X-ray Fluorescence Spectrometry

Akiko HOKURA

Department of Applied Chemistry, School of Engineering, Tokyo Denki University, 5 Senju-Asahi-cho, Adachi, Tokyo 120-8551, Japan

X-ray spectrometry techniques are powerful tools for the elemental, chemical, crystalline, structural and dynamic analysis of a wide variety of materials in a broad range of fields. These techniques provide a highly versatile and nondestructive analysis.^{1,2} Their application is generally not limited by the physicochemical state of a sample: the materials can be in solid, liquid, powder, filtered or other forms. Consequently, X-ray fluorescence (XRF) spectrometry is widely used for determining the elemental composition in environmental, biological, cultural heritage and industrial samples.^{1,2}

In the last few years, the potential for the analytical performance of XRF techniques has dramatically increased due mainly to two factors: miniaturization made in developing X-ray instrumentation,³ such as detectors and focusing devices; and the analytical requirements of an exceptional spatial resolution for complex and heterogeneous samples.⁴

By developing miniaturized instruments, a portable XRF spectrometry technique undoubtedly occupies a prominent place for conduction *in situ* analysis over a wide range of applications. Hagiwara *et al.* proposed a rapid, simple technique that combines disk solid-phase extraction and handheld XRF spectrometry for the on-site determination of As, Se and Cr(VI) in drinking water.⁵ A Ti-loaded anion-exchange disk was used to collect As(III), As(V), Se(IV), Se(VI), and Cr(VI) in water without requiring oxidation and reduction. The detection limits of As, Se, and Cr(VI) were all 1.0 $\mu\text{g L}^{-1}$. Kato *et al.* demonstrated a rapid determination of sub-ppm Cd in the solution state *via* portable XRF based on homogeneous liquid-liquid extraction in the water-ethanol-dimethyl phthalate ternary component system.⁶ The percentage of Cd extracted into the sedimented liquid phase was 91.3% and the volume ratio of the

aqueous phase and the sedimented liquid phase was 121 (29.0 $\rightarrow$ 0.240 mL). The presence of Cd was determined over a concentration range of 0.100 – 4.00 mg L^{-1} . Kunimura *et al.* proposed a method for the detection of a trace amount of cyanocobalamin (Vitamin B₁₂) using a combination of solid-phase extraction and the measurement of Co in vitamin B₁₂ by a portable total-reflection XRF spectrometer (TXRF). Using this combination, a detection limit of 1 ng mL^{-1} was achieved for vitamin B₁₂.⁷ The publication of the ISO standard 20289 for the TXRF spectrometry analysis of water, particularly drinking and ground water, represented a major advance in using of the technique.⁸

As complex and heterogeneous systems, a corrosion behavior of hot-dip galvanized steel sheets immersed in an aqueous NaCl solution was observed by a confocal micro-XRF instrument developed by Akioka *et al.*⁹ The confocal 3D-XRF system combining two polycapillary lenses in a vacuum provided cross-sectional elemental maps without sample destruction. This analytical method is an effective means of elucidating the corrosion mechanism at the solid-liquid interface between a Zn coating layer and its base steel substrate.

High-resolution XRF spectrometry is also a powerful tool for estimating the chemical states of 3d transition metal compounds. Hayashi *et al.* made low-cost tube-type sample cells from plastic straws for the XRF spectrometry of solutions, sols, and gels.¹⁰ High-resolution Fe K $\beta_{1,3}$ spectra were obtained by using plastic straw cells for position-dependent measurements. The Prussian-blue precipitation bands in gels were clearly detected as reaction-diffusion processes in hydro-gels.

Synchrotron-based XRF spectrometry was used to explore the elemental distribution of heterogeneous biological samples.⁴ Fukuda *et al.* determined a striking sub-cellular distribution of Cd and Zn in a hyperaccumulating plant utilizing micro-XRF with high-energy synchrotron radiation.¹¹ The micro-XRF imaging clearly showed that Cd and Zn were preferentially accumulated in trichomes on the leaf, while the distribution of Cd in the leaf was changed by a Zn treatment.

X-ray fluorescence spectrometry is well established and widely used for multi-elemental determination as a rapid, simple, and easy-to-use analysis. Furthermore, the instrumental technique and the analytical applications keep on evolving to provide new attractive features, such as elemental imaging and real-time analysis for complex and heterogeneous samples.

Keywords Portable, confocal, synchrotron-based, on-site determination, imaging

The XRF technique and application keep on evolving to provide new attractive features.

E-mail: hokura@mail.dendai.ac.jp

References

1. K. Tsuji, K. Nakano, Y. Takahashi, K. Hayashi, and C-U. Ro, *Anal. Chem.*, **2012**, 84, 636.

2. C. Vanhoof, J. R. Bacon, U. E. A. Fittschen, and L. Vincze, *J. Anal. At. Spectrom.*, **2020**, *35*, 1704.
 3. Analytical Methods Committee AMCTB No. 89, *Anal. Methods*, **2019**, *11*, 2498.
 4. R. Terzano, M. A. Denecke, G. Falkenberg, B. Miller, D. Paterson, and K. Janssens, *Pure Appl. Chem.*, **2019**, *91*, 1029.
 5. K. Hagiwara, Y. Koike, M. Aizawa, and T. Nakamura, *Anal. Sci.*, **2018**, *34*, 1309.
 6. T. Kato, Y. Nagashima, A. Manaka, C. Nakamura, S. Oshite, and S. Igarashi, *Anal. Sci.*, **2019**, *35*, 939.
 7. S. Kunitamura, Y. Tokuoka, and U. Aono, *Anal. Sci.*, **2018**, *34*, 1401.
 8. L. Borgese, F. Bilo, S. Federici, E. Margui, T. Hase, Y. Y. Huang, B. Beckhoff, and L. E. Depero, *Surf. Interface Anal.*, **2020**, *52*, 119.
 9. K. Akioka, T. Doi, S. Mita, T. Matsuyama, and K. Tsuji, *Anal. Sci.*, **2020**, *36*, 55.
 10. H. Hayashi and M. Takaishi, *Anal. Sci.*, **2019**, *35*, 651.
 11. N. Fukuda, N. Kitajima, Y. Terada, T. Abe, I. Nakai, and A. Hokura, *Metallomics*, **2020**, *12*, 193.
-