“Green analytical chemistry: Trace elemental analysis on water samples by liquid-liquid microextration (LLME)-laser-induced breakdown spectroscopy (LIBS)”

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5-6 June 2012, Plovdiv, Bulgaria

- **Introduction**
  - ✓ **Green chemistry**
    - **Green analytical chemistry**
- **Sample preparation**
  - ✓ **Miniaturization on sample preparation**
    - **Liquid-liquid microextraction (LLME)**
- **Detection techniques for LLME**
  - ✓ **Laser-induced breakdown spectroscopy (LIBS) for trace elemental analysis**
    - **Evaluating LIBS for the analysis of Mn in microdroplets**
    - **Direct microdroplets on aluminium substrates**
    - **Testing the combination of LLME-LIBS: preliminary results**

Introduction

Green Chemistry

“Sustainable development”

“protection of the environment”

“a form of development that meets the needs of the present without compromising the ability of future generations to meet their own needs”

Green Analytical Chemistry(I)

"it is an unfortunate irony that environmental analytical methods often contribute to further environmental problems through the chemicals used in the analysis"

From : P.T. Anastas, Crit. Rev. Anal. Chem., 29(3), 167-175 (1999)

Green Analytical Chemistry(II)

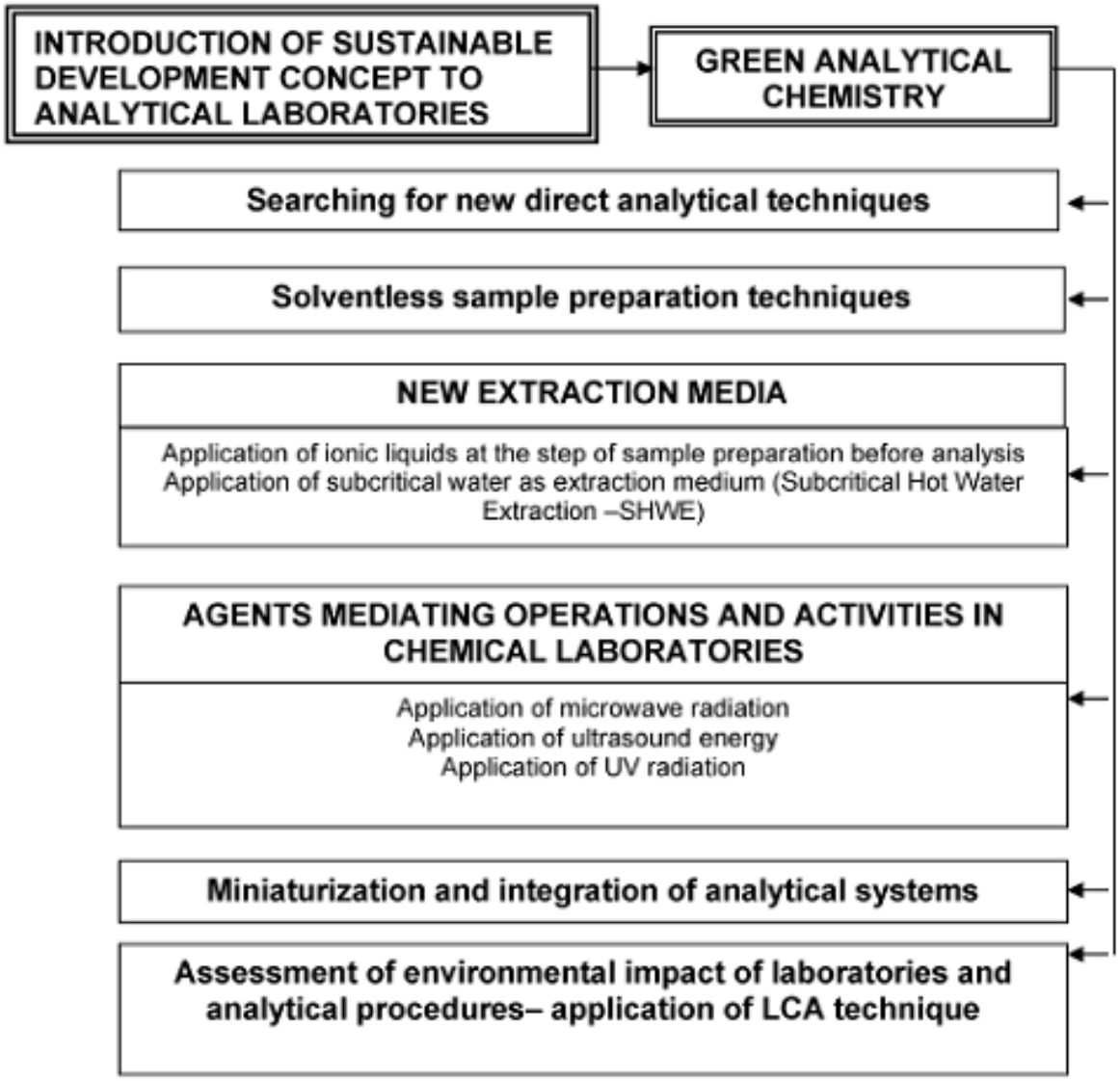
"The goal of Green Analytical Chemistry is to use analytical procedures that generate less hazardous waste and that are safer to use and more benign to the environment"

Twelve Principles of Green Chemistry on Analytical Chemistry

- The elimination (or at least, the significant reduction) of reagents, particularly organic solvents, from analytical procedures
- Reduced emissions of vapours and gases, as well as liquid and solid wastes generated in analytical laboratories
- The elimination of highly toxic and/or eco-toxic reagents from analytical procedures (e.g., the substitution of benzene with other solvents)
- Reduced labour and energy consumption of analytical procedures (per single analyte)
- *Reduced time gap between sampling and the desired information becoming available (i.e., real time analysis)*

From: M. Tobiszewski, A. Mechlinska, J. Namiesnik, Chem. Soc. Rev., 39, 2869–2878 (2010)

Challenges in Green Analytical Chemistry



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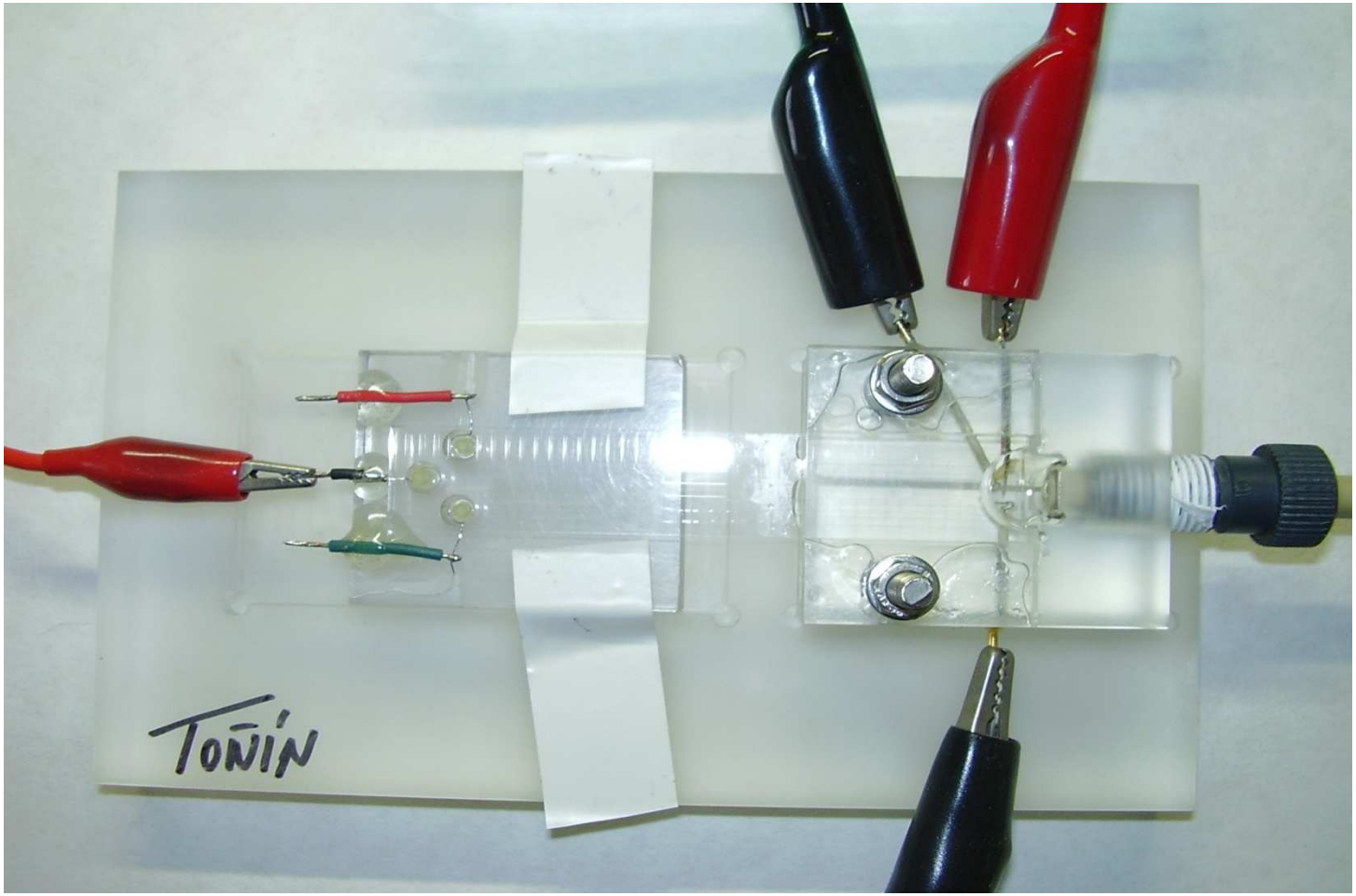
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Sample preparation

