



## BACKUP DATA REPORT NIOSH Method No. 6001

---

**Title:** Arsine

**Analyte:** Arsine

**Author/developer:** Developed under contract

**Date:** 1976

**Note:** Method 6001 is a combination of two older, previously published methods: S229 and P&CAM 265. Therefore, the backup data report is a combination of the two methods' reports. The backup data report for method S229 is a regular written report. The backup data report for P&CAM 265, however, is in the form of a published journal article.

The written report for S229 follows, the journal article for P&CAM can be seen [here](#) as a pdf.

**Disclaimer:** Mention of any company or product does not constitute endorsement by the National Institute for Occupational Safety and Health, Centers for Disease Control and Prevention. In addition, citations to websites external to NIOSH do not constitute NIOSH endorsement of the sponsoring organizations or their programs or products. Furthermore, NIOSH is not responsible for the content of these websites. All web addresses referenced in this document were accessible as of the publication date.

## Backup Data Report Method S229

Substance: Arsine  
OSHA Standard: 0.2 mg/m<sup>3</sup>  
Chemical Used: Arsine in Nitrogen (14 ppm), Linde Specialty Gases

### Procedure

The general procedure used is described in NIOSH Method 6001. The collection method has been adapted from P&CAM 127. The charcoal used was Lot 105 activated coconut charcoal supplied by SKC, Inc., Pittsburgh, PA. Desorption efficiency tests have not been carried out because the low concentration of the arsine source would require that large volumes of gas (200-800 ml) had to be injected directly into the charcoal tube. The arsine vapor samples were collected using the sample collection equipment described in the Butyl Acetate S47 Backup Data Report. The samples were desorbed in 10.0 ml of 0.01 M nitric acid with ultrasonic agitation for 10-15 minutes. The samples were then allowed to stand for one hour with occasional shaking. Tests indicate that this desorption period is sufficient for adequate desorption.

The samples were analyzed in a Perkin-Elmer Atomic Absorption Spectrophotometer, Model 503, equipped with a heated graphite atomizer, HGA Model 2100, and a Deuterium Background Corrector. A Hewlett Packard Recorder, Model 17501A was used. The source was an Electrodeless Discharge Lamp powered by a Perkin-Elmer EDL power supply. The arsenic absorption line at 193.7 nm was used for the assay.

With the aid of an Eppendorff automatic pipettor with disposable plastic tips, duplicate 50 microliter aliquots of the desorbed sample solutions were injected directly into selected graphite tubes. Argon was used as the inert gas stream flowing through the furnace. The furnace conditions were as follows:

**Table 6001-1.** Furnace conditions

Sample cycle	Time in seconds	Temperature (°C)
Sample drying	40	150
Sample charring	20	250
Sample atomization	10	2200

Peak areas of the absorption peaks, as determined using the Perkin-Elmer 503 integrator accessory, were used to determine the quantity of arsenic present in the sample. The analyses were carried out such that the samples were carefully alternated with standards of about the same response as the sample in order to minimize errors due to observed instrument response variations.

### Discussion

The development of an analytical and sampling method for arsine was initiated by testing the arsine evolution method using the Perkin-Elmer Arsine Generator and sodium borohydride as reducing agent; the atomic absorption was measured at 193.7 nm. The reproducibility of calibration standards was

studied from 0.1 to 1.0 µg of arsenic; poor precision was observed with a relative standard deviation of 15.6% over that concentration range. The precision was also tested for the 18-sample analytical set over a fourfold concentration interval by adding 0.2, 0.4, and 0.8 µg of arsenic as sodium arsenate into the generator. As shown in Table 6001-2, the observed poor precision does not favor the use of this method; the relative standard deviation was 9.7%.

**Table 6001-2.** Reproducibility of Calibration Standards (Arsine by arsine evolution using Perkin-Elmer arsine generator with AA at 193.7 nm)

µg added	µg found	Mean	Std dev	CV
0.2	0.21			
0.2	0.17			
0.2	0.24			
0.2	0.23			
0.2	0.22			
0.2	0.20	0.21	0.025	0.118
0.4	0.42			
0.4	0.40			
0.4	0.34			
0.4	0.44			
0.4	0.40			
0.4	0.42	0.40	0.034	0.086
0.8	0.84			
0.8	0.73			
0.8	0.79			
0.8	0.74			
0.8	0.82			
0.8	0.67	0.77	0.063	0.082

The alternative approach studied is the heated graphite atomizer (HGA) method for the analytical measurement of arsine; the absorbance at 193.7 nm was used. Initial analytical studies were done by considering both silver nitrate/impingers and charcoal tubes as viable routes for collection.

