Synthesis and characterization of a new nanosorbent based on functionalized magnetic nanoparticles and its use in the determination of mercury by FI-CV-ETAAS

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In this work, a new chelating sorbent which employs 1,5-bis(di-2-pyridil)methylene thiocarbohydrazide as the functional group and magnetic nanoparticles (MNPs) as its support (DPTH-MNP) was synthetized and characterized. The MNPs were prepared by coprecipitation of Fe^{+2} and Fe^{+3} with NH_3 and then coated with silica in order to easily bind the support and the functionalizing molecule. The aim of the synthesis of this material is applying it as a solid-phase extracting agent and evaluating its potential for the extraction and pre-concentration of trace amounts of analytes present in biological and environmental samples with on-line methods. The MNPs' magnetic core would allow overcoming the usual backpressure problems that happen in solid-phase extraction methods thanks to the possibility of immobilizing the MNPs by applying an external magnetic field. From the study of its adsorption capacity toward metal ions, mercury and antimony were the most retained. Thus, a flow injection solid phase extraction and cold vapor generation method for mercury determination based on the use of this new chelating nanosorbent was optimized. The greatest efforts were put into the reactor design to minimize compaction and loss of nanosorbent. The knotted reactor shown in Figure 1 was chosen as the best. Then, chemical and flow variables were optimized by Central composite designs (CCDs). The method developed has showed to be useful for the automatic pre-concentration and determination of mercury in environmental and biological samples. The determination was performed using electrothermal atomic absorption spectrometry (ETAAS). Under the optimum conditions, pH 5 and 120 s preconcentration time, the enrichment factor was 5.33; the detection limit (3σ) was 7.8 ng L^{-1}; the determination limit (10σ) was 99 ng L^{-1}; and the precisions (calculated for 10 replicate determinations at a 1 and 5 µg L^{-1} standards) were 1.7 and 1.9 % (RSD), respectively. Two linear calibration graphs were obtained, from the determination limits to 10 µg L^{-1} and from 10 to at least 50 µg L^{-1}. From the comparison with other similar methods found in the bibliography, the detection limit and precisions calculated with our method were better. In order to evaluate the accurate and applicability of the method, the analysis of five certified samples LGC 6016 estuarine water, TMDA 54.4 fortified lake water, SRM 2976 mussel tissue, TORT-1 lobster hepatopancreas and DOLT-1 dogfish liver by standard addition and external calibration, were addressed. The results showed good agreement between the certified values, or added amounts of mercury, and the found concentrations. The method was successfully applied to the determination of mercury in sea-water samples collected in the Málaga Bay.

Figure 1. Knotted reactor to a Nd magnet as a sandwich between other two Nd magnets