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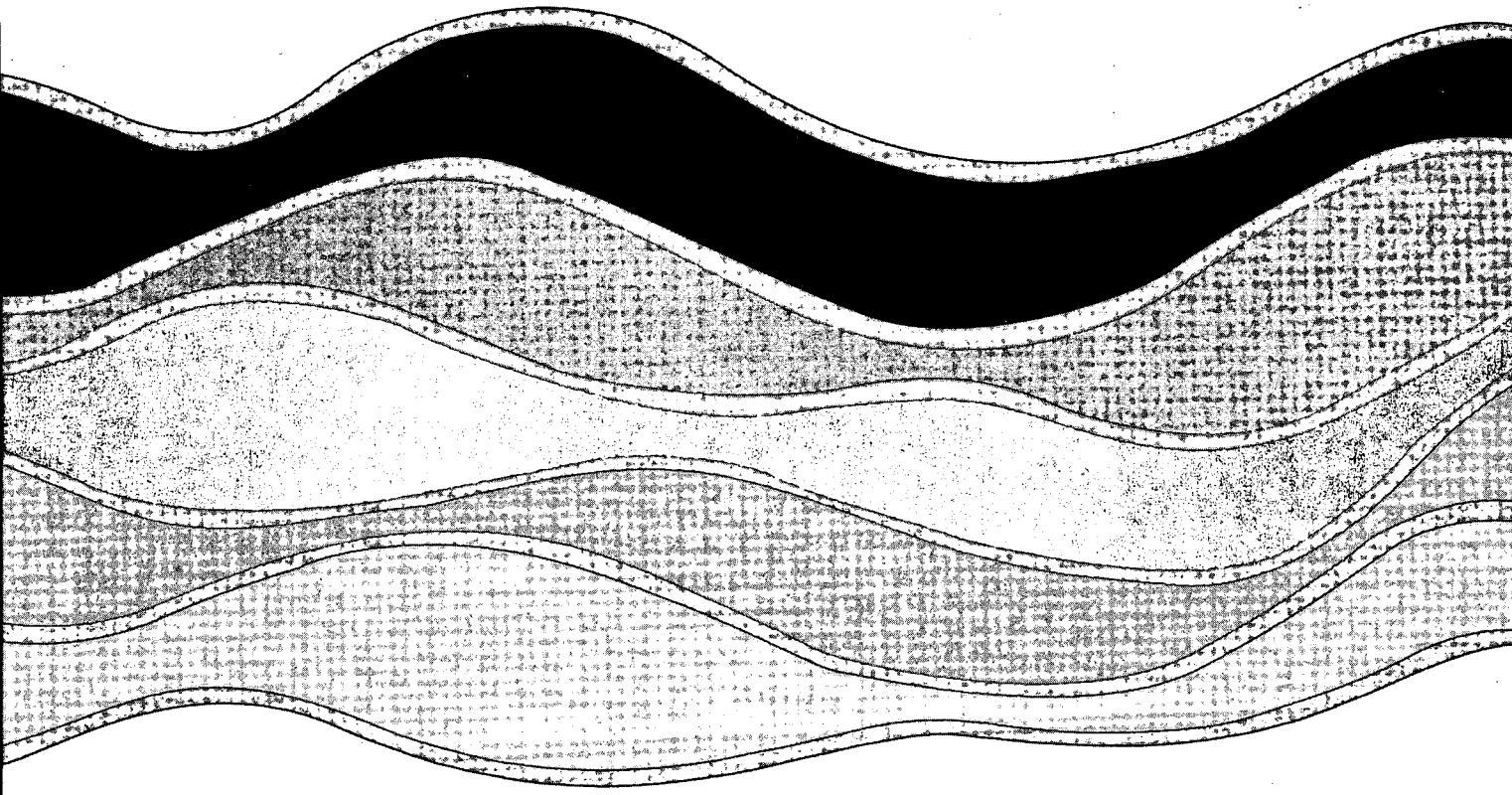

LARGE-SAMPLE EXTRACTION SYSTEMS WITH ANALYTICAL SOLVENT RECOVERY FOR LOW-FLOW APPLICATIONS

D.H.J. Anthony

NWRI Contribution No. 94-69

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In Memoriam of Dr. Peter D. Goulden

This report is dedicated to the memory of Dr. Peter D. Goulden whose ideas and work produced the GLSE\WEEK and a near-completed version of the GLSE/SR before his sudden death in 1987. Peter's work on continuous-flow, liquid-liquid extraction and his development of the Large-Sample Extractor (named the Goulden Large-Sample Extractor (GLSE) in memoriam) for trace organic contaminants determination in environmental samples is one of the highlights of his career in environmental analytical chemistry research. Others include his book "Environmental Pollution Analysis" and his contributions to the Water Quality Branch Analytical Methods Manual and the Analytical Protocol for Monitoring Ambient Water Quality of the Niagara River.

MANAGEMENT PERSPECTIVE

The Goulden Large-Sample Extractor (GLSE), developed within the RAB/NWRI, has been used by the Department (WQB/OR) since 1986 in Niagara River monitoring to determine trends in organic contaminants loadings to the system. The GLSE preconcentration technology has served well analytically in this application. A perceived drawback to the technique is the finite solubility of the extraction solvent in water (1.3% v/v) and the consequent need to treat the extraction effluent to remove dissolved solvent before returning processed sample to the water system being sampled. This report describes the development of a GLSE prototype (GLSE/SR) having on-line analytical solvent recovery capability and a design which minimizes exposure of operating staff to solvent vapour. The system is essentially environmentally "friendly". Testing to date has shown the technique to be analytically equivalent to the original GLSE prototype.

SOMMAIRE À L'INTENTION DE LA DIRECTION

Dans le cadre du programme de surveillance de la rivière Niagara, le ministère (DQE/RO) se sert depuis 1986 de l'extracteur Goulden pour échantillons de grand volume (GLSE), mis au point à la DRPA/INRE, pour évaluer la tendance des charges en polluants organiques. La technique de pré-concentration convient tout à fait dans ce type d'analyse. On a toutefois constaté un inconvénient : le solvant d'extraction étant soluble dans l'eau (1,3 % v/v), il faut traiter l'effluent d'extraction pour en éliminer le solvant dissous avant de renvoyer l'échantillon traité au bassin hydrographique étudié. Dans ce rapport, on décrit la mise au point d'un prototype d'extracteur Goulden avec capacité de récupération du solvant en circuit (GLSE/RS) conçu de façon que l'exposition de l'utilisateur aux vapeurs de solvant soit réduite au maximum. Il s'agit d'un système écologiquement «compatible». D'après les essais réalisés jusqu'ici, il équivaut au premier prototype d'extracteur pour les analyses.

ABSTRACT

This report describes development of a large-sample extractor prototype (GLSE/SR) which has been designed to operate in an "environmentally friendly" manner. The prototype possesses on-line analytical solvent recovery capability and minimizes exposure of operating staff to solvent vapour. The prototype has been laboratory- and field- tested in the Niagara River Toxics Management Program (NRTMP) and shown to be analytically equivalent to the original GLSE prototype which has been used in this program since 1986.

The system is designed around a "standard" (for Niagara River monitoring) processing rate of 35 mL/min to collect a time-integrated extract of 50 L of sample over a 24 h period.

RÉSUMÉ

On décrit la mise au point d'un prototype d'extracteur pour échantillons de grand volume (Goulden/RS) «écologiquement compatible». Cet appareil permet de récupérer le solvant en circuit et réduit au maximum l'exposition de l'utilisateur aux vapeurs de solvant. On a fait des essais en laboratoire et sur le terrain dans le cadre du Programme canado-américain de gestion des toxiques de la rivière Niagara; les résultats montrent qu'il équivaut, pour les analyses, au premier prototype utilisé dans le cadre du programme depuis 1986.

Le système a été mis au point en fonction d'une «norme» de vitesse de traitement (pour la surveillance de la rivière Niagara) de 35 mL/min, ce qui permet de traiter un échantillon de 50 L prélevé sur une période de 24 heures.

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INTRODUCTION

The Goulden Large-Sample Extractor (GLSE), described originally by Goulden and Anthony in 1986 (1-3), was designed to provide a convenient means by which hydrophobic organic contaminants in environmental aqueous matrices could be preconcentrated to levels allowing reliable quantitation by existing analytical methods. The GLSE technique, by virtue of its continuous-flow design, can provide preconcentration factors from 10-1000+ times greater than those commonly achieved using batch extraction techniques which, practically, can be applied only to relatively small samples (1-20 L). These large preconcentration factors are essential for water quality programs designed to monitor ambient levels and trends of hydrophobic organic contaminants in aquatic ecosystems (4). The GLSE technique has been used, since its introduction in 1985, in continuous (weekly) monitoring of organic contaminants in the Niagara River system for evaluation of the impact of the Niagara River Toxics Management Program (NRTMP) (5). Numerous other applications of early prototypes of the GLSE technology have been documented (4).

The physical and chemical properties of DCM, especially its volatility, stability, and density (relative to water), make it an ideal solvent for the extraction of hydrophobic compounds from aqueous matrices for environmental analytical purposes (1). Industrially, the solvent is widely used in many applications for similar reasons (10). In the last two decades, DCM has become one of the most frequently used solvents for analytical extractions and is included in U.S. EPA methods It is currently preferred over "freons" (9,12) in this application.

Understanding of the human health effects, environmental fate and environmental impact of DCM is limited. Existing knowledge (7,8,17), however,

particularly its characteristics as an experimental carcinogen, is sufficient to consider that it's discharge to aqueous systems without treatment (11,13,14) is unacceptable.

The GLSE technique was designed around use of dichloromethane (DCM) as the extractant. This solvent is preferred for several practical reasons associated with solvent extraction techniques in general and with the subsequent analytical fractionation and "cleanup" steps involved in determination of analytes of interest (1,2,15).

Dichloromethane (DCM) has a finite solubility of 1.3% (v/v) in water (6). Discharge of sample effluent processed by DCM extraction is perceived as environmentally unacceptable. The large-sample extraction systems described in this report were designed to perform a continuous return of recovered solvent to the analytical extraction process. The technique has been termed "analytical solvent recovery" by the author. Solvent recovery for continuous-flow processing is desirable for reasons other than removing a perceived negative environmental impact. The most important analytical reason is that it limits the significance of a solvent blank, maintaining it at the level of the blank associated with the initial DCM "charge" (≈ 200-300 mL). This allows much larger samples to be processed without a corresponding increase in solvent blank. Blank values associated with the initial solvent charge are normally non-existent or insignificant. Another advantage of analytical solvent recovery is minimization of the expense and hazards associated with transportation, storage and handling of large amounts of DCM. Additionally, the closed-system operation necessary for analytical solvent recovery reduces exposure of operating personnel to solvent vapour.

