

# A Visual Method for the Detection of Arsenic 0 to 500 µg/L

By Dan Kroll R&D Chemist. Hach Co., Loveland Colorado

## Introduction:

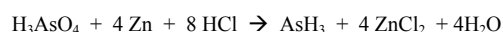
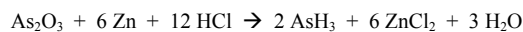
Arsenic is a common contaminant of ground water that has been found to adversely effect human health at levels as low as 10 µg/L. The current USEPA maximum contaminant level (MCL) for arsenic is 50 µg/L, however; the MCL is being considered for revision to between 5 and 20 µg/L. The current World Health Organization (WHO) recommended MCL for arsenic in drinking water is 10 µg/L. The quantification of trace amounts of arsenic in water samples has always been problematic. Current methods rely on expensive apparatus, complicated procedures, and dangerous chemical reagents. Lower cost test kit-type systems have been available in the past, but they only had a working range of 100 to 3000 µg/L, which is not sensitive enough to monitor drinking water supplies. The new Hach Arsenic Kit addresses many of the problems associated with other methods.

## Summary of the New Method:

Hydrogen sulfide is first oxidized to sulfate to prevent interference, and the oxidizing environment is then neutralized. Sulfamic acid and powdered zinc react to create strong reducing conditions in which inorganic arsenic is reduced to arsine gas (AsH<sub>3</sub>). The arsine gas then reacts with mercuric bromide impregnated test paper to form mixed arsenic/mercury halogenides (e.g. AsH<sub>2</sub>HgBr). These compounds discolor the test strip depending upon the concentration of the arsenic in the sample. The color change is from white to yellow to tan to brown.

## Reducing Chemical Hazards:

Most tests for arsenic, including the Hach method, rely on the conversion of arsenic to arsine gas.



The liberated arsine gas is then reacted with a detector paper that has been impregnated with mercuric bromide.

As the reaction above indicates arsine gas is commonly generated by reduction with zinc metal and hydrochloric acid. Hydrochloric acid is dangerous and difficult to work with. The Hach method substitutes a solid acid (sulfamic) packaged in a granular powder form for the hydrochloric. This alleviates the hazards and difficulties associated with using Liquid hydrochloric acid. The zinc powder and all other reagents in the Hach method are packaged in unit dose form for convenience and to minimize handling. The mercuric bromide test paper is on the end of a long plastic strip to eliminate the need to come into contact with the mercuric bromide.

Another concern in arsenic testing is the generation of toxic arsine gas. The unique design of the cap for Hach's reaction vessel focuses the arsine gas on a very small surface. The test strip is held in position so the generated arsine is forced to react with the test strip. A 0.5 x 0.5-inch mercuric bromide coated reaction pad is used as the indicator in the test, but the exposed hole is only 3/16 inch in diameter. This arrangement allows all of the generated gas to come into contact with the mercuric bromide and be reacted. The excess paper around the hole provides sufficient reactant to absorb all of the generated arsine. This increases the sensitivity of the test pad and at the same time reduces the exposure of the operator to arsine gas.

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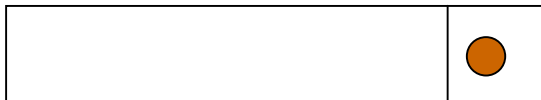
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### Reaction Vessel with Cap and Strip

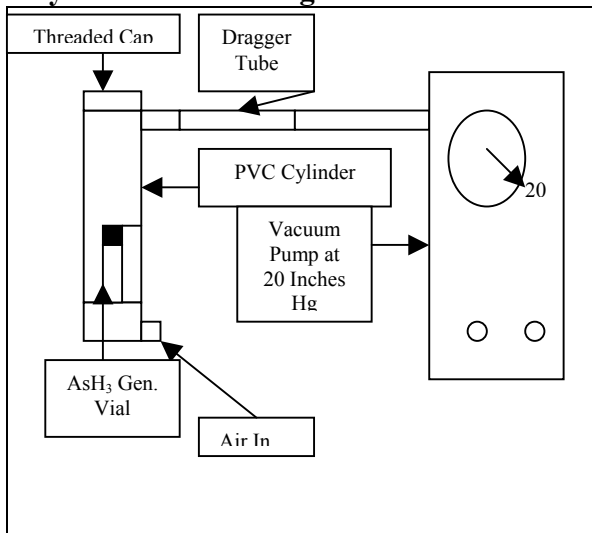


**Test strip exposed to 500  $\mu\text{g/L}$  arsenic**



To verify that arsine exposure is in fact minimized the following experiment was conducted. The ability of the Hach apparatus to absorb all of the arsine was compared to a currently available test kit. The system below was used to make the comparison.

