METHOD 3600C

CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Method 3600 provides general guidance on selection of cleanup methods that are appropriate for the target analytes of interest. Cleanup methods are applied to the extracts prepared by one of the extraction methods, to eliminate sample interferences.

1.2 The following table lists the cleanup methods and provides a brief description of the type of cleanup.

Method No.	Method Name	Cleanup Type
3610	Alumina Cleanup	Adsorption
3611	Alumina Cleanup and Separation of Petroleum Wastes	Adsorption
3620	Florisil Cleanup	Adsorption
3630	Silica Gel Cleanup	Adsorption
3640	Gel-Permeation Cleanup (GPC)	Size-Separation
3650	Acid-Base Partition Cleanup	Acid-Base Partitioning
3660	Sulfur Cleanup	Oxidation/Reduction
3665	Sulfuric Acid/Permanganate Cleanup	Oxidation/Reduction

1.3 The purpose of applying a cleanup method to an extract is to remove interferences and high boiling material that may result in:

- errors in quantitation (data may be biased low because of analyte adsorption in the injection port or front of the GC column or biased high because of overlap with an interference peak);
- false positives because of interference peaks falling within the analyte retention time window;
- false negatives caused by shifting the analyte outside the retention time window;
- rapid deterioration of expensive capillary columns; and,
- instrument downtime caused by cleaning and rebuilding of detectors and ion sources.

1.4 The following techniques have been applied to extract purification: adsorption chromatography; partitioning between immiscible solvents; gel permeation chromatography; oxidation of interfering substances with acid, alkali, or oxidizing agents. These techniques may be used individually or in various combinations, depending on the extent and nature of the co-extractives.

1.5 Most extracts of soil and waste require some degree of cleanup, whereas, cleanup for water extracts may be unnecessary. Highly contaminated extracts (e.g. sample extracts of oily waste or soil containing oily residue) often require a combination of cleanup methods. For example, when analyzing for organochlorine pesticides and PCBs, it may be necessary to use gel permeation

chromatography (GPC), to eliminate the high boiling material and a micro alumina or Florisil column to eliminate interferences with the analyte peaks on the GC/ECD.

1.6 Prior to employing this method, analysts are advised to consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in this procedure is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to meet the data quality objectives or needs for the intended use of the data.

2.0 SUMMARY OF METHOD

Refer to the specific cleanup method for a summary of the procedure.

3.0 INTERFERENCES

3.1 Analytical interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware. All of these materials must be routinely demonstrated to be free of interferences, under the conditions of the analysis, by running laboratory reagent blanks.

3.2 More extensive procedures than those outlined in the methods may be necessary for reagent purification.

4.0 APPARATUS AND MATERIALS

Refer to the specific cleanup method for apparatus and materials needed.

5.0 REAGENTS

Refer to the specific cleanup method for the reagents needed.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

7.0 PROCEDURE

7.1 Prior to using the cleanup procedures, samples normally undergo solvent extraction. Chapter Two, Sec. 2.0, may be used as a guide for choosing the appropriate extraction procedure based on the physical composition of the waste and on the analytes of interest in the matrix (see also Method 3500 for a general description of the extraction technique). For some organic liquids, extraction prior to cleanup may not be necessary.

7.2 Most soil/sediment and waste sample extracts will require some degree of cleanup. The extract is then analyzed by one of the determinative methods. If interferences still preclude analysis for the analytes of interest, additional cleanup may be required.

7.3 Many of the determinative methods identify cleanup methods that should be used when determining particular analytes (e.g., Method 8061, gas chromatography of phthalate esters, recommends using either Method 3610 (alumina column cleanup) or Method 3620 (Florisil column cleanup) if interferences prevent analysis. However, the experience of the analyst may prove invaluable in determining which cleanup methods are needed. Many matrices may require a combination of cleanup procedures in order to ensure proper analytical determinations, however, each cleanup step has the potential to decrease the analytical sensitivity through small losses of analytes during the cleanup. As a result, when multiple cleanup procedures are necessary, additional care is recommended to mnimize analyte loss during each individual cleanup procedure.

7.4 Specific guidance on each cleanup technique is listed in the individual cleanup methods that follow. The amount of extract cleanup required prior to the final determination depends on the concentration of interferences in the sample, the selectivity of both the extraction procedure and the determinative method and the required detection limit. The following Sections give a description of the different cleanup approaches:

7.4.1 Adsorption chromatography - Alumina (Methods 3610 and 3611), Florisil (Method 3620), and silica gel (Method 3630) are useful for separating analytes of a relatively narrow polarity range away from extraneous, interfering peaks of a different polarity. These are primarily used for cleanup of a specific chemical group of relatively non-polar analytes, i.e., organochlorine pesticides, polynuclear aromatic hydrocarbons (PAHs), nitrosamines, etc.. Solid phase extraction cartridges have been added as an option.

7.4.2 Acid-base partitioning (Method 3650) - Useful for separating acidic or basic organics from neutral organics. It has been applied to analytes such as the chlorophenoxy herbicides and phenols. It is very useful for separating the neutral PAHs from the acidic phenols when analyzing a site contaminated with creosote and pentachlorophenol.

