

# **Accelerated Solvent Extraction for Sample Preparation of Chemical Weapon Degradation Compounds**

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with support from the

**Defense Threat Reduction Agency**



**Constellation  
Technology**



**DTRA**  
DEFENSE THREAT REDUCTION AGENCY

# Background

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- **Analytical methods are needed for the monitoring of chemical weapons (CW) under the Chemical Weapons Convention**
- **One approach involves the detection of degradation compounds that remain following exposure of CW agents to the environment**
- **However, time is severely limited for conducting on-site analyses, therefore instrumentation which performs fast soil extractions and analyses is of great interest to those performing such analyses**



# Scope of Work

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**Assess the feasibility of employing an Accelerated Solvent Extraction (ASE) system to selectively extract CW degradation compounds from environmental samples (soils) for determinative chemical analysis**

- Develop and implement method for derivitization and characterization of CW degradation compounds via gas chromatography-mass spectrometry (GC-MS)
- Optimize ASE experimental parameters for extraction of CW degradation compounds spiked onto characterized soils and determine overall performance



# Target Compounds

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<b><u>Compound Name</u></b>	<b><u>Abbreviation</u></b>	<b><u>CW Source</u></b>
<b>Thiodiglycol sulfone</b>	<b>TDGS</b>	<b>Mustards</b>
<b>Thiodiglycol</b>	<b>TDG</b>	<b>Mustards</b>
<b>Ethylmethyl phosphonic acid</b>	<b>EMPA</b>	<b>Sarin, Soman, VX</b>
<b>Methyl phosphonic acid</b>	<b>MPA</b>	<b>Sarin, Soman</b>
<b>Pinacolylmethyl phosphonic acid</b>	<b>PMPA</b>	<b>Soman</b>
<b>Ethylmethyl phosphonothioic acid</b>	<b>EMPTA</b>	<b>VX</b>
<b>Diisopropylamino ethanol</b>	<b>DIPAE</b>	<b>VX</b>
<b>Triethanol amine</b>	<b>TEA</b>	<b>Mustards</b>



# GC-MS Characterization

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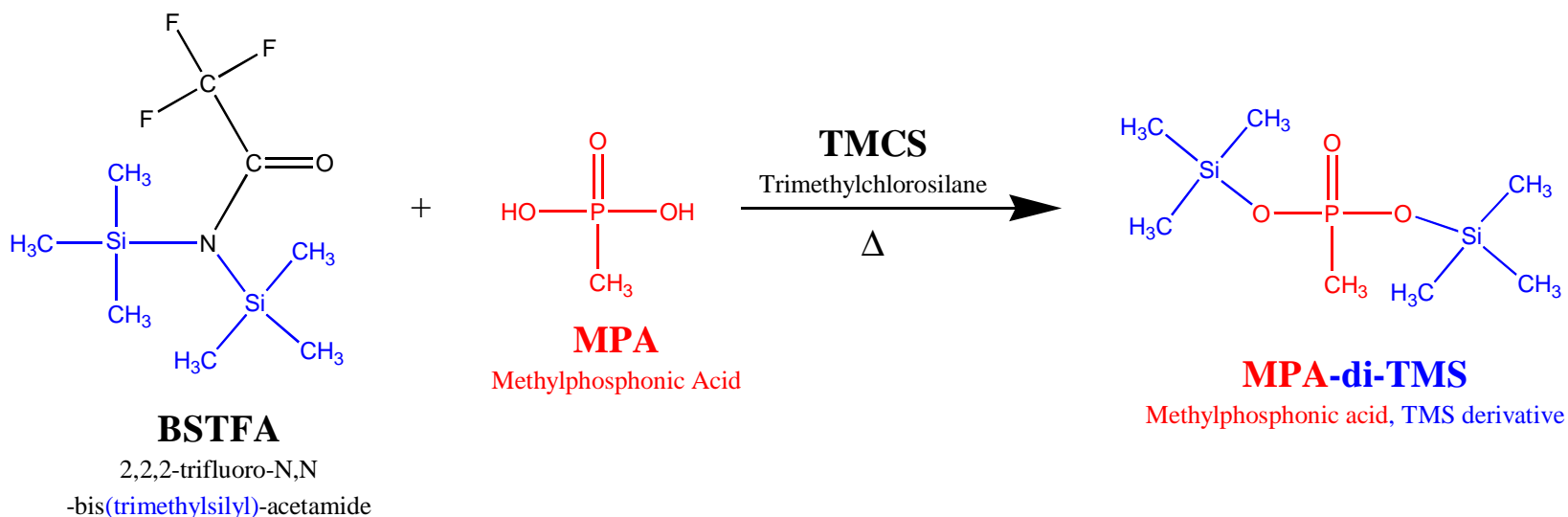
- **Implement instrument operating method using ROP\* as a guide**
  - Establish sample prep and derivitization procedures
  - Develop method for quantitative analysis of target compounds following ASE extraction

