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Measurements of Linear Alkylbenzenes by GC/MS with Interference from Tetrapropylene-Based Alkylbenzenes: Calculation of Quantitation Errors Using a Two-Component Model

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Linear alkylbenzenes (LABs) and tetrapropylene-based alkylbenzenes (TABs) are often used as molecular tracers of domestic waste inputs. Due to the overlapping usage of LABs and TABs in the past, these compounds have been found to co-exist in environmental samples. They elute closely under normal gas chromatographic conditions and contain similar mass spectral ion fragments, which makes it difficult to separate contributions from LABs and TABs even by the gas chromatography/mass spectrometry (GC/MS) method. This paper presents a two-component model that deals with the quantitation error (*E*) in measurements of LABs (or TABs) because of the interference from TABs (or LABs). By taking advantage of the GC/MS chromatographic characteristics of LABs and TABs, a simple equation derived from the model can calculate *E* with the knowledge of relative abundances of *m*/*z* 91 and *m*/*z* 119 in samples, LAB standards, and TAB standards. The model was applied to a sediment core collected from Santa Monica Bay near the Hyperion 7-mi sludge outfall. This model is also applicable to other similar two-component systems, as long as they satisfy the assumptions made under the present study.

Introduction

Linear alkylbenzenes (LABs) have been used to synthesize linear alkylbenzenesulfonate (LAS) surfactants, raw materials in the manufacture of commercial detergents, since the early 1960s. LABs completely replaced highly branched tetrapropylene-based alkylbenzenes (TABs) that had been used previously as precursors for the alkylbenzenesulfonate (ABS) surfactants since the early 1950s. Unsulfonated LAB residues in detergents may be carried into the aquatic environment with wastewater discharges. The presence of LABs has been reported in a variety of media, e.g., municipal wastewater effluent (*1*), sediments (*2*−*6*), water column particles (*7*), and marine species (*8*, *9*). Due to the limited sources for LABs, LABs are useful tracers of domestic waste inputs in the environment (*1*, *10*−*12*).

The difficulty of accurately measuring LABs in environmental samples often arises from the co-existence of TABs, partially due to the overlapping usage of these chemicals in the past. TABs are believed to have over 80 000 possible congeners that make up a complex suite of largely unresolved chromatographic peaks (*13*). Most TABs and LABs elute closely under normal chromatographic conditions. The ion fragments of LABs and TABs from GC/MS essentially overlap, although the relative abundances of their characteristic ion fragments are generally different. Therefore, interference is inevitable.

In this paper, we will present a two-component model that can calculate quantitation errors in measuring LABs using GC/MS in the presence of TABs. Interference by TABs has been recognized for a long time (*1*, *13*), but its magnitude was only discussed (*13*, *14*). Particularly, in sediments where both LABs and TABs have been well preserved, any attempt to use these compounds as time tracers is questionable without consideration of their mutual interference. The model to be described in this paper provides for the first time a quantitative approach to this problem. We have attempted to quantitate errors associated with LAB measurements due to the TAB interference and to enhance the confidence of using LABs and TABs in tracing sedimentation histories. Sections of a sediment core collected in Santa Monica Bay near the Hyperion 7-mi sludge outfall (Los Angeles, CA), which was in use between 1957 and 1987, have been analyzed to demonstrate the usefulness of this model. Since the commercial usage of LABs and TABs overlapped in the early 1960s, buried sediments near the 7-mi outfall were expected to preserve both LABs and TABs.

LABs normally found in environmental samples contain 10−14 carbons in the alkyl chain. The phenyl ring may be located at various positions of the alkyl chain except the terminal carbon, resulting in several LAB isomers for each alkyl chain length. In this paper, individual LABs are often labeled as C_i-LAB-n, where i = 10−14 and n = position number of the phenyl ring (e.g., 1 indicates the terminal position of the alkyl chain). We will first present the analytical procedure for characterization of a pure LAB mixture (secondary standard) that was used for analyses of the sediment samples. We will then derive the two-component model and apply it to the LAB and TAB interference problem found in the core sediments.

Experimental Section

Materials. We were grateful to obtain the pure LAB mixture from Dr. Robert Bowen (Science Applications International Corporation, Narragansett, RI) and a diluted TAB mixture from Dr. Robert Eganhouse (United States Geological Survey, Reston, VA). 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 was purchased from Pfaltz & Bauer (Waterbury, CT). Internal (2-fluorobiphenyl and *p*-terphenyl-d_{14}) and surrogate

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(phenanthrene-d_{10}) standards were acquired from Ultra Scientific, Inc. (North Kingstown, RI). Ultra resi-analyzed grade hexane and methylene chloride and Baker-analyzed grade methanol were obtained from J. T. Baker Inc. (Phillipsburg, NJ). All standard solutions were prepared in hexane. A 60−200 mesh silica gel from EM Science (Gibbstown, NJ) and a 60−235 mesh basic alumina from Fisher Scientific (Pittsburgh, PA) were treated with methanol and methylene chloride, dried in a hood overnight, and activated at 180 and 250 °C, respectively, overnight.

