Measurements of Linear Alkybenzenes by GC/MS and GC/FID

Linear alkylbenzenes (LABs) have been used since the early 1960s to synthesize linear alkylbenzene-sulfonate (LAS) surfactants, the raw materials used in the manufacture of commercial detergents. LABs replaced the highly branched tetraproplene-based alkylbenzenes (TABs) that had been used previously as precursors for detergents. LASs are synthesized by sulfonation of LABs with H_2SO_4 or SO_3. Incomplete sulfonation introduces LABs into detergents with LASs.

Linear alkylbenzenes were first discovered in coastal sediments of Tokyo Bay (Ishiwatari *et al*. 1983) and Southern California Bight (Eganhouse *et al*. 1983a). These compounds end up in aquatic environments as a result of the disposal of domestic wastes containing unsulfonated residues of LABs (Ishiwatari *et al*. 1983, Eganhouse *et al*. 1983a, 1988, Takada and Ishiwatari 1987, Takada *et al*. 1994). The LABs normally found in environmental samples contain 10-14 carbons in the alkyl chain. The phenyl ring can be located at various positions of the alkyl chain, resulting in several LAB isomers for each identical alkyl chain. LABs are sometimes labeled as C_i-LAB-n, where i=10 to 14 and n=position number of the phenyl ring (e.g., 1 is the end of the alkyl chain). A standard analytical method does not exist for the analysis of LABs, probably because their residues are not considered a major environmental concern. However, LABs are useful as indicators of domestic wastes.

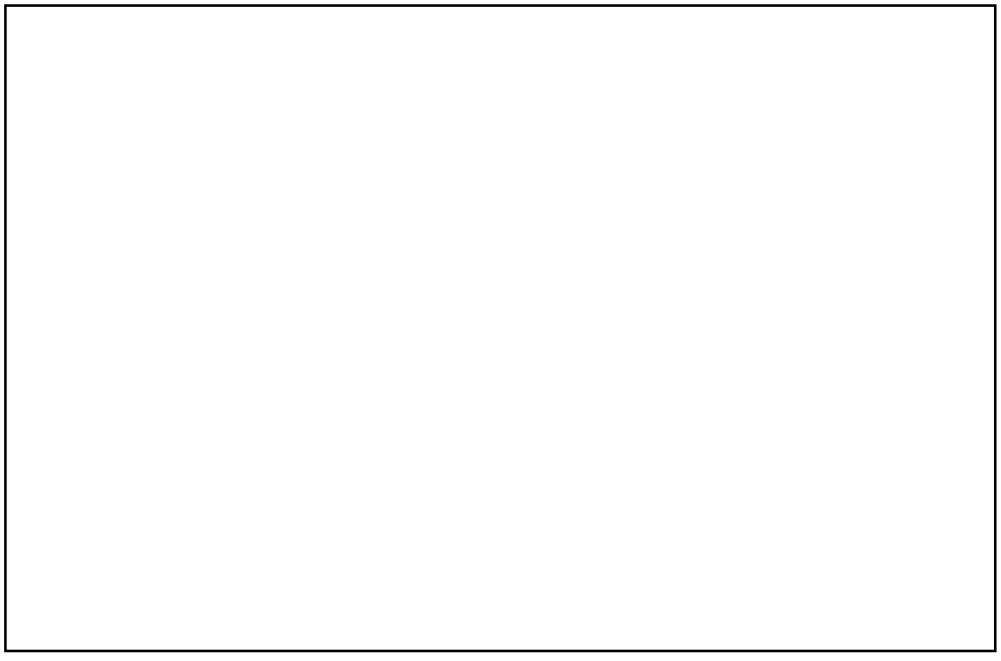
The objective of this study was to develop a reliable analytical procedure for analysis of LABs. Since there are only a few individual LAB standards available commercially (all are C_i-LAB-1), we quantified a pure LAB mixture (secondary standard) by individual LAB standards (primary standards). The components of the LAB mixture were identified by GC/MS using retention times and molecular ion fragments. Calibration curves were established by GC/FID for the primary standards. The characterized LAB mixture was used for instrument calibration and sample analysis with GC/MS.

