PHENOLICS (SPECTROPHOTOMETRIC, MBTH WITH DISTILLATION)

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the analysis of ground water, drinking, surface, and saline waters, and domestic and industrial wastes.

1.2 The method is capable of measuring phenolic materials at the 2 ug/L level when the colored end product is extracted and concentrated in a solvent phase using phenol as a standard.

1.3 The method is capable of measuring phenolic materials that contain from 50 to 1,000 ug/L in the aqueous phase (without solvent extraction) using different kinds of phenols.

1.4 It is not possible to use this method to differentiate between different kinds of phenols.

2.0 SUMMARY OF METHOD

2.1 This method is based on the coupling of phenol with MBTH in an acid medium using ceric ammonium sulfate as an oxidant. The coupling takes place in the p-position; if this position is occupied, the MBTH reagent will react at a free o-position. The colors obtained have maximum absorbance from 460 to 595 nm. For phenol and most phenolic mixtures, the absorbance is 520 and 490 nm.

3.0 INTERFERENCES

3.1 For most samples a preliminary distillation is required to remove interfering materials.

3.2 Color response of phenolic materials with MBTH is not the same for all compounds. Because phenolic-type wastes usually contain a variety of phenols, it is not possible to duplicate a mixture of phenols to be used as a standard. For this reason, phenol has been selected as a standard and any color produced by the reaction of other phenolic compounds is reported as phenol. This value will represent the minimum concentration of phenolic compounds present in the sample.

3.3 Interferences from sulfur compounds are eliminated by acidifying the sample to a pH of less than 4.0 with H_2SO_4 and aerating briefly by stirring.

3.4 Oxidizing agents such as chlorine, detected by the liberation of iodine upon acidification in the presence of potassium iodide, are removed immediately after sampling by the addition of an excess of ferrous ammonium

sulfate (see Paragraph 5.11). If chlorine is not removed, the phenolic compounds may be partially oxidized and the results may be low.

3.5 Phosphate causes a precipitate to form; therefore, phosphoric acid should not be used for preservation. All glassware should be phosphate free.

3.5 High concentrations of aldehydes may cause interferences.

4.0 APPARATUS AND MATERIALS

4.1 Distillation apparatus: All glass, consisting of a 1-liter Pyrex distilling apparatus with Graham condenser.

4.2 pH Meter.

4.3 Spectrophotometer.

4.4 Funnels.

4.5 Filter paper.

4.6 Membrane filters.

4.7 Separatory funnels.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Sulfuric acid, 1 N: Add 28 mL of concentrated H_2SO_4 to 900 mL of Type II water, mix, and dilute to 1 liter.

5.3 MBTH solution, 0.05%: Dissolve 0.1 g of 3-methyl-2-benzo-thiazolinone hydrazone hydrochloride in 200 mL of Type II water.

5.4 Ceric ammonium sulfate solution: Add 2.0 g of $Ce(SO_4)_2 \cdot 2(NH_4)_2SO_4 \cdot 2H_2O$ and 2.0 mL of concentrated H_2SO_4 to 150 mL of Type II water. After the solid has dissolved, dilute to 200 mL with Type II water.

5.5 Buffer solution: Dissolve, in the following order: 8 g of sodium hydroxide, 2 g EDTA (disodium salt), and 8 g boric acid in 200 mL of Type II water. Dilute to 250 mL with Type II water.

5.6 Working buffer solution: Make a working solution by mixing an appropriate volume of buffer solution (5.5) with an equal volume of ethanol.

5.7 Chloroform.

5.8 Stock phenol: Dissolve 1.00 g phenol in 500 mL of Type II water and dilute to 1,000 mL. Add 1 g $CuSO_4$ and 0.5 mL concentrated H_2SO_4 as preservative (1.0 mL = 1.0 mg phenol).

5.9 Standard phenol solution A: Dilute 10.0 mL of stock phenol solution (5.8) to 1,000 mL (1.0 mL = 0.01 mg phenol).

5.10 Standard phenol solution B: Dilute 100.0 mL of standard phenol solution A (5.9) to 1,000 mL with Type II water (1.0 mL = 0.001 mg phenol).

5.11 Ferrous ammonium sulfate: Dissolve 1.1 g ferrous ammonium sulfate in 500 mL Type II water containing 1 mL concentrated H_2SO_4 and dilute to 1 liter with freshly sorted and cooled Type II water.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Biological degradation is inhibited by acidification to a pH of <4 with H_2SO_4. The sample should be kept at 4°C and analyzed within 28 days of collection.

7.0 PROCEDURE

7.1 Distillation:

7.1.1 To 500 mL of sample, adjust the pH to approximately 4 with 1 N sulfuric acid solution (5.2).

7.1.2 Distill over 450 mL of sample, add 50 mL of warm Type II water to flask, and resume distillation until 500 mL has been collected.

