Rapid Determination of Sub-ppm Heavy Metals in the Solution State via Portable X-ray Fluorescence Spectrometry Based on Homogeneous Liquid–Liquid Extraction in a Ternary Component System

Takeshi KATO,*1,*2† Yuki NAGASHIMA,*1 Atsushi MANAKA,*3 Chihiro NAKAMURA,*4 Shigekatu OSHITE,*5 and Shukuro IGARASHI*6

*1 Industrial Technology Innovation Center of Ibaraki Prefecture, 3781-1 Nagaoka, Ibaraki-machi, Ibaraki 311–3195, Japan
*2 Science and Technology Promotion Division, Ibaraki Prefectural Government, 978-6 Kasahara, Mito, Ibaraki 310–8555, Japan
*3 Department of Applied Chemistry and Chemical Engineering, National Institute of Technology, Toyama College, 13 Hongo, Toyama 939–8036, Japan
*4 HORIBA Techno Service Co., Ltd., 2-6 KandaAwaji-cho, Chiyoda, Tokyo 101-0063, Japan
*5 Department of Applied Chemistry and Biochemistry, National Institute of Technology, Fukushima College, 30 Nagao, Kamiarakawa, Taira, Iwaki, Fukushima 970-8034, Japan
*6 Department of Biomolecular Functional Engineering, Faculty of Engineering, Ibaraki University, 4-12-1 Nakanaurosawa, Hitachi, Ibaraki 316–8511, Japan

The rapid determination of sub-ppm heavy metals in the solution state was examined via portable X-ray fluorescence spectrometry (XRF) based on homogeneous liquid–liquid extraction (HoLLE) in the water-ethanol-dimethyl phthalate ternary component system. The percentage of cadmium extracted into the sedimented liquid phase was 91.3%. After phase separation, the volume ratio ($V_a/V_s$) of the aqueous phase ($V_a$) and the sedimented liquid phase ($V_s$) was 121 (29.0 → 0.240 mL). Based on an analysis of the sedimented liquid phase in the solution state via the portable XRF, the presence of cadmium was determined over a concentration range of 0.100 – 4.00 mg L$^{-1}$. Keywords: Portable X-ray fluorescence spectrometry, homogeneous liquid–liquid extraction, HoLLE, heavy metals

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Introduction

Heavy metals are commonly defined as elements with a high specific density (more than 4 – 5 g/cm$^3$). Some trace heavy metals are essential elements for the human body. However, excessive amounts of heavy metals will result in symptoms of poisoning.1 Heavy metal pollution causes serious problems all over the world. Examples of where pollution occurs include river water,2 groundwater,3 soil,4 mining sites,5 and industrial wastewater.6,7 For these reasons, it is necessary to perform on-site determinations of heavy metals to monitor such situations.

Human biomonitoring and the environmental assessment of heavy metals have been conducted by atomic absorption spectrometry (AAS),8 inductively coupled plasma-optical emission spectrometry (ICP-OES),9 and inductively coupled plasma-mass spectrometry (ICP-MS).10 These determination results can then be compared to the maximum tolerance limits set by the World Health Organization (WHO).11 AAS, ICP-OES, and ICP-MS have the advantage of enabling an accurate analysis. These methods, however, require extensive preparation as well as skilled analysis procedures. In addition, transporting such analysis equipment for on-site determination is difficult. For an on-site determination, it is essential to have a simple procedure to ensure rapid detection results. A variety of on-site determinations, such as the electrochemical method,12 fluorescence,13 and atomic emission spectrometry,14 have been developed for heavy metals. Even though these methods are superior in their portability and sensitivity, there is still room for improvement with respect to selectivity and the influence of coexisting substances.