We chose GC/MS for analysis of municipal wastewater effluent and marine sediment because of the ability to distinguish overlapping components with different characteristic ion fragments, which is especially important in analysis of complex samples. The existence of TABs in sediments deposited near sewage outfalls may complicate measurements of LABs, even with GC/MS. We demonstrate how GC/MS can minimize the interference of LABs from TABs by choosing appropriate ion fragments for quantitation.

MATERIALS AND METHODS

Individual LAB compounds (primary standards), C_{10}-LAB-1, C_{12}-LAB-1, and C_{13}-LAB-1 were purchased from Aldrich (St. Louis, MO) and C_{14}-LAB-1 from Pfaltz & Bauer (Waterbury, CT). A pure LAB mixture (secondary standard) was obtained from Mr. Robert Bowen at SAIC (Narragansett, RI). This mixture contains isomers of C_{11}-LABs, C_{12}-LABs, C_{13}-LABs, and C_{14}-LABs except for Ci-

Sample analysis in the chemistry laboratory.



LAB-1 (i=11-14). Two internal standards, 2-fluorobiphenyl and p-teraphenyl-d_{14}, and one surrogate standard, phenanthrene-d_{12}, were acquired from Ultra Scientific, Inc. (North Kingstown, RI). Ultra resi-analyzed grade hexane and methylene chloride were manufactured by J.T. Baker Inc. (Phillipsburg, NJ). Ultra high purity He, H_2, N_2, and compressed air were supplied by Oxygen Service (Orange, CA). GF/C (1.2 µm pore size) glass fiber filters were obtained from Whatman International Ltd. (Maidstone, England). All standard solutions were prepared in hexane.

Sample Collection and Extraction

A 24-h composite of final effluent was collected in a one-gallon bottle on June 27, 1994 from the Point Loma Wastewater Treatment Plant (City of San Diego). The sample was kept on ice and transported to SCCWRP. Ten liters of effluent were filtered with Whatman GF/C glass fiber filters under vacuum. A new filter was installed when the flow rate dropped to about half of the initial value. The filters were extracted by methods used for sediment samples (see *Post-Depositional Distribution of Organic Contaminants Near the Hyperion 7-Mile Outfall in Santa Monica Bay*, in this volume). Filtrates were extracted using the liquid-liquid extraction technique detailed elsewhere (see *Extraction of Hydrophobic Organics from Aqueous Samples with 90-MM C-18 Bonded Disks,* in this volume). The final extract volume was 0.5 mL for all the samples.

Marine sediments were collected from station E6 in Santa Monica Bay by gravity core on June 20, 1994. Results from analyses of four sections (0-2, 38-40, 68-70, 80-82 cm) of a 96-cm core are presented. Procedures for collection and extraction of sediment samples are available elsewhere (see *Post-Depositional Distribution of Organic Contaminants Near the Hyperion 7-Mile Outfall in Santa Monica Bay*, in this volume). The final volume was 0.5 mL for each sample.

GC/MS Analysis

Identification of individual LABs and the LAB mixture was performed by GC/MS. The chromatographic conditions were described elsewhere (see *Post-Depositional Distribution of Organic Contaminants Near the Hyperion 7-Mile Outfall in Santa Monica Bay*, in this volume). One internal standard, p-teraphenyl-d_{14}, and one surrogate standard, phenanthrene-d_{12}, were used in quantitation.

GC/FID Analysis

The composition of the LAB mixture was determined by GC/FID. A Varian 3500 GC was equipped with a 60 m x 0.25 mm ID (0.25 µm film thickness) DB-1 and a 60 m x 0.25 mm ID (0.25 µm film thickness) DB-5 capillary columns. This configuration was used for analyses of hydrocarbon compounds with no additional confirmation needed. The DB-1 column was used for quantitation, since it provided better separation for the LABs, internal standards, and surrogate standard than did the DB-5 column. The initial oven temperature was set at 80°C and immediately ramped to 285°C at 3°C/min, where the temperature was held for 8 min; total run time was 76 min. A sample volume of 2 µL was injected manually into a split/splitless injector with a split time of 1 min. Helium was the carrier gas with a flow rate of 1.8 mL/min at 80°C. The gas flow rates were: H_2 ~24 mL/min, make-up gas N_2 + carrier gas ~20 mL/min, and air ~280 mL/min. Data were acquired and processed using the PE Nelson Turbochrom 3.3 software running on an IBM compatible PC. A PE Nelson 900 series interface unit was used to connect the GC and computer. Two internal standards, 2-fluorobiphenyl and p-terphenyl-d_{14}, and one surrogate standard, phenanthrene-d_{12}, were used for internal calibration and recovery evaluation.

