35 John Street
Ottawa, Ontario
May 19, 1950

GUTZEIT METHOD for ARSENIC

PREPARATION of SAMPLE

Samples can be prepared in the same manner as described under the molybdenum blue method. It is advisable to keep the amount of concentrated sulphuric acid used at a minimum since it must be neutralized later.

CHEMICALS and REAGENTS

Stannous chloride solutions. Dissolve 40 grams "arsenic free" stannous chloride dihydrate in constant boiling hydrochloric and make up to 100 ml with same acid.

Zinc Baker and Adamson 20 mesh "low arsenic" material was used.

Potassium iodide. 15 grams potassium iodide are dissolved in distilled water and diluted to 100 ml. This is prepared fresh at the time of a determination.

Sand. 30 mesh sand is washed with hot sodium hydroxide, hot concentrated nitric acid and hot distilled water, then dried.

Mercuric bromide paper. Paper supplied by Hanford Pratt was impregnated for 1 hour in freshly prepared mercuric bromide solution (5 grams salt dissolved in 95% alcohol and diluted to 100 ml). After removal from sensitizing solution strips are dried in the sheet for 5 minutes with a fan and placed between sheets of filter paper for ½ hour in the dark. At the end of this period, paper is ready for use. Sensitized paper is not stored but prepared fresh each time.

Standard Arsenic Solution

0.869 grams of sodium arsenite is dissolved in distilled water and made up to 500 ml volume. 1 ml of this solution contains 1000 micrograms of trivalent arsenic.from which suitable dilutions can be made.

Constant Boiling HCl

This is prepared by distilling hydrochloric acid S.G. 1.1 from pyrex. The distillate is then distilled once more from pyrex.

Distilled Water. This is prepared as outlined in the molybdenum blue method.

Generators. The generator used are a stock item available from Ace Glass, or Scientific Glass Apparatus Co., of pyrex, with standard taper joints. The top tube has an internal diameter of 2.6 - 2.7 mm for easy and accurate centering of the paper.

Glass wool is placed in the lower end of the middle section and 3 grams of sand are added. The sand is moistened with 10% lead acetate solution. Excess lead acetate is removed by suction.

The arsenic containing sample is neutralized with concentrated sodium hydroxide if it contains free sulphuric acid. It is then placed in arsenic flask. 5 ml. of constant boiling HCl is added, then 5 ml potassium iodide solution and four drops of stannous chloride solution. The contents are then diluted to 40 ml with distilled water and allowed to stand for 30 minutes at room temperature.

Prepare individual paper strips by cutting the large sheet across the middle. For a given run, take strips from the one half of the paper and orient them all the same way in the top tubes. Ensure that top tubes are clean and dry and insert paper strips.

Add 2 grams of zinc to flask and connect the apparatus carefully. Swirl contents of flask to distribute zinc evenly over flask bottom. A series of arsenic standards containing 5 tp 30 micrograms As can be prepared at the same time as the unknown. All generators, prepared as above are placed in a circular holder. A glass bell jar is used to cover generators and evolution of gas is allowed to proceed for 1½ hours.

Lengths of unknown and standard strips are compared at the end of this time from which the amount of arsenic shown by the method can be determined. If the arsenic found is less than 5 or more than 30 micrograms per determination, the sample should be repeated taking larger or smaller aliquots as necessary, together with fresh standard, until the unknown stain length will fit into the group stain lengths.

May 11, 1950

DETERMINATION OF ARSENIC

PREPARATION of SAMPLES

Biological samples up to 150 grams in weight may be ashed in a Kjeldahl flask with 10-20 ml. of concentrated sulphuric acid and concentrated nitric acid as necessary until digest is colourless or only slightly yellow. As nitric is driven off, more may be added, if the colour of the digest indicates it to be necessary. Take to white fumes of SO_3 when digestion deemed to be complete. Cool, and add 60-100 ml. of distilled water. Take to white fumes a second time. This is to eliminate traces of nitric acid, which interferes.

The cooled digest is now transferred to a volumetric flask and made up to 100 ml. A suitable aliquot containing not more than 5 ml. concentrated sulphuric is taken and transferred to a 50 ml. pyrex or vycor erlenmeyer. Concentrated sulphuric is added as necessary to bring the total amount of concentrated sulphuric present to 5 ml. Contents of flask are evaporated to first sign of white fumes and then transferred to two-necked distilling flask. Erlenmeyer is rinsed out with 5 ml. distilled water which is transferred to distilling flask.

Samples of water of 100-500 ml. volume can be evaporated nearly to dryness with 5 ml. concentrated sulphuric acid and 1 ml. concentrated nitric acid in a series of successively smaller beakers. If the concentration of arsenic is not known, or thought to be low, the whole water sample can be run as one determination. Take to white fumes, cool, add 5 ml distilled water, and take to white fumes again. Transfer sulphuric digest to two-necked distilling flask. Rinse out beaker into a distilling flask with 5 ml. distilled water.

Air samples may be taken with a standard impinger in water and treated as water samples.

DISTILLATION

With the 10 ml. of test solution in the boiling flask, add 3 ml. distilled water to still trap, connect condenser, still head, boiling flask, and dropping funnel. Be sure all joints are tight. Place 2 ml. potassium bromide solution in dropping funnel. Place, already hot, Cenco hot cone heater under boiling flask. Blow in the 2 ml. potassium bromide and start stop watch. Rinse dropping funnel into boiler with 2 ml. distilled water. Allow distillation to proceed for exactly 4 minutes. Check at start, and during distillation, that all standard taper connections are tight. Remove at exactly 4 minutes and break connections. Pour out distillate into volumetric flask of 15-25 ml. capacity. Rinse still with distilled water and transfer to volumetric flask.