**\*Recommended Operating Procedure (ROP) for On-Site Analysis by Gas Chromatography - Mass Spectrometry**  
(Version 2.0 of Report of the Specialist Task Force on Analytical Issues to the Expert Group on Inspection Procedures (13.06.1996))



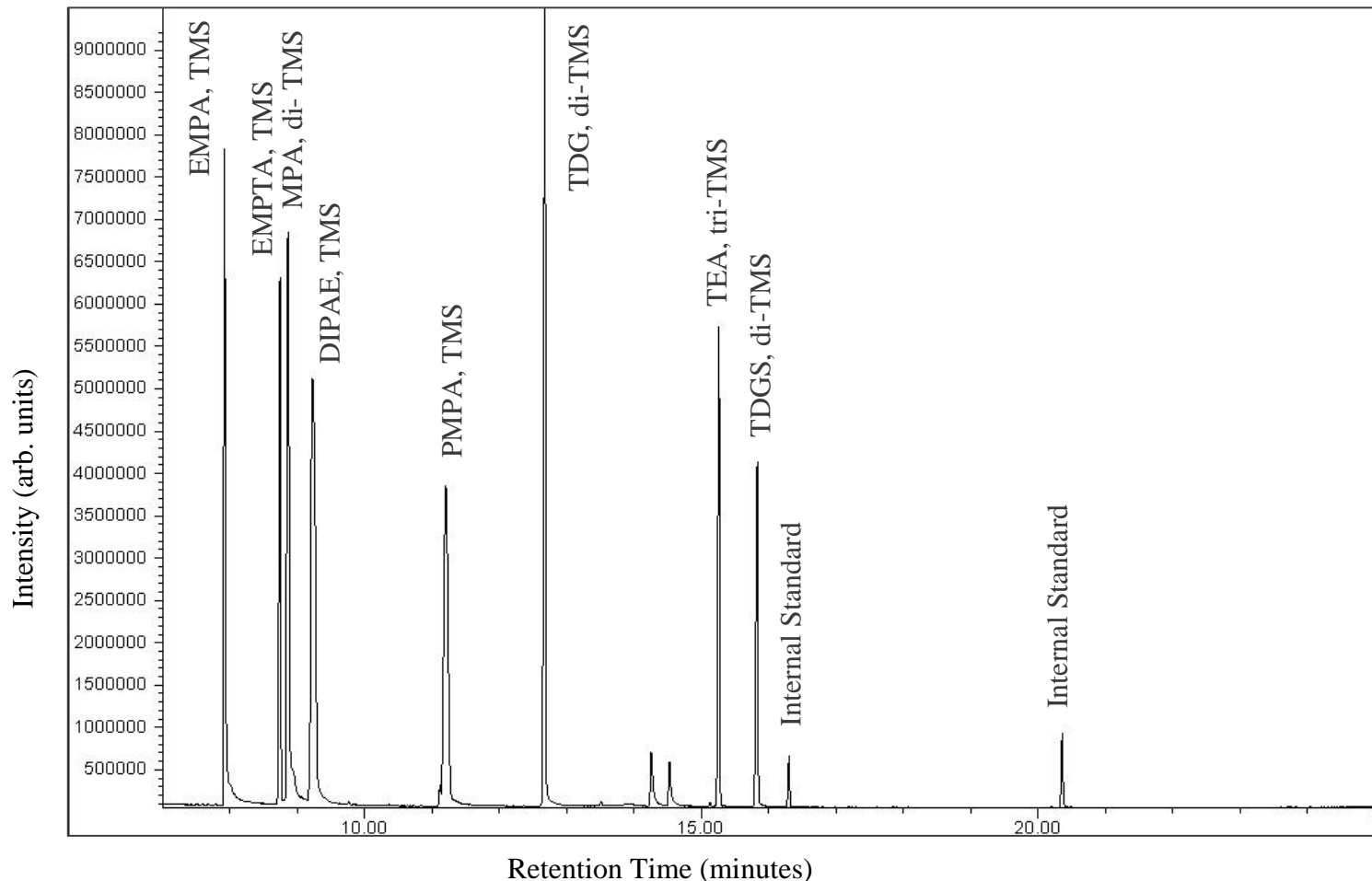
# Derivitization of Target Compounds

Target compounds cannot be detected directly by GC-MS; they must be derivitized by BSTFA prior to GC-MS analysis



