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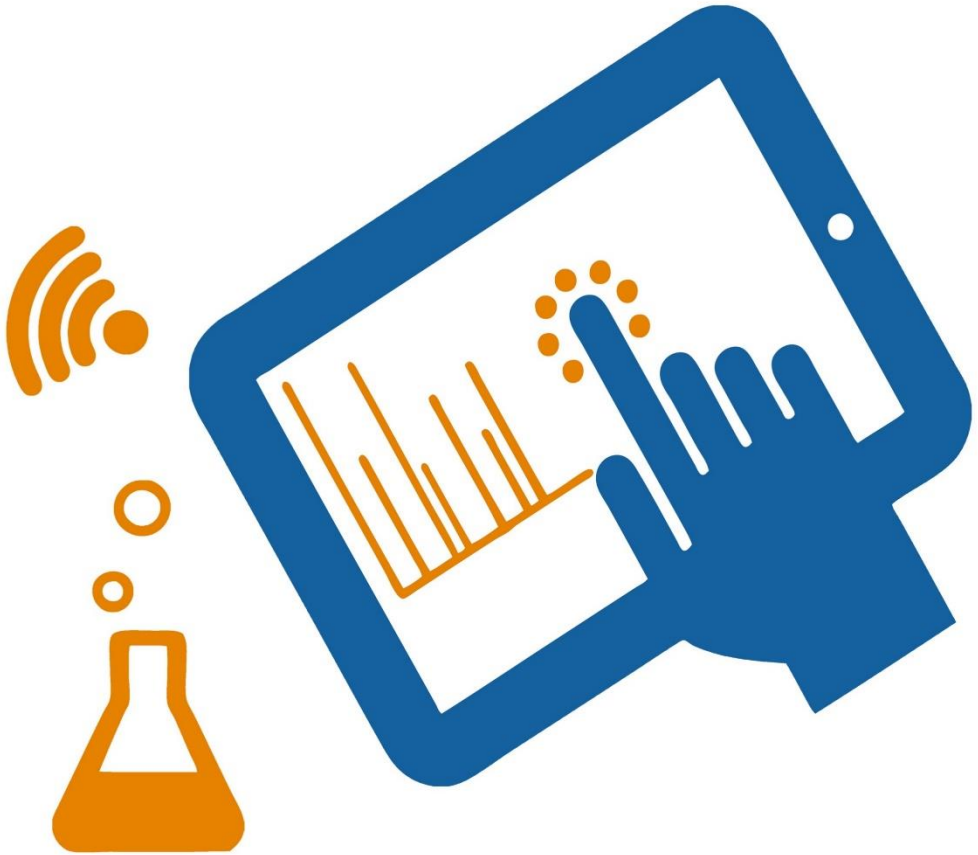

# NETCHEM

# NETCHEM Remote Access Lecture Guide

## Use of GCxGC/MS in environmental chemistry

**In this lecture, you will:**

- ✓ Get familiar with the GCxGC-MS basic principles
- ✓ Learn about sample preparation
- ✓ Learn about GCxGC/MS, applications
- ✓ Learn about GCxGC/MS **Image Patterns**
- ✓ Learn about GCxGC/MS **Separation of Overlapping Peaks**
- ✓ Discussion

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# Background

Comprehensive two-dimensional gas chromatography (GCxGC) has enormous potential for characterizing complex chemical mixtures in the environment.
The GCxGC technique was developed in the 90s, but recently commercial GCxGC systems have become available.
Today GCxGC can be used for environmental forensics, environmental risk assessment, biomonitoring, identification of non-conventional compounds in petroleum and other natural mixtures and products.

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# Comprehensive Gas chromatography/Mass spectrometry technique (GCxGC/MS)

GCxGC/MS is an instrumental technique by which most of the compounds from complex matrices can be separated, identified, and quantitatively determined. Like in the GC, in order for a compound to be analyzed by this technique, it must be relatively volatile (medium and low molecular weight) and thermostable. However, separation also occurs based on polarity as well.

