METHOD 8151

CHLORINATED HERBICIDES BY METHYLATION OR PENTAFLUOROBENZYLATION DERIVATIZATION: CAPILLARY COLUMN TECHNIQUE

1.0 SCOPE AND APPLICATION

1.1 Method 8151 is a capillary column gas chromatographic (GC) method for determining certain chlorinated acid herbicides in solid waste samples. Specifically, Method 8151 may be used to determine the following compounds:

Compound	CAS Registry Number[a]
2,4-D	94-75-7
2,4-DB	94-82-6
Dicamba	1918-00-9
Dichlorprop	120-36-5
Dinoseb	88-85-7
MCPA	94-74-6
MCPP	93-65-2
Silvex (2,4,5-TP)	93-72-1
2,4,5-T	93-76-5
Pentachlorophenol	87-86-5

[a]Chemical Abstract Services Registry Number.

add circled analytes on attached list & footnote

Because these compounds are produced and used in various forms (i.e. acid, salt, ester, etc.), Method 8151 includes a hydrolysis step to convert the herbicide to the acid form prior to analysis.

1.2 When Method 8151 is used to analyze unfamiliar samples, compound identifications should be supported by at least one additional qualitative technique. Step 8.3 provides gas chromtograph/mass spectrometer (GC/MS) criteria appropriate for the qualitative confirmation of compound definitions.

1.3 The estimated detection limits for each of the compounds in solid waste samples are listed in Table 1. The detection limits for a specific waste sample may differ from those listed, depending upon the nature of the interferences and the sample matrix.

1.4 Only experienced analysts should be allowed to work with diazomethane due to the potential hazards associated with its use (explosive, carcinogenic). Method 8151 is restricted to use by or under the supervision of analysts experienced in the use of gas chromatography and in the interpretation of gas chromatograms.

2.0 SUMMARY OF METHOD

2.1 Method 8151 provides extraction, esterification, and gas chromatographic conditions for the analysis of chlorinated acid herbicides in solid waste samples. Extraction is accomplished by escalation of the acidified sample with methylene chloride. The methylene chloride extract is washed with base to remove the free acid herbicides, and the remaining methylene chloride solution of esters is hydrolyzed using potassium hydroxide. Extraneous organic material is removed by a solvent wash. The free acid herbicides and hydrolyzed ester herbicides can be combined to give total herbicides or they can be analyzed separately. After acidification, the acids are extracted with methylene chloride and converted to their methyl esters using diazomethane or pentafluorobenzyl as the derivatizing agent. After excess reagent is removed, the esters are determined by gas chromatography with an electron capture detector (GC/EC). The results are reported as the acid equivalents.

2.2 The sensitivity of Method 8151 depends on the level of interferences in addition to instrumental limitations. Table 1 lists the GC/EC and GC/MS limits of detection that can be obtained in solid waste in the absence of interferences. Detection limits for a typical waste sample should be higher.

3.0 INTERFERENCES

3.1 Refer to Method 8000.

3.2 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts or elevated baselines in gas chromatograms. All these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by analyzing reagent blanks as described in Step 8.1.

3.2.1 Glassware must be scrupulously cleaned. Clean each piece of glassware as soon as possible after use by rinsing it with the last solvent used in it. This should be followed by detergent washing with hot water and rinses with tap water, then with distilled water. Glassware should be solvent-rinsed with acetone and pesticide-quality hexane. After rinsing and drying, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store glassware inverted or capped with aluminum foil. Immediately prior to use, glassware should be rinsed with the next solvent to be used.

3.2.2. The use of high purity reagents and solvents helps minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.3 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from waste to waste, depending upon the nature and diversity of the waste being sampled.

3.4 The sonication extraction must be optimized for each type of sample. It is suggested that tar-like samples be mixed with kaolin clay (Type P, Westwood Ceramic Supply, City of Industry, California or equivalent) to allow efficient extraction. Clay samples are extracted efficiently in the pH range 1 to 2.5 using 80 to 90 mL of buffer and ultrasonic power of 5 to 7.

3.5 Organic acids, especially chlorinated acids, cause the most direct interference with the determination. Phenols, including chlorophenols, may also interfere with this procedure.

3.6 Alkaline hydrolysis and subsequent extraction of the basic solution removes many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electronic capture analysis.

3.7 The herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware must be acid-rinsed and then rinsed to constant pH with water.

4.0 APPARATUS AND MATERIAL

4.1 Glassware

4.1.1 Beaker - 400-mL, thick walled.

4.1.2 Funnel - 75 mm diameter, 58°.

4.1.3 Separatory funnel - 500-mL, with Teflon stopcock.

4.1.4 Centrifuge bottle - 500-mL (Pyrex 1260 or equivalent).

4.2 Kuderna-Danish (K-D) apparatus

4.2.1 Concentrator tube - 10-mL graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.2.2 Evaporation flask - 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.2.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.2.4 Springs - 1/2-inch (Kontes K-662750 or equivalent).

