Free webinar

September 28, 2021
10am EDT, 7am PDT, 2pm BST
1pm EDT, 10am PDT, 6pm BST

Evaluationg Stormwater to Identify & Quantify Causal Toxins from Tire Degradants in Coho Salmon Mortality

For decades, scientists had been concerned about water quality impacts on Pacific Northwest coho salmon that returned from the Pacific Ocean to spawn in local streams and rivers. After rain events in the area, acute and widespread mortality of adult coho salmon in the streams occurred; this was subsequently called urban runoff mortality syndrome (URMS). The cause of this phenomena was unknown for many years with many regulated chemicals and pathogens ruled out as culprits.

This webinar will take you through the journey of researchers at the University of Washington successfully identifying the primary chemical cause of this mortality – 6PPD-quinone. 6PPD-quinone is an oxidation product of 6PPD, an industrial antioxidant compound commonly used in tires. Ed Kolodziej will go through how his team were the first to identify the emerging contaminant using effect-directed analysis workflows paired with a high-resolution LC-Q/TOF and software tools. He will also demonstrate the steps that the led to linking coho mortality to 6PPD and its degradation product 6PPD-quinone.

Following this, researchers at Vogon Laboratories will discuss developing a routine quantitative method on a liquid chromatograph coupled to a triple quadrupole mass spectrometer (LC/TQ) for analysis of 6PPD-quinone. This presentation describes a fast, direct-inject analytical method for the quantitation of 6PPD-quinone in surface water.

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SOME MASS SPECTRAL AND ANALYTICAL ASPECTS OF DEUTERIUM LABELING OF STRAIGHT-CHAIN OLEFINS*

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Abstract—A calculation method has been developed to enhance the effect of deuterium labeling in the mass spectra of linear vicinal dideuterioalkanes (LVDA). Individual LVDA can be identified from these enhanced spectra. Single carbon-number mixtures of LVD nonanes and LVD decanes have been analyzed successfully using matrices derived from spectra of standards. In addition, enhanced mass spectra have been predicted for all of the LVD heptadecanes and LVD nonadecanes. Matrices have been constructed from the predicted spectra, and preliminary tests of these matrices have been conducted. All identifications and analytical results on the LVDA studied can be used to identify the precursor olefins.

INTRODUCTION

ONE PHASE of research at the Bureau of Mines Laramie Energy Research Center is the analysis of the olefinic fraction of shale oil. The composition of this fraction is of considerable interest because shale oil contains as much as 30 to 40% olefinic material. Many of the olefinic compounds in shale oil are in the C_{10} to C_{20} carbon-number range; thus it is important to have analytical methods for determining olefins in this molecular weight range. These methods should allow the qualitative and the quantitative determinations of olefins, including the elusive position of the double bonds.

Application of mass spectroscopy to analysis of olefins and mixtures of olefins is difficult, if not impossible. Problems arise because of the almost indistinguishable mass spectra obtained from olefins of close structural similarity, differing only in the position of the double bond.[2 to 5] To overcome these difficulties, others have obtained derivatives of olefins and mass spectra of the derivatives were correlated with the structure of the original olefin.[6 to 10]

As a first step in characterizing the olefins in shale oil, we have studied the feasibility of analyzing the linear monoolefins. This was done by specifically deuterating the double bonds in known olefins and single-carbon-number mixtures of known olefins. The spectra of the resulting linear vicinal dideuterioalkanes were then used for the study. When deuterated alkanes were not available for direct measurement of their spectra, a first approximation to spectral intensities was made by calculation, using a simple model for the fragmentation of the alkanes. In the method reported, the significance of deuterium labeling was enhanced by a calculation that will be described. Mixtures of linear single-carbon-number monoolefins can be analyzed after they have been deuterated to the corresponding dideuterioalkanes.

Our work is based on the interpretation of the mass spectra of several linear vicinal dideuterioalkanes (LVDA). Correlations of the mass spectra of these LVDA are made with the double-bond position of the original olefin. A matrix similar to those often used for type analysis[11] has been constructed for analyzing C_8, C_9 and C_{10}

* See Ref. 1.

linear monoolefins using spectra of the corresponding LVD octanes, LVD nonanes and LVD decanes. As a test of the method, two mixtures have been successfully analyzed. One of the mixtures contained LVD nonanes; the other contained LVD decanes.

This work includes the prediction of spectra for all the C_{17} and C_{19} LVDA and construction of matrices for the analysis of mixtures of LVD heptadecanes or mixtures of LVD nonadecanes. Refinement and further extension will lead to a more widely applicable mass spectral method for the analysis of LVDA and, consequently, their precursor olefins. Preliminary work has been done on the prediction of other spectra for LVDA in the C_{11} to C_{20} range.