The instrument consists of two parts: a **gas chromatograph**, with two columns, which serves to separate the components (analytes and other compounds present) based on volatility (1$^{st}$ column) and polarity (2$^{nd}$ column) and the **mass spectrometer** which allows the identification and quantification of the analyte. The entire system can be divided into several segments:

1. Carier gas;
2. Chromatograph (system for introduction of analytes to a column, 1st column, 2$^{nd}$ column);
3. Thermal modulator
4. Detector - mass spectrometer

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# Comprehensive GCxGC/MS
## Basic principle

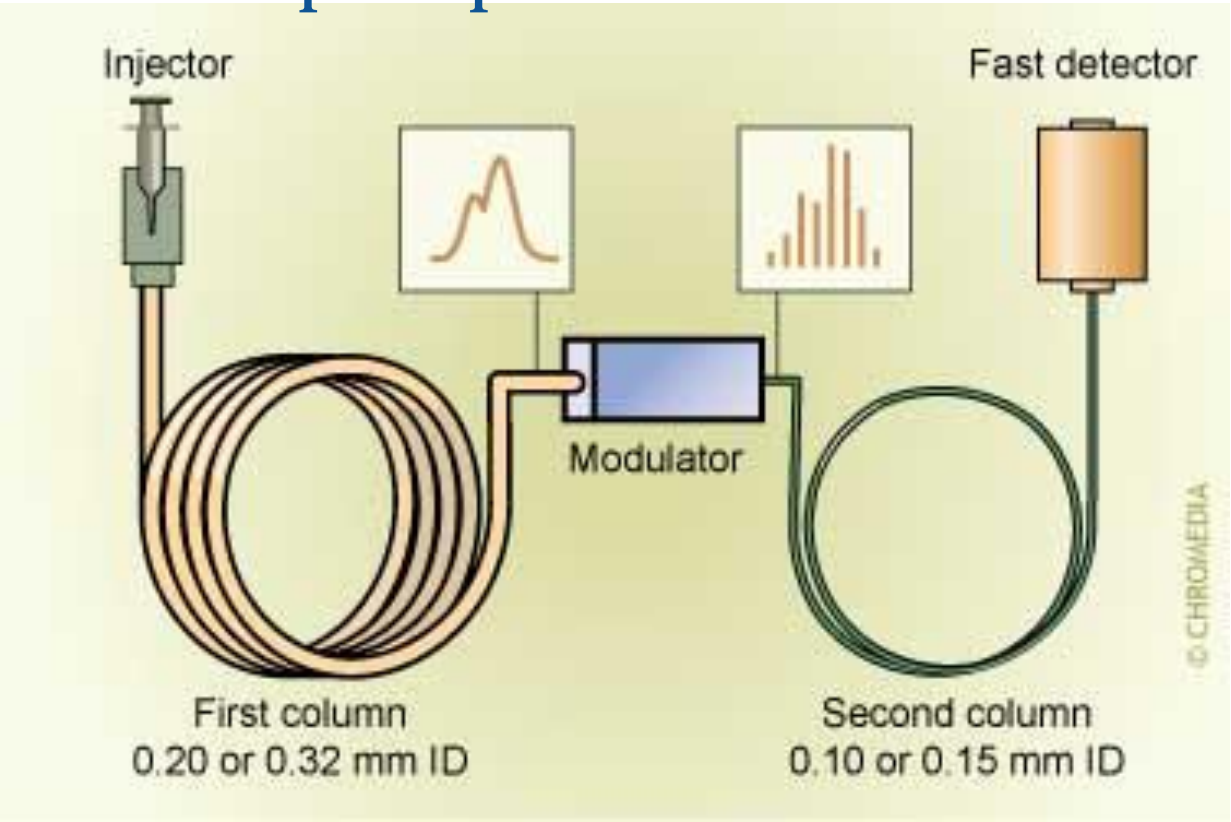


Figure 1. Schematic representation of instrumental technique

https://www.lume.ufrgs.br/bitstream/handle/10183/153852/Poster_46164.pdf?sequence=2