Sample Collection and Extraction. A 96-cm sediment core was collected at station E6 near the Hyperion 7-mi outfall (33°55.7′ N/118°33.34′ W) on June 20, 1994, using a modified gravity corer (*15*). The core was sliced into 2-cm subsections and frozen in the field before being transported to the laboratory. In this paper, the subsections are defined by the depth of the upper edge of the core. For example, a depth of 38 cm means a section from 38−40 cm down the core.

The sediments were thawed and homogenized with a glass rod prior to extraction. About 40 g of the sample was centrifuged in a 250-mL glass bottle to remove excess water and mixed with approximately 50 g of anhydrous sodium sulfate and 100 mL of methylene chloride. The sample bottle was rolled on a roller table for 16, 6, and 16 h. Extract was removed, and new solvent was added between extractions. The combined extract was concentrated to about 3 mL using a rotary evaporator at 30 °C and reduced pressure and then exchanged into hexane. Activated copper granules were added to the extract (overnight in the dark) to remove sulfur. The extract was concentrated to 1 mL under gentle nitrogen flow. Total extractable hydrocarbon (TEH) was determined by weighing, and an appropriate amount of the extract was applied to a 30 cm × 1 cm i.d. 1:2 alumina/silica gel glass column. After the first fraction containing aliphatic hydrocarbons (not analyzed in the present study) was collected, the second fraction, which contained LABs, was collected by eluting 5 mL of dry hexane and 30 mL of a 30/70 mixture of methylene chloride/hexane through the alumina/silica gel column. The extract was concentrated to approximately 1 mL using the rotary evaporator and further concentrated to 0.5 mL under gentle nitrogen flow.

GC/MS Analysis. An HP 5890 Series II GC with a 5970 mass selective detector (MSD) was equipped with a 60 m × 0.25 mm i.d. (0.25 μm film thickness) DB-5 column (J&W Scientific, Folsom, CA). The MSD was operated at the electron impact ionization mode with an electron energy of 70 eV. A mass scanning range of m/z 45−400 was used at 1.7 scan/s. The electron multiplier voltage was set at 1600 V, and the ion source was maintained at 250 °C. The instrument was tuned with decafluorotriphenylphosphine (DFTPP) using U.S. EPA criteria before analysis. Data acquisition and processing were controlled by an HP DOS-based ChemStation data system. Carrier gas used was ultra high purity helium at a flow rate of 2 mL/min at 70 °C. The initial oven temperature was 70 °C, immediately ramped to 200 °C at 6 °C/min and to 285 °C at 10 °C/min, and held for 42 min. 2-Fluorobiphenyl and phenanthrene-d_{10} at 2 μg/mL were used as internal and surrogate standards, respectively.

GC/FID Analysis. A Varian 3500 GC was equipped with a flame ionization detector (FID) and a 60 m × 0.25 mm i.d. (0.25 μm film thickness) DB-1 column. The initial oven temperature of 80 °C was ramped to 285 °C at a rate of 3 °C/min and held for 8 min. A 1-μL sample was injected manually into a split/splitless injector (maintained at 280 °C) with a split time of 1 min and analyzed under the following conditions: carrier gas He ~1.8 mL/min at 80 °C, makeup gas N_2 + He ~20 mL/min, combustion gas H_2 ~24 mL/min, air ~280 mL/min, and the detector temperature at 300 °C. Data were acquired and processed using the PE Nelson Turbochrom 3.3 data system running on an IBM-compatible PC and a PE Nelson 900 Series interface unit. 2-Fluorobiphenyl and *p*-terphenyl-d_{14} were used as internal standards, and phenanthrene-d_{10} was used as a surrogate standard, all at 2 μg/mL.

Results and Discussion

Characterization of the LAB Mixture. Identification of individual LAB components in the LAB mixture was done using the GC/MS method (qualitative analysis), while the composition of the LAB mixture was determined by GC/FID (quantitative analysis). Since there are only a few individual LAB standards available commercially and the LAB-1 compounds are not present in significant quantities in the LAB mixture, this mixture was quantified using the LAB-1 standards, assuming that the responses of all the LABs in an isomer group were identical on GC/FID.

The secondary standard contains isomers of C_{11}−C_{14}-LABs except for C_i-LAB-1 (i = 11−14), a total of 22 components. Two LABs (C_{13}-LAB-7 and C_{13}-LAB-6) co-eluted on the DB-5 column. C_{14}-LAB-7 and C_{14}-LAB-6 were only partially resolved. The selection of a DB-5 column instead of a DB-1 column for GC/MS was due to the reason that the GC/MS system was also simultaneously used for measuring some other organic compounds (e.g., polycyclic aromatic hydrocarbons or PAHs) and the DB-5 column was more suitable than DB-1 in this case. That the eluting sequence of the LAB compounds was identical on the DB-5 (used in GC/MS) and DB-1 columns (used in GC/FID) was confirmed by the analysis of the secondary standard using GC/MS and DB-1 column. For the same reason, internal and surrogate standards used in the present study were primarily chosen for PAH measurements. The use of these standards for LAB measurements was validated by excellent calibration results with these standards and LABs, by the fact that PAHs and LABs were eluted in the same fraction in sample preparation, and by the similarity between the average recovery of all LAB compounds (77.5 ± 3.8%) and that of the surrogate standard (81.5 ± 10.2%) in five spiked sediment samples.