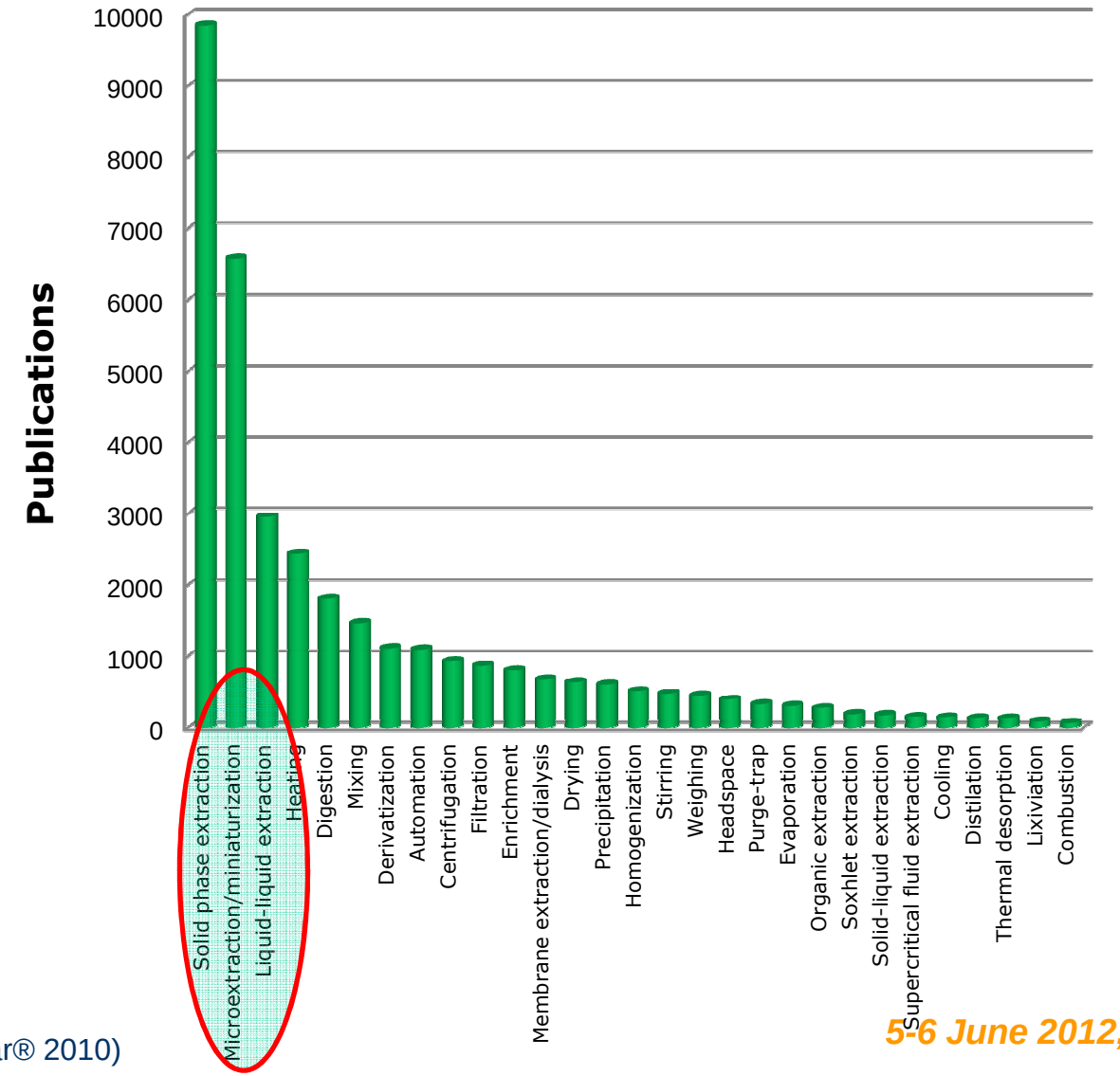
- **Sample conditioning:** Adapt the physical or chemical state to the requirements of the instrument.

- **Removal of interfering species:** Masking or **separation** techniques (e.g., adsorption, absorption, dialysis, precipitation, supercritical fluid extraction, liquid-liquid extraction (LLE), solid phase extraction (SPE), etc.)

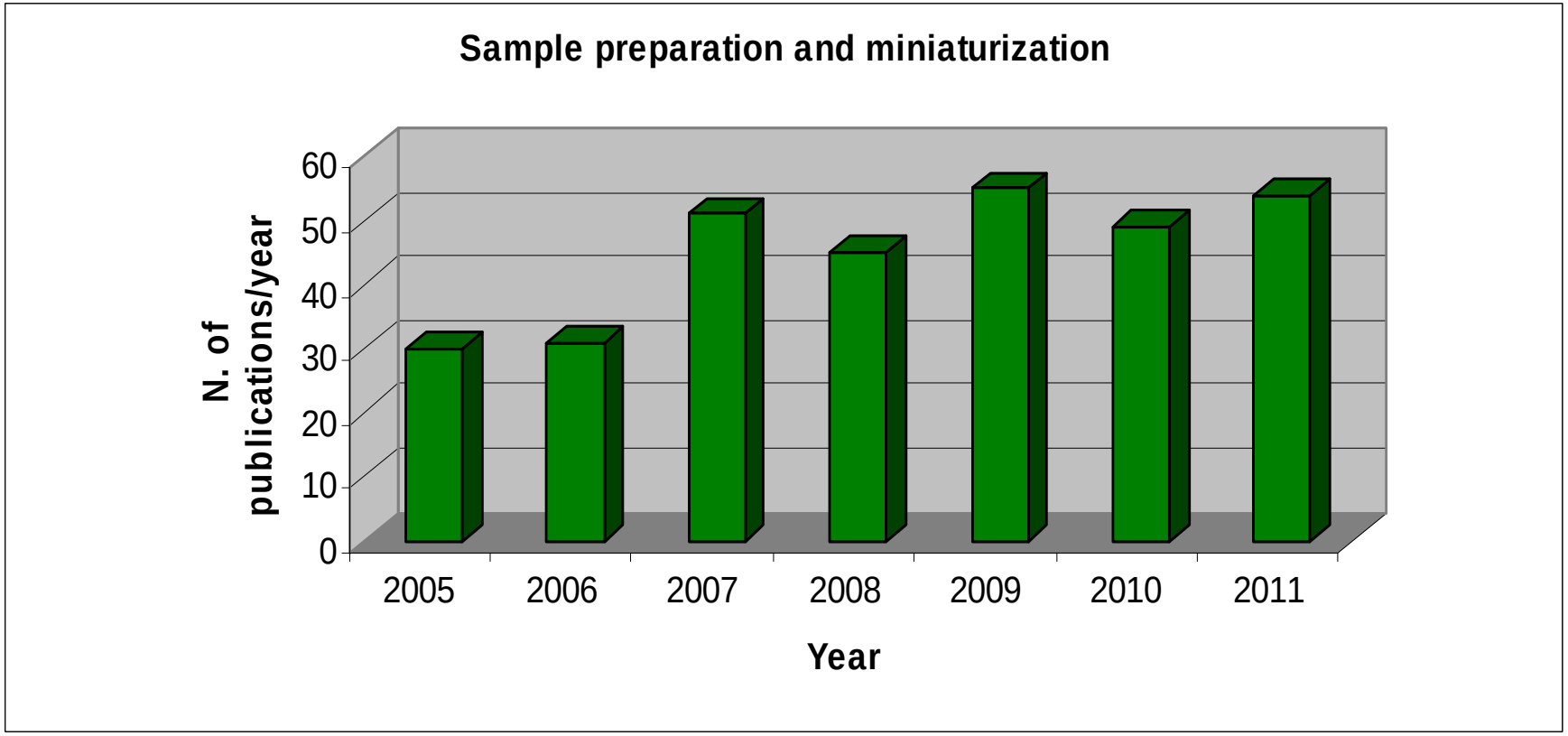
- **Additional operations:** Dilution, **(pre)concentration**, chemical transformations and derivatization, etc.

Sample preparation is the Achilles' Heel of total analytical process!!!!