7.1.3 If the distillate is turbid, filter through a prewashed membrane filter.

7.2 Concentration above 50 ug/L:

7.2.1 To 100 mL of distillate or an aliquot diluted to 100 mL, add 4 mL of MBTH solution (5.3).

7.2.2 After 5 min, add 2.5 mL of ceric ammonium sulfate solution (5.4).

7.2.3 Wait another 5 min and add 7 mL of working buffer solution (5.6).

7.2.4 After 15 min, read the absorbance at 520 nm against a reagent blank. The color is stable for 4 hr.

7.3 Concentration below 50 ug/L:

7.3.1 To 500 mL of distillate in a separatory funnel, add 4 mL of MBTH solution (5.3).

7.3.2 After 5 min, add 2.5 mL of ceric ammonium sulfate solution (5.4).

7.3.3 After an additional 5 min, add 7 mL of working buffer solution (5.6).

7.3.4 After 15 min, add 25 mL of chloroform. Shake the separatory funnel at least 20 times. Allow the layer to separate and pass the chloroform layer through filter paper.

7.3.5 Read the absorbance at 490 nm against a reagent blank.

7.4 Calculation:

7.4.1 Prepare a standard curve by plotting absorbances against concentration values.

7.4.2 Obtain concentration value of sample directly from prepared standard curve.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination has occurred.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

