ALLOWAY

STANDARD OPERATING PROCEDURES FOR METHOD 515.1

DETERMINATION OF CHLORINATED ACIDS IN DRINKING WATER BY GAS CHROMATOGRAPHY WITH AN ELECTRON CAPTURE DETECTOR – MARION, OHIO

SOP #: 515.1

Alloway Revision 8.0

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<th>Section Supervisor:</th>
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Section 1.0 Scope and Application

1.1 This is a gas chromatographic (GC) method applicable to the determination of certain chlorinated acids in ground water and finished drinking water. The following compounds can be determined by this method:

<table>
<thead>
<tr>
<th>Analyte</th>
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<tbody>
<tr>
<td>2,4-D</td>
</tr>
<tr>
<td>Dalapon</td>
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<tr>
<td>Dicamba</td>
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<tr>
<td>Dinoseb</td>
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<tr>
<td>Pentachlorophenol</td>
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<tr>
<td>Picloram</td>
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<tr>
<td>2,4,5-TP(Silvex)</td>
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1.2 This method is restricted to use by or under the supervision of analysts experienced in the use of GC and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 11.0

1.3 Analytes that are not separated chromatographically, i.e., which have very similar retention times, cannot be individually identified and measured in the same calibration mixture or water sample unless an alternate technique for identification and quantitation exist

1.4 When this method is used to analyze unfamiliar samples for any or all of the analytes above, analyte identifications must be confirmed by at least one additional qualitative technique.

Section 2.0 Summary of Method

2.1 A measured volume of sample of approximately 1 L is adjusted to pH 12 with sodium hydroxide and shaken for 1 hour to hydrolize derivatives. Extraneous organic material is removed by a solvent wash. The sample is then acidified, and the chlorinated acids are extracted with ethyl ether by shaking in a separatory funnel. The acids are converted to their methyl esters. Excess derivitizing reagent is removed, and the esters are determined by capillary column/GC using an electron capture detector (ECD).
Section 3.0 Definitions

3.1 **Acceptance Criteria** – specified limits placed on characteristics of an item, process, or service defined in required documents.

3.2 **Analytical Batch** – composed of prepared environmental samples which are analyzed together as a group. It can include prepared sample originating from various environmental matrices and cannot exceed 20 samples.

3.3 **Calibration** – to determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter, instrument, or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

3.4 **Calibration Curve** – the graphical relationship between the known values, such as concentrations, of a series of calibration standards and their instrument response.

3.5 **Calibration Standard (CAL)** – A solution prepared from the primary dilution standard solution. The CAL is used to calibrate an instrument.

3.6 **Field Blank or Trip Blank** – blank prepared in the field or laboratory by filling a clean container with pure de-ionized water and appropriate preservative, if any, for the specific sampling activity being undertaken.

3.7 **High Quality Pure Reagent Water** – water in which no target analytes or interferences are detected as required by the analytical method.

3.8 **Holding Times (Maximum Allowable Holding Times)** – the maximum times that samples may be held prior to analysis and still be considered valid or not compromised.

3.9 **Internal Standard** – a known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

3.10 **Laboratory Duplicates** – Two samples aliquots taken in the laboratory, prepared identically and analyzed separately. Duplicate analysis gives a measure of precision associated with laboratory procedures.
3.11 **Laboratory Performance check solution** - A solution containing method analytes, surrogates and internal standards which is used to monitor the performance of the instrument system within a defined set of method criteria.

3.12 **Laboratory Reagent Blank (LRB)** -- An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.13 **Laboratory Fortified Blank (LFB)** -- An aliquot of reagent water to which a known quantity of the method analyte is added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the method is in control, and whether the laboratory is capable of making accurate and precise measurements at the required method detection limit.

3.14 **Matrix** – the component or substrate that contains the analyte of interest.

3.15 **Matrix Spike (MS) or Laboratory Fortified Matrix (LFM)** – a sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Used to determine the effect of the matrix on a method’s recovery efficiency. The background concentration of the analyte in the sample matrix must be determined in a separate aliquot and the measured value in the LFM corrected for background concentration.

3.16 **Primary Dilution Standard Solution (PDS)** - A solution of several analytes purchased from a commercial source and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.17 **Procedural Standard Calibration** - A calibration method where aqueous calibration standards are prepared and processed (e.g., purged, extracted, and/or derivatized) in exactly the same manner as a sample. All steps in the process from addition of sampling preservatives through instrumental analyses compensates for any inefficiencies in the processing procedure.

3.18 **Quality Control** – the overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.

3.19 **Raw Data** – any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes,
or exact copies thereof that are necessary for the reconstruction and evaluation of
the report activity.

3.20 **Reference Method** – a method of known and documented accuracy and precision
issued by an organization recognized as competent to do so.

3.21 **Standard Operating Procedures (SOPs)** – a written document which details the
method of an operation, analysis or action whose techniques and procedures are
thoroughly prescribed and which is accepted as the method for performing certain
routine or repetitive tasks.

3.22 **Stock Standard Solution** -- A concentrated solution containing a single certified
standard that is a method analyte, or a concentrated solution of a single analyte
prepared in the laboratory with an assayed reference compound. Stock standard
solutions are used to prepare primary dilution standards.

3.23 **Surrogate** – a substance with properties that mimic the analyte of interest. It is
unlikely to be found in environment samples and is added to them for quality
control purposes. Calculated as percent recovery.

**Section 4.0 Interferences**

4.1 Method interferences may be caused by contaminants in solvents, reagents,
glassware, and other sample processing apparatus that lead to anomalous peaks or
elevated baselines in gas chromatograms. The LRB is used as a tool to monitor
for the presence of interferences.

4.2 Glassware must be carefully cleaned as detailed in the laboratory’s Standard
Operating Procedure for Glassware Preparation.

