Indian Standard (Reaffirmed 1999)

METHODS OF SAMPLING AND TEST (PHYSICAL AND CHEMICAL) FOR WATER AND WASTEWATER

PART 37 ARSENIC

(First Revision)

Water Sectional Committee, CDC 26; Panel for Methods of Test for Water, Wastewaters and Effluents, CDC 26 : P1 [Ref : Doc : CDC 26 (9308)]

1. Scope — Prescribes three methods for determination of arsenic. In the atomic absorption spectrometric method, arsenic is converted into its hydride and the atomized to gas phase atoms. The silver diethyl dithiocarbamate method is applicable when interferences are absent. Mercuric bromide stain method requires care and experience. The choice depends upon the accuracy required.

1.1 The silver diethyl dithiocarbamate method shall be the refree method.

2. Atomic Absorption Method

2.1 *Scope and Application* — Arsenic is converted into its volatile hydride by sodium borohydride reagent in acid solution. The hydride is purged continuously by argon or nitrogen into an appropriate atomizer of an atomic absorption spectrometer and converted to gas phase atoms. The sodium borohydride reducing agent, by rapid generation of elemental hydrides in an appropriate reaction cell, minimizes dilution of hydrides by the carrier gas and provides rapid, sensitive determination.

2.2 *Interferences* — Interferences are minimized because arsenic hydride is removed from solution containing most potential interfering substances. Slight response variations occur when acid matrices are varied. Treating the samples and standard in the same manner control this variations. Low concentrations of noble metals, copper, lead, nickel at or greater than 1 mg/l and hydride forming elements like bismuth, antimony, tin and telurium at concentrations between 0·1 and 1 mg/l may suppress the response of arsenic.

2.3 *Apparatus*

2.3.1 *Atomic absorption spectrometer* — Equipped with gas flow meters for argon (or nitrogen) and hydrogen, arsenic electrodeless discharge lamps with power supply background correction at measurement wavelengths and appropriate stripchart recorder.

2.3.2 *Atomizer* — Use one of the following:

a) Boiling-type burner head for argon (or nitrogen) air entrained-hydrogen flame.

b) Cylindrical quartz cell, 10 to 20 cm long electrically heated by external nichrome wire to 800-900°C.

c) Cylindrical quartz cell with internal fuel rich hydrogen-oxygen flame. The sensitivity of quartz cells deteriorates over several months of use. It may be restored by treatment with 40 percent hydrofluoric acid.

2.3.3 *Reaction cell for producing arsenic hydride* — Any commercially available system if it utilizes liquid sodium borohydride reagent, accepts samples digested in accordance with **2.5.3** to **2.5.5**; accepts 4 to 6 N hydrochloric acid; and is efficiently and precisely stirred by the purging gas and/or a magnetic stirrer.

2.3.3.1 *Eye dropper of syringe* — Capable of delivering 0·5 to 3·0 ml sodium borohydride reagent. Exact and reproducible addition is required so that production of hydrogen gas does not vary significantly between determinations.

2.4 *Reagents*

2.4.1 *Sodium borohydride reagent* — Dissolve 8 g sodium borohydride in 200 ml of 0·1 N sodium hydroxide solution. Prepare fresh daily.

2.4.2 *Sodium iodide pre-reductant solution* — Dissolve 50 g of sodium iodide in 500 ml water. Prepare fresh daily.

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2.4.3 *Sulphuric acid* — 18 N.

2.4.3.1 *Sulphuric acid* — 2·5 N.

2.4.4 *Potassium persulphate* — 5 percent solution. Dissolve 25 g of potassium persulphate in water and dilute to 500 ml. Store in glass and referigerate. Prepare weekly.

2.4.5 *Nitric acid* — Concentrated.

2.4.6 *Perchloric acid* — Concentrated.

2.4.7 *Hydrochloric acid* — Concentrated.

2.4.8 *Argon (or nitrogen)* — Commercial grade.

2.4.9 *Arsenic (III) solutions*

2.4.9.1 *Stock arsenic (III) solution* — Dissolve 1·320 g arsenic trioxide in water containing 4 g of sodium hydroxide. Dilute to 1 litre. 1 ml = 1·00 mg arsenic (III).

2.4.9.2 *Intermediate arsenic (III) solution* — Dilute 10 ml arsenic stock solution to 1 000 ml with water containing 5 ml concentrated hydrochloric acid 1·00 ml = 10·0 µg arsenic (III).

