UN environment

Equipment overview and analytical techniques

Module 5

Objectives

Understand inspection protocols, sampling, laboratory specifications and accreditation; laboratory analysis techniques for standard procedures, data quality verification, reporting, communication and disputes. Demonstrate the photo-ionization detectors (PID) equipment with notes on application and limitations; QA/QC.

Topics

- Units of measurement
- TPH analysis and PAH analysis
- VOC analysis and NAPL analysis
- Reporting & interpretation of analysis results
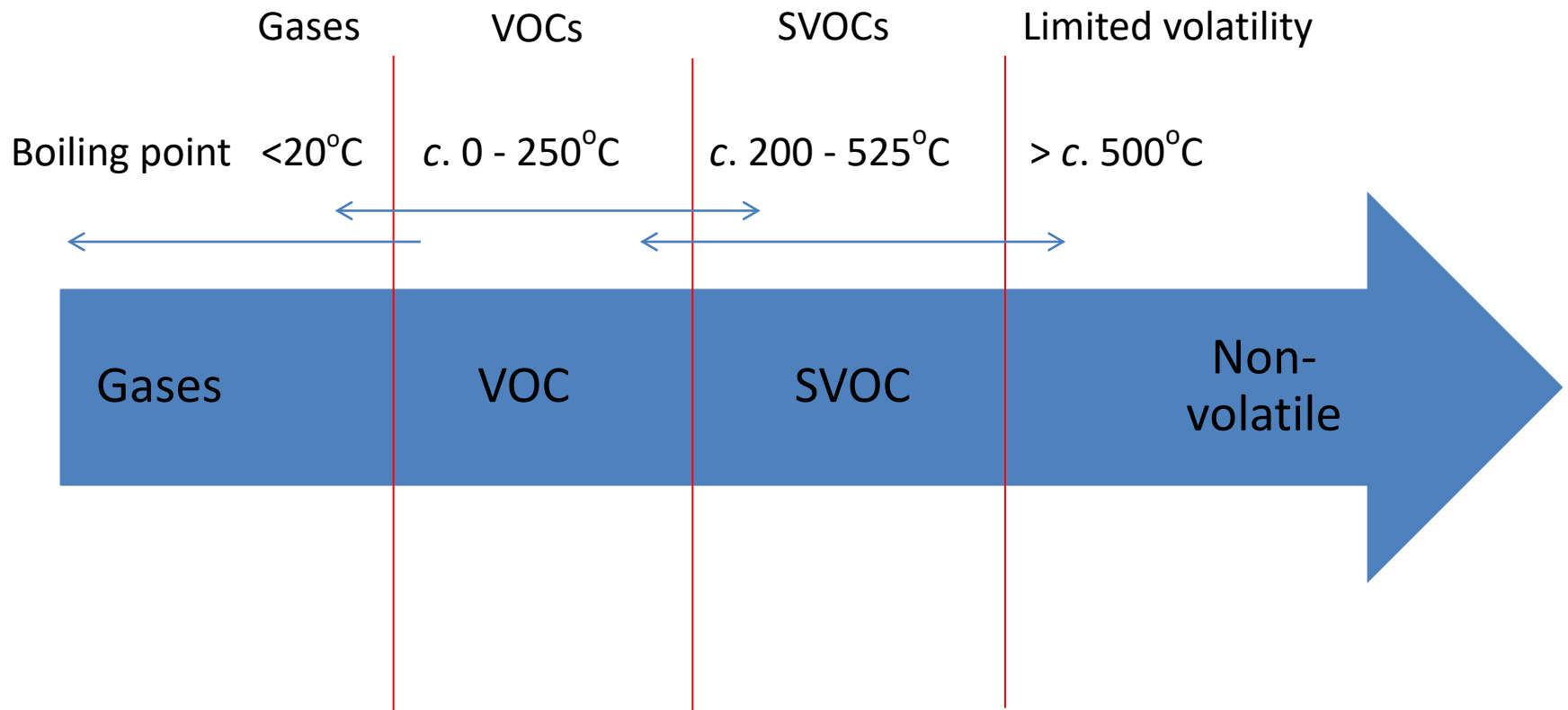- Forensic analysis

Units of measurement

%	ppm **mg/kg**	ppb **ug/kg**	ppt **ng/kg**
%	mg/l	ug/l	ng/l
100	1,000,000		
10	100,000		
1	10,000		
0.1	1,000	1,000,000	
0.01	100	100,000	
0.001	10	10,000	
0.0001	1	1,000	1,000,000
0.00001	0.1	100	100,000
0.000001	0.01	10	10,000
0.0000001	0.001	1	1,000
	0.0001	0.1	100
	0.00001	0.01	10
	0.000001	0.001	1

Boiling point ranges of organic chemicals

	Gases	VOCs	SVOCs	Limited volatility
Boiling point	<20°C	$c.$ 0 - 250°C	$c.$ 200 - 525°C	> $c.$ 500°C

Gases VOC SVOC Non-volatile

Learn what TPH is

GRO

DRO

EPH

PRO

Mineral

GC-MS

NAPL

VOC

Oil

TPH

VPH

Ran out of Space!

Let's untangle these terms!

