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GERSTEL AppNote 282

# Determination of Methylene Chloride in Indoor Air using Thermal Desorption GC-MS with Automated Internal Standard Addition

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## Keywords

Air sampling, methylene chloride, thermal desorption, gas chromatography, mass spectrometry

## Abstract

Methylene chloride has long been used in industry, academia and has been one of the primary extraction solvents for environmental applications. In recent years, the US EPA has issued several risk assessments and regulations regarding the use of methylene chloride.

In March 2019, the EPA regulated sales of methylene chloride in paint and coating removers for consumer use. In November 2022, the EPA released a final revised risk determination for methylene chloride, which found that it presented an unreasonable risk of injury to health. In April 2024, the US EPA finalized a rule that prohibits nearly all uses of methylene chloride, with some exceptions.

For those who continue to use methylene chloride, a workplace chemical protection plan may be required, which includes baseline air monitoring.

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for methylene chloride is 25 ppmV. The average exposure to methylene chloride over an eight-hour period should not exceed 25 ppmV. The short-term exposure limit (STEL) is 125 ppmV over any 15-minute period.

This document outlines methodology for determination of methylene chloride in air using active air sampling with analysis by thermal desorption GC-MS. The GERSTEL Internal Standard/Dry Purge module is a station that attaches to the MPS rail and is used for automated spiking of internal standards. The ISDP can also be used to dry purge sorbent tubes where excess water or solvent may adversely affect the trapping and transfer of analytes from the adsorbent tube to the GC column.

## Introduction

In active air sampling, the sample is collected by passing air through a tube containing a sorbent. This concentrates the analytes onto the tube. Once sampling is complete, the tube is placed in the thermal desorber. The thermal desorber is then sealed, and heat and gas flow are applied to gently desorb the compounds from the sorbent.

The released compounds pass directly into a focusing trap just below the tube. The focusing trap can be held at a low temperature to trap compounds on an inert surface (such as glass beads or quartz wool) or at higher temperatures using additional sorbents.

After the compounds have been trapped, the focusing trap is rapidly heated, and analytes are passed directly onto the GC column for separation, followed by detection with a mass spectrometer. As with the transfer from the thermal desorber, the transfer can be performed in a split or splitless mode to further dilute or concentrate the analytes before they reach the GC column.

Active air sampling can be used for PEL and STEL monitoring.

This work shows indoor air sampling for methylene chloride in our laboratories and office space at GERSTEL, Inc.

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## Experimental

### *Instrumentation*

GERSTEL TD Core System with liquid nitrogen cooling option, GERSTEL ISDP, and Agilent 8890 GC/7000E TQ MS.

### *Analysis Conditions TD Core System*

| | |
|---|---|
| TD 3.5+ | splitless |
| | 50 °C (0 min); 400 °C/min; 300 °C (5 min) |
| CIS 4 | Tenax TA filled liner |
| | solvent vent (50 mL/min) |
| | split 50:1 |
| | -10 °C (0 min); 12 °C/sec; 280 °C (3 min) |

### *Analysis Conditions Agilent 8890 GC / 7000E TQ MS*

| | |
|---|---|
| Column | 60 m HP- 624 UI (Agilent) |
| | $d_i$=0.25 mm, $d_f$=1.4 µm |
| Pneumatics | constant flow 1 mL/min |
| Oven | 35 °C (3.5 min); 10 °C/min; 240 °C (0 min); |
| | 30 °C/min; 280 °C |
| MS1 Scan | 45-300 amu |

### *Sample Description*

Air samples were drawn through a Carbopack B/X tube.

### *Sample Preparation*

Air samples were pulled through the TD tubes at a 100 mL/min flow rate for 10 minutes for a total sample volume of 1 liter. Sampling was performed using an SKC, Inc. Pocket Pump Touch.

### *Standard Preparation*

Standards of methylene chloride in methanol were prepared. One microliter of standard was spiked onto the fritted end of a TD 3.5+ tube filled with Carbopack B/X. The tube was then attached to the GERSTEL Tube Spiking Apparatus, and dry nitrogen was run through the tube for 3 minutes at 50 mL/min. A transport adapter was then attached to the tube. A four-point calibration curve was prepared in the 13-1300 ng range on tube.

