ANALYTICAL PROTOCOL FOR MONITORING AMBIENT WATER QUALITY AT THE NIAGARA-ON-THE-LAKE AND PORT ERIE STATIONS

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NOVEMBER 23, 1987

METHOD FOR THE ANALYSIS OF SEMIVOLATILES IN WATER AND SUSPENDED SEDIMENT FROM THE NIAGARA RIVER

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INTRODUCTION

This document describes the analytical protocol for the determination of trace contaminants in water and suspended sediments collected at the Niagara-on-the-Lake (NOTL) and Fort Erie (FE) stations. The protocol is written with sufficient details to assist non-chemists, chemists, users of the data and non-experts to undertake a desk review. As well, novice analysts should be able to reproduce the procedures to obtain analytical data with an acceptable degree of reliability. The extensive use of the notes is made where appropriate to aid the understanding and highlight the critical aspects. The notes also serve as a warning to analysts to pay special attention to certain practices in order to minimize variability and obtain improved reproducibility.

A companion document dealing with performance verification and performance characteristcs limits for the above protocol is also being prepared. This will briefly describe the principles, theory and scope of the procedures, standard operational practices carried out within various laboratories, quality control procedures as well as supporting data for assessing and/or estimating repeatability, reproducibility, precision, bias and estimate of accuracy for the methods. The above document will be available to readers upon request.

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November 23, 1987

Dr. B.K. Afghan
Chairperson
Analytical Protocol Group, B Committee
Niagara River Long Term Monitoring Program
867 Lakeshore Road, P.O. Box 5050
BURLINGTON, Ontario
L7R 4A6

Dear Dr. Afghan:

On behalf of Environment Canada, I would like to inform you that the members of the Analytical Protocol Group, B Committee of the Niagara River Long Term Monitoring Program have reviewed the final draft of the protocol entitled, "Analytical Protocol for Monitoring Ambient Water Quality at the Niagara-on-the Lake and Fort Erie Stations" and find the document acceptable.

We are authorizing you to forward this document to the A/Chairperson of the River Monitoring Management Commitee on behalf of the Analytical Protocol Group.

Yours sincerely,

Kenneth W. Kuntz

K. Kuntz
Member, Analytical Protocol Group, B Committee
Niagara River Long Term Monitoring Program

Ontario Ministry of the Environment
Drinking Water Organics Section
Laboratory Services Branch
P.O. Box 213, 125 Resources Road
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November 23, 1987

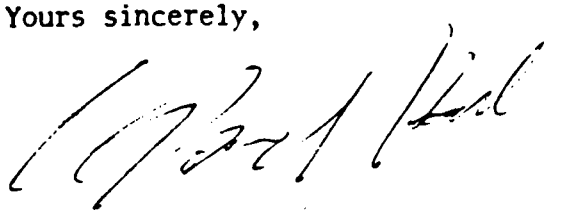
Dr. B.K. Afghan
Chairperson
Analytical Protocol Group, B Committee
Niagara River Long Term Monitoring Program
867 Lakeshore Road, P.O. Box 5050
BURLINGTON, Ontario
L7R 4A6

Dear Dr. Afghan:

On behalf of the Ontario Ministry of the Environment, I would like to inform you that the members of the Analytical Protocol Group, B Committee of the Niagara River Long Term Monitoring Program have reviewed the final draft of the protocol entitled, "Analytical Protocol for Monitoring Ambient Water Quality at the Niagara-on-the Lake and Fort Erie Stations" and find the document acceptable.

We are authorizing you to forward this document to the A/Chairperson of the River Monitoring Management Commitee on behalf of the Analytical Protocol Group.

Yours sincerely,



Dr. C. D. Hall
Member, Analytical Protocol Group, B Committee
Niagara River Long Term Monitoring Program

New York State Department of Environmental Conservation
50 Wolf Road, Albany, New York 12233-1010

Thomas C Jorling
Commissioner

December 8, 1987

Dr. B.K. Afghan
Chairperson
Analytical Protocol Group
B Committee
Niagara River Long Term Monitoring Program
867 Lakeshore Road
P.O. Box 5050
Burlington, Ontario, Canada L7R 4A6

Dear Dr. Afghan:

On behalf of the New York State Department of Environmental Conservation, I would like to inform you that the members of the Analytical Protocol Group, B Committee of the Niagara River Long Term Monitoring Program have reviewed the final draft of the protocol entitled, "Analytical Protocol for Monitoring Ambient Water Quality at the Niagara-on-the-Lake and Fort Erie Stations" and find the analytical procedures acceptable.

We are authorizing you to forward this document to the A/Chairperson of the River Monitoring Management Committee on behalf of the Analytical Protocol Group.

Sincerely,

Lawrence T. Bailey
Member, Analytical Protocol Group, B Committee
Niagara River Long Term Monitoring Program

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION II
EDISON, NEW JERSEY 08837

DEC 14 1987

Dr. B.K. Afghan, Chairperson
Analytical Protocol Group, B Committee
Niagara River Long Term Monitoring Program
867 Lakeshore Road, P.O. Box 5050
Burlington, Ontario L7R 4A6

Dear Dr. Afghan:

As the U.S. Environmental Protection Agency Region II representative on the B Committee, I would like to state that I and the other Regional members of the Analytical Protocol Group have reviewed the final draft of the protocol entitled, "Analytical Protocol for Monitoring Ambient Water Quality at the Niagara on-the-Lake and Fort Erie Stations" and find the description of the methods in the document to be acceptable. The methods are written in a clear and understandable manner and follow good scientific practices. Although we have not had a chance to thoroughly evaluate the verification data in the document, they do indicate that the methods are valid and should produce reliable data within the specifications given.

I am authorizing you to forward this document to the Acting Chairperson of the River Monitoring Management Committee on behalf of the Analytical Protocol Group.

If you have any questions, please call me at 201-321-6709.

Sincerely yours,

Lloyd Kahn

Lloyd Kahn, Member
Analytical Protocol Group, B Committee
Niagara River Long Term Monitoring Program

PROCEDURES FOR REVISING AND UPDATING METHODOLOGIES

The following procedures for revising and updating methodologies were agreed to by the Group "B" Committee:

1. A description of the proposed modification or new protocol along with appropriate supporting information will be distributed by the Proponent to all memebers of the Group for review.

2. Any modification and notification of modification will be reported to the Agencies within 90 days. Major changes will be subject to Criteria Modification Procedure.

3. The review period will be a minimum of 30 days from the date on which the proposed changes are sent out.

4. After the review period, the Group will meet to discuss the proposed changes and agree on their adoption.

5. Once agreement has been reached, the RMMC will be advised of the changes and subject to their approval the changes will be implemented within 90 days.

METHODS FOR THE ANALYSIS OF SEMIVOLATILE ORGANIC CONTAMINANTS IN WATER AND SUSPENDED SEDIMENT FROM THE NIAGARA RIVER

1.0 SUMMARY OF PROCEDURES:

The procedure consists of three operational phases.

(a) The first phase is continuous collection of raw river water carried out using a Westfalia Centrifuge to separate the suspended sediments from the water. Three different samples are collected:

  (i) an on site extract of neutral organic compounds from 40-50 L water into 200 mL of dichloromethane (CH_2Cl_2);

  (ii) a twenty L grab sample of water (acidified in the field) for determination of phenols;

  (iii) sediment for determination of both neutral and phenolic organic compounds;

(b) The second phase is preparation of the extracts for instrumental analysis.

(c) The third phase is instrumental analysis and interpretation.

Sample preparation procedures require concentration and fractionation of the analytes. The flow chart of the extraction procedure and the sample preparation is shown in FIGURE 1. The neutral organics, comprised of chlorobenzenes; organochlorine pesticides; polychlorinated biphenyls; 2,3,7,8-TCDD (tetrachlorodibenzo-p-dioxin) and aromatic hydrocarbons, are extracted on site with a large volume extractor (LVX). The twenty liters of acidified water are returned to the laboratory and extracted by a LVX for determination of phenols including chlorinated phenols. Sediment collected from the Westfalia centrifuge is analyzed for both neutral organics and phenols. Instrumental analysis is by gas chromatography using electron capture and mass spectrometric detection.

Quality control is an integral and essential part of the procedure as this permits monitoring of performance of the method on an ongoing basis. It is particularly important in the Niagara River Program as this will be the only laboratory involved in the study at this time. Quality control involves three distinct phases:

(a) the analysis of standard compounds (termed standard surrogates) added directly to the sample as a control of processes carried out on the actual analytes in real samples of environmental origin;

(b) the determination of analytes from solutions containing known amounts of compounds at appropriate concentrations as a control of the reproducibility of the overall procedure as well as the sub-procedures.

(c) the determination of appropriate blanks.

The quality control program includes the availability of the required solutions and their addition into the analysis at the appropriate point in the analytical procedure.

NOTE: NOTES ARE INCLUDED THROUGHOUT THE TEXT TO HIGHLIGHT CERTAIN REQUIREMENTS FOR THE NON EXPERT READER OR THE NOVICE ANALYST.

2.0 DESCRIPTION OF THE LVX:

The LVX (1)(2) is an apparatus consisting of:

(a) an all glass unit composed of the mixing chamber, settling chambers, separator trap, and solvent reservoir. The mixing chambers, settling chambers and separator trap constitute the flow containment system in which the extracting solvent (CH_2Cl_2) and water are contained and in which extraction occurs;

(b) metering pumps to permit accurate control of the flow of water, make-up CH_2Cl_2 and spiking solution through the system;

(c) a motor and stirring propeller for mixing the two immiscible phases.

The agitator and the containment system are mounted on a support stand. The support stand and the metering pump are secured to 3/4 inch plywood so that all three components become a single unit which can be either secured to a laboratory bench or moved at will to sites remote from the laboratory. The design details are shown in FIGURES 2 - 4 and specifications of the mechanical components appear in TABLE 1.

During normal operation the water is pumped continuously through the mixing chamber of the containment system and is constantly in contact with CH_2Cl_2 and is also constantly being agitated. (A diagram of liquid flow in the containment system is presented in FIGURE 2). Extraction with high recovery requires in part an efficient separation of the organic and aqueous phases. The containment system has four regions in which such separation and settling can take place: the first is the mixing chamber; the second and third are two settling chambers for separation of CH_2Cl_2 and water, returning the separated solvent to the mixing chamber. The last region for separation and settling is a trap

which contains a packed column of short sections of Teflon tubing (approximately 4 mm x 6 mm o.d.) which ensures a visible separation of the CH_2Cl_2 from the water by separating the microdroplets of CH_2Cl_2 from the water.

NOTE: THE LVX WILL NOT FUNCTION EFFICIENTLY WITHOUT TEFLON RINGS.

This trap is required because if the microdroplets of CH_2Cl_2 in water are lost to waste, the yield of extracted analytes would be severely reduced.

The LVX system is designed to recover as much CH_2Cl_2 as possible but some solvent (approximately 1.5% of the volume extracted) is still lost to evaporation or to solubility of CH_2Cl_2 in water. These losses are made up by replacement from the solvent reservoir. This is done by the metering pump.

NOTE: THE MECHANISM FOR REPLACEMENT OF CH_2Cl_2 MUST BE FULLY FUNCTIONAL FOR EFFECTIVE OPERATION OF THE INSTRUMENT.

2.1 Operation:

NOTE: AN EQUIVALENT VOLUME OF DICHLOROMETHANE MUST BE TESTED FOR POTENTIAL INTERFERENCES AND QUALITY ASSURANCE DATA MUST BE REPORTED WITH THE SAMPLE DATA.

A 300 mL portion of dichloromethane is evaporated down to 1 mL using a Goulden evaporator (FIGURE 6) and injected into an electron capture gas chromatograph with OCA and OCB standards (TABLE 3A) to check for interferences.

2.1.1 Extraction of neutral organic analytes: The extractor is filled with reagent water, 200 mL CH_2Cl_2 is added to the mixing chamber and the solvent reservoir is filled with CH_2Cl_2. A 100 mL volumetric flask is filled with solution FSM1 (TABLE 4) which will deliver 40 ng each of 1,3,5-tribromobenzene and 1,2,4,5-tetrabromobenzene and 20 ng of δ-BHC to the 40 to 50 liters of water which is extracted and concentrated to a 2 mL extract (section 4.1-ii).

NOTE: THE METHANOLIC SOLUTION OF SURROGATE STANDARDS IS PREPARED MONTHLY IN THE NATIONAL WATER QUALITY LABORATORY (NWQL) AT THE CANADA CENTER FOR INLAND WATERS (C.C.I.W) AND 100 mL OF THIS SOLUTION IN 100 mL VOLUMETRIC FLASKS IS SENT TO THE FIELD. THIS SOLUTION WAS FOUND TO BE STABLE OVER FIVE WEEKS.

The extractor, the solvent reservoir and the volumetric flask containing surrogate standards are connected to the appropriate metering pumps and at this point the system is ready to be used for extraction of large volumes of water.

The agitator is started at 800 rpm. At this recommended speed of rotation, the 4.5 cm diameter agitating blades produce efficient mixing and minimal emulsion which can occur at higher rpm. The flow of water is begun at a rate of 35 mL/min and the metering pump is set to deliver CH_2Cl_2 flow from the solvent reservoir at 0.70 mL/min to make up for solvent lost to solubility in water and/or evaporation. The pump delivering the surrogate standard solution is set at 0.07 mL/min. After 23.5 hours an additional 10 mL MeOH is added to the 100 mL volumetric flask for rinsing purposes and the metering pump is set at full speed.

NOTE: THE EXTRACTION IS CONSIDERED COMPLETE ONLY AFTER WASHING OF THE SURROGATE STANDARDS FLASK TO COMPLETE TRANSFER OF SURROGATE STANDARDS TO THE AQUEOUS PHASE.

The agitator is then stopped and the system is allowed to settle in order to let the CH_2Cl_2 separate. The solvent in the bottom of the mixing chamber is collected through stopcock A (see FIGURE 2) and solvent remaining in the packed column is brought down into the mixing chamber by draining the water through stopcock B (FIGURE 2). The packed column of teflon rings is washed with 25 mL of CH_2Cl_2 which is combined with the extracts. The separator trap is checked for solvent carryover. Under normal operation this trap should be free of CH_2Cl_2. If, however, any CH_2Cl_2 is present it is isolated and combined on site with the rest of the organic extract before transport to the laboratory.

NOTE: IF THERE IS ANY CH_2Cl_2 VISIBLE IN THE FINAL TRAP THE MECHANICAL SYSTEM MAY BE SUSPECT AND ADJUSTMENT OF PUMPS MAY BE REQUIRED.

NOTE: EXTRACTS ARE COLLECTED INTO CLEANED AMBER SCREW CAP BOTTLES AND SEALED WITH TEFLON LINED SCREW CAPS. THE LEVEL OF CH_2Cl_2 COLLECTED IN THE BOTTLE IS MARKED WITH A FELT TIP MARKER AND THE MARK IS THEN COVERED WITH CLEAR SCOTCH TAPE IN ORDER TO PRESERVE THE MARK WHICH WILL BE USED FOR DETERMINATION OF THE VOLUME COLLECTED FROM THE LVX. THE VOLUME IS AN INDICATOR OF THE QUALITY OF SAMPLING PROCEDURE. THE BOTTLE SHOULD CONTAIN A MINIMUM 200 mL TO A MAXIMUM OF 400 mL. IF THE VOLUME IS SUBSTANTIALLY DIFFERENT OR THE LEVEL IS NOT MARKED WHEN THE BOTTLE ARRIVES IN THE LABORATORY THE OMISSION IS NOTED IN THE LAB BOOK AND THE LEVEL IS MARKED IN THE LABORATORY BEFORE THE BOTTLE IS OPENED. THE CAUSE OF THE UNEXPECTED VOLUMES OR MISSING INFORMATION IS ASCERTAINED BEFORE OTHER FIELD SAMPLES ARE RECEIVED INTO THE LABORATORY.

2.1.2 Extraction of the acidic fraction for phenols: A twenty liter grab sample of water acidified with H_2SO_4 (1 mL/L) is received at the NWQL in glass solvent bottles (these bottles are used once and then discarded). The acidic fraction is extracted and concentrated into CH_2Cl_2 in the laboratory by the LVX procedure as described in section 2.1.1.

3.0 PRINCIPLE OF SAMPLE PREPARATION, CLEANUP AND GAS CHROMATOGRAPHY:

The analytes will be received in solution in a minimum volume of 200 mL and a maximum volume 400 mL of CH_2Cl_2 that will be contained in a clean amber bottle sealed with a teflon lined screw cap. The solvent is dried and evaporated in a controlled manner using a relatively high boiling solvent, iso-octane, as a "keeper solvent" during the evaporation of CH_2Cl_2 in the Goulden Evaporator FIGURES 6 - 8 (section 4.1.ii). As this solvent is non-polar it can also be used to transfer the analyte extract to a chromatographic column for fractionation prior to analysis. The procedure separates analytes into two fractions on the basis of polarity as shown in the schematic flow chart in FIGURE 5.

3.1 General Description of Apparatus and Equipment: The preparation, cleanup and analysis of extract requires laboratory apparatus of an organic analytical chemistry laboratory. This includes glassware, custom evaporation devices for concentrating solutions and/or removing solvents (FIGURES 6 - 8), ovens, furnaces and two gas chromatographs equipped with electron capture detectors. One GC is configured for dual capillary column work and the other for packed column work. The actual clean-up is as follows. Glassware is first washed with heavy duty soap and in hot water. The glassware is then soaked overnight in chromic acid. After soaking the glassware is drained and washed with hot tap water until the washings are no longer coloured. Subsequently glassware is washed with distilled water, acetone and pesticide grade petroleum ether and air dried.

Glassware that is to be used for volumetric measurement is heated at 130°C overnight. The glassware is then cooled and capped with CH_2Cl_2 washed aluminum foil until use. Prior to use glassware is rinsed with the solvent that is to be used in that piece of equipment

NOTE: ALL GLASSWARE USED IN SAMPLE HANDLING IS SEGREGATED FROM THE REST OF THE LABORATORY GLASSWARE.

NOTE: BEFORE USE, GLASSWARE IS WASHED THREE TIMES WITH A 10% VOLUME OF HEXANE (eg A 500 mL FLASK IS WASHED WITH 50 mL HEXANE). THE HEXANE WASHINGS ARE CONCENTRATED TO 1 mL ON A GOULDEN EVAPORATOR AND 1-2 uL ARE ANALYZED BY GC. IF ANY INTERFERENCES ARE FOUND THE GLASSWARE IS AGAIN WASHED WITH HEXANE BEFORE USE.

3.1.1 Equipment for Measuring Liquids: The following glassware items are required for measurement of liquids and preparation of solutions.

(i) Volumetric flasks with capacities ranging from 5 mL to 100 mL.

(ii) Fifteen mL stoppered centrifuge tubes calibrated by the manufacturer are checked for accuracy using 1 and 2 mL volumetric pipettes. Tubes deviating by more than 5% are rejected.

(iii) Graduated cylinders with a 5 mL to 100 mL capacity.

(iv) Volumetric pipettes with capacities ranging from 1 mL to 25 mL.

(v) Eppendorf pipettes for preparing stock solutions with capacities ranging from 10 uL to 1000 uL. THESE EPPENDORF PIPETTES ARE FITTED WITH PREWASHED GLASS TIPS.

3.1.2 Solvent Handling Equipment: The following glassware items will be required for transferring, evaporating or handling liquids and preparation of solutions.

(i) Disposable pipettes and pipette bulbs

(ii) One hundred and 500 mL round bottom flasks with 24/40 ground glass joints

(iii) Glass separatory funnels with a 500 mL capacity

(iv) An Allihn funnel which is a 10 cm by 4 cm filter funnel with a reservoir and a Porosity B sintered glass disk (FIGURE 9)

(v) Stainless steel beakers

(vi) Sonicating bath Bronsted Sonicator model 250 capable of continuously generating 200 watts

(vii) Buchi rotary evaporator (Model RE 111)

(viii) Goulden Evaporators for concentration from CH_2Cl_2, hexane (FIGURES 6 - 7)

(ix) Limited volume glass inserts for concentrating extracts for GC/ MS analysis: Waters Associates, Catalog number 72704.

3.1.3 Chromatographic Columns: The procedure calls for column chromatography to fractionate the extract into two fractions and gas chromatography as the method of qualitative and quantitative analysis.

(i) Fractionation column: A 12 mm X 350 mm glass column with a teflon stopcock or its equivalent.

(ii) Packed column for gas chromatography: 1.8 M X 2 mm glass gas chromatographic column packed with 3% OV 101 on 80/100 mesh chromosorb W-H-P commercially available from Chromatographic Specialties, Brockville Ont.

(iii) Gas chromatographic capillary columns: All capillary columns are made of fused silica, 30 M x 0.25 mm i.d. The phases have a thickness of 0.25 um. The phases used are selected from the following and are listed as the Supelco products; [J & W products which are acceptable replacements appear in squared brackets after the chemical name]: SPB 1 (Polydimethyl siloxane) [DB-1]; SPB 5 (5% phenyl 95% methyl polysiloxane) [DB 5]; SPB 608 or equivalent.

(iv) Guard column: fused silica 0.3 mm i.d and 1.0 M in length.

3.1.4 Miscellaneous Items: Small items that are required at various stages include: glass rod for breaking emulsions; glass marker; felt tip pen marker; water proof and solvent proof transparent tape. In addition the following items are required: glass wool; teflon boiling chips and aluminum foil; Teflon rings cut from teflon tubing (for the LVX 6 mm o.d. tubing is used and for both Goulden Evaporators, 3 mm tubing is used).

NOTE: THE ABOVE ITEMS ARE TO BE WASHED WITH CH_2CL_2 BEFORE USE.

Lastly the procedure requires a cabinet desiccator for storage of sodium sulphate and silica gel.

3.1.5 Heating Apparatus: The following equipment is required for drying and cleaning various reagents and glassware: Two ovens capable of controlling temperatures in excess of 400°C and 130°C respectively; Muffle furnace for drying and cleaning capable of controlling temperatures in excess of 1000°C.

3.2 Gas Chromatographic Analysis Systems: The laboratory utilizes HP gas chromatographs and autosamplers with the following pairings:

GC	AUTOSAMPLER	TYPE OF COLUMN
5700	7672A	1.8 M x 2 mm i.d. glass with 3% OV 101 on Chromosorb W H-P 80/100
5730	7671A	Dual capillary (Section 3.1.3-iii)
5890	7673A	Dual capillary (Section 3.1.3-iii)

Both 5730 and 5890 GC's are equipped with injectors that split the sample onto the two columns for simultaneous analysis.

The detection system for all the above gas chromatographs is Ni^{63} frequency pulsed linearized electron capture detectors. All data are recorded by an HP 1000 computer which has an HP3350 software system Laboratory Automation System (LAS) with a CPLOT package. The 5700 series of gas chromatographs are linked to the LAS by HP 18652A A/D converters and are run in a "LOOP" mode, whereas the 5890 and 5730 GC's are interfaced to the LAS by 3392A integrators, controlled from the computer. Results are stored in the appropriate files in the computer for further examination and are then stored on tape. If needed, stored data can be smoothed by altering integration parameters, and critical segments of a chromatogram.

Results are retained in the computer for up to 7 days for further analysis such as examining critical areas of a chromatogram or re-adjusting the integration parameters. All data are transferred to magnetic tape for storage. Ancillary equipment includes an HP 7914A ST tape drive unit, an HP 2934A line printer and an HP 7550A graphics plotter.

3.3 Reagents: Reagents required are solvents and solids used in column chromatography, reagents for drying organic extracts and pure compounds for preparation of standard solutions of analytes.

(i) Solvents: The following solvents must be of pesticide grade quality: acetone; hexane; petroleum ether; iso-octane; acetonitrile; CH_2Cl_2. Acetone for washing glassware is of reagent grade.

(ii) Solid Reagents: Silica gel from ICN Adsorbent 100-200 mesh for chromatography. Available from TERROCHEM (Catalogue # 02747) in metal bottles in 500 g amounts. This material is dried at 130°C in batches

of 194 g. After drying the Silica gel is deactivated by shaking 194 g with 6 mL reagent water. The prepared silica gel is transferred to a screw cap glass bottle capped with aluminum foil. This container is stored inside a desiccator dried with a mixture of blue and white drierite to keep an anhydrous atmosphere. The 3% deactivated silica gel is not kept for more than three weeks. Anhydrous granular sodium sulphate is heated in a muffle furnace at 600°C for a minimum of 18 hrs and is stored in a desiccator under anhydrous conditions.

(iii) Standards: Reference analytes are obtained from the EPA Repository. Purity of the standards are stated by the supplier and should be at least 95% pure. Upon opening, record batch number, date of acquisition at National Water Quality Laboratory and date of opening of the container . Storage is at -4°C. Corrections for purity are made when standards are prepared.

NOTE: UPON REMOVING FROM STORAGE AND PRIOR TO OPENING, THE BOTTLES MUST BE ALLOWED TO REACH ROOM TEMPERATURE.

(iv) Stock Solutions: Approximately 10 + 1 mg of primary grade standards are weighed on a microbalance to the nearest ug and then dissolved in a volume of iso-octane to give a concentration of 1000 ng/uL. These stock solutions are stored at -4°C in the absence of light. Under these conditions the shelf life is in excess of one year. Concentrations are checked by GC against independent solutions for accuracy. If concentrations differ by more than ± 5% new solutions are prepared. When 1 mL of these solutions remain a new batch of stock solutions is prepared and checked against the old solution. Concentration of these solutions should be within 5% of those initially prepared.

(v) Intermediate and Working Solutions of Parameters, Surrogates and Calibration Standards. These solutions are described in TABLES 2 to 4.

(vi) In-house sediment reference material. One kg of NOTL sediment was collected from the Westfalia centrifuge according to the sampling protocol (3). This material was homogenized and stored at -4°C.

4.0 Preparation of Methylene Chloride Extracts for Analysis:

This phase of the procedure involves concentration of the analytes by selective evaporation of the solvent and separation into two fractions by column chromatography.

4.1 Concentration of Neutral Analytes: The sequence for concentration consists of drying of the CH_2Cl_2 extract from the LVX and concentration of the extract into iso-octane in preparation for fractionation.

NOTE: THE LEVEL OF CH_2Cl_2 COLLECTED IN THE BOTTLE SHOULD BE MARKED IN THE FIELD ON THE BOTTLE WITH A FELT TIP MARKER. THE VOLUME IS AN INDICATOR OF THE QUALITY OF SAMPLING PROCEDURE. THE BOTTLE SHOULD CONTAIN A MINIMUM OF 200 mL AND A MAXIMUM OF 400 mL. IF THE VOLUME IS SUBSTANTIALLY DIFFERENT OR THE LEVEL IS NOT MARKED WHEN THE BOTTLE ARRIVES IN THE LABORATORY THE OMISSION IS NOTED IN THE LAB BOOK AND THE LEVEL IS MARKED IN THE LABORATORY BEFORE THE BOTTLE IS OPENED. THE CAUSE OF THE UNEXPECTED VOLUMES OR MISSING INFORMATION IS ASCERTAINED BEFORE OTHER FIELD SAMPLES ARE RECEIVED. SUCH ANOMALOUS SAMPLES ARE IDENTIFIED AT ALL STAGES OF THE PROCESS AND PARTICULARLY SO WHEN REPORTING RESULTS.

(i) Transfer the CH_2Cl_2 extract into a glass separatory funnel and swirl gently to separate emulsions. Collect CH_2Cl_2 onto an Allihn suction funnel (section 3.1.2-iv) containing 5 cm of clean and dried sodium sulphate (3.3-ii). The Allihn funnel is fitted with a 500 mL round bottom flask. Transfer the CH_2Cl_2 extract to the Allihn funnel and allow the solvent to drain through the sodium sulphate into the round bottom flask. Extract the aqueous layer with an additional 25 mL of CH_2Cl_2 and drain through the sodium sulphate as before. Finally wash the sodium sulphate cake twice with 25 mL of CH_2Cl_2 using gentle suction (not greater than 2 psi).

(ii) Add 2.0 mL of iso-octane to the CH_2Cl_2 extract. The iso-octane acts as a keeper solvent during the concentration stage which involves selective evaporation of the CH_2Cl_2 from, and transfer of analytes to, the keeper solvent. (This process will be called stripping). Add 20 uL of SM2 (TABLE 2A) to the CH_2Cl_2 which delivers 100 ng of dibromobenzene to the final 2 mL extract concentrate and serves as a control for loss of chlorobenzenes and other relatively more volatile analytes. Add several boiling chips to prevent bumping. Evaporate the CH_2Cl_2 in a Goulden Evaporator (FIGURE 7) maintaining the temperature of the jacket condenser at 40°C with a

four hour evaporation time. Remove from evaporator while there is still about 4 mL left and concentrate the iso-octane (while holding the round bottom flask in hand) to less than 2 mL using a gentle stream of nitrogen. Transfer the iso-octane solution to a 15 mL graduated and calibrated centrifuge tube and make up to 2 mL with iso-octane. Add 20 uL SM3 (TABLE 2A) to the 2 mL of the concentrate which delivers 40 ng of 2,3,5,6-tetrachlorobiphenyl and 20 ng of endrin ketone as controls for the subsequent fractionation. One mL of this concentrate is transferred to the column with a 1000 uL glass syringe (section 4.2-ii). The volume remaining in the tube is exactly determined using the same glass syringe and subsequently sent for GC/MS analysis (section 6).

4.1.1 Concentration of Acidic Extract: The CH_2Cl_2 extract from 20 L of acidified water is concentrated to 1 mL using a Goulden evaporator (section 4.1.-ii) and sent for GC/MS analysis (section 6.1).

4.2 Chromatographic Fractionation: The extract is fractionated by column chromatography on 3% deactivated silica gel (section 3.3-ii).

NOTE: CHROMATOGRAPHIC PHASES ARE SENSITIVE TO MOISTURE: DURING PACKING AND/OR STORAGE OF THE COLUMN THIS MUST BE REDUCED TO MAINTAIN ACTIVITY.

NOTE: CHROMATOGRAPHIC PHASES ARE BULK MATERIALS AND NOT ALL PARTS MAY BE EQUALLY ACTIVE. THE 3% DEACTIVATED SILICA GEL (section 3.3-ii) IN THE CONTAINER IS ROTATED GENTLY 10 TIMES PRIOR TO EACH OPENING TO ALLOW FOR A COMPLETE MIXING OF THE MATERIAL THUS AVERAGING POTENTIAL INHOMOGENEITIES.

(i) Preparation of the column: A plug of silanized glass wool is inserted into the column and covered with 2.5 cm of sodium sulfate to retain the silica gel. Transfer 3.4 g of 3% deactivated silica gel (section 3.3-ii) to the column and cap with 2.5 cm of sodium sulfate.

NOTE: THE COLUMN IS WETTED AND WASHED WITH 40 ML OF HEXANE. SUFFICIENT HEXANE IS RETAINED TO PREVENT THE TOP OF THE SODIUM SULPHATE FROM DRYING OUT BEFORE FRACTIONATING THE EXTRACT.

(ii) Fractionation of the concentrated extract: Transfer 1 mL of the concentrated extract (section 4.1-ii)to the head of the hexane wetted column and elute FRACTION A with 40 mL hexane and FRACTION B with 60 mL of 1:1 CH_2Cl_2/Hexane.

FRACTION A contains the following analytes:
1,3-dichlorobenzene; 1,4-dichlorobenzene;
1,2-dichlorobenzene; 1,3,5-trichlorobenzene;
1,2,4-trichlorobenzene; 1,2,3-trichlorobenzene;
hexachlorobutadiene; 1,2,3,4-tetrachlorobenzene;
pentachlorobenzene; hexachlorobenzene; heptachlor;
aldrin; p,p'-DDE; p,p'-TDE; o,p'-DDT; p,p'-DDT;
mirex; PCB's.

FRACTION A also contains the four surrogates:
1,3-dibromobenzene; 1,3,5-tribromobenzene; 1,2,4,5-tetrabromobenzene and 2,3,5,6-tetrachlorobiphenyl.

FRACTION B contains the following analytes:
α-BHC; lindane; heptachlor epoxide; γ-chlordane;
α-endosulfan; α-chlordane; dieldrin; endrin;
β-endosulfan; p,p'-TDE; methoxychlor.

FRACTION B contains surrogates δ-BHC and endrin ketone.

NOTE: p,p'-TDE(p,p'-DDD) SPLITS BETWEEN THE TWO FRACTIONS. THE SPLIT RATIO (FR. A/FR. B) IS APPROXIMATELY 5/95(± 5%).

(iii) Preparation of Fractions for Instrumental Analysis:
Add 1 mL iso-octane to each fraction then carefully concentrate Fraction A on a Goulden Evaporator (FIGURE 8) to a final volume of 1 mL. Conditions for use of the Evaporator are as follows: the jacket condenser is maintained at 70°C for evaporation of hexane with a two hour cycle.

The one mL of isolate of FRACTION A is treated with 0.2 mL of prepurified mercury and stirred on a vortex genie for one minute. If necessary (ie if any mercury sulfide appears as evidenced by a darkened colouration on the surface of the mercury) the solution is further treated for removal of sulfur by transferring to a clean 15 mL centrifuge tube and repeating the procedure using 0.1 mL of prepurified mercury.

FRACTION B is concentrated on a roto evaporator with the water bath at 30°C. No treatment with mercury is required for this fraction.

Ten uL of OCN solution containing 24 ng octachloronaphthalene as the indicator of GC/ECD performance is added to the final 1 mL isolate from each fraction.

5.0 GAS CHROMATOGRAPHY:

Qualitative identification of an analyte is based upon relative retention times on two columns of dissimilar chromatographic properties. Quantitation is by external standard calibration method and is based on the responses of the GC system to the accurate injection of aliquots of solutions OCA, OCB and PCB (TABLE 3A). Typical chromatographic traces appear in FIGURES 10 - 12. Relative retention times and average responses for each analyte are presented in TABLE 5A, B and C.

5.1 Determination of Chlorobenzenes and Organochlorine Pesticides: Identification and quantitative determination of the other organochlorines is based on analysis on two capillary columns with pairing of the following: SPB 1 and SPB 5; SPB 1 and SPB 608 (section 3.1.3-iii). The sample is injected in splitless mode with a time delay of 0.5 min after injection. The injection is split onto the two columns. The initial oven temperature of 80°C is held for 2 min. and then programmed at 4°C/min to 280°C, and this final temperature was held for a further 16 min. The injector temperature is 250°C and the Ni 63 EC detector is maintained at 300°C. The carrier gas is hydrogen with a column head pressure of 13 p.s.i. and with argon/methane as the makeup gas maintained at a flow rate of 30 mL/min although adjustment may be necessary to maximize response.

5.1.2 Calculations: The concentrations of chlorobenzenes and organochlorine pesticides are calculated by single point calibration. For each set of environmental samples the GC/ECD instrument is calibrated using an external standard mix (TABLE 3A) and 10 uL OCN/mL (TABLE 2A). A measured aliquot of the standards solution is injected onto the column. The response of the GC to each analyte is the basis of the single point calibration. Concentration of each analyte is calculated by as follows.

$$C_{sam} = R_{sam}/R_{std} \times C_{std} \times V_{ex}/V_{water} \times 1000$$

Where:

C_{sam} = Concentration of the parameter in sample (ng/L);

R_{sam} = Response of the instrument to injection of parameter;

R_{std} = Response of the instrument to injection of standard (TABLE 5A);

C_{std} = Concentration of parameter in standard (pg/uL) (TABLE 3A);

V_{ex} = Final volume of extract (mL);

V_{water} = Volume of water extract (L).

5.2 DETERMINATION OF POLYCHLORINATED BIPHENYLS: The polychlorinated biphenyls are determined and reported as total PCB's by packed column chromatography. Samples containing mixed Aroclors or predominantly one Aroclor can be analyzed by this technique. Compounds are identified by comparison of retention times and quantitated by comparison of responses from sample chromatograms to those from standards.

5.2.1 Gas Chromatographic Conditions for Determining PCB's: For PCB determinations, the HP 5710 gas chromatograph is equipped with packed glass columns. The samples are analyzed isothermally at 190°C with an injection temperature of 250°C and the detector at 300°C. Argon/methane (95/5) (abbreviated as Ar/Me) is used both as the carrier gas and as the make up gas. Flow rate of carrier and make up gas are both 30 ml/min.

5.2.2 Mixed Aroclors: For mixed Aroclors a 1:1:1 mixture of Aroclors 1242:1254:1260 (TABLE 2A) serves as the standard and this gives 24 distinct peaks on packed column GC. In environmental samples it is frequently not possible to identify all 24 peaks. In order to report an Aroclor the specific pattern of peaks similar to the mixture must be present and a minimum of 8 peaks with distinct Aroclor patterns are required to confirm the presence of PCB's.

During analysis the chromatographic reproducibility should be assessed by comparing relative retention times (RRT) of the sample peaks with corresponding peaks in the PCB standard mixture run under identical GC conditions. The RRT variance should not exceed +/- 2.5 % when compared to Peak # 15 RRT

NOTE: THE ANALYST SHOULD REJECT ANY SAMPLE PEAKS WHICH ARE JUDGED TO BE PROPORTIONALLY MUCH GREATER IN PEAK AREA OR HEIGHT WHEN COMPARED TO THE CORRESPONDING PEAK OF THE EXTERNAL PCB ANALYTICAL STANDARD. SUCH PEAKS THAT ARISE AT THE RETENTION TIME OF ALDRIN MAY BE DUE TO SULPHUR. IN ADDITION p,p'-DDE MAY GIVE LARGE PEAKS WITH RETENTION TIMES SIMILAR TO THOSE OF PEAKS 11 AND 12. UNRESOLVED CHROMATOGRAPHIC PCB PEAKS WITH RETENTION TIMES SIMILAR TO THAT OF SURROGATE SPIKES ARE REJECTED.

For quantitation the 1:1:1 mixture of Aroclors 1242: 1254: 1260 at a concentration 200 pg/uL serves as a standard. Two to five uL of this standard and an identical aliquot of sample are injected. Peak heights or areas of a minimum of six identified peaks in the chromatogram are summed and the total response in the sample versus total response in the standard is calculated as described in section 5.2.4. PCB

presence is confirmed by qualitative examination of Fraction A capillary column chromatograms.

5.2.3 Determination of Samples With One Predominant Aroclor: For samples containing one predominant Aroclor the above procedure (section 5.2.2) may be modified to ensure that the analytical standard used for quantitation closely matches the Aroclor in the sample. A minimum of 30% of peaks from an individual Aroclor must correspond to chromatographic peaks present in the sample before establishing identification of the individual Aroclor.

5.2.4 Calculation of Concentration of PCB's: For PCB's in water the concentration in the water sample (C_{sam}) is given as follows:

$$C_{sam} = V_e \times C_e / V_{sam} \times 1000$$

Where:

C_{sam} = Concentration of PCB in sample (ng/L);

V_e = Volume of Extract (mL);

V_{sam} = Volume of sample (L);

C_e = Σ sample response/Σ standard response x Standard conc^n (pg/uL) (summed over all n peaks in sample and standard).

Typical results for the analysis of water are shown in TABLE 8.

6.0 GC/ MS DETERMINATION OF SELECTED AROMATIC ANALYTES:

MASS SPECTROMETER/ DATA SYSTEM: The mass spectrometer is a Finnigan 4500 quadrupole instrument. For analysis of volatiles, electron impact ionization (EI) at 70 EV is used. High sensitivity quantitative determination of target analytes utilizes appropriate multiple ion detection.

The GC/MS data from both standard and sample analyses is collected and stored on the data system. Standard libraries are created by determining pure standards under exactly the same conditions used for sample acquisition and processing. Hardcopies of standard and sample data are created for spectra of interest. Sample spectra are displayed with standard spectra and the purity or fit as an indication of the degree of match are recorded. Positive confirmations are hardcopied showing spectra of samples and standard library comparison. The base peak of the mass spectrum is used for quantitation.

The polynuclear aromatic hydrocarbons (PAH), phthalate esters (PhthE), 2,3,7,8-tetrachlorodibenzodioxin (TCDD) and phenols are determined by capillary gas chromatography with electron impact, multiple ion monitoring (MIM) mass spectrometric detection. The identification is based on both gas chromatographic retention time and the ratios of selected ions characteristic of analyte. The protocol was developed by SHRADER LABORATORIES (3814 Vinewood, Detroit Mich. 48208) under contract to NWQL. It is an effective compromise between two modes of mass spectrometric analysis: the highly sensitive single ion monitoring mode which lacks structural information and the full scan mode which is considerably less sensitive. In order to ensure unit resolution and maximum sensitivity over the mass range of interest, the mass spectrometer is calibrated using perfluorotributylamine (FC 43).

6.1 Sample Preparation: Five uL of ISTD containing 10 ng of perdeuterated anthracene (anthracene D 10) is added to the 1 ml iso-octane concentrate received from the work-up of the LVX neutral and acidic extract (sections 4.1.-ii and 4.1.1 respectively). The anthracene D 10 serves as a standard for internal calibration of retention times for the analytes and for calibration of relative response factors used in calculation of quantities. The 1 mL analyte solution is carefully concentrated under a gentle of nitrogen in glass inserts to 25 uL and 1-2 uL of this solution is injected on capillary column for GC/MIM analysis.

6.2 Determination of Aromatic Analytes: Analysis of the concentrated extract is carried out under the following conditions. The column is a DB 5 with dimensions 30 M by 0.25 mm i.d and a coating of 0.25 u. One uL of sample is injected through a J & W on-column injector linked to the analytical column through the guard column (section 3.1.3-iv). The initial oven temperature of 70°C is held for 3 min. and then programmed at 10°C/min to 300°C, and this final temperature was held for a further 10 min. The ion source of the mass spectrometer is maintained at 150°C. The carrier gas is helium with a column head pressure was 10 p.s.i.

6.3 Calibration of Quantitation Library for GC/MIM Determination: The concentration is calculated by a two point calibration. For each set of environmental samples the GC/MS library is calibrated using two standard mixtures. The first contains the polynuclear aromatic hydrocarbon, phthalate ester and phenolic analytes ranging from 0.2 to 0.8 ng/uL (TABLE 3B). The second solution contains the same analytes in the range 0.025 to 0.2 ng/uL as well as 2,3,7,8-TCDD in the same range. Both solutions contain anthracene D 10 at 0.1 and 0.4 ng/uL respectively. The retention time and response of each analyte relative to anthracene D 10 is the basis of the calibration used in the Shrader Protocol.

The responses obtained from the two standards are averaged and compared with the cumulative average from previous runs. If this is within 20%, the current value is included in the cumulation. If it is outside these limits a new cumulative average is begun.

Before the samples are run a retention time window for each analyte is set. During a given time window the mass spectrometer will be monitoring 4 to 8 ions characteristic for the analyte(s) that appear(s) in that particular window. The window is set at 60 and 120 seconds for standard and samples respectively. This is sufficiently wide to allow for a 5% retention time window. A 1 uL aliquot of the sample is then injected for GC/MIM determination.

NOTE: IT IS IMPORTANT IN THE SEQUENCE OF ANALYSES THAT ONE SET OF STANDARDS ARE RUN FOR EACH SET OF 5 SAMPLES. THIS INFORMATION IS ADDED TO THE DATA BASE IN THE LIBRARY. THIS CONTROLS FOR ANY POTENTIAL CHANGES IN GC OR MS CONDITIONS THAT COULD POTENTIALLY ALTER EITHER THE RETENTION TIME OR THE FRAGMENTATION PATTERN. ANY MAJOR CHANGES IN THESE MAY INDICATE A POTENTIAL PROBLEM. SUCH CHANGES SHOULD BE DOCUMENTED AND REMEDIAL ACTION TAKEN IF DEEMED NECESSARY. THE NATURE OF THE REMEDIAL ACTION AND THE DATE TAKEN ARE TO BE RECORDED.

6.4 Identification and Quantitation: All the data is stored on disk. Identification of structure and quantitation are carried out after completion of the GC/MIM procedure. The program searches the mass chromatogram and confirms the following;

(a) a chromatographic peak at the relative retention time of the analyte and

(b) the occurrence of the appropriate ions at that time. The molecular ion or base peak comprises the identifying ion and the other high to medium intensity ions are the confirming ions. This data is summarized in TABLE 6 and 7.

NOTE: THE FIT IS CALCULATED BASED ON BOTH RELATIVE RETENTION TIMES AND MASS SPECTRAL INFORMATION ACCORDING TO EQUATIONS DEFINED IN THE SHRADER PROTOCOL AND SUMMARIZED BELOW.

$$FIT_{gc} = 1 - (RT_{std} - RT_{an})/RT_{std}$$

$$FIT_{ms} = 1 - \Sigma(I_{std} - I_{an})/n\text{-}1$$

Where:

RT = Relative Retention time

std = Standard

an = Analyte

n = number of ions in the spectrum.

I = Intensity of ions normalized to the ANTHRACENE D 10.

$$FIT_{total} = FIT_{gc} \times FIT_{ms}$$

If the relative retention time is correct within the precision of the method and both the identification and confirming ions are present and in correct ratio then a positive identification is made. A FIT value greater than 0.9 is taken as a positive identification. In this case the mass fragmentograph and the attenuated mass spectrum appear briefly on the screen, the analyst either accepts or rejects the information and then the program moves to the next GC peak.

If the fit is between 0.75 and 0.9 then a tentative identification is made; the mass chromatogram and both library and attenuated mass spectrum of the analyte appear on the screen. The analyst must carry out further manipulation of the data to complete the identification. If the fit is below 0.75 then the program makes the decision that the analyte does not have a library match, no identification is made and the program does not pause or display the spectrum.

If a positive identification is made then it is possible to obtain a quantitative determination of the now identified analyte. This quantitation is by internal calibration method with the anthracene D 10 as the calibration standard according to the following equations and RF is defined as follows.

$$RF = (W_i/A_i) \times (A_{an}/W_{an})$$

Where:

RF = Response factor (average)

W = Weight (ug);

A = Area under the gc peak;

i = Internal standard;

an = Analyte.

Once the RF for a compound has been determined the amount of analyte in the sample can be determined. The calculation is based on two point calibration by external standardization according to the following equation.

$$W_{an} = (W_i/A_i) \times (A_{an}/RF)$$

NOTE: THE REPORTED VALUE OF W_{an} CANNOT BE SMALLER THAN THE INSTRUMENTAL DETECTION LIMIT. IF W_{an} IS CALCULATED AS LESS THAN THE INSTRUMENTAL DETECTION LIMIT THIS VALUE IS REJECTED AND REPORTED AS ZERO.

7.0 QUALITY CONTROL:

The purpose of quality control is to monitor the performance of a procedure. There are two aspects to the monitoring exercise. The first is to identify when the entire procedure does not function according to specifications. The second is to determine which sub process has failed. In this program each sample will be subjected to control for the entire procedure based on recovery of surrogate standards added to the LVX mixing chamber during the extraction phase. In addition, method spike recovery of analytes added to the reagent water during an extraction will be determined with every 20 samples to provide data on the variability of the method. Sub-processes will be monitored by running solutions of analytes in the appropriate solvent through evaporation, concentration and clean-up phases.

7.1 Control of the Entire Isolation Process: For each sample collected in the field 100 mL of solution FSM1 containing 40 ng of 1,3,5-tribromobenzene and 1,2,4,5-tetrabromobenzene and 20 ng of δ-BHC is added directly to the LVX mixing chamber. Recovery of these surrogates acts as a monitor of the entire extraction, concentration and fractionation steps of the procedure.