TPH Carbon Bands and Extractable PHs

Product	Approximate carbon band range	Boiling point range (°C)
Gasoline / petrol	$C_4 - C_{12}$	25 - 215
Kerosene / jet fuel	$C_{10} - C_{15}$	160 - 260
Diesel	$C_8 - C_{28}$	260 - 380
Heavy fuel oils	$C_{19} - C_{35}$	315 - 540
Lubricating or lube oil (motor oil)	$C_{20} - C_{44}$	425 - 540

- Requires solvent extraction
- Non-volatile component of the TPH
- Useful for identification of diesel and kerosene
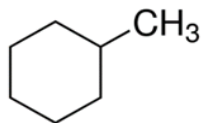- Detection limit – typically <35 mg/kg

TPH Constituents − Key Properties

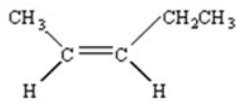## Aliphatic Hydrocarbons
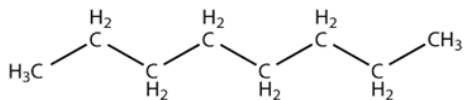
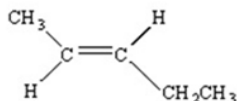**n-paraffins/normal-alkanes**
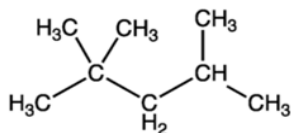
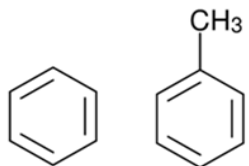**iso-paraffins/i-alkanes**

naphthenes/
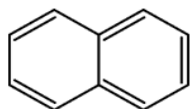cycloalkanes

cis-2-pentene   *trans-2-pentene*

olefins/alkenes
(not in crude)

Aromatic Hydrocarbons

benzenes

polyaromatic hydrocarbons
(PAHs)

Aliphatic Hydrocarbons:
- Straight, branched and cyclic
- Non-polar
- Low water solubility

Aromatic Hydrocarbons:
- Ring structures
- Some polarity
- Increased solubility in water

# Petroleum Hydrocarbons - Human Health Risk Assessment

- Substance-specific risk assessment of non-threshold indicator compounds (Benzene, Benzo(a)pyrene)

- Combined assessment of compounds with similar toxicity and other properties (TPH Criteria Working Group)

Chromatograms are not just pretty pictures

Provide information on

- Type of material
- Presence of non-hydrocarbons
- Presence of solvents
- Presence of non-dissolved hydrocarbons
- Poor integration
- Weathering
  - Degree of weathering
 - Type of weathering
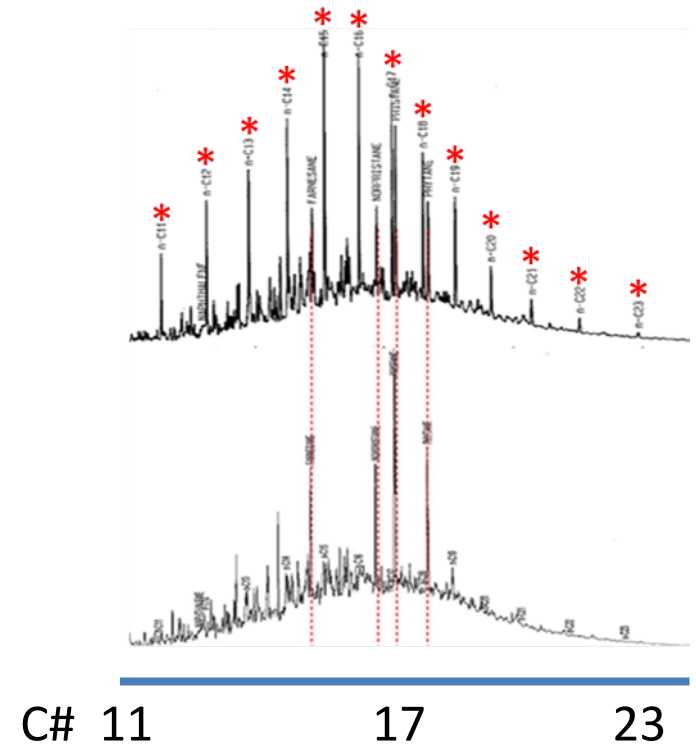
Ask your lab for specific details

C#   11   17   23

TPH Analysis

Total Petroleum Hydrocarbon Criteria Working Group (TPH CWG)

- Volume 1: Analysis of Petroleum Hydrocarbons
- Volume 2: Composition of Petroleum mixtures
- Volume 3: Selection of TPH fractions
- Volume 4: Fraction-specific classes and reference concentrations
- Volume 5: Risk Evaluation

Total Petroleum Hydrocarbon Criteria Working Group Series

Volume 1

Analysis of Petroleum Hydrocarbons in Environmental Media
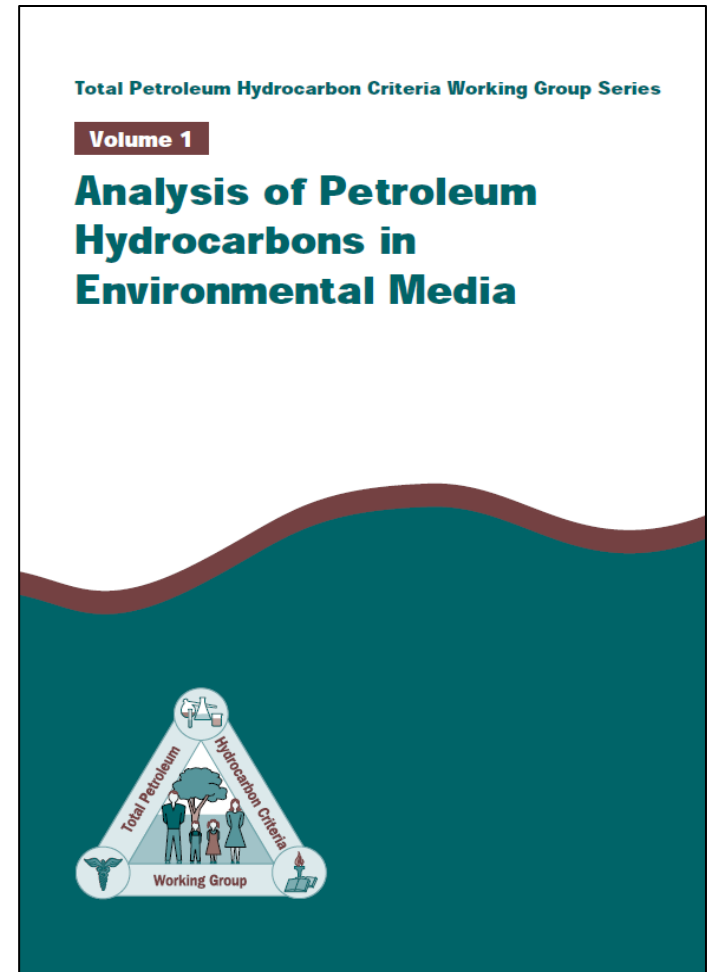
Fractionation

