METHOD 5031

VOLATILE, NONPURGEABLE, WATER-SOLUBLE COMPOUNDS BY AZEOTROPIC DISTILLATION

1.0 SCOPE AND APPLICATION

1.1 This method describes a procedure for separation of nonpurgeable, water-soluble, and volatile organic compounds in aqueous samples or leachates from solid matrices using azeotropic distillation. The appropriate gas chromatographic/mass spectrometric (GC/MS) determinative steps are found in Method 8260. The appropriate gas chromatographic/flame ionization (GC/FID) determinative steps are found in Method 8015. This separation method should be used as an alternative to Method 5030 for compounds that are difficult to purge and trap. Method 5031 is useful in the determination of the following compounds:

Compound Name	CAS No.[a]
Acetone	67-64-1
Acetonitrile	75-05-8
Acrylonitrile	107-13-1
Allyl alcohol	107-18-6
1-Butanol	104-51-8
t-Butyl alcohol	75-65-0
Crotonaldehyde	123-73-9
1,4-Dioxane	123-91-1
Ethanol	64-17-5
Ethyl Acetate	141-78-6
Ethylene oxide	75-21-8
Isobutyl alcohol	78-83-1
Methanol	67-56-1
Methyl ethyl ketone	78-93-3
Methyl isobutyl ketone	108-10-1
N-Nitroso-di-n-butylamine	924-16-3
Paraldehyde	123-63-7
2-Pentanone	107-87-9
2-Picoline	109-06-8
1-Propanol	71-23-8
2-Propanol	67-63-0
Propionitrile	107-12-0
Pyridine	110-86-1
o-Toluidine	95-53-4

[a] Chemical Abstract Service Registry Number

1.2 Additional compounds may be separated successfully using this method. However, use of this method to detect and measure additional analytes may be done only after the laboratory obtains acceptable accuracy and precision data for each additional analyte. In general, compounds that form a water azeotrope that is greater than 50% analyte, with this azeotrope boiling at less than

100°C, can be successfully distilled. The initial study (Reference 5) to determine the ability of this method to separate compounds found that the following compounds perform poorly in this method:

Compound	CAS No.	Compound	CAS No.
Acrolein	107-02-8	Methacrylonitrile	126-98-7
Aniline	62-53-3	Phenol	108-95-2
Dimethylformamide	68-12-2	Propargyl alcohol	107-19-7
2-Ethoxyethanol	110-80-5		

1.3 The method detection limits (MDLs) and analyte concentration ranges are listed in the appropriate determinative methods. The MDL for a sample may differ from those listed, depending on the nature of interferences in the sample matrix.

1.4 This method is restricted to use by or under the supervision of analysts experienced in procedures involving quantitative separation techniques. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 An azeotrope is a liquid mixture of two or more substances which behaves like a single substance, in that it boils at a constant temperature and the vapors released have a constant composition. Azeotropic distillation is a technique which uses the ability of selected organic compounds to form binary azeotropes with water to facilitate the separation of the compounds from a complex matrix.

2.2 Macrodistillation technique: One liter of the sample is buffered to pH 7, spiked with the surrogate spiking solution, and brought to boiling in a 2 L distillation flask. The polar, volatile organic compounds (VOCs) distill into the distillate chamber for 1 hour, and are retained there (Figure 1). The condensate overflows back into the pot and contacts the rising steam. The VOCs are stripped by the steam and are recycled back into the distillate chamber. Analytes are detected and quantitated by either direct aqueous injection GC/MS or GC/FID.

2.3 Microdistillation technique: An aliquot (normally 5 g or 40 mL) of sample is azeotropically distilled, and the first 100 µL to 300 µL of distillate are collected. The water soluble volatile organic compounds are concentrated into the distillate using a microdistillation system. Most semi- and non-volatile interferences remain in the boiling flask. Use of an internal standard is recommended to improve method precision. Concentration factors are typically one and two orders of magnitude for soil and water matrices, respectively. The distillation takes five to six minutes. Analytes are detected and quantitated by either direct aqueous injection GC/MS or GC/FID.

3.0 INTERFERENCES

3.1 Method interference may be caused by contaminants in solvents, reagents, glassware and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory method blanks.

3.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with methanol, followed by a distilled water rinse and drying in a

105°C oven between analyses. Detergent solutions may also be used, but care must be taken to remove the detergent residue from the glassware. After drying and cooling, glassware should be stored in a clean environment to prevent any accumulation of dust or other contaminants. Other approaches to cleaning glassware may also be employed, provided that the laboratory can demonstrate that they are effective in removing contaminants.

3.1.2 Interfering contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations. One or more blanks should be run to check for cross-contamination.

3.1.3 After analysis of a sample containing high concentrations of volatile organic compounds, one or more blanks should be analyzed to check for cross contamination.

3.2 Matrix interferences may be caused by contaminants that are in the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the matrix being sampled. If significant interferences occur in subsequent samples, additional cleanup may be necessary.

4.0 APPARATUS AND MATERIALS

4.1 Macrodistillation System

4.1.1 Round bottom flask - 2-L, 14/20 ground-glass joint.

4.1.2 Vigreux column - 20 cm long, 14/20 ground-glass joint.

4.1.3 Modified Nielson-Kryger apparatus (Figure 1) - This glassware can be made by a glassblower, or a similar apparatus can be purchased and then modified by a glassblower according to the dimensions given in Figure 1.

