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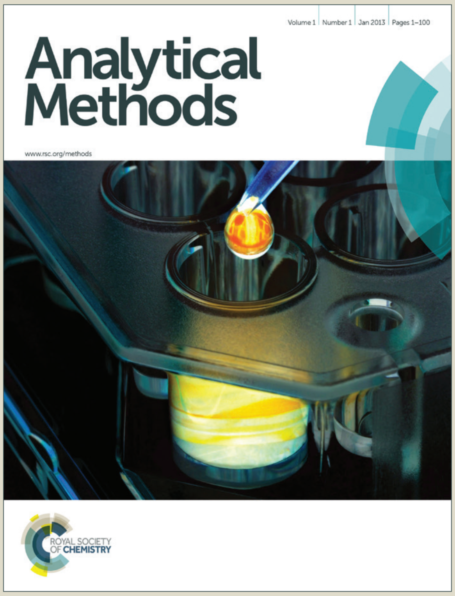

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PAPER

Visual colorimetry for trace arsenic in ground water based on improved molybdenum blue spectrophotometry

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A sensitive visual colorimetry was proposed for the on-site determination of arsenic in drinking water supplied from ground water. The method was based on an advanced molybdenum blue (MB) colorimetry combined with enrichment technique using membrane filter. A portable device equipped with two attachments of a $CaCO_3$-cartridge was used to eliminate interference from phosphate and a tiny membrane holder to retain the MB was proposed for on-site analysis. Ten mL of sample solution containing 0.1-0.4 μg arsenic was passed through the $CaCO_3$-cartridge. The arsenic in the sample solution was converted into MB and collected on a membrane filter as an ion-associate with a cationic surfactant. The arsenic was determined visually from the color intensity of the filter using color chart made from standard solution. The sensitivity is sufficient to detect the concentration of 10 μg L^{-1} adopted by the WHO standard. The speciation analysis for As(III) and As(V) was also successfully performed. The proposed method was applied to several ground water samples, and the analytical results were well comparable with those obtained by HG-AAS.

Introduction

Arsenic contamination of ground water used for drinking is still one of the critical issues for human health in many countries. For example, a large population of people living in Bangladesh and West Bengal, India are under the threat of consuming water contaminated with As.[1-3] Therefore, routine monitoring of As concentration in drinking water is essential for health safety reasons.

Arsenic in ground water exists mainly as inorganic arsenite (As(III)) and arsenate (As(V)). The speciation of arsenic as well as determination of total arsenic is important because the environmental behavior and toxicity of As(III) and As(V) are quite different. Arsenic(III) could be oxidized to As(V) during transportation and storage of the sample before analysis is performed in laboratory.[4] In order to avoid such a problem, an effective on-site analytical method that is simple, rapid, safe and cost-effective is necessary to specify As(III) and As(V).

Currently, field kits for arsenic determination are the most popular practice for on-site analysis. One of these methods is based on a colorimetric reaction of arsine produced by reducing arsenic in a sample with mercuric bromide permeated into a piece of paper.[5] Although this method is simple, rapid and selective, but it has the following problems. The determination limit of sensitivity and accuracy is not sufficient to determine arsenic at a lower concentration than 10 μg L^{-1} as recommended by WHO for the standard of drinking water. The lower accuracy of the method has been previously pointed out by Rahman *et al.*[6] This method is not considered safe because it generates toxic arsine gas. Hussam *et al.* suggested that field kits expose people to high level of arsenic.[7] Furthermore, the use of mercury in this method is also undesirable.

Several attempts involving molybdenum-loaded chelating resin, modified CdTe quantum dots, membrane filter (MF) impregnated with a chelating reagent or modified field kits have been performed to develop an advanced on-site method for arsenic.[8-14] However, more advanced method for on-site analysis of arsenic in ground water to satisfy simplicity, cost-effectiveness, sensitivity, selectivity, safety and speciation accuracy is required. Solid phase extraction of colored species on an MF has been applied to visual colorimetry of phosphate nickel, antimony(V), chromium(VI), manganese, formaldehyde and urinary protein.[15-21] These methods are based on collection of colored species through affinity to MF material and comparison of MF color with standard colors.