7.4.3 Gel permeation chromatography (GPC) (Method 3640) - The most universal cleanup technique for a broad range of semivolatile organics and pesticides. It is capable of separating high molecular-weight, high boiling material from the sample analytes. It has been used successfully for all the semivolatile base, neutral, and acid compounds associated with the EPA Priority Pollutant and the Superfund Target Compound list prior to GC/MS analysis for semivolatiles and pesticides. GPC may not be applicable to elimination of extraneous peaks on a chromatogram which interfere with the analytes of interest. It is, however, useful for the removal of high boiling materials which would contaminate injection ports and column heads, prolonging column life, stabilizing the instrument, and reducing column reactivity.

7.4.4 Sulfur cleanup (Method 3660) - Useful in eliminating sulfur from sample extracts, which may cause chromatographic interference with analytes of interest.

7.4.5 Sulfuric acid/permanganate cleanup (Method 3665) - Useful for the rigorous cleanup of sample extracts prior to analysis for polychlorinated biphenyls (PCBs). This method should be used whenever elevated baselines or overly complex chromatograms prevent accurate quantitation of PCBs. This method cannot be used to cleanup extracts for other target analytes, as it will destroy most organic chemicals including the pesticides Aldrin, Dieldrin, Endrin, Endosulfan (I and II), and Endosulfan sulfate.

7.5 Fractionation is a useful technique that can aid in the separation of complex mixtures of analytes. For instance, an analyst may use Method 3630 (Silica Gel) for separating the PCBs away from most organochlorine pesticides. Method 3611 (Alumina) may be used for fractionation of aliphatic, aromatic, and polar analytes. Method 3620 (Florisil) provides for fractionation of the organochlorine pesticides.

7.6 Cleanup capacity is another factor that must be considered in choosing a cleanup technique. The adsorption methods (3610, 3620, and 3630) provide the option of using standard column chromatography techniques or solid phase extraction cartridges. The decision process in selecting between the different options available generally depends on the amount of interferences/high boiling material in the sample extract and the degree of cleanup required by the determinative method. The solid phase extraction cartridges require less elution solvent and less time, however, their cleanup capacity is drastically reduced when comparing a 0.5 g or 1.0 g Florisil cartridge to a 20 g standard Florisil column. The same factor enters into the choice of the 70 g gel permeation column specified in Method 3640 versus a high efficiency column. As with any other method choice issue, the responsibility for ensuring that the use of a cartridge cleanup is appropriate lies with the laboratory. If the results from a sample analysis suggest that the cleanup was not effective because the capacity of the cartridge was exceeded, then it may be necessary to repeat the procedures with either a larger cartridge or the standard column chromatographic procedure.

7.7 Table 1 indicates the recommended cleanup techniques for the indicated groups of compounds. This information can also be used as guidance for compounds that are not listed. Compounds that are chemically similar to these groups of compounds should behave similarly when taken through the cleanup procedure. However, this must be demonstrated by determining recovery of standards taken through the method.

7.8 Following cleanup, the sample is concentrated to whatever volume is listed in the determinative method using the procedures described in the appropriate 3500 series method. Analysis follows as per the appropriate determinative procedure.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control procedures.

8.2 The analyst must demonstrate that the compounds of interest are being quantitatively recovered by the cleanup technique before the cleanup is applied to actual samples. For sample extracts that are cleaned up, the associated quality control samples (e.g. spikes, blanks, replicates, and duplicates) must also be processed through the same cleanup procedure.

8.3 The analysis using each determinative method (GC, GC/MS, HPLC) lists instrument calibration procedures using stock standards. It is recommended that cleanup also be performed on a series of the same type of standards to validate chromatographic elution patterns for the compounds of interest and to verify the absence of interferences from reagents.

9.0 METHOD PERFORMANCE

Refer to the specific cleanup method for performance data.

10.0 REFERENCES

Refer to the specific cleanup method.

TABLE 1.

RECOMMENDED CLEANUP TECHNIQUES FOR INDICATED GROUPS OF COMPOUNDS

Analyte Group	Determinative[a] Method	Cleanup Method Options
Phenols	8041	3630[b], 3640, 3650, 8041[c]
Phthalate esters	8061	3610, 3620, 3640
Nitrosamines	8070	3610, 3620, 3640
Organochlorine pesticides	8081	3620, 3640, 3660
PCBs	8082	3620, 3630, 3665
Nitroaromatics and cyclic ketones	8091	3620, 3640
Polynuclear aromatic hydrocarbons	8100/8310	3611, 3630, 3640
Haloethers	8111	3620, 3640
Chlorinated hydrocarbons	8121	3620, 3640
Aniline and derivatives	8131	3620, 3640
Organophosphorus pesticides	8141	3620
Chlorinated herbicides	8151	8151[d], 3620
Semivolatile organics	8270	3640, 3650, 3660
Petroleum waste	8270	3611, 3650
PCDDs and PCDFs by LR/MS	8280	8280
PCDDs and PCDFs by HR/MS	8290	8290
N-methyl carbamate pesticides	8318	8318

[a] The GC/MS Method 8270 is also an appropriate determinative method for all analyte groups, unless lower detection limits are required.

[b] Cleanup applicable to derivatized phenols.

[c] Method 8041 includes a derivatization technique followed by GC/ECD analysis, if interferences are encountered using GC/FID.

[d] Method 8151 incorporates an acid-base cleanup step as an integral part of the method.