Sample preparation



(Source: SciFinder Scolar® 2010)

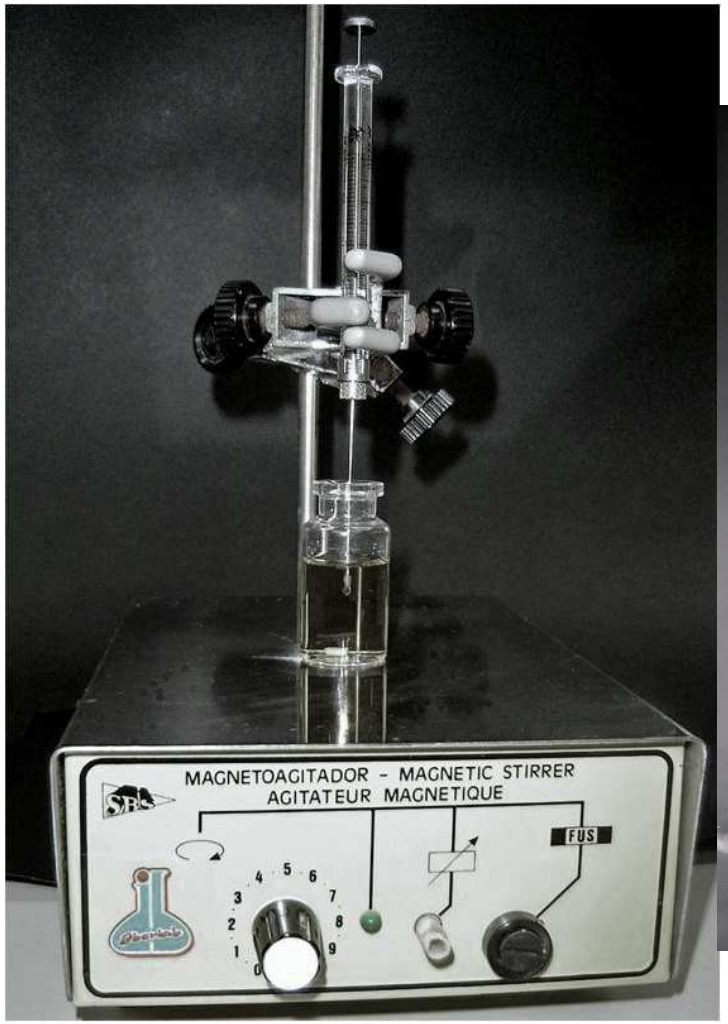


Source: SciFinder® (26/05/2012)

Classification of main extraction techniques:

- **Headspace extraction techniques:**
  - ✓ Static Headspace (SH)
  - ✓ Purge & Trap (dynamic headspace, P&T)
- **Membrane extraction techniques**
- **Sorptive extraction techniques:**
  - ✓ Solid-phase extraction (SPE)
  - ✓ Stir bar sorptive extraction (SBSE)
  - ✓ Solid-phase microextraction (SPME)
- **Solvent extraction techniques:**
  - ✓ Liquid-liquid extraction (LLE)
  - ✓ Liquid-liquid microextraction (LLME)
    - Hollow fiber-liquid phase microextraction (HF-LPME)
    - Single drop microextraction (SDME)
    - Dispersive liquid-liquid microextraction (DLLME)

SDME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Detection techniques for LLME

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Detection techniques for LLME

- **Organic analytes**

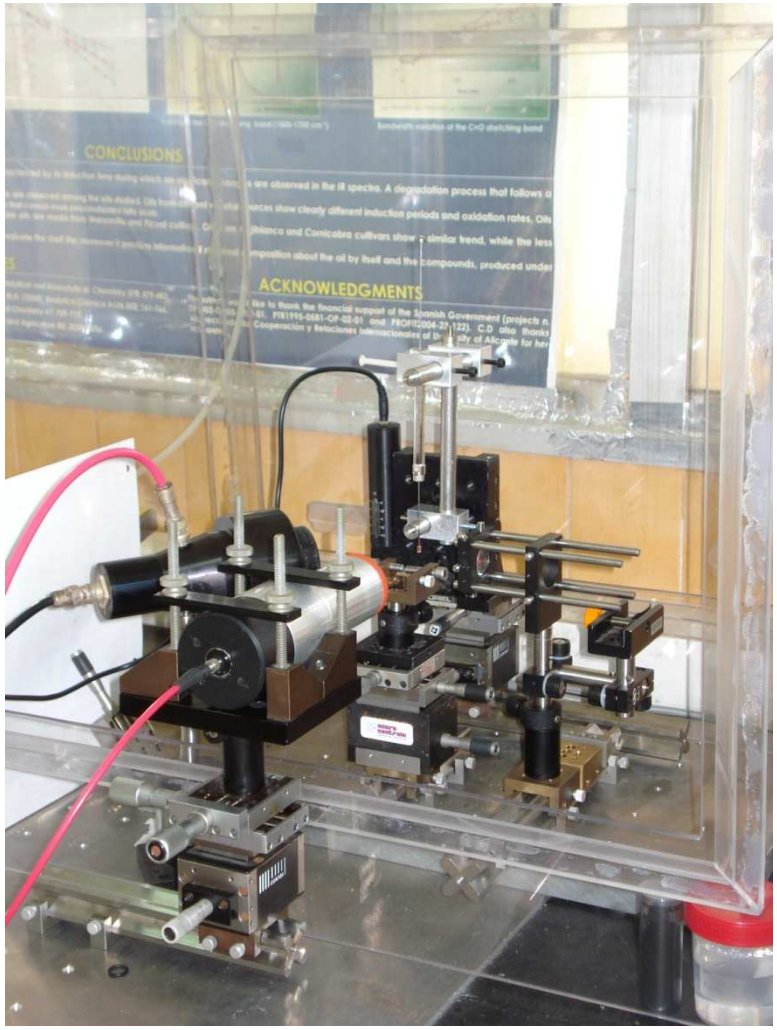
  - ✓ **HPLC, GC, CE before FID, ECD, UV-Vis, MS, etc.**

- **Inorganic analytes**

  - ✓ **ETAAS, ETV-ICP-OES/MS, others (FAAS, CV-AFS, ICP-MS and ICP-OES)**


THIS IS NOT PORTABLE INSTRUMENTATION!!!

Laser-induced breakdown spectroscopy (LIBS) for trace elemental analysis



LIBS

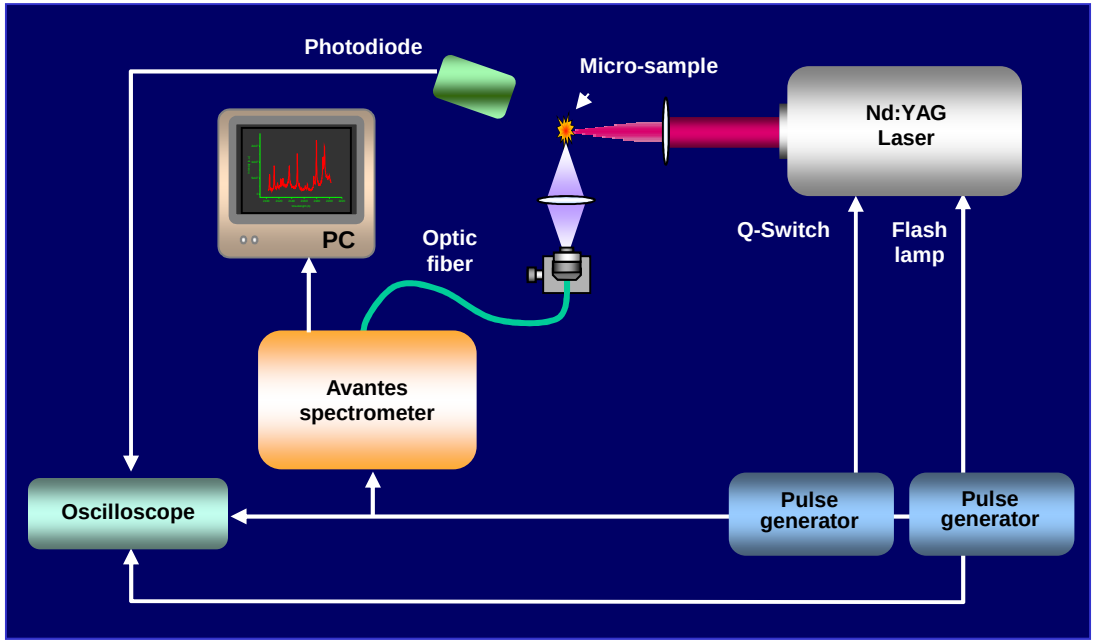
- **Disadvantage: low sensitivity ➔ high LODs**
- **Advantages:**
  - ✓ Multielement analysis
  - ✓ Fast
  - ✓ Portability
  - ✓ Easy to automate
  - ✓ **Capability to analyze very small quantities (microdroplets) of sample**

LLME and LIBS could be combined for trace metal analysis

Evaluating LIBS for the analysis of Mn in microdroplets

LIBS system

- ns Nd:YAG laser (1064 nm)
- Avantes modular spectrometer (Czerny-turner configuration + CCD - covering from 300 nm – 400 nm)
- Delay system (pulse generators) for acquisition time delay control
- Oscilloscope and photodiode to monitor plasma formation and acquisition delay



