Determination of Methylene Chloride Airborne Concentrations Using TD-GC-FID

Tsvetan Popov, PhD, CIH, CSP

Associate Professor

University of Central Missouri

Education

University of Chemical Technology and Metallurgy, Sofia, Bulgaria;

- Master of Science Degree (1997);

Defense Staff Military Academy - Defense Advanced Research Institute, Sofia, Bulgaria;

- PhD Degree (2005)

University of Central Missouri;

- Master of Science Degree in Industrial Hygiene (2019);

Courses/Certifications

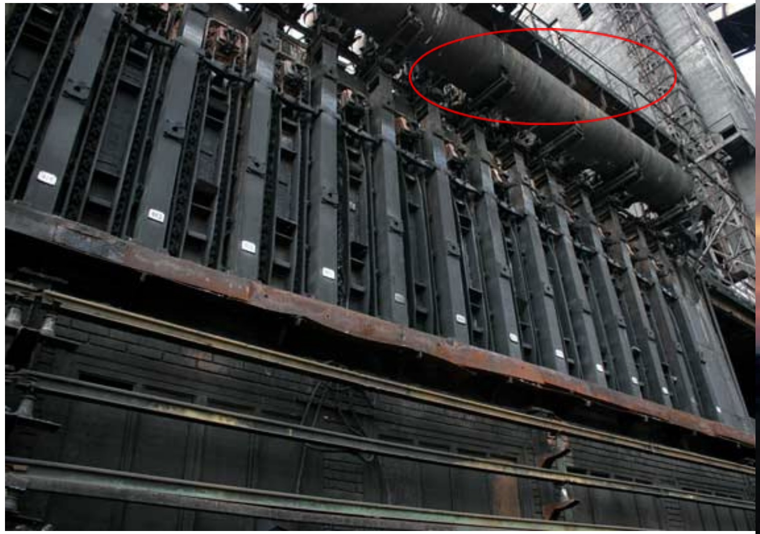
- Certified Safety Professional (2020);
- Certified Industrial Hygienist (2019);
- Analytical Chemistry and Agent Handling Course, January 2009, DSTL Porton Down, The United Kingdom;
- Hazardous Waste Operations and Emergency Response (HAZWOPER), Destruction of Chemical Warfare Agents (CWA), October 2008, Aberdeen Proving Ground, USA;
- Implementation of fluoride reactivation method, July 2006, TNO Defence Security and Safety, The Netherlands;
- Analytical Skills Development Course (ASCD 2006), June 2006, VERIFIN, Helsinki, Finland;

Work Experience

“Kremikovtzi” AD, Coke Plant

Technologist (December 1997 – February 2002)

- Largest metallurgical company in the country and the region.



Work Experience (cont.)

State Agency for Emergency Management and Civil Protection

Chief Inspector (February 2002 – June 2005)

- Experience working with various detectors, direct reading instruments, including gas detectors using sensor technology, photoionization detectors (PID), ion mobility spectrometry (IMS), infrared spectrometry, gas chromatography-mass spectrometry (GC-MS);
- Certified to work with self-contained breathing apparatus (SCBA) and encapsulated suits.

Work Experience (cont.)

Military Medical Academy – Laboratory of Experimental Toxicolog

Analytical Chemist (June 2006 – May 2008)

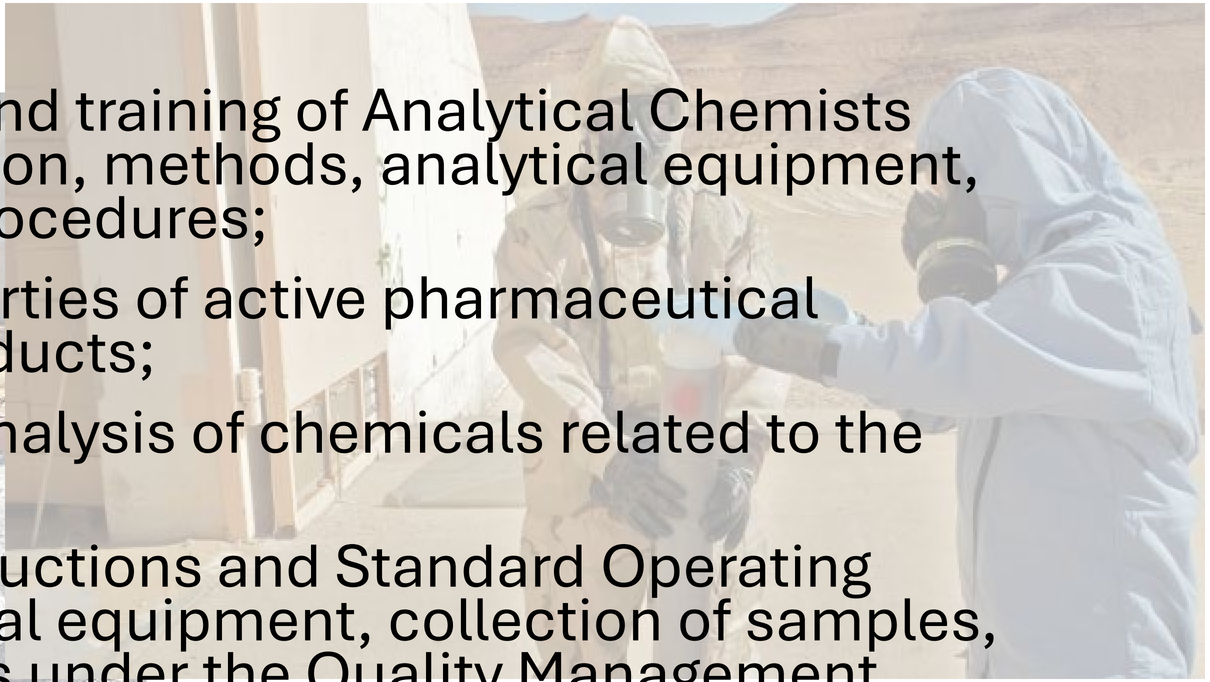
- Development of methods for analysis of chemicals related to the Chemical Weapons Convention and organophosphorus pesticides using Gas Chromatography, coupled to FID, NPD and MS in biological samples, including in vivo and in vitro samples;
- Development of methods for analysis of reactivators of inhibited cholinesterase (oximes) using HPLC, including in vivo and in vitro samples;
- Development of methods for analysis of medications (Sennosides A and B) using HPLC;
- Development of methods for analysis of essential oils (rose, peppermint and lavender) using Gas Chromatography;
- Synthesis, purification, and stability studies of reactivators of inhibited cholinesterase (oximes).

