United States
Environmental Protection
Agency

Environmental Monitoring and Support
Laboratory
Cincinnati OH 45268

Research and Development

EPA-600/S4-82-041 August 1982

EPA

Project Summary

Application of EPA Method 610 to the Analysis of Polynuclear Aromatic Hydrocarbons in Leachate Samples

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EPA Method 610, Determination of Polynuclear Aromatic Hydrocarbons in Industrial and Municipal Wastewaters, was designed for the analysis of 16 PNA compounds in municipal and industrial discharges. Samples of a leachate from a sanitary landfill were obtained and analyzed using method 610 to determine if this method is applicable for the analysis of PNA compounds in a leachate matrix. Leachate samples were also spiked and analyzed to determine the precision and accuracy of method 610 for a leachate matrix.

This Project Summary was developed by EPA's Environmental Monitoring and Support Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

This report summarizes the results of a spiking study performed on a sanitary landfill leachate matrix. Fifteen polynuclear aromatic hydrocarbons (PNAs) were dosed into the landfill leachate and analyzed using EPA method 610. The results show that the PNAs containing two, three, or four fused rings gave recoveries greater than 50% (see Table 1). Those PNAs containing five or six fused rings gave recoveries less than 50%. All PNAs were spiked at the low μg/L to the mid ng/L range.

The leachate matrix was also analyzed by gas chromatography/mass spectrometry (GS/MS) to identify the compounds present in this complex matrix. Forty-three compounds were given a tentative or confirmed identification after packed column and capillary column GC/MS analysis. There were an additional 65 compounds present in the leachate extract that could not be identified.

Further research needs to be performed to improve the accuracy for the analysis of high molecular weight PNAs in leachate samples.

In order to more fully understand the complexity of this leachate matrix, final extracts were subsequently analyzed by GC/MS. The extracts obtained correspond to both the neutral extraction procedure as specified in method 610 and to the basic and acidic extraction procedure specified in method 625. The complex extracts obtained after neutral extraction showed little difference from the extract obtained using the basic extraction. The neutral extraction procedure gave lesser emulsion problems than did the basic extraction procedure. Since the matrix was quite complex, phenols were almost quantitatively extracted during the basic extraction. The only phenol found in the

Table 1. *Recovery and Precision of PNAs Spiked into Landfill Leachate Analysis by Method 610*

		Spike Level µg/L	Recovery[a] From Leachate % ± RSD	Background[b] In Leachate µg/L	Recovery[c] Reagent Water % ± RSD
A	Naphthalene	10.4	115 ± 5	35.3[d]	79 ± 4
B	Acenaphthylene	13.7	85 ± 6	-	80 ± 4
C	Acenaphthene	17.7	94 ± 7	1.9 [d]	81 ± 3
D	Fluorene	1.15	117 ± 6	3.41[d]	84 ± 2
E	Phenanthrene	6.31	81 ± 11	5.05[d]	85 ± 2
F	Anthracene	8.57	71 ± 15	-	71 ± 2
G	Fluoranthene	0.26	119 ± 8	0.81[d]	92 ± 7
H	Pyrene	2.35	62 ± 8	0.52[d]	85 ± 7
I	Benzo (a) Anthracene	0.21	59 ± 10	0.19	82 ± 5
J	Benzo (b) Fluoranthene	0.20	32 ± 14	0.03	90 ± 3
K	Benzo (k) Fluoranthene	0.09	29 ± 14	0.01	94 ± 2
L	Benzo (a) Pyrene	0.20	26 ± 12	0.06[d]	67 ± 2
M	Dibenzo (ah) Anthracene	0.50	15 ± 22	-	86 ± 2
N	Benzo (ghi) Perylene	0.51	16 ± 21	-	86 ± 4
O	Indeno (1,2,3-cd) Pyrene	0.14	10 ± 27	-	94 ± 2

[a] *six aliquots*
[b] *one aliquot*
[c] *three aliquots*
[d] *confirmed by GC/MS*

acidic fraction was 2-fluorophenol, the surrogate standard, and it also carried over into the basic fraction.

A summary of the confirmed and tentative identifications of 43 compounds found in the leachate sample using both packed column and capillary column chromatography is given in Table 2. Fourteen additional compounds were identified after using capillary column chromatography; however, there are still 65 additional peaks in the capillary run that defy interpretation and identification. Packed column chromatography of the post cleanup leachate extract gave identifications for some PNA compounds that were not resolved when the precleanup extract was analyzed using capillary column chromatography.

Results

The leachate spiking study revealed a serious matrix effect for PNA compounds containing five or six fused rings. The results are summarized in Table 1 and demonstrate a trend for much lower recovery with an increasing number of fused rings.

