Derwentside Environmental Testing Services

Chlorinated Solvents

Hazel Davidson
Technical Marketing Manager
Derwentside Environmental Testing Services

Chlorinated Solvents

Contents

- Introduction and definitions
- Behaviour of chlorinated solvents in soil
- Sampling and storage
- Analysis
- Remediation chemistry

Chlorinated solvents Introduction

- A volatile organic compound (VOC)is considered to have a boiling point in the range -25°C to 200°C and lie within the carbon range C_4 – C_{12}
- Solvents are a common legacy of many industrial processes
- VOCs can consist of both LNAPLs and DNAPLs (Light or Dense Non-Aqueous Phase Liquids)
- Solubility in groundwater is highly variable

Chlorinated solvents Introduction

Chlorinated VOCs - examples

Dichloroethylene	Trichloroethylene
Trichloroethane	Chloroform
Bromochloromethane	Dichloromethane
Carbon tetrachloride	Trichloroethene
Tetrachloroethene	Hexachlorobutadiene
Vinyl chloride	Chlorobenzene

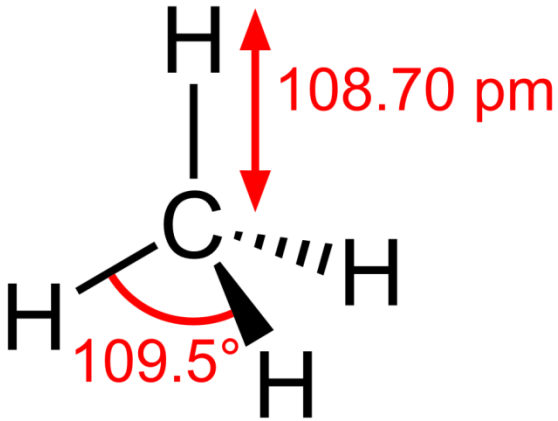
Most VOC suites contain 60+ compounds
(USEPA target list)

Chlorinated solvents Introduction

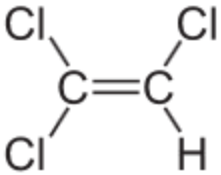
Some definitions:

- Halogenated compounds – hydrocarbons containing one or more of the halogens - chlorine, bromine, fluorine or iodine
- Trihalomethanes – containing 3 halogen atoms, e.g. chloroform, $CHCl_3$
- Aromatic compounds – hydrocarbons including one or more benzene rings
- Alkanes – aliphatics containing no double bonds
- Alkenes – aliphatics containing double bonds
- Synonyms: methylene chloride = dichloromethane
  vinyl chloride = chloroethene
  trichloromethane = chloroform
  trichloroethene = trichloroethylene, TCE, Trike
  tetrachloroethene = perchloroethene, PCE, Perc

