# Alumina Column Cleanup of Organic Extracts

References: USEPA Office of Solid Waste and Emergency Response, Methods 3610B and 3611B Alumina Cleanup in Test Methods for Evaluating Solid Waste, SW846, Third Edition, Final Update, Revision 2, December 1996.

NOAA 1998. Sampling and Analytical Methods of the National Status and Trends Program. Mussel Watch Project 1984-1996. NOAA Technical Memorandum NOS ORCA 130.

## 1. Scope and Application

**Matrices:** This method is suitable for the cleanup of organic sample extracts from chromatographically interfering material prior to analysis for PAHs and PCBs, and in some cases where the analyte list is limited, for Pesticides. The sample extracts may have originated from water, soil, sediment, neat petroleum or tissue matrices.

**Definitions:** Refer to Alpha Analytical Quality Manual.

Alumina is a highly porous and granular form of aluminum oxide. This method is applicable to the cleanup of organic sample extracts prior to analysis by the appropriate determinative method.

The applicable extraction SOPs are:

- Extraction of Liquid Samples by Separatory Funnel-Method 3510C (OP-001),
- Tissue Preparation and Homogenization (OP-003),
- Microscale Solvent Extraction (MSE) (OP-016),
- Shaker Table Extraction (OP-013)
- Organic Waste Diution Extraction, EPA 3580A (OP-021)

The applicable analytical SOPs are:

- Determination of PCB Homologs, Individual Congeners and Pesticides by GC/MS-SIM (O-015),
- Method 8082-PCBs as Aroclors or Congeners by GC/ECD, (O-012),
- Analysis of PAH by GC/MS-SIM (O-007),
- Analysis of Parent and Alkylated PAHs and Selected Heterocyclic Compounds by GC/MS-SIM (O-008),
- Total Petroleum Hydrocarbons and Saturated Hydrocarbons by GC-FID (O-003)

This method should be used whenever elevated baselines or overly complex chromatograms prevent accurate quantification of the target compounds, and is recommended for samples with high lipid content, polymers, proteins, natural resins, cellular components and dispersed high molecular weight compounds.

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one or more of the following laboratory

personnel before performing the modification: Area Supervisor, Department Supervisor, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of experienced analysts. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability, analyzing a proficiency test sample and completing the record of training.

After initial demonstration, ongoing demonstration is based on acceptable laboratory performance of at least a quarterly laboratory control sample or acceptable performance from an annual proficiency test sample. A major modification to this procedure requires demonstration of performance. The identification of major method modification requiring performance demonstration is directed by the Quality Assurance Officer and/or Laboratory Director on a case-by-case basis.

# 2. Summary of Method

A measured sample volume or amount, approximately 1L for aqueous samples, and 0.1-30g for solid/tissue/oil samples, is extracted using the appropriate extraction protocol for the matrix (Section 3.1.1). The extract is concentrated to a measured volume, in most cases, 2mL. 1mL of the samples is loaded onto the alumina column, and 1mL is archived. Note: The pre- and post- cleaned sample volumes may vary on a project to project basis. The pre-alumina column sample volume is determined with the gross gravimetric weight of the extract following the procedures in Alpha Analytical SOP OP-017, *Gravimetric Determination*, so as not to overload the alumina.

Samples will be copper cleaned before samples are loaded onto the column. Samples should be in contact with activated copper for a minimum of two hours.

The appropriate sample volume is eluted through the alumina column with 100mL of methylene chloride. The sample extract is re-concentrated to an appropriate volume and submitted to the next cleanup step, or submitted for instrument analysis. Post-alumina cleaned sample gravimetric determination may be made.

## 2.1 Method Modifications from Reference

None.

# 3. Reporting Limits

Not applicable.

# 4. Interferences

Solvents, reagents and glassware may introduce interferences. These must be demonstrated to be free of interferences by the analysis of a method blank. See the Alpha Analytical SOP *Reagent, Solvent and Standard Control* (G-008) and *Laboratory Glassware Cleaning* (G-002), for additional details. Alumina reagent purification is included in Section 10.3.1.

