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**

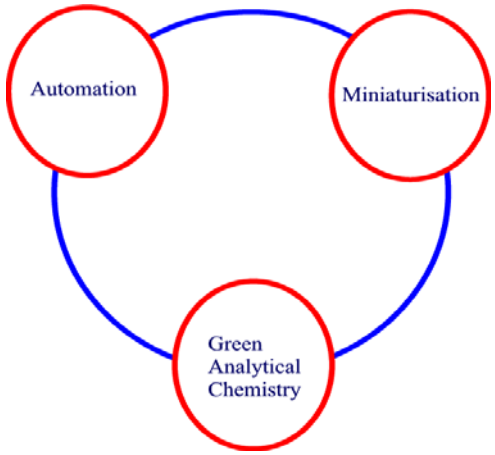
- a simple technique
- **wide range of available organic solvents**

✓**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**



L. Kocúrová, I.S. Balogh, V. Andruch, *Solvent microextraction: A review of recent efforts at automation,* Microchem. J. 110 (2013) 599-607.

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.“

J.M. Kokosa, *Advances in solvent microextraction techniques*, Trends Anal. Chem. 43 (2013) 2-13

Dispersive liquid-liquid microextraction

DLLME

DLLME

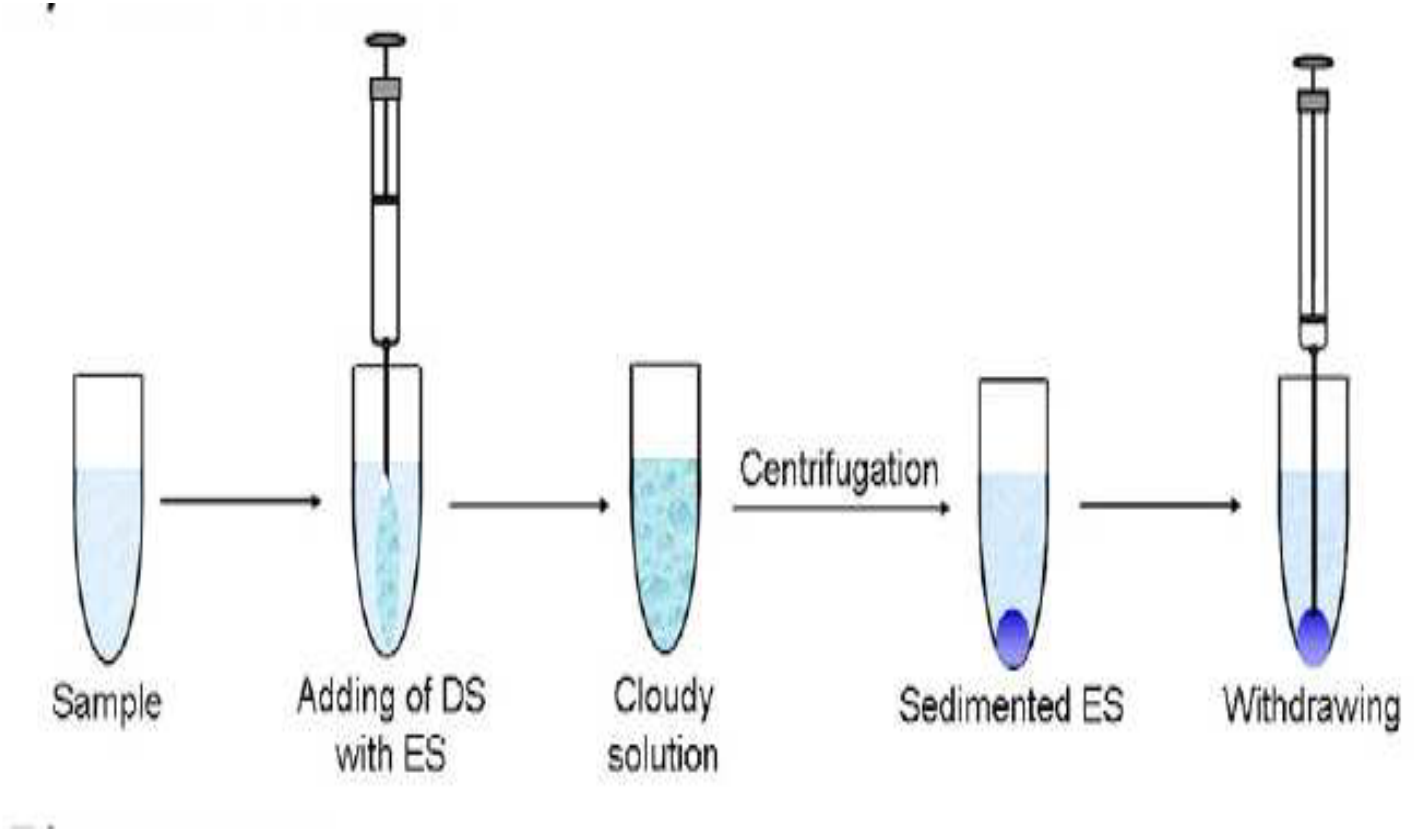
- ✓ Developed by Rezaee et al. in 2006