EXPERIMENTATION IN ANALYTICAL SOLVENT RECOVERY

The "Weekly" Sampler (GLSE/WEEK)

Initial experiments with incorporation of an analytical solvent recovery feature for the GLSE were conducted in cooperation with the WQB/OR during 1986/87 at their

Niagara-on-the-Lake monitoring station. The object of the project was to integrate a newly-designed sample-intake system (for automated pumping of water from the river and fractionating the sediment phase from the aqueous phase) (24) with a GLSE apparatus (designated "GLSE/WEEK") incorporating features to analytically recover dissolved solvent from extraction effluent (25). This prototype was designed to operate in a semi-automated mode, processing a 100 L time-integrated sample over the period of seven days with the option to collect the daily extracts selectively if desired. A condensation of this work is given below.

Design of the GLSE/WEEK Prototype

A schematic diagram of major components of the GLSE/WEEK prototype extraction apparatus is provided in **Fig.1**

Phase Mixing

Early prototypes of the GLSE (GLSE-95, GLSE-70, (1,2)) were open to the atmosphere to allow use of an overhead stirrer as the mixing device. Sealing a glass apparatus with overhead stirring was not considered feasible as stirrer vibration at the high operating speeds required would be almost certain to eventually fracture the glass apparatus.

Instead, the extractor body was redesigned to incorporate a magnetically-coupled centrifugal pump (Micropump, Model No. 101-405) as the mixing device. This type of pump is very efficient at mixing immiscible phases when operated at high speed due to segmentation of pumped fluid caused by the vanes of the centrifugal impeller. Further mixing is provided by the vigorous swirling action created in the mixing chamber by introducing the pumped mixture tangentially to the chamber at high velocity ($\approx$ 2 L/min). This type of pump is, as well, non-contaminating as pumphead components are magnetically operated and therefore not exposed to lubricants used in most other pump types.

Earlier GLSE prototypes incorporated a Teflon "Rashig Ring" scrubber column to coalesce fine droplets of DCM, caused by vigorous phase mixing, from effluent leaving the extractor body. The coalesceate was then returned to the mixing chamber via a solvent return arm. In the GLSE/WEEK prototype, redesign of the extractor body (narrow vertical extensions of the mixing chamber and settling chamber) and the very low sample input rate (≈ 10 mL/min), and the need for a separator trap, unnecessary (**Fig.1**).

Sealing the Apparatus

The mixing mechanism used in this prototype allowed modification of the extractor to effectively seal the major open point of previous prototypes, leaving only small ventilation points to maintain atmospheric pressure within the apparatus. These ventilation points were connected by Teflon tubing to a common collector (4 L solvent reagent bottle) which was continuously purged with nitrogen (UHP) at 20 mL/min through a baffle (Technicon, large mixing coil) to prevent diffusion of atmospheric contaminants into the extraction apparatus.

Automated Operation

The extraction apparatus was integrated with a water intake system designed within the WQB/OR to pump water from the river, and separate the suspended sediment phase from the aqueous phase (24). The latter process was accomplished using continuous-flow centrifugation. The overall collection process was automated to start-up and shut-down at specific times for collection of extracts both from the GLSE/WEEK and the "standard" GLSE/70 prototype (24-hr collection) which was being used in routine processing.

The extraction apparatus was integrated with the collection system to operate only when the continuous-flow centrifuge was operating. Otherwise, it was independently automated to provided a daily extract for each of seven days, emptying each daily extract into a common collection vessel, so that at the end of seven days, an integrated extract (≈ 850 mL), representative of the average contaminants loading over this time period, was

obtained. Manual override of this system permitted collection of an extract for any specific day.

Automated operation was accomplished using an eight- channel programmable timer (Davis Controls, Model No. "Maxirex" D4) powered by a 12 VDC automotive battery which was recharged before each seven day collection period. This approach was used as similar 115 VAC devices were found to be strongly effected by EMI (electromagnetic interference) and line voltage transients caused by centrifuge start-up, etc.

Daily Extraction Cycle

The timing (ie. time of day) of the DCM empty/fill cycle was controlled by the programmable controller powering two (empty, fill) solenoid valves (General Valve, Model No. 2-15- 900). A magnetic float device activating a Reed relay activated the empty/fill process during this time. After the previous day's extract (≈ 120 mL) had been collected (ie., Reed relay is deactivated and "empty" solenoid is closed), the "fill" solenoid is opened and an aliquot of fresh solvent (≈ 150 mL) is delivered to the extractor via gravity from the overhead solvent reservoir. Solvent delivery is stopped as the float reaches the "full" level, activates the Reed relay and closes the "fill" solenoid.

Simultaneously with this event, the sample pump, surrogate standards pump, mixing pump and solvent recovery heater were turned on via the programmable controller. The extraction continued until the next day to the time selected for the controller to shut off the pumps and heater and open the "empty" solenoid. This process was repeated for seven days. On the seventh day, the entire sample collection and extraction system was shut down for collection of the integrated extract, collection of suspended sediment, and cleaning of the apparatus.

Solvent Recovery System

This extractor prototype operates at a low flow rate (≈ 10 mL/min) making near-complete solvent recovery a facile operation. A simple means of distilling a volatile, non-azeotropic, solvent from water is to heat the solution vigorously to the boiling point of water. At this point, some water will boil off as well ("steam-stripping, -distillation"). In this apparatus, both condensed DCM and water are returned to the extraction process. In a continuous-flow system, it remains only to control the vigour of boiling so that a minimal amount of water is vaporized. The return of large amounts of water condensate to the system will raise the temperature of the extraction mixture.

In this prototype, a simple heater (silica) and cold- finger condenser (**Fig.1**) were used to accomplish the distillation.

This type of operation is not suited, practically, for use in other versions of the GLSE since they all operate at much higher sample input rates at which power requirements become formidable, particularly for field operation.

Experimental Results/Discussion

The field experiment at the WQB/OR Niagara-on-the-Lake monitoring station was conducted for a total period of eight months to test physical performance of the extraction system and the newly-installed sample collection system. The final seven weeks of this period were used to obtain analytical data for evaluation of extractor performance.

Extraction efficiency was determined by the use of surrogate standards used to evaluate performance of previous versions of the GLSE (1,2,4,15,26,27). Surrogate standards recoveries are shown in **Table I.** These recoveries were commensurate with those obtained in performance studies of earlier GLSE prototypes and a decision was made to continue development of the solvent recovery feature.

A comparison was also made of ambient contaminant levels as determined using the GLSE/WEEK prototype and the "standard" GLSE/70 version which had been used since 1985 at both WQB/OR Niagara River monitoring stations (Niagara-on-the-Lake (NOTL) and Ft. Erie (FE)). These results are shown in **Table II.** Note should be made that the GLSE/70 collects a 50 L sample over the period of 24 h while the GLSE/WEEK processes a 100 L sample over the period of seven days and represents an average contaminant level over this time period. This comparison was made to suggest how different the values obtained might be, considering the difference in sample size and the variations that may exist in contaminant loadings to the river.

The "24-hr Sampler" (GLSE/SR)

Experimentation with the GLSE/WEEK prototype showed that "environmental isolation" of the solvent extraction process was feasible although certain modifications to the design of the apparatus would be necessary for extension of the capability to the higher sample input rates used in prototypes developed for other applications (35-1000 mL/min).

More specifically, it was realized that the "steam-stripping" technique used in this prototype was unsuited for distillation at these higher sample input rates due to the high power input required. Redesign of the solvent recovery unit to incorporate a more efficient means of "stripping" dissolved DCM from the effluent was therefore necessary. Secondly, the performance of the centrifugal pump as a phase mixing device was not entirely satisfactory. Frequent replacement the motor brushes due to continuous operation was found necessary. In addition, the "free-running" (ie. no feedback provision for constant torque operation) nature of the motor caused changes in the pump speed, and therefore mixing performance, with variations in the composition and viscosity of the pumped mixture. A more suitable means of achieving effective phase-mixing, while still permitting "isolation" of the extraction process, was therefore necessary.

A third improvement found necessary was that of the condenser design used in the GLSE/WEEK prototype. This simple design, in which tap water was used for cooling, was sufficient for the low sample input rate used in the experiment. At higher sample input rates, this device was found to be essentially ineffective. Other alterations made to prototype designs are noted in the following description.

Description of the GLSE/SR Apparatus

As with all GLSE prototypes, an effort was made to ensure that all components wetted by sample, solvent, and the extraction mixture were composed of materials generally accepted as being chemically inert and non-contaminating. Borosilicate glass, Teflon, ceramic and stainless steel are the only materials that contact the critical liquids. A schematic diagram of the overall GLSE/SR assembly is shown in **Fig.2.**

Phase Mixing

This process is accomplished by "remote" magnetic stirring acting on a custom-made Teflon impeller which is centered by the sample inlet. This impeller provides sufficient phase mixing without creating an extremely fine dispersion of DCM in the sample and is thus well-suited to processing aqueous matrices which tend to form stable emulsions (ie. clearing of phases is not immediate on cessation of mixing).

Isolation of the Extraction Process

As with the GLSE/WEEK, the GLSE/SR has pressure relief vents installed at appropriate locations on the glassware apparatus. These may be connected to a common manifold and vented as described for the GLSE/WEEK or vented through activated carbon. In either case, the venting device must not introduce significant pressure in the apparatus as it is designed to operate with gravity flow at atmospheric pressure.

Sample/Surrogate Standards Addition

As with all GLSE prototypes, the pumps used to deliver the sample and standards are positive displacement, piston- type pumps, the pumpheads of which are composed of chemically inert, non-contaminating materials.

A solvent compensation pump (to replace solvent lost by virtue of its water solubility) is, of course, unnecessary for the GLSE/SR prototype.

Sample is first pumped through a cooling coil (set in a refrigerated water bath) to cool it to ≈ 6°C. The cooled sample is the passed through the condenser, where it acts as the coolant, before entering the extractor. On passing through the condenser, the sample, in the heat exchange process, is warmed to ≈ 20°C. Sample is then delivered to the base of the Teflon impeller where it enters the extraction mixture through ports in the impeller.