2.4.9.3 *Standard arsenic (III) solution* — Dilute 10 ml of intermediate arsenic (III) solution to 1000 ml with water containing the same concentration of acid used for sample preparation. 1·00 ml = 0·100 µg arsenic (III). Prepare diluted solutions daily.

2.4.10 *Arsenic (V) solutions*

2.4.10.1 *Stock arsenic (V) solution* — Dissolve 1·534 g arsenic pentaoxide in distilled water containing 4 g of sodium hydroxide. Dilute to 1 litre. 1·00 ml = 1·00 mg arsenic (V).

2.4.10.2 *Intermediate arsenic (V) solution* — *see* **2.4.9.2.** 1 ml = 10·0. µg arsenic (V).

2.4.10.3 *Standard arsenic (V) solution* — *see* **2.4.9.3.** 1 ml = 0·100 µg arsenic (V).

2.4.11 *Organic arsenic solutions*

2.4.11.1 *Stock organic arsenic solution* — Dissolve 1·842 g dimethyl arsenic acid (cacodylic acid) in water containing 4 g of sodium hydroxide. Dilute to 1 litre. 1 ml = 1·00 mg arsenic.

2.4.11.2 *Intermediate organic arsenic solution* — Prepare as given in **2.4.9.2.** 1 ml = 10·0 µg arsenic.

2.4.11.3 *Standard organic arsenic solution* — Prepare as given in **2.4.9.3.** 1·00 ml = 0·100 µg arsenic.

2.5 *Procedure*

2.5.1 *Setting up of apparatus* — Set up as given in Fig. 1 or according to manufacturer's instructions. Connect inlet of reaction cell with auxilary purging gas by flow meter. If a drying cell between the reaction cell and atomizer is necessary, use only anhydrous calcium chloride but not calcium sulphate. Before using the hydride generation/analysis, system, optimize operating parameters. Aspirate aqueous solutions of arsenic directly into the flame to facilitate atomizer alignment. Align quartz automizers for maximum absorbance. Establish purging gas flow, concentration and rate of addition of sodium borohydride reagent solution volume and rate of the stirring for optimum instrument response. If quartz atomizer is used, optimize cell temperature. The recommended wavelength is 193·7 nm for arsenic.

2.5.2 *Calibration* — Transfer 0·00, 1·00, 2·00, 5·00, 10·00, 15·00 and 20·00 ml standard solutions of arsenic (III) to 100 ml volumetric flasks and make up to mark with water containing same acid concentration used for sample preservation. This yields standard solutions of 0, 1, 2, 5, 10 and 20 µg arsenic.

2.5.3 *Preparation of samples and standards for total recoverable arsenic* — Add 50 ml sample or arsenic (III) standard to 200 ml beaker. Add 7 ml of 18 N sulphuric acid and 5 ml concentrated nitric acid. Add a small boiling chip of glass beads. Evaporate to sulphur trioxide fumes. Maintain oxidizing conditions at all times by adding small amounts of nitric acid. Maintain an excess of nitric acid until all organic matter is destroyed. Complete digestion usually as indicated by a light coloured solution. Cool slightly, add 25 ml water and 1 ml concentrated perchloric acid, and evaporate to fumes of sulphur trioxide to expel oxides of nitrogen. After final evaporation of sulphur trioxide fume, dilute to 50 ml.