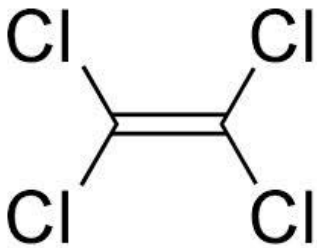
Chlorinated solvents Introduction



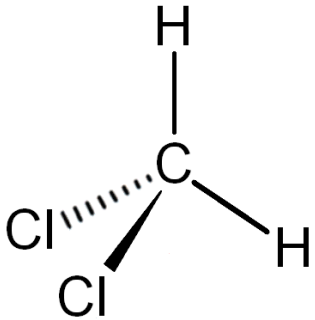
Methane



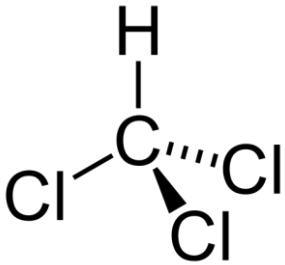
Trichloroethene



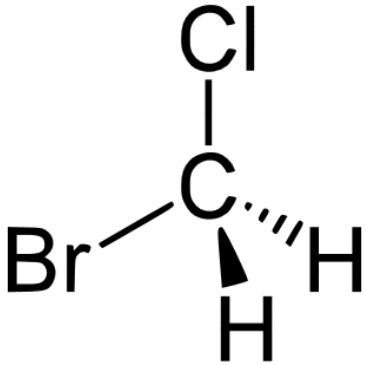
Tetrachloroethene



Dichloromethane



Trichloromethane



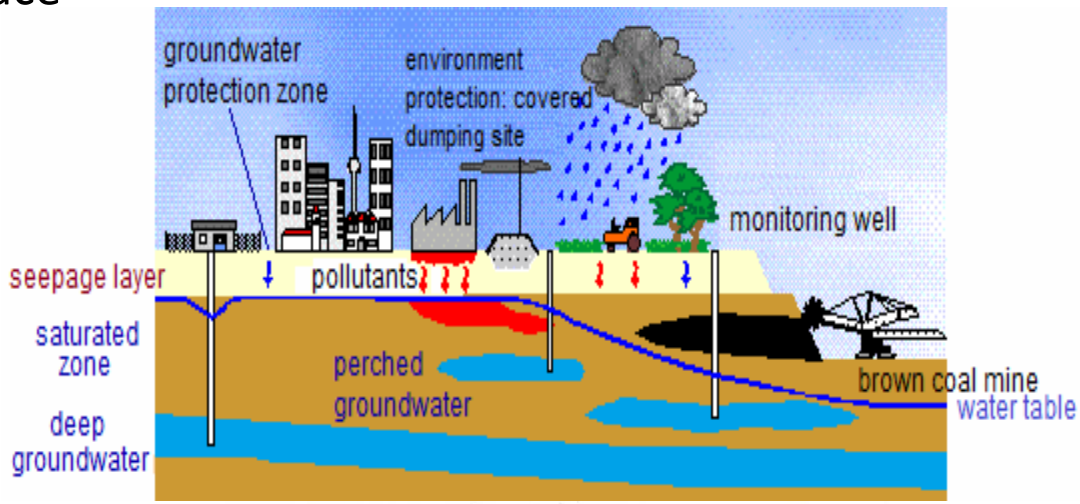
Bromochloromethane

Behaviour in Soil

Presence in soil and groundwater

VOCs and SVOCs can enter the soil and permeate through to any underlying aquifer. The risk to the aquifer depends on several factors:

- Depth from the surface
- Aquifer porosity
- Contaminant load
- Hydrogeology



Behaviour in Soil

Chlorinated solvents will break down or be removed by:

- Sorption
- Degradation
- Dispersion
- Volatilisation
- Advective flow – carried along by groundwater
- Diffusive flow – movement along a concentration gradient

Behaviour in Soil

Presence in soil

- Liquid film around particles
- Adsorbed onto the surface of particles
- Absorbed into soil particles
- Occupation of pore spaces

Presence in groundwater

- Truly dissolved – varying solubilities
- Colloidal suspension – ultra fine droplets
- Free product film or layer

Behaviour in Soil

	Density (g/cm^3)	B. Pt. (^oC)	Solubility (g/l) in water
Vinyl chloride	0.91	- 13.4	2.7
Dichloromethane	1.32	39.8	1.7
Trichloroethene	1.46	87.3	1.28
Chloroform	1.48	61.2	0.8
Tetrachloroethene	1.62	121	0.15
Bromochloromethane	1.99	68.3	16.7

Behaviour in Soil

Rate of dispersion/degradation in the ground depends on:

- Chemical, biochemical, and physical reactions
- Organic content of soil
- Particle size of soil
- Soil composition (matrix)
- Bacterial composition and concentration
- Moisture content
- pH
- Partition coefficient of each compound

Behaviour in Soil

Partition Coefficients, Kd

- Describes the rate of contaminant transport relative to that of groundwater
- Defined as 'the ratio of the contaminant concentration in/on the solid to the concentration in the surrounding aqueous solution once the system has reached equilibrium'
- The Kd value of a compound can be used to estimate the potential for adsorption in soil
- Due to their volatility, VOCs also have a partition coefficient from liquid to air
- This function is used in the headspace analysis