4.3 Boiling chips - Solvent extracted with methylene chloride, approximately 10/40 mesh (silicon carbide or equivalent).

4.3 Diazald Kit - Recommended for the generation of diazomethane (Aldrich Chemical Co., Cat No. Z10, 025-0 or equivalent).

4.3.1 Assemble from two 20 mm x 150 mm test tubes, two Neoprene rubber stoppers, and a source of nitrogen. Use Neoprene rubber stoppers with holes drilled in them to accommodate glass delivery tubes. The exit

tube must be drawn to a point to bubble diazomethane through the sample extract. The generator assembly is shown in Figure 1. The procedure for use of this type of generator is given in Step 7.3.3.

4.4 Water bath - Heated, with concentric ring cover, capable of temperature control (± 2°C). The bath should be used in a hood.

4.5 Filter paper - 15 cm diameter (Whatman No. 1 or equivalent).

4.6 Balance - Analytical, capable of accurately weighing to the nearest 0.0001 g.

4.7 Pipet - Pasteur, glass, disposable (140 mm x 5 mm i.d.).

4.8 Centrifuge.

4.9 Sonabox - Recommended with disrupters for decreasing cavitation sound (Heat Systems - Ultrasonics, Inc., Model W375 or equivalent, with 20 KHz Ultrasonic Converter Model C3 or equivalent).

4.10 Capillary Columns

4.10.1 Column 1 - 30 m x 0.32 mm DB-5 (J & W Scientific, or equivalent) with 1 um film thickness. Used with diazomethane derivatization.

4.10.2 Column 1 - 30 m x 0.25 mm DB-5 (J & W Scientific or equivalent) with 25 um film thickness. Used with Pentafluorobenzylation derivatization.

4.10.3 Column 2 - 30 m x 0.25 mm SP-2550 (Supelco or equivalent) with 25 um film thickness. Used with Pentafluorobenzylation derivatization.

4.10.4 Column 3 - 30 m x 0.32 mm DB-5 (J & W Scientific or equivalent) with 1.0 um film thickness. Used with Pentafluorobenzylation derivatization.

4.11 Gas chromatograph - Analytical system complete with gas chromatograph suitable for Grob-type injection using capillary columns and all required accessories including syringes, capillary analytical column, gases, detector, and stripchart recorder. A data system for measuring peak areas and/or peak heights is recommended.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all inorganic reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified.

5.3 Sodium hydroxide solution (0.1N), NaOH. Dissolve 4 g NaOH in water and dilute to 1000 mL.

5.4 Potassium hydroxide solution (37% aqueous solution (w/v)), KOH. Dissolve 37 g potassium hydroxide pellets in water and dilute to 100 mL.

5.5 Phosphate buffer pH = 2.5 (0.1M). Dissolve 12 g sodium phosphate (NaH_2PO_4) in water and dilute to 1000 mL. Add phosphoric acid to adjust the pH to 2.5.

5.6 Methylene chloride, CH_2Cl_2. Pesticide quality or equivalent.

5.7 Acetone, CH_3COCH_3. Pesticide quality or equivalent.

5.8 Methanol, CH_3OH. Pesticide quality or equivalent.

5.9 Carbitol (diethylene glycol monoethyl ether), $C_2H_5OCH_2CH_2OCH_2CH_2OH$.

5.10 N-methyl-N-nitroso-p-toluenesulfonamide (Diazald). High purity, available from Aldrich Chemical Co or equivalent.

5.11 Silicic acid, $H_2Si_iO_5$. 100-mesh powder, store at 130°C.

5.12 Potassium carbonate, K_2CO_3.

5.13 2,3,4,5,6-Pentafluorobenzyl bromide (PFBBr), $C_6F_5CH_2Br$. Pesticide quality or equivalent.

5.14 Toluene, $C_6H_5CH_3$. Pesticide quality or equivalent.

5.15 Stock standard solutions (500 ng/uL) - Stock standard solutions may be prepared from pure standard materials or purchased as certified solutions.

5.15.1 Prepare stock standard solutions by accurately weighing 0.500 g of pure acid. Dissolve the material in pesticide quality acetone and dilute to volume in a 100-mL volumetric flask. If compound purity is certified at 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.15.2 Transfer the store stock standard solutions to bottles with Teflon lined screw-caps and store at 4°C protected from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially immediately prior to preparing calibration standards from them.

5.15.3 Stock standard solutions must be replaced after 1 year, or sooner, if comparison with check standards indicates a problem.

5.16 Calibration standards - Calibration standards at a minimum of five concentration levels for each parameter of interest should be prepared through dilution of the stock standards with diethyl ether. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner if comparison with check standrds indicates a problem.

5.17 Internal standards (if internal standard calibration is used) - To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. The standard 1,4-dichlorobenzene is suggested as one possibility.

5.17.1 Prepare calibration standards, at a minimum of five concentration levels for each parameter of interest as described in Step 5.16.

5.17.2 To each calibration standard, add a known constant amount of one or more internal standards and dilute to volume with diethyl ether.

