FACILITY SOP ATTACHMENT

SOP NUMBER: IR-GCS-PEST, Rev 1 (9/28/2012)	**CHANGE FORM ID: CF2**

SOP TITLE: ORGANOCHLORINE PESTICIDES BY GC (EPA METHODS 608 & 8081A)

REASON FOR ADDITION OR CHANGE (Use additional sheets if necessary):

1) Clarification of how Arizona DHS requirement to follow 8000C affects the way the 8081A analysis is performed and evaluated.(Audit finding 160.QA-F-12g)

2) Updated data review checklist to ensure target analytes are not reported off a column on which they co-eluted.

3) Added optional procedure for verification of suspect peaks by GCMS-SIM

CHANGE OR ADDITION (Use additional sheets if necessary):

ITEM #1:

Note on 5th main bullet under 9.2.3 reads:

> **NOTE that Arizona follows method 8000C. EPA 8000C does not allow the use of the grand mean RSD to evaluate calibration linearity.**

Change to read:

> NOTE **that all samples submitted for 8081A analysis are analyzed in accordance with EPA 8000B** WITH THE EXCEPTION OF SAMPLES FROM ARIZONA which must follow method 8000C. EPA 8000C does not allow the use of the grand mean RSD to evaluate calibration linearity. **If any 8081A samples in the analysis batch are from an Arizona-based client (or fall under a project requiring AZ certification), all reported analytes must individually meet calibration criteria.**

ITEM #2: Revised checklists (attached)

ITEM #3:

In cases when a target analyte is detected on both instrument channels but the retention time is not well-centered in the RT window on one or both channels, the laboratory may opt to analyze the sample semi-quantitatively by GCMS-SIM. The sample extract to be checked must be analyzed in conjunction with a check standard at or below the required reporting limit. If the presence of the analyte is confirmed by GCMS, the original GC result is to be reported in the manner described in the GC-pesticides SOP. If the presence is NOT confirmed, the analyte will be reported as ND but must be accompanied by an NCM that describes that this reported result is based on GCMS confirmation and not the GC raw data.

Prepared By: D. Dawes

***APPROVED BY:**

FACILITY SOP ATTACHMENT

SOP NUMBER: IR-GCS-PEST, Rev 1 (9/28/2012)	CHANGE FORM ID: CF2
Technical Review Signature	Date 2/27/13
Quality Assurance Manager	Date 2-27-2013
Environmental Health and Safety Coordinator	Date 02/27/2013
Interim Laboratory Director	Date 2/28/13

Control Copy Number _____

GC INITIAL CALIBRATION CHECK LIST
EPA 608/8081A - Organochlorine Pesticides

Analyst: _____ 2nd Level Review: _____
Calibration Date: _____ Date: _____
Calibration batch#: _____ GC #: _____
Method Compliance: ☐ EPA 608 ☐ EPA 8081A

Analyst Rev	2nd Level Rev	
		• 608: minimum 3-point calibration • 8081A: Minimum 5-point calibration (6-point for quadratic regression) • Lowest calibration standard at or below Reporting Limit (but >MDL)
		Calibration Factors (CF): • RSD <= 10% for each compound or if
		• RSD >10% (but <50%): Generate a linear or quadratic curve, r^2>=0.99 (Do NOT use linear calibration curve for Negative or abnormally Positive results).
		• For 8081A only if needed: Average RSD is used and <=20% (Must not be used for Arizona work)
		2nd Source ICV: • Immediately after initial calibration
		• %Recovery: 85 – 115
		Check and verify calibration data for: • Correct retention times
		• All peaks are identified correctly
		• Saturated chromatographic peaks
		• Manual integration
		• All graphics uploaded
		• P flags checked
		• Due to co-elution, the following compound(s) cannot be reported off channel A: _____ B: _____

Comments: _____

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Rev 02/28/13

DAILY DATA CHECKLIST

EPA 608/8081A – Pesticides, Toxaphene, Chlordane

Analyst:		2nd Level Review:	
Analysis Date:		Date:	
Method Compliance:	☐ EPA 608 ☐ EPA 8081A	GC #:	
Prep Batches:		Primary Channel (A/B):	
Analytical Batches		Confirm. Channel (A/B):	

Analyst Rev	2nd Level Rev	
		Instrument blank before sample analysis : <=Reporting Limit
		Pesticides: Endrin (aldehyde & ketone) / DDT(DDE & DDD) Breakdown: <=15%
		ICV/CCV (1rst or 2nd source)
		• At the beginning of every 12-hour shift, every 10-20 samples and at the end of analysis
		• Two different levels during the daily analysis.
		• %Recovery = 85 - 115
		• For Chlordane & Toxaphene, ICV/CCV outside of limits: valid for qualification only
		Method blank every extraction batch: <= Reporting limit, or Method blank contaminated, but samples ND or > 20 times MB.
		Due to co-elution, the following compound(s) cannot be reported off channel A: B:
		LCS every extraction batch of 20 samples or less (refer to in-house limits in LIMS system)
		MS/MSD every extraction batch of 20 samples or less (refer to in-house limits in LIMS system)
		All samples checked for:
		• Dilution Factor
		• Manual integration
		• Surrogates within limits (refer to in-house limits)
		• Precision between channels: <= 40 % (or otherwise justified)
		• All graphics were uploaded.
		• Frequency of 10 (recommended) to 20 between compliant ICV/CCV
		GC Calibration Check Criteria form attached (if average % recovery if ICV/CCV is used)
		All standards used are uniquely identified and are not expired
		All data flags correctly applied and NCMs written, as required
		Run logs printed

Comments: _____

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Rev 02/28/13

FACILITY SOP ATTACHMENT

SOP NUMBER: IR-GCS-PEST, revision 1 (09/28/12)	**CHANGE FORM ID: CF1**

SOP TITLE: Organochlorine Pesticides by GC EPA Methods 608 and 8081A

REASON FOR ADDITION OR CHANGE (Use additional sheets if necessary):

Correction to Retention Time window study section 12.2.4. Both regular and low level pesticides are analyzed from the same base Chrome method. RT windows cannot be different.

CHANGE OR ADDITION (Use additional sheets if necessary):

Currently reads:

If the standard deviation is less than 0.01 minutes, use a default RT window of 0.03 minutes for regular-level pesticides and an **RL** window of 0.01 minutes for low-level pesticides.

Change to read:

If the standard deviation is less than 0.01 minutes, use a default RT window of 0.03 minutes.

Prepared By: D. Dawes

***APPROVED BY:**

Technical Review Signature	Date 11/29/12
Quality Assurance Manager	Date 11-29-2012
Environmental Health and Safety Coordinator	Date 11/29/2012
Interim Laboratory Director	Date 11/29/12

*Should be the same signature authorities of SOP being revised.

Control Copy Number _____

Title: Organochlorine Pesticides by GC
EPA Methods 608 and 8081A

Approvals (Signature/Date):

Paul Monroy, Technical Manager — Date 9/21/12	William Nash, Health & Safety Coordinator — Date 9/21/2012
David Dawes, Quality Assurance Manager — Date 9/21/12	Fred Haley, Laboratory Director — Date 9/21/12

Facility Distribution No. _____ **Distributed To:_____**

1.0 SCOPE AND APPLICATION

EPA 608 method is used to determine the concentration of various organochlorine pesticides in ground water, surface water or wastewater samples.

EPA 8081A method is used to determine the concentration of various organochlorine pesticides in extracts from solid and liquid matrices.

Both methods are combined in this standard operating procedure (SOP).

1.1 Analytes, Matrix(s), and Reporting Limits

The common pesticides to be analyzed include:

Aldrin	4,4'-DDD	Endrin Aldehyde
a-BHC	4,4'-DDE	Endrin Ketone
b-BHC	4,4'-DDT	Heptachlor
d-BHC	Dieldrin	Heptachlor Epoxide
g-BHC	Endosulfan I	Methoxychlor
Chlordane	Endosulfan II	Toxaphene
a-Chlordane	Endosulfan Sulfate	
g-Chlordane	Endrin	

.

