

“Capacity Building and Strengthening Institutional Arrangement”

Analysis and sampling of water and water pollution

Environmental analytical methods (soil)

CHN Analyzer and soil sample treatment: general principles

Ms. Elisa Calabretta

APAT

Agency for Environmental Protection and Technical Services

CHN determination

The elementary analysis CHN represents a useful technique to determine the percentage content of carbon, nitrogen and hydrogen in organic and inorganic compound solid and liquid.



CHN Analyzer

Element description

Carbon (C)

- Its elementary form is graphite and diamond;
- It is composed of coals;
- Its carbon monoxide is a very toxic gas, colourless and odourless;
- The carbon dioxide is formed by combustion of carbon in excess of oxygen.

Hydrogen (H)

- The hydrogen is the most abundant element in the universe;
- It is present overall in the water and in the hydrocarbons.

Nitrogen (N)

- The nitrogen, even if it is not one of the most abundant element, is fundamental for life because it is one of the organism constituent;
- It is present commonly as molecular form N_2 and it is an inert gas in ordinary temperature but more reactive at high temperature;
- Nitrogen fixation in nature is caused by the same bacteria that transform it into nitrates or Sal ammoniac;
- The plant absorb nitrogen compounds, necessary for their growth, also like fertilizing with nitrogen and these are obtained especially with ammonia

Principle of the CHN Analyzer

The analysis can be divided into three phases:

- combustion in excess of oxygen ($T=900-1000\text{ }^{\circ}\text{C}$),
- separation of the gases developed (CO_2 , N_2 , H_2O) via gas chromatography (He carrier gas),
- detection of the gases developed (thermoconductivity detector).

The resulting data are weight percentage of carbon, hydrogen and nitrogen (CHN).

The calibration of the instrument is performed via combustion of a Certified Reference Material