7.2 Monitoring of Recovery of Parameters: With every 20 samples the entire process is tested to determine recoveries and any possible procedural interferences. Recoveries are determined by adding 20 uL of SS1, SS2 and SS3 containing neutral analytes at concentrations shown in TABLE 2A to the 100 mL of FSM1 and the resulting solution is spiked into 40 liters of the reagent water and subjected to the entire isolation procedure as described in section 4.

7.3 Control of Concentration Sub-process: Solution SM2 (TABLE 2A) containing 1,3-dibromobenzene is added to every extract of water received from the field. This surrogate spiked into the sample prior to the concentration step (section 4.1-ii) acts as a control for losses of the chlorobenzenes during evaporation.

7.4 Control of Fractionation: Solution SM3 (TABLE 2A) is spiked into the 2 mL of each sample concentrate prior to fractionation (section 4.2-ii). The surrogate 2,3,5,6-tetrachlorobiphenyl monitors separation into fraction A and endrin ketone monitors separation into fraction B.

7.5 Recording of and Acting on Quality Control Data: The data from the surrogate standards and the samples from the sub-processes are charted as percent recoveries (FIGURE 13). The graph contains the

expected concentration and the upper and lower control limits which are defined as + two standard deviations. The daily results are recorded and a value outside of these control limits indicates a problem that requires assessment.

7.6 **Maintaining Instrument Performance**: The two separated fractions A and B are both spiked with solution OCN (TABLE 2A) in order to monitor instrument performance. The relative retention times of the parameters with respect to octachloronaphthalene is used as a calibration of the time axis.

7.7 **Proficiency Study**: Capability of the laboratory and individuals must be established through proficiency studies. Water is analyzed in controlled situations. For water the CB's, OCPEST., PCB's, (TABLE 2A) were spiked into one L of reagent and Niagara river water at concentrations ranging from 5 to 200 ng/L. These samples and corresponding blanks were extracted and analyzed as described in section 4.2 and 5. These results are presented in TABLE 9.

8.0 ANALYTICAL LIMITS:

In the National Water Quality Laboratory the terms: Instrumental detection limit (IDL), Method detection limit (MDL) and Practical detection limit (PDL) are used to characterize various aspects of the measured process. These also form a basis for comparison between various instruments, techniques and procedures. IDL, MDL and PDL are defined as the lowest concentrations which can be determined to be statistically different from the background signal. IDL is calculated from the standard deviation obtained from the replicate analysis of the calibrating solution using the same instrumental settings as those used for the analysis of samples. MDL and PDL are derived from standard deviations of spiked replicates in solvent and sample matrix respectively, carried through the entire procedure. These limits represent concentration levels at which there is 95% confidence that the analyte signal is statistically different from the background noise. These limits are established as follows:

(a) The IDL is established by analysing a calibrating standard solution which contains a final concentration of individual analytes at five to ten times the estimated IDL. The standard deviation from replicate injections is calculated and the IDL is derived using the following equation:

$$IDL = t_{(n-1)} \times s_I$$

IDL IS EXPRESSED IN TERMS OF ng OF ANALYTE INJECTED ONTO THE COLUMN.

Where:

$t_{(n-1)}$ = the value of a one sided Student's t-distribution for n-1 degrees of freedom (at 95% confidence limits);

s_I = standard deviation determined by replicate analysis of standard solutions.

NOTE: THE EQUATION FOR THE INSTRUMENT DETECTION LIMIT DIFFERS FROM THE MDL ONLY IN THAT FOR THE IDL, THE S_b TERM IS ZERO BECAUSE THE BLANK UNDER STANDARD OPERATING CONDITIONS DOES NOT PRODUCE A DETECTABLE SIGNAL.

(b) Method Detection Limit (MDL) is the lowest concentration of analyte that can be reliably detected after spiking the analyte into solvent used for extraction and being carried through the entire procedure including extraction, concentration and instrumental analysis and still be statistically distinguished from reagent water carried through the entire procedure. The MDL is given by:

$$MDL = t_{(n-1)} \times s_M$$

Where:

$t_{(n-1)}$ = the value of a one sided Student's t-distribution for n-1 degrees of freedom (at 95% confidence limits);

s_M = standard deviation determined by analysis analytes spiked into solvent.

NOTE: FOR CALCULATION OF $t_{(n-1)}$ OR s, A MINIMUM OF 7 REPLICATE ANALYSES ARE REQUIRED.

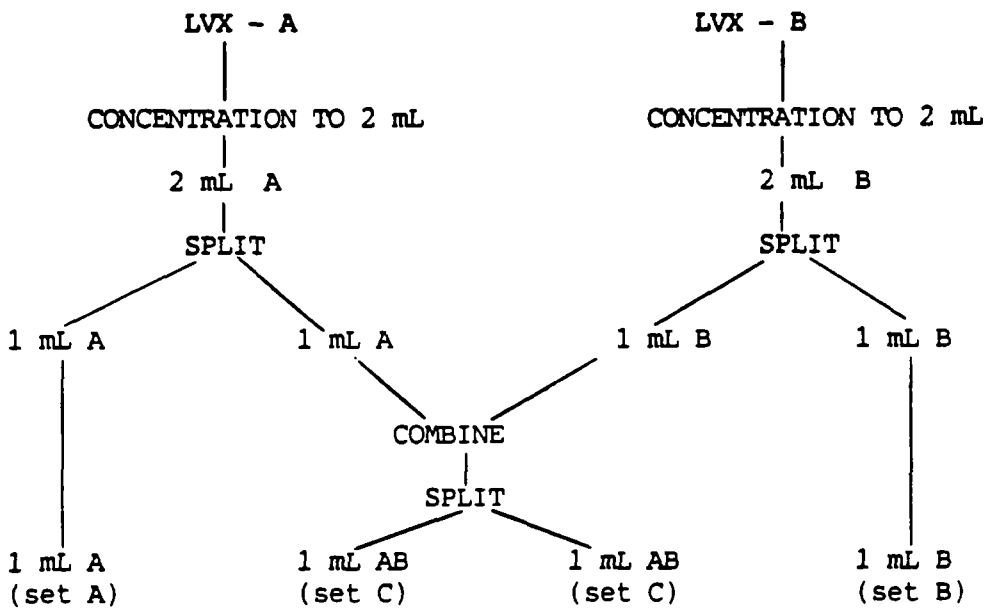
(c) Practical Detection Limit (PDL) is the lowest concentration that can be determined in a real sample matrix and is statistically distinct from the background response of a sample carried through the same procedure. It is determined by the same method as the MDL.

Calculated detection limits for water are presented in TABLE 10A & B.

9.0 OVERALL VERIFICATION PROCEDURE FOR SEMIVOLATILE ORGANIC POLLUTANTS:

The initial verification of the procedure was performed during the period of April-June 1986, by spiking organochlorine pesticides into 40 L of distilled-deionized water and carrying the spiked water through the entire extraction procedure. The results of spike recovery are shown in TABLE 11.

The procedure was further verified by undertaking a specially designed experiment where two extractors were simultaneously used at the NOTL station to collect 16 samples which were then processed using the following flow chart.



In this special experiment, 8 replicates of natural water were extracted in the field in duplicate using two identical LVX extractors operating simultaneously. The sampling stream was divided, spiked in each extractor with the compounds listed in TABLE 2 and extracted continuously at a flow rate of 600 mL/min. Over an 83 minute cycle time approximately 50 L of water was extracted. An additional 30 minutes was required to set up for the next extraction. These samples were collected continously over an 18 hour period.

The 8 pairs of extracts were concentrated in the laboratory to 2 mLs each. One mL of each pair were combined and re-split as per the flow chart. A total of 32 samples were analysed according to the procedure outlined in section 5. Results of the 8 samples of set A were compared to the 8 samples of set B to establish sampler variability. These results are presented in TABLE 12A. Analysis of the 16 samples of set C (TABLE 12B) established total variability of the procedures from the sampling to the quantitative analysis.

The whole excerise demonstrated that the performance of the paired extractors and the overall variation of the procedure was within acceptable limits (+/- 2 standard deviations).

In addition, 7 samples over 7 days were collected and analysed to complement the special experiment to establish total varaibility (background levels + extractor and laboratory varaibility). These results are presented in TABLE 13.

10.0 ORGANICS IN SEDIMENTS:

This method is designed to determine the semi-volatile organics that are present in the suspended sediment of the Niagara River. Sediment is separated from water in the Westfalia centrifuge and organics are isolated by solvent extraction at neutral and acidic pH. The two extracts are combined and are then analyzed in a manner similar to that described for the extracts from the LVX (sections 2-3). Thus the combined solvent extracts are concentrated to 10 mL and then this isolate is split into two 5 mL portions. One portion is used for mass spectral determination of phenols, polynuclear aromatic hydrocarbons and phthalate esters (section 6). The remaining 5 mL are used for determination of chlorobenzenes, organochlorine pesticides and PCB's as described in section 5.

11.0 PROCEDURE:

11.1 EXTRACTION OF WET SEDIMENT: Weigh approximately 10 g of wet sediment, which has been collected according to the sampling protocol (3), accurately (± 0.02 g) into a 250 ml stainless steel beaker. Add 100 mL of a 1:1 hexane:acetone (v/v) solution and 100 uL of SM1 (TABLE 2A) to the sample of sediment. This will deliver 200 ng of 1,3,5-tribromobenzene, 200 ng of 1,2,4,5-tetrabromobenzene and 100 ng of δ-BHC to the final 10 mL of extract. Sonicate the mixture of liquid and solid at full power for 3 minutes in an ice bath. A representative sample of wet suspended sediment is dried at 105°C to a constant weight to determine moisture.

NOTE: SONICATION GENERATES A CONSIDERABLE AMOUNT OF HEAT. THE ICE BATH IS REQUIRED IN ORDER TO PREVENT OVERHEATING WITH LOSS OF SOLVENT AND/OR SAMPLE.

Subsequent to sonication allow the fine particles of sediment to settle to the bottom of the beaker (1 to 2 minutes). Transfer the supernatant to the top of a prewashed 5 cm celite column in a glass filter funnel and allow to drain into a 1 L round bottom flask. Repeat the extraction, including sonication one more time. This fraction of the extract contains neutral organics which includes the polynuclear aromatic hydrocarbons. The latter class of compound is acid sensitive at atmospheric conditions.

NOTE: POLYNUCLEAR AROMATIC HYDROCARBONS ARE ALSO LIGHT SENSITIVE PARTICULARLY WHEN WIDELY DISTRIBUTED ON A SURFACE (SUCH AS A SEDIMENT). CARE MUST BE TAKEN TO REDUCE THE AMOUNT OF LIGHT EXPOSURE TO THE SAMPLE.

Acidify the remaining sediment sample to pH 2 by adding 6 drops of 50% H_2SO_4 and repeat the extraction twice more with 100 ml of the extracting solvent which is filtered through the same celite bed as used for the neutral fraction. This fraction of the extract contains the acidic phenols.

Add 100 uL SM2 (TABLE 2A) containing 500 ng of dibromobenzene and reduce the combined fractions to approximately 200 mL on the rota-evaporator. This 200 mL will contain predominantly hexane which is transferred to a 1 L glass separatory funnel.

NOTE: THE VOLUME OF SOLUTION REMAINING IN THE ROUND BOTTOM FLASK CAN BE ESTIMATED BY MONITORING THE VOLUME OF ACETONE IN THE RECEIVING RESERVOIR

Add 100 mL reagent water to the hexane isolate and then shake the resulting two phase mixture for 2 minutes and allow the phases to separate. If an emulsion occurs add 25 mL of a saturated sodium sulphate solution and again shake the emulsified mixture for 1 minute. The layers should quickly separate.

The water layer is drained into a 500 mL separatory funnel and extracted once with 100 mL CH_2Cl_2 and twice with 50 mL CH_2Cl_2. The CH_2Cl_2 layers are then combined with the hexane isolate in the original funnel. Residual water is removed from the combined extract by filtering through 5 cm of anhydrous sodium sulfate (section 3.8-ii) in an Allihn funnel (section 3.3-iv) and into a 500 mL round bottom flask.

Add 30 mL iso-octane as a keeper solvent to the volatile organic solvents. Using a rotary evaporator with a water bath at 30°C concentrate the extract to 20 mL. Add an additional 20 mL iso-octane and concentrate to 3-4 mL on the rotary evaporator under the same conditions. Transfer the extract to a calibrated 15 mL centrifuge tube using four 1 mL washes of iso-octane to wash the round bottom flask and dilute to 10 mL with iso-octane.

NOTE: EACH mL OF THIS EXTRACT CONTAINS THE ORGANICS FROM ONE GRAM OF SEDIMENT.

NOTE: LARGE VOLUMES OF ISO-OCTANE ARE USED AS KEEPER VOLUMES AND TO PREPARE DILUTIONS. AS THESE VOLUMES ARE EVAPORATED THE POLAR AND VOLATILE SOLVENTS SUCH AS ACETONE AND CH_2Cl_2 ARE EFFECTIVELY REMOVED FROM SOLUTION AND THUS DO NOT CAUSE VARIATIONS IN THE SUBSEQUENT CHROMATOGRAPHIC STEPS.

11.2 CHROMATOGRAPHIC FRACTIONATION: Add 100 uL solution SM3 (TABLE 2A) containing 200 ng of tetrachlorobiphenyl and 100 ng endrin ketone to the 10 mL isolate (section 11.1). Divide into two equal portions and fractionate one aliquot using a modification of the procedure described in section 4.2. The variations in the procedure are:

(a) After elution 10 mL of iso-octane are added to each fraction and the solutions concentrated to 2 mL.

(b) The 2 mL of concentrate are diluted to 5 mL in a calibrated 15 mL centrifuge tube with three 1 mL washes of iso-octane. Fifty uL of OCN solution (TABLE 2A) containing 120 ng of Octachloronaphthalene are added to the 5 mL of both fractions.

After the fractionation and concentration steps treat the 5 mL portion of Fraction A with 0.2 mL of prepurified mercury to remove sulfur. If necessary (ie if sulfur is still present as evidenced by a darkened colouration of the surface of the mercury) repeat this by decanting the iso-octane and add an additional 0.2 mL of prepurified mercury. The final preparation which is free of sulfur is now ready for use in gas chromatographic analysis.

12.0 INSTRUMENTAL ANALYSIS OF SEDIMENT EXTRACTS:

The instrumental techniques and calibration standards used in the analysis of organics in sediment are those described in sections 5 (GC/ECD) and 6 (GC/MIM). Equations for calculating amounts of analyte are similar to those in section 5.1.2 and 5.2.4 with the only change being that sample amount is expressed in grams instead of a volume measure. Typical results for the analysis of suspended sediment calculated on a wet and dry weight basis are shown in TABLE 14A and B.

13.0 QUALITY CONTROL:

The purpose of quality control is to monitor the performance of a procedure. There are two aspects to the monitoring exercise. The first is to identify when the entire procedure does not function according to specifications. The second is to determine which sub process has failed. In this program each sample will be subjected to control for the entire procedure based on recovery of surrogate standards added to the sample of sediment. In addition, method spike recovery of analytes added to the reference sediment (section 3.3-vi) will be determined with every 20 samples to provide data on the variability of the method. Sub-processes will be monitored by running solutions of analytes in the appropriate solvent through evaporation, concentration and clean-up phases.

13.1 Control of the Entire Isolation Process: For each sample collected in the field solution SM1 containing 1,3,5-tribromobenzene, 1,2,4,5-tetrabromobenzene and δ-BHC is added directly to the sample of sediment. Recovery of these surrogates acts as a monitor of the entire extraction, concentration and fractionation steps of the procedure.

13.2 Monitoring of Recovery of Parameters: With every 20 samples the entire process is tested to determine recoveries and any possible procedural interferences. Recoveries are determined by spiking SS1, SS2 and SS3 containing neutral analytes at concentrations shown in TABLE 2A and SM1 containing surrogates to reference and subjected to the entire isolation procedure as described in section 10.

13.3 Control of Concentration Sub-process: Solution SM2 (TABLE 2A) containing 1,3-dibromobenzene is added to every extract of sediment received from the field. This surrogate spiked into the sample prior to the concentration step (section 4.1-ii) acts as a control for losses of the chlorobenzenes during evaporation.

13.4 Control of Fractionation: Solution SM3 (TABLE 2A) is spiked into the 10 mL of each sample concentrate prior to fractionation (section 4.2-ii). The surrogate 2,3,5,6-tetrachlorobiphenyl monitors separation into fraction A and endrin ketone monitors separation into fraction B.

13.5 Recording of and Acting on Quality Control Data: The data from the surrogate standards and the samples from the sub-processes are charted as percent recoveries (FIGURE 14). The graph contains the expected concentration and the upper and lower control limits which are defined as + two standard deviations. The daily results are recorded and a value outside of these control limits indicates a problem that requires assessment.

13.6 Maintaining Instrument Performance: The two separated fractions A and B are both spiked with solution OCN (TABLE 2A) in order to monitor instrument performance. The relative retention times of the parameters with respect to octachloronaphthalene is used as a calibration of the time axis.

13.7 Proficiency Study: At initiation of the investigation capability of the laboratory and individuals is established through proficiency studies. Sediment is analyzed in controlled situations. The CB's, OCPEST. and PCB's (TABLES 2) were spiked into 10 g of wet matrix sediment (section 3.3-vi) concentrations ranging from 5 to 200 ng/g these samples and corresponding unspiked sediment were extracted and analyzed as described in section 10. These results are presented in TABLE 15.

14.0 OVERALL VERIFICATION FOR PROCEDURE FOR SEMIVOLATILE ORGANIC POLLUTANTS:

A bulk sediment collected at the Niagara on the Lake sampling site was routinely spiked with chlorobenzenes, organochlorine pesticides, PCB's, PAH's and phenols and processed with every batch of 16 sediments collected from Fort Erie and Niagara on the Lake . The spike recovery and associated information is presented in TABLE 16.

15.0 DETECTION LIMITS:

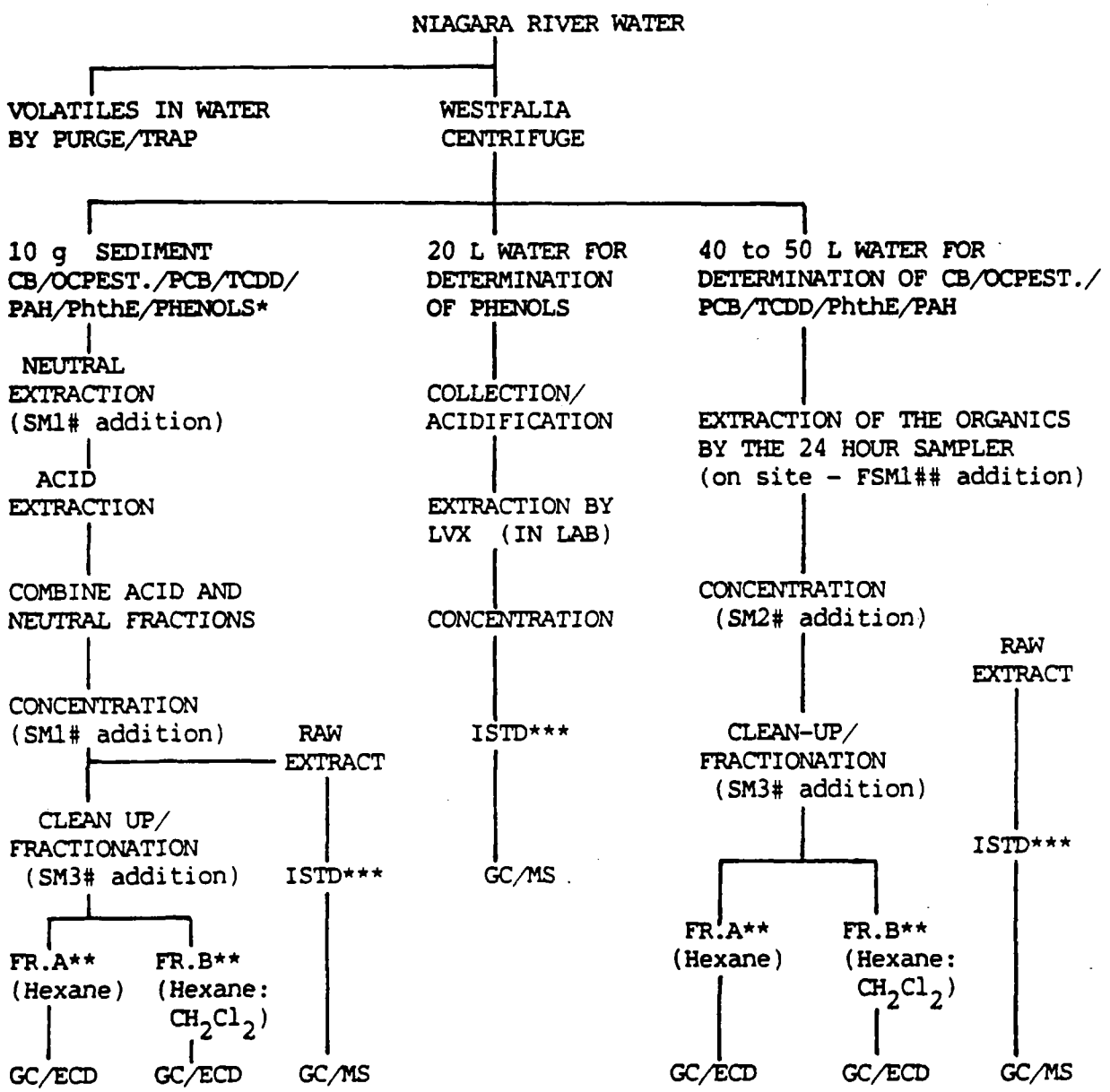
Detection limits are calculated as described in section 8 and on a per gram wet and dry weight basis and are summarized in TABLE 17A and B.

16.0 REPORTING OF DATA:

All water data are calculated as ng/L and suspended sediments are calculated on a dry weight basis as ng/g. Results are entered into a computer onto a spread-sheet. Data is transferred electronically for use by the project managers. Hard copies of data in the form computer printouts are generated and submitted as well.

FIGURE 1:

SCHEMATIC OF ANALYSES FOR ORGANICS IN NIAGARA RIVER

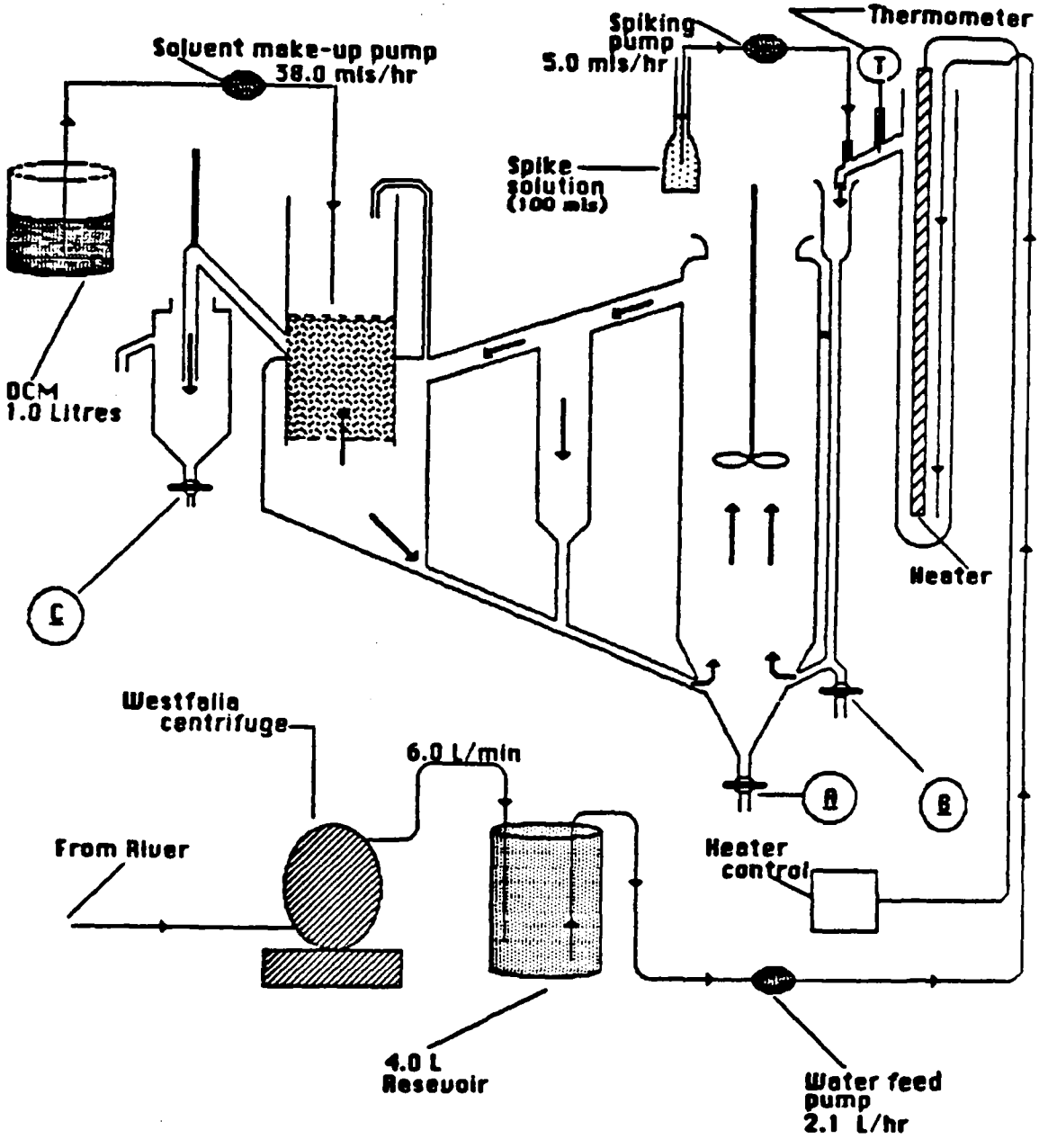


* CB = chlorobenzenes; OCPEST.= organochlorine pesticides; PCB = polychlorinated biphenyls; TCDD = 2,3,7,8 TCDD; PhthE = phthalate esters; PAH = polynuclear aromatic hydrocarbons

** FR = FRACTION (section 4.2.ii) # TABLE 2A

*** ISTD = INTERNAL STANDARD (anthracene D 10) ## TABLE 4

FIGURE 2: FLOW DIAGRAM OF THE LARGE VOLUME EXTRACTOR



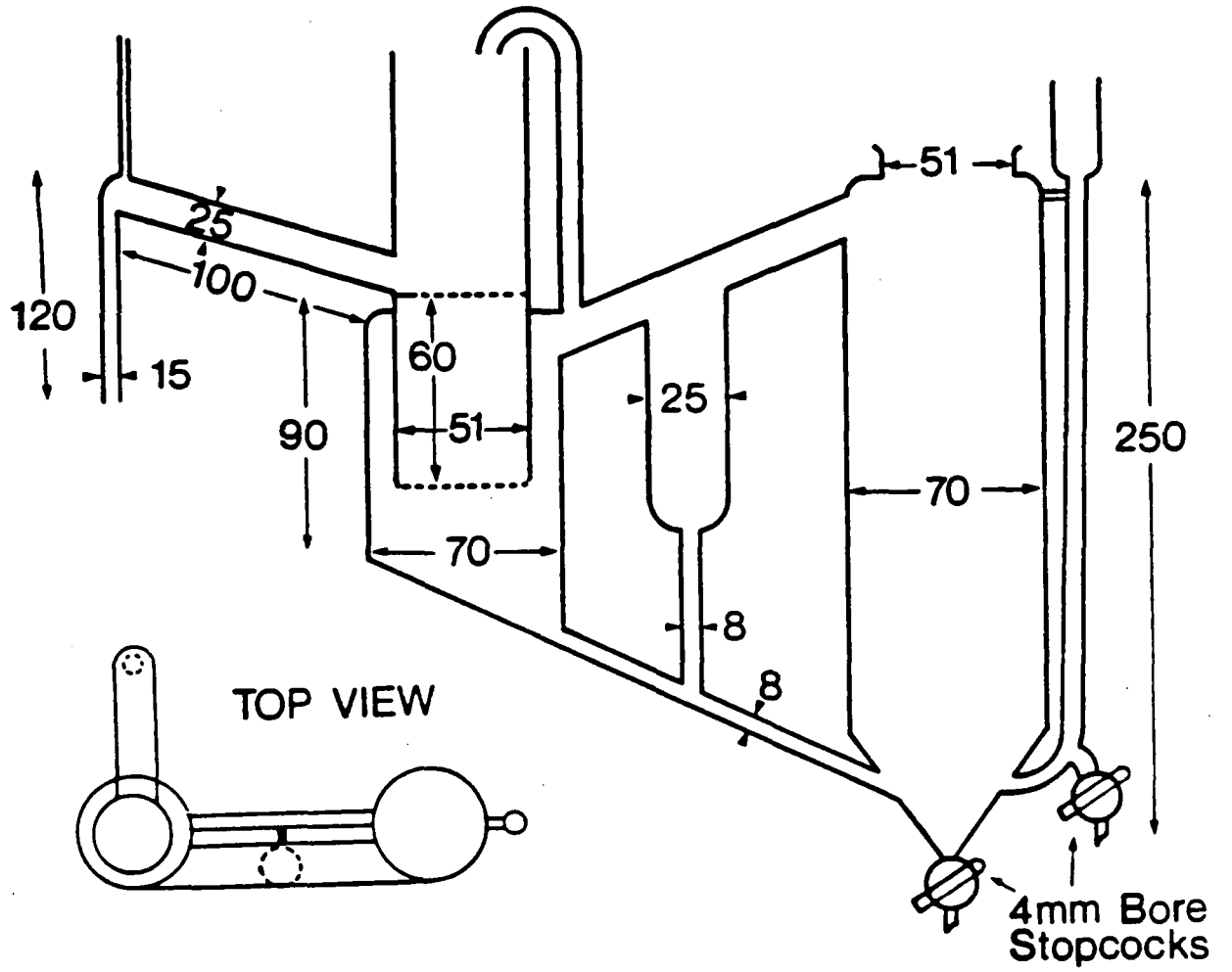


FIGURE 3: THE 38 mL PER MINUTE EXTRACTOR
(field)

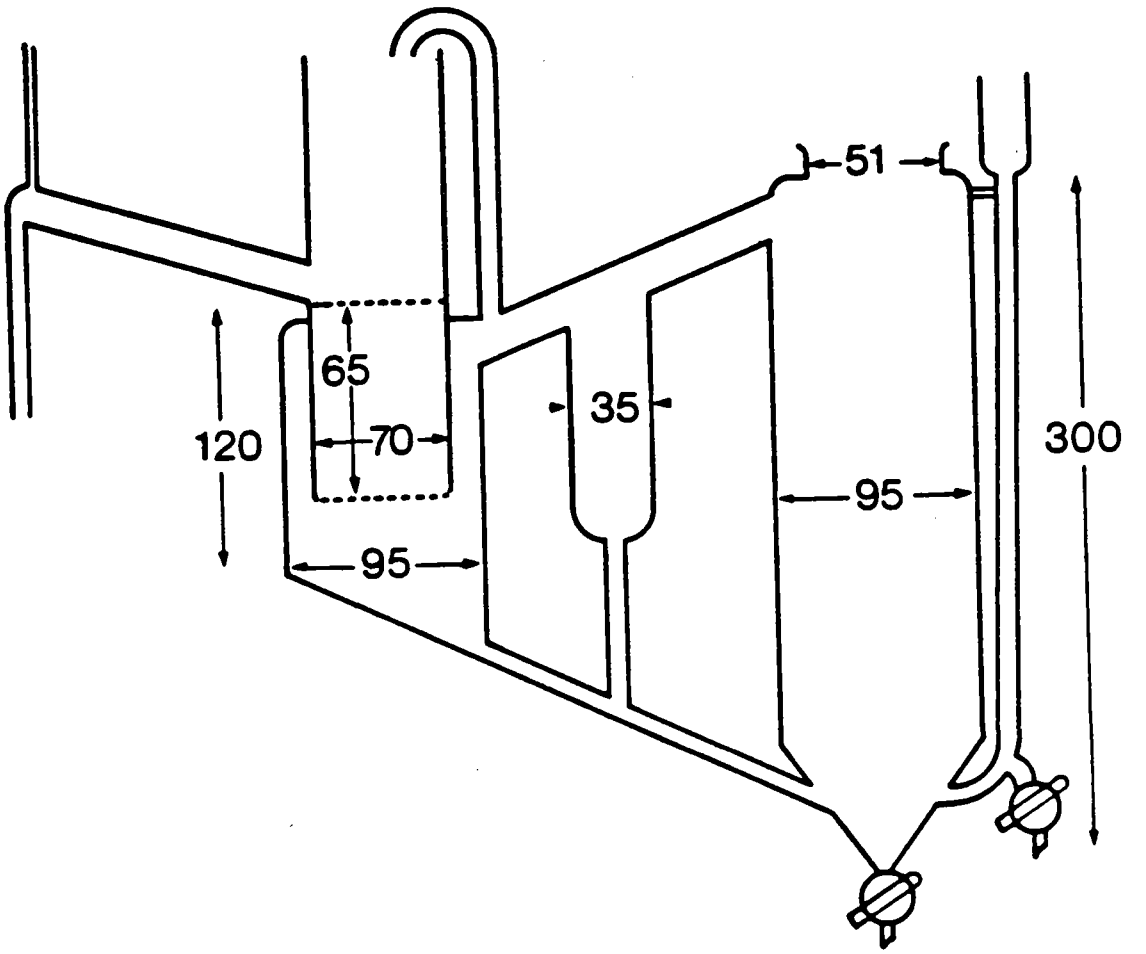


FIGURE 3: continued
THE 600 mL PER MINUTE EXTRACTOR
(lab)

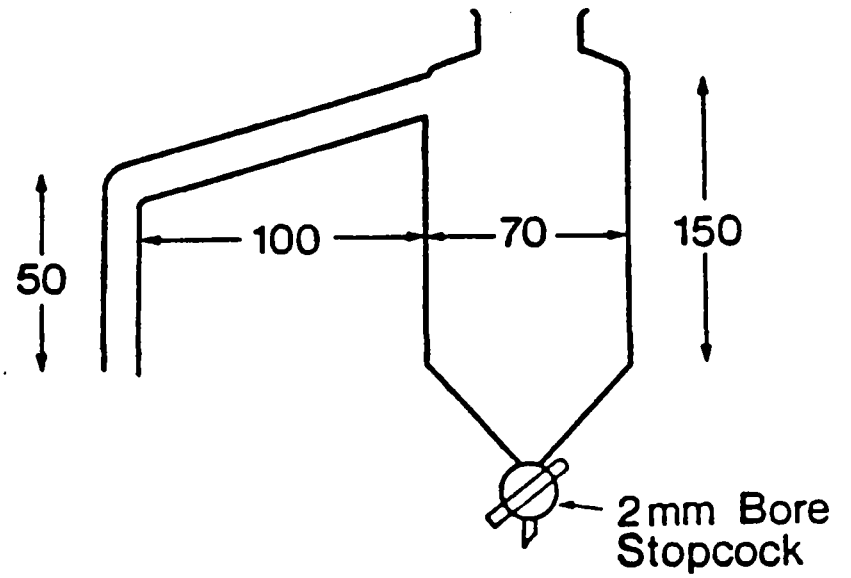
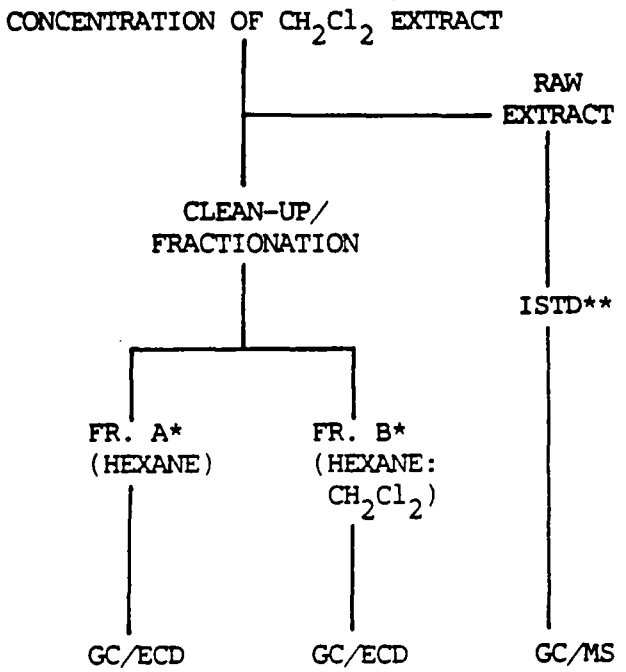


FIGURE 4: DETAIL OF THE SEPARATOR TRAP
(dimensions are in mm)

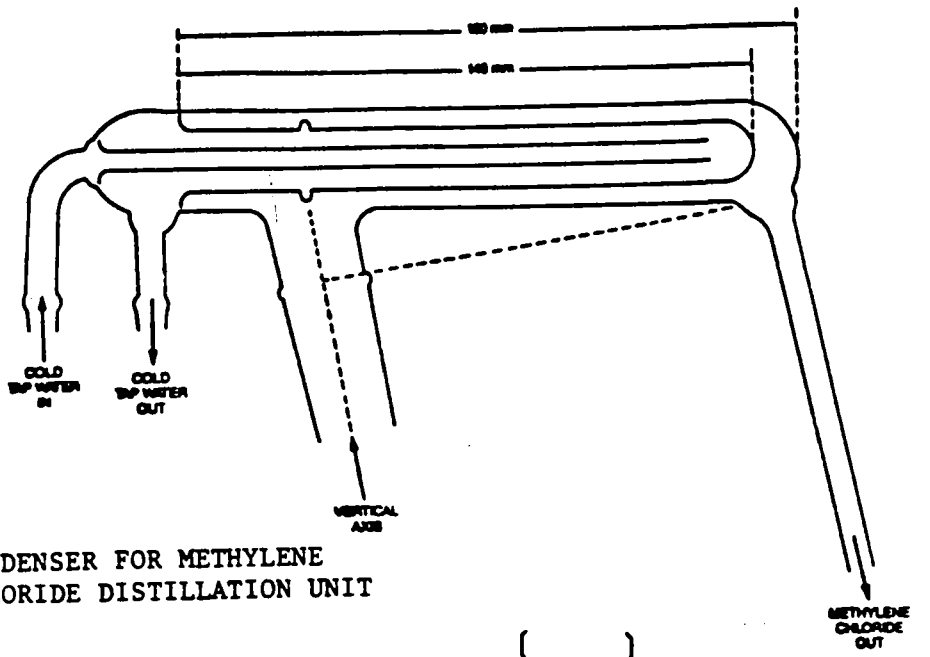
FIGURE 5:

SCHEMATIC FOR THE POST-EXTRACTION PHASE OF SAMPLE PREPARATION

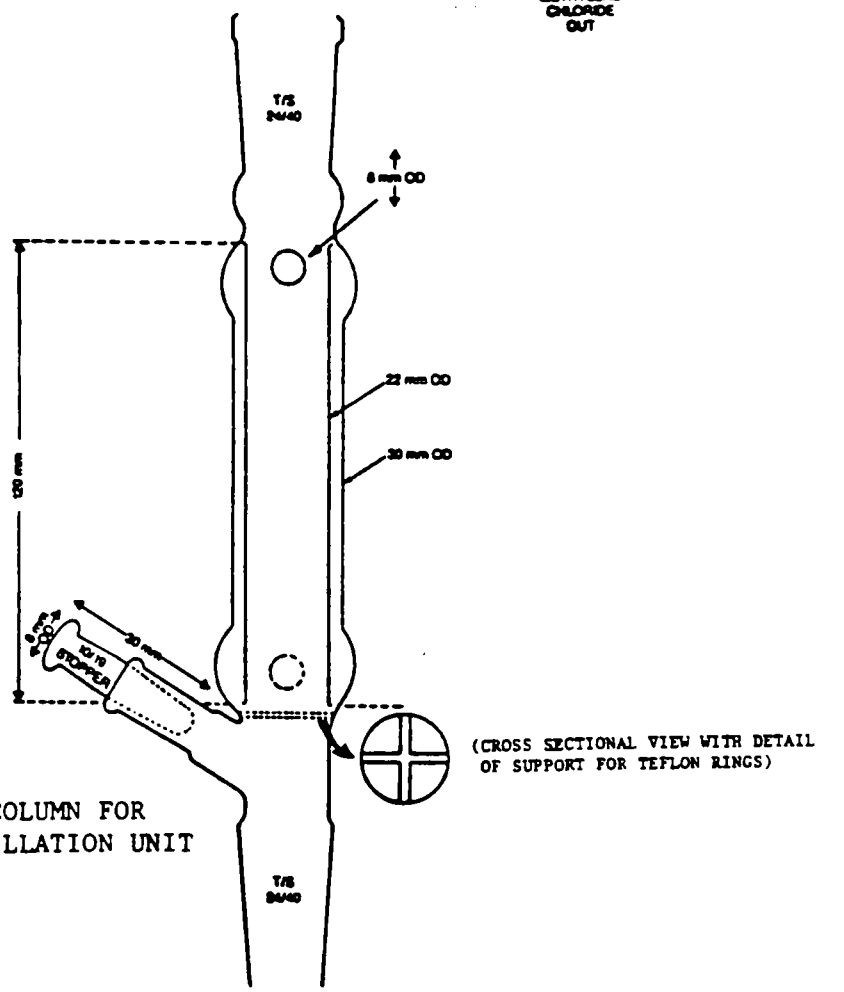


* FR.= CHROMATOGRAPHIC FRACTION (SECTION 4.2-ii)

** ISTD = INTERNAL STANDARD (anthracene D 10)



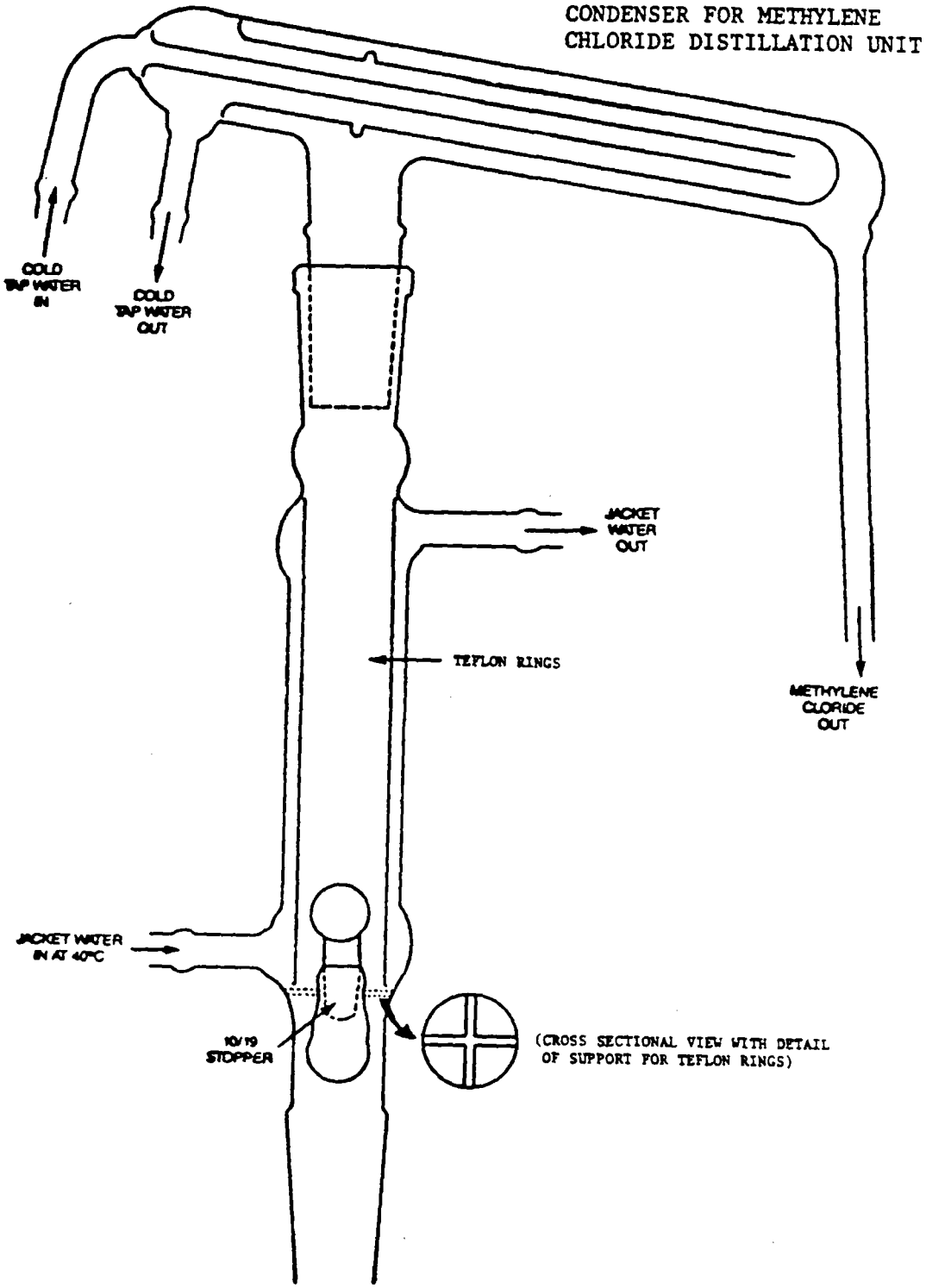
CONDENSER FOR METHYLENE
CHLORIDE DISTILLATION UNIT



(CROSS SECTIONAL VIEW WITH DETAIL OF SUPPORT FOR TEFLON RINGS)