Additional compounds that may be analyzed by this SOP include:

2,4'-DDD	2,4'-DDT
2,4'-DDE	Mirex

These methods can be used to analyze generally down to 0.1 µg/L in liquids and 5.0 µg/Kg in solids. See attached analysis information for detailed reporting and QC limits. NOTE: See LIMS data system for current MDL and Control Limit values.

1.2 Differentiation between EPA 608 and EPA 8081A

Although overlapping each other in many aspects, 608 method and 8081A method do differ in certain analysis requirements, notably:

- Method 8081A requires a higher number of calibration points (5 vs. 3 in 608).
- Method 608 requires a more stringent calibration factor RSD (10% vs. 20% in 8081A).
- Method 8081A/8000B does NOT allow the calibration curve to be forced through the point of origin.
- Method 608 requires a calibration verification (CCV) daily while Method 8081A specifies it at the beginning of each 12-hour shift.
- Method 608 does NOT allow averaging of calibration factor RSD and ICV/CCV recoveries.
- Method 8081A requires result confirmation from a secondary column.
- Surrogates are discussed only in method 8081A.
- The breakdown check of DDT and Endrin is discussed only in method 8081A.

The more stringent quality control will take precedent if the analysis is to be used for both methods. Additionally, this SOP will include the surrogates, the breakdown check and the 12-hour CCV in all cases.

On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in "Validation of Methods" in the Quality Assurance Manual.

2.0 SUMMARY OF METHOD

Liquid sample extraction: A measured volume of sample, approximately 1L, is extracted with methylene chloride using a separatory funnel. The methylene chloride extract is dried and exchanged to hexane during concentration to a volume of 10 mL or less.

Solid sample extraction: A measured aliquot of soil is extracted with hexane-acetone (1:1) using Method 3546 (microwave extraction). The extract is dried and exchanged to hexane during concentration to a volume of 10 mL or less. (Oil by Method 3580A).

The extract is separated by gas chromatography and the parameters are then measured with an electron capture detector (ECD). Single analytes and multi-component pesticides are identified using retention times and pattern recognition.

3.0 DEFINITIONS

3.1 The primary column is defined as the column that demonstrates the least interference throughout the sequence.

3.2 BHC is an acronym for benzene hexachloride. It is also sometimes referred to as hexachlorocyclohexane or HCH. (Lindane, a general trade name is used for this class of compounds.)

3.3 There are no additional specific definitions associated with this test. See the laboratory QA manual and EPA methods 608 and 8081A for general definitions.

4.0 INTERFERENCES

The following are three broad categories of sources of interferences in EPA Methods 608 and 8081A:

4.1 Contaminated solvents, reagents, glassware, or other sample processing hardware. Cross-contamination of clean glassware can easily occur when plastics are handled during extraction, especially when solvent-wetted surfaces are handled. Flexible plastic used during sample preparation can introduce Phthalate esters.

4.2 Contaminated GC carrier gas, parts, column surfaces, or detector surfaces.

4.3 Non-target compounds extracted from the sample matrix to which the detector will respond.

For a detailed discussion on cleanup procedures, refer to Section 11 of Method 608, or sections 3.7 and 7.2 of Method 8081A. Some recommended cleanups are as follows:

- Interferences from **phthalate esters** can be minimized by avoiding contact with any plastic material, and by checking all solvents and reagents for phthalate contamination.
- Phthalate esters can be removed prior to analysis by using Method 3640 (Gel Permeation Cleanup), Method 3630 (Silica Gel Cleanup), or Method 3610 (Alumina).
- The presence of **elemental sulfur** will result in broad peaks that interfere with the ECD detection of early eluting organochlorine pesticides. Sulfur contamination should be expected with sediment samples. It can be removed by the technique described in Method 3660, in Section 11.3 of Method 608 or the sample may be diluted.
- **Waxes, lipids** and other high molecular weight materials can be removed by Method 3640 (GPC cleanup-pesticide option).
- Other halogenated pesticides or industrial chemicals may interfere with the analysis of pesticides. These may be removed by Method 3620B (Florisil).

5.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

Personal Protective Equipment required: Safety Glasses/Face Shield, Labcoat, and Nitrile Gloves.

The gas chromatograph contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

There are areas of high voltage in the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 EQUIPMENT AND SUPPLIES

6.1 Instrumentation

6.1.1 Gas Chromatograph - AT 5000, 6000 and 7000 Series, or equivalent
6.1.2 Column A: RTX-CLP (30m x 0.32mm x 0.32µm) or equivalent
6.1.3 Column B: RTX-CLP2 (30m x 0.32mm x 0.25µm) or equivalent
6.1.4 Electron capture detector (ECD)

6.1.5 Autosampler – AT 7673A, 7683, or equivalent
6.1.6 Injector liners

6.2 Supplies
6.2.1 Assorted volumetric flasks, class A
6.2.2 Assorted micro syringes – 5, 10, 50, 100, 500 and 1000 µl
6.2.3 Assorted glass and minert vials – 2, 10, 40 mL with Teflon-lined screw caps or crimp tops

7.0 REAGENTS AND STANDARDS

7.1 Reagents
All purchased and prepared reagents must be made from a traceable (NIST) source material, if available, and documentation of this traceability must be maintained by the laboratory.

7.1.1 Acetone, pesticide grade or equivalent
7.1.2 n-Hexane, pesticide grade or equivalent.
7.1.3 Methanol, pesticide grade or equivalent

7.2 Standards
All purchased standards must be accompanied by a Certificate of Analysis (C of A) which is kept available at the laboratory in order to demonstrate traceability of the standard to certified (NIST-traceable, if available) source material.
All prepared standards must be made from a traceable (NIST) source material, if available, and documentation of this traceability must be maintained by the laboratory.
7.2.1 Pesticides Mix - 1000 µg/ml by UltraScientific, Restek or equivalent
7.2.2 Pesticides Surrogate Spike solution - 200 µg/ml by Restek or equivalent
7.2.3 Toxaphene solution - 1000 µg/ml by UltraScientific or equivalent
7.2.4 Chlordane solution - 1000 µg/ml by Supelco & Restek or equivalent
7.2.5 DDT/Endrin standard - 500 µg/ml by Supelco or equivalent
7.2.6 Mirex solution - 100 µg/ml by UltraScientific or O2Si
7.2.7 2,4-DDD, 2,4-DDE, 2,4-DDT standard - 100 µg/ml by Acustandard or equivalent
7.2.8 2,4,5-trichlorophenol, 1000 µg/ml stock standard, Restek or equivalent

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Waters	1L amber glass	2 bottles	Cool >0 to 6°C	7 Days* from collection to extraction. 40 days from extraction to analysis	40 CFR Part 136.3 and SW846, Chapter 4

Soils	4 oz jar	100 g	Cool >0 to 6°C	14 Days from collection to extraction. 40 days from extraction to analysis	SW846, Chapter 4

* For 608 Only: Water samples shall be extracted within 72 hours of collection or 7 days if pH-adjusted to 5.0 – 9.0 using sulfuric acid or sodium hydroxide. Document the pH on the worksheet.

9.0 QUALITY CONTROL

9.1 Sample QC

The following quality control samples are prepared with each batch of samples. Each of these QC samples may be re-analyzed once if it doesn't pass, in order to verify the failure wasn't due to a physical or mechanical problem.

If the sample extract(s) require any cleanup procedure, the associated batch QC (i.e. MB, MS/MSD and LCS) must also undergo the same cleanup procedure with the sample extract(s).

9.1.1 Method Blank (MB)

Prepare and analyze a method blank (MB) for each matrix and with every batch of 20 samples, or less. Check that there are no analytes detected at or above the reporting limit. If the method blank shows contamination, re-prepare all samples in the batch unless:

- The samples are ND (flag the results accordingly).
- The sample result is > 20x the blank level (flag the result accordingly).