Experimental procedure

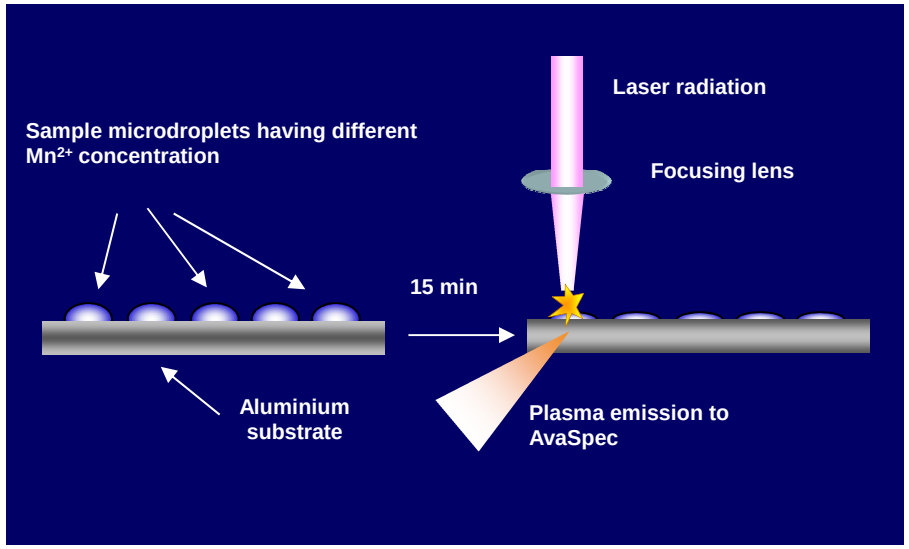
- Synthetic samples with different Mn^{2+} concentration were prepared
- Microvolumes of the prepared samples were analyzed by using two different LIBS experimental strategies:

✓ Analysis by direct laser irradiation of microdroplets
✓ Analysis by laser irradiation of microdroplets on a metallic (aluminium) substrate

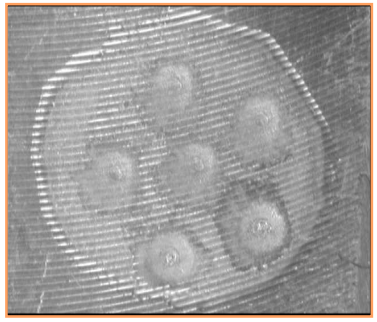
Direct microdroplets on aluminium substrates

Experimental procedure

- 10 μL microdroplets were placed on an aluminium substrate and left to dry for 15 minutes
- Laser radiation was focused on the dried microdroplet to create the LIBS plasma
- Plasma emission was detected by the Avantes spectrometer
- Five spectra were taken for each single droplet. Spectra of one single droplet were averaged

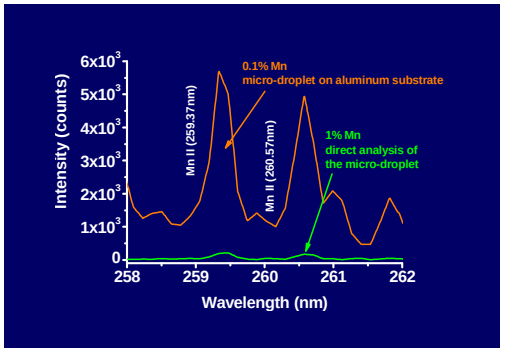


Results



Several laser shots on a single, dried, 10 μL sample droplet

Since laser radiation can be focused on a extremely low sample area, this configuration allows several replicate measurements to be carried out in a single microdroplet.



LIBS emission signal markedly improves when microdroplets are analyzed by using aluminium substrates.

Direct analysis of microdroplets vs. the use of aluminium substrates
Orange spectrum corresponds to an analyte concentration 10 times lower than that of green spectrum

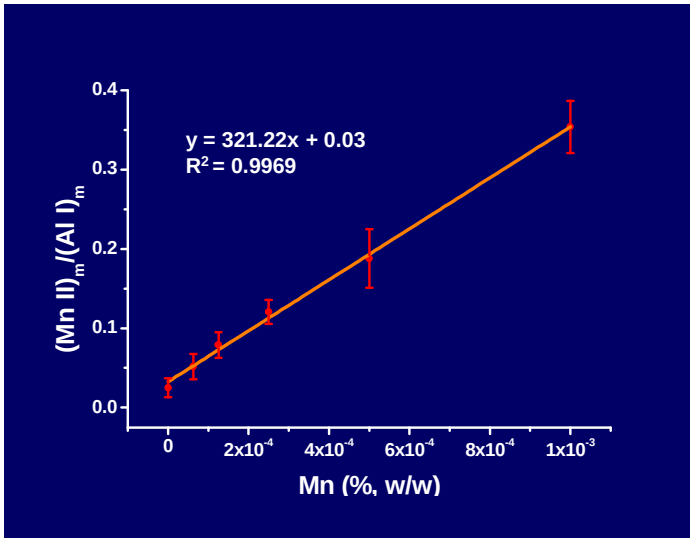
Direct microdroplets on aluminium substrates

Results

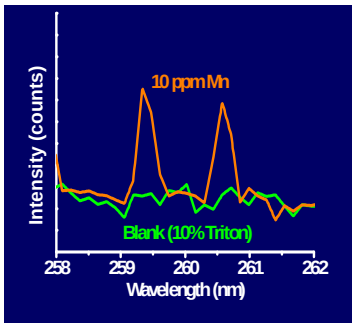
- Higher reproducibility and better linearity (R^2= 0.9969 compared to direct analysis of droplets
- Limit of detection was found to be 6x10^{-4} % of Mn (6 ppm)

Considering that microextraction methodologies can lead to micro-volumes of extractants and high enrichment factors (more than 200, in some cases)

LIBS analysis of microdroplets on solid substrates appears to be a promising alternative to be combined with LLME methodologies for trace elemental analysis



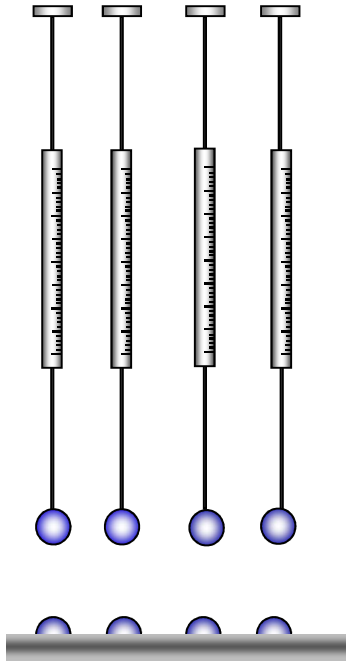
Analysis of microdroplets on aluminium substrates (Al was used as internal standard)



LIBS signal of a 10 ppm Mn sample

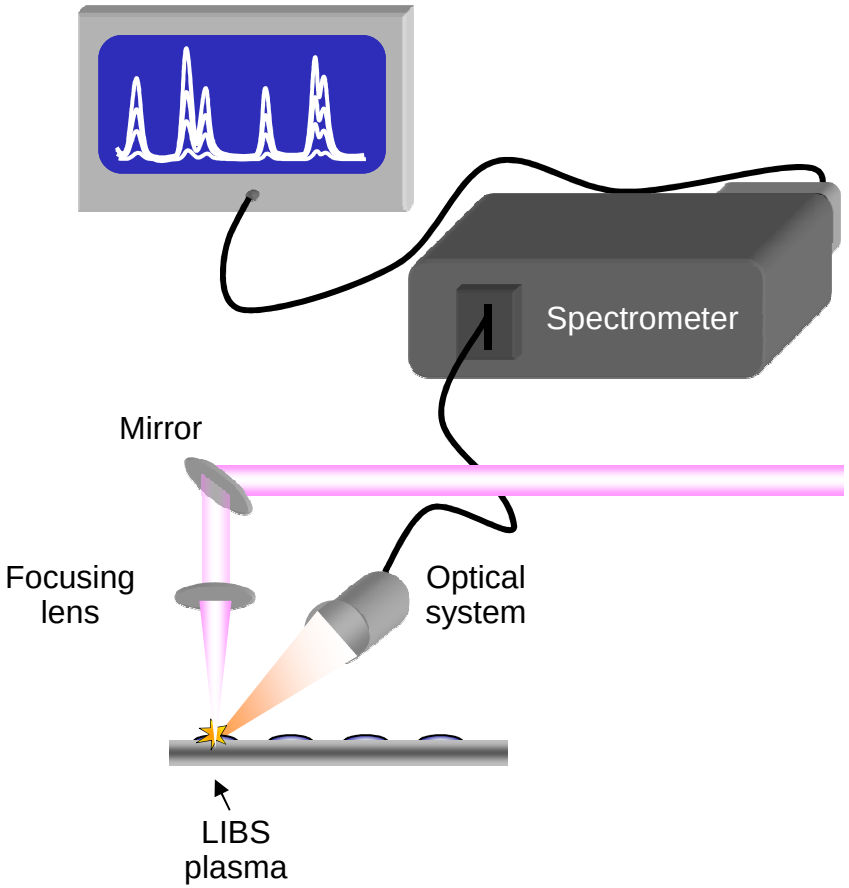
Testing the combination LLME-LIBS: preliminary results