4.1.4 Recirculating, submersible pumps - One for each distillation apparatus. Alternatively, a water chiller may be used in place of a recirculating submersible pump, with ice water, if the chiller can maintain a temperature of 0°C to 5°C in all distillation condensers.

4.1.5 Five-gallon container - Preferably insulated, holds ice water to maintain condenser temperature.

4.1.6 Volumetric glassware - 10-mL class A volumetric flasks and volumetric pipets of various sizes, 1 to 3 mL.

4.1.7 Sample/standard vials - 4-dram glass, with polytetrafluoroethylene (PTFE)-lined screw cap or crimp top vials.

4.1.8 pH Paper - narrow range (6.0-8.0).

4.2 Microdistillation System

4.2.1 Wadsworth MicroVOC System - Shamrock Glass, or equivalent.

4.2.1.1 Round bottom flask - 100-mL, 14/20 ground-glass joint.

4.2.1.2 Fractionation column - 14/20 ground-glass joint, 1.6 cm OD, 1.3 cm ID, 60 cm length (see Figure 2).

4.2.1.3 Pipe insulation - polyurethane foam, 1.5 inch OD, 0.5 inch ID, 55 cm in length.

4.2.1.4 Glass beads, 5 mm OD.

4.2.1.5 Keck clamps for 14/20 ground-glass joint.

4.2.1.6 Glass reducing union - 14/20 ground-glass joint to 6 mm OD tube (see Figure 3).

4.2.1.7 Stainless steel reducing union - 1/16 inch to 1/4 inch.

4.2.1.8 Air condenser - PTFE tubing, 1/16 inch OD to 1/32 inch ID (40 cm in length, or equivalent).

4.2.2 Support stand with rod - 1 meter.

4.2.3 Three-finger clamps.

4.2.4 Heating mantle - Glas-Col, 115 volts, 230 watts, STM 400, or equivalent.

4.2.5 Temperature controller - Glas-Col PL-115-Cordtrol, 115 volts, 600 watts, or equivalent.

4.2.6 Porous carbon boiling chips - VWR Catalog No. 26397-409, or equivalent.

4.2.7 Autosampler vials - glass, with PTFE-lined screw cap or top vials.

4.2.8 Autosampler vial inserts, 100-µL - The vial may be calibrated by dispensing a known volume of liquid into it, and marking the side of the vial.

4.3 Balance - Analytical, capable of weighing 0.0001 g.

4.4 Microsyringes - Various sizes.

5.0 REAGENTS

5.1 Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all 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 Organic-free Reagent Water - All references to water in this method refer to organic-free reagent water as defined in Chapter One.

5.3 Potassium phosphate, monobasic, KH_2PO_4 (macrodistillation technique).

5.4 Sodium phosphate, dibasic, Na_2HPO_4 (macrodistillation technique).

5.5 Sodium chloride, NaCl (macrodistillation technique).

5.6 Stock Standard Solutions - Prepared from pure standard materials or from purchased certified solutions.

5.6.1 Prepare, in organic-free reagent water, a set of stock standard solutions each containing one of the target analytes. Place about 9.0 mL of organic-free reagent water in a 10 mL tared, ground-glass stoppered volumetric flask. Weigh the flask to the interest 0.0001 g. Add the assayed reference material, as described below:

5.6.1.1 Liquids - Using a 100-µL syringe, immediately add two or more drops of assayed reference material to the flask using the known density as an approximate guide to place 0.100 g in the flask. The liquid must fall directly into the water without contacting the neck of the flask.

5.6.1.2 Solids - Add enough material to achieve approximately 0.100 g in the flask.

NOTE: The solubility of N-nitroso-di-n-butylamine in water is approximately 1000 mg/L. All other stock solutions should be 10,000 mg/L.

5.6.2 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 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.

5.6.3 Transfer the stock standard solution into a PTFE-sealed screw cap bottle. Store, with minimal headspace, at 4°C, and protect from light.

5.6.4 Prepare fresh stock standard every month. Reactive compounds, such as acrylonitrile and N-nitroso-di-n-butylamine, may need to be prepared more frequently. Standards must be monitored closely. See individual determinative methods for calibration requirements.

5.7 Secondary dilution standards - Using stock standard solutions, prepare secondary dilution standards, in organic-free reagent water, containing the compounds of interest, either singly or mixed together. Secondary dilution standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Store in a vial with minimal headspace in a refrigerator free of organic solvents. Standards should be monitored frequently and replaced when comparisons to independent check standards indicate a change of greater than 20%.

5.8 Stock Surrogate Solutions and Surrogate Spiking Solution

5.8.1 GC/MS Surrogates - Recommended surrogates for GC/MS analysis (Method 8260) include d_6-acetone, d_3-acetonitrile, d_3-methanol, d_5-pyridine, d_8-1,4-dioxane, and d_5-phenol. Although not all the analytes will have corresponding surrogates readily available, their use allows very accurate quantitation by isotope dilution methods. The stock surrogate

solutions should be prepared as in Sec. 5.6, and a surrogate spiking solution should be prepared from the stocks at a concentration so that addition of 50 µL of the spiking solution to the sample will produce a sample distillate with a concentration in the middle of the instrument calibration range, nominally 1000 mg/L. Each sample undergoing GC/MS analysis must be spiked with the spiking solution prior to distillation (nominal 50 µg added to the sample).