5.17.3 Analyze each calibration standard according to Section 7.0.

5.18 Surrogate standards - The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and blank with one or two herbicide surrogates (e.g. herbicides that not expected to be present in the sample) recommended to encompass the range of the temperature program used in this method. Deuterated analogs of analytes should not be used as surrogates for gas chromatographic analysis due to coelution problems.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Step 4.1.

7.0 PROCEDURE

7.1 Sample preparation

7.1.1 Extraction

7.1.1.1 To a 400-mL, thick-wall beaker add 50 g (dry weight) of the well-mixed, moist solid sample. Acidify solids in each beaker with 85 mL of 0.1M phosphate buffer (pH = 2.5) and thoroughly mix the contents with a glass stirring rod.

7.1.1.2 Add 100 mL methylene chloride to the beaker and sonicate the sample for 3 minutes with output control knob set at 6.3

and in the pulsed mode at 50 percent duty cycle. Allow the solids to settle. Transfer the organic layer into a 500-mL centrifuge bottle.

7.1.1.3 Sonicate the sample twice more using 100 mL of methylene chloride and the same ultrasonic condition.

7.1.1.4 Combine the three organic extracts from the sample in the centrifuge bottle and centrifuge 10 minutes to settle the fine particles. Filter the combined extract through Whatman #1 filter paper into 500-mL separatory funnel.

7.1.2. Hydrolysis

7.1.2.1 Wash the organic extracts two times with 100-mL portions of 0.1N aqueous sodium hydroxide. Combine the aqueous layers containing the salts of the free acid herbicides in a beaker and save. The organic layer contains the herbicide esters, which must be hydrolyzed as follows:

7.1.2.2 Transfer the methylene chloride solution into a 500-mL Kuderna-Danish flask. Add boiling chips and attach the macro-Snyder column. Evaporate the methylene chloride on the water bath to a volume of approximately 25 mL. Remove the flasks from the water bath and allow them to cool.

7.1.2.3 Add 5 mL of 37% aqueous potassium hydroxide, 30 mL of water and 40 mL of methanol to the extract. Add additional boiling chips to the flask. Reflux the mixture on a 60-65°C water bath for 2 hours. Remove the flasks from the water bath and cool to room temperature.

7.1.3 At this point the basic solutions containing the herbicide salts obtained in Step 7.1.2.1 can be combined or they can be analyzed separately.

7.1.4 Solvent Cleanup

7.1.4.1 Adjust the pH of the basic aqueous extract to $\leq$ 1 with phosphoric acid.

7.1.4.2 Transfer the acidified aqueous solution to a 500-mL separatory funnel and extract the solution two times with 100 mL of methylene chloride.

7.1.4.3 Combine the organic extracts in a 500-mL Kuderna-Danish flask. Add boiling chips to the extract and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top. Place the apparatus on a hot water bath (15°-20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 15-20 minutes. At the

proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.1.4.4 Evaporate the extracts just to dryness under a stream of nitrogen.

7.1.4.5 Reconstitute with 1 mL of isooctane and 0.5 mL of methanol. Dilute to a volume of 4 mL with diethyl ether. The sample is now ready for methylation with diazomethane. If PFB is being performed, dilute with 4 mL acetone.

7.2 Esterification

7.2.1 For PFB derivatization refer to Step 7.2.4. For diazomethane derivatization continue with Step 7.2.1.1.

7.2.1.1 Two methods may be used for the generation of diazomethane: the bubbler method (see Figure 1) and the Diazald kit method. The bubbler method is suggested when small batches (10-15) of samples require esterfication. The bubbler method works well with samples that have low concentrations of herbicides (e.g. aqueous samples) and is safer to use than the Diazald kit procedure. The Diazald kit method is good for large quantities of samples needing esterification. The Diazald kit method is more effective than the bubbler method for soils or samples that may contain high concentrations of herbicides (e.g. samples such as soils that may result in yellow extracts following hydrolysis may be difficult to handle by the bubbler method). The diazomethane derivatization (U.S. EPA, 1971) procedures, described below, will react efficiently with all of the chlorinated herbicides described in this method and should be used only by experienced analysts, due to the potential hazards associated with its use. The following precautions should be taken:

CAUTION: Diazomethane is a carcinogen and can explode under certain conditions

- Use a safety screen
- Use mechanical pipetting aides.
- Do not heat above 90°C - EXPLOSION may result.
- Avoid grinding surfaces, ground-gas joints, sleeve bearings, and glass stirrers - EXPLOSION may result.
- Store away from alkali metals - EXPLOSION may result.
- Solutions of diazomethane decompose rapidly in the presence of solid materials such as copper powder, calcium chloride, and boiling chips.

7.2.2 Diazald kit method - Instructions for preparing diazomethane are provided with the generator kit.

7.2.2.1 Add 2 mL of diazomethane solution and let the sample stand for 10 minutes with occasional swirling. The yellow color of diazomethane should be evident and should persist for this period.

7.2.2.2 Rinse inside wall of ampule with 700 uL of diethyl ether. Reduce the sample to approximately 2 mL to remove excess diazomethane by allowing solvent to evaporate spontaneously at room temperature. Alternatively, 10 mg silicic acid can be added to destroy the excess diazomethane.

