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Edgewood Chemical Biological Center

Analysis of Chemical Warfare Agents: processes for unknown environmental samples

11 August 2017

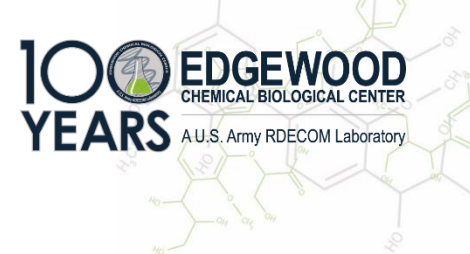
Joy Ginter, Alex Jestel, Stanley Ostazeski

Forensic Analytical Branch

Overview

- ECBC Forensic Analytical Center (ECBC FAC)
- Chemical Weapons Convention (CWC)
- Organization for the Prohibition of Chemical Weapons (OPCW)
- Environmental Proficiency Tests
 - Overview
 - Techniques employed by ECBC FAC

Forensic Analytical Center



- Edgewood Chemical/Biological Forensic Analytical Center (EC/B FAC) – located at Edgewood Area of Aberdeen Proving Ground, MD
- Forensic chemical analysis for both chemical and biotoxin threat agents, explosives, etc.
 - US Army and Department of Defense
 - US Department of Homeland Security (DHS)
 - FBI and other Government agencies
- Sample analysis missions for various clients and Government agencies
- US representative laboratory to the Organization for the Prohibition of Chemical Weapons (OPCW)
- Compliance analysis facility for the US Army Chemical Agent Standard Analytical Reference Material (CASARM) Program and several demilitarization programs
- Deploy and support mobile laboratories for chemical analysis



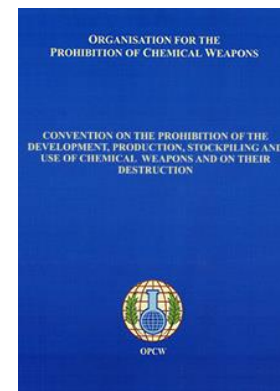
Chemical Weapons Convention (CWC)

- Entered into force April 29, 1997
- Prohibits the development, production, stockpiling and use of chemical weapons (CW)
- 190 Member States (98% of global population)
- Signed but not ratified:
 - Israel, Myanmar (1993)
- Unsigned:
 - Angola, North Korea, Egypt

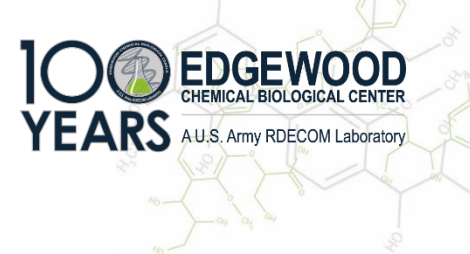


CWC Schedules

- Schedule 1: Classic CWAs
 - Sarin, soman, tabun, VX, sulfur mustards, lewisite(s), nitrogen mustards, saxitoxin, ricin
- Schedule 2: “Chemicals, except for those listed in Schedule 1, containing a phosphorus atom to which is bonded one methyl, ethyl or propyl (normal or iso) group but not further carbon atoms,”
- Schedule 3: Toxic chemicals that often have large-scale industrial use as well
 - Phosgene, Cyanogen chloride, Hydrogen cyanide



Organization for the Prohibition of Chemical Weapons (OPCW)



- Headquarters: The Hague, Netherlands
- ~500 employees
- Implementing body of CWC to ensure compliance and oversees destruction of chemical weapons
- Provides on-site inspection/verification activities
- Provides off-site verification and analysis via an international network of “Designated Laboratories”
- Administers “Proficiency Tests” to annually certify competence of Designated Laboratories
- Awarded Nobel Peace Prize in 2013



OPCW Designated Laboratory

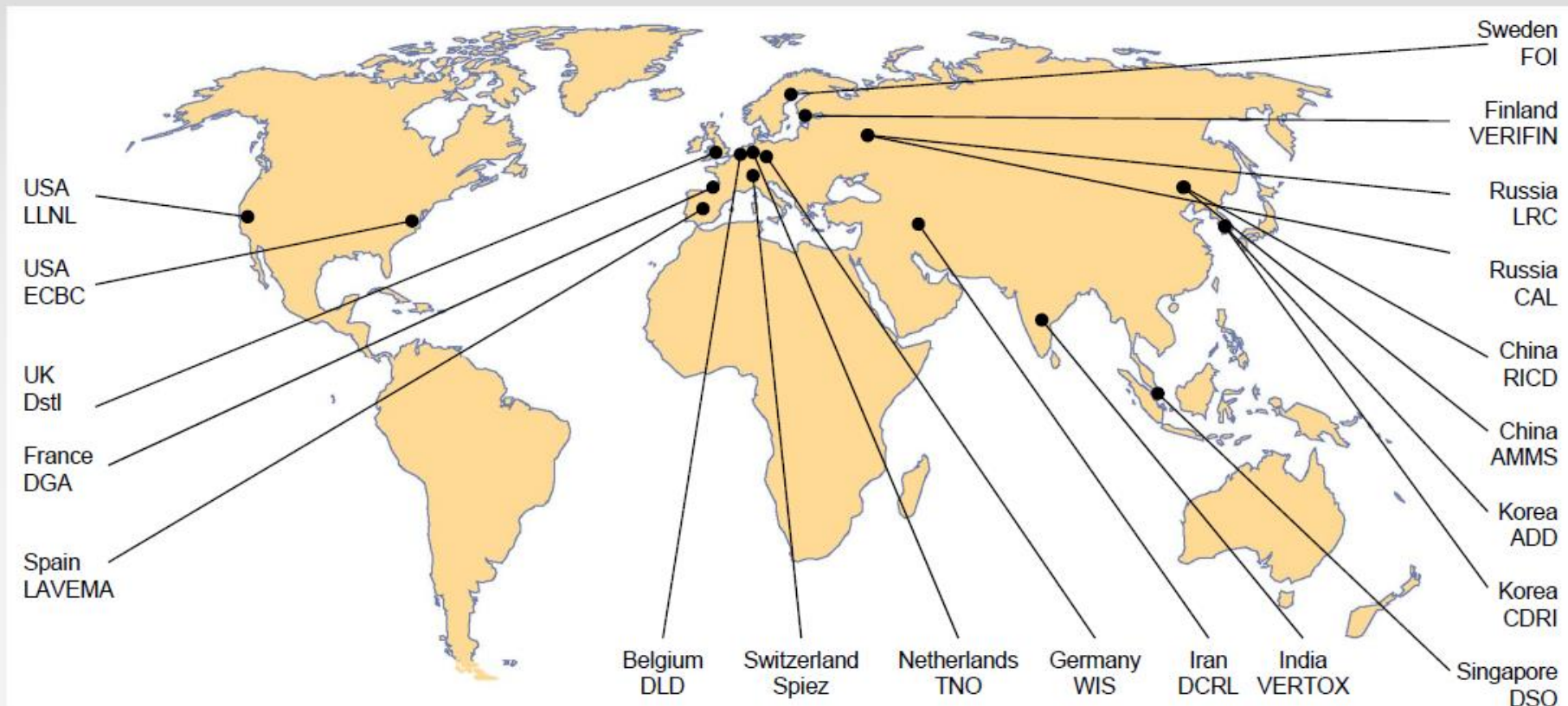
- Primary role – off-site forensic analysis of authentic samples collected during OPCW inspections
 - Challenge inspections – key role
 - Investigation of Alleged Use – key role (Syria)
 - Routine inspections – limited to ambiguities not resolved by on-site analysis



- Other roles
 - Assist OPCW in preparing and evaluating proficiency tests
 - Development and validation of analytical methods
 - Synthesis of chemicals and collection of reference data
 - Technical training