- ✓ 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

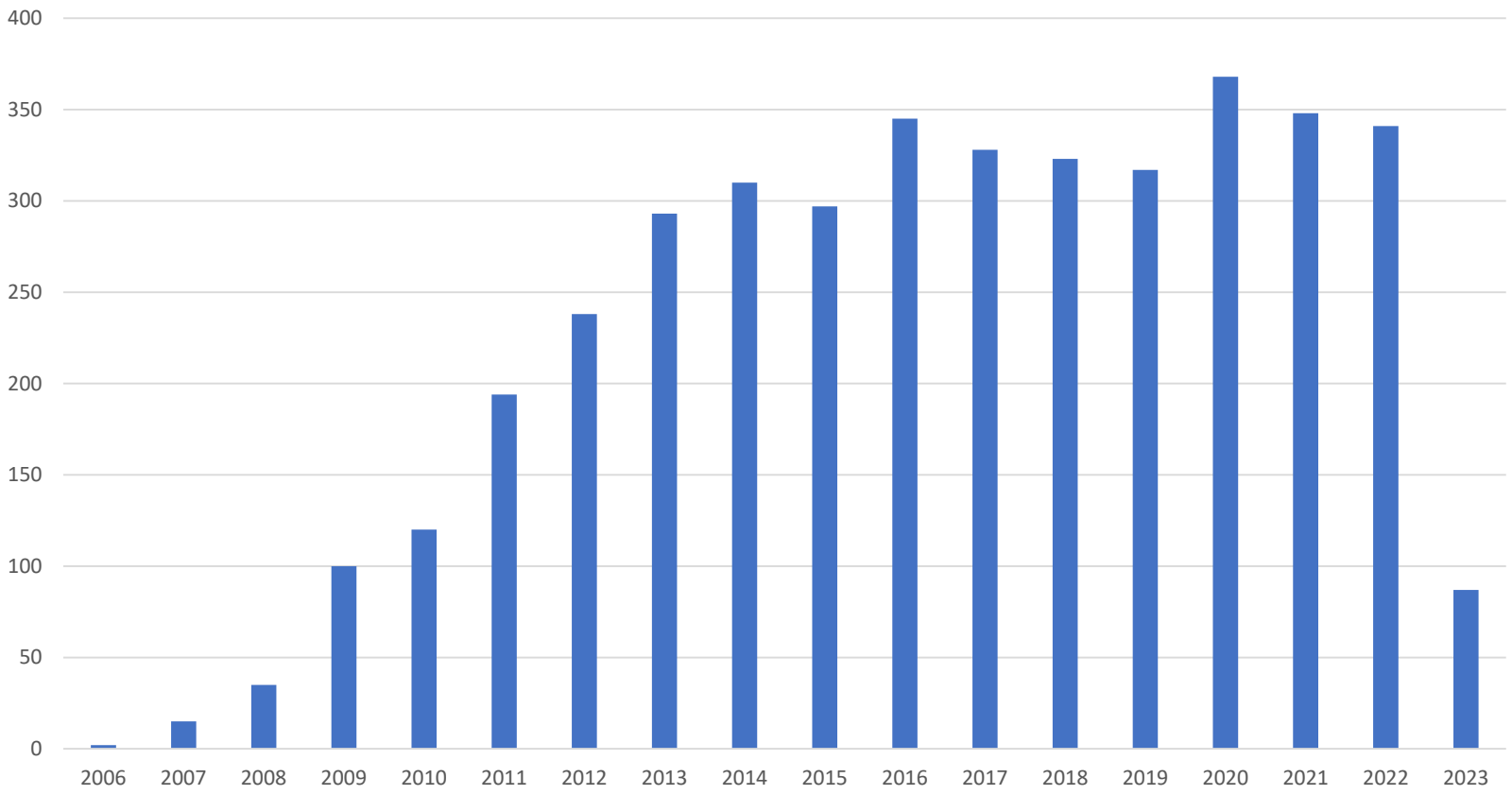
M. Rezaee, Y. Assadi, M.R. Milani Hosseini, E. Aghaee, F. Ahmadi, S. Berijani, *Determination of organic compounds in water using dispersive liquid–liquid microextraction*, J. Chromatogr. A *1116* (2006) 1–9

DLLME – schematic



L. Kocúrová, I.S. Balogh, J. Šandrejová, V. Andruch, *Recent advances in dispersive liquid-liquid microextraction using organic solvents lighter than water. A review*, Microchem. J. *102* (2012) 11-17

Evolution of number of papers



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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.

