



STANDARD OPERATING PROCEDURES

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FIELD DETERMINATION OF CHLORINATED BENZENES IN PRODUCT SAMPLES BY GC/FID AT THE STANDARD CHLORINE-METACHEM SITE

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1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the method to be used for the on-site analysis of chlorinated benzenes (CBs) present in pure product and other matrices using gas chromatography (GC) with a flame ionization detector (FID). This method is applicable to the target analytes listed in Table 1, Appendix A. On-site field laboratories provide quick turnaround on critical data needed for field decisions concerning site characterization, treatability, separation, and remediation/removal activities. The sample preparation may be modified depending on the type of matrix.

2.0 METHOD SUMMARY

A weighed sample of product is dissolved in methylene chloride and mixed by inverting several times. An aliquot of the sample solution is spiked with an internal standard mix and injected into a GC/FID. Chlorinated benzenes are identified by their retention times and quantitated using their response factors.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

Samples are typically analyzed immediately upon receipt. In the event that samples cannot be analyzed immediately, samples must be diluted within 14 days and analyzed within 40 days. Sample dilutions should be stored at 4 ± 2 degrees Celsius ($^{\circ}\text{C}$) when not in use. All unused portions must be maintained in appropriate containers until disposal.

Samples, sample dilutions, and standards must be stored separately in an atmosphere free of all potential contaminants.

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

- Peaks having co-eluting retention times can interfere with this method.
- There may be down-time associated with electrical spikes/power outages due to thunderstorms in the site area.
- Improper cleaning or storage of glassware may cause interferences.
- Organic impurities in the carrier gas, the instrument, carryover from a previous sample, or solvents used may contribute to contamination.

5.0 EQUIPMENT/APPARATUS

- GC/FID, gas chromatograph with flame ionization detector, capable of temperature programming (Agilent Technologies 6890 GC equipped with Chemstation software or equivalent).
- Chromatographic column, capillary column, 30 meter (m) x 0.32 millimeter (mm) inner diameter (ID), 0.50 micron (μm) film thickness (Restek Inc. Rtx-5MS or equivalent).
- Balance, capable of weighing 0.1 gram (g) to the nearest 0.001g (Ohaus, Inc. or equivalent).



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- Hydrogen Generator, capable of producing ultra pure 99.999 - 99.9999 percent (%) dry hydrogen gas from deionized water and electricity (Parker Hannifin, Corp. or equivalent).
- Syringe, standard microliter (μL) volume syringes with cemented needles: 25, 100, 500, and 1000 μL (Hamilton, Inc. or equivalent).
- Liners, split/splitless low pressure drop liner with FS wool (Restek or equivalent).
- Refrigerators, explosion -proof for sample and standard storage (Lab-Line or equivalent).
- Hot plate, capable of heating samples up to 120°C (Thermolyne Corp. or equivalent).
- Glass vials with Teflon-lined crimp caps, 10 mL.
- GC autosampler glass vials with Teflon-lined crimp caps, 2 mL.
- Helium, ultra high purity 99.999% - 99.9999%, used as carrier gas and as purge gas in the thermal desorber.
- Air, ultra high purity, 99.999% - 99.9999%, used for FID fuel mix.

6.0 REAGENTS

- Calibration stock standard, neat chlorinated benzenes, ranging from 98- 100% (Aldrich or equivalent).
- Working calibration standards, prepared from the stock standard mix in methylene chloride, ranging from 10 to 1000 micrograms per milliliter ($\mu\text{g}/\text{mL}$).
- Time Reference Standard, 2-Chlorotoluene, neat material ranging from 98-100% (Aldrich or equivalent).
- Internal Standards (IS), 1-Chlorooctane and d_{10} -Phenanthrene, neat materials, ranging from 98-100% (Aldrich or equivalent).
- Stock Internal/Time Reference Standard Solution, containing 1-chlorooctane, d_{10} -phenanthrene, and 2-chlorotoluene, prepared at 2000 $\mu\text{g}/\text{mL}$ in methylene chloride from the neat substance. Spike 20 μL of this solution in all calibration standards and samples for a final concentration of 40 $\mu\text{g}/\text{mL}$.
- Dichloromethane, pesticide or GC grade, for standard preparation and sample extraction (Burdick & Jackson or equivalent).

7.0 PROCEDURES

7.1 Sample Preparation

Weigh approximately 0.1g ($\pm 0.001\text{g}$) of sample in a 10-mL glass vial. Dissolve the sample in 10 mL of methylene chloride and mix by inverting. An aliquot of this sample will be diluted 10 times prior to



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analysis. One milliliter of the sample solution is transferred to a GC autosampler vial and spiked with 20 μL of the working IS/time reference standard solution for analysis by GC/FID.

7.2 GC/FID Chromatographic Conditions

Typical operating conditions for analysis are as follows:

Initial Temperature:	50.0°C
Initial Time:	0.50 minutes (min.)
Ramp Rate 1:	8.0°C/min for 0.10 min.
Ramp Rate 2:	20.0°C/min for 1.00 min.
Ramp Rate 3:	20.0°C/min for 2.50 min.
Final Temperature:	240.0°C
Final Time:	0.50 min.
Post Temperature:	50.0°C
Post Time:	0.00 min.
Run Time:	23.98 min.
Injection Volume:	1 μL

7.3 Initial Calibration

Prior to any sample analysis, calibrate the GC/FID using target analytes typically consisting of five concentration levels (10, 50, 250, 500 and 1000 $\mu\text{g}/\text{mL}$). One of the calibration standards should be near the detection limit for the compounds of interest. Following analysis of all calibration points, a calibration report listing the average relative response factors (RRF_{ave}) and the percent relative standard deviation (%RSD) is generated. The %RSD must be less than or equal to (\leq)30% for each compound with 2 compounds up to 40%. A typical chromatogram for chlorinated benzenes can be found in Figure 1, Appendix B.