Sampling and Storage of VOC Samples

- Stored in the correct type of container
- Stored for the minimum period of time
- Analysed as soon as possible, ideally within five days
- Water and soil samples stored at 5°C
- The more volatile the component the more critical are the above factors

Sampling and Storage of VOCs

Soils - disturbed samples

- Suitable for VPH and chlorinated solvents
- Also require a tub of soil for moisture content
- No headspace – press soil into jar, overfill, level off

60 g glass jar

Waters

- Volatile organic compounds: VPH, chlorinated solvents
- Minimise aeration and agitation when sampling
- No headspace - check by inverting vial

40 ml glass vial with septum

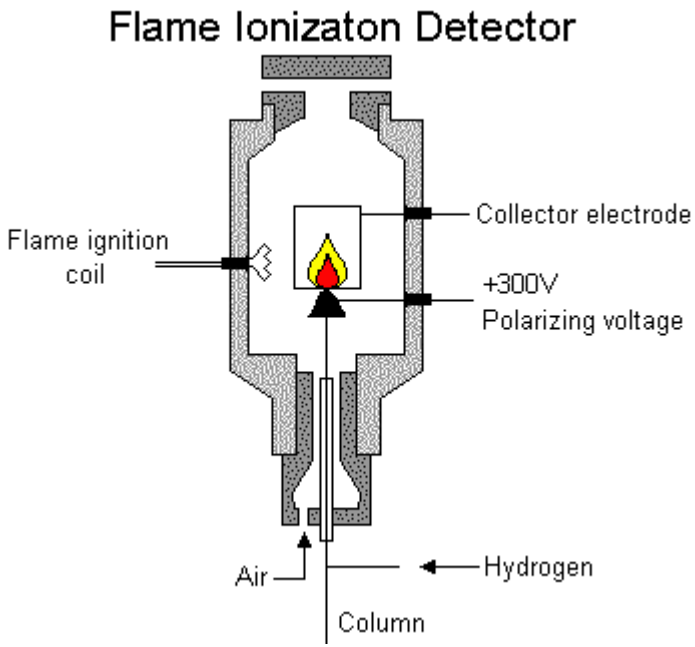
It is good practice to take a duplicate for <u>each</u> of the above analyses

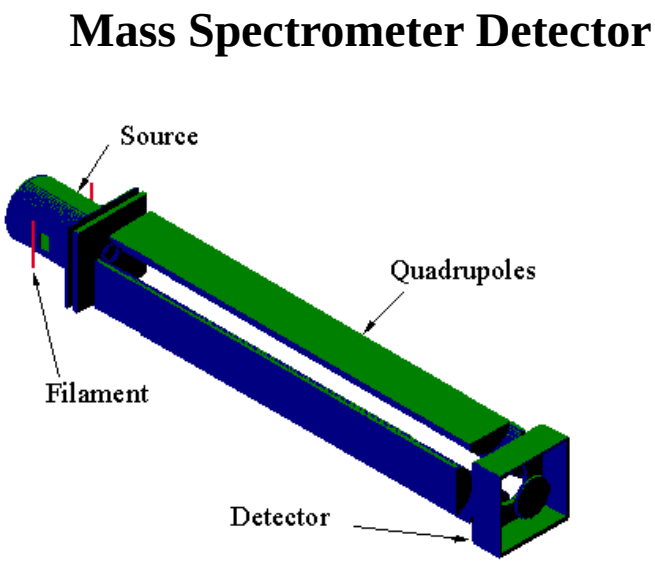
Sampling and Storage

Temperature considerations

- MCERTS for waters states: 'the sample storage environment shall maintain a temperature of '5 +/- 3°C' – now extended down to 1°C
- If possible, pre-chill samples before packing
- Use a minimum of three ice packs per cool box
- Ice packs should be freshly frozen, preferably in a freezer
- Completely fill the cool box, to minimise headspace