7.2.2.3 Dilute the sample to 10.0 mL using hexane. Analyze by gas chromatography.

7.2.3 Bubbler method - Assemble the diazomethane bubbler (see Figure 1).

7.2.3.1 Add 5 mL of diethyl ether to the first test tube. Add 1 mL of diethyl ether, 1 mL of caribtol, 1.5 mL of 37% KOH, and 0.1-0.2 g Diazald to the second test tube. Immediately place the exit tube into the concentrator tube containing the sample extract. Apply nitrogen flow (10 mL/min) to bubble diazomethane through the extract for 10 minutes or until the yellow color of diazomethane persists. The amount of Diazald used is sufficient for esterification of approximately three sample extracts. An adxditional 0.1-0.2 g of Daizald may be added (after the initial Diazald is consumed) to extend the generation of the diazomethane. There is sufficient KOH present in the original solution to perform a maximum of approximately 20 minutes of total esterification.

7.2.3.2 Remove the concentrator tube and seal it with a Neoprene or Teflon stopper. Store at room temperature in a hood for 20 minutes.

7.2.3.3 Destroy any unreacted diazomethane by adding 0.1-0.2 g silicic acid to the concentrator tube. Allow to stand until the evolution of nitrogen gas has stopped. Adjust the sample volume to 10.0 mL with hexane. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. It is recommended that the methylated extracts be analyzed immediately to minimize the trans-esterification and other potential reactions that may occur. Analyze by gas chromatography.

7.2.4 PFB Method

7.2.4.1 Add 30 uL of 10% K_2CO_3 and 200 uL of 3% PFBBr in acetone. Close tube with glass stopper and mix on vortex mixer. Heat tube in heater at 60°C for 3 hours.

7.2.4.2 Evaporate the solution to 0.5 mL with a gentle stream of nitrogen. Add 2 mL hexane and repeat evaporation just to dryness at ambient temperature.

7.2.4.3 Redissolve residue in 2 mL toulene:hexane (1:6) for column cleanup.

7.2.4.4 Top silica column with 0.5 cm hydrous sodium sulfate. Prewet column with 5 mL hexane and let the solvent drain to top of adsorbent. Quantitatively transfer reaction residue with several rinsings of toluene:hexane solution (total 2-3 mL).

7.2.4.5 Elute column with toluene:hexane to collect 8 mL. Discard this fraction which contains excess reagent.

7.2.4.6 Elute the column with toluene:hexane (1:9) to collect 8 mL containing PFB drivatives. Analyze by GC/EC.

7.3 Gas chromatography conditions (recommended)

7.3.1 GC/EC - Column temperature is set at 50°C for 1 minute, then programmed at 25°C/min to 100°C, and held for 1 minute, then programmed at 25°C/min to 100°C, held for 1 minute then programmed at 12°C/min to 220°C and held for 12 minutes. The retention times of each analyte are shown in Table 1.

7.4 Calibration - Refer to Method 8000 for proper calibration techniques. Use Table 1 for guidance on selecting the lowest point on the calibration curve.

7.4.1 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.5 Gas chromatographic analysis

7.5.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 uL of internal standard to the sample prior to injection.

7.5.2 Follow Step 7.6 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level standard after each group of 10 samples in the analysis sequence.

7.5.3 An example of a chromatogram for a methylated chlorophenoxy herbicide is shown in Figure 1.

7.5.4 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.5.5 Using either the internal or external calibration procedure (Steps 5.10 and 5.11 of Method 8000), determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes.

7.5.6 If calibration standards have been prepared and analyzed in the same manner as the samples (e.g. have undergone hydrolysis and

esterification), then the calculation of concentration given in Method 8000, Step 7.8 should be used. However, if calibration is performed using standards made from methyl ester compounds (compounds not esterified by application of this method), then the calculation of concentration must include a correction for the molecular weight of the methyl ester versus the acid herbicide.

7.5.7 If peak detection and identification are prevented due to interferences, further cleanup is required. Before using any cleanup procedure, the analyst must process a series of standards through the procedure to validate elution patterns and the absence of interferences from reagents.

8.0 QUALITY CONTROL

8.1 Chapter to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Procedures to check the GC system operation are found in Method 8000, Step 8.6.

8.2.1 Select a representative spike concentration for each compound (acid or ester) to be measured. Using stock methods, prepare a check standard concentrate in acetone 1,000 times more concentrated than the selected concentrations.

8.2.2 Table 2 indicates single operator accuracy and precision for this method. Compare the results obtained with the results given in Table 2 to determine if the data quality is acceptable.

8.3 Calculate surrogate standard recovery on all standards, samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000, Step 8.10).

8.3.1 If recovery is not within limits, the following procedures are required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

8.4 GC/MS confirmation

8.4.1 GC/MS techniques should be judiciously employed to support qualitative identifications made with this method. Refer to Method 8270 for the appropriate GC/MS operating conditions and analysis procedures.