DISCUSSION AND RESULTS

Fragmentation model and enhancement treatment

The fragmentation model used for this work assumes that: 1. The principal fragment ions of *n*-alkanes arise from simple carbon-carbon bond cleavage followed by hydrogen loss; and that 2. Both of these reactions occur exactly the same in the LVDA as they occur in the corresponding perprotioalkanes.* Consecutive reactions involving deuterium loss are also probable, but correction for these reactions was small and not considered significant. Consequently, they were not used in this work.

Each spectrum was corrected for naturally occurring isotopes. Also, a procedure was developed that will strip a spectrum of all ions except those produced by single carbon-carbon bond cleavages. This procedure enhances the effect of deuterium labeling by showing more clearly the position of double bonds in precursor olefins. (See Appendix A.)

Fig. 1 shows a partial mass spectrum of *n*-decane, a partial mass spectrum of *n*-decane-2,3-d_2 and an enhanced partial mass spectrum of *n*-decane-2,3-d_2. Figs. 1a and 1b show the differences between the spectra of *n*-decane and *n*-decane-2,3-d_2. Fig. 1c shows the effect of the enhancement procedure. This partial spectrum shows that the assumption made for the enhancement calculation is adequate for all carbon-number regions of the spectrum above C_5. If the assumption were totally correct, the enhanced spectrum (Fig. 1c) should contain peaks only at *m/e* 57, 59; 71, 73; 85, 87; 99, 101; 114, 115 and 144. For the regions C_6, C_7 and C_8, the calculation removes nearly all of the peaks except those predicted by the model. In the C_4 and C_5 regions, the simple model is not adequate because large peaks remain at *m/e* 58, 70 and 72. Apparently fragments at C_5 and below are not produced by simple cleavage of the carbon-carbon bond. Ring formation prior to fragmentation could explain this result, as suggested by earlier workers on mass spectra of alkanes.[12,13]

Other small positive or negative residuals are seen in the C_6 and above regions of the enhanced spectra of this dideuteriodecane but are not of sufficient importance to invalidate the use of these spectra. Enhanced spectra of all the other dideuteriodecanes showed small residual or negative peaks of comparable size. The peaks in the C_6-C_8 region are produced by simple cleavage with little or no deuterium rearrangement and are sufficient to identify each of the five LVD decanes. Fig. 2 shows the enhanced spectra of the C_6-C_8 region of the following *n*-decanes: -1,2-d_2, -2,3-d_2, -3,4-d_2, -4,5-d_2 and -5,6-d_2. The enhanced partial spectra shown in Fig. 2 are readily

* Validity for the fragmentation model has been shown by Weinberg and Scoggins[8] in work on several dideuteriooctanes.

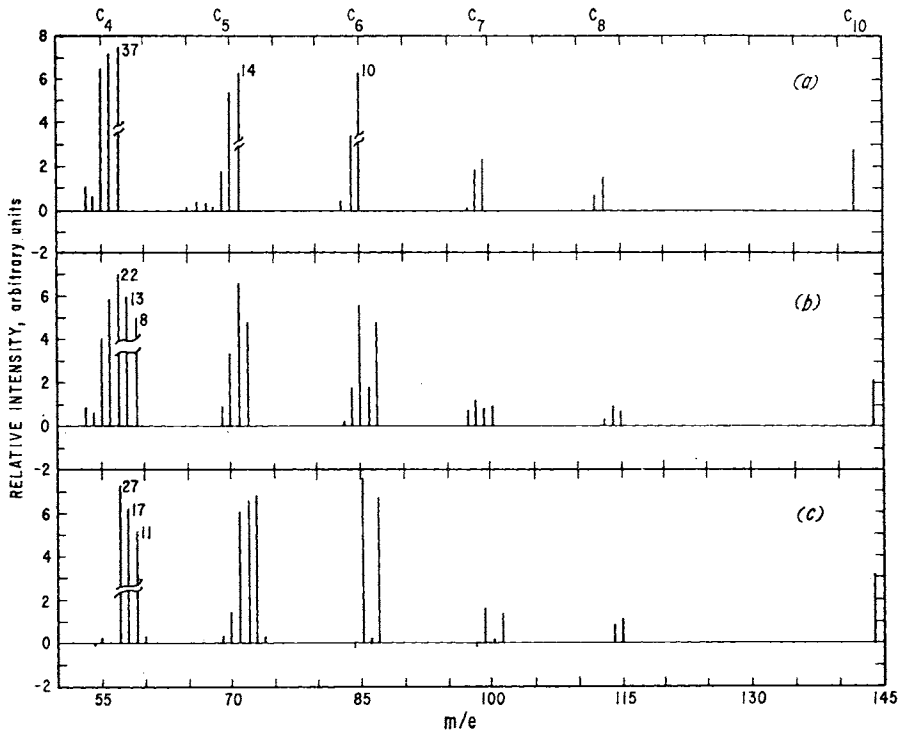

FIG. 1. Partial mass spectra of (a) *n*-decane, (b) *n*-decane-2,3-d_2 and (c) enhancement-corrected *n*-decane-2,3-d_2.

distinguishable from each other, making it easy to identify the five vicinal dideuteriodecanes. The spectra are explained by the simple carbon-carbon bond cleavages as indicated. For example, a peak at *m/e* 115 of *n*-decane-1,2-d_2 is formed by cleavage of the bond between the eighth and the ninth carbon atoms and the charge left with the larger fragment containing two deuterium atoms. The *m/e* 113 peak arises from analogous cleavage between the second and third carbon atoms. The latter fragment does not contain deuterium.