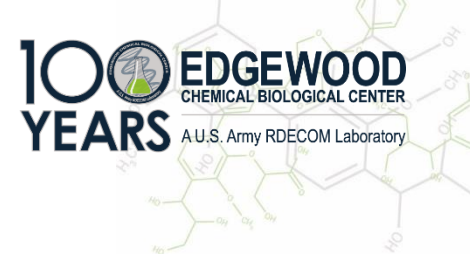
OPCW Laboratory Network

OPCW Designated Laboratories



20 Designated Laboratories (1 suspended) in 16 countries
as of July 2017

US Designated Laboratories



- Congress mandates that all samples collected in the U.S. must remain in the U.S.
- CWC requires samples be sent to at least two OPCW-designated laboratories
- To meet the above requirements, U.S. has two OPCW-designated laboratories
 - U.S. Army ECBC Forensic Analytical Center (FAC) 1998
 - Lawrence Livermore National Laboratory (LLNL) 2003



Requirements for Designation

- Must score a minimum of 2 A's and 1 B on 3 consecutive tests and maintain on a rolling basis
- Must participate in at least 1 proficiency test per calendar year (2 offered per year)
- Must have an established quality system that is accredited by an internationally recognized body
- ECBC/FAC has participated in 25 proficiency tests and received 22 A's since 1996.

Environmental Proficiency Tests

- Samples from 2 different matrices are provided, each containing:
 - Test sample (spiking chemicals >1 ppm)
 - Control sample (spiked at >5 ppm)
 - Blank (no relevant chemicals)
- Samples received blind with random IDs
- Objective: identify scheduled chemicals, their precursors and degradation/reaction products (5-9 spiked chemicals per test)
 - Also must report any chemicals that are “one reaction step away from a scheduled chemical”
 - Non-Scheduled Reportable Chemicals
- Test time for analysis and reporting: 15 calendar days (report ~100 pages)

Test Sample Matrices

- Commonly used matrices

- Organic (DCM, hexane, decane, toluene, $C_{12}H_{26}$, chlorobenzene, pump oil)
- Aqueous
- Soil



- Other matrices previously used

- Decon solutions, wipes, painted plates, emulsions, wall plaster, floor tile, agar gel, aluminum

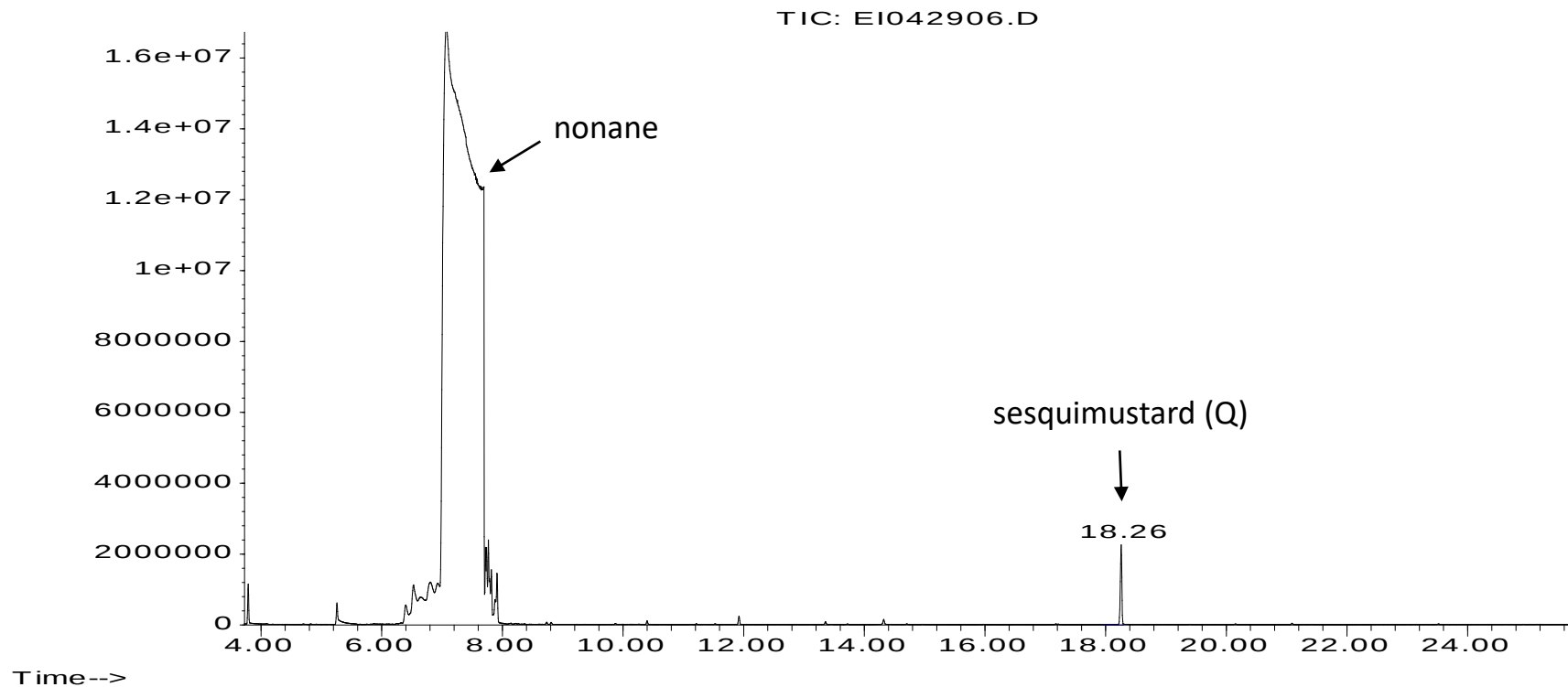


Sample Interferents

- Organic and soil
 - Diesel fuel (~500 ug/mL, but as high as 1%)
 - Mineral grease, machine oil
- Aqueous
 - Polyethylene glycols (PEG, ~0.5 mg/mL)
 - Metals/salts/acids (Borax, degreaser, CaCl_2 , MgSO_4 , fatty acids, 2-methoxyethanol, etc), paramagnetic (NMR)
- All
 - Pesticides and other irrelevant compounds containing P, S, Cl and N

GC/MS Chromatogram of a Test Sample

Abundance

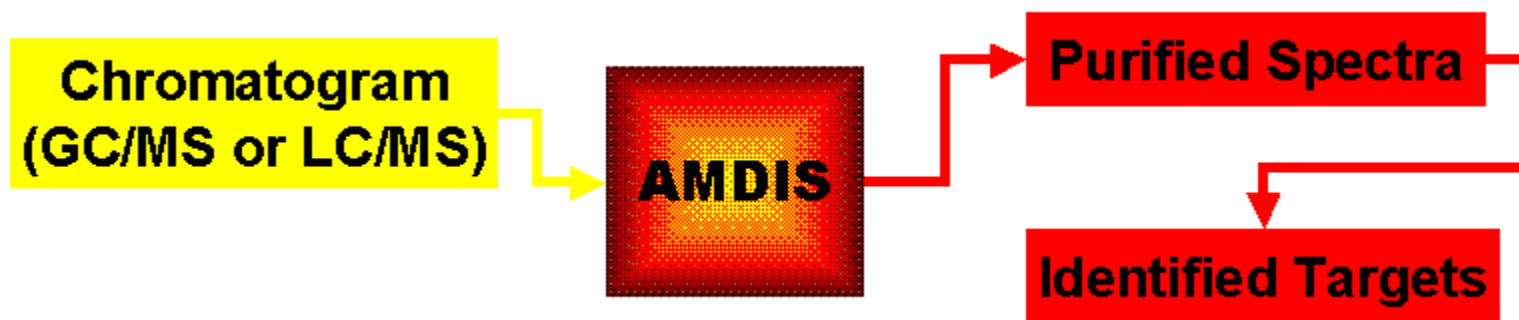


Sample 128: Organic, Direct Split
25th OPCW Proficiency Test

Strategies for Detecting Analytes Under Nonane Interferent

- AMDIS library search
- Selective detectors (dFPD, AED)
- Sample cleanup (SPE or solvent extraction)
- Different phase GC column (DB-1701)