Figure 1 shows typical ion profiles for C_{12}-LAB-n (n = 2−6). The distinct fragmentation patterns within a specific isomer group allowed identification of the individual components in the LAB mixture by comparing the mass spectra of the components to the reference spectra stored in the ChemStation data system. The fits were normally better than 80 with 100 being perfect.

The relative response factor (RRF) of a LAB congener relative to an internal standard was obtained by a linear fit of the peak area ratio versus the concentration ratio of the LAB congener and a related internal standard in a series of solutions in 0.1, 0.4, 1, 2, 5, and 10 μg/mL of each primary standard. These RRFs were used to quantify three secondary standard solutions prepared at total concentrations of 25, 50, and 100 μg/mL and analyzed twice using GC/FID. Since C_{11}-LAB-1 was not available to us at the time of this study, C_{10}-LAB-1 was used to quantify C_{11}-LABs. Our measurements obtained similar RRFs for all the primary standards; therefore, it was expected that the relative

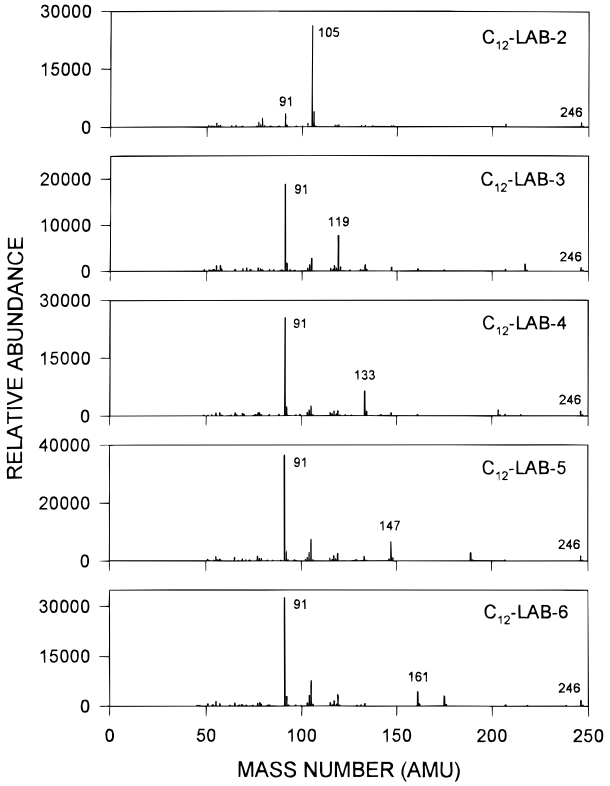

FIGURE 1. Typical ion profiles of C_{12}-LAB-2, C_{12}-LAB-3, C_{12}-LAB-4, C_{12}-LAB-5, and C_{12}-LAB-6.

TABLE 1

Measured Composition of Secondary Standard (LAB Mixture) by GC/FID Using DB-1 Column

LAB compounds[a]	av ($n = 6$)	RSD (%)
6-phenylundecane*	0.0142	9.1
5-phenylundecane*	0.0269	8.5
4-phenylundecane*	0.0200	8.2
3-phenylundecane*	0.0190	9.0
2-phenylundecane*	0.0180	9.8
6-phenyldodecane*	0.0686	11.1
5-phenyldodecane*	0.0628	10.8
4-phenyldodecane*	0.0459	10.9
3-phenyldodecane*	0.0432	12.1
2-phenyldodecane*	0.0398	12.7
7&6-phenyltridecane**	0.1446	10.2
5-phenyltridecane**	0.0886	9.7
4-phenyltridecane**	0.0635	9.8
3-phenyltridecane**	0.0593	9.3
2-phenyltridecane**	0.0546	7.9
7-phenyltetradecane**	0.0178	8.5
6-phenyltetradecane**	0.0168	8.4
5-phenyltetradecane**	0.0163	7.7
4-phenyltetradecane**	0.0111	7.4
3-phenyltetradecane**	0.0098	9.2
2-phenyltetradecane**	0.0083	6.3
∑LAB	0.8489	9.4 (av)

[a] Relative to 2-fluorobiphenyl indicated by *. [b] Relative to *p*-terphenyl-d_{14} indicated by **.

response factors of C_{10}-LAB-1 and C_{11}-LAB-1 were also similar. Table 1 presents an average composition of the secondary standard from six measurements. The average recovery of total LABs from the measurements was 84.9% relative to the gravimetric weight of the secondary standard injected (the average recovery of the surrogate standard was 87%), probably suggesting the presence of some unknown residues in the LAB mixture.

