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Multi-element Determination of Heavy Metals in the Han River of Korea Using Liquid-Liquid Extraction-Flame Atomic Absorption Spectrometry

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A method of multi-element determination of hazardous heavy metals such as Cd, Cu and Pb in the water of the Han River is described in this paper. The liquid-liquid extraction (LLE) methods using *N,N'*-diethyldithiocarbamate-methylisobutylketone (DDTC-MIBK) and ammonium pyrrolidine dithiocarbamate-methylisobutylketone (APDC-MIBK) were compared by flame atomic absorption spectrometry (FAAS). For quantitative analysis, DDTC-MIBK extraction was adopted due to its good recoveries (average 93.0% for 3 elements), detection limits (3.4–18.6 ng/l), repeatability (C.V. 1.13–4.57%) and accuracy (average 97.5%). The multi-element determination was available because no interference effect was observed on 3 kinds of metal coexisting in an aqueous matrix. The heavy metal concentrations in the aqueous samples collected from 12 separate points of the Han River averaged 4.204 ppb for Cd, 8.563 ppb for Cu and 2.462 ppb for Pb, respectively. Cd existed almost in suspended particles in water, Cu existed half in suspended particles and half in dissolved form and Pb was almost completely found in particles and only 7% in dissolved form.

Key words — heavy metals; cadmium; copper; lead; LLE; FAAS

Introduction

Water is an essential resource for life.¹⁾ Although the availability of fresh water varies widely with geographic location, the Earth's water cycle is an important provider.²⁾ An important component in determining the safety of water is the toxic element content.³⁾ The Environmental Protection Agency (EPA) now considers toxic pollution in drinking water supplies to be one of the greatest environmental hazards.⁴⁾ Water pollution sources include municipal (home and business), industrial and non-point, the latter meaning the source is broad and cannot be easily identified. Toxic chemicals affect a river's ecosystem- not only the water, but the

plants and fish that live there as well. Thus the contamination of drinking water by heavy metals is potentially hazardous to human health.⁵⁾ Long-term exposure to heavy metals can cause various damage to the brain, kidneys, nervous system, and red blood cells.⁶⁾ The toxicity of heavy metals can cause problems to appear such as the denaturation of the tissue protein or necrosis of cells.^{7,8)} The Han River is an important supply source for drinking water, and from agriculture to industry, from rangeland to domestic use, the residents of Seoul and its satellite cities depend on that water.⁹⁾ To determine the Cd, Cu and Pb levels in the Han river water using a selective analytical method, liquid-liquid extraction (LLE) with *N,N'*-diethyldithiocarbamate-

methyisobutylketone (DDTC-MIBK) followed by flame atomic absorption spectroscopy was used.

Materials and Methods

Apparatus and Chemicals — An atomic absorption spectrometer equipped with a single element hollow cathode lamp (Perkin Elmer AAS 5100-DS 7700, U.S.A.) was used. A field type pH meter (Horiba U-7) was used to analyse the pH of the aqueous samples. All glassware was soaked in 10% HNO_3 and rinsed with distilled water to avoid contamination. All reagent solutions were of analytical reagent grade purchased from Wako Pure Chemicals (Japan). Distilled and deionised water was obtained by a Milli Q water purifier (Millipore, U.S.A.)

Water Sampling — Water samples were collected from 12 separate points along the Han River at constant intervals during March 13–17, 1996. A map representing the sampling points is illustrated in Fig. 1. The North Han River (3 sampling points) and the South Han River (3 sampling points) flow to confluence through Seoul city (6 sampling points).

Water samples were collected from 2–3 sites about 20 m apart and a total of 1.5–4.2 l was obtained at each sampling point. Details of sampling amount, pH, and circumstances are tabulated in Table 1.

Liquid-Liquid Extraction — Two LLE methods to determine the elements in aqueous samples were investigated in this experiment. The DDTC-MIBK method is as follows: A 400 ml

Fig. 1. Map Showing Sampling Points

—→, sampling points; - - -, border of city

Table 1. Sampling Information

Classification	Sampling point	Sampling amount	pH	Circumstance
North Han River	Kapyung	4l	7.32	Agricultural region
	Chungpyung	4l	7.14	Agricultural region
	Yangsung	4l	7.35	Agricultural region
South Han River	Sangri	1.5l	7.33	Agricultural region
	Yangpyung	2.5l	7.39	Agricultural region
	Yeoju	4l	7.17	Industrial region
Confluent Han River	Paldang	4l	7.44	Water supply origin
	Hanam	4l	7.48	Residential area
	Chonho bridge	4l	7.27	Residential area
	Dongho bridge	4l	6.70	Residential area
	Wonhyo bridge	4.2l	7.10	Residential area
	Hengju bridge	2.5l	7.12	Residential area