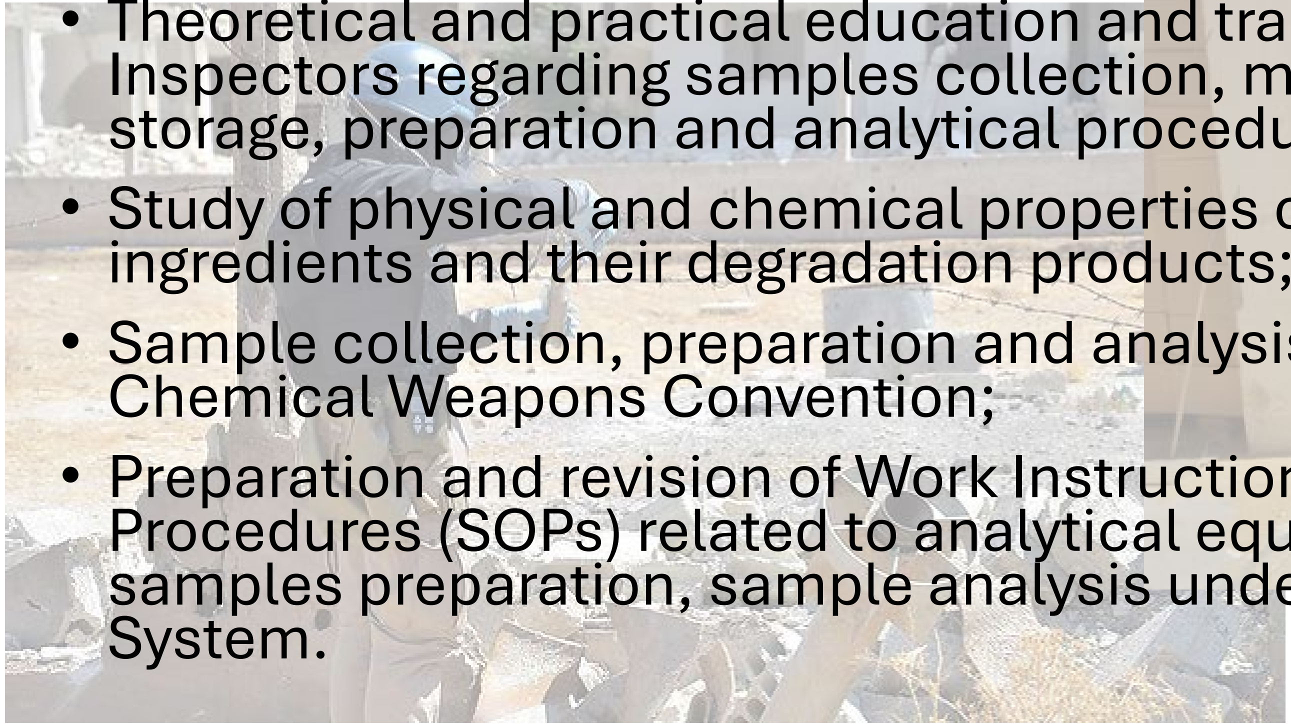
Work Experience (cont.)

Organization for the Prohibition of Chemical Weapons, The Hague, The Netherlands

Inspector Analytical Chemist, Inspection Team Leader

(June 2008 – April 2016)





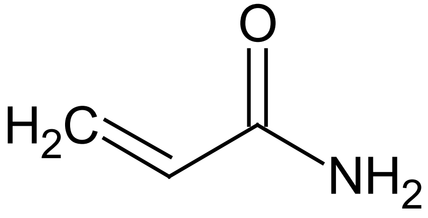
- Theoretical and practical education and training of Analytical Chemists Inspectors regarding samples collection, methods, analytical equipment, storage, preparation and analytical procedures;
- Study of physical and chemical properties of active pharmaceutical ingredients and their degradation products;
- Sample collection, preparation and analysis of chemicals related to the Chemical Weapons Convention;
- Preparation and revision of Work Instructions and Standard Operating Procedures (SOPs) related to analytical equipment, collection of samples, samples preparation, sample analysis under the Quality Management System.

