

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

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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 (μ FIA-TLM) which was recently shown to provide limits of detection at ng/mL level in sub μ L 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 on diffusive gradients in thin-film (DGT) technique, which is increasingly used for monitoring of environmental pollution due to its robustness, versatility, precision and capacity of pre-concentrating bioavailable trace-level pollutants [2].

Validation of FIA-TLS and μ FIA-TLM techniques for Fe determination in comparison to UV-Vis spectrometry showed that despite 100 times shorter optical path length (comparing to UV-Vis spectrophotometry), μ FIA-TLM offers LODs of 0.10 and 0.07 μ mol/L for Fe(II) and Fe(total), respectively, and analysis of only 3 μ mol/L samples. This is sufficiently low for cloudwater analysis, since concentrations, lower than 0.1 μ mol/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 μ g/mL for HPLC-DAD while TLS detection offered about 10 times lower detection limits (0.004 - 0.007 μ g/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 μ g/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:

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