RESULTS AND DISCUSSION

Identification of the LAB Compounds by GC/MS

A mixture of the primary standards (C_{10}-LAB-1, C_{12}-LAB-1, C_{13}-LAB-1, and C_{14}-LAB) was prepared with a concentration of 5 µg/mL for each component and run on

FIGURE 1. Total ion chromatogram of the LAB mixture acquired by GC/MS.

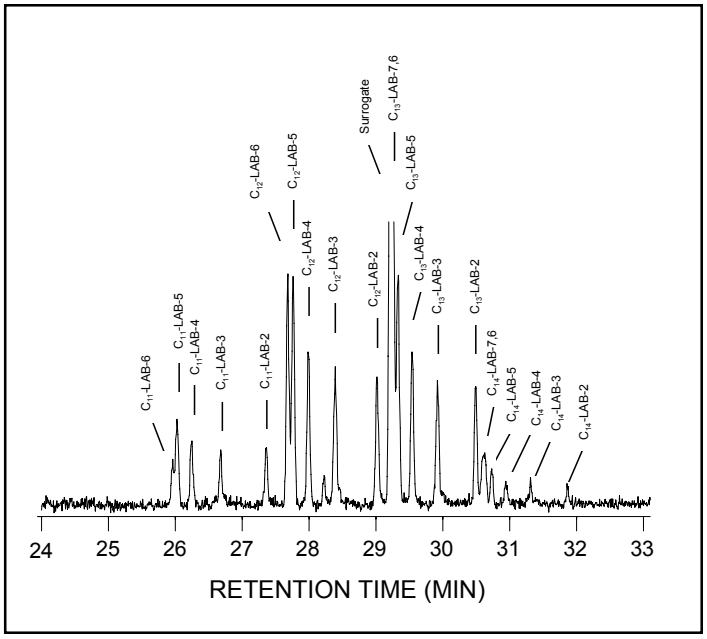


TABLE 1. Retention times (R.T.), parent ions, and characteristic fragments of LAB compounds acquired by GC/MS.

Primary Standard	R.T. (min.) DB-5	R.T. (min) DB-1	Parent Ion (m/z)	Characteristic Fragment
1-phenyl decane	27.30	24.02	218	92, 91
1-phenyl dodecane	30.61	27.48	246	92, 91
1-phenyl tridecane	32.00	28.96	260	92, 91
1-phenyl tetradecane	33.33	30.24	274	92, 91
Secondary Standard				
6-phenyl undecane	25.99	23.21	232	91, 161
5-phenyl undecane	26.06	23.27	232	91, 147
4-phenyl undecane	26.28	23.47	232	91, 133
3-phenyl undecane	26.72	23.88	232	91, 119
2-phenyl undecane	27.40	24.55	232	105, 91
6-phenyl dodecane	27.72	25.01	246	91, 161
5-phenyl dodecane	27.81	25.10	246	91, 147
4-phenyl dodecane	28.03	25.31	246	91, 133
3-phenyl dodecane	28.42	25.71	246	91, 119
2-phenyl dodecane	29.05	26.32	246	105, 91
7&6-phenyl tridecane	29.26	26.63	260	91, 175, 161[a]
5-phenyl tridecane	29.37	26.75	260	91, 147
4-phenyl tridecane	29.57	26.96	260	91, 133
3-phenyl tridecane	29.96	27.32	260	91, 119
2-phenyl tridecane	30.53	27.87	260	105, 91
7-phenyl tetradecane	30.64	28.07	274	91, 175
6-phenyl tetradecane	30.67	28.13	274	91, 161
5-phenyl tetradecane	30.78	28.23	274	91, 147
4-phenyl tetradecane	30.99	28.42	274	91, 133
3-phenyl tetradecane	31.35	28.77	274	91, 119
2-phenyl tetradecane	31.90	29.27	274	105, 91
Internal Standards				
p-terphenyl-d_{14}	34.63	31.20	244	
Surrogate Standard				
Phenanthrene-d_{10}	29.29	25.74	188	

[a]Ions 91 and 175 are for 7-phenyl tridecane; ions 91 and 161 are for 6-phenyl tridecane.