Further examination of Fig. 2 shows that fragmentation model assumptions permit the determination for fragment ions down to as low as the C_6 region. The spectra a, b and c can be distinguished from one another in the C_8 region; the spectra b, c and d can be distinguished from one another in the C_7 region; and finally, the spectra c, d and e can be distinguished from one another in the C_6 region. From the information in Fig. 2, we infer that our model is valid for all bond cleavages that produce ions larger than one-half the molecular ion. Thus C_8 and C_9 molecules must produce C_5 ions and above that fit the model; C_{10} and C_{11} molecules must produce C_6 ions and above that fit the model; and C_{12} and C_{13} molecules must produce C_7 ions and above that fit the model. We have examined all the 1,2-d_2 LVDA from C_8 to C_{19} and find that fragmentation fits the model well enough to positively identify all of them. Consequently, all the precursor olefins can also be identified.

Data are given in Table 1 for all the LVD octanes, nonanes and decanes. Data are given in Table 2 for 1,2- and 8,9-heptadecane-d_2 and 1,2- and 9,10-nonadecane-d_2. The data in both Tables are presented as fractions of the sum of the three possible

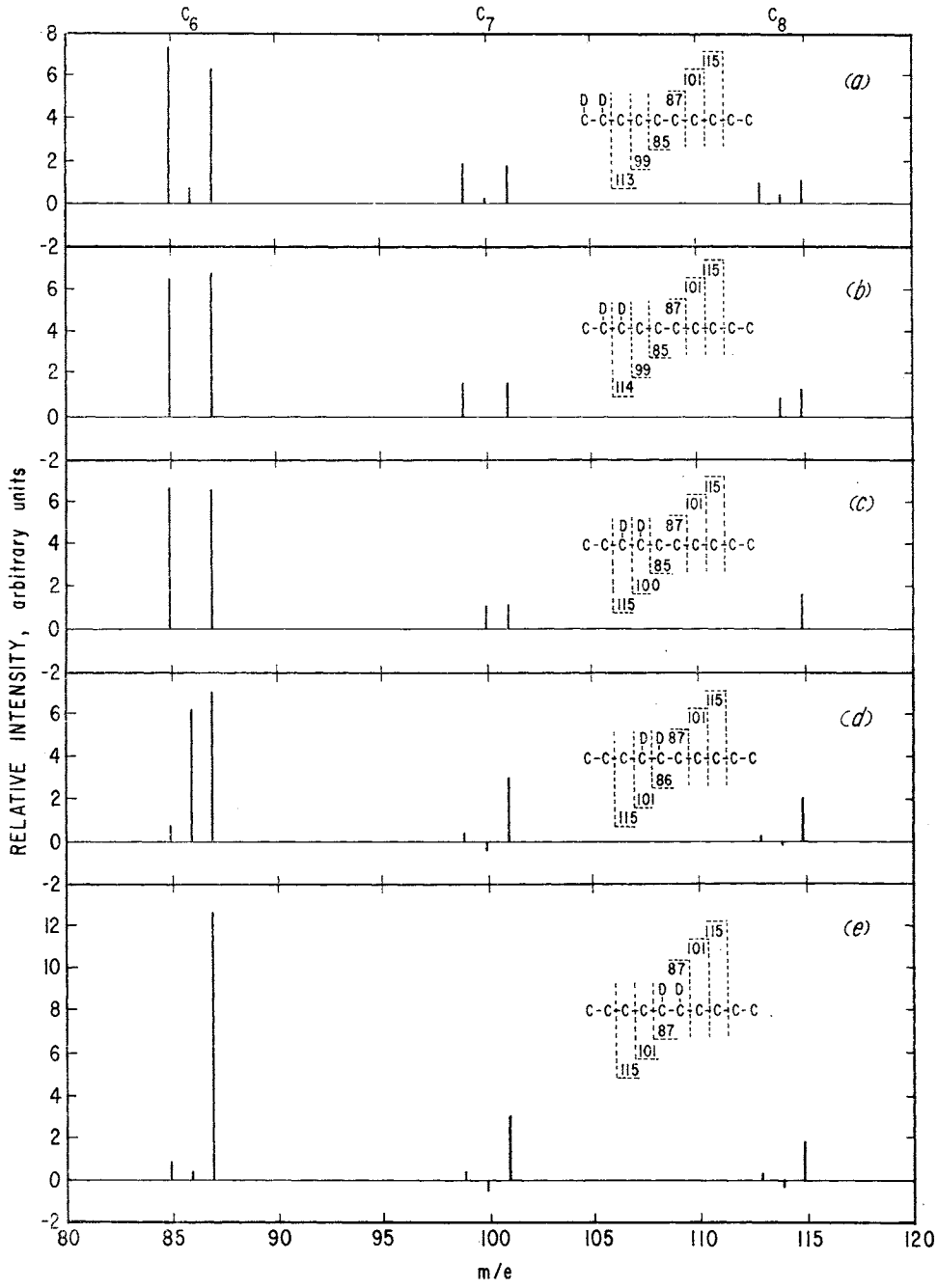

FIG. 2. Enhanced partial spectra of (a) *n*-decane-1,2-d_2, (b) *n*-decane-2,3-d_2, (c) *n*-decane-3,4-d_2, (d) *n*-decane-4,5-d_2 and (e) *n*-decane-5,6-d_2.

TABLE 1. MASS SPECTRAL PATTERNS OF LVD OCTANES, LVD NONANES AND LVD DECANES

Carbon number of fragment	*m/e* of fragment	Fraction of total ionization[a]												
		D positions in LVD octanes[b]				D positions in LVD nonanes				D positions in LVD decanes				
		1,2	2,3	3,4	4,5	1,2	2,3	3,4	4,5	1,2	2,3	3,4	4,5	5,6
	71	0·50[c]	0·54	0·08	0·11	0·47	0·52	0·52	0·10					
C_5	72	−0·01	−0·04	0·47	−0·03	0·05	0·02	0·04	0·45					
	73	0·51	0·51	0·45	0·93[c]	0·48	0·46	0·44	0·45					
	85	0·48	0·06	0·07	0·07	0·49	0·48	0·05	0·07	0·51	0·52	0·50	0·05	0·06
C_6	86	−0·01	0·48	0·01	0·03	0·01	0·01	0·42	−0·01	0·04	0·02	0·02	0·45	0·03
	87	0·53	0·46	0·92	0·90	0·50	0·51	0·53	0·95	0·45	0·46	0·48	0·50	0·92
	99					0·44	−0·04	0·12	0·16	0·51	0·53	0·10	0·13	0·15
C_7	100					0·02	0·56	−0·06	−0·14	0·02	0·04	0·44	−0·11	−0·13
	101					0·54	0·48	0·94	0·98	0·47	0·44	0·46	0·98	0·98
	113									0·42	0·02	0·09	0·11	0·12
C_8	114									0·08	0·43	−0·01	−0·07	−0·11
	115									0·50	0·55	0·92	0·97	0·99

[a] Patterns are given as fractions of total ionization for the three possible primary peaks in each carbon-number region after enhancement.