Surrogate standards or "spiking" standards are delivered to the sample in the "spiking" inlet so that they are dissolved in sample before reaching the extraction mixture. The "spiking" inlet incorporates an intentional "break" in fluid lines so that under no circumstance can the extraction mixture, with standards (which are toxic), be siphoned back into the medium being sampled.

Solvent Recovery Unit

The solvent recovery unit consists of four major components; a boiler, a heated gas-stripping coil, a heated packed gas stripping/distillation column, and a jacketted, "cold-finger" condenser.

Extraction effluent is delivered, by gravity flow, to the jacketted gas stripping coil which is heated with "polished" effluent exiting from the boiler. In this coil, DCM is visibly stripped from solution and probably the bulk of dissolved DCM is removed here.

The gas/liquid mixture is then directed to the heated packed column where the gaseous DCM vents to the condenser and liquid falls through the warmed column, stripping off more DCM, to the boiler. In the boiler, any DCM remaining in the liquid is vaporized and passes up the packed column to the condenser. The distillation column allows a separation of water and DCM by refluxing water while passing DCM to the condenser. "Polished" effluent at ≈ 100 deg C overflows to the jacket of the gas stripper, where it is used to heat effluent exiting from the extractor, and to the drain tube.

Condensed DCM is returned directly the mixing chamber and is delivered just under the surface of the stirred mixture.

Performance Testing

As the important features of the GLSE affecting analyte recovery have remained essentially unchanged in the GLSE/SR prototype and this performance has been well documented for specific analytes (CBs, OC/PCBs), an extensive study of this aspect of performance was not considered useful. Performance testing of early prototypes of the GLSE was restricted to the CB and OC/PCB classes of contaminants. In the present study, PAHs, phthalates and phenols were included although documentation on PAH recoveries by DCM extraction is limited and the latter two classes are most efficiently recovered in acidic extraction. The data are provided here for discussion and documentation purposes.

The major points requiring attention, considering the intended use of the apparatus in the Niagara River Toxics Management Program (NRTMP), were the following:

(i) Demonstration that surrogate standards recoveries used to estimate extraction efficiency were comparable with those obtained using the "standard" GLSE/70 prototype used in Niagara River monitoring since 1985,

(ii) Demonstration that the recovery of specific classes of contaminants being determined in the Niagara River using the two prototypes were comparable,

(iii) Demonstration that DCM discharge in extraction effluent from the GLSE/SR prototype is significantly reduced over that of the GLSE/70 prototype, and,

(iv) The GLSE/SR should not be substantially more complex to operate than the "standard" GLSE/70 prototype.

These points were addressed with a combination of laboratory and field experiments. Extraction recoveries were determined using a solution of surrogate standards ("FSM1" (15)) and a second solution of analytes (CBs, OCs/PCBs, PAHs, phthalates, chlorophenols) being determined in the Niagara River (NR) monitoring program (5). These solutions were prepared in methanol for on-line addition to the extraction process (1,15,17,27,30). A reference extraction was done in replicate (n=5) by extended mixing (3 h, magnetic stirrer) of 2 L solutions "spiked" with the NR analytes. The extractions were done using a solvent-to-water (SWR) ratio typical of GLSE preconcentration (≈ 0.1) (1,3,4). These extractions remove the concern of "contact time" in continuous-flow extractions and represent a "best-case" recovery reference.

Physical Performance

The GLSE/SR design was tested and "optimized" for physical performance characteristics (solvent recovery, phase mixing, sample input rates, etc.) before analytical testing.

Ultrapure "organics free" water (Millipore MQ2 water purification system fed by distilled water, fitted with a Model "Q" activated carbon "polishing" cartridge for removal of organics - this water is referred to as "MQ2" water) was used in all laboratory

experiments. Water for the 24 hr experiments was stored in 50 gal stainless steel barrels (27).

Solvent recovery was assessed by measurement of the volume of condensed DCM over 24 hr periods of operation. DCM content of the extraction effluent was determined by UV/VIS spectrometry. Dichloromethane has a strong UV absorbence near the oxygen cutoff extending into the vacuum UV (6); the test mixture contains no other UV absorbing components, other than oxygen and possibly chlorine, in significant amounts. DCM discharge in extraction effluent was measured using a Hewlett-Packard model 8451A single beam photodiode array (PDA) UV/VIS spectrometer. A Gilson Minipuls II peristaltic pump and a 1.0 cm silica flowcell (Hellma, PN 178.711/Z:15), arranged as shown in **(Fig.3)**, were used to make continuous measurements of the DCM concentration in the extraction effluent after being cooled to room temperature in a "straight-through" heat exchanger. Background noise in UV measurements due to pump pulsations was minimized by high-speed (setting 1000) pumping through narrow-bore (1/16" heavy wall) teflon tubing. Measurements were made at 210 nm giving ≈ 0.5 au for a 1 % (v/v) solution of DCM in water. Linear response over this range was confirmed by calibration. Water saturated with DCM (1.3% v/v), prepared fresh for each experiment, was used as the calibration standard from which dilutions were prepared. MQ2 water, freshly boiled to remove dissolved oxygen and chlorine, was used as the blank solution and for preparation of standards. This matrix is equivalent to that of the extraction effluent which is boiled during the solvent recovery process.

Laboratory Testing

On establishing "optimal" physical operating parameters, analytical performance was determined by conducting a two- week experiment in which 24 hr extractions were conducted, alternately, with "spiked" and blank 50 L samples. The "spike" samples consisted of 50 L of MQ2 water "spiked" on-line during the extraction using the surrogate standards addition delivery system. The standards "spike" consisted of "target" analytes sought in the NRTMP (5) and comprise the classes of chlorobenzenes

(CBs), organochlorine pesticides and industrial materials (OCs/PCBs), polynuclear aromatic hydrocarbons (PAHs), phthalates and chlorophenols. This standards solution was delivered "on-line", as with the surrogate standards, to eliminate the concern of container adsorption of analytes.

Field Testing

Completion of the laboratory studies and review of the results showed the system to be effective and that the next step, a field study of comparative recoveries of ambient contaminants, should be conducted. The experimental design selected was the "paired comparison" technique as the expected differences in the two preconcentration methods were likely to be small, requiring a sensitive statistical technique to test significance of differences (28). A schematic of the test set-up is shown in **Fig.5.**

Testing was conducted at the WQB/OR Niagara-on-the-Lake (NOTL) monitoring station during March 1991. The sample collection system at this station has been described elsewhere (23,29). As the water temperature of the Niagara River at the time of testing (27 Feb.-13 March, 1991) was ≈ 5°C, use of the refrigerated water bath to cool the sample was unnecessary.

Paired samples for the two extractor prototypes were drawn from a small (≈ 4L) common, continuously fed and flushed reservoir of clarified river water. The experiment was conducted over a two week period during which six paired samples were collected (total of twelve samples).

Experimental Results/Discussion

Physical Performance

Physical testing of the GSLE/SR prototype showed the system to be very effective in purging dissolved DCM from the extraction effluent. This is to be expected

as the high volatility of DCM as compared to that of water and the absence of chemical interaction between the two solvents which might be conducive to azeotrope formation. The complete distillation of DCM from aqueous solution is very easily accomplished; recovering the DCM by condensation is somewhat more difficult. On temperature stabilization, DCM in extraction effluent is reduced to less than 1% of its saturation concentration in water (ie. < 1% of 1.6%(w/w) = < 160 ppm). Measurement of condensed DCM in 24 h experiments showed the system to be 60-70 % effective in recovering dissolved solvent. Evaporative losses and possible loss due to decomposition of DCM in contact with water at elevated temperatures (10) account for this efficiency. The evaporative losses most likely occur in the condenser rather than in the extractor itself, although the condenser's design is considerably more effective than that of earlier prototypes (5-10 % effective). These losses may be reduced somewhat by slightly pressurizing the system (as withthe GLSE/WEEK) but are more effectively dealt with by improved condenser design. The apparatus must ultimately be vented to avoid pressurization. Over-pressurization results in the introduction of condensed steam and warm DCM vapour to extraction unit causing the temperature of the extraction mixture to rise, thus increasing DCM volatilization and system pressure and defeating the gravity drain.

The GLSE/SR unit proved to be no more complex to use than the existing GLSE/70 prototype although "cleaning" of the solvent recovery apparatus after continued use is an additional chore.

Analytical Performance

Analyte recoveries for this study are expressed as nanograms per sample (or % for surrogate standards) since this is the fundamental quantity being compared and conversion to ambient concentrations is unnecessary for the purpose of this work. Corrections for extraction and analytical surrogate recoveries have not been made as these were generally found to be comparable and to have precision sufficient for comparisons

of "raw" data. "Corrections" within these limits of analytical precision are meaningless. The data presented are not to be construed as surveillance data.

Laboratory Testing

Analytical Blanks

In an ultratrace technique such as that used for contaminant monitoring of the Niagara River (4,5,15,26,30), particularly one so dependent on preconcentration steps (solvent extraction, evaporative concentration), great care must be exercised in avoiding contamination of the sample. Distinguishing between contamination at specific points in the overall procedure is difficult due to the complexity involved. For example, contamination in the extraction process is difficult to distinguish in a particular data set from contamination in the analytical process (carry-over in extraction, concentration, analytical cleanup/fractionation, chromatographic "ghosting", use of high-level standards with low level samples, contamination of standards, contamination of "blank water"). In laboratory experiments, samples were interspersed with "blanks" to sort out this aspect of the overall analysis. For the few cases of contamination observed, some results appeared to result from "swamping out" of extraction blank by contamination in further processing of samples; some contamination (particularly by phthalates) appears to be due to the MQ2 "blank water". This has since been confirmed by GC\FTIR analysis (the MQ2 water purification system contains an activated carbon "polishing" cartridge for organics, the cartridge and distribution components are made of plastics). Most analytes showed no or minimal (< 5 %) blank response. Exceptions included the phthalates, PCBs, some PAHs and 1,4-dichlorobenzene. These blank values have been subtracted from analyte responses where they seem to be attributable to the laboratory extraction process (blank water, extraction, sample containers). A previous study, with a designed blank experiment has suggested that contamination from the extraction process is minimal if properly conducted; observed contamination appears to arise elsewhere in the analytical procedure (28). The materials used in construction of all GLSE prototypes were selected for their

non-contaminating properties (glass, stainless steel, teflon, ceramic (1,4,17). The blank problem in this study was minimal and does not appear to be reflected in the field test data, except possibly for PCBs (**Table IV**, 5/8).