J.M. Kokosa, *Advances in solvent-microextraction techniques*, TrAC - Trends Anal. Chem., 43 (2013) 2-13

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**.

J. Šandrejová, N. Campillo, P. Viñas, V. Andruch, *Classification and terminology in dispersive liquid–liquid microextraction*, Microchem. J. 127 (2016) 184-186

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 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

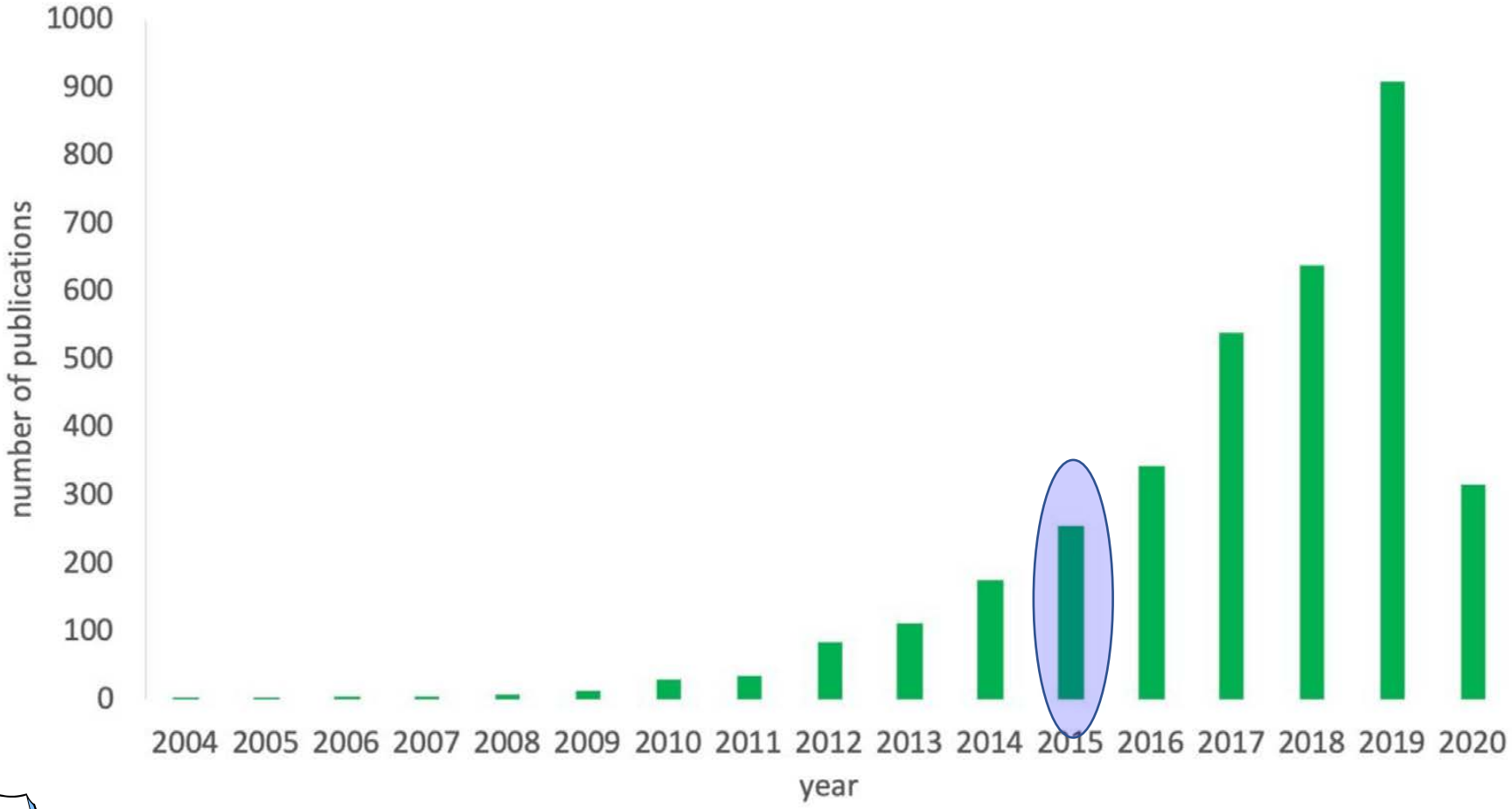
Green solvents

- ✓ 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



www.scopus.com

Selected references

✓ **Sample pre-treatment**

- A. Jain, K.K. Verma, *Recent advances in applications of single-drop microextraction: A review*, Analytica Chimica Acta 706 (2011) 37-65
- Li Xu, Chanbasha Basheer, Hian Kee Lee, *Developments in single-drop microextraction. Review*, J. Chromatogr. A, 1152 (2007) 184-192
- A. Kloskowski, W. Chrzanowski, M. Pilarczyk, J. Namiesnik, *Modern techniques of sample preparation for determination of organic analytes by gas chromatography*, Crit. Rev. Anal. Chem., 37 (2007) 15-38
- J.M. Kokosa, *Advances in solvent microextraction techniques*, Trends Anal. Chem. 43 (2013) 2-13

✓ **Green chemistry**

- P.T. Anastas, M.M. Kirchhoff, *Origins, Current Status, and Future Challenges of Green Chemistry*, Acc. Chem. Res. 2002, 35, 686-694
- S. Armenta, S. Garrigues, M. de la Guardia, *Green analytical chemistry*, Trends Anal. Chem. 27 (2008) 497-511.

Selected references

✓ DLLME

- S. Berijani, Y. Assadi, M. Anbia, M.R. Milani Hosseini, E. Aghaee, *Dispersive liquid-liquid microextraction combined with gas chromatography-flame photometric detection. Very simple, rapid and sensitive method for the determination of organophosphorus pesticides in water*, J. Chromatogr. A, 1123 (2006) 1-9
- M. Rezaee, Y. Assadi, M.R. Milani Hosseini, E. Aghaee, F. Ahmadi, S. Berijani, *Determination of organic compounds in water using dispersive liquid-liquid microextraction*, J. Chromatogr. A, 1116 (2006) 1-9