4.3 Interfering contamination may occur when a sample containing low
concentrations of compounds is analyzed immediately after a sample containing
relatively high concentrations of compounds. Syringes and injection port liners
must be cleaned carefully or replaced as needed. After analysis of a sample
containing high concentrations of compounds, a solvent blank or an LRB is
analyzed to ensure that accurate values are obtained for the next sample. If
suspicion of carryover exists, reanalysis of the affected samples is performed.

4.4 Samples and standards must be contained in the same solvent to ensure
chromatographic comparability.
4.5 Interferences by phthalate esters can pose a major problem in pesticide analysis using the electron capture detector. Common flexible plastics, gloves, and tubing contain varying amounts of phthalates that are easily extracted or leached during laboratory operations.

4.6 Matrix interferences may be caused by contaminants that are coextracted from the sample.

Section 5.0 Safety

5.1 The toxicity or carcinogenicity of each chemical and reagent used in this method has not been precisely defined. However, each one must be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each analyst is responsible for adherence to the procedures outlined in the Chemical Hygiene Plan. Material Safety Data Sheets are stored in the Quality Assurance Section of the laboratory.

5.2 Some method analytes have been tentatively classified as known or suspected human or mammalian carcinogens. Pure standard materials and stock standard solutions of these compounds should be handled with suitable protection to skin, eyes, etc.

5.3 Safety glasses, gloves, and lab coats must be worn when handling samples and solvents. Safety glasses must be worn when handling glassware and chromatographic columns. Safety glasses must be worn when handling equipment within the laboratory.

5.4 Ethyl ether is an extremely flammable solvent. Avoid sparks or equipment that has not been demonstrated to be safe around flammable fumes.

Section 6.0 Equipment and Supplies

6.1 Sample Bottle -- Borosilicate, 1-L volume with graduations fitted with screw caps lined with TFE-fluorocarbon. Protect samples from light. Cap liners are also used.

6.2 Glassware

6.2.1 Nalgene FEP Funnel – 2000-mL
6.2.2 Kuderna-Danish (K-D) apparatus – 500-mL equipped with a 10 or 25 mL concentrator tube and 3-ball Snyder column.

6.2.3 Erlenmeyer flasks – 500-mL with 24/40 ground glass joints fitted with stoppers.

6.2.4 Autosampler vials (17-mL) – with Teflon lined caps

6.2.5 Disposable pipettes – clean borosilicate glass free from dust or residues.

6.3 **Tumbler** – Capable of holding sample bottles and tumbling them end-over-end at 30 turns/minute.

6.4 **Boiling stones** -- Carborundum, #12 granules.

6.5 **Diazomethane Generator**

6.6 **Water bath** -- Heated, capable of temperature control (±2°C). The bath should be used in a hood.

6.7 **Balance** -- Analytical, capable of accurately weighing to the nearest 0.001 g.

6.8 **N-EVAP**

6.9 **Thermometer**

6.10 **Metal spatula**

6.11 **Rinsed glasswool**

6.12 **Permanent ink marker**

6.13 **Prep sheet**

6.14 **1-mL autosampler vial**

6.15 **Crimp caps**

6.16 **Crimper**

6.17 **Rubber pipette bulb**
6.18 Disposable Pasteur pipettes

6.19 50-µL Pipettor

6.20 pH paper – pH range 9.0 to 14, pH Hydrion Insta Check Fisher Scientific Catalog # 14-850-10T or equivalent and pH range 0 to 5.5, pH Hydrion Insta Check 14-850-10A, or equivalent. All pH litmus paper must be entered into Reagent Traceability Software.

6.21 Glass rods

6.22 Syringes (of various sizes)

6.23 Bottle top dispenser for solvent bottles

6.24 Gas Chromatograph – Analytical system complete with temperature programmable GC suitable for use with capillary columns and all required accessories including syringes, analytical columns, gases, detector and data collection.

6.24.1 Column 1 (Primary column) – RTX CLPesticides, 30m Length x 0.32 mm ID x 0.5µm film (cat: 11139 or equivalent)

6.24.1.1 Conditions:

Oven – 40°C, hold for 1 minute. Ramp at 3°C/minute to 185°C and hold for 0 minute. Ramp at 25°C/minute to 300°C and hold for 0 minute.

Inlet Temperature - 250°C

Detector - 315°C

Injector – 1 µL

6.24.2 Column 2 (Confirmation column) – RTX CLPesticide2, 30m Length x 0.32mm ID x 0.25 um film (cat: 11324 or equivalent).

6.24.2.1 Conditions:
Oven – 40°C, hold for 1 minute. Ramp at 3°C/minute to 185°C and hold for 0 minute. Ramp at 25°C/minute to 300°C and hold for 0 minute.

Inlet Temperature - 250°C

Detector - 315°C

Injector – 1 µL

6.24.3 Detector -- Electron Capture Detector (ECD). This detector has been proven effective in the analysis of fortified reagent and artificial ground waters. Alternative detectors, including a mass spectrometer, may be used.

**Section 7.0  Reagents and Calibration Standards**

7.1 **Acetone** – Pesticide quality or equivalent

7.2 **Methylene chloride** - Pesticide quality or equivalent

7.3 **Methyl tert-butyl ether (MTBE)** – Pesticide quality or equivalent.

7.4 **Ethyl Ether** – Anhydrous (1.5-2.5 % ethanol).

7.5 **Sodium sulfate, granular** - Anhydrous, ACS grade.

7.6 **Sodium Hydroxide (NaOH)** – Pellets, ACS grade. Dissolve 200-g of NaOH in 500-mL of Reagent Water with cooling.

7.7 **Sulfuric Acid** – Concentrated, ACS grade.