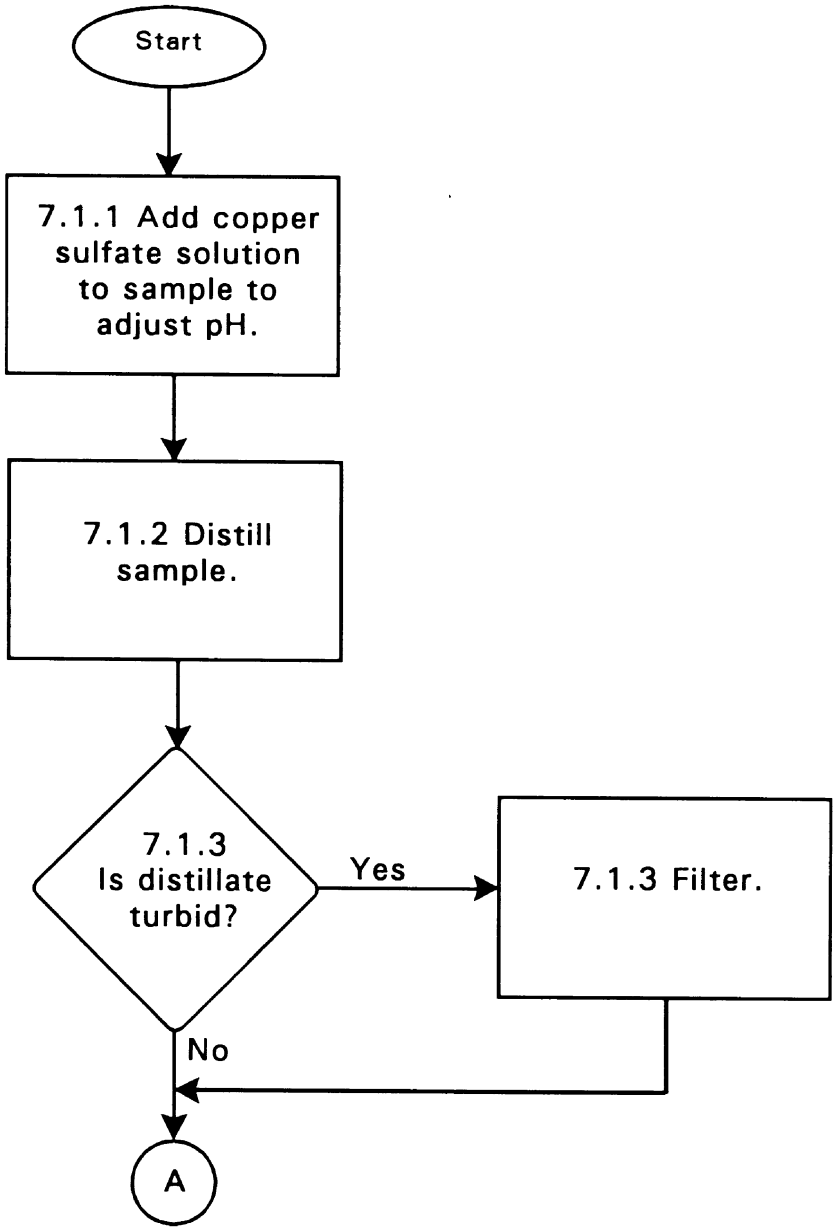
9.0 METHOD PERFORMANCE

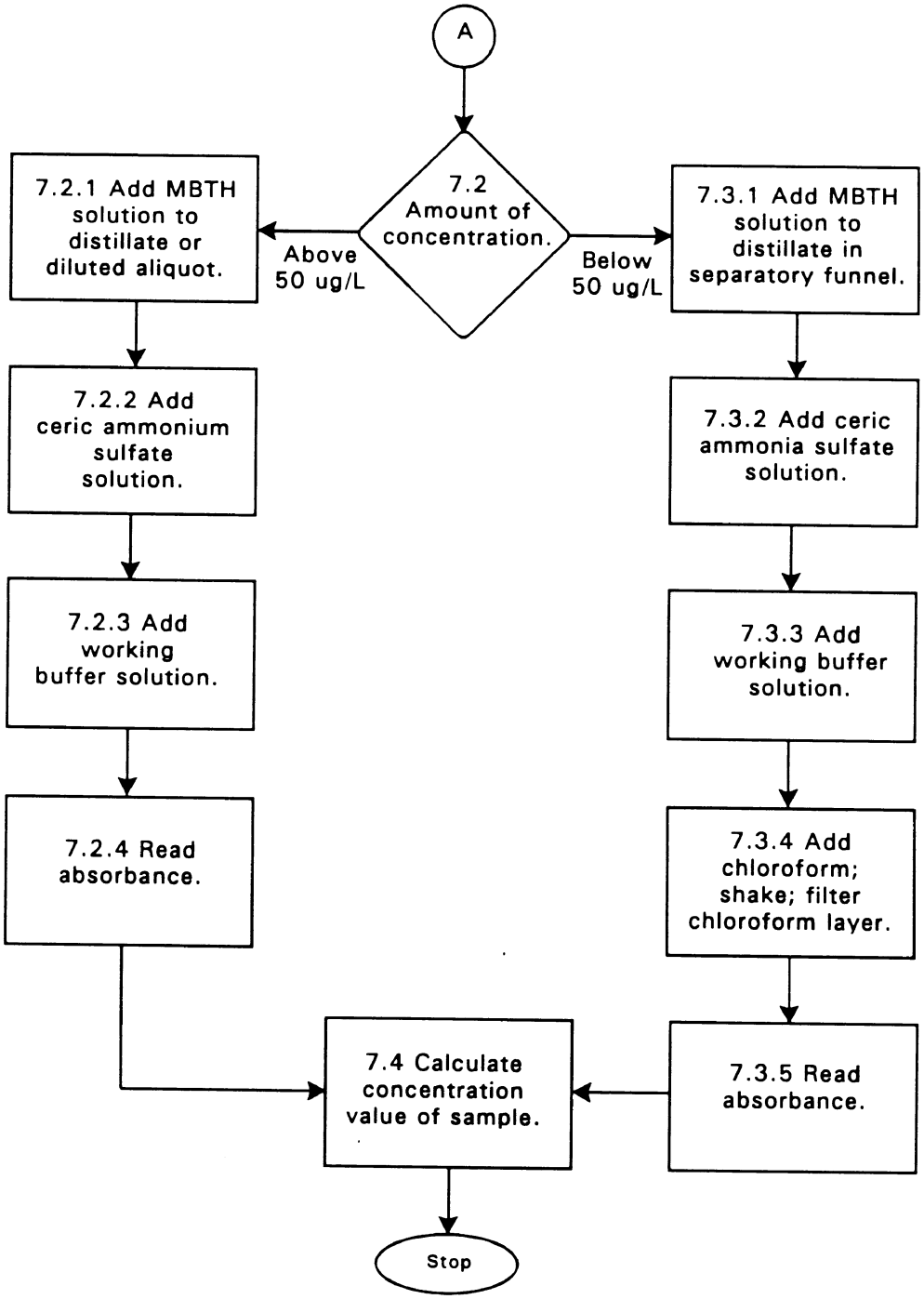
9.1 Precision and accuracy data are not available at this time.

10.0 REFERENCES

1. Friestad, H.O., E.E. Ott, and F.A. Gunther, "Automated Colorometric Micro Determination of Phenol by Oxidative Coupling with 3-Methyl-benzothiazolinone Hydrazone," Technicon International Congress, 1969.

2. Gales, M.E., "An Evaluation of the 3-Methyl-benzothiazolinone Hydrazone Method for the Determination of Phenols in Water and Wastewater," Analyst, 100, No. 1197, 841 (1975).


Start
7.1.1 Add copper sulfate solution to sample to adjust pH.
7.1.2 Distill sample.
7.1.3 Is distillate turbid?
Yes
7.1.3 Filter.
No
A


A
7.2 Amount of concentration.
Above 50 ug/L
Below 50 ug/L
7.2.1 Add MBTH solution to distillate or diluted aliquot.
7.2.2 Add ceric ammonium sulfate solution.
7.2.3 Add working buffer solution.
7.2.4 Read absorbance.
7.3.1 Add MBTH solution to distillate in separatory funnel.
7.3.2 Add ceric ammonia sulfate solution.
7.3.3 Add working buffer solution.
7.3.4 Add chloroform; shake; filter chloroform layer.
7.3.5 Read absorbance.
7.4 Calculate concentration value of sample.
Stop