Reference Extraction

Five replicate extractions of "spiked" MQ2 ("blank") water were conducted to provide a reference for the best possible recoveries to be expected with a solvent/water ratio (SWR) and a contact time well in excess of that in the GLSE/SR. The procedure used is described elsewhere (31).

Reference recoveries are reported in **Table III.** Phthalates, chlorophenols, and neutral herbicides were not determined in the reference extracts. For the surrogate standards, OCs/PCBs, PAHs and most CBs, recoveries were generally statistically indistinguishable from the spike level. The more volatile dichloro-CBs are recovered with less efficiency. This is typical for the ultratrace procedure used in these analyses (15,26) and relates to evaporative loss in the preconcentration and evaporative concentration procedures. Several of the OCs show > 100 % recovery (eg. /-endosulfan, up to 128 % in reference extraction). This, as well, is typical of the analytical procedure and may be related to, among other things, the accuracy with which a multicomponent stock solution can be prepared and subsequently diluted and manipulated to reflect the nominal values. Overall, the recoveries achieved in the reference extraction were very good and in agreement with theoretical (1,3) and published recoveries of the CB, OC/PCB and PAH classes of compounds (15,26).

GLSE/SR Analyte Recoveries (Laboratory)

Surrogate standard and analyte recoveries observed in the laboratory performance study are shown in **Table III.** A more extensive examination of surrogate standard recoveries is shown in **Table V.**

Surrogate standard recoveries in laboratory testing were good in comparison with the reference extraction and typical for these analytes in extractions with the GLSE-70 and GLSE- 95 (4,15,26,27,30). The somewhat lower recoveries seen with the GLSE/SR compared with the reference extraction may be related to the volatility of the compounds in being stirred in an open system (**Tables III, V**).

Recoveries of CBs, and OCs/PCBs were good in comparison with the reference extraction (**Table III**) and with nominal "spike" levels. PAH recoveries were very good in the reference extraction but the earlier eluting PAHs were less effectively recovered in the GLSE/SR process (44-66%). This apparent "recovery" may be due to a kinetic situation in PAH extraction (the contact time for the reference extraction (3 h) far exceeded that of the GLSE/SR (≈ 4 min)) or to an analytical artefact (calibration, "spike" preparation). The PAH and phthalate determination procedures were, in fact, experimental at the time of this work. Difficulties in solvent extraction and solid-phase extraction of PAHs are currently being reported (33).

Phthalate, chlorophenol and neutral herbicide recoveries were not assessed as they were not determined in the reference extraction and no comparative recovery data is available. As these determinations were in an experimental stage at the time of this work, recovery data is merely presented in **Table III** along with the nominal "spike" level and no comment is made regarding recoveries. These data, again, may be the result of analytical artefacts and not reflect extraction behaviour. Normally, the phthalates and chlorophenols would be extracted from acidified solutions.

The recoveries obtained in this work refer to neutral extractions in which the dissociation of some of these compounds would influence recovery greatly.

Field Testing

In a paired comparison (**Table IV**), no significant difference was determined in surrogate standards recoveries (extraction standards) by the two extractions techniques (GLSE-70 "standard" apparatus, GLSE/SR). Endrin ketone, one of the analytical process standards, did appear to be more effectively recovered from GLSE/SR extracts and this may relate to the tendency of this apparatus to reduce formation of stable "emulsions" which may have an effect in subsequent analytical processing ("cleanup", fractionation).

Generally, no significant difference was seen in recovery of chlorobenzenes by the two techniques. 1,2- dichlorobenzene appears to be less effectively recovered by the GLSE/SR. This may result from incorporation of the solvent recovery feature and the volatility of the analyte.

For most OCs determined, no significant difference was seen between recoveries by the two processes. Those analyte recoveries which appeared marginally higher were generally seen in the GLSE/SR extractions. This may be related to the avoidance of stable "emulsion" formation discussed above.

The high PCB values seen in two samples from GLSE/SR processing are not unusual in PCB determination in the Niagara River matrix (32) and as no explanation is available, these values were statistically rejected from calculations.

PAHs, phthalates and neutral herbicides generally showed no significant differences in recoveries with the two extraction processes. It is noted here that these compounds are normally extracted under acidic conditions and that the data included in this report were obtained from extractions at near neutral ambient pH. They are reported for interest only.

TECHNOLOGY TRANSFER

The results of the limited laboratory and field testing of the GLSE/SR prototype were considered to be sufficient to warrant further field testing before replacement of the "standard" GLSE/70 units at the two WQB/OR Niagara River monitoring stations. Three replicas of the prototype apparatus have been manufactured for the WQB/OR for this purpose; one unit being loaned to the New York State Department of Environmental Conservation (NYSDEC) through Mann Testing Laboratories (under contract with the WQB/OR) for monitoring in Buffalo Creek, a tributary of the Niagara River. Two replicas of the GLSE/SR have been deployed in the joint (Environment Canada, Environment Ontario, NYSDEC and the U.S. EPA) Niagara River Monitoring program. The WQB/OR has since conducted an extensive field study comparing performance of the "standard" GLSE/70 and the GLSE/SR in Niagara River monitoring (34).

CONCLUSIONS

The GLSE/SR is better than 99% effective in removing dissolved dichloromethane from extraction effluent and 60-70% effective in analytical recovery of dissolved solvent from the extraction process. This solvent recovery process, however, is ineffective at sample input rates substantially higher than that used in 24 h extractions in the Niagara River monitoring program (≈ 35 mL/min). The GLSE/SR, with some accessory equipment, could be used to perform the 7-day time-integrated sampling demonstrated with the GLSE/WEEK prototype. "Scale-up" of the GLSE/SR to process samples at higher sample input rates required in surveillance activities (500-1000 mL/min) is not feasible and alternative solvent recovery techniques are being investigated.

The analytical solvent recovery process used in the GLSE/SR does not appear to introduce "new" compounds (GC/ECD) to the extraction process as a result of the reaction conditions provided in the solvent recovery process.

In terms of recovery of analytes, laboratory and field testing of the GLSE/SR prototype show recoveries of CBs and OC/PCBs to be statistically indistinguishable from the GLSE-70 prototype which has been used in the Niagara River monitoring program since 1986.

Laboratory studies suggest that investigation is due in processing (extraction and subsequent analytical processing) of PAHs, phthalates, phenolic compounds and neutral herbicides. These compounds were not included in original performance testing of the "standard" GLSE (GLSE/70), which was restricted to surrogate standards, CBs and OC/PCBs. Comparative data is therefore not available.

The GLSE\SR has the potential to be "automated", as was the more complex GLSE/WEEK, to provide a 7-day time-integrated extract with improved detection limits ($\simeq$ x 7).

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Figure 1. GLSE/Week Components Arrangement