COLOUR DEVELOPMENT

Three ml. of acid - molybdate solution are added to flask with a pipette inserted nearly to bottom of flask and without allowing solution to run down flask neck. Two ml. of hydrazine sulphate solution are added by pipette in the same way. Distilled water is added to make the volume about 1 or 2 ml. less than the total capacity of the flask.

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The flask is then heated for exactly 10 minutes in a boiling water bath, after which the flask is cooled to room or standard temperature and made up to volume. Transmittance is read in a suitable colorimeter or spectrophotometer. We use a Beckman spectrophotometer, model DU, with transmittance read at a wavelength of 840 mm. with a slit width of .04 mm., against water as a blank.

A reagent blank should be carried through the determination along with the samples being analysed.

CHEMICALS & REAGENTS

All chemicals should be purest obtainable, and as low in arsenic as possible. Accept "arsenic free" on a label with reservations.

Sulphuric acid. Grasselli reagent grade, specific gravity 1.84, arsenic content on label given as .00000%.

Concentrated nitric acid. Reagent grade concentrated nitric acid specific gravity 1.47, was redistilled from pyrex.

Potassium bromide. Thirty grams potassium bromide diluted to 100 ml with distilled water.

Hydrazine sulphate. 0.05 grams hydrazine sulphate diluted to 100 ml. with distilled water.

Molybdate reagent. One gram ammonium molybdate and 60 ml. concentrated sulphuric acid diluted to 100 ml. with distilled water.

Hydrochloric acid. 180 grams pyrex distilled constant boiling hydrochloric acid diluted to 1 litre with distilled water.

Acid molybdate reagent. 50 ml. of molybdate reagent alone, and 25 ml. of 1 normal hydrochloric acid.

Distilled water. All distilled water used for arsenic determinations, and for preparation of reagents, was triple distilled. First distillation was made in a Barnstead still, and the second and third from pyrex. It might be pointed out that distilled water from the Barnstead type still is unsatisfactory for arsenic determinations, being higher in arsenic content than the original tap water by a factor of 10. In this case, the only useful function of the Barnstead still was to remove scale-forming materials, so that the pyrex stills could be used without sludge formation.

STANDARD ARSENIC SOLUTION

As the arsenic must be pentavalent to be determined by this method, it is convenient to make up standards using pentavalent arsenic 0.384 grams arsenic pentoxide (best reagent grade) are dissolved in 15 ml. normal sodium hydroxide. After solution is complete, 15 ml. normal hydrochloric acid is added and the solution is then made up to a volume of 500 ml. with distilled water. One ml. of this stock solution contains 500 micrograms of elemental arsenic. Suitable dilutions can be made to get down to the 0-100 microgram range.

INTERFERENCES

Due to insufficient time, interferences were not investigated. Germanium, phosphorus, and silica according to Boltz and Mellon (1) also form a molybdenum blue colour with maximum absorption at 840 millimicrons. It should be possible to eliminate phosphate or silica interferences, if large amounts should be present, by repeating the distillation a second time, since it is thought that any phosphorus or silica found in the first distillate is due to mechanical carry over. In connection with germanium Chaney and Magnuson (2) claim that no blue colour is formed with molybdate reagent. If germanium might be expected, a complete investigation of both statements should be made. According to Chaney and Magnuson (2), selenium, antimony, and germanium if present will distill with the arsenic. They also say that Se and Sb do not interfere.

As nitrate interferes, all nitric acid should be eliminated before distillation. It might be worth while to investigate the possibility of digestion without nitric.

REMARKS

Recoveries of known amounts of arsenic carried through the distillation procedure have run 98% on 30 microgram amounts.

In comparison with the Gutzeit method, this method is more reliable. The Gutzeit method cannot be used for all materials, and often requires a preliminary separation by distillation, which, of course, is interent in the method outlined. Unlike Gutzeit, the molybdenum blue method is reproducible from day to day and from run to run. It is of sufficiently high sensitivity for most purposes.

The attached curve is based on colour sample volumes of 25 ml. and a light path of 1 cm. Higher sensitivities might be obtained by working with smaller sample volumes and a longer light path, although Boltz and Mellon (1) claim the response is linear only from 0 to 3 ppm. of arsenic (0-75 micrograms per 25 ml.). A curve however, is satisfactory, if reproducible.

The method above outlined, is essentially that of Magnuson and Watson (3) as modified by Maren (4). It depends on being able to distill pentavalent arsenic quantitatively. This represents a change in the thinking of one of the authors (Magnuson) who previously went to considerable lengths to ensure the arsenic was trivalent before distillation, since pentavalent arsenic would not distill!

As the acid concentration of the final colour sample affects the intensity of the colour (2,3,4) it is recommended that development be made in the same volume each time, preferably in the total flask volume. Results were erratic until development was carried out in a nearly filled flask each time rather than one -half or three-quarters full.

The still referred to is available commercially from Scientific Glass Apparatus Co., Inc., under #M1586. It is necessary only to order parts sufficient to make a complete still, or stills. The digestion set up, derived from (2) is unnecessary, as digestion can be carried out in Kjeldahl flasks, erlenmeyers, or beakers.

LITERATURE CITED

1 - D. F. Boltz and M. A. Mellon. Ind. Eng. Chem., Anal. Ed. 19, 873 (1947).
2 - Chaney, A. L. and Magnuson, H. J. Ind. Eng. Chem., Anal. Ed. 12, 691 (1940).
3 - Magnuson, H. J. and Watson, E. B. Ind. Eng. Chem. 16, 339, (1944).
4 - Maren, T. H. Ind. Eng. Chem. Anal. Ed. 18, 521, (1946).