[b] Derived from literature data.[8]
[c] Each of the listed values is underlined if its theoretical value is 0·50 and boxed if its theoretical value is 1·0.

primary peaks in each carbon-number region (the enhancement correction is done before determining total ion concentration). The fractions in each region should total 1·00.

Theoretical values for all peaks should be 1·00, 0·50 or 0. For the values that should be 0·50, the range of observed values is 0·34 to 0·62. For the values that should be 1·0, the range of observed values is 0·85 to 0·99. For easy comparison, each of the actual values shown in Tables 1 and 2 is boxed if its theoretical value is 1·00 and underlined if its theoretical value is 0·50. For the values that should be 0·0, the range of observed values is −0·14 to 0·20. The greatest deviations from theoretical values occur, Table 2, for the C_{10} and C_{11} regions in the 1,2-d_2-*n*-heptadecane and 1,2-d_2-*n*-nonadecane. Inspection of the data in Tables 1 and 2 shows that there is no difficulty identifying the compound even when these regions are used.

The large deviations from 0 at *m/e* 128 for C_{17} and *m/e* 142 for 1,2-d_2 C_{17} and C_{19} indicate that: 1. A single hydrogen is lost more readily in the labeled compound than in the unlabeled compound, or 2. There is cleavage between the carbon atoms holding the two deuterium atoms. If hydrogen were lost more readily we should see this effect throughout all the spectra, but this is not observed. Therefore, we believe that the bond between the two carbon atoms holding the deuterium is broken. A C_{10} fragment formed by cleavage of this bond has been shown by other workers.[13] Perhaps ring closure occurs prior to the formation of this fragment.

Another interesting phenomenon is the distribution of ions in the 1,2-C_{17}-d_2 and C_{19}-d_2 compounds for the higher-carbon-number fragments. The C_{15} region of the *n*-C_{17} and the C_{17} region of the *n*-C_{19} show a dideuterio fragment to perprotio fragment ratio of nearly 2. This supports the view that a considerable amount of C_2 loss comes from other than terminal carbons. We suggest that this type of loss occurs by ring closure with subsequent cleavage of that ring. Notice that the effect continues into the lower weight fragments until the dideuterio to perprotio fragment ratio approaches 1·0. This would suggest that the larger the cleaved neutral fragment, the better the chance of including the deuterium atoms.