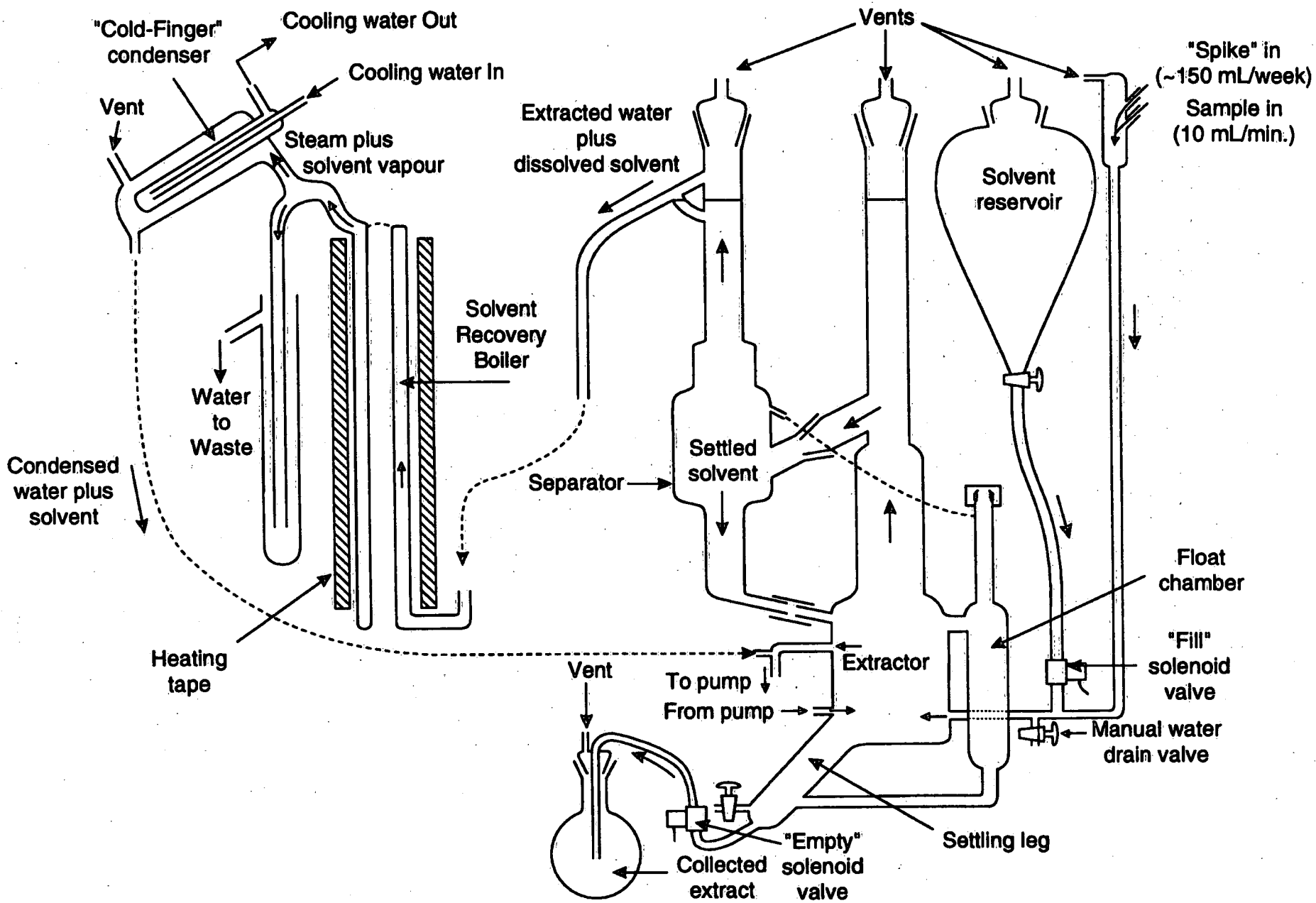


FIGURE 2

G.L.S.E./SR: MAJOR COMPONENTS

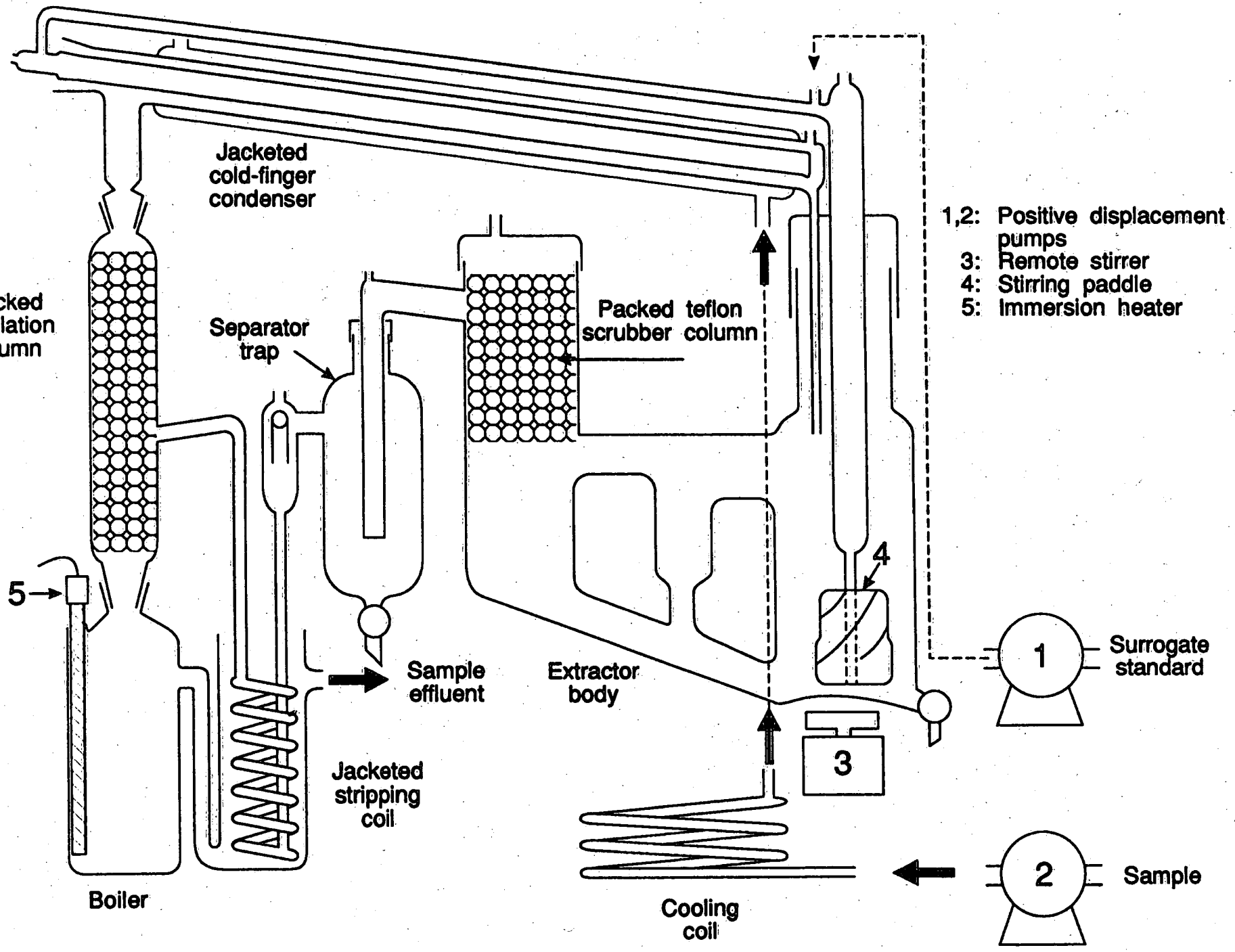


Figure 3. Sample Cooling Arrangement for Laboratory Study

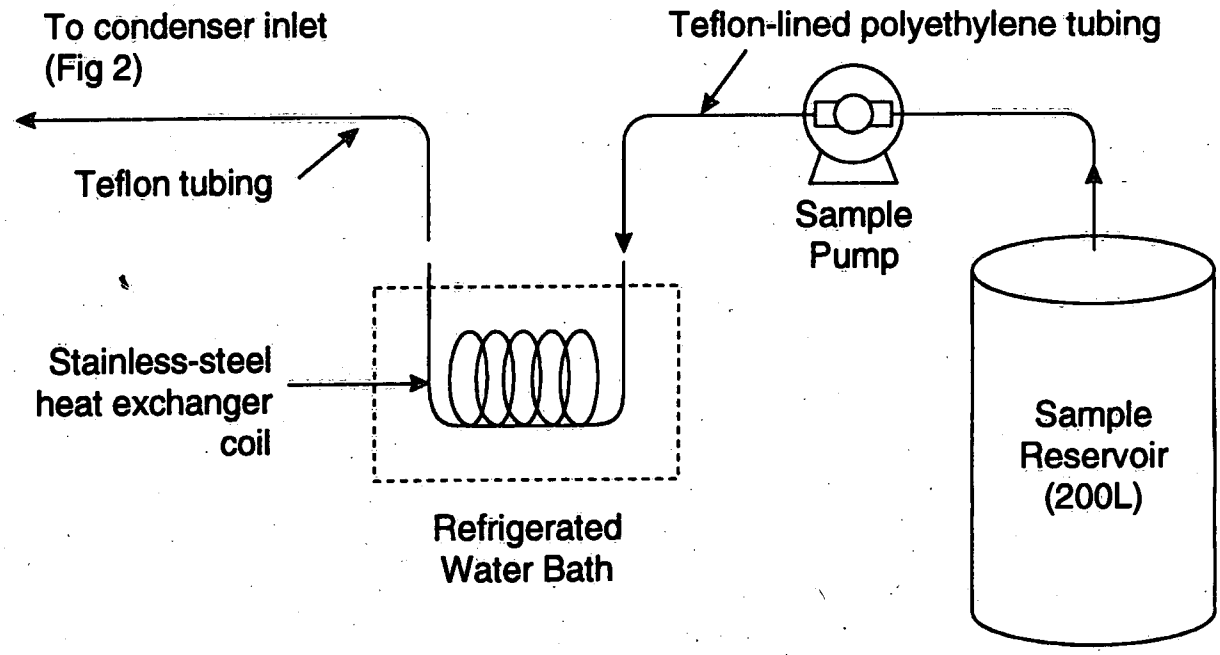


Figure 4. Measurement of DCM in GLSE/SR Extraction Effluent

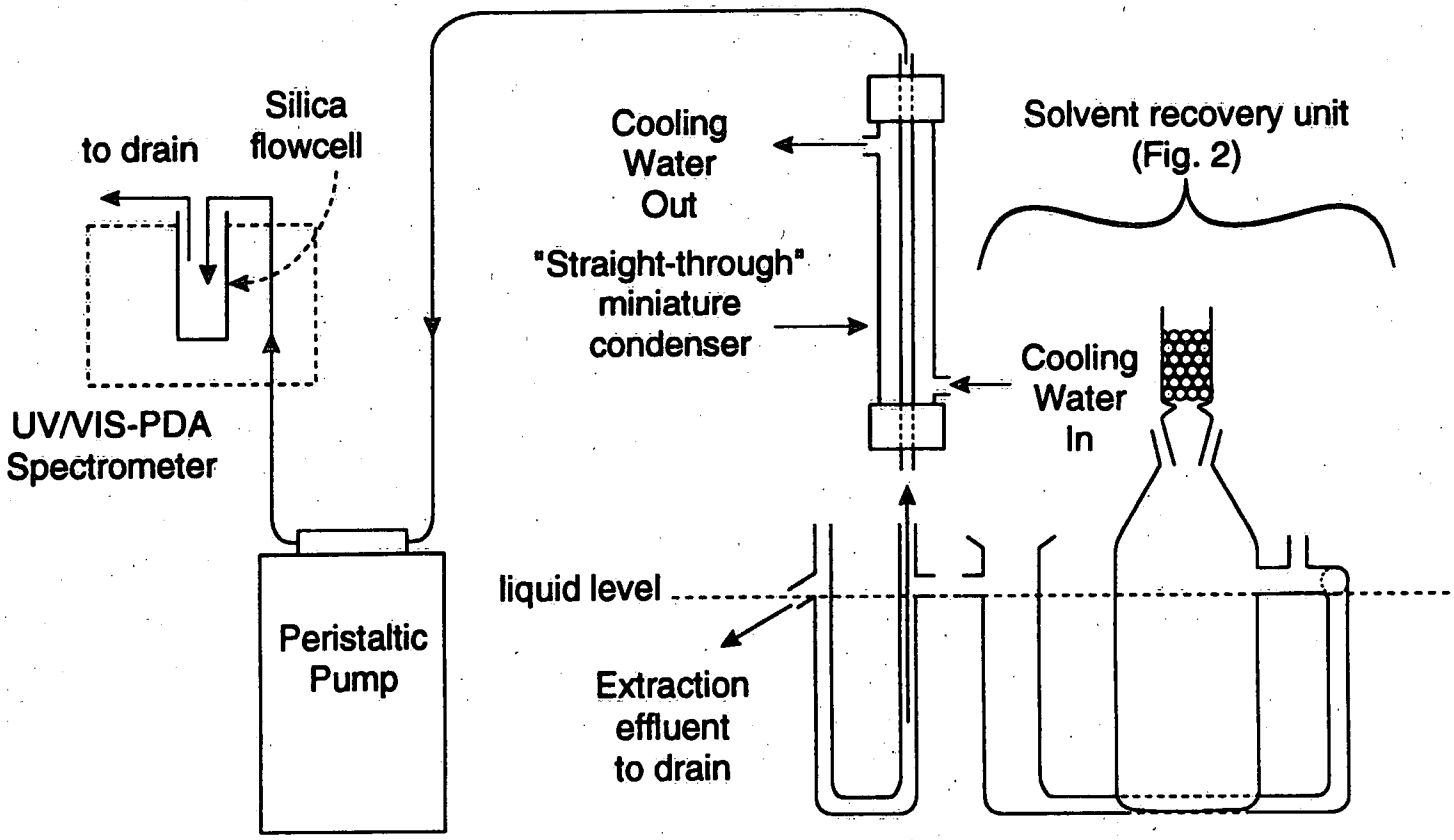


TABLE I : Surrogate Standards Recoveries (Extraction) in Field Study of GLSE/WEEK (%)

Compound	Week							
	1	2	3	4	5	6	7	Mean (+/- sd)
1,3-dibromobenzene	87.3	73.0	85.2	74.5	84.8	91.9	95.4	84.6 (8.3)
1,3,5-tribromobenzene	118	83.1	95.3	93.1	93.4	105	104	98.8 (11.2)
1,2,4,5-tetrabromobenzene	127	95.5	106	92.3	97.3	112	119	107 (13.0)
2,3,5,6-tetrachlorobiphenyl	104	87.9	104	76.9	98.4	105	112	98.3 (12.0)

TABLE II: Comparison of Niagara River Contaninant Levels Results as Determined using the GLSE/70 (24-HR sampler, 50 L sample) and the GLSE/WEEK (weekly sampler, 100 L sample). (ng/100L, n=7).