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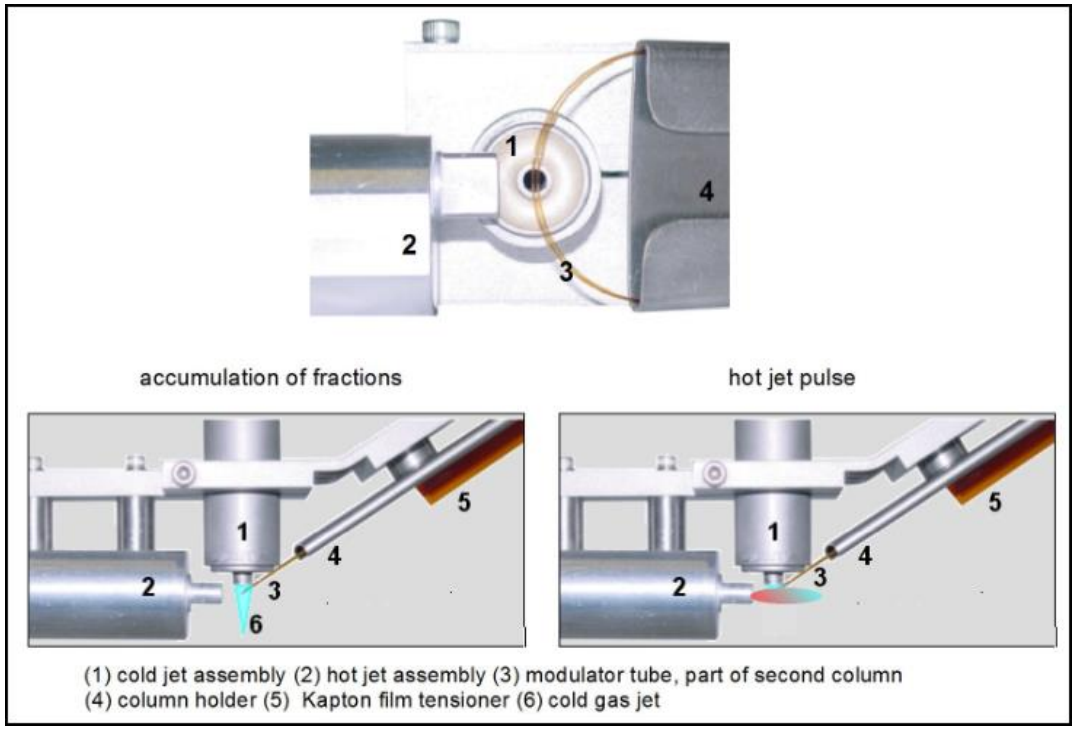
# Comprehensive GCxGC/MS
# Thermal modulation by Zoex-Modulator




(1) cold jet assembly (2) hot jet assembly (3) modulator tube, part of second column
(4) column holder (5) Kapton film tensioner (6) cold gas jet

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# *Analysis of petroleum diesel fuel aromatic fraction on GCxGC/MS*

## *Sample preparation*

Sample preparation is the same as for the regular GC and include homogenization, extraction and extract purification. Purification of the samples is usually performed using polar adsorbents (silica, alumina, Florisil) followed by elution using nonpolar solvent such as hexane. However, for the analysis of the polar compounds after elution with hexane elution with polar solvents such as dichloromethane can be conducted. Also some natural products are extracted using dichloromethane and after filtration using 0.2μm filters directly analyzed using GCxGC.

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# Analysis of petroleum diesel fuel aromatic fraction on GCxGC/MS

## Sample preparation

Petroleum diesel fuel (5 mL) is passed through a column (30 ×1.5 cm), with 10g of silica gel (70-230 mesh, Merck KGaA, Germany). The first two fractions (alkanes and branched/cyclic alkanes) are eluted with 30 mL and 10 mL of hexane, respectively. The third, aromatic fraction is eluted with a mixture of hexane:toluene (3:1, v/v).

Extracts that passed through a clean-up column are evaporated to constant weight, dissolved in 1 mL of hexane and analyzed using GC×GC-MS gas chromatograph-quadrupole mass spectrometer GCMS-QP2010 Ultra (Shimadzu, Kyoto, Japan) and ZX2 thermal modulation system (Zoex Corp.) as Total Ion Chromatograms (TIC). A Rtx®-1 (first column: RESTEK, Crossbond® 100% dimethyl polysiloxane, 30 m, 0.25 mm ID, df=0.25 µm) and a BPX50 (SGE Analytical Science, 1 m, 0.1 mm ID, df=0.1 µm) column were connected through the GC×GC modulator as the first and second capillary columns, respectively.

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# Analysis of petroleum diesel fuel aromatic fraction on GCxGC/MS

## GCxGC conditions

The temperature program start with an isothermal step at 40 °C for 5 min. Next, the temperature increase from 40 to 300 °C by 5.2 °C $min^{-1}$. The program finish with an isothermal step at 300 °C for 5 min. The modulation applied for the comprehensive GC×GC analysis is a hot jet pulse (300 ms) every 6000 ms. The MS data are collected with Shimadzu GC/MS Real Time Analysis. The GC×GC-MS data are analyzed using ChromeSquare 2.1 software, which is capable of directly reading GC×GC data obtained with GC-MS solution, converting it to a 2-dimensional image. Individual compounds are identified by a search of the MS spectrum with the MS libraries NIST 11, NIST 11s, and Wiley 8.