Analytical applications

Data from the literature[8] were used to construct a matrix to analyze mixtures of LVD octanes and spectra on standards of LVD nonanes, and LVD decanes were used to construct matrices to analyze mixtures of C-9's or C-10's. Data from the standards were corrected for naturally occurring isotopes to construct these matrices.

Matrix elements were determined by taking the three most significant peaks from selected carbon-number regions and normalizing to 1·000—for example, two carbon-number regions (C_5 and C_6) were selected for the LVD octanes. In the C_5 region the 71, 72 and 73 peaks were summed and normalized because these peaks are the three primary peaks that can arise from carbon-carbon bond cleavage. For the C_6 region the primary peaks were 85, 86 and 87. From all the peaks determined in this manner, those having the most leverage were used in the matrices. The elements were arranged in the matrices to put the largest on the diagonal. The matrices for the LVD octanes, LVD nonanes and LVD decanes are shown in Table 3, and their corresponding inverses are shown in Table 4.

The data in Table 5 show that the test mixtures of LVD nonanes and LVD decanes are analyzed within ±5% absolute using the matrices shown in Table 4. Because of

TABLE 2. MASS SPECTRAL PATTERNS OF LVD HEPTADECANES AND LVD NONADECANES

Carbon number of fragment	m/e fragment	Fraction of total ionization[a] D positions in LVD heptadecanes 1,2	8,9	D positions in LVD nonadecanes 1,2	9,10
	127	0·41[b]	0·09		
C_9	128	0·20	0·42		
	129	0·39	0·49		
	141	0·42	0·03	0·46	0·08
C_{10}	142	0·13	0·13	0·15	0·43
	143	0·44	0·85[b]	0·39	0·49
	155	0·45	0·08	0·48	0·03
C_{11}	156	0·08	−0·01	0·11	0·11
	157	0·47	0·93	0·41	0·86
	169	0·46	0·09	0·51	0·07
C_{12}	170	0·03	−0·04	0·02	0·03
	171	0·51	0·96	0·47	0·90
	183	0·43	0·11	0·49	0·09
C_{13}	184	0·05	−0·02	0·02	−0·01
	185	0·52	0·91	0·49	0·92
	197	0·41	0·09	0·46	0·09
C_{14}	198	0·05	0	0·05	−0·01
	199	0·54	0·91	0·49	0·92
	211	0·34	0·08	0·42	0·10
C_{15}	212	0·06	−0·03	0·04	−0·03
	213	0·60	0·95	0·54	0·92
	225			0·42	0·08
C_{16}	226			0·03	0
	227			0·55	0·92
	239			0·35	0·07
C_{17}	240			0·03	−0·01
	241			0·62	0·94

[a] Patterns are given as fractions of total ionization for the three possible primary peaks in each carbon-number region after enhancement.

[b] Each of the listed values is underlined if its theoretical value is 0·50 and boxed if its theoretical value is 1·0.

the method for preparing the test mixtures (i.e. deuterating a mixture of olefins) one can see that the method can be applied to mixtures of linear olefins, not just to mixtures of LVDA. These data demonstrate that both qualitative and quantitative analyses can be obtained for mixtures of LVDA and their precursor olefins.

Predictions of spectra of C_{11}-C_{19} n-*alkanes*-1,2-d_2

The ultimate aim of this research is to extend the methods described to higher-molecular-weight compounds. Predictions of their spectra would obviate the

TABLE 3. MATRIX ELEMENTS FOR LVD OCTANES, LVD NONANES AND LVD DECANES AS FRACTIONS OF TOTAL ION INTENSITY FOR PRIMARY PEAKS

	Fraction of total ionization				
	Deuterium positions				
m/e	1,2	2,3	3,4	4,5	5,6
			LVD octanes[a]		
85	0·419	0·134	0·063	0·064	
86	0·118	0·475	0·177	0·188	
72	0·210	0·185	0·457	0·292	
73	0·383	0·383	0·309	0·593	
			LVD nonanes		
99	0·362	0·189	0·090	0·093	
100	0·237	0·497	0·311	0·271	
86	0·129	0·130	0·449	0·210	
72	0·241	0·219	0·229	0·450	
			LVD decanes		
113	0·362	0·157	0·077	0·083	0·094
114	0·246	0·465	0·288	0·259	0·239
100	0·270	0·268	0·464	0·355	0·345
86	0·161	0·147	0·152	0·459	0·248
87	0·381	0·393	0·406	0·371	0·672

[a] Derived from literature data.[8]