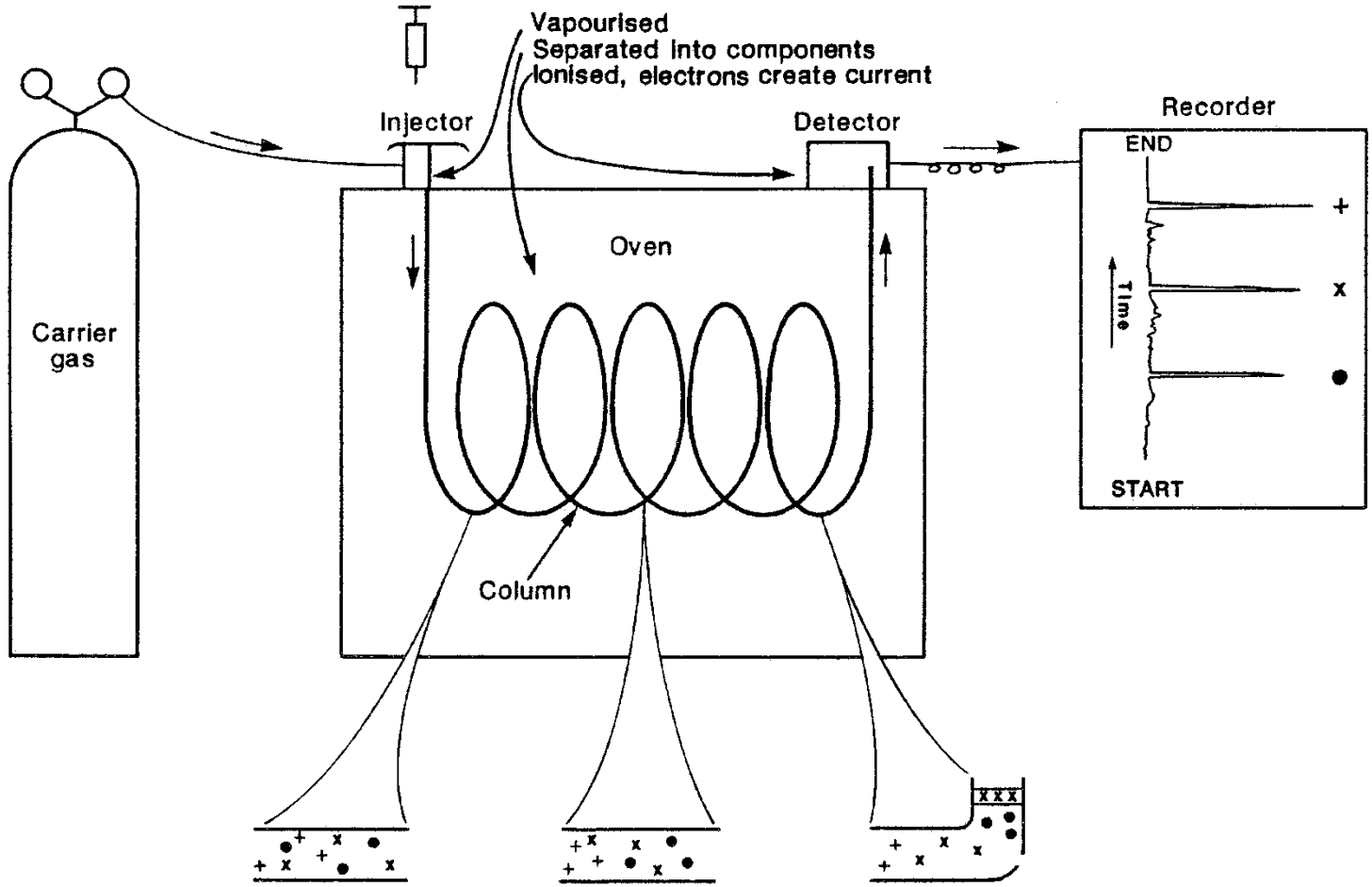
Analytical Methods





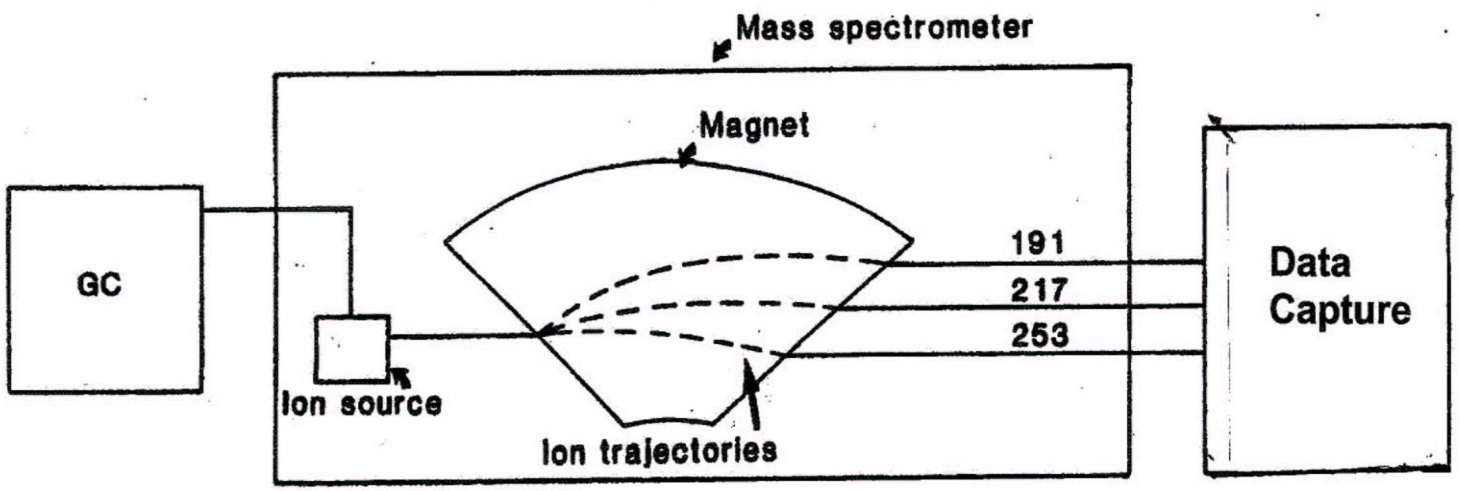
Gas chromatography followed by mass spectroscopy

GC-FID


Vapourised
Separated into components
Ionised, electrons create current
Injector
Detector
Recorder
END
Time
START
Oven
Carrier gas
Column

GCMS

- After exiting the GC oven, the compounds are bombarded with electrons within a system under vacuum
- Molecules of the compound became positively charged due to loss of electrons, forming fragmented ions.
- These fragmented ions pass through a magnetic field where they are separated according to their mass



What is chromatography?

Chromatography can be defined as:

The separation of components in a mixture by partitioning between a mobile phase (gas or liquid) and a stationary phase (the column)