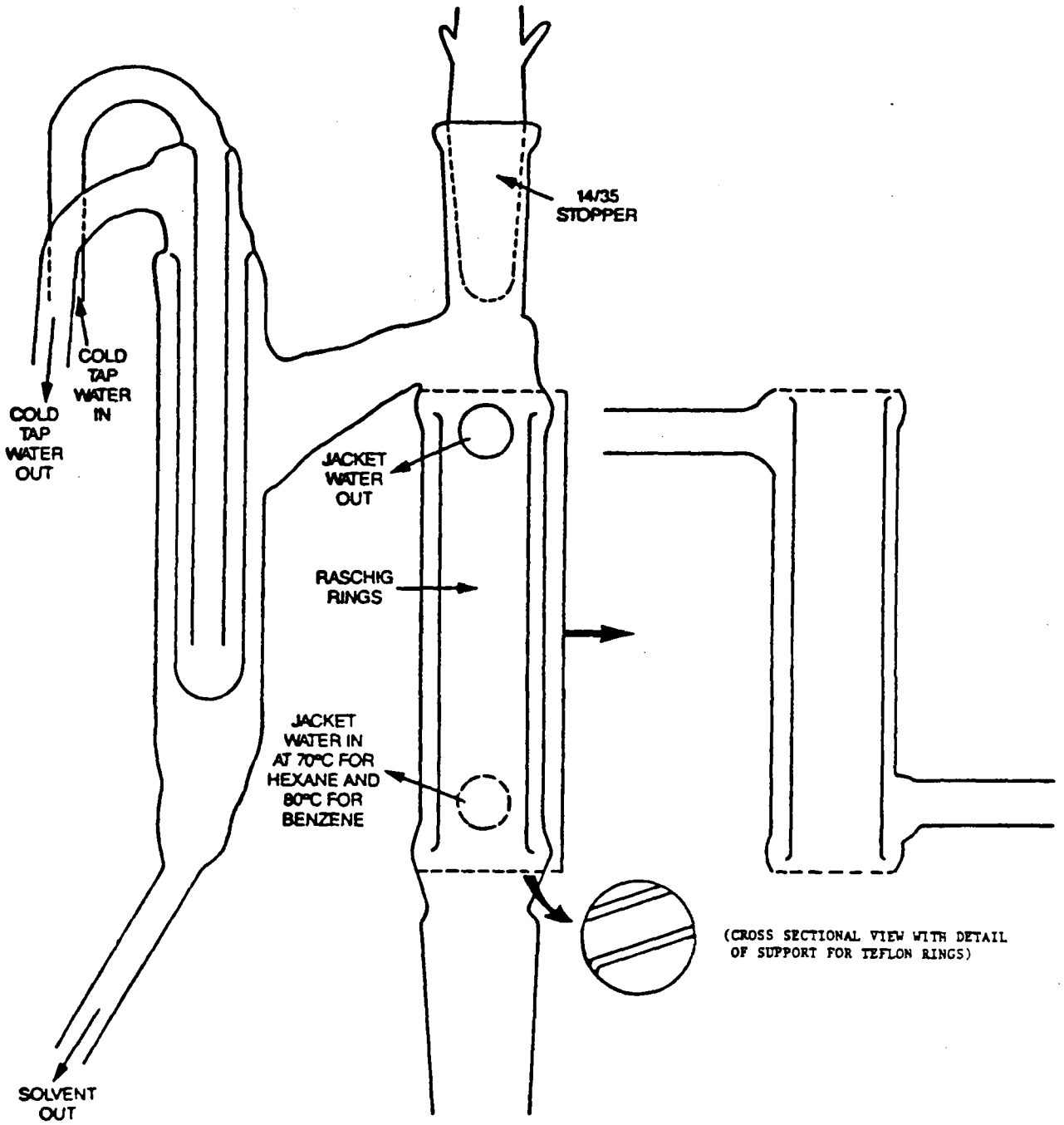
JACKETED FRACTIONATION COLUMN FOR
METHYLENE CHLORIDE DISTILLATION UNIT

FIGURE 6: EXPLODED VIEW OF THE GOULDEN EVAPORATOR FOR DISTILLATION OF CH_2Cl_2



JACKETED FRACTIONATION COLUMN FOR
METHYLENE CHLORIDE DISTILLATION UNIT

FIGURE 7: GOULDEN EVAPORATOR FOR DISTILLATION OF CH_2Cl_2



HYDROCARBON DISTILLATION UNIT

FIGURE 8: GOULDEN EVAPORATOR FOR DISTILLATION OF HEXANE

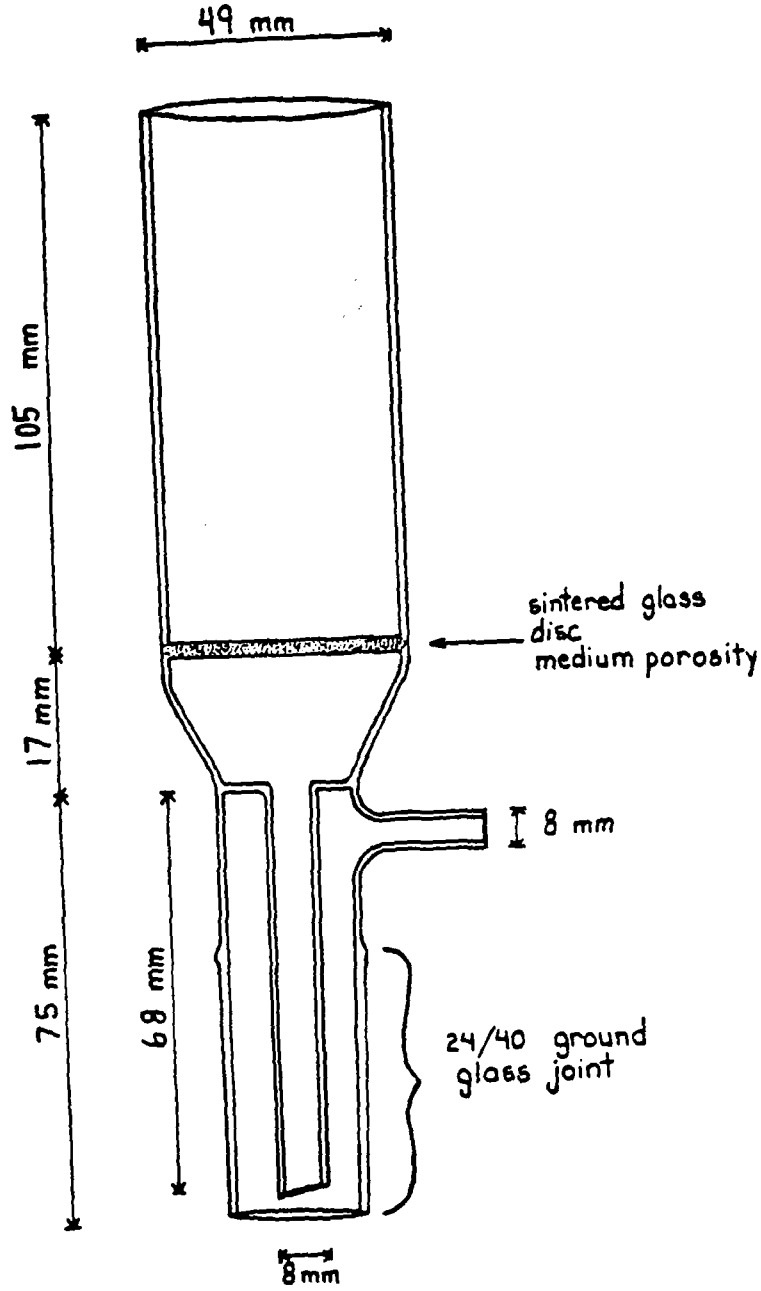


FIGURE 9: ALLIHN FUNNEL

FIGURE 10: CAPILLIARY COLUMN GC/ECD TRACE OF FRACTION A STANDARDS

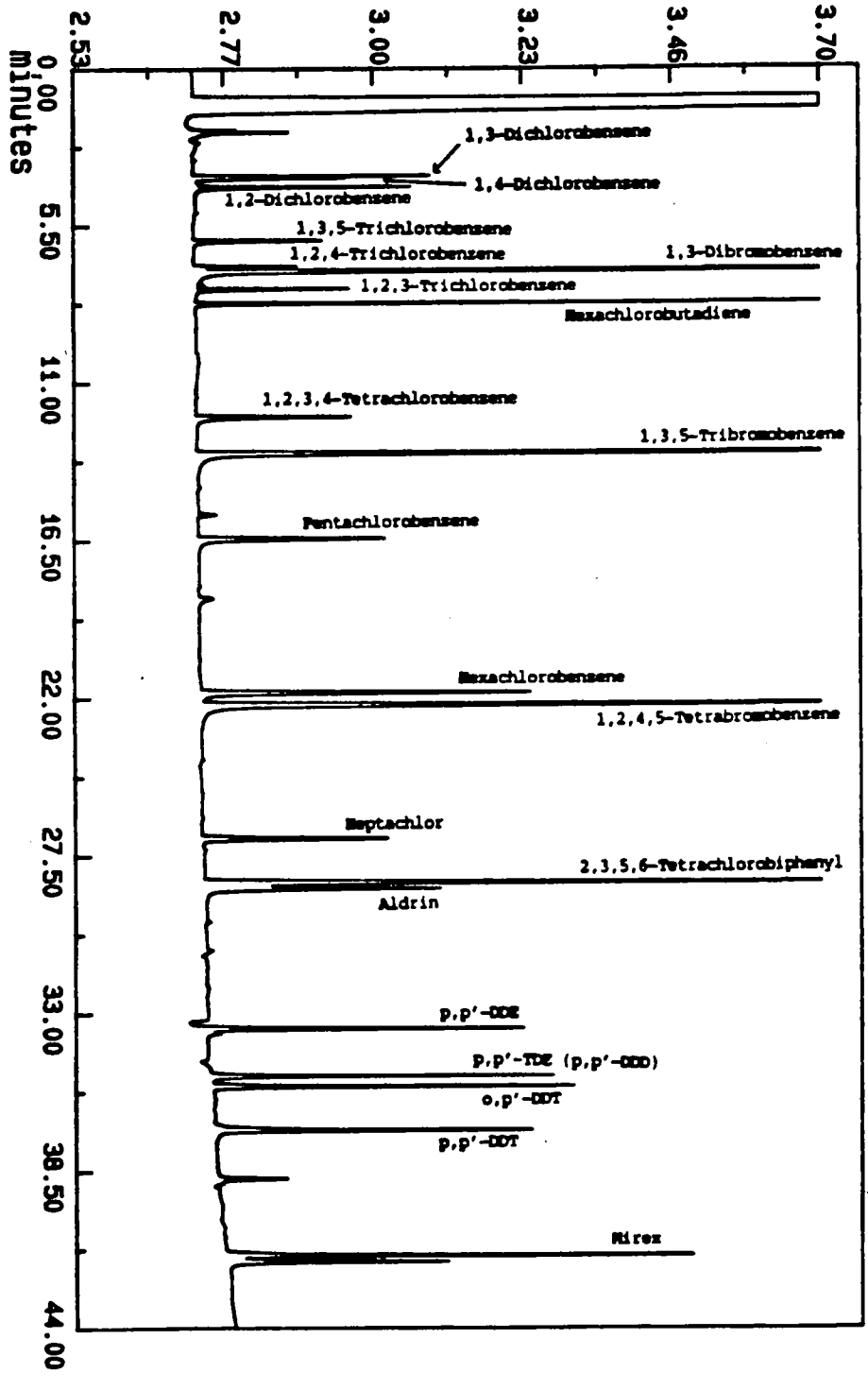


FIGURE 11: CAPILLIARY COLUMN GC/ECD TRACE OF FRACTION B STANDARDS

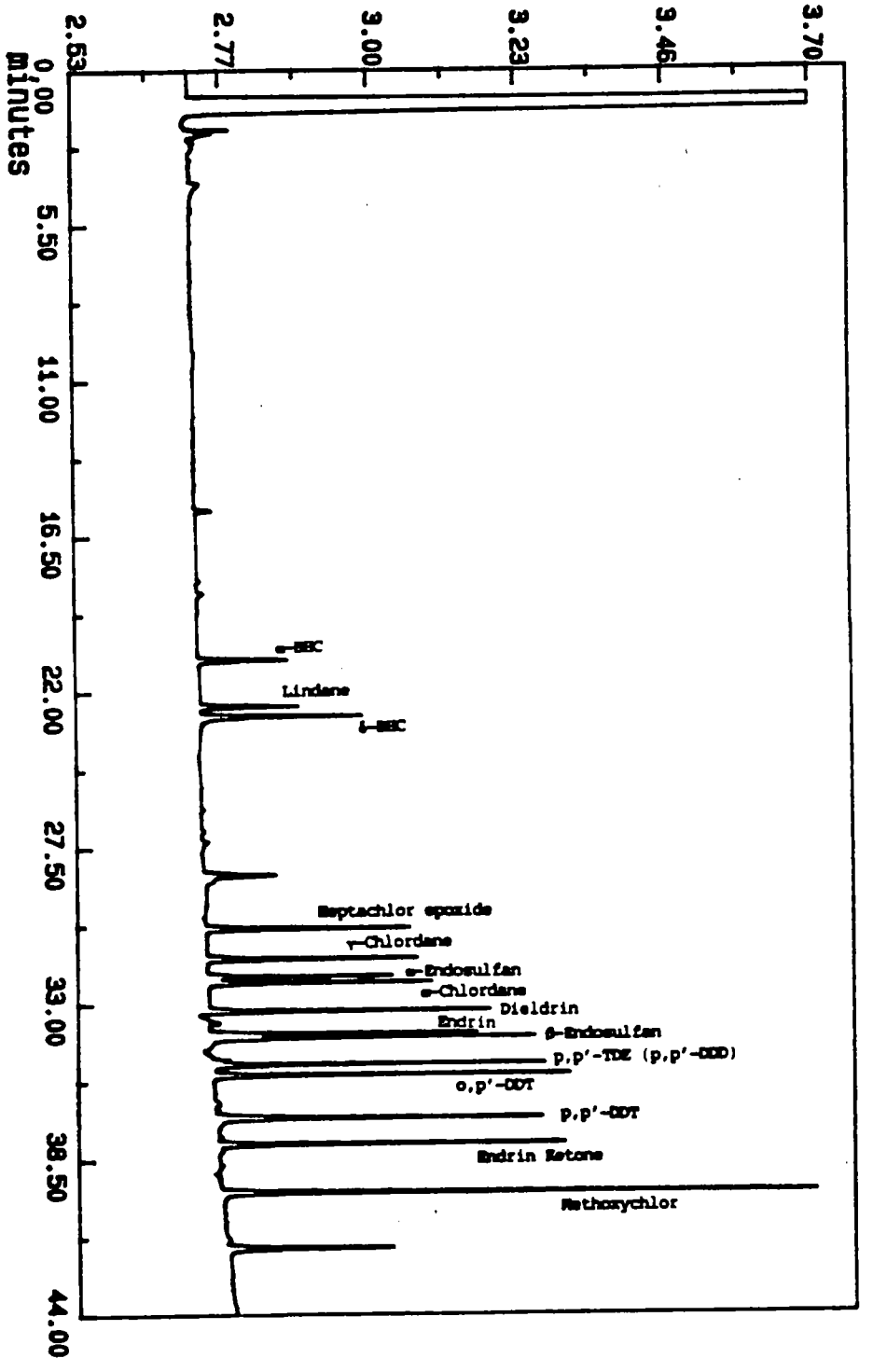


FIGURE 12: PACKED COLUMN GC/ECD TRACE OF FRACTION A PCB's

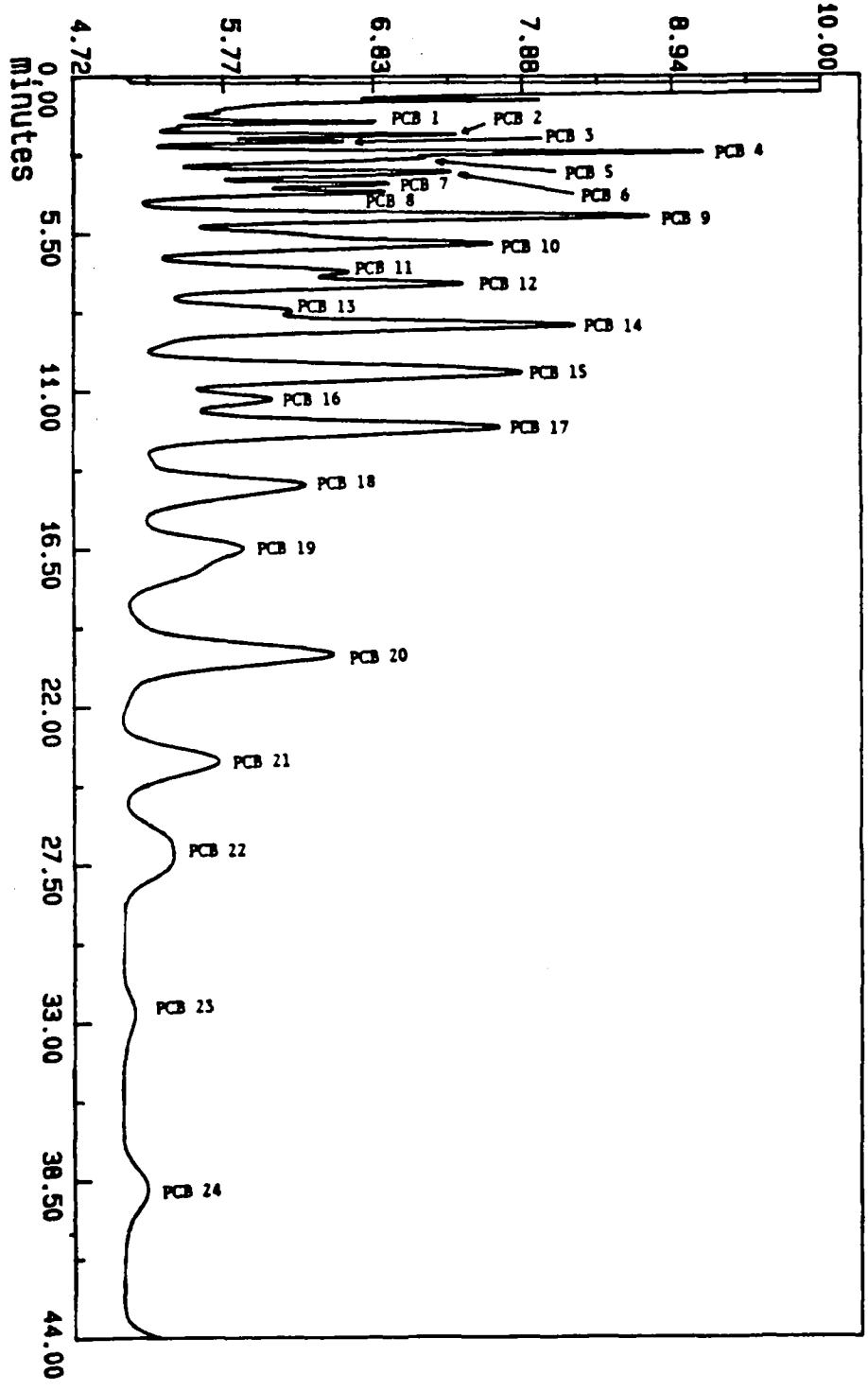
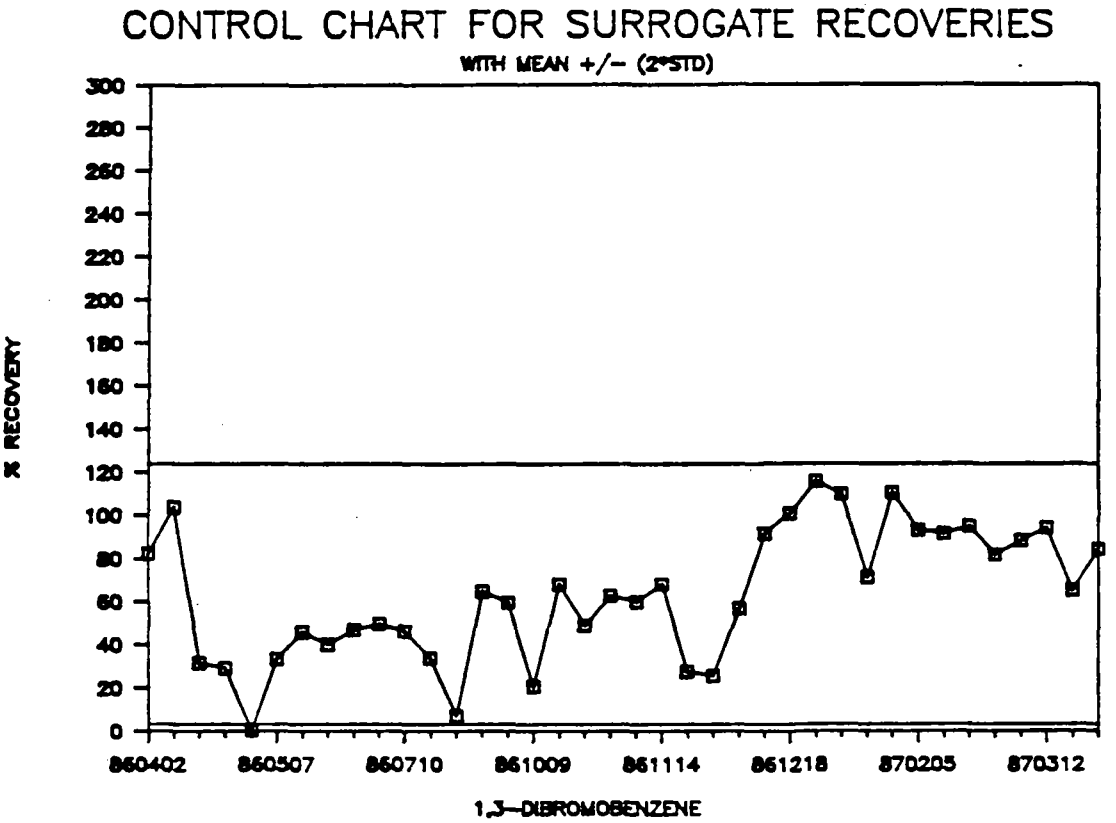


FIGURE 13: CONTROL CHARTS FOR WATER



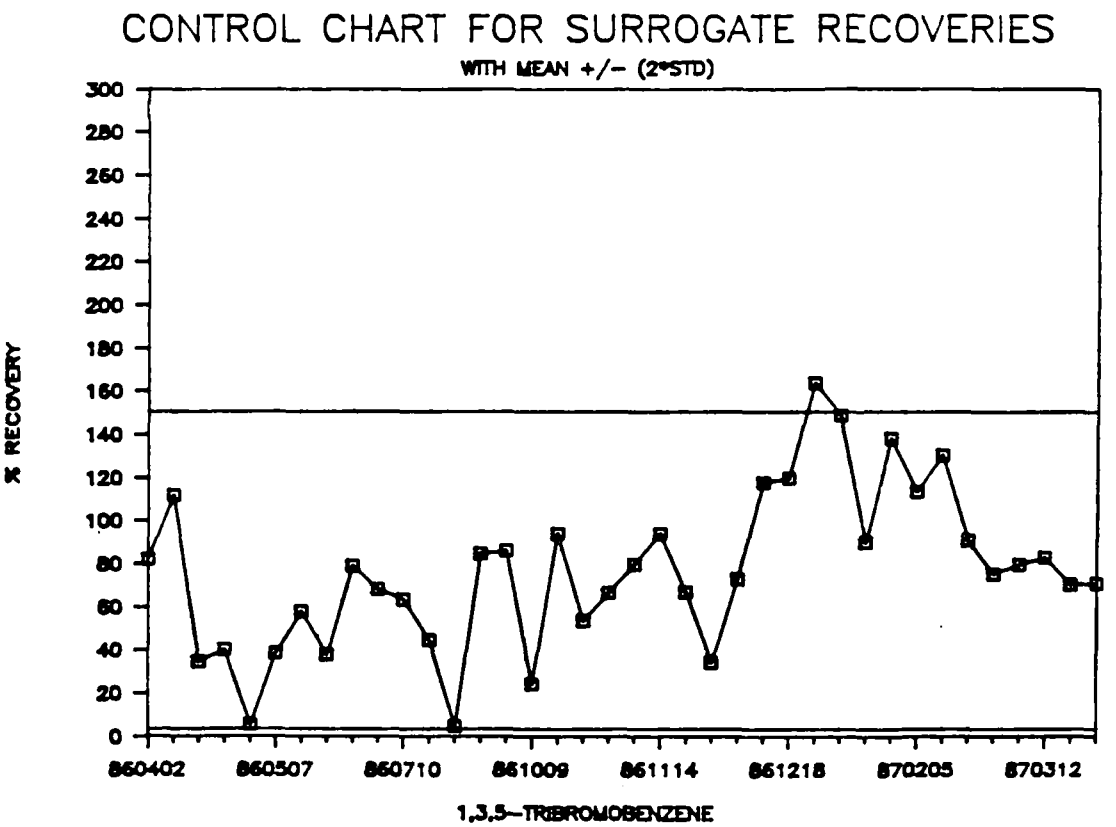
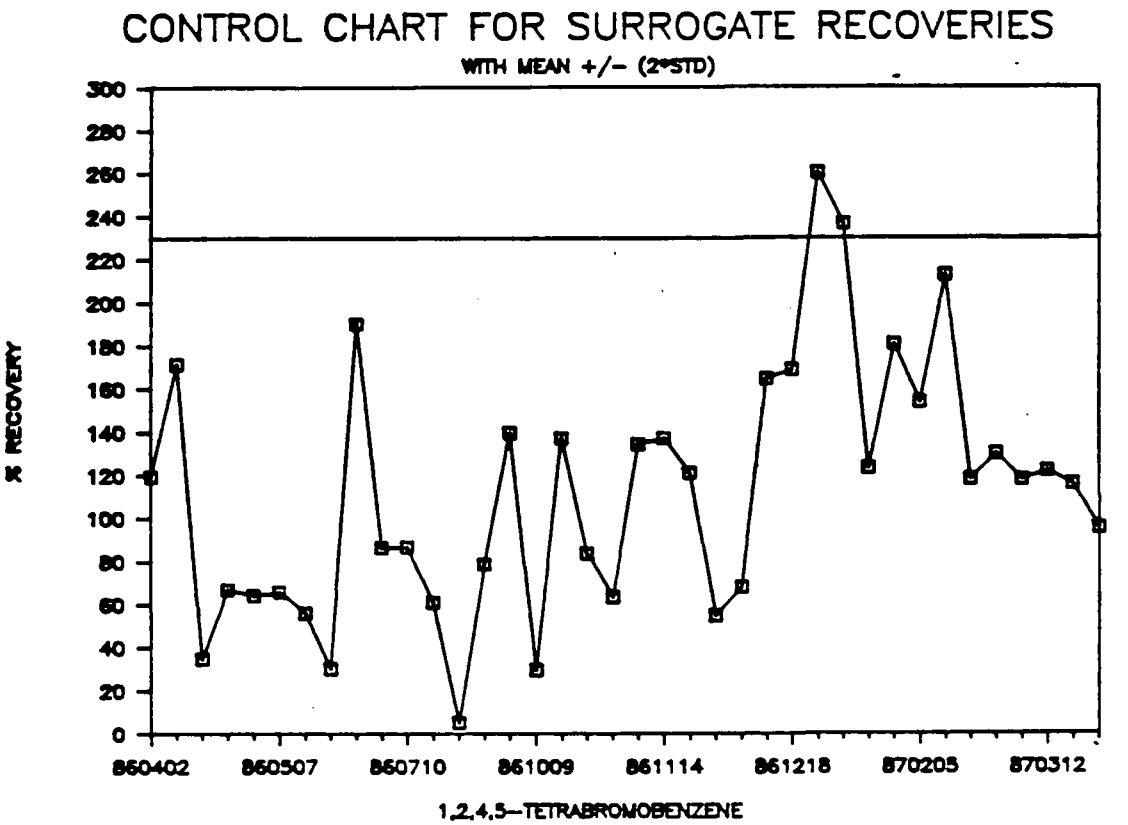


FIGURE 13: continued



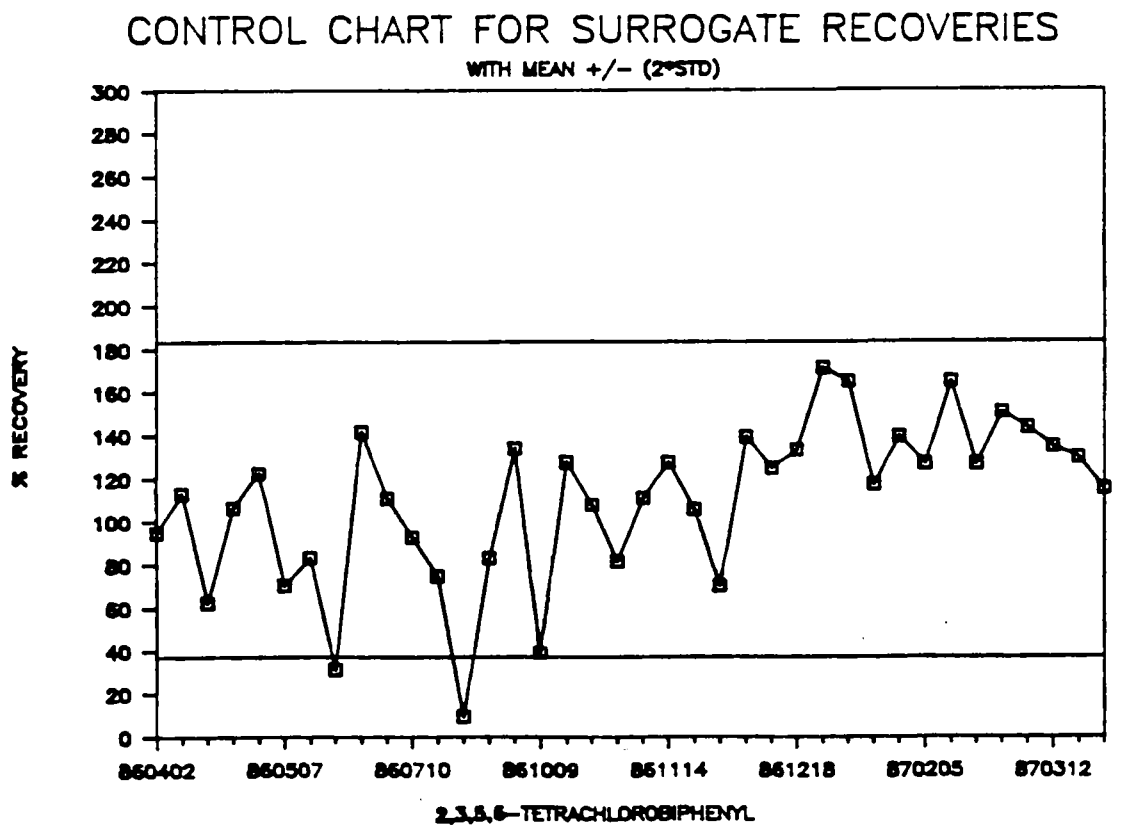
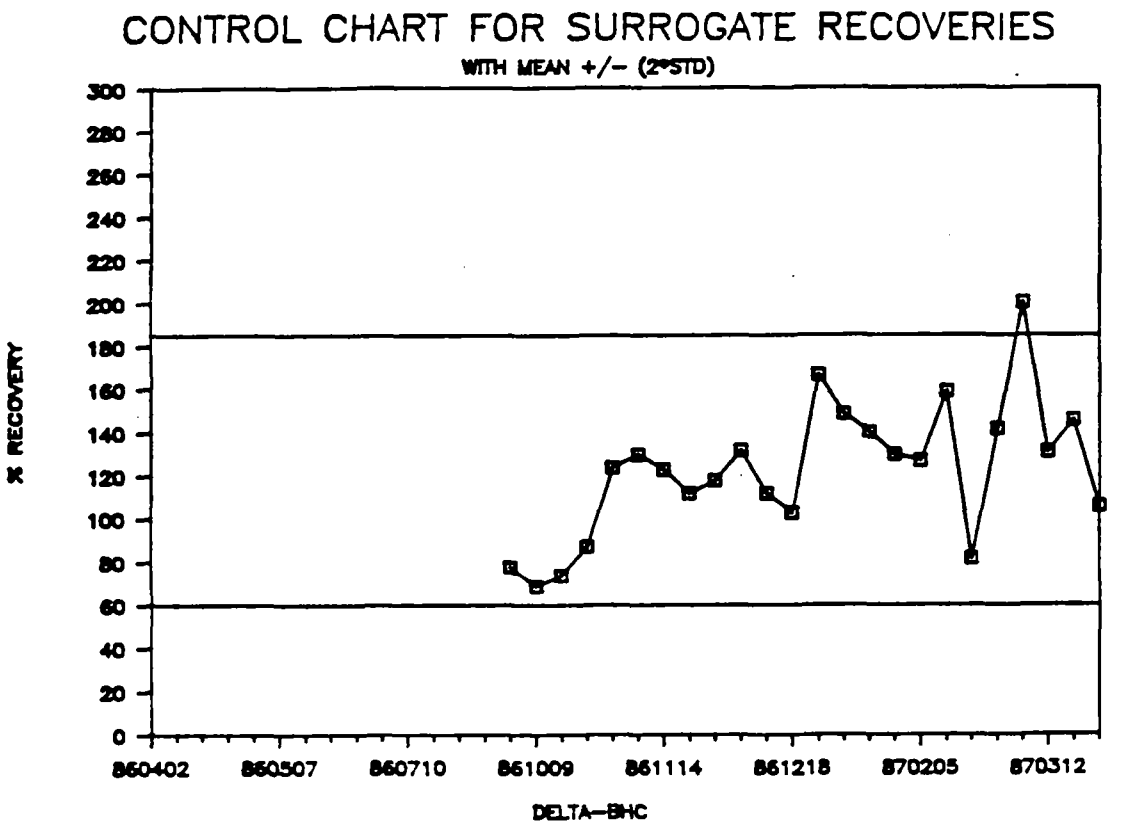


FIGURE 13: continued



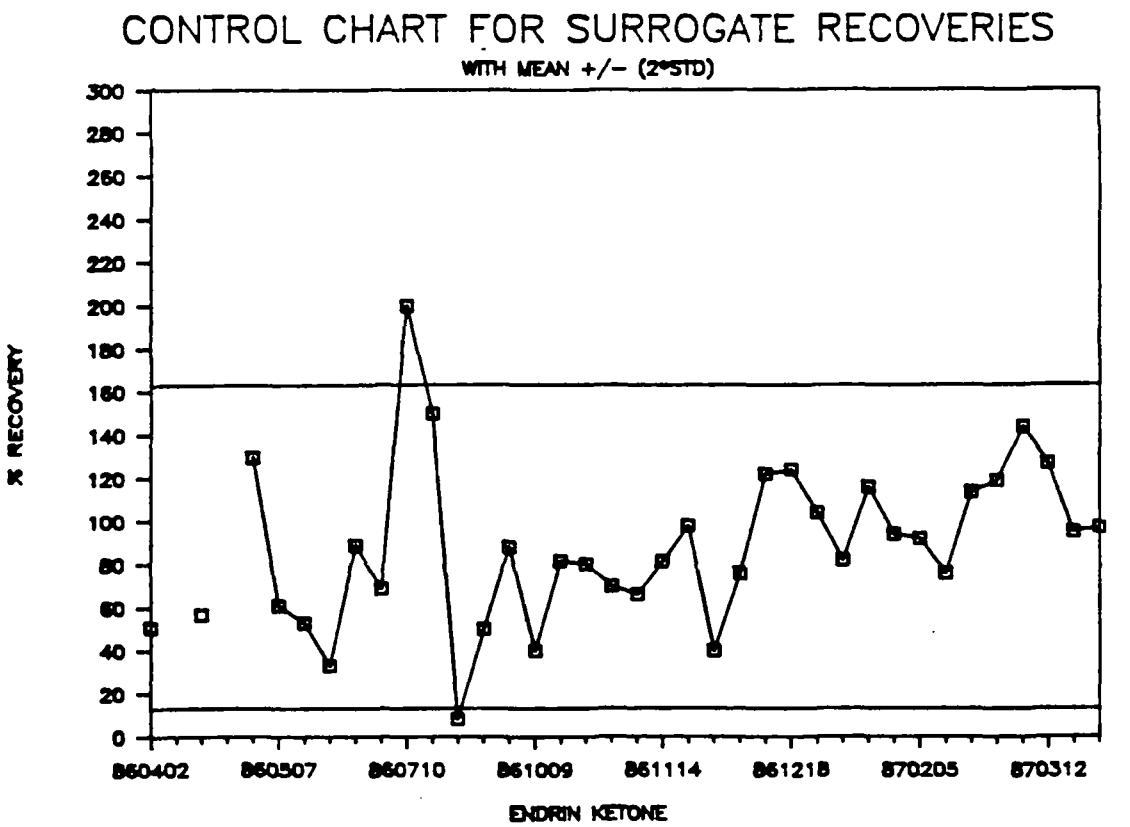
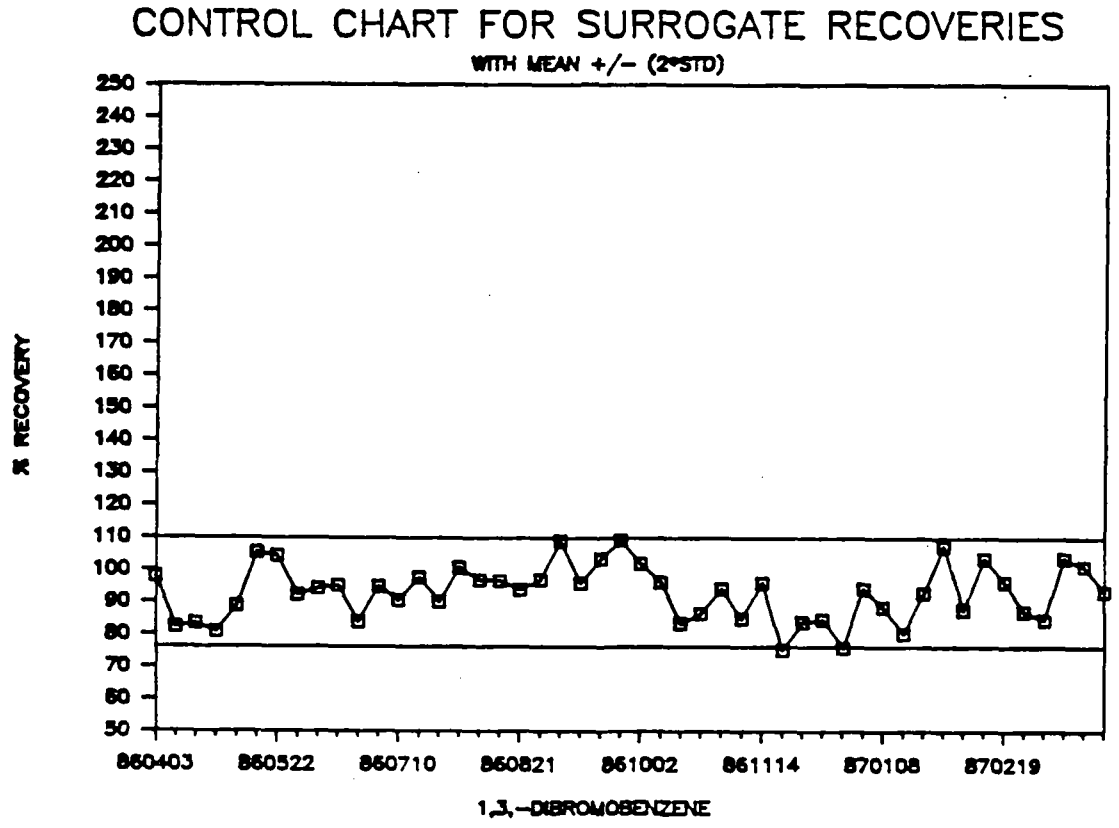


FIGURE 14: CONTROL CHARTS FOR SUSPENDED SEDIMENT



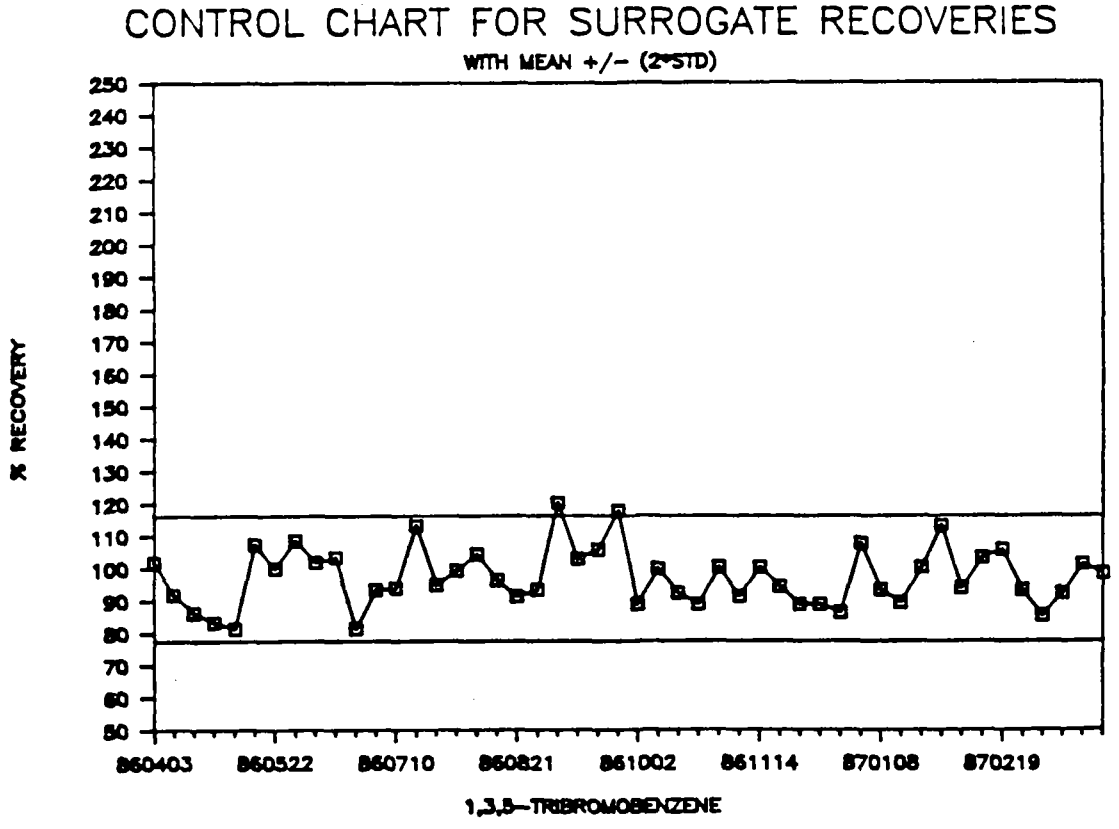
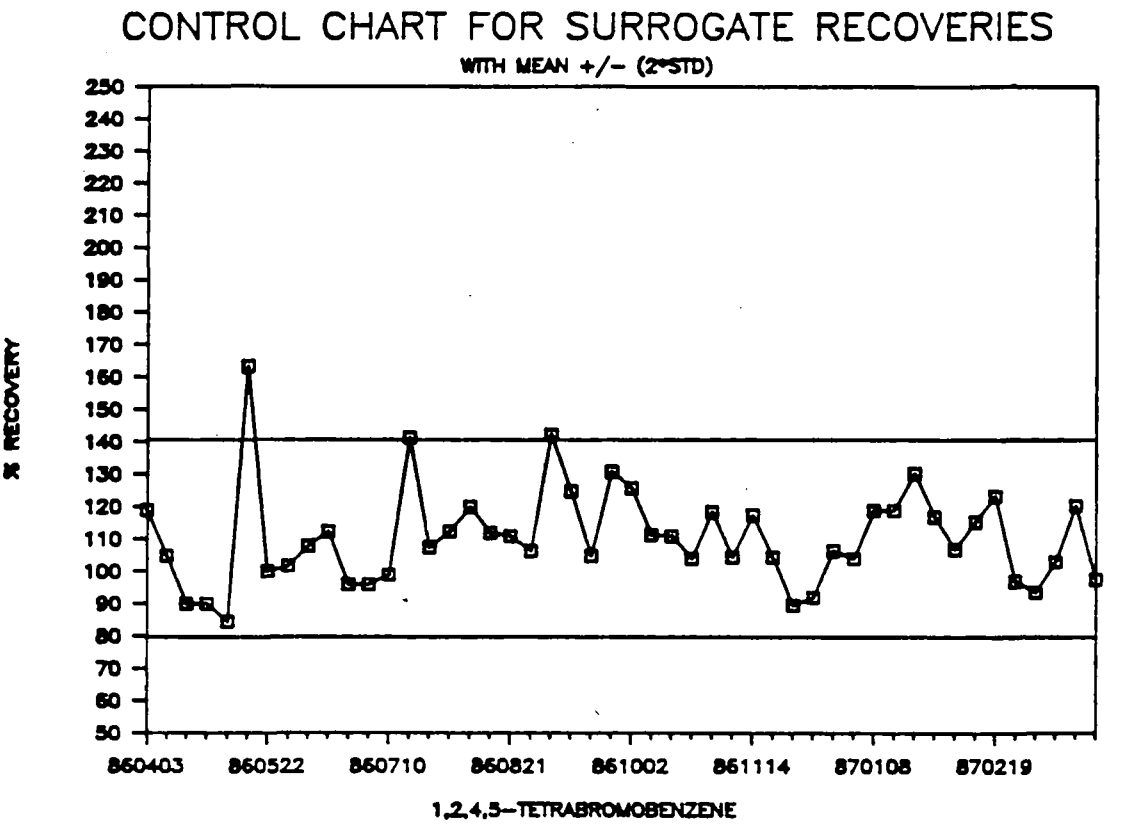


FIGURE 14: continued



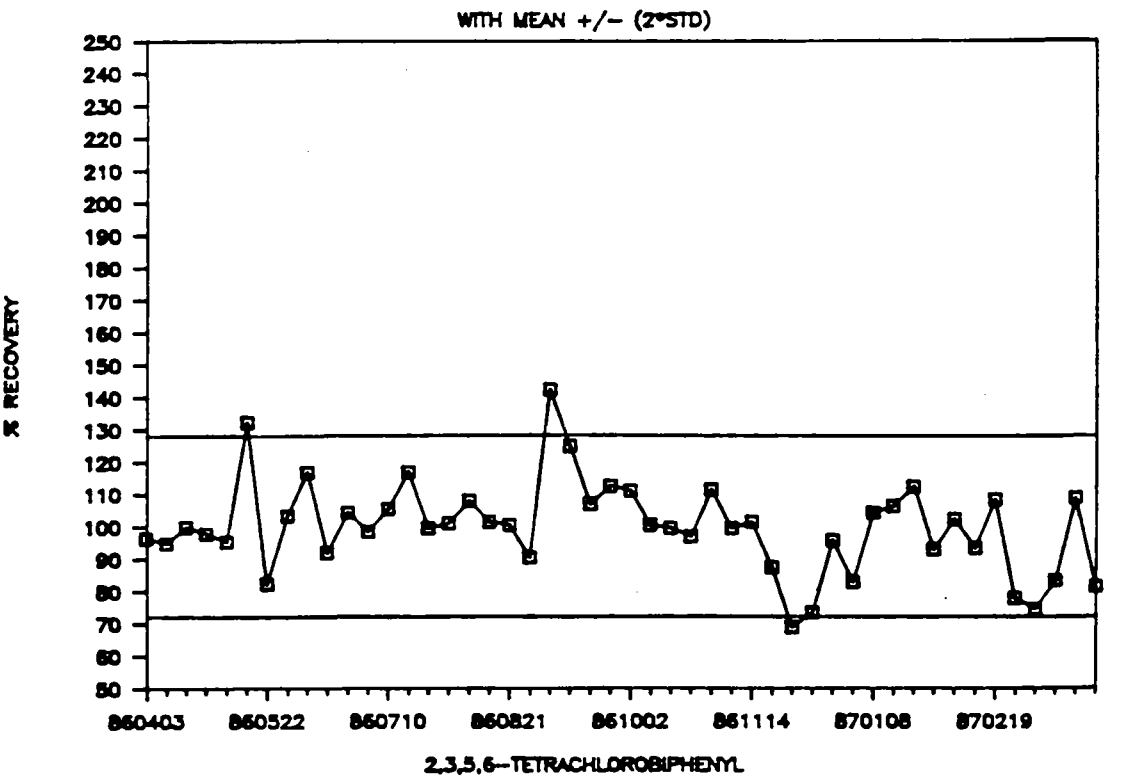
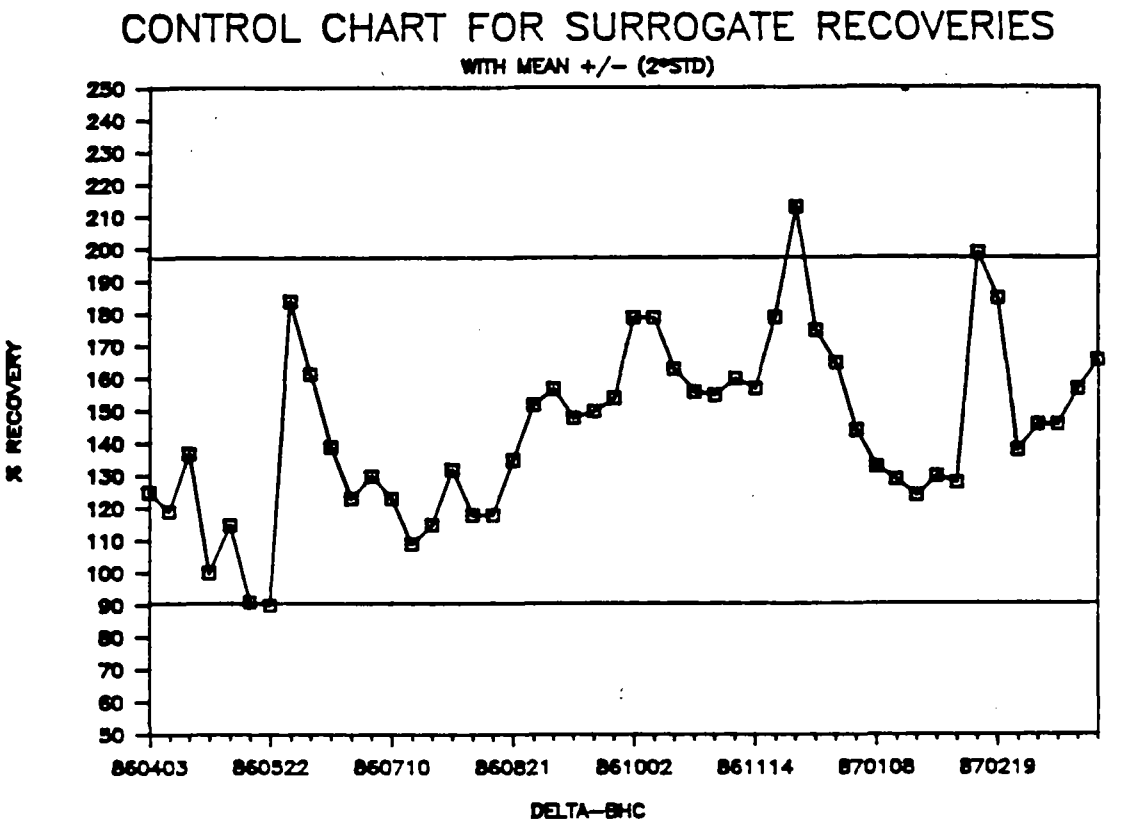


FIGURE 14: continued



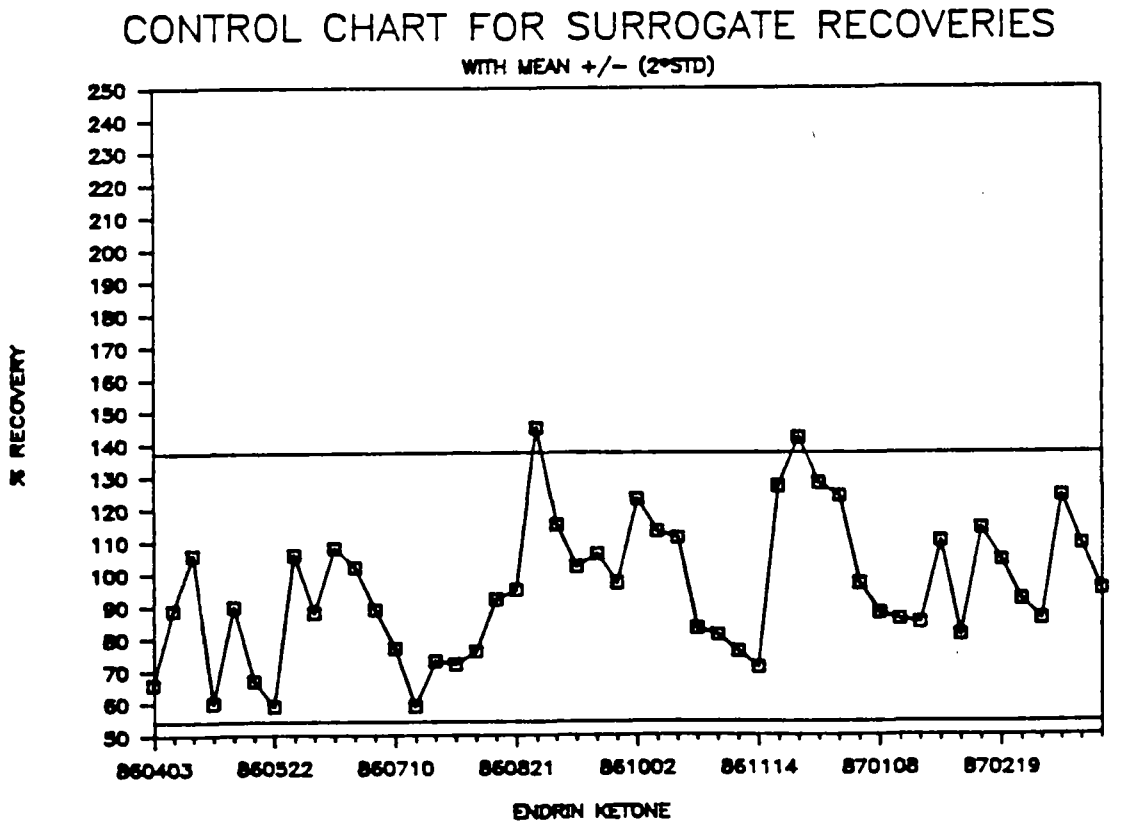


TABLE 1:

MECHANICAL COMPONENTS OF THE LVX

(a) Metering pumps to control (i) flow of water
(ii) flow of spiking solutions
(iii) flow of CH_2Cl_2.

