

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**

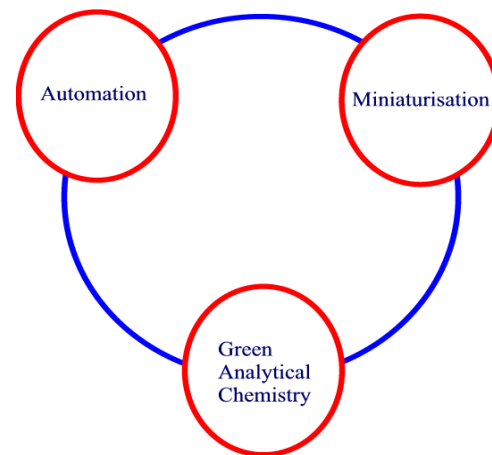
- time-consuming
- tedious
- **large volumes of organic solvents used**
- **production of vast amounts of organic waste**

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

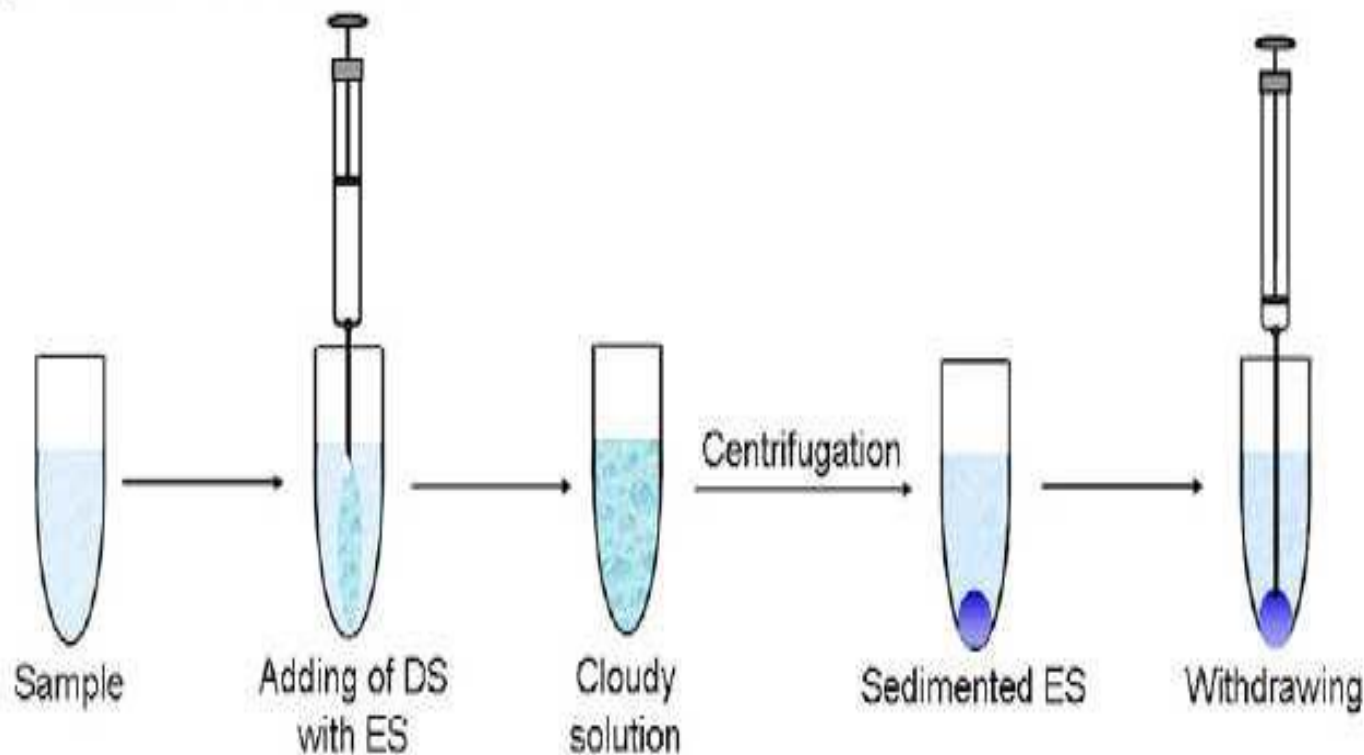
DLLME

DLLME

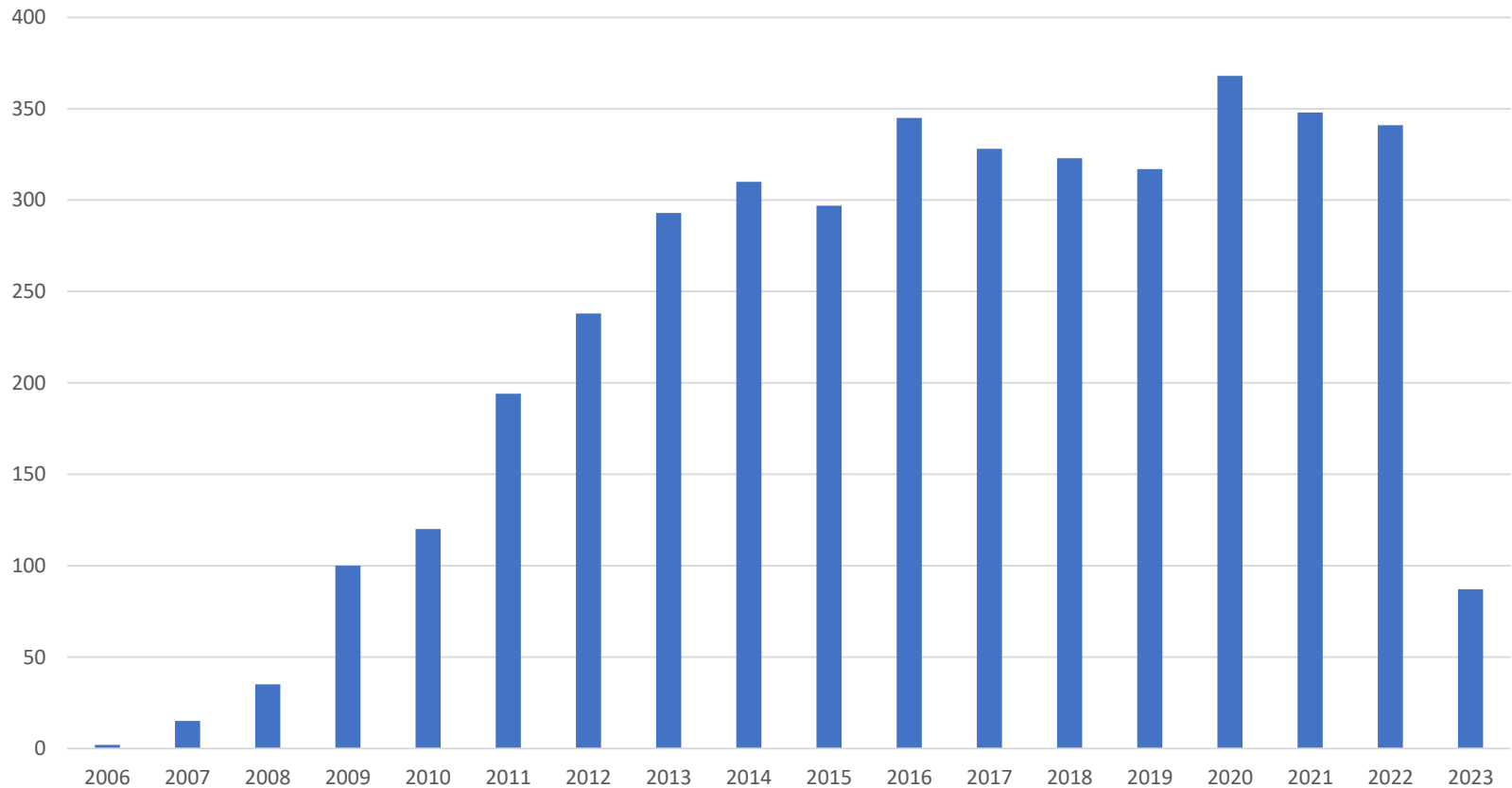
- ✓ Developed by Rezaee et al. in 2006
- ✓ A ternary component system
 - sample solution
 - extraction solvent – **density higher than that of water**
 - dispersive solvent – **miscible with both water and extraction solvent**
- ✓ When injected into the sample, a cloudy solution is formed and a large 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

DLLME

- ✓ 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*

DLLME

- ✓ 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**.



