

# Theoretical Considerations

The amount of compound absorbed by the silica-coated fibre at equilibrium is directly related to its concentration in the sample

$$n = \frac{KV_2C_0V_1}{KV_2} \times V_1$$

$n$  = the number of moles of the compound absorbed by the stationary phase

$K$  = the partition coefficient of a compound between the stationary phase and the aqueous phase

$C_0$  = the initial concentration of compound in the aqueous phase

$V_1$  = the volume of the aqueous sample and

$V_2$  = the volume of the stationary phase.



- The polymeric stationary phases used for SPME have a high affinity for organic molecules and hence the values of  $K$  are large.
- These large values of  $K$  lead to good pre-concentration of the target compounds in the aqueous sample and a corresponding high sensitivity in terms of the analysis.
- The dynamics of extraction are controlled by the mass transport of the compounds from the sample to the stationary phase of the silica-coated fibre.

**How might the dynamics of extraction be increased?**



# Classical Approaches for Solid–Liquid Extraction

- The extraction of organic compounds, including pesticides, polycyclic aromatic hydrocarbons and phenols from matrices (soils, sewage sludges, vegetables, plants), has historically been carried out by using Soxhlet extraction.
- The apparatus for Soxhlet extraction consists of a solvent reservoir, extractor body, an electric heat source (e.g. an isomantle) and a water-cooled reflux condenser.
- Soxhlet extraction uses a range of organic solvents to remove organic compounds from predominantly solid matrices.



Two variations of the apparatus are possible: one in which the solvent vapour passes outside (a), or alternatively within the body of the apparatus (b).

The mode of operation of both is the same.

**(a)** Solvent vapour passes external to the sample-containing thimble, which results in cooled organic solvent passing through the sample. This extraction process is relatively slow.

**(b)** Solvent vapour surrounds the sample-containing thimble. The hot organic solvent allows more rapid extraction.



# Microwave-Assisted Extraction

- The components of a microwave system are as follows:
  - a microwave generator;
  - a waveguide for transmission;
  - a resonant cavity;
  - a power supply.
- The microwave generator is called a **magnetron**.
- At the microwave frequency (2.45 GHz), electromagnetic energy is conducted from the magnetron to the resonant cavity using a waveguide. The sample placed inside the resonant cavity is therefore subjected to microwave energy.



- The solvent must be able to absorb microwave radiation and thereby becomes hot.
- The ability of an organic solvent to be useful for MAE can be assessed in terms of its dielectric constant,  $\epsilon$  ; the larger the value of the dielectric constant, the better the organic solvent's ability to become hot.



# Instrumentation

## Open (atmospheric) MAE system

- The sample is located in an 'open vessel' to which an appropriate organic solvent is added.
- Microwaves are directed via the waveguide onto the sample/solvent system.
- Hot solvent then comes into contact with a water-cooled reflux condenser.
- This causes the solvent to condense and return to the vessel.
- This process is repeated for a short period of time so enabling organic compounds to be desorbed from the sample matrix into the organic solvent.



## Closed (pressurized) MAE system

- Microwaves enter the cavity (the 'oven') and are dispersed via a mode stirrer.
- The latter allows an even distribution of microwaves within the cavity.
- The other major difference in the pressurized MAE system is that the sample and solvent are located within the sealed vessels which are usually made of microwave-transparent materials.