9.1.2 Laboratory Control Sample (LCS)

Prepare and analyze a primary source laboratory control sample (LCS) for every batch of 20 samples or less. The LCS recovery must be within laboratory acceptance limits (see Attachment 1). If the LCS is outside of these limits, re-analize the LCS once. If the second run of LCS is still outside of these limits, then determine as follows:

- If the analyte(s) in both runs of the LCS is above the acceptance limits and the associated sample results are ND, report the data and flag the results accordingly to indicate the high LCS recovery.
- If the analyte(s) in both runs of the LCS is above the acceptance limits and the associated sample results are positive, re-extract and re-analyze the affected samples with acceptable QC criteria.
- If the analyte in both runs of the LCS is below the acceptance limits, re-extract and re-analyze the affected samples.
- Notify Project Manager immediately if there is insufficient sample left to re-extract. Flag samples results and fill out NCM if sample results are still to be reported with failed QC.

LCS Duplicate (LCD) is performed only when insufficient sample is available for the MS/MSD or when requested by the client/project/contract.

For Oil and Product matrices, LCS/LCSD must be extracted by EPA 3580A.

For samples requiring chlordane or toxaphene analysis only, extract an LCS/LCSD with the appropriate standard.

9.1.3 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

The sample for MS/MSD is randomly selected, unless specifically requested by a client.
Prepare and analyze a matrix spike (MS) and a matrix spike (MSD) duplicate for each matrix and with every batch of 20 samples, or less. The recovery and relative percent difference must be within laboratory acceptance limits (see Attachment 1).

- If the MS/MSD are outside of the acceptance limits due to matrix effect, flag the reported and write an NCM.
- If the MS/MSD are outside of the acceptance limits due to non-matrix related causes (instrument problems, analyst error, etc), re-analyze the samples after taking corrective action. If re-analyzing the MS/MSD is not possible, fill out an NCM with detailed explanation.

9.2 Instrument QC

The following instrument QC samples are run with each analytical sequence. Each of these QC samples may be re-analyzed once if it does not pass, in order to verify the failure wasn't due to a physical or mechanical problem. Re-analysis must be performed before any batch QC or client samples are analyzed.

9.2.1 Initial Degradation Check (8081A only)

- Prime (or deactivate) the GC column after one or more days of non-operation by injecting the highest pesticide calibration standard. Inject this standard prior to calibration to prevent column adsorption.
- Analyze a degradation standard containing DDT and Endrin initially and every 12 hours. Look for the degradation products of 4,4'-DDT (4,4'-DDE and 4,4'-DDD) and of Endrin (Endrin Ketone and Endrin Aldehyde).
- NOTE: Even though EPA 608 method does not require initial degradation check, this SOP complies this the most stringent criteria of EPA 8081 regarding the initial degradation check for all single component pesticide analyses.
- Calculate the percent breakdown of DDT and Endrin on both the primary and secondary columns and verify that it is < 15%.
- Take corrective action if degradation of either DDT or Endrin exceeds 15%. Corrective action may include:
    - Replace the glass injection port insert
    - Change the "Y" connector or replace as needed
    - Prepare a new standard
    - Trim the first few inches (up to 12") of the column
    - Change the precolumn
    - Backflush the column with solvent according to the manufacturer's instructions
    - Deactivate the metal injector body with Sylon-CT or equivalent
    - Replace the column

- Record all performed maintenance in the instrument maintenance logbook.

9.2.2 Initial Calibration Verification (ICV)

Immediately after the initial calibration, analyze secondary source verification (ICV) with a concentration near the mid-point. Verify that its response is within ± **15**% of spiked value and the retention times are within their respective accepted windows.

- If not, re-prepare the ICV standard.
- If the ICV is still out of control, re-calibrate the system

If Toxaphene or Chlordane ICVs do not meet the 15% criteria, the standard is used for pattern recognition only and any positive results must be reanalyzed under a new calibration with an acceptable ICV.

9.2.3 Continuing Calibration Verification (CCV)

- On a daily basis, verify calibration at the beginning of each 12-hour shift by injecting calibration verification standards (CCV) prior to conducting any sample analysis. A verification must also be checked at intervals of 10 to 20 samples – alternated between two different calibration levels (e.g. 100 and 200 ppb) – and at the end of the analysis sequence. CCV standards can be from either the primary or secondary source.
- NOTE: Though EPA Method 608 does not require calibration verification more than once each working day, this SOP complies to the more stringent criteria of EPA Method 8081A regarding the CCV frequency.
- On a daily basis, analyze a CCV standard for Toxaphene and Chlordane for pattern recognition purpose at the beginning of each analysis sequence. If Toxaphene and Chlordane CCVs fail, samples that present any of these patterns must be re-run against its respective calibration and with passing bracketing CCVs.
- Verify that the recovery of each CCV is within ±15% of the initial calibration.
    - If retention times have slightly shifted, perform the necessary instrument maintenance and/or reset the RT (but not the RT window).
    - If the CCV fails the acceptance criteria, re-prepare and reanalyze a fresh standard once.
    - If the second CCV also fails, end the analysis sequence. Perform any necessary maintenance (such as replacement of liner, etc.) and start a new sequence, reanalyzing the samples that were not bracketed by a passing CCVs in the previous sequence.
    - If Toxaphene or chlordane CCVs fail, re-run samples that show pattern with passing CCVs.
- For 8081A analysis only: If ±15% recovery limit is exceeded for any analyte, then the mean percent difference (Grand mean) of all calibrated analytes can be used (8000B only). Attach a complete GC Calibration Check Criteria Form (attachment 2) (For 608 analysis, re-calibrate the instrument for the analytes that failed to meet recovery specifications).
  NOTE that Arizona follows method 8000C. EPA 8000C does not allow the use of the grand mean RSD to evaluate calibration linearity.
    - If the CCV result is > 115% of the expected value and all samples are ND for the compound then report the results with an NCM (if the mean percent recovery is used per EPA 8000B).
    - NOTE: If any compound in a sample has a result above the RL, it must be reanalyzed against a calibration that meets the ±15% CCV criteria.

- If any analyte is detected in a sample and the ICV/CCV recovery is outside of the acceptance limits (high or low):
  - Reanalyze the sample one time with a passing opening QC.
  - If the ending CCV is still out because of matrix effect, flag the results accordingly.
- When a particular sample or project causes any CCV to fail the recovery verification two times, matrix interference is considered confirmed, the data is reported and flagged accordingly.
- When a suspected matrix interfered sample was bracketed by failing CCVs (opening and ending) in a previous analysis sequence, it only needs to be re-run once with a passing opening CCV.
- Recalibrate the system in all other cases.
- All of the criteria listed above for CCV also apply to the analysis sequence from the confirmation column if it is used to report data.
- If the CCV fails in the secondary column, the results from the primary column may be reported as long as the results from the primary and the secondary column are within 40% RPD.
- For Oil and Product matrices (extracted by EPA 3580A), LCS/LCSD may be used as CCVs.

9.2.4 Surrogates

Calculate the surrogate recoveries for tetrachloro-m-xylene (TCMX) and decachlorobiphenyl (DCB). Both surrogates should be within the historically generated acceptance limits, however if one surrogate is out in a QC sample (e.g. CCV, LCS, MS/MSD) and the target analytes are within the QC limits, the data shall be deemed acceptable as the target analytes are more critical. Use the recovery of the surrogates to monitor for unusual matrix effects, gross sample processing errors, etc.

- Verify that there are no errors in calibration, calculations, or surrogate standard solutions in use.
- Check instrument performance.
- Recalculate the data and/or re-analyze the extract if any of the above checks reveals a problem.
- Re-extract and re-analyze the sample if none of the above are a problem or flag the data and provide a NCM.

9.2.5 Calibration Acceptance Summary

Refer to the “Calibration Curves” SOP and the “Selection of Calibration Points” SOP for more information on calibrating the instrument.

- Prepare a calibration curve by plotting the response (peak area) against the concentration of at least 3 standards for 608 and 5 standards for 8081.
- For Method 608, the % RSD of the Calibration Factors (CFs) for each target analyte and surrogate must be < 10% for both the primary and secondary columns in order to quantitate the compound using the average CF.

