Spectrophotometric Microdetermination of Arsenic in Natural Waters and its Application to Silicate and Biological Materials

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Introduction

Ordinary natural waters are usually very poor in arsenic. As shown later, well water on the Higashiyama campus of Nagoya University contains only 0.4 μg./l. of this element and the sea water off Sugashima Island in Ise Bay contains 1.8 μg./l. For determining arsenic in such dilution, various methods[1,2,3] already proposed are not satisfactory. Some are liable to be contaminated, thus causing a considerable error while others are of low sensitivity. The neutron activation method by Smales and Pate[4] which boasts the highest sensitivity is usable only to those to whom a nuclear reactor is accessible.

After considering these points and closely examining the merits and defects of the current methods, the writers finally succeeded in establishing the following time-saving method fulfilling every requirement for water analysis with fair accuracy.

Our method consists of five steps; (a) coprecipitation with ferric hydroxide, (b) mineralization of the filtered precipitate, (c) extraction of arsenic xanthate by carbon tetrachloride, (d) oxidation of the xanthate into quinque-valent arsenic followed by extraction by water, and (e) final spectrophotometry of the extracted element as molybdenum blue.

Thus, usually using 3 l. of the sample, 2 μg. of arsenic can be safely determined with an error of only 5%. With appropriate pretreatment, the method is also applicable to silicate and biological materials.

Experimental

Reagents.—*Ferric Chloride.*—4.84 g. of arsenic-free ferric chloride ($FeCl_3 \cdot 6aq.$) is dissolved in 25 ml. of sulfuric acid and diluted to 100 ml. This solution contains 10 mg. of iron per ml.

Bromcresol Purple.—0.1% W/V solution.

Ammonia (1 : 3).—Reagent quality.

Nitric acid.—Reagent quality, freshly distilled.

Sulfuric acid.—Reagent quality, arsenic free.

Potassium iodide.—25% W/V solution.

Sodium thiosulfate.—5% W/V solution.

Carbon tetrachloride.—Reagent quality.

Potassium xanthate.—0.1% W/V solution, reagent quality.

Carbon tetrachloride containing bromine (1 : 25).—One part of bromine is mixed with 25 parts of carbon tetrachloride.

Sulfuric acid (1 : 9).

Ammonium molybdate.—2% W/V solution, reagent quality.

Hydrazine sulfate.—0.1% W/V solution, reagent quality.

Arsenic standard solution.—0.132 g. of arsenous oxide is dissolved in 2 ml. of 1 N sodium hydroxide solution, slightly acidified with dilute sulfuric acid, and diluted to 100 ml. This solution contains 1.00 mg. of arsenic per ml. A working standard solution is prepared by adequately diluting this solution.

Apparata.—Automatic Filtering Apparatus (Fig. 1).—This apparatus consists of three parts: a funnel (A), its receptacle (B), and a siphon (C).

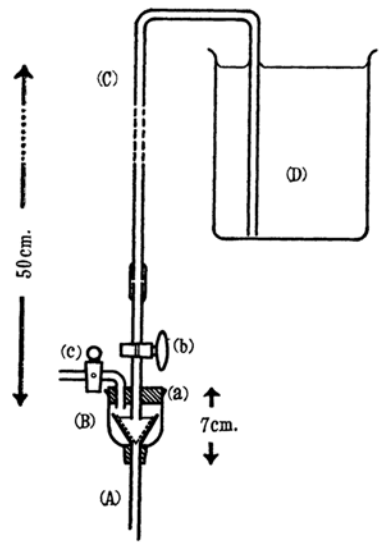

Fig. 1. Automatic filtering apparatus.