8.4.2 When available, chemical ionization mass spectra may be employed to aid the qualitative identification process.

8.4.3 Should these MS procedures fail to provide satisfactory results, additional steps may be taken before reanalysis. These steps may include the use of alternate packed or capillary GC colums or additional cleanup.

9.0 METHOD PERFORMANCE

9.1 In a single laboratory, using clay/still bottom samples, the mean recoveries presented in Table 2 were obtained. The standard deviations of the percent recoveries of these measurements are also in Table 2.

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

3. Fed. Regist. 1971, 38, No. 75, Pt. II.

4. Goerlitz, D. G.; Lamar, W. L. "Determination of Phenoxy Acid Herbicides in Water by Electron Capture and Microcoulometric Gas Chromatography"; U.S. Geol. Survey Water Supply Paper 1967, 1817-C.

5. Burke, J. A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects"; J. Assoc. Off Anal. Chem. 1965, 48, 1037.

6. "Extraction and Cleanup Procedures for the Determination of Phenoxy Acid Herbicides in Sediment"; U.S. Environmental Protection Agency. EPA Toxicant and Analysis Center: Bay St. Louis, MS, 1972.

7. Shore, F.L.; Amick, E.N.; Pan, S. T. "Single Laboratory Validation of EPA Method 8150 for the Analysis of Chlorinated Herbicides in Hazardous Waste"; U.S. Environmental Protection Agency. Environmental Monitoring Systems Laboratory. Office of Research and Development, Las Vegas, NV, 1985; EPA-600/4-85-060.

TABLE 1.
CHROMATOGRAPHIC CONDITIONS[a] AND ESTIMATED DETECTION LIMITS
FOR METHOD 8151 USING DIAZOMETHANE DERIVATIZATION

Analyte	Retention Time (minutes)	GC/EC Estimated Detection Limit[b] (ng/g)	GC/MS Estimated Identification Limit[c] (ng)
Dicamba	13.47	0.12	0.5
MCPP	13.77	66	0.40
MCPA	13.96	43	0.3
Dichlorprop	14.51	0.38	0.65
2,4-D	14.76	0.34	0.44
Silvex	16.33	0.11	1.25
2,4,5-T	16.72	0.16	1.3
2,4-DB	17.82	4.0	1.7
Dinoseb	18.00	0.28	4.5

[a] Gas chromatography conditions:
GC/EC - DB-5 capillary column, 0.25 um film thickness, 0.25 um i.d. x 30 m long. Grob-type 30-second splitless injection. Column temperature, programmed: Initial 50°C for 1 minute, program 25°C/min to 100°C, hold for 1 minute, program 12°C/min to 220°C, hold for 12 minutes.

GC/MS - DB-5 capillary column, 1.0 um film thickness, 0.23 um i.d. x 30 m long. Grob-type 30-second splitless injection. Column temperature programmed: Initial 60°C for 2 minutes, program 13°C/min to 220°C, hold for 10 minutes.

[b] Detection limits determined from standard solutions corrected back to 50 g samples, extracted and concentrated to 10 mL with 5 uL injected.

[c] The minimum amount of analyte to give a Finnigan INCOS FIT value of 800 as the methyl derivative vs. the spectrum obtained from 50 ng of the respective free acid herbicide.

TABLE 2.
ACCURACY AND PRECISION FOR METHOD 8151
USING DIAZOMETHANE DERIVATIZATION

Analyte	Mean[a] Percent Recovery	Linear[b] Concentration Range (ng/g)	Percent Relative[c] Standard Deviation (n=20)
Dicamba	95.7	0.52- 104	7.5
MCPP	98.3	620 -61,800	3.4
MCPA	96.9	620 -61,200	5.3
Dichlorprop	97.3	1.5 - 3,000	5.0
2,4-D	84.3	1.2 - 2,440	5.3
Silvex	94.5	0.42 - 828	5.7
2,4,5-T	83.1	0.42 - 828	7.3
2,4-DB	90.7	4.0 -8,060	7.6
Dinoseb	93.7	0.82 -1,620	8.7

[a] Mean percent recovery calculated from 10 determinations of spiked clay and clay/still bottom samples over the linear concentration range.

[b] Linear concentration range was determined on standard solutions and corrected to 50 g solid samples.

[c] Percent relative standard deviation was calculated on standard solutions, 10 samples high in the linear concentration range, and 10 samples low in the range.

TABLE 3.
RETENTION TIMES (MINUTES) OF HERBICIDE-
PFB DERIVATIVES

Herbicide	Gas chromatography column		
	Thin-film DB-5[a]	SP-2250[b]	Thick-film DB-5[c]
Dalapon	10.41	12.94	13.54
MCPP	18.22	22.30	22.98
Dicamba	18.73	23.57	23.94
MCPA	18.88	23.95	24.18
Dichlorprop	19.10	24.10	24.70
2,4-D	19.84	26.33	26.20
Silvex	21.00	27.90	29.02
2,4,5-T	22.03	31.45	31.36
Dinoseb	22.11	28.93	31.57
2,4-DB	23.85	35.61	35.97

[a] DB-5 capillary column, 0.25 um film thickness, 0.25 mm i.d. x 30 m long. Column temperature, programmed: Initial 70°C for 1 minute, program 10°C/min to 240°C, hold for 17 minutes.

