Efficient determination of ultra-trace elements in complex matrices issues a serious challenge to analysts despite the intensive development of instrumental techniques. Difficulties usually result from the insufficient sensitivity of analytical techniques as well as serious matrix interferences. Therefore, a preliminary preconcentration and separation of ultra-trace metal ions from a complex matrix are usually required. Unfortunately, sample preparation is considered as the most time-consuming and error-prone step of the chemical analyses. Therefore, the development of sensitive, precise and selective methods is very important. Solid-phase extraction (SPE) is the most common technique used for preconcentration/separation of analytes. However, this technique based on "classical" adsorbents (activated carbon, modified or unmodified silica) requires relatively high amounts of adsorbents and other chemical reagents. In recent years, the solid-phase microextraction has become the most valuable alternative technique to classical SPE. These new miniaturized preconcentration/separation techniques allow reducing the amount of toxic solvents and reagents according to the green chemistry rules. Two main issues related to the development of microextraction techniques are: (a) new adsorbents with exceptional adsorptive properties that can be used in micro-amounts, (b) spectroscopic techniques enabling analysis of micro-samples. The discovery of carbonaceous nanomaterials, i.e. graphene oxide (GO) and carbon nanotubes (CNTs) was a key milestone in the development of carbon-based adsorbents as well as new methods based on solid-phase microextraction. In the view of the second issue, total-reflection X-ray fluorescence spectrometry (TXRF) seems to be extremely interesting. In this technique, the micro-sample (liquid or suspension) is deposited on smooth surfaces of reflector. Due to special measurement geometry (the incident angle of the X-ray beam is below the critical angle of external total reflection), the measured spectral background is extremely reduced and the analytes are excited by both primary and reflected beam. As a consequence, the excellent signal to noise ratio is achieved and the limits of detection are typically in the range of pg or ng mL^{-1}. Such low limits of detection can be obtained for extremely small samples, i.e. 5-10 µL.

The aim of the project is to develop micro-analytical methods based on new modified carbon-based nano-adsorbents and TXRF spectrometry. The crucial issue is to synthesize carbon-based nanomaterials of new adsorptive properties suitable for dispersive micro-solid phase extraction (DMSPE) and TXRF measurements. GO and CNTs have impressive adsorptive properties (the adsorption capacity of GO is much higher than the capacity of any of the currently reported sorbents). However, GO-adsorbents are not selective and, in consequence, determination of analytes in complex matrix can be seriously hampered. In a word, the suitable modification of GO and CNTs is required. In this project, the surface of GO and CNTs will be modified with salen, porphine, thiosemicarbazone and thiosemicarbazide molecules containing functional groups that can efficiently bind the metal ions. It can be expected that suitable surface modification of GO and CNTs with different molecules can improve selectivity and adsorption capacity towards metal ions. Therefore, the speciation and ultratrace analysis of complex matrix sample (difficult to analyze by spectroscopic techniques) will be possible. The developed methods will be solvent-free alternative based on miniaturized preconcentration/separation technique (e.g. 10 µg of nano-adsorbent per 1 mL of the sample) and microanalytical measurement such as TXRF using very low-power instrument. Therefore, procedures developed in this project can be considered as environmental friendly and consistent with the green analytical chemistry rules. It is particularly important to combine the advantages of-new nanomaterials in: (a) DMSPE (high adsorption capacity, dispersibility, selectivity) and (b) TXRF measurement (micro-amount of adsorbent and no interferences with analytes – the proposed nanomaterials containing only C, H, O, N and S do not emit X-ray fluorescence radiation in the region of interest). Since TXRF technique enables the direct measurement of suspensions to be performed, the another advantage resulting from the application of modified CNTs and GO nanomaterials is the possibility to obtain smooth and thin samples deposited onto a quartz reflector, which is a crucial issue in X-ray fluorescence measurement under the total reflection conditions.

New nano-adsorbents will be characterized by microscopy and spectroscopy techniques. The chemical nature of adsorption of metal ions (Cr(III), Cr(VI), Co(II), Ni(II), Cu(II), Zn(II), As(III), As(V), Se(IV), Se(VI), Cd(II), Hg(II), Pb(II)) on new nanomaterials will be investigated by adsorption isotherms, kinetic and thermodynamic studies, as well as by photoelectron spectroscopy. Therefore, our project will lead not only to the development of new micro-analytical procedures but also it will broaden fundamental knowledge on adsorption of trace metal ions on GO and CNTs modified with salen, porphine, thiosemicarbazone and thiosemicarbazide.