Automated *M*ass Spectral *D*econvolution & *I*dentification *S*ystem



Software supplied by NIST

GCMS (EI) Libraries

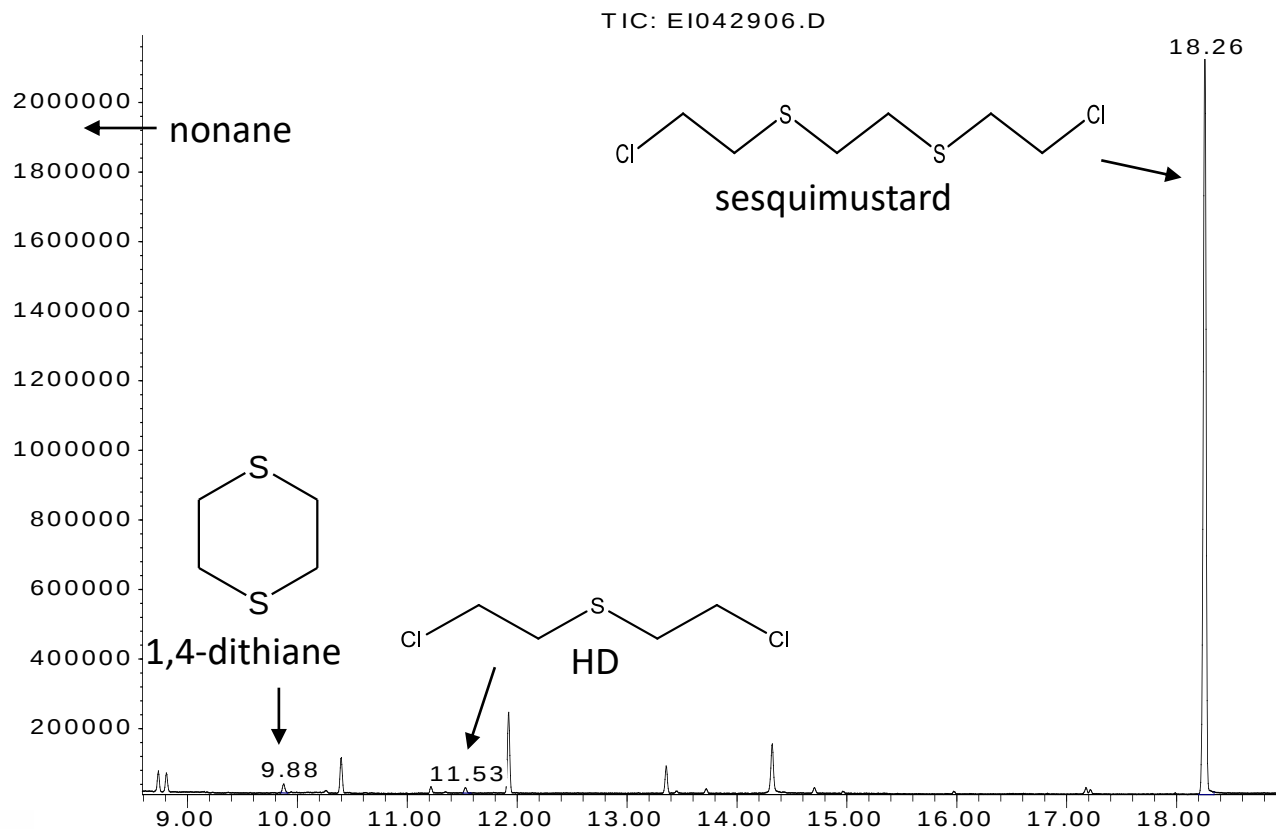
- **OPCW Central Analytical Database (OCAD)**
 - scheduled compounds only
 - MS (3940), GC-RI (3324), NMR (1391), IR (925)
- **Validation Group Working Database (VGWD)**
 - OCAD + unscheduled agent degradation products
- NIST and other commercial libraries
- In-house user libraries

AMDIS Matches

- **Divinylsulfoxide [DVSO]** (RT 7.05 min, RI_c 885)
CH2=CHS(=O)CH=CH2
- **Sesquimustard [Q]** (RT 18.26 min, RI_c 1731)
ClCH2CH2SCH2CH2SCH2CH2Cl
- **1,4-Dithiane** (RT 9.87 min, RI_c 1074)
C4H8S2
- **Mustard gas [HD]** (RT 11.53 min, RI_c 1180)
ClCH2CH2SCH2CH2Cl

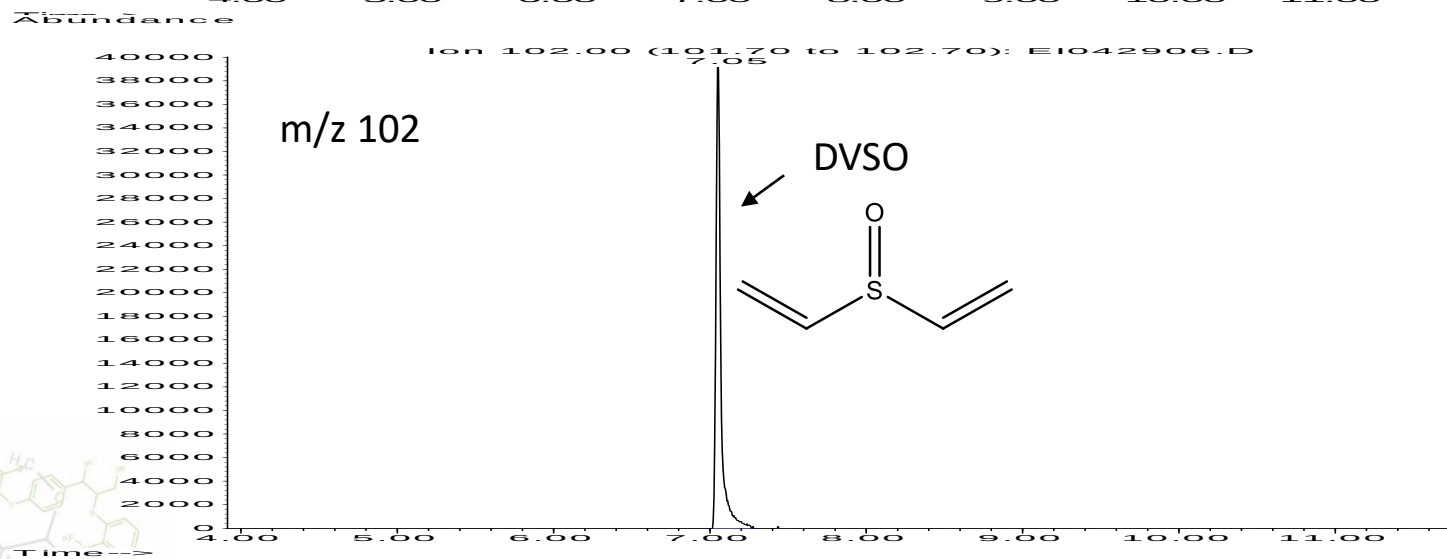
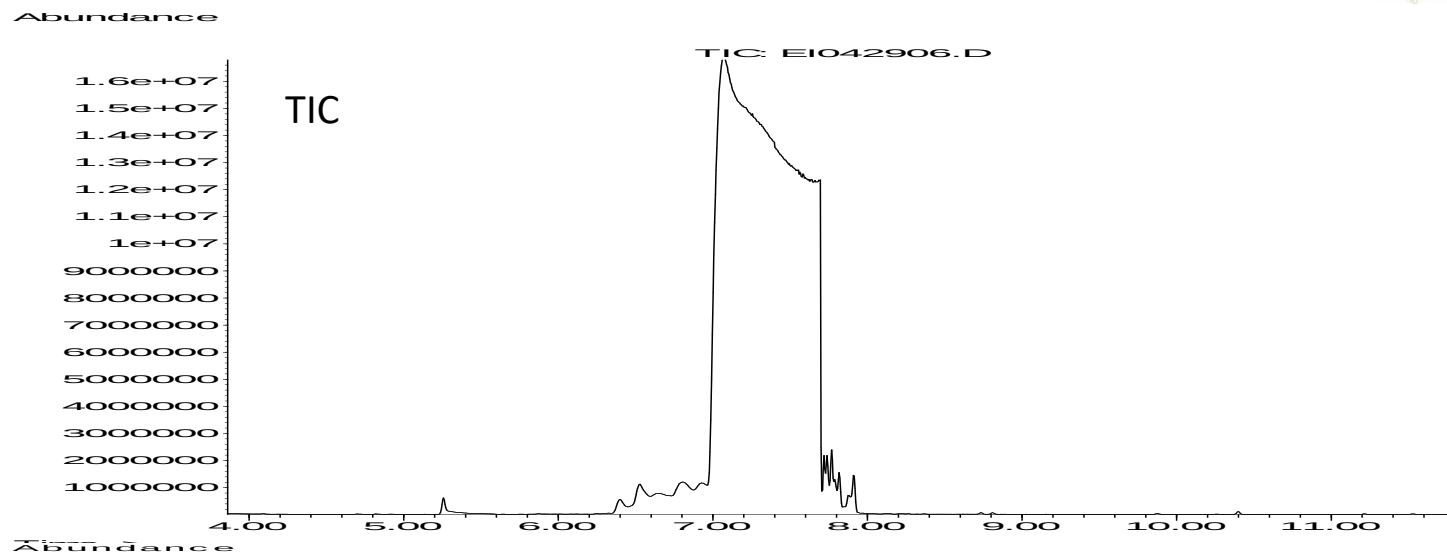
GC-MS Chromatogram