GC/MS. The LAB compounds were characterized by almost equally strong fragments at m/z 92 and 91 and weak signals from their parent molecular ions (Table 1).

The LAB mixture contained four isomer groups for a total of 22 components. To identify individual components, a 25-ppm solution of the LAB mixture was prepared and analyzed using GC/MS (Figure 1, Table 1). Two LABs, 7-phenyl tridecane (C_{13}-LAB-7) and 6-phenyl tridecane (C_{13}-LAB-6), could not be separated on the DB-5 column. Two LABs, 7-phenyl tetradecane (C_{14}-LAB-7) and 6-phenyl tetradecane (C_{14}-LAB-6) were only partially resolved. To confirm that the eluting sequence of the LAB compounds was identical on the DB-5 and DB-1 columns, the LAB mixture was also analyzed using GC/MS and the DB-1 column (Table 1). Each LAB isomer group in the mixture was distinguished by their strong characteristic fragments and weak parent molecular ions. Within an isomer group, individual components had various amounts of ion fragments due to differences in molecular structure. Generally, C_i-LAB-n (n=3-7) had a strong fragment at m/z 91 and C_i-LAB-2 had a strong peak at m/z 105. Among the LABs with n=3-7, different prominent fragments were identified. For instance, C_{12}-LAB-3 had a second strong fragment at m/z 119, C_{12}-LAB-4 at m/z 133, C_{12}-LAB-5 at m/z 147, and C_{12}-LAB-6 at m/z 161. This allowed identification of the components of the LAB mixture by comparing the ion profile spectra acquired by the GC/MS with the reference spectra stored in the ChemStation data system (Figure 2). The matching qualities were normally better than 80 (100 was perfect).

Quantitation of the LAB Mixture by GC/FID

The primary standards (C_{10}-LAB-1, C_{12}-LAB-1, C_{13}-LAB-1, and C_{14}-LAB-1) were used to characterize the LAB mixture using GC/FID. Solutions of 0.1, 0.4, 2, 5, and 10 µg/mL of each primary standard were prepared with 2 µg/mL of internal and surrogate standards. Five-point calibration curves were established with GC/FID. The relative response factor (RRF) of a sample compound relative to an internal standard is:

$$RRF = \frac{\left(\frac{A_S}{A_I}\right)}{\left(\frac{C_S}{C_I}\right)} \qquad (1)$$

where:

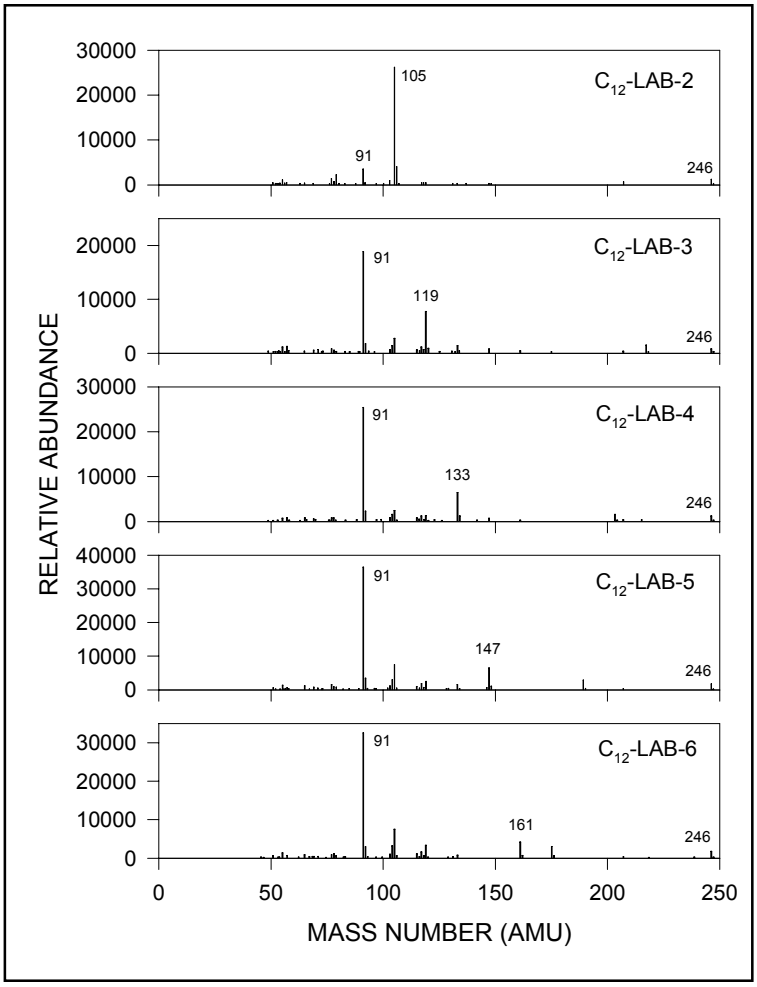
A_S = peak area of the sample compound,
A_I = peak area of the internal standard,
C_S = concentration of the sample compound, and
C_I = concentration of the internal standard.