environmental sample was added to 16 ml of *c*-nitric acid, the watch glass was then covered, heated on a hot plate (below 500°C) until the liquid was reduced to 100 ml, and 25% (w/v) of ammonium citrate debasic and bromothymol blue was then added. The pH level was adjusted to 6.5 with 25% NH₄OH solution. Successively, 40% (w/v) (NH₄)₂SO₄ 10 ml, and 10% (w/v) DDTC 5 ml were added to the sample. The sample solution was transferred to a 500 ml separatory funnel, 20 ml MIBK added and the mixture shaken for 1 min. The aspirated MIBK (top layer) was analysed by atomic absorption spectroscopy. The ammonium pyrrolidine dithiocarbamate (APDC)-MIBK method was as follows: A 400 ml environmental sample was added to 6 ml *c*-nitric acid and 4 ml 50% (w/v) HCl, the watch glass was then covered, heated on a hot plate (below 500°C) until the liquid was reduced to 100 ml. The pH level was adjusted to 2.5 with *c*-HCl, and 5 ml of 1% APDC was added. The sample solution was transferred to a 500 ml separatory funnel, 20 ml MIBK was then added and shaken for 1 min. The aspirated organic supernatant was then analysed by atomic absorption spectroscopy. The procedures of the above methods are illustrated in Fig. 2.

To learn whether the metal existed in a dissolved form or in suspended particles, a water sample 400 ml was collected from Wonhyo bridge and then separated into residue and water parts by filtering with a 0.45 µm pore size membrane

filter. The residue was dissolved in 16 ml *c*-HNO₃ and cooled. This solution was added to 10 ml of H₂O₂ and diluted with 50 ml of distilled water, then evaporated to dryness by heating on a hot plate. Forty ml of 0.5 N HNO₃ was then added to the solid sample, then heated and filtered. This solution was quantitatively transferred to a 100 ml volumetric flask and diluted to volume with a 0.5 N HNO₃ solution. The water part was extracted using the DDTC-MIBK method.

Results and Discussion

Investigation of the Most Appropriate LLE Method

To complete a selective method, a number of extraction methods are available.^{10,11)} As selective LLE methods, the DDTC-MIBK and APDC-MIBK methods were compared. To compare the recoveries, an appropriate amount of mixed standard solution involving 0.05 µg or 0.50 µg of each element was extracted by each of the two methods, respectively. Twenty ml of the MIBK layer was obtained repeatedly and analysed 6–7 times. The result was calculated as found (µg) × 100/added (µg) as shown in Table 2. The DDTC-MIBK method showed 93.9% recovery, while the APDC-MIBK showed poor recoveries averaging 58.3% for 3 elements.

The detection limits of the DDTC-MIBK method obtained by preparation equal to the recovery method was calculated by the tech-

Fig. 2. Procedures of the 2 Liquid-Liquid Extraction Methods

Table 2. Recoveries of Cd, Cu, Pb by DDTC-MIBK and APDC-MIBK LLE Methods

Metal element	n^a	DDTC-MIBK			APDC-MIBK		
		Added(μ g)	Found(μ g)	Recovery(%)	Added(μ g)	Found(μ g)	Recovery(%)
Cd	6	0.05	0.050 ± 0.004	100.0	0.05	0.495 ± 0.037	99.0
Cu	7	0.05	0.048 ± 0.002	96.0	0.05	0.038 ± 0.014	76.0
Pb	7	0.50	0.416 ± 0.019	83.2	0.50	N.D. ^{b)}	0
Average recovery				93.0%	58.3%		

^{a)} number of analyses. ^{b)} Not detected.

Table 3. Detection Limits of Cd, Cu, Pb Pretreated with DDTC-MIBK and APDC-MIBK by Flame Atomic Absorption Spectroscopy

Metal element	DDTC-MIBK				APDC-MIBK			
	Injected conc. ($\mu\text{g/ml}$)	n^a	Dlim ^{b)}	Qran ^{c)}	Injected conc. ($\mu\text{g/ml}$)	n^a	Dlim ^{b)}	Qran ^{c)}
Cd	0.001	6	0.00420	0.1430	0.005	3	0.03970	0.1323
	0.005	6			0.010	5		
	0.010	6			0.500	8		
	0.050	6						
Cu	0.005	7	0.00348	0.0116	0.005	5	0.01700	0.0566
	0.010	7			0.010	5		
	0.050	7			0.050	8		
Pb	0.010	6	0.01860	0.0620	0.010	3	N.C. ^{d)}	N.C.
	0.050	6						
	0.100	6						
	0.500	7						

a) number of analyses. *b)* detection limits ($\mu\text{g/ml}$) of injection sample. *c)* quantitative ranges ($\mu\text{g/ml}$). *d)* not calculated due to bad recoveries.