The HGA studies were initiated by testing the effect of silver nitrate concentration on the analytical scheme. It was observed that high concentrations of silver nitrate interferes with the assay because of the dense smoke formed during the ignition process, but a 0.01 M solution of silver nitrate was acceptable. Six analytical samples were prepared by adding 2 µg of arsenic (as sodium arsenate) into 10 ml of 0.01 M silver nitrate. This concentration is equivalent to a 10-liter sample at the OSHA standard level. Duplicate 50 µl aliquots of these six samples were analyzed by the HGA method. The data summarized in Table 6001-3 indicate that poor precision was obtained when peak height measurements were used, but the precision was improved considerably when some form of peak area measurement was used. The relative standard deviation was 0.293 for peak height determined concentrations but dropped to 0.033 when the planimeter-integrated areas were used.

**Table 6001-3.** Reproducibility of Calibration Standards (Arsine as arsenic by HGA; in 0.01M AgNO<sub>3</sub>; peak height vs peak area.)

µg added	µg found (peak height)	µg found (peak area) <sup>1</sup>
2.0	2.06	1.99
2.0	3.58	2.03
2.0	2.04	2.03
2.0	3.62	2.09
2.0	1.98	1.90
2.0	2.54	2.01
Mean	2.64	2.01
Std dev	0.77	0.066
CV <sub>1</sub>	0.293	0.033

1. Peak area determined by planimeter integration of areas of absorption peak. Recorder chart speed was run at fast mode i.e., 1"/sec.

Subsequent studies were done using the Model 503 integrator accessory in the 10-second integration mode; the peak width of the absorption peaks was 3-5 seconds. Five calibration solutions containing 6-44 µg As/10 ml (3-22 ng/50 µL) were analyzed repetitively six times and the observed relative standard deviation over this concentration interval was 2.7%

To test the precision of the method, eighteen samples were prepared by spiking 10 ml of 0.01 M silver nitrate with sodium arsenate containing arsenic equivalent to that present in a 10-liter sample at 0.5, 1, and 2X OSHA standard for arsine. The data summarized in Table 6001-4 show an average recovery of 99.5% with average CV<sub>1</sub>=0.065, indicating that the HGA method is acceptable.

**Table 6001-4.** Arsine\* (10 mL 0.01 M silver nitrate)

µg added	µg found	Recovery	Mean	Std dev	CV1
1.0	1.14	1.14			
1.0	1.84	1.84**			
1.0	0.90	0.90			
1.0	1.00	1.00			
1.0	0.92	0.92			
1.0	0.96	0.96	0.984	0.095	0.097
2.0	1.96	0.98			
2.0	1.80	0.90			
2.0	2.06	1.03			
2.0	2.02	1.01			
2.0	1.98	0.99			
2.0	1.94	0.97	0.980	0.045	0.046
4.0	3.92	0.980			
4.0	3.98	0.995			
4.0	3.84	0.960			
4.0	4.26	1.065			
4.0	4.32	1.080			
4.0	4.16	1.040	1.020	0.049	0.048

$$\overline{CV}_1 = 0.0651; \overline{CV}_{A+DE} = 0.0705$$

\*Samples spiked with sodium arsenate containing arsenic equivalent to 10 liters at 0.5, 1 and 2X OSHA standard for arsine.

\*\*These values excluded from statistical analysis

In order to determine the most suitable collection media, a "quick-screening" process was set up using a single stage, six outlet miniature generator to test a series of alternative collection media for arsine. The experimental results summarized in Table 6001-5 indicated that 0.1 M silver nitrate and charcoal could both be acceptable.

**Table 6001-5.** Comparison of various collection media for Arsine (test conc: 0.324 mg/m<sup>3</sup>)

Collection media	Flowrate (L/min)	% Recovery
0.01 M AgNO <sub>3</sub> /0.01 M HNO <sub>3</sub>	1.5	18
0.10 M AgNO <sub>3</sub> /0.01 M HNO <sub>3</sub>	1-1.5	75
0.1 M AgNO <sub>3</sub>	1-1.5	91
3% hydrogen peroxide	1	10
Charcoal	1	50 (front); 18 (backup)
Charcoal	0.2	93 (front); 0 (backup)

Further studies were conducted to evaluate both silver nitrate and charcoal for collection. The recommended method is collection on charcoal and desorption with 0.01 M nitric acid; the experimental data with silver nitrate is also presented, to indicate that the overall recovery with this method is low.

The collection efficiency in 10 ml of 0.1 M silver nitrate is 91%, as shown in Table 6001-6 for a 110-liter sample. The solutions were diluted to 100 ml with 0.01 M nitric acid prior to analysis to decrease the silver nitrate concentration to 0.01 M.