To apply the least-squares linear regression fitting, Equation (1) was rearranged as:

$$\left(\frac{A_S}{A_I}\right) = (RRF)\left(\frac{C_S}{C_I}\right) \qquad (2)$$

By plotting (A_S/A_I) versus (C_S/C_I), and forcing the regression through the origin, RRF is the slope (Table 2). The RRF of the surrogate standard was an average of five values.

FIGURE 2. Typical ion profiles of C_{12}-LAB-2, C_{12}-LAB-3, C_{12}-LAB-4, C_{12}-LAB-5, and C_{12}-LAB-6.



Three secondary standard solutions were prepared in total concentrations of 25, 50, and 100 µg/mL with 2 µg/mL of internal and surrogate standards. These solutions were analyzed twice using GC/FID and quantified with the relative response factors of the primary standards. Since the secondary standard contained C_{11}-LABs to C_{14}-LABs, C_{11}-LABs were quantified using the calibration curve of C_{10}-LAB-1, C_{12}-LABs were quantified using C_{12}-LAB-1, C_{13}-LABs were quantified using C_{13}-LAB-1, and C_{14}-LABs were quantified using C_{14}-LAB-1; this assumed that the relative response factors of all LABs in an isomer group were identical. Six measurements were made for each of the LAB components in the secondary standard. The average recovery of total LABs was 84.9%, indicating the presence of unknown residues. Therefore, the composition of the secondary standard was calculated by normalizing the measured concentrations of individual LABs to the injected amount of the secondary standard instead of the measured sum. An average composition was obtained from six calculations (Table 3).

Analysis of Effluent and Sediment Samples by GC/MS

After the secondary standard was characterized, it was used in calibrating the GC/MS for sample analysis. Calibration standards were prepared in 2, 5, 20, 50, and 200 µg/mL from the secondary standard, along with 2 µg/mL p-teraphenyl-d_{14} (internal standard) and phenanthrene-d_{12} (surrogate standard). The 5-point calibration curves for all LAB compounds were established with GC/MS. Relative response factors were obtained from least-squares linear regression [Eq. (2)].

The ion profile patterns between C_{11}- and C_{14}-LABs were similar for the standard and the effluent particle sample except for the relative abundance among isomer groups (Figure 3). The LAB standard was dominated by C_{13}- and C_{12}- LABs, while C_{11}-, C_{12}- and C_{13}-LABs were about equally prominent in the effluent (measured by the abundance of m/z 91). The major difference was that the effluent particles contained significant amounts of C_{10}-LABs that were not present in the LAB mixture. These C_{10}-LAB compounds were quantified by the response factor of C_{11}-LAB-6. The ion profiles of the effluent filtrate were identical with those of the effluent particle and therefore are not shown.

With more than 80,000 isomers, TABs are a complex suite of largely unresolved chromatographic peaks; the major ion fragments are m/z 119, 105, or 113 (Eganhouse *et al*. 1983a,b). Due to lack of TAB standards, we only compared the ion profiles at m/z 91, 105, 119, and 133 to identify the presence of TABs in the samples. The clean ion chromatograms with well resolved peaks suggested that the Point Loma Treatment Plant effluent does not contain TABs (Figure 3).