7.8 **Potassium Hydroxide (KOH)** – 37%. Dissolve 200-g of KOH pellets in 500-mL of reagent water and dilute to 100-mL.

7.9 **Carbitol (Diethylene Glycol Monoethyl Ether)** – ACS Grade.

7.10 **Diazald** – ACS Grade
7.11 **Diazald Solution** – Prepare a solution containing 10g of Diazald in 100-mL of a 50:50 volume mixture of ethyl ether and carbitol. This solution is stable for one month longer when stored at 4°C in an amber bottle with a Teflon lined screw cap.

7.12 **Internal Standard Solution** – 4,4’-dibromooctafluorobiphenyl (DBOB). 100 µg/mL in MTBE. Addition of 10-µL in 10-mL sample extract results in an extract concentration of 100 ng/mL.

7.13 **Surrogate Standard Solution** - The surrogate solution is purchased as a certified solution. The surrogate solution contains 2,4-Dichloro-phenylacetic acid (DCAA) at a concentration of 100 µg/mL.

7.14 **Calibration Standards** -- The calibration standard solutions are diluted from the certified custom standard mix. The standards are purchased in the methyl ester form and do not require extraction. The calibration standards are prepared at six different concentrations as listed in Table 1.

7.14.1 The standards are prepared by diluting the initial volumes to a 10-mL final volume with MTBE. 10-µL of the internal standard solution is also added to each 10-mL volume calibration standard. The dilution results and analyte concentrations are specified in Table 1.

7.14.2 The finished calibration standard solutions are stored at 4°C. These solutions are used for 60 days from date of production.

<table>
<thead>
<tr>
<th>ANALYTE</th>
<th>Initial Conc. (µg/mL)</th>
<th>Final Standard Concentrations (µg/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>2,4-D</td>
<td>10</td>
<td>0.01</td>
</tr>
<tr>
<td>Dalapon</td>
<td>100</td>
<td>0.1</td>
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<tr>
<td>Dicamba</td>
<td>20</td>
<td>0.02</td>
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<td>Silvex</td>
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<td>Daclthal</td>
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<td>0.1</td>
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<tr>
<td>DCAA (Surrogate)</td>
<td>100</td>
<td>0.1</td>
</tr>
</tbody>
</table>

7.15 **LFB/LFM Spiking Solution** – The LFB/LFM stock spike solution is diluted from the certified custom spiking mix. It is prepared by taking 1-mL of the
custom spiking mix to a 100-mL final volume with acetone. Table 2 lists the initial concentrations of the custom spiking mix and the stock concentration.

Table 2. Initial Concentrations and Stock Concentration of Spike Solution

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Initial Concentration (µg/mL)</th>
<th>Stock Concentration (µg/mL)</th>
</tr>
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<tr>
<td>2,4-D</td>
<td>40</td>
<td>0.4</td>
</tr>
<tr>
<td>2,4-DB</td>
<td>40</td>
<td>0.4</td>
</tr>
<tr>
<td>2,4,5-TP (Silvex)</td>
<td>80</td>
<td>0.8</td>
</tr>
<tr>
<td>2,4,5-T</td>
<td>80</td>
<td>0.8</td>
</tr>
<tr>
<td>Dalapon</td>
<td>400</td>
<td>4.0</td>
</tr>
<tr>
<td>Dicamba</td>
<td>80</td>
<td>0.8</td>
</tr>
<tr>
<td>Dacthal</td>
<td>400</td>
<td>4.0</td>
</tr>
<tr>
<td>Dinoseb</td>
<td>80</td>
<td>0.8</td>
</tr>
</tbody>
</table>

7.16 High Quality Pure Reagent Water

7.17 Ascorbic Acid – ACS Grade. Fisher Scientific Catalog # AC352685000 or equivalent.

Section 8.0 Sample Collection, Preservation, Shipment, and Storage

8.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be prewashed with sample before collection.

8.2 Add 80 mg of sodium thiosulfate per liter of sample to the sample bottle prior to collecting the sample.

8.3 After the sample is collected in a bottle containing preservative, seal the bottle and shake vigorously for 1 minute, or until all sodium thiosulfate has been dissolved.

8.4 The samples must be iced or refrigerated at 4°C away from light from the time of collection until extraction.

8.5 Preservation study results indicate that most method anlaytes present in samples are stable for 14 days when stored under these conditions.

8.6 Extracts should be stored at 4°C away from light. Preservation study results indicate that most analytes are stable for 28 days.
Section 9.0  Calibration and Standardization

9.1  Establish GC operating parameters. The GC system should be calibrated using the internal or external standard technique. All analytes should be resolved before continuing with analysis.

9.2  Internal Standard Calibration Procedure

9.2.1  The system is calibrated using a minimum of five different concentrations of the calibration standards. One μL of each calibration standard is analyzed and the area of each peak is tabulated against the concentration of each compound. The response factor (RF) for each compound relative to the internal standards is determined as follows:

\[
RF = \frac{(A_x)(C_{is})}{(A_{is})(C_x)}
\]

Where:
- \(A_x\) = Area of the peak ion for the compound being measured.
- \(A_{is}\) = Area of the characteristic ion for the specific internal standard.
- \(C_{is}\) = Concentration of the specific internal standard (ng/uL).
- \(C_x\) = Concentration of the compound being measured (ng/uL).

9.2.2  The tabulated peak areas and concentrations are used to generate a calibration curve for each compound and the surrogate. The curve must have a correlation coefficient of greater than or equal to 0.995.

9.3  Continuing Calibration Verification (CCV)

9.3.1  A calibration standard at mid concentration containing all of the compounds must be analyzed every 10 samples during analysis. For each compound the calculated value must be within 20% of the working value. If not corrective action must be taken and the check standard re-analyzed. If the check standard passes, routine analyses may continue, if not, additional corrective action must be completed and new calibration curves established.

