

SIMPLIFIED ACID EXTRACTION METHODS OF HEAVY METAL IONS FROM CONTAMINATED SOILS

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ABSTRACT: Early detection of heavy metal contaminations of soil and ground water has great importance for human health. In this study, single acid extraction methods have been tested and evaluated for the extraction of heavy metal ions for rapid and on-site soil sample preparations. Parametric studies have been performed including sample to acid volume ratio, extraction time, and acid concentration, and the performance of the proposed method has been compared with standard laboratory based protocol using soil samples spiked with target metal ions. The proposed protocol utilizing three different single acids (EDTA, HNO₃, HCl) has shown the comparable extraction efficiency over ~80% for heavy metal ions of major concerns, Pb, Hg, and As. Compared to standard method based on aqua regia digestion, single acid extraction provides reduced processing steps and reagent volume, possibly enabling the on-site processing of contaminated soils and analysis.

Keywords: Soil Analysis, Heavy metals, Ionic Extraction

1. INTRODUCTION

Heavy metal contaminations of soil and ground water have been one of major concern in the world due to their toxicity and numerous effects on human health [1]-[4]. Although conventional laboratory based detection methods are well established, rapid and on-site monitoring of soil contamination which is essential for preventing the environmental pollution in a very early stage is still limited[5]-[8]. Conventional analytical techniques are based on the large scale system involving time-consuming and serial processing of samples with hazardous materials, complicated instruments, central laboratories, and high skilled personnel are required [9]. Thus, the development of miniaturized procedures is crucial for on-site analysis.

Soil samples generally require sample pretreatment with efficient purification and extraction of target analytes before a specific analysis, and the preprocessing has been recognized as one of the most critical step for maximizing analytical accuracy. However, sample preprocessing usually involves labor-intensive and tedious process and has been the actual bottle neck of developing a rapid, automated and portable soil monitoring system [10], [11]. In this work, simplified extraction protocols for heavy metal detection from contaminated soils are presented. For the adaption in a syringe like miniaturized format, single acid based extraction methods have been designed and tested for the extraction of heavy metal ions of major concerns in South Korea, which are Hg, Pb, and As. Metal ions are extracted using acid solution first and filtered to remove any

undesirable debris. In order to assess the performance of the proposed simplified and miniaturized preprocessing protocol, mock-up soil samples with known quantity of ions have been processed, and the comparison with the standard protocol has been made by measuring the ion concentration. The proposed protocol has shown the comparable extraction efficiency over 80% while the required processing steps and the reagent volume have been reduced significantly. Thus, the proposed method can be applied for on-site analysis of contaminated soils, enabling simplified and rapid analytical procedures.

2. MATERIALS AND EQUIPMENT

Two reference soils, CRM 109-03-002 (Korea Research Institute of Standards and Science, KRISS, South Korea) and BAM-U112a (Odlab, South Korea) were purchased and tested. Selected ion concentration in reference soils are shown in Table 1.

Table 1 Ion concentration in reference soils (mg/kg)

	Hg	Pb	As
KRISS-CRM	0.98	3945.3	1200
BAM-U112a	16.3	198	10.3

Ions of interest (Hg, Pb, As) were extracted and total concentrations of metal ions were analyzed by using inductively coupled plasma optical emission spectrometry (ICP-OES) and mercury analyzer. All test samples were filtered by filter

paper (F1001, Chmlab) before the analysis. EP grade Ethylenediaminetetraacetic acid (EDTA), Hydrochloric acid (HCl) and Nitric acid (HNO₃) were purchased (Daejung, South Korea). 18 MΩcm DI water was purified with a Pure Power System (Human corp., South Korea).

3. METHODS

3.1 Standard Method

For the comparison of the extraction efficiency with the standard extraction protocol, ES07000 from Korea Ministry of Environment was selected and applied, which is based on aqua regia digestion.

3.2 EDTA Extraction

1~4g of soil samples were mixed with 40 ml of 0.05M EDTA in a centrifuge tube and homogenized with tube shaker (Finepcr, South Korea) for 0.5~3 hours. After the extraction, samples were filtered through a filter paper, then collected.

3.3 HNO₃ Extraction

5~200 mg of soil samples were mixed with 5~50 ml of 10% and 50 % HNO₃ in a centrifuge tube, and were sonicated for 30 min at 35°C (Hwashin, South Korea). Samples were then diluted with DI water and filtered through the filter paper and collected.

