



Cloud point extraction and flame atomic absorption spectrometric determination of cadmium(II), lead(II), palladium(II) and silver(I) in environmental samples

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ABSTRACT

The phase-separation phenomenon of non-ionic surfactants occurring in aqueous solution was used for the extraction of cadmium(II), lead(II), palladium(II) and silver(I). The analytical procedure involved the formation of understudy metals complex with bis((1H-benzo [d]imidazol-2yl)ethyl)sulfane (BIES), and quantitatively extracted to the phase rich in octylphenoxypolyethoxyethanol (Triton X-114) after centrifugation. Methanol acidified with 1 mol L⁻¹ HNO₃ was added to the surfactant-rich phase prior to its analysis by flame atomic absorption spectrometry (FAAS). The concentration of BIES, pH and amount of surfactant (Triton X-114) was optimized. At optimum conditions, the detection limits of (3 sdb/m) of 1.4, 2.8, 1.6 and 1.4 ng mL⁻¹ for Cd²⁺, Pb²⁺, Pd²⁺ and Ag⁺ along with preconcentration factors of 30 and enrichment factors of 48, 39, 32 and 42 for Cd²⁺, Pb²⁺, Pd²⁺ and Ag⁺, respectively, were obtained. The proposed cloud point extraction has been successfully applied for the determination of metal ions in real samples with complicated matrix such as radiology waste, vegetable, blood and urine samples.

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1. Introduction

Monitoring the presence of toxic trace elements in biological fluids is an extremely important task to evaluate the occupational and environmental exposure [1–3]. The common availability of the instrumentation, simplicity of the procedures, speed, precision and accuracy of the technique still make flame atomic absorption method an attractive alternative [4–7]. Monitoring of trace element concentrations in biological materials, particularly biological fluids, might be considered a difficult analytical task, mostly due to the complexity of the matrix and the low concentration of these elements, which requires sensitive instrumental techniques and often a preconcentration step [8–11]. The traditional liquid–liquid extraction and other conventional separation methods are time-consuming and labor-intensive approaches, besides requiring relatively large amounts of high-purity and frequently toxic solvents, which have to be disposed off properly. Cloud point extraction (CPE) is an alternative suitable separation technique, which is based on the phase behavior of non-ionic and zwitter ionic surfactants in aqueous solutions, which exhibit phase separation after an increase in temperature or the addition of a salting-out agent [12,13]. The cloud point is the temperature above which aqueous solutions of

non-ionic and zwitter ionic surfactants become turbid. Specifically, above the cloud point the solution is separated into two phases: a rich phase containing a high surfactant concentration in a small volume and a poor phase with a surfactant concentration close to the critical micelle concentration (cmc) [14]. This simple procedure called cloud point extraction [15–19] enables to avoid hazardous organic solvents and allows to achieve a much higher concentration of recovered metal ions than in the case of liquid–liquid extraction, because the micellar phase volume is about 10–100-fold less than the volume of an aqueous phase [16]. Accordingly, any metal ions that either directly interact with micelles or after prerequisite binding with hydrophobic chelating ligand, can be extracted from the parent solution by CPE procedure. Trace elements can be extracted to the surfactant-rich phase usually after formation of a hydrophobic complex with an appropriate chelating agent [20]. This approach has been successfully employed to extract and preconcentrate several trace elements from a variety of matrices [21–27]. Method development for CPE requires the optimization of several experimental parameters, such as pH, concentrations of chelating agent and surfactant. Hydrophobic species (hydrophobic organic compounds or metal ions after reaction with a suitable hydrophobic ligand) present in samples are able to interact with the micelles, thus being concentrated in the small volume of the surfactant-rich phase [27]. The small volume of the surfactant-rich phase obtained with this methodology permits the design of extraction schemes that are simple, cheap, highly efficient, fast, and of lower toxicity than those

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extractions that use organic solvents. The CPE method has important practical application and used to separate and preconcentrate analyte compounds as a step prior to their determination after the formation of sparingly water-soluble complexes [26–33].

Since, our survey through literature did not show any application of bis((1H-benzo [d] imidazol-2yl)ethyl)sulfane (BIES) as complexing agent for metal ions in CPE. This paper reports the simultaneous preconcentration of Pb^{2+} , Pd^{2+} , Cd^{2+} and Ag^{+} , after the formation of a complex with BIES and later analysis by flame atomic absorption spectrometry (FAAS), using Triton X-114 as surfactant. The proposed method was applied for the determination of metal ions in radiology waste, vegetable, blood and urine samples.