### *Internal Addition with ISDP*

A gas standard mix (Restek, 34408) of 1 ppmV each, chlorobenzene-$d_5$, 1,4-difluorobenzene, bromochloromethane and p-bromofluorobenzene in nitrogen was used as the internal standard.

The GERSTEL ISDP provides precise, reproducible, and fully automated addition of gaseous internal standards using GERSTEL TD 3.5+ tubes and other 3.5" tubes delivered via a high precision regulator and a fixed volume loop. The addition of gaseous internal standards via the ISDP is often recommended in methods for air analysis, such as US EPA TO-17. In addition to adding internal standards, the GERSTEL ISDP also uses a mass flow controller for precise and reproducible dry purging of the tube in the sampling direction to remove water from humid samples.

### *Sample Introduction*

The Carbopack B/X tubes were placed in a VT-40t tray on the autosampler. The standard was desorbed in splitless mode under a 50 mL/min helium flow @ 300 °C for 5.0 minutes. Analytes were trapped in the CIS inlet at -10 °C on a Tenax-TA liner. When desorption was complete, analytes were transferred to the column in split mode (50:1) by heating the inlet rapidly to 280 °C.

## Results and Discussion

Figure 1 shows a picture of a TD 3.5+ with ISDP. The gripper on the MPS Universal syringe tool is used to move the thermal desorption tubes to and from the tray, ISDP, and thermal desorption unit.


**Figure 1:** Picture of GERSTEL TD 3.5+ with ISDP.

The ISDP unit is controlled through the GERSTEL Maestro software using a Preplet or PrepSequence. A Maestro Preplet was used in this study and is part of the actual method, such that any tube thermally desorbed with the method is automatically spiked with the internal standard. Figure 2 shows the steps used in the preplet.

