Measurements using cellulosic microsystems with magnetic inclusions

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Outline

1. A liquid membrane system containing magnetic particles and thio-calix[4]arene embedded in the pores of a cellulose membrane which was realized in two ways:

a) the carrier dissolved in the solvent of the magnetic fluid and

b) with the carrier bound to the magnetic particles from the magnetic fluid

were used for a turbulent transport through the membrane system of metallic cations.

2. Based on the evaluation of the results obtained it was proposed a cause and effect diagram to identify and analyze uncertainty sources, and the combined standard uncertainty was derived.

MAGNETIC LIQUID MEMBRANE ON MICROPOROUS CELLULOSE SUPPORT

- no mechanical moving components;
- alternate operation (with phases' recirculation, equicurrent, cascade or parallel countercurrent with the concentration gradient in source phase with variable pH during the experiment);
- low loss of membrane solvent in aqueous phases.

Applications of micro- and nano-systems based on functionalized, derivatized and embedded magnetic particles for the following applications:

- *The transport and medicine and pharmaceutical products controlled release;*
- *Decontamination, detox and inactivation of organisms and / or environment;*
- *Development of the chemical sensors and biosensors.*

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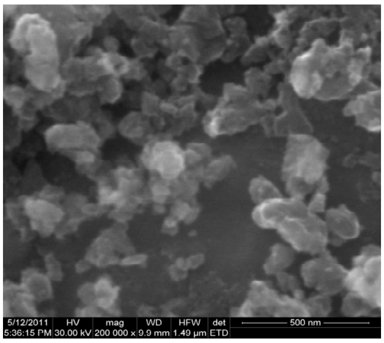
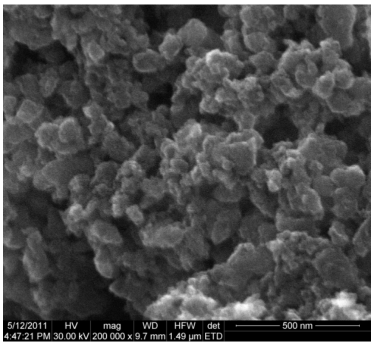
THE MAGNETIC LIQUID

- ❑ **medium alcohol: n-octanol ;**
- ❑ **magnetic particles from ferroferric oxide with dimensions: 10 - 15 nm.**





Magnetic nanoparticles based on magnetite, HFSEM

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EXPERIMENTAL
MICROPOROUS CELLULOSE SUPPORT

➢ **Obtaining the liquid membranes on cellulosic support**

➢ Commercial cellulose membranes were activated for 48h in $ZnCl_2$ 10%

➢ different types of liquid membranes on cellulose support were obtained:

❑ based on 10^{-5}M thio-calix [4] arene in n-octanol, immobilized by soaking, on a commercial cellulosic support enabled (**MCS**);

❑based on magnetic fluid with 10^{-5} M thio-calix [4] arene grafted onto magnetic nanoparticles in n-octanol, immobilized by soaking, on a commercial cellulosic support (**MCF2**).

❑

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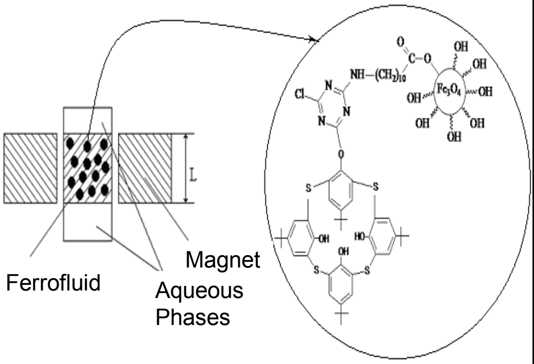
The liquid membrane system containing magnetic particles and thio-calix[4]arene embedded in the pores of a cellulosic membrane was studied in two ways:

- *With the carrier dissolved in the magnetic liquid solvent (**MCF1**);*
- *With the carrier bounded to the magnetic particles of the magnetic fluid (**MCF2**);*



The Influence of The Source Phase and of The Receiving Phase pH on The Transport Efficiency through Membranes

The studied general characteristics of the lead ions transport through liquid membranes on cellulosic support were:

- **The continuous decrease of the lead ions concentrations from the source phase during the operating period;**
- **The continuous increase of the lead ions concentrations in the receiving phase during the operating period;**
- **The existence of a crossing point of the two curves, representing the lead ions concentration in source and receiving phases.**