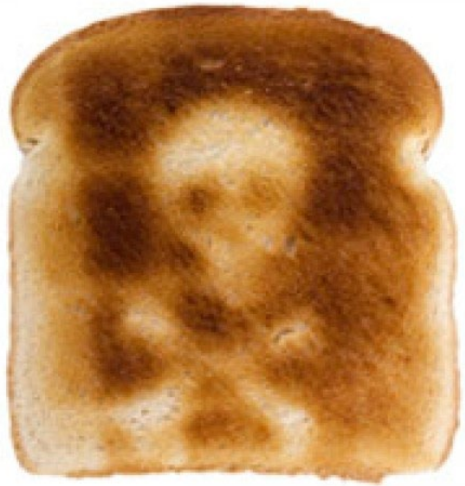
Work Experience (cont.)

ALcontrol Laboratories, Oosterhout, The Netherlands

Development Engineer, May 2016 – July 2017

- Determination of acrylamide using LC-MS/MS;
- Classified as neurotoxin and potential carcinogen;
- Acrylamide is formed when certain amino acids (mostly asparagine) interact with sugars in presence of heat.





Work Experience (cont.)

University of Central Missouri

Associate Professor of Safety Sciences (August 2022 – Present)

Assistant Professor of Safety Sciences (August 2017 – July 2022)

- Teaching undergraduate and graduate courses in Safety Science;
- Development of online and lecture courses in undergraduate and graduate levels;
- Safety and Health Laboratory testing, maintenance and repair of equipment and instruments;
- Sound knowledge and understanding of PID, FID, FTIR, Portable GCs and GC-MS, Gas Analyzers, Detector Tubes, Aerosol Monitors, Noise Level meters, and other sampling and analytical techniques.

Scope

This presentation will cover:

- Methylene chloride: use, toxicity;
- OSHA and EPA exposure limits;
- Direct-reading instruments: advantages and disadvantages;
- Sampling and analytical methods: advantages and disadvantages;
- Use of thermal desorption and gas chromatography; and
- Implementation of hierarchy of controls.

Introduction

Why methylene chloride?

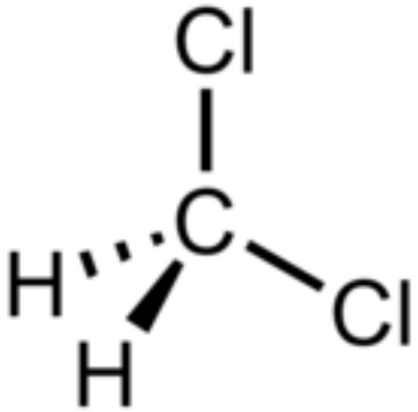
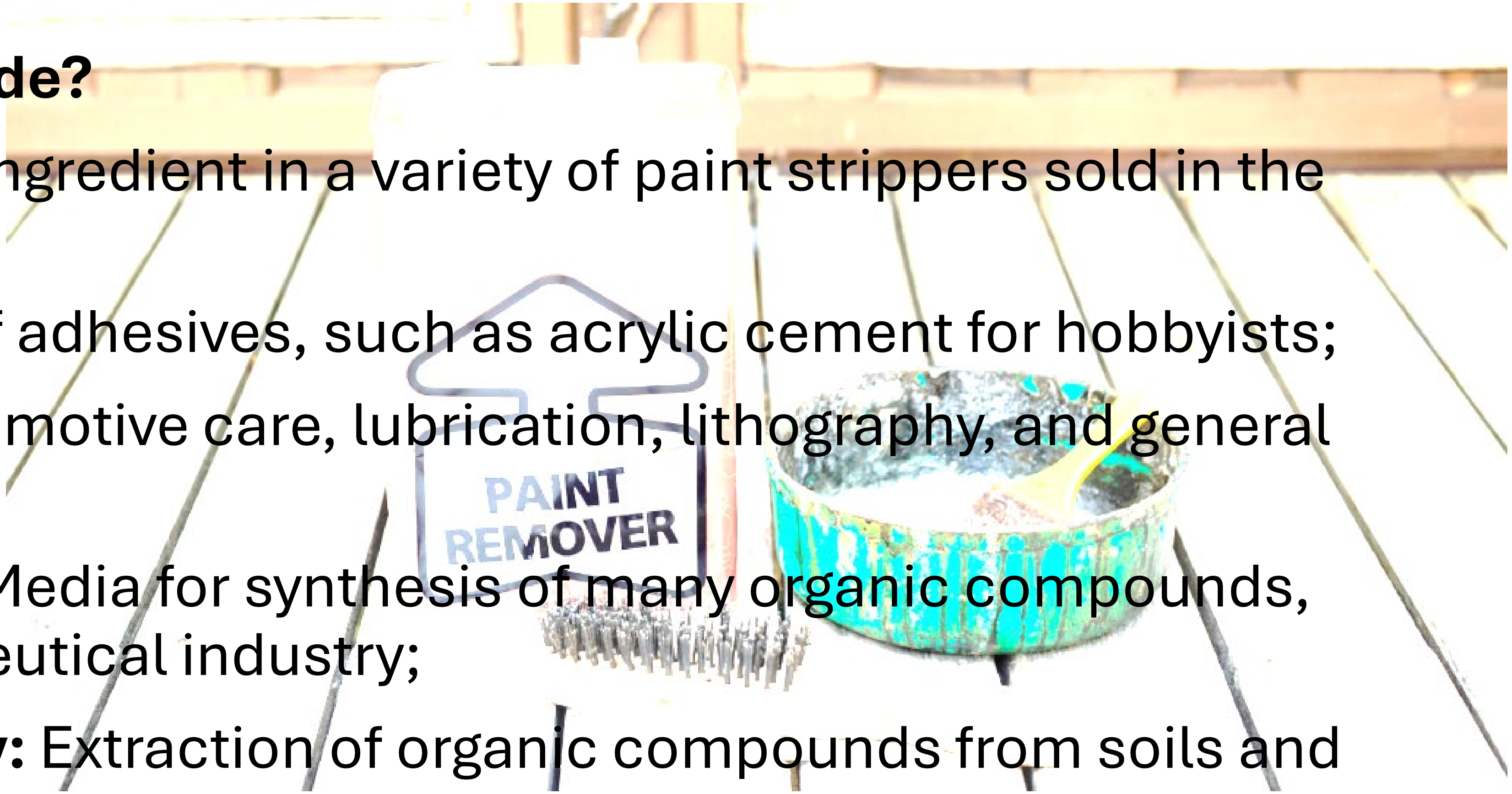