2. Experimental

2.1. Reagents

All solutions were prepared with deionized water. Analytical-grade of acids, bases and other chemicals used in this study was obtained from Merck, Darmstadt, Germany. A 1.0% (w/v) Triton X-114 (E. Merck, Darmstadt, Germany) was prepared by dissolving 1.0 g of Triton X-114 in 100 mL volumetric flask. The ligand BIES as shown in Scheme 1, was synthesized according to literature [33].

2.2. Instrumentation

A Shimadzu V-570-atomic absorption spectrometer equipped with deuterium background correction and cadmium, palladium, silver and lead hollow-cathode lamp as the radiation source. The instrumental parameters were adjusted according to the manufacturer's recommendations. The acetylene flow rate and the burner height were adjusted in order to obtain the maximum absorbance signal, while aspirating the analyte solution in methanol containing 0.1 mol L^{-1} nitric acid. A Hettich centrifuge (Buckinghamshire, UK) was used to accelerate the phase-separation process. A Metrohm 692 pH/ion meter furnished with a combined glass-saturated calomel electrode was used for pH measurements.

2.3. Test procedure

A cloud point experiment has been carried out according to the following procedure. Taken an aliquot of 15 mL of a aqueous solution containing $0.13 \mu\text{g mL}^{-1}$ of metal ions added 0.13% (w/v) of Triton X-114 and 0.13 mmol L^{-1} of BIES at pH 8 was prepared. The mixture was shaken for 1 min kept for 20 min in a thermo-stated bath at 45°C . Separation of the phases was achieved by centrifugation at 3500 rpm for 15 min. The whole system was cooled in an ice bath for 20 min so that the surfactant-rich phase would regain its viscosity and the bulk aqueous phase was easily decanted. The remaining micellar phase was dissolved in 0.5 mL of 1.0 mol L^{-1} HNO_3 in methanol and then the analyte contents were determined by FAAS.

2.4. Application

The waste radiographic samples were prepared for the measurement of their analytes content as follows: duplicate 20 mL of the sample was taken in a flask (50 mL in capacity) and added 10 mL of 3 mol L^{-1} nitric acid. The content of flasks was heated on electric hot plate to reduce the volume up to 20 mL. The resulting solution was neutralized with sodium hydroxide solution to desired value and filtered. The filtrate and washings were diluted to 50 mL with deionized water in a volumetric flask and then CPE procedure given in Section 2.3 was applied.

Three vegetables (oscimum basilicum and allium ampeloprasum persicum and spinach) were purchased from Firouzabad, Iran, and mixed their equal mass to make a triplicate composite sample. Afterwards, the composite vegetable samples were dried at 110°C in an electric oven and were ground to small mesh. A 10 g mixture was heated in silica crucible for 3 h on a hot plate and the charred material was transferred to furnace for overnight heating at 650°C . The residue was cooled, treated with 10.0 mL concentrated nitric acid and 3 mL of 30% H_2O_2 and kept in a furnace for 2 h at the same temperature so that no organic compound traces are left. The final residue was treated with 3 mL concentrated hydrochloric acid and 2–4 mL of 70% perchloric acid and heated to evaporate the fumes, so that all the metals change to respective ions [10]. The solid residue was dissolved in water, filtered and made up to 25 mL in volumetric, keeping the pH at 8.0 by diluted KOH. Blank digestions were also performed. Then the preconcentration procedure given above was applied.

Taken 2.0 mL of blood and urine homogenized samples in flasks (50 mL incapacity).

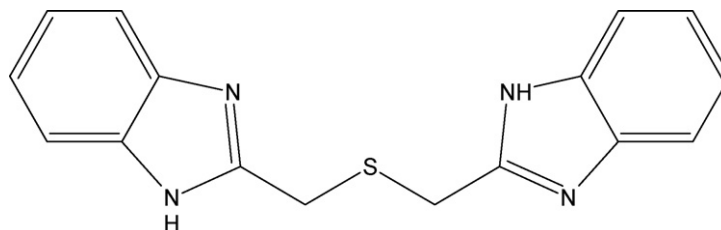
The digestion procedure was carried out by heating the samples for 1 h after addition of 10 mL concentrated HNO_3 and 2 mL HClO_4 70%. The content of the flasks was diluted with deionized water and filtered through a Whatman No. 40 filter paper into a 25 mL calibrated flask and its pH was adjusted to desired value [10]. Then the procedure given in Section 2.3 was performed.

