METHOD 9066

PHENOLICS (COLORIMETRIC, AUTOMATED 4-AAP WITH DISTILLATION)

1.0 SCOPE AND APPLICATION

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

1.2 The method is capable of measuring phenolic materials from 2 to 500 ug/L in the aqueous phase using phenol as a standard.

2.0 SUMMARY OF METHOD

2.1 This automated method is based on the distillation of phenol and subsequent reaction of the distillate with alkaline ferricyanide ($K_3Fe(CN)_6$) and 4-amino-antipyrine (4-AAP) to form a red complex which is measured at 505 or 520 nm.

3.0 INTERFERENCES

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

3.2 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 (5.5). If chlorine is not removed, the phenolic compounds may be partially oxidized and the results may be low.

3.3 Background contamination from plastic tubing and sample containers is eliminated by filling the wash receptacle by siphon (using Kel-F tubing) and using glass tubes for the samples and standards.

4.0 APPARATUS AND MATERIALS

4.1 Automated continuous-flow analytical instrument:

4.1.1 **Sampler:** Equipped with continuous mixer.

4.1.2 **Manifold.**

4.1.3 **Proportioning pump II or III.**

4.1.4 **Heating bath with distillation coil.**

4.1.5 **Distillation head.**

4.1.6 **Colorimeter:** Equipped with a 50 mm flowcell and 505 or 520 nm filter.

4.1.7 **Recorder.**

5.0 REAGENTS

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

5.2 Distillation reagent: Add 100 mL of concentrated phosphoric acid (85% H_3PO_4) to 800 mL of Type II water, cool and dilute to 1 liter.

5.3 Buffered potassium ferricyanide: Dissolve 2.0 g potassium ferricyanide, 3.1 g boric acid, and 3.75 g potassium chloride in 800 mL of Type II water. Adjust to pH of 10.3 with 1 N sodium hydroxide (5.3) and dilute to 1 liter. Add 0.5 mL of Brij-35 (available from Technicon). (Brij-35 is a wetting agent and is a proprietary Technicon product.) Prepare fresh weekly.

5.4 Sodium hydroxide (1 N): Dissolve 40 g NaOH in 500 mL of Type II water, cool and dilute to 1 liter.

5.5 4-Aminoantipyrine: Dissolve 0.65 g of 4-aminoantipyrine in 800 mL of Type II water and dilute to 1 liter. Prepare fresh each day.

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

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

CAUTION: This solution is toxic.

5.8 Standard phenol solution A: Dilute 10.0 mL of stock phenol solution (5.6) to 1,000 mL (1.0 mL = 0.01 mg phenol).

5.9 Standard phenol solution B: Dilute 100.0 mL of standard phenol solution A (5.8) to 1,000 mL with Type II water (1.0 mL = 0.001 mg phenol).

5.10 Standard phenol solution C: Dilute 100.0 mL of standard phenol solution B (5.9) to 1,000 mL with Type II water (1.0 mL = 0.0001 mg phenol).

5.11 Using standard solution A, B, or C, prepare the following standards in 100-mL volumetric flasks. Each standard should be preserved by adding 2 drops of concentrated H_2SO_4 to 100.0 mL:

Standard Solution (mL)	Concentration (ug/L)
Solution C	
1.0	1.0
2.0	2.0
3.0	3.0
5.0	5.0
Solution B	
1.0	10.0
2.0	20.0
5.0	50.0
10.0	100.0
Solution A	
2.0	200.0
3.0	300.0
5.0	500.0

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 the acidification to a pH <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 Set up the manifold as shown in Figure 1.

7.2 Fill the wash receptacle by siphon. Use Kel-F tubing with a fast flow (1 liter/hr).

7.3 Allow colorimeter and recorder to warm up for 30 min. Run a baseline with all reagents, feeding Type II water through the sample line. Use polyethylene tubing for sample line. When new tubing is used, about 2 hr may be required to obtain a stable baseline. This 2-hr time period may be necessary to remove the residual phenol from the tubing.

7.4 Place appropriate phenol standards in sampler in order of decreasing concentration. Complete loading of sampler tray with unknown samples, using glass tubes. If samples have not been preserved as instructed in Paragraph 6.2, add concentrated H_2SO_4 to 100 mL of sample. Run with sensitivity setting at full scale or 500.