### System for Checking Arsenic Emissions



The dragger tube is a detection system that is used to measure arsine in air. The length that a purple color travels up the tube quantifies the amount of arsine present. Samples containing 500  $\mu\text{g/L}$  arsenic were tested using both methods. The Hach method uses a 50 mL sample and the competitor uses a 5 mL sample. The vacuum pump was set at 20 inches of Hg and allowed to run continually for the full 30 minutes of each test. The results of the experiment are in the table below.

### Results of Arsine Exposure Test

Apparatus	mg/L $\text{AsH}_3$ after 30 min.
Competitor with no test strip	0.8 ppm
Competitor with test strip	0.3 ppm
Hach with no test strip	> 3.0 ppm
Hach with test strip	0.0 ppm

The new Hach apparatus does a good job of preventing release of arsine to the atmosphere where an operator could be exposed even though, as a whole it generates more arsine due to the larger sample volume.

### Improved Sensitivity:

The unique design of the cap for Hach's reaction vessel focuses the arsine gas on a very small surface. The test strip is held in position so the generated arsine is forced to react with the test strip before it can exit the reaction vessel. This combined with the large (50 mL) sample size allows for a calibrated range of 0 to 500  $\mu\text{g/L}$  (ppb). The calibration scale is graduated at 0, 10, 30, 50, 70, 300, and 500  $\mu\text{g/L}$ . Each step is distinct and allows for quantification at the levels needed to ensure health and safety standards.

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### Sulfide Interference:

Unfortunately, in the reduction of arsenic to arsine gas, sulfides are also reduced concurrently with the arsenic to form hydrogen sulfide (H<sub>2</sub>S). Hydrogen sulfide also reacts with the mercuric bromide test paper. The current methods of removing sulfide interference entail passing the arsine gas stream through a scrubber to remove the hydrogen sulfide. These scrubbers are usually cotton soaked in lead acetate solution (zinc and copper have also been utilized but have been found to be less efficient). The sulfide reacts with the lead on the cotton to form solid lead sulfide, thus effectively removing the sulfide contaminant from the arsine gas stream.

There are two major drawbacks to this method. First, it is difficult to ensure that a tight seal has been formed that will obligate the passage of all of the gas through the scrubber. The rate of gas evolution must also be controlled to allow adequate contact time for all of the sulfide to react. Secondly, the operator is forced to handle hazardous lead acetate and lead sulfide, and after the test is over, there remains the problem of disposing of these toxic materials.

Hach's new method eliminates the need to rely on hazardous lead acetate to remove sulfide interference. The patent pending Hach method employs the addition of 3 unit dose reagent pillows to convert the sulfide present in the sample to a form that will not interfere in the test. This is done without hazardous chemicals such as lead acetate.

First, sodium phosphate dibasic and potassium monopersulfate (Oxone®) are added to the sample. This results in formation of strong oxidizing conditions. Sulfides are oxidized under these conditions to sulfate in which form they no longer interfere with the arsenic test. Next a mixture of disodium and tetrasodium EDTA is added to the sam-

ple to remove any residual Oxone® that could interfere in the subsequent reduction and evolution of arsine gas.

Tests were run to determine the quantities of sulfide that could be tolerated by this method. A sulfide concentration was said to interfere if the color developed in the arsenic test exceeded more than ½ of the step between 0 and 10 µg/L arsenic on the color chart or approximately 5 µg/L arsenic.