Many interferences can be removed by sample cleanup. Only appropriate cleanup techniques must be performed based on the suspected interference and the compounds of interest.

Soapy residue may result in basic conditions on glassware and may cause degradation of the pesticides Aldrin and Heptachlor, and some organophosphorous pesticides. All glassware must be

rinsed thoroughly with deionized water and solvent to remove soapy residue. See the Alpha Analytical SOP (G-002) *Laboratory Glassware Cleaning,* for additional details.

Phthalate esters can be a major source of contamination if any material containing plasticizers (phthalates) comes in contact with the sample during the extraction process. Use of plastic or any material containing plasticizers (phthalates) must be avoided during extraction, concentration and analysis.

# 5. Health and Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

# 6. Sample Collection, Preservation, Shipping and Handling

## 6.1 Sample Collection

Refer to applicable extraction SOPs listed in Section 1.

## 6.2 Sample Preservation

Refer to applicable extraction SOPs listed in Section 1.

## 6.3 Sample Shipping

Refer to SOP/01-01 Sample Receipt and Login for sample shipping requirements.

## 6.4 Sample Handling

Refer to applicable extraction SOPs listed in Section 1.

# 7. Equipment and Supplies

## 7.1 13mm glass column with Teflon stopcock.

**7.2 General Lab supplies:** Disposable glass Pasteur pipettes with bulbs, glass wool, 250mL glass beakers, gas tight syringes (25uL, 50uL, 100uL, 250uL, 500uL, 1mL, 2.5mL, 5mL and 10mL), 250mL KD concentration apparatus, 20mL concentrator tubes, 1L certified pre-cleaned amber jars.

## 7.3 Muffle Furnace.

## 7.4 Top loading balance.

## 7.5 Pyrex baking sheet, 9x12

## 7.6 Glass rod

# 8. Reagents and Standards

**8.1 Methylene Chloride:** Pesticide grade.

**8.2 Organic free reagent water.** Deionized (DI) water is ASTM Type II laboratory reagent grade water.

**8.3 Sodium Sulfate:** Baked at 400C for 4 hours.

**8.4 Activated copper:** See Alpha Analytical SOP OP-007 Sulfur Cleanup with Copper (Method 3660B), for details.

**8.5 Alumina:** MP alumina B Super 1 thin layer chromatography grade – baked at 400°C for 4 hours and pre-tested for cleanliness. Store at 105°C until used.

# 9. Quality Control

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

All associated quality control samples must undergo the same cleanup regiment as the samples. Method blanks must be deemed acceptable and free from contamination as soon as practical.

Refer to the appropriate extraction/preparation and determinative method SOPs, listed in Section 3.0, for specific QC criteria for surrogates, matrix spikes, duplicates and laboratory control spikes.

## 9.1 Blank(s)

Method blanks must be deemed acceptable and free from contamination as soon as practical.

## 9.2 Laboratory Control Sample (LCS)

Refer to the appropriate extraction/preparation and determinative method SOPs listed in Section 1.

## 9.3 Initial Calibration Verification (ICV)

Not applicable to this method.

## 9.4 Continuing Calibration Verification (CCV)

Not applicable to this method.

## 9.5 Matrix Spike

Refer to the appropriate extraction/preparation and determinative method SOPs listed in Section 1.

## 9.6 Laboratory Duplicate

Refer to the appropriate extraction/preparation and determinative method SOPs listed in Section 1.

## 9.7 Method-specific Quality Control Samples

Refer to the appropriate extraction/preparation and determinative method SOPs listed in Section 1.

### 9.8 Method Sequence

- Alumina preparation
- Column preparation
- Sample Cleanup
  - Load sample onto column
  - Rinse with 1mL methylene chloride 2x
  - Add 100mL methylene chloride
  - Flow through column
- Sample concentration
- Final volume

## 10. Procedure

### 10.1 Equipment Set-up

Samples are prioritized by the Organic Manager or Preparation Group Leader for extraction and cleanup based on hold time and client due date. All samples must first be copper cleaned. See the Alpha Analytical SOP OP-007 *Sulfur Cleanup with Copper (Method 3660B)*, for details.