TABLE 4. INVERTED MATRICES FOR LVD OCTANES, LVD NONANES AND LVD DECANES

	Deuterium positions				
m/e	1,2	2,3	3,4	4,5	5,6
			LVD octanes		
85	2·64595	−0·69423	−0·07737	−0·02738	
86	0·06697	2·80324	−0·73331	−0·53485	
72	−0·18501	0·08179	3·27715	−1·61967	
73	−1·65578	−1·40476	−1·18408	2·89344	
			LVD nonanes		
99	3·61316	−1·44375	0·27976	−0·00781	
100	−0·85942	3·19201	−1·50770	−1·04109	
86	−0·10477	−0·18960	3·03183	−1·27902	
72	−1·46348	0·68375	−0·95894	3·38395	
			LVD decanes		
113	3·58563	−1·20122	0·37839	−0·11398	−0·25654
114	−0·82983	3·75189	−2·03651	−0·33759	−0·04818
100	−0·68883	−0·65982	4·35690	−1·89235	−1·20741
86	−0·21733	0·05761	−0·04085	3·12679	−1·12305
87	−1·01147	−1·14631	−1·63328	−0·32090	2·99421

TABLE 5. MASS SPECTRAL ANALYSES OF LVD NONANES AND LVD DECANES IN PERCENT[a]

Deuterium position	Known[b]	Calculated	Difference
		LVD nonanes	
1,2	31·2	27·0	−4·2
2,3	21·8	24·4	+2·6
3,4	32·2	31·8	−0·4
4,5	14·8	16·8	+2·0
		LVD decanes	
1,2	31·5	26·6	−4·9
2,3	0	−3·3	−3·3
3,4	17·5	20·1	+2·6
4,5	23·5	24·7	+1·2
5,6	27·5	31·9	+4·4

[a] Volume, mole and weight percent are all equivalent.
[b] Individual olefins were mixed and deuterated.[14,15]

TABLE 6. PREDICTED SPECTRA FOR THE EIGHT LVD HEPTADECANES[a]

Carbon number of fragment ions	m/e	Fraction of total ionization — Deuterium positions 1,2	2,3	3,4	4,5	5,6	6,7	7,8	8,9
	127	0·40[b]	0·40	0·40	0·40	0·40	0·40	0·40	0·10
C_9	128	0·20	0·20	0·20	0·20	0·20	0·20	0·20	0·40
	129	0·40	0·40	0·40	0·40	0·40	0·40	0·40	0·50
	141	0·44	0·44	0·44	0·44	0·44	0·44	0·06	0·03
C_{10}	142	0·14	0·14	0·14	0·14	0·14	0·14	0·44	0·12
	143	0·42	0·42	0·42	0·42	0·42	0·42	0·50	0·85[b]
	155	0·46	0·46	0·46	0·46	0·46	0·04	0·07	0·07
C_{11}	156	0·07	0·07	0·07	0·07	0·07	0·46	0·03	
	157	0·47	0·47	0·47	0·47	0·47	0·50	0·90	0·93
	169	0·46	0·46	0·46	0·46	0·04	0·07	0·07	0·07
C_{12}	170	0·04	0·04	0·04	0·04	0·46			
	171	0·50	0·50	0·50	0·50	0·50	0·93	0·93	0·93
	183	0·43	0·43	0·43	0·04	0·07	0·07	0·07	0·07
C_{13}	184	0·04	0·04	0·04	0·43				
	185	0·53	0·53	0·53	0·53	0·93	0·93	0·93	0·93
	197	0·40	0·40	0·04	0·07	0·07	0·07	0·07	0·07
C_{14}	198	0·04	0·04	0·40					
	199	0·56	0·56	0·56	0·93	0·93	0·93	0·93	0·93
	211	0·35	0·04	0·07	0·07	0·07	0·07	0·07	0·07
C_{15}	212	0·04	0·35						
	213	0·61	0·61	0·93	0·93	0·93	0·93	0·93	0·93

[a] Spectra are tabulated as fractions of total ionization for the three possible primary peaks in each carbon-number region after enhancement.
[b] Each of the listed values is underlined if its theoretical value is 0·50 and boxed if its theoretical value is 1·0.

TABLE 7. MATRICES FOR LVD HEPTADECANES AND LVD NONADECANES COMPILED FROM PREDICTED SPECTRA[a]

Deuterium position	Fraction of total ionization								
	Deuterium positions								
m/e	1,2	2,3	3,4	4,5	5,6	6,7	7,8	8,9	8,9
	LVD heptadecanes-C_{17}								
211	0·35	0·04	0·07	0·07	0·07	0·07	0·07	0·07	
212	0·04	0·35							
198	0·04	0·04	0·40						
184	0·04	0·04	0·04	0·43					
170	0·04	0·04	0·04	0·04	0·46				
156	0·07	0·07	0·07	0·07	0·07	0·46	0·03		
142	0·14	0·14	0·14	0·14	0·14	0·14	0·43	0·12	
128	0·20	0·20	0·20	0·20	0·20	0·20	0·20	0·40	
	LVD nonadecanes-C_{19}								
239	0·34	0·07	0·07	0·07	0·07	0·07	0·07	0·07	0·07
240	0·04	0·34							
226	0·04	0·04	0·38						
212	0·04	0·04	0·04	0·41					
198	0·04	0·04	0·04	0·04	0·44				
184	0·04	0·04	0·04	0·04	0·04	0·50			
170	0·05	0·05	0·05	0·05	0·05	0·05	0·50	0·02	
156	0·10	0·10	0·10	0·10	0·10	0·10	0·10	0·48	0·10
142	0·14	0·14	0·14	0·14	0·14	0·14	0·14	0·14	0·44