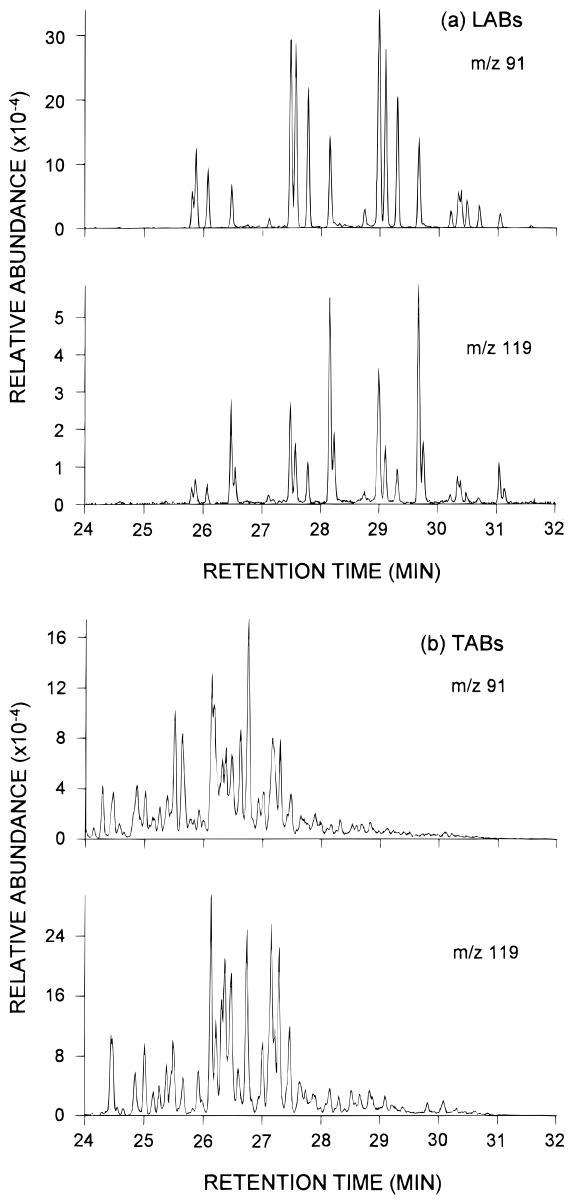

FIGURE 2. Ion chromatograms of *m/z* 91 and 119 for (a) LAB mixture and (b) TAB mixture.

Analysis of Sediment Samples by GC/MS. The secondary standard characterized was used to prepare calibration standards at 2, 5, 20, 50, and 200 μg/mL total LABs and analyzed using GC/MS. RRFs of individual LABs in the secondary standard were obtained using the same procedure as described above and used to quantify LAB components in the sediment samples. Since our intention was to identify the magnitude of interference by TABs in measuring LABs in the sediment samples, only qualitative results from the analysis of three sections (38−40, 68−70, and 80−82 cm) are described here; some of the quantitative data can be found elsewhere (*16*).

TABs generally have a strong fragment at m/z 119 and relatively weak signals at m/z 91, 105, and 133 under the chromatographic conditions used in the present study. The fragmentation patterns of TABs significantly differ from those of LABs. As a comparison, Figure 2 shows the ion chromatograms of m/z 91 and 119 from the LAB and TAB standards. Ion chromatograms of m/z 91 and 119 were also extracted from GC/MS chromatograms of the samples (Figure 3). The pattern of LABs in the sediment samples