3. Results and discussion

Since the BIES ligand possesses nitrogen and sulfur donor atoms and a conjugated π system, it should form stable complexes with cadmium(II), lead(II), palladium(II) and silver(I). Thus, we decided to examine its capability as a suitable reagent for sensitive and efficient ligand formation for CPE of these ions.

3.1. Effect of pH

The influence of pH on method sensitivity has been carried out by conducting a replicate set of similar CPE experiments by changing the pH of aqueous solution of sample in the range of 2.0–9.0. Fig. 1 shows the effect of pH on the sensitivity of method. It was found that at pH of eight maximum sensitivities were achieved. Therefore, a pH of 8 was selected for subsequent work. In acidic medium, a weak complexation and uptake occurs, which



Scheme 1. The structure of ligand.

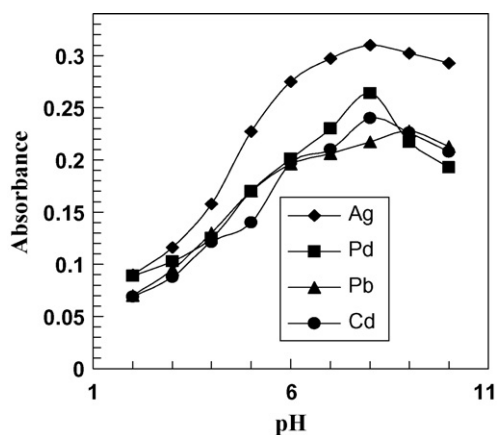


Fig. 1. Effect of pH on cloud point extraction of ions ($n = 3$).

is explained by competition between metal ions and hydrogen ions for the binding to ligand. On the other hand by increasing the pH, the potential of active sites of ligand for metal ion binding and consequently the metal ions uptake were increased. The uptake capacities increased with increasing pH, reaching plateau values at around pH 8 (Fig. 1). The uptake of metal ion beyond $\text{pH} > 8$ is attributed to the formation of metal hydroxide species such as soluble $\text{M}(\text{OH})^+$ and/or insoluble precipitate of $\text{M}(\text{OH})_n$. To achieve high efficiency and good selectivity a pH of 8.0 was selected for subsequent work.

3.2. Effect of ligand concentration

The CPE can be used for the preconcentration of metal ions after the formation of sparingly water-soluble complexes. The CPE efficiency depends on the hydrophobicity of the ligand and the complex formed the apparent equilibrium constants in the micellar medium, the kinetics of the complex formation, and the transference between the phases [14,34]. It was proved that Triton X-114 effectively extracts the derivatized metal species from sample concentration of 13% (v/v). In this work ligand was used in tetrahydrofuran (THF) solution since the solubility and stability of ligand is relatively high in this solvent and it is a water-soluble solvent. It was found that the extraction efficiency decreased above a THF concentration of 5% (v/v) due to dissolution of the surfactant phase and decreasing the volume of this phase. The concentration of the chelating agent was subsequently studied for its effect on the extraction of metal ions and the results are presented in Fig. 2. The ligand concentration increased up to certain values, which were sufficient for total complexation, and the obtained responses were improved. However, using an excessive amount of reagent, decrease

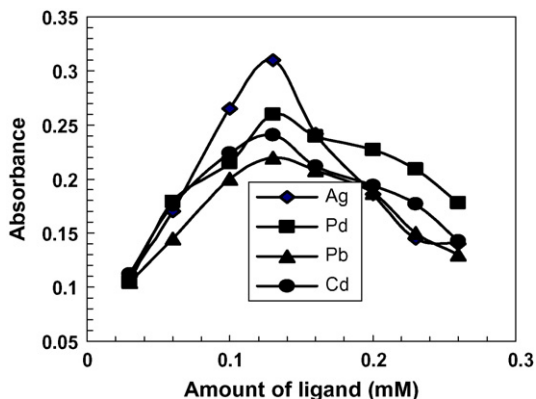


Fig. 2. Effect of ligand concentration on CPE of ions ($n = 3$).