[a] Spectra are tabulated as fractions of total ionization for the three possible primary peaks in each carbon-number region after enhancement.

necessity for preparing these compounds and obtaining their mass spectra. Initial attempts have been made to predict the spectra of the C_{11}-C_{19}*n*-alkanes-1,2-d_2. Because the effect of labeling is more discernible after enhancement, the predicted spectra from which the trial matrices are produced are enhanced.

The spectra for all of the LVD heptadecanes and LVD nonadecanes were predicted even though two standard spectra were available for each. The predicted spectra were generated intuitively after a study of the data in Table 2. The prediction process was tested by constructing matrices from the predicted spectra and analyzing mixtures simulated by combining the standard spectra.

Predicted spectra for the eight LVDA heptadecanes are shown in Table 6. Trial matrices were set up for the LVD heptadecanes and LVD nonadecanes using elements from predicted spectra. These matrices are shown in Table 7. Inverse matrices for the LVD heptadecanes and LVD nonadecanes are shown in Table 8.

The actual spectra of 1,2-d_2 heptadecane and 8,9-d_2 heptadecane were averaged to simulate one 50–50 mixture and the actual spectra of 1,2-d_2 nonadecane and 9,10-d_2 nonadecane were averaged to simulate another. Test results of these simulated mixtures are shown in Table 9. The results show that the matrices based on predicted spectra analyzed a mixture of two components to within $\pm 5\%$ absolute. We recognize that a 2-component mixture does not test an entire 8- or 9-component matrix. Our

TABLE 8. INVERTED MATRICES FOR LVD HEPTADECANES AND LVD NONADECANES

	Deuterium positions								
m/e	1,2	2,3	3,4	4,5	5,6	6,7	7,8	8,9	9,10
					LVD heptadecanes				
211	3·34327	0·11746	−0·16441	−0·16862	−0·17264	−0·20362	−0·29186	−0·49752	
212	−0·38209	2·84372	0·01879	0·01927	0·01973	0·02327	0·03336	0·05686	
198	−0·29612	−0·29612	2·51456	0·01493	0·01529	0·01804	0·02585	0·04407	
184	−0·24791	−0·24791	−0·22037	2·33809	0·01280	0·01510	0·02164	0·03689	
170	−0·21019	−0·21019	−0·18683	−0·19162	2·18477	0·01280	0·01835	0·03128	
156	−0·30979	−0·30979	−0·27537	−0·28243	−0·28916	2·22304	−0·14697	0·09830	
142	−0·39940	−0·39940	−0·35503	−0·36413	−0·37280	−0·43971	2·70308	−0·74103	
128	−0·74888	−0·74888	−0·66567	−0·68274	−0·69900	−0·82446	−1·18172	2·98557	
					LVD nonadecanes				
239	3·42660	−0·24939	−0·24939	−0·25613	−0·26254	−0·25112	−0·27902	−0·35245	−0·46504
240	−0·40313	2·97052	0·02934	0·03013	0·03089	0·02954	0·03283	0·04146	0·05471
226	−0·31826	−0·28643	2·65474	0·02379	0·02438	0·02332	0·02592	0·03274	0·04319
212	−0·26392	−0·23753	−0·23753	2·45875	0·02022	0·01934	0·02149	0·02715	0·03582
198	−0·22194	−0·19974	−0·19974	−0·20514	2·28973	0·01626	0·01807	0·02283	0·03012
184	−0·17755	−0·15979	−0·15979	−0·16411	−0·16821	2·01301	0·01446	0·01826	0·02410
170	−0·19293	−0·17364	−0·17364	−0·17833	−0·18279	−0·17484	2·02795	−0·06995	0·04659
156	−0·28127	−0·25314	−0·25314	−0·25998	−0·26648	−0·25490	−0·28322	2·27383	−0·47203
142	−0·49878	−0·44891	−0·44891	−0·46104	−0·47256	−0·45202	−0·50224	−0·63441	2·49626

TABLE 9. MASS SPECTRAL ANALYSES OF SIMULATED TEST MIXTURES OF LVD HEPTADECANES AND LVD NONADECANES IN PERCENT[a]

