

METHOD 3660B

SULFUR CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Elemental sulfur is encountered in many sediment samples (generally specific to different areas in the country), marine algae, and some industrial wastes. The solubility of sulfur in various solvents is very similar to the organochlorine and organophosphorus pesticides. Therefore, the sulfur interference follows along with the pesticides through the normal extraction and cleanup techniques. In general, sulfur will usually elute entirely in Fraction 1 of the Florisil cleanup (Method 3620).

1.2 Sulfur will be quite evident in gas chromatograms obtained from electron capture detectors, flame photometric detectors operated in the sulfur or phosphorous mode, and Coulson electrolytic conductivity detectors in the sulfur mode. If the gas chromatograph is operated at the normal conditions for pesticide analysis, the sulfur interference can completely mask the region from the solvent peak through Aldrin.

1.3 Two techniques for the elimination of sulfur are detailed within this method: (1) the use of copper powder; and (2) the use of tetrabutylammonium sulfite. Tetrabutylammonium sulfite causes the least amount of degradation of a broad range of pesticides and organic compounds, while copper may degrade organophosphorus and some organochlorine pesticides.

1.4 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 The sample to undergo cleanup is mixed with either copper or tetrabutylammonium (TBA) sulfite. The mixture is shaken and the extract is removed from the sulfur cleanup reagent.

3.0 INTERFERENCES

The copper technique requires that the copper powder be very reactive, as evidenced by a bright shiny appearance (see Sec. 5.5 for the preparation of this reagent). However, care must be taken to remove all traces of the acid used to prepare the copper, in order to avoid degradation of some analytes.

4.0 APPARATUS AND MATERIALS

4.1 Mechanical shaker or mixer - Vortex Genie or equivalent.

4.2 Pipets, disposable - Pasteur type.

4.3 Centrifuge tubes, calibrated - 12 mL.

4.4 Glass bottles or vials - 10 mL and 50 mL, with polytetrafluoroethylene (PTFE)-lined screw caps or crimp tops.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Nitric acid, HNO_3 , dilute.

5.4 Solvents

5.4.1 Acetone, CH_3COCH_3 - Pesticide quality or equivalent.

5.4.2 Hexane, C_6H_{14} - Pesticide quality or equivalent.

5.4.3 2-Propanol, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ - Pesticide quality or equivalent.

5.5 Copper powder - Remove oxides by treating with dilute nitric acid, rinse with organic-free reagent water to remove all traces of acid, rinse with acetone and dry under a stream of nitrogen. (Copper, fine granular Mallinckrodt 4649 or equivalent).

5.6 Tetrabutylammonium (TBA) sulfite reagent

5.6.1 Tetrabutylammonium hydrogen sulfate, $[\text{CH}_3(\text{CH}_2)_3]_4\text{NHSO}_4$.

5.6.2 Sodium sulfite, Na_2SO_3 .

5.6.3 Prepare reagent by dissolving 3.39 g tetrabutylammonium hydrogen sulfate in 100 mL organic-free reagent water. To remove impurities, extract this solution three times with 20 mL portions of hexane. Discard the hexane extracts, and add 25 g sodium sulfite to the water solution. Store the resulting solution, which is saturated with sodium sulfite, in an amber bottle with a PTFE-lined screw cap. This solution can be stored at room temperature for at least one month.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Removal of sulfur using copper.

7.1.1 Concentrate the sample to exactly 1.0 mL or other known volume. Perform concentration using the techniques described in the appropriate 3500 series method.

CAUTION: When the volume of solvent is reduced below 1 mL, semivolatile analytes may be lost.

7.1.2 If the sulfur concentration is such that crystallization occurs, centrifuge to settle the crystals, and carefully draw off the sample extract with a disposable pipet leaving the excess sulfur in the concentration vessel. Transfer 1.0 mL of the extract to a calibrated centrifuge tube.

7.1.3 Add approximately 2 g of cleaned copper powder to the centrifuge tube. (The copper will fill the tube to approximately the 0.5 mL mark). Vigorously mix the extract and the copper powder for at least 1 min on the mechanical shaker. Allow the phases to separate.

7.1.4 Separate the extract from the copper by drawing off the extract with a disposable pipet and transfer to a clean vial. The volume remaining still represents 1.0 mL of extract.

NOTE: This separation is necessary to prevent further degradation of the pesticides.

7.2 Removal of sulfur using TBA sulfite

7.2.1 Concentrate the sample extract to exactly 1.0 mL or other known volume. Perform concentration using the techniques described in the appropriate 3500 series method.

CAUTION: When the volume of solvent is reduced below 1 mL, semivolatile analytes may be lost.

7.2.2 Transfer 1.0 mL of the extract to a 50 mL clear glass bottle or vial with a PTFE-lined screw-cap. Rinse the concentrator tube with 1 mL of hexane, adding the rinsings to the 50 mL bottle.

7.2.3 Add 1.0 mL TBA sulfite reagent and 2 mL 2-propanol, cap the bottle, and shake for at least 1 min. If the sample is colorless or if the initial color is unchanged, and if clear crystals (precipitated sodium sulfite) are observed, sufficient sodium sulfite is present. If the precipitated sodium sulfite disappears, add more crystalline sodium sulfite in approximately 0.100 g portions until a solid residue remains after repeated shaking.

7.2.4 Add 5 mL organic free reagent water and shake for at least 1 min. Allow the sample to stand for 5-10 min. Transfer the hexane layer (top) to a concentrator tube and concentrate the extract to approximately 1.0 mL using the techniques described in the appropriate 3500 series method. Record the actual volume of the final extract.

7.3 Analyze the cleaned up extracts by gas chromatography (see the determinative methods, Sec. 4.3 of this chapter).

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 All reagents should be checked prior to use to verify that interferences do not exist.

9.0 METHOD PERFORMANCE

9.1 Table 1 indicates the effect of using copper to remove sulfur on the recovery of certain pesticides.

10.0 REFERENCES

1. Goerlitz, D.F. and L.M. Law, Bulletin for Environmental Contamination and Toxicology, 6, 9 (1971).
2. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, Revision, July 1985.

TABLE 1
EFFECT OF COPPER ON PESTICIDES

Pesticide	Percent Recovery ^a Using Copper
Aroclor 1254	104.26
Lindane	94.83
Heptachlor	5.39
Aldrin	93.29
Heptachlor epoxide	96.55
DDE	102.91
DDT	85.10
BHC	98.08
Dieldrin	94.90
Endrin	89.26
Chlorobenzilate	0.00
Malathion	0.00
Diazinon	0.00
Parathion	0.00
Ethion	0.00
Trithion	0.00

- a Percent recoveries cited are averages based on duplicate analyses for all compounds other than for Aldrin and BHC. For Aldrin, four and three determinations were averaged to obtain the result for copper. Recovery of BHC using copper is based on one analysis.

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