

METHOD 3600B

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

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<u>Method #</u>	<u>Method Name</u>	<u>Cleanup Type</u>
3610	Alumina Cleanup	Adsorption
3611	Alumina Cleanup & Separation for Petroleum Waste	Adsorption
3620	Florisil Cleanup	Adsorption
3630	Silica Gel Cleanup	Adsorption
3640	Gel-Permeation Cleanup	Size-Separation
3650	Acid-Base Partition Cleanup	Acid-Base Partitioning
3660	Sulfur Cleanup	Oxidation/Reduction
3665	Sulfuric Acid/Permanganate Cleanup	Oxidation/Reduction

1.2 The purpose of applying a cleanup method to an extract is to remove interferences and high boiling material that may result in: (1) 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); (2) false positives because of interference peaks falling within the analyte retention time window; (3) false negatives caused by shifting the analyte outside the retention time window; (4) rapid deterioration of expensive capillary columns; and, (5) instrument downtime caused by cleaning and rebuilding of detectors and ion sources. 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.

1.3 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.

1.3.1 Adsorption column 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.

1.3.2 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.

1.3.3 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.

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

1.4 Several of the methods are also useful for fractionation of complex mixtures of analytes. Use the solid phase extraction cartridges in Method 3630 (Silica Gel) for separating the PCBs away from most organochlorine pesticides. Method 3611 (Alumina) is for the fractionation of aliphatic, aromatic and polar analytes. Method 3620 (Florisil) provides fractionation of the organochlorine pesticides.

1.5 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.

1.6 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.

2.0 SUMMARY OF METHOD

2.1 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

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

5.0 REAGENTS

5.1 Refer to the specific cleanup method for the reagents needed.

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 Prior to using the cleanup procedures, samples normally undergo

solvent extraction. Chapter Two, Section 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 specify 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. As indicated in Section 1.0 of this method, many matrices may require a combination of cleanup procedures in order to ensure proper analytical determinations.

7.4 Guidance for cleanup is specified in each of the 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.

7.5 Following cleanup, the sample is concentrated to whatever volume is required in the determinative method. Analysis follows as specified in the determinative procedure.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One 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) specifies 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

9.1 Refer to the specific cleanup method for performance data.

10.0 REFERENCES

10.1 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	8040	3630 ^b , 3640, 3650, 8040 ^c
Phthalate esters	8060/8061	3610, 3620, 3640
Nitrosamines	8070	3610, 3620, 3640
Organochlorine pesticides & PCBs	8080/8081	3620, 3640, 3660
PCBs	8080/8081	3665
Nitroaromatics and cyclic ketones	8090	3620, 3640
Polynuclear aromatic hydrocarbons	8100/8310	3611, 3630, 3640
Chlorinated hydrocarbons	8120/8121	3620, 3640
Organophosphorus pesticides	8140/8141	3620
Chlorinated herbicides	8150/8151	8150 ^d , 8151 ^d , 3620
Semivolatile organics	8250/8270	3640, 3650, 3660
Petroleum waste	8250/8270	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 Methods, 8250 and 8270, are also appropriate determinative methods for all analyte groups, unless lower detection limits are required.

^b Cleanup applicable to derivatized phenols.

^c Method 8040 includes a derivatization technique followed by GC/ECD analysis, if interferences are encountered using GC/FID.

^d Methods 8150 and 8151 incorporate an acid-base cleanup step as an integral part of the methods.

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