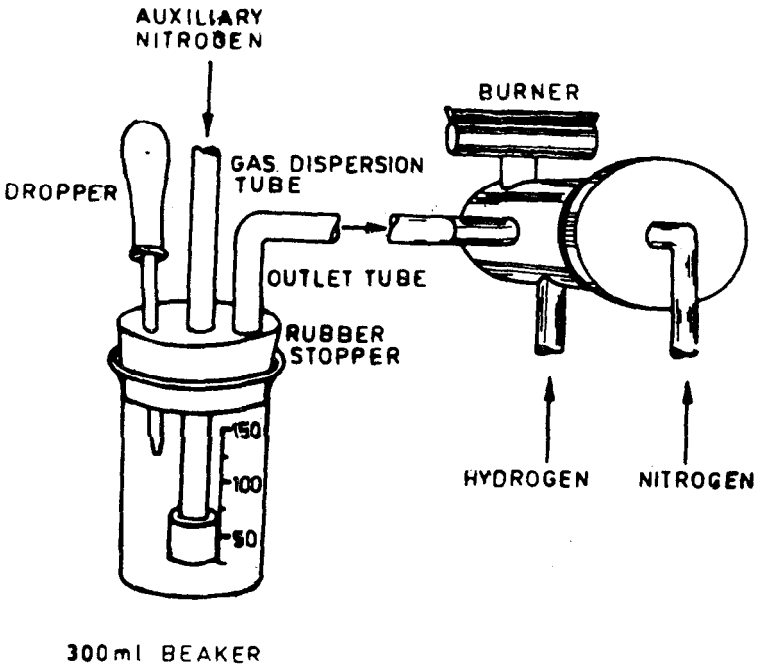

FIG. 1 REACTION CELL FOR PRODUCING ARSENIC HYDRIDE

2.5.4 *Preparation of samples and standards for total arsenic* — Add 50 ml sample or standard to 200 ml beaker. Add 1 ml of 2·50 N sulphuric acid and 5 ml of 5 percent potassium persulphate. Boil gently on a preheated hot plate for about 30 minutes or until the final volume is reduced to 10 ml. Do not let sample go to dryness. After manual digestion, dilute to 50 ml.

2.5.5 *Determination* — To 50 ml digested standard or sample in a 200 ml beaker, add 5 ml concentrated hydrochloric acid and mix. Add 5 ml of sodium iodide pre-reductant solution, mix and wait at least 30 minutes. Attach one beaker at a time to the rubber stopper containing the gas dispersion tube for the purging of gas, sodium borohydride reagent inlet and the outlet to the atomizer. Turn on strip chart recorder and wait until the base line is established by the purging gas and all is expelled from reaction cell. Add 0·5 ml of sodium borohydride reagent. After the instrument absorbance has reached a maximum and returned to the base line, remove beaker, rinse dispersion tube with water and proceed to next sample or standard. Periodically compare arsenic (III) and arsenic (V) curves for response consistency. Check for presence of chemical interferences that supress instrument response for arsenic by treating a digested sample with 10 µg/l arsenic (III) or arsenic (V) as appropriate. Average recoveries should be not less than 90 percent.

2.6 *Calculation* — Construct a standard curve by plotting peak heights of standards *versus* concentration of standards. Measure peak heights of samples and read concentrations from the curve. If sample was diluted before digestion, apply an appropriate factor.

3. Silver Diethyl Dithiocarbamate Method

3.1 *Scope and Application* — Inorganic arsenic is reduced to arsine by zinc in acid solution in an arsine generator. The arsine is then passed through scrubber containing glass wool impregnated with lead acetate solution and into an absorber tube containing silver diethyl dithiocarbamate dissolved in pyridine or chloroform. In the absorber, arsine reacts with silver salt forming a soluble red complex suitable for spectrophotometric measurement.

3.2 *Interference* — Certain metals like chromium, cobalt, copper, mercury nickel, potassium and silver interfere in the generation of arsine. The concentration of these metals normally present in water and wastewaters do not interfere significantly. Antimony salt interferes with colour developments.

3.2.1 The minimum detectable quantity is 1 µg of arsenic.

3.3 *Apparatus*

3.3.1 *Arsine generator and absorption tube* — *See* Fig. 2.

3.3.2 *Spectrophotometer* — For use at 535 nm with 1 cm cells.

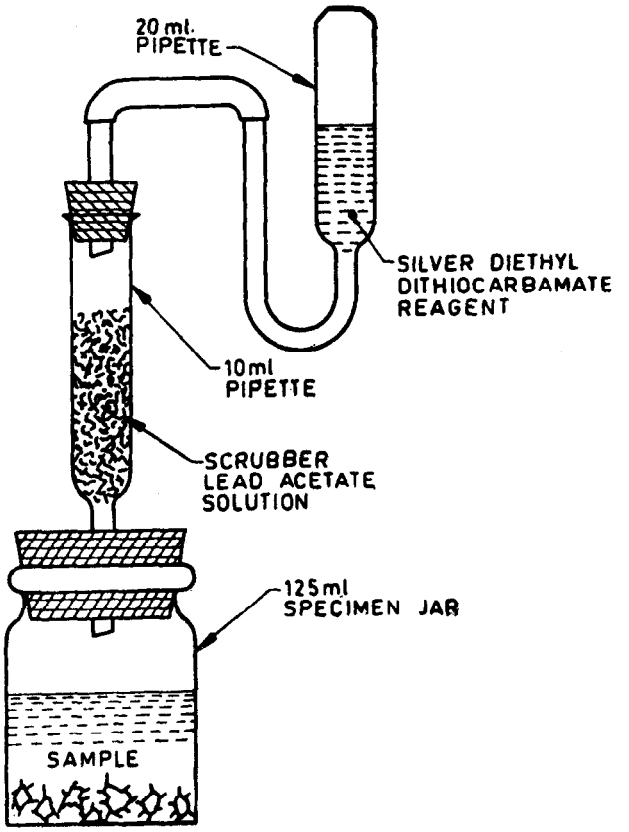

FIG. 2 ARSINE GENERATOR AND ABSORBER ASSEMBLY

3.4 *Reagents*

3.4.1 *Hydrochloric acid* — concentrated.