After SDME



Drying

LIBS analysis



Testing the combination LLME-LIBS: preliminary results

Univariate optimization

Variables

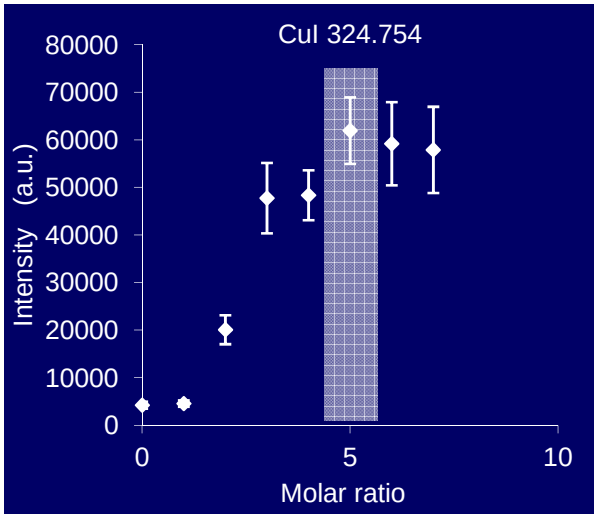
- **Molar ratio (APDC/analytes)**
- **pH**
- **Extraction time**
- **Stirring speed**
- **Droplet volume**

Testing the combination LLME-LIBS: preliminary results

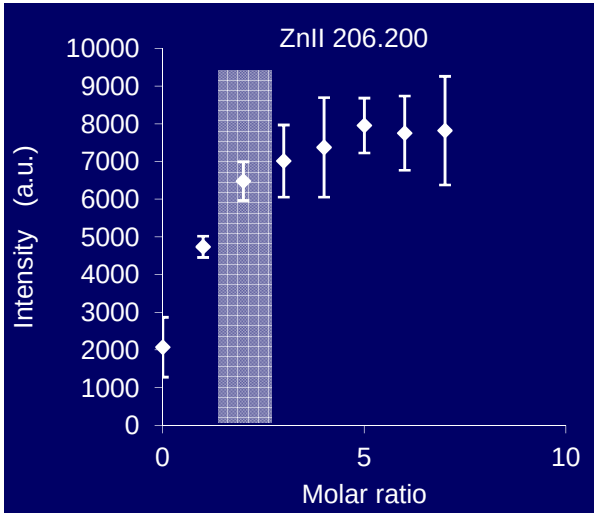
Variable → **Molar ratio (APDC/analytes)**

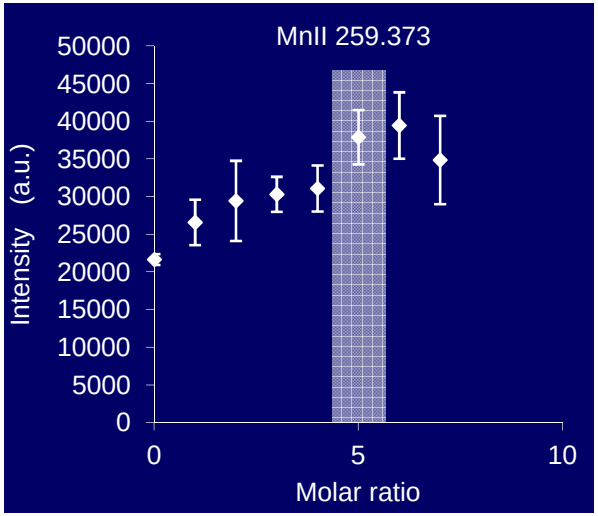
Constants

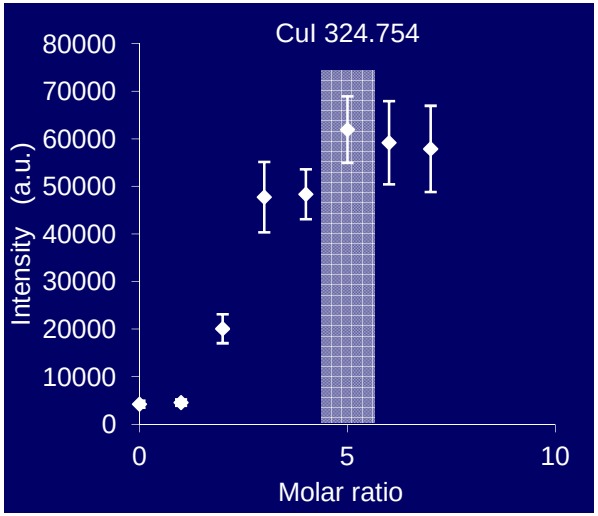
- **pH = 10**
- **Extraction time = 10 min**
- **Stirring speed = 1700 r.p.m.**
- **Droplet volume = 5 µL**

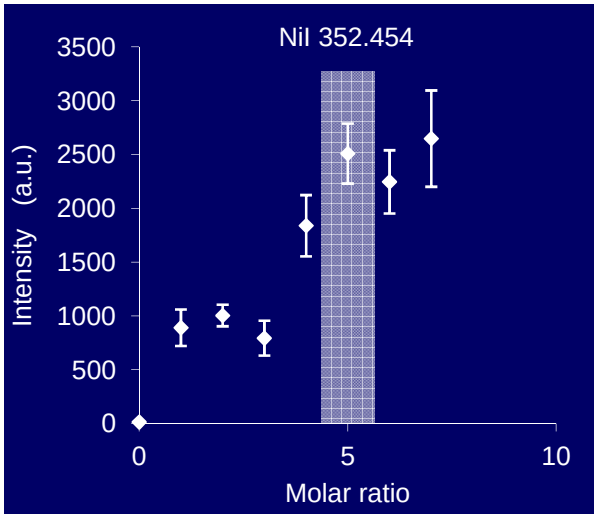


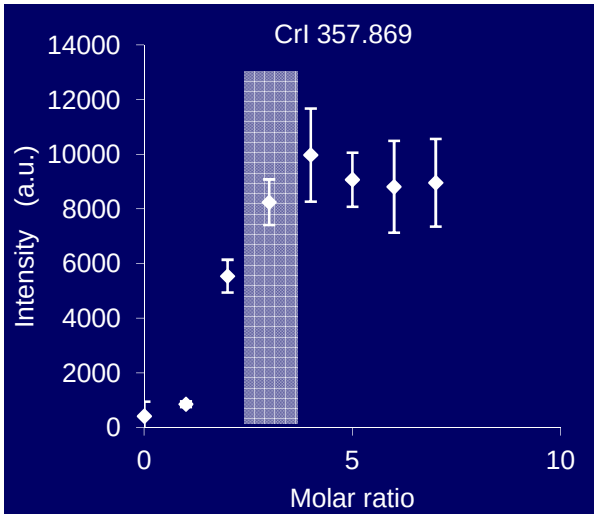
Testing the combination LLME-LIBS: preliminary results









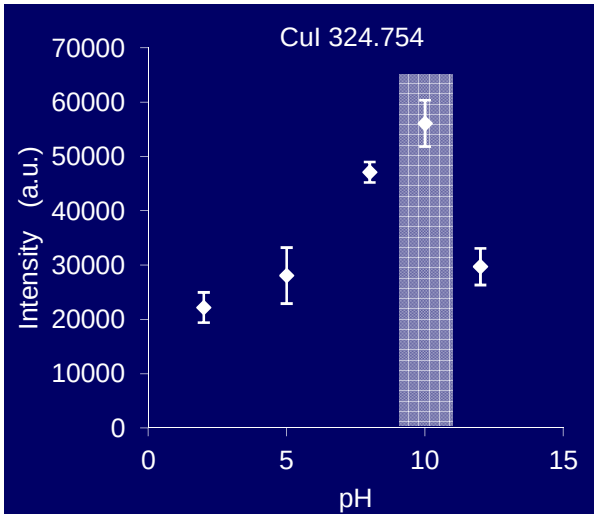


Testing the combination LLME-LIBS: preliminary results

Variable → **pH**

Constants

- **Molar ratio (APDC/analytes) = 5**
- **Extraction time = 10 min**
- **Stirring speed = 1700 r.p.m.**
- **Droplet volume = 5 µL**