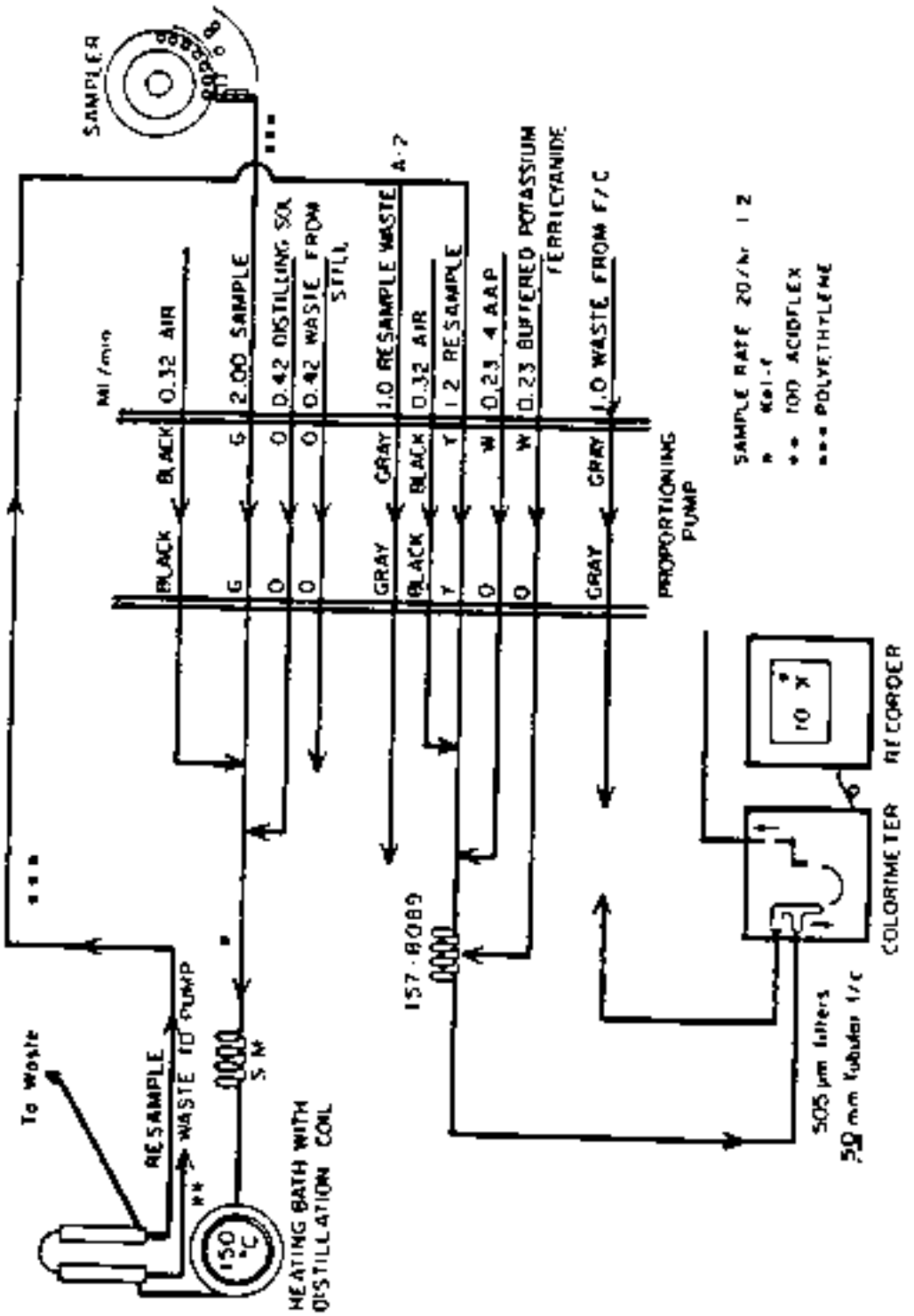


Figure 1 Phenol Autoanalyzer II

7.5 Switch sample from Type II water to sampler and begin analysis.

7.6 Calculation:

7.6.1 Prepare a linear standard curve by plotting peak heights of standards against concentration values. Compute concentration of samples by comparing sample peak heights with standards.

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 In a single laboratory using sewage samples at concentrations of 3.8, 15, 43, and 89 ug/L, the standard deviations were $\pm$0.5, $\pm$0.6, $\pm$0.6, and $\pm$1.0 ug/L, respectively. At concentrations of 73, 146, 299, and 447 ug/L, the standard deviations were $\pm$1.0, $\pm$1.8, $\pm$4.2, and $\pm$5.3 ug/L, respectively.