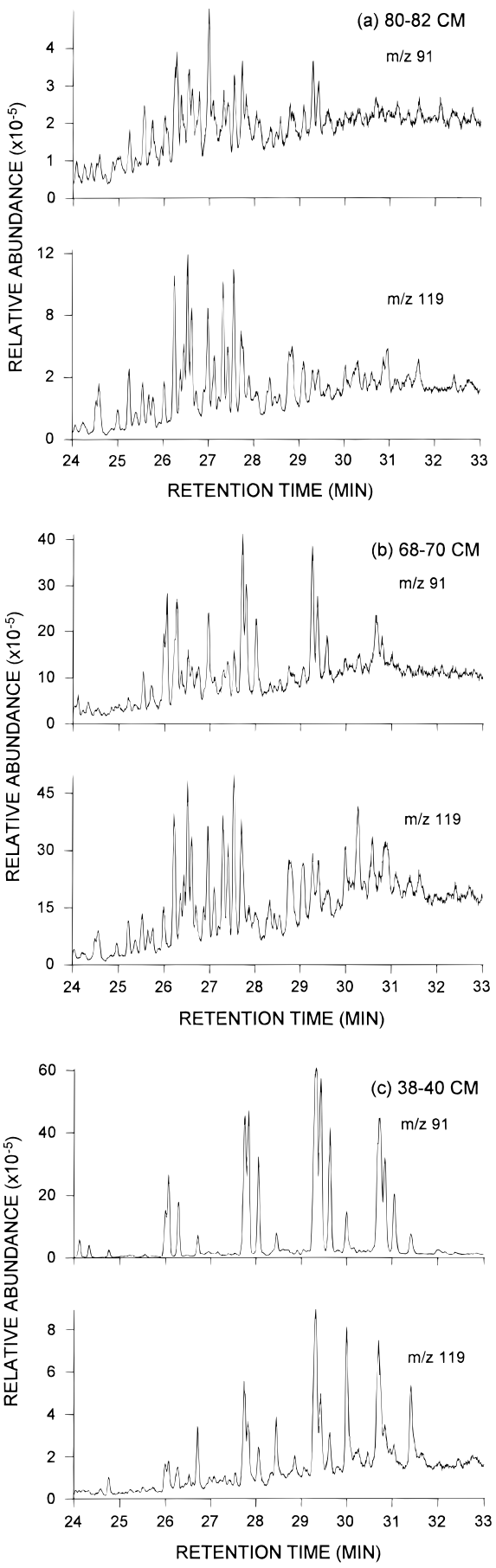

FIGURE 3. Ion chromatograms of *m/z* 91, 105, 119, and 133 for the E6 core sediments at (a) 80−82 cm, (b) 68−70 cm, and (c) 38−40 cm.

(especially at the upper sections) resembled that of the secondary standard, i.e., C_{13}-LABs were most prominent with little or no C_{10}-LABs present. The LABs found in the Hyperion 7-mi outfall effluent had a similar pattern (*1*). The presence of TABs was apparent, reflected in the relative abundances of m/z 91 and 119 and overall patterns throughout the sediment core.

At the 80-cm depth, the m/z 119 fragment was qualitatively more abundant than m/z 91 (Figure 3a). The most prominent and resolved group of peaks occurred between the retention times of C_{11}-LABs and C_{12}-LABs. This was consistent with the fact that the majority of TABs contain 12 carbons in the branched side chain (*14*). The ion chromatogram of m/z 91 contained only partially baseline-resolved peaks with an elevated baseline. The contribution to m/z 91 from LABs might have overlaid on top of the TAB background. The total LAB concentration at this depth was considerably low with high measurement uncertainty. At 68 cm, the abundances of m/z 91 and 119 became comparable (Figure 3b). In addition, the pattern of m/z 91 similar to that of the secondary standard (Figure 2a) started to appear. In core sections at and above 38 cm, the characteristic pattern of m/z 119 associated with TABs nearly disappeared (Figure 3c). An ion chromatogram of m/z 91 with a fairly clean background was observed, and the relative abundance of m/z 91 to m/z 119 was close to that found in the LAB mixture (Figures 2a and 3c).

The above observations led to the conclusion that TABs were dominant at 80 cm and detectable at 68 cm of the sediment core. Due to the similar characteristics of LABs and TABs in retention time and ion fragment (Figure 2), especially between the retention times of C_{11}-LABs and C_{12}-LABs, even the GC/MS method was unable to effectively differentiate the contributions from LABs and TABs based on the characteristic ions. In an area with both LABs and TABs present, quantitation of LABs might be quite inaccurate. Obviously, to obtain accurate LAB contents, additional considerations are needed to account for or evaluate the impact of the TAB interference. This is especially crucial when low levels of LABs are encountered.

Quantitative Approach to the TAB Interference Problem. Herein we will derive an equation that can quantitatively calculate the magnitude of interference by TABs. In our approach, three assumptions are made: (I) only LABs and TABs contribute to m/z 91 and 119; (II) LABs contain a strongest ion fragment at m/z 91 and a minor component of m/z 119; and (III) TABs contain a strongest ion fragment at m/z 119 and a minor component of m/z 91.

Assumption I basically assumes a two-component model for the equation to be derived. Assumption II is designed specifically for all LABs except C_i-LAB-2 for which the major fragment considered should be m/z 105. Assumption III indicates that TABs may interfere with the quantitation of LABs by contributing m/z 91 to the measured abundance of m/z 91 in a given sample. Assumptions II and III imply that the relative abundance of m/z 91 to m/z 119 is always greater than 1 for LABs (except for LABs-2) and less than 1 for TABs, which appears to be the case as shown in Figure 2. It is impossible to distinguish the contributions from LABs and TABs if assumptions II and III are not satisfied.

For a given chromatographic peak in a sample, A and A' are defined as abundances of m/z 91 and 119, respectively; B and B' are abundances of m/z 91 and 119 contributed from a LAB compound (or mixture); and C and C' are

abundances of m/z 91 and 119 contributed from a TAB compound (or mixture). According to assumption I:

$$A = B + C \tag{1}$$

$$A' = B' + C' \tag{2}$$

In mass spectroscopy, the relative abundance of certain characteristic fragments for a given compound is fairly invariant under given chromatographic conditions, which is the basis for peak identification. Hence, we may define

$$B' = XB \tag{3}$$

$$C' = X'C \tag{4}$$

where X and X' are the relative abundances of m/z 119 to m/z 91 contributed from a LAB compound and a TAB compound, respectively. In particular

$$0 < X < 1 \text{ and } X' > 1 \tag{5}$$

must be satisfied based on assumptions II and III. Substituting eqs 3 and 4 into 2 yields