- For Method 8081A, the requirement for the % RSD of the CFs is < 20%. Only Method 8081A allows averaging the % RSD of the CFs.
- If one or more of the compounds has an %RSD above the acceptable limit then:
  - A first order (linear) or quadratic (non-linear) regression may be used for quantitation. The use of a weighted curve (1/X or 1/X2) is recommended in order for better quantitation at the RL of the analyte.
  - Examine the linearity and the accuracy in quantitating at the low calibration standard and at the point of origin in both options before selecting the better curve (1rst order regression may be less accurate than 2nd order near the point of origin).
  - The Coefficient of Determination (r2) must be ≥ 0.99 (Correlation Coefficient (r) ≥ 0.995) for the curve to be acceptable. If r2 is < 0.99 then the instrument must be recalibrated for that compound.
- When evaluating results near the RL review them carefully to ensure they make sense (i.e. no significantly negative values or false hits when the response area is below the lowest standard). If a result is questionable, the sample should be re-analyzed on another instrument or the result reported as estimated.

9.3 Other QC

Florisil Cartridge Testing Check

Monthly, or with every lot of Florisil clean-up cartridges, whichever comes first, a solution of 2,4,5-trichlorophenol and an LCS-level spike of pesticides is passed through a Florisil column, evaporated down and analyzed. 2,4,5-trichlorophenol recovery must be less than 5% of true value and pesticide recoveries must be 80-110% of true value. If criteria are not met, repeat twice more. If recoveries are still outside of limits, cartridges from this lot cannot be used.

10.0 PROCEDURE

10.1 Standard Preparation

10.1.1 Store standards at > 0 to 6°C in PTFE sealed containers, in the dark. Check the solutions frequently for signs of degradation or evaporation. Stock standard solutions must be replaced after one year from the date opened or according to the manufacturer's expiration date (sooner if routine QC indicates a problem). All other standards must be replaced every 6 months (sooner if routine QC indicates a problem).

10.1.2 All working standards (surrogates, BS/BSD and MS/MSD spiking standards) used in water samples must be prepared using Acetone instead of hexane.

10.1.3 Prepare all standards by using a calibrated syringe to deliver the required volume to a volumetric flask. Fill to the mark with the appropriate solvent.

10.1.4 Transfer each solution from the volumetric flasks into 40 mL or 12 mL VOA vials with Teflon-lined screw caps. Store the solutions at > 0 to 6°C and protect from light.

10.1.5 Enter the standard information into the LIMS system. All standard information must be reviewed for accuracy by a peer or department manager before the standard can be used.

10.1.6 Prepare new calibration standards every 6 months, or sooner, if comparison with check standards indicates a problem. Enter the standard information into the LIMS system.

Prepare the calibration standards by adding the volumes of spike solutions shown in the following tables (see attachments):

Table Number	Title
Table 1	Pesticides, regular list
Table 2	A26—Regular list + 2,4'-series + Mirex
Table 3	Chlordane
Table 4	Toxaphene
Table 5	Surrogate and Endrin/DDT Breakdown

10.1.7 2,4,5-trichlorophenol, 100 ug/L working standard. Add 10 ul of 1000 ug/ml stock standard to 100 ml final volume of acetone. Refrigerate for up to 6 months.

10.2 Sample Preparation

Sample extracts are received from the extraction department. Upon receipt:

- Store extracts in crimp-top vials at > 0 to 6°C until analysis.
- Verify that the extract has not exceeded its 40 day holding time.
- If a sample is suspected to contain sulfur, perform a dilution in order to eliminate matrix interference from the sulfur. Record the dilution performed in the sample worklist.

10.3 Instrument Initialization

The following are suggestive instrument conditions. These may vary slightly between instruments, or because of necessary instrument maintenance (e.g. column trimming) or because of column age.

Detectors: Dual Electron Capture Detector (ECD) or Dual Electron Capture Micro ECD.

Injection Volume: 1 µl

Refer to the following table for additional details:

	Option 1	Option 2
Column A:	Restek CLP (30m x .32mm ID x 0.25um	Restek CLP (30m x .32mm ID x 0.25um
Column B:	Restek CLP2 (30 m x .32 mm ID x 0.5um	Restek CLP2 (30 m x .32 mm ID x 0.5um
Helium flow rate:	10 mL/min	10 mL/min
ECD make-up Nitrogen:	60 mL/min	35 mL/min
Electronic pressure control:	10	22
Injector t °C	240 °C	240 °C
Detector t °C	310 °C	310 °C
Oven initial t °C	125 °C	140 °C
Initial Hold time	3 minute	1 minute
Rate 1	7 °C/min	30 °C/min

Final Temp 1 °C:	200 °C	240 °C
Hold time 2:	10 minutes	2 minutes
Rate 2	17 °C/min	30 °C/min
Final temp 2 °C:	285 °C	300 °C
Final Time 2:	8 minutes	2.67 minutes
Run Time:	36 minutes	11 minutes

Verify that the solvent bottles in the autosampler are full, and the solvent waste vials are empty.

10.4 Calibration

10.4.1 For a new calibration, load the calibration standards in ascending concentration order followed by the ICV. Verify all calibration criteria are met before proceeding.

10.4.2 For Method 608, analyze a minimum of three standard points for a working calibration curve.

10.4.3 For Method 8081A, use a minimum of five standard points (or six if using a quadratic curve).

10.4.4 Calibrate the primary and secondary columns simultaneously.

10.4.5 Repeat for Toxaphene and Chlordane.

10.4.6 The surrogates are calibrated at ascending levels at the same time as the pesticides standards.

10.4.7 To continue using a previous calibration, copy the worklist from the previous sequence, analyze an instrument blank and a CCV.

- Re-center the RT windows based upon the initial CCV for that day.
- Verify all acceptance criteria are met before proceeding

10.5 Sample Analysis

10.5.1 Load one or two high level pesticides standards to prime the column

10.5.2 Load and inject an instrument blank (IB) after priming.

10.5.3 Verify that the instrument blank (hexane) is free of contamination.

10.5.4 Analyze a degradation standard containing DDT and Endrin and check for breakdown of DDT and Endrin. Repeat this step every 12-hour shift. (Not applicable for Toxaphene and Chlordane).

10.5.5 Proceed with a CCV analysis for single component analytes. Analyze a CCV for Toxaphene or Chlordane for pattern recognition.

10.5.6 NOTE: If the degradation check fails, change the liner and re-run the degradation check.

10.5.7 Analyze the method blank (MB) and verify that it is free of contamination (<RL).

10.5.8 Analyze the LCS and verify that it meets the QC limits.

10.5.9 Follow with 10-20 sample extracts.

10.5.10 Load an instrument blank after a dirty extract to prevent carry-over. Instrument blanks (and standards) do not count towards the 10-20 samples between CCVs.

10.5.11 Analyze the matrix spike (MS) and matrix spike duplicate (MSD) sometime during the sequence. The recoveries of the MS/MSD should be within in-house control limits.

Prime
Prime
Instrument Blank
Degradation Standard (DDT and Endrin)
CCV
CCV - Toxaphene
CCV - Chlordane
MB
LCS
10-20 samples (incl. MS/MSD)
CCV2

10.6 Identification of Single-Component Analytes

Refer to the "Reporting results for methods that require second-column confirmation" policy (CA-T-P-003) for information on reporting single component analytes.

10.6.1 Analyte identification will be confirmed if a peak falls within the retention time of both the primary and secondary confirmation column.

- If the analyte is confirmed, verify that the result from the confirmation column agrees with the primary column (RPD ≤ 40%). Otherwise, check for co-elution or other error.
- If there is an explanation for the discrepancy in quantitated results, report the result from the unaffected column.
- If no discrepancy is found, re-run the sample on a different instrument or report the lower of the two results.
- NOTE: Confirmation analysis for detected analytes on a secondary column is only required by Method 8081A, but strongly recommended for all pesticides analyses.

10.6.2 Manual adjustments can be performed for situations such as

- RT shifts evident in surrogates,
- Inadequate automated integrations (e.g., split peaks, co-elution)
- Any such adjustments must be fully documented with before and after chromatograms, analyst initial, date and reason.