Three FMI lab pumps are used for all three functions with pistons of different diameter to control the flow rates.

Solution Pumped	Flow Rate (mL/hour)	Pump	Pump Head
Spiking solution	5.0	RPG6	RHOCKC
Solvent makeup	38	RPG6	2CSC
Water feed	2100	RPSY	2CSC

(b) A stirrer consisting of a motor rated at 115 volts 60 hz 100 watt and a propeller approximately 4.5 cm (some adjustment of the size may have to be made due to slight differences in the size of the stirring chambers of individual LVX units).

TABLE 2A:

SPIKING SOLUTION FOR CHLOROBENZENES, ORGANOCHLORINES PESTICIDES, PCB's AND HALOGENATED SURROGATES.

Parameter	Volume Stock Req'd (uL)*	Spiking** Solution	Conc (ng/uL)
1,3-Dichlorobenzene	500	SS1	5.0
1,4-Dichlorobenzene	500	SS1	5.0
1,2-Dichlorobenzene	500	SS1	5.0
1,3,5-Trichlorobenzene	50	SS1	0.5
1,2,4-Trichlorobenzene	50	SS1	0.5
1,2,3-Trichlorobenzene	50	SS1	0.5
1,2,3,4-Tetrachlorobenzene	50	SS1	0.5
Pentachlorobenzene	50	SS1	0.5
Hexachlorobenzene	50	SS1	0.5
α-BHC	50	SS1	0.5
Lindane	50	SS1	0.5
Heptachlor	50	SS1	0.5
Aldrin	50	SS1	0.5
Heptachlor epoxide	50	SS1	0.5
γ-Chlordane	50	SS1	0.5
α-Chlordane	50	SS1	0.5
α-Endosulfan	50	SS1	0.5
p,p'-DDE	100	SS1	1.0
Dieldrin	100	SS1	1.0
Endrin	100	SS1	1.0
o,p'-DDT	150	SS1	1.5
p,p'-TDE (p,p'-DDD)	150	SS1	1.5
p,p'-DDT	150	SS1	1.5
β-Endosulfan	100	SS1	1.0
Mirex	100	SS1	1.0
Methoxychlor	500	SS1	5.0
Hexachlorobutadiene	50	SS1	0.5
PCB (Aroclor 1242;1254;1260)	2000	SS3	20.0
1,3,5-Tribromobenzene	200	SM1	2.0
1,2,4,5-Tetrabromobenzene	200	SM1	2.0
δ-BHC	100	SM1	1.0
1,3-Dibromobenzene	500	SM2	5.0
2,3,5,6-Tetrachlorobiphenyl	200	SM3***	2.0
Endrin Ketone	100	SM3***	1.0
Octachloronaphthalene	240	OCN***	2.4

* Volume of stock solution req'd for dilution to 100 mL with MeOH to provide 100 mL of spiking solution. All stock solutions are at 1000 ng/uL; (for PCB's the concentration of each Aroclor in the stock solution is 333 ng/uL).

** SS = Spiking Solution; SM = Surrogate Mix

*** In isooctane

TABLE 2B:

SPIKING SOLUTION SS2 FOR POLYNUCLEAR AROMATIC HYDROCARBONS, PHTHALATE ESTERS AND PHENOLS.

Parameter	Volume* Stock Sol^{n} Req'd (uL)	Conc in SS2 (ng/uL)
Fluoranthene	2000	20
Pyrene	2000	20
Benzo(a)anthracene	2000	20
Chrysene	4000	40
Benzo(b)fluoranthene	4000	40
Benzo(k)fluoranthene	4000	40
Benzo(a)pyrene	4000	40
2,4,6-Trichlorophenol	4000	40
2,4,5-Trichlorophenol	4000	40
Pentachlorophenol	8000	80
Phenol	8000	80

* Volume of stock solution required for dilution to 100 mL with MeOH to provide 100 mL of spiking solution SS2. All stock solutions are at 1000 ng/uL.

TABLE 3A:

INTERMEDIATE AND CALIBRATION SOLUTIONS FOR CHLOROBENZENES, ORGANOCHLORINE PESTICIDES, PCB's AND FOR HALOGENATED SURROGATES.

Parameter	Volume* Stock Sol^n(uL)	Inter. Sol^n	Conc Inter. Sol^n (ng/l)	Calib. Sol^n**	Final Conc (pg/uL)
1,3-Dichlorobenzene	500	I1	5.0	OCA	50
1,4-Dichlorobenzene	500	I1	5.0	OCA	50
1,2-Dichlorobenzene	500	I1	5.0	OCA	50
1,3,5-Trichlorobenzene	50	I1	0.5	OCA	5
1,2,4-Trichlorobenzene	50	I1	0.5	OCA	5
1,2,3-Trichlorobenzene	50	I1	0.5	OCA	5
1,2,3,4-Tetrachlorobenzene	50	I1	0.5	OCA	5
Pentachlorobenzene	50	I1	0.5	OCA	5
Hexachlorobenzene	50	I1	0.5	OCA	5
α-BHC	50	I2	0.5	OCB	5
Lindane	50	I2	0.5	OCB	5
Heptachlor	50	I1	0.5	OCA	5
Aldrin	50	I1	0.5	OCA	5
Heptachlor epoxide	50	I2	0.5	OCB	5
γ-Chlordane	50	I2	0.5	OCB	5
α-Chlordane	50	I2	0.5	OCB	5
α-Endosulfan	50	I2	0.5	OCB	5
p,p'-DDE	100	I1	1.0	OCA	10
Dieldrin	100	I2	1.0	OCB	10
Endrin	100	I2	1.0	OCB	10
o,p'-DDT	150	I1,I2	1.5	OCA,OCB	15
p,p'-TDE (p,p'-DDD)	150	I1,I2	1.5	OCA,OCB	15
p,p'-DDT	150	I1,I2	1.5	OCA,OCB	15
β-Endosulfan	100	I2	1.0	OCB	10
Mirex	100	I1	1.0	OCA	10
Methoxychlor	500	I2	5.0	OCB	50
PCB (Aroclor 1242;1254;1260)	2000	I3	20.0	PCB	200
Hexachlorobutadiene	50	I1	0.5	OCA	5
1,3-Dibromobenzene	500	I1	5.0	OCA	50
1,3,5-Tribromobenzene	200	I1	2.0	OCA	20
1,2,4,5-Tetrabromobenzene	200	I1	2.0	OCA	20
2,3,5,6-Tetrachlorobiphenyl	200	I1	2.0	OCA	20
δ-BHC	100	I2	1.0	OCB	10
Endrin Ketone	100	I2	1.0	OCB	10

* Volume of stock solution required for dilution to 100 mL with iso-octane to provide 100 mL of Intermediate Solutions I1, I2 and I3. All stock solutions are at 1000 ng/uL; (for PCB's the concentration of each Aroclor in the stock solution is 333 ng/uL).

** OCA = Fraction A; OCB = Fraction B

NOTE: To prepare Calibration Solution OCA dilute 1000 uL I1 to 100 mL with iso-octane.

To prepare Calibration Solution OCB dilute 1000 uL I2 to 100 mL with iso-octane.

To prepare Calibration Solution PCB dilute 1000 uL I3 to 100 mL with iso-octane.

TABLE 3B:

CALIBRATION SOLUTIONS FOR DETERMINATION OF POLYNUCLEAR AROMATIC HYDROCARBONS, PHTHALATE ESTERS, PHENOLS AND 2,3,7,8-TCDD.

Parameter	Volume* Stock Sol^{n} Req'd (uL)	Final Conc in MS1* (pg/uL)	Final Conc in MS2* (pg/uL)
Fluoranthene	100	200	50
Pyrene	100	200	50
Benzo(a)anthracene	100	200	50
Chrysene	200	400	100
Bis (2-ethylhexyl) phthalate	200	400	100
Dioctylphthalate	200	400	100
Benzo(b)fluoranthene	200	400	100
Benzo(k)fluoranthene	200	400	100
Benzo(a)pyrene	200	400	100
2,4,6-Trichlorophenol	200	400	100
2,4,5-Trichlorophenol	200	400	100
Pentachlorophenol	400	800	200
Phenol	400	800	200
2,3,7,8-TCDD	2500	N/A	25

* Volume of stock required for dilution to 100 mL with iso-octane to provide high standard. Calibration solution MS1, the high point of the two point calibration is prepared by diluting 20 mL of high standard to 100 mL in iso-octane. Injection solution MS2 is prepared by diluting 25 mL MS1 plus 2500 uL 2,3,7,8-TCDD to 100 mL in iso-octane. All stock solutions are at a concentration of 1000 ng/uL except 2,3,7,8-TCDD which is 1 ng/uL.

TABLE 4:

FIELD SPIKING SOLUTION (FSM1)

Surrogate	Volume* Stock Soln Req'd (uL)	Int** Soln	Conc of FI1 (pg/uL)	Final Conc FSM1 (pg/uL)	Amount of Spike (ng)
1,3,5-Tribromobenzene	100	FI1	1000	0.4	40
1,2,4,5-Tetra-bromobenzene	100	FI1	1000	0.4	40
δ-BHC	50	FI1	500	0.2	20

* This column describes the volume of 1000 ng/uL stock solution required for dilution to 100 mL in MeOH to provide 100 mL of Intermediate Solution FI1. Field Spike Solution FSM1 is prepared by diluting 40 uL FI1 to 100 mL with MeOH.

** FI1 = Field Intermediate 1 solution.

TABLE 5A:

RETENTION TIMES AND RESPONSES OF PARAMETERS DETERMINED BY GC/ECD WITH SPB 1.

Parameter	Retention Time	Relative Retention Time (%)	Mean* Response (n = 10)	Std Dev	Coeff. of Var.**
1,3-Dichlorobenzene	3.16	6.9	33353	734	2.2
1,4-Dichlorobenzene	3.22	7.0	20394	467	2.3
1,2-Dichlorobenzene	3.54	7.7	31885	757	2.4
1,3,5-Trichlorobenzene	5.42	11.8	22151	629	2.8
1,2,4-Trichlorobenzene	6.35	13.8	14692	632	4.3
1,2,3-Trichlorobenzene	7.15	15.6	24643	641	2.6
1,2,3,4-Tetrachlorobenzene	11.70	25.5	27254	551	2.0
Pentachlorobenzene	16.00	34.8	41980	824	2.0
Hexachlorobenzene	21.44	46.6	81805	1684	2.1
α-BHC	20.51	44.6	25148	756	3.0
Lindane	22.16	48.2	28482	1068	3.7
Heptachlor	26.61	57.9	42137	960	2.3
Aldrin	28.37	61.7	60066	1351	2.2
Heptachlor epoxide	30.12	65.5	46633	2086	4.5
γ-Chlordane	31.21	67.9	49222	2333	4.7
α-Chlordane	32.06	69.7	55470	2791	5.0
α-Endosulfan	31.83	69.2	44830	2332	5.2
p,p'-DDE	33.36	726	88547	3538	4.0
Dieldrin	33.07	71.9	91930	5031	5.5
Endrin	33.88	73.7	83055	9373	11.3
o,p'-DDT	35.41	77.0	109874	6337	5.8
p,p'-TDE (p,p'-DDD)	35.02	76.2	77900	4961	6.4
p,p'-DDT	36.97	80.4	108908	6660	6.1
β-Endosulfan	34.03	74.0	83573	4299	5.1
Mirex	41.36	90.0	156990	4040	2.6
Methoxychlor	39.65	86.3	167246	7927	4.7
Hexachlorobutadiene	7.71	16.8	83651	4381	5.2
1,3-Dibromobenzene	6.50	14.1	266874	8163	3.1
1,3,5-Tribromobenzene	12.99	28.3	181100	3632	2.0
1,2,4,5-Tetrabromobenzene	21.86	47.6	141559	6962	4.9
2,3,5,6-Tetrachlorobiphenyl	28.16	61.3	167933	3899	2.3
δ-BHC	22.43	48.8	43177	2424	5.6
Endrin Ketone	37.82	82.3	105679	9364	8.9
Octachloronaphthalene	45.97	100.0	308872	14851	4.8

* RESPONSE IS THE PEAK HEIGHT COUNT REPORTED BY THE 3392 INTEGRATOR.

** Coeff. of Var. = STANDARD DEVIATION/MEAN RESPONSE X 100%

TABLE 5B:

RETENTION TIMES OF PCB's DETERMINED BY GC/ECD WITH OV 101.

Parameter	Retention Time(min.)	Relative Retention Time (%)
PCB 1	1.60	3.5
2	2.04	4.5
3	2.26	5.0
4	2.67	5.9
5	2.85	6.3
6	3.34	7.4
7	3.75	8.3
8	4.03	8.9
9	4.89	10.8
10	5.83	12.9
11	6.78	15.0
12	7.21	15.9
13	8.12	17.9
14	8.66	19.1
15	10.29	22.7
16	11.17	24.7
17	12.17	26.0
18	14.14	31.2
19	16.31	36.0
20	19.96	44.1
21	23.64	52.2
22	26.69	58.9
23	32.32	71.4
24	38.42	84.8
OCNE	45.28	100.0

TABLE 5C:

RELATIVE RETENTION TIMES (%) FOR SPB 1, SPB 5, SPB 608 AND OV 101.

Parameter	SPB 1	SPB 5	SPB 608	OV 101
1,3-Dichlorobenzene	6.9	8.4	8.3	xx
1,4-Dichlorobenzene	7.0	8.6	8.7	xx
1,2-Dichlorobenzene	7.7	9.4	9.9	xx
1,3,5-Trichlorobenzene	11.8	13.6	13.5	xx
1,2,4-Trichlorobenzene	13.8	15.9	16.9	xx
1,2,3-Trichlorobenzene	15.6	17.9	19.7	xx
1,2,3,4-Tetrachlorobenzene	25.5	27.9	29.8	xx
Pentachlorobenzene	34.8	36.8	37.8	xx
Hexachlorobenzene	46.6	48.2	48.7	4.1
α-BHC	44.6	47.5	50.8	-
Lindane	48.2	51.2	54.9	-
Heptachlor	57.9	58.9	58.6	6.7
Aldrin	61.7	62.4#	61.8	8.0
Heptachlor epoxide	65.5	66.7	67.5	-
γ-Chlordane	67.9	69.1	69.3	-
α-Chlordane	69.7	70.7	70.8@	-
α-Endosulfan	69.2	70.2	70.8@	-
p,p'-DDE	72.6	73.3	73.6	15.4
Dieldrin	71.9	72.9	73.7	-
Endrin	73.7	74.9	76.9	-
o,p'-DDT	77.0	77.6	78.4*	20.7
p,p'-TDE (p,p'-DDD)	76.2	77.4	78.7	19.7
p,p'-DDT	80.4	81.0	81.4	26.1
β-Endosulfan	74.0	75.9	78.4*	-
Mirex	90.0	89.7	89.2	48.2
Methoxychlor	86.3	86.8	88.9^	-
Hexachlorobutadiene	16.8	18.2	17.2	xx
1,3-Dibromobenzene	14.1	16.4	18.4	1.3
1,3,5-Tribromobenzene	28.3	30.6	32.9	1.5
1,2,4,5-Tetrabromobenzene	47.6	49.6	52.6	4.2
2,3,5,6-Tetrachlorobiphenyl	61.3	62.4#	63.3	8.1
δ-BHC	48.8	54.2	59.7	-
Endrin Ketone	82.3	84.5	88.9^	-
Octachloronaphthalene	100.0	100.0	100.0	100.0

@, #, ^, * = Co-eluting peaks

xx = Retention time too early

TABLE 6:

DETECTION CHARACTERISITICS OF THE AROMATIC HYDROCARBONS.

Parameter	Quantitation Mass	Retention times relative to Anthracene D 10	Relative Response Factor
Anthracene D 10	188.0	1.0000	1.00
Fluoranthene	202.0	1.17624	0.964
Pyrene	202.0	1.20935	1.084
Benzo(a)anthracene	228.0	1.39435	1.211
Chrysene	228.0	1.40214	1.093
Bis(2-ethylhexyl) phthalate	149.0	1.42649	2.638
Dioctylphthalate	149.0	1.52580	3.065
Benzo(b)fluoranthene	252.1	1.56573	0.992
Benzo(k)fluoranthene	252.1	1.57254	1.083
Benzo(a)pyrene	252.1	1.61733	0.722
Phenol	94.0	0.30867	1.029
2,4,6-Trichlorophenol	196.0	0.66602	0.194
2,4,5-Trichlorophenol	196.0	0.67478	0.131
Pentachlorophenol	265.9	0.97955	0.099
2,3,7,8-TCDD	321.9	1.33951	0.429

TABLE 7:

MULTIPLE ION MONITORING LIBRARY

Parameter	Masses(intensity relative to base peak = 100)
Anthracene D 10	188.0
Fluoranthene	202.0(100);203.0(18);200.0(22);101.0(52)
Pyrene	202.0(100);203.0(18);200.0(21);101.0(65)
Benzo(a)anthracene	228.0(100);229.0(20);226.0(27);114.0(25)
Chrysene	228.0(100);229.0(20);226.0(27);114.0(26)
Bis(2-ethylhexyl) phthalate	149.0(100);167.0(40);279.1(10)
Dioctylphthalate	149.0(100);150.0(9);279.1(10)
Benzo(b)fluoranthene	252.1(100);253.1(18);250.1(20);126.0(21)
Benzo(k)fluoranthene	252.1(100);253.1(19);250.1(21);126.0(26)
Benzo(a)pyrene	252.1(100);253.1(20);250.1(22);126.0(23)
Phenol	94.0(100);95.0(7);66.0(40)
2,4,6-Trichlorophenol	196.0(100);198.0(94);200.0(28);132.0(49)
2,4,5-Trichlorophenol	196.0(100);198.0(94);200.0(28);132.0(49)
Pentachlorophenol	265.9(100);263.9(61);267.9(57);269.9(20)
2,3,7,8-TCDD	321.9(100);319.9(81);323.9(48);325.9(10) 256.9(20);258.9(20)

TABLE 8:

TYPICAL RESULTS FOR WATER SAMPLES FROM NIAGARA ON THE LAKE FOR THE PERIOD APRIL-86 TO MARCH-87.

Parameter	n*	Mean (ng/L)	Std Dev (ng/L)	Min. Value (ng/L)	Max. Value (ng/L)
1,3-Dichlorobenzene	34	1.46	0.56	0.42	2.62
1,4-Dichlorobenzene	35	2.53	1.21	0.17	5.70
1,2-Dichlorobenzene	26	2.17	1.41	0.38	6.10
1,3,5-Trichlorobenzene	31	0.15	0.05	0.07	0.26
1,2,4-Trichlorobenzene	34	1.60	0.77	0.60	4.44
1,2,3-Trichlorobenzene	34	0.35	0.23	0.16	1.38
1,2,3,4-Tetrachlorobenzene	35	0.73	0.49	0.03	2.14
Pentachlorobenzene	33	0.25	0.14	0.08	0.61
Hexachlorobenzene	38	0.12	0.05	0.05	0.23
α-BHC	38	2.44	0.81	1.00	4.86
Lindane	37	0.66	0.18	0.32	1.21
Heptachlor	0				
Aldrin	0				
Heptachlor epoxide	33	0.15	0.12	0.04	0.80
γ-Chlordane	4	0.03	0.01	0.02	0.04
α-Chlordane	27	0.03	0.01	0.01	0.07
α-Endosulfan	8	0.08	0.06	0.01	0.19
p,p'-DDE	30	0.03	0.01	0.01	0.06
Dieldrin	35	0.32	0.10	0.04	0.45
Endrin	24	0.06	0.03	0.02	0.13
o,p'-DDT	3	0.01	0.01	0.01	0.02
p,p'-TDE (p,p'-DDD)	4	0.09	0.08	0.02	0.20
p,p'-DDT	5	0.04	0.05	0.01	0.13
β-Endosulfan	3	0.05	0.02	0.03	0.07
Mirex	0				
Methoxychlor	4	0.07	0.03	0.03	0.10
PCB (Aroclor 1242;1254;1260)	32	1.53	0.53	0.78	3.20
Hexachlorobutadiene	33	0.11	0.06	0.03	0.29
		(%)	(%)	(%)	(%)
1,3-Dibromobenzene	38	64	30	0.5	116
1,3,5-Tribromobenzene	38	77	37	5	164
1,2,4,5-Tetrabromobenzene	38	113	59	5	260
2,3,5,6-Tetrachlorobiphenyl	38	110	37	10	171
δ-BHC	24	123	31	69	201
Endrin Ketone	36	88	38	8	200

* Number of positive values

TABLE 9:

RESULTS OF RECOVERY FROM PROFICIENCY TESTING (WATER)(n = 15)

Parameter	Amount of spike (ng)	Mean Recovery (ng)	Recovery (%)	Std Dev (ng)	Coeff. of Var. (%)
1,3-Dichlorobenzene	50.0	30.5	61	4.8	16
1,4-Dichlorobenzene	50.0	28.6	57	3.8	13
1,2-Dichlorobenzene	50.0	33.2	66	4.9	15
1,3,5-Trichlorobenzene	5.0	4.2	84	0.7	16
1,2,4-Trichlorobenzene	5.0	4.4	89	0.6	14
1,2,3-Trichlorobenzene	5.0	4.4	88	0.6	14
1,2,3,4-Tetrachlorobenzene	5.0	4.9	98	0.7	15
Pentachlorobenzene	5.0	5.1	101	0.7	14
Hexachlorobenzene	5.0	5.3	106	0.8	14
α-BHC	5.0	5.4	108	0.2	3
Lindane	5.0	5.3	106	0.2	4
Heptachlor	5.0	5.3	106	1.0	20
Aldrin	5.0	5.5	110	0.8	15
Heptachlor epoxide	5.0	4.9	98	0.3	7
γ-Chlordane	5.0	4.8	96	0.3	5
α-Chlordane	5.0	4.7	94	0.4	8
α-Endosulfan	5.0	4.5	90	0.3	6
p,p'-DDE	10.0	13.9	139	2.9	21
Dieldrin	5.0	4.7	93	0.3	7
Endrin	5.0	4.6	92	0.4	8
o,p'-DDT	10.0	13.6	136	10.0	73
p,p'-TDE (p,p'-DDD)	10.0	11.7	117	7.8	67
p,p'-DDT	10.0	12.5	125	7.4	60
β-Endosulfan	5.0	4.3	86	0.4	9
Mirex	5.0	5.3	106	1.2	22
Methoxychlor	30.0	25.1	84	4.9	19

TABLE 10A:

DETECTION LIMITS FOR CHLOROBENZENES, ORGANOCHLORINE PESTICIDES, PCB's AND SURROGATES IN WATER.

Parameter	IDL * (pg)	MDL * (ng/L)	PDL * (ng/L)
1,3-Dichlorobenzene	3.0	0.25	0.50
1,4-Dichlorobenzene	3.2	0.29	0.82
1,2-Dichlorobenzene	3.3	0.45	0.55
1,3,5-Trichlorobenzene	0.38	0.03	0.04
1,2,4-Trichlorobenzene	0.59	0.16	0.33
1,2,3-Trichlorobenzene	0.36	0.03	0.07
1,2,3,4-Tetrachlorobenzene	0.28	0.04	0.11
Pentachlorobenzene	0.28	0.05	0.05
Hexachlorobenzene	0.29	0.05	0.07
α-BHC	0.41	0.12	1.3
Lindane	0.51	0.04	0.40
Heptachlor	0.32	0.08	0.11
Aldrin	0.30	0.05	0.07
Heptachlor epoxide	0.62	0.04	0.06
γ-Chlordane	0.65	0.07	0.04
α-Chlordane	0.69	0.09	0.07
α-Endosulfan	0.71	0.05	0.05
p,p'-DDE	1.1	0.10	0.20
Dieldrin	1.5	0.10	0.18
Endrin	1.6	0.10	0.14
o,p'-DDT	2.4	0.12	0.26
p,p'-TDE (p,p'-DDD)	2.6	0.31	0.22
p,p'-DDT	2.5	0.32	0.28
β-Endosulfan	1.4	0.15	0.09
Mirex	0.71	0.08	0.11
Methoxychlor	6.5	1.4	1.6
PCB (Aroclor 1242;1254;1260)	40	1.2	3.3
Hexachlorobutadiene	0.71	0.04	0.08
1,3-Dibromobenzene	4.3	-	-
1,3,5-Tribromobenzene	1.1	-	-
1,2,4,5-Tetrabromobenzene	2.7	-	-
2,3,5,6-Tetrachlorobiphenyl	1.3	-	-
δ-BHC	1.5	-	-
Endrin Ketone	2.5	-	-
Octachloronaphthalene	2.3	-	-

* IDL, MDL and PDL as defined in section 8.0-(a),(b),(c)

TABLE 10B:

DETECTION LIMITS FOR POLYNUCLEAR AROMATIC HYDROCARBONS, PHENOLS AND 2,3,7,8-TCDD IN WATER.

Parameter	IDL (pg)	MDL (ng/L)	PDL (ng/L)
Fluoranthene	43	0.40	0.35
Pyrene	49	0.41	0.32
Benzo(a)anthracene	82	0.40	0.26
Chrysene	107	0.49	0.57
Bis(2-ethylhexyl) phthalate	159	0.16	
Dioctylphthalate	148	0.15	
Benzo(b)fluoranthene	161	0.72	0.50
Benzo(k)fluoranthene	204	0.46	0.49
Benzo(a)pyrene	159	0.46	0.46
2,4,6-Trichlorophenol	165	0.17	
2,4,5-Trichlorophenol	134	0.13	
Pentachlorophenol	198	0.20	
Phenol	192	0.19	
2,3,7,8-TCDD	21	0.02	

TABLE 11:

RESULTS OF RECOVERY FROM 40 LITER SPIKES.

Parameter	Conc in Water (ng/L)	n	Mean Recovery (ng/L)	Recovery (%)	Std Dev (ng/L)	Coeff of Var (%)
Hexachlorobenzene	0.25	11	0.13	52	0.05	42
α-BHC	0.25	11	0.19	76	0.05	26
Lindane	0.25	11	0.20	80	0.05	23
Heptachlor	0.25	11	0.12	48	0.04	33
Aldrin	0.25	11	0.14	56	0.05	38
Heptachlor epoxide	0.25	11	0.18	72	0.04	21
γ-Chlordane	0.25	11	0.17	68	0.05	31
α-Chlordane	0.25	11	0.18	72	0.05	27
α-Endosulfan	0.25	10	0.12	48	0.08	69
p,p'-DDE	0.25	11	0.28	112	0.07	25
Dieldrin	0.25	11	0.18	72	0.07	37
Endrin	0.25	9	0.18	72	0.07	38
p,p'-TDE (p,p'-DDD)	1.0	11	0.78	78	0.27	35
p,p'-DDT	1.0	11	0.76	76	0.38	47
β-Endosulfan	0.25	7	0.16	64	0.08	47
Mirex	0.25	11	0.15	60	0.06	38
Methoxychlor	1.5	11	1.11	74	0.45	40
PCB (Aroclor 1242;1254;1260)	10	21	6.41	64	2.01	31
Hexachlorobutadiene	0.25	5	0.12	48	0.05	42

TABLE 12A:

RESULTS TO SHOW VARIABILITY OF TWO LVX EXTRACTORS ON SITE (n = 8)

		SET A			SET B		
Parameter	Am't of Spike (ng/L)	Mean Comp'd Meas'd (ng/L)	Std Dev (ng/L)	Coeff Of Var (%)	Mean Comp'd Meas'd (ng/L)	Std Dev (ng/L)	Coeff of Var (%)
1,3-Dichlorobenzene	2.0	2.2	0.59	12	2.1	0.23	11
1,4-Dichlorobenzene	2.0	3.4	0.36	11	3.3	0.40	12
1,2-Dichlorobenzene	2.0	2.4	0.28	12	2.3	0.25	11
1,3,5-Trichlorobenzene	0.2	0.22	0.02	10	0.22	0.02	8
1,2,4-Trichlorobenzene	0.2	1.20	0.18	15	1.25	0.16	12
1,2,3-Trichlorobenzene	0.2	0.37	0.04	12	0.37	0.03	8
1,2,3,4-Tetrachlorobenzene	0.2	0.48	0.05	11	0.48	0.07	14
Pentachlorobenzene	0.2	0.27	0.03	11	0.27	0.03	10
Hexachlorobenzene	0.2	0.24	0.04	18	0.26	0.05	19
α-BHC	0.2	6.24	0.79	13	6.46	0.61	10
Lindane	0.2	1.40	0.25	18	1.51	0.18	12
Heptachlor	0.2	0.09	0.07	74	0.12	0.06	50
Aldrin	0.2	0.16	0.03	18	0.19	0.04	21
Heptachlor epoxide	0.2	0.29	0.03	11	0.32	0.03	9
γ-Chlordane	0.2	0.16	0.02	11	0.18	0.03	17
α-Chlordane	0.2	0.19	0.03	17	0.23	0.05	22
α-Endosulfan	0.2	0.13	0.02	12	0.17	0.04	24
p,p'-DDE	0.4	0.38	0.09	25	0.43	0.15	36
Dieldrin	0.4	0.71	0.09	14	0.77	0.12	16
Endrin	0.4	0.40	0.08	20	0.45	0.06	13
o,p'-DDT	0.6	0.44	0.15	33	0.56	0.18	33
p,p'-TDE (p,p'-DDD)	0.6	0.62	0.13	20	0.73	0.11	15
p,p'-DDT	0.6	0.41	0.14	33	0.54	0.20	37
β-Endosulfan	0.4	0.30	0.05	16	0.34	0.05	15
Mirex	0.4	0.28	0.04	16	0.28	0.13	47
Methoxychlor	2.0	2.78	1.07	38	2.94	0.86	29
Hexachlorobutadiene	0.2	0.21	0.07	32	0.21	0.03	14
1,3-Dibromobenzene	2.0	1.87	0.28	15	1.76	0.20	11
1,3,5-Tribromobenzene	0.8	0.62	0.09	15	0.64	0.12	19
1,2,4,5-Tetrabromobenzene	0.8	0.66	0.12	18	0.69	0.13	19
2,3,5,6-Tetrachlorobiphenyl	0.8	0.85	0.12	13	0.87	0.18	21
δ-BHC	0.4	0.65	0.12	18	0.74	0.10	14
Endrin Ketone	0.4	0.44	0.08	19	0.48	0.08	17
Octachloronaphthalene	0.96	1.28	0.62	48	1.23	0.43	35

TABLE 12A: continued

RESULTS TO SHOW VARIABILITY OF TWO LVX EXTRACTORS ON SITE (n = 8)

		SET A			SET B		
Parameter	Am't of Spike (ng/L)	Mean Comp'd Meas'd (ng/L)	Std Dev (ng/L)	Coeff Of Var (%)	Mean Comp'd Meas'd (ng/L)	Std Dev (ng/L)	Coeff of Var (%)
Fluoranthene	8	7.4	2.1	29	7.2	1.9	27
Pyrene	8	7.4	1.6	21	8.0	1.8	22
Benzo(a)anthracene	8	7.3	1.6	22	7.2	0.9	14
Chrysene	16	15.7	3.9	25	15.2	2.4	16
Benzo(b)fluoranthene	16	11.4	2.7	24	11.6	2.0	17
Benzo(k)fluoranthene	16	13.6	3.7	27	13.0	2.6	20
Benzo(a)pyrene	16	12.2	3.7	30	12.0	2.4	20

TABLE 12B:

RESULTS TO SHOW VARIABILITY OF DUPLICATE EXTRACTIONS (n = 16).

	SET C			
Parameter	Amount of Spike (ng/L)	Mean Compound Measured (ng/L)	Std Dev (ng/L)	Coeff Of Var (%)
1,3-Dichlorobenzene	2.0	2.2	0.34	15
1,4-Dichlorobenzene	2.0	3.4	0.58	17
1,2-Dichlorobenzene	2.0	2.4	0.40	17
1,3,5-Trichlorobenzene	0.2	0.21	0.05	24
1,2,4-Trichlorobenzene	0.2	1.31	0.22	17
1,2,3-Trichlorobenzene	0.2	0.36	0.10	28
1,2,3,4-Tetrachlorobenzene	0.2	0.49	0.07	14
Pentachlorobenzene	0.2	0.28	0.04	13
Hexachlorobenzene	0.2	0.26	0.04	15
α-BHC	0.2	6.23	0.84	14
Lindane	0.2	1.46	0.26	18
Heptachlor	0.2	0.13	0.07	56
Aldrin	0.2	0.17	0.04	25
Heptachlor epoxide	0.2	0.30	0.04	13
γ-Chlordane	0.2	0.17	0.03	15
α-Chlordane	0.2	0.20	0.06	28
α-Endosulfan	0.2	0.14	0.05	37
p,p'-DDE	0.4	0.40	0.11	27
Dieldrin	0.4	0.75	0.11	14
Endrin	0.4	0.41	0.10	24
o,p'-DDT	0.6	0.52	0.13	26
p,p'-TDE (p,p'-DDD)	0.6	0.62	0.20	33
p,p'-DDT	0.6	0.49	0.15	32
β-Endosulfan	0.4	0.31	0.06	19
Mirex	0.4	0.28	0.10	34
Methoxychlor	2.0	2.91	1.03	35
Hexachlorobutadiene	0.2	0.22	0.04	18
1,3-Dibromobenzene	2.0	1.90	0.30	16
1,3,5-Tribromobenzene	0.8	0.66	0.10	15
1,2,4,5-Tetrabromobenzene	0.8	0.70	0.12	17
2,3,5,6-Tetrachlorobiphenyl	0.8	0.89	0.12	14
δ-BHC	0.4	0.69	0.15	22
Endrin Ketone	0.4	0.47	0.11	23
Octachloronaphthalene	0.96	1.24	0.52	42

TABLE 12B: continued

RESULTS TO SHOW VARIABILITY OF DUPLICATE EXTRACTIONS (n = 16).

	SET C			
Parameter	Amount of Spike (ng/L)	Mean Compound Measured (ng/L)	Std Dev (ng/L)	Coeff of Var (%)
Fluoranthene	8	7.5	2.2	29
Pyrene	8	7.7	2.2	28
Benzo(a)anthracene	8	7.4	1.8	24
Chrysene	16	16.4	3.6	22
Benzo(b)fluoranthene	16	12.6	3.5	28
Benzo(k)fluoranthene	16	13.3	2.8	21
Benzo(a)pyrene	16	12.7	2.4	19

TABLE 13:

RESULTS FOR CHLOROBENZENES, ORGANOCHLORINE PESTICIDES, PCB's AND SURROGATES IN 7 NATURAL WATER SAMPLES COLLECTED OVER 7 DAYS.

Parameter	Amount of Spike (ng/L)	Mean Compound Measured (ng/L)	Std Dev (ng/L)	Coeff Of Var (%)
1,3-Dichlorobenzene	2.0	1.28	0.16	12
1,4-Dichlorobenzene	2.0	2.96	0.92	31
1,2-Dichlorobenzene	2.0	2.4	0.76	32
1,3,5-Trichlorobenzene	0.2	0.92	0.02	16
1,2,4-Trichlorobenzene	0.2	1.44	0.32	22
1,2,3-Trichlorobenzene	0.2	0.30	0.08	26
1,2,3,4-Tetrachlorobenzene	0.2	0.64	0.46	71
Pentachlorobenzene	0.2	0.16	0.11	65
Hexachlorobenzene	0.2	0.08	0.01	14
α-BHC	0.2	7.52	0.68	9
Lindane	0.2	1.32	0.17	13
Heptachlor	0.2			
Aldrin	0.2			
Heptachlor epoxide	0.2	0.13	0.01	7
γ-Chlordane	0.2			
α-Chlordane	0.2	0.02	0.004	21
α-Endosulfan	0.2			
p,p'-DDE	0.4	0.02	0.01	34
Dieldrin	0.4	0.35	0.04	10
Endrin	0.4	0.05	0.01	22
o,p'-DDT	0.6			
p,p'-TDE (p,p'-DDD)	0.6			
p,p'-DDT	0.6			
β-Endosulfan	0.4			
Mirex	0.4			
Methoxychlor	2.0			
PCB (Aroclor 1242;1254;1260)		1.44	0.72	50
Hexachlorobutadiene	0.2	0.06	0.02	27
1,3-Dibromobenzene	2.0	1.88	0.30	16
1,3,5-Tribromobenzene	0.8	0.68	0.12	18
1,2,4,5-Tetrabromobenzene	0.8	0.80	0.10	13
2,3,5,6-Tetrachlorobiphenyl	0.8	0.92	0.10	11
δ-BHC	0.4	0.72	0.13	19
Endrin Ketone	0.4	0.43	0.07	17
Octachloronaphthalene	0.96	1.08	0.16	15

TABLE 14A:

TYPICAL RESULTS FOR SUSPENDED SEDIMENT FROM NIAGARA ON THE LAKE FOR THE PERIOD APRIL-86 TO MARCH-87 (BASED ON WET WEIGHT).

Parameter	n*	Mean (ng/g)	Std Dev (ng/g)	Min. Value (ng/g)	Max. Value (ng/g)
1,3-Dichlorobenzene	12	11.5	8.0	3.7	20.2
1,4-Dichlorobenzene	28	12.1	7.8	2.8	38.9
1,2-Dichlorobenzene	12	4.6	1.3	2.6	6.9
1,3,5-Trichlorobenzene	30	1.0	0.9	0.1	4.2
1,2,4-Trichlorobenzene	49	6.8	6.5	0.4	30.4
1,2,3-Trichlorobenzene	46	1.6	2.7	0.2	17.3
1,2,3,4-Tetrachlorobenzene	47	13.3	15.5	1.0	66.7
Pentachlorobenzene	47	8.7	8.6	0.8	36.7
Hexachlorobenzene	49	10.3	17.2	0.1	84.5
α-BHC	17	3.9	1.8	1.3	8.2
Lindane	1	2.5		2.5	2.5
Heptachlor	0				
Aldrin	1	1.2		1.2	1.2
Heptachlor epoxide	0				
γ-Chlordane	0				
α-Chlordane	0				
α-Endosulfan	5	1.3	0.3	0.9	1.7
p,p'-DDE	49	2.1	0.7	0.9	5.6
Dieldrin	17	1.7	0.9	0.8	3.7
Endrin	0				
o,p'-DDT	33	0.4	0.2	0.2	0.8
p,p'-TDE (p,p'-DDD)	5	2.2	0.5	1.6	2.7
p,p'-DDT	40	2.1	1.7	0.3	10.2
β-Endosulfan	1	1.7		1.7	1.7
Mirex	34	1.7	2.7	0.2	15.5
Methoxychlor	8	4.7	1.8	2.6	7.3
PCB (Aroclor 1242;1254;1260)	49	77	39	31	231
Hexachlorobutadiene	45	6.5	15.8	0.2	70.5
		(%)	(%)	(%)	(%)
1,3-Dibromobenzene	49	93	8	75	109
1,3,5-Tribromobenzene	49	97	10	71	121
1,2,4,5-Tetrabromobenzene	49	110	15	85	164
2,3,5,6-Tetrachlorobiphenyl	49	100	14	69	142
δ-BHC	49	144	27	90	213
Endrin Ketone	49	96	21	59	145

* Number of positive values.

TABLE 14B:

TYPICAL RESULTS FOR SUSPENDED SEDIMENT FROM NIAGARA ON THE LAKE FOR THE PERIOD APRIL-86 TO MARCH-87 (BASED ON DRY WEIGHT).

Parameter	n*	Mean (ng/g)	Std Dev (ng/g)	Min. Value (ng/g)	Max. Value (ng/g)
1,3-Dichlorobenzene	11	35.9	24.0	8.7	98.6
1,4-Dichlorobenzene	27	35.5	25.8	7.3	136
1,2-Dichlorobenzene	11	13.8	6.5	5.5	27.8
1,3,5-Trichlorobenzene	29	3.0	2.2	0.3	10.1
1,2,4-Trichlorobenzene	48	19.8	19.8	1.0	90.9
1,2,3-Trichlorobenzene	45	4.7	8.3	0.4	51.5
1,2,3,4-Tetrachlorobenzene	46	40.7	50.0	2.0	199
Pentachlorobenzene	46	26.7	28.1	1.6	116
Hexachlorobenzene	48	29.7	50.6	0.2	295
α-BHC	16	8.2	6.3	3.2	28.7
Lindane	1	7.4		7.4	7.4
Heptachlor	0				
Aldrin	1	4.2		4.2	4.2
Heptachlor epoxide	0				
γ-Chlordane	0				
α-Chlordane	0				
α-Endosulfan	5	3.1	0.6	2.3	3.9
p,p'-DDE	48	5.8	2.1	2.2	14.2
Dieldrin	16	4.2	1.6	1.9	7.3
Endrin	0				
o,p'-DDT	32	1.1	0.5	0.4	2.6
p,p'-TDE (p,p'-DDD)	4	5.1	0.8	4.0	5.9
p,p'-DDT	39	5.3	3.2	0.7	17.7
β-Endosulfan	0				
Mirex	33	5.0	8.0	0.4	46.1
Methoxychlor	8	14.0	6.8	5.4	25.5
PCB (Aroclor 1242;1254;1260)	48	220	136	76	688
Hexachlorobutadiene	44	17.6	40	0.4	181

* Number of positive values.