5.8.2 GC/FID Surrogates - Fluorinated alcohols and ketones may be used as surrogates when GC/FID analysis (Method 8015) is used, provided that the surrogates do not coelute with the target analytes. No single surrogate can be recommended, at present, when every compound listed in Sec. 1.1 is included in the analyte list. Nominally 50 µg of each fluorinated surrogate should be added to each sample prior to distillation.

NOTE: For small volume samples, the use of a spike volume greater than 200 µL may excessively dilute the sample and reduce analyte recovery.

5.9 Internal standards

5.9.1 GC/MS Internal Standards - The recommended internal standards when using GC/MS analysis (Method 8260) are d_{14}-diglyme (diethylene glycol dimethyl ether), d_6-isopropyl alcohol, d_7-dimethyl formamide, and d_5-benzyl alcohol. Other compounds may be used as internal standards provided they exhibit similar retention times to the compounds being detected. Care should be taken to avoid using compounds in which active hydrogens are deuterium labeled, as isotopic exchange would be expected in an aqueous matrix. The concentration of the secondary dilution standard and the spiking volume added to each distillate after distillation and just before GC/MS analysis should be consistent with the choice of a determinative method.

5.9.2 GC/FID Internal Standards - Halogenated alcohols, ketones, and nitriles may be used as internal standards when GC/FID analysis (Method 8015) is used. The recommended internal standards are hexafluoro-2-propanol, hexafluoro-2-methyl-2-propanol, and 2-chloroacetonitrile, however, these compounds may not be appropriate for all matrices. Nominally, 5 to 50 µg of each internal standard should be added to each sample prior to distillation. The total spike volume should be less than 1 mL to avoid excessive dilution of the sample and lower analyte recovery. However, the concentration of the secondary dilution standard and the spiking volume added to each prior to distillation should be consistent with the choice of a determinative method. Ethanol or other alcohols may be used as internal standards, provided that they are neither target analytes nor present in the sample.

5.10 Calibration standards

5.10.1 Prepare calibration standards using the recommended analyte, surrogate, and internal standard concentrations as specified in the appropriate determinative method (Methods 8015 or 8260). All calibration standards should be distilled by the same procedure as the samples for the microdistillation procedure.

5.11 All standards should be stored at 4°C in PTFE-lined, screw-capped vials with minimal headspace.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

NOTE: At this time, the effect of reducing agents or preservatives on method performance has not been evaluated. Preservation of samples is difficult because almost all preservatives could potentially interfere with the analysis. Storage at 4°C appears to be the best way to preserve most samples until analysis.

6.2 Samples should be analyzed within the designated holding time initiated at sample collection.

6.3 The distillate should be stored in a tightly sealed vial at 4°C in a refrigerator free of organic solvents. It is recommended that the distillate be analyzed within 24 hours of distillation. Distillates must be analyzed within 7 days of distillation.

7.0 PROCEDURE

7.1 Macrodistillation procedure

7.1.1 Set up the azeotropic distillation apparatus as shown in Figure 1. Fill the 5-gallon insulated container with ice and water, or connect the condenser to a chiller. It is very important to maintain a temperature of 0°C to 5°C in the condensers.

7.1.2 Measure a 1-L aliquot of sample with a 1000-mL graduated cylinder, and transfer it to a 1-L Erlenmeyer flask. Add 3.40 g KH_2PO_4, and 3.55 g Na_2HPO_4, and slowly stir with a stir bar and stir plate until dissolved. Check the pH with narrow range pH paper. The pH of the sample should be between 6.8 and 7.0. Add more Na_2HPO_4 if too acidic, or more KH_2PO_4 if too basic.

7.1.3 Transfer the buffered sample to a 2-L round-bottomed flask. Add 250 g of NaCl. Addition of salt has been shown to increase method efficiency for some of the compounds.

7.1.4 Spike the sample with 50 µL of the surrogate spiking solution (See Sec. 5.8).

7.1.5 Attach the Vigreux column to the flask and then the condenser.

7.1.6 Turn on the circulating pumps or chiller and heating mantles. After boiling has begun, the heating mantle voltage can be reduced approximately 10% to 15% to maintain an even boiling.

7.1.7 30 min after boiling begins, use a 5-mL syringe to remove the distillate from the reservoir and place it into a preweighed PTFE-lined screw cap vial. Take a second sample after an additional 30 minutes have elapsed and combine it with the first sample. Determine the weight of the distillate.

7.1.8 Add an amount of internal standard spiking solution so that the distillate will have a concentration of 10 mg/L. (For example, a 6-mL distillate would need 60 µg of internal standard). Mix well and store at 4°C until analysis.

7.2 Microdistillation procedure

7.2.1 Aqueous samples

7.2.1.1 Add 40 mL of the well-mixed sample to a 100-mL round-bottom flask. The sample volume should be the same volume used for the calibration standards. A smaller volume may be used if sample volume is limited, but the concentration factor will be reduced accordingly. If a smaller volume of sample is used, the analyst should add organic-free reagent water to the sample to make the volume approximately the same as that used for the standards and other samples.

