

## Microextraction in preconcentration and determination of trace metal ions by X-ray fluorescence techniques

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Nowadays, commonly applied analytical techniques allow determination of analytes on trace or ultratrace levels. However, the direct analysis of sample is not always possible due to low concentrations of analytes or too complicated matrix. Therefore prior isolation and/or preconcentration step is necessary before the analysis. The one of the most popular sample pretreatment methodologies are extraction techniques such as liquid-liquid extraction (LLE) or solid-phase extraction (SPE). In order to eliminate the disadvantages of the classical extraction techniques, associated mainly with use of large amounts of organic solvents, microextraction techniques based on miniaturization of classical extraction modes are introduced. In microextraction techniques small sample volumes are analysed, therefore the volume of organic solvent is reduced and, in consequence, the amount of generated organic waste decreases. The aim of the PhD thesis is development of the analytical procedures enabling preconcentration and determination of a number of trace elements using X-ray fluorescence (XRF) techniques. The proposed procedures combine:

- **DLLME/EDXRF** - dispersive liquid-liquid microextraction and energy-dispersive X-ray fluorescence spectrometry (EDXRF) for simultaneous determination of Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ga(III), Se(IV) and Pb(II) ions with the use of ammonium pyrrolidinedithiocarbamate (APDC) and sodium diethyldithiocarbamate (Na-DDTC) as chelating agents and carbon tetrachloride as an extraction solvent,
- **DMSPE/TXRF** - dispersive micro-solid phase extraction and total-reflection X-ray fluorescence spectrometry for determination of Cd(II) and Pb(II) ions with multiwalled carbon nanotubes MWCNTs as an adsorbent,
- **DMSPE/EDXRF** - dispersive micro-solid phase extraction and energy-dispersive X-ray fluorescence spectrometry (EDXRF) for simultaneous determination of Co(II), Cu(II), Ni(II) and Pb(II) ions and speciation of Se, with graphene applied as an adsorbent.

In order to obtain the best signal to background ratio, different modes of sample deposition onto the sample carrier were evaluated. Moreover, various parameters affecting recovery of extracted elements such as the sample pH, the amount of chelating agent (APDC or Na-DDTC), sample volume, the volume of extraction solvent/adsorbent and extraction/adsorption time were investigated. The proposed procedures enable very low detection limits to be obtained: (i) DLLME/EDXRF - from 1.6 to 4.1 ng mL<sup>-1</sup> for 5 mL samples, (ii) DMSPE/TXRF - from 1.0 to 2.1 ng mL<sup>-1</sup> for Pb (20 mL sample), (iii) DMSPE/EDXRF - from 0.23 to 1.1 ng mL<sup>-1</sup> (for 50 mL samples) and 0.032 ng mL<sup>-1</sup> for speciation of Se (for 75 mL samples). It is noteworthy that receiving such low detection limits was possible to obtain due to high enrichment factor values: DLLME/EDXRF - 250, DMSPE/TXRF - 40 and DMSPE/EDXRF - 418 (Pb) -2553 (Cu).

The proposed procedures are promising tools in multielemental analysis due to the possibility of simultaneous determination of enriched elements, low detection limits, simplicity, rapidity and low costs. Moreover, microextraction procedures extend the scope of XRF usage to liquid samples analysis and enable decreasing obtained detection limits over 1000 times.