Molybdenum blue (MB) spectrophotometry based on the reaction of As(V) with molybdate is simple, rapid, cost-effective and free from mercury and arsine. In our previous work, we proposed an improved high sensitive MB spectrophotometry for arsenic where by the MB anion was collected on an MF as an ion-associate with a cationic surfactant and the MF was dissolved

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in a small volume of organic solvent.[22-24] In our current study, this MF collection technique combined with $CaCO_3$-column treatment was advanced to a visual colorimetry using small sample volume in a shorter time. A portable device equipped with two attachments of $CaCO_3$ packed cartridge and a tiny MF holder is proposed. The optimization of $CaCO_3$-cartridge to remove phosphate and selection of membrane materials were carried out. The interferences from other substances and the reliability of the proposed method were demonstrated. The analytical results for ground water samples were compared with those obtained by HG-AAS.

Experimental

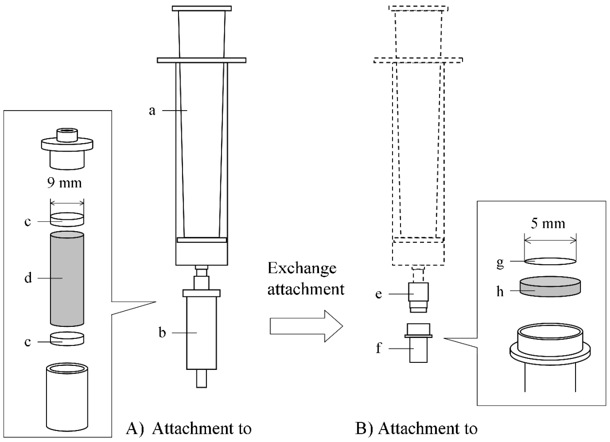
Reagents

The chemical conditions, such as concentrations of molybdate and hydrazinium sulfate added for color development, and C_{12}TMAB solution added as counter ion to the molybdenum blue anion, were the same as reported in previous studies.[22-24] Molybdate solution for As(V) was dissolved in 0.6 g of hexaammonium heptamolybdate tetrahydrate and 0.024 g of potassium antimonyl tartrate in a 50 mL of 2.9 M sulfuric acid. For the determination of total As, As(III) must be oxidized to As(V) in sulfuric acid solution before coloration. In that case, the concentration of the sulfuric acid dissolving molybdate should be 2.2 M. Hydrazinium sulfate solution was prepared by dissolving 0.135 g of hydrazinium sulfate in 10 mL of water. A mixed reagent was prepared from 5 mL of the ammonium molybdate solution and 1 mL of the hydrazinum sulfate solution, and used within 20 min. *n*-Dodecyltrimethylammonium bromide (C_{12}TMAB) solution was prepared by dissolving 0.2 g of C_{12}TMAB in 250 mL of water. The following procedure was carried out to remove the phosphate present as an impurity in this solution: add 2 mL of 6.5% aluminum chloride solution to the C_{12}TMAB solution, adjust the pH to 8.5 with aqueous ammonia, and after mixing the solution for 25 min, remove the aluminum hydroxide by filtration.[25] Calcium carbonate with particle size 12-15 µm was obtained from Kanto Chemical Co. All reagents used were of guaranteed grade.

Apparatus

A Canon model CanoScan 5000 scanner was used for reading standard colors into a computer. A commercial digital camera was used for shooting the image of sample after MF collection. A Varian model SpectrAA-55B with VGA-77 hydride generation-atomic absorption spectrometer (HG-AAS) was used for the determination of As in ground water samples.

A $CaCO_3$-cartridge was prepared by packing 0.5 g of calcium carbonate to a 2 mL polypropylene cartridge (13 mm in diameter, 49 mm in length) purchased from SUPELCO as shown in Fig. 1(A). For rapid operation, a smaller sample volume is desirable, therefore, 10 mL of sample volume was used in this method. In the case of colorimetry using membrane filtration technique, the filtration area is very important because it controls the sensitivity. An MF with 5 mm in diameter and MF holder with 4 mm in filtration diameter was adopted as shown in Fig. 1(B). The MF holder was connected to the syringe by hollow connector. The tiny MF holder and a hollow connector were provided by Kyoritsu Chemical-Check Lab. Corp.



A) Attachment to remove phosphate

B) Attachment to collect MB

Fig. 1 Proposed device and attachments. (A): Attachment to remove phosphate, (B): Attachment to collect molybdenum blue. a: polypropylene syringe; b: polypropylene cartridge; c: fritted disk; d: calcium carbonate powder; e: polypropylene hollow connector; f: membrane filter holder; g: membrane filter; h: sintered beads to support filter.