Add approximately 0.14 g KH_2PO_4 and 0.14 g Na_2HPO_4, and slowly stir or swirl the sample until these buffering agents dissolve. Check the pH with narrow range pH paper. The pH of the sample should be between 6.8 and 7.0. Add more Na_2HPO_4 if too acidic, or more KH_2PO_4 if too basic.

7.2.1.2 Add appropriate volumes of the surrogate standards, internal standards and matrix spiking solutions.

7.2.1.3 Add 5 to 10 boiling chips to the flask, and place the flask in the heating mantle.

7.2.2 Solid samples

7.2.2.1 Add 5 g of sample to a 100-mL round bottom flask.

7.2.2.2 Add appropriate volumes of the surrogate standards, internal standards, and matrix spiking solutions.

7.2.2.3 Add 40 mL of organic-free reagent water to the flask, and place the flask in the heating mantle.

7.2.3 Assemble the micro distillation system (see Figure 4).

7.2.3.1 Attach the air condenser to the stainless steel reducing union (see Figure 3). The air condenser and reducing unions must be completely dry to avoid diluting or contaminating the distillate.

7.2.3.2 Fill the fractionation column with glass beads. The fractionation column and glass beads must be completely dry.

7.2.3.3 Insulate the column with polyurethane foam. Attach the fractionation column to the 100-mL round bottom flask. Adjust a three finger clamp to hold the column upright.

7.2.3.4 Attach the reducing union assembly to the top of the fractionation column, and hold in place with a Keck or three-finger clamp.

7.2.3.5 Place the free end of the air condenser into the collection vial.

7.2.4 Heat the sample at a rate sufficient to bring it to a boil in 2-4 minutes for water samples, and 3-5 minutes for solid samples. Using the heating mantle assembly described in Sec. 4.2.4, these rates correspond to settings of 75% and 60% on the rheostat, respectively.

7.2.5 Collect the first 100 to 300 µL of distillate in a calibrated microvial.

7.2.5.1 Some bubbles may be present in the condenser. This may make collecting exactly 100 µL difficult, but acceptable results can be obtained with practice.

NOTE: Once steam begins to condense at the top of the fractionation column, it normally takes less than 10 to 30 seconds for 100 µL of distillate to be collected.

7.2.5.2 As the distillate collects in the collection vial, slowly back the air condenser tube out of the micro-vial as it fills. This allows the bubbles to escape without dislodging the distillate from the micro-vial. Remove the free end of the condenser from the vial when the collected volume reaches 100 µL.

7.2.5.3 A larger volume of distillate may be collected by using a larger vial. In this case, the concentration factor will be reduced accordingly. Collecting a larger volume will require longer condensation times, and may require water cooling of the condenser. The steam flow rate continues to increase after the first 100 µL of distillate is produced. This flow can overwhelm the cooling capacity of the air condenser. Lengthening the condenser to 100 cm may also be helpful.

NOTE: When 100 µL of distillate is collected from a 40-mL or 5-g sample, the theoretical concentration factors are 400 and 50, respectively. Typical absolute recoveries of target analytes are 10% to 40%. Thus, the actual concentration factor is about 2 orders of magnitude for water samples and 1 order of magnitude for solid samples. Distilling all calibration standards compensates for low absolute recoveries.

7.2.6 Cap the collection vial and store at 4°C until the distillate is analyzed.

7.2.7 Turn off the heating mantle and allow the system to cool. Do not attempt to disassemble the apparatus while it is hot. Significant steam pressure has built up within the system during distillation. Disassembly could lead to a sudden release of steam. The use of a smaller ID condenser or higher heating rates is not recommended, since this may cause the steam within the system to reach an unsafe pressure.

7.3 Sample Analysis

7.3.1 The samples prepared by this method may be analyzed by the appropriate GC or GC/MS method, such as Methods 8015 and 8260. Refer to these methods for appropriate analysis conditions.

7.3.2 All distillates and standards must be allowed to warm to ambient temperature before analysis.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control procedures.

8.2 To establish the ability to generate data of acceptable accuracy and precision refer to Method 8000 and the determinative method to be used.

9.0 METHOD PERFORMANCE

See Methods 8015 and 8260 for performance data.

10.0 REFERENCES

1. Peters, T.L. "Steam Distillation Apparatus for Concentration of Trace Water Soluble Organics"; Anal Chem., 1980, 52(1), 211-213.

2. Cramer, P.H., Wilner, J., and Stanley, J.S., "Final Report: Method for Polar, Water Soluble, Nonpurgeable Volatile Organics (VOCs)", For U.S. EPA, Environmental Monitoring Support Laboratory, EPA Contract No. 68-C8-0041.

3. Lee, R.P., Bruce, M.L., and Stephens, M.W., "Test Method Petition to Distill Water Soluble Volatile Organic Compounds from Aqueous Samples by Azeotropic Microdistillation", submitted by Wadsworth/ALERT Laboratories Inc., N. Canton, OH, January, 1991.

4. Bruce, M.L., Lee, R.P., and Stephens, M.W., "Concentration of Water Soluble Volatile Organic Compounds from Aqueous Samples by Azeotropic Microdistillation", Environ. Sci. Technol., 1992, 26, 160-163.