**Table 6001-6.** Collection efficiency of Arsine (0.1M silver nitrate/impingers; sample size of 110 L)

µg found (1 <sup>st</sup> impinger)	µg found (2 <sup>nd</sup> impinger)	Total	Collection efficiency
35.0	3.9	38.9	0.900
33.5	3.8	37.3	0.898
33.9	3.3	37.2	0.911
34.7	3.0	37.7	0.920
34.9	2.6	37.5	0.931
33.9	3.1	37.0	0.916

Avg collection efficiency=0.913; CV=0.014

Two sets of 18 samples were collected- one set was analyzed immediately while the other set was stored for six days. The experimental results tabulated in Tables 6001-7 and 6001-8 show an average recovery of 89% for the fresh samples and 86% for the stored samples with an average precision of 0.066 and 0.038 respectively. All data have been corrected for a desorption efficiency of 0.91.

**Table 6001-7** Sampling and Analysis (0.1M Silver Nitrate/Impingers, stored for 0 days)

µg found	Corrected µg found	Liters found	mg/m <sup>3</sup> found	mg/m <sup>3</sup> taken	Recovery	Mean	Std dev	CV <sub>2</sub>
7.80	8.57	111.3	0.0770	0.095				
8.63	9.48	109.5	0.0866	0.095				
9.05	9.95	109.5	0.0909	0.095				
9.46	10.40	111.1	0.0936	0.095				
8.53	9.37	110.4	0.0849	0.095				
8.22	9.03	109.9	0.0822	0.095	90.4	0.0859	0.0060	0.696
16.43	18.05	110.6	0.1632	0.201				
18.62	20.46	111.2	0.1840	0.201				
18.30	20.11	112.6	0.1786	0.201				
21.22	23.32	111.5	0.2091	0.201				
16.95	18.63	111.5	0.1671	0.201				
18.30	20.11	110.6	0.1818	0.201	89.9	0.1806	0.0162	0.0898
36.4	40.0	109.1	0.367	0.415				
34.8	38.2	108.8	0.351	0.415				
35.3	38.8	110.3	0.352	0.415				
36.1	39.7	110.8	0.358	0.415				
36.3	39.9	110.7	0.360	0.415				
35.2	38.7	109.5	0.353	0.415	86.0	0.357	0.0061	0.0171

**Table 6001-8** Sampling and Analysis (0.1M Silver Nitrate/Impingers, stored for 6 days)

µg found	Corrected µg found	Liters found	mg/m <sup>3</sup> found	mg/m <sup>3</sup> taken	Recovery	Mean	Std dev	CV <sub>2</sub>
7.86	8.64	111.4	0.0776	0.098				
7.92	8.70	109.7	0.0793	0.098				
7.80	8.57	109.7	0.0781	0.098				
7.68	8.44	111.2	0.0759	0.098				
8.69	9.55	110.6	0.0863	0.098				
8.36	9.19	110.1	0.0835	0.098	81.7	0.0801	0.0040	0.0495
18.11	19.90	110.8	0.1796	0.204				
18.18	19.98	111.3	0.1795	0.204				
17.46	19.19	112.8	0.1701	0.204				
18.75	20.60	111.6	0.1846	0.204				
18.06	19.85	111.6	0.1779	0.204				
16.83	18.49	110.8	0.1669	0.204	86.5	0.1764	0.0066	0.0375
28.5*	31.3*	109.3	0.286*	0.415				
37.0	40.7	108.9	0.374	0.415				
37.2	40.9	110.5	0.370	0.415				
37.2	40.9	110.9	0.369	0.415				
38.3	42.1	110.8	0.380	0.415				
36.2	39.8	109.7	0.363	0.415	89.4	0.371	0.0063	0.0169

\*These values excluded from statistical analysis

### Generation

The test atmosphere samples at 0.5, 1 and 2X OSHA standard were generated by delivering arsine from a gas cylinder via a needle valve into the vapor generation equipment described in the Butyl Acetate S47 Backup Data Report. The arsine source is a mixture of arsine in nitrogen with a manufacturer's reported concentration of 14 ppm. The arsine content of the tank was independently calibrated by using the silver diethyldithiocarbamate/pyridine method described in P&CAM 140 and also by collection in 0.1 M silver nitrate and analysis by HGA. In both cases, known volumes of arsine from the gas cylinder were collected directly into either of the two collection media referred to above; the volume of arsine gas collected was determined by water displacement. The determined arsine concentration of the gas cylinder by the silver diethyldithiocarbamate method and by the silver nitrate/HCA method was 16.5 ppm and 15.8 ppm respectively. The generator concentration was calculated on the basis of the silver nitrate/HCA assay because this method appeared to be more reliable than the silver diethyldithiocarbamate method. The latter method required the preparation of a calibration curve by generating arsine by the action of metallic zinc on trivalent arsenic and absorbing the arsine formed in the pyridine-silver diethyldithiocarbamate. The conversion of arsenic to arsine may not be complete and this introduces a bias in the assay of the arsine tank concentration.