- L. Lili, H. Xu, D. Song, Y. Cui, S. Hu, G. Zhang, *Analysis of volatile aldehyde biomarkers in human blood by derivatization and dispersive liquid-liquid microextraction based on solidification of floating organic droplet method by high performance liquid chromatography*, J. Chromatogr. A, 1217 (2010) 2365-2370
- K.-J. Huang, C.-Y. Wei, W.-L. Liu, W.-Z. Xie, J.-F. Zhang, W. Wang, *Ultrasound assisted dispersive liquid-liquid micro- extraction combined with high performance liquid chromatography-fluorescence detection for sensitive determination of biogenic amines in rice wine samples*, J. Chromatogr. A, 1216 (2009) 6636–6641
- E. Yantzi, E. Psillakis, K. Tyrovola, N. Kalogerakis, *Vortex-assisted liquid-liquid microextraction of octylphenol, nonylphenol and bisphenol-A*, Talanta 80 (2010) 2057–2062

Selected references

✓ **DLLME**

- Q. Wu, Q. Chang, Ch. Wu, H. Rao, X. Zeng, Ch. Wang, Z. Wang, *Ultrasound assisted surfactant-enhanced emulsification microextraction for the determination of carbamate pesticides in water samples by high performance liquid chromatography*, J. Chromatogr. A 1217 (2010) 1773–1778
- B. Horstkotte, R. Suarez, P. Solich, V. Cerdà, *In-syringe-stirring: A novel approach for magnetic stirring-assisted dispersive liquid–liquid microextraction*, Anal. Chim. Acta 788 (2013) 52-60
- H. Chen, R. Chen, S. Li*, Low-density extraction solvent-based solvent terminated dispersive liquid-liquid microextraction combined with gas chromatography-tandem mass spectrometry for the determination of carbamate pesticides in water samples*, J. Chromatogr. A, 1217 (2010) 1244-1248
- J.M. Kokosa, *Advances in solvent-microextraction techniques*, TrAC - Trends Anal. Chem., 43 (2013) 2-13
- F. Pena-Pereira, I. Lavilla, C. Bendicho, *Miniaturized preconcentration methods based on liquid–liquid extraction and their application in inorganic ultratrace analysis and speciation: A review*, Spectrochim. Acta B 64 (2009) 1-15