3.4 HCl Extraction

200 mg of soil samples were mixed with 10~40 ml of HCl in different concentrations from 1.7 % to 10 % in a centrifuge tube and homogenized with the tube shaker for 0.5~12 hours. If needed, sonication was applied at 60°C for 0.5~2 hours. Samples were then diluted with DI water and filtered through the filter paper and collected.

4. RESULTS AND DISCUSSION

Table 1 summarizes extraction efficiencies of different acids together with the results by standard method. For the extraction of Pb, most of acid extractions showed comparable efficiencies, while the extraction of Hg and As were achieved only for HNO₃ and HCl, respectively. Standard extraction efficiencies for Pb and Hg ions were appeared as over than 80% for both KRISS-CRM and BAM-U112a soils. For each acid, the protocol was empirically optimized and tested to achieve target efficiencies over 80% for future applications.

EDTA was first tested for the extraction of

three ions. EDTA is the well-known chelating agent for soil washing method, and many studies have shown that EDTA is effective especially in removing Pb, while the efficiency can be affected by various parameters including acid concentrations and the acid to soil ratio [12]-[16]. The test results of Pb extraction with 0.05M EDTA also showed good efficiencies over 70% for BAM-U112a soils even within relatively short incubation time. However, the efficiency was lowered in the case of KRISS-CRM. To further examine the EDTA extraction efficiencies for KRISS-CRM, the effects of incubation time and acid to soil ratio were tested.

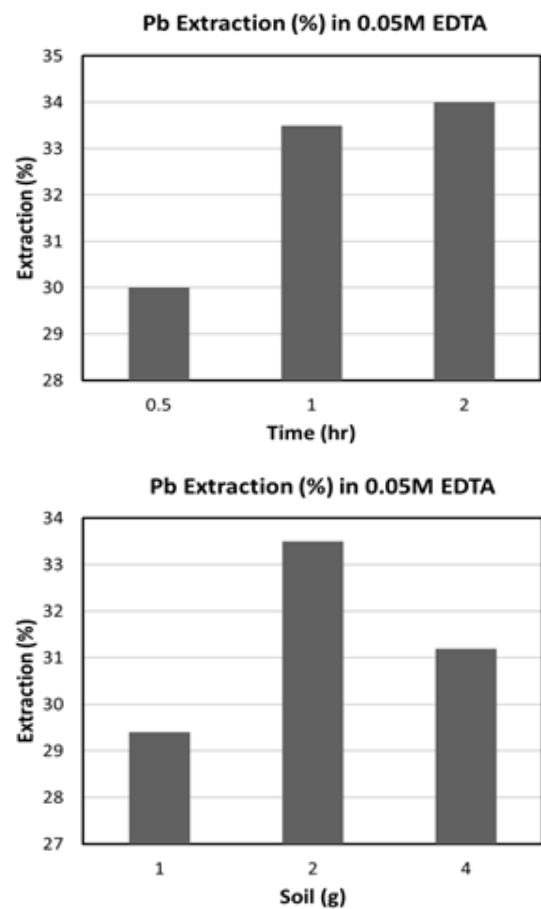


Fig. 1 Lead ion extraction efficiency in 0.05M EDTA as increased time (top) and soil mass (bottom).

Figure 1 shows the variation of Pb extraction efficiencies with different incubation time and soil mass in 0.05M EDTA. As seen on the figure, elongated incubation time increased the extraction efficiency, but the efficiency increase became saturated if incubated over 2 hours. Meanwhile, the test result of different soil amounts informs that the optimal acid to soil ratio exists. In this case, the incubation was performed for 1 hour for all

Table 2 Acid extraction efficiency for heavy metal ions

Acid	Soil	Extraction	Efficiency	Remarks
0.05M EDTA	KRISS	40ml acid & 1-4g soil 0.5-3 hour	Pb 29-34%	Standard extraction (ES 07000)
	BAM	40ml acid & 1-4g soil 0.5-3 hour	Pb 70-107%	
10% HNO ₃	KRISS	5-50ml acid & 5-200mg soil 30 min sonication at 35C	Pb 33-42%	KRISS CRM . Pb 96-104% . Hg 90%
	BAM	5-50ml acid & 5-200mg soil 30 min sonication at 35C	Pb 74-102%	
50% HNO ₃	BAM	12ml acid, & 200mg soil 45 hour	Pb 75% Hg 87%	BAM-U112a . Pb 77-95% . Hg 88-93% . As 107%
1.7% HCl	BAM	40 ml acid & 0.2g soil 1 hour shaking	Pb 77% As 78%	
2.5% HCl	BAM	10ml acid+11.5% ethanol & 0.2g soil 90-120min sonication at 60C	Pb 75-83% Hg 33-38%	
10% HCl	BAM	40 ml acid & 0.2g soil 1-12hour shaking	Pb 76-91% As 78-136%	