$$\frac{A'}{X'} = \left(\frac{X}{X'}\right)B + C \tag{6}$$

Subtracting eq 6 from eq 1 gives

$$A - \frac{A'}{X'} = B - \left(\frac{X}{X'}\right)B$$

or

$$B = \frac{X'A - A'}{X' - X} \tag{7}$$

In eq 1, A is measured directly from sample analysis and B is the contribution of m/z 91 of a LAB compound. Therefore, we may define the quantitation error, E, as

$$E\,(\%) = 100 \times \left(\frac{A - B}{B}\right) \tag{8}$$

By substituting eq 7 into eq 8 and performing a simple calculation, we obtain

$$E\,(\%) = 100 \times \left(\frac{1 - \beta X}{\beta X' - 1}\right) \tag{9}$$

with

$$\beta = A/A' \tag{10}$$

Since E is always positive by definition, as shown in eq 8, there are constraints for the combined values of β, X, and X'. Specifically, the following relations must be satisfied under any circumstances:

$$\beta X \le 1 \text{ and } \beta X' > 1 \tag{11}$$

or

$$\beta X \ge 1 \text{ and } \beta X' < 1 \tag{12}$$

In fact, eqs 11 and 12 are equivalent. While eq 11 complies with assumptions II and III and will be used here, eq 12 only interchanges the designation of the relative abundances of m/z 91 and m/z 119 for LABs and TABs. Since eq 5 already limits the ranges of X and X', β has to vary accordingly. In addition, $\beta X' = 1$ in eq 9 is a singular point mathematically. Practically, at $\beta X' = 1$, we have $A/A' = B/B' = C/C'$, and contributions from LABs and TABs cannot be distinguished. $\beta X' = 1$ also violates assumptions II and III. In summary, any error in quantifying a particular LAB compound (or mixture) in the presence of TABs may be calculated from eq 9 with the constraints given in eqs 5 and 11.

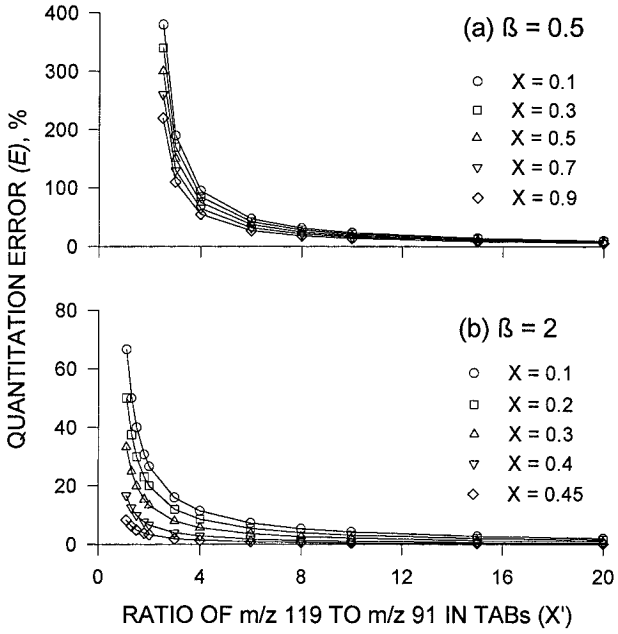

FIGURE 4. Relationships between *E* and *X'* at various *X*: (a) β = 0.5 and (b) β = 2.

Using eq 9, we may elucidate some generalizations regarding the TAB interference problem. Three conclusions can be made from Figure 4, showing the trends of E with respect to X' under various X and β values. First, E decreases almost exponentially with increasing X' at small X's and becomes nearly linear at large X's. This indicates that a TAB compound with a larger ratio of m/z 119 to m/z 91 will exert less interference than one with a small ratio at fixed X and β. Secondly, as β increases (from Figure 4, panel a to panel b) or m/z 91 is enhanced relative to m/z 119 in the sample, the quantitation error will decline. This is a direct consequence of assumptions II and III. Since m/z 91 is a major fragment in LABs and a minor one in TABs, enhanced m/z 91 abundance at fixed X and X' can only be contributed largely from LABs, thus reducing the error. Finally, large X values give small E's. A large X value at fixed X' and β means high B' or high m/z 119 abundance in LABs, leading to low abundance of C' or m/z 119 in TABs. Since X' is fixed, C is also lowered with decreasing C', resulting in small E. Practically, this states that quantitation of C_i-LAB-3 (with a larger X) is impacted less by TABs compared to other LABs at fixed X' and β. However, as shown below, E is not very sensitive to X, as compared to X'.

It should be noted that the above conclusions portray only one of the scenarios in each case. Since Figure 4 was constructed directly from eq 9 which is limited only by assumptions I–III, the conclusions strictly reflect the facts. Other scenarios are possible but have to satisfy assumptions I–III.