11.0 SAFETY

The following target analytes are known or suspected to be human carcinogens: acrylonitrile and 1,4-dioxane. Pure standard materials and stock standard solutions of these compounds should be handled in a hood.

FIGURE 1
AZEOTROPIC MACRODISTILLATION SYSTEM

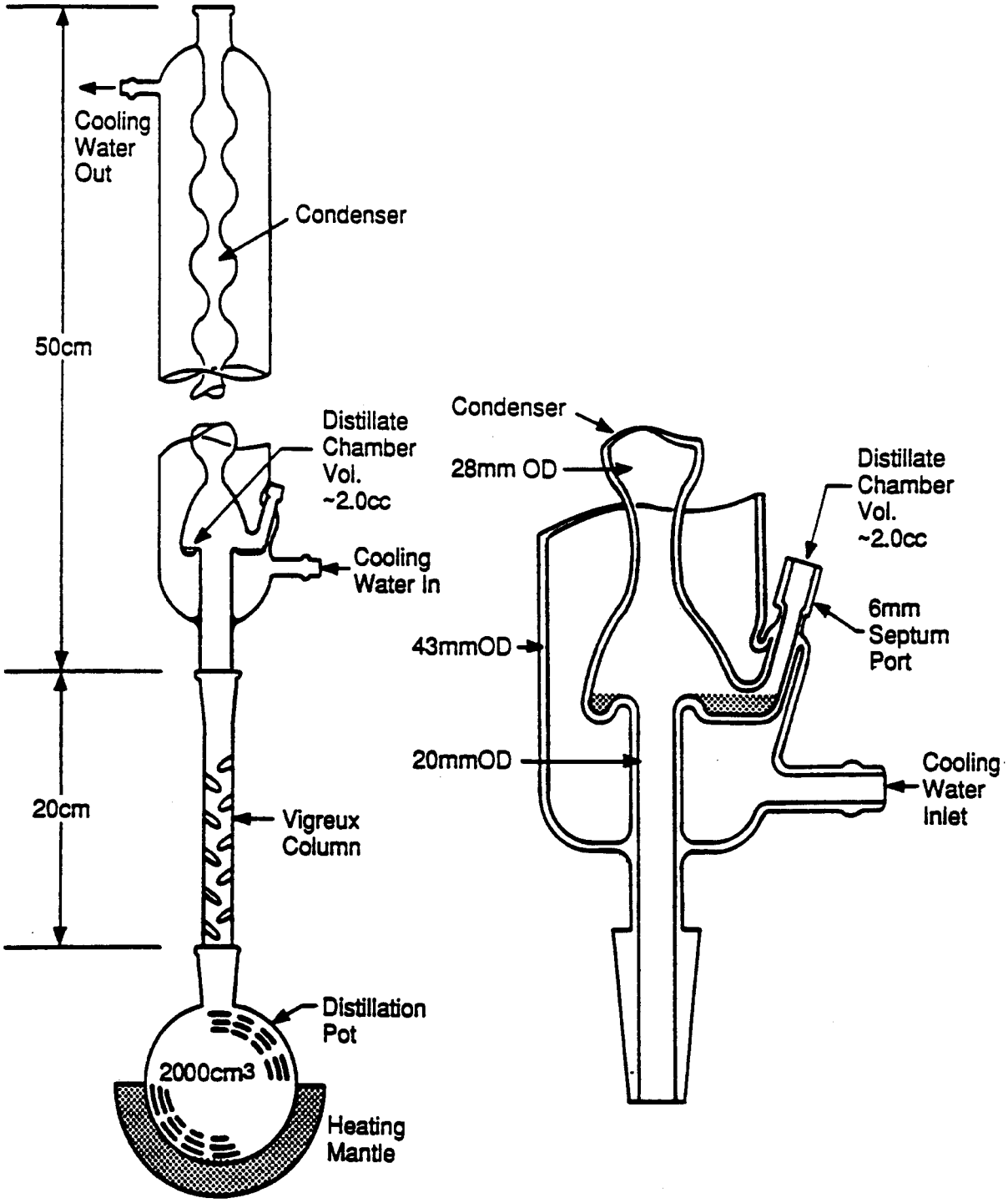


FIGURE 2
FRACTIONATION COLUMN

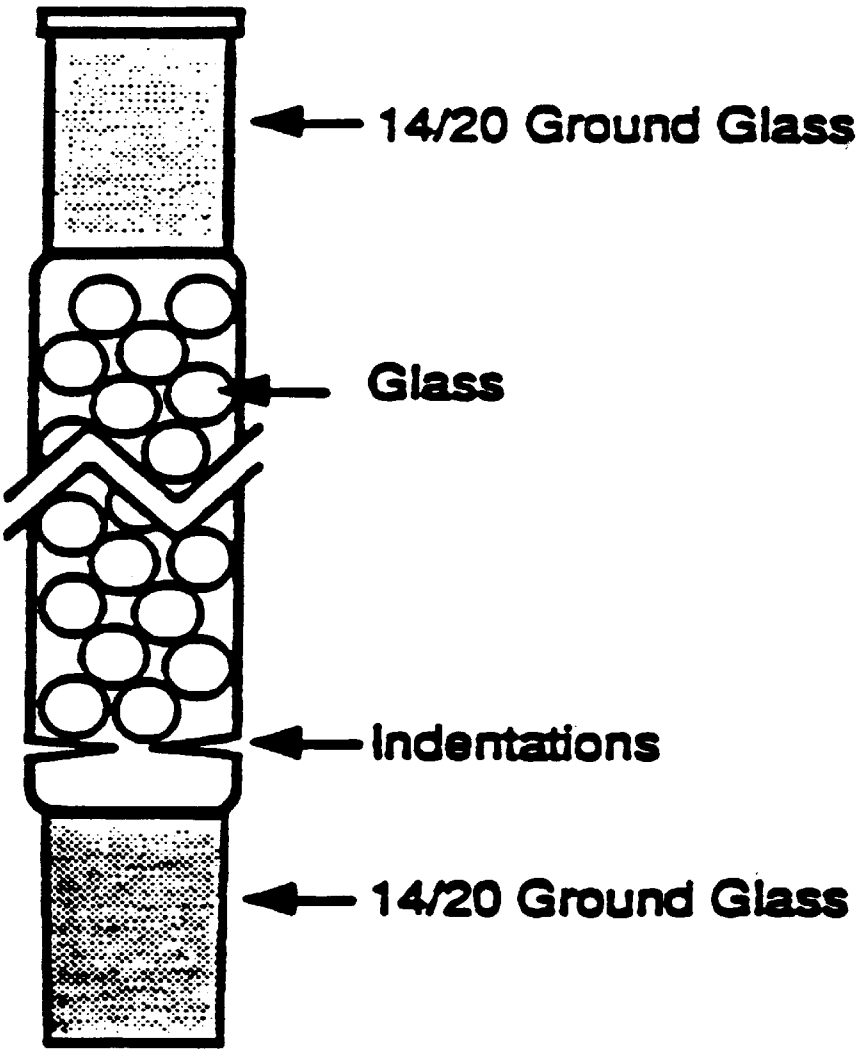