TABLE 15:

RESULTS OF PROFICIENCY STUDY FOR SUSPENDED SEDIMENT SPIKES (n = 10 February 1987).

Parameter	Spiked Amount (ng/g)	Initial Analysis (ng/g)	Blank Value (ng/g)	Mean Recovery (ng/g)	Recovery (%)	Coeff. Of Var. (%)
1,3-Dichlorobenzene	50.0	5.5		5.5	11	38
1,4-Dichlorobenzene	50.0	18.0		18.0	36	22
1,2-Dichlorobenzene	50.0	13.4		13.4	27	33
1,3,5-Trichlorobenzene	5.0	4.0		4.0	80	25
1,2,4-Trichlorobenzene	5.0	11.8		11.8	236	34
1,2,3-Trichlorobenzene	5.0	2.5		2.5	50	8
1,2,3,4-Tetrachlorobenzene	5.0	12.1		12.1	242	7
Pentachlorobenzene	5.0	9.2		9.2	184	7
Hexachlorobenzene	5.0	9.8	5.6	4.2	84	24
α-BHC	5.0	4.6	1.4	3.2	64	16
Lindane	5.0	4.4		4.4	88	9
Heptachlor	5.0	3.9		3.9	78	8
Aldrin	5.0	4.2		4.2	84	7
Heptachlor epoxide	5.0	4.3		4.3	86	7
γ-Chlordane	5.0	4.9		4.9	98	14
α-Chlordane	5.0	3.7		3.7	74	8
α-Endosulfan	5.0	4.3		4.3	86	5
p,p'-DDE	5.0	5.2	1.6	3.6	72	14
Dieldrin	5.0	5.1	1.5	3.6	72	14
Endrin	5.0	4.6		4.6	92	11
o,p'-DDT	10.0	7.3		7.3	73	5
p,p'-TDE (p,p'-DDD)	10.0	10.6	2.5	8.1	81	25
p,p'-DDT	10.0	10.4	1.2	9.2	92	20
β-Endosulfan	5.0	4.3		4.3	86	16
Mirex	5.0	4.5	0.6	3.9	78	31
Methoxychlor	25.0	29.0		29.0	116	14
1,3-Dibromobenzene	50.0	56.1		56.1	112	10
1,3,5-Tribromobenzene	20.0	10.4		10.4	52	12
1,2,4,5-Tetrabromobenzene	20.0	16.4		16.4	82	7
2,3,5,6-Tetrachlorobiphenyl	20.0	21.3		21.3	106	34
δ-BHC	10.0	7.9		7.9	79	9
Endrin Ketone	10.0	14.7		14.7	147	14

TABLE 16:

RESULTS OF CONTINUING VERIFICATION FOR SUSPENDED SEDIMENT SPIKES (n = 10 from March to May 1987).

Parameter	Spiked Amount (ng/g)	Initial Analysis (ng/g)	Blank Value (ng/g)	Mean Recovery (ng/g)	Recovery (%)	Coeff. Of Var. (%)
1,3-Dichlorobenzene	50.0	11.6		11.6	23	19
1,4-Dichlorobenzene	50.0	21.1		21.1	42	11
1,2-Dichlorobenzene	50.0	17.6		17.6	35	16
1,3,5-Trichlorobenzene	5.0	2.4		2.4	48	15
1,2,4-Trichlorobenzene	5.0	10.0	7.1	2.9	58	24
1,2,3-Trichlorobenzene	5.0	4.3	1.5	2.8	56	14
1,2,3,4-Tetrachlorobenzene	5.0	15.6	11.2	4.4	88	12
Pentachlorobenzene	5.0	12.7	6.7	6.0	120	12
Hexachlorobenzene	5.0	11.0	6.2	4.8	96	24
α-BHC	5.0	6.1	0.9	5.2	104	9
Lindane	5.0	5.9		5.9	118	9
Heptachlor	5.0	4.1		4.1	82	7
Aldrin	5.0	4.6		4.6	92	7
Heptachlor epoxide	5.0	5.7		5.7	114	6
γ-Chlordane	5.0	4.5		4.5	90	7
α-Chlordane	5.0	4.6		4.6	92	10
α-Endosulfan	5.0	4.1		4.1	82	6
p,p'-DDE	10.0	12.7	2.3	10.4	104	11
Dieldrin	10.0	10.3	1.1	9.2	92	7
Endrin	10.0	10.2		10.2	102	6
o,p'-DDT	15.0	14.1		14.1	94	10
p,p'-TDE (p,p'-DDD)	15.0	18.7	2.6	16.1	107	7
p,p'-DDT	15.0	17.6	0.9	16.7	111	9
β-Endosulfan	10.0	8.4		8.4	84	7
Mirex	10.0	9.7	0.9	8.8	88	10
Methoxychlor	50.0	55		55	109	7
PCB (Aroclor 1242;1254;1260)	200	272	75	197	99	8
Hexachlorobutadiene	5.0	2.5		2.5	50	33
1,3-Dibromobenzene	50.0	47		47	94	7
1,3,5-Tribromobenzene	20.0	15.8		15.8	79	6
1,2,4,5-Tetrabromobenzene	20.0	22.5		22.5	112	4
2,3,5,6-Tetrachlorobiphenyl	20.0	21.7		21.7	108	4
δ-BHC	10.0	10.7		10.7	107	16
Endrin Ketone	10.0	10.4		10.4	104	10
Octachloronaphthalene	24.0	24.9		24.9	104	8

TABLE 16 continued.

RESULTS OF CONTINUING VERIFICATION FOR SUSPENDED SEDIMENT SPIKES (n = 10 from March to May 1987).

Parameter	Spiked Amount (ng/g)	Initial Analysis (ng/g)	Blank Value (ng/g)	Mean Recovery (ng/g)	Recovery (%)	Coeff. Of Var. (%)
Fluoranthene	200	370	210	160	80	24
Pyrene	200	360	170	190	95	19
Benzo(a)anthracene	200	380	210	170	85	31
Chrysene	400	630	260	370	92	26
Bis(2-ethylhexyl) phthalate		390	390	390		17
Dioctylphthalate		210	210	210		13
Benzo(b)fluoranthene	400	530	110	420	105	20
Benzo(k)fluoranthene	400	530	110	420	105	20
Benzo(a)pyrene	400	470	90	380	95	18
2,4,6-Trichlorophenol		500	500	500		29
2,4,5-Trichlorophenol		450	450	450		13
Pentachlorophenol		890	890	890		13
Phenol	800	1050	460	590	74	29

TABLE 17A:

DETECTION LIMITS FOR CHLOROBENZENES, ORGANOCHLORINE PESTICIDES PCB's AND SURROGATES IN SUSPENDED SEDIMENTS.

Parameter	IDL (pg)	WET WEIGHT MDL & PDL* (ng/g)	DRY WEIGHT MDL & PDL* (ng/g)
1,3-Dichlorobenzene	3.0	4.1	11.1
1,4-Dichlorobenzene	3.2	4.2	11.7
1,2-Dichlorobenzene	3.3	5.3	14.7
1,3,5-Trichlorobenzene	0.38	0.66	1.8
1,2,4-Trichlorobenzene	0.59	1.3	3.6
1,2,3-Trichlorobenzene	0.36	0.69	1.9
1,2,3,4-Tetrachlorobenzene	0.28	0.98	2.7
Pentachlorobenzene	0.28	1.4	3.7
Hexachlorobenzene	0.29	2.3	6.3
α-BHC	0.41	0.83	2.3
Lindane	0.51	1.0	2.9
Heptachlor	0.32	0.50	1.4
Aldrin	0.30	0.60	1.6
Heptachlor epoxide	0.62	0.69	1.9
γ-Chlordane	0.65	0.56	1.5
α-Chlordane	0.69	0.84	2.3
α-Endosulfan	0.71	0.49	1.4
p,p'-DDE	1.1	2.0	5.6
Dieldrin	1.5	1.2	3.2
Endrin	1.6	1.0	2.9
o,p'-DDT	2.4	2.5	7.0
p,p'-TDE (p,p'-DDD)	2.6	2.2	6.0
p,p'-DDT	2.5	2.7	7.5
β-Endosulfan	1.4	1.0	2.9
Mirex	0.71	1.6	4.3
Methoxychlor	6.5	6.5	18
PCB (Aroclor 1242;1254;1260)	40	28	77
Hexachlorobutadiene	0.71	1.5	4.2
1,3-Dibromobenzene	4.3	-	-
1,3,5-Tribromobenzene	1.1	-	-
1,2,4,5-Tetrabromobenzene	2.7	-	-
2,3,5,6-Tetrachlorobiphenyl	1.3	-	-
δ-BHC	1.5	-	-
Endrin Ketone	2.5	-	-
Octachloronaphthalene	2.3	-	-

* MDL and PDL are operationally the same.

TABLE 17B:

DETECTION LIMITS FOR POLYNUCLEAR AROMATIC HYDROCARBONS, PHENOLS AND 2,3,7,8-TCDD IN SUSPENDED SEDIMENT.

Parameter	IDL (pg)	WET WEIGHT MDL & PDL* (ng/g)	DRY WEIGHT MDL & PDL* (ng/g)
Fluoranthene	43	77	195
Pyrene	49	66	182
Benzo(a)anthracene	82	97	270
Chrysene	107	178	490
Bis(2-ethylhexyl) phthalate	159	119	330
Dioctylphthalate	148	51	141
Benzo(b)fluoranthene	161	156	430
Benzo(k)fluoranthene	204	154	420
Benzo(a)pyrene	159	126	350
2,4,6-Trichlorophenol	165	260	720
2,4,5-Trichlorophenol	135	106	290
Pentachlorophenol	198	220	600
Phenol	192	310	860
2,3,7,8-TCDD	21	N/A	N/A

* MDL and PDL are operationally the same.

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(1) Goulden, P. D. and D. H. J. Anthony 1985. Design of a Large Sample Extractor for the Determination of Organics in Water. Analytical Methods Division, NWRI, CCIW, Burlington, Ontario. Report No. 85-121.

(2) Goulden, P. D. and D. H. J. Anthony 198 . A Modified Large Sample Extractor for a 24-Hour Sampling Period. Analytical Methods Division, NWRI, CCIW, Burlington, Ontario.

(3) Sampling Protocols Group (Group A). Niagara River Sampling Protocol. 1986.

METHOD FOR THE ANALYSIS OF VOLATILES IN WATER FROM THE NIAGARA RIVER

1.0 SCOPE AND APPLICATION:

This method is designed to determine volatile organic pollutants (in this document such analytes will be referred to as volatiles) in Niagara River water samples. A comprehensive measurement of all volatiles is not attempted but rather special emphasis is placed on those volatiles required by the Niagara River Monitoring project. These compounds are: Methylene Chloride; Chloroform; Benzene; 1,2-Dichloroethane; Carbon Tetrachloride and Tetrachloroethylene.

2.0 PRINCIPLE AND THEORY:

A sample of Niagara River water that has been collected in duplicate in 40 mL glass bottles according to the Sampling Protocol (1) is transferred into an Environchem 810A purge and trap unit. Volatiles are purged from the water sample and concentrated on a large bore, primary trap containing sorbent resins. An estimation of the purged volatiles is obtained by monitoring these analytes from the first trap using an FID as a screen for the level of contamination. Subsequent to the FID screening procedure residual water vapour is then removed from the trap and plumbing with a stream of helium (He). Retained organic compounds are then transferred to a small bore secondary trap. This is also an adsorbent trap containing five discrete sorbent materials packed in series. The end result of the two trap system is an effective purging and trapping of the analytes from the water and concentration of the volatiles on a trap with a small internal diameter that is designed for efficient transfer of analytes to the analytical capillary column.

Subsequent to the purge and trap sequence, the secondary trap is rapidly heated and the analytes are desorbed directly into a capillary column connected to a Finnigan 4500 GC/MS for mass spectral identification of analyte structure and determination of the concentration of each analyte.

3.0 INSTRUMENTATION

3.1 Purge/Trap Unit: The purge/trap unit is an Environchem model series 810A Universal Automated Concentrator (UNACON) with two proportional flow controllers (FIGURE 1). It functions as an isolation/ concentration system for volatiles from the matrix and as an inlet to the capillary column for GC/MS analysis. The unit consists of a 13 mL purging apparatus (FIGURE 2), two sorbent traps and associated systems for transferring volatiles to

analytical instruments. Sorbent materials in the traps are selected for the following characteristics: good adsorption during the isolation phase of the procedure; good desorption characteristics during the heating cycle and thermal stability. All sorbent materials used are stable to at least 350°C and are conditioned at 300°C to reduce background. The characteristics of the sorbents are described in TABLE 1.

The large bore primary trap (205 mm X 4 mm) contains three sorbent resins: Glass beads, Tenax, and Ambersorb XE 340 as well as glass wool packing. (Ambersorb XE 340 is the most anhydrous of the Ambersorb series). Both the large bore of the column as well as the anhydrous, hydrophobic nature of the sorbents are important features of the primary trap. This design permits a large flow of He sparging gas to be passed through the sample with a relatively high degree of efficiency for selective concentration of the volatiles of interest.

The secondary trap is a narrow bore system (205 mm X 1 mm) with approximately 1/10 the capacity of the first trap. This is also a sorbent trap containing the five discrete sorbent materials listed in TABLE 1 and glass wool packing and is used to trap organics desorbed off the primary trap. The small bore allows for an efficient transfer of volatiles to the capillary column. This is due to the relatively high linear velocity of gas through the small inner diameter of the trap even at the low flow rates required by capillary column GC. Efficiency of transfer from trap to column is also ensured by the thermal stability of sorbents which allows for a rapid increase to high temperature for desorption. Finally, efficient transfer of analyte to column is also ensured by heating the transfer lines between the two instruments to 250°C.

The traps are linked to the GC column through a flow controlled and NOT a pressure controlled system. This approach is used because in a capillary column the linear velocity of carrier gas changes with temperature. When flow is controlled the retention times are more reproducible.

3.2 GAS CHROMATOGRAPH: Gas chromatography is carried out on fused silica capillary columns coated with polydimethyl siloxane (SPB-1) 60 M by 0.32 mm I.D. with a 1.0 u film thickness. The oven temperature of the GC is maintained at 60°C for 5 minutes, programmed to 200°C at 10°C/min. and held at 200°C for 10 min. The temperature is then ramped to 250°C at 15°C/min. with no hold at 250°C. The GC column is inserted directly into the ion source and positioned approximately 1 mm away from the orifice of the ion volume.

3.3 MASS SPECTROMETER/ DATA SYSTEM: The mass spectrometer is a Finnigan 4500 quadrupole instrument. For analysis of volatiles, electron impact ionization (EI) at 70 EV is used. High sensitivity quantitative determination of target analytes utilizes appropriate multiple ion detection. In order to ensure unit

resolution and maximum sensitivity over the mass range of interest the mass spectrometer is calibrated using perfluorotributylamine (FC 43).

The GC/MS data from both standard and sample analyses is collected and stored on the data system. Standard libraries are created by determining pure standards under exactly the same conditions used for sample acquisition and processing. Hardcopies of standard and sample data are created for spectra of interest. Sample spectra are displayed with standard spectra and the purity or fit as an indication of the degree of match are recorded. Positive confirmations are hardcopied showing spectra of samples and standard library comparison. The base peak of the mass spectrum is used for quantitation.

4.0 REAGENTS AND STANDARDS.

4.1 Organic Free Water: Organic free water (OFW) is prepared by purging previously boiled milli-Q water with U.H.P. He for an hour. This sample is then tested for organics by the procedures described above. Matrix water is water from the Niagara River that has been sparged twice and on the second analysis shown to be free of organics. This water serves as a control of any matrix effects.

4.2 Organic Compounds: Pure organic solvents as supplied from B & J or Caledon are used. These volatile organic compounds are checked before standard preparation by injecting 1 uL of each solvent directly onto the column in the split mode (20:1 or greater) and monitoring the response by GC/MS. The internal standards used for calibration is perdeuterated benzene (benzene D 6).

4.3 Preparation Of Stock Solutions: The stock solution is prepared by diluting the analyte to a concentration of 10,000 ng/uL (or 10 ug/uL or 10 mg/mL) in methanol (MeOH). This concentration need not be prepared accurately at 10,000 ng/uL but it must be exactly known. Concentrations in this range are prepared by transferring an appropriate and accurately measured volume (calculated to weigh 0.1 g based on density) into a 10 mL volumetric flask containing 9.0 mL methanol. This solution is then brought to volume with methanol.

NOTE: TRANSFER OF VOLUMES OF KNOWN WEIGHT MUST BE CARRIED OUT AT 25°C (TABLE 2). IF DILUTIONS ARE MADE AT A DIFFERENT TEMPERATURE THE DENSITY AT THAT TEMPERATURE MUST BE KNOWN AND RECORDED.

Intermediate solutions are prepared as needed by spiking 10 uL of the 10^4 ng/uL stock solution into 10 mL of reagent water. This gives an intermediate solution at a concentration of 10 ng/uL. The working solution is prepared daily by diluting 10 uL of the

intermediate into 10 mL reagent water which gives a solution with a concentration of 10 pg/uL. Working standards at medium and low concentrations are prepared daily by diluting 5.0 and 2.5 uL of stock into 10 mL and proceeding as for the 10 pg/uL solutions. All standard solutions are also spiked with 50 ng of perdeuterated benzene (benzene D 6) to serve as an internal standard for identification and quantitation.

4.4 Quality Control: A previously analysed sample is reanalysed as a blank to establish that background is low and then the it is spiked with a standard and analysed. If the recovery of the standard containing the volatiles of interest varies by more than 3 standard deviations, the spiking and reanalysis is repeated. The same sample is then repurged for blank purposes. During the daily run of samples one of the purged samples is spiked with a standard and reanalysed. If the recovery of the standard varies by more than 3 standard deviations, the spiking and reanalysis is repeated. At the end of the day the last sample is repurged as a blank. If a sample shows unusual concentrations (ie. greater than three times the MDL) the analysis is repeated.

5.0 SAMPLING PROCEDURES:

5.1 Preparation of Bottles and Septa: Proper preparation of sample bottles and septa (ie those surfaces in contact with the sample) is one essential prerequisite to obtaining reliable data. The described procedures must be adhered to, or if alterations are made they must first be shown to produce equally clean bottles and septa. Common to all cleaning procedures that are used in conjunction with volatiles is the requirement that these be carried out in an environment free of analytes.

Sample bottles are first washed with detergent followed by a hot water rinse to flush away flotated soil. The bottles are then drained. Subsequently, the bottles are rinsed twice with acetone, twice with hexane and then dried using nitrogen. Finally the bottles are heated in an oven maintained at 175°C overnight.

Septa are prepared an hour before use and washed in a similar manner: specifically washed with detergent, hot water, distilled water, and are then air dried in an organic-free environment.

5.2 Control of Contamination: Sampling of water for trace organic analysis demands absolute care in all respects including personal cleanliness. Samples can be contaminated from the following sources:

(a) persons carrying out the investigations - dirty hands; hand lotion, perfume, after shave lotion and cigarette smoke etc.

(b) equipment and laboratory environment - intermediate transferring devices like plastic hoses, rubber seals

and glue, etc; solvents used in the nearby area.

This or any other contamination source list must be considered to be incomplete and both laboratory analysts and field investigators must be aware of unexpected sources. When these are identified the list will be expanded. Such identification is completely dependent upon stringent observation and reporting by all investigators.

5.3 Sample Collection Procedures: It is the intent that all samples are to be collected, at least in duplicate. If replicate samples are not available due to extenuating circumstances these circumstances are noted in the log book.
The sample bottle is rinsed several times with water to be sampled. The bottle is filled to overflowing and placed on a level surface. The septum seal is positioned with the teflon side upon the convex meniscus and the bottle is sealed by screwing the cap on tightly. The sample is inverted and the cap is lightly tapped on a solid surface. Absence of entrapped air indicates a successful seal. If bubbles are present, the bottle is opened, a few additional drops of sample are added and the bottle resealed.

5.4 Labeling, Shipment and Storage of samples: Following collection according to the sampling protocol (1), all bottles must be properly labelled in a clear and legible manner. All labelling must include the following information:

(i) sample or site identification

(ii) original (A), duplicate (B)

(iii) date sampled

Bottles of each sample set are stored in a sealed plastic bag and in a cooler (not frozen) for shipment to the laboratory. Samples are shipped to the National Water Quality Laboratory where laboratory identification numbers are added. Included with each shipment is a list of all samples to be analyzed and a list of all complete and incomplete sample sets. Maximum storage time at $4^{o}C$ is 14 days.

6.0 PURGE AND TRAP TECHNIQUE:

Ten ml of sample is transferred from the bottle by pouring into the 13 mL purge/trap unit. The sample is sparged with U.H.P. He at a flow rate of 60 cc/min at room temperature for 13 minutes. Volatiles are concentrated on a large bore, primary trap and are monitored for level of contamination by FID.

NOTE: SHOULD SAMPLE RESULTS EXCEED ANALYTICAL LIMITS, THE ORIGINAL SAMPLE SHOULD BE DILUTED AND REANALYZED.

NOTE: SOME WATER IS RETAINED IN THE PLUMBING AND ON THE RESINS OF THE PRIMARY TRAP. DRYING OF THE SYSTEM PRIOR TO TRANSFER TO THE SECONDARY TRAP IS ESSENTIAL AS THE SECONDARY TRAP CONTAINS SILICA GEL WHICH CAN ADSORB WATER THUS INVALIDATING SUBSEQUENT STEPS IN THE ANALYSIS.

Drying of the primary trap is affected by passing dry gas (He) through the system at a flow of 60 cc/min. for 8 minutes. Subsequent to drying, the first trap is heated to 250°C in 20 sec. desorbing retained compounds onto a small bore, secondary trap for 3 minutes at a flow of 2 cc/min. This trap is then quantitatively, reproducibly, and quickly desorbed directly onto a capillary column by heating to 250°C in 20 sec. at a flow of 2 cc/min.(Section 3.1). For maximum sensitivity the capillary column is inserted directly into the MS source.

Full scan EI data are acquired and stored. Relative retention time (relative to benzene D 6) and mass spectral match of sample and library standards will determine the structure. Quantitative analysis is affected by the internal standard method using volatile compounds that are not in the matrix. Single point calibration technique is used and the concentrations are calculated from the following equations using the AUTOQU.PR Finnegan quantitation program:

$$Cs = (R_{an}/R_{is})_{sample} / RF$$

Where:

C_s = concentration of analyte in sample (ug/L)

R_{an} = response of system to analyte in the sample

R_{is} = response of system to internal standard in the sample (benzene D 6)

RF = Response Factor $= (A_{an}/A_{is})_{std} / C_{std}$

Where:

C_{std} = concentration of analyte in the standard solution (ug/L)

A_{an} = response of the system to analyte in the standard solution

A_{is} = response of the system to internal standard in the standard solution (benzene D 6)

Typical traces are shown in FIGURE 3 and gas chromatographic characteristics are summarized in TABLE 3.

Detection limit is based on seven replicate determinations and defined statistically according to the following equation:

$$DL = B + S \times t_{(n-1)}$$

Where:

DL = Detection Limit (ug/L)

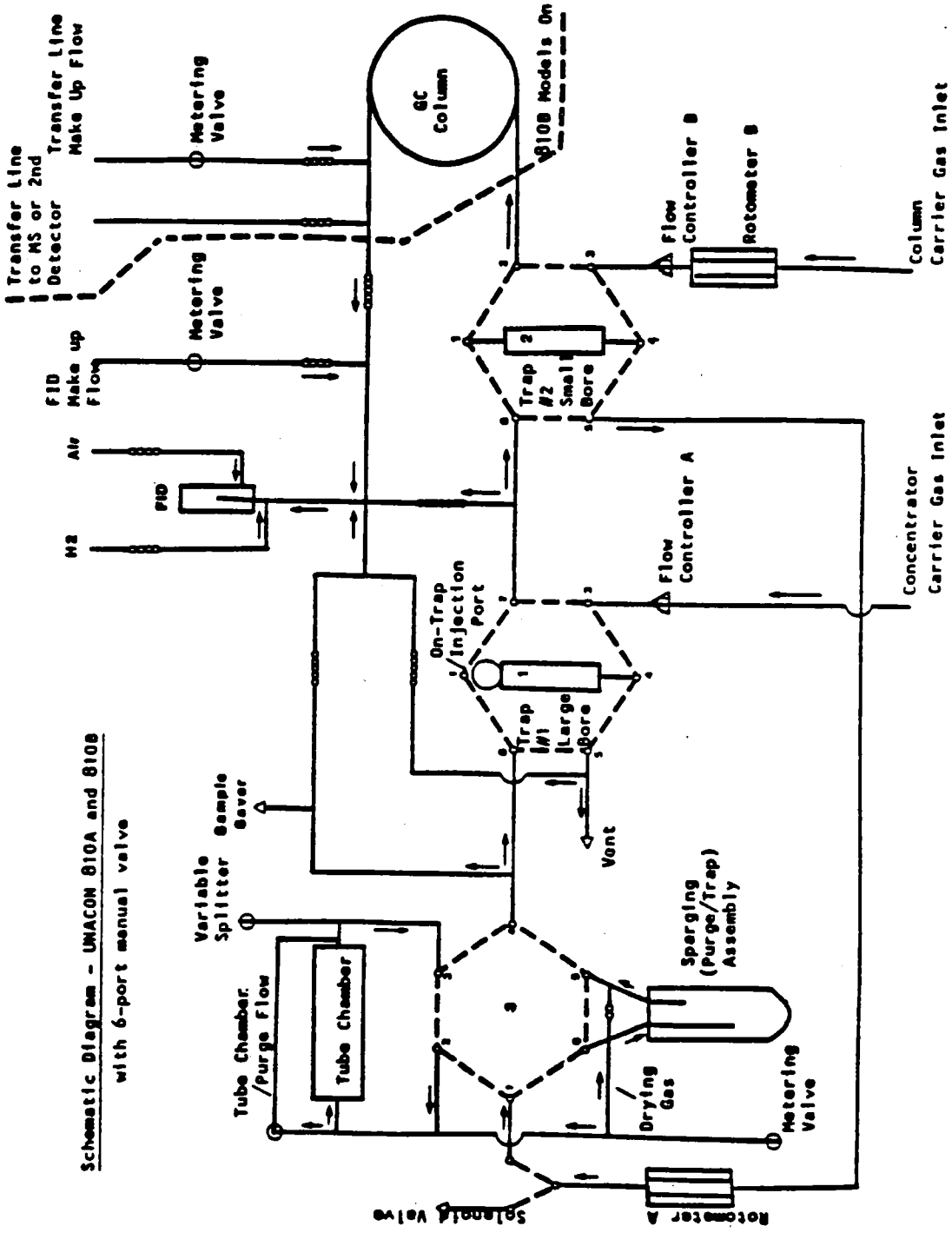
B = signal in the blank

S = Standard Deviation (ug/L)

t = Student's T value (For n = 7, t = 1.943).

The performance characteristics of the method are shown in TABLE 4. These were defined using OFW to which known concentrations of analyte had been added. The seven volatiles are monitored using the information in the Volatile Library (TABLE 5) and the Descriptor (FIGURE 4).

FIGURE 1



Schematic Diagram - UNACON 810A and 8108

with 6-port manual valve

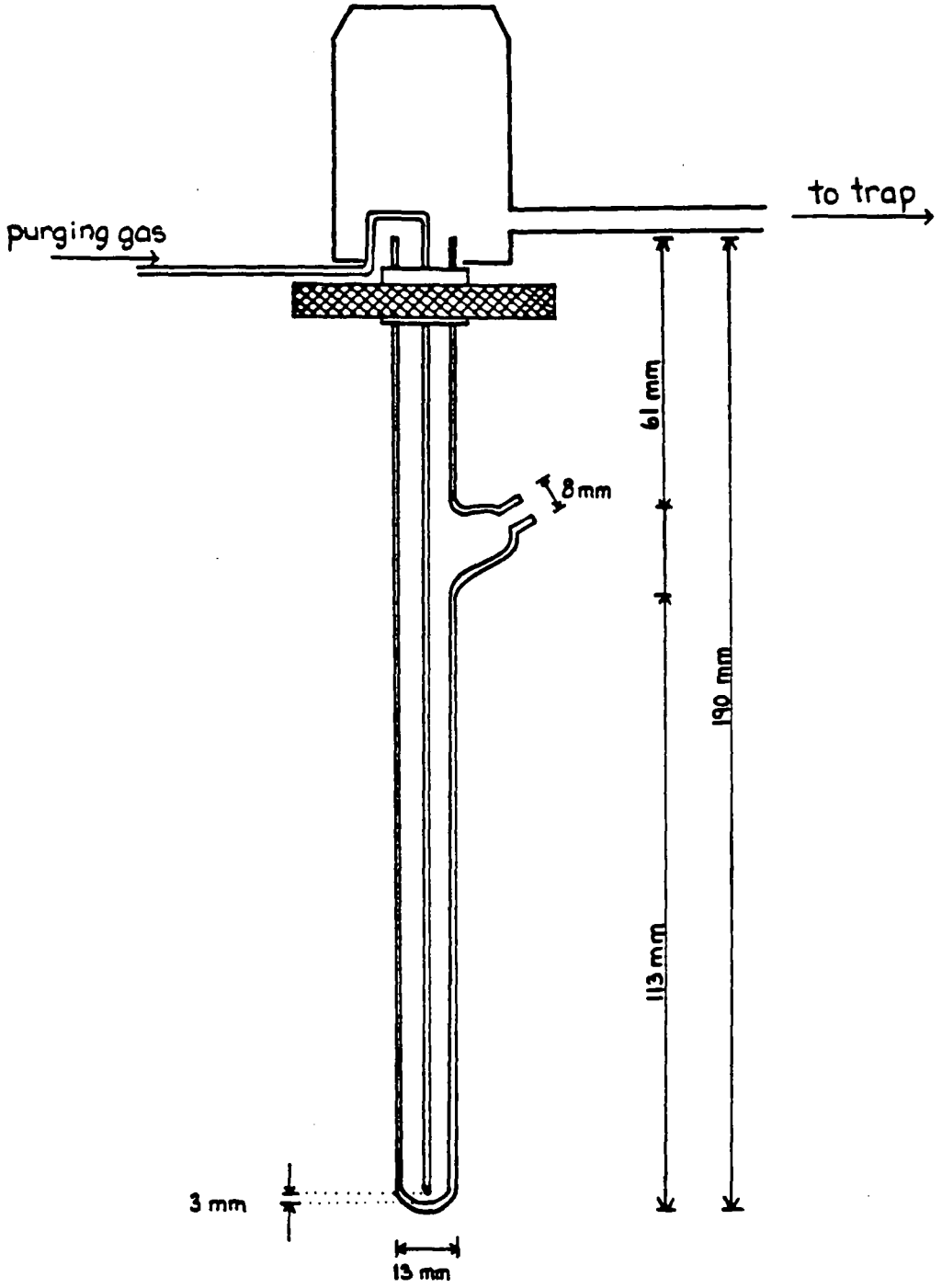


FIGURE 2: PURGING APPARATUS

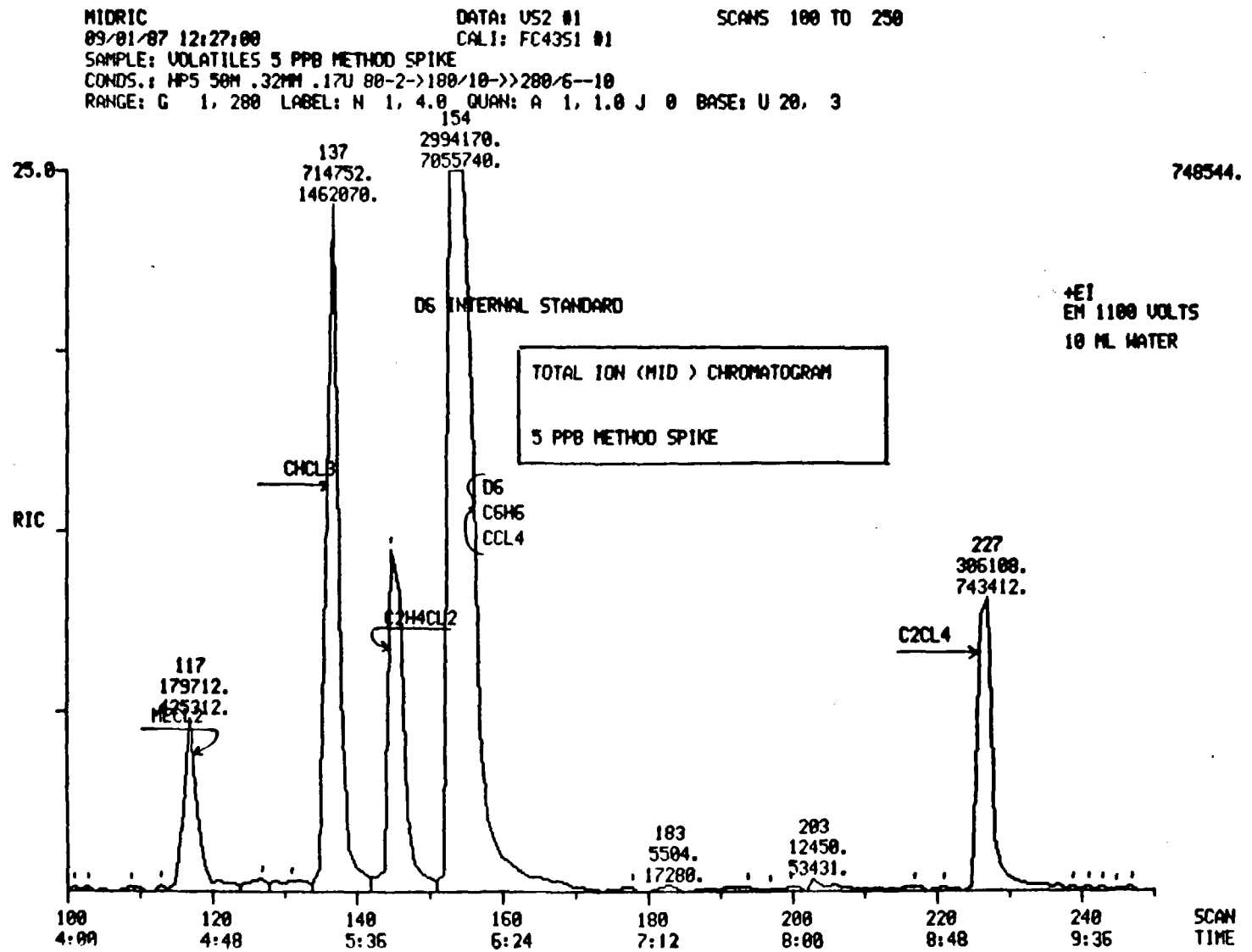

MIDRIC
09/01/87 12:27:00
SAMPLE: VOLATILES 5 PPB METHOD SPIKE
CONDS.: HP5 50M .32MM .17U 80-2->180/10->>280/6--10
RANGE: G 1, 200 LABEL: N 1, 4.0 QUAN: A 1, 1.0 J 0 BASE: U 20, 3
DATA: V52 #1
CALI: FC4351 #1
SCANS 100 TO 250
25.0
RIC
748544.
+EI
EM 1100 VOLTS
10 ML WATER
TOTAL ION (MID) CHROMATOGRAM
5 PPB METHOD SPIKE
137
714752.
1462070.
154
2994170.
7055740.
D6 INTERNAL STANDARD
CHCL3
D6
C6H6
CCL4
C2H4CL2
117
179712.
425312.
MECL2
227
306100.
743412.
C2CL4
183
5504.
17280.
203
12450.
53431.
100
4:00
120
4:48
140
5:36
160
6:24
180
7:12
200
8:00
220
8:48
240
9:36
SCAN
TIME

FIGURE 3

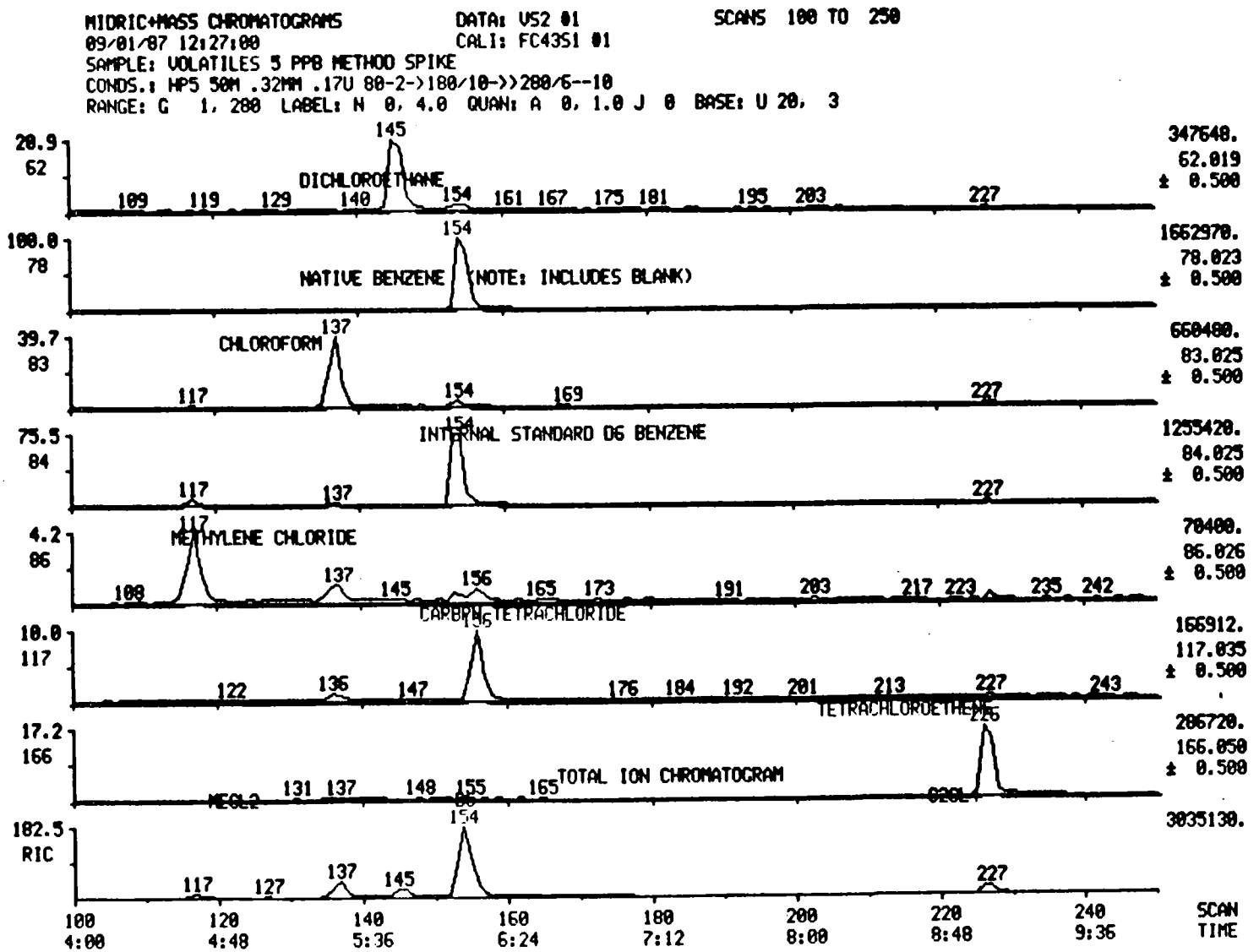


FIGURE 3 continued

Quantitation Report File: VS2

Data: VS2.TI
09/01/87 12:27:00
Sample: VOLATILES 5 PPB METHOD SPIKE
Conds.: HP5 50M .32MM .17U 80-2->180/10->>280/6--10
Formula: PFBR HERBS Instrument: FINN Weight: 180.000
Submitted by: NWQL Analyst: JC/AC Acct. No.: 300-400

AMOUNT=HEIGHT * REF AMNT/(REF HEIGHT * RESP FACT)
Resp. fac. from Library Entry

No	Name
1	DEUTERATED BENZENE D6 INTERNAL STD
2	METHYLENE CHLORIDE
3	CHLOROFORM
4	DICHLOROETHANE
5	NATIVE BENZENE
6	CARBON TETRACHLORIDE
7	TETRACHLOROETHYLENE

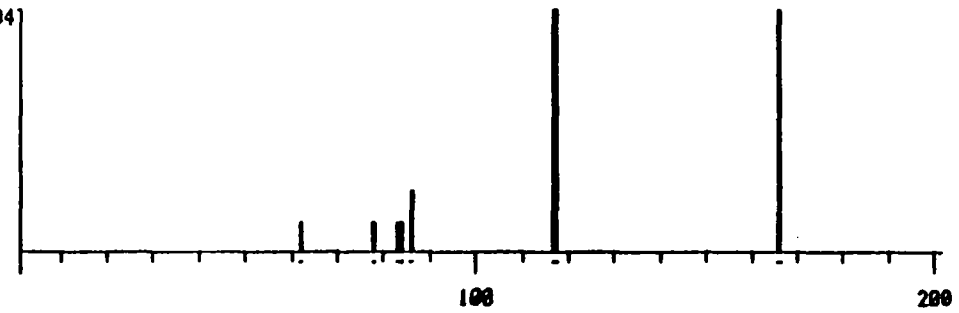
No	m/z	Scan	Time	Ref	RRT	Meth	Area(Hght)	Amount	%Tot
1	84	154	6:10	1	1.000	A BB	1249110. *	5.000 PPB	14.29
2	86	117	4:41	1	0.760	A BV	68905. *	5.000 PPB	14.29
3	83	137	5:29	1	0.890	A BB	653078. *	5.000 PPB	14.29
4	62	145	5:48	1	0.942	A VV	343386. *	5.000 PPB	14.29
5	78	154	6:10	1	1.000	A BB	1654440. *	5.000 PPB	14.29
6	117	156	6:14	1	1.013	A BB	161750. *	5.000 PPB	14.29
7	166	226	9:02	1	1.468	A BB	284709. *	5.000 PPB	14.29

No	Ret(L)	Ratio	RRT(L)	Ratio	Amnt	Amnt(L)	R.Fac	R.Fac(L)	Ratio
1	6:05	1.01	1.000	1.00	5.00	5.00	1.000	1.000	1.00
2	4:38	1.01	1.000	0.76	5.00	5.00	0.055	0.055	1.00
3	5:26	1.01	1.000	0.89	5.00	5.00	0.523	0.523	1.00
4	5:46	1.01	1.000	0.94	5.00	5.00	0.275	0.275	1.00
5	6:07	1.01	1.000	1.00	5.00	5.00	1.324	1.324	1.00
6	6:12	1.01	1.000	1.01	5.00	5.00	0.129	0.129	1.00
7	9:00	1.00	1.000	1.47	5.00	5.00	0.228	0.228	1.00

FIGURE 3 continued

MID DESC: V2
INST: FINN CALI: FC43N10

MASS DEFECT AT 100 U 30 MMU
MASTER RATE 16384
TOTAL ACQU TIME 2.310 S
TOTAL SCAN TIME 2.400 S
CENT SAMP INT 0.200 MS
CALI MASS RANGE 69 TO 502 U



7.	61.750	166.250	1.000	2.400	1	80	0	1	0	POS
INT	BEGIN	END	TIME	(SECS)	MPW	MFW	MA	TH	BL	ION
0	MASS	MASS	REQUEST	ACTUAL						
1.	61.750	62.250	0.100	0.102	1	80	30	1	0	POS
2.	77.750	78.250	0.100	0.111	1	80	30	1	0	POS
3.	82.750	83.250	0.100	0.105	1	80	30	1	0	POS
4.	83.750	84.250	0.100	0.105	1	80	30	1	0	POS
5.	85.750	86.250	0.200	0.210	1	80	30	1	0	POS
6.	116.750	117.250	0.600	0.839	1	80	30	1	0	POS
7.	165.750	166.250	0.600	0.839	1	80	30	1	0	POS

FIGURE 4: DESCRIPTOR

TABLE 1:

SORBENT MATERIALS USED IN THE ENVIROCHEM UNACON TRAPS*

SORBENT MATERIAL*	CHEMICAL DESCRIPTION	LARGE BORE TRAP (length of layer mm)	SMALL BORE TRAP (length of layer mm)	SORPTION CHARACTERISTICS
Glass Beads	SiO_2	30	2	Retains high boiling, high molecular weight organics
TENAX	Porous Polymer	75	80	Retains medium to low boiling organics
Silica gel	$Si(OH)_n$	-	30	Retains medium to low boiling, polar organics and water.
Ambersorb XE 340	Carbonaceous Adsorbent	35	30	Retains low boiling organics.
Charcoal	Activated Carbon	-	14	Retains all organics

* as supplied by the manufacturer

TABLE 2:

PHYSICAL CHARACTERISTICS OF ANALYTES

Parameter	Boiling point (^{o}C) (760 mm)	Density (25^{o}C)	Volume to prepare 10 mL standard stock mix at 10^{4} ng/uL (uL)
Dichloromethane	40	1.3266	75
Chloroform	61.7	1.4832	67
Carbon tetrachloride	76.5	1.5940	63
Benzene	80.1	0.8765	114
1,2-Dichloroethane	83.5	1.2351	81
Tetrachloroethylene	121	1.6227	62
Benzene D 6	80	0.95	NA

TABLE 3:

GC/ MS CHARACTERISTICS OF THE VOLATILES

Parameter	Ions Monitored	Relative Retention Time	Spiking Level (ug/L)	Mean Response (Area) (n = 7)	Coeff. of Variation (%)
Benzene D6	84	1.00	1.00	188992	20.5
Dichloro-methane	86	0.757	1.00	42498	8.5
Chloroform	83	0.888	1.00	109360	9.6
1,2-Dichloro-ethane	62	0.947	1.00	80389	9.4
Benzene	78	1.007	1.00	186496	20.7
Carbon tetrachloride	117	1.020	1.00	19248	8.9
Tetrachloro-ethylene	166	1.487	1.00	59460	20.5

TABLE 4:

DETECTION CHARACTERISTICS OF THE METHOD (n = 7)

Parameter	Spiking Level (ug/L)	Mean (ug/L)	Std Dev (ug/L)	Coeff. of Var. (%)	MDL & PDL* (ug/L)
Benzene D6	1.00	0.777	0.160	20.5	0.31
Dichloro-methane	1.00	0.953	0.081	8.5	0.16
Chloroform	1.00	1.176	0.112	9.6	0.22
1,2-Dichloro-ethane	1.00	1.130	0.106	9.4	0.21
Benzene	1.00	0.806	0.167	20.7	0.32
Carbon tetrachloride	1.00	1.068	0.095	8.9	0.18
Tetrachloro-ethylene	1.00	0.877	0.180	20.5	0.35

* In this method MDL and PDL are operationally the same.

MDL = Method detection limit.

PDL = Practical detection limit.