9.3.2  The CCV must be from a different source than that of the standard used in the initial calibration curve.
9.4 Reporting Limit Check Standard

9.4.1 A reporting limit check standard must be analyzed every day that samples are run and a new curve is not established. The reporting limit check is from the lowest point in the curve. The calculated values must be within 50%–150% of the expected value (this range has been dictated by one of the state agencies that certifies our laboratory).

Section 10.0 Quality Control

10.1 Minimum quality control (QC) requirements are: initial demonstration of laboratory capability, determination of surrogate compound recoveries in each sample and blank, monitoring internal standard peak area or height in each sample and blank (when internal standard calibration procedures are being employed), analysis of laboratory reagent blanks, laboratory fortified samples, laboratory fortified blanks, and QC samples. An MDL for each analyte must also be determined.

10.2 Laboratory Reagent Blanks (LRB)/Method Blank -- Before processing any samples, the analyst must demonstrate that all glassware and reagent interferences are under control. Each time a set of samples is extracted or reagents are changed, a LRB must be analyzed. If a target analyte is detected but falls below the reporting limit, then samples may be reported. If an analyte of interest is detected in the LRB at or above the reporting limit, samples that have results below the reporting limit can be reported with qualification. Sample results that are 10 times higher than the LRB can be reported with the following qualifying statement: Analyte detected in the Method Blank is $\geq 1/10$ of the amount detected in this sample. Evaluate data accordingly. If the sample result is not 10 times higher than the result in the method blank then the samples should be reanalyzed or if reported the results must be qualified with the following statement: Analyte detected in the Method Blank is $\leq 1/10$ of the amount detected in this sample. Evaluate data accordingly. If within the retention time window of any analyte of interest the LRB produces a peak that would prevent the determination of that analyte, determine the source of contamination and eliminate the interference before processing samples.

10.3 Initial Demonstration of Capability

10.3.1 Select a representative fortified concentration (about 10 times MDL or at a concentration that represents a mid-point of the calibration range for each analyte. Prepare a primary dilution standard (in methanol) containing each
analyte at 1000 times selected concentration. With a syringe, add 1-mL of the concentrate to each of four to seven 1 L aliquots of reagent water, and analyze each of these LFBs according to procedures beginning in Section 11.0.

10.3.2 For each analyte, the recovery value for all replicates must fall in the range of the laboratories in-house control limits and must not exceed the limits set from Table 4. The precision of the measurements, calculated as relative standard deviation (RSD), must be 20% or less. For those compounds that fail these criteria, this procedure must be repeated using four fresh samples until satisfactory performance has been demonstrated.

10.4 The analyst is permitted to modify GC columns, GC conditions, concentration techniques (i.e., evaporation techniques), and internal standards or surrogate compounds. Each time such method modifications are made, the analyst must repeat the procedures in Section 10.3.

10.5 Method Detection Limit Study

10.5.1 For each analyte, determine the method detection limit (MDL). Prepare a minimum of seven LFB’s at a low concentration. Extract and analyze each replicate according to Section 11.0. The LFB’s should be prepared over a period of several days so that day to day variations are reflected in precision measurements. The standard deviation of the average of seven results for each analyte is then multiplied by 3.143 to obtain the calculated MDL. The reporting limit check standard when analyzed daily may be used to calculate the MDL.

10.6 Assessing Surrogate Recovery

10.6.1 When surrogate recovery from a sample, lab blank, LFB or matrix spike is <70% or >130%, check calculations to locate possible errors, fortifying solutions for degradation, contamination or other obvious abnormalities, and instrument performance. If those steps do not reveal the cause of the problem, reanalyze the extract.

10.6.2 If reanalysis of the blank extract fails the 70-130% recovery criterion, the problem must be identified and corrected before continuing.

10.6.3 If sample extract reanalysis meets the surrogate recovery criterion, report only data for the reanalyzed extract. If sample extract reanalysis continues
to fail the surrogate recovery criterion, report all data for that sample as suspect.

10.7 Assessing the Internal Standard

10.7.1 The analyst is expected to monitor the internal standard response of all samples (including but not limited to samples, Blanks, LFB’s and matrix spikes) during each analytical day. The internal standard response for any sample chromatogram should not deviate from the daily calibration check standard by more than 30%.

10.7.2 If > 30% deviation occurs with an individual extract, inject a second a aliquot of that extract.

10.7.2.1 If the re-injected aliquot produces an acceptable internal standard response, report results for that aliquot.

10.7.2.2 If a deviation of > 30% is obtained for the reinjected extract, analysis of the samples should be repeated beginning with Section 11, provided the sample is still available and meets the holding time. Otherwise, report the results from the reinjected extract as suspect.

10.7.3 If consecutive samples fail the internal standard response criteria, immediately analyze a calibration check standard.

10.7.3.1 If the check standard provides a response factor within 20% of the predicted value, then follow procedures itemized for each sample failing the response criterion.

10.7.3.2 If the check standard deviates more than 20% of the predicted value, then the analyst must recalibrate, as specified in Section 9.0.

10.8 Assessing Laboratory Performance -- Laboratory Fortified Blank (LFB)

10.8.1 The laboratory must analyze at least one LFB sample with every 20 samples or one per sample set (all samples extracted within a 24-hour period) whichever is greater. The concentration of each analyte should be approximately 10 times the MDL or a concentration that represents a mid-point of the curve. Calculate the accuracy as percent recovery and
determine control limits (using 20 data points) with periodic review of the control charts.