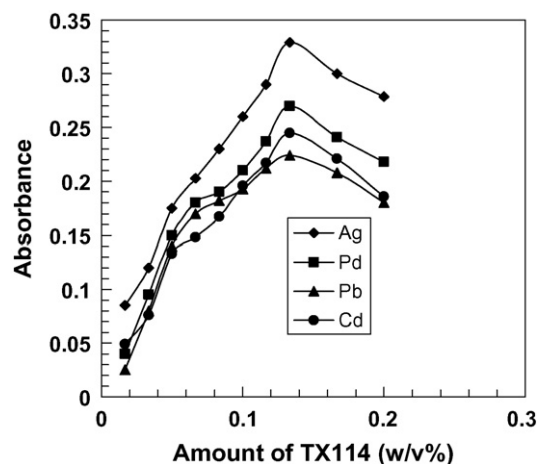


Fig. 3. Effect of surfactant concentration on CPE of ions ($n = 3$).

in extraction performance was observed, because utilizing a higher concentration of ligand causes more volume of organic as solvent to enter the solution that can prevent the micelle formation and reduce the extraction efficiency or maybe lead to the formation of charged species. The starting points of the horizontal parts of the curves are consistent with the formation constants of the complexes. Therefore, 0.13 mmol L^{-1} of a BIES concentration was chosen for subsequent experiments.

3.3. Effect of Triton X-114 concentration

The presence of active groups in the surfactant molecule can be considered to be advantageous under certain circumstances when electrostatic interactions are favorable. The non-ionic surfactant, Triton X-114, is the most frequently used surfactant to perform CPE experiments. A successful cloud point extraction should maximize the extraction efficiency by minimizing the phase volume ratio ($V_{\text{org}}/V_{\text{aqueous}}$), thus improving its concentration factor. The variation of the analytical signal as a function of the concentration of Triton X-114 in the range of 0.02–0.2% (w/v) was also investigated. Fig. 3 also shows a considerable change in the absorbance signal at different surfactant concentrations. An increase in the surfactant amounts also increases the volume of the surfactant-rich phase that is obtained after centrifugation of the analyte. Extract is therefore more diluted when higher amounts of surfactants are used, resulting in a loss of sensitivity with increase of Triton X-114 concentration above 0.13% (w/v), the signals decrease because of the increment in the overall analyte volumes and the viscosity of the surfactant phase. Due to the increase of the surfactant volume, deteriorating the FAAS signal. At concentrations below this value, the extraction efficiency of complexes was low because there are few molecules of the surfactant to entrap the ligand-metal complexes quantitatively [34]. Therefore, in order to achieve a good enrichment factors and high extraction efficiency, Triton X-114 concentration of 0.13% (w/v) was chosen. In this condition, it was shown that the recovery of the analytes using a single step extraction was quantitative. The optimum surfactant concentration used for the four metals was the same, 0.13% Triton X-114, in order to achieve the optimal analytical signal high and good enhancement factor in conjunction with the highest possible extraction efficiency.

3.4. Effect of NaCl concentration

It was observed that the presence of electrolytes decreases the cloud point (salting-out effect), resulting in low extraction efficiency. The lower cloud point extraction efficiency is attributed to

electrolytes promoting dehydration of the poly(oxyethylene) chains [35]. According to Komaromy-Hiller et al. [36] the salting-out phenomenon is directly related to desorption of ions to the hydrophilic parts of the micelles, increasing interaction between micelles and consequently leading to the precipitation of surfactant molecules. Based on this discussion, NaCl was investigated as electrolyte in the concentration range from 0.5 to 5% (w/v) with the goal of obtaining the cloud point without heating. It was observed that the highest absorbance was obtained at 1% (w/v) NaCl concentration. The signal decreased considerably for increasing NaCl concentrations (3–5%, w/v). This effect might be explained by the additional surface charge when the NaCl concentration is very high, thus changing the molecular architecture of the surfactant and consequently the micelle formation process. It is necessary to emphasize that different blank solutions were also evaluated and no significant signal was obtained. In this way, 1% (w/v) NaCl concentration was used in all further experiment.

3.5. Effect of methanol volume

The surfactant-rich phase obtained after cloud point preconcentration is very viscous owing to the Triton X-114 that it contains. In the phase-separation step, the surfactant-rich phase with high viscosity was settled. The addition of a diluent, such as 2 mol L⁻¹ HNO₃ reduces the surfactant phase viscosity and facilitates its transfer into the flame nebulizer. Therefore, 0.5 mL of diluent was chosen as the optimized value and added to the surfactant-rich phase in order to ensure a sufficient volume of the sample for aspiration. The final surfactant-rich phase volume was 0.5 mL. The best results were obtained for methanol and, to prevent its vaporization during the experiments at room temperature, methanol-diluted HNO₃ (3:1) mixture solution was employed. On addition of small volumes of acidified methanol, the signal was lower because of the inappropriate properties of the solution for aspiration and nebulization, whereas for greater volumes, there was a decrease in the signal due to dilution. An optimal volume of 0.5 mL of acidified methanol was chosen in order to ensure good absorbance signal.