FIGURE 3
AIR CONDENSER AND REDUCING UNIONS

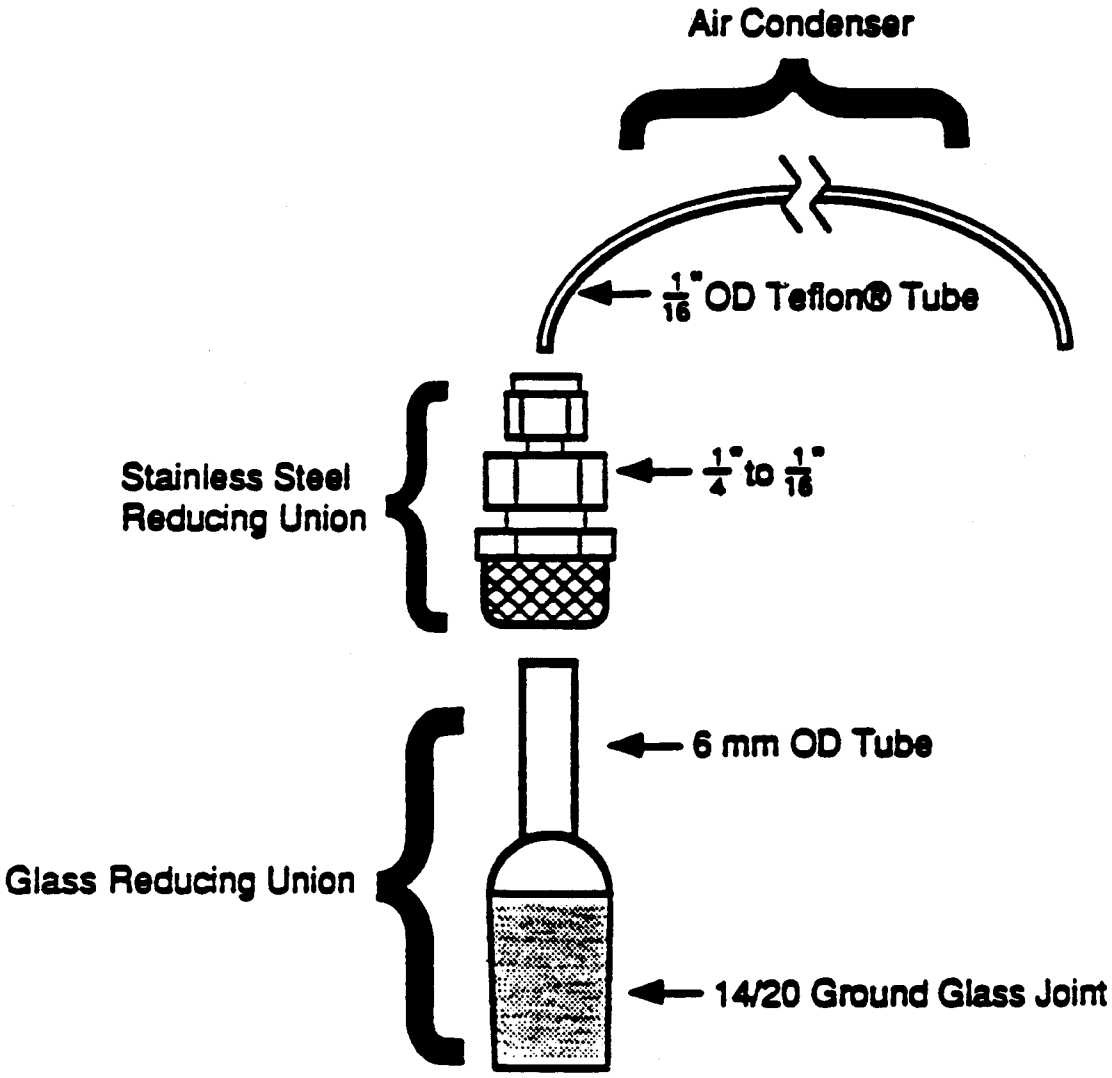
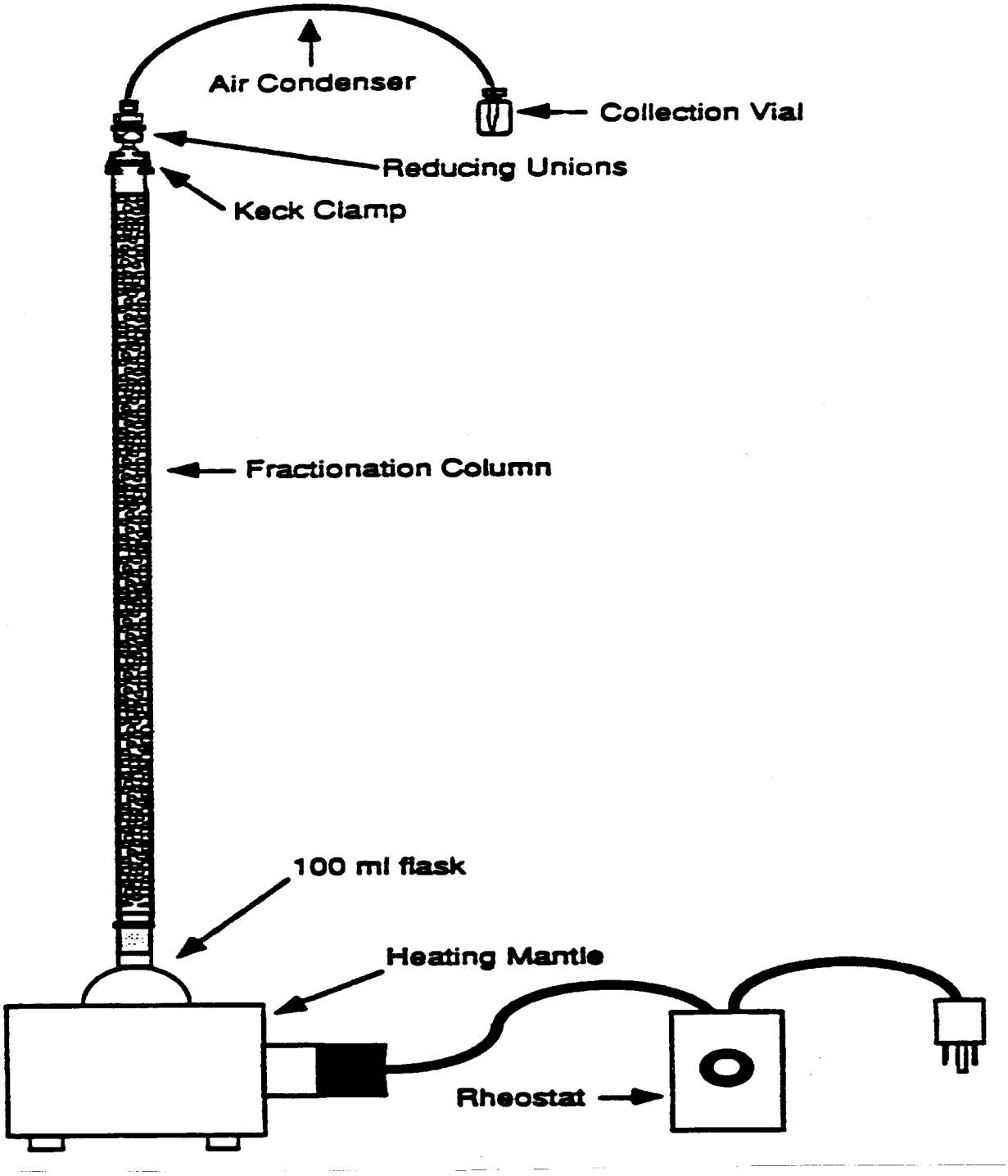
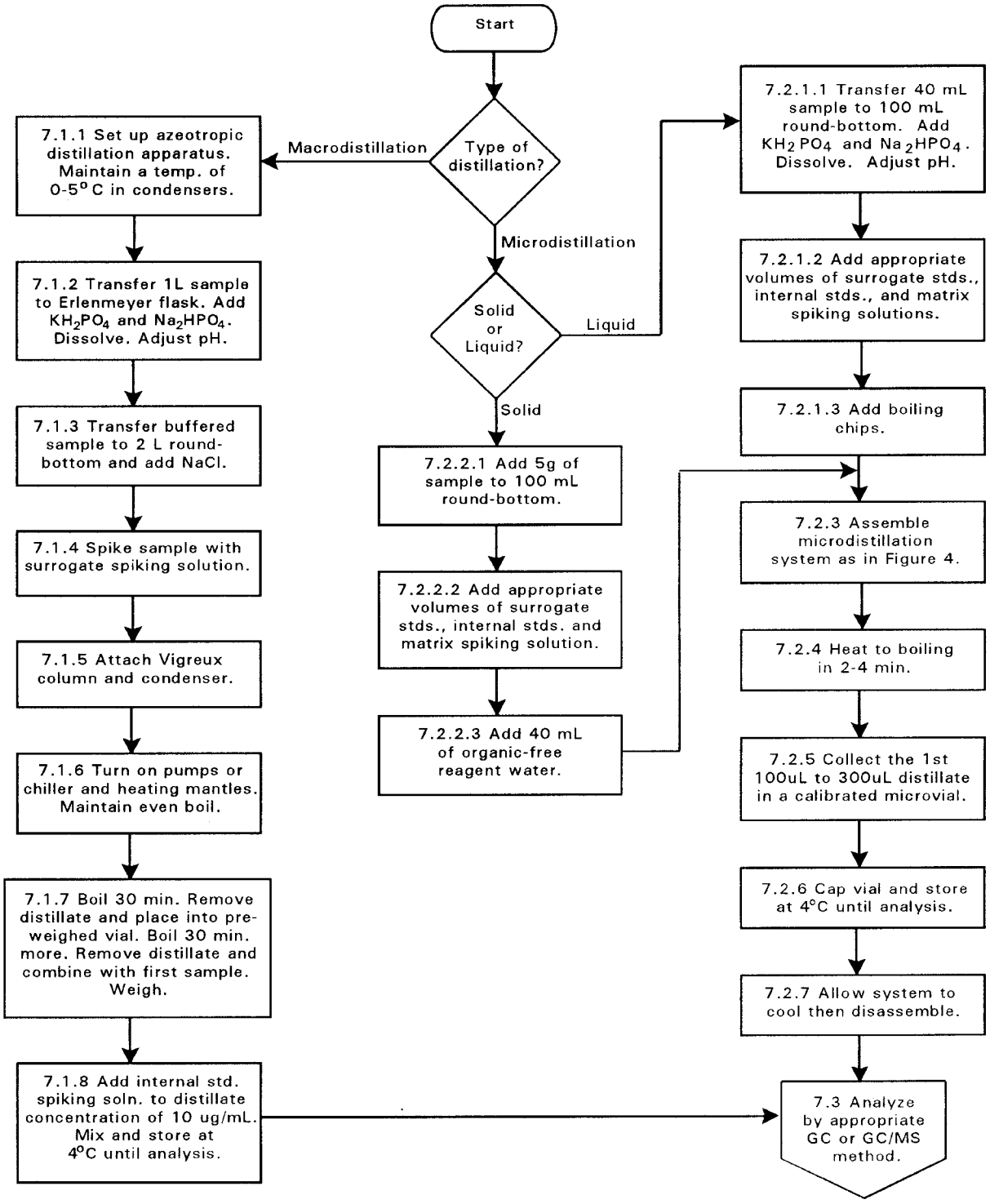