The high recoveries for A-naphthalene, D-fluorene, and G-fluoranthene are due to the relative magnitude of the amount spiked to the amount present in the background. In each of these three cases, the leachate was spiked at approximately one-third the background level. The remaining PNA compounds were spiked at a level at least twice the background level. All recoveries from reagent water are consistent and show no trend. The correlation coefficients for recovery versus number of fused rings are -0.867 for the leachate matrix and 0.414 for reagent water when the results for compounds A,D, and G are included and are -0.954 and 0.448 when these three compounds are not included.

Conclusions

Landfill leachates contain a large number of polar and nonpolar materials. Method 610 performs reasonably well for leachate samples containing µg per liter levels of PNA compounds containing two, three or four fused rings. PNA compounds containing five or six fused rings exhibit low recoveries from landfill leachates. Almost all polar interferences are removed using the silica gel chromatography cleanup procedure. Confirmation of identity in the post cleanup extract is easily performed by GC/MS using packed column chromatography.

Recommendations

Since these leachate samples exhibit a serious matrix effect of low recovery for PNA compounds containing five and six fused rings, further research must be performed to improve the accuracy of the analytical method for measuring the high molecular weight PNA compounds in landfill leachates.

Table 2. *Compounds Identified in Leachate Samples*

	Compound	Retention Times Relative to 4,4'-Dibromobiphenyl[a] Packed Column	Capillary Column	Identification[b]
	Tetrachloroethene	—	0.051	T
	Chlorobenzene	—	0.097	T
	Dimethylbenzene	—	0.132	T
	2-Fluorophenol-Surrogate Standard	—	0.142	—
	Cumene	—	0.212	T
	Camphene	—	0.253	T
1	1,2,4-Trimethylbenzene	0.117	0.296	C
2	1,3-Dichlorobenzene	0.184	0.316	C
3	2,3-Dihydro-1H-indene	0.199	0.343	T
4	1,2-Dichlorobenzene	0.216	0.343	C
	4-Methylbenzene amine	—	0.388	T
	Camphor	—	0.398	T
	Tetramethylbenzene	—	0.426	T
	Triethylphosphate	—	0.432	T
5	Naphthalene	0.392	0.483	C
6	t-Butylphenol	0.482	0.567	T
7	2-Methylnaphthalene	0.482	0.571	C
8	1-Methylnaphthalene	0.506	—	C
	2,6-Di-t-Butylbenzoquinone	—	0.690	T
9	Dicyclohexylamine	0.523	0.700	T
10	Dimethylnaphthalene	0.558	0.649	T
11	Dimethylnaphthalene	0.570	—	T
12	Acenaphthene	0.652	0.705	C
13	Dibenzofuran	0.675	0.725	T
14	Octylphenol	0.705	0.776	T
15	Fluorene	0.734	0.767	C
16	Tributylphosphate	0.754	0.801	T
17	N,N-Dimethyl 4-toluenesulfonamide	0.830	—	T
	2(3H)-Benzothiazolone	—	0.824	T
18	Phenanthrene	0.854	0.884	C
19	N-Ethyl-4-toluenesulfonamide	0.874	0.835	T
20	Methyl phenanthrene	0.936	—	T
21	Dibutylphthalate	0.959	0.969	C
	Phenobarbitol	—	0.989	T
22	4,4'-Dibromobiphenyl-Surrogate Standard	1.000	1.000	-
23	Unknown mol. wt. 238	1.015	1.045	T
24	Fluoranthene	1.044	1.058	C
25	Pyrene	1.082	—	C
26	Tetramethylphenanthrene	1.088	1.102	T
27	N-cyclohexyl 4-toluenesulfonamide	1.111	1.070	T
28	4,4'-(1-methylethylidene) bisphenol	1.140	1.077	T
29	Tributoxyethyl phosphate	1.187	1.173	T
30	Bis (2-ethyhexyl) phthalate	1.225	—	C
31	Dioctyl phthalate	1.263	1.230	C
	Benzo (a) pyrene	—	1.413	C

[a]Ret. time of 4,4=-dibromobiphenyl is 35.4 min on packed column, and 20.0 min on capillary column.
[b]T-tentative by similarity of mass spectra; C - confirmed identification by retention time and similarity of mass spectra.

★ U.S. GOVERNMENT PRINTING OFFICE: 1988 - 559-017/0788

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The complete report, entitled "Application of EPA Method 610 to the Analysis of Polynuclear Aromatic Hydrocarbons in Leachate Samples," (Order No. PB 82-221 235; Cost: $6.00, subject to change) will be available only from:

National Technical Information Service
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