Novel Methods and Applications of Photothermal Techniques for Speciation Studies in Environmental Samples

Mladen FRANKO

Laboratory for Environmental and Life Sciences, University of Nova Gorica, Nova Gorica, Slovenia

The objective of this lecture is to present the most recent and novel approaches to speciation of iron in environmental samples by exploiting the advantages of photothermal techniques such as thermal lens spectrometry (TLS) and beam deflection spectrometry (BDS). This includes determination of iron redox species by coupling of TLS to flow injection analysis (FIA) and TLS microscopy to microfluidic systems (μFIA-TLM) which was recently shown to provide limits of detection at ng/mL level in sub μL samples [1]. TLS was also applied for detection in liquid chromatography for determination of fluorescing pyoverdines as well as nonfluorescing Fe(III)-pyoverdine complexes in a single chromatographic run. Application of BDS was related to analysis of passive samplers based ondiffusive gradients in thin-film (DGT) technique, which is increasingly used for monitoring of environmentalpollution due to its robustness, versatility, precision andcapacity of pre-concentrating bioavailable trace-level pollutants [2].

Validation of FIA-TLS and μFIA-TLM techniques for Fe determination in comparisson to UV-Vis spectrometry showed that despite 100 times shorter optical path length (comparing to UV-Vis spectrophotometry), μFIA-TLM offers LODs of 0.10 and 0.07 μmol/L for Fe(II) and Fe(total), respectively, and analysis of only 3 μmol/L samples. This is sufficiently low for cloudwater analysis, since concentrations, lower than 0.1 μmol/L (5 ng/mL) are not expected [3]. Analysis of spiked synthetic cloud water has shown recoveries in the 102-105% range for Fe(total), which confirms good specificity of the method.

In case of pyoverdines and Fe(III)-pyoverdine complexes,LODs were estimated to be 0.05-0.06 μg/mL for HPLC-DAD whileTLS detection offered about 10 times lower detection limits (0.004 - 0.007 μg/mL) for determination of all pyoverdine species in a single run. Still, about 10 times lowest LODs of fluorescent pyoverdines (not complexed with Fe) were achieved by spectrofluorimetric (SF) detection.However, SF does not offer a possibility of measuring nonfluorescent Fe(III)-pyoverdines.

Combined DGT-BDS has provided LODs between 40-80 nmol/L (2.2 – 4.4 μg/L)Fe(II), which depends strongly on the type of the resin used in the DGT sampler. These values correspond to about 30 ng of total Fe amount diffused into the DGT gel and compare favorably to the LODs obtained by UV-Vis spectrometry which were between 200 and 400 nmol/L, respectively.

References:

1. M. Liu, S. Malovrh, M. Franko**,**Analytical Methods, **8**, 5053 (2016) doi: 10.1039/C6AY00932H
2. W. Bennett, M. Arsic, J.G. Panther, D.T. Welsh, P.R. Teasdale,in: W. Davison (Ed.): Diffusive Gradients in Thin-Filmsfor Environmental Measurements. 1.ed. Cambridge UniversityPress, Cambridge, UK, 2016, pp. 66–92.DOI:10.1017/CBO9781316442654.005

3. L. Deguillaume, T. Charboullot, M. Joly, M.Vaïtingom, M. Parazols, A. Marinoni, P. Amato, A.M. Delort,V. Vinatier, A. Flossmann, N. Chaumerliac, J.M. Pichon, S. Houdier, P. Laj, K. Sellegri, A. Colomb, M. Brigante,G. Mailhot, Atmospheric Chemistry and Physics. **12**, 1485 (2014)

CV-Mladen Franko

Mladen Franko, born 31 March 1958, is a Professor of Chemistry at the University of Nova Gorica, where he currently serves as the *Vice-rector for education* and *Head of the Laboratory for Environmental and Life Sciences.*

He earned Ph.D. degree in analytical chemistry from Marquette University (Milwaukee, Wisconsin, USA) in 1990.

His current research interests and expertise include: development and application of new analytical methods based on laser photothermal spectroscopy for detection of heavy metals and their species and organic compounds following chromatographic separation and FIA including microfluidic systems; development of new biosensors and laser detection techniques for determination of toxic and essential compounds in environmental and biological samples; and investigations of photochemical degradation of organic environmental pollutants and related toxicity.

His research achievements are reported in over 150 works registered in Web of Science database, which were cited by other authors over 2200 times. In addition, he published 5 book chapters and presented over 60 invited lectures at international conferences and meetings, universities and other institutions. For his scientific achievements in analytical chemistry he was awarded the *"Zois Prize" - State Award for Science of the Republic of Slovenia* in 2005.

From 2004 till 2017 he served as the *Vice-president of the Slovenian Chemical Society* and till 2014 he was *Associate editor of Acta Chimica Slovenica*.

Mladen Franko lectured regular undergraduate and graduate courses on *General Chemistry*, *Fundamentals of Environmental Science*, *Analytical Chemistry, Analytical Instrumentation*, *Remote Sensing*, *Environmental Chemistry, Environmental Impacts of Agriculture* and *Toxicology* at the University of Nova Gorica, and University of Maribor. He was guest and visiting professor at University of Turin (Italy), University of Zagreb, China University of Geosciences in Wuhan, and at Azerbaijan State Agricultural University in Ganja (Azerbaijan), where he was awarded the title of Honorary Doctor in 2019.