Chromatography Theory

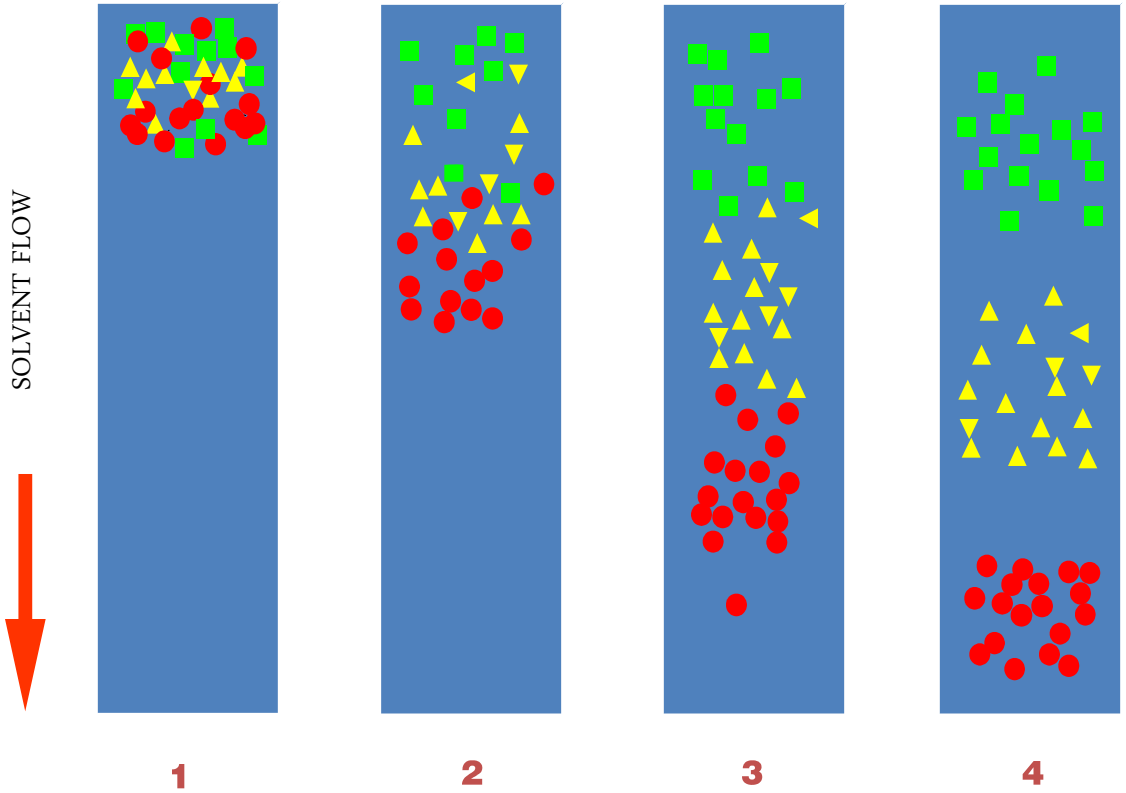


Image by ALcontrol Laboratories

VOC Sample Preparation

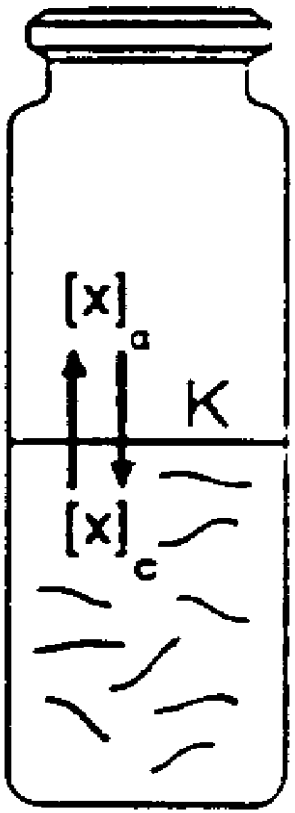
Disturbed Soils

- Top layer of soil is discarded
- Approx. 5 g is placed into a headspace vial and weighed
- 5 ml of water and matrix modifier are added
- Internal standard is added
- Vial is sealed
- For highly contaminated samples, methanol extraction is required

Waters

- 10 cm^3 of sample is removed by syringe into headspace vial
- Internal standard and matrix modifier are added
- Vial is sealed

VOC Sample Preparation



- An analyte has a constant distribution coefficient between matrix and headspace
- Enhanced in the headspace with heat
- Sample and internal standard added to vial and sealed
- Sample agitated and heated for a fixed time period
- Injected onto the column