The core from Santa Monica Bay contained sediments deposited prior to 1957 when the Hyperion 7-mile outfall

TABLE 2. Five-point calibration levels of individual LABs on GC/FID. R.T. = retention time, RRF = relative response factor.

Primary LAB Standards	R.T. (min)	RRF	R^2
1-phenyl decane[a]	30.00	1.31	0.996
1-phenyl dodecane[a]	37.43	1.23	0.995
1-phenyl tridecane[b]	40.91	1.08	0.998
1-phenyl tetradecane[b]	44.23	1.15	0.999
Surrogate Standard			%RSD
Phenanthrene-d10[a]	32.82	0.94	9.76

[a]Relative to 2-flourobiphenyl.
[b]Relative to p-teraphenyl-d14.

TABLE 3. Composition of the LAB mixture by GC/FID. SD = standard deviation.

Total LAB Conc. (µg/mL)				Composition				
	25	50	100	25	50	100		
LAB Compound							Ave.	SD
6-phenyl undecane[a]	0.0132	0.0146	0.0162	0.0128	0.0150	0.0134	0.0142	0.0013
5-phenyl undecane[a]	0.0252	0.0274	0.0307	0.0248	0.0282	0.0253	0.0269	0.0023
4-phenyl undecane[a]	0.0188	0.0204	0.0227	0.0184	0.0208	0.0188	0.0200	0.0016
3-phenyl undecane[a]	0.0176	0.0196	0.0217	0.0172	0.0198	0.0179	0.0190	0.0017
2-phenyl undecane[a]	0.0172	0.0184	0.0209	0.0160	0.0188	0.0167	0.0180	0.0018
6-phenyl dodecane[a]	0.0636	0.0700	0.0817	0.0616	0.0718	0.0631	0.0686	0.0076
5-phenyl dodecane[a]	0.0592	0.0640	0.0747	0.0564	0.0652	0.0574	0.0628	0.0068
4-phenyl dodecane[a]	0.0432	0.0476	0.0543	0.0412	0.0478	0.0415	0.0459	0.0050
3-phenyl dodecane[a]	0.0388	0.0456	0.0516	0.0384	0.0450	0.0395	0.0432	0.0052
2-phenyl dodecane[a]	0.0372	0.0410	0.0485	0.0348	0.0414	0.0358	0.0398	0.0050
7&6-phenyl tridecane[b]	0.1328	0.1412	0.1275	0.1560	0.1428	0.1673	0.1446	0.0148
5-phenyl tridecane[b]	0.0808	0.0860	0.0792	0.0944	0.0892	0.1021	0.0886	0.0086
4-phenyl tridecane[b]	0.0584	0.0622	0.0561	0.0680	0.0630	0.0731	0.0635	0.0062
3-phenyl tridecane[b]	0.0548	0.0582	0.0528	0.0632	0.0588	0.0678	0.0593	0.0055
2-phenyl tridecane[b]	0.0520	0.0534	0.0488	0.0580	0.0544	0.0608	0.0546	0.0043
7-phenyl tetradecane[b]	0.0164	0.0176	0.0160	0.0188	0.0178	0.0201	0.0178	0.0015
6-phenyl tetradecane[b]	0.0156	0.0166	0.0151	0.0176	0.0168	0.0190	0.0168	0.0014
5-phenyl tetradecane[b]	0.0160	0.0162	0.0144	0.0172	0.0160	0.0181	0.0163	0.0013
4-phenyl tetradecane[b]	0.0108	0.0108	0.0099	0.0116	0.0110	0.0123	0.0111	0.0008
3-phenyl tetradecane[b]	0.0100	0.0094	0.0086	0.0092	0.0104	0.0111	0.0098	0.0009
2-phenyl tetradecane[b]	0.0080	0.0080	0.0077	0.0084	0.0082	0.0092	0.0083	0.0005
Measured Total	0.7896	0.8482	0.8591	0.8440	0.8622	0.8903	0.8489	

[a]Relative to 2-fluorobiphenyl.
[b]Relative to p-teraphenyl-d_{14}.

started operation (see *Post-Depositional Distribution of Organic Contaminants Near the Hyperion 7-Mile Outfall in Santa Monica Bay*, in this volume). The presence of TABs was identified from the change in the relative abundances of m/z 91 and 119, and the overall pattern at various core depths (Figure 4). At 80-82 cm, the m/z 119 fragment was relatively abundant compared to m/z 91. The most prominent and resolved group of peaks occurred between the retention times of C_{11}-LABs and C_{12}-LABs, which is consistent with the fact that the majority of TABs contains 12 carbons in the branched side chain. The ion profile of m/z 91 was also relatively abundant. However, it generally had no baseline-resolved peaks and mostly consisted of an enhanced baseline.