Abundance



Time-->

GCMS Chromatogram

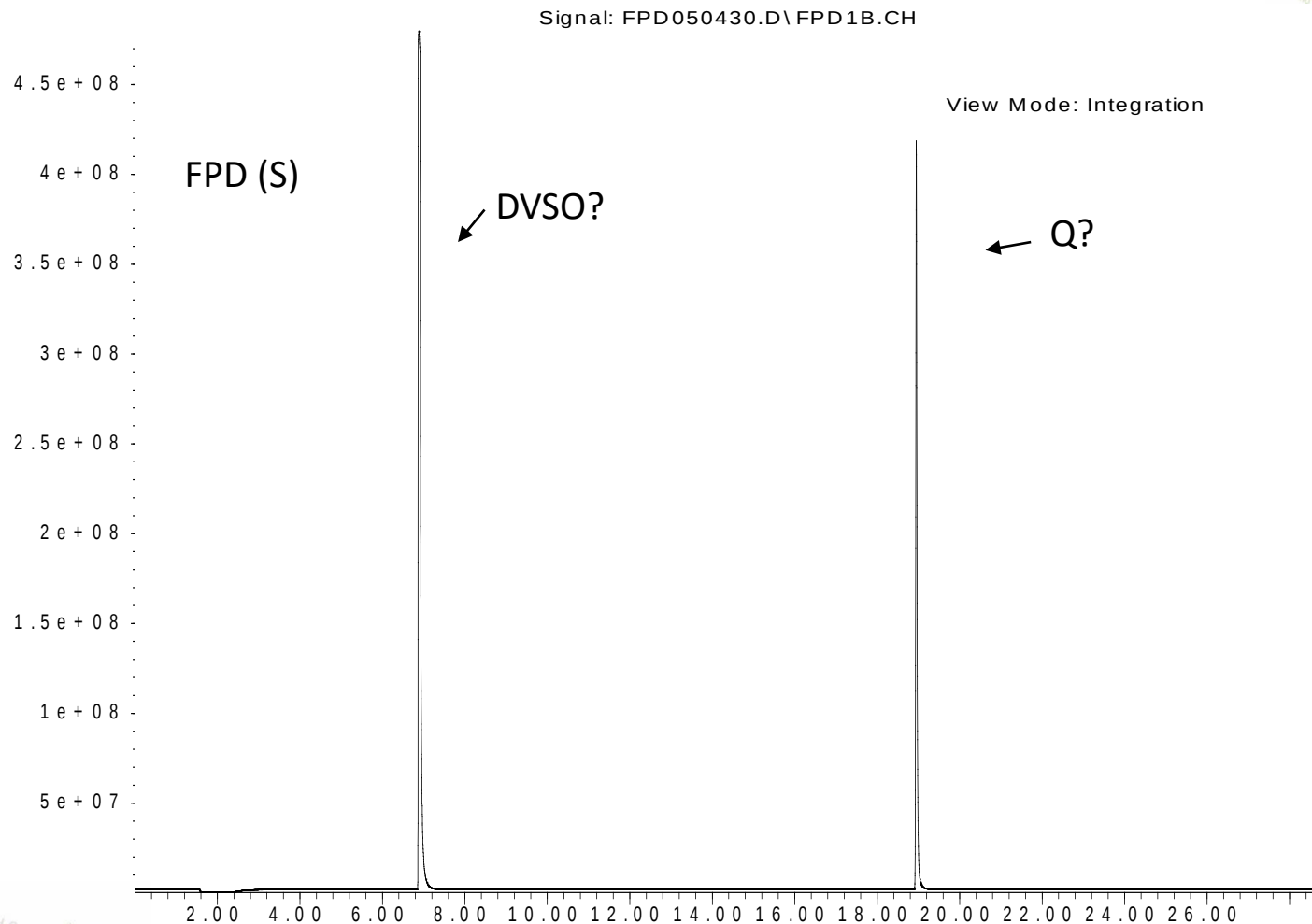


Strategies for Detecting Analytes Under Nonane Interferent

- AMDIS library search
- Selective detectors (dFPD, AED)
- Sample cleanup (SPE or solvent extraction)
- Different phase GC column (DB-1701)