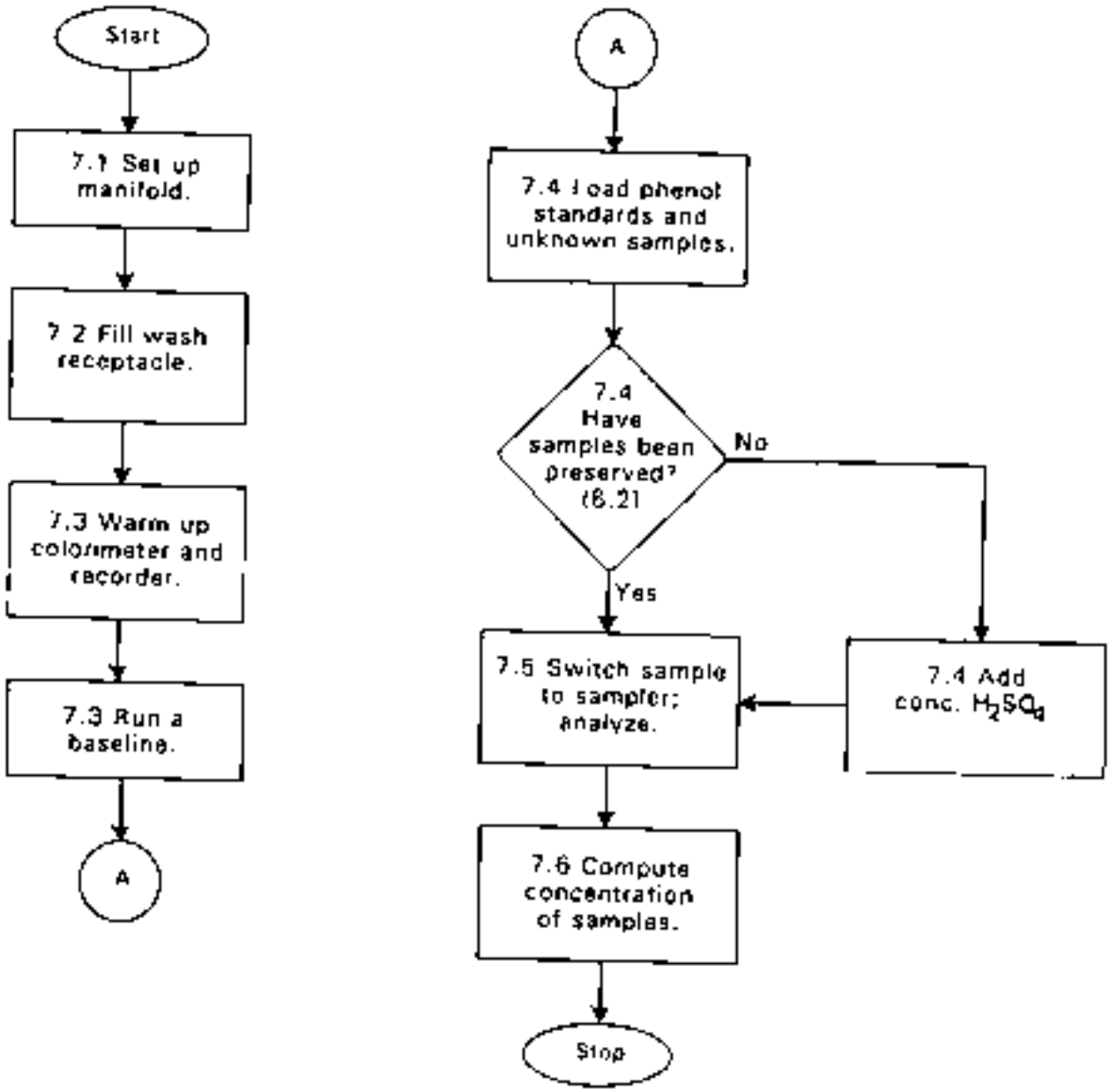
9.2 In a single laboratory using sewage samples at concentrations of 5.3 and 82 ug/L, the recoveries were 78% and 98%, respectively. At concentrations of 168 and 489 ug/L, the recoveries were 97% and 98%, respectively.

10.0 REFERENCES

1. Gales, M.E. and R.L. Booth, "Automated 4AAP Phenolic Method," AWWA 68, 540 (1976).

2. Standard Methods for the Examination of Water and Wastewater, 14th ed., p. 574, Method 510, (1975).

3. Technicon AutoAnalyzer II Methodology, Industrial Method No.127-71W, AA II.


Start
7.1 Set up manifold.
7.2 Fill wash receptacle.
7.3 Warm up colorimeter and recorder.
7.3 Run a baseline.
A
A
7.4 Load phenol standards and unknown samples.
7.4 Have samples been preserved? (6.2)
No
Yes
7.4 Add conc. H_2SO_4
7.5 Switch sample to sampler; analyze.
7.6 Compute concentration of samples.
Stop