10.7 Identification of Multi-Component Analytes (Chordane and Toxaphene)

Refer to the "Reporting of multi-component organochlorine analytes" SOP for more Information on reporting multi-component analytes

10.7.1 Multi-component pesticides are identified using pattern recognition and characteristic "fingerprint" retention time. Visually compare the Chlordane or Toxaphene chromatogram with the CCV standard chromatogram. Overlay and expand the chromatograms using Chrom's "compare" feature. Check for retention time shifting by verifying that the surrogate RTs coincide. Expanding the baseline helps in identifying multi-component groups. Use of overlays (for multi-component analytes only) and the experience of the analyst are heavily weighted in regards to the interpretation of these complex chromatograms. If Chlordane or Toxaphene is detected above the reporting limit, reanalyze the samples against the calibration curve of the identified compound.

10.7.2 Quantitate the chlordane or toxaphene based on the prior identification.

10.7.3 Submit the sample extract for Florisil cleanup whenever interferences prevent peak detection and identification. Soil samples always undergo the Florisil cleanup.

10.7.4 Re-analyze the cleaned extract and re-evaluate the extract chromatogram.

10.8 Quantitation of Multi-Component Analytes (Toxaphene/Chlordane)

10.8.1 3 – 6 major peaks are used to quantitate chlordane.

10.8.2 Total area/time group is used to quantitate toxaphene. NOTE: DDE, DDT, DDD and Dieldrin peaks are removed from the total toxaphene area.

10.9 Total Area Measurement

10.9.1 Construct the baseline in the sample chromatogram between the retention times of the first and last eluting Toxaphene component in the standard.

10.9.2 In order to use the total area/time group approach, the pattern in the sample chromatogram must be compared to that of the standard. Note: If the pattern does not match the standard pattern completely, the sample concentration may be significantly underestimated.

10.10 Major peaks Meassurement

10.10.1 For chlordane select 3 to 6 major peaks.

10.10.2 The chosen peaks may not exactly match the sample with the standard in relative areas. However, analyst should not use peaks from the sample chromatogram whose areas appear to be disproportionately larger or smaller relative to the standard peaks.

10.10.3 If possible, compare samples with standards from different suppliers to see if a better match is available.

10.10.4 The areas of the selected peaks should be added together and used to determine the concentration.

10.9.1 These calibration factors are then used to calculate the concentration of each corresponding peak in the sample chromatogram and the resulting concentrations are averaged to provide the final result for the sample.

10.11 Chlordane by 8081A only

The presence of alpha and gamma chlordane in a sample in approximately the correct proportion (i.e as seen in a technical chlordane standard) is sufficient evidence to call the sample positive for

the presence of technical chlordane. It is quantitated based on the peaks that are recognizable as part of technical chlordane (note: DO NOT include heptachlor), even if this is only alpha and gamma chlordane. Also, even if the pattern match is poor for the other chlordane components, the presence of alpha and gamma chlordane is definitive proof of the presence of technical chlordane.

When reporting and quantifying chlordane that does not closely match the technical chlordane standard, it is mandatory that this is explained in the report (narrative or NCM) as follows:

"The sample shows clear evidence of the presence of chlordane based on the presence of alpha and gamma chlordane, but the chlordane peaks in the sample do not closely match the technical chlordane standard. As a result, there is increased quantitative uncertainty associated with this result. This is consistent with the guidance in section 7.6.2 of SW-846 method 8081B."

10.12 Preventative Maintenance

10.11.1 If degradation of either DDT or Endrin exceeds 15%, take corrective action (See instrument QC)

10.11.2 To prevent carryover from a dirty extract, load one or two instrument blanks immediately after all dirty extracts.

10.11.3 If an instrument is unusable or has limitation to its use (bad port, not for low level samples, etc), it must be tagged accordingly until such a time the problem has been corrected.

10.11.4 Record the problem, solution and verification of proper operation into the instrument maintenance logbook.

10.11.5 Record all performed maintenance in the instrument maintenance logbook.

11.0 CALCULATIONS / DATA REDUCTION

11.1 Accuracy

$$\text{ICV / CCV, LCS \% Recovery} = \frac{\text{observed concentration}}{\text{known concentration}} \times 100$$

$$\text{MS \% Recovery} = \frac{\text{(spiked sample) - (unspiked sample)}}{\text{spiked concentration}} \times 100$$

11.2 Precision (RPD)

$$\text{Matrix Duplicate (MD)} = \frac{|\text{orig. sample value - dup. sample value}|}{[(\text{orig. sample value + dup. sample value})/2]} \times 100$$

11.3 Concentration

Water and Soil Samples:

$$C_f = C_i \times PF \times DF$$

where C_f = Final concentration in µg/L or µg/Kg
C_I = Concentration in µg/L from instrument
PF = Preparation Factor
DF = Any additional Dilution Factor (post-extraction)

11.4 Percent Difference

$$\% \text{ Difference} = \frac{[\text{Apparent conc}(\mu g/L) - \text{True conc } (\mu g/L)] \times 100}{\text{True conc } (\mu g/L)}$$

12.0 METHOD PERFORMANCE

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure as described in laboratory's SOP, IR-QA-MDL. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.2 Retention Time Window Study

12.2.1 Retention time window studies are to be performed as often as necessary, whenever a new type of column is installed, and at a minimum annually.

12.2.2 Perform a retention time window study on each instrument and column by analyzing a triplicate run of a check standard (ICV/CCV) over a 72-hour period.

12.2.3 Calculate the mean and standard deviation of the retention time for each analyte and surrogate to three decimal places. The width of each retention time window is then calculated as three times the standard deviation.

12.2.4 If the standard deviation is less than 0.01 minutes, use a default RT window of 0.03 minutes for regular-level pesticides and an RL window of 0.01minutes for low-level pesticides.

12.2.5 NOTE: The experience of the analyst must be used in conjunction with the RT window calculations to ensure an appropriate window is established, one that minimizes the occurrence of both false positive and false negative results.

12.3 Demonstration of Capabilities

Every analyst must perform an Initial Demonstration of Capability (IDOC) before performing analyses on any client samples. An IDOC can be 1) 4 consecutive LCS samples (prepared from

a source other than that used for the ICAL) with an average recovery and RSD within the in-house statistical limits, or 2) passing results on a blind or PT study.

12.4 Training Requirements

The analyst must have documented training, including reading of the SOP and source methods, conducted by the department manager, senior chemist, or other analyst with training documentation and a passing DOC.

13.0 POLLUTION CONTROL

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in the "Waste Management and Pollution Prevention" section of the Corporate Environmental Health and Safety Manual (CW-E-M-001).

14.0 WASTE MANAGEMENT

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the laboratory's Waste Disposal SOP (IR-EHS-WASTE). The following waste streams are produced when this method is carried out:

- **Autosampler vials** – Once the analysts have reported the sample results, they store the autosampler vials in the appropriate refrigerator in the semivolatiles area. After 40 day minimum that the vials have been stored, the analysts remove the vials and disposed them into the Step-on waste container located in the extractions lab. The Step-on container is label "Autosampler vials". Waste bulked as autosampler vials.
- **Hexane/Acetone waste**. This waste is generated when analysts prepare sample and standards. The waste is store in a 4 L bottle, the bottle is placed inside the fume hood. Waste bulked as mixed flammable solvents.
- **Pesticides waste** – After the 40 day of storage, the extracts with equal or higher concentration of the analytes indicated in the table below are placed in plastic container label as "Hazardous waste". The container is taken by the analyst into the main waste storage area and placed in the appropriate shelf labeled "Hazardous waste". The analysts fill out the Hazardous Sample Notice Form and give it to the sample control manager (or designee), so the samples can be disposed as Hazardous waste when sample archive technicians dispose of the samples.

Analyte	TTLC Level (mg/kg)	STLC Level (mg/L)
Aldrin	1.4	0.14
Chlordane	2.5	0.25
DDT/DDE/DDD	1.0	0.1
Dieldrin	8.0	0.8
Endrin	0.2	0.02
Heptachlor	4.7	0.47
Lindane	4.0	0.4
Methoxychlor	100	10
Mirex	21	2.1
PCBs	50	5.0
Toxaphene	5	0.5

- **Unused standards**. If hazardous standards cannot be collected with one of the waste streams generated in the method, then analyst and technicians take this standard and placed it on the shelves labeled "hazardous waste" in the main waste storage area. The standard will be lab packed (example: mercury standard). If the standard can be collected in the satellite waste container for one of the waste streams of the method, then pour the standard in the right satellite container, rinse the original container, and collect the rinsate in the satellite container. The original container can be placed in the regular trash.