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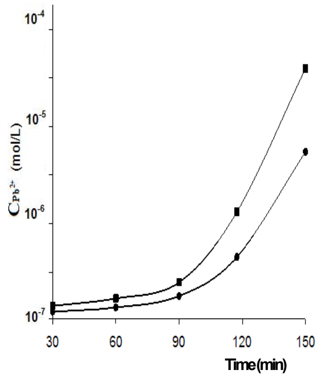
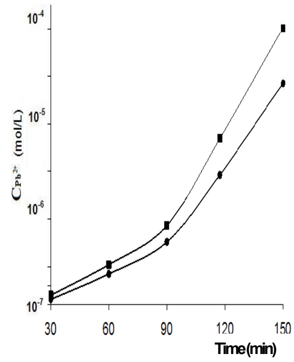
Influence of The Receiving Phase pH



Variation of Pb^{2+} concentration in time for receiving phase, MCS; source phase Pb^{2+}, 10^{-4} M, receiving phase HCl. 10^{-1} M (■) ; 10^{-2} M (●)



Variation of Pb^{2+} concentration in time for receiving phase, **MCF2**; source phase Pb^{2+}, 10^{-4} M, receiving phase HCl. 10^{-1} M (■) ; 10^{-2} M (●)

Lead Concentration Determination

Procedure for concentration through cellulosic membranes with magnetic inclusions and GFAAS analysis of solution for Lead concentration determination

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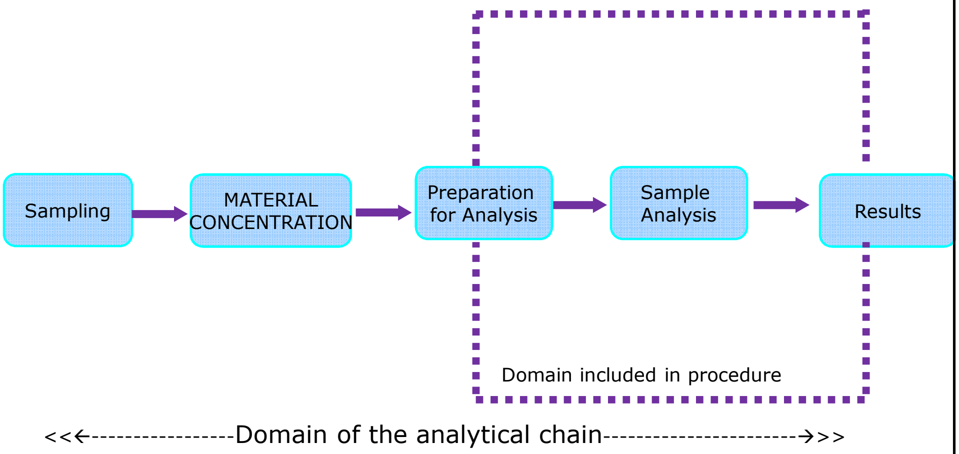
Synoptic Diagram of the Applicability Domain



Flux diagram of activities

Preparation of lead solutions for analysis (mineralization, concentration through membranes, volume quotation, etc.)

⇩

Determination of Pb in solution

⇩

Results calculation

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Preparation of lead solutions for analysis

- *Concentration*

most important stage for the solutions' preparation

- Labs could develop working procedures associated to this process.
- ISO 15586 : 2003 – dealing with the procedure for preparing the lead samples for analysis makes no reference regarding a compulsory development (validation) of a such method in this sense

is only giving an operational protocol model which could be applied by labs according to their facilities

it is the user's responsibility to ensure the validity of the test methods for solutions of untested matrices

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Determination of Pb in solution

- ISO 15587-2 : 2002 mentions the necessity to develop and validate a working procedure for mineralized solutions' analysis.
- The determination method is based on a GFAAS technique.
- ISO 15586:2003 mentions a list of minimum procedures for quality assurance which have to be developed and integrated in the quality assurance system at the lab's level.