Scheme of an CHN Analyzer

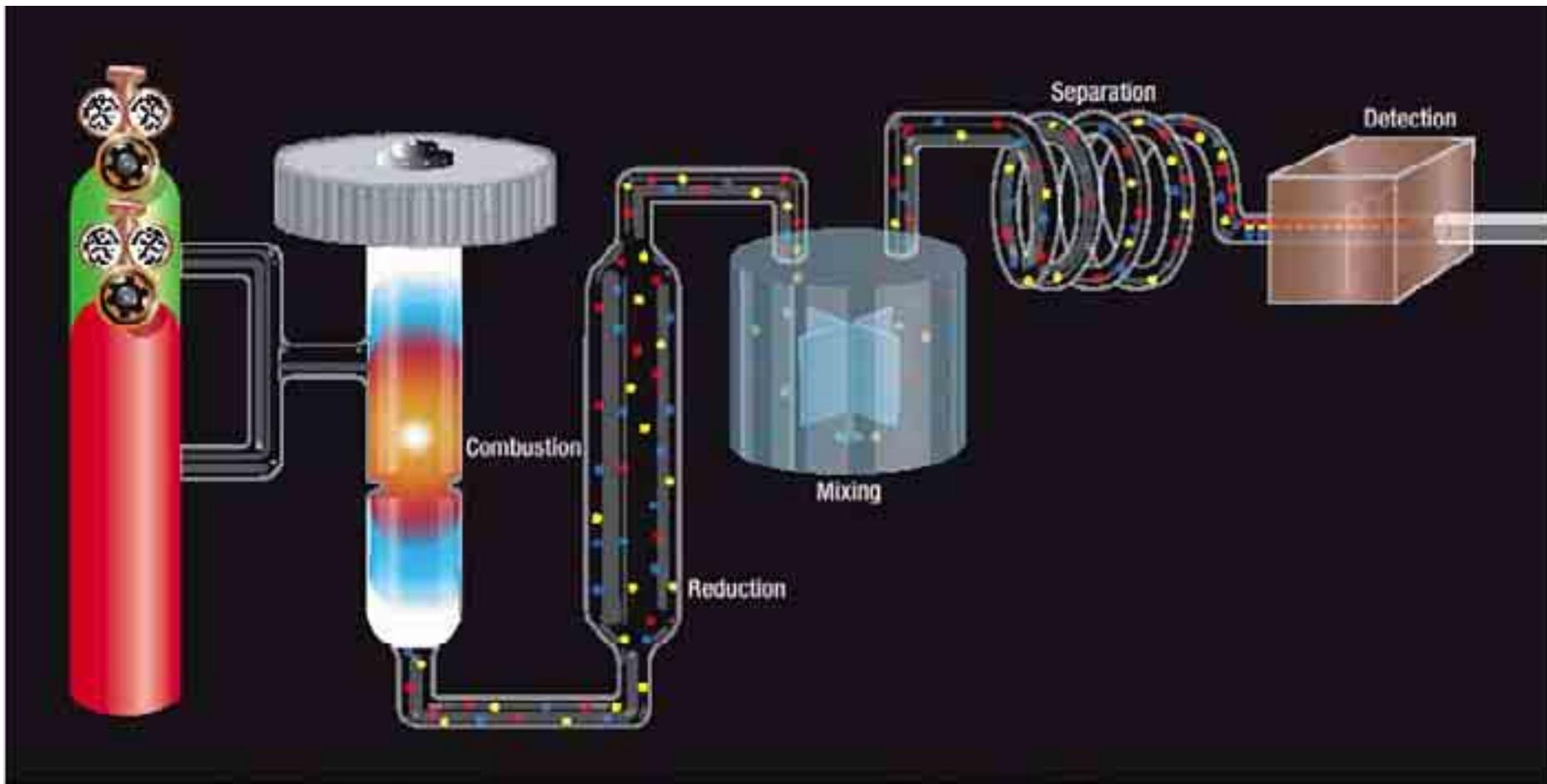


Figure 1. 2400 Series II CHNS/O Schematic

Instrument (1)

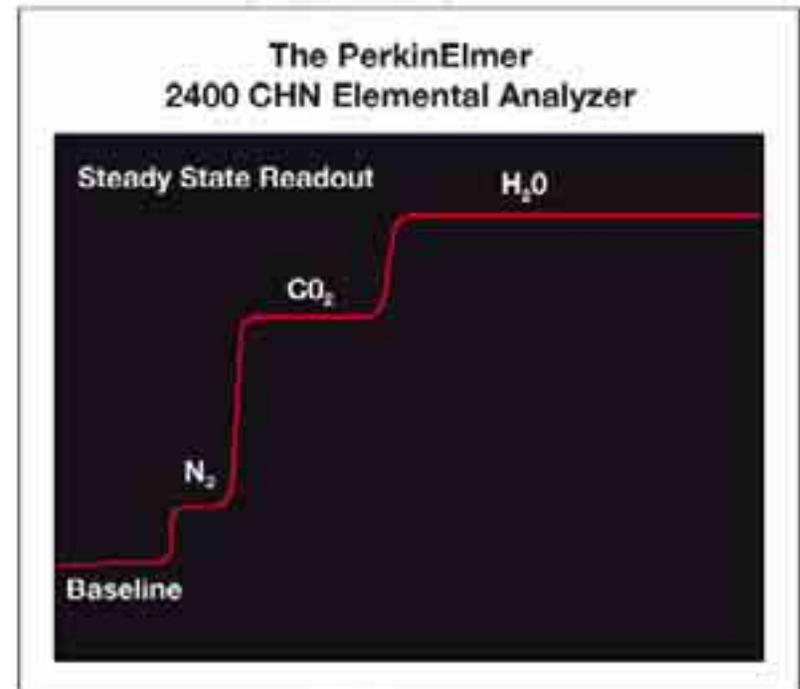
- *Auto sampling*: manual or automatic system of introduction of the samples collected in capsule.
- *Combustion tube*: containing a tungsten trap to gather the ashes, filled in the second part of reagents separated one from each other by a layer of quartz wool. A flux of ultrapure oxygen is introduced into this tube.
- *Reduction tube* it is filled by power copper to reduce:
 - the nitrogen oxides (previously formed during the oxidation phase) to elemental nitrogen,
 - the oxigen in CuO

The reduction tube has a limited life because copper is oxidized by the excess of oxygen during the oxidation reaction.

Instrument (2)

