in chemical plants.

GC-IMS

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GAS

OVERVIEW GC-IMS – KEY FEATURES

- Stand alone operation due to integrated computer unit
- Manual or automatic operation including data acquisition, analysis, visualisation and data export
- High reproducibility
- Access to all relevant parameters for method development: temperature control for IMS, column and sample loop, flow control of internal sampling pump, drift and carrier gas
- Heating mode up to 100 °C for fast cleaning of the system
- Direct sampling using electrical six-port-valve and integrated pump
- Software controlled switching between positive and negative ionization mode
- Chromatographic pre-separation of water; suitable for samples with high moisture content
- Simultaneous calibration/ quantification of different compounds
- Adjustable alarm thresholds
- Comprehensive self-monitoring check-up features
- Integrated hardware watchdog to control hardware failures
- Status of the instrument (correct temperatures, pressures, flows) are continuously checked
- Calibrated test-substance to verify readiness scope of supply

TECHNICAL SPECIFICATION

Ionisation method: ß-radiation
Source: Tritium (3H)
Activity: 300 MBq, below the exemption limit of 1 GBq acc.to EURATOM guideline, no licence required
Column type: Multi Capillary Column (MCC) or Capillary Column (CC) – various stationary phases available
Sampling: Integrated pump plus heated electrical 6-port-valve (stainless steel), gas tight loop (1-10 mL)
Detection limit: Typically low ppb_v-range
Dynamic range: 1-3 orders of magnitude
Display: Touchscreen 6.4”TFT
Communication: RS232, USB, Ethernet
Power: 100 – 240 V AC, 50-60 Hz (external) 24 V DC / 8.3A, XLR-connector (internal)
Power consumption: < 200 Watt
Dimensions: 449 x 435 x 177 mm (WxDxH)
Weight: 15,5 kg or 34,2 lb
Housing: 19” compatible, IP 20 enclosure, CE Marking

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