Trace heavy element analysis for wastewater and river water by X-ray fluorescence spectrometry

—Examples for ppm to sub ppm level analysis of heavy elements—

Takao Moriyama*

1. Introduction

There has been a growing demand globally for the analysis of environmental hazardous substances. In Japan, The Japanese environmental regulation for a trace of zinc in wastewater has been recently revised from 5 mg/*l* (5 ppm) down to 2 mg/*l* (2 ppm).

This report introduces an X-ray fluorescence (XRF) analysis for the detection of ppb level of a trace of zinc in wastewater and also hazardous heavy elements in river water using a high sensitivity micro-droplet filter paper, "Ultracarry"†, and the newly developed vacuum dryer, "Ultradry".

2. Sample preparation

A liquid sample of wastewater or river water is dropped onto an Ultracarry filter paper, and the maximum dropping amount per specimen on an Ultracarry is 500 μl (see Fig. 1).

If a solution dropped on an Ultracarry is dried by a regular dryer, it normally may take about two hours. In order to shorten the drying time, an Ultradry, which dries the solution by decompression and heating, was employed (see Fig. 2).

The Ultradry can dry a batch of Ultracarry pads and Microcarry filters. Microcarry is a filter paper for the micro-droplet method. The drying time for a batch of filters in the Ultradry is about 20 to 30 minutes. Several samples can be prepared together at the same time. The dried Ultracarry pads were mounted on aluminum or titanium cups to avoid scattered X-rays. The cups were set in the sample holders of the XRF instrument. (see Fig. 3).

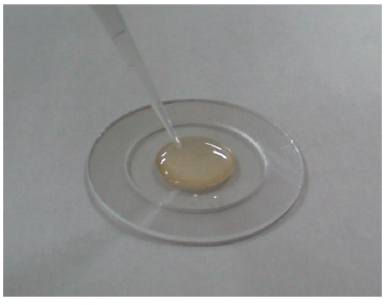

Fig. 1. Ultracarry and a dropped solution with a micro pipette.

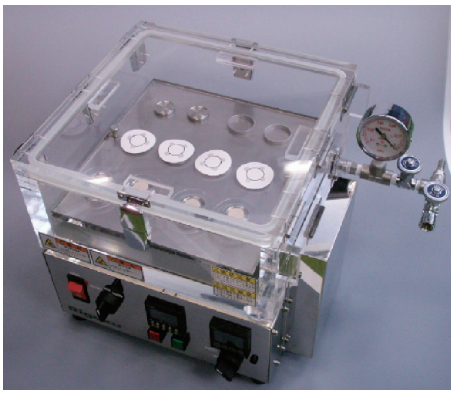

Fig. 2. Vacuum dryer Ultradry.

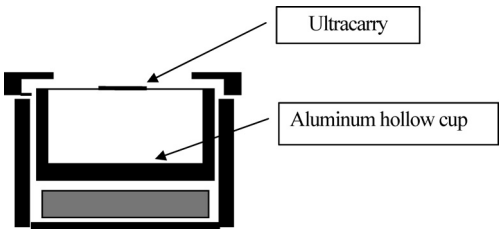

Fig. 3. Schematic diagram of setting an Ultracarry in a sample holder for a tube-above type spectrometer.

3. XRF Analyses

3.1. Detection of a trace amount of zinc in wastewater

A Rigaku wavelength-dispersive X-ray fluorescence spectrometer ZSX Primus II was used. The spectrometer system has a high spectral resolution that enables a high precision analysis of wastewater with a complex sample matrix.

The solutions with 1, 2, 5, and 10-ppm zinc were prepared by diluting the standard solution used for atomic absorption spectrometry. 500 μl of the solutions were dropped onto Ultracarry pads and then dried with an Ultradry. The XRF spectra for the samples are shown in Fig. 4. The Zn-Kα peak is clearly detectable in the XRF spectrum for the sample with 2-ppm zinc, which is

* Application Laboratory-XRF, Rigaku Corporation.

† U. S. patent No. 7,016,463, EPC Patent No.1650559, Korean patent No. 0713742, Russian patent No. 12005110658, and Taiwanese patent No. I300477.

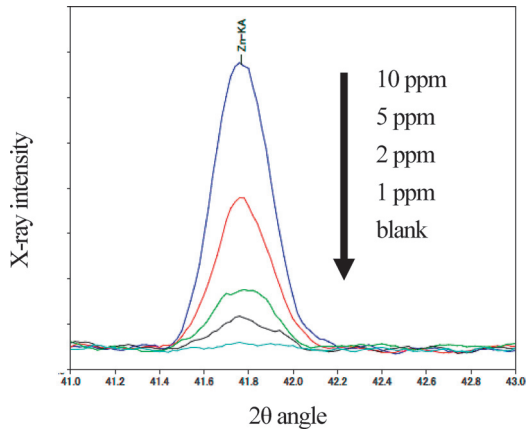

Fig. 4. Kα XRF peaks for Zinc in wastewater (LiF (200) analyzing crystal, 50 kV and 50 mA).