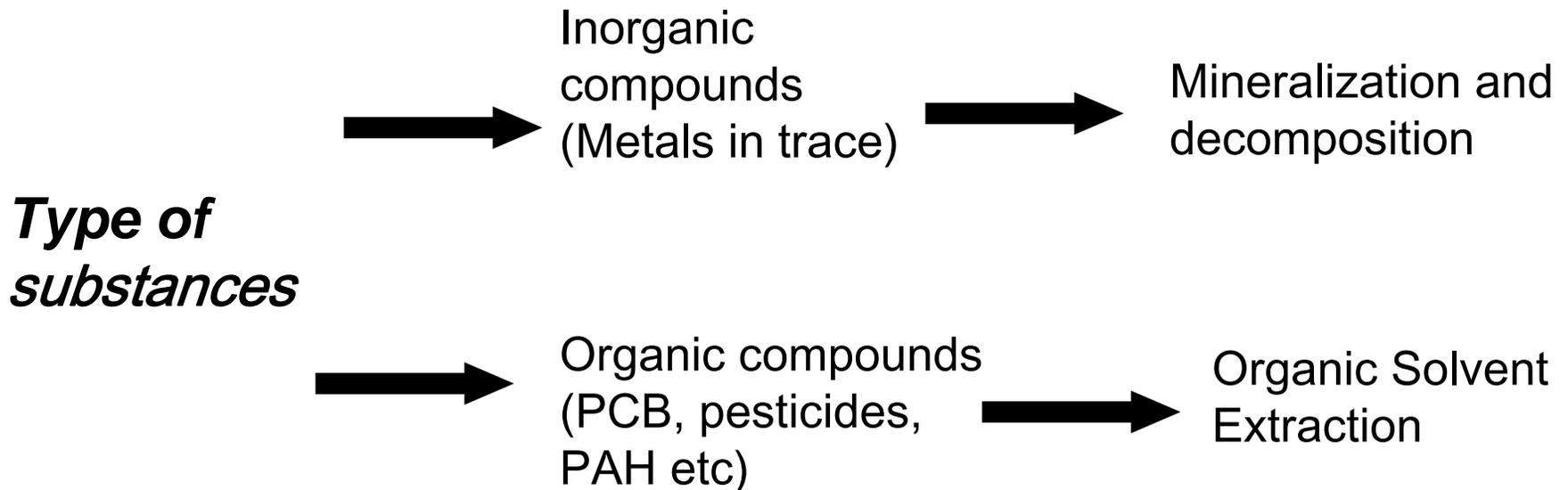
- *Mixing chamber*: the gases are perfectly homogenized and sent to the separative column;
- *Column* separation of the gases;
- *Detector* (conductivity detector).

Not a chromatogram is acquired but a stepped graphic, each step corresponds to one gas.



SOIL SAMPLE TREATMENT: PURPOSE

- transformation of the sample in the suitable state for the instrumental analysis;
- to separate the analytes from interfering compounds and matrix
- preconcentration.



INORGANIC MICROPOLLUTANTS

Mineralization and decomposition

The sample is treated with concentrated acids (a mixture) at high temperature. The metals are dissolved in water solution.

The choice of the acid to use depends on:

- the metals to determine,
- the type of matrix (Cr in silicates needs harder mineralization adding HF),
- the instrumental technique utilized for the analysis (the presence of Cl can interfere during ICP-MS analysis).

Mineralization reagents

HNO_3 displays the properties of a strong acid and it is a powerful oxidising agent. It dissolves nearly all the metals transforming them in nitrates. Its oxidising strength can be increases adding ClO_4^- , MnO_4^- , H_2O_2 , increasing the temperature or the pressure.

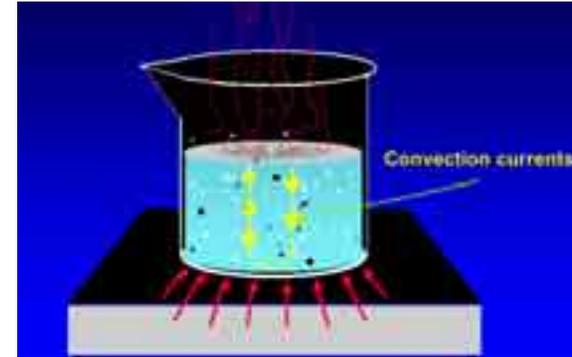
HCl it is a not powerful reducing agent. It dissolves many carbonates, Alkaline hydroxy, and several Metals (AgCl , HgCl_2 are insoluble!!). Mixed with HNO_3 (3:1) aqua regia.

HF it is not a oxidising agent but a complexing agent. It is most utilized in inorganic analyses because it can dissolve the silicates. To increase the dissolution often HF is mixed with HNO_3 .

H_2SO_4 only at high concentration it is a powerful oxidising agent. It must be utilized in quarts containers, improve the oxidising power of the HClO_4 .