Selected results

[1]. R. Karosi, V. Andruch, J. Posta, J. Balogh, Separation of chromium (VI) using complexation and its determination with GFAAS, Microchem. J., 82 (2006) 61-65
[2]. N. Urbanová, M. Kádár, K. Tóth, B. Bogáti, V. Andruch, I. Bitter, Fluorescent Iminodiacetamide Derivatives as Potential Ionophores for Optical Zinc Ion-selective Sensors, Anal. Sci., 24 (2008) 727-733
[3]. I.S. Balogh, M. Ruschak, V. Andruch, F. Billes, Determination of Cu(III) in semiconductor ceramics using cationic violet reagent, Microchim. Acta, 166 (2009) 145-150
[4]. L. Kocúrová, I.S. Balogh, J. Şkrlíková, J. Posta, V. Andruch, A novel approach in dispersive liquid-liquid microextraction based on the use of an auxiliary solvent for adjustment of density UV-VIS spectrophotometric and graphite furnace atomic absorption spectrometric determination of gold based on ion pair formation, Talanta, 82 (2010) 1958-1964
[5]. L. Kocúrová, I.S. Balogh, L. Nagy, F. Billes, A. Simon, V. Andruch, Application of a bisindocarbocyanine reagent for dispersive liquid-liquid microextraction of silver with subsequent spectrophotometric determination, Microchem. J., 99 (2011) 514-522
[6]. L. Rusnáková, V. Andruch, I.S. Balogh, J. Škrlíková, A dispersive liquid-liquid microextraction procedure for determination of boron in water after ultrasound-assisted conversion to tetrafluoroborate, Talanta, 85 (2011) 541-545
[7]. J. Škrlíková, V. Andruch, I.S. Balogh, L. Kocúrová, L. Nagy, Y. Bazeľ, A novel, environmentally friendly dispersive liquid-liquid microextraction procedure for the determination of copper, Microchem. J., 99 (2011) 40-45

Selected results

[8]. J. Škrlíková, V. Andruch, I.S. Balogh, J. Posta, Y. Bazeľ, A. Hudák, V. Jalčoviková, L. Kocúrová, A novel, environmentally friendly procedure for copper extraction using dimethylindodicarbocyanine dye and subsequent graphite furnace atomic absorption spectrometric detection, Anal. Methods, 3 (2011) 2412
[9]. J. Škrlíková, V. Andruch, H. Sklenářová, P. Solich, I.S. Balogh, F. Billes, A Novel Non-Extractive Sequential Injection Procedure for Determination of Cadmium, Anal. Lett., 44 (2011) 431-445
[10]. M. Alexovič, I.S. Balogh, J. Škrlíková, V. Andruch, A dispersive liquid-liquid microextraction procedure for UV-Vis spectrophotometric determination of chromium(VI) in water samples, Anal. Methods, 4 (2012) 1410-1414
[11]. V. Andruch, C.C. Acebal, J. Škrlíková, H. Sklenářová, P. Solich, I.S. Balogh, F. Billes, L. Kocúrová, Automated on-line dispersive liquid-liquid microextraction based on a sequential injection system, Microchem. J., 100 (2012) 77-82
[12]. V. Andruch, L. Kocúrová, I.S. Balogh, J. Škrlíková, Recent advances in coupling single-drop and dispersive liquid–liquid microextraction with UV-vis spectrophotometry and related detection techniques, Microchem. J., 102 (2012) 1-10
[13]. I.S. Balogh, L. Rusnáková, J. Škrlíková, L. Kocúrová, M. Török, V. Andruch, A spectrophotometric method for manganese determination in water samples based on ion pair formation and dispersive liquid-liquid microextraction, Int. J. Environ. Anal. Chem., 92 (2012) 1059-1071
[14]. R. Karosi, K. Boruzs, Á. Béni, J. Posta, J. Balogh, V. Andruch, Using dimethyl indocarbocyanide (DIC) as ion-pair agent for chromium speciation and its application in GFAAS analysis of water, Anal. Methods, 4 (2012) 2361

Selected results

[15]. L. Kocúrová, I.S. Balogh, J. Šandrejová, V. Andruch, Recent advances in dispersive liquid-liquid microextraction using organic solvents lighter than water. A review, Microchem. J., 102 (2012) 11-17
[16]. M. Alexovič, V. Andruch, I.S. Balogh, J. Šandrejová, A single-valve sequential injection manifold (SV-SIA) for automation of air-assisted liquid-phase microextraction: stopped flow spectrophotometric determination of chromium(vi), Anal. Methods, 5 (2013) 2497-2502
[17]. V. Andruch, I.S. Balogh, L. Kocúrová, J. Šandrejová, Five years of dispersive liquid-liquid microextraction, Appl. Spectrosc. Rev., 48 (2013) 161-259
[18]. V. Andruch, I.S. Balogh, L. Kocúrová, J. Šandrejová, The present state of coupling of dispersive liquid-liquid microextraction with atomic absorption spectrometry, J. Anal. At. Spectrom., 28 (2013) 19-32
[19]. V. Andruch, M. Burdel, L. Kocúrová, J. Šandrejová, I.S. Balogh, Application of ultrasonic irradiation and vortex agitation in solvent microextraction, TrAC - Trends Anal. Chem., 49 (2013) 1-19
[20]. M. Burdel, J. Šandrejová, I.S. Balogh, A. Vishnikin, V. Andruch, A comparison of various modes of liquid-liquid based microextraction techniques: Determination of picric acid, J. Sep. Sci., 36 (2013) 932-938
[21]. L. Kocurova, I.S. Balogh, V. Andruch, Solvent microextraction: A review of recent efforts at automation, Microchem. J., 110 (2013) 599-607