Test atmosphere samples at a concentration two times the OSHA standard level were generated by delivering 40.8 mg/min (818 ml/min of 15.8 ppm arsine in nitrogen, at 27.6°C and 761 mm Hg) of arsine from a gas cylinder into a dry air stream flowing at a rate of 0.1011 m<sup>3</sup>/min. The three sample lines were maintained at dilution ratios of 0.233, 0.479 and 1.000 to produce the 0.5, 1 and 2X OSHA standard test levels. All six samples at the three test levels were collected simultaneously at 0.22 L/min for 45

minutes (10 liters). The data are summarized in Table 6001-9. The samples were stored for 6 days before desorption and analysis.

**Table 6001-9.** Sampling and Analysis (lot 105 charcoal, sample stored 6 days)

Test level	µg Found	Liters found	mg/m <sup>3</sup> found	mg/m <sup>3</sup> taken	Recovery	Mean	Std dev	CV <sub>2</sub>
0.5S	0.865	10.16	0.0851	0.0941				
0.5S	0.832	10.25	0.0812	0.0941				
0.5S	0.857	10.20	0.0840	0.0941				
0.5S	0.859	10.43	0.0824	0.0941				
0.5S	0.859	10.02	0.0857	0.0941				
0.5S	0.809	10.16	0.0796	0.0941	88.2	0.830	0.00236	0.0284
1S	1.957	10.25	0.1909	0.1935				
1S	1.907	10.20	0.1870	0.1935				
1S	1.917	10.43	0.1838	0.1935				
1S	1.857	10.25	0.1812	0.1935				
1S	1.936	10.25	0.1889	0.1935				
1S	1.956	10.25	0.1908	0.1935	96.7	0.1871	0.00393	0.0210
2S	4.16	10.16	0.409	0.404				
2S	3.99	10.25	0.389	0.404				
2S	4.07	10.66	0.382	0.404				
2S	4.05	10.25	0.395	0.404				
2S	3.94	10.25	0.384	0.404				
2S	3.93	10.20	0.385	0.404	96.8	0.391	0.0101	0.0258

### Breakthrough

The collection efficiency on charcoal was determined based on the analysis of the front and backup sections of the charcoal tubes for sampling periods of 45-240 minutes at 0.22 liters per minute. Data are summarized in Table 6001-10.

The first section of the charcoal tube was found to hold at least 0.022 mg of arsine when a test atmosphere containing 0.405 mg/m<sup>3</sup> of arsine in air was sampled at 0.227 L/min for 240 minutes; i.e., at that time the concentration of analyte in the effluent was less than 5% of that in the influent.



**Table 6001-10.** Collection efficiency\* of arsine (lot 105 charcoal, 0.22 L/min, 0.405 mg/m<sup>3</sup>)

Sample size (L)	Arsine found front	Arsine found backup	Total arsine found	% front
10.16	4.16	0.01	4.17	99.8
10.25	3.99	0.00	3.99	100
10.66	4.07	0.00	4.07	100
10.25	4.05	0.00	4.05	100
10.25	3.94	0.00	3.94	100
10.20	3.93	0.00	3.93	100
27.01	10.58	0.01	10.59	99.9
27.25	11.70	0.01	11.71	99.9
42.5	16.66	0.01	16.67	99.9
40.9	17.06	0.00	17.06	100.0
54.5	21.01	0.00	21.01	100.0
54.3	22.57	0.00	22.57	100.0

Overall collection efficiency=99.96%

\*all values have not been corrected for desorption efficiency

### Precision and Accuracy

The statistical procedures used are described in Reference 1.

$$\overline{CV}_2 = 0.0253 \quad \overline{CV}_T = 0.056$$

The average recovery of the generated samples over all levels was 93.9%.

Because the desorption efficiency was not determined as explained in the procedure section, the results should be corrected by this average recovery to reflect the undetermined desorption efficiency factor. The NIOSH Method 6001, however, was written with the usual protocol of determining desorption efficiency for the concentration range studied. The DE experiments can be done using a more concentrated arsine source, such as 15% in nitrogen. With a 15% arsine source, only 20-80 microliters of gas are needed to cover the 0.5, 1, and 2X OSHA standard and no complications are anticipated in directly injecting these small sample volumes into the charcoal tubes.

## References

1. Stanford Research Institute [1976]. Documentation of NIOSH Validation Tests. Menlo Park, CA: Stanford Research Institute, NIOSH Contract No. CDC-99-74-45.