### 10.2 Initial Calibration

Not applicable to this method.

### 10.3 Equipment Operation and Sample Processing

#### 10.3.1 Alumina Preparation and Deactivation

**10.3.1.1** A 500g – 1000g aliquot of alumina is poured into a 1L beaker, and then spread in a thin layer onto a Pyrex baking sheet. This is placed into the muffle furnace for 4 hours at 400°C. Baked alumina can be stored at 100C-105°C to keep moisture out, until it is ready for deactivation and use. Additionally, the alumina MUST be tested for cleanliness after baking to ensure background cleanliness.

**10.3.1.1.1** Alumina Cleanliness Test: Aliquot 20g of baked alumina into a 60mL VOA vial. Add enough methylene chloride to fill the headspace of the vial. Spin the vial on the mechanical spinner for approximately 20 minutes. Pour off the methylene chloride and concentrate via KD to 1mL. Submit the extract for FID analysis. The extract is compared to non-extracted methylene chloride analysis under the same instrument conditions. The Section Supervisor can ensure the alumina lot is clean and acceptable for use. All FID chromatograms are kept for reference in the log book located in the preparation lab.

**10.3.1.2** Remove the alumina from the furnace and allow it to cool for at least 20 minutes. Weigh the needed amount (20g per column) in a 1L pre-cleaned amber jar with Teflon lined cap. Adjust the weight of alumina to be used for the sample batch to the next 50$^{th}$ increment so that the water that needs to be added for deactivation

can be measured with a syringe. Volume of water should be a whole number (*i.e.*, for 12 columns the amounts used should be; 250g of alumina = 15mL of water, not 240g of alumina = 14.4mL of water) Add 6% (alumina weight) of de-ionized water to the alumina to deactivate it. Close the amber jar tightly and place in the tumbler for 2 hours.

**10.3.2 Column Preparation**

**10.3.2.1** Solvent rinse 13mm glass columns with methylene chloride, or acetone first then methylene chloride if water is present in the column. Ensure stopcocks are rinsed by turning five times. Add a plug of baked glass wool to the top of the column and rinse again with methylene chloride, allowing it to flow through column. Turn stopcock to prevent methylene chloride from exiting column and add enough methylene chloride to cover glass wool. Using glass rod, bring glass wool to the bottom of the column and tap out any bubbles.

**10.3.2.2** Weigh 20 grams ± 0.05g of the 6 % de-activated alumina into a solvent rinsed 250mL beaker and immediately add methylene chloride to create slurry. Add this directly to the column. Rinse any remaining alumina out of the beaker into the column and allow it to settle. Start methylene chloride flowing through the column to rinse down any alumina that may be stuck onto the side walls of the column. Add approximately ½ inch of sodium sulfate to the top of the alumina.

**10.3.2.3** Pre-elute column with 50mL of methylene chloride. ***At <u>no time</u> should the bed of alumina be exposed to the air***. Leave approximately ½ inch of methylene chloride over the top of sodium sulfate.

**10.3.2.4** Place solvent rinsed 250mL KD concentration setup under the column to receive the eluant.

**10.3.3 Sample Cleanup**

**10.3.3.1** Load the sample at the correct pre-determined volume onto the column with a Pasteur pipette ensuring alumina bed is not disturbed. A new pipette must be used for each sample.

**10.3.3.2** Open the stopcock and allow the sample to move onto alumina bed through sodium sulfate layer and close the stopcock when the sample is on the alumina.

**10.3.3.3** Rinse the original sample vial with approximately 1mL of methylene chloride, and load this onto the column. Open the stopcock to move the methylene chloride onto the alumina bed. Repeat 1 more time for a total of two rinses of the original sample vial.

**10.3.3.4** Once both rinses have been pulled onto the alumina column bed, add 100ml of methylene chloride for total sample elution, without disturbing the alumina bed. Start methylene chloride flowing through the column at approximately 5-7 mL/min.

**10.3.3.5** Samples are then concentrated via KD (see Section 1 for the applicable extraction SOPs, which provide this procedure) on a 75°C water bath to approximately 5mL.