# Total Ion Chromatogram

Derivatization and separation of all 8 target compounds



# Principles of ASE

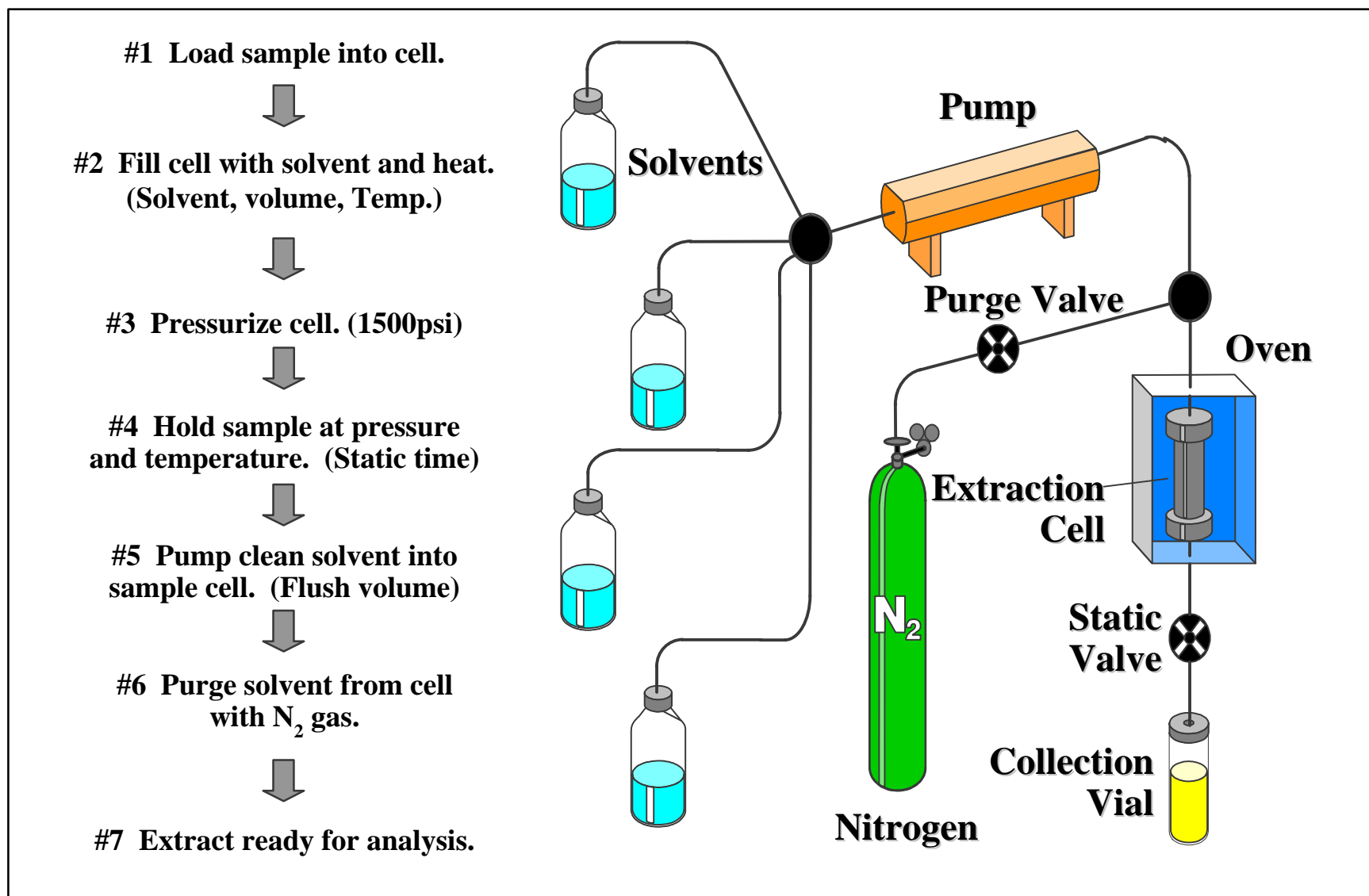
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**Accelerated Solvent Extraction is accomplished by applying high pressure and temperature to an extraction cell containing the sample and solvent**