3.6. Effect of temperature

Temperature can effect complexation reactions and micelle formation. The mechanism of phase separation is due to an increase in the micellar aggregation number when temperature is increased [37–42], may be caused by a change in micellar interactions, which are repulsive at low temperatures but predominantly attractive at high temperatures. This can be explained on the basis of the dehydration process that occurs in the external layer of the micelles of non-ionic surfactants when temperature is increased [40]. The dielectric constant of water is also decreases by increasing temperature, rendering it to a poorer solvent for the hydrophobic portion of the surfactant molecule [41]. It appears that the phase volume ratio of all non-ionic surfactants decreases as the equilibration temperature increases. The greatest analyte enrichment factors are, thus, expected where the CPE is conducted using equilibration temperatures that are well above the cloud point temperature of the surfactant [37].

The temperature at which phase separation occurs is a function of the surfactant concentration and can be altered (either increased or decreased) in the presence of other materials (i.e. salts, alcohols, non-ionic surfactants and some organic compounds). To achieve easy phase separation and preconcentration as efficient as possible, optimal incubation time and equilibration temperature are necessary to complete reactions. It was desirable to employ the shortest equilibration time and the lowest possible equilibration temperature as a compromise between completion of extraction and efficient separation of phases. The dependence of extraction

Table 1

Effects of the interferences ions on the recoveries of the examined metal ions ($n = 3$).

Ions	Tolerable level (mg L ⁻¹)
Na ⁺ , K ⁺ , Ti ³⁺ , Al ³⁺ , HCO ₃ ⁻	1000
Ba ²⁺ , Ca ²⁺ , Mg ²⁺	700
Co ²⁺ , Cu ²⁺ , CH ₃ COO ⁻	400
Ni ²⁺	350
Cr ³⁺	200
Fe ³⁺ , Hg ²⁺ , Zn ²⁺	100

efficiency upon equilibration temperature and time was studied with 50 °C in the time range of 5–30 min, respectively. The results from the optimization experiments showed that an incubation time of 10 min is adequate for quantitative complexation of all species in a single step without the need of extra cloud point extraction experiments. The effect of the equilibration temperature was investigated from room temperature to 50 °C. The excellent extraction efficiency achieved for equilibration temperature from 50 to 70 °C. Above this temperatures lead to the decomposition of complexes and the reduction of extraction efficiency. A temperature of 55 °C was further used in all experiments.

3.7. Effect of centrifuge time and rates

It was found that the increase of centrifuge rate has no considerable effect upon the extraction efficiency and analytical signal. Keeping the optimized temperature, the influence of centrifuge time on CPE was studied within a range of, immediately after the preparation to 20 min. It was observed that, the incubation time before centrifugation has no significant effect upon the extraction efficiency. So, in order to keep analysis time as short as possible the turbid solution was centrifuged immediately after the preparation at room temperature. The effect of centrifugation time upon analytical signal was also studied in the range of 5–20 min. A centrifugation time of 10 min at 4000 rpm was selected for the entire procedure, since complete separation occurred for this time and no appreciable improvements were observed for longer times.

3.8. Effect of interference

Selectivity and utility of the method were further examined in the presence of various ions. The interfering capacity of water matrix constituents such as calcium, magnesium, sodium, potassium, chloride, sulfate and some other ions on understudy analyte ions recoveries was also considered. A series of mixture of metal ions such as at weight ratios of 1000 was subjected to the proposed procedure and no significantly decrease in metal ions recoveries was detected. An error of ±5% in the recovery error of ±5% in the recovery was considered to be tolerable. As results indicates (Table 1) that most of the cations and anions are tolerable at weight ratios of 1000. So it was confirmed that deposition efficiency would not be affected by the presence of high concentrations of matrix cations.

3.9. Characteristics of the method

The precision of the procedure was determined as the relative standard deviation of seven independent measurements carried out in solutions containing all ions. The limits of detection (LOD) the lowest analyte concentration that produces a response detectable above the noise level based on 3 times the standard deviations of the blank ($n = 20$, $LOD = Xb + 3s$, where Xb is the blank value and s is the standard deviation (s.d.) of the blank ($n = 10$) were found to be (3 sdb/m) of 1.4, 2.8, 1.6 and 1.4 ng mL⁻¹ for Cd²⁺, Pb²⁺, Pd²⁺ and Ag⁺ ion along with preconcentration factors of 30. The enrichment factors which were calculated from slope of calibration