10.9 Assessing Method Performance -- Laboratory Fortified Sample Matrix

10.9.1 The laboratory must add a known concentration to a minimum of 10% of the routine samples or one sample per set, whichever is greater. The added concentration should not be less than the background concentration of the sample selected for fortification. The percent recovery must fall within the in-house limits of the fortified concentration.

10.9.2 If the recovery for any analyte falls outside of the designated range, and all other QC is in control then the recovery is matrix not system related. The data should be qualified appropriately.

10.10 Assessing Instrument System -- Laboratory Performance Check (LPC)

10.10.1 Laboratory performance check (LPC) -- After initial demonstration of capability, instrument performance should be monitored on a daily basis by analysis of the LPC sample. The LPC sample contains compounds designed to monitor instrument sensitivity, column performance (primary column) and chromatographic performance. Refer to Table 3 in the Appendix for the acceptance criteria. If the criteria are not met, the system must be evaluated to determine the problem.

10.11 Duplicate Analysis

10.11.1 A duplicate analysis is done one per every ten samples with an RPD of \( \leq 20\% \). If the duplicate results are outside acceptance limits, report result of the sample used for the duplicate with the following qualification statement: The duplicate fell outside method limits and the result for this sample should be evaluated accordingly.

10.12 The laboratory may adopt additional quality control practices for use with this method such as the use of additional control charts. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. For example, field or laboratory duplicates may be analyzed to assess the precision of the environmental measurements or field reagent blanks may be used to assess contamination of samples under site conditions, transportation and storage.
Section 11.0  Analytical Procedure

11.1  Extraction

11.1.1  Measure 500 mLs of sample into a clean sample bottle.

11.1.2  Add 0.5 mL DCAA surrogate to all samples. Add 0.5 mL of the stock spike solution to LFM and LFB and shake.

11.1.3  Add 125 g of baked sodium chloride to sample. Tumble for 15 minutes to dissolve.

11.1.4  Add 9 mL of 6N Sodium hydroxide to the sample to pH > 12. Verify with pH paper. Add more 6N Sodium hydroxide if necessary. Allow sample to sit at room temperature (with periodic shaking & pH checks) to properly hydrolyze the target analytes for a minimum of 1 hour before proceeding with the next step. Perform a final pH check to ensure the pH > 12. Rinse a separatory funnel 1 time with CH₂Cl₂. Drain and discard CH₂Cl₂.

11.1.5  Pour sample into separatory funnel.

11.1.6  Add 60-mL CH₂Cl₂ to the sample bottle. Swirl and pour into the separatory funnel. Shake the separatory funnel several times by hand and vent. Drain the CH₂Cl₂.

11.1.7  Repeat steps 11.1.6 one more time.

11.1.8  Add 20-mL sulfuric acid to sample - seal and shake. Make sure the pH is < 2. Check pH using pH strips in range of 0-5.5.

11.1.9  Prepare flask – rinse flask first with 10% nitric acid, next with reagent water, then acetone, finally ethyl ether.

11.1.10 Add 120 ml ethyl ether to sample quart - rinse and add to sample. Vent and then shake 2 minutes. Allow to separate 10 minutes.

11.1.11 Drain sample back into container. Drain ether layer into round flask that has been rinsed with ethyl ether. Pour sample back into separatory funnel.

11.1.12 Repeat steps 11.1.10 and 11.1.11 twice using 60-mL of ethyl ether instead of 120-mL.
11.1.13 Add 10-15g of ether rinsed acidified baked sodium sulfate to each sample. Place Teflon stopper on flask and shake vigorously.

11.1.14 Leave sit two hours or overnight.

11.1.15 Rinse K-D with ethyl ether. Add 1 Teflon boiling chip.

11.1.16 Rinse funnel with acidified glass wool in it with ethyl ether.

11.1.17 Pour extract through funnel – Do not allow sodium sulfate to enter funnel. Rinse flask with 20-mL of ethyl ether vigorously and pour through funnel.

11.1.18 Repeat 11.1.17 two more times. On the last rinse, let sodium sulfate enter the funnel.

11.1.19 Rinse again in funnel with ethyl ether. Rinse stopper with ethyl ether.

11.1.20 Attach a 3-ball Snyder column and concentrate to approximately 8-9 mL. Add 10-mL MTBE and concentrate down into receiver.

11.1.21 Remove concentrator. Allow to stand for 10 minutes. The volume should be 5-8 mL.

11.1.22 Transfer extract into MTBE rinsed volume test tube.

11.1.23 Rinse walls of test tube with 1-mL of MTBE 3 times.

11.1.24 Concentrate the extract by gentle heating and passing nitrogen over the extract to 2-3 mL. Add 250-µL methanol and 0.5 to 1mL diazomethane. Solution must stay yellow for two minutes. Let the extract sit for 30 minutes.

11.1.25 Adjust extract to 5-mL with MTBE.

11.1.26 Transfer sample to 10-mL vial.

11.1.27 Add a small amount silicic acid and cap.

11.1.28 Shake by hand and let the extract settle.
11.1.29 Fill a 1-mL vial with extract. Leave the rest of the extract in the 10-mL vial.

11.1.30 Add 5-µL of internal standard

11.1.31 Complete prep sheet with finish dates and lot numbers of solvents. Place the extracts in the appropriate refrigerator.

11.2 Gas Chromatography

11.2.1 Section 6.24 summarizes the recommended operating conditions for the GC.

11.2.2 GC must be calibrated at least quarterly or sooner if LPC and/or CCV fail to meet acceptance criteria.

11.2.3 If samples are suspected to have very low concentrations of analytes, fortify the extract with 50 µL/10mL with the internal standard solution and analyze. If a dilution is suspected, adjust extract to exactly 5 or 10 mL and accurately dilute the extract and spike the resulting solution with 5 µL internal standard per 1-mL of extract. Thoroughly mix sample and place aliquot in a GC vial for subsequent analyses.

