Bull. Environm. Contam. Toxicol. 29, 539–543 (1982)

Isolation of Hydrocarbon Residues from Sediment by Steam Distillation

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Knowledge of the impact of petroleum on freshwater systems is minimal. As part of a study of freshwater ecosystems in western Pennsylvania oil fields, it was necessary to analyze sediment taken from streams receiving effluents from nearby oil wells.

A number of procedures have been published for extracting oil in sediments. POUTANEN (1981) extracted hydrocarbons from freeze-dried sediment with benzene/methanol and ultrasonic agitation. PAASIVITRA (1981) saponified sediment mixture for 4 h and partitioned hydrocarbons from the alkaline digest with hexane. GEIGER & BLUMER (1974) extracted hydrocarbons from wet sediments by soxhlet with benzene/methanol for 48 h. BROWN et al (1980) extracted sediments three times in a ballmill tumbler with dichloromethane/methanol for 16, 6, and 16 h.

All of the above extraction methods require some sort of column chromatography to clean up the extract and/or the use of selective gas chromatography-mass spectrometry (GC-MS) to cope with the presence of compounds interfering with GC analysis of specific hydrocarbons.

The purpose of this study was to determine if a quicker and more efficient cleanup procedure could be found for the residue analysis of wet sediment possibly polluted with oil.

A method was devised that included extraction and cleanup of sediment in a modified Nielson-Kryger steam distillation device (VEITH & KIWUS 1977). Steam distillation, based on the independent vapor pressure contribution each component makes to the combined vapor pressure over the boiling mixture, appears to provide convenient cleanup of sediment for analysis by gas chromatography.

Co-extraction of interfering chemicals with lower vapor pressures (MACKAY 1973), e.g., higher molecular weight organic compounds and certain water-soluble chemicals, can be restricted by distilling the mixture for the minimum time needed for recovery of more volatile target compounds.

0007-4861/82/0029-0539 $01.00

MATERIALS & METHODS

A 50 g sample of sandy-type sediment from a western Pennyslvania stream was introduced into a 500 ml flat bottom boiling flask fitted with a 24/40 glass joint.

The sediment was spiked at levels of 0.04 and 4.0 ppm with each of 14 aliphatic and 9 aromatic petroleum hydrocarbons known to accumulate in animal tissues (BELISLE et al 1981). About 200 ml of distilled water was blended with the mixture. Unspiked portions of the same sediment mixture were run as controls. A Kontes K-523026 distillation condenser (Kontes, Vineland, NJ) was attached to the flask and 20 ml isooctane was added to the solvent trap through the top of the column. The samples were boiled vigorously for 2 h. The unit was cooled, and the lower aqueous phase trapped in the distillation column was discarded. The upper isooctane layer was collected together with several 2-3 ml petroleum ether rinses of the column. The volume of extract was reduced to 5 ml with a rotary evaporator. The concentrated eluate was separated into aliphatic and aromatic fractions on a 30 cm x 2.4 cm id glass column packed with 20 g silica gel (100-200 mesh, deactivated with 1.2% water) and prewashed with 100 ml methylene chloride followed by 100 ml petroleum ether. The aliphatics were eluted with 100 ml petroleum ether and then aromatics were eluted with 130 ml 40% methylene chloride in petroleum ether. Each fraction was concentrated to about 5 ml on a rotary evaporator, transferred to 10 ml Mills tubes, and reduced to a final concentration of $\geq$ 2.5 g/ml on a Kontes tube heater with a stream of nitrogen for analysis by gas chromatography (GC).

The GC analyses were performed on a Hewlett-Packard 5710A gas chromatograph equipped with a flame ionization detector (FID). Each sample was introduced by splitless injection onto a Quadrex glass capillary column (50 M x 0.25 mm id) coated with OV-101. Inlet purge activation time was 99 sec. Column temperature was held at 100 C for 8 min, then programmed to a final temperature of 230°C at 2°C/min. For field samples, the absolute detection limit is about 0.50 ng for all compounds, or 0.002 ppm based on a 50 g sample.

RESULTS & DISCUSSION

Recoveries of the reference hydrocarbons ranged from 33% to 100% when spiked at 0.04 ppm and from 72% to 93% at a concentration of 4.0 ppm (see Table 1). No reference compounds were detected in the control sediment extracts (see Fig. 1). Separate procedural studies showed that most of the losses were co-distillation losses occurring during the final concentration step. Losses were most severe for the more volatile compounds.

Increasing distillation time from 2 h to 4 h did not improve recoveries. GC chromatograms of these sediments, as well as oil-contaminated sediments we analyzed later, were free of interferences. Our results indicate that steam distillation offers relatively simple cleanup and acceptable efficiency for extraction of aliphatic and aromatic hydrocarbons in wet sediment.