Initial d-FPD Screening

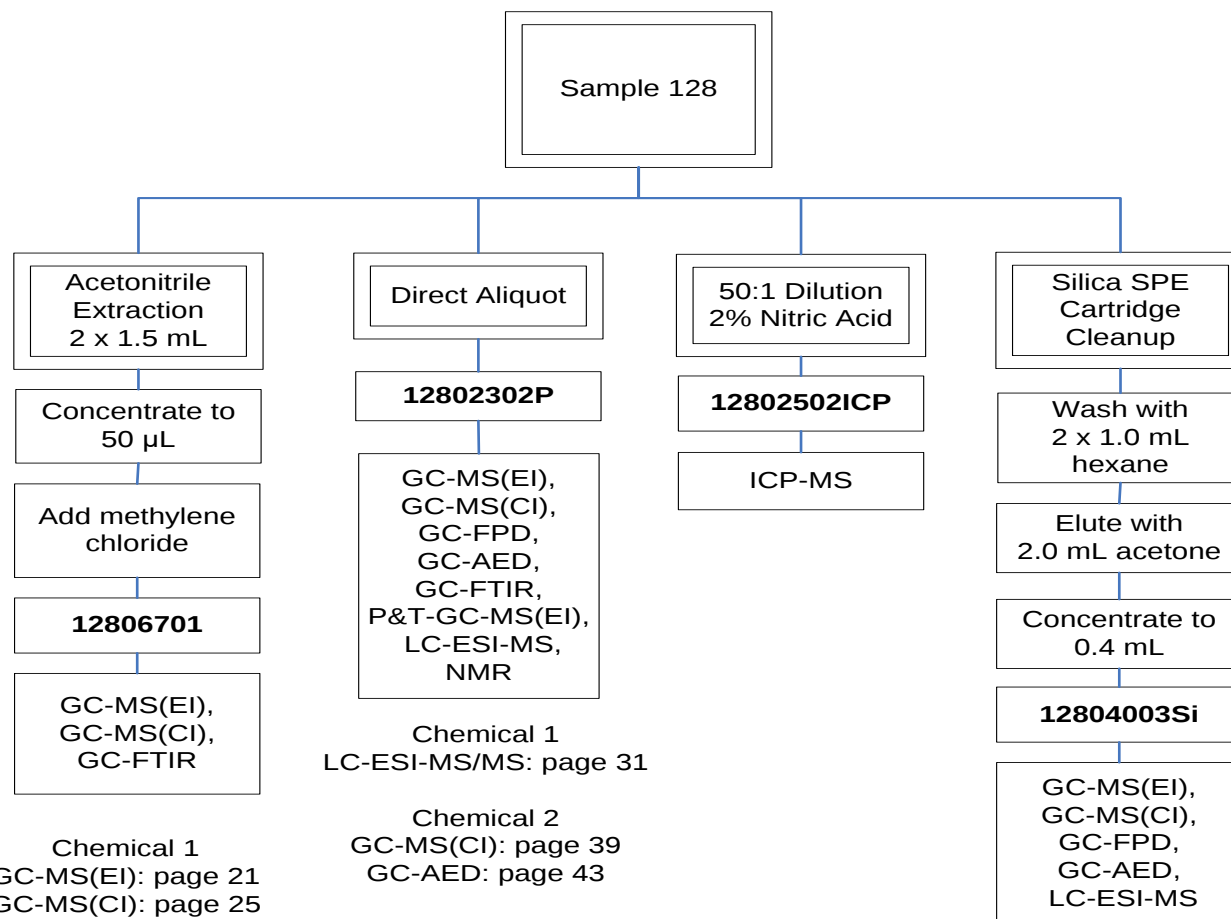
Response_



Strategies for Detecting Analytes Under Nonane Interferent

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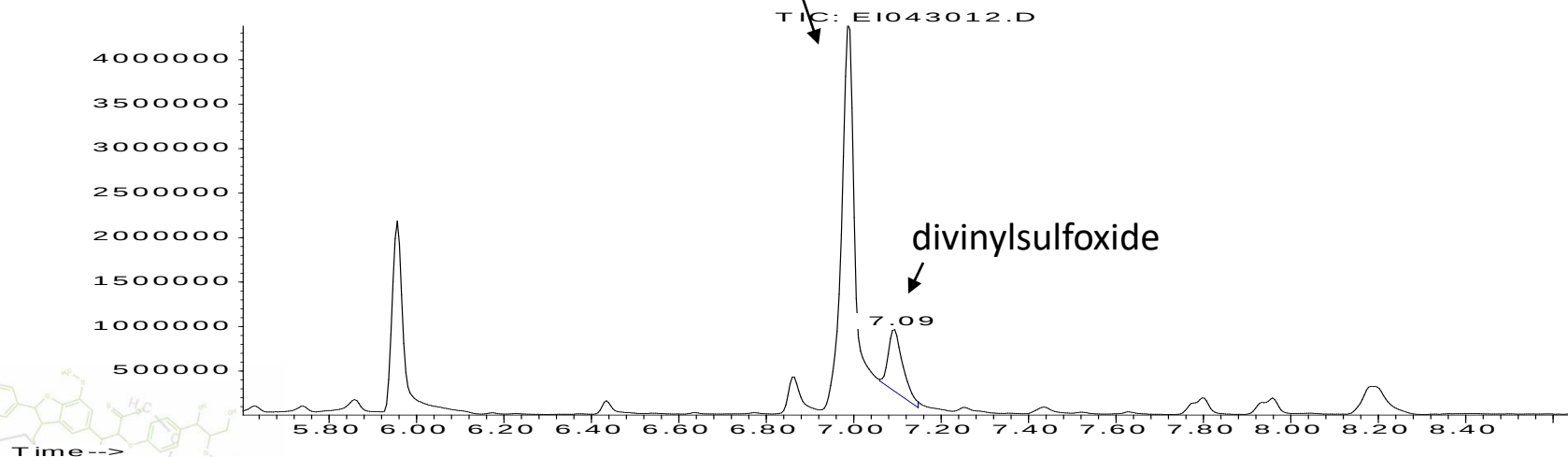
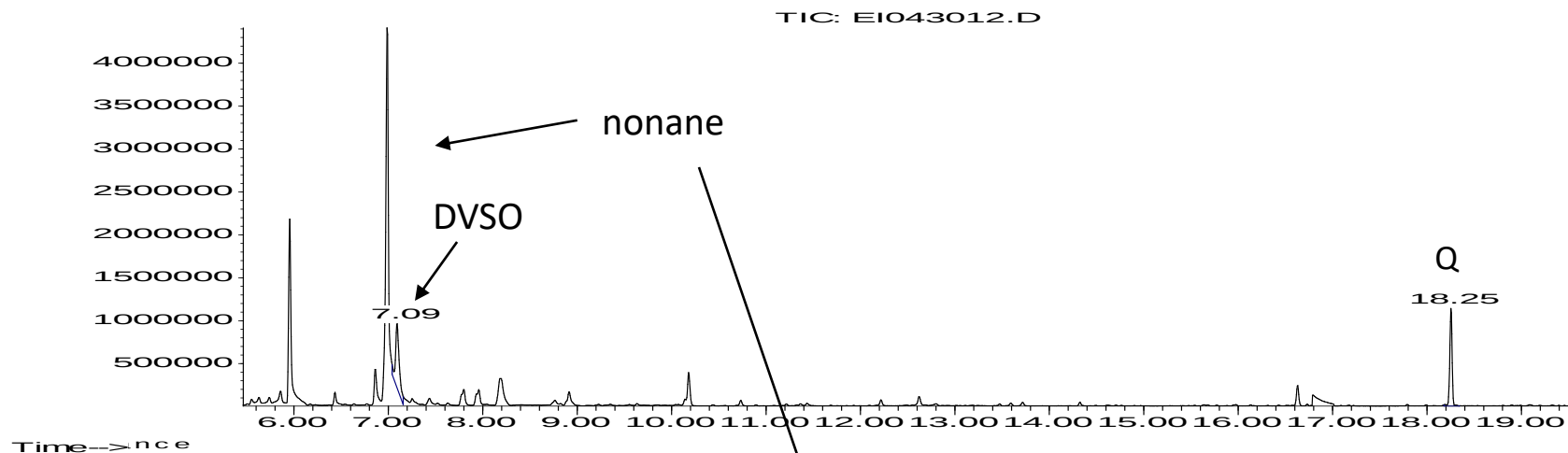
Sample Preparation Scheme