11.2.4 Inject 1-µL of the sample extract. Record the resulting peak size in area units.

11.2.5 If the response for the peak exceeds the working range of the system, dilute the extract and reanalyze.

11.2.6 Routine maintenance is performed on the GC. Usually septa are changed every 100 injections. At this time, the lines are inspected along with the detectors. Column maintenance is also performed at this time. Gases are checked daily for adequate pressure.
### 11.3 Example Analytical Sequence

<table>
<thead>
<tr>
<th>Injection Number</th>
<th>Sample Description</th>
<th>Acceptance Criteria</th>
<th>Remedial Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>LPC (once per day of analytical run)</td>
<td>Must meet criteria of Table 3 of the Appendix</td>
<td>Identify and correct the source of the problem, instrument maintenance</td>
</tr>
<tr>
<td>2</td>
<td>Initial Calibration Verification</td>
<td>Target analyte peak matches retention time of curve and recovers 80-120% of expected value</td>
<td>Identify and correct source of problem, instrument maintenance, recalibration.</td>
</tr>
<tr>
<td>3</td>
<td>PQL Check (once a day per analytical run)</td>
<td>50-150% of true value</td>
<td>Identify and correct source of problem, instrument maintenance, recalibration.</td>
</tr>
<tr>
<td>4</td>
<td>Laboratory Reagent Blank</td>
<td>&lt; PQL, Surrogate / internal standard passes criteria.</td>
<td>Identify and correct source of contamination and/or re-extract batch.</td>
</tr>
<tr>
<td>5</td>
<td>LFB</td>
<td>Acceptable recovery is based on current control criteria. Surrogate/internal standard passes criteria.</td>
<td>Find and correct source of problem Re-extract batch.</td>
</tr>
<tr>
<td>6</td>
<td>LFSM1 (matrix spike)</td>
<td>Acceptable recovery is based upon current control criteria, and with %RPD &lt; 20 if LFB dup. %RPD &lt; 20%. Surrogate / Internal Standard pass criteria.</td>
<td>If %Recovery is out of designated range, but laboratory performance for all other QC is acceptable, the recovery problem is judged to be matrix related. Label sample a &quot;suspect matrix&quot; but still report.</td>
</tr>
<tr>
<td>7 .. 16</td>
<td>Field samples, 1-10</td>
<td>Pass RT, surrogate, and internal standard criteria</td>
<td>Identify and correct source of problem, re-extract</td>
</tr>
<tr>
<td>17</td>
<td>Mid Sequence calibration Verification</td>
<td>80-120% of true value</td>
<td>Identify and correct source of problem, instrument maintenance, recalibration.</td>
</tr>
<tr>
<td>18</td>
<td>LFSM2 (matrix spike)</td>
<td>Acceptable recovery is based upon current control criteria, and with %RPD &lt; 20 if LFB dup. %RPD &lt; 20%. Surrogate / Internal Standard pass criteria.</td>
<td>If %Recovery is out of designated range, but laboratory performance for all other QC is acceptable, the recovery problem is judged to be matrix related. Label sample a &quot;suspect matrix&quot; but still report.</td>
</tr>
<tr>
<td>19 .. 28</td>
<td>Field samples, 11-20</td>
<td>Pass RT, surrogate, and internal standard criteria</td>
<td>Identify and correct source of problem, re-extract</td>
</tr>
<tr>
<td>29</td>
<td>End Sequence calibration Verification</td>
<td>80-120% of true value</td>
<td>Identify and correct source of problem, instrument maintenance, recalibration.</td>
</tr>
</tbody>
</table>
11.4 **Reviewing Data**

11.4.1 Load Method

11.4.2 If a curve was run, choose the correct curve for the method. Work the curve according to Section 9 to make sure that it meets all criteria. If all criteria is met, save the new curve. If a curve was not run, go to Section 11.4.3.

11.4.3 Examine all check standards and quality control samples before any samples to ensure that the data is reportable. Use manual integrations if necessary (printing a before and after copy and including the reason code, date, and initials).

11.4.4 Load Data File

11.4.5 After Data File is loaded, all samples will be listed on the left-hand side of the box. Double click on each sample to pull it up on the screen. If a sample is clean, print only a copy from the column that was used for the check standards. If a target compound is detected, copies from both columns must be printed.

11.5 **Identification of Analytes**

11.5.1 Identify a sample component by comparison of its retention time to the retention time of a reference chromatogram. If the retention time of an unknown corresponds, within limits, to the retention time of a standard compound on both columns, then identification is considered positive.

11.5.2 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation can be used to calculate a suggested window size for a compound. However, the experience of the analyst should weigh heavily in the interpretations of chromatograms.

### Section 12.0 **Calculations and Quantitative Analysis**

12.1 The identification of compounds is based on retention times on both the primary and confirmation columns.
12.2 The retention time of any suspected target analyte in a sample must fall within the established retention time window (Rt window). The retention time window is equal to the average absolute retention time of the injected standards for each analyte for the run plus or minus .02 min. This window may expand as the Retention time increases, but depends heavily on the experience of the analyst.

12.3 When a compound has been identified by the HP ChemStation, the quantification of that compound will be based on the integrated abundance of the identified peak.