Methods of digestion:

- *hot plate open vessel digestion* (traditional method),
- *microwave assisted digestion.*

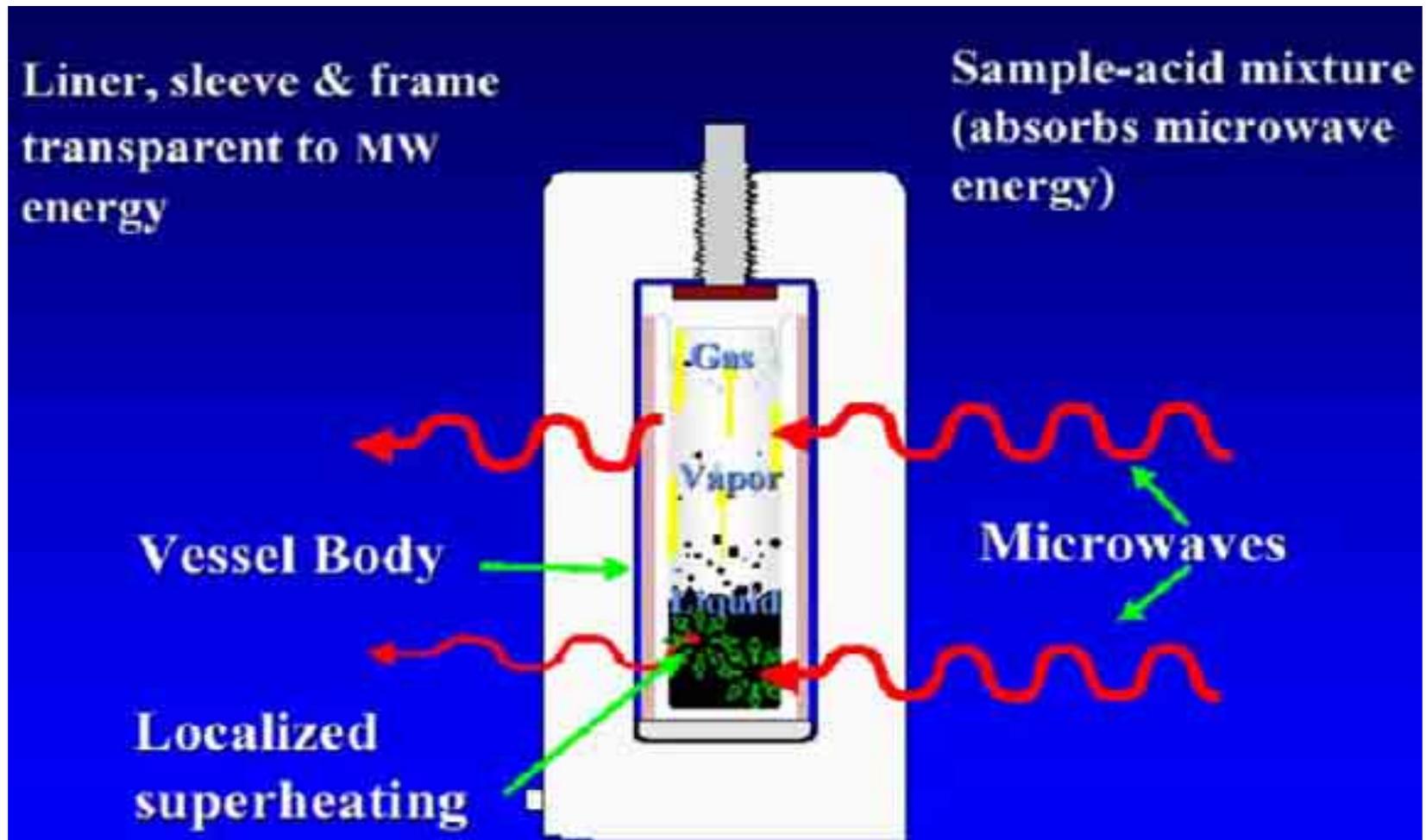


For the microwave assisted digestion the sample, placed inside a microwave transparent vessel with a polar liquid or ionic solution (usually acid) is subjected to rapid heating in the case of a sealed vessel, elevated pressure, causing the sample to digest or dissolve in a short time.

In this system the temperature and the pressure are controlled.

Higher reproducibility than hot plate open vessel digestion can be obtained .

Heating process of the sample in the microwave digestion system



Advantages of the Microwave-assisted digestion method:

- the environment in which the reaction takes place is clean, closed and controlled (less contamination),
- the amount of acid is diminished to stoichiometric quantities of the reagents, further reducing contamination,
- shorter reaction time and improved digestion due to higher temperature (far above the normal boiling point of the reagents),
- no losses of volatile elements.