Chemical 1 = DVSO
Chemical 2 = Q

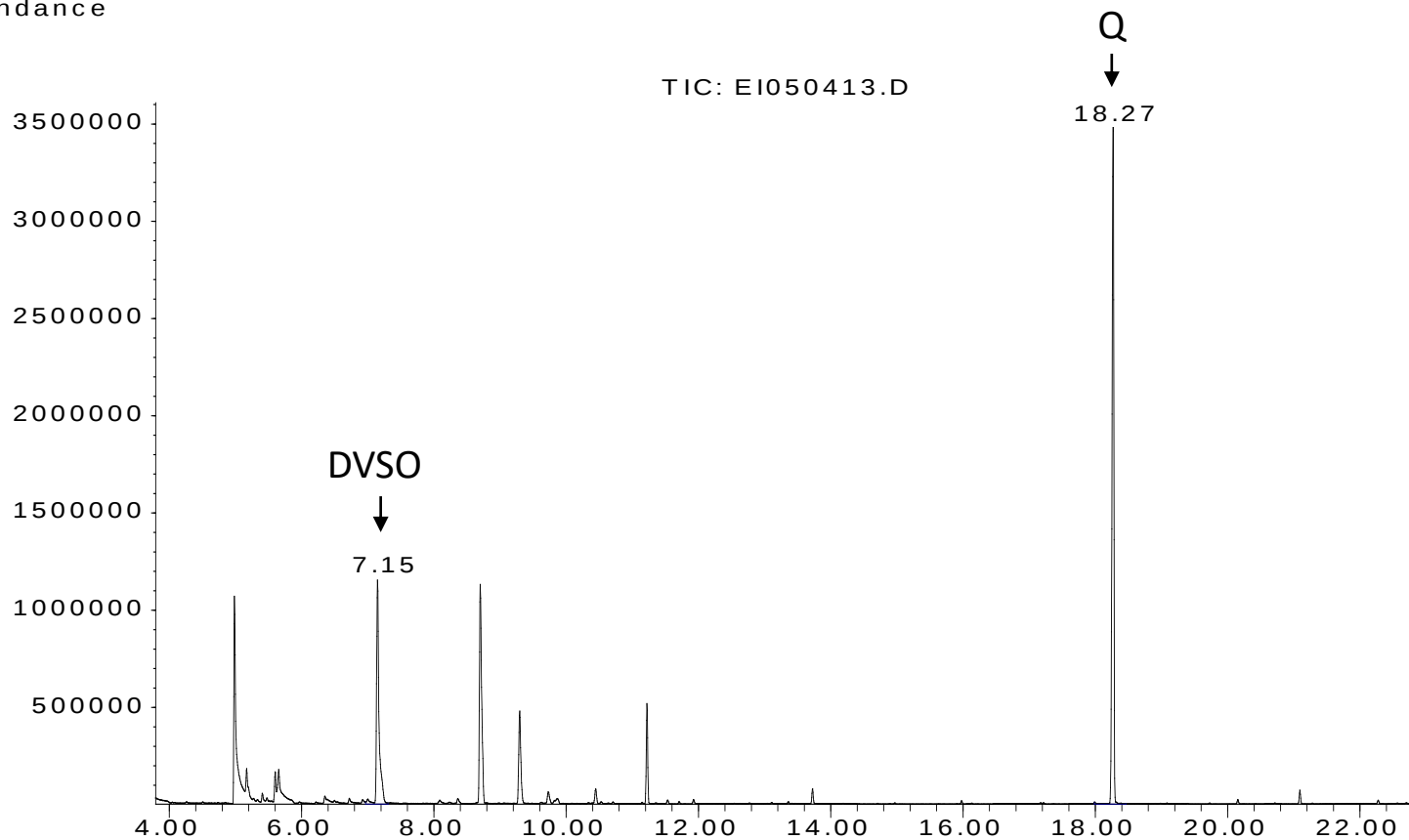
GC/MS Chromatogram after Silica Solid Phase Extraction Cleanup

Abundance



GC-MS Chromatogram of Sample after Acetonitrile Extraction

Abundance



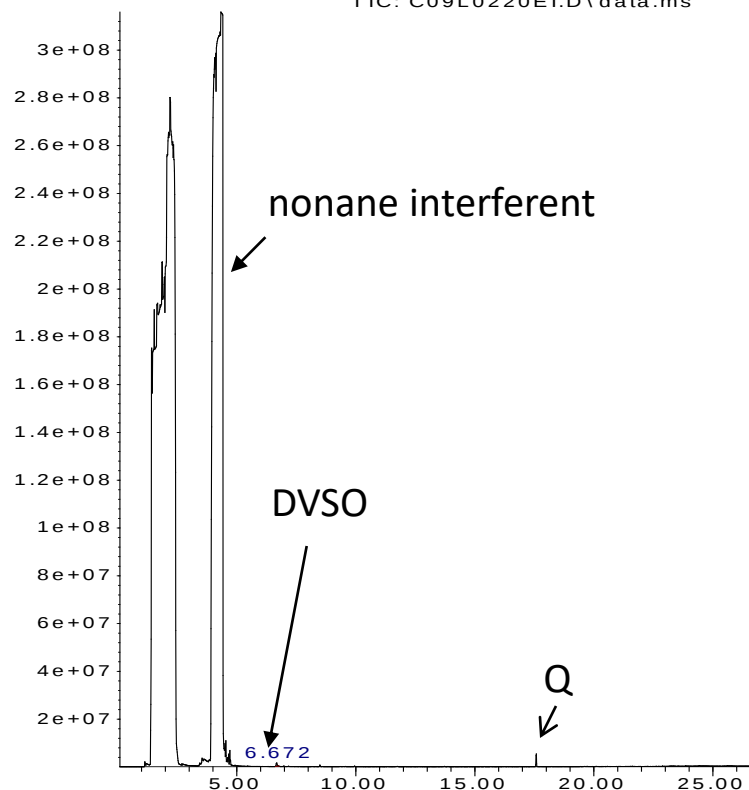
Strategies for Detecting Analytes Under Nonane Interferent

- AMDIS library search
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Analysis of Direct Split using VF 1701 MS Column

Abundance

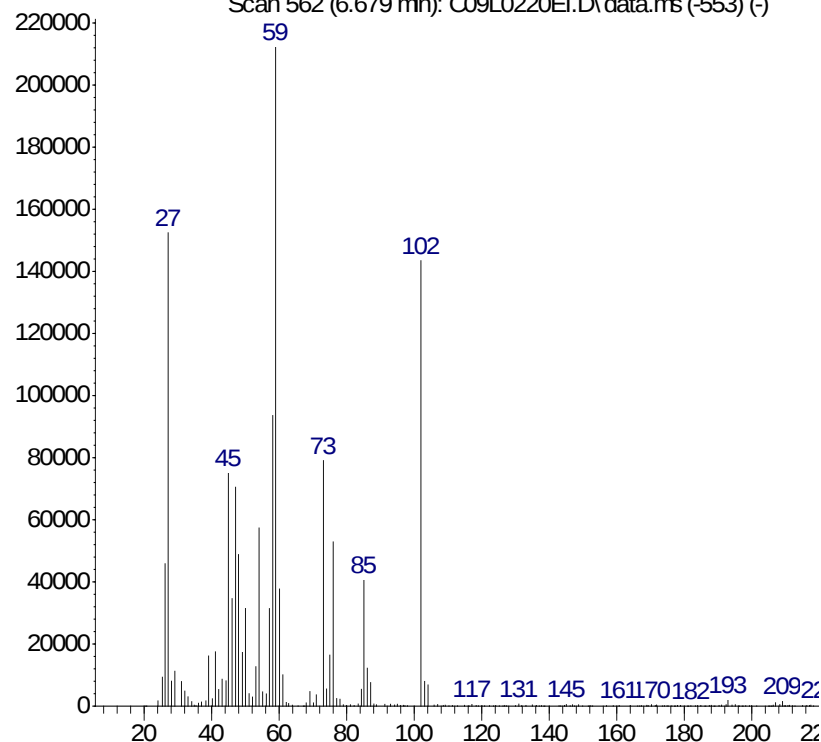
TIC: C09L0220EI.D\data.ms



Time-->

Abundance

Scan 562 (6.679 min): C09L0220EI.D\data.ms (-553) (-)



