

DETERMINATION OF PAHs, PCBs AND PCDD/Fs IN SURFACE WATER USING THE GOULDEN LARGE-SAMPLE EXTRACTOR AND HIGH RESOLUTION MASS SPECTROMETRY.

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Introduction

Guidelines for surface water quality in Canada and United States for priority pollutants such as PAHs, PCBs and PCDD/Fs have been set to extremely low concentrations. Actual analytical methods on a conventional 1-L sample do not allow to reach these low concentrations even if high resolution mass spectrometry is used as the detection technique. The preconcentration of these contaminants from a large-volume water sample represents one approach that can be used to reach these extremely low MDL. The Goulden large-sample extractor (GLSE) has already been validated as a preconcentration technique for the analysis of pesticides in surface water (ref 1,2). In this study, the GLSE is evaluated for the analysis of PAHs, PCB congeners and PCDD/Fs from a 53 litre surface water sample.

Materials and Methods

Extractor Design

The GLSE is basically a mixer-settler in which the water sample is continuously passed through a vessel containing the solvent. Water sample and solvent are circulated around an extraction loop by a three blades propeller. The separation of the organic phase from the water is enhanced by passing the sample through a packed column containing Teflon ring which help break emulsion formed.

Procedure

Prior to the extraction with the GLSE, the water sample (53 L) is pumped from a stainless steel reservoir (Spartanburg) through a 293 mm Gelman 0.7 um filter. The dry filter is Soxhlet extracted with toluene overnight and is identified as the « particulate phase ». For the extraction of the dissolved phase, the GLSE is initially charged with 200 ml of dichloromethane (DCM) in the mixing chamber and the stirrer is started. The water sample (room temperature) is then pumped through the GLSE at a flow rate of 475 mL/min (pump P1). Simultaneously, a methanol solution containing labelled surrogates of PAHs, PCBs and PCDD/Fs is continuously added to the sample (1mL/min) and fresh DCM is pumped (10 mL/min) to maintain the solvent level (pumps P2 and P3). After the sample has passed through the GLSE, the solvent in the bottom of the mixing chamber (600 - 700 ml) is drained in a precleaned amber bottle. The extract is then concentrated and purified over a silver loaded alumina column to isolate PAHs from PCBs and PCDD/Fs. The

PCB and PCDD/F fraction is passed through an alumina column to isolate PCBs from PCDD/Fs. (ref. 3). Internal standard is added to each fraction for quantification by HRGC/HRMS on an Autospec Q (Micromass, UK) at 10 000 resolution (final volume: PAHs 500 uL, PCBs 500 uL, PCDD/Fs 25 uL) . All results were corrected for surrogate recoveries.

Validation Study

In order to validate the efficiency of the GLSE system for the extraction of ultratrace levels of organic contaminants, five distilled water samples of 53 L were spiked at 500 pg/L for PAHs, 15 pg/L for PCBs and 0.5 pg/L for PCDD/Fs. These samples were not filtered and extracted immediately after spiking with the GLSE. Differences between the average measured concentrations on these five samples and the expected concentration expressed as percent deviations (%D) are presented in figure 1. For PCBs, contribution of each homologue group to the total PCBs concentration were used for the calculation of the %D values. The percent deviation for most of these contaminants is under 25%. Higher positive %D value have been obtained for fluoranthene. Higher negative %D values were calculated for indeno(1,2,3,cd)pyrene, benzo(a)pyrene, hepta and octachlorinated dioxins and furans. This behavior could be explain by sorption of these contaminants to the container walls.

Method Reproducibility

Replicates of surface water (n=3) were collected in april 97 and february 98 on the St. Lawrence river near Quebec city. The particle phase and the dissolved phase were analysed according to the procedure previously described for PCBs and PAHs. The method reproducibility expressed in %RSDs are listed in table 1. The %RSD ranged from 0 % to 28 % while method detection limits for PAHs ranged from 10 to 100 pg/L and 0.1 to 0.8pg/L for PCBs. The 53 L extractions resulted in an average 25-35 fold decrease of the MDL relative to the conventional 1 L extraction.

Conclusion

This study has demonstrated that the GSLE combined to the HRGC/HRMS is a reliable procedure for the quantification of organic compounds at picogram and sub-picogram levels. This protocol is presently in application in our laboratory and more than 200 samples have been processed for the quantification of PAHs, PCBs and PCDD/Fs.