The $CaCO_3$-cartridge operation and the collection of ion-associate were carried out by connecting the cartridge or the MF holder to 25 mL polypropylene syringe purchased from HSW. Cellulose acetate and mixed cellulose ester MF (0.8 µm pore size, 5 mm diameter) were purchased from Advantec Toyo.

The outline of the proposed method

The flow which consists of three main procedures for As(III), total As (=As(III) plus As(V)) and modified procedure for the sample containing high level Fe are shown in Figure 2 to outline the method proposed in this study.

Treatment with $CaCO_3$ cartridge before color development

Ten milliliter of sample solution containing less than 0.05 µg of As(III) was placed into a beaker. One hundred microliter of 0.1 M calcium chloride solution was added to the sample solution. The solution was passed through the $CaCO_3$-cartridge to a syringe for the removal of P and As(V).

Visual colorimetry for As (III)

The $CaCO_3$-cartridge was taken off from the syringe and the MF holder was placed on it. Two hundred microliter of 2.5 M sulfuric acid was added to the sample solution in the syringe. The 0.3 % potassium permanganate solution was added until the solution became light pink. The solution was set aside for 2 min to oxidize As(III) to As(V). Nine hundred microliter of the mixed reagent was added to the solution. The solution was set aside for 15 min to form MB anion. One hundred microliter of the C_{12}TMAB solution was added to the sample to form ion-associate with the MB anion. The solution was passed through the MF to retain the ion-associate by inserting the syringe. Measuring of As(III) was carried out by comparing the sample color with standard color chart.

Visual colorimetry for As(III) plus As(V)

Two hundred microliter of 2.5 M sulfuric acid and 0.08 mL of 0.08 M sodium thiosulfate were added to 10 mL of sample

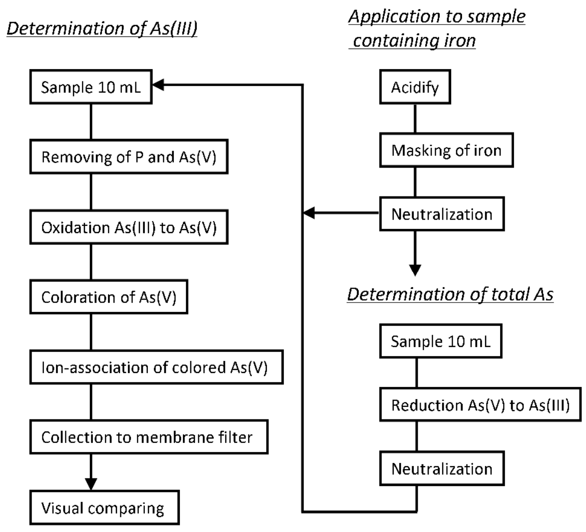


Fig. 2 Schematic flow diagram of the visual measurement procedure.

solution, and set aside for 15 min to reduce As(V) to As(III). Ammonia solution was added to neutralize the solution. The determination of the As (III) was carried out by the same procedure as described above.

Application to ground water containing iron at high concentration

When brown precipitate caused by the presence of iron was observed in the $CaCO_3$-cartridge, the following additional procedure was useful to eliminate the interference from iron. Acidified sample solution containing more than 0.05 µg of arsenic and less than 0.01 mg of iron was taken and diluted to 10 mL with pure water by adding 0.1 mL of Na_2HPO_4 solution containing 10 mg L^{-1} of P. The solution was neutralized with ammonia before cartridge operation.