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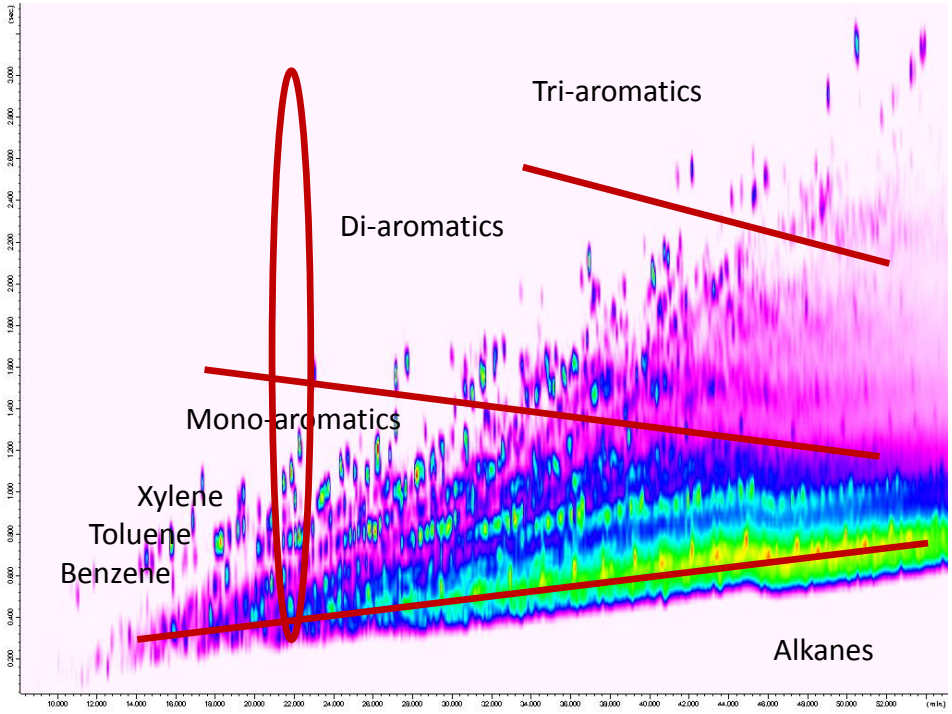
# Analysis of petroleum diesel fuel aromatic fraction on GCxGC/MS

## RESULTS - Image Patterns

GCxGC provides image patterns that can be correlated to compound structure.

This capability is especially useful for grouping analysis of mixtures containing many components.

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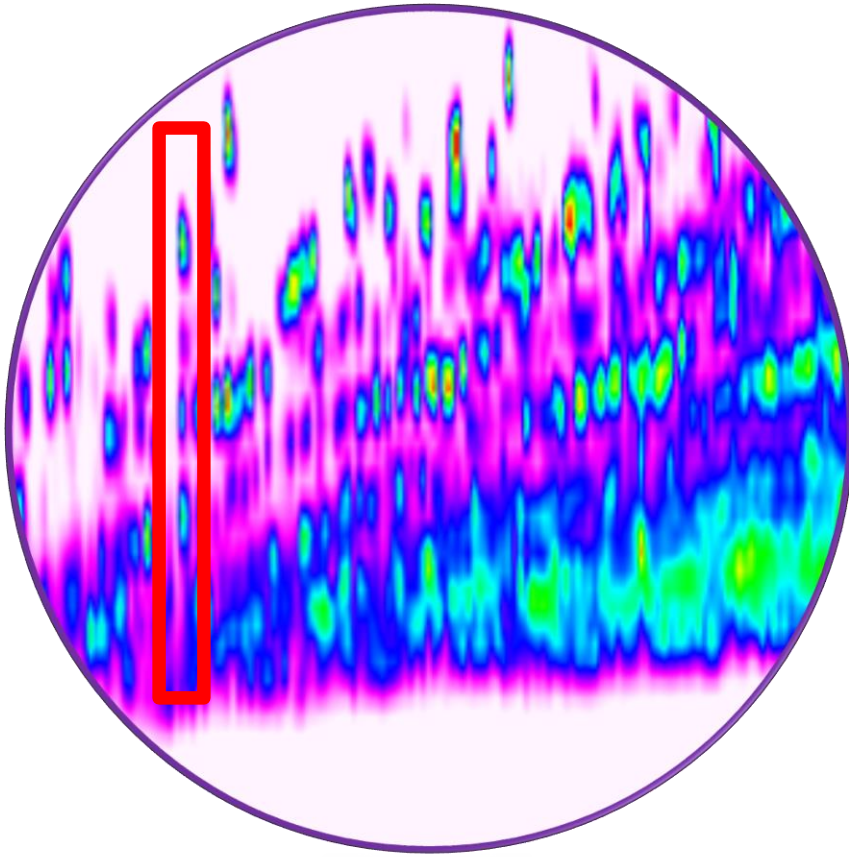
# *Analysis of petroleum diesel fuel aromatic fraction on GCxGC/MS*