Compared to AAS, ICP-OES, and ICP-MS, X-ray fluorescence spectrometry (XRF) has several merits, such as being gas free, low cost, and easy to operate. By miniaturizing this technology, a portable XRF allows on-site determinations in soil and biological samples.15,16 The portable XRF is based on energy dispersive XRF to enable space-saving and low cost. X-ray fluorescence has a peculiar energy value for every element in energy dispersive XRF. It is thus less subject to the influence of coexisting elements. Moreover, the energy value for heavy metals (cadmium) is far from that for the elements which can exist in the environment (such as iron, copper, calcium, and so on). Homogeneous liquid–liquid extraction (HoLLE) was combined with the portable XRF to compensate the sensitivity of XRF. In the general solvent
extraction, an interface exists between the aqueous phase and the water-immiscible organic solvent phase. Thus, mechanical shaking is required, which increases the surface area of the contact interface and causes the solute to move through the interface. On the other hand, in HoLLE, the target solute (metal) is concentrated into a small liquid phase on the basis of its phase separation from the homogeneous solution. There is no interface between the aqueous and organic solvent phases because the solution is homogeneous under initial conditions. Therefore, no vigorous mechanical shaking is necessary in HoLLE. HoLLE can rapidly achieve high concentration rates down to very low sample volumes.\(^{13,21}\) The HoLLE procedure is easy to operate and requires only the addition of a solution. Using a homogeneous solution before HoLLE leads to a high-efficiency phase separation. From the viewpoint of workability, it is thought that the portable XRF and HoLLE are suitable for on-site determinations.

In this study, we adopted HoLLE in the water-ethanol-dimethyl phthalate ternary component system owing to environmental reasons and on-site workability. Regarding XRF for heavy metals, the sorbent method,\(^{23}\) the ion exchange membrane method,\(^{23}\) the precipitation method,\(^{23}\) and the electrochemical deposition method by energy dispersive XRF,\(^{24}\) and the filter paper method by wavelength dispersive XRF\(^{26}\) have been reported. However, there are several problems in on-site workability. Therefore, in this study, we report the effect of determination of heavy metals at sub-ppm levels for on-site determination via a combination of HoLLE and a portable energy dispersive XRF. Soft acceptors like cadmium are likely to form complexes with soft donors containing phosphorus or sulfur atoms. Because the generation of suitable complexes is an important procedure in the determination, several ligands, such as di(2-ethylhexyl) dithiophosphoric acid,\(^{27}\) bis(2,4,4-trimethylpentyl) phosphinic acid,\(^{28}\) diethylidithiocarbamic acid,\(^{29}\) and 1-(2-thiazolylazo)-2-naphthol,\(^{30}\) have been investigated for cadmium in liquid-liquid extractions such as solvent extraction and cloud point extraction. Based on the cadmium extraction percentage and the solubility in HoLLE, 1-(2-thiazolylazo)-2-naphthol (TAN) was selected for this study.

### Experimental

**Reagents and chemicals**

An aqueous solution of cadmium ions was prepared by diluting 1000 mg L\(^{-1}\) standard solutions obtained from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). The metal salt used was Cd(NO\(_3\))\(_2\) (in HNO\(_3\)). The complexing agent TAN was selected for this study. The following instruments were employed in this study: an AS185 centrifugal separator manufactured by AS ONE Corporation (Osaka, Japan); and a MESA-50 portable X-ray fluorescence spectrometer manufactured by Horiba (Kyoto, Japan). The mass and size of the MESA-50 were 12 kg and 202 mm (wide) \(\times\) 280 mm (long) \(\times\) 178 mm (height), respectively.

**Procedure**

**Evaluation by the portable XRF of the cadmium in the solution state.** Approximately 200 \(\mu\)L of the solution was injected into a columnar-shaped cavity with the X-ray transmission film set below. The area of the base in the cavity with X-ray transmission film was 8 mm. X-ray transmission film was made of polypropylene with a thickness of 4 \(\mu\)m. A schematic diagram of the analysis section is shown in Fig. 1. The XRF measurement conditions were as follows: an X-ray tube of palladium anode, an X-ray diameter of 3.0 mm, a time of 100 s, and a voltage of 50 kV. The XRF intensities were obtained from the Cd-K\(\alpha\) peak (23.1 keV) of the XRF spectrum.