The funnel with a filter paper is fixed in the receptacle. A rubber stopper (a) with two leading tubes (b and c) is then tightly fixed into the mouth of the receptacle and the upper end of tube (b) is connected to the end of one of the arms of the siphon. Filteration is carried out as follows: Cocks (b and c) are opend and lips are placed to the end of tube (c) to gently suck,

1) R. Pieruccini, *Spectrochim. Acta*, **4**, 189-99 (1950).
2) M. Ishibashi, T. Shigematsu, Y. Nakagawa and Y. Ishibashi, *Bull. Inst. Chem. Research Kyoto Univ.*, **24**, 68 (1951).
3) A.K. Klein and F.A. Vorhes, Jr., *Assoc. Offic. Agr. Chemists*, **23**, 121-30 (1939).
4) A.A. Smales and B.D. Pate, *Analyst*, **77**, 188-95 (1952).

while the stem-end of the funnel is closed with a finger. When the liquid in vessel (D) flows down to the end of tube (b), both cocks are closed. Then the cock (b) is opend and the liquid is allowed to drop down into the funnel. Filtration continues under automatic control by the pressure change in the closed receptacle. Thus when the water level difference is kept at 50 cm., liquid continues to filter at a rate of about 500 ml. per hr.

Digestion Apparatus[5] (Fig. 2).—This apparatus

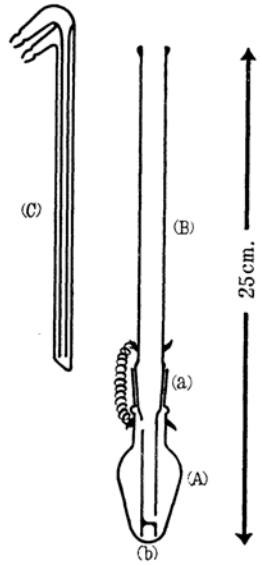

Fig. 2. Digestion apparatus.

consists of three parts: a digestion flask (A), a chimney (B), and a Schirm's[6] condenser (C). The chimney is so designed as to fit into the mouth of the digestion flask with ground joint (a). The small elongation of the chimney extending into the flask has a septum near its opening (b) bearing a small air space. When the chimney is fixed and the liquid in the flask is heated to boiling the open space immersed in the liquid continuously supplies air bubbles whereby bumping is avoided so that boiling continues smoothly. The chimney elongation has two openings, one near the mouth of the flask and the other just above the septum, through which the vapour evolving in the flask is led into the chimney where it is cooled and condensed by the previously inserted Schirm's condenser.

Procedure.—Co-precipitation.—To a suitable amount of the sample containing 1–5 μg. of arsenic, 1 ml. of ferric chloride solution is added per liter. After warming to 70–80°C, the solution is neutralized with ammonia (1 : 3) using bromcresol purple as indicator. While stirring vigorously, 1 ml. of the same reagent is added in excess per liter of the solution. When the solution is sufficiently cooled, the ferric hydroxide precipitate is filtered off through the automatic filtering apparatus just described.

Mineralization—The filter paper with precipitate is placed in the digestion flask and the chimney with Schirm's condenser is fixed in the flask. Gradually 2 ml. of nitric acid and 5 ml. of sulfuric acid are successively added through the chimney. A violent reaction occurs. When the reaction slows down, the contents of the flask are digested for 1–3 hr. During this digestion period repeated additions of nitric acid in small portions are necessary to avoid carbonization. After completion of mineralization, the contents of the flask are transferred into a quartz evaporating dish and heated on a water bath to drive off the excess nitric acid.

Extraction.—The residual solution in the dish is transferred into a 100 ml. beaker. After dilution with 25 ml. of water, it is warmed on a water bath and 2 ml. of potassium iodide solution added. After the solution is left to cool sufficiently for about thirty min., sodium thiosulfate solution is added with care in order to remove the liberated iodine. Any excess addition of the reagent must be avoided. Then the solution is transferred into a 100 ml. separatory funnel to which 5 ml. of potassium xanthate solution and 3 ml. of carbon tetrachloride were previously added. The funnel is vigorously shaken for two min. When carbon tetrachloride layer separates on the bottom, it is drawn out into a 25 ml. separatory funnel. The carbon tetrachloride extraction is repeated with 5 ml. of potassium xanthate solution and 3 ml. of carbon tetrachloride, and this second extract is joined to the first.