Results and Discussion

Membrane filter

The most important thing in the MF-separation technique is the material constituting MF, because in most of the cases the affinity between the chemical species will be retained and MF material will greatly affect the collection efficiency. In our previous work, we reported that ion-associates are collected on MF by hydrophobic interaction besides electrostatic interaction between polar functional group of the MF material and ion-associate.[26] In this visual colorimetry, the color homogeneity of membrane filter retaining the MB is very important as well as quantitative collection of the MB. Therefore, the effect of MF materials on the color intensity and homogeneity was investigated. Figure 3 shows MFs after collection of 0.1 µg/10 mL of As(V) as an ion-associate with the MB and the cationic surfactant. The investigated MFs were made from mixing cellulose ester (0.8 µm, Advantec Toyo), cellulose acetate (0.8 µm, Advantec Toyo), polyethersulfone (0.8 µm, Advantec Toyo) and nylon 6,6 (1.2 µm, Pall Life Science). The MFs made from mixed cellulose ester and cellulose acetate produced almost the same color intensity. The polyethersulfone MF did not retain the ion-associate. The nylon 6,6 MF produced uneven color intensity on the MF. This is probably due to the polarity of the molecule constructing the MF material which affects the collection behavior. Mixed cellulose ester and cellulose acetate have polar sites on their molecules due to oxygen atom charged negative in nitro and acetate groups, whereas polyethersulfone does not have such site. Although nylon 6,6 has polarity due to amide group, it gave uneven color intensity of the MF. Therefore, this MF is not suitable in this method. The exact reason for such uneven color of the MF is unclear. However, mixed cellulose ester and cellulose acetate are equivalently usable in this method.

The optimization of the MF pore size for ion-associate collection was also investigated. The mixed cellulose ester filters (Advantec Toyo) with pore size 0.45, 0.8, 1, 3 and 5 µm were used for ion-associate obtained from 0.01 mg L^{-1} As(V). The color intensity of the MFs increased with decreasing their pore size. However, a very strong force was required to push out the solution from the syringe in the case of 0.45 µm. Therefore, 0.8 µm of the MF is recommend.

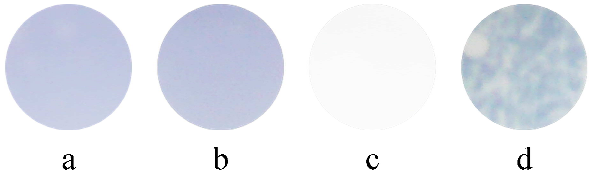


Fig. 3 Materials of membrane filter for the collection of the ion-associate of MB. a: mixed cellulose ester (0.8 µm, Advantec Toyo); b: cellulose acetate (0.8 µm, Advantec Toyo); c: polyethersulfone (0.8 µm, Advantec Toyo); d: nylon 6,6 (1.2 µm, Pall Life Science).

Standard colors

Figure 4 shows the MFs photographs taken after collecting 0-40 µg L^{-1} arsenic as MB. The color intensity increased with increasing the concentration of As with the rage tested in this experiment. It is obvious that 5 µg L^{-1} of As is detectable by this method. The precisions at various As concentrations will be described later. Since the color of MF retaining MB is stable for only 30 minutes, therefore the color standard was prepared by printing for convenience. The print out of the scanned color does not reveal the original color. Therefore, in overcome this the standard color chart was created using graphical software and only after that it was printed by a commercial printer.

Precision of the visual reading

Color intensity matching test was carried out to investigate the precision of the proposed method. Forty teachers and students volunteered to participate in this investigation. They matched the color intensity of a given MF with the standard color, and answered by matching the corresponding concentration. The arsenic concentrations used for the standard color chart were 0, 5, 10, 15, 20, 25, 30, 35, 40 and 50 µg L^{-1}.

Figure 5 shows the result of the matching test. The numbers in Fig. 5 are the number of persons for each matching results in 40 monitors. The numbers in parentheses are the percentage of frequency. In the case of 0 and 10 µg L^{-1}, the percentage of right answer was 90 %. And false answer ranged ± 5 µg L^{-1}. The limit

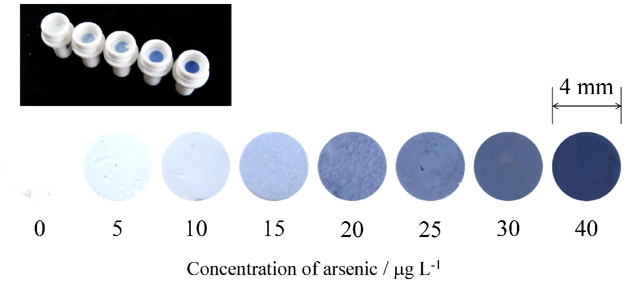


Fig. 4 Color variation of membrane filter obtained from different arsenic concentrations. The pore size of cellulose acetate membrane filter was 0.8 μm.

of detection based on three times the standard deviation obtained from reading results at 0 μg L^{-1} was ca. 5 μg L^{-1}. This clearly indicates that the method is useful for screening the threshold concentration of 10 μg L^{-1} adopted by the WHO standard. At higher concentrations than 30 μg L^{-1}, the As concentrations are slightly smaller than the prepared ones. In order to obtain an accurate result for a highly polluted sample, we recommend dilution with pure water before the procedure.

