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A PRELIMINARY CHEMICAL EXAMINATION OF HYDROPHOBIC TIRE LEACHATE COMPONENTS

PART II

ON-SITE, LARGE-SAMPLE PRECONCENTRATION OF TIRE LEACHATE COMPONENTS FOR CHEMICAL CHARACTERIZATION

D.H.J. Anthony and D.W. Barclay

NWRI Technical Report 93-25

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Analytical Chemistry Research Project,
Research and Applications Branch,
National Water Research Institute.

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MANAGEMENT PERSPECTIVE

This document is one of a series describing methodological developments for the identification / characterization of toxic organic contaminants in tire leachate.

This report describes a large-sample extraction procedure used in on-site preconcentration of hydrophobic components from 100 L samples of tire leachate used in assessing the toxicity of the material to fish. The procedure employs a variation of the Goulden Large-Sample Extraction (GLSE) technique as a means of providing sufficient material for development of a comprehensive toxicity-based chemical characterization of toxic, hydrophobic tire leachate components. The work forms one part of a larger study within the Analytical Chemistry Research Project (ACRP) / Research and Applications Branch (RAB) to identify toxic components of tire leachate. Results of this study will be reported separately as work progresses.

ABSTRACT

Large volume samples of water used in studies of tire leachate toxicity to fish were processed on-site, using a variation of the Goulden Large-Sample Extraction (GLSE) technique, to isolate the hydrophobic fraction of leachate components. Samples of extraction effluent (aqueous phase) were retained for HPLC and LC/MS examination of water-soluble components. Non-processed water was collected for microbial toxicity testing.

The large-sample extraction technique was used to provide a sufficient quantity of analyte material for a comprehensive toxicity-based characterization of the toxic component(s) of the leachate samples. As applied, the technique allowed processing of the three test samples in one working day and could process twice this amount in the same time period.

INTRODUCTION

Problems encountered thus far in the identification of toxic tire leachate components have been discussed in Part I and a more comprehensive analytical approach to these problems has been proposed.

This report descibes the technique and preconcentration rationale used in on-site large-sample processing of water used in toxicity studies conducted by B.A.R. Environmental Inc., Guelph, Ontario (1,2), for the preconcentration of hydrophobic compounds in the leachate and identification / characterization of toxic components.

PRECONCENTRATION / ANALYTICAL RATIONALE

Extraction of large volumes of the leachate samples, using the Goulden Large-Sample Extraction (GLSE) technique (3), was applied as the first step in the approach proposed in Part I. The technique provides sufficient preconcentration for detection of hydrophobic contaminants at trace and ultratrace levels, provides sufficient material for characterization by less-sensitive molecular spectrometric techniques (eg. FTIR, UV/VIS) and provides an initial separation of hydrophobic and hydrophilic compounds required for a broad-spectrum analysis using GC and HPLC techniques with a variety of detectors. The processing of large samples by the GLSE technique also provides a sufficient amount of extract for initial experimentation with fractionation techniques appropriate for the matrix and necessary for toxicity-testing of isolated components.

Due to the efficiency of the GLSE technique, the ideal application for the technique is on-site preconcentration as this eliminates difficulties related to cleaning large sample containers and the transport and storage of large samples (4,5,6).

An environmental concern regarding use of dichloromethane (DCM) as an extractant, is the treatment of extraction effluent to remove dissolved DCM before discharge of the effluent to a water system. B.A.R. (2) discharges its aqueous waste to a septic system and in some cases to a holding lagoon. Discharge of extraction effluent, without treatement, to such systems was considered inappropriate. The extraction effluent was collected in pails and returned to the laboratory for treatment using a prototype continuous-flow solvent recovery system.