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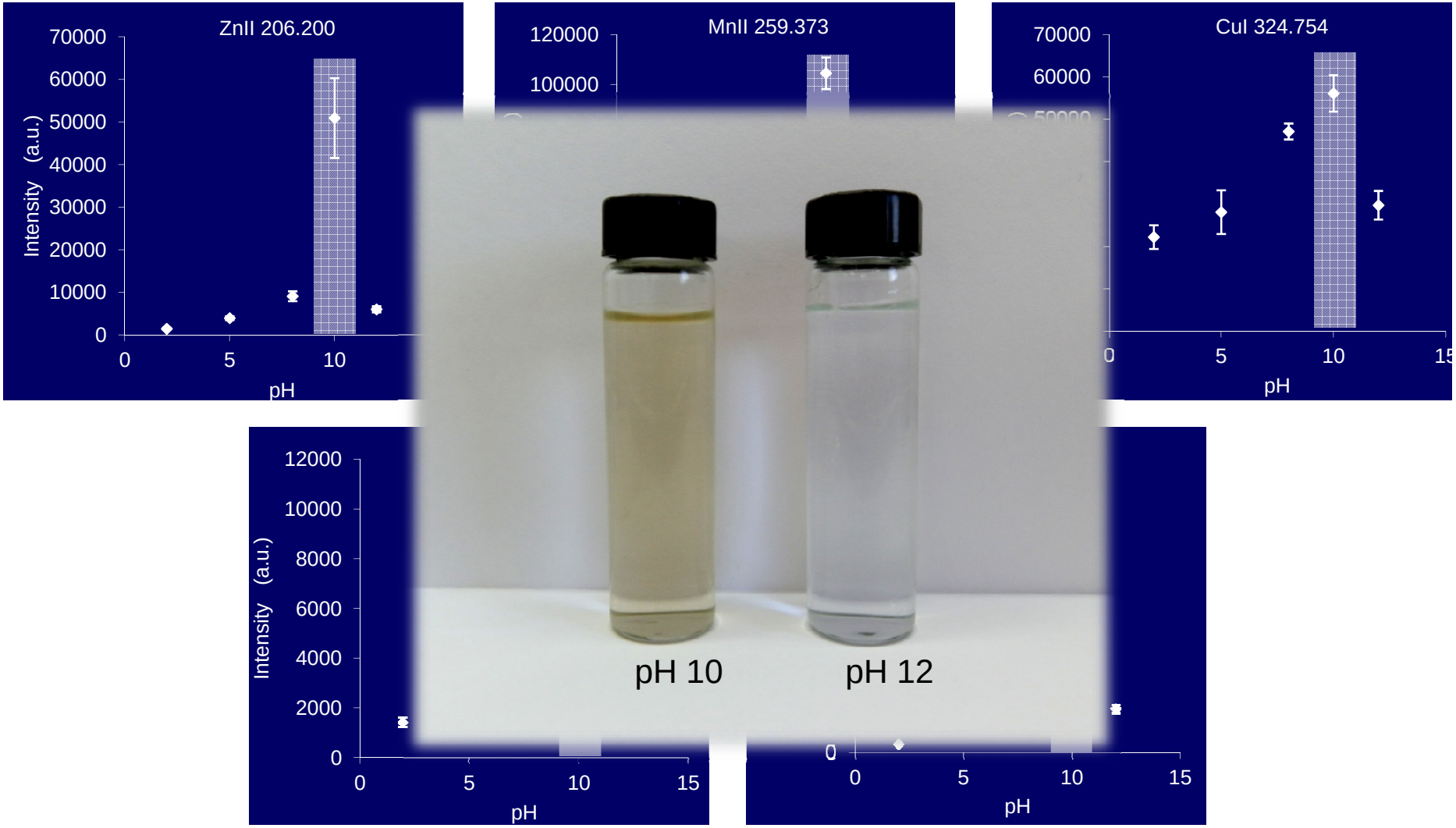
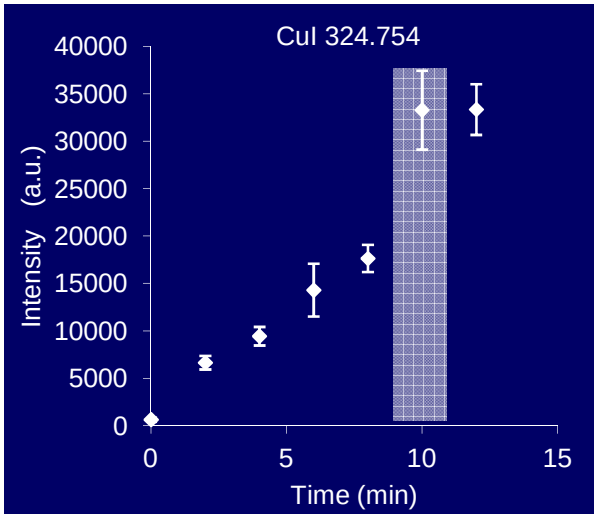


Testing the combination LLME-LIBS: preliminary results

Variable → **Extraction time**

Constants

- **Molar ratio (APDC/analytes) = 5**
- **pH = 10**
- **Stirring speed = 1700 r.p.m.**
- **Droplet volume = 5 µL**



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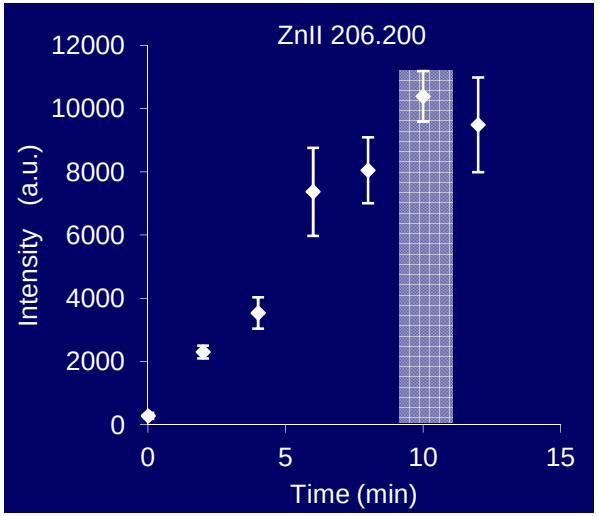
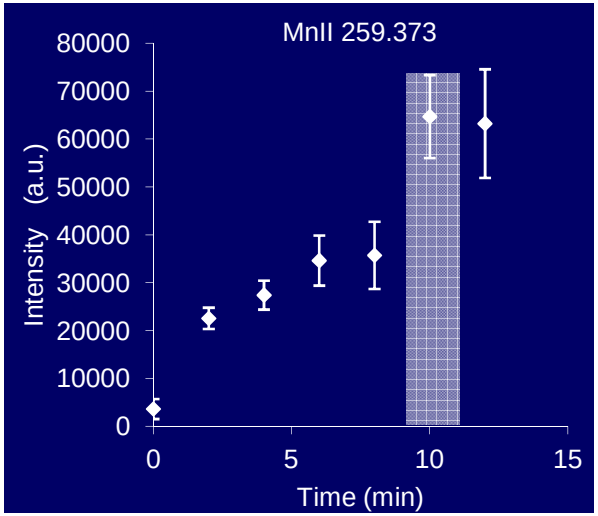
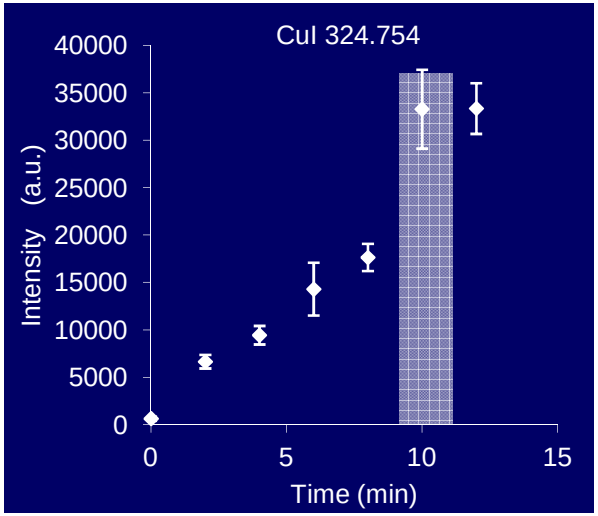
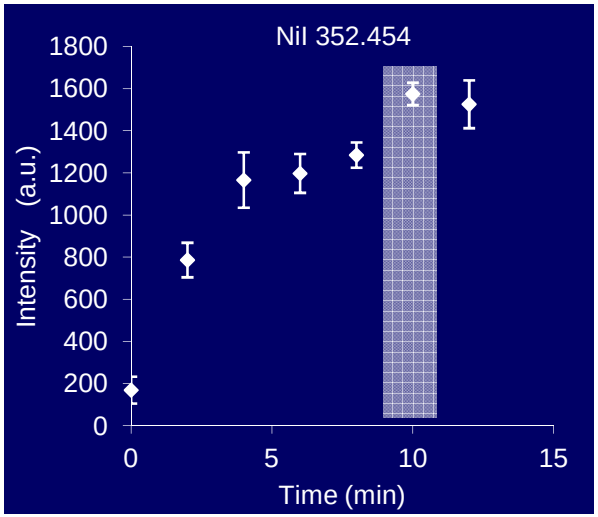
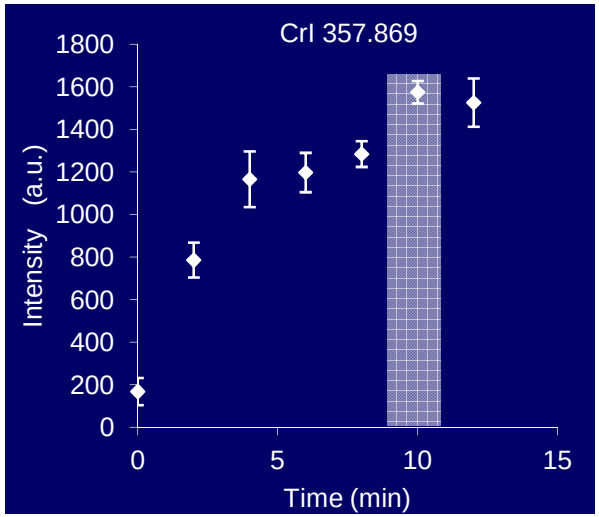