15.0 REFERENCES / CROSS-REFERENCES

15.1 EPA Method 608, 40 CFR part 136, Appendix A

15.2 EPA Method 8081A, EPA SW-846 Update III, December 1996

15.3 EPA Method 8000B, EPA SW-846 Update III, December 1996

15.4 EPA Method 8000C, EPA SW-846 Update IV, Revision 3, March 2003

15.5 CA-Q-S-005, Calibration Curves (General)

15.6 CA-T-P-002, Selection Of Calibration Points

15.7 CA-Q-QM-003 Reporting of multi-component organochlorine analytes

15.8 CA-T-P-003_r1 Reporting results for methods that require second-column confirmation

15.9 Arizona DHS Information Update #37, June 13, 1997

16.0 METHOD MODIFICATIONS

Item	Method 608	Modification
1	Section 7.2.1	EPA Method 608 requires a calibration verification daily while EPA Method 8081A specifies it at the beginning of each 12-hour shift. The laboratory complies with the more stringent criteria specified in EPA method 8081A for this SOP.
2	No reference	Surrogate spikes are not discussed in EPA Method 608. The laboratory follows the criteria specified in EPA Method 8081A in this SOP
3	No reference	EPA Method 608 does not require the use of confirmation from a secondary column. The laboratory follows the criteria specified in EPA 8081A in this SOP
4	No reference	Method EPA 608 does not require the breakdown check of DDT and Endrin. The laboratory follows the criteria specified in EPA 8081A in this SOP
5	EPA 8000B. Section 7.10.4	The reference method indicates to report the higher result in instances where the RPD between the results of the two columns is >40%. The laboratory follows the TestAmerica approach of reporting the lower result which is in alignment with 8000C.

17.0 ATTACHMENTS

17.1 Attachment 1: Analysis Information
17.2 Attachment 2: GC Calibration Check Criteria Form
17.3 Attachment 3: Datatypes
17.4 Attachment 4: Standard Preparation Tables
17.5 Attachment 5: Data Review Checklist
17.6 Attachment 6: ICAL Review Checklist

18.0 REVISION HISTORY

18.1 Revision 0, dated 30 October 2009

- This revision supersedes Pesticides.SOP, revision 0, 08/17/06
- Changes made include
  - Addition of Safety sections 5.1, 5.2, and table in 5.2
  - Addition of Pollution Control wording
  - Addition of Waste Management wording
  - Addition of table for method modifications
- Prepared by GM & DD

18.2 Revision 1, dated 28 September 2012

- This revision supersedes IR-GCS-PEST, rev 0, 10/30/09
- Added dataypes
- Added reference to Calibration Curves and Selection of calibration points corporate SOPs
- Updated RT window section
- Remove reference to Alachlor, Benefin, Chlorantonil, Pentachloronitrobenzene and Trifluralin.
- Updated ICAL and daily checklists
- Remove reference to the use of combined methods
- Added shelf life of standards prepared in acetone (one month)
- Changed requirement of reporting the higher result to report the lower when the RPD between the two channels is greater than 40% and there is no evidence of chromatographic problems per CA-T-P-003 and 8000C.
- Added GC Calibration Check Criteria Form as attachment 2
- Added clarification that if the CCV fails in the secondary column, the data can still be reported as long as the results are within the 40%.
- Prepared by PM, CN and AS

Attachment 1a:
Analysis Information

TestAmerica Irvine **8/10/2012**

Analytical Method Information

Analyte	MDL	Reporting Limit	Surrogate %R	Duplicate RPD	Matrix Spike %R	Matrix Spike RPD	Blank Spike / LCS %R	Blank Spike / LCS RPD
8081A-Pesticides in Water (EPA 3510C/8081A) & 608-Pesticides in Water								
Preservation: 4 C, Cool								
Container: 1 L Amber			**Amount Required:** 2000 ml			**Hold Time:** 7 days		
4,4'-DDD	0.030	0.10 ug/l			50 - 125	30	55 - 120	30
4,4'-DDE	0.030	0.10 ug/l			45 - 125	30	50 - 120	30
4,4'-DDT	0.030	0.10 ug/l			50 - 125	30	55 - 120	30
Aldrin	0.030	0.10 ug/l			35 - 120	30	40 - 115	30
alpha-BHC	0.020	0.10 ug/l			40 - 120	30	45 - 115	30
alpha-Chlordane	0.030	0.20 ug/l						
beta-BHC	0.040	0.10 ug/l			50 - 120	30	55 - 115	30
delta-BHC	0.020	0.20 ug/l			50 - 120	30	55 - 115	30
Dieldrin	0.030	0.10 ug/l			50 - 120	30	55 - 115	30
Endosulfan I	0.030	0.10 ug/l			50 - 120	30	55 - 115	30
Endosulfan II	0.040	0.10 ug/l			50 - 125	30	55 - 120	30
Endosulfan sulfate	0.050	0.20 ug/l			55 - 125	30	60 - 120	30
Endrin	0.030	0.10 ug/l			50 - 120	30	55 - 115	30
Endrin aldehyde	0.050	0.10 ug/l			45 - 125	30	50 - 120	30
Endrin ketone	0.040	0.10 ug/l			50 - 125	30	55 - 120	30
gamma-BHC (Lindane)	0.030	0.10 ug/l			40 - 120	30	45 - 115	30
gamma-Chlordane	0.030	0.20 ug/l						
Heptachlor	0.030	0.10 ug/l			40 - 120	30	45 - 115	30
Heptachlor epoxide	0.030	0.10 ug/l			50 - 120	30	55 - 115	30
Methoxychlor	0.040	0.10 ug/l			55 - 125	30	60 - 120	30
Chlordane	0.30	1.0 ug/l						
Toxaphene	0.80	5.0 ug/l						
surr: Decachlorobiphenyl			45 - 120					
surr: Tetrachloro-m-xylene			35 - 115					

Attachment 1b:
Analysis Information

TestAmerica Irvine **8/10/2012**

Analytical Method Information

Analyte	MDL	Reporting Limit	Surrogate %R	Duplicate RPD	Matrix Spike %R	Matrix Spike RPD	Blank Spike / LCS %R	Blank Spike / LCS RPD
8081A-Pesticides in Soil (EPA 3545/8081A)								
Preservation: 4 C, Cool								
Container: 4 oz Jar			**Amount Required:** 100 grams				**Hold Time:** 14 days	
4,4'-DDD	1.5	5.0 ug/kg			40 - 130	30	60 - 120	30
4,4'-DDE	1.5	5.0 ug/kg			35 - 130	30	60 - 120	30
4,4'-DDT	1.5	5.0 ug/kg			35 - 130	30	65 - 120	30
Aldrin	1.5	5.0 ug/kg			40 - 115	30	50 - 115	30
alpha-BHC	1.5	5.0 ug/kg			40 - 115	30	60 - 115	30
alpha-Chlordane	2.0	5.0 ug/kg						
beta-BHC	1.5	5.0 ug/kg			40 - 120	30	60 - 115	30
delta-BHC	1.5	10 ug/kg			45 - 120	30	60 - 115	30
Dieldrin	1.5	5.0 ug/kg			40 - 125	30	65 - 115	30
Endosulfan I	1.5	5.0 ug/kg			40 - 120	30	40 - 120	30
Endosulfan II	1.5	5.0 ug/kg			40 - 125	30	55 - 120	30
Endosulfan sulfate	2.0	10 ug/kg			45 - 120	30	65 - 115	30
Endrin	1.5	5.0 ug/kg			45 - 125	30	55 - 120	30
Endrin aldehyde	1.5	5.0 ug/kg			30 - 120	30	55 - 115	30
Endrin ketone	2.0	5.0 ug/kg			40 - 120	30	65 - 115	30
gamma-BHC (Lindane)	1.5	5.0 ug/kg			40 - 120	30	55 - 115	30
gamma-Chlordane	1.5	5.0 ug/kg						
Heptachlor	2.0	5.0 ug/kg			40 - 115	30	55 - 115	30
Heptachlor epoxide	2.0	5.0 ug/kg			45 - 115	30	55 - 115	30
Methoxychlor	1.5	5.0 ug/kg			40 - 135	30	65 - 120	30
Chlordane	10	50 ug/kg						
Toxaphene	50	200 ug/kg						
surr: Decachlorobiphenyl			45 - 120					
surr: Tetrachloro-m-xylene			35 - 115					