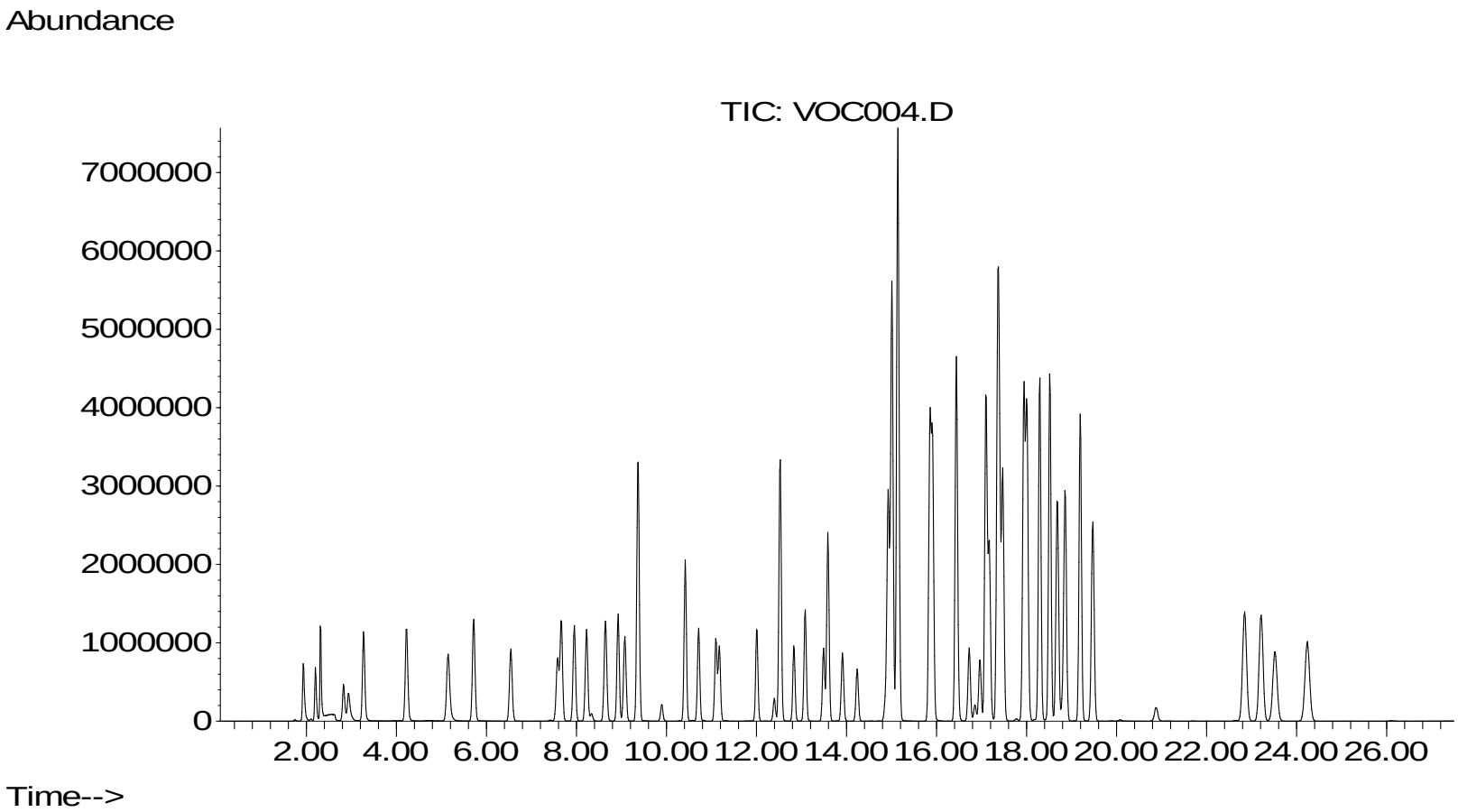
Headspace Autosampler

Volatile Organic Compounds– GC/MS Headspace

- VOC suite is based on USEPA 8260B methodology
- Contains approx. 60 target compounds
  - Chlorinated alkanes
  - Chlorinated alkenes
  - Aromatic Hydrocarbons
- Detection to between 1 and 10 ppb
- Tentatively identified compounds also available