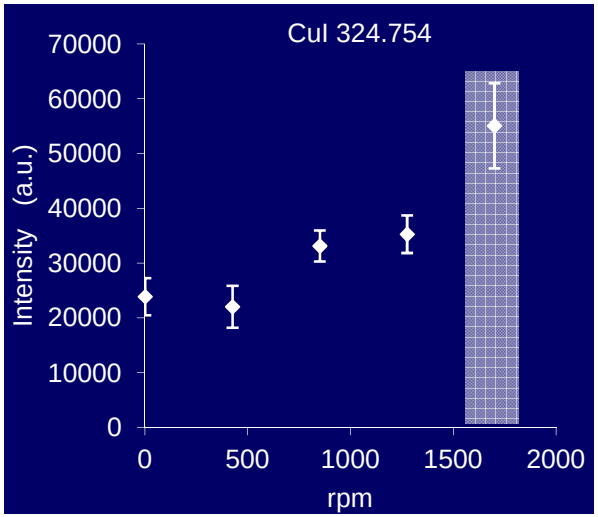


Testing the combination LLME-LIBS: preliminary results

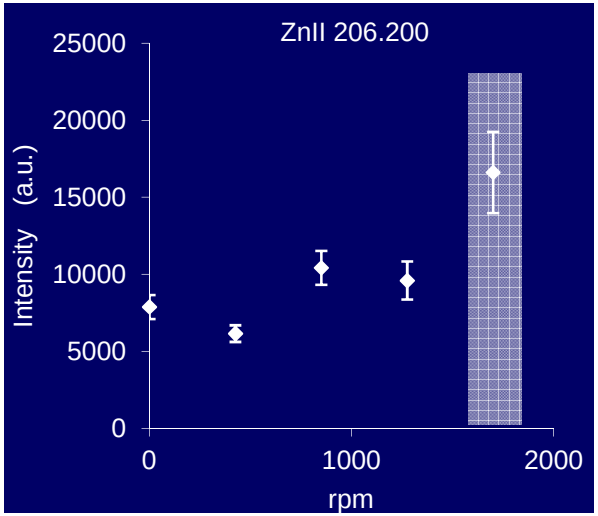
Variable → **Stirring speed**

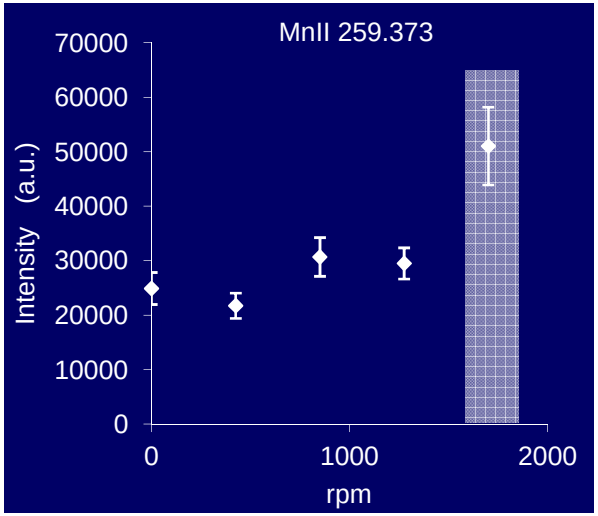
Constants

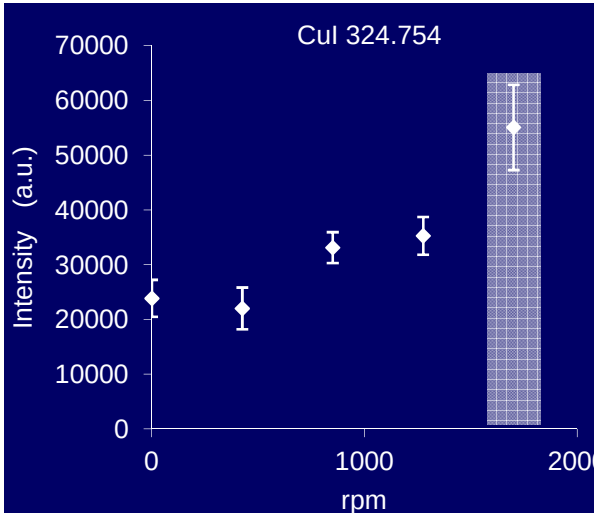
- Molar ratio (APDC/analytes) = 5
- pH = 10
- Extraction time = 10 min
- Droplet volume = 5 µL

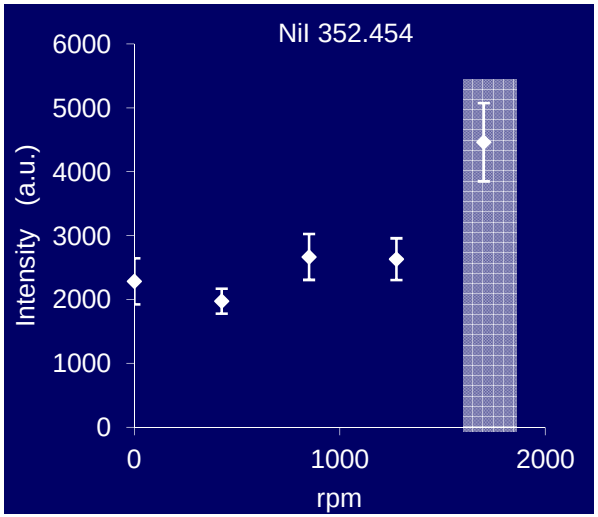


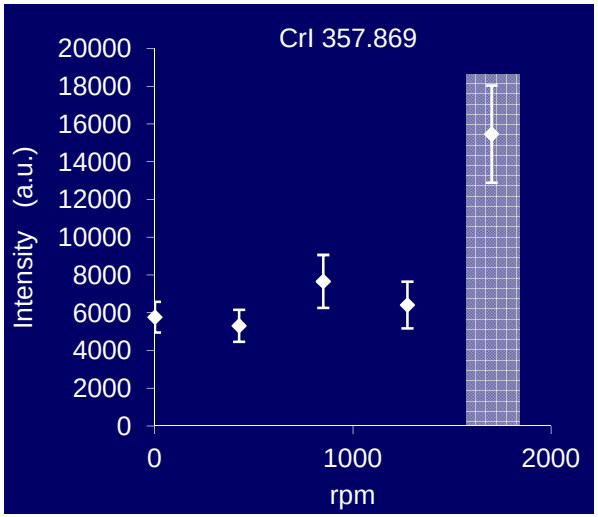
Testing the combination LLME-LIBS: preliminary results









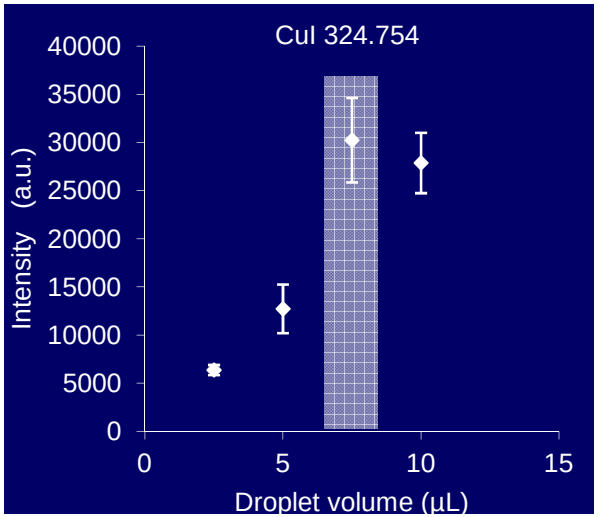


Testing the combination LLME-LIBS: preliminary results

Variable → **Droplet volume**

Constants

- **Molar ratio (APDC/analytes) = 5**
- **pH = 10**
- **Extraction time = 10 min**
- **Stirring speed = 1700 r.p.m.**