Table 4. Repeatability of Atomic Absorption Spectroscopic Analysis to Determine Cd, Cu and Pb in DDTC-MIBK Extracted Sample

Metal element	Injected conc. ($\mu\text{g/ml}$)	n^a	Mean $\pm$ S.D.	Coefficient of variance (%)
Cd	0.50	10	0.5033 $\pm$ 0.0070	1.391
Cu	0.10	10	0.1190 $\pm$ 0.0014	1.176
Pb	0.50	7	0.4160 $\pm$ 0.0190	4.567

a) number of analyses.

nique previously reported.¹²⁾ As shown in Table 3, the detection limits for Cd, Cu and Pb by DDTC-MIBK were 0.210, 0.170, 0.930 ppb, respectively, while those by APDC-MIBK were 1.850, 0.850 and not detected.

The repeatability of the DDTC-MIBK method was also evaluated by repeated analyses as shown in Table 4. The repeatabilities expressed with coefficients of variation for the 3 elements were below 5% in this experiment.

Based on the above results, the DDTC-MIBK method provided better recoveries and detection limits for the 3 surveyed metals. It was concluded that the LLE method using DDTC-MIBK was preferable to the APDC-MIBK to determine the 3 metals in an aqueous matrix.

Multi-element Determination

The interference effect of analyte coexistence should be considered for a multi-element determination of metals. Separate stock standard solutions and mixed standard solutions containing a constant amount of metals are repeatedly analysed and compared to each other. As shown in Table 5, no interference effect was observed because almost the same results were obtained whether the elements coexisted or separately existed.

Metal Concentrations in the Han River

The Cd, Cu and Pb levels at 12 points of the Han River basin are tabulated in Table 6.

The Cd levels slightly increased from the North Han River to the confluent stream except that constant levels of 3.700 ppb, 3.763 ppb, 3.325 ppb were determined at the South

Table 5. Interference Effect of Coexistence of Cd, Cu, Pb in an Aqueous Matrix Extracted with DDTC -MIBK Solution

Metal element	Injected standard conc.(ppm)	Coexisted ^{b)}			Separately existed ^{c)}		
		<i>n</i> ^{a)}	Calculated Mean±S.D.	Accuracy (%)	<i>n</i> *	Calculated Mean±S.D.	Accuracy (%)
Cd	2	11	2.168±0.041	108.4	12	2.179±0.029	108.9
Cu	2	12	2.045±0.034	102.2	11	2.017±0.037	100.8
Pb	2	12	1.641±0.141	82.0	20	1.597±0.181	79.8
Average accuracies				97.5%	96.5%		

a) number of analyses. b) Mixed standard soln. containing Cd, Cu, Pb each 2 ppm was analyzed. c) Standard solns. containing Cd, Cu, Pb 2 ppm respectively, were analyzed.

Table 6. Metal Concentration in Aqueous Samples from the Han River (nuit : ppb)

Stream	Sampling point	Cd			Cu			Pb		
		<i>n</i> ^{a)}	Mean±S.D.	Min.—Max.	<i>n</i>	Mean±S.D.	Min.—Max.	<i>n</i>	Mean±S.D.	Min.—Max.
North Han River	Kapyung	5	3.975±0.168	3.700—4.300	5	4.613±0.022	4.600—4.650	5	N.D.*	
	Chungpyung	5	4.000±0.094	3.850—4.150	5	4.288±0.022	4.250—4.300	5	N.D.	
	Yangsu	5	4.500±0.106	4.400—4.650	5	5.563±0.022	5.550—5.600	5	N.D.	
	Average	4.145			4.821				N.D.	
South Han River	Sangri	3	3.700±0.087	3.550—4.250	3	6.775±0.025	6.750—6.850	3	N.D.	
	Yeoju	5	3.763±0.022	3.600—4.050	5	25.625 ^{b)} ±0.053	25.500—25.750	5	N.D.	
	Average	3.596		12.412			N.D.			
Confluent Han River	Paldang*	5	3.850±0.219	3.550—4.250	5	5.975±0.043	5.900—6.000	5	N.D.	
	Hanam	5	3.975±0.075	3.900—4.100	5	4.625±0.065	4.500—4.750	5	9.875±1.635	7.500—12.000
	Chonho bridge	5	4.088±0.143	4.050—4.300	5	8.413±0.023	8.400—8.450	5	N.D.	
	Dongho bridge	5	4.050±0.070	3.950—4.150	5	4.613±0.041	4.550—4.650	5	3.750±3.250	5.000—7.000
	Wonhyo bridge	5	2.888±0.583	1.900—3.650	5	8.825±0.025	8.800—8.900	5	6.833±2.953	3.000—11.000
	Hengju bridge	5	4.138±0.102	4.050—4.400	5	10.050±0.065	9.950—10.100	5	6.625±2.073	4.500—11.500
	Average	4.831				7.083			4.513	
	Total average	4.204				8.563			2.462	

a) origin of the water supply. b) see text.

