METHOD 3660A

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 Three techniques for the elimination of sulfur are detailed within this method: (1) the use of copper powder; (2) the use of mercury; and (3) the use of tetrabutylammonium sulfite. Tetrabutylammonium sulfite causes the least amount of degradation of a broad range of pesticides and organic compounds, while copper and mercury may degrade organophosphorus and some organochlorine pesticides.

2.0 SUMMARY OF METHOD

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

3.0 INTERFERENCES

3.1 Removal of sulfur using copper:

3.1.1 The copper must be very reactive. Therefore, all oxides of copper must be removed so that the copper has a shiny, bright appearance.

3.1.2 The sample extract must be vigorously agitated with the reactive copper for at least one minute.

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 Teflon-lined screw caps or crimp tops.

4.5 Kuderna-Danish (K-D) apparatus.

4.5.1 Concentrator tube - 10 mL graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.5.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.5.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.5.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.5.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

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, $CH_3CH(OH)CH_3$ - 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 Mercury, triple distilled.

5.7 Tetrabutylammonium (TBA) sulfite reagent

5.7.1 Tetrabutylammonium hydrogen sulfate, $[CH_3(CH_2)_3]_4NHSO_4$.

5.7.2 Sodium sulfite, Na_2SO_3.

5.7.3 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 Teflon-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, Section 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 Kuderna-Danish (K-D) Technique (Method 3510, Sections 7.10.1 through 7.10.4).

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 K-D tube. 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 0.5 mL mark) to the centrifuge tube. Mix for at least 1 min on the mechanical shaker.

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 mercury

NOTE: Mercury is a highly toxic metal. All operations involving mercury should be performed in a hood. Prior to using mercury, it is recommended that the analyst become acquainted with proper handling and cleanup techniques associated with this metal.

7.2.1 Concentrate the sample extract to exactly 1.0 mL or other known volume. Perform concentration using the Kuderna-Danish (K-D) Technique (Method 3510, Sections 7.10.1 through 7.10.4).

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

7.2.2 Pipet 1.0 mL of the extract into a clean concentrator tube or Teflon-sealed vial.

7.2.3 Add one to three drops of mercury to the vial and seal. Agitate the contents of the vial for 15-30 sec. Prolonged shaking (2 hr) may be required. If so, use a mechanical shaker.

7.2.4 Separate the sample from the mercury by drawing off the extract with a disposable pipet and transfer to a clean vial.

7.3 Removal of sulfur using TBA sulfite

7.3.1 Concentrate the sample extract to exactly 1.0 mL or other known volume. Perform concentration using the Kuderna-Danish (K-D) Technique (Method 3510, Sections 7.10.1 through 7.10.4).

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

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

7.3.3 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.

7.3.4 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 with the micro K-D Technique (Section 7.3.5) or the Nitrogen Blowdown Technique (Section 7.3.6). Record the actual volume of the final extract.

7.3.5 Micro-Snyder Column Technique

7.3.5.1 Add another one or two clean boiling chips to the concentrator tube and attach a two ball micro-Snyder column. Prewet the column by adding about 0.5 mL of hexane to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 minutes. At the

proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joints with about 0.2 mL of solvent and add to the concentrator tube. Adjust the final volume to approximately 1.0 mL with hexane.

7.3.6 Nitrogen Blowdown Technique

7.3.6.1 Place the concentrator tube in a warm water bath (approximately 35°C) and evaporate the solvent volume to 1.0-2.0 mL, using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

CAUTION: Do not use plasticized tubing between the carbon trap and the sample.

7.3.6.2 The internal wall of the tube must be rinsed down several times with the appropriate solvent during the operation. During evaporation, the solvent level in the tube must be positioned to prevent water from condensing into the sample (i.e., the solvent level should be below the level of the water bath). Under normal operating conditions, the extract should not be allowed to become dry.

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

7.4 Analyze the cleaned up extracts by gas chromatography (see the determinative methods, Section 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 and mercury to remove sulfur on the recovery of certain pesticides.

