Highly Sensitive Flow Analysis of Trace Level Arsenic in Water Based on Vaporization-collection In-line Preconcentration

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Vaporization-collection in-line preconcentration (VCIP) is proposed for simple and highly sensitive measurement of vaporizable water pollutants. In this work, VCIP has been applied to arsenic analysis to develop an instrument for use in the field. The signal is 200 times higher than with conventional direct injection. Low ppb levels of As can be analyzed automatically in one step. This method is expected to be applicable to the measurement of very low levels of other water vaporizable pollutants as well.

In natural water, many species are generally present at very low concentrations. This means that they are difficult to determine by conventional methods, even though they play important roles in mineral cycles of the natural water environment or have significant toxicity. Most of them are unstable and should be determined on-site. We developed a novel method to determine such species present at low levels, based on automatic vaporization and efficient vapor collection that could be performed in the field. It should be possible to determine vaporizable species such as NH_4^+, CN^-, S^{2-}, arsenite and arsenate by this method. In this work, the method has been applied to arsenic measurement.

Arsenic (As) is the inorganic contaminant of most concern in drinking and natural water. Water polluted with As can cause many serious diseases.[1] Most As pollution is from natural sources, so control of As contamination is almost impossible. Levels of As in drinking water at waterworks etc. need to be monitored routinely. In highly polluted areas, such as Bangladesh, well water can be checked by an As detection kit, especially for screening.[2] However, the World Health Organization (WHO) recently reduced the allowable level of As from 50 to 10 ppb.[3] Low levels of As close to this new level cannot be measured by the kit, nor by conventional direct measurement methods. Hence, As measurement usually requires troublesome preconcentration (e.g., coprecipitation with iron hydroxide[4]) or expensive laboratory instrumentation (e.g., ICP-MS). Trace level As is not stable in its speciation or even its total soluble content.[5] Hence, ideally samples are measured on-site, in the field. We developed an automatic system for highly sensitive measurement of As in water in the field.

The novel method proposed here is vaporization-collection in-line preconcentration (VCIP) coupled with flow analysis. The first step of VCIP is vaporization of the analyte to evacuate it from the solution into the gas phase. The As contained in a sample is completely released as the hydride, AsH_3. To obtain good reproducibility and efficient AsH_3 generation, relatively mild conditions were maintained for several minutes by adding a reducing agent at a constant rate with a small solenoid pump. The AsH_3 generated is forced out of the solution with the help of air bubbling. The second step is collection of the vapor in the gas phase with a diffusion scrubber (DS), into a very small volume of absorbing solution. We have developed a good DS for highly effective concentration of atmospheric trace gases,[6,7] and the same DS is used in this work. It is an annular DS with a very small porous tube made of polypropylene. In the final step, the collected As reacts with reagents in a flow system and its concentration is determined from its absorbance signal.

A flow diagram of the system is shown in Figure 1. Three kinds of solutions, namely $NaBH_4$ solution (0.66 M $NaBH_4$ + 0.1 M NaOH), absorbing solution (15 mM $KMnO_4$ + 10 mM NaOH), and reagent solution (10 mM $(NH_4)_6Mo_7O_{24}$ + 0.06 M ascorbic acid + 0.9 M H_2SO_4) were put in drip bags, BHB, ASB, and RSB, respectively. The absorbing solution and the reagent solution were both flowed at 0.2 mL/min using a small dual peristaltic pump. Twenty milliliters of sample was put in a generator together with 2.5 mL of 9 M HCl. When a start button, SS, was pushed, a solenoid pump, SP, carried the $NaBH_4$ solution at a constant rate of 2 mL/min. Concurrently, air went

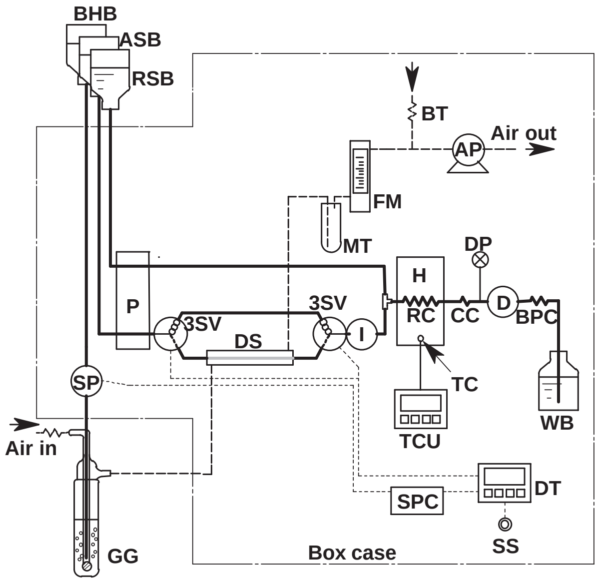

Figure 1. Flow diagram of VCIP As measurement system. BHB: $NaBH_4$ solution bag; ASB: absorbing solution bag; RSB: reagent solution bag; P: dual peristaltic pump; 3SV: three-way solenoid valve; DS: diffusion scrubber; I: 6-port sample injector; RC: reaction coil; H: heater; TC: thermistor; TCU: temperature control unit; CC: cooling coil; DP: debubble port; D: absorbance detector with LED and photodiode; BPC: back pressure coil; WB: waste bottle; SP: solenoid pump; GG: gas generator; MT: mist trap; FM: flow meter; BT: ballast tube; AP: air pump; DT: digital timer; SS: start switch; SPC: pulse generator for solenoid pump control.

