

Analysis of arsenic in contaminated soil SRM by two extraction methods : Ultrasonic extraction method and Microwave extraction method

Youn-Tae Kim, Hyeon Yoon*, Mi-Young Shin*
Cheol-Ho Yoon*, Nam-Chil Woo

*Dep. of Earth System Sciences, Yonsei University, *Korea Basic Science Institute (yountae@kbsi.re.kr)*

Abstract

Two extraction techniques, Ultrasonic and Microwave extraction method, were tested for the determination of arsenic in contaminated soil SRM (Montana Soil). The extraction mixture was prepared by mixing 1 M ortho-phosphoric acid and 0.1 M ascorbic acid. This extractant was known to preserve arsenic species. The appropriate extraction time was 10 min to 20 min and the recovery rate was about 80%. A coupled system, SPE-HG-ICP-AES, was used for the determination of inorganic arsenic species. The detection limit was around 2 µg/l and the linearity of calibration curve was better than $R^2=0.99$.

key word : arsenic species, HG-ICP-AES, soil extraction method, recovery rate

1. Introduction

Arsenic can occur in many natural environments as consequences of mining activities and uses of arsenic containing pesticides and herbicides. Since arsenic is known to a carcinogen, it is critical to evaluate correct arsenic contents in contaminated soils. Arsenic has a various toxicity according to present species. Therefore, effective, accurate, and reproducible techniques for determination of arsenic are increasingly important as a consequence of the highly toxic nature of arsenic.

Ultrasonic and Microwave extraction methods have been widely used in many contaminated soil samples. However, the practical efficiency of two methods has not been compared with reliable certified Standard Reference Material (SRM) as well as with real samples. Therefore, in this study, we present the preliminary results to optimize the sample preparing procedure.

2. Method

Apparatus. A Sonic Dismembrator model 500 (117V, 50/60Hz, power 60%) and a MLS-1200 Mega microwave digestion system (MDR Tech, USA) were used for soil extraction. Total arsenic concentration for recovery rate was analysed using ICP-AES (Ultima 2C, Jobin Yvon), and HG-ICP-AES (138Ultrac, Jobin Yvon). A coupled system, SPE-HG-ICP-AES, was used for the determination of the arsenic species. For separation of arsenic species, QMA cartridge was used.

Reagents. A extractant was prepared from a mixture of 1.0 M sodium dihydrogen phosphate ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$) and 0.1 M L(+) ascorbic acid. Then, the solution was purged with Ar stream for 15 minutes. For hydride generation, 6 M HCl solution and 1.0% sodium borohydride (NaBH_4) in 0.1% NaOH solution were made and aged for 2 days. Mobile phase was 20 mM phosphate buffer solution at pH 6.5.

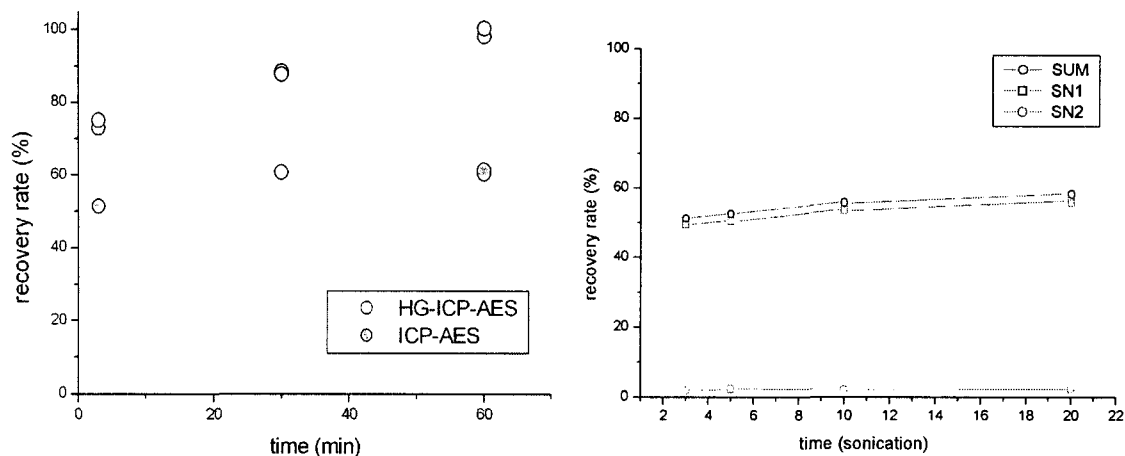
Standard Reference Material. SRM 2710(Montana soil) from NIST is a highly contaminated soil. The certified value of arsenic in SRM 2710 is 626 ± 38 mg/kg.

