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METHOD 335.4

I. SCOPE AND APPLICATION:

This is a general purpose procedure for the collection of water samples for the analysis of cyanide in drinking water supplies, ground waters, surface waters, as well as saline waters, domestic and industrial wastes. The applicable range is 5 to 500 µg/liter.

Analyte	Chemical Abstract Services Registry Numbers (CASRN)
Cyanide	151-50-8

II. REAGENTS:

- *Sodium hydroxide solution, 1.25 N*; Dissolve 50 grams of NaOH in reagent water and dilute to 1 liter with reagent water.
- *Sodium hydroxide solution, 10 N*, Dissolve 400 grams of NaOH pellets into 750 ml of reagent free water. QS (quantity sufficient) to 1-liter.
- *Ascorbic acid solution*:
- *Acetic acid buffer solution*: Dissolve 146 g anhydrous sodium acetate ($NaC_2H_3O_2$), or 243g of $NaC_2H_3O_2 \cdot 3H_2O$, in 400 ml distilled water. Add 480 g concentrated acetic acid and dilute to 1 liter with chlorine-demand-free water.
- *Lead acetate*: ACS (American Chemical Society) reagent grade in powder form.
- *Lead carbonate*: ACS (American Chemical Society) reagent grade powder form.

III. MATERIALS:

- 1 liter (32 oz) high density polyethylene bottles with poly-foamed lined screw on caps.
- pH indicator paper (high end)
- Latex gloves
- Paper towels & Kim Wipe napkins
- Plastic container for disposal of used pipette tips
- Disposable glass pipettes and rubber bulb.
- Potassium iodide-starch indicator paper
- Lead acetate test paper
- Funnel
- Filter paper
- Protective eyewear.

IV. PROCEDURE:

1. Remove any attachments such as hoses, screens or aeration devices on the faucet. Inspect the faucet for anything that may fall into the sample container.

2. Open the tap and allow the system to flush for approximately 10 minutes. This should be sufficiently long enough to get a representative sample.

3. Place a 1-inch strip of potassium iodide-starch indicator paper (KI-starch paper) on a dry opened paper towel. Obtain an aliquot of the sample directly from the tap using a clean glass pipette. Place a drop of the sample water on the KI-starch paper. A blue color indicates the presence of oxidizing agents and requires ascorbic acid treatment. as outline in step 4. An absence of a blue color on the KI-starch paper however, indicates the absence of oxidizing agents and therefore proceed to step 7.

4. *For systems that contain oxidizing agent interferents:* Obtain an empty 1-liter polyethylene or glass sample bottle (containing no NaOH solution) and remove the cap t fill, tip the bottle at about a 45° angle into the stream of water. The stream of water should be sufficiently slow so as to be able to anticipate when the bottle is nearly full and thus avoid over flowing. Fill the bottle to the fill line or within ½ inch of the top. This will allow enough space for mixing after ascorbic acid has been added to reduce the oxidizing agents.

IV. PROCEDURE (continued):

5. Add 10 drops of ascorbic acid, recap the bottle, and invert 5 times. Uncap the bottle and obtain an aliquot of the sample using a clean glass pipette. Test the water sample using another strip of KI-starch paper to determine if the ascorbic acid has neutralized the oxidizers. If the KI-starch paper indicates all of the oxidizing agents have been neutralized by the ascorbic acid (no blue color on the KI-starch paper), record the results in the field sampling notebook and proceed to step 7.

6. Continue the cycle of adding ascorbic acid, capping, mixing, and testing the sample with a clean glass pipette until the KI-starch paper indicates there are no more oxidizing agents present in the sample. Record the amount of ascorbic acid required to reduce all the oxidizing agents in the field sampling notebook.

7. *For systems that contain oxidized product interferents:* Place a 1-inch strip of lead acetate test paper on a dry opened paper towel. Moisten the lead acetate paper by placing a few drops of acetic acid buffer test solution (pH4) using a clean glass pipette. Test for sulfide (S^{-2}) by obtaining an aliquot of the sample from the bottle using a clean glass pipette and placing a drop of the sample on the lead acetate test paper that has been previously moistened with acetic acid buffer solution. A darkening of the paper indicates the presence of S^{-2} and requires that lead acetate is added to the water sample. Recap and invert the bottle 5 times to mix the sample. If the S^{-2} concentration appears too high (extreme blackening of the paper or the water sample emits a sulfur odor), add powdered lead carbonate [$Pb(CO_3)_2$] to avoid reducing the pH of the water sample.

8. Repeat the cycle of adding lead acetate (or lead carbonate) capping, mixing, and testing the sample using lead acetate test paper until a drop of sample no longer darkens the acidified lead acetate test paper.