Selected results

[22]. L. Kocúrová, I.S. Balogh, V. Andruch, A glance at achievements in the coupling of headspace and direct immersion single-drop microextraction with chromatographic techniques, J. Sep. Sci., 36 (2013) 3758-3768
[23]. L. Kocúrová, I.S. Balogh, V. Andruch, Dispersive liquid-phase microextraction procedure for spectrometric determination of cadmium, Microchem. J., 107 (2013) 3-9
[24]. M. Falkova, M. Alexovič, M. Pushina, A. Bulatov, L. Moskvin, V. Andruch, Fully automated on-line flow-batch based ultrasound-assisted surfactant-mediated extraction and determination of anthraquinones in medicinal plants, Microchem. J., 116 (2014) 98-106
[25]. L. Kocúrová, I.S. Balogh, M. Fatl'ová, Y. Bazel, A. Simon, R. Serbin, M. Badida, R. Rusnák, V. Andruch, A novel, donor-active solvent-assisted liquid-phase microextraction procedure for spectrometric determination of zinc
[26]. J. Brazilian Chem. Soc., 25 (2014) 313-319
[27]. M. Alexovič, M. Wieczorek, J. Kozak, P. Košcielniak, I.S. Balogh, V. Andruch, An automatic, vigorous-injection assisted dispersive liquid-liquid microextraction technique for stopped-flow spectrophotometric detection of boron, Talanta, 133 (2015) 127-133
[28]. F. Billes, L. Elečková, H. Mikosch, V. Andruch, Vibrational spectroscopic study of dehydroacetic acid and its cinnamoyl pyrone derivatives, Spectrochim. Acta Part A, 146 (2015) 97-112

Selected results

[29]. L. Eleckova, M. Alexovic, J. Kuchar, I.S. Balogh, V. Andruch, Visual detection and sequential injection determination of aluminium using a cinnamoyl derivative, Talanta, 133 (2015) 27-33
[30]. K. Medinskaia, S. Garmonov, J. Kozak, M. Wieczorek, V. Andruch, P. Kościelniak, A. Bulatov, Stepwise injection determination of isoniazid in human urine samples coupled with generalized calibration method, Microchem. J., 123 (2015) 111-117
[31]. P. Viñas, N. Campillo, V. Andruch, Recent achievements in solidified floating organic drop microextraction, TrAC - Trends Anal. Chem., 68 (2015) 48-77
[32]. S. Zaruba, A.B. Vishnikin, V. Andruch, Application of solidification of floating organic drop microextraction for inorganic anions: Determination of phosphate in water samples, Microchem. J., 122 (2015) 10-15
[33]. K. Medinskaia, C. Vakh, D. Aseeva, V. Andruch, L. Moskvin, A. Bulatov, A fully automated effervescence assisted dispersive liquid-liquid microextraction based on a stepwise injection system. Determination of antipyrine in saliva samples, Anal. Chim. Acta, 902 (2016) 129-134
[34]. J. Šandrejová, N. Campillo, P. Viñas, V. Andruch, Classification and terminology in dispersive liquid–liquid microextraction, Microchem. J., 127 (2016) 184-186
[35]. Shishov, A. Zabrodin, L. Moskvin, V. Andruch, A. Bulatov, Interfacial reaction using particle-immobilized reagents in a fluidized reactor. Determination of glycerol in biodiesel, Anal. Chim. Acta, 914 (2016) 75-80