Compound (sampler)	Week								
	1	2	3	4	5	6	7	Mean (+/- sd)	
Hexachlorobenzene (GLSE/70)	14	9	12	15	13	12	23	14 (4)	
(GLSE/WEEK)	3.3	2.4	2.9	1.7	2.5	1.9	4.3	2.7 (0.9)	
a-BHC	176	238	200	236	315	242	258	238 (44)	
	305	234	213	206	216	74	201	207 (69)	
Lindane	59	75	58	64	60	63	71	64 (6)	
	78	59	53	48	53	27	47	52 (15)	
Heptachlorepoxide	12	11	13	13	14	16	13	13 (2)	
	4.5	6.1	5.1	4.1	6.2	5.9	8.5	5.8 (1.5)	
g-chlordane	nd	nd	4	nd	nd	nd	nd	nd (-)	n=1
	1.7	1.9	2.0	1.3	2.0	1.9	3.0	2.0 (0.5)	
p,p'-DDE	6	3	2	nd	3	3	5	3 (2)	n=6
	3.5	1.5	1.9	1.0	1.6	2.3	3.3	2.2 (0.9)	
Dieldrin	nd	29	35	29	38	43	38	35 (6)	n=6
	32	36	31	23	30	26	33	30 (4)	
Endrin	13	6	10	nd	9	8	5	8.5 (2.9)	n=6
	3.1	3.8	3.0	2.5	5.1	5.8	6.2	4.2 (1.5)	

n : number of determinations
sd : standard deviation
nd : not detected

TABLE III : Reference and GLSE/SR Extraction Recoveries in Laboratory Testing

Compound	Nominal spike amount (ng)	Reference Extraction Recovery (ng +/- s) (n=5)		Recovery (% +/- CV)		Recovery GLSE/SR (ng +/- s) (n=5)		Recovery (% +/- CV)	
Surrogate standards									
1,3,5-tribromobenzene	80			89	16			71	5
1,2,4,5-tetrabromobenzene	80			96	11			117	6
d-BHC	40			106	12			125	12
Chlorobenzenes (CBs)									
1,3-dichlorobenzene	200	132	12	66	9	137	11	69	8
1,4-dichlorobenzene	200	173	26	87	15	167	15	83	9
1,2-dichlorobenzene	200	144	12	72	8	146	10	73	7
1,3,5-trichlorobenzene	20	18.8	2.1	94	11	16.5	0.9	83	5
1,2,4-trichlorobenzene	20	19.9	0.8	100	4	19.4	1.5	97	6
1,2,3-trichlorobenzene	20	19.6	0.6	98	3	19.2	1.1	96	6
1,2,3,4-tetrachlorobenzene	20	22.0	3.5	110	16	20.7	1.2	104	6
Pentachlorobenzene	20	23.5	3.6	118	15	23.7	1.1	119	5
Organochlorine Pesticides and Industrial Materials (OCs/ PCBs)									
Hexachlorobenzene	20	23.7	3.0	119	13	25.2	1.2	126	5
a-BHC	20	22.4	1.0	112	5	21.5	1.7	108	8
g-BHC	20	23.4	0.5	117	2	24.2	1.9	121	7
Heptachlor	20	23.1	1.6	116	7	not determined			
Aldrin	20	20.7	1.9	104	9	not determined			

TABLE III (continued)

Heptachlor epoxide	20	19.5	1.5	98	8	24.0	1.7	120	7
q-chlordane	20	21.5	1.7	108	8	25.4	2.4	127	10
a-endosulphan	20	25.5	2.6	128	10	not determined			
a-chlordane	20	21.0	2.6	105	12	22.0	1.7	110	8
p,p'-DDE	40	48.9	11.5	122	24	33.7	3.1	84	9
Dieldrin	40	41.7	2.4	104	6	24.2	5.7	61	24
Endrin	40	39.6	2.3	99	6	41.1	4.5	103	11
o,p'-DDT	60	67.2	13.9	112	21	44.1	2.5	74	6
p,p'-TDE	60	62.5	11.0	104	18	58.5	7.0	98	12
p,p'-DDT	60	62.9	11.3	105	18	51.5	5.0	86	10
b-endosulphan	40	39.4	3,2	99	8				
Endrin aldehyde	not determined								
Photomirex	not determined								
Mirex	40	40.8	5.1	102	13	37.9	2.3	95	6
Methoxychlor	200	213	18	107	9	146.7	19.0	73	13
Hexachlorobutadiene	20	18.9	2.6	95	14	18.8	1.1	94	6
Hexachlorocyclopentadiene	not determined								
PCB (total)	800	733	62	92	9	761	71	95	9
Polynuclear Aromatic Hydrocarbons (PAHs)									
Naphthalene	1000	not determined				514	8 (4)	51	2
2-methylnaphthalene	2000	1735	239	87	14	1078	49 (4)	54	5
1 methylnaphthalene	2000	1721	245	86	14	992	57 (4)	50	6
2-chloronaphthalene	4000	3582	516	90	14	2647	33 (4)	66	13

TABLE III (continued)

Acenaphthylene	1000	894	140	89	16	538	69	54	13
Fluorene	2000	2096	349	105	17	1282	193	64	15
Anthracene	1000		not determined			467	26	47	6
Phenanthrene	1000	866	158	87	18	440	49	44	11
Fluoranthene	1000	1005	234	101	23	636	48	64	8
Pyrene	1000	935	213	94	23	655	39	66	6
Benzo(a)anthracene	1000		not determined			708	79	71	11
Chrysene	1000		not determined			777	151	78	20
Benzo(b)fluoranthene	1000	837	32 (3)	84	4	892	84	89	10
Benzo(k)fluoranthene	1000	865	40 (3)	87	5	1066	136	107	13
Benzo(a)pyrene	1000	847	29 (3)	85	3	941	98	94	10
Indenopyrene	1000	1023	84 (3)	102	8	987	133	98	14
Dibenzo(ah)anthracene	2000		not determined			1786	213	89	12
Benzo(ghi)perylene	1000	906	122 (3)	91	14	916	150	92	16
<u>Phthalates</u>									
Dimethylphthalate	2000		not determined			853	58		
Diethylphthalate	2000		"			1168	155		
Di-n-butylphthalate	1000		"			4668	919		
Benzylbutylphthalate	2000		"			1473	252		
Bis(2-ethylhexyl)phthalate	1000		"			18074	6141		
Dioctylphthalate	1000		"			1004	406		

TABLE III (continued)

Chlorophenols				
Phenol	4000	"	not determined	
2,4-dichlorophenol	4000	"	1485	221
2,3-dichlorophenol	6000	"	1680	249
2,6-dichlorophenol	4000	not determined	1562	338
3-methyl,4-chlorophenol	5000	"	804	148
2,3,5-trichlorophenol	6000	"	3342	172
2,4,6-trichlorophenol	6000	"	3286	147
2,4,5-trichlorophenol	6000	"	3152	447
2,3,4-trichlorophenol	6000	"	2663	390
3,5-dichlorophenol	4000	"	643	129
2,3,6-trichlorophenol	4000	"	2613	361
3,4-dichlorophenol	5000	"	613	98
3,4,5-trichlorophenol	6000	"	1709	280
Pentachlorophenol	10000	"	16897	3016
Neutral Herbicides				
Atrazine	4000	"	2114	146
Metolachlor	2000	"	1120	61

s : standard deviation
CV: coefficient of variation

TABLE IV: ABBREVIATIONS USED IN TABLE

n number of paired observations.

x mean difference between paired observations of row [2] and row [1] ([2] -[1]).

s standard deviation of mean difference.

SE standard error of mean difference.

T t-test value

P p-value

* : low surrogate standard recoveries (see text)

** : value rejected due to low surrogate standard recovery (see text)

++ : value rejected (non-parametric test). Excursions of this magnitude are not unusual in PCB determinations (32) but no explanation has been provided. These values were therefore rejected statistically. .(see text)

nd : not detected / not determined

TABLE IV : Paired Comparison of Niagara River Contaminant Data (ng / mL). (Surrogate Standards recoveries in %)

For each analyte, data in row [1] was obtained with the "standard" GLSE unit (GLSE-70) and data in row [2] was obtained with the prototype under study (GLSE/SR) having analytical solvent recovery capability.

Sample		1	2	3	4	5	6	n	x	s	SE	T	P
Surrogate Standards Recoveries (%)													
Extraction Standards													
1,3,5-tribromobenzene	[1]	88.16	72.87	94.85	89.59	74.14	33.22*	5	0.988	10.37	4.639	0.21	0.8
	[2]	84.39	81.32	80.55	92.44	85.85	96.83						
1,2,4,5-tetrabromobenzene		113.69	105.04	108.08	102.60	93.81	46.41*	5	1.830	6.79	3.038	0.60	0.5
		114.18	111.51	98.68	107.03	100.97	112.05						
d-BHC		104.91	107.72	98.14	125.97	107.59	92.55	6	4.140	27.08	11.057	0.37	0.7
		119.19	123.06	95.37	85.35	109.38	131.35						
Analytical Process Standards													
1,3-dibromobenzene		86.09	78.25	81.83	82.54	77.85	69.35	6	3.420	12.65	5.163	-0.66	0.5
		74.25	70.56	64.13	81.92	76.35	88.18						
2,3,5,6-tetrachlorobiphenyl		124.77	116.43	118.20	108.44	94.35	82.86	6	5.892	17.02	6.947	0.85	0.
		110.88	109.41	120.94	117.12	104.01	118.04						
Endrin Ketone		80.15	88.09	81.63	84.08	74.14	93.92	6	4.675	7.38	3.011	1.15	0.
		92.56	95.03	89.50	92.89	73.99	86.09						

continued ...