TABLE 5:

VOLATILE LIBRARY

Code/Entry:	Name / Ret Time / CAS-Number / Rel Ret Tm	B Pk / Qn	Area / Mass	MW / Amount	Formula / Units	Mass/Intensity Pairs / Res	Fac	Fit	Th	Sch	W	Ref.	Peak
V3	1: D6 BENZENE INTERNAL STD				C6.D6								
	4:53	84											
	0.000		0.000	(	62, 574)(	78, 353)(	83, 36)						
	1.000	84.00		2.50	UG/L	1.000		84		4595710.		V3:	1
V3	2: METHYLENECHLORIDE				C.H2.CL2								
	3:17	84											
	0.000		0.000	(	78, 0)(	83, 42)(	84,1000)						
	1.000	84.00		2.50	UG/L	0.453		84		791552.		V3:	1
V3	3: CHLOROFORM				C.H.CL3								
	4:24	83											
	0.000		0.000	(	78, 0)(	83,1000)(	84, 34)						
	1.000	83.00		2.50	UG/L	0.547		120		2445310.		V3:	1
V3	4: CARBONTETRACHLORIDE				C.CL4								
	4:46	117											
	0.000		0.000	(	78, 0)(	83, 27)(	84, 134)						
	1.000	117.00		2.50	UG/L	0.072		152		393728.		V3:	1
V3	5: DICHLOROETHANE				C2.H4.CL2								
	4:53	84											
	0.000		0.000	(	62, 574)(	78, 353)(	83, 36)						
	1.000	62.00		2.50	UG/L	0.237		98		4595710.		V3:	1
V3	6: BENZENE, NATIVE + TRAP BLANK				C6.H6								
	4:55	78											
	0.000		0.000	(	62, 489)(	78,1000)(	83, 12)						
	1.000	78.00		2.50	UG/L	0.828		78		3764220.		V3:	1
V3	7: TETRACHLOROETHENE				C2.CL4								
	7:29	166											
	0.000		0.000	(	78, 0)(	83, 19)(	84, 16)						
	1.000	166.00		2.50	UG/L	0.091		164		593920.		V3:	1

REFERENCES

(1) Sampling Protocols Group (Group A). Niagara River Sampling Protocol. 1986.

METHODS FOR METAL ANALYSIS IN WATER AND SUSPENDED SEDIMENT

I INTRODUCTION AND SUMMARY OF PROCEDURES:

Three operational phases are involved in the determination of metals from Niagara River samples:

(a) a collection phase

(b) sample preparation prior to instrumental analysis

(c) instrumental analysis and interpretation.

A quality control program is carried out in parallel to the analyses of samples. Both the determination of the analytes and quality control are integral to the reporting of the final data. Data on water and sediment are obtained and reported in this investigation.

Raw river water is passed through a Westfalia Centrifuge which separates sediments from water. The water and sediment for these analyses are collected at this stage. In general, sample preparation procedures require acid digestion and/or concentration of the metals prior to instrumental analysis as shown in FIGURE I - 1. Special procedures are used in the sample preparation of Mercury, Silver, Arsenic, Selenium and Antimony. Instrumental analysis is either by Atomic Emission Spectroscopy (AES) or Atomic Absorbtion Spectroscopy (AAS). In the case of AES, Inductively Coupled Plasma (ICP) is used as an excitation technique to provide a maximum dynamic range for determinations. Automated sample injection techniques are used to reduce cost of analysis and time required for reporting data.

Quality control is an integral and essential part of the final report as this permits a rigorous and quantitative evaluation of data. It is particularly important in the Niagara River Program as this will be the only laboratory involved in the study at this time. Quality control involves:

(a) determination of appropriate blanks

(b) analysis of selected samples in duplicate

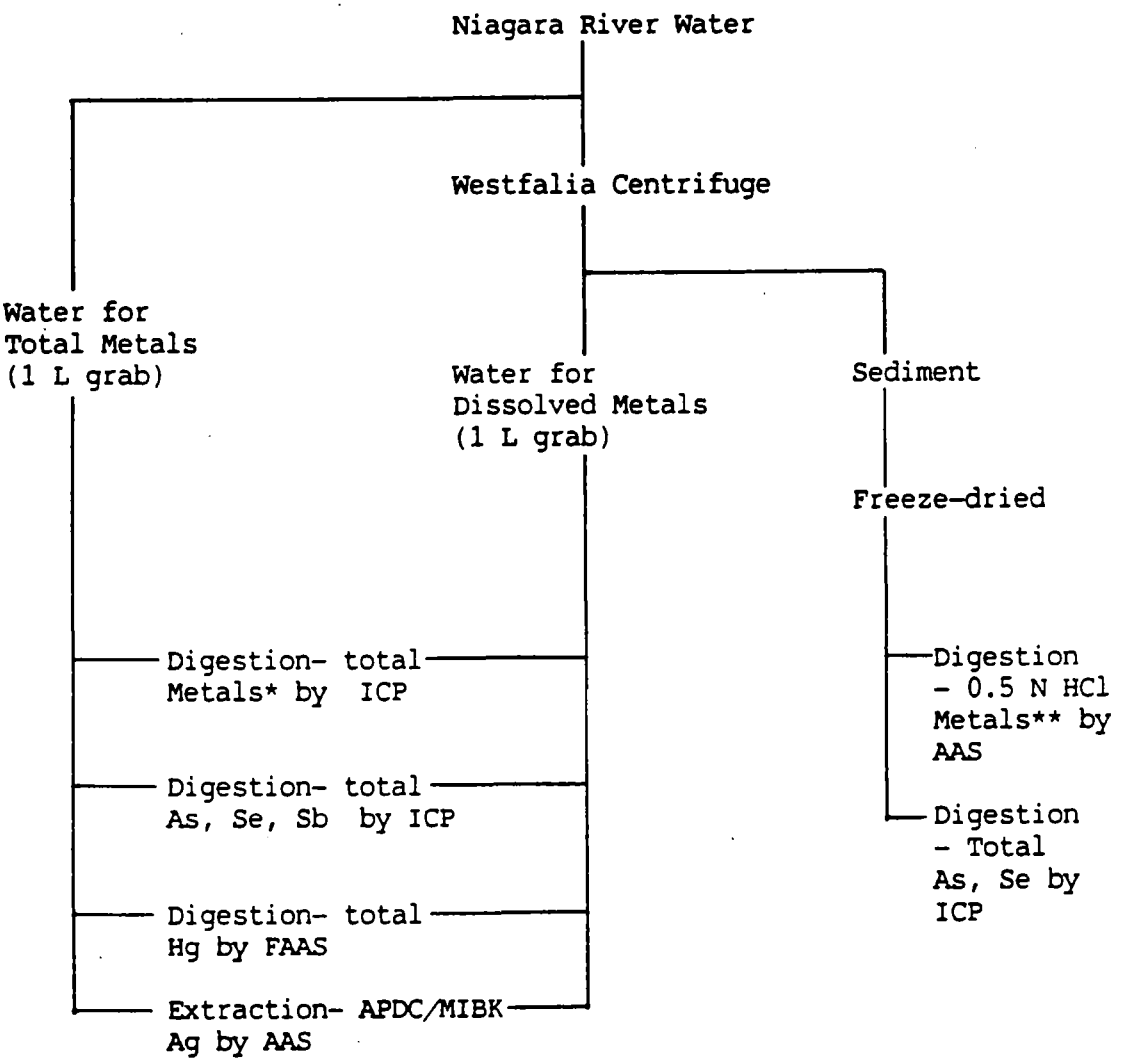
(c) analysis of control samples

(d) analysis of spike samples.

Data from the quality control program is used to ensure that procedures carried out on a given day were in control.

FIGURE I - 1:

SCHEMATIC FOR TRACE METAL ANALYSIS IN THE NIAGARA RIVER



* Al, Ba, Be, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Sr, V, Zn.

** Cd, Cr, Co, Cu, Pb, Ni, Zn.

II DETERMINATION OF SELECTED METALS IN WATER BY INDUCTIVELY COUPLED ARGON PLASMA/ATOMIC EMISSION SPECTROSCOPY (ICP-AES)

1.0 SCOPE AND APPLICATION:

This method is designed to determine the following metals in surface water by ICP/AES: Al, Ba, Be, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Sr, V, Zn. Matrix matching is used to compensate for high concentrations of Ca, Mg, Na and K that are found in such water.

2.0 PRINCIPLES AND THEORY:

The following characteristics are required of a technique to be used on the Niagara River Monitoring project:

(a) High sensitivity to permit detection of analytes at low concentrations

(b) Specificity to permit detection of numerous analytes in a complex matrix

(c) Large linear dynamic range to permit the analysis of samples with highly variable concentrations of any analyte

(d) Reproduciblity at low concentrations.

All of the above characteristics are best met by a combination of ICP/AES.

ICP-AES is used for exciting metals in a gas phase with sufficiently large amounts of thermal energy to promote atoms to various elevated states. As these excited atoms return to the electronic ground state they emit light at discrete wavelengths. The intensity of the emitted light is proportional to the concentration of the metal providing the analyte is sufficiently dilute which is the case with environmental samples. Because of the specificity of emission spectra, the species emitting the light can be identified from a complex matrix of metals. The high intensity of the emitted light allows determination of metals at the part per billion level providing that the appropriate methods of excitation of metals and detection of signal are used. While all elements can be excited by ICP, certain elements with emission lines in the vacuum UV range are not useful. In practical terms, about 70 elements, primarily the metals and the metaloids can be determined in this way.

An important feature of ICP is the method of supplying high temperatures required for excitation. A plasma is produced by seeding electrons into argon which acts as a carrier gas flowing through a tube that is surrounded by an induction coil. These electrons provide some conductivity so that when an oscillating magnetic field is applied the

electrons and ions flow in an annular fashion and are accelerated each half cycle. Resistance to flow causes heating and subsequent excitation. The high temperatures (9000 to 10000°K) and reproducibilty of the source produces the high sensitivity and large linear dynamic range. The ICP provides an additional advantage over other types of excitation techniques, as no electrodes are involved and thus contamination risk is much reduced. Instrumentation used in this investigation is further modified by incorporation of a modified sample introduction system (1). As in the standard introduction system the liquid is first converted to an aerosol spray and passed through a vertical chamber heated by radiant energy. In the present system small water droplets produced in the aerosol spray are dried. The lighter, finer particles produce a more abundant and stable aerosol.

3.0 APPARATUS AND REAGENTS:

It is essential that all items are of a quality consistent with requirements of a trace metals analysis laboratory.

3.1 Apparatus: The following items are required:

(i) Applied Research 3580 Model Inductively Coupled Argon / Atomic Emission Spectrometer

(ii) Modified Sample Introduction System (Heated Spray Chamber), see FIGURE II - 1

(iii) Gilson Model 222 Autosampler

(iv) Two Technicon flow rated pump tubes: one orange/orange (wash) and one black/black (sample)

(v) Gilson Minipuls 2 Peristaltic Pump

(vi) Haake F3 Refrigerated Waterbath

(vii) Rotameter: Model 1355Xb1C1AAA 947 L010BMA

(viii) Low flow gas service flow controller: Model 8844

(ix) Pure quartz glass 150 mL digestion flasks

(x) Sampler tubes to fit 10 mL sampler trays

(xi) Gas or electric hotplate

(xii) Staco E1010VA Variable Autotransformer

(xiii) CGE Photographic Lamp DYH (120 Volt / 600 Watt)

(xiv) High Purity Argon (minimum purity 99.995%)

(xv) Pressure gauge (regulator) rated at 0-60 PSI

(xvi) One liter polyethylene Bottles.

NOTE: POLYETHYLENE BOTTLES ARE ACID WASHED USING DOUBLY DISTILLED METAL FREE WATER ACIDIFIED WITH ULTREX NITRIC ACID. THE ACIDIFIED WATER IS THEN REMOVED BY WASHING WITH DOUBLY DISTILLED METAL FREE WATER.

NOTE: POLYETHYLENE BOTTLES USED FOR ANALYSIS OF NIAGARA RIVER WATER ARE USED ONLY FOR THIS PROJECT. BOTTLES USED FOR ANALYSIS OF OTHER WATERS ARE NOT USED FOR NIAGARA RIVER WATER.

3.2 Reagents:

(i) Doubly distilled metal free water (DDMFW)

NOTE: CENTRAL DISTILLED WATER IS REDISTILLED IN THE LABORATORY IN AN ALL GLASS STILL,CORNING APPARATUS.

(ii) Concentrated Nitric Acid (HNO_3): Ultrex, J.T. Baker Chemical Co. Purchased from John's Scientific 175 Hansen St. Toronto, Ont. M4C 1A7

(iii) Concentrated Hydrochloric Acid (HCl): Ultrex Grade, J.T. Baker Chemical Co. Purchased from John's Scientific 175 Hansen St. Toronto, Ont. M4C 1A7

(iv) Set 1 of metal standards for ICP/AES. The following metals of Set 1 are available as standard solutions at 1000 mg/L from Spex Industries Edison N.J. and are purchased from Seignory Chemical Products 2367 Guenette St. Laurent Que. H4R 2E9 (catalogue numbers appear in brackets):

Al (PLAL-2), Ba (PLBA-2), Be (PLBE-2),
Cd (PLCD-2), Co (PLCO-2), Cr (PLCR-2),
Cu (PLCU-2), Fe (PLFE-2), Li (PLLI-2),
Mn (PLMN-2), Mo (PLMO-2), Ni (PLNI-2),
Pb (PLPB-2), Sr (PLSR-2), V (PLV-2),
Zn (PLZN-2).

(v) Set 2 of metal standards for ICP/AES. The following metals of Set 2 are available as standard solutions at 10,000 mg/L from Spex Industries Edison N.J. and are purchased from Seignory Chemical Products 2367 Guenette St. Laurent Que. H4R 2E9 (catalogue numbers appear in brackets):

Ca (PLCA-3), Mg (PLMG-3),
Na (PLNA-3), K (PLK-3).

(vi) Stock matrix solution consisting of:
3600 mg/L Ca, 800 mg/L Mg, 800 mg/L Na and 100 mg/L K.

3.3 Quality Control And Intermediate Solutions: The following solutions are used for quality control and for calibration of the instrument. Accuracy of solutions is checked against NBS SRM's.

(i) Intermediate solutions: Solutions A through C are of intermediate concentrations and are used in subsequent preparations of quality control and calibration solutions. These are prepared in DDMFW as described in FIGURE II - 2. Concentrations in these and subsequent solutions required for quality control are presented in TABLE II - 1. Solutions required for calibration of the instruments are summarized in TABLE II - 2.

(ii) Quality control solutions: The spiking procedure requires additional solutions of intermediate concentration (Solutions D through I). This solutions are prepared in DDMFW as described in FIGURE II - 2.

(iii) Calibration Solutions: Calibration solutions are prepared from solution A through C; the mixtures are summarized in TABLE II - 2.

NOTE: ALL STANDARD SOLUTIONS CONTAIN MATRIX IONS AT THE FOLLOWING CONCENTRATIONS: Ca 360 mg/L, Mg 80 mg/L, Na 80 mg/L and K 10 mg/L. THESE ARE SET 2 METALS (section 3.2-v).

The stock standards of set 2 metals (Ca, Mg, Na, and K) at a concentration of 10,000 mg/L are used to prepare the matrix mix. The following volumes of these solutions are added to a 100 mL volumetric flask: Ca stock 36 mL; Mg stock 8 mL; Na stock 8 mL and K stock 1 mL. The combined volumes are then diluted to 100 mL and this solution contains 3600 mg/L of Ca; 800 mg of Mg; 800 mg of Na and 100 mg/L of K.

4.0 SAMPLING PROCEDURES:

Samples are collected in acid cleaned polyethylene bottles (see section 3.1-xvi). The water is taken from the effluent of the Westfalia Centrifuge. Prior to taking the grab sample the water is allowed to run until the temperature has stabilized. This temperature is noted and recorded. WHEN A STABLE TEMPERATURE HAS BEEN ACHIEVED AND RECORDED, the river water is added to the bottles and acidified with 4 mL of 50% HNO_3/L of sample. Field blanks consisting of DDMFW in collection bottles are acidified in the field in a similar manner. All water samples are stored in polyethylene bottles at room temperature until analysis.

Lab blanks are prepared by adding DDMFW to the collection bottles in the laboratory and acidifying with the same acid as that used in the field. Water in these bottles is stored and analyzed in exactly the same way as the samples of Niagara River Water.

5.0 PROCEDURE:

In order to report a concentration of metals the following procedures are required: preparation of calibration standards; analysis of samples; analysis of standards; and analysis of quality control solutions.

5.1 **Sample Preparation Procedure:** A volume of homogenized sample (100 mL maximum) is pipetted into a weighed 150 mL digestion flask, placed on a hotplate and evaporated gently (**NO BUMPING**) at 100°C to near dryness. The flask is removed from heat, cooled, 0.5 mL HCl is added and sample is evaporated to near dryness again. HCl addition and evaporation is repeated one more time. Sufficient distilled water is added to increase weight to 10% of original volume. Water is carefully swirled to dissolve any solids deposited on the flask and the sample is transferred directly to sampler tubes. (ie. For 100 mL sample, water is added to increase weight of flask to 10 g over initial weight of the empty flask).

5.2 **Instrumental Analysis:** The ICP/AES is set in operation with 0.2% HCl being pumped through the nebulizer. The heating lamp is turned on and allowed to stabilize. The samples and standards are then pumped to the spray chamber. The operating conditions are as follows:

(a) Observation height - 2 mm above the top of the RF(Radio Frequency) coil
(b) Plasma forward power - 1200W
(c) Plasma reflected power - less than 10W
(d) Argon cooling flow - 12 L/min.
(e) Argon plasma flow - 0.8 L/min.
(f) Nebulizer gas flow - 1.00 L/min.

Argon is adjusted to give a maximum reading for a 1 mg/L standard. The sample is pumped to the nebulizer at a rate of 2.0 mL/min.

Calibration of the instrument is made with matrix matched solutions containing various concentrations of each of the metals (section 3.2-vi). The background intensity for each standard and sample is determined by making measurements "off-peak" by moving the spectrometer primary slit to the wavelengths described in TABLE II - 3. On-peak off-peak measurements are made with a 50 sec. integration time. The sample is aspirated for 2.5 min. and between each sample a 0.5 min. wash of 0.2% HCl at 2.0 mL/min. is included to clean the system. The wash receptacle is washed with 0.2% HCl at 2.6 mL/min.

5.3 Calculations: All calculations are performed on a PDP 11/23+ data system using SAS/DPS software under copyright protection to Applied Research Laboratories.

5.4 Detection Limit: The various detection limits are summarized in TABLE II - 4 according to definitions outlined in the procedures for Semivolatiles . These are determined from 20 replicate analysis of a typical sample.

6.0 QUALITY CONTROL:

Two types of solutions are required for quality control; spiking solutions for standard additions and control solutions.

The quality control program involves the following protocol. One sample in every 10 is treated with a 10 mL spike of SOLUTION E to 100 mL of sample and a spike recovery is calculated as a percentage. In addition a matrix blank is spiked with 10 mL SOLUTION E to 100 mL matrix water run to determine the possible matrix effects on the analyses. Three replicates of control SOLUTIONS H and I are analyzed with each run. Field blanks submitted with the samples and laboratory blanks are run to control for possible interferences or contamination arising from different sources.

A minimum of 7 observations of the control sample are used to calculate a mean(x) and standard deviation(σ). The upper and lower control limits are computed as $x \pm 1.96\sigma$, within which at least 95% of the measurements of the control sample fall. If during routine sample analysis, any results of the control sample fall outside $x \pm 3\sigma$ (upper and lower warning limits), the measurements of the samples is discontinued and the source of the deviation is traced and corrected.

7.0 COMPARISON OF ICP/AES AND ATOMIC ABSORPTION SPECTROSCOPY FOR THE ANALYSIS OF TRACE METALS:

Traditionally, the N W Q L analysed all heavy metals by Atomic Absorption Spectroscopy (AAS). During the last 2 years the laboratory has adapted ICP/AES for multi-element analysis. The laboratory has conducted trace metal analysis in Niagara River samples using both ICP/AES and AAS for over a 12 month period. A comparison of the data from both methods is illustrated in FIGURE II - 3.

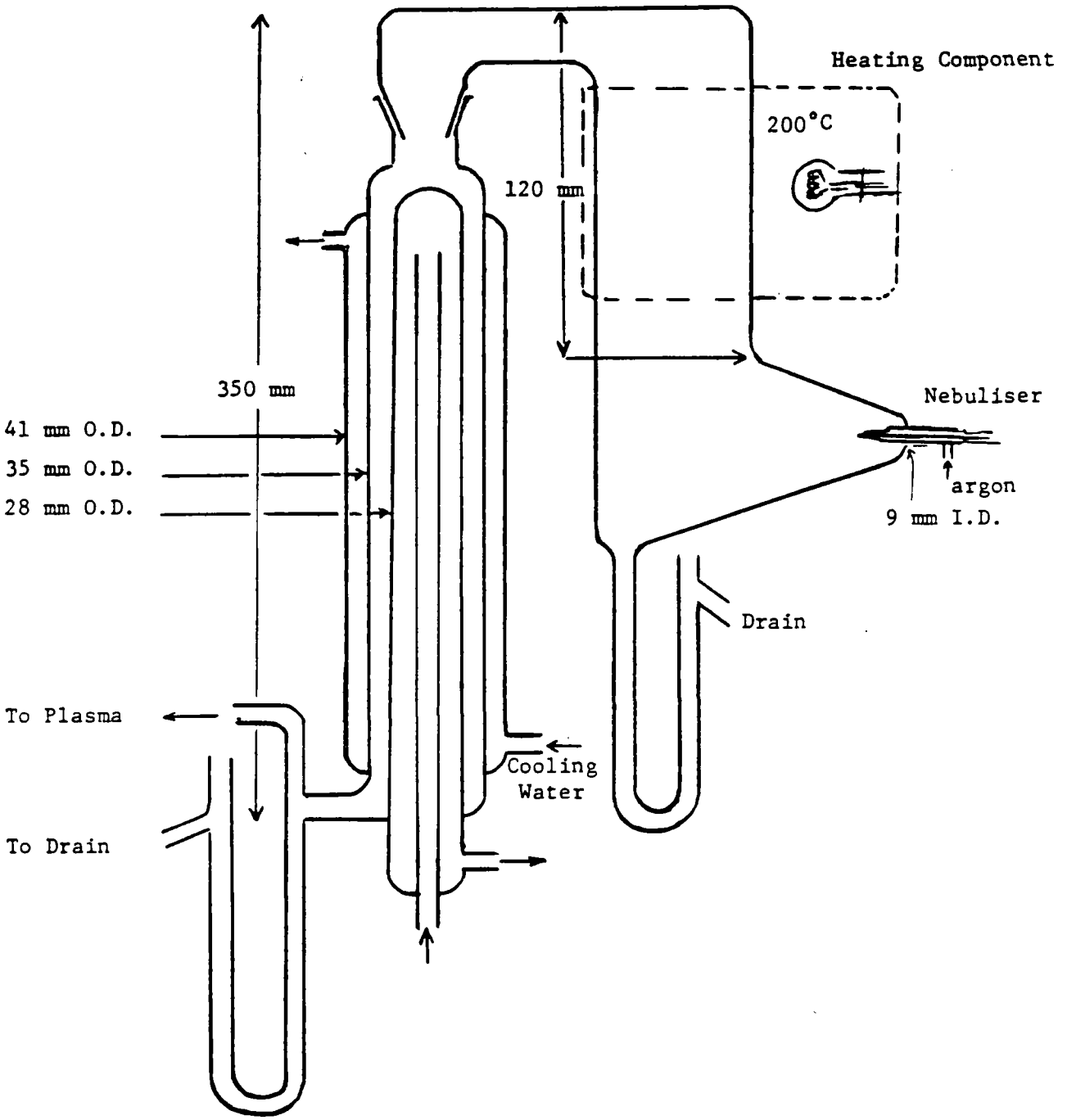


FIGURE II - 1 HEATED SPRAY CHAMBER

FIGURE II - 2:

SOLUTIONS REQUIRED FOR METAL ANALYSIS

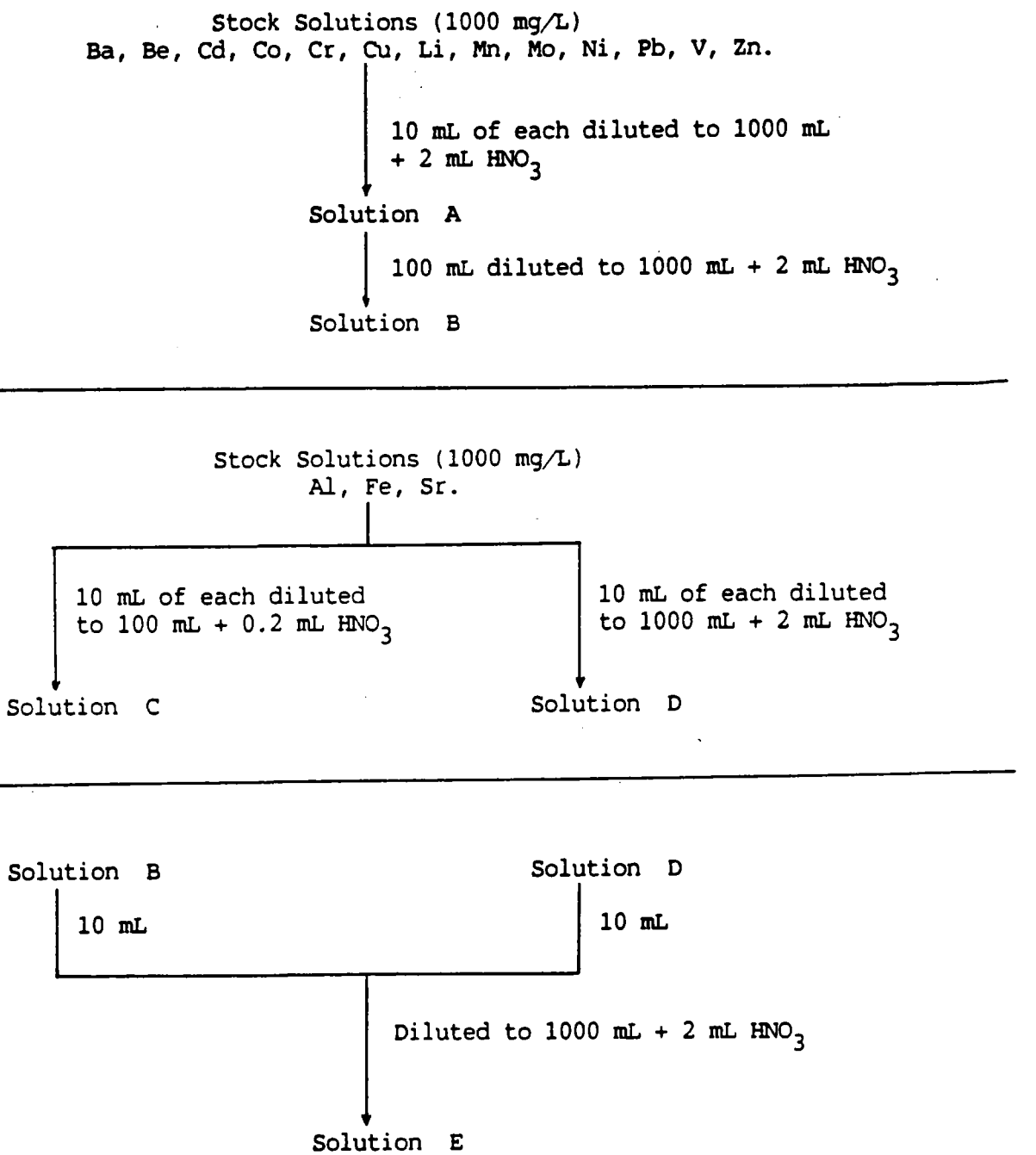


FIGURE II - 2 continued.

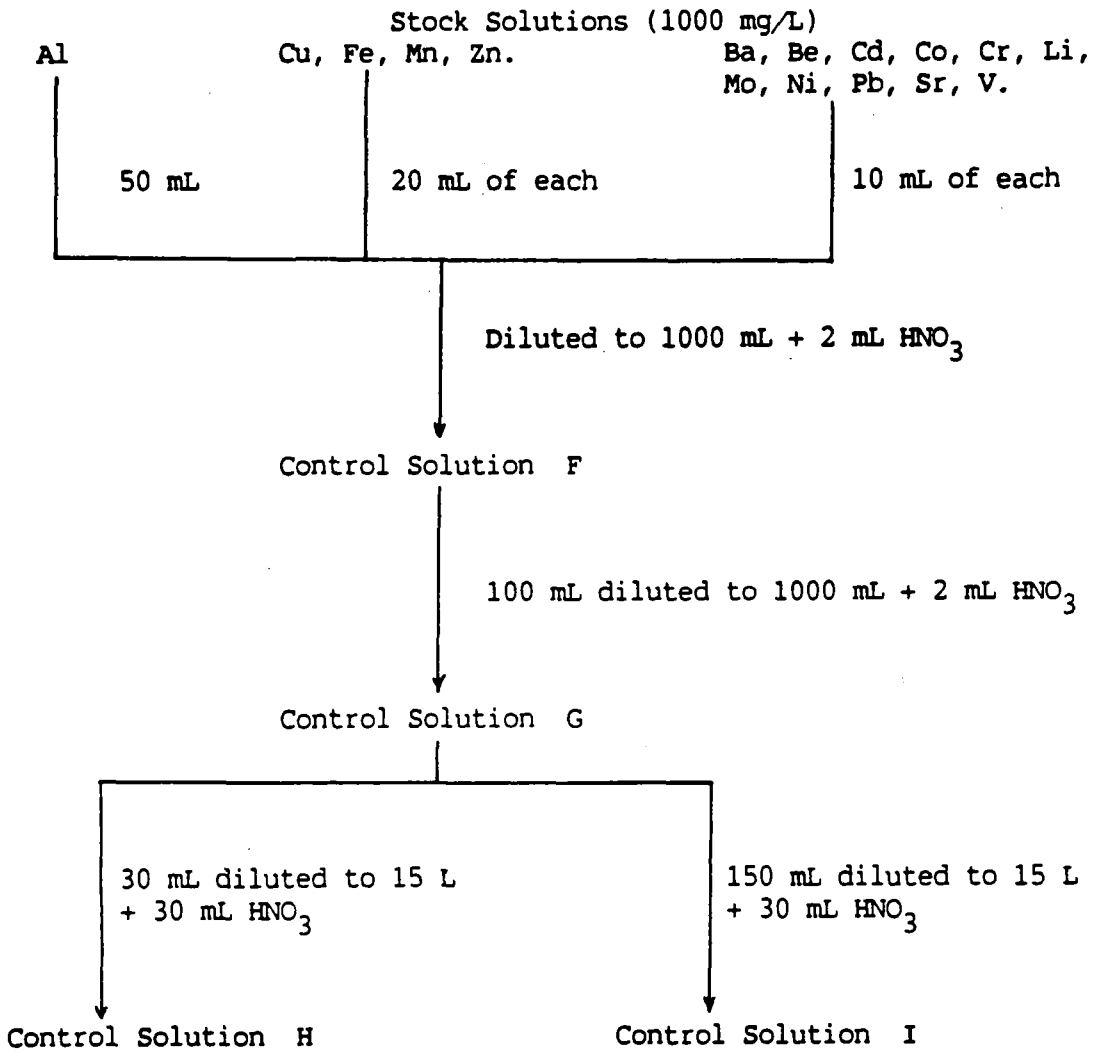
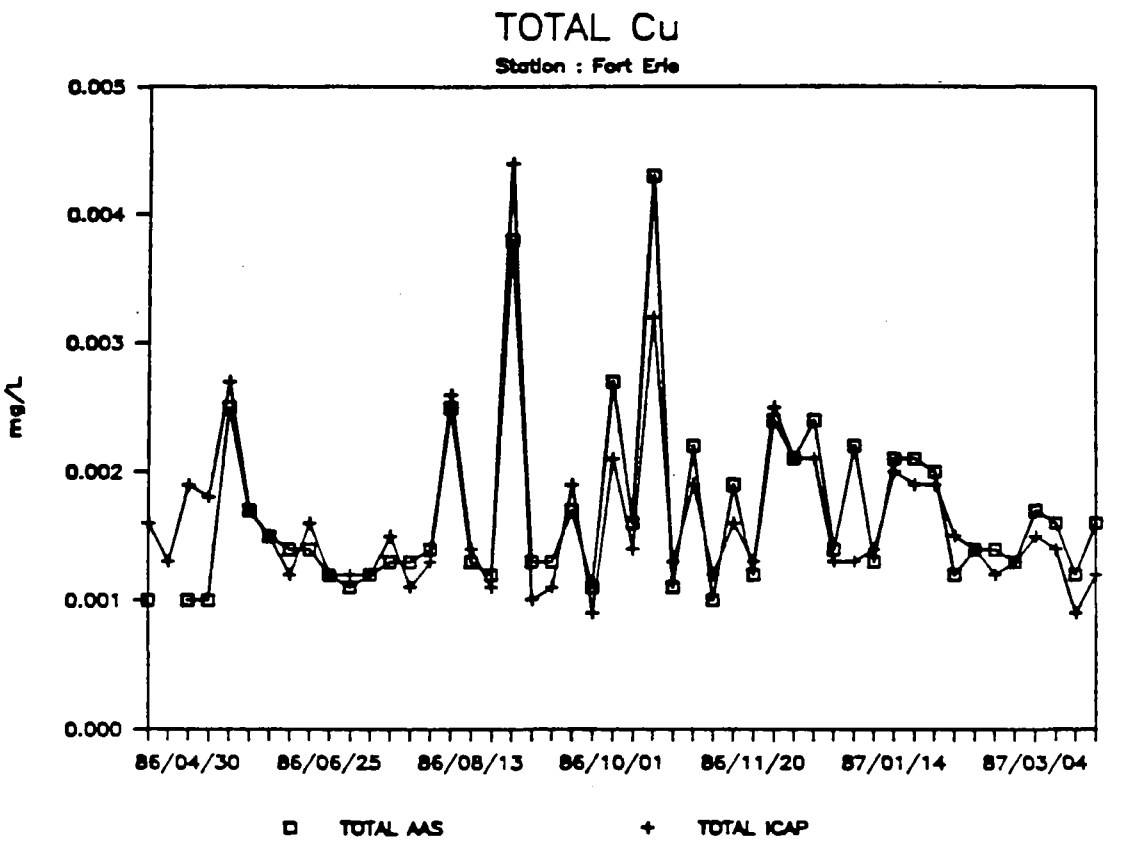


FIGURE II - 3


TOTAL Cu
Station : Fort Erie
0.005
0.004
0.003
0.002
0.001
0.000
mg/L
86/04/30
86/06/25
86/08/13
86/10/01
86/11/20
87/01/14
87/03/04
TOTAL AAS
TOTAL ICAP

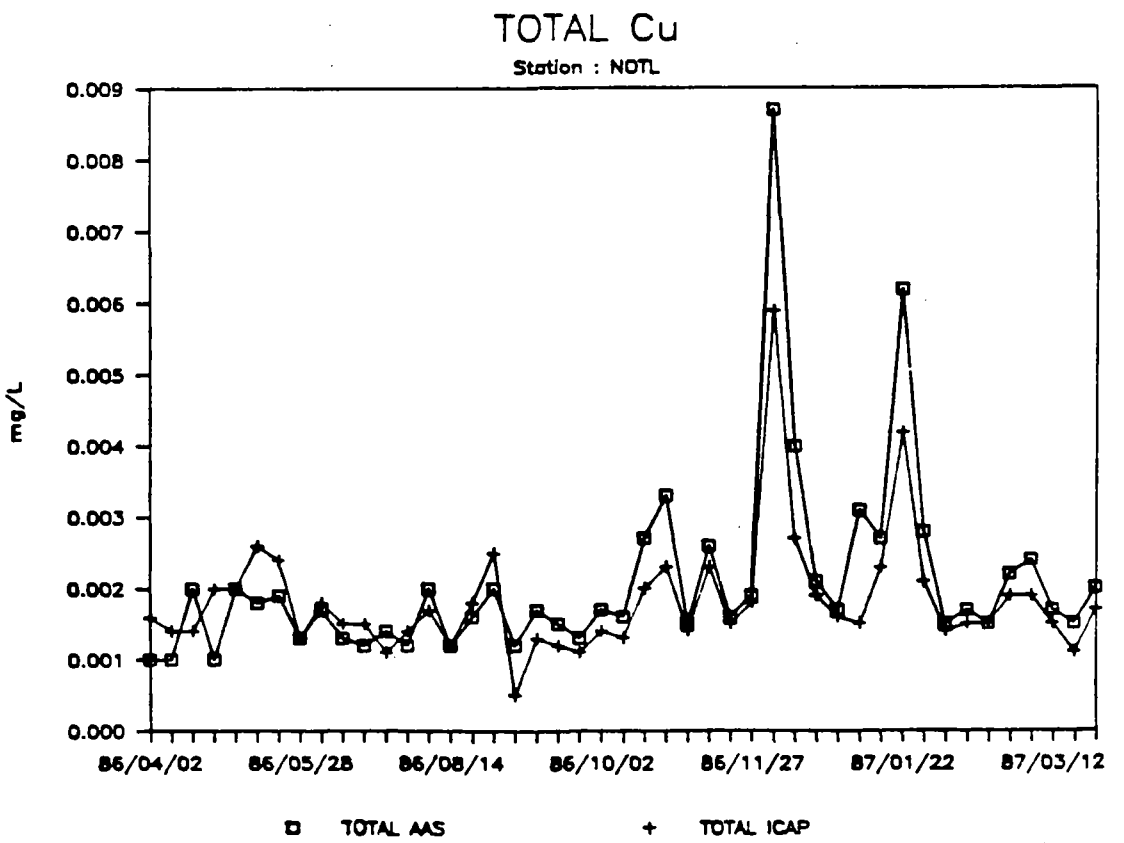
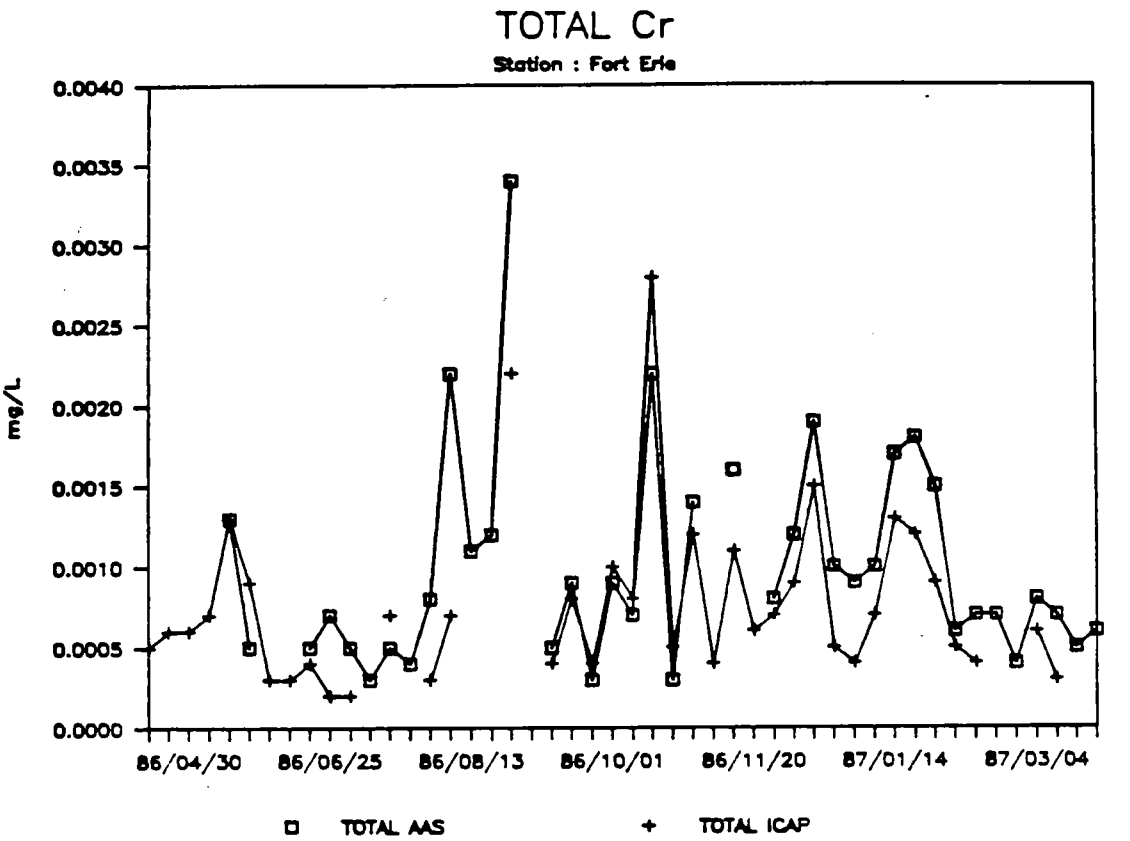

TOTAL Cu
Station : NOTL
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0.000
mg/L
86/04/02
86/05/28
86/08/14
86/10/02
86/11/27
87/01/22
87/03/12
TOTAL AAS
TOTAL ICAP

FIGURE II - 3 continued



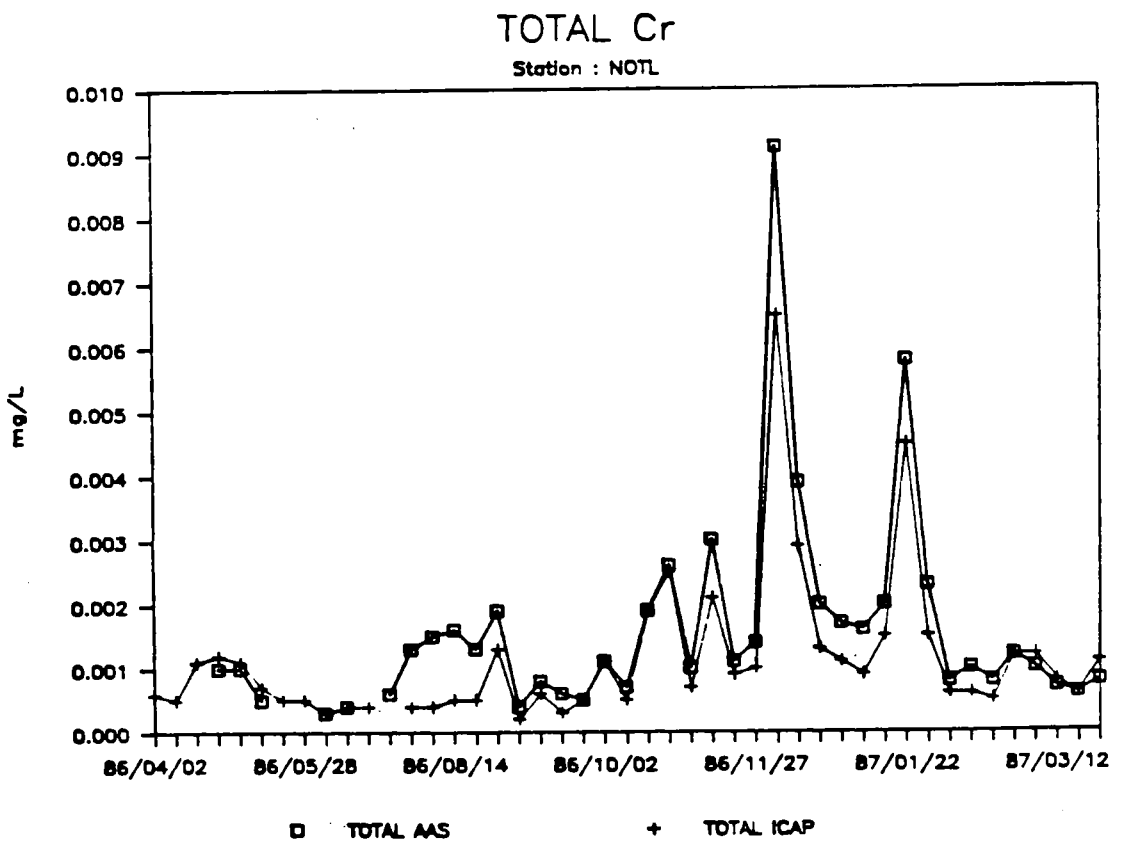
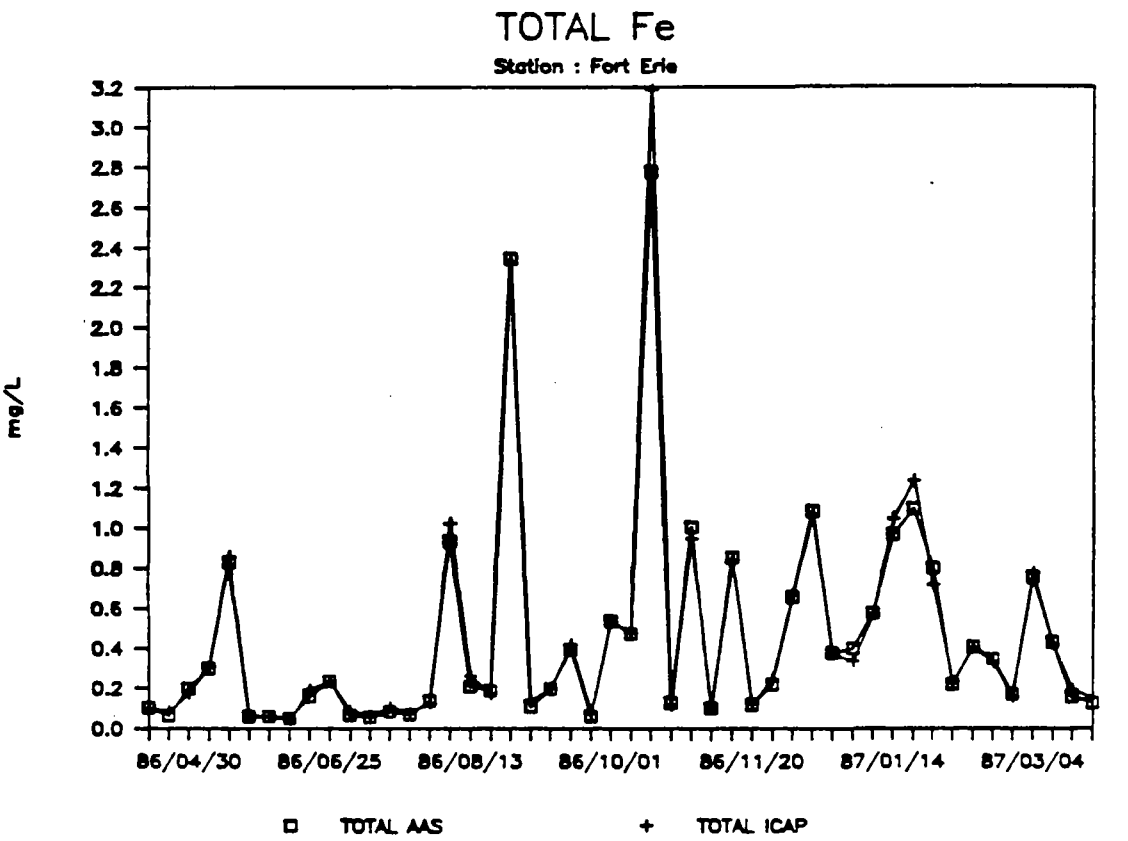