Attachment 1c:
Analysis Information

TestAmerica Irvine 8/10/2012

Analytical Method Information

Analyte	MDL	Reporting Limit	Surrogate %R	Duplicate RPD	Matrix Spike %R	Matrix Spike RPD	Blank Spike / LCS %R	Blank Spike / LCS RPD
8081A-All Pesticides (LowRL) in Water (EPA 8081A) & 608-All Pesticides (LowRL)								
Preservation: 4 C, Cool								
Container: 1 L Amber		**Amount Required:** 2000 ml				**Hold Time:** 7 days		
4,4'-DDD	0.0020	0.0050 ug/l			50 - 125	30	55 - 120	30
4,4'-DDE	0.0030	0.0050 ug/l			45 - 125	30	50 - 120	30
4,4'-DDT	0.0040	0.010 ug/l			50 - 125	30	55 - 120	30
Aldrin	0.0015	0.0050 ug/l			35 - 120	30	40 - 115	30
alpha-BHC	0.0025	0.0050 ug/l			40 - 120	30	45 - 115	30
alpha-Chlordane	0.030	0.10 ug/l				30		30
beta-BHC	0.0040	0.010 ug/l			50 - 120	30	55 - 115	30
delta-BHC	0.0035	0.0050 ug/l			50 - 120	30	55 - 115	30
Dieldrin	0.0020	0.0050 ug/l			50 - 120	30	55 - 115	30
Endosulfan I	0.0020	0.0050 ug/l			50 - 120	30	55 - 115	30
Endosulfan II	0.0030	0.0050 ug/l			50 - 125	30	55 - 120	30
Endosulfan sulfate	0.0030	0.010 ug/l			55 - 125	30	60 - 120	30
Endrin	0.0020	0.0050 ug/l			50 - 120	30	55 - 115	30
Endrin aldehyde	0.0020	0.010 ug/l			45 - 125	30	50 - 120	30
Endrin ketone	0.0030	0.010 ug/l			50 - 125	30	55 - 120	30
gamma-BHC (Lindane)	0.0030	0.010 ug/l			40 - 120	30	45 - 115	30
gamma-Chlordane	0.030	0.10 ug/l				30		30
Heptachlor	0.0030	0.010 ug/l			40 - 120	30	45 - 115	30
Heptachlor epoxide	0.0025	0.0050 ug/l			50 - 120	30	55 - 115	30
Methoxychlor	0.0035	0.0050 ug/l			55 - 125	30	60 - 120	30
Chlordane	0.040	0.10 ug/l						
Toxaphene	0.25	0.50 ug/l						
surr: Decachlorobiphenyl			45 - 120					
surr: Tetrachloro-m-xylene			35 - 115					

Attachment 2
GC Calibration Check Criteria Form

GC CALIBRATION CHECK CRITERIA
(ICV / CCV)

Method : 8081A
GC #: _____
Channel (circle one): A / B
Worklist # _____
Prep batches _____
Analytical batches _____

Analyst: _____
Analysis date: _____
2nd Level review: _____
Review Date: _____

Per Method 8000B of SW-846, the % recovery of the calibration checks (**ICV/CCV**) for GC analyses must be within ± 15 % from the true value for each individual analyte or when averaged across **all** analytes in the solution. Per Method 8000B, the end user is to be notified if the latter situation occurs.

☐ All analytes met the individual calibration check requirement of ± 15 % recovery.

☐ The % recovery for the following individual analytes fell outside of the ± 15 % criteria. However the average % recovery of **all** analytes in the ICV/CCV solution was within ± 15%, thus meeting the overall calibration check criteria.

Raw Data File	Analytes	% D (ICV/CCV)	RL Area count

G:\quality\data_rev\chcklist\gc_sv\pesticides\gc_icv_r1
Rev 08/20/2012

Attachment 3
Datatypes

Method Code	Level	Datatype Description	Value to Enter	Units
608_Pest	**BATCH**	**Analysis comment**	**If needed**	**N/A**
608_Pest	**ANALYSIS**	**Batch Comment**	**If needed**	**N/A**
608_Pest	ANALYSIS	Final weight/volume of sample	n/a	mL
8081A	**BATCH**	**Analysis comment**	**If needed**	**NONE**
8081A	ANALYSIS	Injection volume	n/a	uL
8081A	**ANALYSIS**	**Batch Comment**	**If needed**	**NONE**
8081A	ANALYSIS	Final weight/volume of sample	n/a	N/A
8081A	ANALYSIS	Fractional Volume Multiphasic Samples	n/a	L
8081A	ANALYSIS	Initial weight/volume of sample	n/a	N/A

Attachment 4
Table 1: Regular Pesticide Standards

Pesticides Calibration Mother Solution

Final volume (mL): 25 mL
Analyte /Surrogate concentration (ppb): 5K/5K

Stock (1st source)	Conc (µg/mL)	Vol (mL)
Pesticide Mix	1,000	0.125
Surrogate	200	0.625

Pesticides Cal ICV Std

Final volume (mL): 50 mL
Analyte /Surrogate concentration (ppb): 100/100

Stock (2nd source)	Conc (µg/mL)	Vol (mL)
Pesticide Mix	200	0.0250
Surrogate	200	0.0250

CCVs

	Final Conc (ppb)	Vol Mother Solution (mL)	Final volume (mL)
P 2	2/2	0.04	100
P 25	25/25	0.5	100
P 100	100/100	2	100
P 200	200/200	4	100
P 300	300/300	6	100

Pesticides LCS

Final volume (mL): 500 mL
Analyte concentration (ppb): 500

Stock (1st source)	Conc (µg/mL)	Vol (mL)
Pesticide Mix	1,000	0.250

Pesticides Cal Regular & Low-Level

Calibration	Final Conc (ppb)	Vol of Mother Solution (mL)	Bring to Vol (mL)
#1	2/2	0.010	25
#2	10/10	0.050	25
#3	25/25	0.125	25
#4	50/50	0.250	25
#5	75/75	0.375	25
#6	100/100	0.500	25
#7	200/200	1.000	25
#8	300/300	1.500	25
#9	500/500	2.500	25

Pesticides Surrogate for Extractions

Final volume (mL): 1000 mL
Analyte /Surrogate concentration (ppb): 500

Stock (1st source)	Conc (µg/ml)	Vol (ml)
Surrogate	200	2.5

Attachment 4
Table 3: A26 Regular list + 2,4' series + Mirex

A26 Calibration Mother Soln

Final volume (mL): 10 mL
Analyte/Surrogate concentration (ppb): 2.5K/2.5K

Stock (1st source)	Conc (µg/mL)	Vol (mL)
Pesticide Mix	1,000	0.025
8080 surrogate stock	200	0.125
2,4-DDD	100	0.250
2,4-DDE	100	0.250
2,4-DDT	100	0.250
Mirex	100	0.250

A26 Calibration Stds

Calibration	Final Conc (ppb)	Vol of Mother soln (mL)	Bring to Vol (mL)
#1	25/25	0.1	10
#2	50/50	0.2	10
#3	100/100	0.4	10
#4	200/200	0.8	10
#5	300/300	1.2	10
#6	500/500	2.0	10

A26 ICV Std

Final volume (mL): 50 mL
Analyte/Surrogate concentration (ppb): 100/100

Stock (2nd source)	Conc µ/mL)	Vol (mL)
Pesticide Mix	200	0.025
8080 surrogate stock	200	0.025
Mirex	100	0.050
2,4-DDD	100	0.050
2,4-DDE	100	0.050
2,4-DDT	100	0.050