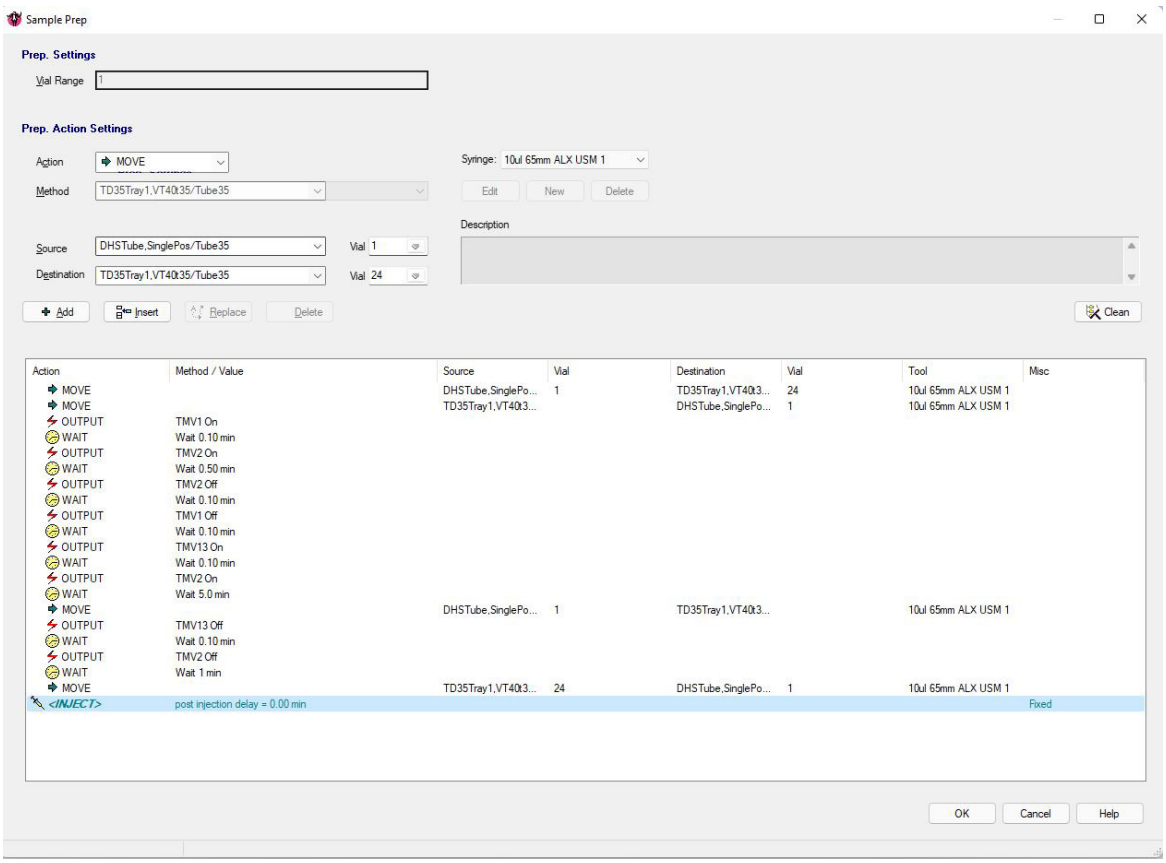


**Figure 2:** GERSTEL preplet for internal standard tube spike.

Table 1 shows the results for the four compounds in the internal standard spiked onto the Carbopack B/X tubes. The data shows good precision (n=9) for all four analytes.

**Table 1:** Precision data for ISDP.

| Chloro-benzene-$d_5$ | 1,4-Difluoro-benzene | Bromochloro-methane | p-Bromofluoro-benzene |
|---|---|---|---|
| 2.29% | 3.64% | 3.17% | 3.64% |

A four-point calibration curve was generated for methylene chloride from 13-1300 ng on tube. The r-squared value for the linear regression without internal standard was 0.9989. For this study, chlorobenzene-$d_5$ was used for the internal standard. With the internal standard, the r-squared value for the linear regression improved to a value of 0.9993.

Air samples were drawn from several laboratory and office areas around the building. A typical chromatogram is shown in Figure 3. Methylene chloride and hexane are the most prominent peaks in the chromatogram.