In the quantitative determination of "target" compounds, use of the surrogate standard technique is mandatory as a QA technique for the "on-line" estimation of extraction efficiency for a particular matrix, analyte and operating conditions (3,4,5). With the unknown identity of the contaminant(s), the technique is essentially meaningless as the surrogate standard(s) must possess chemical characteristics approximating those of the analyte(s). These characteristics are unknown as well. It has been shown that, for uncomplicated aqueous matrices, recovery of hydrophobic compounds (log Kow > 3) by the GLSE

technique is sufficiently quantitative for this application (4,6). As the purpose of this study was to identify, by "fingerprinting" and profile differentiation techniques, rather than to quantitate a "culprit" contaminant, the surrogate standard technique was not applied.

The more hydrophilic compounds in an aqueous matrix can be recovered with greater efficiency by solvent extraction using higher solvent / water (SWR) ratios (3,4,5). In this work, the SWR was increased to its practical limit (≈ 0.5). Aliquots (≈ 20 L) of extraction effluent of each leachate sample were collected for complementary processing in the laboratory (exhaustive extraction techniques (5,7), base/neutral - acid extraction, "salting out" extraction). The on-site extractions were conducted at ambient pH (pH 7.7) (3).

EXPERIMENTAL

(I) Preparation

Containers for extracts and processed aqueous samples

Extracts were contained in 1 L amber soft-glass Boston Round bottles fitted with teflon-lined screw caps and additional aluminum foil liners. The bottles and aluminum liners were cleaned as described in (5) and weighed. Aqueous samples were collected in 4L amber solvent (DCM) reagent bottles which had been used for no other purpose than to contain the original high purity solvent.

GLSE apparatus

The extraction apparatus used was the GLSE-95 (LaSalle Scientific Inc. "package" (8,9,) which is capable of processing non-complex aqueous matrices at an input rate up to 1 L/min (4,5,6). This unit was modified by use of a Fisher "Stedi-speed" stirrer and replacement of the heater tube assembly with an accessory "spiking" inlet. The extractions were carried out at ambient temperature (22°C)). The surrogate standard port of the fitting was plugged to prevent aspiration of air into the extractor inlet. The surrogate standards pump was not used. The extractor was cleaned as described in (5,9). Before transporting to the site, the extractor was further "cleaned" by extracting an "extractor-full" of ultrapure water (Millipore MQ2 system with organics "polishing" cartridge) with three successive 300 mL aliquots of DCM. The final aliquot was saved as an **Extractor Blank** (Table I).

Solvent (DCM)

The solvent used for the extractions was Burdick & Jackson "High Purity" grade (product #300-4) dichloromethane (methylene chloride), Lot # BA209. The purity of this solvent had been previously tested for suitability in ultratrace determinations (4,5) but a portion was reserved as a solvent blank (Table I).

(II) On-site extractions

The extractions were carried out on 21 July, 1992 (Day 25 of tire exposure to the water used in the toxicity test). The site (2) was a well-ventilated "warehouse-type" area containing aquaria for fish toxicity testing, well separated from office and laboratory operations. This site was agreed on by the authors and management and staff of B.A.R. as being appropriate for "open" use of DCM.

Samples for biological toxicity testing

Before extraction of the samples, aliquots were collected for biological toxicity testing ("Battery of Tests", (10,11,)). Four 4L aliquots of each sample were collected by pumping sample from the aquaria using the sample pump of the GLSE fitted with an accessory outlet line. These samples were collected in 4L amber solvent reagent containers.

Extractions

The samples to be extracted were contained in 300 L glass aquaria with ≈150 L remaining after toxicity testing (the tires were leached in the aquaria for the specified period then aliquots were removed for toxicity testing according to standard procedures). The aquaria and the test tires had been precleaned with detergent ("Ivory", liquid) and rinsed to remove extraneous material. The aquaria were covered with transparent "food grade" plastic sheeting for the duration of the leaching period. The samples consisted of a "control" (no tire, aerated well water), water exposed to a used "scrap" tire, and water exposed to a "new" tire (2). The samples were processed in this order.

Before processing the samples, the GLSE was given a final cleaning by stirring with an "extractor-full" of "control" water and 800 mL of DCM for 15 min.