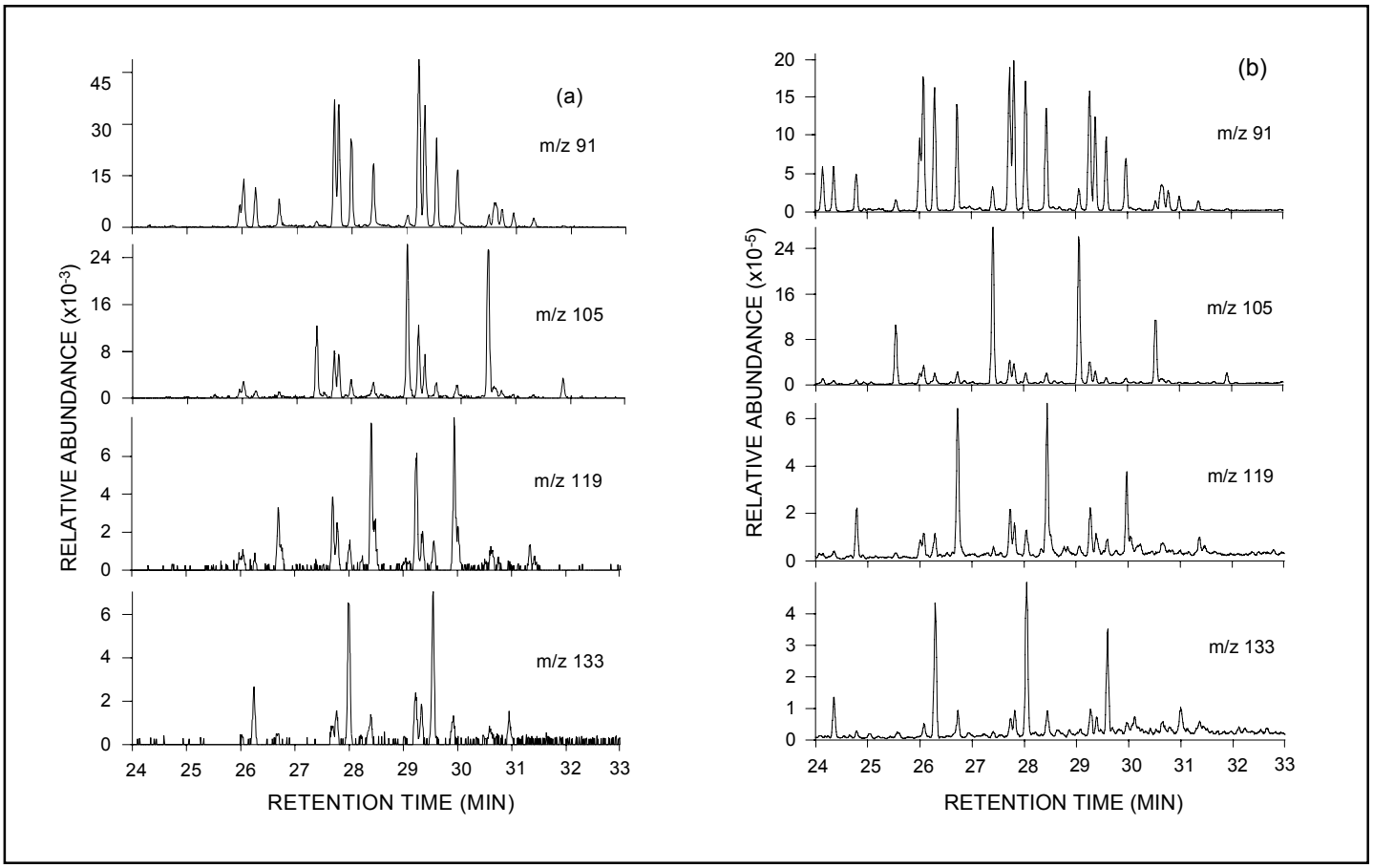
The contribution from LABs to m/z 91 may have added to the TAB background and was identified by their retention times and patterns. The total LAB concentration at 80-82 cm measured by this approach was low despite the high abundance of m/z 91. The abundance of m/z 119 was lower at 68-70 cm than at 80-82 cm. The abundance of m/z 91 was also lower, but not as much as m/z 119. In addition, more resolved peaks of m/z 91 appeared. At 38-40 cm, the characteristic TAB pattern of m/z 119 essentially disappeared. The m/z 91 signals dominated the ion chromatograms at 38-40 cm and at the surface (0-2 cm). The results indicate that interference from TABs can be minimized by using m/z 91 as the quantitation ion and comparing the abundance of m/z 119 to m/z 91.