Standard Method

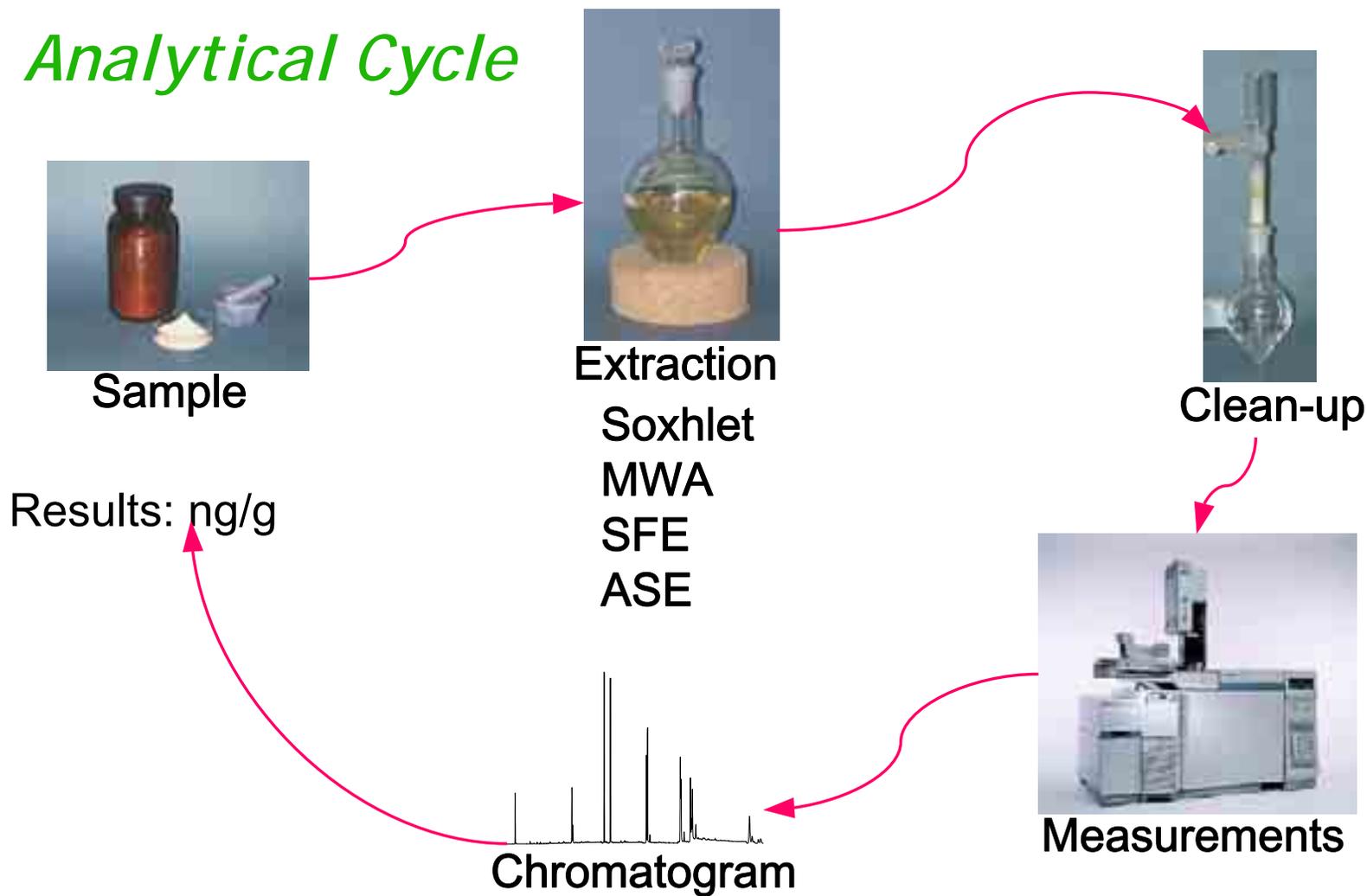
- US-EPA 3050B Acid digestion of sediments, sludges and soils
- US-EPA 3051 Microwave Assisted Acid Digestion of sediments, sludges and soils
- US-EPA 3052 Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrix

Standard Reference

EN 13656: 2002 Characterization of waste-Microwave assisted digestion with hydrofluoric(HF), nitric (HNO_3), and hydrochloridric (HCl) and mixture for subsequent determination of elements