Image Sources: Toxic-Free Future, OCWR

Introduction (cont.)

Why methylene chloride?



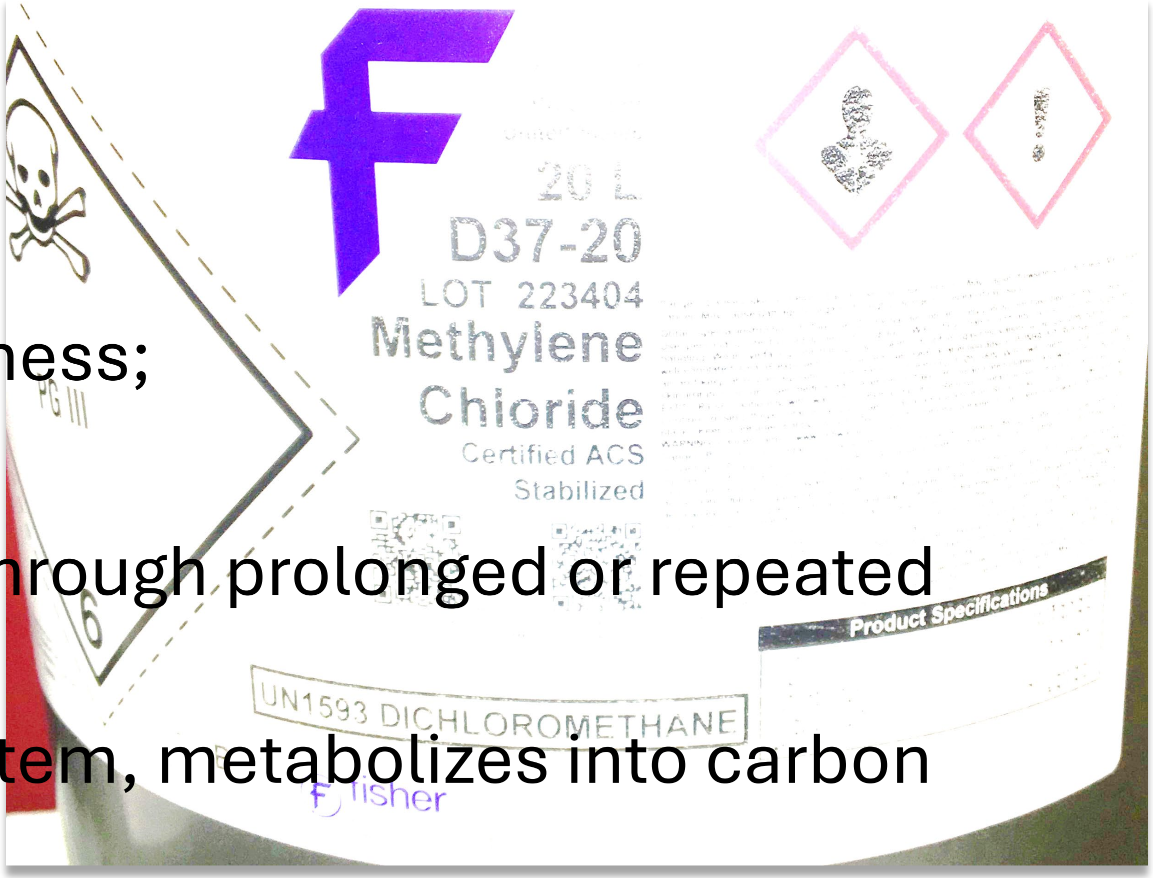
- **Paint Strippers:** Key ingredient in a variety of paint strippers sold in the U.S. (in the past);
- **Adhesives:** A range of adhesives, such as acrylic cement for hobbyists;
- **Other Products:** Automotive care, lubrication, lithography, and general cleaning;
- **Organic Chemistry:** Media for synthesis of many organic compounds, including in pharmaceutical industry;
- **Analytical Chemistry:** Extraction of organic compounds from soils and aqueous samples.

Sources: Toxic-Free Future

Introduction (cont.)

Why methylene chloride?