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 sedimented phase
- Viscosity of the sedimented phase

✓ Solution

- evaporation and reconstitution of the sedimented phase
- back extraction step
- dilution of the sedimented phase

Using an optical probe as the microdrop holder in headspace single drop microextraction

Determination of sulfite in food samples

S. Zaruba, A.B. Vishnikin, J. Škrlíková, V. Andruch, *Using an optical probe as the microdrop holder in headspace single drop microextraction: Determination of sulfite in food samples*, Anal. Chem., 88 (2016) 10296-10300



HS-SDME

- ✓ 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

S. Zaruba, A.B. Vishnikin, J. Škrlíková, A. Diuzheva, I. Ozimaničová, K. Gavazov, V. Andruch, *A two-in-one device for online monitoring of direct immersion single-drop microextraction: An optical probe as both microdrop holder and measuring cell*, RSC Adv., 7 (2017) 29421-29427



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

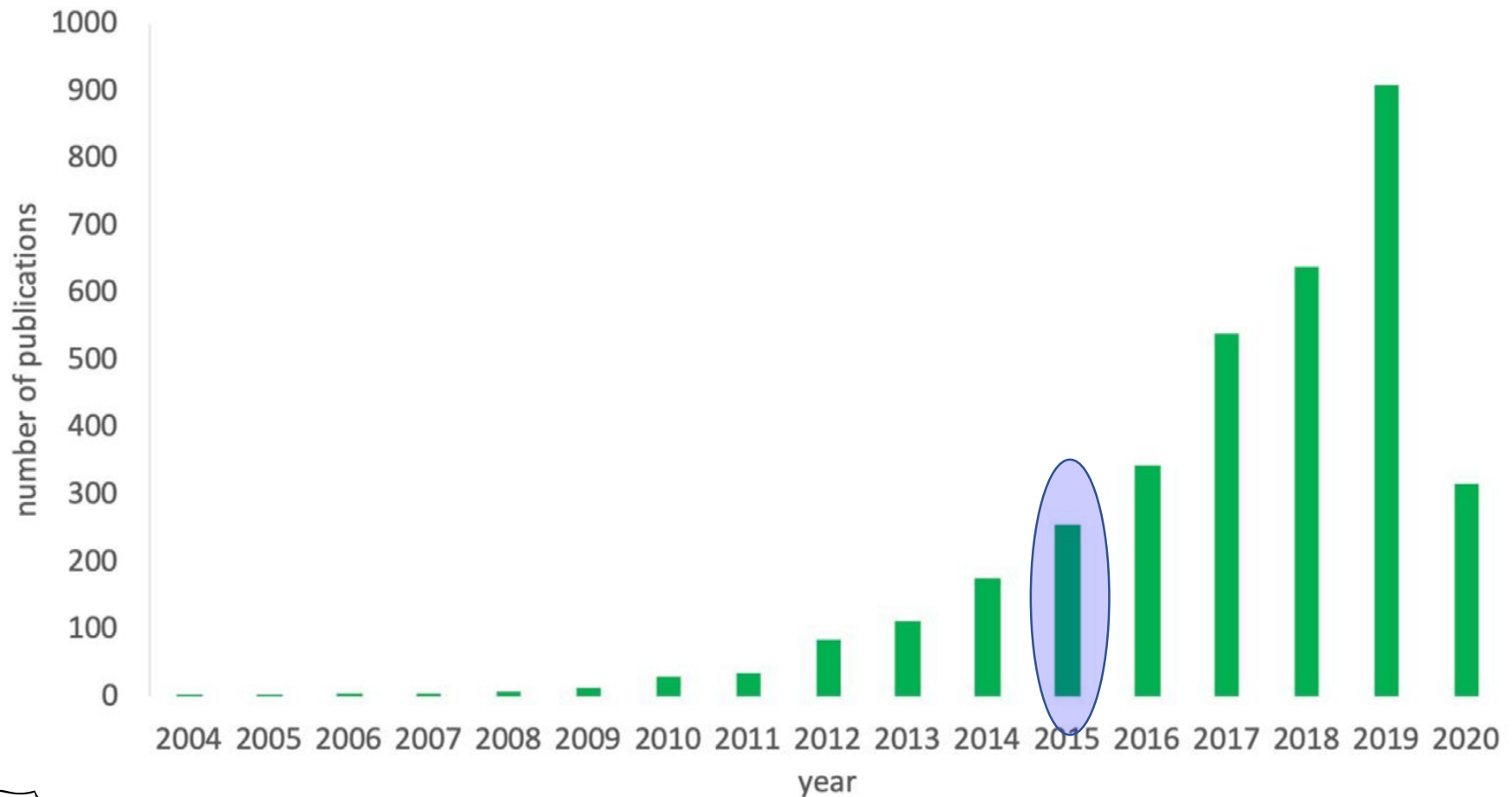
Green solvents

- ✓ 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



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