ORGANIC MICROPOLLUTANTS

Analytical Cycle



Extraction techniques

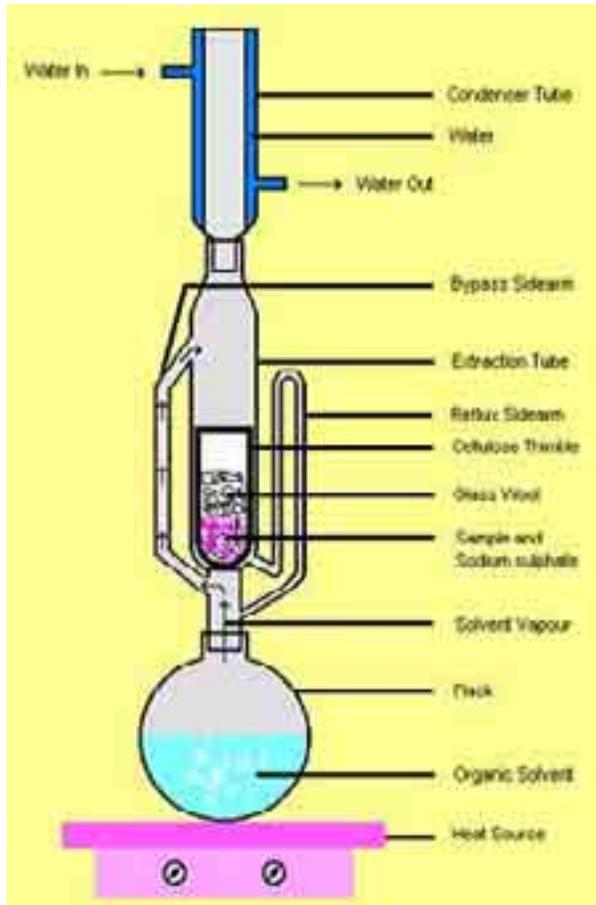
The organic micropollutants (PAH, PCB, PCDD...) are lypophilic substances and tend to be bound to the organic fraction of the soil. Their extraction from the solid matrix is possible only utilizing an organic solvent.

The choice of the suitable solvent depends as usually in chromatography on the polarity of the substance to extract. The law is : *like with like*.

Some of the main extraction techniques are:

- Soxhlet extraction;
- Supercritical fluid extraction;
- Microwave assisted extraction;
- ASE -Accelerated Solvent extraction.

Soxhlet Extraction



The sample is contained in a cellulose thimble. This thimble is placed in the extraction tube, which itself sits on a flask containing an organic solvent. The solvent is boiled, and its vapour travels upward through the extraction tube into the condenser tube. The cool water flowing around the outside of the condenser tube condenses the vapor, which then drips into the thimble, containing the sample. Once the liquid reaches the level of the bypass arm, it is siphoned back into the flask.

The sample in the thimble is continuously re-exposed to fresh, heated solvent, thus greatly increasing the extraction rate. But it 's time consuming (up to 24 h) and utilize large volume of solvent.

**Reference extraction
technique !!!**

Automated Soxhlet extraction

It includes three stage extraction system:

1. The sample- loaded extraction thimble is immersed into the boiling solvent to ensure very rapid intimate contact
2. The thimble is elevated above the solvent and is rinse-extracted
3. Evaporation of the solvent

It allows nearly the same recovery obtained with the traditional Soxhlet extraction system but in a less time (few hours), however the time is long with half the solvent!!

Supercritical fluid extraction

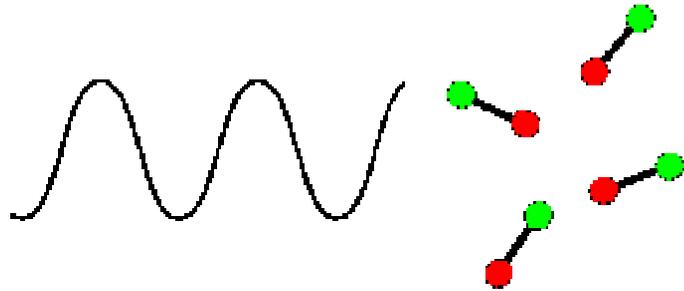
SFE utilizes CO₂ or another chemical (N₂O, CHClF₂) at high pressure and moderate temperature in lieu of an organic solvent. Above the critical point, these supercritical fluids have higher diffusivity and lower viscosity than liquids which contribute to their often superior extraction capabilities. Selective extraction can be performed by suitably modifying the density of the supercritical fluid results in an increase of the extraction yield of high molecular weight compounds. The density of the fluid can be varied by varying its temperature and pressure..

