微量分析およびスペシエーション分析への固相の応用

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Application of the solid phase to the micro and speciation analysis greatly improved the analytical methods including chromatography, i.e., solid phase can be used as the concentration and separation media. For a novel purpose of expanding the application of solid phase to the analytical methodologies, the solid phase could be used as a medium for spectroscopy in solid-phase spectrophotometry (SPS) and as a medium for the chemical reactions in on-line concentration/separation/reaction method by ion exchanger columns. In the present thesis, the two methodologies were used to establish high sensitive, simple, less-cost and greener analytical methods.

In Chapter 1 in Part 1, a new solid-phase spectrophotometry (SPS) method that is easy and simple enough in operation of on-site analyses was developed. A commercially available portable spectrophotometer was optimized for the solid-phase light measurements. LEDs were used as the light source and were powered by rechargeable battery to be usable as portable equipment, and applicability to on-site analyses was realized. The selection of appropriate LED lamps and the stability of the light source were described in detail since they were the important factors for achieving high precision measurements. In addition, the analytical application for the determination of phosphate, chromium(VI) and iron(II) concentrations at µg dm\(^{-3}\) levels in natural water samples were conducted to examine the effectiveness of this proposed SPS method.

In Chapter 2 in Part 1, the SPS method was also developed to determine the total iron concentration of boiler water systems in power generation plants. 2,4,6-Tris(2-pyridyl)-1,3,5-triazine method (TPTZ) was used as the coloring reagent for Fe. The reagents and of cation exchanger was put into the boiler water sample, and the produced Fe(TPTZ)\(_2\) colored complex was adsorbed on the cation exchanger, resulting a 625 times concentration of the target iron in 30 min without any other procedure. The detection limit of 0.1 µg dm\(^{-3}\) was obtained. The optimum conditions for digestion procedure for particulate iron in boiler water and color developing reaction were discussed in detail in this chapter. As for the application to the real samples, the proposed SPS method is the best one because of the shorter analysis time, simpler operation and very low-cost equipment compared to the conventional methods such as TPTZ solution spectrophotometric method, inductively coupled plasma mass spectrometry (ICP-MS) and Atomic absorption spectrometry (AAS).

In Part 2, application of solid phase to the micro and speciation analysis of chemical species was reported. In Chapter 1, speciation analysis of ultratrace chromium in water was realized by on-line reaction/concentration/separation method using a cation exchange column. Cr(VI) and 1,5-diphenylcarbazide (DPC) were mixed and on-line reacted in a flow tube of an HPLC system to form Cr(III)-1,5-diphenylcarbazone (DPCO) complex. When the reagents and complex flowed into the cation-exchange column (TSK IC-Cation, 4.6 mm i.d., 10 mm long), both DPC and the corresponding Cr(III)-DPCO complex were concentrated on the column. The higher DPC concentration on the column accelerated the remaining Cr(VI) to quickly complete the reaction with the DPC on the column. After the complexation and preconcentration, the complex and the extra DPC were eluted with a mixed solution.
containing lanthanum chloride and 1-propanol. The absorbance of the Cr(III)-DPCO complex at 540 nm was continuously monitored. In addition, the dissolved Cr(III) could be oxidized to Cr(VI) by 185-nm irradiation using a low pressure ultraviolet (UV) lamp for 8 min, and then analyzed by the present method as total chromium, thus the quantitative speciation analysis of Cr(III) and Cr(VI) was realized. The analytical time was 8 min for Cr(VI) and 24 min for total Cr. The detection limit (3σ) of the method was 0.6 ng dm$^{-3}$ for Cr(VI) and 0.8 ng dm$^{-3}$ for total chromium when using a 3.9-cm$^3$ water sample. The present method was successfully applied to the speciation analysis of dissolved chromium in natural water.

In Chapter 2 Part 2, the application of the method to the speciation analysis of leached Cr(III) and Cr(VI) from stainless steel was reported. Speciation analysis data of leached chromium is very valuable to understand the leaching mechanisms of leaching procedure. Because of the high sensitivity, a small amount of stainless steel sample is enough to obtain a detectable concentration of Cr at interested leaching time. It made the leaching procedure even simpler than the RoHS standard extraction method.

Above all, both the methodologies are very sensitive (detection limit of sub-µg dm$^{-3}$ level for SPS and ng dm$^{-3}$ level for the on-line reaction/concentration/separation method) and simple since the pretreatment of the sample can be saved. Especially, the cost of both methods is greatly lower than other sophisticated methods. The SPS methods developed so far can be applied to on-site speciation analysis of unstable chemical species (i.e., Fe(II) in oxic condition) in natural water, and also applicable to the real-time monitoring of special species in industries; the developed on-line reaction/concentration/separation method for speciation analysis of chromium can be applied to various fields in which chromium should be determined, such as the evaluation of environmental pollution potential, regulation of stainless-steel waste management, and the inspection of imported and exported chromium-containing products (i.e., leather, and stainless steel), since a short leaching time is sufficient to obtain a detectable concentration of the chromium because of the high sensitivity.