Interference from phosphate and iron

Phosphate forms MB anion under the same conditions as for As(V). We have proposed using $CaCO_3$ to remove phosphate in the presence of calcium ion.[22] In this study, the details of the performance of the $CaCO_3$ packed cartridge for 10 mL sample solution were investigated. Several samples of 10 mL containing 10 μg L^{-1} of As(V), 0.1 mg L^{-1} of P as Na_2HPO_4, and 1 mM $CaCl_2{\cdot}2H_2O$ were prepared. They were passed through a cartridges packed with various amounts of $CaCO_3$. A positive error due to phosphate was observed when 0.2 and 0.3 g of $CaCO_3$ was used. However, the interference from 0.1 mg L^{-1} of phosphate to determine 10 μg L^{-1} of arsenic was prevented by using more than 0.4 g of $CaCO_3$.

The arsenic-rich ground water in west Bengal is also heavily contaminated with Fe resulted from the dissolution of arsenopyrite (FeAsS).[27] The decrease of As(III) could be influenced from iron (II) and iron (III) which appears as brown precipitate on the surface of $CaCO_3$. Probably iron forms hydroxide and As(III) is eliminated by coprecipitation with the hydroxide on the surface of $CaCO_3$.[28]

The effect of phosphate added as masking reagents has been investigated to eliminate the interference from iron in our previous study.[22] For the visual determination of 10 μg L^{-1} of As(III) in 10 mL solution, the effect of phosphate on the masking of Fe added as iron(II) sulfate was demonstrated. Without phosphate, 1 mg L^{-1} Fe gave lower recovery of As(III). On the other hand, in the presence of 0.1 and 0.2 mg L^{-1} phosphate, 1 mg L^{-1} Fe did not cause any interferences. Probably, iron was removed as complex with phosphate, and the excess phosphate also adsorbed on the surface of the $CaCO_3$. More than 0.3 mg L^{-1} of phosphate produced positive error. This error was probably caused by the phosphate that exceeded the sorption ability of the $CaCO_3$. When iron exceeds 1 mg L^{-1}, dilution of the sample with pure water was effective to avoid the interference from Fe. This is due to the fast that in most cases, the levels of As and Fe in the ground waters were reported to be less than 100 μg L^{-1} and 10 mg L^{-1}, respectively.[29-31]

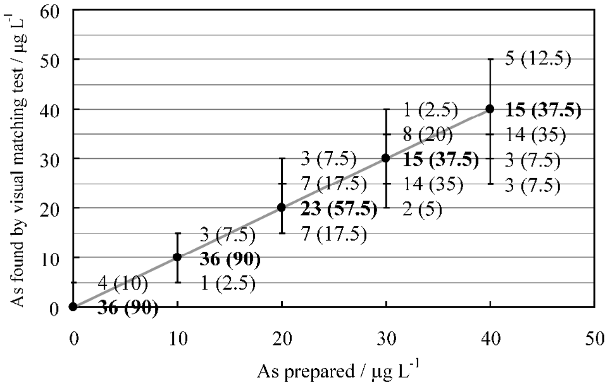


Fig. 5 Calibration and precision for the proposed method. The standard color series for visual matching test was made from 0, 5, 15, 20, 30, 35, 40 and 50 μg L^{-1} of arsenic. The numbers in the figure are the number of persons for each matching results in 40 monitors. The number in the parenthesis is the response rate % for the monitors.

Interferences from other ions

The interference from other ions on the determination of As was investigated. The concentrations of the foreign ions were set up to almost the same or higher as those in ground water sampled in Bengali.[32-33] The ions of Na^+ 1000 mg L^{-1}, K^+ 1000 mg L^{-1}, Ca^{2+} 200 mg L^{-1}, Mg^{2+} 100 mg L^{-1}, Mn^{2+} 100 mg L^{-1}, NH_4^+ 2700 mg L^{-1}, Cl^- 1550 mg L^{-1}, NO_3^- 226 mg L^{-1}, HCO_3^- 100 mg L^{-1} and SO_4^{2-} 4800 mg L^{-1} did not interfere with the determination of 10 μg L^{-1} As.