- High temperature = greater solubility and solvent capacity, increased migration rate of analyte
- High pressure maintained to keep solvent in liquid phase at high temperatures



# Dionex ASE<sup>®</sup> 200 Schematic



# ASE Instrument Parameters

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## Parameters

- Solvent
- Solvent Temperature
- Solvent Flush Volume
- Static (Extraction) Time
- Number of Static Cycles
- Cell Pressure

## Experimental Values

Methanol

100 °C - 200 °C

60% of 22 mL Extraction Cell

5 minutes

1 cycle

1500 psi



# Experimental Procedure

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- **Characterized soils obtained from R.T. Corporation**
  - Soil #1 - sandy loam
  - Soil #2 - sandy clay-loam
  - Soil #3 - loam
  - Inert Sand (Ottawa Sand, 20 - 30 mesh: Fisher Scientific)
- **Soils spiked with ~ 500mg target compound per 10g of soil prior to ASE extraction (50ppm target/10g soil)**
- **Optimize ASE instrument parameters (mainly temperature) by determining percent recoveries of analytes**



# Experimental Procedure

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- **ASE extractions performed in sets of 12, 3 cells for each soil matrix, for each of the 8 target compounds and using extraction temperatures of 100°C, 125 °C, 150 °C, 175 °C, and 200 °C.....480 extractions!**

⇒ Time required for extraction of 24 samples: 6 - 8 hours + sample prep time (loading and cleaning of extraction cells, etc.)



# Experimental Procedure

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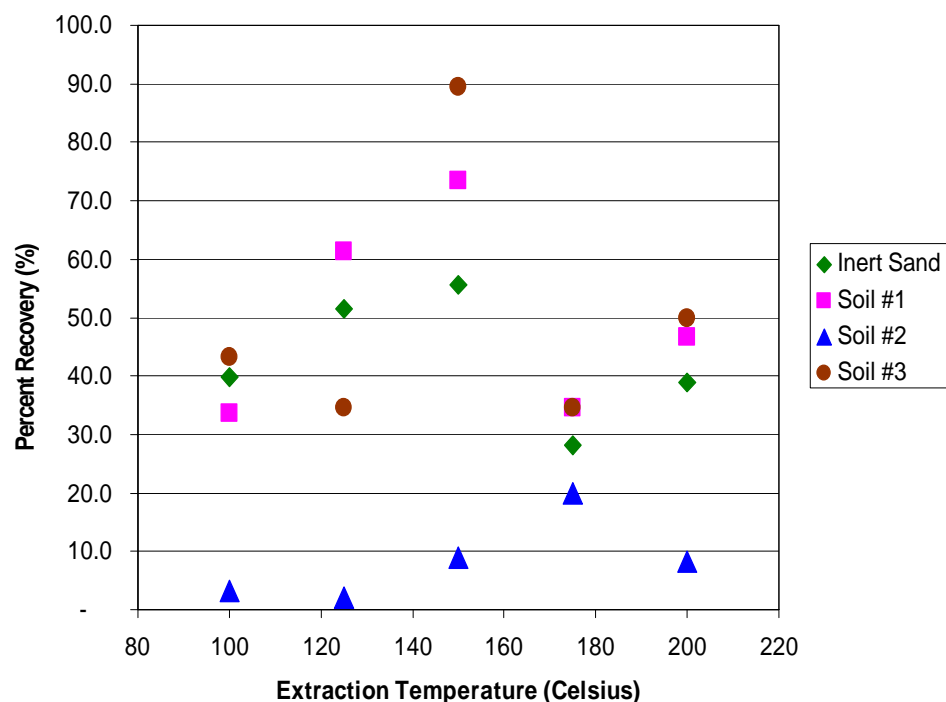
- **Evaporation of solvent by nitrogen blowdown**
- **Derivitization of extracted target compounds**
  - ⇒ Time required for solvent evaporation and derivitization: 6 - 8 hours
- **Dilution of derivitized samples and addition of internal standards followed by GC-MS analysis**
  - ⇒ Time required for GC-MS analysis of 30 samples (24 ASE extractions + 6 daily QC samples): 24 hours