## *Separation of Overlapping Peaks*

The peaks which are overlapped in GC are separated as blobs in GCxGC, and the chromatogram of Diesel oil shows that most of the compounds are clearly distinguished and separated.

Analysis can be conducted as TIC and SIM, like in regular GC.



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| DESCRIPTION OF THE EDUCATIONAL ELEMENT | |
|---|---|
| Educational element title | **Working principles of 2 dimensional gas chromatography** |
| Educational field | **Chemistry** |
| Level of study | **Master academic studies** |
| Title of course in which Educational element is implemented (lecture or lab exercise) | **Remediation (lab exercise)** |
| **Title** of teaching unit | **Use of GCxGC/MS in environmental chemistry** |
| Teacher | **PhD Vladimir Beškoski, assoc. prof.**<br>**PhD Branimir Jovančićević, prof.** |
| Target group (study program, year of study) | **Master Study Programme - Environmental Chemistry, Module: Remediation, 1st year** |
| Educational objectives of educational element | **To explain basic principles of GCxGC/MS** |
| Required preliminary knowledge and skills | **GC-MS instrumentation & working principle basics** |
| Material available at Moodle platform for the educational element:<br>- Type (.mp4/.avi/.ppt/.pdf/.doc/.jpeg …):<br>- Size (MB):<br>- Used language in the material: | **PowerPoint presentation**<br>**2.8 MB**<br>**english** |
| Remote access classroom-laboratory | **Yes** |

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| DESCRIPTION OF REMOTE ACCESS | |
|---|---|
| **1. NETCHEM COMMUNICATION SIDES**<br>(NOTE: NETCHEM Communication is defined as event that involves all kinds of internet interactions (in real time and not in real time) between participants via devices (PCs, laptops, tablets andmobilephones)) | |
| host side<br>(NOTE: Host side of NETCHEM Communication is defined as PC who invites other users to join the session) | **participant's PC in classroom** |
| guest side<br>(NOTE: Guest side of NETCHEM Communication is defined as PC who joins the invitation to session) | **participant's PC in laboratory** |
| **1. COMMUNICATION SOFWARE** | |
| Team Viewer | Meeting: **No** |
| | Remote control: **No** |
| | Meeting and Remote control simultaneously: **No** |
| Skype | Call 1:1: **No** |
| | Conference Call: **Yes** |
| **1. COMUNICATION HARDWARE** | |
| on host side | **1 PC** |
| on guest side | **1 PC** |
| **1. INFORMATION EXCHANGE TYPE** | |
| Educational<br>(one side is dominantly receptive) | **Yes** |
| | Place of Educator participant: **guest side** |
| | Number of educator(s):**1** |
| | Place of student participant: **host side** |
| | Number of student participant(s):**~ 10** |
| Consultative<br>(two sides are equal in giving-receiving information) | **No** |
| | Number of host side participant(s): **No** |
| | Number of guest side participant(s): **No** |

# Author, Editor and Referee References

This remote access laboratory was created thanks to work done primarily at University of Niš.

Contributors to this material were: Vladimir Beskoski

Date of creation: September, 2018.

Refereeing of this material was done by: _____

Editing into NETCHEM Format and onto NETCHEM platform was completed by: _____

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# References and Supplemental Material

The NETCHEM platform was established at the University of Nis in 2016-2019 through the Erasmus Programme.

Please contact a NETCHEM representatives at your institution or visit our website for an expanded contact list.

The work included had been led by the NETCHEM staff at your institution.

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