**10.3.3.6** Samples are then adjusted to the appropriate final volume on the N-Evap. Additional sample cleanup (silica gel, GPC, or acid) may be required depending upon project requirements. If no further cleanups are required, samples are spiked with the appropriate internal standard and submitted for determinative instrument analysis.

### 10.4 Continuing Calibration

Not applicable to this method.

### 10.5 Preventive Maintenance

An instrument service company calibrates temperature of the furnace on an annual basis. Certificates are kept on file.

## 11. Data Evaluation, Calculations and Reporting

Procedures for data and record management must adhere to the Quality Systems Manual, other subordinate documents covering record keeping, and the Alpha Analytical *Document Control* SOP (08-01). All records must be stored in such a manner as to be safe and accessible for at least 10 years.

The extraction/cleanup bench sheets and other relevant laboratory notebooks must follow the specifications in the Logbook Useage Work Instructions, WI 108-01, and all record keeping and document control practices. All relevant observation must be recorded onto the bench sheets during the procedure.

See the appropriate Alpha Analytical SOPs for details on sample analysis, data evaluation, calculations and data reporting.

## 12. Contingencies for Handling Out-of-Control Data or Unacceptable Data

All results for the organic compounds of interests are reportable without qualification if extraction and analytical holding times are met, preservation (including cooler temperatures) are met, all QC criteria defined in the table below are met, and matrix interference is reduced and not suspected during extraction, cleanup and/or analysis of the samples. If any of the below QC parameters are not met, all associated samples must be evaluated for re-extraction and/or re-analysis.

| QC Parameter | Acceptance Criteria |
|---|---|
| Method Blank | < reporting limit |
| Laboratory Control Samples | See the applicable Alpha Analytical SOP for acceptance criteria |
| Sample Duplicate | See the applicable Alpha Analytical SOP for acceptance criteria |
| Matrix Spike | See the applicable Alpha Analytical SOP for acceptance criteria |
| Matrix Spike Duplicate | See the applicable Alpha Analytical SOP for acceptance criteria |
| Standard Reference Material | See the applicable Alpha Analytical SOP for acceptance criteria |

If non-compliant organic compound results are to be reported, the Organic Manager and the QA Manager must approve the reporting of these results. The laboratory Project Manager shall be notified, and may chose to relay the non-compliance to the client or other QA oversight individual,

for approval, or other corrective action, such as re-sampling, re-extraction and/or re-analysis. The analyst or QA Specialist performing the secondary analytical review initiates the project narrative, and the narrative must clearly document the non-compliance and provide a reason for acceptance of these results.

# 13. Method Performance

## 13.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP/08-05. These studies performed by the laboratory are maintained on file for review.

The Method Detection Limits (MDL) do not apply to this SOP. However, when determining MDLs for a given extraction and/or analytical technique, any cleanup methods that would routinely be used, must be employed.

## 13.2 Demonstration of Capability Studies

Refer to Alpha SOP/08-12 for further information regarding IDC/DOC Generation.

### 13.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

### 13.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

# 14. Pollution Prevention and Waste Management

Once satisfactory organic compound results have been generated, the cleaned extracts and any archive extract portion is held for 30 days, or longer if specified by a client contract, then discarded into a 55-gallon drum labeled “Vial Waste”.

All waste generated during sample extract cleanup must be discarded in the 55-gallon drum labeled “Solvent Flammable” or “Solvent non-flammable” waste

Refer to Alpha’s Chemical Hygiene Plan and Waste Management and Disposal SOP for further pollution prevention and waste management information.

# 15. Referenced Documents

Chemical Hygiene Plan

CQSM Quality Systems Manual

SOP/01-01 Sample Receipt and Login

SOP G-008 Reagent, Solvent and Standard Control

SOP/08-05 MDL/LOD/LOQ Generation

SOP/08-12 IDC/DOC Generation

G-006 Hazardous Waste and Sample Disposal

WI 108-01 Laboratory Notebook Useage Work Instructions

SOP G-002 Laboratory Glassware Cleaning

SOP/08-01 Document Control

# 16. Attachments

None.