▶ Fractionation typically relies on the use of silica gel to separate the sample into aliphatic and aromatic *classes**

▶ The fractions are then injected into a Gas Chromatographer (GC) for separation into *carbon ranges*

▶ However, they

- Cost more than bulk TPH
- Raise the reporting limits
- Non-hydrocarbons will be removed from analysis (results)

Volatility?

Hydrocarbons?

Solubility?

Toxicity?
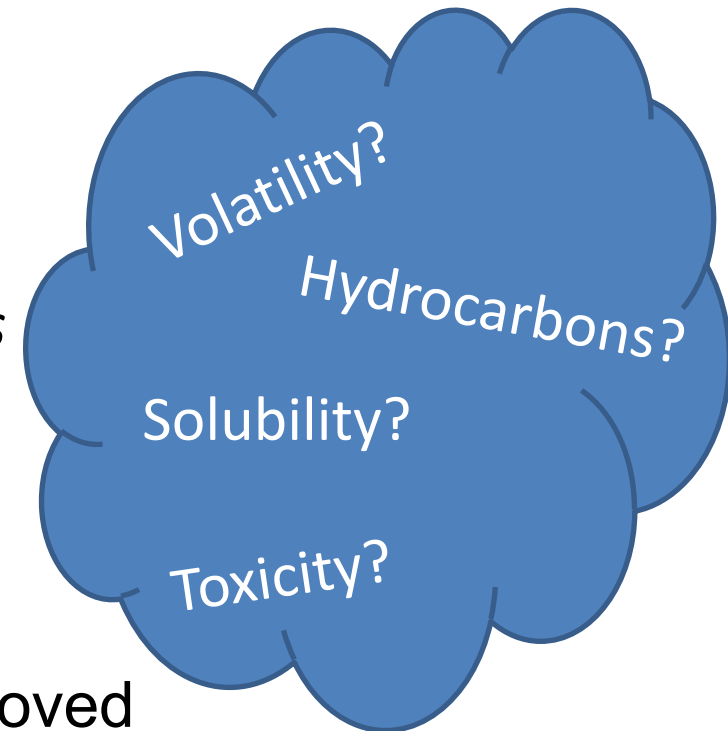
* Class separation in the volatile range does not rely on use of silica gel
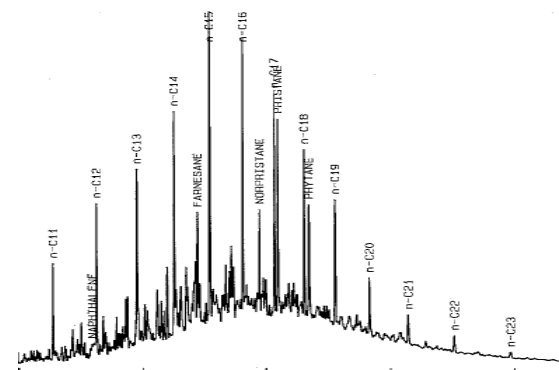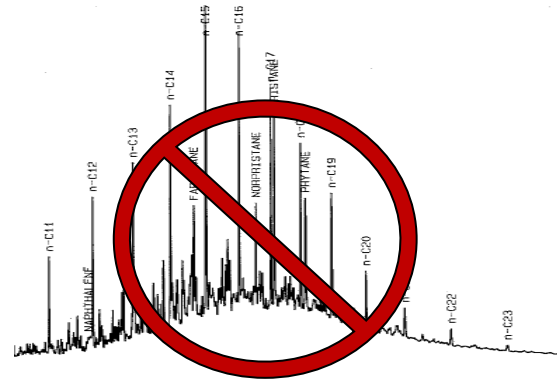
Not all TPH methods are the same

Extraction Solvent

- n-pentane
- dichloromethane

Baseline Correction

Carbon Ranges

- C6-C10 vs. C6-C12
- C12-C26 vs. C12-C28

Calibration Standard

Don't assume a change has occurred at a site if the TPH value suddenly changes!

Naturally occurring compounds

- Most soils contain hydrocarbons derived from organic matter (vegetation)
- Humic acids
- Fatty acids both volatile and non-volatile
- Tannic acids – from peat
- Alkanes – from waxy coating on leaves
- Sterols – from plants

TPH CWG

- Breakdown into narrow carbon bands
- Includes VPH and EPH
- Extract is cleaned up (removes naturally occurring compounds)
- Detection limit <100 µg/kg
- Used for risk assessment - in conjunction with indicator compounds