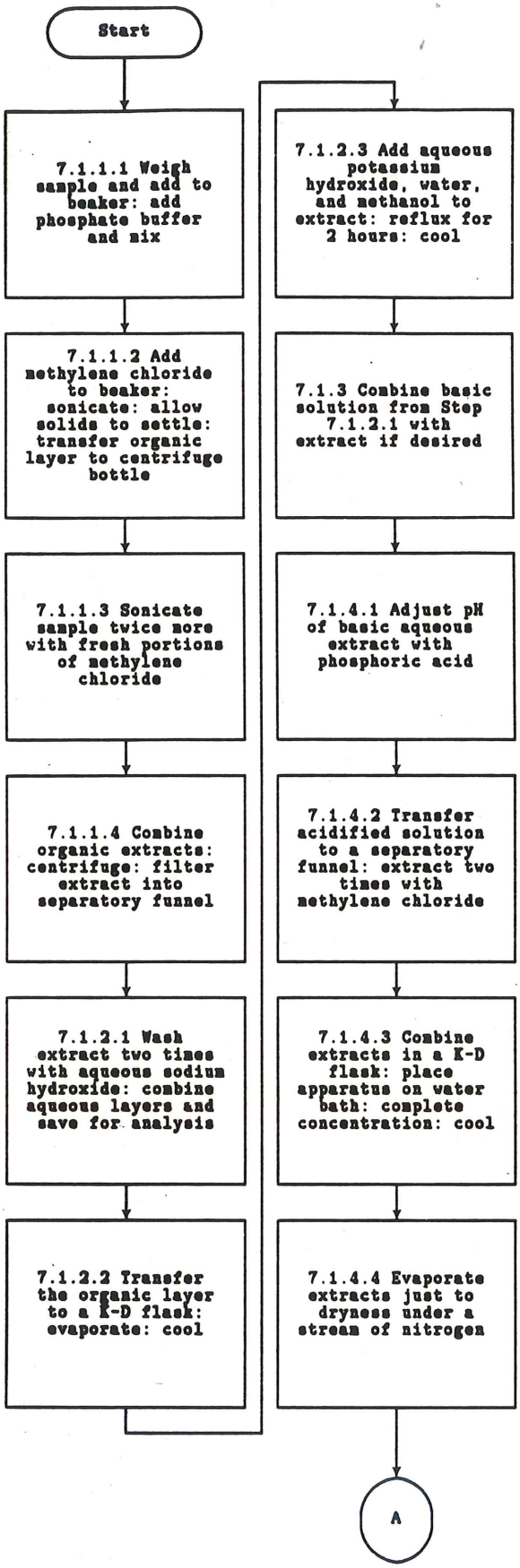
[b] SP-2550 capillary column, 0.25 um film thickness, 0.25 mm i.d. x 30 m long. Column temperature, programmed: 70°C for 1 minute, program 10°C/min to 240°C, hold for 10 minutes.