# Percent Recoveries

- Example of data generated for one of the 8 target compounds; each data point is the average of 3 identical runs

**TDG**



	100°C	125°C	150°C	175°C	200°C
Inert Sand	39.8 ± 2.9	51.4 ± 2.1	55.7 ± 6.6	28.1 ± 2.9	38.9 ± 14.3
Soil #1	33.6 ± 3.6	61.4 ± 19.1	73.5 ± 17.1	34.6 ± 5.8	46.7 ± 3.1
Soil #2	3.1 ± 2.8	2.1 ± 3.6	8.9 ± 13.4	19.8 ± 20.1	8.2 ± 7.1
Soil #3	43.2 ± 7.7	34.6 ± 30.4	89.4 ± 9.8	34.5 ± 6.6	49.9 ± 7.7

# Maximum Recoveries of Target Compounds Using ASE

	Inert Sand	Soil #1 Sandy Loam	Soil #2 Sandy Clay-Loam	Soil #3 Loam
TDG	56 ± 7 %	74 ± 17 %	8 ± 7 %	89 ± 10 %
TDGS	99 ± 3 %	95 ± 19 %	1 ± 1 %	77 ± 1 %
EMPTA	95 ± 9 %	57 ± 7 %	4 ± 2 %	42 ± 2 %
PMPA	40 ± 4 %	30 ± 3 %	1 ± 1 %	6 ± 2 %
EMPA	28 ± 2 %	14 ± 1 %	1 ± 1 %	4 ± 2 %
MPA	2 ± 2 %	0 %	0 %	0 %
DIPAE	74 ± 10 %	23 ± 3 %	5 ± 4 %	14 ± 3 %
TEA	60 ± 4 %	2 ± 2 %	2 ± 2 %	4 ± 0 %



# CONCLUSIONS

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- **Highest recoveries obtained at 100°C to 150°C**
- **High extraction temperatures (175°C and 200°C) yield lower recoveries, possibly due to:**
  - ⇒ Greater extraction of interfering organic compounds
  - ⇒ Breakdown of target compounds
- **Poor recoveries in Soil #2, possibly due to smaller particle size (greater surface area)**
- **Inert sand and Soil #1 yield highest recoveries**



# CONCLUSIONS

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**With the exception of Soil #2...**

- **Excellent recovery of TDG, TDGS, EMPTA (50 - 90%)**
- **Moderate recovery of EMPA, TEA, DIPAE in sand (25 - 50%), poor recovery in soil #1, #3**
- **Moderate recovery of PMPA in sand, soil #1 (30 - 40%), poor recovery in soil #3**
- **Poor recovery of MPA in all matrices (< 10%)**



# Evaluation of ASE for CW Sample Prep

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- **Advantages of ASE for CW Sample Prep**
  - Automation of solvent extraction
  - Fast extraction time
  - Low volumes of solvent used
  - High recoveries of TDG, TDGS, and EMPTA
- **Disadvantages of ASE for CW Sample Prep**
  - Cost of equipment and maintenance required after 100's of extractions
  - Moderate recoveries of EMPA, PMPA, TEA, DIPAE in inert sand only
  - Poor recovery of MPA in all matrices
  - Poor recoveries of all analytes from soil #2



# Future Work

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- **Investigate “fast” GC technology to reduce GC-MS analysis time and increase sample throughput**

- **Equipment to be used:**

Agilent Tech. 6890 fast GC equipped with an O.I. Analytical pulsed-flame photometric detector (PFPD) or an Agilent 5973 mass-selective detector