Selected results

[36]. Vakh, A. Pochivalov, V. Androuch, L. Moskvin, A. Bulatov, A fully automated effervescence-assisted switchable solvent-based liquid phase microextraction procedure: Liquid chromatographic determination of ofloxacin in human urine samples, Anal. Chim. Acta, 907 (2016) 54-59
[37]. S. Zaruba, A.B. Vishnikin, V. Androuch, A novel vortex-assisted liquid-liquid microextraction approach using auxiliary solvent: Determination of iodide in mineral water samples, Talanta, 149 (2016) 110-116
[38]. S. Zaruba, A.B. Vishnikin, J. Škrlíková, V. Androuch, 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
[39]. N. Campillo, P. Viñas, J. Šandrejová, V. Androuch, Ten years of dispersive liquid–liquid microextraction and derived techniques, Appl. Spectrosc. Rev., 52 (2017) 267-415
[40]. L. Nugbienyo, Y. Malinina, S. Garmonov, M. Kamencev, I. Salahov, V. Androuch, L. Moskvin, A. Bulatov, Automated sugaring-out liquid-liquid extraction based on flow system coupled with HPLC-UV for the determination of procainamide in urine, Talanta, 167 (2017) 709-713
[41]. L. Nugbienyo, A. Shishov, S. Garmonov, L. Moskvin, V. Androuch, A. Bulatov, Flow method based on liquid-liquid extraction using deep eutectic solvent for the spectrofluorimetric determination of procainamide in human saliva, Talanta, 168 (2017) 307-312
[42]. Pochivalov, C. Vakh, V. Androuch, L. Moskvin, A. Bulatov, Automated alkaline-induced salting-out homogeneous liquid-liquid extraction coupled with in-line organic-phase detection by an optical probe for the determination of diclofenac, Talanta, 169 (2017) 156-162

Selected results

[43]. Shishov, A. Bulatov, M. Locatelli, S. Carradori, V. Andruch, Application of deep eutectic solvents in analytical chemistry. A review, Microchem. J., 135 (2017) 33-38
[44]. Shishov, D. Nechaeva, L. Moskvin, V. Andruch, A. Bulatov, Automated solid sample dissolution coupled with sugaring-out homogenous liquid-liquid extraction. Application for the analysis of throat lozenge samples, J. Mol. Liq., 233 (2017) 149-155
[45]. T. Stefanova-Bahchevanska, N. Milcheva, S. Zaruba, V. Andruch, V. Delchev, K. Simitchiev, K. Gavazov, A green cloud-point extraction-chromogenic system for vanadium determination, J. Mol. Liq., 248 (2017) 135-142
[46]. S. Zaruba, V. Bozóová, A.B. Vishnikin, Y.R. Bazeľ, J. Šandrejová, K. Gavazov, V. Andruch, Vortex-assisted liquid-liquid microextraction procedure for iodine speciation in water samples, Microchem. J., 132 (2017) 59-68
[47]. 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
[48]. Diuzheva, S. Carradori, V. Andruch, M. Locatelli, E. De Luca, M. Tiecco, R. Germani, L. Menghini, A. Nocentini, P. Gratteri, C. Campestre, Use of Innovative (Micro)Extraction Techniques to Characterise Harpagophytum procumbens Root and its Commercial Food Supplements, Phytochem. Anal., 29 (2018) 233–241
[49]. Mocan, A. Diuzheva, S. Carradori, V. Andruch, C. Massafra, C. Moldovan, C. Sisea, J.P. Petzer, A. Petzer, S. Zara, G.D. Marconi, G. Zengin, G. Crișan, M. Locatelli, Development of novel techniques to extract phenolic compounds from Romanian cultivars of Prunus domestica L. and their biological properties, Food Chem. Toxicol., 119 (2018) 189-198

Selected results

[50]. Diuzheva, J. Balogh, Y. Studenyak, Z. Cziáky, J. Jekő, A salting-out assisted liquid-liquid microextraction procedure for determination of cysteine followed by spectrophotometric detection, Talanta, 194 (2019) 446-451
[51]. Diuzheva, H. Dejmková, J. Fischer, V. Andruch, Simultaneous determination of three carbamate pesticides using vortex-assisted liquid–liquid microextraction combined with HPLC-amperometric detection, Microchem. J., 150 (2019) 104071
[52]. K.B. Gavazov, I. Hagarová, R. Halko, V. Andruch, Recent advances in the application of nanoparticles in cloud point extraction, J. Mol. Liq., 281 (2019) 93-99
[53]. Mocan, A. Diuzheva, S. Badarau, C. Moldovan, V. Andruch, S. Carradori, C. Campestre, A. Tartaglia, M. De Simone, D. Vodnar, M. Tiecco, R. Germani, G. Crisan, M. Locatelli, Liquid Phase and Microwave-Assisted Extractions for Multicomponent Phenolic Pattern Determination of Five Romanian Galium Species Coupled with Bioassays, Molecules, 24 (2019)
[54]. M. Rutkowska, J. Płotka-Wasylka, M. Sajid, V. Andruch, Liquid–phase microextraction: A review of reviews, Microchem. J., 149 (2019) 103989
[55]. Shishov, R. Chromá, C. Vakh, J. Kuchár, A. Simon, V. Andruch, A. Bulatov, In situ decomposition of deep eutectic solvent as a novel approach in liquid-liquid microextraction, Anal. Chim. Acta, 1065 (2019) 49-55
[56]. N. Campillo, K. Gavazov, P. Viñas, I. Hagarova, V. Andruch, Liquid-phase microextraction: update May 2016 to December 2018, Appl. Spectrosc. Rev., 55 (2020) 307-326