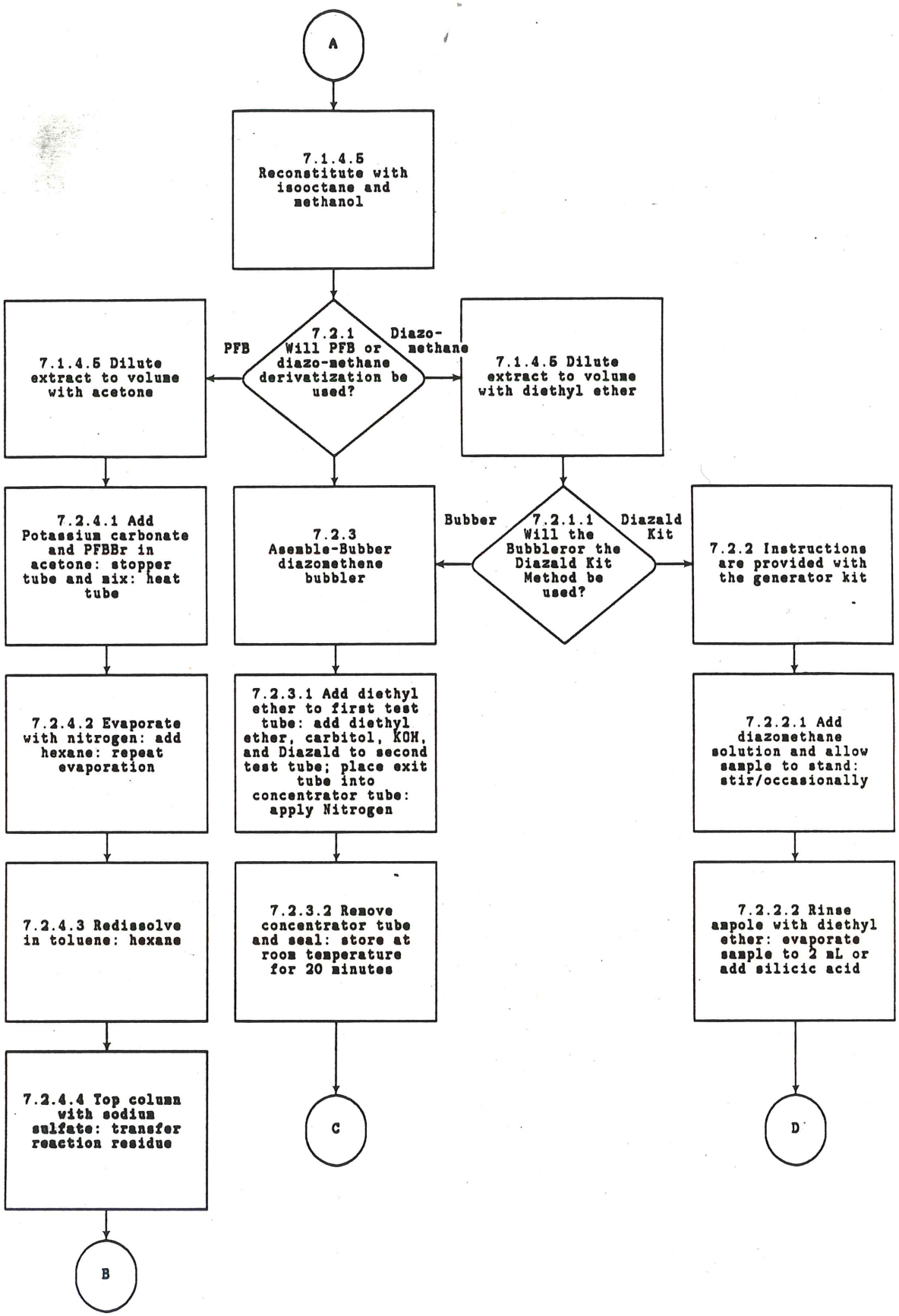
[c] DB-5 capillary column, 1.0 um film thickness, 0.32 mm i.d. x 30 m long. Column temperature, programmed: 70°C for 1 minute, program 10°C/min to 240°C, hold for 10 minutes.