- Causes skin irritation;
- Causes serious eye irritation;
- May cause drowsiness or dizziness;
- May cause cancer;
- May cause damage to organs through prolonged or repeated exposure;
- Affects the central nervous system, metabolizes into carbon monoxide in the body



Sources: Fisher Scientific, EPA

Exposure Limits

OSHA:

Methylene chloride

Print

SYNONYMS & TRADE NAMES

Dichloromethane, Methylene dichloride

CAS NO.	RTECS NO.	DOT ID & GUIDE
75-09-2	PA8050000	1593 160

FORMULA	CONVERSION	IDLH
CH_2Cl_2	1 ppm = 3.47 mg/m^3	Ca [2300 ppm] See: 75092

EXPOSURE LIMITS

NIOSH REL
Ca See Appendix A
OSHA PEL
[1910.1052] TWA 25 ppm ST 125 ppm

MEASUREMENT METHODS

NIOSH 1005 , 3800;
OSHA 59 , 80
See: NMAM or OSHA Methods

Source: NIOSH Pocket Guide

Exposure Limits (cont.)

EPA:

FACT SHEET
2024 Final Risk Management Rule for Methylene Chloride under TSCA

EPA

Compliance Timelines* for the Workplace Chemical Protection Program

Initial Monitoring	Exposure Limits and Dermal Protections	Exposure Control Plan	Other Monitoring
Complete initial monitoring. Demarcate regulated area within 3 months of initial monitoring data. Provide respiratory protection within 3 months of initial monitoring data but no later than 15 months after final rule.	Ensure methylene chloride inhalation exposures do not exceed the ECEL (2 ppm as an 8-hr TWA) and EPA STEL (16 ppm as a 15-min TWA) for all potentially exposed persons. Provide respiratory and/or dermal protection if applicable.	Develop and implement an exposure control plan. Notify potentially exposed persons of completion of exposure control plan within 30 days of its completion. Provide requested records by a potentially exposed person within 15 days	<u>Periodic Monitoring</u> Conduct at a minimum **every 5 years, but could occur as frequently as every 3 months,** dependent upon initial monitoring results. <u>As Needed Monitoring</u> Conduct additional monitoring after any change that may introduce additional sources of methylene

Source: EPA

Exposure Limits (cont.)

OSHA vs EPA:

Table 1: Comparison of the OSHA methylene chloride exposure limits to the new EPA rule.

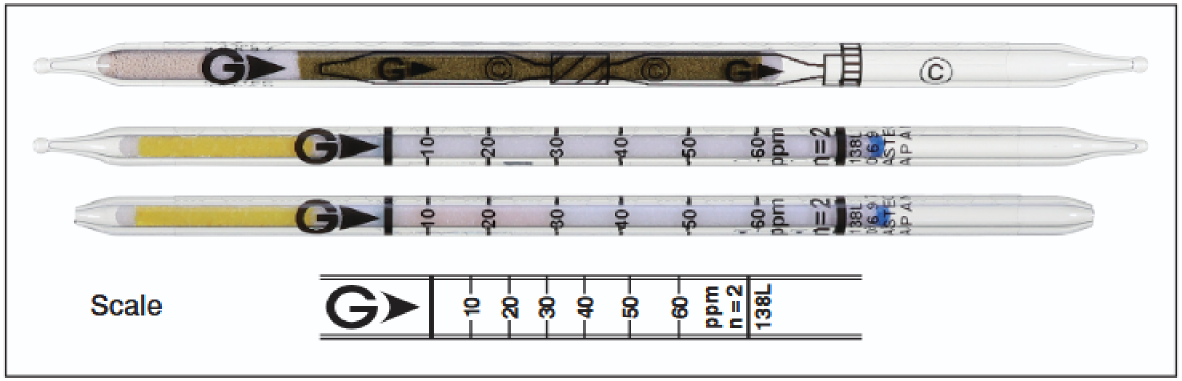
Rule	OSHA	New EPA
8-Hour Time Weighted average (TWA)	25 ppm	2 ppm
15-Minute Short Term Exposure Limit (STEL)	125 ppm	16 ppm
Action Level	12.5 ppm	1 ppm

Source: University of Minnesota

Monitoring: Direct-Reading Instruments

Detector Tubes:

Methylene Chloride CH_2Cl_2 No.138L



Performance

When used, these tubes are to be connected.

Measuring range	4 to 10 ppm	10 to 60 ppm	60 to 150 ppm
Number of pump strokes	4 (400 mL)	2 (200 mL)	1 (100 mL)
Correction factor	0.4	1	2.5
Sampling time	12 min	6 min	3 min
Detecting limit :	3 ppm (4 pump strokes)		

Methylene Chloride 20/a

Order No. 81 03 591

Application Range

Standard Measuring Range:	20 to 200 ppm
Number of Strokes n:	8
Time for Measurement:	approx. 7 min.
Standard Deviation:	± 15 to 25 %
Color Change:	yellow → red

Ambient Operating Conditions

Temperature:	17 to 30 °C At 25 °C to 30 °C/77 °F to 86 °F multiply the reading with the factor 0.6.
Absolute Humidity:	3 to 25 mg H_2O / L

Source: Gastec and Drager

Monitoring: Direct-Reading Instruments (cont.)