Table 1. Recovery of reference hydrocarbons from 50 g of wet sediment by steam distillation, N = 3

Hydrocarbon	Cmpd No.	0.04 ppm spike Avg. %	0.04 ppm spike S.D.	4.0 ppm spike Avg. %	4.0 ppm spike S.D.
ALIPHATIC					
t-decalin	1	50	0.85	91	7.5
n-C_{12}	2	55	4.0	93	6.1
n-C_{13}	3	60	2.9	91	5.7
n-C_{14}	4	65	7.5	91	5.6
Octylcyclohexane	5	65	2.9	92	4.5
n-C_{15}	6	70	6.0	85	7.2
Nonylcyclohexane	7	75	2.9	91	4.5
n-C_{16}	8	75	2.9	80	6.0
n-C_{17}	9	75	2.9	85	11.1
Pristane	10	75	2.9	85	9.3
n-C_{18}	11	80	8.5	83	8.9
Phytane	12	80	7.5	91	7.6
n-C_{19}	13	75	6.0	83	14.
n-C_{20}	14	75	2.9	84	10.
AROMATIC					
Tetralin	15	33	2.9	76	13.
Naphthalene	16	50	5.0	79	9.6
1-methylnaphthalene	17	55	5.0	72	14.
2-ethylnaphthalene	18	55	7.5	82	5.9
1,5-dimethylnaphthalene	19	90	13.	84	6.4
4-phenyltoluene	20	70	6.0	81	4.9
1,3,5-trimethylnaphthalene	21	70	5.0	80	7.6
Fluorene	22	75	6.0	86	5.3
Phenanthrene	23	100	13.	90	7.6

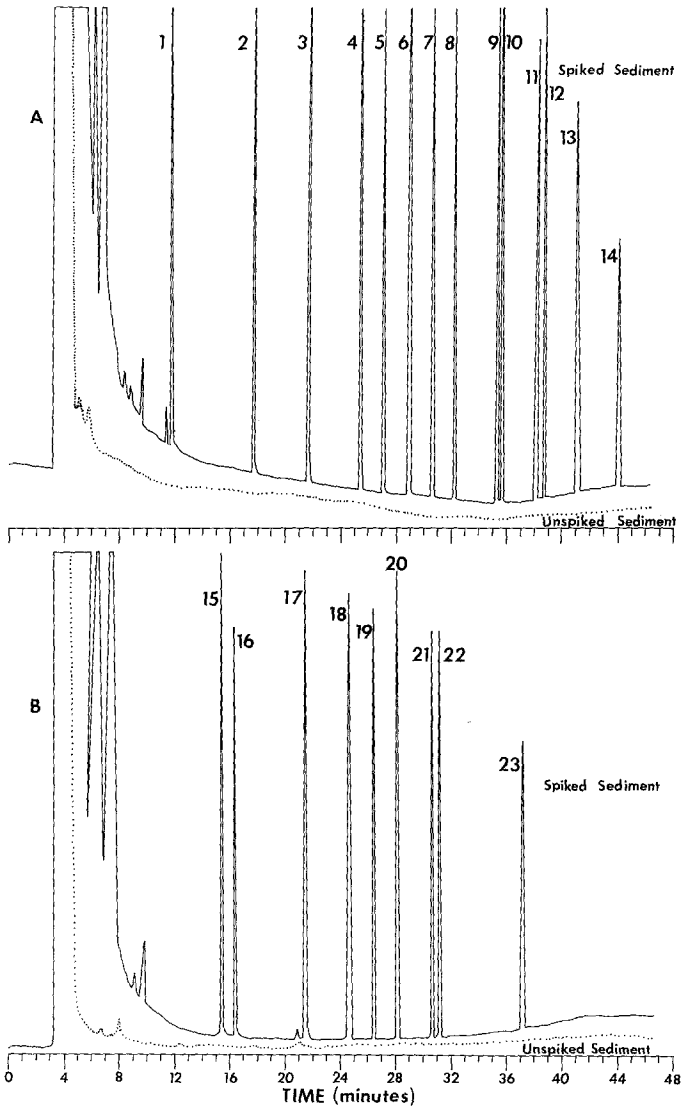

FIGURE 1. Gas chromatograms of 40 ng each hydrocarbon from 50 g spiked sediment. Reference compound numbers are identified in Table 1. (A) Aliphatic fraction. (B) Aromatic fraction.

Acknowledgements. We appreciate the technical assistance of D. Swineford, A. Krynitsky, and M. Kreamer. We would also like to thank W. Reichel for many helpful suggestions.

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Accepted September 21, 1982