

The Potential Use of Some Sampling/Preservation and Analysis Methods for Arsenic Speciation in Natural Waters

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ABSTRACT

The arsenic, the problematic toxic contaminant, has many chemical forms having different toxicities and mobilities. Among of these, inorganic arsenic species, arsenite [As(III)] and arsenate [As(V)], are dominant in a natural water. And some organic arsenic species like monomethylarsonate (MMA) and demethylarsinate (DMA) exist in a small fraction. It is well known that the toxicity of inorganic species As(III) are 3~5 times more toxic than As(V) while the toxicities of organic species are not yet clearly revealed. So, for an accurate risk assessment for arsenic, resolving the information about the arsenic species present in natural waters without causing changes in its electro-chemical state during preparation is essential.

Developing the analytical technique, separation of different species and detection to low concentration for commented species is desirable. However arsenic species can be transformed rapidly by slight changes in redox condition. Therefore sampling/preservation method which was applied is very important. Arsenic speciation methods are reported in many field, but mostly targeted on a measurement of inorganic species. Besides, the methods regarding organic species was only tested in a laboratory not until than recently it has been start to be applied in natural waters. For this application, we should know factors which can affect a stability of arsenic species at that circumstance. Arsenic speciation is controlled by iron, pH and redox potential.

The potential use of various analytical methods for sampling/preservation was tested for the groundwater and the surface water samples from two abandoned mines, Guryong and Ulsan, Korea. Various analytical methods were used to measure concentrations of total arsenic and arsenic species. The Guryong is Au-Ag-Cu mine having high iron content and low pH, and samples from the Guryong mine showed low arsenic concentrations. While, the Ulsan Fe mine is formed by a skarn deposit and has

considerable amount of arsenopyrite. Therefore, sample materials showed high arsenic concentrations with neutral pH. The total concentration of arsenic and arsenic species strongly affected according to the sampling/preservation methods which were applied in samples from two different sites.

In groundwater and acid mine drainage samples which have high iron content like ones from Guryong mine, the chemical reagent needs to prohibit the precipitation of iron. Phosphoric acid used to this purpose. When sample has high clay content, it was divided to two sub-samples, the one filtered then phosphoric acid added and the other by a reverse procedure. Samples were analyzed by HG-ICP-AES for total arsenic and by HG-SPE-ICP-MS for arsenic species. Hydride generation method was used to lower the detection limit and prevent matrix interference.

The groundwaters and surface waters from not only creek but also a pond and a spring has neutral pH like one from Ulsan mine, the chemical reagent is necessary for long period storage. Filtered sample in which reagent was not added maintained present arsenic species at least for 3 days. Then, samples were analyzed by ICP-AES (Ultima 2C, JY) for total arsenic and by HPLC (PRP X-100)-ICP-MS (Elan6100, Perkin Elmer) for arsenic speciation analysis.

The occurrence of precipitation strongly affected to total arsenic concentration. In raw samples unlike the preservative reagent added samples, arsenic was not detected. The sub-samples of clay rich groundwater showed very different pattern inferred an effect of sorption. In neutral samples, raw samples were not different to preserved samples at least for 3 days. Hydride generation method improves the detection limit but over- or under-estimate of total arsenic concentration can occur because of different hydride efficiencies by species. Using SPE is good for a measurement of inorganic arsenic species especially for AMD and using HPLC column for neutral water. Therefore site characters like pH and iron content are very important to decision making for selecting sampling/preservation and analysis method.

Key words: arsenic species, sampling/preservation methods, analytical methods, groundwater, surface water