Since LABs and TABs are interchangeable as two components in the model, an equation equivalent to eq 9 may be derived to calculate the quantitation errors in measurements of TABs with interference from LABs. This can be done by redefining the quantitation error given in

TABLE 2

Values of X and β Calculated from Analyses of LAB Mixture and E6 Core Sediments

LABSs	X	β 80 cm	68 cm	58 cm	48 cm	38 cm
C_{11}-LAB-6	0.074	0.45	1.06	7.0	7.9	10.4
C_{11}-LAB-4	0.068	0.63	0.84	4.4	14.0	10.6
C_{11}-LAB-3	0.588	0.35	0.38	1.9[a]	2.1[a]	2.6[a]
C_{12}-LAB-6	0.101	0.33	0.79	5.2	7.1	8.9
C_{12}-LAB-4	0.054	0.76	1.40	6.3	7.5	13.6
C_{12}-LAB-3	0.413	0.52	0.23[b]	2.2	2.3	2.8[a]

[a] These values give $\beta X > 1$; hence, the related E's were given a zero value in Figures 5 and 6. See text for details. [b] Not included in Figures 5 and 6 due to violation of $\beta X' > 1$ ($X' = 3.1$). See text for details.

eq 8. If E' is defined as the quantitation error in measuring TABs with interference from LABs, using a process similar to that in obtaining eq 9, we may obtain

$$E'\,(\%) = 100 \times \left(\frac{A - C}{C}\right) = \left(\frac{1 - \beta X'}{\beta X - 1}\right) \qquad (13)$$

Equations 9 and 13 are different only in the positions of X and X'.

Application of the Two-Component Model. The quantitation errors from the measurements of LABs in the E6 sediment core were calculated using eq 9 and are demonstrated below. Since TABs mainly appeared between the retention times of C_{11}-LABs and C_{12}-LABs (Figure 2), we considered C_{11}-LABs and C_{12}-LABs only.

β values were obtained directly from the abundance ratios of m/z 91 to m/z 119 in the samples. It was found that the m/z 119 abundances of C_{11}-LAB-5 and C_{12}-LAB-5 gradually decreased with increasing core depth and disappeared at the bottom sections. This might indicate that little or no TAB interference for these two compounds was present; therefore, they were not included in the calculation. Figure 2 indeed shows that the abundances of m/z 91 in the TAB standard at the retention times similar to those of C_{11}-LAB-5 and C_{12}-LAB-5 were fairly low. The contributions of m/z 91 from TABs at these retention times might be absent in the samples. However, the retention times of C_{11}-LAB-5 and C_{12}-LAB-5 were close to those of C_{11}-LAB-6 and C_{12}-LAB-6, respectively. As illustrated below, the quantitation errors in measurements of C_{11}-LAB-6 and C_{12}-LAB-6 were fairly high. More data are needed to verify this observation.

X values were obtained from the analysis of the pure LAB mixture (no significant amounts of TABs present) and considered constant for each LAB compound throughout the core. Table 2 lists the X and β values for the selected LAB compounds. β increased with decreasing core depth for all but C_{11}-LAB-4 (higher β at 48 cm than at 38 cm) and C_{12}-LAB-3 (higher β at 80 cm than at 68 cm). This general trend verified the findings shown in Figure 3, i.e., lower TAB contents were found at shallow-depth sediments. There were four βX values (see footnote in Table 2) that violated eq 11. TABs at these particular depths might actually be very low, making the ratio of m/z 91 to m/z 119 in the sample close to that in the standard. Consequently, a small fluctuation in the measurement of m/z 91 and 119 in the sample would have violated the constraint $\beta X \leq 1$. Nevertheless the extremely low TAB concentrations indicated negligible quantitation errors at these depths; hence a zero was given to the E value for each of these samples.

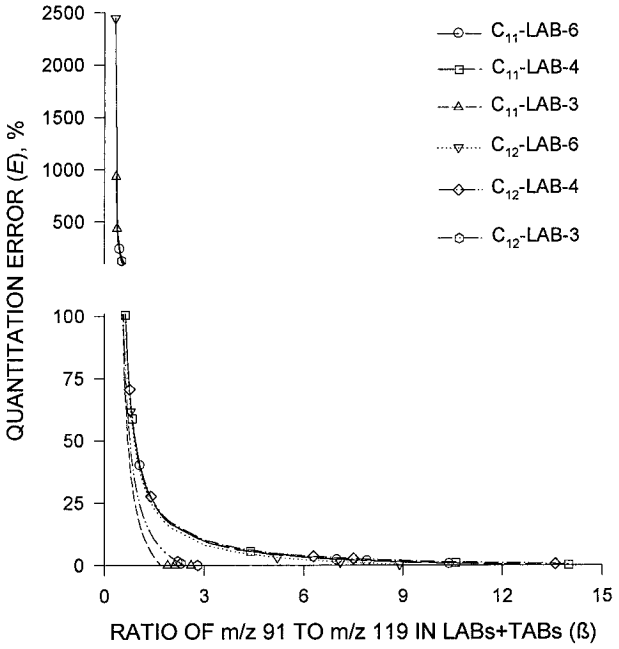

FIGURE 5. Relationships between E and β at $X' = 3.1$ and various X (see text for details).