CONCLUSIONS

A procedure was developed to characterize an LAB mixture using GC/MS and GC/FID capillary column techniques. The components of the LAB mixture were identified by GC/MS using retention times and molecular ion fragments. Calibration curves were established by GC/FID for the primary standards. The responses by GC/FID were assumed identical for all LABs in an isomer group and the composition of the LAB mixture was determined using the calibration curves of the primary standards. This mixture was used as a calibration standard for measuring LABs in municipal wastewater effluent and marine sediments by GC/MS.

Effluent from the Point Loma Wastewater Treatment Plant contained no TABs. The strong signals of m/z 119 indicated that significant amounts of TABs were detected near the bottom of a sediment core from Santa Monica Bay. The characteristic pattern of m/z 119 gradually disappeared toward the top of the core, while the relative abundance of m/z 91 increased. By using the m/z 91 fragment as the quantitation ion and comparing the relative abundance of m/z 119, interference with analyses of LABs by TABs was minimized. The methods developed here will enable us to measure LABs in complex samples and use them as an indicator of domestic waste inputs in the coastal marine environment.

FIGURE 3. Ion chromatograms of m/z 91, 105, 119, and 133 for (a) the LAB mixture and (b) municipal wastewater effluent particles from the Point Loma Municipal Wastewater Treatment Plant.



REFERENCES

Eganhouse, R.P., D.L. Blumfield, and I.R. Kaplan. 1983a. Long-chain alkylbenzenes as molecular tracers of domestic wastes in the marine environment. *Environ. Sci. Technol.* 17:523-530.

Eganhouse, R.P., E.C. Ruth, and I.R. Kaplan. 1983b. Determination of long-chain alkylbenzenes in environmental samples by argentation thin-layer chromatography/high-resolution gas chromatography and gas chromatography/mass spectrometry. *Anal. Chem.* 55:2120-2126.

Eganhouse, R.P., D.P. Olaguer, B.R. Gould, and C.S. Phinney. 1988. Use of molecular markers for the detection of municipal sewage sludge at sea. *Mar. Environ. Res*. 25:1-22.

Ishiwatari, R., H. Takada, S.J. Yun, and E. Mastsmoto. 1983. Alkylbenzene pollution of Tokyo Bay sediments. *Nature* 301:599-600.

Takada, H. and R. Ishiwatari. 1987. Linear alkylbenzenes in urban riverine environments in Tokyo: Distribution, source, and behavior. *Environ. Sci. Technol*. 21:875-883.

Takada, H., J.W. Farrington, M.H. Bothner, C.G. Johnson, and B.W. Tripp. 1994. Transport of sludge-derived organic pollutants to deep-sea sediments at deep water dump site 106. *Environ. Sci. Technol*. 28:1062-1072.

ACKNOWLEDGMENTS

Authors Charlie Yu and Eddy Zeng sincerely thank R. Bowen (SAIC) for generously providing the LAB mixture, H. Stubbs and D. Diehl for sample collection, C. Vista and A. Khan for laboratory assistance, and J. Cross for reviewing the manuscript.

FIGURE 4. Ion chromatograms of m/z 91, 105, 119, and 133 for marine sediments at (a) 80-82 cm, (b) 68-70 cm, (c) 38-40 cm, and (d) 0-2 cm in a core from Santa Monica Bay.