<i>Advantages</i>	<i>Disadvantages</i>
<ul style="list-style-type: none"> · High solvent power · CO₂ and other SFE solvents are non toxic (less postextraction concentration problem and laboratory safety and waste disposal concerns) · quite rapid analysis · on-line analysis (GC-HPLC) 	<ul style="list-style-type: none"> · requirement for a special equipment

Typical SFE apparatus consists of a high performance liquid chromatography pump for the delivery of the supercritical fluid to a tubular cell packed with 1 g or less of sample.

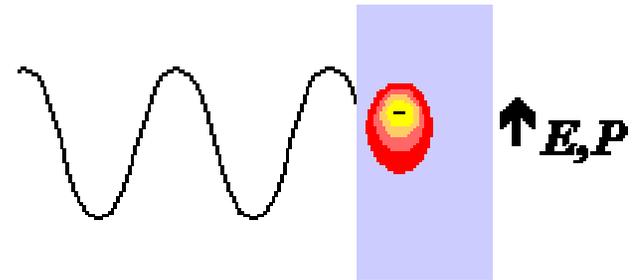
Microwave Assisted Extraction (principle)

1. Dipolar Polarisation



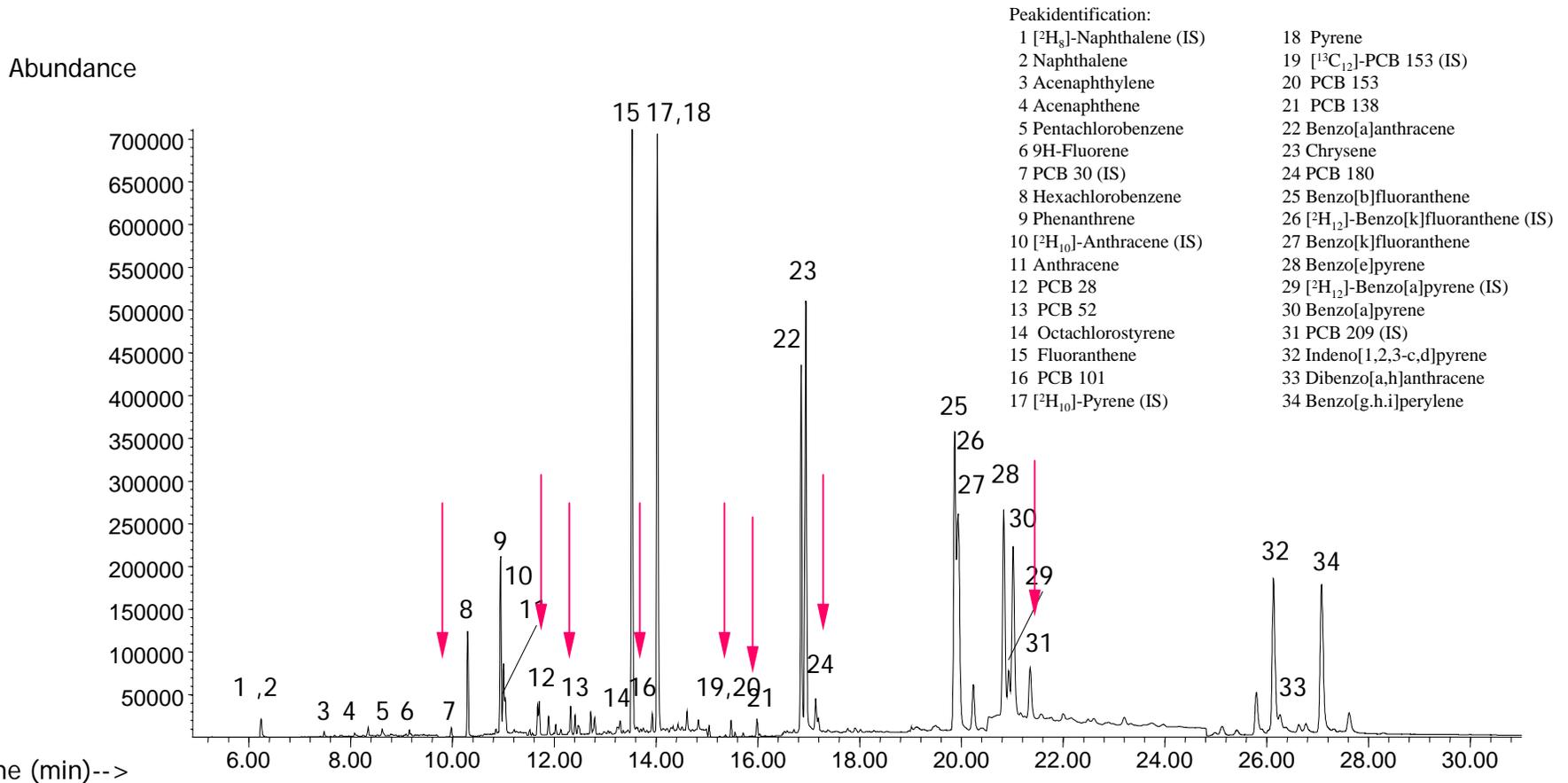
- Sample: Polar molecules
- Intermediate frequency electric field – molecules almost in phase with field polarity
- Heating due to random motion – molecules jostle (trying following the field)
- Dependent on frequency

