

Determination of mercury with dithizone

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Sect. I. Reagents

All reagents should be of highest purity. Any sulphuric acid used is preferably tested for the presence of mercury.

Oxidation mixture I: Dissolve 7 g of potassium permanganate in 100 ml of distilled water. Add carefully 10 ml of conc. Sulphuric acid. This solution should be renewed daily.

Oxidation mixture II (for digestion of samples of animal tissues and alike): Mix 1 volume of conc. sulphuric acid with 2 volumes of conc. nitric acid.

Hydroxylamine hydrochloride: Dissolve 20 g of hydroxylamine hydrochloride ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ) in 100 ml of distilled water.

Sulphuric acid, 3 M: Add carefully 1 volume of conc. sulphuric acid to 5 volumes of distilled water.

Hydrochloric acid, 0.1 M: Dilute 8 ml of hydrochloric acid (sp.gr. 1.19) to 1000 ml with distilled water.

Dithizone: Dissolve 50 mg of dithizone in 100 ml of carbon tetrachloride. This stock solution will keep for several months when stored dark and cold.

A working solution is made by diluting 4 ml of the stock solution to 100 ml with carbon tetrachloride. The solution should be shielded from direct light by covering the flask with aluminum foil.

Potassium iodide, 0.2 M: Dissolve 33 g of potassium iodide in distilled water, add 10 ml of hydroxylamine hydrochloride (to prevent oxidation) and dilute to 1000 ml.

Mercuric chloride stock solution: Dissolve 135 mg of mercuric chloride in 1000 ml of 0.1M hydrochloric acid. This solution will contain 100  $\mu\text{g}$  of Hg per ml.

Sect. II. Calibration curve

Transfer 0, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 ml of the mercuric stock solution to 100 ml volumetric flasks. Add to each of the flasks 5 ml of 3 M sulphuric acid and 10 ml of 0.1 M hydrochloric acid and make up to the mark with distilled water. These solutions will contain mercury equivalent to 0, 0.5 ..... 3.0  $\mu\text{g Hg/ml}$ , respectively. Transfer 10.0 ml of each of the solutions to a 100 ml separatory funnel and add 10.0 ml of dithizone solution. Shake efficiently for ca. 60 seconds and allow the phases to separate. Run as much as possible of the organic layer into a second separatory funnel containing 50 ml of distilled water and 2 ml of 3 M sulphuric acid. Shake for ca. 30 seconds and let the phases separate. Run approximately half of the organic phase into a 1 cm cuvette. Add 4 ml potassium iodide to the aqueous phase and replace the stopper. Turn the funnel upside down and open the stopcock to return the dithizone trapped in the bore. After this shake for 60 seconds and run, after separation of the phases, the dithizone phase into another 1 cm cuvette. Use the latter as blank on measurement of the extinction at 500 nm.

The measured extinctions are plotted against the content of mercury present in the aliquots taken. The calibration curve is approximately linear up to 30  $\mu\text{g}$  of Hg. The amount of dithizone available corresponds to ca. 80  $\mu\text{g}$  of Hg. Note that any work with dithizone should be done in diffuse light and that extinctions should be measured as soon as possible.

Sect. III A. Pretreatment of industrial waste waters

To 100 ml of sample add 10 ml of potassium permanganate solution. Heat on a steam bath for one hour. Cool the solution and add 5 ml of hydroxylamine solution and let stand with occasional shaking for a few minutes to complete the reduction of the permanganate. Ensure that any manganic dioxide has dissolved. Transfer the solution to a 200 ml volumetric flask and make up to the mark with distilled water. If the original sample contains chloride, allow 1-2 hours for the reduction of any chlorine formed before the analysis is continued as described in section IV. Otherwise proceed directly to avoid that reduction of  $\text{Hg}^{2+}$  to  $\text{Hg}_2^{2+}$  takes place.

In case the sample contains suspended solids which do not dissolve at the oxidation filter the solution through filter paper (acid-washed quality) into the volumetric flask. Wash the filter with 25 ml of 0.1 M hydrochloric acid, added in small portions.