TABLE IV (continued)

Sample		1	2	3	4	5	6	n	x	s	SE	T	P
Analytes													
Chlorobenzenes (CBs)													
1,3-dichlorobenzene	[1]	13.75	20.72	35.37	30.99	11.05	9.56**	5	-0.530	4.599	2.057	-0.26	0.81
	[2]	13.15	19.11	28.47	31.52	16.98	17.57						
1,4-dichlorobenzene		67.68	83.10	155.14	189.72	55.53	46.94**	5	-6.476	19.073	8.530	-0.76	0.49
		62.41	79.59	129.34	168.95	78.50	81.82						
1,2-dichlorobenzene		35.59	46.62	79.56	127.02	31.65	28.16**	5	-6.200	7.008	3.134	-1.98	0.12
		33.64	45.23	65.30	113.62	44.45	47.73						
1,3,5-trichlorobenzene		1.58	1.91	3.12	2.74	0.85	0.81**	5	-0.024	0.443	0.198	-0.12	0.91
		1.45	1.76	2.53	2.87	1.47	1.50						
1,2,4-trichlorobenzene		35.21	39.16	135.08	144.31	31.92	26.26**	5	-3.878	13.759	6.153	-0.63	0.56
		29.09	37.17	116.03	134.09	49.91	45.88						
1,2,3-trichlorobenzene		11.53	11.78	40.50	49.78	9.95	5.73**	5	-1.194	4.167	1.865	-0.64	0.56
		9.44	11.03	35.52	45.95	15.63	14.33						
1,2,3,4-tetrachlorobenzene		8.10	9.19	121.30	78.95	9.95	6.07**	5	-2.398	8.361	3.739	-0.64	0.56
		6.99	14.49	106.57	72.70	14.75	12.38						
Pentachlorobenzene		2.11	2.85	22.71	11.40	1.79	1.41**	5	-0.336	1.154	0.516	-0.65	0.55
		2.13	2.67	20.38	11.58	2.42	2.38						
Hexachlorobenzene		1.44	1.77	3.91	2.39	1.11	0.94**	5	-0.024	0.229	0.102	-0.23	0.83
		1.30	1.68	3.60	2.60	1.32	1.34						

continued...

TABLE IV : (continued)

Sample		1	2	3	4	5	6	n	x	s	SE	T	
Organochlorine Pesticides and Industrial Materials (OCs/PCBs)													
a-BHC	[1]	32.96	39.35	40.13	36.58	30.29	35.45	6	3.613	4.413	1.802	2.01	0.
	[2]	43.16	37.17	45.90	42.09	31.02	37.10						
g-BHC		11.57	13.69	13.50	12.87	10.85	13.24	6	1.123	1.287	0.525	2.14	0.
		14.69	13.34	15.15	14.63	11.03	13.62						
Heptachlor		nd	nd	nd	nd	nd	nd						
Aldrin		nd	nd	nd	nd	nd	nd						
Heptachlor epoxide		2.46	2.95	1.99	2.76	2.65	3.15	6	0.280	0.564	0.230	1.22	0.
		2.81	2.77	3.19	3.40	2.52	2.95						
g-Chlordane		nd	nd	nd	nd	nd	nd						
a-Endosulphan		nd	0.89	1.08	0.89	0.98	0.86	4	0.047	0.108	0.054	0.88	0
		nd	0.84	1.20	1.05	nd	0.82						
a-Chlordane		nd	nd	nd	nd	nd	nd						
p,p'-DDE		nd	1.13	2.19	1.75	0.63	0.70	4	0.048	0.119	0.059	0.80	0
		0.79	nd	2.15	1.73	0.66	0.92						
Dieldrin		5.40	6.65	6.68	6.13	6.41	7.13	6	0.130	0.765	0.312	0.42	0
		6.21	6.27	7.30	7.12	5.59	6.69						
Endrin		nd	nd	nd	nd	nd	nd						
o,p'-DDT		nd	nd	nd	nd	nd	nd						
p,p'-TDE		1.84	2.20	2.30	2.02	1.97	2.51	6	-0.025	0.286	0.117	-0.21	0
		1.98	1.87	2.54	2.29	1.88	2.13						
p,p'-DDT		nd	nd	nd	1.39	nd	nd						
		nd	nd	1.56	1.54	nd	nd						

continued ...

TABLE IV : (continued) OCs/PCBs

Sample		1	2	3	4	5	6	n	x	s	SE	T	P
b-endosulphan	[1]	0.65	0.80	1.22	nd	nd	0.84	3	-0.067	0.087	0.050	-1.32	0.32
	[2]	nd	0.66	1.25	0.92	nd	0.75						
Endrin aldehyde		nd	nd	nd	nd	nd	nd						
Photonirex		nd	nd	nd	nd	nd	nd						
Mirex		nd	nd	nd	nd	nd	nd						
		0.66	0.61	0.44	nd	nd	nd						
Methoxychlor		nd	5.57	2.08	nd	nd	nd	2	0.840	1.061	0.750	1.12	0.46
		nd	7.16	2.17	1.94	nd	nd						
Hexachlorobutadiene		1.86	2.34	5.27	3.53	1.35	1.09	6	0.080	0.696	0.284	0.28	0.79
		1.68	2.16	4.28	3.76	1.95	2.09						
Hexachlorocyclopentadiene		nd	nd	4.30	1.36	0.51	nd	3	-0.263	0.728	0.421	-0.63	0.60
		nd	nd	3.20	1.44	0.74	nd						
PCB (total)	(i)	16.97	19.69	26.59	19.94	15.17	15.02	6	9.560	10.070	4.111	2.33	0.06
		18.27	45.12++	44.76++	25.05	22.29	15.25						
	(ii)							4	3.440	3.226	1.613	2.13	0.12
2,3,7,8-TCDD		nd	nd	nd	nd	nd	nd						

continued...

TABLE IV : (continued)

Sample		1	2	3	4	5	6	n	x	s	SE	T	P
Polynuclear Aromatic Hydrocarbons (PAHs)													
Naphthalene	[1]	41.46	65.89	42.67	10.85	17.70	17.82	6	7.685	13.520	5.520	1.39	0.2
	[2]	31.46	82.97	66.21	28.54	18.49	14.83						
2-Methylnaphthalene		15.10	41.77	32.76	19.57	7.00	12.10	6	5.873	7.058	2.281	2.04	0.(
		17.85	45.90	46.45	34.43	10.31	8.60						
1-Methylnaphthalene		13.51	27.30	20.81	17.47	15.55	10.21	6	3.423	3.701	1.511	2.27	0.(
		13.37	31.89	28.44	24.38	14.03	13.28						
2-Chloronaphthalene		nd	nd	nd	nd	nd	nd						
Acenaphthylene		nd	11.12	13.72	11.13	8.71	6.04	4	1.217	1.922	0.961	1.27	0.2
		5.70	15.10	14.72	11.36	8.37	nd						
Fluorene		12.66	21.12	26.47	21.42	9.04	10.21	6	2.320	7.098	2.898	0.80	0.
		10.00	36.74	23.06	23.73	12.72	8.59						
Anthracene		nd	nd	nd	nd	nd	nd						
Phenanthrene		49.45	77.63	101.52	104.84	36.52	35.62	6	-0.042	7.091	2.895	-2.78	0.(
		36.27	70.91	96.40	85.25	35.96	32.64						
Fluoranthene		nd	77.54	48.81	60.06	14.77	15.28	5	4.896	10.296	4.886	1.00	0.
		nd	101.75	47.11	59.61	14.36	18.21						
Pyrene		16.76	39.95	30.99	31.88	6.63	7.99	6	5.502	8.840	3.609	1.52	0.
		19.00	63.43	31.96	33.87	9.72	9.23						
Benzo(a)anthracene		nd	13.30	19.44	17.28	nd	1.21	2	-1.755	0.615	0.435	-4.03	0.
		8.13	nd	18.12	15.09	5.10	nd						
Chrysene		11.39	20.38	17.56	17.25	7.49	3.25	5	1.416	3.088	1.381	1.03	0.
		9.53	nd	21.03	21.61	5.45	7.40						
Benzo(b)fluorene		7.49	10.65	21.33	24.89	8.04	10.45	6	4.688	5.951	2.429	1.93	0.
		7.23	24.15	32.06	28.22	8.64	10.68						

continued...

TABLE IV : (continued)

Sample		1	2	3	4	5	6	n	x	s	SE	T	P
PAHs (continued)													
Benzo(k)fluorene	[1]	6.97	10.65	21.33	24.89	8.04	9.90	6	0.938	2.995	1.223	0.77	0.48
	[2]	5.88	14.80	17.44	28.22	8.64	12.88						
Benzo(a)pyrene		nd	6.34	12.83	19.21	4.03	5.42	4	1.073	1.208	0.604	1.78	0.17
		nd	5.77	14.83	21.17	4.93	nd						
Indenopyrene		nd	3.84	nd	7.84	nd	nd	2	3.210	5.643	3.990	0.80	0.57
		3.95	11.04	nd	7.06	nd	nd						
Dibenzo(ah)anthracene		nd	nd	nd	nd	nd	nd						
		nd	8.11	nd	nd	nd	nd						
Benzo(ghi)perylene		nd	6.12	nd	5.93	nd	nd	2	3.890	0.608	0.430	9.05	0.07
		4.53	10.44	nd	9.39	nd	nd						

continued...