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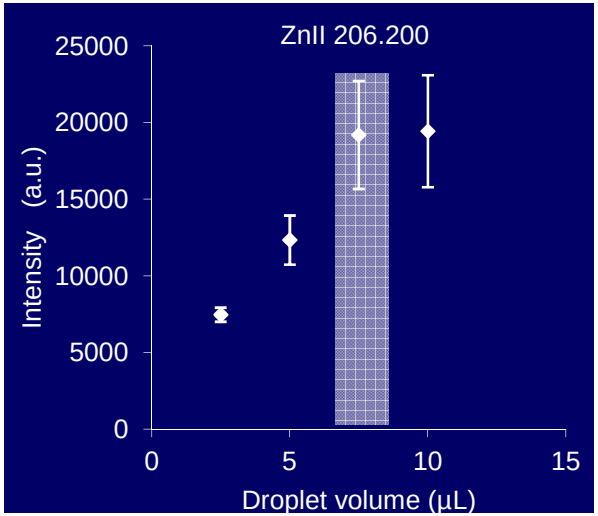
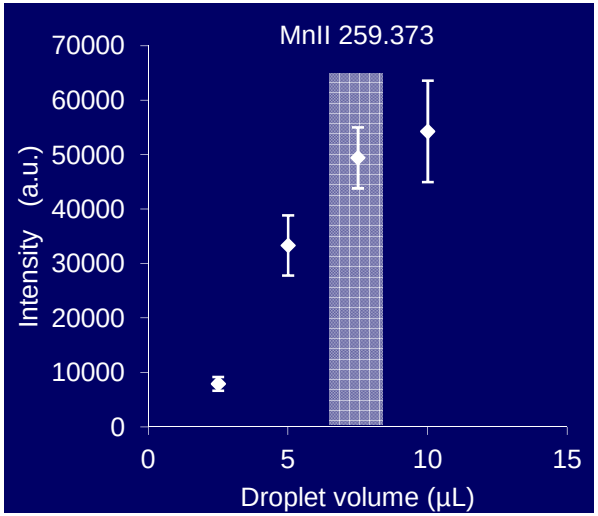
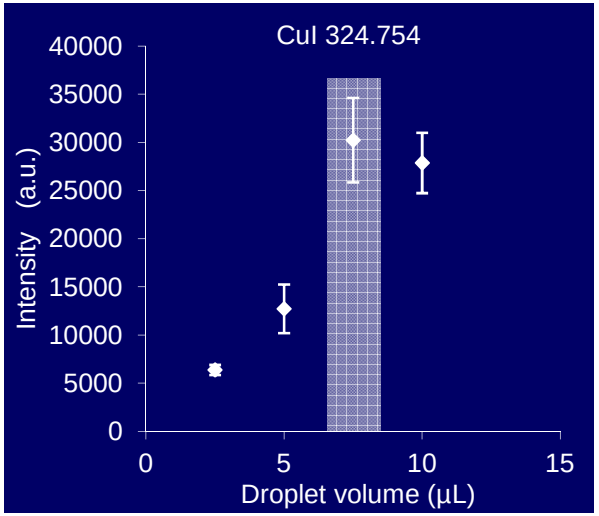
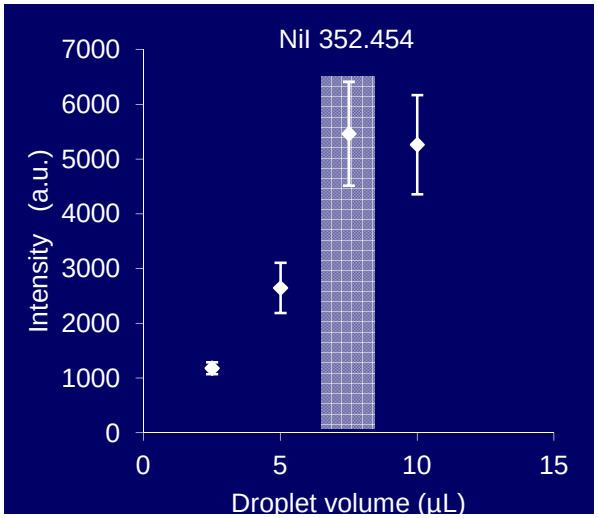
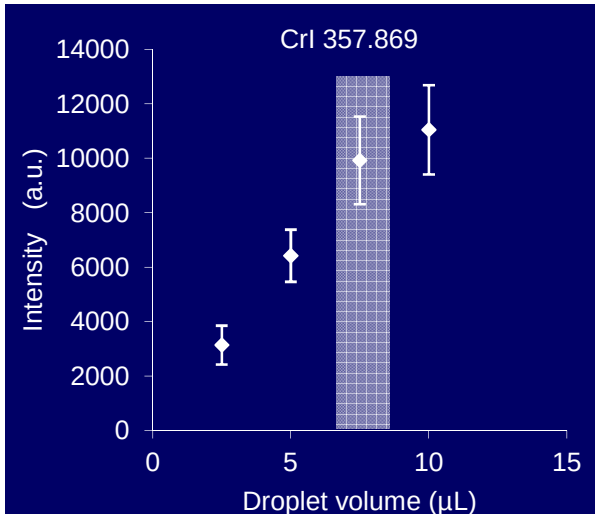








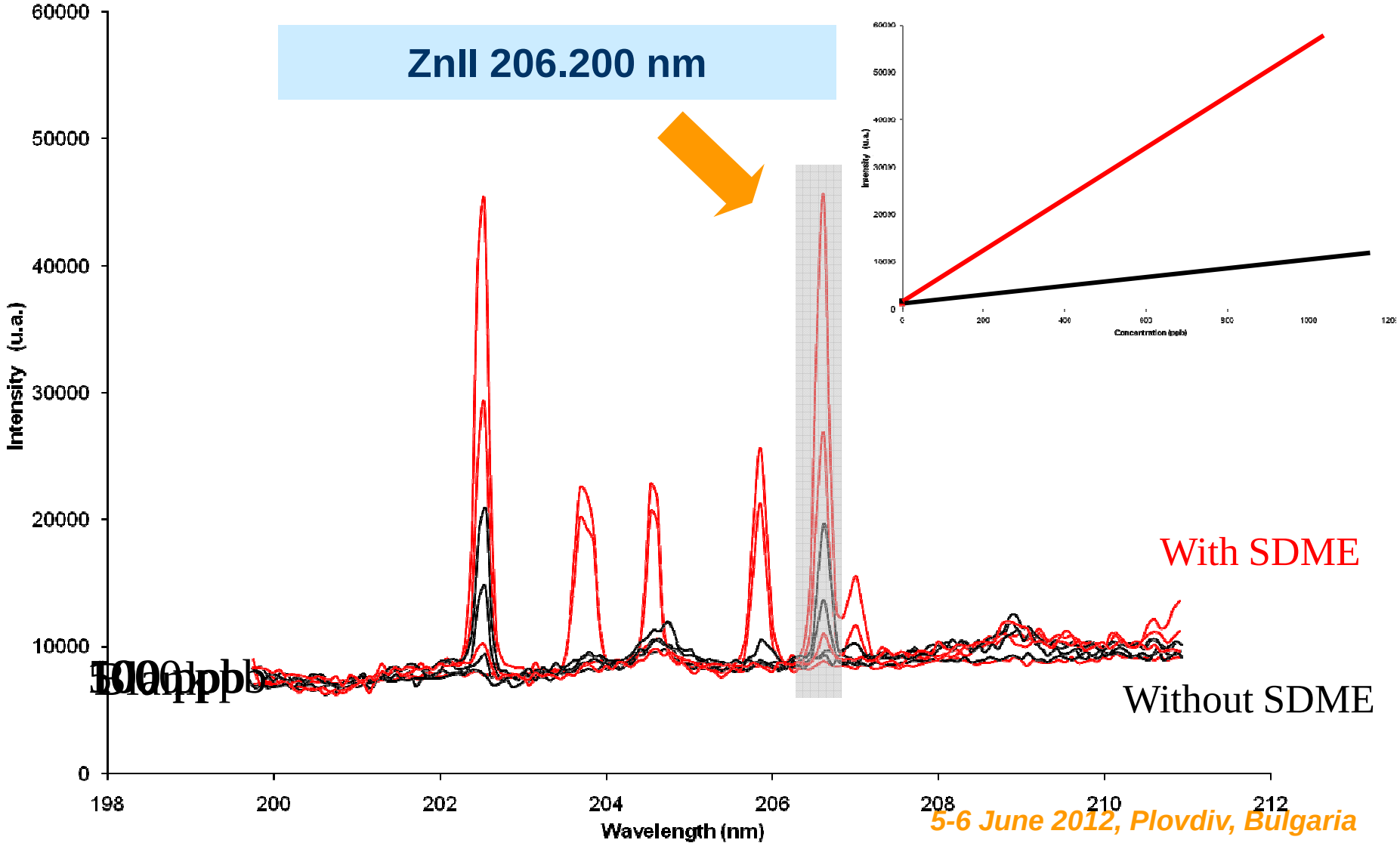


Testing the combination LLME-LIBS: preliminary results

Optimized values

- **Molar ratio (APDC/analytes) = 5**
- **pH = 10**
- **Extraction time = 10 min**
- **Stirring speed = 1700 r.p.m.**
- **Droplet volume = 7.5 µL**

Testing the combination LLME-LIBS: preliminary results



Testing the combination LLME-LIBS: preliminary results

	Without SDME		With SDME	
Emission line (nm)	Slope (ppb^{-1})	LOD (ppb)	Slope (ppb^{-1})	LOD (ppb)
ZnII (206.200)	7.6±0.4	171	54±3	23
MnII (259.373)	29±4	427	59±4	301
CuI (324.754)	26±5	141	55±5	54
NiI (352.454)	2.0±0.2	149	11.3±0.6	67
CrI (357.869)	7.0±1.0	143	17.6±1.2	50

Conclusions

For the first time, the capability for elemental analysis of LLME + LIBS has been experimentally proved

Nevertheless, much work is still needed in order to definitively assess the analytical capabilities of LIBS to be coupled with several microextraction methodologies

Future work

- Study and optimization of the best solid substrate to be used as solid-sample holder
- Study of the influence of the extraction solvent (concentration and nature – surfactants, ionic liquids, organic solvents, etc.) on LIBS signal
- Study of the double pulse LIBS methodology as a mean to obtain further emission intensity and S/N enhancement
- Miniaturized/portable LIBS system

Acknowledgements

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The SP-BG team

5-6 June 2012, Plovdiv, Bulgaria

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Thank you

for

your

attention

5-6 June 2012, Plovdiv, Bulgaria