7.4 Continuing Calibration

For each 12-hour shift of analysis, the GC/FID calibration is checked before sample analysis using a daily standard at the 250 $\mu\text{g}/\text{mL}$ level. The continuing calibration is acceptable when the percent difference (%D) for each compound in the daily standard is plus or minus (\pm) 30% of the RRF_{ave} of the initial calibration curve. If any standard component varies more than $\pm 30\%$ of the RRF_{ave} , re-run the continuing calibration standard. If the re-injection does not meet the criterion, re-inject the five levels of the working calibration standard mix to generate a new initial calibration before analyzing samples.

7.5 Retention Time Windows

Typical retention times for the target analytes are listed in Table 1, Appendix A. The retention time window for each analyte is defined as ± 0.04 min. from the daily calibration standard.

8.0 CALCULATIONS

Concentrations of target compounds are calculated by the laboratory generated macros which uses the RF_{ave} , from



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the initial calibration. Calculate the relative response factor (RRF), RRF_{ave} , %RSD, and %D using the equations in Table 2, Appendix A. Input the sample information to calculate the chlorinated benzene concentrations in the sample. Refer to Figure 2, Appendix B.

9.0 QUALITY ASSURANCE/QUALITY CONTROL

The following quality assurance/quality control procedures apply:

- Initial Calibration - An acceptable five-point standard calibration must be run prior to sample analysis. A calibration range is acceptable if the %RSD \leq 30% for each compound with 2 compounds up to 40%.
- Continuing Calibration - A continuing calibration standard must be run for each 12-hour shift when analyzing samples. The %D must be within \pm 30%.
- Time Reference Standard - 2-Chlorotoluene is added to all standards and samples. The retention time must not drift more than \pm 0.04 min. from the latest 12-hour calibration check standard.
- Internal Standards - 1-Chlorooctane and d10-phenanthrene area responses must not vary by more than 50 - 200% between the sample and the most recent valid calibration check standard. The retention times must not drift more than \pm 0.04 min. from the latest 12-hour calibration check standard.
- All target analyte concentrations must be within linear range. Use the results of the initial analysis to determine the appropriate dilution factor (DF). The DF should bring the target compounds within the upper half of the initial calibration.

10.0 DATA VALIDATION

Analytical data will be reviewed by Scientific, Engineering, Response and Analytical Services (SERAS) field laboratory chemists prior to release according to the Quality Assurance/Quality Control considerations listed in Section 9.0.

11.0 HEALTH AND SAFETY

Field laboratory instrumentation and analytical methods must meet all relevant United States Environmental Protection Agency/Environmental Response Team (U.S. EPA/ERT), SERAS, and Occupational Safety and Health Administration (OSHA) regulations to ensure the safety of personnel working in the laboratory. All applicable U.S. EPA and U.S. Department of Transportation (DOT) regulations regarding handling, accumulation, storage and removal of hazardous wastes must be met. More specifically, refer to SERAS SOP #1501, *Hazardous Waste Management* and SERAS SOP #3013, *SERAS Laboratory Safety Program*.

12.0 REFERENCES

This section is not applicable to this SOP.

13.0 APPENDICES



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APPENDIX A
Tables
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TABLE 1. Method Target Analytes and Corresponding Internal Standards

<u>Compound</u>	<u>RT</u>	
Chlorobenzene	7.81	
Bromobenzene	9.51	
2-Chlorotoluene	9.89	(Time Reference Standard)
1,3-Dichlorobenzene	10.98	
1,4-Dichlorobenzene	11.11	
1,2-Dichlorobenzene	11.59	
1-Chlorooctane	11.83	(Quant. Internal Standard)
4-Bromochlorobenzene	12.86	
1,3,5-Trichlorobenzene	13.40	
1,2,4-Trichlorobenzene	14.11	
1,2,3-Trichlorobenzene	14.63	
1,2,4,5-Tetrachlorobenzene	15.97	
1,2,3,4-Tetrachlorobenzene	16.47	
Pentachlorobenzene	17.67	
Hexachlorobenzene	18.99	
d ₁₀ -Phenanthrene	19.41	(Quant. Internal Standard)

RT=Retention Time



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TABLE 2. Equations for Calculating RRF, RRF_{ave} , %RSD, and %D

$$RRF = \frac{(A_x)(C_{is})}{(A_{is})(C_x)}$$

where:

A_x = area of analyte X

A_{is} = area of internal standard

C_{is} = concentration of internal standard

C_x = concentration of analyte X

$$\%RSD = \frac{SD}{RRF_{ave}} \times 100$$

$$SD = \sqrt{\frac{\sum_{i=1}^n (RF_i - RRF_{ave})^2}{4}}$$

$$RRF_{ave} = \frac{RF_1 + \dots + RF_5}{5}$$