2. Conduction Mechanism



- Sample: Electrical conductor
- Electric field E – Polarisation P
- Heating due to electrical resistance
- Good conductor: complete P in 10-18 s (electrons move in phase)
- Too conducting: Microwave energy is reflected – colossal surface voltage: arcing

MAE- Analysis of PCBs and PAH

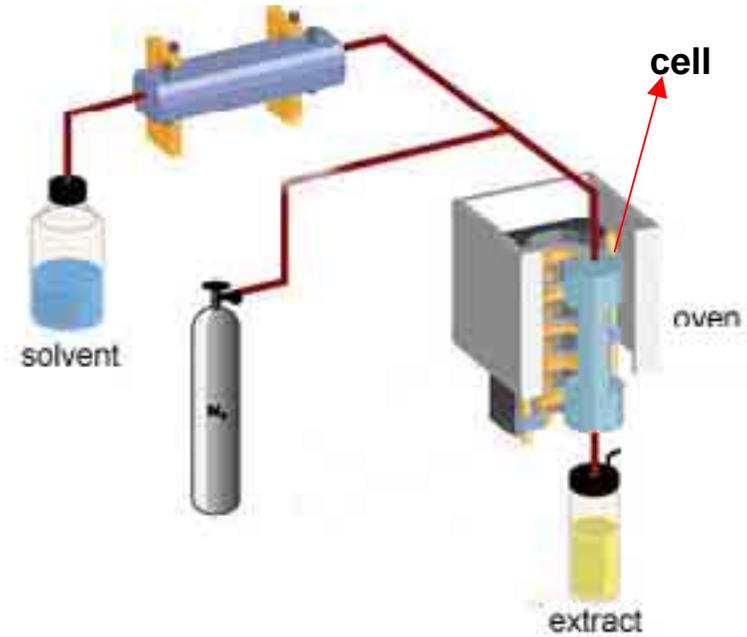


Accelerated Solvent Extraction

ASE uses conventional liquid solvents at elevated temperature and pressure to increase the efficiency of the extraction process.

The sample is loaded in a stainless steel cell with an adsorbent (hydromatryx) to remove eventual interferences (a preliminary clean-up) in the cell itself. The extract is collected in a vial of 40 or 60 mL upon the number of cycles done.

Increase temperature accelerates the extraction kinetics, while elevated pressure keeps the solvent below its boiling point, thus enabling safe and rapid extractions.



Clean-up

Clean-up removes co-extracted compounds before the final determination step can be executed.

The technique most frequently used are adsorption and gel permeation chromatography.

For the adsorption chromatography the most used adsorbent are:

- ❖ synthetic magnesium silicate (Florisil),
- ❖ silica,
- ❖ alumina,
- ❖ Carbon,
- ❖ C₁₈.

The first three materials progressively retard elution according to increasing polarity. The reverse occurs with the last two adsorbents.

Comparison of extraction techniques

	Soxhlet	MAE	SFE	ASE
Sample Weight (g)	30	5	< 1	2-5
Solvent Volume (mL)	150-250	20-30	10	10-30
Extraction time	24 h	35 min	20-120 min	10-20 min
Extraction	1	10-12	1	1
System	open	closed	closed	closed
Solvent	-	polar	CO ₂ + Modifier	-
Cost	Low	High	High	High

Standard Methods

- US-EPA 3500B Organic Extraction and Sample Preparation
- US-EPA 3540C Soxhlet Extraction
- US-EPA 3541 Automated Soxhlet Extraction
- US-EPA 3545 Pressurized Fluid Extraction (PFE)
- US-EPA 3561 Supercritical Fluid Extraction of PAH
- US-EPA 3600C Cleanup
- US-EPA 3610 Alumina cleanup
- US-EPA 3620B Florisil cleanup
- US-EPA 3630C Silica Gel Cleanup
- US-EPA 3640A Gel-Permeation Cleanup