m/z-->

Presented by French CEB laboratory at evaluation meeting July 2009

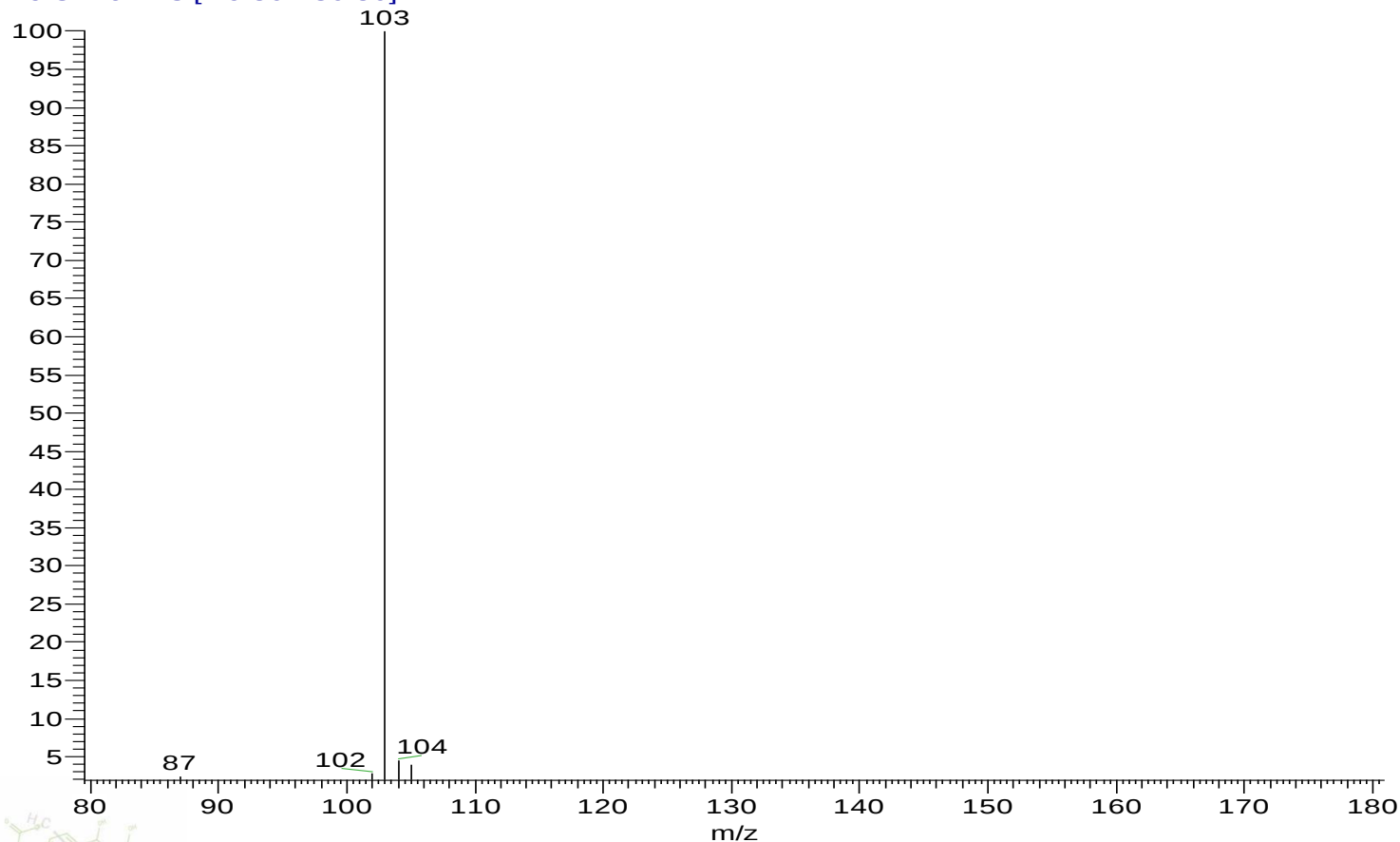
Identification of DVSO Supporting CI (isobutane) Data

D:\XCALIBUR\...\25th OPCW\IBCI050602

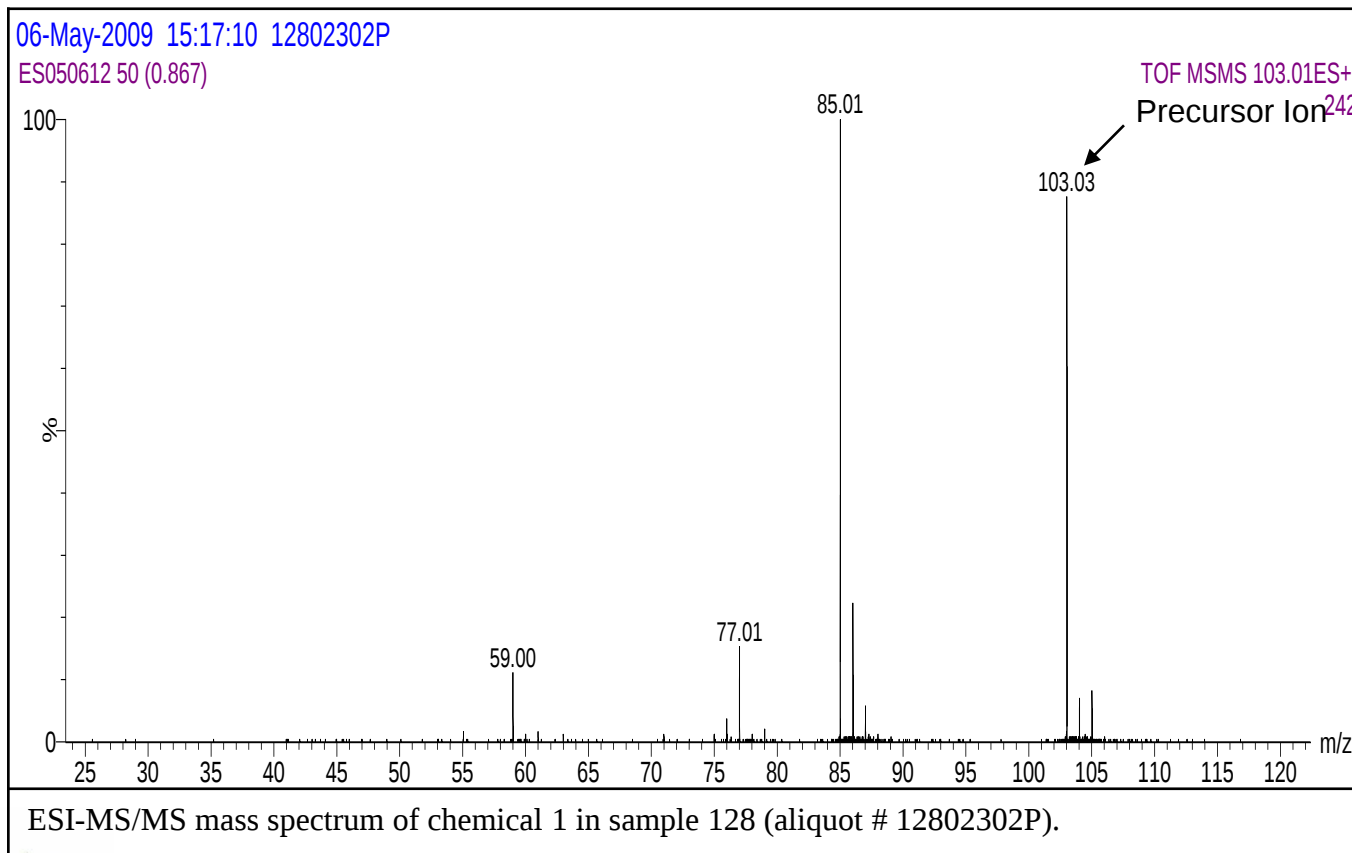
5/6/2009 2:25:57 PM

12806701

IBCI050602 #704-710 RT: 11.46-11.56 AV: 7 SB: 56 10.3
T: + c CI Full ms [79.50-430.50]



Identification of DVSO Supporting ESI-MS/MS Data



Other Techniques if Conventional Sample Cleanup Fails

- GC-MS/MS and LC-MS/MS
 - Product or parent ion scan
- HRMS
- GCxGC/MS
- SPME-GC-MS