Petroleum Hydrocarbons − TPH CWG

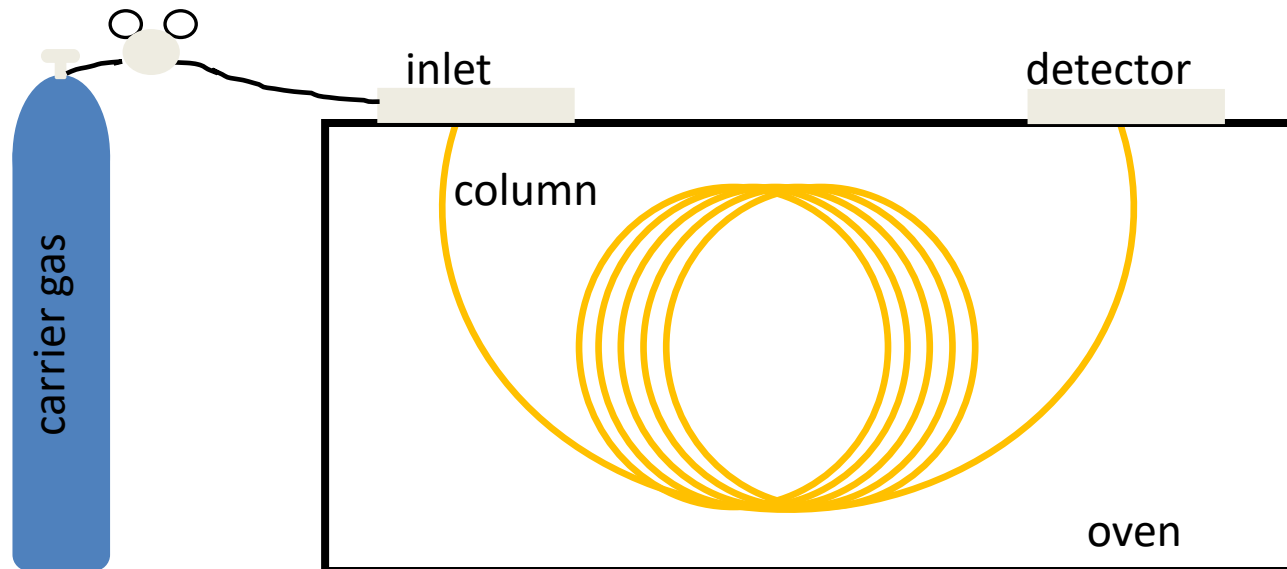| Aliphatic fraction	Aromatic fraction
$C_{>5}$ - C_6	$C_{>5}$ - C_7
$C_{>6}$ - C_8	$C_{>7}$ - C_8
$C_{>8}$ - C_{10}	$C_{>8}$ - C_{10}
$C_{>10}$ - C_{12}	$C_{>10}$ - C_{12}
$C_{>12}$ - C_{16}	$C_{>12}$ - C_{16}
$C_{>16}$ - C_{35}	$C_{>16}$ - C_{21}
$C_{>35}$ - C_{44}	$C_{>21}$ - C_{35}
	$C_{>35}$ - C_{44}

Preferred Method

Laboratory method for TPH analysis: Gas Chromatography

- For separating mixtures into components
- Based on volatility of molecules
- Several options for detectors

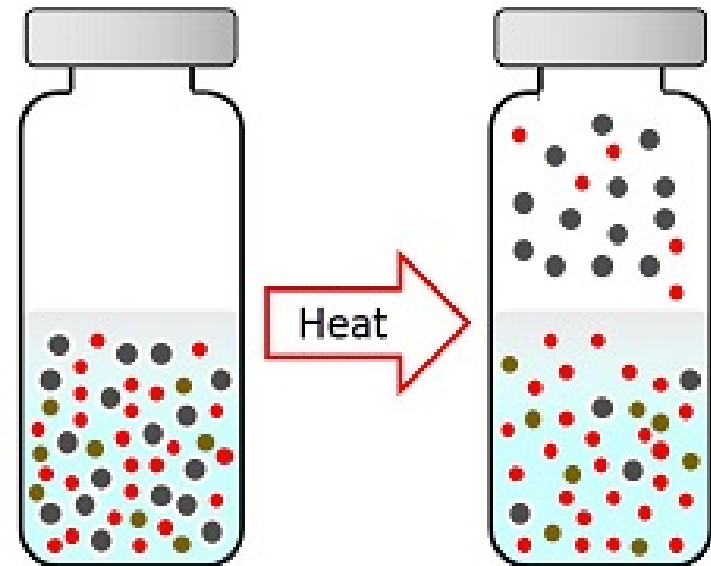# Equipment for organic analysis (1)

GC-FID used for EPH analysis

The majority of organic chemistry testing for environmental contaminants is done by Gas Chromatography with different autosamplers and detectors

VOC Analysis
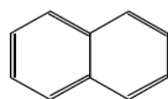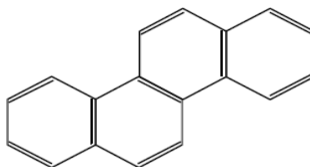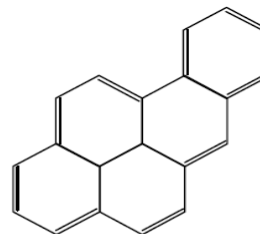