10.0 REFERENCES

1. Loy, E.W., private communication.

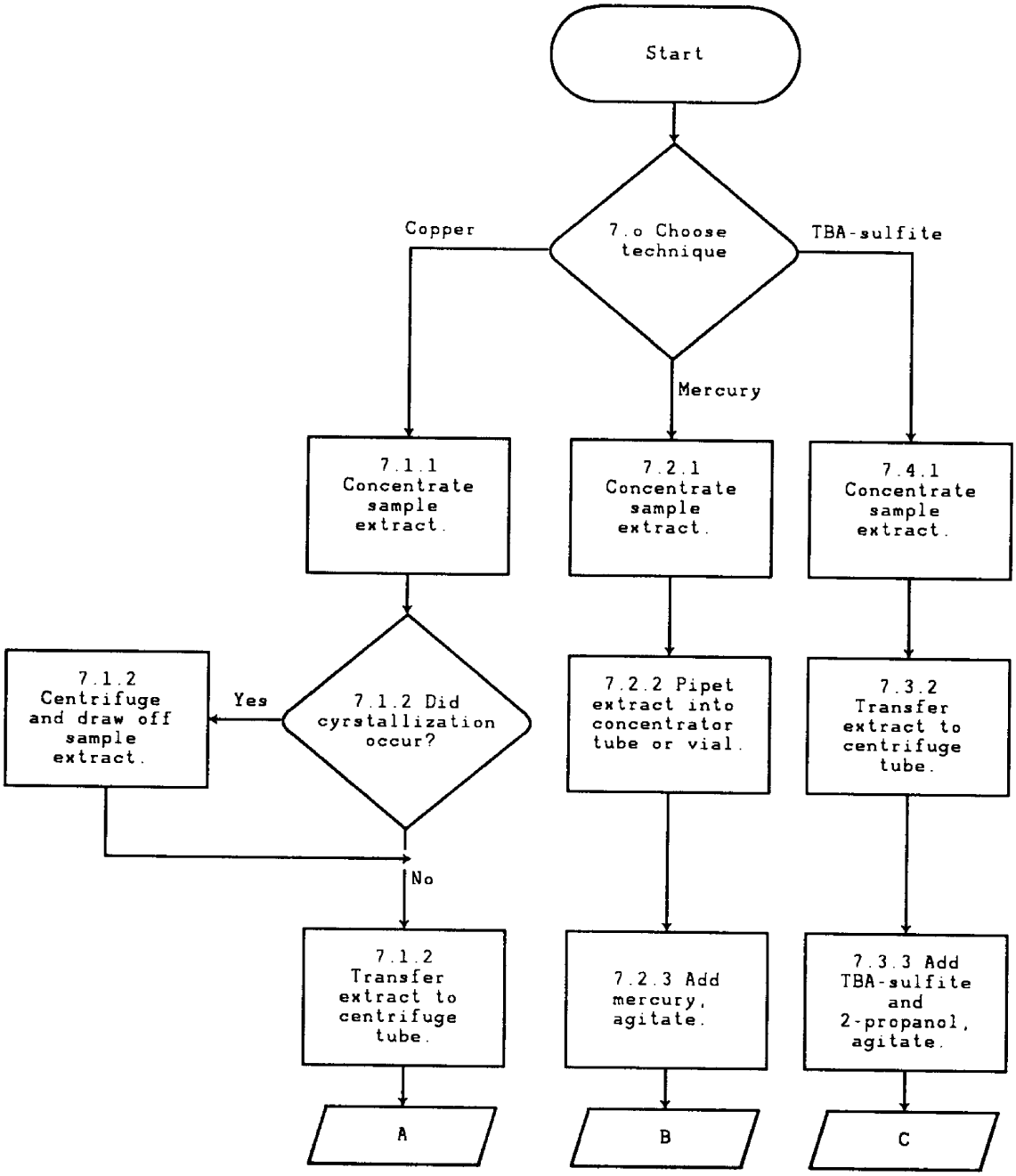
2. Goerlitz, D.F. and L.M. Law, Bulletin for Environmental Contamination and Toxicology, 6, 9 (1971).