It is often the case that a part of the carbon tetrachloride is emulsified into numberless small droplets, their unification being difficult. This difficulty, however, is easily solved by filtering through a cotton plug 1 mm. thick placed at the bottom of the funnel. The droplets are united by passing through the plug and running down to form larger drops associated with some considerable amount of water. This water can be completely removed by repeated separatory funnel treatment.

To the joined carbon tetrachloride extract, are added 1.2 ml. of sulfuric acid (1 : 9), 2 ml. of water and one or more of carbon tetrachloride containing bromine (1 : 25), to give a deep red color to the organic layer. After thorough shaking, the funnel is left to stand until two perfectly separate layers form. A greater part of the oxidized arsenic has gone into the acid layer. The bottom carbon tetrachloride layer is separated into another 25 ml. separatory funnel and shaken with 3 ml. of water to remove the last trace of arsenic in carbon tetrachloride by the water. The acid extract and the water extract are united and washed with two portions of 3 ml. of carbon tetrachloride to remove the remaining bromine. Then the joined extract is transferred into a 10 ml. measuring flask. The separatory funnels are washed with 3 ml. of water and this washing is also added to the flask.

Determination.—After first adding 0.4 ml. of ammonium molybdate solution and 0.4 ml. of hydrazine sulfate solution and then making it up

5) M. Tanaka and S. Kanamori, *Anal. chim. Acta* **14**, 263 (1956).
6) E. Schirm, *Z. anorg. Chem.*, **25**, 1225 (1912).

to 10 ml., the flask is kept in boiling water for thirty min. and then cooled with tap water. Now the extinction measurement is made using a wave length greater than 700 mμ, preferably 840 mμ. The value obtained is corrected by referring to the value of a blank test which was conducted, omitting no step of the procedure. Finally the amount of arsenic is determined by referring to a standard curve constructed by using various known amounts of arsenic.

Discussion

In the analysis of minute quantities of arsenic, special care must be paid to avoid the slightest contamination. Glass and enamel vessels are sources of considerable contamination, particularly when they are warmed in the process of evaporation or co-precipitation. The following experiment proved this: 100 ml. of 1 N suluric acid was put in each of three beakers, glass, enamel, and porcelain, of equal size. They were heated on an electric plate for thirty min. Then the arsenic from each beaker was determined with the result that 2 μg., 50 μg., and below 0.1 μg. were the arsenic values for glass, enamel, and porcelain beakers respectively. Thus a porcelain vessel is recommended as the best for our purpose.

The reason why co-precipitation with ferric hydroxide was adopted is that it suffers the least from contamination and also saves considerable time when compared with evaporation.

Ferric hydroxide, however, co-precipitates not only dissolved arsenic but also other suspended particulates which might contain combined arsenic. Therefore the obtained arsenic value indicates the total amount of arsenic.

The recovery of tri-valent and quinquevalent arsenic in the co-precipitation process was separately examined as follows: Various quantities of each arsenic species were dissolved in 1 l. of water and co-precipitated with 10 mg. of ferric hydroxide. The precipitate filtered off through a fine glass filter was dissolved in dilute sulfuric acid and determined according to the prescribed procedure. The results given in Table I show that the recovery is between 98 and 100%. The experiment also proved that 10 mg. of ferric hydroxide is sufficient to complete co-precipitation of arsenic in ordinary waters even if they contain other substances susceptible to ferric hydroxide co-precipitation.

The optimum pH for the co-precipitation is around 9 and in order to bring the pH of the solution up to this value, approximately 1 ml. of ammonia (1: 3) must be added in excess beyond the neutral point for bromcresol purple. The addition must be made with vigorous stirring so that a uniform shifting of pH is ensured.