curve after preconcentration to slope of calibration curve before preconcentration of 48, 39, 32 and 42 for Cd²⁺, Pb²⁺, Pd²⁺ and Ag⁺, respectively. It should be mentioned that the enrichment factor of our method can be improved by using larger volumes of initial solute. The limit of quantification (LOQ) is the lowest level of analyte that can be accurately and precisely measured. The limits of quantification, defined as 10 times the standard deviation (*s*) of the blank (*n* = 10), were found to be 6.6, 11.8, 8.9 and 5.1 ng mL⁻¹ for Cd²⁺, Pb²⁺, Pd²⁺ and Ag⁺, respectively. The relative standard deviations (r.s.d.) were 3.6, 2.0, 2.7, 2.1% for these ions, respectively.

3.10. Accuracy and applications

We have explored the feasibility of the CPE methodology using preconcentration with BIES ligand in surfactant media for the determination of concentration of Cd²⁺, Pb²⁺, Pd²⁺ and Ag⁺ ions in different matrices. A wide variety of samples were tested by our proposed method and these included radiology waste, vegetable, blood and urine samples by standard addition method. Spiking experiments checked reliability. The results are presented in Table 2. The recovery of spiked samples is satisfactory reasonable, which indicate the capability of the system in the determination of analytes in real samples. In view of the high selectivity provided by flame atomic absorption spectrometry, the only interferences studied were those related to the preconcentration step: cations that may react with ligand, anions that may form complexes with the

metal ions and decrease extraction efficiency. The interferences induced by other cations which readily complex with ligand can be avoided by increasing the amount of ligand dissolved in solution.

4. Conclusion

The combined advantages of the cloud point methodology (easy, safe, rapid and inexpensive) and the use of as a chromogenic reagent (selectivity and sensitivity) for these metal ions were utilized for their determination in real samples. The separation occurred efficiently, resulting in good enrichment factor and low LOD. In contrast to some other preconcentration techniques, no organic solvent is employed; therefore, the environmental pollution is limited to a small amount of surfactant, Triton X-114 (at 0.013% (w/v)) which is commercially available at low cost. Due to physical–chemical characteristics such as lower cloud point and higher density, which make phase separation easily by centrifugation. Complexing agent is stable in acidic medium, which is of advantage because samples are prepared and preserved at low pH values thus facilitating the conditions for cloud point development. Another advantage concerns the green chemistry concept. The small volume of the surfactant-rich phase (0.5 mL), permitting a design for extraction strategy, having lower toxicity than those using organic solvents. The proposed method shows very good sensitivity and precision and has some good advantages over other preconcentration methods reported in the literature [42–52].

Table 2

Recovery of trace elements from spiked real samples after application of presented procedure (final volume: 0.5 mL, *n* = 3).

Sample	Ion	Added (μg L ⁻¹)	Found (μg L ⁻¹)	r.s.d. (%)	Recovery (%)
Radiology waste	Pd	0	0.0429	3.7	–
		0.1	0.145	–	103.2
	Ag	0	0.224	2.2	–
		0.1	0.326	1.5	98.6
	Pb	0	0.056	2.4	–
		0.1	0.157	1.4	102.2
Cd	0	0.065	3.8	–	
	0.1	0.163	2.3	97.2	
Vegetable	Pd	0	N.D.	–	–
		0.1	0.104	3.6	103.2
		0.2	0.218	2.4	–
	Ag	0	N.D.	2.6	–
		0.1	0.105	1.8	97.8
		0.2	0.207	–	–
Pb	0	0.462	2.7	–	
	0.1	0.567	1.6	97.6	
Cd	0	0.386	1.8	–	
	0.1	0.499	1.0	101.0	
Blood	Pd	0	N.D.	–	–
		0.1	0.228	4.3	103.2
		0.2	0.330	2.7	–
	Ag	0	N.D.	–	–
		0.1	0.295	3.1	97.8
		0.2	0.195	2.2	–
Pb	0	0.105	3.6	–	
	0.1	0.209	2.3	101.6	
Cd	0	0.057	3.8	–	
	0.1	0.161	2.2	96.0	
Urine	Pd	0	N.D.	3.8	–
		0.1	0.104	2.3	101.2
		0.2	0.208	–	–
	Ag	0	N.D.	3.4	–
		0.1	0.107	1.7	102.0
		0.2	0.204	–	–
Pb	0	0.079	3.7	–	
	0.1	0.174	2.8	102.0	
Cd	0	0.090	3.8	–	
	0.1	0.195	3.0	98.0	

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