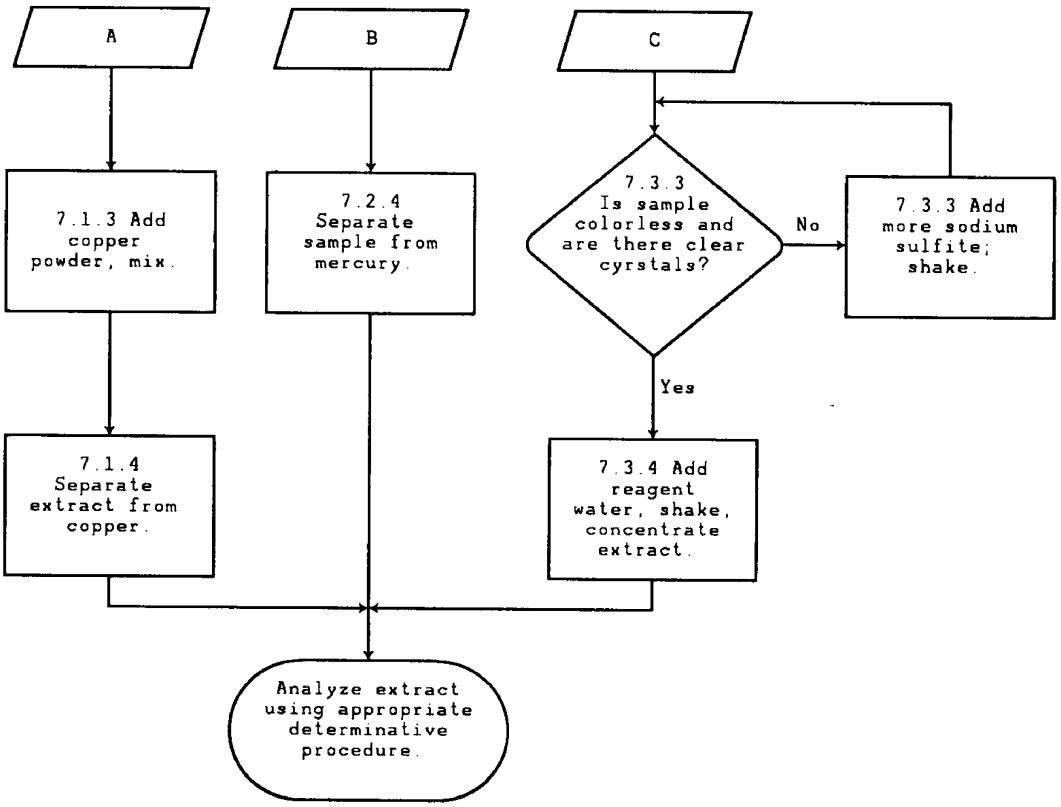
3. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, Revision, July 1985.

Table 1.
EFFECT OF MERCURY AND COPPER ON PESTICIDES

Pesticide	Percent Recovery[a] using: Mercury	Copper
Aroclor 1254	97.10	104.26
Lindane	75.73	94.83
Heptachlor	39.84	5.39
Aldrin	95.52	93.29
Heptachlor epoxide	69.13	96.55
DDE	92.07	102.91
DDT	78.78	85.10
BHC	81.22	98.08
Dieldrin	79.11	94.90
Endrin	70.83	89.26
Chlorobenzilate	7.14	0.00
Malathion	0.00	0.00
Diazinon	0.00	0.00
Parathion	0.00	0.00
Ethion	0.00	0.00
Trithion	0.00	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 mercury and copper, respectively. Recovery of BHC using copper is based on one analysis.


Start
7.0 Choose technique
Copper
Mercury
TBA-sulfite
7.1.1 Concentrate sample extract.
7.2.1 Concentrate sample extract.
7.4.1 Concentrate sample extract.
7.1.2 Did cyrstallization occur?
Yes
7.1.2 Centrifuge and draw off sample extract.
7.2.2 Pipet extract into concentrator tube or vial.
7.3.2 Transfer extract to centrifuge tube.
No
7.1.2 Transfer extract to centrifuge tube.
7.2.3 Add mercury, agitate.
7.3.3 Add TBA-sulfite and 2-propanol, agitate.
A
B
C


A
B
C
7.1.3 Add copper powder, mix.
7.2.4 Separate sample from mercury.
7.3.3 Is sample colorless and are there clear cyrstals?
No
7.3.3 Add more sodium sulfite; shake.
Yes
7.1.4 Separate extract from copper.
7.3.4 Add reagent water, shake, concentrate extract.
Analyze extract using appropriate determinative procedure.