TABLE I

CO-PRECIPITATION OF ARSENIC WITH FERRIC HYDROXIDE

Fe used mg.	As^{III} added μg.	As^{III} co-pptd. μg.
10	2	1.9
10	5	5.2
10	100	97
10	1000	990
Fe used mg.	As^{V} added μg.	As^{V} co-pptd. μg.
10	2	2.1
10	5	4.8
10	100	98
10	1000	990

As for extraction of tri-valent arsenic, it is complete even with an acidity of 1 N sulfuric acid so long as co-existing elements are poor. With an increase of such elements, the pH range for a complete extraction is narrowed, a fact by the consideration of which the writers adopted an acidity of 6 N sulfuric acid in the present procedure.

Fig. 3 shows interferences with the extraction of arsenic xanthate by various elements.

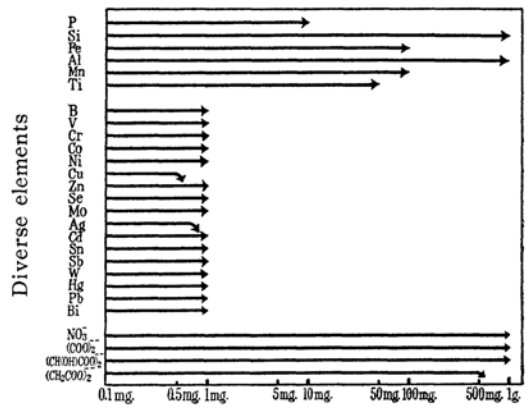

Fig. 3. Interferences of diverse elements.

Straight arrows indicate interference ranges no greater than 3%. A greater interference is first visible at the points where arrows begin to bend. Downward bending indicates a negative interference greater than 3%.

It is remarkable to find that phosphorus and silicon show no considerable interference despite the fact that they are likely to develop the same molybdenum blue as arsenic.

The interferences by alkalis, alkaline earths, aluminum, manganese, zinc, cadmium, vanadium, and boron cause no greater error than the minor unavoidable error straying in through mechanical treatment.

If selenium is in the original sample, it is reduced into metal partly during the course of potassium iodide treatment and in part in the hydrazine sulfate treatment. The first selenium metal can be easily removed by filtering off through a cotton plug similar to that used in the treatment of carbon tetrachloride droplets, while the second metallic selenium can be removed by adding a small amount of carbon tetrachloride and shaking.

The results of application of the method are given in Table II. They show the quantitative recoveries of arsenic which was previously added to the original sample.

TABLE II

EXAMPLES OF APPLICATION

Description	Sample taken	As added	As found
Ground water from a well on the campus of Nagoya Univ.	5 l.		2.1 μg.
	5 l.	10 μg.	12.0 μg.
Sea water at Sugashima Is., Mie pref.	2 l.		3.3 μg.
	2 l.	10 μg.	13.6 μg.
Serpentine (Sugashima Is., Mie pref.)	1 g.		0.4 μg.
	1 g.	5 μg.	5.6 μg.
Bottom deposit of Aburagafuchi, a brackish lake, Aichi pref.	1 g.		7.7 μg.
	1 g.	5 μg.	12.5 μg.
York	4.6 g.		0.6 μg.
	4.6 g.	5 μg.	5.4 μg.

Application to Silicate and Biological Materials

Silicate Materials.—To 0.5–1 g. of powdered silicate material weighed in a nickel crucible, 0.5 g. of sodium hydroxide and 1 ml. of water are added and placed on a water bath. When completely dried out, 0.5 g. of sodium peroxide and 2 g. of fused sodium hydroxide are successively added and the crucible is quickly covered with a lid. A violent reaction occurs. When the reaction is over, the crucible is heated to dull-red for 0.5–1 hr. until decomposition is supposed to be complete. The melt is digested with 20 ml. of water and then neutralized with 9 ml. of sulfuric acid (1 : 1). Disregarding any separation of silica, the solution is acidified with 5 ml. of sulfuric acid and processed according to the prescribed procedure.

Biological Materials.—A suitable amount of a biological material is first decomposed in the digestion apparatus. Then the digest is processed to the prescribed procedure.

Results of application of the method to silicate and biological materials are also given in Table II.

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