cases in the consideration of assay time. Even the soil amount may further be optimized, it can be seen that the extraction efficiency is limited about 34%. The difference in extraction efficiencies for two soils may come from the labilities of ions in samples and the saturation due to the high Pb concentration in KRISS-CRM. It can be observed that EDTA extraction can generally be optimized with longer incubation time before saturation and the proper sample and acid volumes. However, besides Pb, EDTA was inefficient or incapable for the extraction of Hg and As.

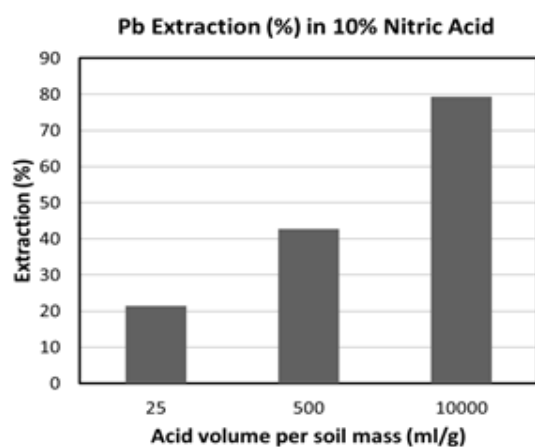


Fig. 2 Lead ion extraction efficiency in 10% nitric acid as increased acid volume per soil mass.

For the extraction of metal ions, nitric acid was tested. First, 10% HNO₃ extraction followed by 30 minutes sonication were performed based on the protocol [15]. The extraction efficiency of Pb ions was appeared as similar to the result of EDTA. Figure 2 shows the efficiency of lead ion extraction in 10% HNO₃. The extraction efficiency is rapidly increasing as the applied acid volume is getting larger. Unlike the laboratory based or large scale soil washing, acid volume should be minimized for field applications, and thus further increase of the acid volume was avoided. Instead, to increase the extraction efficiency and achieve the Hg extraction, acid of higher concentration was applied with elongated incubation time. On the application of 50% HNO₃, the increase in Hg extraction efficiency was achieved while the effect was negligible for Pb. However, Hg extraction over 80% was found to be challenging unless incubated over ~40 hours. Thus, additional complementary mechanism such as ultrasound, which is adequate for field application, will be necessary if reduced processing time is required [16].

HCl was tested with BAM-U112a especially focusing As ions. As KRISS-CRM contains high concentration, only BAM-U112a was tested for excluding saturation effect. 1.7% HCl with 1 hour shaking showed the good extraction efficiency close to 80%. Further increase in acid concentration was found to be ineffective, but the increase in incubation time showed more improved

extraction of As ions. Hg extraction was also tested initially based on the protocol [17]. As expected, simple extraction of Hg ions in HCl could not be achieved, but additional sonication steps at the elevated temperature (60°C) provided significant increase in the extraction efficiency. Pb extraction in HCl also showed comparable efficiencies with other acids regardless of the acid concentration.

5. CONCLUSION

As an alternative approach of standard extraction protocol based on aqua regia, single acid extraction methods have been tested and optimized. Single acid including EDTA, HNO₃, and HCl has shown comparable extraction efficiency compared to the standard protocol. Findings from the presented study can be summarized as follows:

- Single acid extraction of Pb and As ions can possibly be performed with the efficiencies over 78% through a simple incubation in 0.05M EDTA and 1.7% HCl, respectively, with optimized incubation time and acid volumes.
- Single acid extraction of Hg ions can possibly be performed by using 50% HNO₃ with the efficiency of 87%, but requires elongated incubation time more than 40 hours. Additional mechanism such as ultrasound is generally required to reduce the time.

In conclusion, the presented single extraction protocols provide simplicity of the sample preparation by bypassing the complicated procedure of the standard method with comparable ion recovery rates, thus, possibly allow the field applicable sample pre-processing. The developed protocol will be implemented to a field applicable analytical system and validated in our future study.