3.4.2 *Potassium iodide solution* — Dissolve 15 g of potassium iodide in 100 ml distilled water. Store in a brown bottle.

3.4.3 *Stannous chloride solution* — Dissolve 40 g arsenic free stannous chloride ($SnCl_2.2H_2O$) in 100 ml concentrated hydrochloric acid.

3.4.4 *Lead acetate solution* — Dissolve 10 g of lead acetate [$Pb(C_2H_3O_2)_2.3H_2O$] in 100 ml distilled water.

3.4.5 *Silver diethyl dithiocarbamate reagent* — Dissolve 410 mg of 1 ephedrine in 200 ml chloroform, add 625 mg of silver diethyl dithiocarbamate and adjust volume to 250 ml with additional chloroform. Filter and store in brown bottle. Alternatively dissolve 1 g of silver diethyl dithiocarbamate in 200 ml of pyridine. Store in brown bottle.

3.4.6 *Zinc* — 20 to 30 mesh, arsenic free.

3.4.7 *Stock arsenic solution* — Dissolve 1·320 g arsenic trioxide in 10 ml distilled water containing 4 g of sodium hydroxide and dilute to 1 000 ml with distilled water. 1·00 ml = 1·00 mg arsenic.

3.4.7.1 *Intermediate arsenic solution* — Dilute 5 ml of stock solution to 500 ml with distilled water. 1·00 ml = 1·00 µg arsenic.

3.4.7.2 *Standard arsenic solution* — Dilute 10·00 ml intermediate solution to 100 ml with distilled water. 1·00 ml = 1·00 µg arsenic.

3.5 *Procedure*

3.5.1 Pipette 35·0 ml of sample into a clean generator bottle. Add successively with thorough mixing after each addition, 5 ml concentrated hydrochloric acid, 2 ml potassium iodide solution and 8 drops of stannous chloride. Allow 15 minutes for reduction of arsenic to the trivalent state.

3.5.2 *Preparation of scrubber and absorber* — Impregnate glass wool in the scrubber with lead acetate solution. Do not make too wet because water will be carried over into the reagent solution. Pipette 4·00 ml of silver diethyl dithiocarbamate reagent into absorber tubes.

3.5.3 *Arsine generation and measurement* — Add 3 g of zinc to generator and connect scrubber-absorber assembly immediately. Make sure that all connections are fitted tightly. Allow 30 minutes for complete evaluation of arsine. Warm the generator slightly to ensure that all arsine is released. Pour solution from absorber directly into 1 cm cell and measure absorbance at 535 nm, using reagent blank as reference.

3.5.4 Treat portions of standard solutions containing 0, 1, 2, 5, 10 µg arsenic as above. Plot absorbance *versus* concentration of arsenic in the standard.

3.6 *Calculation*

$$\text{Arsenic, mg/l} = \frac{M}{V}$$

where

M = mass in µg of arsenic in 4·00 ml of final solution, and

V = volume in ml of sample.

4. Mercuric Bromide Stain Method

4.1 *Scope and Application* — After sample concentration, arsenic is liberated as arsine by zinc in acid solution in arsine generator. The generated arsine is passed through a column containing a roll of cotton moistened with lead acetate solution. The generated arsine produces a yellow-brown stain on test paper strips impregnated with mercuric bromide. The length of the stain is roughly proportional to the amount of arsine present. This method requires care and experience and is suitable only for qualitative or semi-quantitative determinations.

4.1.1 *Interferences* — Antimony (> 0·10 mg) interferes.

4.1.1.1 *Minimum detectable quality* — 1 µg of arsenic.

4.2 *Apparatus*

4.2.1 *Arsine generator* — *See* Fig. 3.

4.3 *Reagents*

4.3.1 *Sulphuric acid* — 1 : 1.

4.3.2 *Nitric acid* — Concentrated.

4.3.3 *Roll cotton* — Cut a roll of dentist's cotton into 25 mm lengths.