In extraction of the samples, the GLSE was "charged" with an "oversized" volume (≈ 800 mL) of DCM to improve recovery of hydrophilic compounds (4,5). Otherwise, the apparatus was operated according to the general recommendations given in (5,9). The samples were processed at a sample input rate of 1100 ml/min (+/-0.2%) with the solvent compensation pump rate adjusted accordingly. Each sample was processed for 90.0 min., representing a processed sample volume of 99.0 L.

During the first 15 min. of each extraction, 8 L of processed extractor effluent were collected for HPLC investigation of hydrophilic compounds (the dissolved DCM in these samples acting as a preservative against microbial degradation of analyte) (Table I). These samples were collected directly from the separator trap outlet with the "tygon" tubing drain line removed. After collection of each extract, the extractor's scrubber column was rinsed with extracted water to minimize carryover contamination of the subsequent sample. Extracts were placed "on-ice" within an hour of completing the extractions and were refrigerated the following morning (22 July,'92). The extraction effluent samples were also refrigerated at this time. Samples for biological toxicity testing were delivered to F. Yang (RAB) on the same day.

OBSERVATIONS AND RESULTS

The water which had been exposed to the two tires was slightly coloured as compared to the "control" sample; that exposed to the "new" tire, more so, having a definite yellow-green colour. During extraction of these samples, the intensity of colour in the solvent was seen to increase as the extraction proceeded, with the effluent emerging colourless. The "scrap" extract was quite intensely yellow coloured while the "new" extract was very intensely yellow-orange coloured. This colour was becoming so intense that, as a precaution against saturation of the extract, the extraction was stopped at 45.0 min., the extract withdrawn, and a fresh "charge" of DCM added for the remaining half of the extraction. The reader should note that the above observations of colour intensity in the GLSE-95 involve a light path length of ≈95 mm and might not be apparent if viewed through a narrower vessel. The disinct transfer of colour from the aqueous phase to the solvent with these samples indicates that the coloured compound(s) (perhaps a component of the paint used to enhance the appearance of new tires) possess a considerable degree of hydrophobicity. This coloured material may not be implied in the toxicity of the tire leachate since the "scrap" tire (less intensely coloured) leachate had shown greater toxicity to rainbow trout "fry" (2).

As is generally observed in the extraction of any water other than ultrapure (eg., MQ2-processed) water, the two tire leachate samples caused very fine dispersions of DCM in the extraction mix, making a reduction in stirring speed (from setting ≈ 5 to ≈ 4.5 on the Fisher "Stedi-speed" stirrer) necessary to minimize carryover of fine droplets of solvent with the extractor effluent (5,9).

Information regarding the various samples collected for this project is summarized in **Table I.**

EXTRACT TREATMENT

Extract volumes were determined by difference weighing in the event that the extract might be split for subsequent analytical treatment. Normally, in determinations in which the extract is concentrated to a final known volume before splitting, knowledge of the initial extract volume is unecessary (4,5). The extracts, along with the QC samples related to GLSE processing, were transferred to F. Yang (RAB) for further processing (12) and use by the analytical team (Afghan, Scott and Anthony, ACRP / RAB) after the test extracts had been reweighed and a 20.0 mL sample withdrawn from each for UV-VIS / FTIR spectrometric examination (Part III).

The balance of the extracts (Table II) were transferred to separatory funnels and the DCM phase dried through anhydrous sodium sulfate. The dried extracts were then concentrated by evaporation, using methanol as a "keeper", to ≈100 mL., transferred to actinic glass volumetric flasks and made up to 100.00 mL (12). 5.0 mL aliquots were retained in actinic "Minivials" for chromatographic work and the balance retained for spectrometric examination, fractionation and toxicity testing.

Table II. summarizes processing information for the three test samples.