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Concept of Measurement Uncertainty

- 1993 ⟹ ISO “Guide to the Expression of Uncertainty in Measurement” (the GUM)
- 1995 ⟹ EURACHEM Guide for “Quantifying Uncertainty in Analytical Measurement” , 1st Edition
- 2000 ⟹ EURACHEM Guide for “Quantifying Uncertainty in Analytical Measurement” , 2nd Edition (CITAC)

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Concept of Measurement Uncertainty

- 2012 ⟹ ISO-Standard 11352 (2012-07): "Water quality - Estimation of measurement uncertainty based on validation and quality control data“
- 2012 ⟹ EURACHEM Guide for “Quantifying Uncertainty in Analytical Measurement” , 3rd Edition (CITAC)

consistent with the formal ISO Guide principles set out in the ISO Guide to the Expression of Uncertainty in measurement

the requirements of ISO/IEC 17025:2005

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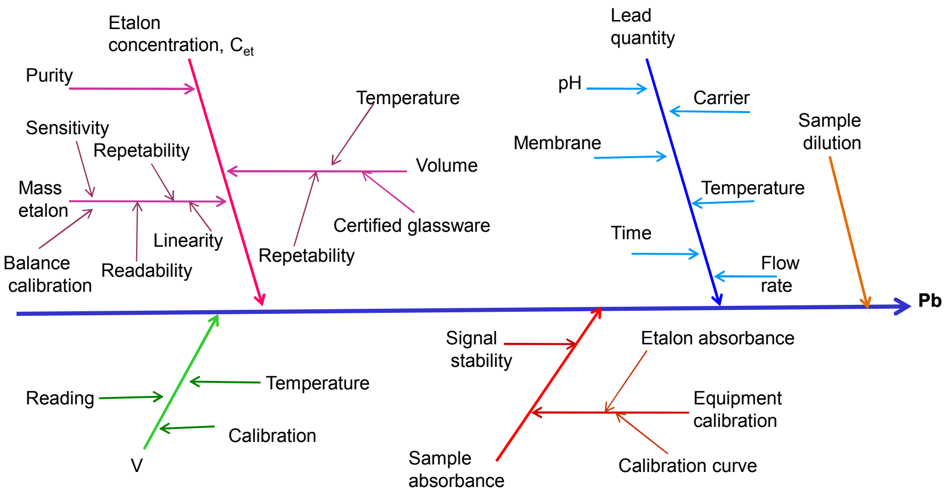
Possible uncertainty sources



Quantifying uncertainty sources

Volume – the glass tank -300 ml

Temperature – 20 ± 2^{0}C

considering a rectangular temperature distribution:

u_T =0.07mL

Calibration: for 300 mL cylinder (class A) a calibration specification of 1.5 mL and considering a triangular volume distribution:

u_C = 0.61mL

Reading: considering an inaccuracy of 1% when measuring volumes with cylinders, then:

u_R = 1.22 mL

For our tank volume (300 mL) the found uncertainy:

$u_{(V)}$ = 1.37 mL

Lead concentration

-each lead solution was measured twice for a set of experimental conditi (pH, flow rate)

- It was applied the linear least square fit (R=0.998)
- Also, 95% confidence interval was considered

u_c = 0.011mg/L

and a residual standard deviation:

S = 0.0027 mg/L

Time

- It is an important factor in the concentration process
- For about 60 min there are small changes in concentration. It could be considered a rectangular distribution for 0.005%/h

u_{time} = 0.02×10^{-3}

Acid concentration (pH) associated uncertainty = 0.0008

Combined standard uncertainty for lead quantity

$u_{c\,(C0)}$ = 0.045mg

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Standard Combined Uncertainty induced by etalon solution preparation taking into account:

Purity	u_P =0.000058	
Mass	u_m= 0.01 mg	
Volume	u_V = 0.04 mL	
Repeatabiliy	u_R = 0.02 mL	$u_{(V)}$ =0.05mL
Temperature	u_T = 0.024 mL	
Concentration of Pb etalon	= 1000.99 mg/L	

$u_{c\,(et)}$ =0.5004 mg/L

Applying all the contributions of the different parameters:

$$\frac{u_c(Pb)}{c_{Pb}} = 0.1098$$

$$u_c(Pb) = 0.045\ mg\ /\ L$$

the expanded uncertainty:

U_{Pb} = 0.0909 mg/L

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CONCLUSIONS

- The use of thiocalix [4] arene as carrier in composite liquid membranes: cellulose - magnetic fluid in n-octanol, allows the transport, separation and concentration of Pb^{2+} ions under a pH gradient and for a concentration from 10^{-4} M to 10^{-7} M.
- It was proposed a cause and effect diagram to identify and analyze uncertainty sources.
- The combined standard uncertainty was derived using spreadsheet method.
- The extended uncertainty was obtained by applying a coverage factor of 2 → U_{Pb} = 0.0909 mg/L

THANK YOU FOR YOUR KIND ATTENTION!

MULTUMESC!

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