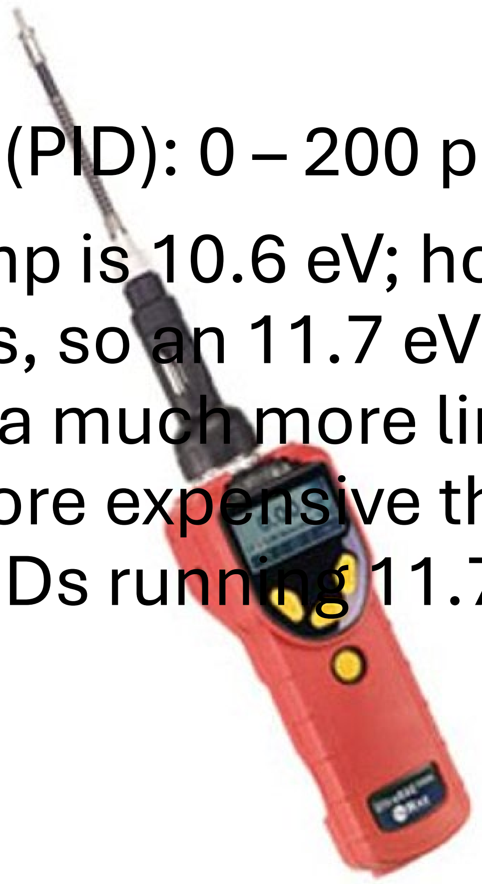
Detector Tubes (MicroTubes): 10 – 500 ppm

Source: SKC and Drager

Monitoring: Direct-Reading Instruments (cont.)

Photoionization Detection (PID): 0 – 200 ppm

The most common PID lamp is 10.6 eV; however, MC's ionization potential is higher than this, so an 11.7 eV lamp must be used. The 11.7 eV lamps in use have a much more limited service life (about 600–800 hours) and are more expensive than the 10.6 eV lamps. It is unclear whether current PIDs running 11.7 eV lamps would detect MC at an MDL of 0.1 ppm.



Sources: Honeywell and The Synergist

Sampling and Analysis

NIOSH Pocket Guide:

Methylene chloride

Print

SYNONYMS & TRADE NAMES

Dichloromethane, Methylene dichloride

CAS NO.	RTECS NO.	DOT ID & GUIDE
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EXPOSURE LIMITS

NIOSH REL
Ca See Appendix A
OSHA PEL
[1910.1052] TWA 25 ppm ST 125 ppm

MEASUREMENT METHODS

NIOSH 1005 , 3800;
OSHA 59 , 80
See: NMAM or OSHA Methods

Source: CDC

Sampling and Analysis (cont.)

NIOSH 1005 Method:

METHYLENE CHLORIDE **1005**

CH_2Cl_2 MW: 84.94 CAS: 75-09-2 RTECS: PA8050000

METHOD: 1005, Issue 3	**EVALUATION: FULL**	**Issue 1: 15 August 1984** **Issue 3: 15 January 1998**

OSHA : 25 ppm; STEL 125 ppm
NIOSH: lowest feasible; carcinogen
ACGIH: 50 ppm; suspect carcinogen
(1 ppm = 3.47 mg/m³)

PROPERTIES: liquids, d 1.323 g/mL @ 20 °C; BP 40 °C; MP -95 °C; VP 47 kPa (349 mm Hg) @ 25 °C, nonflammable

SYNONYMS: dichloromethane, methylene dichloride

SAMPLING		MEASUREMENT	
SAMPLER:	SOLID SORBENT (2 coconut shell charcoal tubes, 100/50 mg)	**TECHNIQUE:**	GAS CHROMATOGRAPHY, FID
		ANALYTE:	methylene chloride
FLOW RATE:	0.01 to 0.2 L/min	**DESORPTION:**	1 mL CS_2
VOL-MIN: **-MAX:**	0.5 L @ 500 ppm 2.5 L	**INJECTION VOLUME:**	1 µL

Source: CDC

Sampling and Analysis (cont.)

OSHA 1025 Method:

OSHA Method 1025, Methylene Chloride

Methylene Chloride

CAS number:	75-09-2
OSHA PEL:	25 ppm (87 mg/m^3) 8-Hour TWA PEL, 12.5 ppm (43 mg/m^3) 8-Hour TWA Action Level, 125 ppm (434 mg/m^3) 15-Minute STEL, General Industry, Construction, Shipyard
Procedure:	Collect samples by drawing workplace air containing methylene chloride vapor through two Anasorb 747 synthetic charcoal sorbent tubes connected in series. Extract samples with 60/40 (v/v) *N,N*-dimethylformamide/carbon disulfide (DMF/CS_2) and analyze by gas chromatography (GC) using a flame ionization detector (FID).
Recommended sampling time and sampling rate:	240 min at 50 mL/min (12 L, 8-Hour TWA) 15 min at 50 mL/min (0.75 L, 15-Minute STEL)
Limit of quantitation:	0.22 ppm (0.77 mg/m^3, 8-Hour TWA), 3.6 ppm (12 mg/m^3, 15-Minute STEL)
Reporting limit:	0.48 ppm (1.7 mg/m^3, 8-Hour TWA), 7.7 ppm (27 mg/m^3, 15-Minute STEL)

Source: OSHA

Sampling and Analysis (cont.)