4.3.4 *Lead acetate solution* — Prepare as prescribed in **3.4.4**.

4.3.5 *Mercuric bromide paper* — Use commercially available arsenic papers. Cut uniformly into strips about 12 cm long and 2·5 mm wide. Soak strips for at least 1 h in filtered solution prepared by dissolving 3 to 6 g of mercuric bromide in 100 ml of 95 percent ethyl or *iso*propyl alcohol; dry by waving in air. Store in dry, dark place. For best results, prepare papers just before use.

4.3.6 *Potassium iodide solution* — Prepare as given in **3.4.2**.

4.3.7 *Stannous chloride reagent* — Prepare as given in **3.4.3**.

4.3.8 *Zinc* — 20 to 30 mesh, arsenic free.

4.3.9 *Standard arsenic solution* — Prepare as given in **3.4.7.2**.

4.4 *Procedure*

4.4.1 Place suitable sample containing 2 to 30 µg of arsenic in a flask or beaker, add 7 ml of 1 : 1 sulphuric acid and 5 ml concentrated nitric acid. Evaporate to sulphur trioxide fumes. Cool, add about 25 ml distilled water, and again evaporate to sulphur trioxide fumes to expel oxides of nitrogen. Maintain an excess of nitric acid until the organic matter is destroyed. Cool, add about 25 ml of water and transfer to generator.

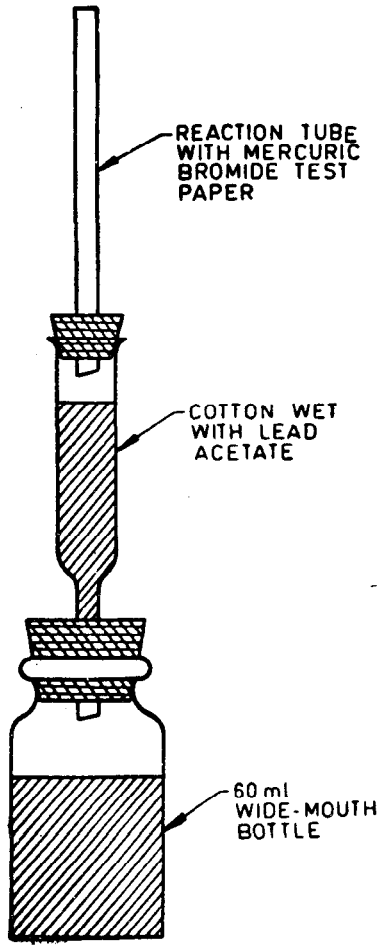

FIG. 3 GENERATOR USED WITH MERCURIC BROMIDE STAIN METHOD

Dip one end of the 2·5 cm length of cotton into lead acetate solution and introduce into glass columns. Then put the dried narrow glass tube in place and insert mercuric bromide test paper. Make sure paper strip is straight.

To the 25 ml sample concentrate in generator, add 7 ml of 1 : 1 sulphuric acid and cool. Add 5 ml of potassium iodide solution, 4 drops of stannous chloride reagent and 2 to 5 g of zinc, immediately connect reaction tube to generator. Immerse the apparatus to within 2·5 cm of the top of the narrow tube in a water bath kept at 20 to 25°C and allow the evolution to proceed for 1½ hours. Remove strip and compute average lengths of stains on both the sides. Using a calibration curve, the preparation of which is given in **4.4.1.1**, estimate the amount of arsenic.

4.4.1.1 Prepare a blank and standards at 3 µg intervals in the range of 0 to 30 µg arsenic with 14 ml of 1 : 1 sulphuric acid and bring total volume to 25 ml. Place in generator and treat as prescribed for sample concentrate in **4.4.1**. Remove strip and compute average lengths in mm of stains on both sides. Plot length in millimetres against micrograms arsenic and use as a standard curve.

EXPLANATORY NOTE

Arsenic may occur in water as a result of mineral dissolution, industrial discharges or application of insecticides. Severe poisoning can arise from ingestion of as little as 100 mg of arsenic. The arsenic concentration on most potable waters seldom exceeds 0·01 mg/l. This standard supersedes **40** of IS ; 3025-1964 ' Methods of sampling and test (physical and chemical) for water used in industry ' and **7** of IS : 2488 (Part 2)-1968 ' Methods of sampling and test for industrial effluents, Part 2 '. In the preparation of this standard, considerable assistance has been derived from Standard Methods for the Examination of Water and Wastewater; published by the American Public Health Association, Washington, U.S.A. 16th edition, 1985.