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7. REFERENCES

- [1] Adriano DC. "Trace elements in the terrestrial environment" Springer Science & Business Media, 2001.
- [2] Smith SR. "A critical review of the bioavailability and impacts of heavy metals in municipal solid waste composts compared to sewage sludge", *Environment international*, Vol. 35, 2009, pp.142-156.
- [3] Nriagu JO. "A global assessment of natural sources of atmospheric trace metals", *Nature*, Vol. 338, 1989, pp.47-49.
- [4] Wuana RA, Okieimen FE. "Heavy metals in contaminated soils: a review of sources, chemistry, risks and best available strategies for remediation", *ISRN Ecology*, 2011.
- [5] Gleyzes C, Tellier S, Astruc M. "Fractionation studies of trace elements in contaminated soils and sediments: a review of sequential extraction procedures", *TrAC Trends in Analytical Chemistry*, Vol 21, 2002, pp.451-467.
- [6] Tessier A, Campbell PGC, Bisson M. "Sequential extraction procedure for the speciation of particulate trace metals", *Analytical chemistry*, vol. 51, 1979, pp. 844-851.
- [7] Quevauviller P. "Operationally defined extraction procedures for soil and sediment analysis I. Standardization", *TrAC Trends in Analytical Chemistry*, Vol. 17, 1998, pp.289-298.
- [8] Sahuquillo A, Rigol A, Rauret G. "Overview of the use of leaching/extraction tests for risk assessment of trace metals in contaminated soils and sediments", *TrAC Trends in Analytical Chemistry*, Vol. 22, 2003, pp.152-159.
- [9] Gu W, Zhou CY, Wong MK, Gan LM. "Orthogonal array design (OAD) for the optimization of mercury extraction from soils by dilute acid with microwave heating", *Talanta*, Vol. 46, 1998. pp.1019-1029.
- [10] Park JH, Lamb D, Paneerselvam P, et al. "Role of organic amendments on enhanced bioremediation of heavy metal (loid) contaminated soils", *Journal of hazardous materials*, Vol. 185, 2011, pp.549-574.
- [11] Pueyo M, Rauret G, Bacon JR, et al. "A new organic-rich soil reference material certified for its EDTA-and acetic acid-extractable contents of Cd, Cr, Cu, Ni, Pb and Zn, following collaboratively tested and harmonised procedures", *Journal of Environmental Monitoring*, Vol. 3, 2001, pp.238-242.
- [12] Elliott HA, Brown GA. "Comparative evaluation of NTA and EDTA for extractive decontamination of Pb-polluted soils", *Water, Air, and Soil Pollution*, Vol. 45, 1989, pp.361-369.
- [13] Elliott HA, Shastri NL. "Extractive Decontamination of Metal-Polluted Soils

- Using Oxalate", *Water, Air, and Soil Pollution*, Vol. 110, 1999, pp.335-346.
- [14] Heil DM, Samani Z, Hanson AT, Rudd B. "Remediation of Lead Contaminated Soil by EDTA. I. Batch and Column Studies", *Water, Air, and Soil Pollution*, Vol. 113, 1999, pp.77-95.
- [15] Katoh M, Masaki S, Sato T, "Single-Step Extraction to Determine Soluble Lead Levels in Soil", *Int. J. of GEOMATE*, Vol. 3, 2012, pp.375-380.
- [16] Moghal AAB, Al-Shamrani MA, Zahid WM, "Heavy Metal Desorption Studies On The Artificially Contaminated Al-Qatif Soil", *Int. J. of GEOMATE*, Vol. 8, 2015, pp.1323-1327.
- [17] Ashley K. "Ultrasonic extraction and field-portable anodic stripping voltammetry of lead from environmental samples", *Electroanalysis*, Vol. 7, 1995, pp.1189-1192.
- [18] De La Calle I, Cabaleiro N, Lavilla I, Bendicho C. "Ultrasound-assisted single extraction tests for rapid assessment of metal extractability from soils by total reflection X-ray fluorescence", *Journal of hazardous materials*, Vol. 260, pp.202-209.
- [19] Han Y, Kingston HM, Boylan HM, et al. "Speciation of mercury in soil and sediment by selective solvent and acid extraction", *Analytical and Bioanalytical Chemistry*, Vol. 375, 2003, pp.428-436.

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