Sulfide standards were prepared from sodium sulfide and their concentrations were verified on a Hach DR-4000 using Hach method # 8131 (Methylene Blue) and the instrument stored program for sulfide. Using 0.45-0.55 g of sodium phosphate, dibasic; 0.55-0.65g Oxone®, and 0.55-0.65 g of 1:1 tetrasodium EDTA/disodium EDTA. It was found that up to 5 mg/L S<sup>2-</sup> could be tolerated before the acceptance criteria of 5 µg/L arsenic equivalence was exceeded.

### Interferences:

Various substances likely to interfere with the method were evaluated using the same criteria as for sulfide (5µg/L As). The following were found to interfere at concentrations greater than those listed. At lower levels they do not interfere.

Ion or Substance	Concentration
Sulfide (S <sup>2-</sup> )	5 mg/L
Selenium (Se)	1 mg/L
Antimony (Sb)	0.25 mg/L
Tellurium (Te)	Likely to interfere, but not tested

The following did not interfere at the levels tested.

Ion or Substance	Level Tested
Hardness	1000 mg/L CaCO <sub>3</sub>
Alkalinity	1000 mg/L CaCO <sub>3</sub>
Iron (Fe)	10 mg/L
Temperature	10 to 40 degrees C

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### Organic Arsenic:

Organic arsenic represents a small proportion of the arsenic found in most systems, however, in some cases where anthropogenic sources of arsenic, such as pesticides are a factor, its contribution to the total arsenic present can be significant. Most tests are not designed to detect organic arsenic without complicated digestions and other manipulations. The instructions, as written, for this method are designed to detect inorganic arsenic. Organic arsenic compounds, such as dimethylarsenic acid, are not detected. To quantify total arsenic including organic arsenic with this method the following simple modification is needed.

Collect the sample in a glass beaker. Add the disodium phosphate and Oxone<sup>®</sup>. Place the beaker in a boiling water bath for 30 minutes. Remove the beaker from the water bath and transfer the contents to the reaction vessel. Allow the sample to cool to room temperature. Complete the rest of the procedure as for inorganic arsenic.

### Results for Various Organic Arsenics

Compound	500 µg/L Std	10 µg/L Std
Cacodylic acid (Dimethyl arsenic acid) C <sub>2</sub> H <sub>8</sub> AsO <sub>2</sub> Na	500	10
o-Arsanilic acid H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> AsO <sub>3</sub> H <sub>2</sub>	500	10
p-Arsanilic acid H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> AsO <sub>3</sub> H <sub>2</sub>	500	10
Arsenazo III C <sub>22</sub> H <sub>18</sub> N <sub>4</sub> O <sub>14</sub> S <sub>2</sub> As <sub>2</sub>	500	10

The results on all organic arsenics tested resulted in 100% recovery at both 10 and 500 µg/L As.

### Real World Samples:

Samples of bottled water from a variety of sources were tested and then spiked and re-tested. Samples that showed an initial arsenic level matched closely with levels reported for these products by the Natural Resource Defense Council (NRDC).

#### Bottled Water Results

Brand	Source	Initial Detected (µg/L)	With 10 µg/L Spike	NRDC Reported Value
Absopure	Plymouth, Michigan	0	10	Not Done
Perrier	France	0	10	0
S. Pellegrino	San Pellegrino, Italy	≈4	Slightly >10	5
Dannon	Henner Valley, Utah	0	10	0
Crystal Geyser	Olancho, California	10	>10	11,12,17
Fiji	Suva, Fiji Islands	≈4	Slightly >10	Not Done
Safeway	Granite County, Montana	0	10	0

Various well water samples obtained from Iowa, which contained large amounts of iron and organic material, were spiked and tested along with tap water from Iowa and Colorado.

#### Well and Tap Water Results

Source	Initial Detected (µg/L)	With 10 µg/L Spike
Well near Madrid, Iowa	Slightly < 10	> 10
Well near Ames, Iowa	0	10
Well near Kelley, Iowa	0	10
Ames, Iowa tap	0	10
Loveland, CO tap	0	10
Ft. Collins, CO tap	0	10

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**Conclusion:**

The method described offers a safe, easy and accurate method for determining arsenic levels in the low µg/L levels without expensive apparatus or equipment. With slight modification it is versatile enough to detect total arsenic including organic compounds.

It doesn't suffer from interference from sulfide like other common methods and has been shown to work on a variety of drinking and ground water samples.