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METHOD 515.1

I. SCOPE AND APPLICATION:

This is a gas chromatographic (GC) method applicable to the determination of certain chlorinated acids in ground water and finished drinking water. The following compounds can be determined using this method.

<u>Analyte</u>	<u>Chemical Abstract Services Registry Numbers (CASRN)</u>
Acifluorfen*	50594-66-6
Benzaton	25057-89-0
Chloramben*	133-90-4
2,4-D	94-75-7
Dalapon*	75-99-0
2,4-DB	94-82-6
DCPA acid metabolites (a)	N/A
Dicamba	1918-00-9
3,5-Dichlorobenzoic acid	51-36-5
Dichloroprop	120-36-5
Dinoseb	88-85-7
5-Hydroxydicamba	7600-50-2
4-Nitrophenol*	100-02-7
Pentachlorophenol (PCP)	87-86-5
Picloram	1918-02-1
2,4,5-T	93-76-5
2,4,5-TP (Silvex)	93-72-1

(a) DCPA monoacid and diacid metabolites included in the method scope; DCPA diacid metabolite was used for the validation studies.

* These compounds are only qualitatively identified. These compounds are not quantitated because control over precision has not been demonstrated.

II. REAGENTS:

- Sodium Thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) solution

III. MATERIALS:

- 1-liter amber borosilicate sample bottle fitted with screw caps lined with TFE-fluorocarbon. Collect duplicate samples.
- Latex gloves
- Protective eyewear
- Plastic container for disposal of used pipette tips
- Disposable glass pipette and a rubber bulb.
- Pool and Spa 3-Way Test Strips (Chem Lab Products, Inc.)
- Paper towels & Kim wipes
- Pliers

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 about 10 minutes. This should be sufficiently long enough to allow the water temperature to stabilize and get a representative sample.
3. Adjust the water flow to about 1000 ml/minute or slow enough that no air bubbles purge the sample when collecting from the flowing stream.
4. Remove the cap from the 1-liter container. Do not rinse the container as it has already been acid rinsed and may already contain sodium thiosulfate as a preservative.
5. To fill, tip the bottle to about a 45° angle into the stream of water. Ensure the stream is sufficiently slow so as to be able to anticipate when the bottle is nearly full and thus avoid over flowing. Fill the bottle to within approximately $\frac{1}{2}$ inch of the mouth.
6. Remove the bottle from the flow and recap. Invert the sample bottle five times.
7. Place a chlorine detector 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 chlorine detector strip with the aliquot from the glass pipette and immediately flick the chlorine detector strip once using a sharp wrist motion to shake off the excess water. Compare the strip with the reference chlorine range. A determination must be made within 30 seconds.

IV. PROCEDURE (continued):

8. If no chlorine is detected, recap the bottle firmly, dry the sample bottle, attach the sample/laboratory label to the bottle and secure the chain of custody seal around the cap. Record the results in the field notebook and place the sample bottle in the ice chest to cool to 4°C. Collect duplicate samples.
9. If chlorine is present, add 5 drops of sodium thiosulfate solution, recap the bottle firmly and invert 5 times. Place a chlorine detector strip on a dry opened paper towel.
10. Remove the screw-on cap and obtain an aliquot of the sample using a glass pipette. Thoroughly moisten the chlorine detector strip with the aliquot from the glass pipette and immediately flick the chlorine detector strip once using a sharp wrist motion to shake off the excess water. Compare the strip with the reference chlorine range. A determination must be made within 30 seconds.
11. If no chlorine is detected, recap the bottle firmly, dry the sample bottle, attach the sample/laboratory label to the bottle and secure the chain of custody seal around the cap. Record the results in the field notebook and place the sample bottle in the ice chest to cool to 4°C. Remember to collect duplicate samples.
12. Continue the process of adding sodium thiosulfate to the sample, recapping, mixing, and testing until no chlorine is detected. Remember to note the number of drops of sodium thiosulfate added to the water sample in the field notebook.

V. SAMPLE TRANSPORT:

After obtaining the water samples, attach the completed chain of custody seal around the plastic cap of each 1-liter bottle. The 1-liter bottle must be amber colored to reflect sunlight since some of the pesticides analyzed for in this method are light sensitive and degrade when exposed to ultraviolet radiation. Place the sample bottle into the ice chest for transport. The samples must 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 voa samples for transportation. Never use “blue ice” as the samples will not adequately chill. 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 PRESERVATION:

If residual chlorine is known to be present, add 80 mg of sodium thiosulfate (or 50 mg of sodium sulfate) per liter of sample to the sample bottle prior to collecting the sample. When collecting the sample, minimize headspace in the bottle. After the sample is collected in the bottle containing the dechlorinating agent, seal the bottle and shake well until the preservative has dissolved. The samples must be iced or refrigerated at 4°C and protected from light from the time of collection until extraction. Holding time studies have indicated that the analytes are stable for up to 14 days if preserved properly.

VII. DEFINITIONS:

- A. *Sodium Thiosulfate (Na₂S₂O₃):* A preservative use to dechlorinate water samples. Reduces free chlorine into acid.
- B. *Eluant:* The solvent that contains the analytes after extraction or desorption.

VIII. SAFETY:

In the past, Method 515.1 required that the sample be preserved using mercuric chloride (Cl₂Hg) so that the samples final Cl₂Hg concentration was 10 mg/l. The purpose of this preservation test was to prevent microbial degradation of the pesticides. But recently EPA has issued a decree that the use of mercuric chloride for preservation is no longer required. EPA has addressed the potential problem of microbial degradation by adjusting the holding times of the sample. The driving force for this change came about because of the highly toxic nature of mercuric chloride. Not only was it an additional hazard to sample handlers and the analysts but it also created more stringent requirements with respect to sample disposal.

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

IX. SUMMARY OF METHOD:

METHOD 515.1: liquid/liquid extraction: A measured volume of sample, approximately 1 liter, is adjusted to a pH of 12 using 6 N sodium hydroxide (NaOH) and shaken for 1 hour to hydrolyze the derivatives. (Note: Since many of the herbicides contained in this method are applied as a variety of esters and salts, it is vital to hydrolyze them to the parent acid prior to their extraction.) Extraneous organic material is removed by a solvent wash. The sample is acidified, and the chlorinated acids are extracted with ethyl ether by shaking in a separatory funnel or by using a mechanical tumbler. The acids are converted to their methyl esters using diazomethane as the derivitizing agent or alternatively, trimethylsilyldiazomethane (TMSD). . The excess derivitizing agent is removed, and the esters are separated using capillary column gas chromatography and identified using an electron capture detector (ECD).