TABLE IV : (continued)

Sample		1	2	3	4	5	6	n	x	s	SE	T	P
Phthalates													
Dimethylphthalate	[1]	29.94	24.24	25.83	20.11	16.38	23.92	6	-1.132	5.899	2.408	-0.47	0.6
	[2]	24.61	30.96	22.02	21.03	20.01	15.00						
Diethylphthalate		277.90	202.78	175.50	126.18	102.91	119.19	6	-42.953	66.290	27.063	-1.59	0.1
		122.73	254.19	131.00	88.68	77.13	72.31						
Di-n-butylphthalate		195.89	144.70	106.51	556.92	185.14	348.22	6	-16.940	309.576	126.384	-0.13	0.9
		218.15	636.63	169.25	117.25	144.74	149.62						
Benzylbutylphthalate		84.47	96.87	87.00	80.38	34.68	54.83	6	15.987	39.501	16.126	0.99	0.3
		98.44	188.05	105.36	59.13	34.45	48.72						
Bis(2-ethylhexyl)phthalate		6167.72	9189.09	1148.76	279.84	319.06	307.49	5	35,352	75,570	33,796	1.05	0.3
		2438.21	179,439	10826.16	nd	793.47	390.40						
Dioctylphthalate		28.28	83.68	20.84	22.17	10.21	15.30	6	24.995	34.859	14.231	1.76	0.1
		116.88	100.99	61.29	21.46	16.25	13.62						
Neutral Herbicides													
Atrazine		1525.44	1646.99	1103.28	1045.63	849.67	807.99	6	-37.960	131.232	58.869	-0.65	0.5
		1404.27	nd	1255.79	866.34	778.10	837.71						
Metolachlor		627.08	537.67	302.72	207.82	144.19	173.36	6	37.59	116.572	47.590	0.80	0.
		675.48	801.97	263.88	158.93	160.73	159.29						

TABLE V : Surrogate Standards Recoveries (%), Laboratory and Field Testing

Laboratory testing

Compound	Sample Number							mean	s	cv(%)	% recovery
	1	2	3	4	5	6	7				
1,3,5-tribromobenzene	29.8	31.7	33.5	28.7	31.1	31.6	32.7	31.30	1.64	5.24	68.04
1,2,4,5-tetrabromobenzene	49.7	53.4	57.3	47.6	51.9	53.2	49.6	51.81	3.21	6.20	84.64
-BHC	21.8	28.0	25.4	28.5	27.3	30.5	31.9	27.63	3.33	12.05	96.85

Field Testing

Compound	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5		Sample 6	
	GLSE	GLSE/SR	GLSE	GLSE/SR	GLSE	GLSE/SR	GLSE	GLSE/SR	GLSE	GLSE/SR	GLSE	GLSE/SR
1,3,5-tribromobenzene	88.16	84.39	72.87	81.32	94.85	80.55	89.59	92.44	74.14	85.85	-	96.83
1,2,4,5-tetrabromobenzene	113.69	114.18	105.04	111.51	108.08	98.68	102.60	107.03	93.81	100.97	-	112.05
-BHC	104.91	119.19	107.72	123.06	98.14	95.37	125.97	85.35	107.59	109.38	-	131.35

Paired t-test (2-tailed), Field Testing

Compound	Mean (n=5) GLSE	s	Mean (n=5) GLSE/SR	s	Calculated t (95% level of significance)	P value
1,3,5-tribromobenzene	83.92	9.84	84.91	4.74	0.21	0.84
1,2,4,5-tetrabromobenzene	104.64	7.34	106.47	6.64	0.60	0.58
-BHC	106.15	11.38	110.62	17.50	0.41	0.70

APPENDIX

OPERATIONAL PROCEDURE FOR THE GLSE/SR

General

This procedure applies to operation of the original GLSE/WEEK prototype using the accessory equipment described in **Performance Studies** (below). In this procedure, a 50 L sample is processed over a period of 24 h. Operational settings for the electromechanical components of the system are given in Table III. Operation of the sample collection system (pumping and clarification of water from the river) is discussed elsewhere (23,29).

As with all GLSE equipment used on a frequent basis, it is recommended that the extractor be stored "wet", filled with ultrapure, "organics-free" water (quality should be determined, not assumed), during the periods it is not in use (16).

Procedure

- The refrigerated water bath and the boiler heater (the boiler must have water in it; normally it is full or nearly full of "polished" water from the previous extraction)

are turned on. Approximately 15 to 20 min will be required for the coolant to reach ≈ 6°C. and the water in the boiler to boil.

- While the above equilibration process is taking place, the extractor is drained of storage water (this will remove some surface-bound extraneous organic material which has solubilized in the water during storage), and an initial "charge" of 500 mL of DCM is added to the extractor through the packed Teflon scrubber column.

- A container of fresh surrogate standards solution is inserted at the standards pickup line inlet.

- The sample pump is started and pumping is continued until the condenser is full of sample and sample is entering the extractor. The sample pump is stopped and the extractor is refilled with "organic free" water. The sample pump, surrogate standards pump and the stirrer are turned on. This represents the beginning of the extraction (0 h) and the time of this event is recorded for estimation of the sample volume extracted.

[During the first ~30 min of operation, the solvent recovery unit will be of limited effectiveness as system temperatures stabilize. Additionally, there may be some overflow of extracted sample during this time at the separator trap overflows as liquid in the gas stripper comes to the required temperature and DCM vapour begins to be purged from

the liquid. This "running in" period represents ≈ 2% of the total processing time. DCM loss during this period likely is < 1% of the potential solubility loss and is not considered significant.]

- After 30 min, system temperatures should have stabilized. This state is visualized by a vigorous evolution of gaseous DCM in the gas stripping coil and the flow of condensed DCM from the condenser to the mixing chamber. At this point, the extraction may be left unattended for the 24 h processing cycle.

[Once some experience is had with the system in a routine operation, the system may be left unattended as soon as the sample pump, surrogate standards pump, and stirrer have been turned on.]

- At ≈ 23.5 h, the surrogate standards solution should have been consumed. The container is rinsed with a few mL of methanol and this is pumped through the delivery system to rinse the pumphead and delivery lines.

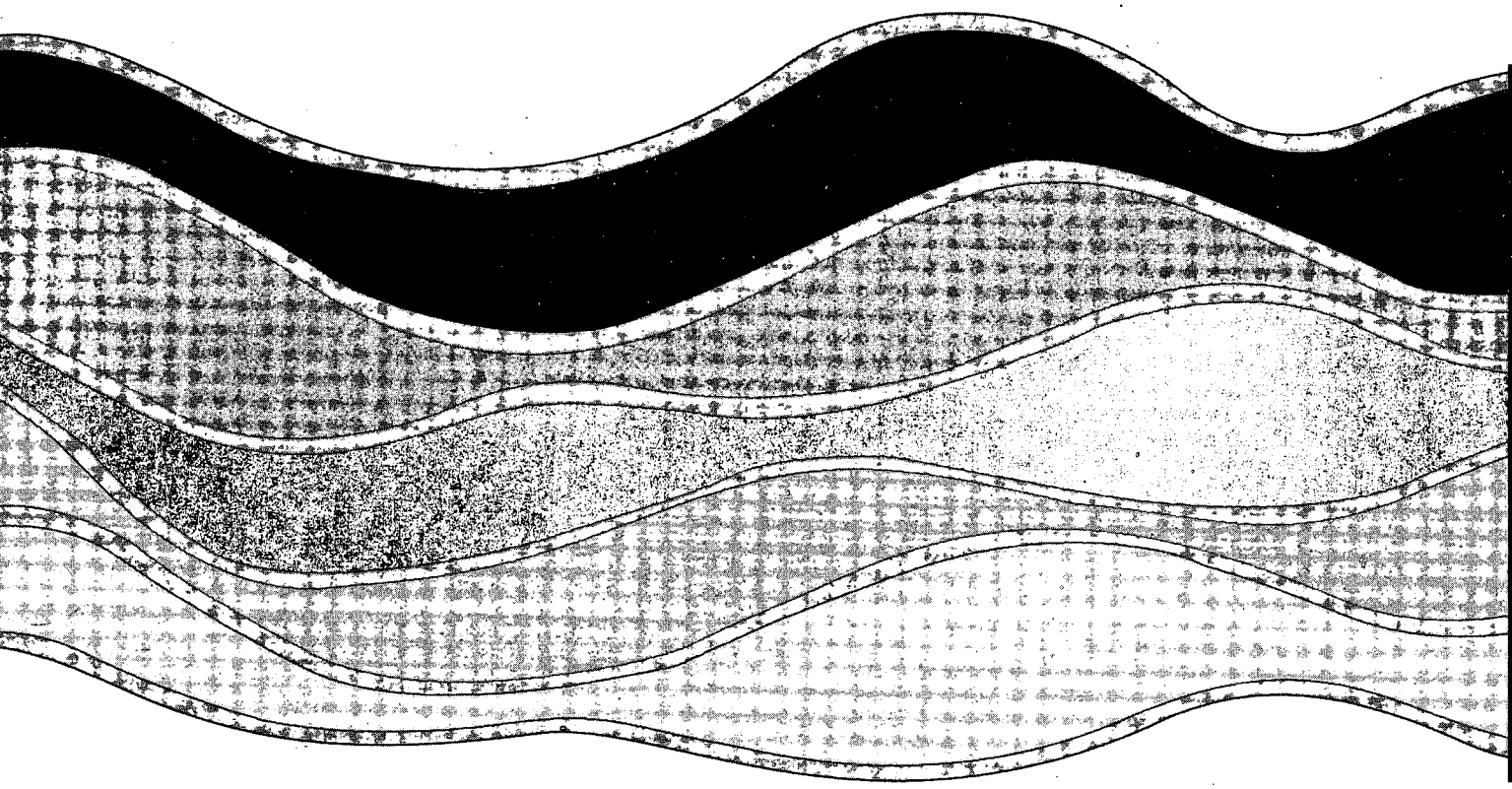
- At 24.0 h the entire extraction system is shut down (sample pump, surrogate standards pump, boiler heater, stirrer, and water bath are turned off) and the phases allowed to separate and clear. If there have been no unusual problems during the unattended period, there should be ≈ 300 mL of DCM remaining in the mixing chamber.

[≈ 200 mL of DCM are lost during the 24 h processing period. The bulk of this loss is due to evaporation with some possible loss due to decomposition in the presence of water at elevated temperatures (10)].

- The extract is collected as per the procedure suggested for most GLSE prototypes (17,30,35,36).

- The apparatus is filled with "organics free" water and left in this state until next use.

[After continued use, the boiler and the portion of the packed column below the gas stripper inlet to the column will become coated with carbonate scale (if sampling "hard" waters). This may be dissolved by flushing the column and boiler with 5-10% nitric acid. These components should then be well flushed with "organics free" water before the next use.]



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