Chloropicrin (PS) Detection in Pump Oil

Abundance

TIC: 04280502.D

After NH₂ SPE Cleanup

PS

Time-->

Abundance

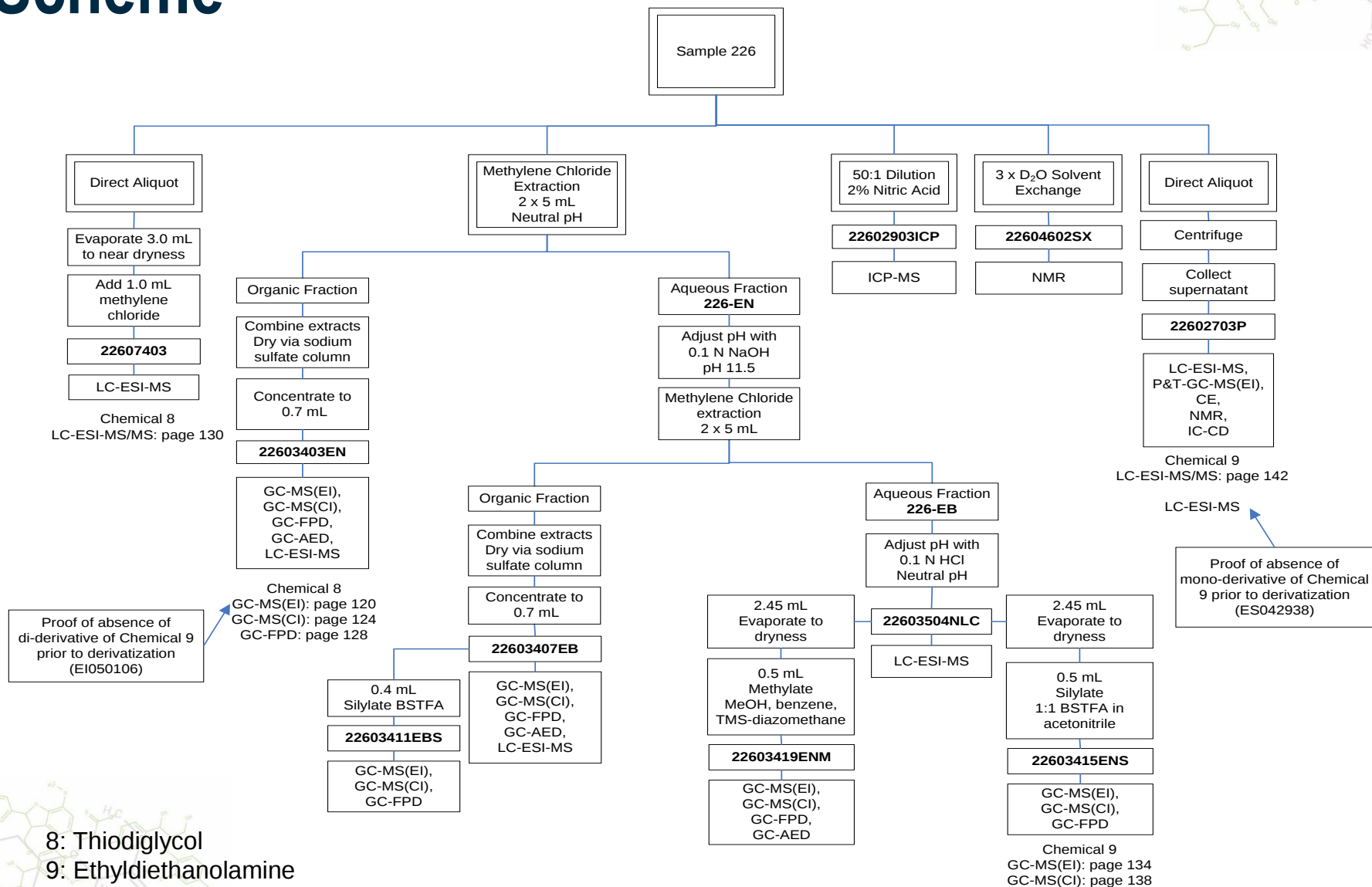
TIC: 05100507.D

SPME (headspace)
3 drops sample
PDMS/DVB Fiber
95°C/30 minutes

PS

Time-->

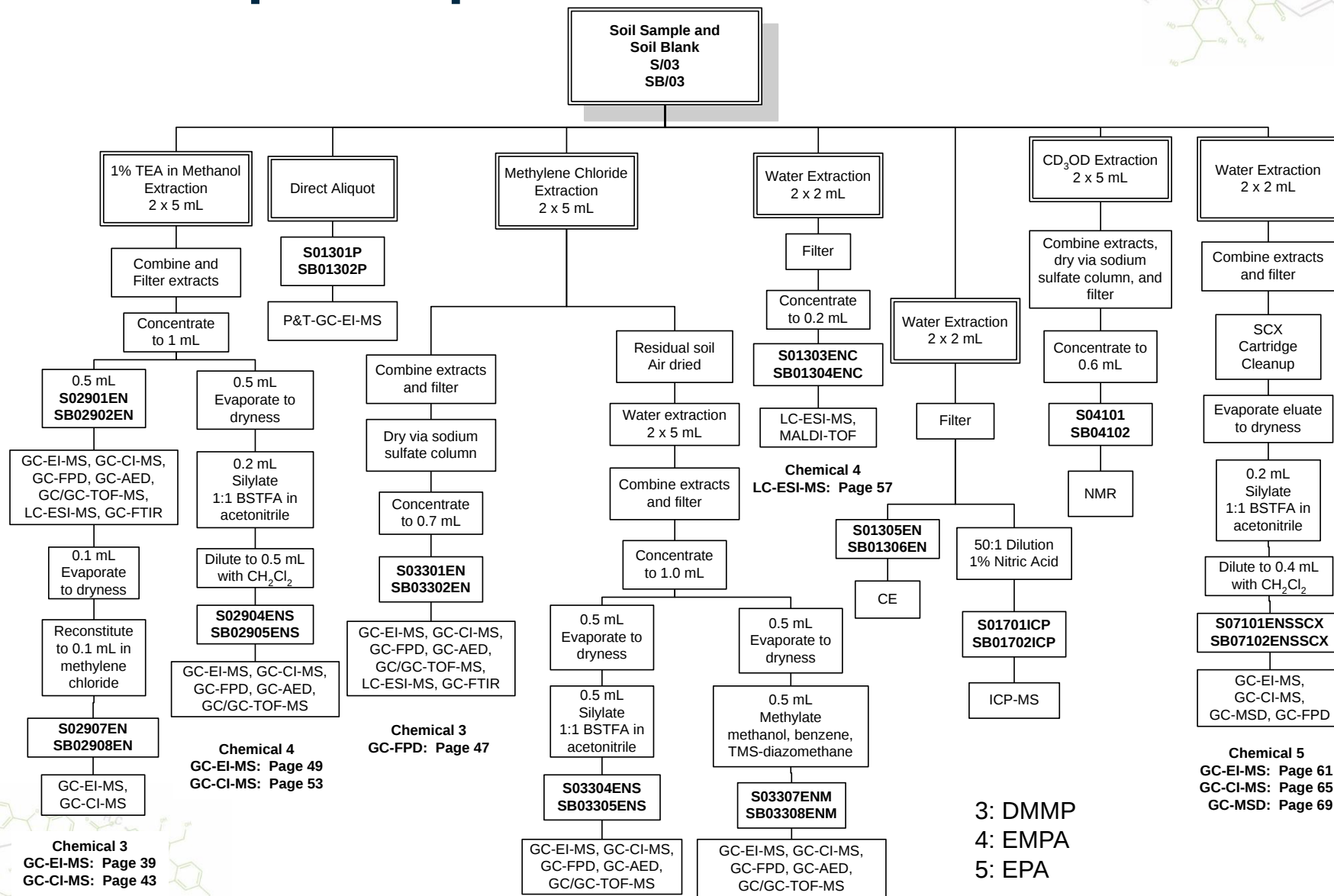
Aqueous Sample Preparation Scheme



8: Thiodiglycol

9: Ethyldiethanolamine

Soil Sample Preparation Scheme



Acknowledgements

- Forensic Analytical Center Colleagues

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