VOC analysis by Headspace GC-MS

PAHs

- Poly(cyclic) Aromatic Hydrocarbons
- A group of organic compounds that contain two or more fused aromatic rings
- Widespread in the environment and in most soils
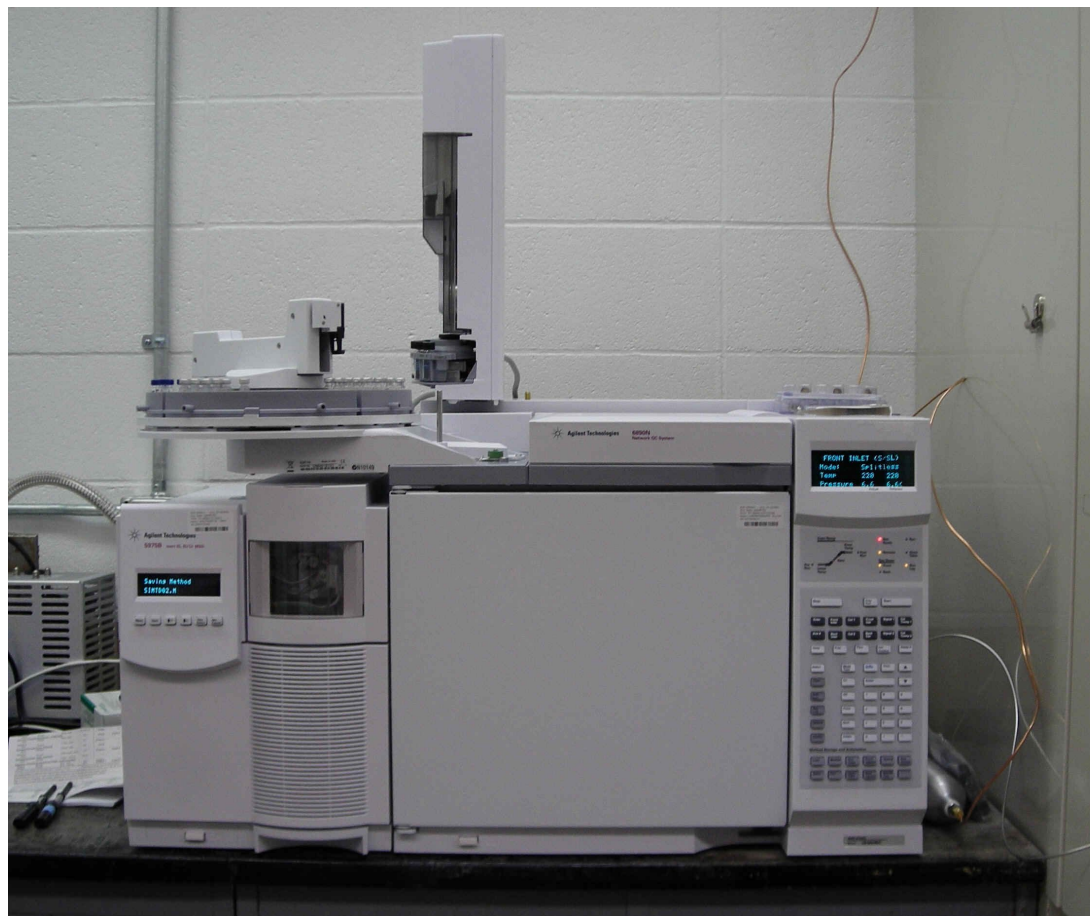- Always complex mixtures – including coal tar, diesel and oils etc.

Naphthalene   Chrysene   Benzo(a)pyrene

Equipment for organic analysis (2)

For targeted analysis of specific compounds, GC-MS is the usual instrument of choice. This is configured for analysis of samples in the semi-volatile range.

GC-MS used for SVOC analysis

Whole oil by GC-FID

- Also known as product ID or product fingerprinting
- Generally 1-2 ml product required
- Gives carbon range by comparison to reference
- Detects hydrocarbons in the range C5 to >C40
- Good resolution of diagnostic peaks e.g. BTEX, nC17, pristane
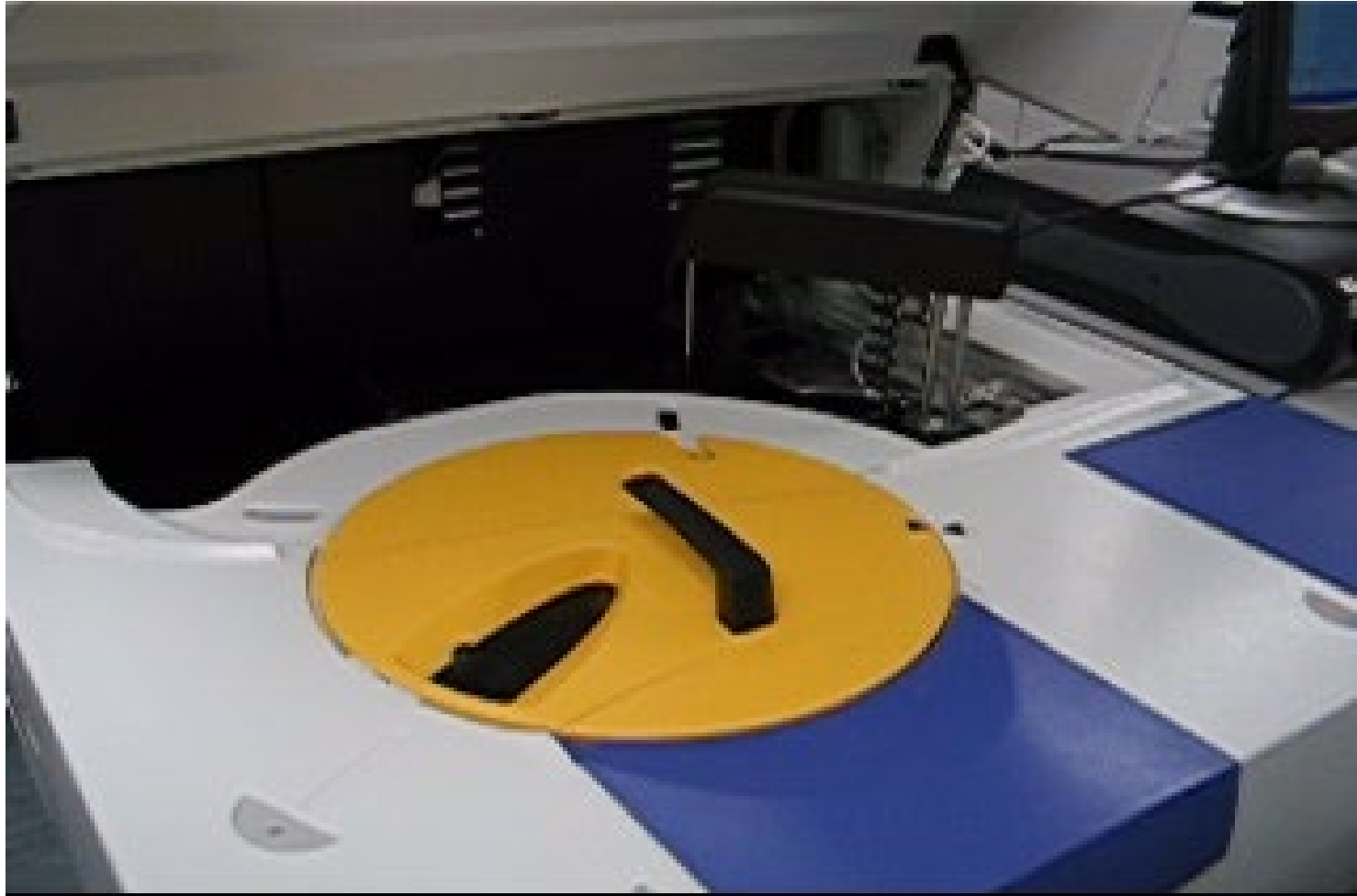
ICP-MS