The selection of X' values was based on the analysis of the TAB mixture (no significant amounts of LABs present) and the restriction $\beta X' > 1$. Due to the actual range of β values in the samples (Table 2), X' had to be greater than 3 to ensure $\beta X' > 1$ for all the LABs at all the depths (except for C_{12}-LAB-3 at 68 cm), especially at 80 cm ($\beta = 0.33$ for C_{12}-LAB-6) where the presence of TABs was obvious. To estimate X' from the TAB mixture, we extracted the ion chromatograms of m/z 91 and 119 (Figure 2b). The abundances of these two ions were summed around the retention times of the LAB compounds given in Table 2. The average ratio, X', of the abundances of m/z 119 and 91 turned out to be ~2.8, a little smaller than expected ($\beta X' > 1$ not satisfied). However, considering the complex nature of the samples and TAB mixture, the discrepancy between the X' value (~2.8) measured from the TAB standard and that (~3.1) derived from the sample analysis using $\beta X' > 1$ was acceptable. We decided to select $X' = 3.1$ to satisfy $\beta X' > 1$. Obviously, the X' value had to be assumed identical for all TABs. Since E decreased with increasing X' (Figure 4), it is apparent that the quantitation errors calculated here represented upper limits.

Figure 5 shows the relationships between E and β obtained from eq 9 with X and β given in Table 2 and $X' = 3.1$. Four of the six curves in Figure 5 essentially overlap. These four curves are associated with C_{11}-LAB-6, C_{11}-LAB-4, C_{12}-LAB-6, and C_{12}-LAB-4 with X values ranging from 0.054 to 0.101 (Table 2). This indicates that E is not sensitive to X at small X values. Two other curves, related to C_{11}-LAB-3 and C_{12}-LAB-3 with larger X values (Table 2), approach zero very quickly as β increases. Since all LABs except for C_i-LAB-3 and C_i-LAB-2 have similar relative abundances of m/z 119 and m/z 91, they may be treated as one entity in using eq 9. This would simplify the estimation of E on a routine basis.

The variation of E with core depth is demonstrated in Figure 6, which was converted from Figure 5. A low β value (0.23, see Table 2) for C_{12}-LAB-3 at 68 cm did not satisfy $\beta X' > 1$, which cannot be explained presently. Otherwise, E increased with increasing core depth (Figure 6). The

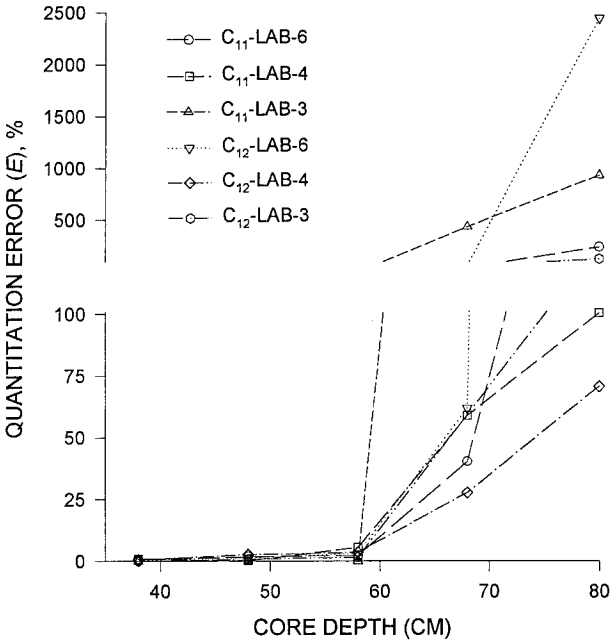

FIGURE 6. Variation of *E* with sediment core depth at station E6.

quantitation errors at 80 cm varied from ~70 to 2450% for six LAB compounds considered. The highest *E* value, 2450%, occurred at 80 cm for C_{12}-LAB-6. Below this depth, the concentrations of both LABs and TABs were extremely low, probably reflecting the sedimentation history prior to the usage of the Hyperion 7-mi sludge outfall. The quantitation errors became significantly smaller at 68 cm than at 80 cm and essentially vanished at or above the 38-cm depth for all LABs.

Summary and Conclusions

It is clear that the magnitude of interference from TABs in measurements of LABs may be quantitatively assessed using eq 9 or vice versa using eq 13 based on the two-component model. *X* values may be obtained for individual LAB compounds, but LABs with similar *X* values can be treated together. On the other hand, it was only possible to obtain an average *X′* for TABs. *X* and *X′* values are obtained from LAB and TAB standards, respectively, and should be relatively invariant under given experimental conditions. Therefore, the key to applying eq 9 or eq 13 in field samples is an accurate measurement of β (=*A*/*A′*) values. The present study demonstrated the application of eq 9 in a sediment core from Santa Monica Bay near the Hyperion 7-mi sludge outfall (Figures 5 and 6). It should be noted that, however, more field studies are needed to test the model. For instance, it would be interesting to apply our model to the LAB and TAB profiles in a sediment core collected from the San Pedro Shelf (*4*).

As mentioned previously, both eqs 9 and 13 were derived based on a two-component system, i.e., assumption I. For systems containing more than two components, additional terms have to be added to eqs 1 and 2. This will greatly complicate the mathematical approach and is beyond the scope of the present study. Finally, the model presented above is actually applicable to any other similar systems, as long as they satisfy assumptions I–III.

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