through the generator. Arsenic was converted into AsH_3 in the generator and went through the DS. The $NaBH_4$ solution was introduced from a porous glass ball used for the air bubbling. The airflow helped introduction of the $NaBH_4$ solution and mixing of the $NaBH_4$ with the sample. The airflow also played an important role in taking the AsH_3 completely out of solution and into the gas phase, and in carrying the AsH_3 to the DS. In the collection, the airflow rate was important, because the collection efficiency, f, at the DS is flow rate dependent as shown by Gormley–Kennedy's equation.[8] Higher flow rates gave a lower f, and a very low flow rate did not carry all the AsH_3 to the DS. A flow rate of 50–70 mL/min was selected. AsH_3 was trapped in the absorbing solution as arsenate. After 5 min of AsH_3 generation, the solenoid pump and the bubbling through the generator were stopped automatically, and then the collected arsenic was introduced to the flow system by switching two 3-way solenoid valves. The collected arsenate reacted with Mo and ascorbic acid in a reaction coil heated at 70 °C. The resulting absorbance was measured with a homemade detector comprising a near-infrared LED (870 nm) and a photodiode. The generator was placed on the side of an aluminum box so that the sample procedure could be carried out easily. All other parts including a battery were incorporated in the box.

Total As was measured with a single generator/collector set. Figure 2 shows the response curves obtained for 0–50 ppb of As. The initial pH of the generator was 0. At this condition, both As(III) and As(V) were converted into AsH_3. The conversion from As(V) is slower, and usually prereduction is required before the vapor generation.[9] With a generation time of 2 min, only 50% of As(V) was converted, while the As(III) recovery was 100%. However, As(III) and (V) gave identical signals when the reaction time was 5 min. The continuous addition of $NaBH_4$ made perfect As(V) conversion possible. The correlation coefficient R^2 of the calibration curve from 0 to 50 ppb was 0.9976. After testing the generation/collection, 4 ppm As(V) was directly injected from the sample injector. The peak area obtained from this direct injection of 4 ppm As(V) was almost the same as that from the 20 ppb VCIP peak, even though the volumes injected into the flow were almost the same (85 and 98 μL for direct injection and VCIP, respectively). This shows that the VCIP gave a signal ca. 200 times greater than that from conventional FIA. The scale of the y axis in Figure 2b is 20 times that in Figure 2a, to show the responses to very low levels of As. As shown in Figure 2b, ppb or sub-ppb levels of As can be directly determined by VCIP. The limit of detection was estimated to be 0.18 ppb, from three times the standard deviation of the baseline signal.

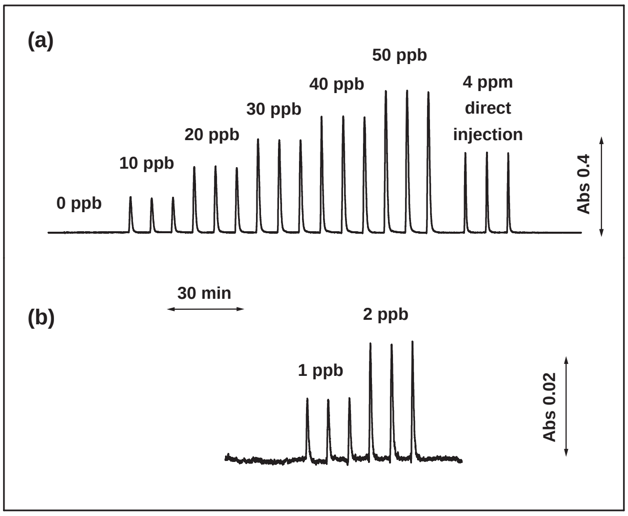

Figure 2. Response charts. (a) Standard solutions of 0–50 ppb As(III) were measured three times each by the VCIP method. After these measurements, 4 ppm As(V) was directly introduced from the injector. (b) Responses for low concentrations. The y axis is expanded to twenty times that of of panel (a).

In flow injection analysis (FIA), usually only several tens or hundreds of microliters of sample are injected into a flow system, so that the measurable range for As analysis is generally in the ppm or sub-ppm range. Some As FIA methods use conversion to AsH_3, where the gas diffuses through a membrane from one solution to another solution directly in "a gas-diffusion cell (GDC)"[10] or a pervaporation cell (PC).[11] The purpose of GDC and PC is selective measurement, these methods do not improve the sensitivity. A preconcentration column can be used to attain good sensitivity, but phosphate behaves similarly to arsenate, and this interference is a big concern. On the other hand, VCIP not only eliminates interference from phosphate but also increases the signal significantly.

Recovery was tested using natural water samples with standard addition of 10-ppb As, which is the new regulatory level. The recovery was 100 ± 2% for both As(III) and (V) for river water, well water and tap water. Though high level heavy metals would decrease the AsH_3 generation rate, there was no problem with total As analysis for any of the samples.

In conclusion, a novel method, VCIP, is proposed here, and it has been successfully applied to As measurement. VCIP is a simple and highly sensitive method, and it is expected to be applicable to any trace species in water that can be vaporized by acidification/alkalization or reduction.

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