Kone Spectrophotometer

The hand-held PID and what it measures

- Very handy and practical field tool for initial assessments
- Measures hundreds of VOCs
- Ionisation potential is the energy required to displace an electron and ionise the gas
- Energy required is measured in Electron Volts (eV)
- If the IP of sample is less than eV of the energy source, the contaminant will be ionised and detected.
- Range of lamps used for different contaminant compounds
- Does not measure nitrogen oxygen, CO2, methane, ethane, freons or ozone

Hydraulic Fracturing − Flowback water

Name	Determinand	LOD	Units
Dissolved Metals	Arsenic	2.5	µg/l
	Barium	3	µg/l
	Boron	12	µg/l
	Cadmium	0.5	µg/l
	Calcium	0.2	mg/l
	Chromium	1.5	µg/l
	Copper	7	µg/l
	Iron	20	µg/l
	Lead	5	µg/l
	Magnesium	0.1	µg/l
	Mercury	1	µg/l
	Nickel	2	µg/l
	Potassium	0.1	mg/l
	Selenium	3	µg/l
	Sodium	0.1	mg/l
	Strontium	.5	µg/l
	Vanadium	1.5	µg/l
	Zinc	3	µg/l
	>C5-C6	5	µg/l
	>C6-C8	5	µg/l
	>C8-C10	5	µg/l
	>C10-C12	5	µg/l
	>C12-C16	10	µg/l
	>C16-C21	10	µg/l
TPH CWG	C21-C35	10	µg/l
Aliphatics	Total aliphatics	10	µg/l
	>C5-EC7	5	µg/l
	>EC7-EC8	5	µg/l
	>EC8-EC10	5	µg/l
	>EC10-EC12	5	µg/l
	>EC12-EC16	10	µg/l
	>EC16-EC21	10	µg/l
TPH CWG	>EC21-EC35	10	µg/l
Aromatics	Total aromatics	10	µg/l
	MTBE	5	µg/l
	Benzene	5	µg/l
	Toluene	5	µg/l
	Ethylbenzene	5	µg/l
	m/p-Xylene	5	µg/l
	o-Xylene	5	µg/l
	Bromide	0.05	mg/l
	Sulphate	0.05	mg/l
	Chloride	0.3	mg/l
	Nitrate as NO3	0.2	mg/l
	Nitrite as NO2	0.02	mg/l

	Determinand	LOD	Units
	Ammonical Nitrogen	0.03	mg/l
	T.Alkalinity as CaCO3	1	mg/l
	BOD (settled)	1	mg/l
	COD (settled)	7	mg/l
	Electrical Conductivity at 25	2	µS/cm
	pH	0.01	pH Units
	Salinity	0.1	%
	Total Dissolved Solids	10	mg/l