Han River. Factors contributing to the aqueous content of Cd are thought to be fallout from air, industrial effluents and commercial phosphate fertilizers containing Cd. The main uses of Cd in industry are electroplating or galvanising because of its noncorrosive properties, colour pigments for paints and plastics and cathode material for nickel-cadmium batteries. The average of Cd in the Han River was 4.204 ppb which is below the 0.01 ppm level of Korea EPA regulations,¹³⁾ but this average exceeds the WHO environmental health criteria for Cd in freshwater (below 1

μg/l).¹⁴⁾ This level is also higher than the 1.7 ppb of the Taba River and much higher than the 0.11 ppb of the Ashida River in Japan.¹⁵⁾

The Cu level also increased from the upper stream to the downward flow and averaged 8.563 ppb with the wide range of 4.250—25.750 ppb. Cu is widely distributed in nature but there is little available information on the concentration in an aqueous environment because of the following contradiction: Cu is well known as an essential element for mammals because its deficiency is characterised by hypochromic, microcytic anemia resulting

from defective hemoglobin synthesis. Oxidative enzymes such as catalase, peroxidase, cytochrome oxidases and others require Cu, but the potential hazardous health effects associated with excess Cu intake have also been reviewed.¹⁶⁾ The Cu level at Yeosu showed a sudden increase to 25.625 ppb, which is thought to be the result of effluent from non-point industry located in this area. No regulation has been established for the amount of Cu in river water in Korea, but there is a maximum level of 1.0 mg/l in U.S.A.¹⁷⁾ The Cu level of rainfall in Montreal Island was reported as 0.21–26.5 ppb.¹⁰⁾ and the average Cu level of the Han River water except the Yeosu area was similar to this report.

Pb, the most ubiquitous toxic metal, is detectable in practically all phases of the inert environment and in all biologic systems but there is no demonstrated biological need. The Pb levels averaged 2.462 ppb with a range of N.D.–12.000 ppb. The sources of aqueous pollution include lead based indoor paints in old dwellings, industrial emissions and lead-containing auto exhausts. The large amount of Pb detected in the Han River is thought to come from the atmosphere existing either in solid forms, dust or particulates of lead dioxide or in the form of vapour, particularly alkyl lead that has escaped by evaporation from automobile fuel system. The Pb contribution from the atmosphere to the river could be traced by annual monitoring of Pb because Pb-added gasoline has been prohibited in Korea recently.

Existence Forms of Metals in Han River Water

As shown in Table 7, no Cd concentration of dissolved metals was detected. Cu concentration exists half in dissolved and half in suspended particles, Pb was not detected. Based on these results, Cd can be entirely eliminated by filtration or coagulation, Pb can also be partially eliminated as can a very small amount of Cu. This means the appropri-

Table 7. Existence Forms of Metals in Aqueous Samples from the Han River Water (unit: ppb)

Sample	Cd	Cu	Pb
Aqueous sample 400 ml	5.550±0.137	3.138±0.079	6.500±0.379
Suspended particles	5.413±0.158	1.606±0.061	5.120±0.548
Dissolved metals	N.D.	1.643±0.112	0.379±0.415

Aqueous samples (400 ml) from Wonhyo bridge were determined 5 times.

ate treatments of filtration, adsorption with charcoal and precipitation can reduce the hazardous heavy metals in the Han River water.

Conclusion

To determine the level of heavy metals in environmental aqueous samples, 2 LLE methods prior to atomic absorption spectroscopy were compared. Between the DDTC-MIBK and APDC-MIBK extraction methods, the former was preferable for its good recovery (about 93.0%), repeatability (C.V. 1.13–4.57%) and linearity ($\gamma=0.99$) for quantitative analysis. Multi-element determination for these 3 metals was possible because no interference effect of coexistence in an aqueous matrix was observed. The heavy metal concentrations in the aqueous samples collected from 12 points along the Han River were averaged at 4.204 ppb for Cd with a range of 1.900–4.650 ppb, 8.563 ppb for Cu with a range of 4.250–25.750 and 2.462 ppb for Pb with a range of N.D.–12.000 ppb, respectively. The metal element levels in river water showed a tendency to increase from upper stream to down and at some points such as Yeosu showed a sudden increase of Cu level. Due to the predominance of Cd, Pb contents in the river water and about the half of the Cu was found to exist in suspended particles, traces of the 3 elements were found in dissolved forms. This result means that appropriate treatment of raw water can eliminate the majority of these heavy metals.

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