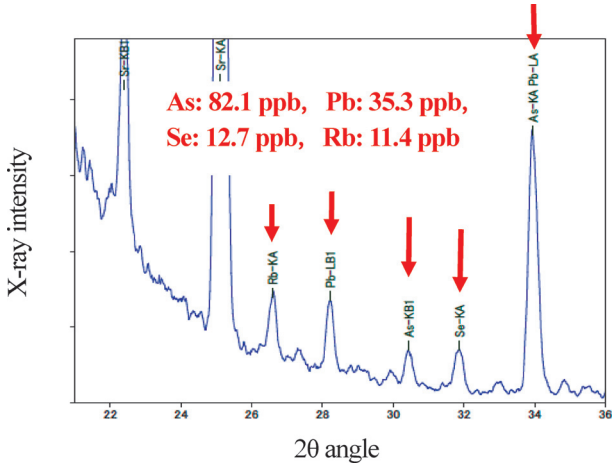

Fig. 5. XRF spectrum of river water (21°–36°2θ, LiF (200) analyzing crystal, Cu primary-beam filter, 50 kV and 50 mA.

the criterion of the Japanese environmental regulation for wastewater. The results plotted in Fig. 4 show that the combination of ZSX Primus II and Ultracarry enables wastewater analysis of a trace of zinc down to 1 ppm. The time for drying the Ultracarry was about 30 minutes, and the time for the XRF qualitative analysis per sample was 2 to 3 minutes. A quantitative XRF analysis of a trace amount of zinc in wastewater is also possible by using a calibration curve.

3.2. Detection of trace amounts of heavy elements in river water

The environmental regulation for hazardous heavy elements in river water is in the 10 ppb levels. It is, therefore, necessary to use condensed sample solutions. The Ultradry can be used for this type of analysis because it is equipped with a decompression evaporating apparatus.

A NIST1643c standard (reference solution of river water) was used in this study. The NIST standard material was first condensed by 50 times with an Ultradry, and then dropped onto an Ultracarry and dried. The XRF spectrum charts of the reference solution are plotted in Figs. 5, 6 and 7. XRF peaks for As (82.1 ppb), Pb (35.3 ppb), Se (12.7 ppb), Rb (11.4 ppb), Zn (73.9 ppb), Cr (19.0 ppb) and V (31.4 ppb) contained in the reference solution are clearly detectable.

4. Conclusions

Our technique of using an Ultracarry filter paper and an Ultradry vacuum dryer shows that the XRF method can be used effectively for a sub ppm level analysis of environmental heavy hazardous elements in wastewater and river water owing to its simple and rapid sample preparation. Since industrial wastewater is likely containing a number of heavy elements, it is therefore useful to perform a prescreening analysis before a normal atomic absorption spectrometer or an inductively coupled plasma spectrometer analysis.

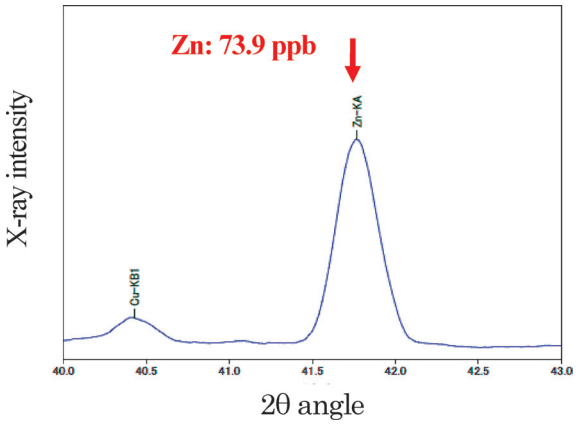

Fig. 6. XRF spectrum of river water (40°–43°2θ, LiF (200) analyzing crystal, 50 kV and 50 mA).

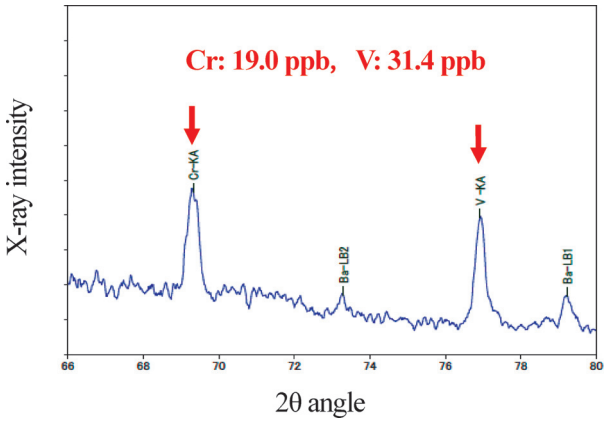

Fig. 7. XRF spectrum of river water (66°–80°2θ, LiF (200) analyzing crystal, 50 kV and 50 mA, and the Cr-Kα peak is overlapped by the V-Kβ1 peak).