

Determination of Particulate Arsenic in Air

1. INTRODUCTION

Arsenic compounds in environmental samples, have been measured in the past by variations of the Gutzeit procedure or the molybdenum blue method. Because the former procedure is not reproducible from one test run to another, much analytical effort is lost in the need for calibration of each run. The molybdenum blue method is seriously affected if the arsenic should not be pentavalent at the stage of color development. Serious errors are often occasioned by the interfering presence of oxidizing or reducing agents. The method of Vasak and Sedivec makes use of the arsine generation procedure, associated with the name Gutzeit. The arsine evolved is trapped in a silver organic reagent with stoichiometric replacement of the silver by arsenic (11.1). Dubois et al have worked out the optimum operating conditions for the method (11.2). The Vasak and Sedivec method, in various forms, is perhaps the most generally accepted method for arsenic and its compounds at present, being reliable, sensitive, accurate and fulfilling the requirements of a reference method (11.3).

There must be a clear understanding of the difficulties associated with the sampling of arsenic compounds, as found in air. Volatile compounds, such as arsine, will not be trapped on dry filter media. Particulate arsenic compounds, such as arsenic trioxide, have an appreciable volatility and this must be taken into account in any sampling procedure. Arsenic oxide, as a vapor in air, is in the form As_4O_6 and the saturated concentration at $25^\circ C$ is calculated to be 0.6 micrograms per cubic metre (11.4). If this equilibrium concentration is comparable to or higher than the amount of particulate As_2O_3 , collected on the filter, the filtration sampling procedure is unsatisfactory. Sample collection and arsenic analysis, based upon such collection, cannot be accurate. The low concentrations of "arsenic oxide" in air 0.01 to $1.0 \mu g/m^3$, reported by various monitoring networks, may well be indicative of poor collection efficiency (11.5).

The same remarks on sampling and volatility apply equally to compounds of mercury and selenium as well as the large number of polycyclic aromatic hydrocarbons found in air.

2. FIELD OF APPLICATION

The method is applicable to the measurement of arsenic compounds, as found in ambient air. The compound encountered most commonly is arsenic trioxide which may be in vapor or solid form, depending upon the concentration present and the temperature. The measuring range of the method is 1 to 15 micrograms of arsenic (As). As little as 0.1 micrograms per determination may be measured with accuracy.

3. PRINCIPLE

A prepared test sample containing the arsenic compound in aqueous solution is put through an arsine generation procedure, the arsenic evolved is trapped in a solution of silver diethyldithiocarbamate in pyridine. A pink to red color is developed in this reagent, the intensity being proportional to the amount of arsine reacting with the reagent. The absorbance is measured with a spectrophotometer and the amount of arsenic in the sample is read from the calibration curve (11.1, 11.2, 11.3).

4. REACTIONS

Arsenic or arsenic compounds, in the form of arsine, displace an equivalent amount of silver from silver diethyldithiocarbamate.

5. REAGENTS

5.1 *Silver diethyldithiocarbamate*

Reagent grade, very pale yellow in color. If yellowish brown, discard or purify by crystallization, at reduced temperature, in the absence of light.

5.2 *Pyridine*

Reagent grade. It is usually necessary to purify before use by passing through a column of activated alumina.

5.3 *Arsine absorbing solution*

Dissolve 0.5 gram silver diethyldithiocarbamate (5.1) in purified pyridine. Dilute with pyridine to final volume of 200ml. Store in an amber glass bottle, with ground stopper, in the refrigerator.

5.4 *Sulfuric acid*

Reagent grade, concentrated, low in arsenic.

5.5 *Hydrochloric acid*

Reagent grade, concentrated, low in arsenic.

5.6 *Potassium iodide 15%*

Dissolve 15 grams of reagent grade material in distilled water, making up solution to 100ml with distilled water.

5.7 *Stannous chloride 40%*

Dissolve 15 grams of reagent grade stannous chloride in 75ml of hydrochloric acid (5.5) making up solution to 100ml with concentrated hydrochloric acid.

5.8 *Zinc metal*

Granular, 20 mesh, low in arsenic.

5.9 *Lead acetate solution*

Dissolve 10 grams reagent grade lead acetate in distilled water and make up to 100ml with distilled water.

5.10 *Nitric acid*

Reagent grade, concentrated, low in arsenic.

5.11 *Sodium hydroxide 40%*

Dissolve 40 grams of reagent grade sodium hydroxide in distilled water and dilute to 100ml with distilled water.

5.12 *Sodium hydroxide 1%*

Dissolve 5 grams reagent grade sodium hydroxide in distilled water and dilute to 500ml with distilled water.

5.13 *Stock arsenic solution*

Dissolve 1.32 grams of reagent grade arsenic trioxide in 10ml of sodium hydroxide (5.13). Dilute to 1 litre with distilled water. One ml of this solution contains 1,000 micrograms arsenic, as the element.