FIGURE II - 3 continued



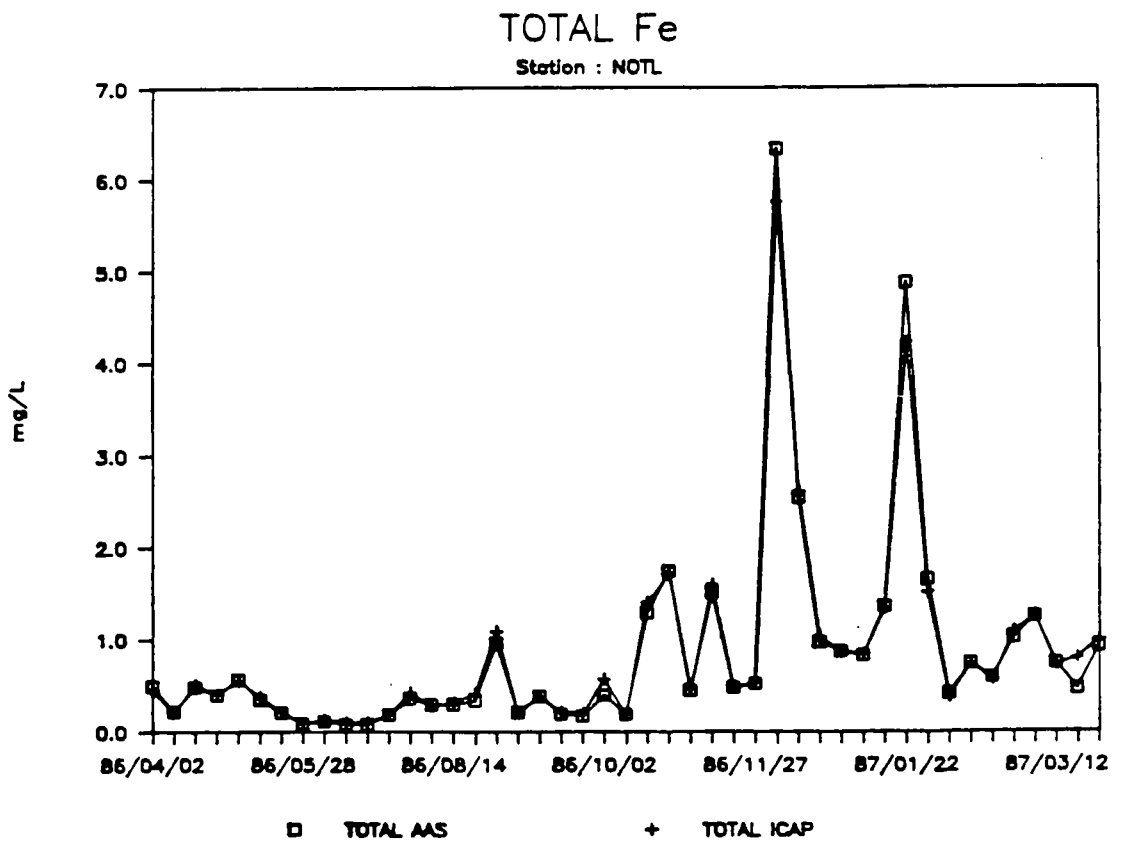
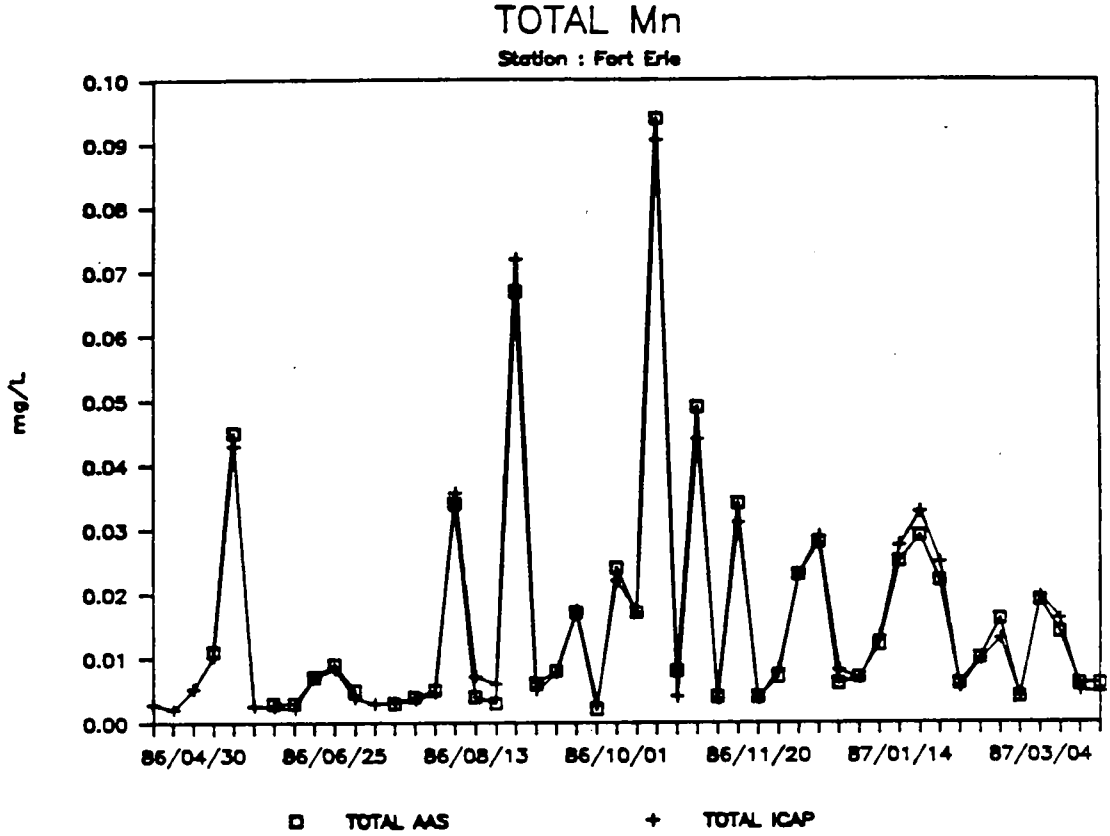


FIGURE II - 3 continued



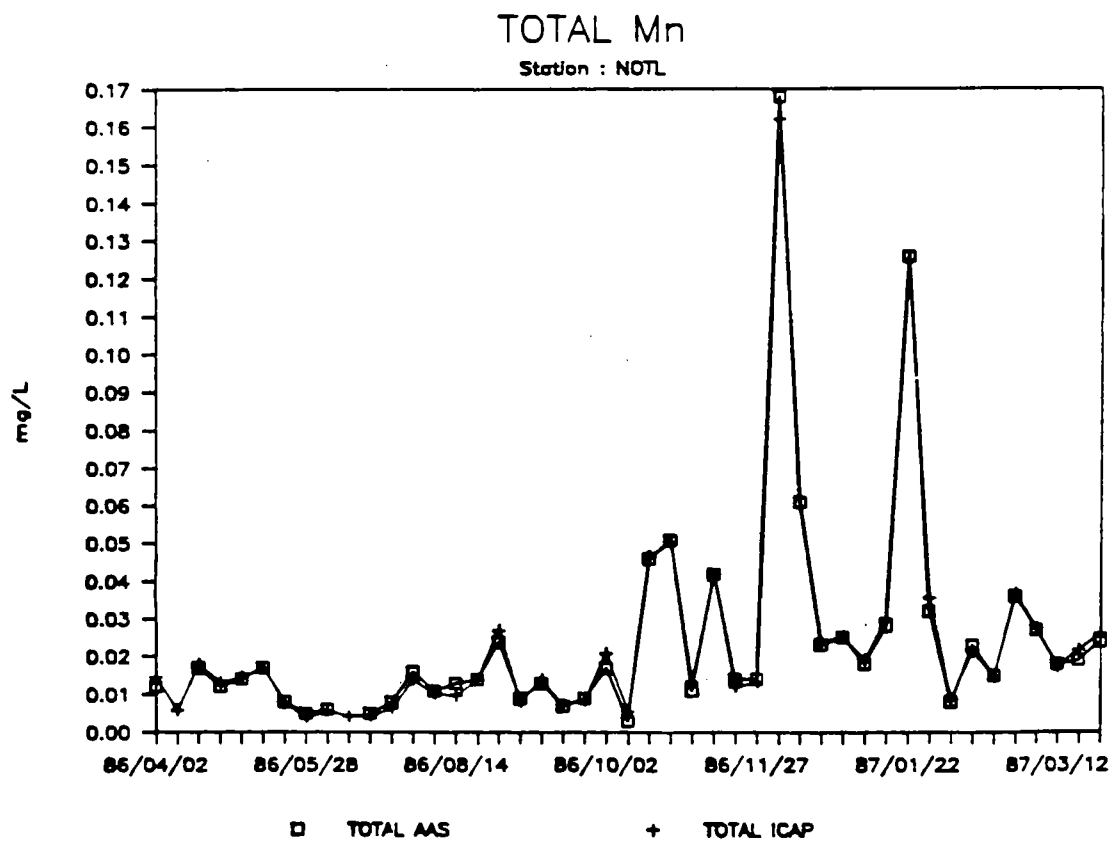
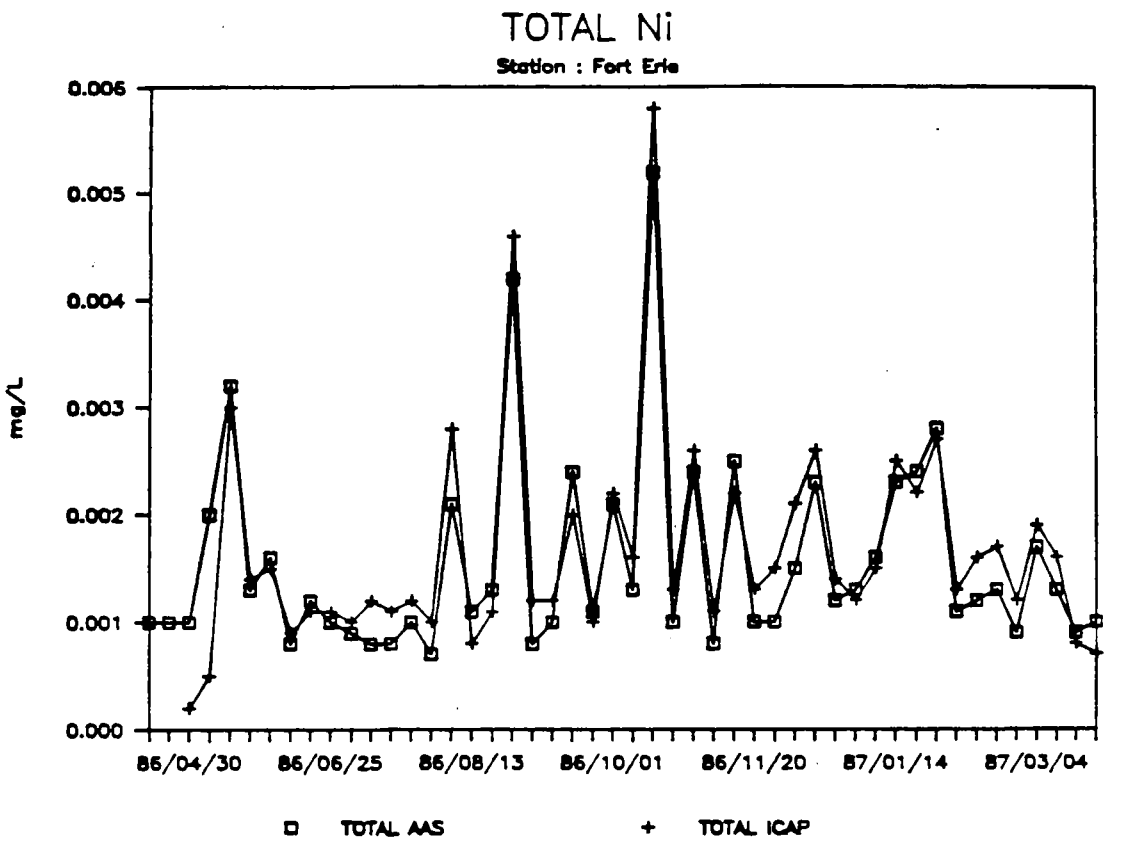
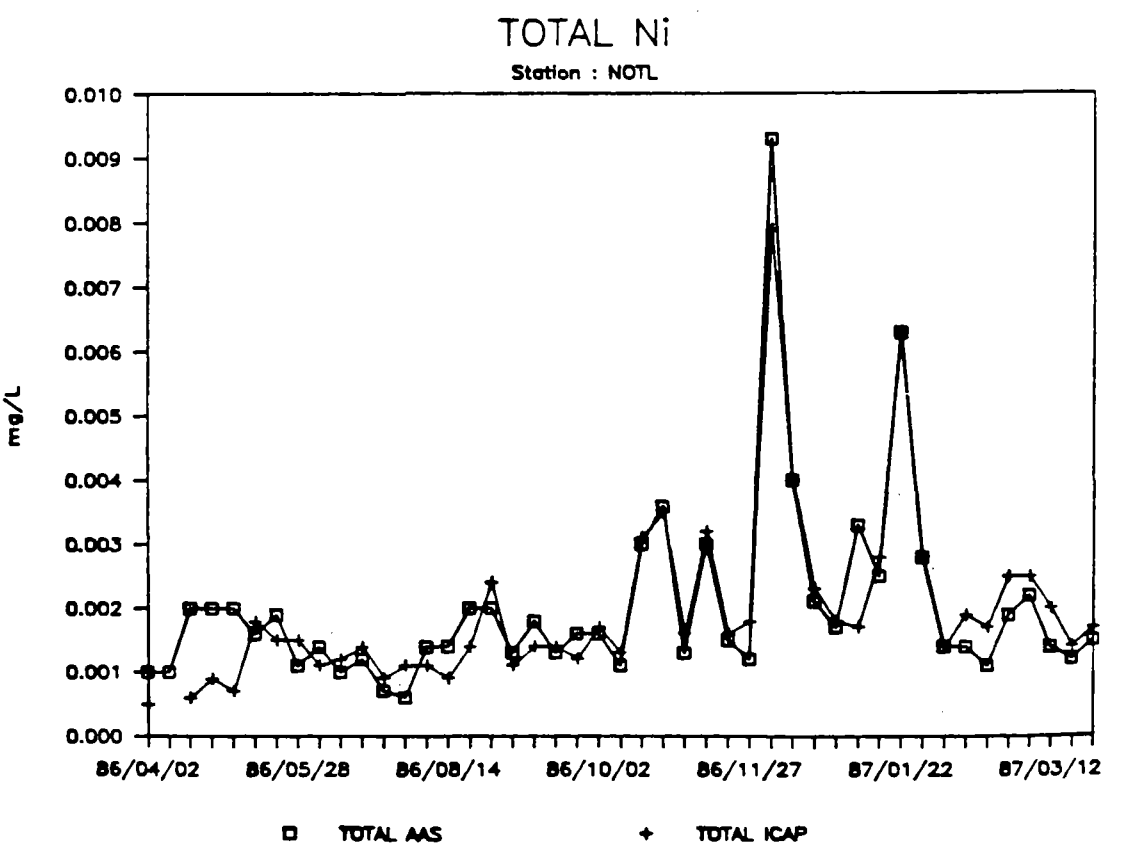
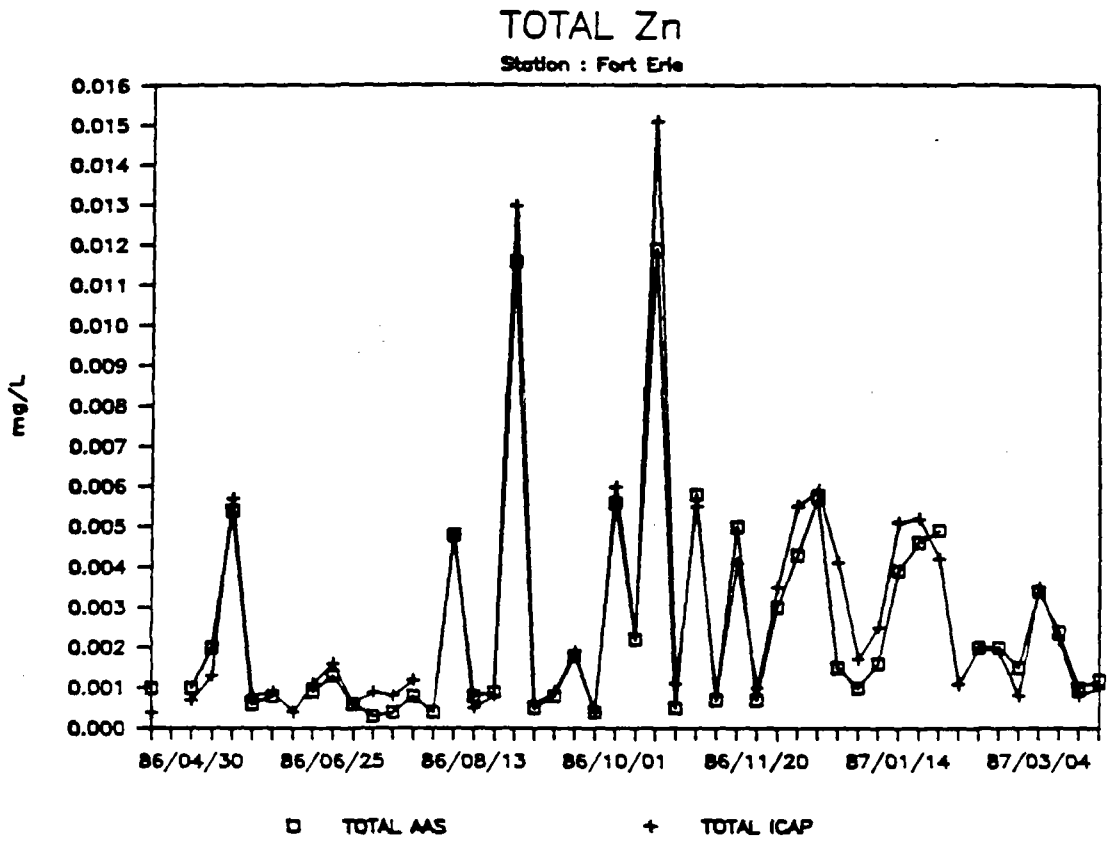


FIGURE II - 3 continued






TOTAL Zn
Station : Fort Erie
mg/L
0.016
0.015
0.014
0.013
0.012
0.011
0.010
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0.000
86/04/30
86/06/25
86/08/13
86/10/01
86/11/20
87/01/14
87/03/04
TOTAL AAS
TOTAL ICAP

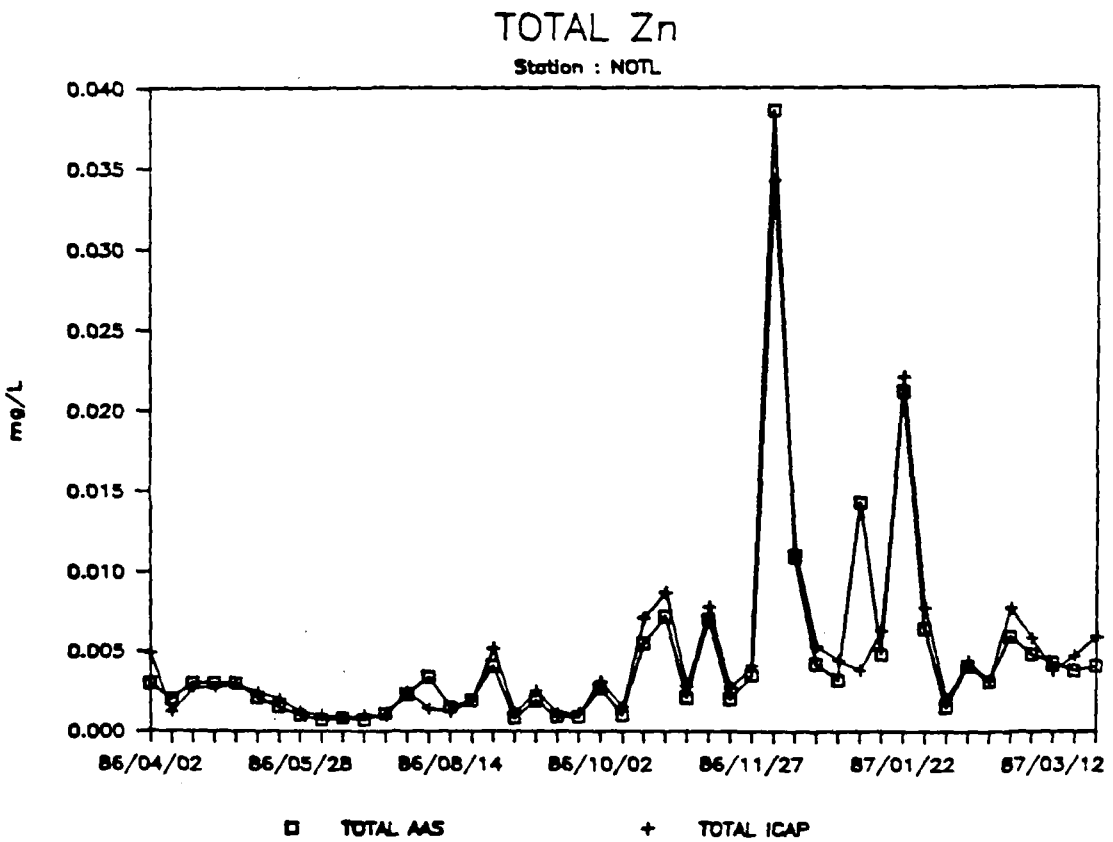

TOTAL Zn
Station : NOTL
mg/L
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
86/04/02
86/05/28
86/08/14
86/10/02
86/11/27
87/01/22
87/03/12
TOTAL AAS
TOTAL ICAP

TABLE II - 1:

CALIBRATION STANDARDS AND QUALITY CONTROL SOLUTIONS REQUIRED

SOLUTION	METALS	CONCENTRATION
A	Ba, Be, Cd, Co, Cr, Cu, Li, Mn, Mo, Ni, Pb, V, Zn.	10 mg/L
B	Ba, Be, Cd, Co, Cr, Cu, Li, Mn, Mo, Ni, Pb, V, Zn.	1 mg/L
C	Al, Fe and Sr.	100 mg/L
D	Al, Fe and Sr.	10 mg/L
E	Ba, Be, Cd, Co, Cr, Cu, Li, Mn, Mo, Ni, Pb, V, Zn.	10 ug/L
	Al, Fe and Sr.	100 ug/L
F	Al.	50 mg/L
	Cu, Fe, Mn, Zn.	20 mg/L
	Ba, Be, Cd, Co, Cr, Li, Mo, Ni, Pb, Sr, V.	10 mg/L
G	Al.	5 mg/L
	Cu, Fe, Mn, Zn.	2 mg/L
	Ba, Be, Cd, Co, Cr, Li, Mo, Ni, Pb, Sr, V.	1 mg/L
H	Al.	10 ug/L
	Cu, Fe, Mn, Zn	4 ug/L
	Ba, Be, Cd, Co, Cr, Li, Mo, Ni, Pb, Sr, V.	2 ug/L
I	Al.	50 ug/L
	Cu, Fe, Mn, Zn.	20 ug/L
	Ba, Be, Cd, Co, Cr, Li, Mo, Ni, Pb, Sr, V.	10 ug/L

TABLE II - 2:

PREPARATION OF THE CALIBRATION SOLUTIONS

VOLUME OF STANDARD TRANSFERRED TO 100 mL VOLUMETRIC FLASK*	CONCENTRATION IN CALIBRATION SOLUTION (ug/L)	METALS IN CALIBRATION SOLUTION
10 mL of SOLUTION B	100	Al, Ba, Be, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Sr, V, Zn.
20 mL of SOLUTION B	200	
50 mL of SOLUTION B	500	
10 mL of SOLUTION A	1000	
20 mL of SOLUTION A	2000	
50 mL of SOLUTION A	5000	
10 mL of SOLUTION C	10,000	Al, Fe, Sr.

* Each 100 mL volumetric flask contains 0.2 mL concentrated HCl and 10 mL of matrix solution with the matrix metals at the following concentrations: Ca at 360 mg/L; Mg and Na at 80 mg/L and K at 10 mg/L.

TABLE II - 3:

SPECTRAL CHARACTERISTICS FOR DETERMINATION OF METALS

Metal	Wavelengths (nm)	Order of Diffraction	Off Line Measurement (nm)
Aluminum	308.215	2	-0.035
Barium	455.403	1	+0.069
Beryllium	313.042	2	+0.035
Cadmium	226.502	3	+0.023
Cobalt	228.616	3	-0.023
Chromium	267.716	2	+0.035
Copper	324.754	2	+0.035
Iron	259.940	2	+0.035
Lithium	670.780	1	+0.069
Manganese	257.610	2	+0.035
Molybdenum	202.030	3	+0.023
Nickel	231.604	2	+0.035
Lead	220.053	3	+0.023
Strontium	407.771	1	+0.069
Vanadium	292.402	2	+0.035
Zinc	213.856	3	+0.023

ON PEAK/OFF PEAK	TIME(sec.)/MEASUREMENT
PRE-INTEGRATION (SAMPLE TUBE TO PLASMA)	90
OFF PEAK MEASUREMENT(ONE POSITIVE, ONE NEGATIVE)	10
ON PEAK MEASUREMENT (THREE)	10
RINSE TIME	40

TABLE II - 4:

DETECTION LIMITS FOR METALS DETERMINED BY ICP

Element	Wavelength (nm)	mV* Reading (1 mg/L)	Replicate Conc (ug/L)	IDL** (ug/L)	MDL** (ug/L)	PDL** (ug/L)
Al	308.215	107	10.0	1.0	1.5	2.0
Ba	455.403	2780	2.0	0.08	0.18	0.2
Be	315.042	8133	2.0	0.02	0.05	0.05
Cd	226.502	2773	2.0	0.06	0.08	0.1
Co	228.616	1114	2.0	0.08	0.09	0.1
Cr	267.716	768	2.0	0.09	0.15	0.2
Cu	324.754	654	4.0	0.16	0.2	0.2
Fe	259.940	914	4.0	0.16	0.36	0.4
Li	670.780	442	2.0	0.06	0.08	0.1
Mn	257.610	6544	4.0	0.04	0.08	0.1
Mo	202.030	1454	2.0	0.06	0.08	0.1
Ni	231.604	602	2.0	0.15	0.16	0.2
Pb	220.053	311	2.0	0.18	0.18	0.2
Sr	407.771	9875	2.0	0.03	0.06	0.1
V	292.402	762	2.0	0.08	0.08	0.1
Zn	213.856	5139	4.0	0.04	0.19	0.2

IDL = Instrument Detection Limit

MDL = Method Detection Limit

PDL = Practical Detection Limit

* Reading from direct aspiration of standard

** Calculated from replicates concentrated 10 X

III ARSENIC, SELENIUM AND ANTIMONY IN WATER

1.0 SCOPE AND APPLICATION:

This method is designed to determine Arsenic (As), Selenium (Se) and Antimony (Sb) in Niagara River water. No distinction is made between organic and inorganic forms. Preliminary sample handling with respect to filtering determines whether total or dissolved metals are determined.

2.0 PRINCIPLE AND THEORY:

The method determines total analytes in Niagara River water. Acid persulfate converts species of As, Se and Sb to AsO_4^{-3}, SeO_4^{-2} and SbO_4^{-3} respectively. Subsequently the oxidized species are reduced to the volatile hydrides which can be sparged into the plasma of the ICP and measured under previously described conditions.

After oxidation with persulfate the AsO_4^{-3} can be reduced with $NaBH_4$ in acidic medium to AsH_3. In contrast reduction of SeO_4^{-2} requires two steps; first reduction with HCl in the oxidizing solution to SeO_3^{-2} which can be subsequently reduced with $NaBH_4$ to the H_2Se. Antimony behaves like arsenic, except it needs a stronger reducing agent to bring it to the correct oxidation state for the formation of the hydride; in this case potassium iodide(KI) is used.

Use of KI requires care with respect to concentration and stability of the solution. Over a period of a day the reducing capacity may be lost. The analysis should not start until one hour after KI introduction to the system as shown in TABLE III - 1, in order to reach a stable condition.

3.0 APPARATUS AND REAGENTS:

Both equipment and reagents must be of a high quality and consistent with a trace metals analysis laboratory.

3.1 Apparatus: The following equipment is required

(i) An Inductively Coupled Argon Plasma (ICAP) system: Model ARL with a QA-137 Spectrometer

(ii) Technicon autoanalyser unit consisting of: Autosampler IV controlled by ICP computer; Carlo Erba 20 channel proportioning pump

(iii) Manifold described in FIGURE III - 1

(iv) Small glass funnels

(v) Twenty five mL graduated cylinder

(vi) Two hundred and fifty mL Erlenmeyer flask

(vii) Electric hot plate (model Thermolyne Type 2200)

(viii) Anti-bumping granules

NOTE: Anti-bumping granules must be washed with 10% H_2SO_4 to remove any traces of interferences.

(ix) 100 mL polypropylene bottles

(x) Gas flow meter capable of controlling flow rates between 0 and 250 mL/min.

(xi) Pressure gauge (regulator) rated at 0-60 PSI

3.2 Reagents:

NOTE: ALL REAGENTS ARE TO BE OF ANALYTICAL GRADE AND APPROPRIATE FOR USE IN A TRACE ANALYSIS LABORATORY.

(i) As, Se and Sb standards purchased from Fisher at concentrations of 1000 mg/L

NOTE: THE FOLLOWING REAGENTS ARE OBTAINED FROM BAKER

(ii) Concentrated Hydrochloric Acid (HCl): Reagent Analytical Grade, Catalogue number 9535-3

(iii) Potassium Persulfate ($K_2S_2O_8$): Catalogue number 3238-1

(iv) Sodium Borohydride ($NaBH_4$): Catalogue number V023-5

(v) Potassium Iodide (KI): Catalogue number 3165-5

(vi) Prepurified Argon.

3.3 Required Solutions:

NOTE: THE FOLLOWING SOLUTIONS ARE STABLE AND CAN BE PREPARED IN ADVANCE.

(i) Solutions of intermediate concentrations in 1% H_2SO_4 :

SOLUTION A 10 mg/L As, Se, Sb
SOLUTION B 0.1 mg/L (100 ug/L) As, Se, Sb 1% H_2SO_4

(ii) A 4% solution of potassium persulfate (W/V) in deionized water

NOTE: THE FOLLOWING SOLUTIONS MUST BE PREPARED DAILY

(iii) A 2.5% solution of $NaBH_4$ (W/V) in 1 N NaOH

(iv) An 8% solution of KI (W/V) in deionized water

NOTE: WAIT 1 HR AFTER KI INTRODUCTION TO THE SYSTEM

4.0 PROCEDURE:

Transfer one hundred mL of sample to an acid washed 250 mL erlenmeyer flask. Add 10 mL of 4% potassium persulfate solution and 3.5 mL of concentrated HCl. Add acid washed anti-bumping granules and evaporate gently at 100°C insuring there is no sample loss, on an electric hot plate until concentrated to 8-10 mL. After cooling transfer the solution to a 25 mL graduated cylinder and make up to 13 mL with deionized water and pour the solution back into the 250 mL erlenmeyer flask. Add 7 mL of concentrated HCl to make a total volume of 20 mL. Place a small conical funnel in the top of the flask to hinder evaporation and reflux at 90°C for 20-30 min. The samples are made back up to 20 mL and transferred to storage bottles.

Transfer a 15 mL portion of the sample to the technicon sampler and analyze As, Se and Sb using the autoanalyzer manifold in FIG. 1 to analyse the samples by automated on-line reduction of the analytes to the corresponding hydrides. These are determined by ICP. This system is capable of analyzing 45 samples per hour using an aspiration time of 45 sec. with a 30 sec. wash. It is operated at the maximum sampling rate. Operating conditions for the system are described in TABLE III-2.

5.0 CALCULATIONS:

The concentrations are calculated from a calibration curve ranging from 0 to 20 ug/L with the lowest non-zero concentration of the calibration curve being 0.5 ug/L. A concentration of zero is used in the curve because there are no significant interferences. Calculations are based on measurements of peak heights and are carried out by the data system. Detection limits based on the analysis of 20 replicates are presented in TABLE III - 4.

6.0 QUALITY CONTROL:

Quality control is based on the following protocol. A duplicate, a spike and one quality control sample are run with each batch of 40 samples (ie approximately once every hour). The spiked sample is prepared by adding 1 mL SOLUTION B to 99 mL tap water which gives a 1 ug/L spike. The quality control sample used in this analysis is a NBS Certified Reference Sample(NBS 1643A). TABLE III - 3 demonstrates the recoveries at the following concentrations, using tap water for sample.

A minimum of 7 observations of the control sample are used to calculate a mean(x) and standard deviation(σ). The upper and lower control limits are computed as $x \pm 1.96\sigma$, within which at least 95% of the measurements of the control sample fall. If during routine sample analysis, any results of the control sample fall outside $x \pm 3\sigma$ (upper and lower warning limits), the measurements of the samples is discontinued and the source of the deviation is traced and corrected.

Arsenic, Selenium and Antimony in Water

Flow Diagram

(Carlo Erba, peristaltic)

Pump

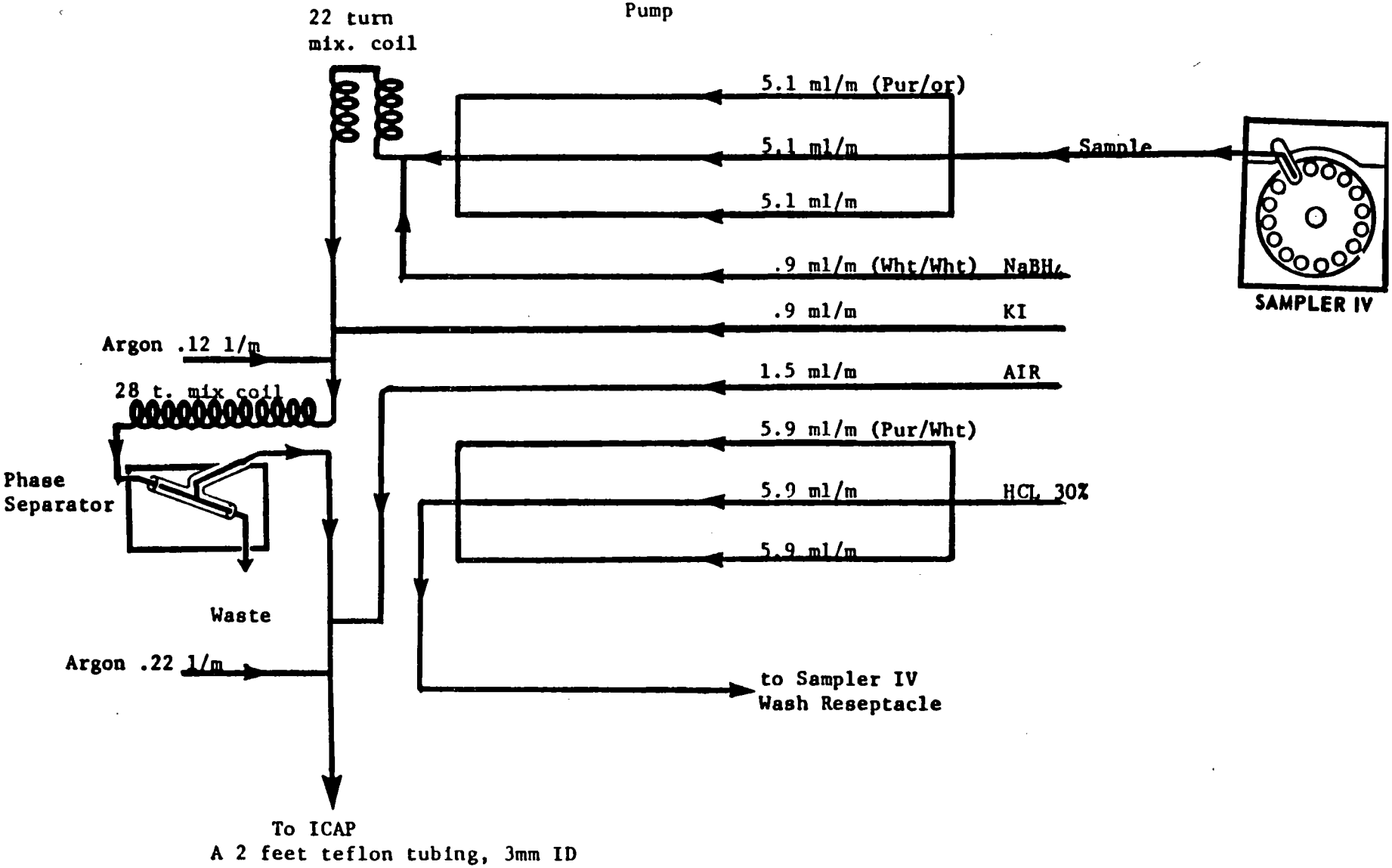


FIGURE III - 1 HYDRIDE MANIFOLD

TABLE III - 1:

THE EFFECT OF KI STABILITY ON AS/SE ANALYSIS

TIME AFTER KI INTRODUCTION TO THE SYSTEM (MIN.)	READING (mV)	
	As	Se
0	60	48
6	71	47
9	70	45
22	69	40
50	69	36
62	69	34
87	68	35
105	68	37

TABLE III - 2:

OPERATING CONDITIONS FOR THE TECHNICON AND ICAP SYSTEMS

POSITION OF GAS FLOW INTO THE SYSTEM (SEE FIGURE II - 1)	FLOW RATE
ARGON BEFORE SEPARATOR	0.12 L/min
ARGON AFTER SEPARATOR	0.22 L/min
ARGON COOLING GAS	12.0 L/min
ARGON PLASMA GAS	0.12 L/min
ARGON INJECTOR FLOW	0.34 L/min
AIR FLOW	1.50 mL/min

OPERATING PARAMETERS FOR THE ICAP

FORWARD POWER	1600 W
REFLECTED POWER	less than 10 W
PRE-INTEGRATION TIME	45 seconds
INTEGRATION TIME	30 seconds

WAVELENGTHS FOR DETERMINATION ANALYTES

ANALYTE	WAVELENGTH* (nm)
As	193.77
Se	203.99
Sb	206.83

* ALL MEASUREMENTS ARE MADE IN THE THIRD ORDER OF DIFFRACTION.

TABLE III - 3:

RECOVERIES OF QUALITY CONTROL SAMPLES USING SPIKING TECHNIQUES

% RECOVERY OF ANALYTES (MEAN +/- ONE STANDARD DEVIATION)

SPIKING AMOUNTS (ug/L)	ARSENIC	SELENIUM	ANTIMONY
1	98.9 ± 5.5	117.1 ± 17.6	86.9 ± 10.0
2	98.6 ± 4.3	115.5 ± 5.9	93.9 ± 7.1
5	97.7 ± 1.0	97.5 ± 1.9	91.2 ± 4.5

TABLE III - 4:

DETECTION LIMITS

PARAMETERS	mV Reading 5 ug/L (Baseline Subtracted)	IDL (ug/L)	MDL & PDL* (ug/L)
Arsenic	194	0.08	0.1
Selenium	72	0.08	0.1
Antimony	56	0.15	0.2

IDL = Instrument Detection Limit

MDL = Method Detection Limit

PDL = Practical Detection Limit

* MDL and PDL are operationally the same.

IV DETERMINATION OF MERCURY IN WATER

1.0 SCOPE AND APPLICATION:

This method is designed to determine mercury (Hg) in Niagara River water. No chemical interferences are noted in mercury analysis.

2.0 PRINCIPLE AND THEORY:

The method is based on reduction of Hg^{2+} with stannous chloride in hydroxylamine sulphate-sodium chloride to elemental Hg. The volatile elemental Hg is sparged directly into an absorption cell situated in the light path of a mercury lamp and the absorption determined at 253.7 nm.

Environmental samples which may contain organomercury compounds are digested with H_2SO_4, $KMnO_4$ and $K_2S_2O_8$ at 100°C to convert all species Hg^{2+} prior to reduction to elemental Hg as shown in equation 1 and 2.

$$R\text{-}Hg \xrightarrow{\text{[oxidants]}} Hg^{2+} \quad \ldots\ldots\ldots\ldots\ldots\ldots \; 1$$

$$Hg^{2+} + Sn^{2+} \longrightarrow Hg^{o} + Sn^{4+} \quad \ldots\ldots\ldots\ldots \; 2$$

3.0 APPARATUS AND REAGENTS:

Quality of equipment and reagents must be consistent with a trace metals analysis laboratory and known to be free of mercury and other elements that may interfere with the analysis of mercury.

3.1 Apparatus: The following equipment is required:

(i) LDC/Milton Roy, Mercury Cold Vapour Monitor

(ii) Automatic analyzer consisting of Auto Sampler IV with mixer equipped to use 15 ml test tubes, manifold, heating bath and proportioning pump, as shown in FIGURE IV - 1. The system is equivalent to a Technicon II system with a Carlo Erba proportioning pump No. 08-59-10202

(iii) Technicon Stirrer on sampler

(iv) Technicon Heater with 105°C thermostat

(v) Gas separator constructed according to the diagram in FIGURE IV - 2

(vi) Packed column constructed according to the diagram in FIGURE IV - 3

(vii) Strip-chart recorder; Hewlett Packard model 7101 B or equivalent

(viii) One hundred and twenty five mL pyrex bottle

(ix) Two liter glass screw cap bottle.

NOTE: GLASSWARE FOR MERCURY ANALYSIS ARE TO BE KEPT SEPARATE FROM ALL OTHER GLASSWARE.

NOTE: GLASSWARE FOR MERCURY ANALYSIS IS WASHED WITH CONCENTRATED NITRIC ACID FOLLOWED BY FIVE WASHES EACH WITH TAP AND DISTILLED WATER.

3.2 Reagents: All reagents are to be of analytical grade and are obtained from Baker (equivalent quality reagents from other sources are acceptable).

(i) Potassium Dichromate ($K_2Cr_2O_7$): Catalogue number 3093-1

(ii) Sulphuric acid (H_2SO_4) with a specific gravity of 1.84: Catalogue number 9681-3

NOTE: THIS REAGENT MUST BE SHOWN TO BE SUITABLE FOR USE IN MERCURY ANALYSIS BY ANALYZING A 1% (W/V) AQUEOUS SOLUTION PRIOR TO USE IN ANY PART OF THE PROCEDURE

(iii) Concentrated Hydrochloric Acid (HCl); Analytical Grade, Catalogue number 9535-3

(iv) Hydroxylamine sulphate [$(NH_2OH)_2.H_2SO_4$]: Catalogue number N 646-7

(v) Potassium permanganate ($KMnO_4$): Catalogue number 3228-5

(vi) Potassium persulphate ($K_2S_2O_8$): Catalogue number 3238-1

(vii) Stannous chloride ($SnCl_2$): Catalogue number 3980-1

(viii) Mercuric chloride ($HgCl_2$): Catalogue number 2594-4

3.3 Solutions:

NOTE: THE FOLLOWING SOLUTIONS ARE STABLE AND CAN BE PREPARED IN ADVANCE.

(i) Prepare potassium dichromate preservative solution (5% W/V) by dissolving 50 g of $K_2Cr_2O_7$ in 1000 mL distilled water

NOTE: ALTHOUGH REAGENT GRADE MATERIAL IS USED, SOME GRADES OF THIS REAGENT CONTAIN Hg. SOLUTIONS OF $K_2Cr_2O_7$ ARE ANALYZED TO DETERMINE THE LEVEL OF Hg CONTAMINATION. MERCURY CAN BE REMOVED FROM ACIDIFIED (pH 1.4 TO 2) AQUEOUS SOLUTION OF $K_2Cr_2O_7$ BY EXTRACTION WITH A 0.1% W/V SOLUTION OF DITHIZONE IN $CHCl_3$. ANY $K_2Cr_2O_7$ SOLUTION, HOWEVER PREPARED, MUST BE SHOWN TO BE FREE OF INTERFERENCES PRIOR TO USE IN ANY PART OF THE PROCEDURE.

(ii) Prepare a stock mercury solution at a concentration of 1000 mg/L Hg by dissolving 1.354 g $HgCl_2$, in 750 mL distilled water in a 1000 mL volumetric flask. Add 10 mL H_2SO_4 (section 3.2-ii) and 10 mL of $K_2Cr_2O_7$ solution (section 3.3-i) and make up to volume with distilled water

NOTE: COMMERCIALLY AVAILABLE STOCK SOLUTIONS OF MERCURY CAN BE USED TO REPLACE THOSE PREPARED IN-HOUSE FROM $HgCl_2$ (section 3.2-vii) PROVIDED THAT THEY ARE CHECKED AGAINST IN-HOUSE STANDARDS TO CONFIRM CONCENTRATION.

(iii) Prepare a working solution, a spiking solution, two calibration solutions and two quality control solutions (FIGURE IV - 4) in distilled water containing 10 mL H_2SO_4/L (section 3.2-ii) and 10 mL of $K_2Cr_2O_7$ solution/L (section 3.3-i) as preservatives.

NOTE: THE FOLLOWING REAGENT SOLUTIONS ARE UNSTABLE AND MUST BE PREPARED WEEKLY OR DAILY AS INDICATED.

(iv) Prepare the $(NH_2OH)_2.H_2SO_4$-NaCl reducing agent daily by dissolving 15 g $(NH_2OH)_2.H_2SO_4$ and 15 g NaCl in 500 mL of distilled water

(v) Prepare the $KMnO_4$ oxidizing solution by dissolving 2.5 g of KMnO4 in 500 mL of distilled water. PREPARE WEEKLY AND STORE IN AN AMBER BOTTLE IN THE ABSENCE OF LIGHT.

(vi) Prepare the $K_2S_2O_8$ oxidizing solution daily by dissolving 2.5 g $K_2S_2O_8$ in 500 mL of distilled water.

(vii) Prepare the $SnCl_2$ reducing solution daily by dissolving 50 g of $SnCl_2$ in 125 mL of concentrated HCl acid dilute to 500 mL.

4.0 SAMPLING AND STORAGE PROCEDURES:

The samples are collected in a clean (3.1-ix) teflon lined screw cap glass bottle containing 1 mL concentrated H_2SO_4 plus 1 mL of 5% (w/v) potassium dichromate ($K_2Cr_2O_7$) solution per 100 mL of sample. Samples are stable for at least 3 months. Generally, the samples are analysed within one week of receipt.

Care is taken to ensure that bottles are shipped in boxes adequate for glass containers (i.e. with enough padding to prevent breakage) and that during shipping the sample is prevented from freezing.

NOTE: IT IS IMPORTANT THAT THE ABOVE PROCEDURES FOR SAMPLING, SHIPPING AND STORAGE BE STRICTLY FOLLOWED. THERE IS CONTROVERSY IN THE LITERATURE REGARDING SUCH PROCEDURES. THOSE DESCRIBED ABOVE HAVE BEEN EXTENSIVELY TESTED AT N W Q L AND FOUND TO BE SUPERIOR FOR THE SPECIFIC APPLICATION. BEFORE ANY CHANGES ARE IMPLEMENTED SUCH MODIFICATIONS MUST BE SHOWN TO PRODUCE RESULTS EQUIVALENT TO EXISTING PROCEDURES.