Groundwater Dissolved Gases Suite

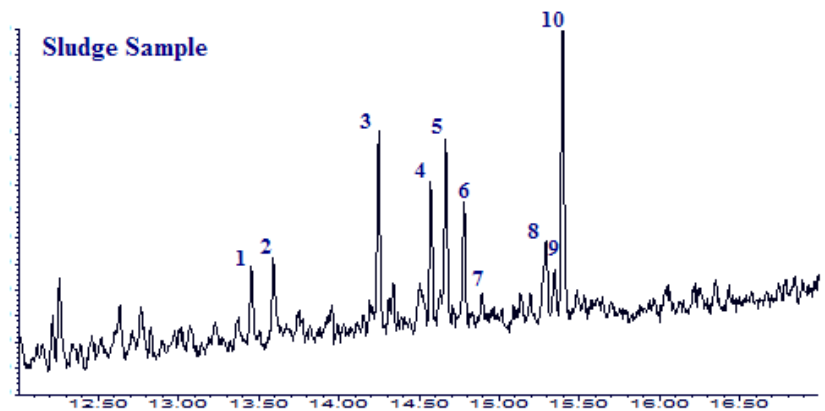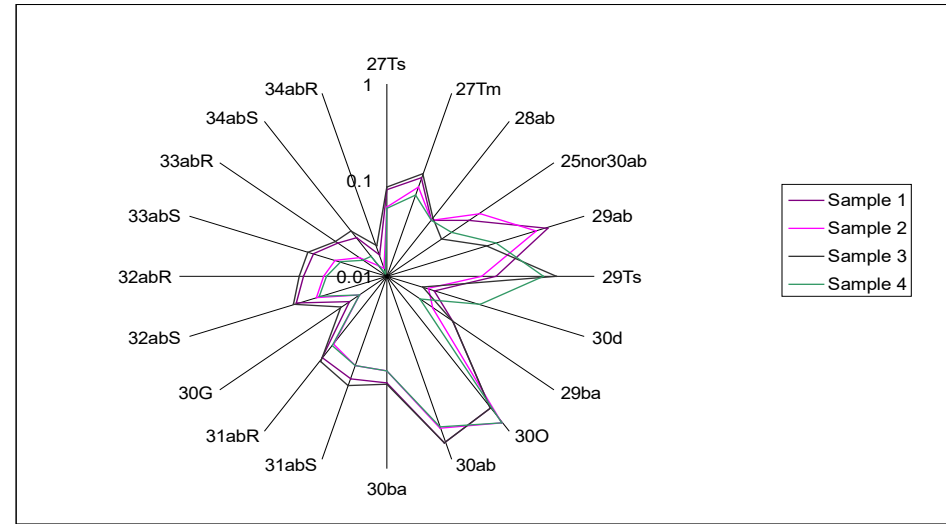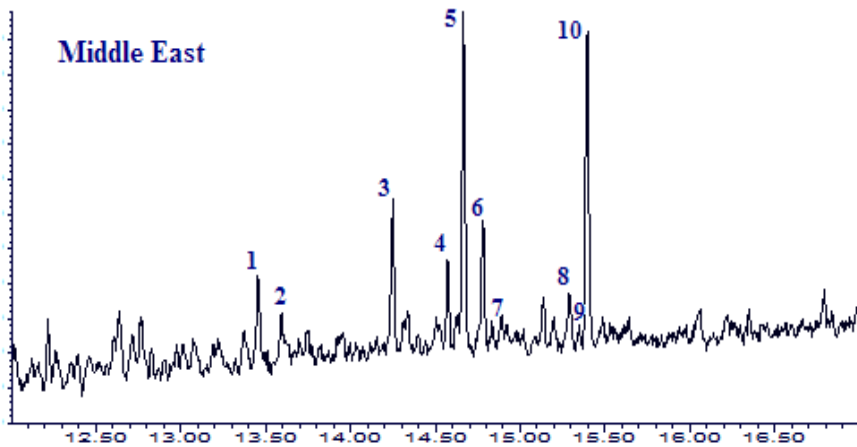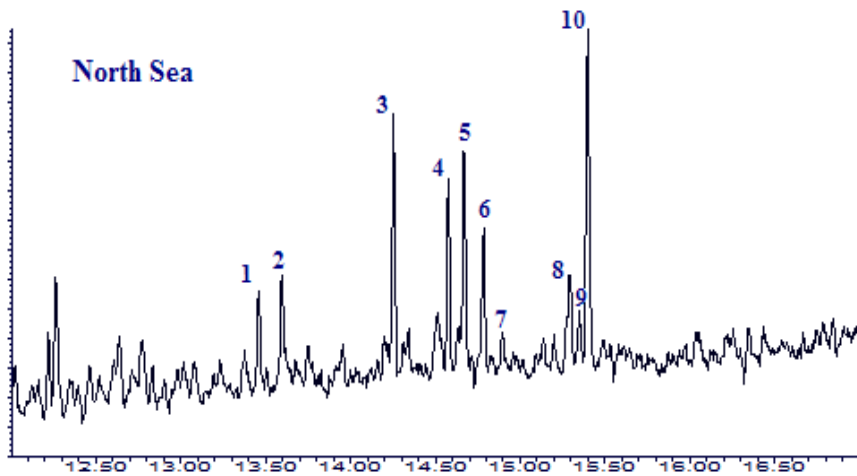| Name	Determinand	LOD	Units
Dissolved Gas	CO2		mg/l
	CH4		mg/l