5.14 *Standard arsenic solution A*

Dilute 10ml of arsenic solution (5.13) to 100ml with distilled water. 1ml = 100 μ g arsenic (As). Prepare fresh daily.

5.15 *Standard arsenic solution B*

Dilute 1ml of standard solution A (5.14) to 100ml with distilled water. 1ml = 1 μ g arsenic (As). Prepare fresh daily.

5.16 *Nonaq stopcock grease*

Water soluble stopcock grease. Available from Fisher Scientific Co., Pittsburgh, Pa.

6. APPARATUS

6.1 *Spectrophotometer*

Able to make measurements in the visible, between 500-600m.

6.2 *Arsine generation apparatus*

An assembly in three pieces, as described (11.2).

6.3 *Support rack*

The above (6.2) should be firmly supported by the neck of the generation flask. A convenient arrangement has been described (11.6). This permits the installation of a complete generation assembly at every four inches of fume hood frontage.

6.4 *Hydrogen sulfide absorbent*

The scrubber section of the glassware (6.2) should contain a *dry* absorbent which might be glass beads, or cotton balls which have been soaked in lead acetate solution and dried (5.9).

6.5 *Miscellaneous*

Reagent bottles, volumetric flasks, cuvettes, etc., as required.

7. SAMPLING AND SAMPLES

7.1 *Air sampling*

The collection of arsine is being excluded from consideration, because it is a gaseous compound associated with specific industrial processes. In volatile compounds of arsenic such as arsenopyrite, FeAsS_2 may be sampled on dry filter media by conventional methods. Special attention has to be given to the sampling of arsenic trioxide because of its volatility at sampling temperatures (11.4). If the temperature at the time of sampling is very low and if the concentration of arsenic in the air being sampled is very high, one may consider the use of dry filter media. As a general rule, it is better to take samples by impinger in dilute aqueous sodium hydroxide.

7.2 Preparation of test sample

Inspect impinger sample to ensure absorbing solution is colorless, transparent and free from turbidity or suspended matter. If amount of arsenic is known to be high, take an aliquot of suitably low volume. If concentration of arsenic is known to be low, it may be necessary to use the entire sample, evaporating carefully to 30ml or less so that all sample may be used.

8. PROCEDURE

8.1 Calibration curve

Prepare a series of arsenic standards in the range of 0.15 micrograms of arsenic, in 1 or 2 microgram intervals, by pipetting suitable volumes of the arsenic working standard B into 125ml Erlenmeyer flasks. Add sufficient distilled water to each flask to make a total liquid volume of 35ml. To each flask add 5ml concentrated hydrochloric acid (5.5), 2ml of potassium iodide solution and 8 drops stannous chloride solution. Swirl the flasks and allow to stand for 15 minutes to ensure reduction of all arsenic to the trivalent form. Place 3ml of the silver absorbing reagent in the receiver and attach to scrubber tube with clamp. Lubricate the ground glass joint with Nonaq stopcock grease or water, add 3 grams of granulated zinc to flask and quickly connect scrubber joint to flask. At room temperature, arsine evolution is completed in about 30 minutes. Transfer the absorbing solution to a 1cm cell and measure the absorbance at 560nm against the absorbing reagent as reference. Prepare calibration curve by plotting measured absorbance against micrograms of arsenic taken.

8.2 Air samples

Treated in the same manner as standards. Depending upon the analyst's knowledge of the sampling conditions, all or part of the sample may be taken for analysis. From previous experience with known amounts of arsenic, the analyst will be able to decide from the color of the absorbing solution, whether the sample (or aliquot) taken is within the range of the calibration curve. Smaller or larger aliquots may be taken and the determination repeated.

9. EXPRESSION OF RESULTS

If a 25ml aliquot of a 50ml prepared sample is taken for analysis and 3ml of absorbing solution has been used, the arsenic concentration, in milligrams element per cubic metre is:

$$\frac{\text{Micrograms arsenic from curve XZ}}{1,000 \times \text{volume air in m}^3}$$

10. NOTES ON PROCEDURE

10.1 *Collection efficiencies*

Little is known about collection efficiencies of arsenic trioxide on dry filter media. It is known that collection is incomplete and for this reason airborne particulates containing arsenic compounds should be sampled by impinger, in dilute acid or alkali solutions (11.5).

10.2 *Temperature and pressure*

The effect of these sampling variables has been largely disregarded in the past. Since these factors have an effect upon the accuracy of the measured air volume, it is recommended that these corrections be introduced routinely. There is increasing agreement, at the international level, that the standard conditions of temperature and pressure should be 25°C and 760mm Hg.

11. REFERENCES

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