In case the sample contains difficultly oxidised, suspended organics, it is recommended to filter the sample through glass fiber paper. The filtrate is analysed as described above while the filter with the removed solids is analysed separately after digestion as described under sect. III D.

Sect. III B. Pretreatment of technical caustic soda

Depending on whether mercury is to be determined as w/w or w/v weigh 10-15 g or measure volumetrically 10 ml of the sample into a 250 ml Erlenmeyer flask. Add a few crystals of solid potassium permanganate and neutralise with 3 M sulphuric acid under simultaneous cooling. When 50 % caustic soda is analysed, approximately 20 ml of the acid will be required. Add an additional 5 ml of acid. If crystals of sodium sulphate start to form, dilute with distilled water. Destroy the excess permanganate by adding 1-2 ml of hydroxylamine solution. Transfer the solution to a 100 ml volumetric flask and make up to the mark. Proceed the analysis immediately as described under Section IV.

Sect. III C. Pretreatment of lake bottom sediments  
and alike

Weigh, alternatively measure volumetrically, approximately 5 g of the material into a 100 ml Erlenmeyer flask and add 10 ml of potassium permanganate solution. Heat on a steam bath for 1 hour. After cooling, add 5 ml of hydroxylamine solution and let stand with occasional shaking for a few minutes. Filter through paper filter (acid-washed quality) into a 100 ml volumetric flask. Wash the filter with 25 ml 0,1 M hydrochloric acid in small portions and make up to the mark with distilled water. Proceed the analysis immediately as described in Section IV.

Sect. IV. Determination of mercury in pretreated samples

For the following to be applicable, the sample should contain less than a 1000-fold excess of copper over mercury. Bromide ion when present at concentrations below 1 g per litre gives practically no interference; at a concentration of 1.65 g per litre the error was 9 per cent at 30  $\mu\text{g}$  of Hg per 10 ml of dithizone. Iodide ion should be virtually absent. If the chloride concentration exceeds 1 M, the sample should be diluted, with distilled water.

The pretreated sample solution should be in a measuring flask filled to the mark. Transfer an aliquot, containing 5-30  $\mu\text{g}$  of Hg to a separatory funnel of adequate size. Add 10.0 ml of dithizone solution and proceed as described for making the calibration curve.

The amount of mercury in the extracted aliquot is then obtained from the calibration curve. Multiplying with the proper volumetric factors gives the content in the original sample.

For "clean" samples or when the highest precision is not required, the treatment with iodide may be omitted. A 5 ml portion of dithizone may then be used for extracting the mercury (sample content 2.5 - 15  $\mu\text{g}$  Hg). The extract is measured at 500 nm against dithizone solution. The calibration is made as described in section II but omitting the iodide step. If the mercuric content of the original sample is known only within a wide range, a rough estimate, serving for instance as a guide to the volume of the aliquot finally taken, may be made as follows: An aliquot, say 10 ml, of the pretreated solution is shaken with 10 ml of dithizone solution. If a moderate

change of the colour of the organic phase takes place, the size of the aliquot was appropriate and the analysis may be proceeded as described above. If virtually no colour change takes place, additional aliquots of sample solution, up to a total of 200-250 ml, are added until a change is noticeable. If the colour turns orange-yellow instead, add further 10 ml portions of dithizone until the colour turns greenish. Measure the extinction in a 1 cm cuvette against pure dithizone solution. Read the corresponding mercury value from the calibration curve and multiply with the number of dithizone portions taken to obtain a crude value of the mercury content of the aliquot taken. Adjust the volume of the aliquot to be taken for precision analysis accordingly.

When the first aliquot taken is too small or too large, the most convenient and simple procedure in many instances is to start from the beginning with a more suitably sized aliquot.



Sect. VI. Cleaning of glass-ware

Used glass-ware is first cleaned thoroughly by conventional methods. Rinse thereafter first with warm permanganate solution, then with 0.1 M hydrochloric acid and finally several times with distilled water. Let dry in air, avoiding contamination with dust.

The cleaning may be checked by running a few drops of dithizone over the surface of the glass. No change in colour should occur.

For transport or storing of samples, glass bottles (Pyrex) are preferred. Polyethylene bottles of good quality may when practical be used as an alternative.