Headspace GCMS

VOC Analysis - Standard



GCMS – VOC list

VOCs
1,1 Dichloroethylene
1,1,1,2-tetrachloroethane
1,1,1-trichloroethane
1,1,2,2-tetrachloroethane
1,1,2-trichloroethane
1,1-dichloroethane
1,1-dichloropropene
1,2,3-trichlorobenzene
1,2,3-trichloropropane
1,2,4-trichlorobenzene
1,2,4-trimethylbenzene
1,2-dibromo-3-chloropropane
1,2-dibromoethane
1,2-dichlorobenzene
1,2-dichloroethane
1,2-dichloroethylene
1,2-dichloropropane
1,3,5-trimethylbenzene
1,3-dichlorobenzene
1,3-dichlorobenzene+p-isopropyltoluene
1,3-dichloropropane
1,4-dichlorobenzene
2,2-dichlororopane

2,2-dichlororopane+1,2-dichloroethylene
2-chlorotoluene
4-chlorotoluene
Benzene
Bromobenzene
Bromochloromethane
Bromodichloromethane
Bromoform
Bromomethane
Carbon Disulphide
Carbon tetrachloride
Carbon tetrachloride + 1,1-dichloropropene
Chlorobenzene
Chloroethane
Chloroform
Chloromethane
cis-1,2-dichloroethylene
cis-1,3-dichloropropene
Dibromochloromethane
Dibromomethane
Dichlorodifluoromethane
Ethylbenzene
Hexachlorobutadiene

Isopropylbenzene
m+p-Xylene
Methylene Chloride
Naphthalene
n-butylbenzene
n-propylbenzene
o-Xylene
p-isopropyltoluene
sec-butylbenzene
Styrene
Tert-butylbenzene
Tetrachloroethylene
Toluene
Trans-1,2-dichloroethylene
trans-1,3-dichloropropene
Trichloroethylene
Trichlorofluoromethane
Vinyl Chloride

VOCs – GCMS Headspace

- Full Scan mode
  - detects all compounds
  - use of TICs (tentatively identified compounds)
  - detection limit is affected
- Selected Ion Monitoring (SIM) mode
  - only detects target compounds
  - detection limit can be 10 x better

Remediation

- Pump and treat (groundwater)
- Pump and remove/reuse (product)
- Dig and dump (soils)
- Soil washing
- In situ bioremediation
- In situ chemical oxidation
- In situ thermal treatment

Chemical Remediation

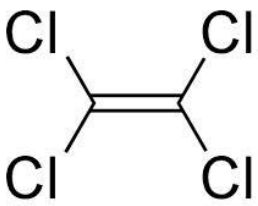
SABRE

- Source Area BioRemediation (SABRE)
- CL:AIRE and DTI LINK 5 year bioremediation project
- Former chemical plant in E. Midlands
- DNAPL contamination, mostly TCE and some PCE (trichloroethene and tetrachloroethene)
- In situ anaerobic reductive dechlorination (RD)
- Use of DNAPL partitioning electron donor to enhance RD (emulsified soya oil)

Chemical Remediation

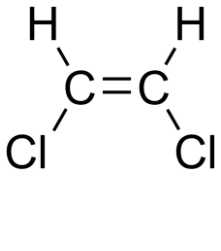
Example of biodegradation:

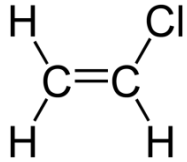
Tetrachloroethene (PCE or ‘perc’)



Reductive ↓ *dechlorination*

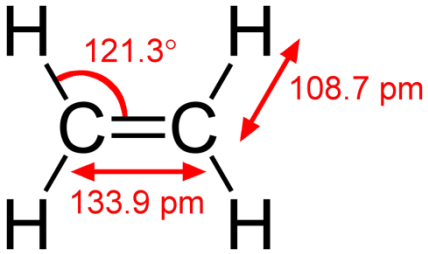
1,2 – dichloroethene and vinyl chloride





Reductive ↓ *dechlorination*

ethene



Analytical Summary

- GCMS is required for lower limits of detection in the 1-10 ppb range (dependent on solubility, volatility and detector response)
- Correct sampling procedures are critical for accurate results
- Correct sample containers and cold storage essential

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Thank you

hazel.davidson@dets.co.uk

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