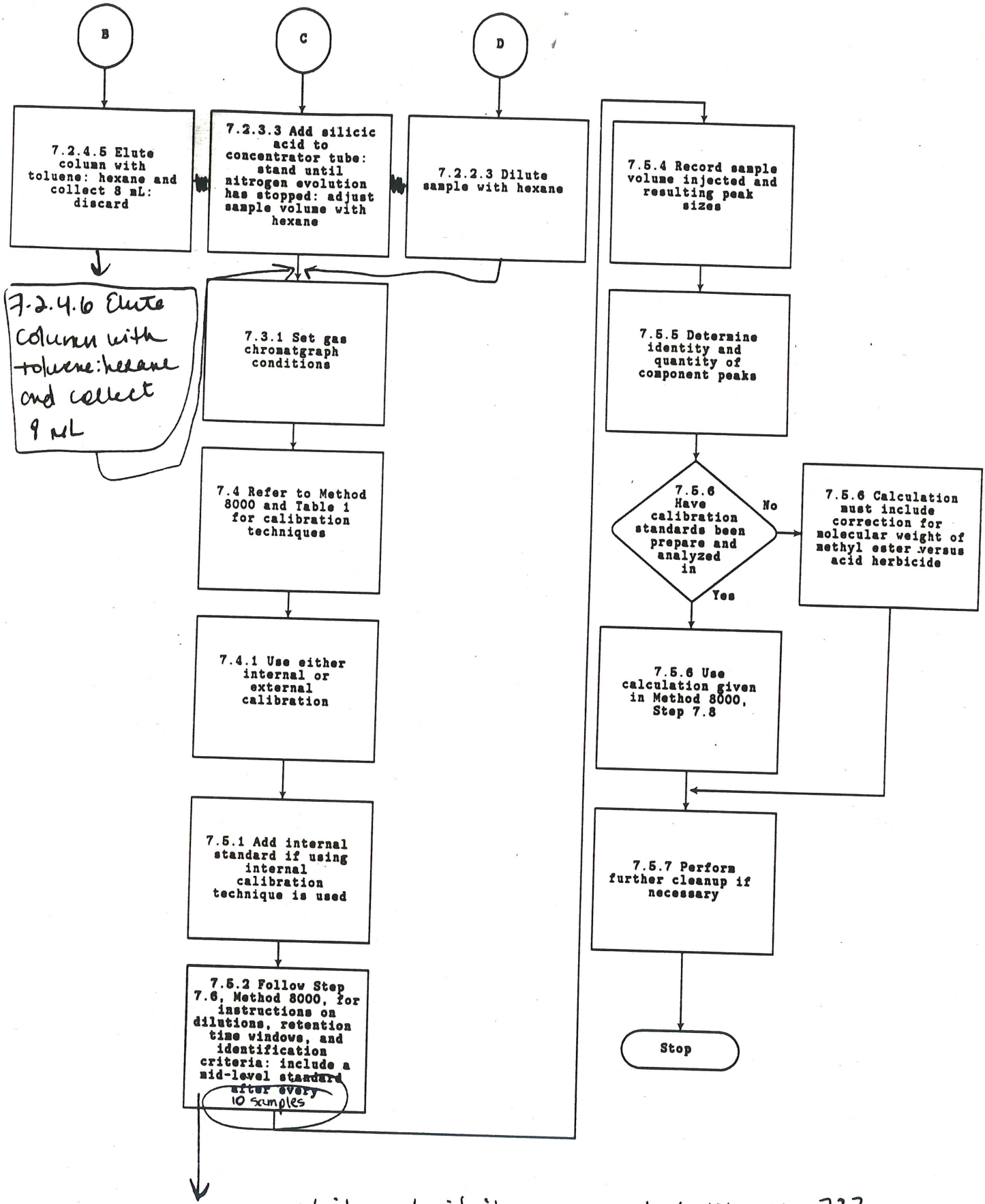
TABLE 4.
RELATIVE RECOVERIES OF PFB HERBICIDES

Analyte	Std. concn, ug/mL	Relative recoveries, % 1	2	3	4	5	6	7	8	Mean
MCPP	5.1	95.6	88.8	97.1	100	95.5	97.2	98.1	98.2	96.3
Dicamba	3.9	91.4	99.2	100	92.7	84.0	93.0	91.1	90.1	92.7
MCPA	10.1	89.6	79.7	87.0	100	89.5	84.9	92.3	98.6	90.2
Dichlorprop	6.0	88.4	80.3	89.5	100	85.2	87.9	84.5	90.5	88.3
2,4-D	9.8	55.6	90.3	100	65.9	58.3	61.6	60.8	67.6	70.0
Silvex	10.4	95.3	85.8	91.5	100	91.3	95.0	91.1	96.0	93.3
2,4,5-T	12.8	78.7	65.6	69.2	100	81.6	90.1	84.3	98.5	83.5
2,4-DB	20.1	99.8	96.3	100	88.4	97.1	92.4	94.2	91.6	95.0
Mean		86.8	85.7	91.8	93.4	85.3	89.0	87.1	91.4	

METHOD 8151
CHLORINATED HERBICIDES BY METHYLATION OR PENTAFLUORBENZYLATION DERIVATIZATION: CAPILLARY COLUMN TECHNIQUE


Start
7.1.1.1 Weigh sample and add to beaker: add phosphate buffer and mix
7.1.1.2 Add methylene chloride to beaker: sonicate: allow solids to settle: transfer organic layer to centrifuge bottle
7.1.1.3 Sonicate sample twice more with fresh portions of methylene chloride
7.1.1.4 Combine organic extracts: centrifuge: filter extract into separatory funnel
7.1.2.1 Wash extract two times with aqueous sodium hydroxide: combine aqueous layers and save for analysis
7.1.2.2 Transfer the organic layer to a K-D flask: evaporate: cool
7.1.2.3 Add aqueous potassium hydroxide, water, and methanol to extract: reflux for 2 hours: cool
7.1.3 Combine basic solution from Step 7.1.2.1 with extract if desired
7.1.4.1 Adjust pH of basic aqueous extract with phosphoric acid
7.1.4.2 Transfer acidified solution to a separatory funnel: extract two times with methylene chloride
7.1.4.3 Combine extracts in a K-D flask: place apparatus on water bath: complete concentration: cool
7.1.4.4 Evaporate extracts just to dryness under a stream of nitrogen
A


A
7.1.4.5 Reconstitute with isooctane and methanol
7.2.1 Will PFB or diazo-methane derivatization be used?
PFB
Diazo-methane
7.1.4.5 Dilute extract to volume with acetone
7.1.4.5 Dilute extract to volume with diethyl ether
7.2.4.1 Add Potassium carbonate and PFBBr in acetone: stopper tube and mix: heat tube
7.2.3 Asemble-Bubber diazomethene bubbler
Bubber
7.2.1.1 Will the Bubbleror the Diazald Kit Method be used?
Diazald Kit
7.2.2 Instructions are provided with the generator kit
7.2.4.2 Evaporate with nitrogen: add hexane: repeat evaporation
7.2.3.1 Add diethyl ether to first test tube: add diethyl ether, carbitol, KOH, and Diazald to second test tube; place exit tube into concentrator tube: apply Nitrogen
7.2.2.1 Add diazomethane solution and allow sample to stand: stir/occasionally
7.2.4.3 Redissolve in toluene: hexane
7.2.3.2 Remove concentrator tube and seal: store at room temperature for 20 minutes
7.2.2.2 Rinse ampole with diethyl ether: evaporate sample to 2 mL or add silicic acid
7.2.4.4 Top column with sodium sulfate: transfer reaction residue
B
C
D



Suzy: would it work if it was worded like this???

Follow step 7.6, Method 8000. for dilution, retention time window, and identification criteria procedures: include a mid-level standard every 10 samples.