

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, ϵ ; 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.