RECOMMENDATIONS

The identity of the "culprit" contaminant(s) being unknown, considerable effort was made in preparation and in the on-site extractions to adhere to procedures appropriate for ultratrace analysis. This was done to accommodate the possibility that the contaminant may be a highly toxic compound expressing its effect at ultratrace levels. The authors advise that similar precautions (eg. ultraclean operations (5,13), use of inert, non-contaminating materials (glass, stainless steel, teflon), careful observations of concentrates during processing (general recommendations in (14)) be taken in the further treatment and analysis of the extracts provided.
It should be noted that, in addition to the highly hydrophobic compounds isolated by the GLSE technique, the procedure used in this application was intentionally modified to include compounds possessing some hydrophilicity (p.6). Additional care must be exercised, therefore, in transferring components to different solvents and in concentrating them in solvents other than DCM, otherwise precipitation of components may occur.

Ideally, in a study of this sort, the toxicity of the extracted water should be tested to ensure that toxic components have been extracted. In this case, the processed effluent is saturated with DCM, a toxic compound. This in itself does not pose a problem as DCM, being very volatile, could be readily purged from the sample by sparging with compressed nitrogen (utra-high purity, UHP). DCM, however, decomposes

in water to form phosgene ($COCl_2$, a highly toxic compound), formic acid and HCl (15). Reagent DCM is preserved with cyclohexene to prevent the formation of phosgene on exposure of the solvent to air. During extraction, however, the cyclohexene is retained in the DCM phase and oxidation of DCM in the aqueous phase (1.3% v/v solubility) can occur. The presence of phosgene in the aqueous sample would seriously affect toxicity tests. The phosgene produced would eventually be hydrolysed to CO and HCl. The kinetics of these two processes (volatilization, decomposition) would have to be considered if "aged" sample were to be tested for toxicity. Immediate purging and re-testing of extracted samples to determine loss of toxicity from the aqueous phase on GLSE processing is recommended.

CONCLUSIONS

The GLSE preconcentration technique, as applied in this work, proved to be very effective in processing sample within a reasonable time period (3x100 L samples plus "set-up" time). At a nominal sampling rate of 1000 L/min, the technique is capable of processing twice the volume (ie. 200 L) of sample tested in this experiment within the period of one working day.

This work demonstrates the ease with which, through large-sample preconcentration, sufficient amounts of analyte can be isolated to allow application of less-sensitive, but chemically informative, structure elucidation techniques (eg, FTIR, UV/VIS, AED), in conjunction with "routine" techniques such as MS, to provide rigorous chemical identification/characterization of unknown organic compounds in aqueous matrices. This approach is readily integrated with toxicity testing to allow identification or characterization of toxic "culprit" compounds in aqueous systems (14,16).

TABLE I : Sample information

DESIGNATION	DESCRIPTION	SAMPLE VOLUME	COMMENTS
Samples for biological toxicity testing			
CONTROL			clear, colorless.
SCRAP	Unprocessed test water pumped directly from aquaria	12 L. (nom.)	clear, slight turquoise color.
NEW			clear, definite yellow-green color.
Processed effluent for HPLC investigation			
CONTROL			
SCRAP	Extraction effluent	8 L. (nom.)	clear, colorless effluent.
NEW			
Extracts			
CONTROL	Aerated well-water	~800 mL DCM (see Table 2)	see Table 2
SCRAP	"scrap" tire leachate (2)	"	
NEW	"new" tire leachate (2)	"	
QA samples			
Container Blank	To assess container cleaning procedure.	~50 mL. DCM @	duplicates
Solvent Blank	To assess level of solvent contamination.	~2100 mL. DCM	represents total DCM used in 100L. extraction (liquid and dissolved)
Extractor Blank	To assess contamination of extract by GLSE.	~800 mL. DCM	-

TABLE II : Test sample extracts

DESIGNATION	AQUEOUS SAMPLE VOLUME (L.)	EXTRACT VOLUME (mL.)	REDUCED VOLUME* (mL.)	CORRN. FACTOR* (x)	COMMENTS
CONTROL	99.0	792	772	1.03	clear, colorless extract
SCRAP	99.0	882	862	1.02	clear, intense yellow extract
NEW	99.0	1797	1777	1.01	clear, very intense yellow-orange extract

* Extract volume reduced by 20.00 mL (p.10). Apply correction factor to any quantitative results.

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