**HoLLE of the Cd-TAN complexes.** A Cd standard solution (10 mg L\(^{-1}\)) was added to a 50-mL centrifuge tube such that a predetermined amount of Cd was added to the tube. A phosphate pH standard solution (10.0 mL, pH 6.86) and a TAN solution (2.63 mL, 3.92 \(\times\) 10\(^{-3}\) mol L\(^{-1}\)) were then added to the centrifuge tube. The volume was adjusted to 26.7 mL with distilled water. Next, a homogeneous solution with ethanol (1.87 mL) and dimethyl phthalate (0.40 mL) was added to the centrifuge tube. After shaking gently, the solution was centrifuged at 2500 rpm for 10 min to hasten phase separation. After phase separation, the sedimented liquid phase was collected using a microsyringe. The sedimented liquid phase via HoLLE was determined using the portable XRF.

### Results and Discussion

**Evaluation by the portable XRF of the cadmium in the solution state**

We studied the XRF evaluation of the heavy metal (cadmium) in the solution state. An evaluation of the undersurface irradiation type portable XRF was examined to perform on-site determinations. In the portable XRF that was used in this study, the X-ray path was set to contact the sample solution directly from the undersurface. Therefore, this system could lead to more sensitive determinations than standard uppersurface irradiation type energy dispersive XRF.\(^{11}\) The XRF intensities were obtained from the Cd-K\(\alpha\) peak (23.1 keV) of the XRF spectrum. The calibration curve for the portable XRF was prepared via 200 \(\mu\)L of a cadmium standard solution at concentrations from 25 to 400 mg L\(^{-1}\) in a columnar-shaped cavity with the X-ray transmission film set below. The XRF intensities were proportional to the cadmium concentration. The relative standard deviation (RSD) in the median of the calibration curve was 1.76% (10 determinations). The detection limit (3\(\sigma\)) was 14.0 mg L\(^{-1}\).

**HoLLE of the Cd-TAN complexes**

HoLLE in a ternary component system has been applied to the
extraction of hydrophobic metal complexes. Due to environmental reasons and on-site workability, water–ethanol–dimethyl phthalate was examined. When a homogeneous solution with a Cd-TAN complex and a homogeneous mixture of ethanol and dimethyl phthalate were added, a small amount of sedimented liquid phase was rapidly generated on the basis of the difference between their various solubilities in water–ethanol–dimethyl phthalate. Phase separation was satisfactorily completed via HoLLE (Fig. 2). The volume ratio, defined as volume ratio = (mL of the aqueous phase)/(mL of the sedimented liquid phase), was 29.0/0.240 = 121. After phase separation, the sedimented liquid phase was collected via a microsyringe. The sedimented liquid phase was analyzed in the solution state by the portable XRF. The portable XRF analysis revealed that the distribution ratio and extraction percentage were 1260 and 91.3%. On the basis of the calibration curve based on the XRF intensities of the cadmium standard solution, a cadmium concentration was determined by the XRF intensity of the sedimented liquid phase concentrated from the solution before phase separation ([Cd]T = 2.00 mg L–1, 29.0 mL). The cadmium extraction percentage was calculated by the above determined cadmium concentration of the sedimented liquid phase. Moreover, HoLLE was conducted on solutions with various cadmium concentrations. The results of the analyses are shown in Fig. 3. Measurement was satisfactorily completed without influence from X-ray background noise and other interference. As shown in Fig. 4, the XRF intensities were proportional to the cadmium concentrations from 0.100 to 4.00 mg L–1. The calibration limit (3σ) was 0.0992 mg L–1. It is thought that this system has the potential to determine heavy metals at the ppb level under optimized conditions. This system can reduce the influence of coexisting metals and organic compounds via an X-ray fluorescence analysis at the energy value particular to each element.

Conclusions

On-site rapid determination of sub-ppm level heavy metals (cadmium) in the solution state has been achieved using a portable XRF based on HoLLE. Under HoLLE in the water-ethanol-dimethyl phthalate ternary component system, the cadmium extraction percentage was 91.3% and the volume ratio was 121 (29.0 \rightarrow 0.240 mL). On the basis of HoLLE, the cadmium was determined in the range of 0.100 to 4.00 mg L–1 using the portable XRF. It was possible to determine cadmium at sub-ppm levels using a small low-cost portable XRF without
using large-scale analysis instruments. In the near future, the proposed system is expected to facilitate on-site determinations of sub-ppm level heavy metals.

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