FIGURE 4
AZEOTROPIC MICRODISTILLATION SYSTEM




Start
Type of distillation?
Macrodistillation
Microdistillation
7.1.1 Set up azeotropic distillation apparatus. Maintain a temp. of 0-5° C in condensers.
7.1.2 Transfer 1L sample to Erlenmeyer flask. Add KH_2PO_4 and Na_2HPO_4. Dissolve. Adjust pH.
7.1.3 Transfer buffered sample to 2 L round-bottom and add NaCl.
7.1.4 Spike sample with surrogate spiking solution.
7.1.5 Attach Vigreux column and condenser.
7.1.6 Turn on pumps or chiller and heating mantles. Maintain even boil.
7.1.7 Boil 30 min. Remove distillate and place into pre-weighed vial. Boil 30 min. more. Remove distillate and combine with first sample. Weigh.
7.1.8 Add internal std. spiking soln. to distillate concentration of 10 ug/mL. Mix and store at 4°C until analysis.
Solid or Liquid?
Liquid
Solid
7.2.2.1 Add 5g of sample to 100 mL round-bottom.
7.2.2.2 Add appropriate volumes of surrogate stds., internal stds. and matrix spiking solution.
7.2.2.3 Add 40 mL of organic-free reagent water.
7.2.1.1 Transfer 40 mL sample to 100 mL round-bottom. Add KH_2PO_4 and Na_2HPO_4. Dissolve. Adjust pH.
7.2.1.2 Add appropriate volumes of surrogate stds., internal stds., and matrix spiking solutions.
7.2.1.3 Add boiling chips.
7.2.3 Assemble microdistillation system as in Figure 4.
7.2.4 Heat to boiling in 2-4 min.
7.2.5 Collect the 1st 100uL to 300uL distillate in a calibrated microvial.
7.2.6 Cap vial and store at 4°C until analysis.
7.2.7 Allow system to cool then disassemble.
7.3 Analyze by appropriate GC or GC/MS method.