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References

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Figure 1 : Percent deviation (%D) between the average concentration (n=5) and the expected concentration. (distilled water ; vol 53 L)

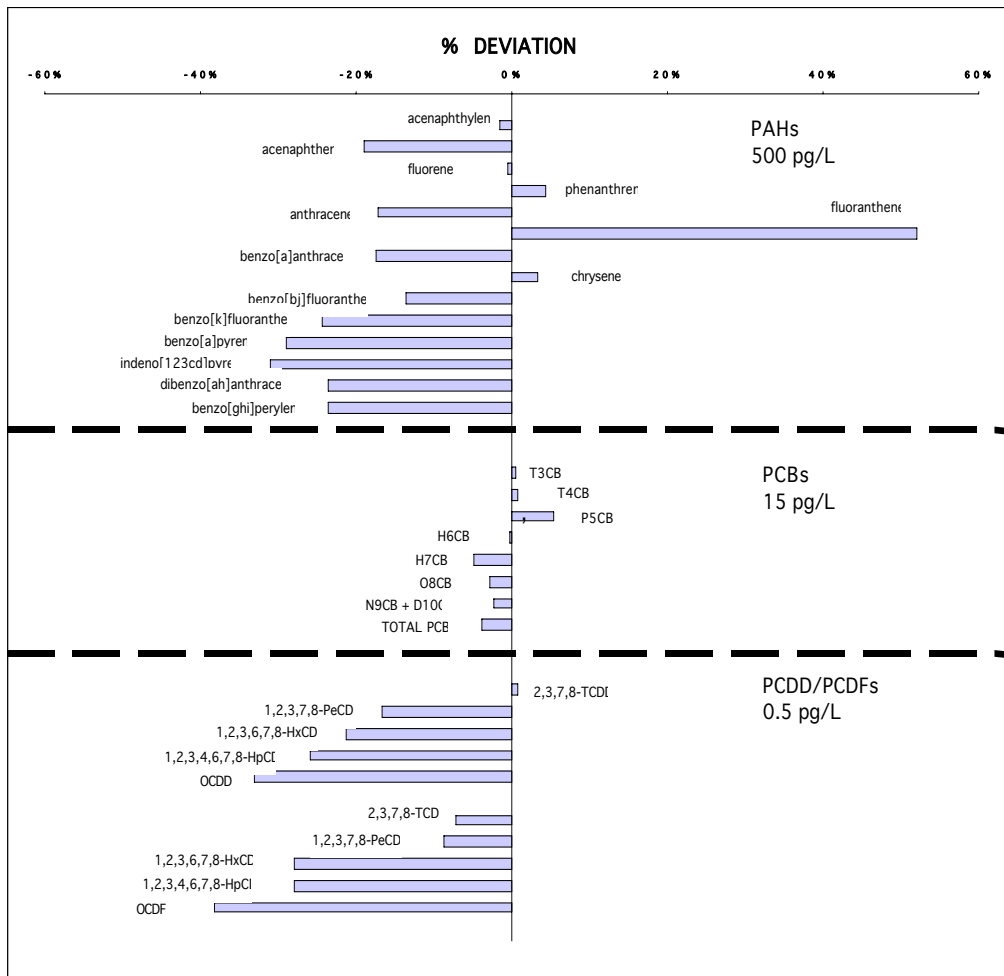


Table 1 : Mean PAHs and PCBs concentration and %RSD of triplicate samples from St. Lawrence river collected in 1997 and 1998.

	DISSOLVED PHASE			PARTICULATE PHASE		
	Mean concentration pg/L	RSD %	MDL pg/L	Mean concentration pg/L	RSD %	MDL pg/L
PAHs	February 1998			February 1998		
acenaphthylene	790	18	80	ND	NA	80
acenaphthene	820	4	80	ND	NA	80
fluorene	1600	6	20	ND	NA	40
phenanthrene	3030	8	60	2400	17	50
anthracene	310	5	100	ND	NA	60
fluoranthene	1800	0	20	580	12	10
benzo[a]anthracene	84	24	20	140	15	10
chrysene	460	17	40	300	17	10
benzo[b]fluoranthene	170	10	10	370	12	10
benzo[k]fluoranthene	46	15	10	100	16	10
benzo(e)pyrène	100	0	10	220	12	10
benzo[a]pyrene	39	27	10	170	19	10
perylene	72	11	10	460	12	10
indeno[123cd]pyrene	43	7	10	160	17	10
dibenzo[ah]anthracene	8	5	10	40	15	10
benzo[ghi]perylene	61	7	10	180	17	10
PCBs	February 1998			April 1997		
T3CB	147	16	0.6	337	12	0.8
T4CB	107	15	0.1	243	20	0.3
P5CB	47	28	0.2	183	10	0.4
H6CB	36	17	0.1	133	7	0.2
H7CB	11	12	0.1	33	10	0.3
O8CB	3	6	0.2	9	8	0.1
N9CB	1	0	0.1	2	22	0.2
D10CB	ND	NA	0.1	1	0	0.2
TOTAL PCB	350	16		927	6	