Forensic Analysis
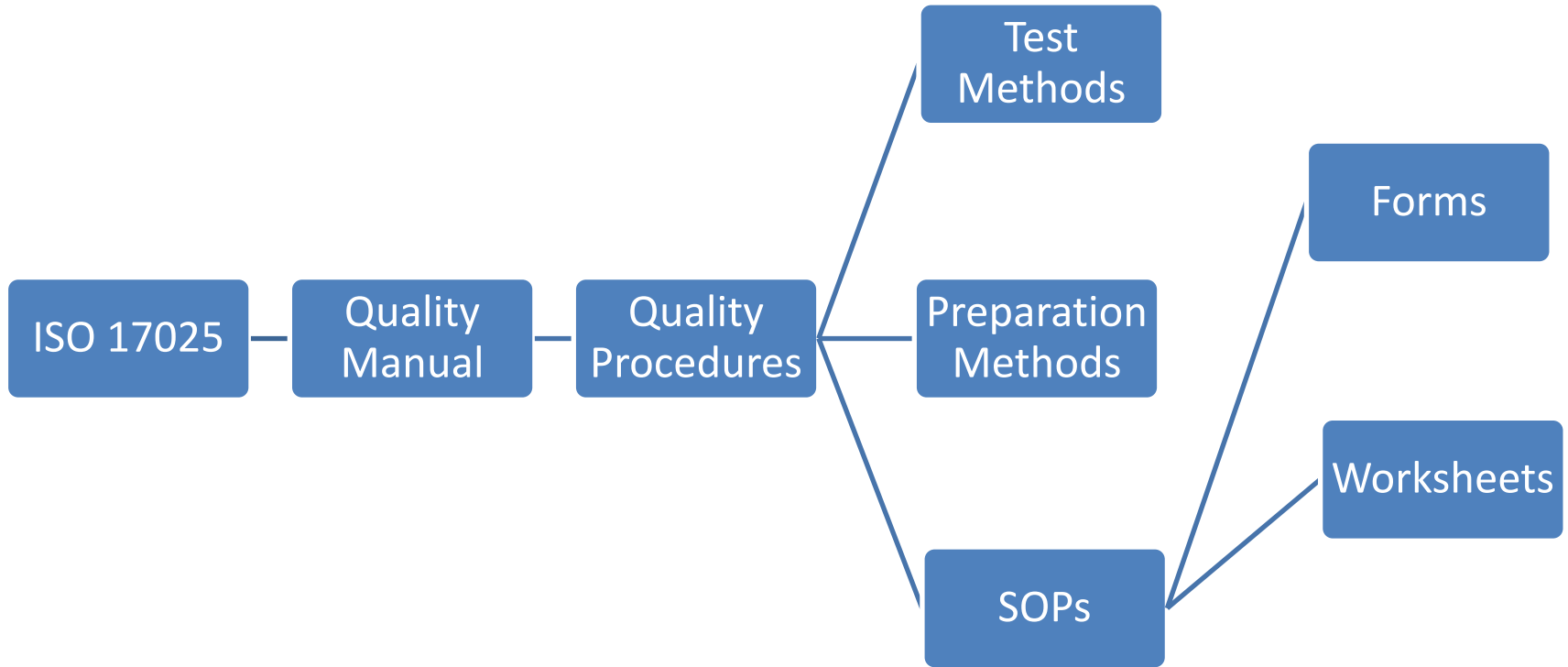
- GC-FID Analysis
- GC-MS Analysis
- Diagnostic Ratio analysis
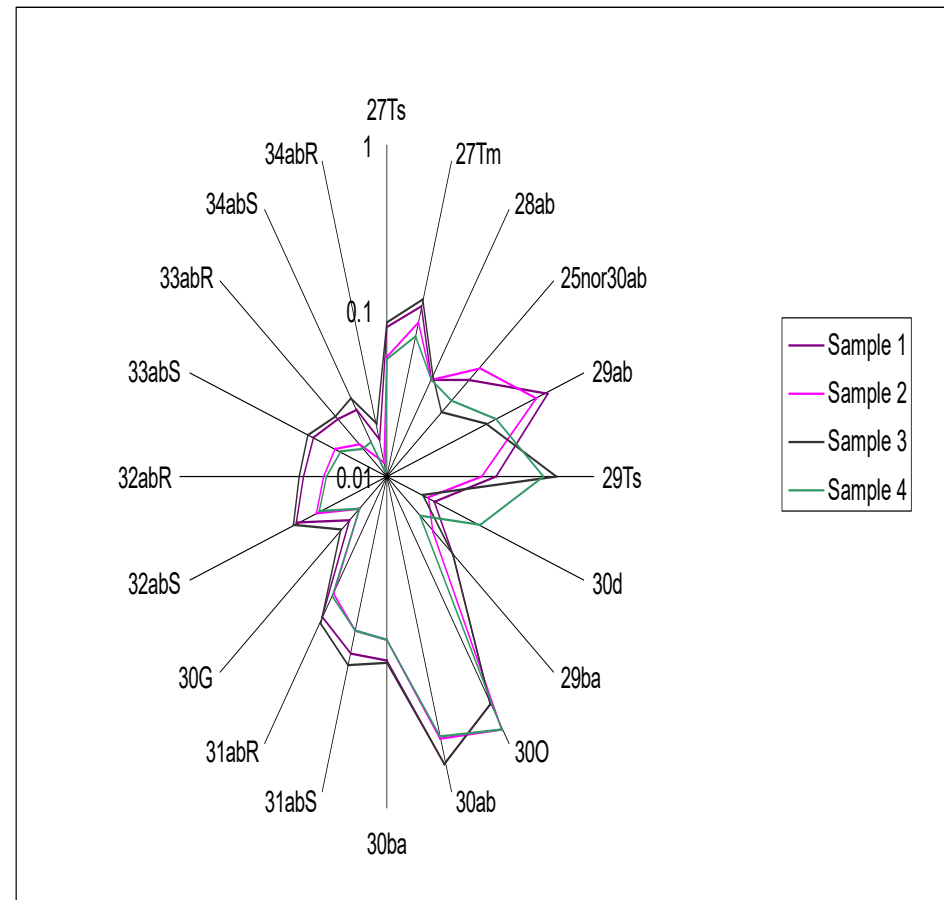
Forensic Analysis

Quality

Some Essential Features of a Quality System

Development and Validation
A test method needs to be set up so we know it "works"
Document Control
Everyone to be working according to a given set of procedures
Audits
We need to know we are doing things right
Complaints
Respond to customer criticisms and questions
Independent Accreditation - UKAS
External checking
AQC charts
An internal means of quality assurance
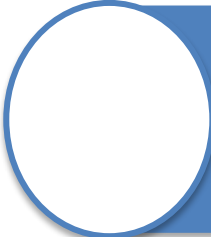**PT Schemes**
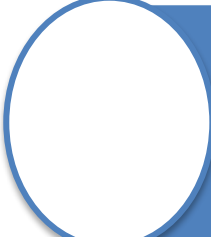An external means of quality assurance

Proficiency Testing

- Proficiency Testing (PT) is an inter-laboratory comparison of results.
- It is run by an external provider and the feedback is used to assess our analytical methods.
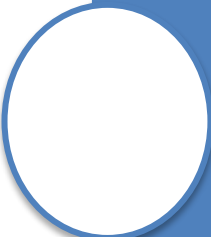- It is a requirement of ISO17025

Key Messages

It is important to understand units of measurement, especially since the quantities and concentrations of toxic chemicals that pose a risk to human and the environment can be very small.

Criteria (concentrations) have been developed by specialists that are considered the maximum levels for safety for most toxic chemicals, including BTEX, PCBs and others.

Gas chromatography, mass spectrometry and spectrophotometry are typical techniques to determine the extremely low levels of contaminants in soil and water.

The quality and reliability of the results depends on many factors, the last of which is the procedure, reagents and equipment used at the laboratory.

Thank you

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