Passive Sampling:

Chemical Name	CAS Number	Badge/ Media	Description	Sampling Rate (mL/ min)	PEL	STEL	8 hr Rpt Lmt	RL (ug)	Vol (L)	TAT	Test Group
Methylene Chloride	75-09-2	546AT	Badge, Charcoal	2.39	OSHA 25 PPM	OSHA STEL 125 PPM	0.75 PPM	3		6	OV List A
Methylene Chloride	75-09-2	525AT	Badge, Charcoal	72.7	OSHA 25 PPM	OSHA STEL 125 PPM	0.025 PPM	3			
Methylene Chloride	75-09-2	J6-001	Tube, Charcoal 50-100mg	0.10 L/min	OSHA 25 PPM	OSHA STEL 125 PPM	0.018 PPM	3	10		
Methylene Chloride	**75-09-2**	**566AT**	**Badge, Charcoal**	**9.54**	**OSHA 25 PPM**	**OSHA STEL 125 PPM**	**0.19 PPM**	**3**			

Sources: Assay Technology

Sampling and Analysis (cont.)

Active and passive sampling reporting limits (RLs): 3 – 5 ug per sample

Methylene chloride	
FEE PER SAMPLE:	$81.00
COMPATIBLE ANALYTES:	
METHOD:	mod. NIOSH 1005; GC/FID Separate tubes as soon as possible after sample collection.
ANALYTICAL TECHNIQUE:	GC/FID
COLLECTION MEDIUM:	Charcoal
ORDER NUMBER:	226-01
VOL. / TIME / AREA / MASS:	0.5-2.5 L
SAMPLING RATE:	0.01-0.2 LPM
LOQ:	5 ug

Methylene Chloride	
FEE PER SAMPLE:	$81.00
COMPATIBLE ANALYTES:	
METHOD:	mod. OSHA 59; GC/FID
ANALYTICAL TECHNIQUE:	GC/FID
COLLECTION MEDIUM:	Charcoal
ORDER NUMBER:	--
VOL. / TIME / AREA / MASS:	10 L
SAMPLING RATE:	0.05 LPM
LOQ:	5 ug

Methylene Chloride [2]	
FEE PER SAMPLE:	$81.00
COMPATIBLE ANALYTES:	$37.00
METHOD:	mod. NIOSH 1005; GC/FID BADGE ✔ For best sampling results, include the charcoal scavenger packet with your returned sampling media. Manufacturer recommends returning samples to the
ANALYTICAL TECHNIQUE:	GC/FID
COLLECTION MEDIUM:	PM
ORDER NUMBER:	N566
VOL. / TIME / AREA / MASS:	15 min. - 12 hrs.
SAMPLING RATE:	--
LOQ:	5 ug

Source: SGS Galson

Sampling and Analysis (cont.)

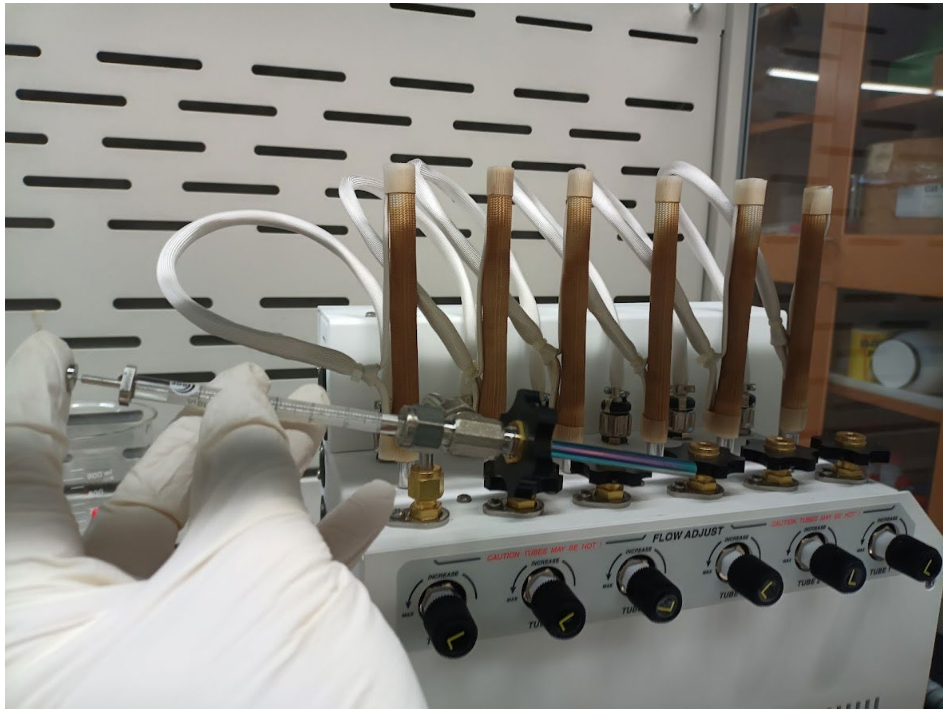
Developed calculator to assist sampling and analysis strategy:

	OSHA, ppm	EPA, ppm			
PEL	25	2			
STEL	125	16			
	Concentration, ppm	Concentration,mg/m3		Amount in Sampled Volume, mg:	Amount in Sampled Volume, ug:
OSHA PEL	25	86.77432543		0.065080744	65.08074407
OSHA STEL	125	433.8716271		0.32540372	325.4037204
EPA ECEL	2	6.941946034		0.00520646	5.206459526
EPA STEL	16	55.53556827		0.041651676	41.65167621
Reporting Limit:	ug	mg			
	5	0.005			
Flow Rate:		L/min			
		0.05			
Sampling Time:		min			
		15			
Sampling Volume:	L	m3			
	0.75	0.00075			

Source: Own image

Sampling and Analysis (cont.)

