Some Green Analytical Approaches

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Sample pre-treatment

✓ No sample pre-treatment
  - Matrix effect
  - Low concentration of the analyte

✓ The main aim
  - Clean up
  - Pre-concentration of the analytes of interest
  - Compatible with the analytical system

✓ Choice of the technique
  - Nature of analyte
  - Nature of sample
  - Detection technique used
Liquid–liquid extraction (LLE)

One of the oldest separation technique

✅ **Advantages**
- a simple technique
- *wide range of available organic solvents*

✅ **Disadvantages**
- time-consuming
- tedious
- *large volumes of organic solvents used*
- *production of vast amounts of organic waste*
Improvement of conventional LLE

✓ Miniaturization

✓ Automation

✓ Convenient to green analytical chemistry

Liquid-phase microextraction

✓ **LPME**
  - Small amount of solvent used
  - High sample-to-acceptor volume ratio

✓ **Main categories:**
  - **SDME**, Single Drop Microextraction
  - **HF-LPME**, Hollow-Fiber Liquid Phase Microextraction
  - **DLLME**, Dispersive Liquid–Liquid Microextraction
  - **HLLE**, Homogeneous Liquid–Liquid (micro)Extraction
What is the microextraction?

„... solvent microextraction (SME) is a technique of sample preparation by extraction ... with solvent volumes of 100 μL or less.“

Dispersive liquid-liquid microextraction

DLLME
DLLME

✔ Developed by Rezaee et al. in 2006

✔ A ternary component system

➤ sample solution

➤ extraction solvent – density higher than that of water

➤ dispersive solvent – miscible with both water and extraction solvent

✔ When injected into the sample, a cloudy solution is formed and a large surface area between extraction solvent and aqueous sample enables quickly achieving of equilibrium

DLLME – schematic

Evolution of number of papers
Factors affecting DLLME

- pH
- Ionic strength
- Extraction solvent nature and volume
- Dispersive solvent nature and volume
- Auxiliary agents
- Auxiliary energies
- Extraction time
DLLME

✓ Advantages
  - quick achieving of the equilibrium
  - very short extraction time
  - simplicity and low costs

✓ Disadvantages
  - limitations to solvents with density higher than water
  - problems with dispersive solvents
  - time-consuming centrifugation step
Therefore there were new techniques developed

- allow the use of extraction solvents lighter than water
- allow to omit the dispersive solvent
- allow to omit centrifugation step
Extraction solvent

✓ **Requirements** for extraction solvents
  ➢ density higher than that of water
    ✓ chlorobenzene, chloroform, tetrachloromethane, tetrachloroethane

✓ **Advantages** of using an extraction solvent heavier than water
  ➢ easy removal of the extraction phase after extraction

✓ **Disadvantages** of using an extraction solvent heavier than water
  ➢ hazardous

✓ **Solution**
  ➢ use of *extraction solvents lighter than water*
The use of extraction *solvents lighter than water*

- use of *special extraction vessels*
  - home-made device is needed
  - tedious
  - laborious

- use of „solidification of floating organic droplet“ (DLLME-SFO)
  - limited number of solvents with melting point between 10-30 °C

- use of *auxiliary solvent* for adjustment of solvents mixture density
Dispersive solvent

✓ **Requirements** for dispersion solvents
  ➢ miscibility with both the sample and the extraction solvent
    ✓ methanol, ethanol, acetone, acetonitrile

✓ **Advantages** of using a dispersion solvent
  ➢ increasing the extraction efficiency *(formation of a cloudy state)*

✓ **Disadvantages** of using a dispersion solvent
  ➢ reducing the extraction efficiency of *polar analytes*

✓ **Solution**
  ➢ DLLME *without the use of dispersive solvent*
Without dispersive solvent

✓ Alternatives to the use of dispersive solvent
  ➢ ultrasonication

➢ vortex mixing

➢ air-assisted DLLME

➢ adding of surfactants

➢ magnetic stirring
Centrifugation

✓ **Requirements** for centrifugation

✓ **Advantages** of using centrifugation
  ➢ perfect separation of the aqueous and organic phases

✓ **Disadvantages** of using centrifugation
  ➢ time-consuming step (**2-20 min**)

✓ **Solution**
  ➢ *DLLME without using centrifugation*
DLLME without centrifugation

✓ Solvent terminated DLLME
DLLME vs DLPME

✓ We should distinguish between two techniques:
  1) dispersive liquid-liquid microextraction (DLLME), and
  2) dispersive liquid-phase microextraction (DLPME).
DLLME vs DLPME

✅ DLLME
  - use a *mixture of extraction and dispersive solvents* and which in some instances, in addition to these two solvents, the formation of the cloudy solution is enhanced by adding *supplementary reagents* or applying *supplementary energy*.

✅ DLPME
  - *no dispersive solvent* is used.
Acronyms

✓ There is a tendency when researchers lightly modify an existing general method to give it
  ➢ a new name and
  ➢ a new acronym,

✓ which greatly complicates a search in the literature.

Acronyms

✓ Ideally, the method name and its acronym should provide the reader *sufficient information*;

✓ however, it should also be *as simple as possible* and not burdened with unnecessary details.

✓ probable *no ideal state is possible*.

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Single drop microextraction

✓ Modalities

- DI-SDME, Direct Immersion Single Drop Microextraction
- HS-SDME, Headspace Single Drop Microextraction
- LLLME, Liquid-liquid-liquid Microextraction
Single drop microextraction

✓ **Disadvantages**
  - Drop instability
  - Time-consuming
  - Low volume of the sedimeted phase
  - Viscosity of the sedimeted phase

✓ **Solution**
  - evaporation and reconstitution of the sedimeted phase
  - back extraction step
  - dilution of the sedimeted phase
Using an optical probe as the microdrop holder in headspace single drop microextraction

Determination of sulfite in food samples

A novel headspace single-drop microextraction method (HS-SDME) for determination of sulfite was developed.

An optical probe was used as the droplet holder in the HS-SDME procedure, and the analytical signal (absorbance) was monitored online during the extraction process.
A two-in-one device for online monitoring of direct immersion single-drop microextraction

An optical probe as both microdrop holder and measuring cell

DI-SDME

✓ An optical probe is proposed as the microdrop holder and simultaneously the measuring cell in a direct immersion single-drop microextraction (DI-SDME) procedure.

✓ This approach enables the analytical signal (absorbance of organic phase) to be monitored online during the extraction process.

✓ Based on the suggested approach, a novel DI-SDME method for the determination of thiocyanate ions in human saliva samples.
Optical probe – advantages

✓ optical probe as the holder of the extraction drop in SDME
✓ optical probe as the measuring cell in SDME
✓ necessity of transferring the extraction phase to a microcuvette is eliminated
✓ allows the absorbance to be recorded online
✓ allows the stirring rate to be increased
✓ setup does not include any homemade components
Green solvents

- Ionic liquids (IL)
- Deep eutectic solvents (DES)
- Switchable-hydrophilicity solvents (SHS)
- Surfactants
Deep eutectic solvents

✓ DES is a mixture of two or more pure compounds for which the eutectic point temperature is lower than that of the ideal liquid mixture, representing a significant negative deviation from ideality.
Deep eutectic solvents
Selected references

✓ **Sample pre-treatment**


✓ **Green chemistry**

Selected references

**DLLME**


Selected references

**DLLME**

Selected results

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Selected results


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