12.4 The concentration in the extract is determined based upon the calibration curve established. The only other calculation that must be made are as follows:

12.4.1 The concentration of the analyte in the liquid phase of the sample is calculated using the concentration of the analyte in the extract and the volume of liquid extracted, as follows:

\[
C(\micro g/L) = \frac{(A_S)(I_S)}{(A_{is})(RF)(V_O)}
\]

Where:
- \(A_S\) = Response for the parameter to be measured
- \(A_{is}\) = Response for the Internal Standard
- \(I_S\) = Amount of Internal Standard added to each extract (µg)
- \(V_O\) = Volume of water extracted (L)

Section 13.0 Data Assessment

13.1 The primary analyst bears the responsibility of producing accurate data. A documented review is performed that includes a check of the following parameters:

- Calibration verification
- QC criteria
- Calculation checks
- Data entry using the LIMS worksheet
- Review of all data to ensure proper peak integration

The initial data review is documented on a checklist that is initiated and dated by the primary analyst. A secondary review must be performed by an individual trained to the standard operating procedure. The specific procedures for data review can be found in Alloway’s data review and manual integration SOPs.
13.2 Data qualifiers are used whenever deviations occur while analyzing the samples. The qualifiers are included on the Certificate of Analysis that is presented to the client. Qualifiers include: samples that were not properly preserved, failed surrogate recovery, failed LFM recovery, qualified due to LRB contamination, estimated or elevated reporting limit due to sample matrix interference, calibration failure (high bias) but sample was <RL for the compound.

13.3 If acceptance limits are not met corrective actions are taken as described in Alloway’s Corrective Action SOP.

Section 14.0 Report Generation

14.1 A report is generated after each analysis run is complete. The report includes the US EPA Method number, sample identification, date acquired, acquisition method, date processed, processing method, analyst’s name, chromatogram and quantitative results. If any manipulation is performed, the result is saved and another report is printed and added to the original.

Section 15.0 Pollution Prevention and Waste Management

15.1 (For information about pollution prevention that may be applicable to laboratory practices, consult “Less is Better: Laboratory Chemical Management for Waste Reduction” available from the American Chemical Society’s Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.)

15.2 (“The Waste Management Manual for Laboratory Personnel”, also available from the American Chemical Society at the address above.)

15.3 It is the laboratory’s responsibility to comply with the requirements as stated in the Alloway’s Chemical Hygiene Plan for waste disposal.

Section 16.0 References

Section 17.0 Revision History

17.1 Revision 4 issued to update format, edited the Table number from 1 to 3 in Appendix section, changed reference in section 10.10 from Table 4 to Table 3 and add Revision History Section.

17.2 Revision 5 issued to specify the pH litmus paper range to use (9.0-14) when verifying the pH is >12 in extraction step (Sections: 6.20 and 11.1.3), specify the pH litmus paper range to use (0.0-5.5) when verifying the pH is <2 (Sections: 6.20 and 11.1.9), indicate the Ascorbic Acid reagent quality/grade and catalog number (Section 7.17) and to change the number of data points from 50 to 20 when generating limits (Section 10.8.1).

17.3 Revision 6 included the following updates.

- Section 3.10 – Added the definition of Laboratory Duplicates.
- Section 3.11 – Added the definition of Laboratory Performance Check Solution.
- Section 3.16 – Matrix Spike Duplicate or Laboratory Fortified Matrix Duplicate. – Deleted the definition. Not required by method.
- Section 8.3 page 11 – Added to sealing and shaking sample.
- Section 9.3.1 page 12 – deleted re-analyze the CCV.
- Section 10.3.2 – deleted and reworded statement concerning replicate analysis of the ODOC/IDOC.
- Section 10.3.3 page 14 – deleted section.
- Section 10.5 – Method Detection Limit Study. Expanded upon definition of MDL’s.
- Section 10.9.1 and 10.9.2 page 16 – Laboratory Fortified Sample Matrix. Added percent recovery qualifications.
- Added Section 18.0 – Data assessment and acceptance criteria for Quality Control Measures.
- Section 6.24 - Updated columns used for analysis.

17.4 Revision 7 included updates to Sections 11.1.2 to 11.1.4 so that sample is allowed to hydrolyze for a minimum of an hour prior to extraction. Modified 11.3 to an example analytical sequence. Added LFSM criteria to the table in Section 10.9.
17.5  Revision 8 issued 3/9/15. Revisions included addition of section 10.11 (duplicate analysis) and updating section 11.2.2 (calibration frequency.)
### Section 18 - Data Assessment and Acceptance Criteria for Quality Control Measures