CCVs

	Final Conc (ppb)	Vol Mother Soln (mL)	Final volume (mL)
CCV1	25/25	0.25	25
CCV2	100/100	1	25
CCV3	300/300	3	25

A26 LCS

Final volume (mL): 50 mL
Analyte concentration (ppb): 500K

Stock (1st source)	Conc (µg/mL)	Vol (mL)
Pesticide Mix	1,000	0.025
2,4-DDD	100	0.250
2,4-DDE	100	0.250
2,4-DDT	100	0.250
Mirex	100	0.250

Attachment 4
Table 4: Chlordane

Chlordane Calibration Mother Soln

Final volume (mL): 10 mL
Chlordane/Surrogate concentration (ppb): 50K/5K

Stock (1st source)	Supplier	Cat#	Vol (mL)
Chlordane	Restek		0.50
Surrogate (200 µg/mL)	Restek	32000	0.25

Chlordane Calibration Stds

Calibration	Vol of Mother Soln (mL)	Final volume (mL)	Final Conc (ppb)
#1	0.01	10	50/5
#2	0.02	10	100/10
#3	0.05	10	250/25
#4	0.10	10	500/50
#5	0.20	10	1K/100
#6	0.40	10	2K/200
#7	0.60	10	3K/300
#8	1.00	10	5K/500

Chlordane Cal ICV Std

Final volume (mL): 25 mL
Chlordane/Surrogate concentration (ppb): 1K/100

Stock (2nd source)	Supplier	Cat#	Vol (mL)
Chlordane Mix (1000 µg/mL)	Supelco		0.0250
Surrogate (200 µg/mL)	Restek	32000	0.0125

Chlordane CCVs

Vol Mother Soln (mL)	Final volume (mL)	Final Conc (ppb)
2	50	2K/200
3	50	3K/300

Chlordane RL

Vol Mother Soln (mL)	Final volume (mL)	Final Conc (ppb)
0.5	100	250/25

Chlordane MDL

Final volume (mL): 50 mL
Chlordane concentration (ppb): 500

Stock (1st source)	Supplier	Vol (mL)
Chlordane Mix (1000 µg/mL)	Restek	0.025

Chlordane LCS

Final volume (mL): 50 mL
Chlordane concentration (ppb): 2000

Stock (1st source)	Supplier	Vol (mL)
Chlordane Mix (1000 µg/mL)	Restek	**0.1**

Attachment 4
Table 5: Toxaphene

Toxaphene Calibration Mother Soln			
Final volume (mL):	25 mL		
Toxaphene concentration/Surrogate (ppb):	50K/2.5K		
Stock (1st source)	**Supplier**	**Cat#**	**Vol (mL)**
Toxaphene (1 mg/mL)	Ultra	EPA-1161	1.2500
Surrogate (200 µg/ml)	Restek	32000	0.3125
Toxaphene Calibration Stds			
Calibration	**Vol of Mother Soln (mL)**	**Final volume (mL)**	**Final Conc (ppb)**
#1	0.05	25	100/5
#2	0.125	25	250/12.5
#3	0.25	25	500/25
#4	0.50	25	1K/50
#5	1.00	25	2K/100
#6	1.50	25	3K/150
#7	2.50	25	5K/250
#8	3.50	25	7K/350
#9	5.00	25	10K/500
Toxaphene Cal ICV Std			
Final volume (mL):	25 mL		
Toxaphene concentration/Surrogate (ppb):	5K/250		
Stock (2nd source)	**Supplier**	**Cat#**	**Vol (mL)**
Toxaphene (1 mg/mL)	Ultra	CUS-3512	0.12500
Surrogate (200 ug/mL)	Restek	32000	0.03125
Toxaphene CCV1			
Vol Mother Soln (mL)	**Final volume (mL)**	**Final Conc (ppb)**	
6	100	3K/150	
Toxaphene CCV2			
Vol Mother Soln (mL)	**Final volume (mL))**	**Final Conc (ppb)**	
14	100	7K/350	
Toxaphene MDL			
Final volume (mL):	50 mL		
Toxaphene concentration (ppb):	2K		
Stock (2nd source)	**Supplier**	**Vol (mL)**	
Toxaphene (1 mg/mL)	Ultra	0.100	
Toxaphene LCS			
Final volume (ml):	50 mL		
Toxaphene concentration (ppb):	6K		
Stock (2nd source)	**Supplier**	**Vol (mL)**	
Toxaphene (1 mg/mL)	Ultra	0.300	

Attachment 4
Table 6: Surrogate & Endrin/DDT Breakdown

8080 Surr. Extraction Soln.

Stock	Volume of 8080 Surr. Stock 200 µg/mL	Final volume	Final Conc.
8080 Surr. Stock 200 µg/mL	2.5 mL	1000 mL	500ppb

4,4 Endrin/DDT Breakdown STD.

Stock	Volume of DDT/Endrin Mix Soln. 500 µg/mL	Final volume	Final Conc.
DDT/Endrin Mix Soln. 500 µg/mL	0.2 mL	250 mL	400 ppb

Attachment 5:
Data Review Checklist

DAILY DATA CHECKLIST

EPA 608/8081A – Pesticides, Toxaphene, Chlordane

Analyst:		2nd Level Review:	
Analysis Date:		Date:	
Method Compliance:	☐ EPA 608 ☐ EPA 8081A	GC #:	
Prep Batches:		Primary Channel (A/B):	
Analytical Batches		Confirm. Channel (A/B):	

Analyst Rev	2nd Level Rev	
_____	_____	Instrument blank before sample analysis : <=Reporting Limit
_____	_____	Pesticides: Endrin (aldehyde & ketone) / DDT(DDE & DDD) Breakdown: <=15%
		ICV/CCV (1rst or 2nd source)
_____	_____	• At the beginning of every 12-hour shift, every 10-20 samples and at the end of analysis
_____	_____	• Two different levels during the daily analysis.
_____	_____	• %Recovery = 85 - 115
_____	_____	• For Chlordane & Toxaphene, ICV/CCV outside of limits: valid for qualification only
_____	_____	Method blank every extraction batch: <= Reporting limit, or
_____	_____	Method blank contaminated, but samples ND or > 20 times MB.
_____	_____	LCS every extraction batch of 20 samples or less (refer to in-house limits in LIMS system)
_____	_____	MS/MSD every extraction batch of 20 samples or less (refer to in-house limits in LIMS system)
		All samples checked for:
_____	_____	• Dilution Factor
_____	_____	• Manual integration
_____	_____	• Surrogates within limits (refer to in-house limits)
_____	_____	• Precision between channels: <= 40 % (or otherwise justified)
_____	_____	• All graphics were uploaded.
_____	_____	• Frequency of 10 (recommended) to 20 between compliant ICV/CCV
_____	_____	GC Calibration Check Criteria form attached (if average % recovery if ICV/CCV is used)
_____	_____	All standards used are uniquely identified and are not expired
_____	_____	All data flags correctly applied and NCMs written, as required
_____	_____	Run logs printed

Comments: _____

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Attachment 6
ICAL Review Checklist

GC INITIAL CALIBRATION CHECK LIST
EPA 608/8081A - Organochlorine Pesticides

Analyst: _____ 2nd Level Review: _____
Calibration Date: _____ Date: _____
Calibration batch#: _____ GC #: _____
Method Compliance: ☐ EPA 608 ☐ EPA 8081A

Analyst Rev	2nd Level Rev	
		• 608: minimum 3-point calibration • 8081A: Minimum 5-point calibration (6-point for quadratic regression) • Lowest calibration standard at or below Reporting Limit (but >MDL)
		Calibration Factors (CF): • RSD <= 10% for each compound or if
		• RSD >10% (but <50%): Generate a linear or quadratic curve, r^2>=0.99 (Do NOT use linear calibration curve for Negative or abnormally Positive results).
		• For 8081A only if needed. Average RSD is used and <=20% (Must not be used for Arizona work)
		2nd Source ICV: • Immediately after initial calibration
		• %Recovery: 85 – 115
		Check and verify calibration data for: • Correct retention times
		• All peaks are identified correctly
		• Saturated chromatographic peaks
		• Manual integration
		• All graphics uploaded
		• P flags checked

Comments: _____

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