9. Filter the sample before raising the pH $\geq$ 12 with sodium hydroxide for stabilization. This step is necessary to remove any excess powdered lead carbonate. Discard the filtrate.

10. Once the oxidizing agents or oxidized products have been neutralized, add 2 ml of 10 N NaOH solution. Cap the bottle and invert 5 times to mix the sample.

11. Place a pH indicator test strip on a dry opened paper towel. Remove the screw-on cap and obtain an aliquot of the sample using a glass pipette. Moisten the pH indicator test strip with the aliquot from the glass pipette and immediately flick the pH indicator test strip once using a sharp wrist motion to shake off the excess water. Compare the strip with the reference pH range on the side of the pH container A determination must be made within 30 seconds.

IV. PROCEDURE (continued):

12. If the pH is not $\geq$ 12, add 3 ml of 1.25 N NaOH solution, recap the bottle firmly and invert the bottle 5 times.

13. Continue the cycle of adding 3 ml of 1.25 N NaOH solution to the sample, recapping, mixing, and testing the sample to ensure the pH has been properly adjusted to $\geq$ 12.

14. Once the sample has been stabilized by properly adjusting the pH to $\geq$ 12, the sample may be recapped, dried, and the sample label and chain of custody affixed to the bottle. Place the bottle in the ice chest to cool to 4°C for storage and transportation.

V. SAMPLE TRANSPORT:

Place the sample bottle(s) into the ice chest for transport. The samples must have the pH adjusted to $\geq$ 12, be chilled and preserved at a temperature of 4°C and maintained at that temperature until analysis. Always use chopped, grated, or dry ice when chilling the samples for transportation. Never use "blue ice" as the samples may not chill adequately. Field samples that will not be received at the laboratory on the day of collection must be packaged for shipment with sufficient ice to ensure they will be at 4°C upon arrival at the laboratory.

VI. SAMPLE STORAGE:

Sample should be analyzed as soon as possible after collection. If storage is required, preserved samples will be maintained at 4°C until analyzed and have a maximum holding time of up to 14 days after collection.

VII. DEFINITIONS:

A. *Aliquot:* A measured portion of a sample taken for analysis.

B. *Oxidizer*: an agent that accepts electrons and becomes reduced as a result.

C. *Matrix Effect*: The influence of the sample matrix or sample components upon the ability of analytical methods to qualitatively identify and quantitatively measure target compounds in environmental samples.

VIII. SAFETY:

The use of protective eyewear and laboratory quality latex gloves is highly recommended when collecting and preserving samples.

NEVER acidify a sample known or suspected of containing cyanide. Acidification of such a sample will result in the release of hydrocyanic (HCN) gas!

Sodium hydroxide present in concentrations of 1.25N and especially 10 N represent extremely strong and concentrated caustic substances. Always wear gloves when handling these solutions (or the pellet form) and protective eyewear.

Lead acetate is a suspected carcinogen. Always wear gloves and a dust mask when handling this compound. Do not breathe in powdered dust and keep separated from foodstuffs.

IX. SUMMARY OF METHOD:

METHOD 335.4: The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a manual reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is converted to cyanogen chloride by reactions with chloramine-T, that subsequently reacts with pyridine and barbituric acid to give a red-colored complex. The amount of cyanide present is directly proportional to the intensity of the red-colored complex that is then quantitated using an ultraviolet-visible (UV-VIS) spectrometer.

X. INTERFERENCES:

Several interferences are encountered with this method. Some of the known interferences are aldehydes, nitrates, nitrites, and oxidizing agents such as chlorine, thiocyanate, thiosulfate, and sulfides. Because chlorine combines with sodium thiosulfate to for thiosulfates and sulfides, ascorbic acid is recommended for reducing the oxidizing agents.

High results may be obtained for samples that contain nitrate and/or nitrite. During the distillation process, nitrate and nitrite will form nitrous acid that will react with some organic compounds to form oximes. These oximes will decompose under analytical conditions to generate hydrocyanic acid (HCN) and thus give a bias high for the result.

X. INTERFERENCES (continued):

Oxidizing agents, such as chlorine, may decompose most of the cyanides during storage and manipulation. Test a drop of the sample with potassium iodide-starch paper (KI-starch paper) at the time of collection; a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. Sodium arsenite has also been employed to remove oxidizing agents but the toxicity associated with this compound makes ascorbic acid the reagent of choice.

Sulfides adversely affect the analytical procedure by producing hydrogen sulfide during the distillation process. Sulfides will distill aver with cyanide and, therefore, adversely affect colorimetric, titrimetric, and electrode procedures.