<table>
<thead>
<tr>
<th>SOP Reference</th>
<th>Requirement</th>
<th>Specification and Frequency</th>
<th>Acceptance Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>Section 9.2</td>
<td>Initial Calibration</td>
<td>Use internal standard calibration technique to generate an average RRF, first, or second order calibration curve.</td>
<td>When average response is used, the %RSD must be less than 20%. When first or second order regression is used, the correlation coefficient must be greater than 0.995. If criteria is not met corrective action is required such as injection port maintenance, new column, and/or recalibration.</td>
</tr>
</tbody>
</table>
| Section 9.3   | Continuing Calibration Check (CCal) | Verify initial calibration by analyzing a calibration standard at the beginning of each analytical day, prior to the analysis of sample batch. All compounds should be represented in this standard. | If Average response is used for the calibration then the response of the analyte should be ± 20% of the average response in the curve.  
1. If the recovery is below criteria, then the results for the analysis must be considered invalid.  
2. If the recovery is above criteria, and there are NO detections in the sample then the results can be reported with a qualifier, otherwise the results should be considered invalid. |
<table>
<thead>
<tr>
<th>Section</th>
<th>Laboratory</th>
<th>Frequency</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.8</td>
<td>Laboratory Fortified Blank (LFB)</td>
<td>Daily, or with each extraction batch or at a rate of 1 in 20 samples</td>
<td>Results of LFB analyses using mid-point fortifications should be within the Laboratories in-house true value for each analyte. 1. If the recovery is below method criteria. Then the results for that extraction batch should be considered invalid. 2. If the recovery is above criteria, and there are NO detections in the sample then the results can be reported with a qualifier, otherwise the results should be considered invalid.</td>
</tr>
<tr>
<td>10.9</td>
<td>Laboratory Fortified Sample matrix</td>
<td>Daily, or at a frequency or 10 percent of samples.</td>
<td>If %Recovery is out of designated range, but laboratory performance for all other QC is acceptable, the recovery problem is judged to be matrix related. Label sample a &quot;suspect matrix&quot; but still report.</td>
</tr>
<tr>
<td>Section 10.2</td>
<td>Laboratory Reagent Blank / Method Blank (LRB)</td>
<td>Daily with each extraction batch or 5% of field samples</td>
<td>Demonstrate that all target analytes are below the PQL, and confirm that possible interferences do not prevent quantification of method. If an analyte of interest is detected in the LRB at or above the reporting limit, samples that have results below the reporting limit can be reported with qualification. See section 10.2. If within the retention time window of any analyte of interest the LRB produces a peak that would prevent the determination of that analyte, determine the source of contamination and eliminate the interference before processing samples.</td>
</tr>
<tr>
<td>Section 9.4</td>
<td>Report Limit Check (RLC)</td>
<td>One RLC each analytical day that a new curve is not established.</td>
<td>The recoveries of the analytes should meet the criteria 50-150%. If the recovery is high and no target analytes are detected in the sample, then the results can be reported. If the recovery is low, then the system does not meet the required sensitivity and analysis cannot proceed until corrective action is taken to restore system sensitivity.</td>
</tr>
<tr>
<td>Section</td>
<td>Internal Standard (IS)</td>
<td>4, 4’-dibromo-octafluorobiphenyl (DBOB). Compare the IS area to the average IS area in the initial calibration and in the calibration check in the immediately preceding Calibration Check.</td>
<td>Peak area counts for the IS in LFBs, LRBs, and sample extracts must be within ± 30% of the average peak area calculated during the initial calibration or ± 30% from the most recent CCC. If the IS does not meet this criterion, corresponding target results are invalid.</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Section 10.4</td>
<td>Surrogate Standards</td>
<td>2, 4-Dichloro-phenylacetic acid (DCAA) is added to all calibration standards and samples, including QC samples. Calculate surrogate recovery.</td>
<td>Surrogate recovery must be within 70-130% of the true value for all aliquots (samples, Blanks, LFB/CCal, and FDs). 1. If the recovery is below criteria then the results for that sample should be considered invalid. 2. If the recovery is above criteria, and there are NO detections in the sample then the results can be reported with a qualifier, otherwise the results should be considered invalid.</td>
</tr>
<tr>
<td>Section 8.5</td>
<td>Sample Holding Time</td>
<td>14 days with appropriate preservation and storage.</td>
<td>Sample results are valid only if samples are extracted within sample hold time.</td>
</tr>
<tr>
<td>Section 8.6</td>
<td>Extract Holding Time</td>
<td>28 days with appropriate preservation and storage</td>
<td>Sample results are valid only if samples are analyzed within extract hold time.</td>
</tr>
</tbody>
</table>
APPENDIX

Table 3: Laboratory Performance Check Solution Criteria

<table>
<thead>
<tr>
<th>Test</th>
<th>Analyte</th>
<th>Conc. (µg/mL)</th>
<th>Requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitivity</td>
<td>Dinoseb</td>
<td>0.004</td>
<td>Detection of analyte; S/N &gt; 3</td>
</tr>
<tr>
<td>Chromatographic performance</td>
<td>4-Nitrophenol</td>
<td>1.6</td>
<td>0.70 &lt; PGF &lt; 1.05&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Column Performance</td>
<td>3,5 Dichlorobenzoic Acid</td>
<td>0.6</td>
<td>Resolution &gt; 0.40&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>4-Nitrophenol</td>
<td>1.6</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>PGF – Peak Guassian Factor. Calculated using the equation:

\[ \text{PGF} = \frac{1.83 \times W(1/2)}{W(1/10)} \]

Where: \( W(1/2) \) = Peak width at half height in seconds
\( W(1/10) \) = Peak width in seconds at 10<sup>th</sup> height

<sup>b</sup>Resolution between the two peaks as defined by the equation:

\[ R = \frac{t}{W} \]

Where: \( t \) = Difference in elution times between the two peaks
\( W \) = the average peak width, at the baseline, of the two peaks
Table 4: Laboratory Accuracy, Precision and Estimated Detection Limits (EDLS) for Analytes from Reagent Water and Synthetic Groundwater.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>EDL</th>
<th>Concentration</th>
<th>Reagent Water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ug/L</td>
<td>ug/L</td>
<td>R</td>
</tr>
<tr>
<td>2,4-D</td>
<td>0.2</td>
<td>1</td>
<td>131</td>
</tr>
<tr>
<td>Dalapon</td>
<td>1.3</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>Dicamba</td>
<td>0.081</td>
<td>0.4</td>
<td>135</td>
</tr>
<tr>
<td>Dinoseb</td>
<td>0.19</td>
<td>0.4</td>
<td>42</td>
</tr>
<tr>
<td>Pentachlorophenol (PCP)</td>
<td>0.076</td>
<td>0.04</td>
<td>130</td>
</tr>
<tr>
<td>Picloram</td>
<td>0.14</td>
<td>0.6</td>
<td>91</td>
</tr>
<tr>
<td>2,4,5-TP</td>
<td>0.075</td>
<td>0.2</td>
<td>134</td>
</tr>
</tbody>
</table>

EDL = estimated detection limit defined as the MDL (appendix B to 40 CFR Part 136-Definition and Procedure for the Determination of the Method Detection Limit). The concentration used to determine the EDL is not the same concentration presented in this table.

R = average percent recovery

S = standard deviation of the percent recovery