5.0 PROCEDURES:

CAUTION: MERCURY IS A MATERIAL COMMON TO MANY LABORATORIES. ALL SOURCES SUCH AS THERMOMETERS AND POLAROGRAPHS SHOULD BE EXCLUDED FROM THE LABORATORY DETERMINING MERCURY IN ENVIRONMENTAL SAMPLES.

The flows of samples and reagents on the manifold of the autoanalyser are established according to the diagram in FIGURE IV - 1. Sample flowing through the system at a rate of 11.7 mL/min. is mixed with H_2SO_4 and $KMnO_4$ (2.55 and 1.2 mL/min. respectively) and heated to 100°C for digestion. Excess $KMnO_4$ is then reduced with hydroxylamine sulphate at a flow of 2.4 mL/min. and the stream is cooled. $SNCl_2$ introduced at a rate of 1.2 mL/min. reduces Hg^{+2} to mercury vapour which is stripped from the stream and passed through a mercury cell. The system is run without sample or standard until a steady baseline is established. At this point the samples are transferred to the technicon IV sampler. When a stable base line has been established samples and standards are analyzed at a rate of 30 per hour.

NOTE: AT THE END OF EVERY DAY THE AUTOMATED SYSTEM IS CLEANED BY:

1- ASPIRATING A SOLUTION OF HYDROXYLAMINE SULFATE (SAME AS THE REAGENT) THROUGH $KMnO_4$ LINE
2- ASPIRATING A 0.1 N NaOH SOLUTION THROUGH SULFURIC ACID LINE
3- FINAL WASH WITH DEION. WATER FOR 15 MIN

5.1 Calculations: Prepare a calibration curve derived from the peak heights obtained with the standard solutions in the range from 0.02 ug/L to 0.5 ug/L (section 3.3-iii). Determine the concentration of mercury in the samples by comparing sample peak heights directly with those obtained from the calibration curve. Detection limits based on the analysis of 20 replicates are presented in TABLE IV - 1.

6.0 QUALITY CONTROL:

The protocol for quality control requires one blank obtained by analyzing deionized distilled water, one duplicate, two control samples (section 3.3-iv) and one spike sample (section 3.3-v) for every 40 samples.

NOTE: THE SPIKE SAMPLE IS PREPARED BY ADDING 50 uL (section 3.3-v) OF SPIKING SOLUTION IN 25 mL VOLUMETRIC FLASK. THIS DELIVERS 5 ng TO THE FLASK. MAKE UP TO VOLUME WITH SAMPLE USED FOR SPIKE. THE CONCENTRATION OF ADDED Hg IN THE SPIKED SAMPLES IS 0.2 ug/L.

A minimum of 7 observations of the control sample are used to calculate a mean(x) and standard deviation(σ). The upper and lower control limits are computed as $x \pm 1.96\sigma$, within which at least 95% of the measurements of the control sample fall. If during routine sample analysis, any results of the control sample fall outside $x \pm 3\sigma$ (upper and lower warning limits), the measurements of the samples is discontinued and the source of the deviation is traced and corrected.

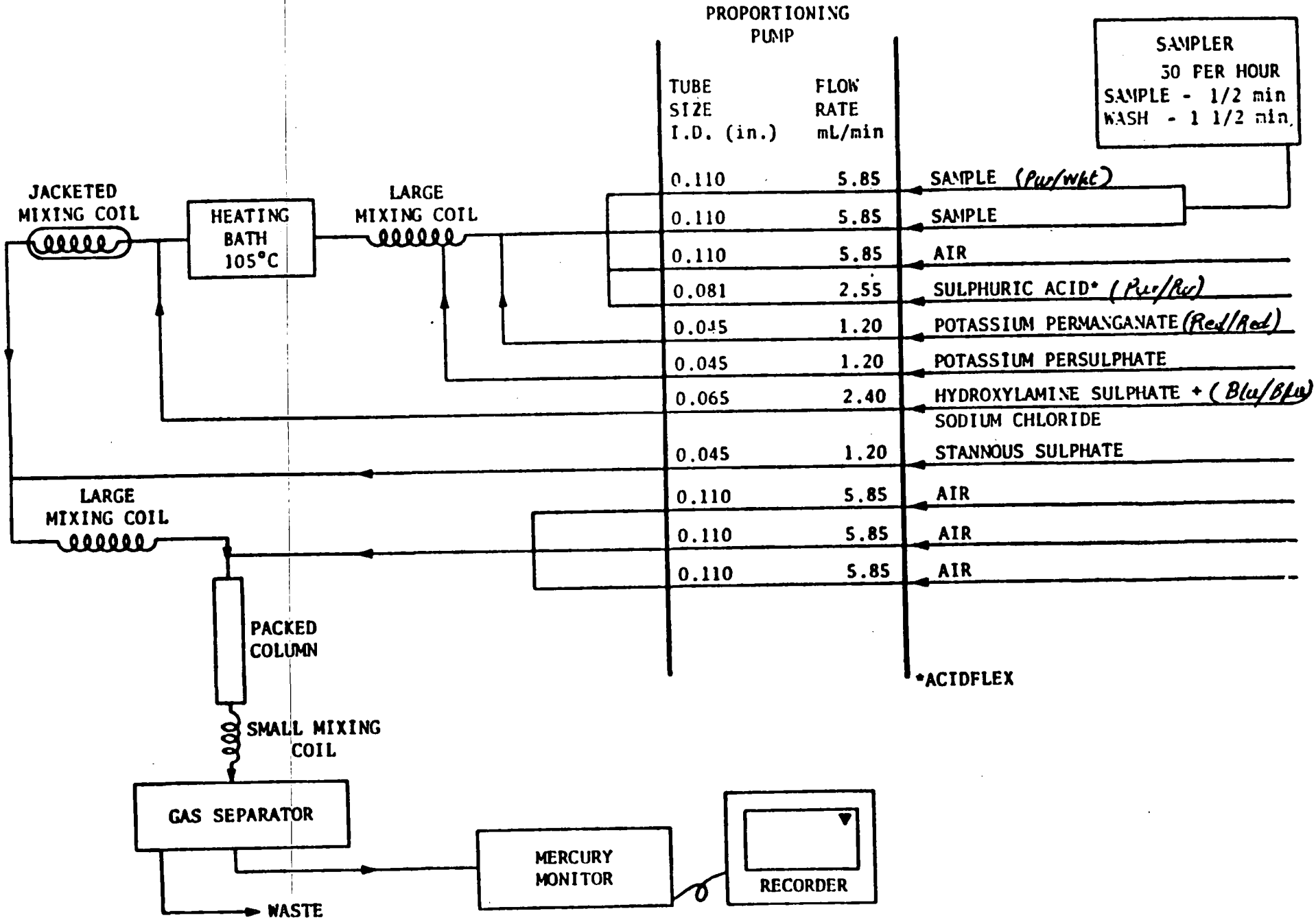


FIGURE IV - 1 MERCURY MANIFOLD

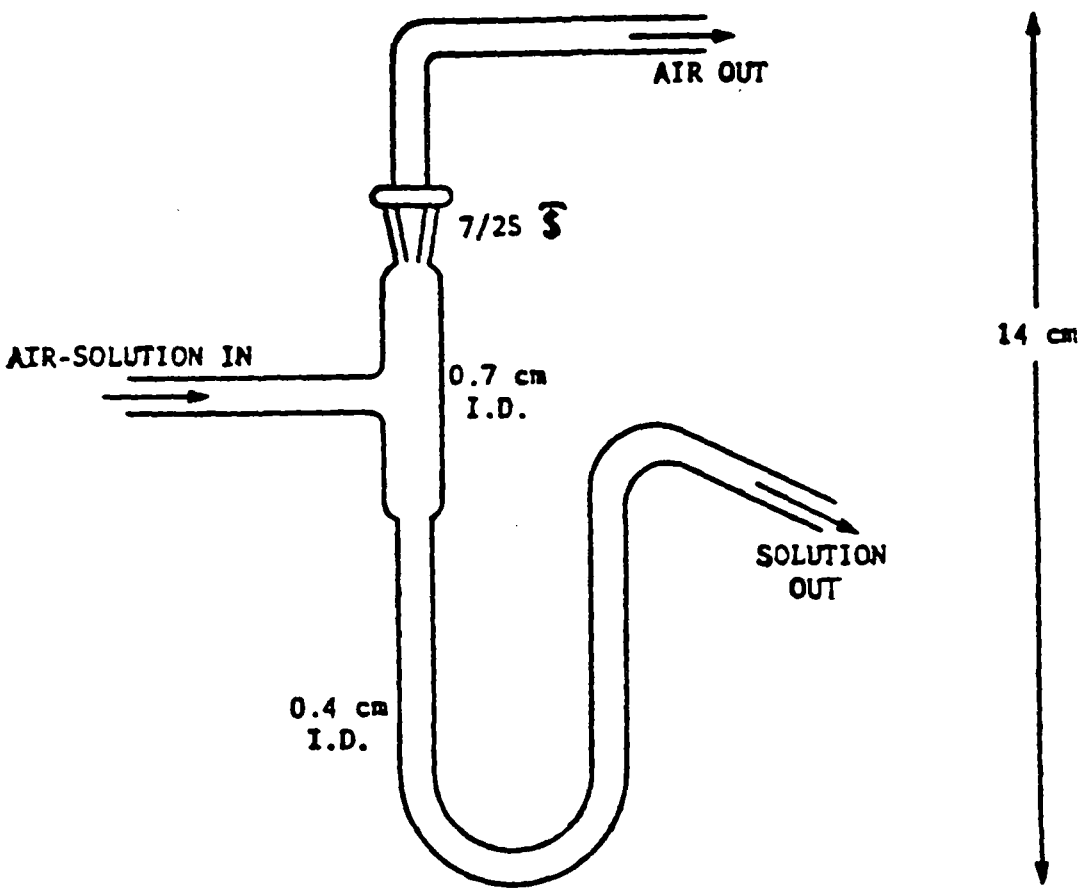


FIGURE IV - 2 GAS SEPARATOR

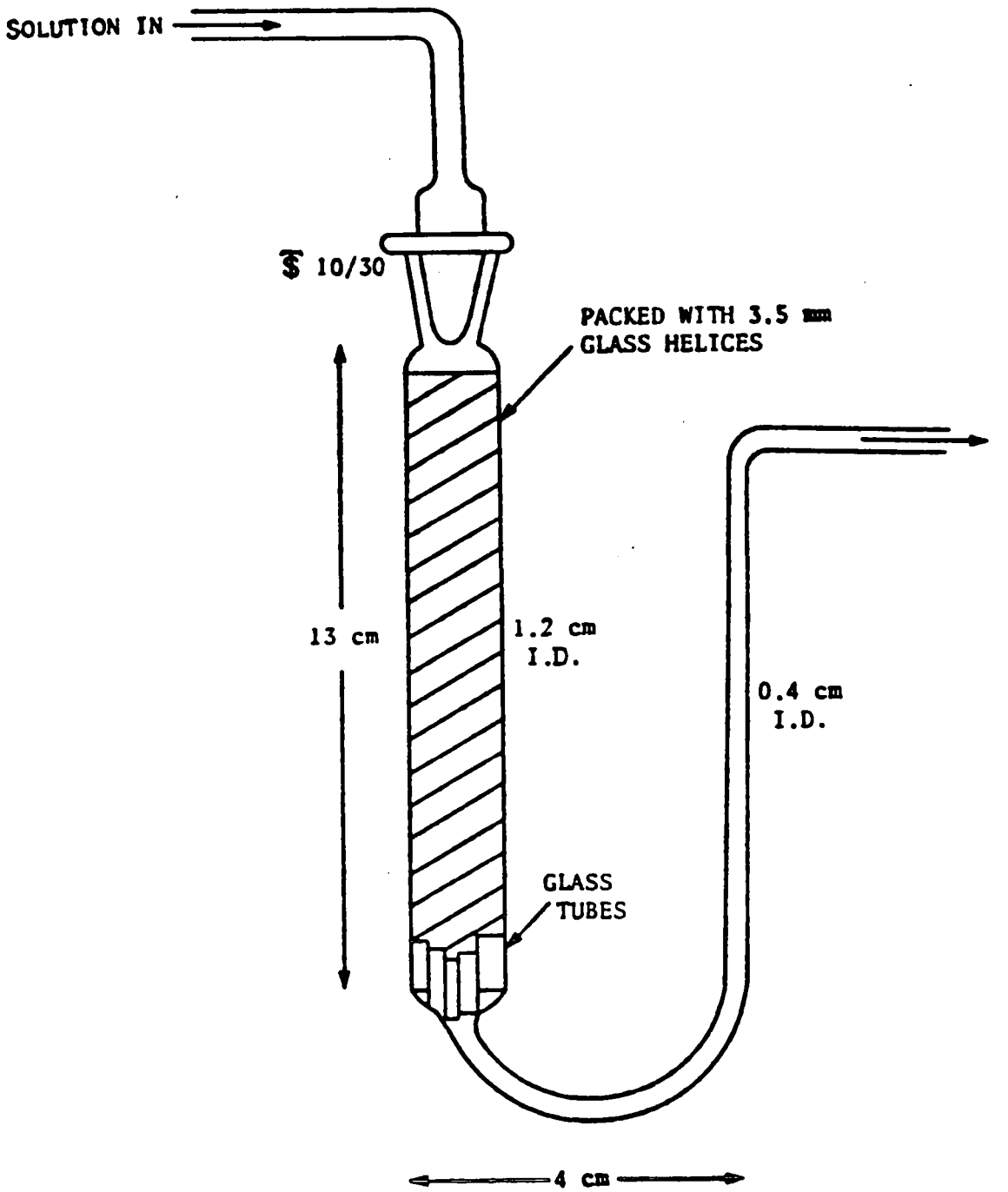


FIGURE IV - 3 PACKED COLUMN

FIGURE IV - 4

PREPARATION OF REQUIRED MERCURY SOLUTIONS

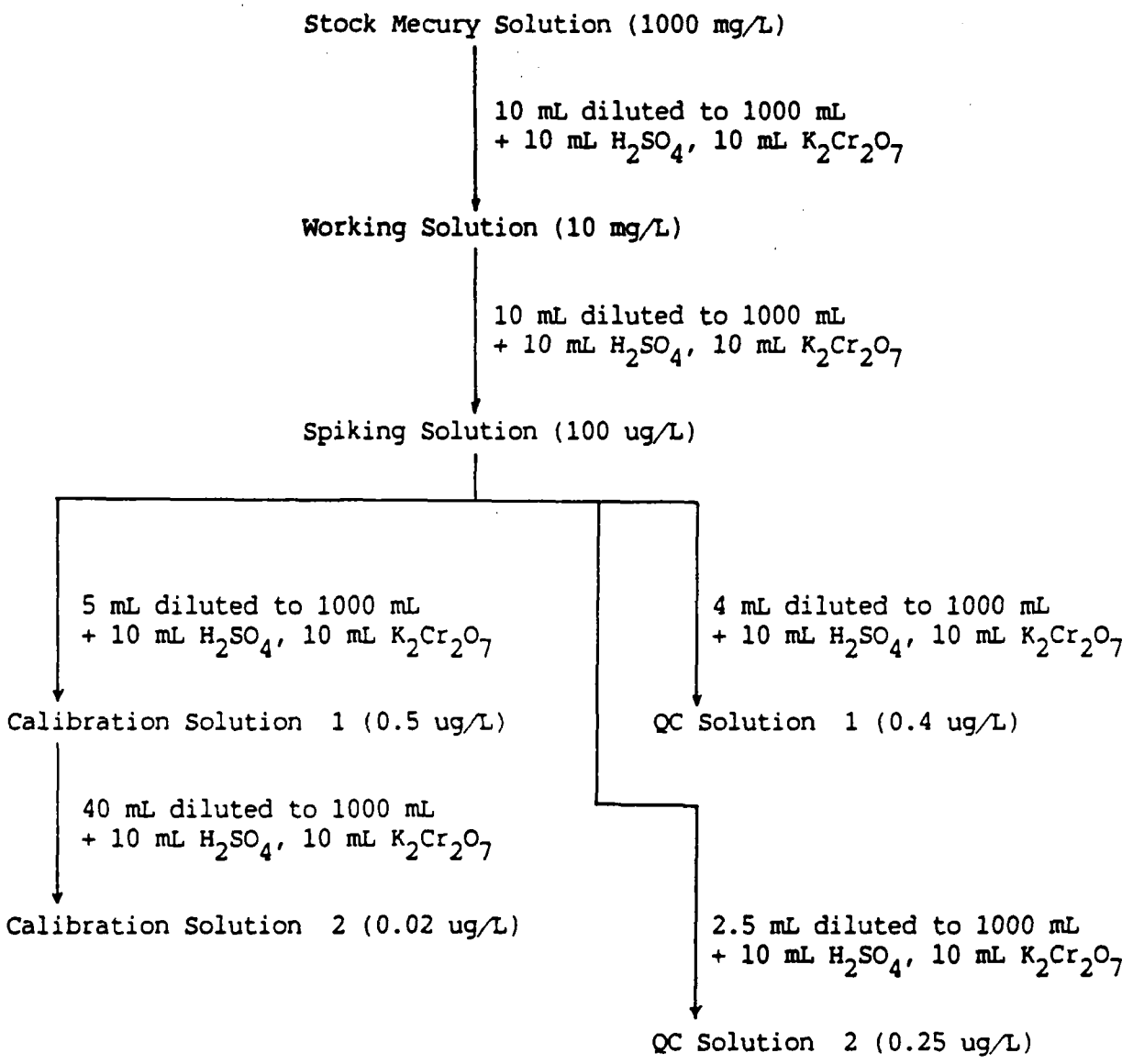


TABLE IV - 1:

DETECTION LIMITS

	Recorder Chart Divisions (% of full scale)		IDL	MDL	PDL
	0.5 ug/L	0.0 ug/L	(ug/L)	(ug/L)	(ug/L)
Mercury	55	0.5	0.0025	0.005	0.02

V DETERMINATION OF SILVER IN WATER

1.0 SCOPE AND APPLICATION:

This method is applicable to the analysis of extactable silver (Ag) in Niagara River water.

2.0 PRINCIPLE AND THEORY:

Two different sample preparation procedures are used to present the analyte to an atomic absorption spectrometer. The first is direct aspiration of a preserved aqueous solution of natural water. When greater sensitivity is required the Ag^+ is extracted as the ammonium pyrrolidene dithiocarbamate (APDC) chelate into methyl isobutyl ketone (MIBK) at pH 3.5. The MIBK extract is then aspirated into the AAS unit. In both the direct aspiration and the extraction method absorption is measured at 328.1 nm to determine Ag^+. With the solvent extraction method interferences are unknown.

3.0 APPARATUS AND REAGENTS:

Equipment and reagents must be of a high quality and consistent with a trace metals analysis laboratory.

3.1 Apparatus: The following equipment is required:

(i) Perkin-Elmer Atomic Absorption Spectrophotometer: Model 5000 with the following equipment:

(a) A Silver hollow cathode Lamp

(b) A 7 Angstom Slit

(c) Triple-slot (boling burner)Burner

(ii) Mechanical shaker

(iii) Accurate and precise pH meter

(iv) Two hundred mL volumetric flask

(v) 250 mL polyethylene bottles.

NOTE: BOTTLES ARE TO BE WASHED WITH A 2% (W/V) SOLUTION OF HNO_3 (section 3.2-vii) IN DEIONIZED DISTILLED WATER.

3.2 Reagents

NOTE: ALL REAGENTS ARE OF REAGENT GRADE AND ARE SHOWN TO BE FREE OF SILVER BEFORE BEING USED IN THE ANALYSIS.

(i) Gases: Acetylene and Air

(ii) Deionized distilled water (DDW) prepared by passing distilled water over a mixed bed ion exchange resin

(iii) Ammonium pyrrolidine dithiocarbamate: Catalogue number BDH 14129-26

(iv) Methyl isobutyl ketone: Catalogue number Caledon 7600-140

(v) Acetone: Catalogue number Baker 9008-3

(vi) Ethylene diamine tetraacetic acid (EDTA): Catalogue number Baker 8991-1

(vii) Concentrated Nitric Acid (HNO_3): Baker Analytical Grade

(viii) Silver nitrate ($AgNO_3$): Catalogue number Baker 3426-1

3.3 Solutions:

NOTE: THESE SOLUTIONS ARE UNSTABLE AND MUST BE PREPARED FRESH DAILY OR JUST PRIOR TO USE AS INDICATED.

(i) Prepare the chelating solution prior to use by dissolving 1 g APDC in 100 mL deionized distilled water.Filter this solution if necessary.

(ii) Prepare silver stock solution daily at a concentration of 100 mg/L by dissolving 0.0787 g of $AgNO_3$ in 500 mL DDW (section 3.2-ii).

(iii) Prepare spiking and calibration solutions (FIGURE V - 1) in DDW daily by diluting the stock solution (section 3.3-ii).

(iv) The control sample used in this method is made by spiking 2 ug/L to tap water

(v) The 100 ug/L (section 3-ii) solution is also the spiking solution.

4.0 SAMPLING PROCEDURE AND STORAGE:

Samples are collected into polyethylene bottles (section 3.1-v) containing 1.0 g EDTA (section 3.2-v) as a preservative.

NOTE: IT IS ESSENTIAL THAT THE EDTA PRESERVATIVE BE IN THE BOTTLE BEFORE THE ADDITION OF THE SAMPLE. ONLY IF THE EDTA IS PRESENT ARE THE SAMPLES STABLE OVER A PERIOD OF 2 WEEKS.

5.0 PROCEDURE:

5.1 Extraction Method: For samples with Ag^+ concentrations in the 0.1 to 10 ug/L range the APDC chelation/MIBK extraction procedure is used. A 100 mL aliquot of preserved sample is transfered into a 200 mL beaker and the pH is determined. In the presence of EDTA preservative the pH should be between 4 and 5. The pH is adjusted prior to extraction to 3.5 using a 3% (V/V) solution of HNO_3 (section 3.2-vii) in DDW (section 3.2-ii).

NOTE: EXTRACTION OF Ag^+ AS THE APDC CHELATE INTO MIBK IS SENSITIVE TO CONTROL OF pH. CARE MUST BE EXERCISED TO ENSURE THAT THE pH IS 3.5 BEFORE PROCEEDING WITH THE EXTRACTION.

The sample is transfered into a 200 mL volumetric flask and 2 mL of APDC and 3.7 mL of MIBK are added. The flask is shaken vigorously on a mechanical shaker for 5 minutes and then let stand until the layers separate. The organic layer is floated to the neck of the flask by slowly adding distilled deionized water. In a similar manner, 100 mL aliquots of standards are also extracted. The MIBK layers are aspirated directly into the AAS unit (section 3.1-i).

NOTE: IF EMULSIONS OCCUR WITH SOME WATERS DURING THE EXTRACTION STEP, ONE DROP OF METHANOL IS ADDED TO DISSOLVE THE INTERFERING LAYER. THE CHANGE IN VOLUME OF THE ORGANIC LAYER IS MONITORED AND THE APPROPRIATE CORRECTION FACTOR IS USED IN THE CALCULATIONS

5.2 Direct Analysis Method: For concentrations above 10 ug/mL the preserved aqueous sample is directly aspirated into the AAS unit.

6.0 INSTRUMENTAL ANALYSIS:

An oxidizing AAS flame is used with a triple slot burner and acetylene as the fuel and air as the oxidizing agent. The lamp is a silver hollow cathode lamp with a 7 Angstrom slit. The wavelength being monitored is 328.1 nm.

NOTE: PREMIX CHAMBER (CLOUD CHAMBER) AND BURNER MUST BE THOROUGHLY RINSED AND CLEANED DAILY WITH ACETONE AND 1:1 (V/V) HNO_3 (section 3.2-vii) IN WATER TO PREVENT CONTAMINATION AND TO ALLOW REPRODUCIBLE DETECTION AT THE 0.0001 mg/L LIMIT.

7.0 CALCULATIONS:

A calibration curve is prepared from the standard solutions (section 3.3-iii) extracted with APDC/MIBK. Peak heights are obtained from these standards. The concentration of Ag^+ in the sample is determined by directly comparing sample peak heights with the calibration curve.

8.0 PRECISION AND ACCURACY:

The precision of the method on 10 replicate analyses of silver spiked into natural water gave recoveries and coefficients of variation which can be found in TABLE V - 1. These data were obtained from a single intralaboratory study. Based on the analysis of 20 replicates the PDL for the extraction procedure is operationally the same as the MDL and is 0.1 ug/L. The IDL does not apply.

9.0 QUALITY CONTROL:

The protocol for quality control requires one blank obtained by analyzing DDW, one duplicate, and two control samples (section 3.3-iv) for every 40 samples. This will determine the method blank, control for recoveries and check the accuracy of the method. In addition one spike sample (section 3.3-v) for every 40 samples is used to determine recoveries.

A minimum of 7 observations of the control sample are used to calculate a mean(x) and standard deviation(σ). The upper and lower control limits are computed as $x \pm 1.96\sigma$, within which at least 95% of the measurements of the control sample fall. If during routine sample analysis, any results of the control sample fall outside $x \pm 3\sigma$ (upper and lower warning limits), the measurements of the samples is discontinued and the source of the deviation is traced and corrected.

FIGURE V - 1

SOLUTIONS REQUIRED FOR SILVER ANALYSIS

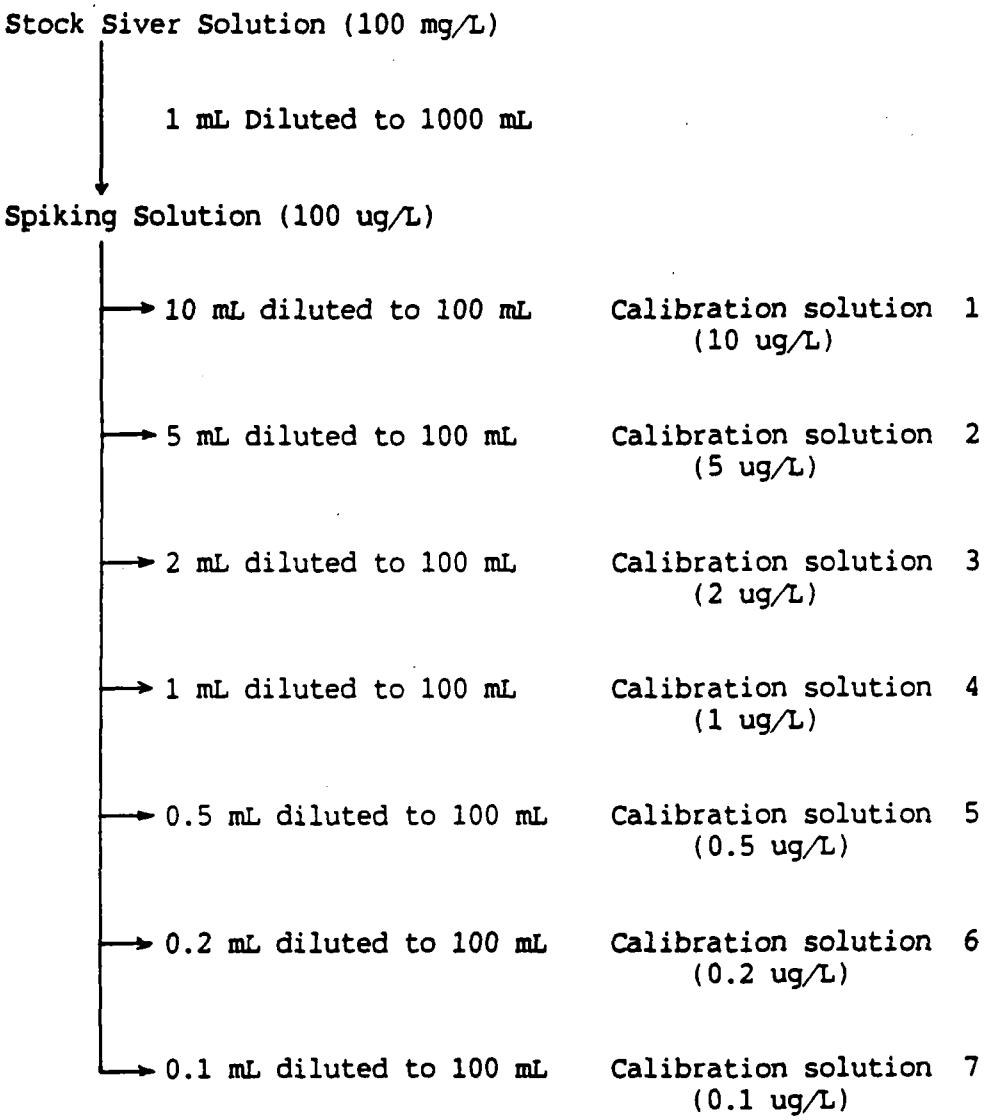


TABLE V - 1:

RECOVERIES OF QUALITY CONTROL SAMPLES USING A SPIKING TECHNIQUE

SPIKING AMOUNTS (ug/L)	RECOVERY (%)	COEFF. OF VAR. (%)
0.5	116	4.9
2.0	106	1.8
5.0	97	2.8

VI NON-RESIDUAL METALS IN SUSPENDED SEDIMENTS

1.0 SCOPE AND APPLICATION:

This method is designed to determine non-residual Cd, Cr, Co, Cu, Pb, Ni and Zn in Niagara River suspended sediments. Detection limits depend on weight of sediment analyzed. Up to 10 g dry weight may be used.

2.0 PRINCIPLE AND THEORY:

Non-residual metals (0.5 N HCl extractable) in a sediment is defined as the fraction of the metal that is not part of the silicate matrix of the rock from which the sediment is derived. This includes metal adsorbed on the sediment particles, complexed by or adsorbed on organic matter and the form of insoluble salts.

In determining non-residual metals, it is necessary to ensure that the sample preparation does not isolate metals from the rock from which the sediment is derived. Consequently a relatively mild acid digestion procedure is used to liberate metals from organic matter, dissolve precipitated salts and extract all easily extracted metals from the sediments.

3.0 APPARATUS AND REAGENTS:

Equipment and reagents used in these analyses are similar to those used in the determination of metals in water. The additional materials required are described below.

3.1 Apparatus: The following equipment is required:

(i) Virtis Company Model Sublimator 100 SRC freeze dryer

(ii) Large petri dishes

(iii) Suction filtration apparatus

(iv) Automatic shaker

(v) 125 mL wide-mouth polyethylene or polypropylene bottles

(vi) 100 mL volumetric flasks

(vii) Glassware and plasticware

NOTE: GLASSWARE AND PLASTICWARE SUCH AS FLASKS, BEAKERS, PIPETTES, FUNNELS, GRADUATED CYLINDERS AND WIDE-MOUTHED BOTTLES SHOULD BE WASHED WITH 1:1 HNO_3 AND THEN RINSED REPEATEDLY WITH DEIONIZED-DISTILLED WATER.

3.2 Reagents:

(i) 0.5 N HCl, Analytical Grade: Baker Catalog Number 9535-3

(ii) 25% W/V of KCl in distilled deionized water, Analytical Grade: Baker Catalog Number 3040-1

(iii) 30% W/V of NH_4Cl in distilled deionized water, Analytical Grade: Baker Catalog Number 0660-1

4.0 SAMPLING PROCEDURE AND STORAGE:

Samples are collected using a Westfalia centrifuge according to the sampling protocol (2).

5.0 SAMPLE PREPARATION:

Samples are freeze dried at -50°C for 5 days at 25 to 30 milli-Torr.

6.0 PROCEDURE:

Five g of the freeze-dried sediment are accurately weighed and placed in a 125 mL polypropylene wide-mouth bottle. 100 mL of 0.5 N hydrochloric acid added to the above and the cap is replaced tightly.

NOTE: DUE TO THE NATURE OF SUSPENDED SEDIMENT, THE AMOUNT OF ACID ADDED SHOULD BE SUFFICIENT. IF BUBBLING OF CO_2 OCCURS AT TIME OF ADDITION OF HCl OWING TO THE PRESENCE OF $CaCO_3$, THE DIGESTION IS REPEATED WITH A SMALLER PORTION OF DRIED SEDIMENT.

Capped bottles are shaken at room temperature in a mechanical shaker overnight (16 hours). The solution is filtered by suction through a 0.45 um cellulose acetate filter. Leached sediment is discarded.

The absorption of chromium is suppressed in the air-acetylene flame by the presence of iron and nickel. The addition of 2% ammonium chloride to samples and standards controls the interference caused by iron. 0.75 mL of a 30% NH_4Cl solution is added to each 10 mL of samples.

The resulting solutions can be analyzed directly on the Perkin Elmer flame atomic absorption spectrometer with background correction used in the calculations. The concentrations of metals in the digest are determined by direct comparison with standards made up in matrix

matched solutions.

NOTE: AN ACID-RESISTANT NEBULIZER IS USED.

7.0 CALCULATIONS:

Extractable metal concentration in the suspended sediment is given by:

$$M = C \times V / W$$

Where:

M = concentration of metal in sediment (mg/kg)

C = concentration of metal in digest solution (mg/L)

V = volume to which the sample is diluted (L)

W = weight of dry sediment used (kg).

8.0 QUALITY CONTROL:

The quality Control program requires the analysis of the following samples: Two blank samples are analyzed with every 50 samples; one duplicate, one spike and one control sample every 25 samples. Detection limits based on the analysis of 20 replicates of 5 g samples are presented in TABLE VI - 1. Standard reference materials from ASTM and NBS are used to ensure good recovery.

A minimum of 7 observations of the control sample are used to calculate a mean(x) and standard deviation(σ). The upper and lower control limits are computed as $x \pm 1.96\sigma$, within which at least 95% of the measurements of the control sample fall. If during routine sample analysis, any results of the control sample fall outside $x \pm 3\sigma$ (upper and lower warning limits), the measurements of the samples is discontinued and the source of the deviation is traced and corrected.

9.0 PRECISION:

The precision of the method is available only from a single laboratory. Precision is expressed as the coefficient of variation at the given level in the sediment and is based on analysis of 10 replicates. This data is presented in TABLE VI - 2.

TABLE VI - 1:

DETECTION LIMITS

Metal	Wavelength (nm)	PDL* (mg/kg)
Cadmium	228.8	0.2
Chromium	357.9	0.2
Cobalt	240.7	0.4
Copper	324.8	0.2
Lead	217.0	1.0
Nickel	232.0	0.6
Zinc	213.9	0.2

* PDL = Practical Detection Limit

TABLE VI - 2:

PRECISION OF THE METHOD FOR DETERMINATION OF NON-RESIDUAL METALS

Metal	Concentration (mg/kg)	Coeff. of Var. (%)
Cd	1.4	8.8
Co	10	0.7
Cr	14	2.9
Cu	40	1.0
Ni	30	2.2
Pb	44	4.0
Zn	70	0.5

VII TOTAL ARSENIC AND SELENIUM IN SUSPENDED SEDIMENT

1.0 SCOPE AND APPLICATION:

This method is designed to determine Arsenic (As) and Selenium (Se) in Niagara River suspended sediments. The standard size of 0.5 g of sample is used.

2.0 PRINCIPLE AND THEORY:

In order to obtain good recovery for As and Se in the whole matrix, organic materials in the sample are destroyed by nitric acid digestion before NaOH fusion. Subsequently the digest is dissolved in HCl at 90°C which also reduces the inorganic Se to the Se^{+4} state. Hydrides of the As and Se are formed by reduction in acidic medium with $NaBH_4$. The hydrides are sparged directly into the ICAP for determination of As and Se.

3.0 APPARATUS AND REAGENTS:

Both equipment and reagents must be of a quality consistent with a trace metals analysis laboratory.

3.1 Apparatus: The following equipment is required:

(i) Virtis Company Model Sublimator 100 SRC freeze dryer

(ii) Thermolyne type 2200 hot plate

(iii) Muffle furnace

(iv) Model IEC Centra centrifuge

(v) Autoanalyzer unit consisting of:

- (a) Technicon Sampler IV with capability to handle glass tubes and 20 - 1:2 cam (to permit analysis of 25 samples per hr. and 1:2 samples to wash ratio)
- (b) 20 channel Carlo Erba proportioning pump
- (c) Manifold as described in (FIGURE VII - 1)

(vi) ARL QA-137 ICAP Spectrometer

(vii) 15 mL zirconium crucibles

(viii) 100 mL volumetric flasks

(ix) 25 mL centrifuge tubes

(x) Glass rod and funnel

3.2 Reagents:

NOTE: ALL REAGENTS ARE TO BE OF ANALYTICAL GRADE AND APPROPRIATE FOR USE IN A TRACE ANALYSIS LABORATORY USING ICAP AS THE INSTRUMENTAL TECHNIQUE.

(i) Sodium Hydroxide (NaOH): Catalogue number 3722-5

(ii) Concentrated Nitric Acid (HNO_3); Analytical Grade Co. Purchased from John's Scientific 175 Hansen St. Toronto, Ont. M4C 1A7

(iii) Concentrated Hydrochloric Acid (HCl); Analytical Grade: Catalogue number 9535-3.

(iv) Sodium Borohydride ($NaBH_4$): Catalogue number V023-5

(iv) Standard Reference Material of Sediment from A.S.T.M and N.B.S.

(v) Prepurified Argon

(vi) 1000 mg/L As and Se standards from Fisher

(vii) Solutions of intermediates concentrations in 1% H_2SO_4 :

SOLUTION A 10 mg/L As and Se
SOLUTION B 0.1 mg/L (100 ug/L) As, Se, in 1% H_2SO_4

NOTE: IF SOLUTIONS ARE DILUTED, CARE SHOULD BE TAKEN TO ENSURE THAT THE REAGENT MATRIX OF THE STANDARDS IS APPROPRIATELY DILUTED. THIS IS IMPORTANT, SINCE THE SENSITIVITY OF THE SYSTEM IS DEPENDENT ON THE REAGENT MATRIX OF THE SAMPLES.

(viii) A 2.5% solution of $NaBH_4$ (W/V) in 100 ml of 1 N NaOH. One N NaOH is to be prepared in deionized water daily.

4.0 SAMPLING PROCEDURE AND STORAGE:

Samples are collected using a Westfalia centrifuge according to the sampling protocol (2).

5.0 SAMPLE PREPARATION:

Samples are freeze dried at -50°C for 5 days at 25 to 30 milli-Torr.

6.0 PROCEDURE:

A 0.5 g portion of freeze-dried homogenized sample weighed into a clean zirconium crucible. 4 mL of HNO_3 is added to the sample and heated on the hot plate at 80-90°C until dryness. If foaming occurs, an additional 4 mL HNO_3 is added after foaming subsides and the digestion is repeated. The crucible is removed from the hot plate and cooled. The sample is now ready for fusion with NaOH.

About 4.5 g of NaOH pellets are added to the cooled zirconium crucible, covered with a lid and placed in a 150 mL beaker to prevent loss of sample during the fusion process. The beaker is placed in a muffle furnace initially at room temperature and the temperature of the furnace is increased 50°C every 15 minutes, up to the limit of 350°C. This temperature is maintained for at least 4 hours.

Furnace and samples are cooled, 50 mL deionized water is added to the cold beaker, which is then heated on a hot plate at 90°C until contents of the crucible are dislodged. Contents of crucible and beaker are transferred to a 250 mL Erlenmeyer flask with rinses of 5 mL deionized water. Crucible is rinsed with 12 mL concentrated HCl and the washings are transferred into the erlenmeyer.

NOTE: VIGOROUS REACTION WILL OCCUR.

The rinsing is repeated with another 30 mL concentrated HCl. All transferred portions are heated at 90°C for 1 hour. While still hot, the contents are transferred to a 100 mL volumetric flask, cooled and made up to the mark with distilled water. About 25 mL of sample is centrifuged at a speed of 3500 rpm for 10 min. This will bring all non-dissolved silicates to the bottom of the centrifuge tubes.

The sample is transferred to the Technicon sampler and analyzed for As, and Se using the autoanalyzer manifold in FIG. 1. These are determined by ICAP.

This system is capable of analyzing 25 samples per hour using an aspiration time of 45 sec. with a 30 sec. wash and a delay of 60 sec. between samples. Operating conditions for the system are described in TABLE VII - 1.

7.0 CALCULATIONS:

A calibration curve is derived from the peak heights obtained by the analysis of standard solutions. The concentration of As and Se in the samples is determined by comparing peak heights obtained by the analysis of samples with the calibration curve.

The concentration of metal in sediment is calculated as follows:

$$M = C \times V / W$$

Where:

M = concentration of metal in sediment (mg/kg)

C = concentration of metal in digest solution (mg/L)

V = volume to which sample is diluted (L)

W = weight of dry sample used (kg)

8.0 QUALITY CONTROL:

The quality control program for this phase of the work requires one duplicate sample, one method blank, two spikes and one reference sample for every 25 samples. Detection limits based on the analysis of 20 replicates of 0.5 g samples are presented in TABLE VII - 2. Standard reference materials from ASTM and NBS are used to ensure good recovery.

A minimum of 7 observations of the control sample are used to calculate a mean(x) and standard deviation(σ). The upper and lower control limits are computed as $x \pm 1.96\sigma$, within which at least 95% of the measurements of the control sample fall. If during routine sample analysis, any results of the control sample fall outside $x \pm 3\sigma$ (upper and lower warning limits), the measurements of the samples is discontinued and the source of the deviation is traced and corrected.

9.0 PRECISION AND ACCURACY:

The precision and accuracy for determination of each analyte by the described method is summarized in TABLE VII - 3.

Arsenic, Selenium in Sediment

Flow Diagram

(Carlo Erba, peristaltic)

Pump

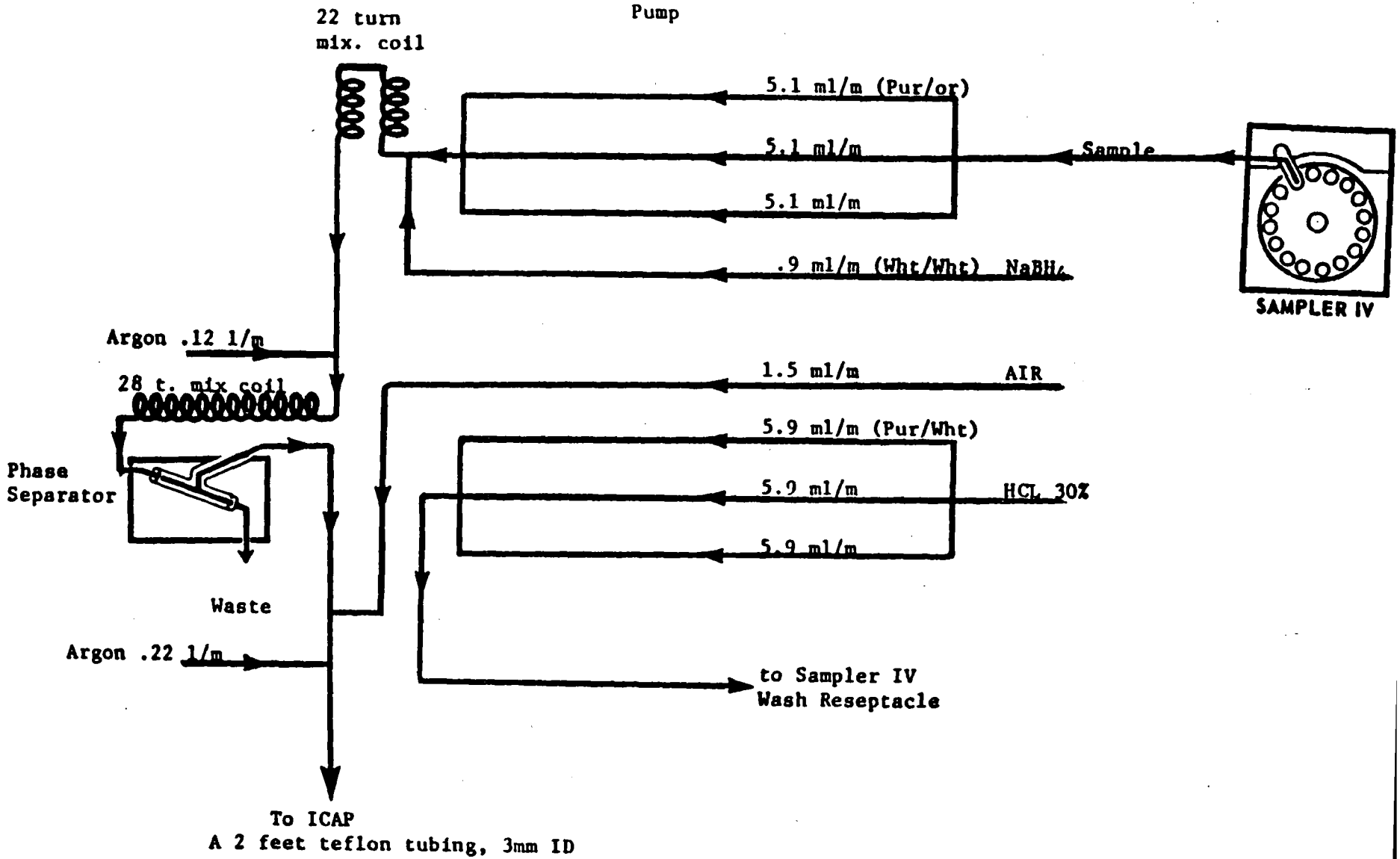


FIGURE VII - 1 HYDRIDE MANIFOLD

TABLE VII - 1:

OPERATING CONDITIONS FOR THE TECHNICON AND ICAP SYSTEMS

POSITION OF GAS FLOW INTO THE SYSTEM (SEE FIGURE II - 1)	FLOW RATE
ARGON BEFORE SEPARATOR	0.12 L/min
ARGON AFTER SEPARATOR	0.22 L/min
ARGON COOLING GAS	12.0 L/min
ARGON PLASMA GAS	0.12 L/min
ARGON INJECTOR FLOW	0.34 L/min
AIR FLOW	1.50 mL/min
OPERATING PARAMETERS FOR THE ICAP	
FORWARD POWER	1600 W
REFLECTED POWER	less than 10 W
PRE-INTEGRATION TIME	45 seconds
INTEGRATION TIME	30 seconds
WAVELENGTHS FOR DETERMINATION ANALYTES	
ANALYTE	WAVELENGTH* (nm)
As	193.77
Se	203.99

* All measurements are made in the third order of diffraction.

TABLE VII - 2:

DETECTION LIMITS

Element	PDL* (mg/kg)
Arsenic	0.2
Selenium	0.2

* PDL = Practical Detection Limit

TABLE VII - 3:

PRECISION AND ACCURACY FOR DETERMINATION OF As AND Se IN SEDIMENT

	Mean		Standard Deviation	
	As (mg/kg)	Se (mg/kg)	As (mg/kg)	Se (mg/kg)
Blanks	0.0007	0.0001	0.0006	0.0004
Difference between duplicates	0.003	-0.048	0.500	0.074
Reference material WQB-1	22.6	1.24	0.8	0.29
	(%)	(%)	(%)	(%)
Spikes	98.0	91.3	7.5	6.5

REFERENCES

(1) Goulden P. D. and D. H. J. Anthony. Determination of Trace Metals in Freshwaters by Inductively Coupled Argon Plasma Atomic Emission Spectrometry with a Heated Spray Chamber and Desolvation. Analytical Chemistry, Vol. 54, 1982. pp 1678-1681.

(2) Sampling Protocols Group (Group A). Niagara River Sampling Protocol. 1986.