Procedure for the extraction of arsenic species. For ultrasonic extraction, 1.0 g of soil and 150 ml extractant were mixed in a glass beaker. Sonication times of sample were 3, 5, 10, 20, 30 and 60 min. For microwave extraction, 100 mg of soil and 15 ml extractant were mixed in a glass beaker. Times of extraction were 10, 20 and 30 min. After microwave extraction, samples were diluted up to 50.0 ml with deionized distilled water. When using both methods, sample condition was equivalent to ultrasonic extraction. Time series of samples which were done first ultrasonic extraction then microwave extraction were sonication 10 min + microwave 5 min, sonication 10 min + microwave 10 min, sonication 15 min + microwave 5 min and sonication 15 min + microwave 10 min. Time series of samples which were done ultrasonic extraction after microwave extraction were microwave 5 min + sonication 15 min and microwave 10 min + sonication 15 min. Samples were centrifuged (2800 rpm, 30 min) for filtering and solutions were kept at 4°C until analysis.

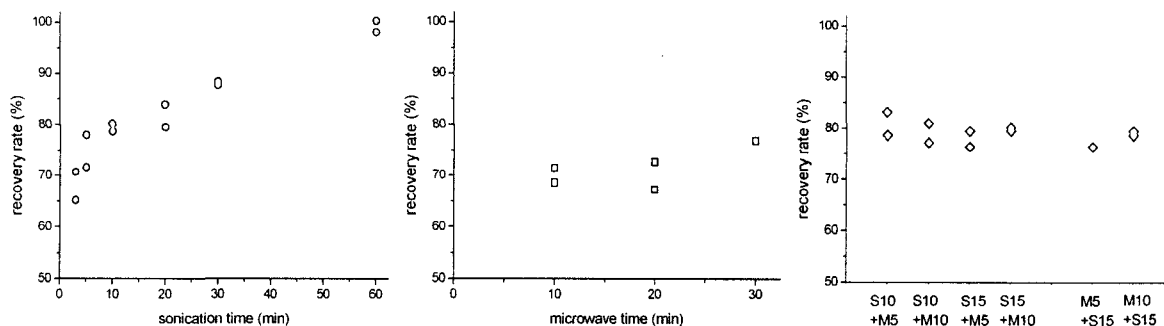
Measurement. Total arsenic concentration was measured by both ICP-AES and HG-ICP-AES. The efficiency of both techniques were compared in terms of recovery rate of total arsenic phase. Arsenic species were analysed by SPE-HG-ICP-MS. In the speciation analysis, the linearity of calibration curve was better than $R^2=0.99$ and a detection limit was around 2 µg/l.

3. Result

For the measurement of arsenic, we used two analytical methods, ICP-AES and HG(hydride generation)-ICP-AES because HG-ICP-AES could offer a lower detection limit than ICP-AES, and avoid the interference of salt in an extractant. The result of ICP-AES analysis showed much lower concentration than those of HG-ICP-AES analysis because of interferences. Therefore, we used the result analysed by HG-ICP-AES after dilution to calculate recovery rates. Two stage ultrasonic extraction didn't significantly improve the recovery efficiency.



The results from various time conditions in ultrasonic extraction method and microwave extraction method showed an improvement of recovery rate by time. The more it took, the more solution loss occurred. At the extraction time longer than 30 min, a significant loss happened resulting apparent extraction efficiency increased. Therefore we decided that the extraction time should not go over 30 min. As the extraction time went over 10 min, recovery rates of arsenic in SRM 2710 were similar, around 80%. To raise the efficiency of extraction, these two methods were combined, resulting stable recovery rates in various set-ups.



To estimate present arsenic species in the extractant, SPE-HG-ICP-AES was used. The calibration curve drawn from 5 $\mu\text{g/l}$ to 200 $\mu\text{g/l}$ and the linearity was better than $R^2=0.99$. The extractant of SRM 2710 was analysed, the result showed that As(V) was the present species.

4. Conclusion

Recovery rates of arsenic species in SRM 2710 were tested by different extraction methods. The appropriate time of extraction was 10 to 20 min. Extraction time over 30 min made solution loss by vaporization and under 10 min gave a low efficiency. The recovery rates extracted for 10 to 20 min were about 80%. SPE-HG-ICP-AES was used for the determination of the inorganic arsenic species. The detection limit was around 2 $\mu\text{g/l}$ and the linearity of calibration curve was better than $R^2=0.99$.

5. Reference

1. USEPA 1995, On-line Test method for evaluating solid waste. SW 846,
2. A. C. Joseph. and M. Montes-Bayon. Elemental speciation studies-new directions for trace metal analysis. *Ecotoxicology and Environmental Safty*. 56, 2003, 148-163.
3. S. Garcia-Manyes, G. Jimenez, A. Padro, R. Rubio, and G. Rauret. Arsenic speciation in contaminated soils. *Talanta*, 58, 2002, 97-109.
4. T. Chirenje, L. Q. Ma, M. Sazulczewski, R. Littell, K. M. Portier, and E. Zillioux. Arsenic Distribution in Florida Urban Soils: Comparison between Gainesville and Miami. *J. Envir. Quality*, 32, 2003, 109-119.
5. Y. Bohari, A. Astruc, M. Astruc, J. Cloud. Improvement of hydride generation for the speciation of arsenic in natural freshwater samples by HPLC-HG-AFS. *J. Anal. At. Spectrom*, 2001, 774-778.