Thermal desorption with gas chromatography:



Sources: Own photos

Sampling and Analysis (cont.)

Thermal desorption vs sorbent tubes (Sampling):

Advantages:

- GC inlet made of alloy (non-fragile)
- No need to brake tube ends (safety hazard)

Disadvantages:

- GC inlet conditioning (heating in flow of inert gas, e.g., nitrogen or helium).
- Air sampling pump and tubing required

Sampling and Analysis (cont.)

Thermal desorption vs sorbent tubes (sample preparation):

Advantages:

- Little to no sample preparation (internal standard)
- Short time to introduce sampler in the instrument
- Hazardous solvents (CS2) not required for extraction

Disadvantages:

- Additional equipment required for thermal desorption if automation needed.

Sampling and Analysis (cont.)

Thermal desorption vs sorbent tubes (analysis):

Advantages:

- Improved sensitivity (sample not diluted 1000 times)
- Excellent recoveries
- Packed GC inlets can be reused after conditioning

Disadvantages:

- Once analyzed, depending on equipment, analysis may not be repeated (duplicates in sample collection)

The Project …

Custom packed sorbent tubes (GC inlets) with deactivated glass wool and sorbent material:

Sources: Own photos

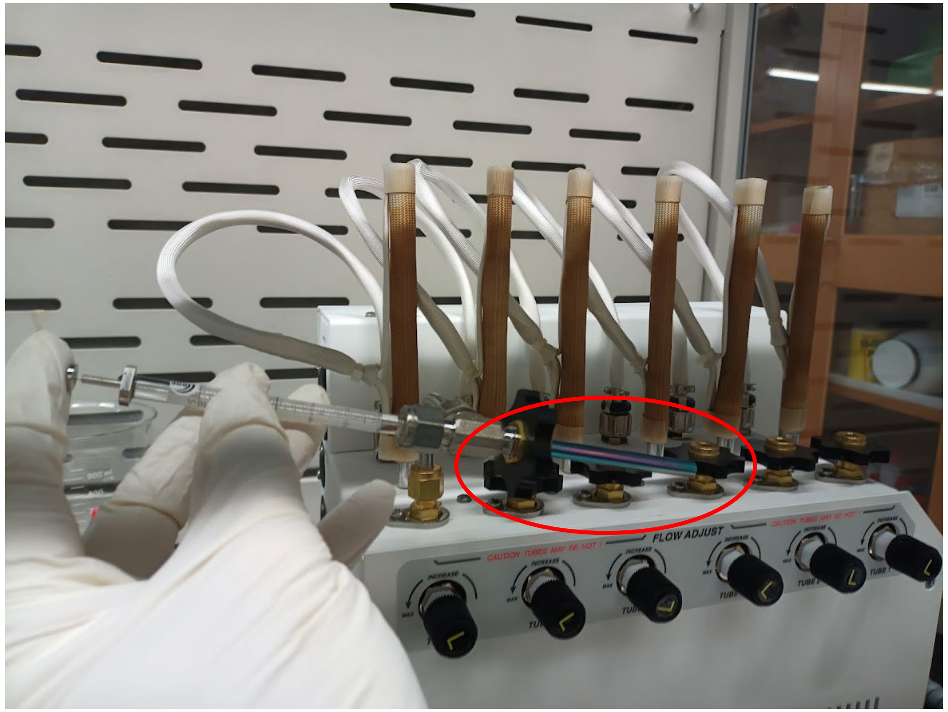
The Project … (cont.)

Tube (GC inlets) conditioning with nitrogen at elevated temperature:

Sources: Own photos

The Project … (cont.)

Tube (GC inlets) spiking with know concentrations of methylene chloride:



Sources: Own photos

The Project … (cont.)

Analysis using gas chromatograph with flame ionization detector and generated hydrogen onsite (used as both carrier and detector gas):

Sources: Own photos

The Project … (cont.)

Current progress:

- Experimenting with different sorbents;
- Recovery studies;
- Chromatography conditions;
- Calibration (internal standard considerations);
- Breakthrough; and
- Sample stability.

Hierarchy of Controls

Paint strippers (substitution):

- Benzyl alcohol;
- Ethylbenzene;
- Toluene;
- Light Aliphatic Hydrocarbons;
- Ethanolamine;
- Formic acid (?);
- Ammonia (?).

Source: Klean Strip

Hierarchy of Controls

Chromatography (substitution):

- Ethyl Acetate;
- Heptanes;
- Methyl *tert*-butyl ether (MTBE).

Extractions and Purifications (substitution):

- Ethyl Acetate;
- MTBE;
- Toluene;
- 2-Methyltetrahydrofuran (2-MeTHF).

Source: University of Minnesota

Conclusions

- Current sampling and analysis methods (active and passive sampling, solvent extraction) have reporting limits covering EPA's ECEL and STEL concentrations (2 and 16 ppm respectively);
- Methods involving thermal desorption and gas chromatography analysis offer improved detection and reporting limits;
- In laboratory conditions, exposures may occur at short period of time during solvent handling while setting up equipment for synthesis (> 15 min). In this case, based on airborne concentrations amount of analyte may be close method reporting limits;
- Attention should be paid to monitor concentrations at storage rooms (long-term exposure), solvent transfer and equipment setup (short-term exposure);
- Implementing the hierarchy of controls by substitution of methylene chloride may require use of other hazardous compounds that also require special attention.

Questions?

Thank you for your attention!