Selected results

[57]. Diuzheva, M. Locatelli, A. Tartaglia, M. Goga, V. Ferrone, G. Carlucci, V. Andruch, Application of liquid-phase microextraction to the analysis of plant and herbal samples, Phytochem. Anal., 31 (2020) 687-699
[58]. J. Płotka-Wasylka, M. de la Guardia, V. Andruch, M. Vilková, Deep eutectic solvents vs ionic liquids: Similarities and differences, Microchem. J., 159 (2020) 105539
[59]. Shishov, A. Pochivalov, L. Nugbienyo, V. Andruch, A. Bulatov, Deep eutectic solvents are not only effective extractants, TrAC - Trends Anal. Chem., 129 (2020) 115956
[60]. M. Vilková, J. Płotka-Wasylka, V. Andruch, The role of water in deep eutectic solvent-base extraction, J. Mol. Liq., 304 (2020) 112747
[61]. R. Chromá, M. Vilková, I. Shepa, P. Makoś-Chełstowska, V. Andruch, Investigation of tetrabutylammonium bromide-glycerol-based deep eutectic solvents and their mixtures with water by spectroscopic techniques, J. Mol. Liq., 330 (2021) 115617
[62]. Diuzheva, E. Fernández, L. Vidal, V. Andruch, A. Canals, Vitamin E determination in edible oils by reversed-phase dispersive liquid-liquid microextraction and screen-printed carbon electrodes, Advances in Sample Preparation, 1 (2021) 100005
[63]. Kalyniukova, J. Holuša, D. Musiolek, J. Sedlakova-Kadukova, J. Płotka-Wasylka, V. Andruch, Application of deep eutectic solvents for separation and determination of bioactive compounds in medicinal plants, Ind. Crops Prod., 172 (2021) 114047

Selected results

[64]. P. Makoś-Chełstowska, R. Chromá, V. Andruch, Closer look into the structures of tetrabutylammonium bromide–glycerol-based deep eutectic solvents and their mixtures with water, J. Mol. Liq., (2021) 116676
[65]. N.P. Milcheva, F. Genç, P.V. Racheva, V.B. Delchev, V. Andruch, K.B. Gavazov, An environmentally friendly cloud point extraction–spectrophotometric determination of trace vanadium using a novel reagent, J. Mol. Liq., 334 (2021) 116086
[66]. J. Płotka-Wasylka, H.M. Mohamed, A. Kurowska-Susdorf, R. Dewani, M.Y. Fares, V. Andruch, Green analytical chemistry as an integral part of sustainable education development, Curr. Opin. Green Sustain. Chem., 31 (2021) 100508
[67]. V. Andruch, R. Halko, J. Tuček, J. Płotka-Wasylka, Application of deep eutectic solvents in atomic absorption spectrometry, TrAC - Trends Anal. Chem., 147 (2022) 116510
[68]. V. Andruch, P. Makoś-Chełstowska, J. Płotka-Wasylka, Remarks on use of the term “deep eutectic solvent” in analytical chemistry, Microchem. J., 179 (2022) 107498
[69]. V. Andruch, A. Varfalvyová, R. Halko, N. Jatkowska, J. Płotka-Wasylka, Application of deep eutectic solvents in bioanalysis, TrAC - Trends Anal. Chem., 154 (2022) 116660
[70]. R. Halko, J. Tuček, K. Chovancová, V. Andruch, Some green approaches in atomic absorption spectrometry. The last 10 years, Appl. Spectrosc. Rev., (2022) 1-48

Selected results

[71]. P. Janicka, J. Płotka-Wasylka, N. Jatkowska, A. Chabowska, M.Y. Fares, V. Andruch, M. Kaykhaii, J. Gębicki, Trends in the new generation of green solvents in extraction processes, Curr. Opin. Green Sustain. Chem., 37 (2022) 100670
[72]. Shishov, P. Makos-Chelstowska, A. Bulatov, V. Andruch, Deep Eutectic Solvents or Eutectic Mixtures? Characterization of Tetrabutylammonium Bromide and Nonanoic Acid Mixtures, J. Phys. Chem. B, 126 (2022) 3889-3896
[73]. V. Andruch, A. Kalyniukova, J. Płotka-Wasylka, N. Jatkowska, D. Snigur, S. Zaruba, J. Płatkiewicz, A. Zgoła-Grześkowiak, J. Werner, Application of deep eutectic solvents in analytical sample pretreatment (update 2017–2022). Part A: Liquid phase microextraction, Microchem. J., 189 (2023) 108509