Silicate and germanium also form molybdenum blues. Fortunately, the conditions for silicate are quite different from those for As(V). Thirty mg L^{-1} of silicate (as SiO_2) did not interfere with the determination of As by the proposed method. In the case of germanium, the requisite concentration of molybdate for color development is six times higher than that employed in this study.[34] Furthermore, there were several reports stating the concentration level of germanium in ground water samples ranges from 10 ng L^{-1} to 10 μg L^{-1}.[35-37] Germanium is not likely to be present at high concentrations to interfere.

Application to ground water

The proposed method was applied to ground water samples collected at three points in Dhaka, Bangladesh and two other points in Toyama city, Japan. The samples at Dhaka were acidified to less than pH 2.0 with HCl and immediately after collection they were transported to Japan by maintaining the temperature at 4°C, and analyzed in our laboratory. The color intensity matching test was carried out by 15 people using standard color chart. Table 1 shows the analytical results for arsenic in ground water samples with and without addition of As, and those by HG-AAS. In the case of Dhaka 1 sample, the proposed method gave 0 and 5 μg L^{-1} of As(III) with 7 and 93% response rates, and 5, 10, 15 μg L^{-1} of total As with 7, 73, 20% response rates, respectively. On the other hand, HG-AAS gave

Table 1 Analytical results and recovery tests for arsenic in ground waters by the proposed method and HG-AAS.

Sample	As added As(III) /μg L^{-1}	As added Total As /μg L^{-1}	As found As(III) /μg L^{-1} (%)*	As found Total As /μg L^{-1} (%)*	HG-AAS Total As /μg L^{-1}
Dhaka 1	0		0 (7) 5 (93)	5 (7) 10 (73) 15 (20)	8.1 ± 0.2
Dhaka 2	0		15 (7) 20 (7) 25 (53) 30 (33)	25 (27) 30 (73)	34 ± 0.9
Dhaka 3	0		20 (7) 25 (33) 30 (60)	20 (7) 25 (47) 30 (47)	27 ± 1.7
Toyama 1	0		0 (100)	0 (80) 5 (20)	<0.3
	5	5	-	5 (7) 10 (93)	-
	10	0	5 (20) 10 (80)	-	
Toyama 2	0		0 (100)	0 (80) 5 (20)	<0.3
	5	5	-	5 (7) 10 (87) 15 (7)	-
	10	0	5 (13) 10 (80) 15 (7)	-	

* The number in parentheses is the response rate % for 15 persons answered.

8.1 μg L^{-1} of total As for the same sample. The proposed method produced well comparable result with that by HG-AAS for total As. Such results were also obtained for Dhaka 2 and Dhaka 3 samples by the proposed method. Incidentally, we have to note that the Dhaka samples were analyzed after transported to Japan, therefore, the results of speciation may not inform us exact original characteristics of the used samples. As in the case of Toyama, the results by HG-AAS were below the detection limit of 0.3 μg L^{-1} (3σ). The proposed method gave 0 μg L^{-1} with more than 80 % response rates for both samples. The recovery tests of added As by the proposed method were performed for the samples. Ten μg L^{-1} of As(III) was added for the As(III)-recovery test, and both 5 μg L^{-1} As(III) and 5 μg L^{-1} As(V) were added for the total As-recovery test. The recoveries of the spiked As(III) and total As were almost satisfactory for both samples. This indicates that foreign species in these samples did not interfere with the determination of As.

Conclusions

A sensitive visual method for on-site determination of trace As in ground water based on the MB colorimetry combined with MF concentration technique and $CaCO_3$-cartidge to eliminate interference species was proposed. The method was successfully applied to the ground waters collected in Toyama and Dhaka without interference from other substances. The proposed method is cost-effective because it only requires a portable device equipped two attachments of a $CaCO_3$-cartridge and a tiny membrane holder, and doesn't need any other detector devise. Another advantage of this method is that it's rapid. The time required for the entire procedure for As(III) from elimination of phosphate to visual analysis is twenty minutes whereas thirty five minutes for total As. The method also proves to be safe because there is no exposure to mercury and arsine. This method is useful for monitoring ground water, and also for on-site screening for arsenic.

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A sensitive on-site visual method for trace arsenic in ground water based on the molybdenum blue colorimetry combined with membrane filtration technique was developed.