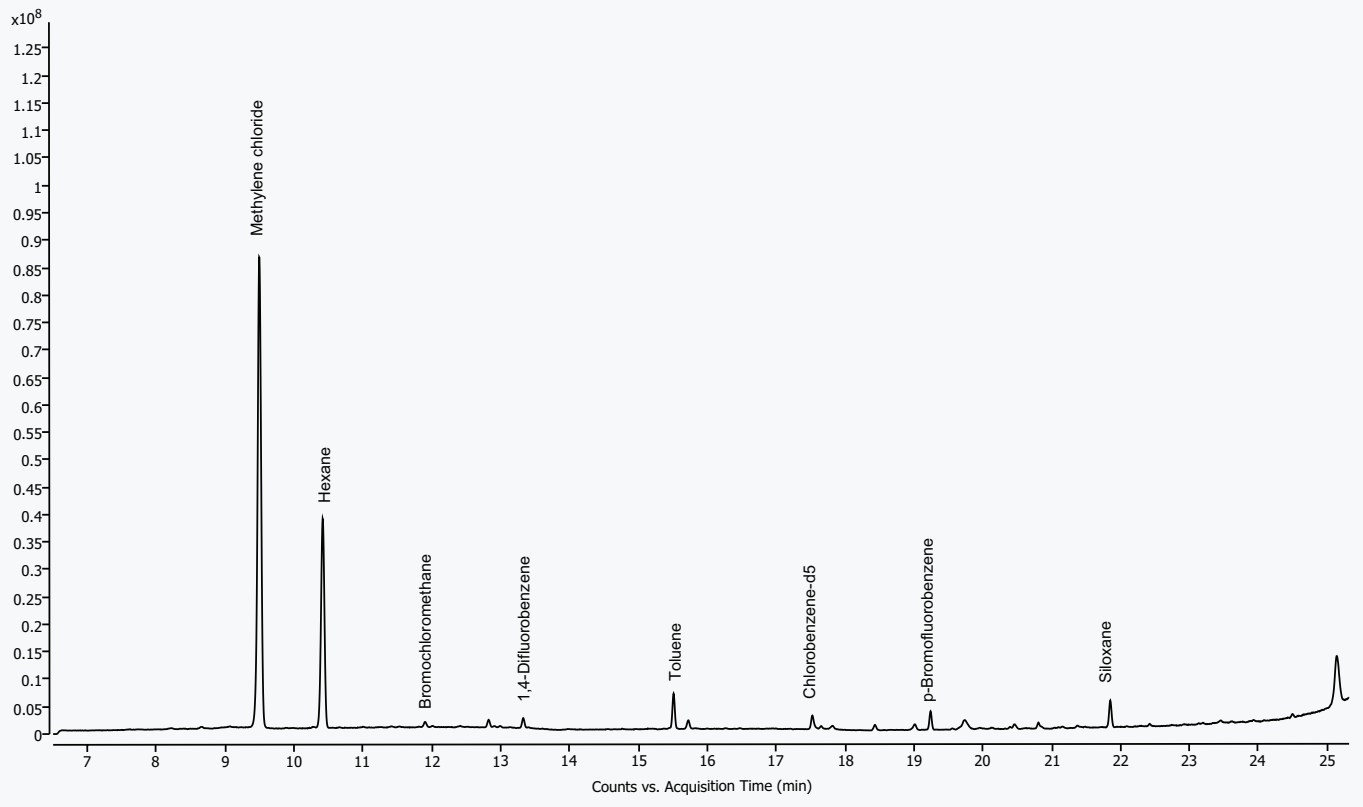


**Figure 3:** Total ion chromatogram for building air sample.

Table 2 shows the quantitative data for the building air samples. All values are well below the 25 ppmV level for the PEL. The highest values were found in the laboratory areas, and the lowest level was found in the warehouse area. Three replicate samples taken in the Main Laboratory area showed good precision at 6.4% with an average value of 0.0302 ppmV.

**Table 2:** Quantitative data for $CH_2Cl_2$.

| Area | $[CH_2Cl_2]$ ppmV |
|---|---|
| Cubical Area | 0.0996 |
| Training Room | 0.0409 |
| Office | 0.0598 |
| Lab 1 | 0.401 |
| Lab 2 | 0.143 |
| Warehouse | 0.0050 |
| Main Laboratory Rep 1 | 0.0319 |
| Main Laboratory Rep 2 | 0.0316 |
| Main Laboratory Rep 3 | 0.0274 |
| Average | 0.0302 |
| RSD | 6.4% |

A timed study was also conducted to see if the concentration of methylene chloride fluctuated during the day. Samples were taken every hour from 0730 to 1530 hrs. in the Main Laboratory. The concentration versus time and average concentration are shown in Figure 4.

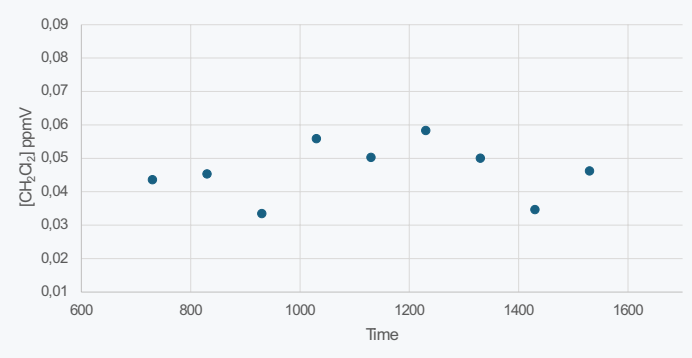


**Figure 4:** Methylene chloride concentration in main laboratory by time of day.

The results show that the concentration of methylene chloride did not vary much from the average value of 0.046 ppmV, which has a range of 0.033-0.058 ppmV.

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## Conclusion

This study demonstrates the use of the GERSTEL TD 3.5+ with ISDP for determining methylene chloride in air using active air sampling. The ISDP delivers precise tube spiking of gaseous standards onto adsorbent tubes, which helps increase the accuracy of the results. This method could establish baseline air concentrations of methylene chloride in an area where the solvent is in use.