Deuterium position	Simulated mixture calculated	Simulated mixture theoretical	Difference
	LVD heptadecanes		
1,2	49·9	50·0	−0·1
2,3	−1·4	0·0	−1·4
3,4	1·4	0·0	+1·4
4,5	−1·2	0·0	−1·2
5,6	−5.2	0.0	−5·2
6,7	1·0	0·0	1·0
7,8	0·4	0·0	0·4
8,9	55·1	50·0	5·1
	LVD nonadecanes		
1,2	51·4	50·0	+1·4
2,3	−3·1	0·0	−3·1
3,4	−1·2	0·0	−1·2
4,5	3·9	0·0	+3·9
5,6	−0·1	0·0	−0·1
6,7	−3·1	0·0	−3·1
7,8	+0·1	0·0	+0·1
8,9	2·5	0·0	+2·5
9,10	49·6	50·0	−0·4
	100·0	100·0	

[a] Mole percent, weight percent and volume percent are all equivalent.

results lead us to believe that the matrices would give analyses of equal accuracy for test mixtures containing more components, however. The method should be usable up to the C_{20}–C_{24} range. We feel that larger fragment ions from molecular-weight alkanes above this range have too low an intensity to be analytically useful.

CONCLUSION

The results of this work indicate that any C_8 to C_{20} linear monoolefin, deuterated to its corresponding vicinal dideuterioalkane, can be identified by its mass spectrum. A procedure has been developed for enhancing the effect of this labeling to show more clearly the position of the double bond in linear olefins. The mass spectra of vicinal dideuterioalkanes have been correlated with the precursor olefin, and matrices have been developed for the analysis of C_8, C_9 and C_{10} LVDA mixtures. Preliminary work has been done to predict the spectra of LVDA in the C_{11} to C_{19} carbon-number region. Predicted spectra are given for the C_{17} LVDA, and preliminary matrices have been developed for the C_{17} and C_{19} LVDA. Research so far indicates that this work can be extended to all the LVDA from C_{11} to C_{24} by synthesizing additional selected compounds and predicting spectra for the rest.

EXPERIMENTAL

Mass spectra The 70-volt spectra of 13 vicinal, straight-chain dideuterioalkanes were obtained using a CEC-21-103C mass spectrometer.* The 13 compounds used in this work were: Four *n*-

* Reference to specific brand names is made for identification purposes only and does not imply endorsement by the Bureau of Mines.

nonanes: 1,2-d_2, 2,3-d_2, 3,4-d_2 and 4,5-d_2; Five *n*-decanes: 1,2-d_2, 2,3-d_2, 3,4-d_2, 4,5-d_2 and 5,6-d_2; Two *n*-heptadecanes: 1,2-d_2 and 8,9-d_2; Two nonadecanes: 1,2-d_2 and 9,10-d_2.

All of these compounds were prepared by the method of Morandi and Jensen,[14] who extended the work of Osborn *et al.*[15] This procedure involves the specific deuteration of the double bond in selected linear olefins through the use of deuterium gas and tris(triphenylphosphine)-rhodium(I) chloride catalyst.

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APPENDIX

Enhancement Procedure

Each spectrum is corrected for naturally occurring isotopes. A further calculation is then made where necessary to enhance the effect of labeling to remove the contribution of ions which result from reactions involving hydrogen loss from fragments formed by carbon–carbon bond cleavage. This enhancement procedure is illustrated for the ions containing six carbon atoms from *n*-decane-2,3-d_2. Table A-1 lists selected data from the mass spectra of *n*-decane and *n*-decane-2,3-d_2. Columns 2 and 4 contain selected peak heights of these two compounds after they have been corrected for naturally occurring isotopes and normalized to a total ionization of 10,000. To make the enhancement correction, the *n*-decane spectrum in the *m/e* region 80 to 87 has been renormalized so that the 85 peak is equal to 1·000.

The resulting pattern, shown in column 3 of Table A-1, is used to make the enhancement correction as shown in Table A-2.

The *m/e* 87 peak height of the *n*-decane-2,3-d_2 is 445 (column 2 of Table A-2). No correction is applied to this peak. It is equivalent to the *m/e* 85 peak of *n*-decane,

TABLE A-1. DATA REQUIRED FOR ENHANCEMENT CALCULATIONS FOR C_6 REGION IN THE MASS SPECTRUM OF *n*-DECANE-2,3-d_2

	Data from mass spectrum of *n*-decane		Data from mass spectrum of *n*-decane-2,3-d_2	Enhanced peak heights for *n*-decane-2,3-d_2		
	Peak		Peak	Corrected for H-loss from		
m/e	heights[a]	Pattern[b]	heights[a]	87	86	85
87	—	—	445	445	445	445
86	—	—	188	36	36	36
85	1030	1·000	535	515	503	503
84	351	0·341	179	174	172	0
83	48	0·046	22	20	20	−3
82	10	0·010	5	5	5	0
81	4	0·004	—			
80	1	0·001	—			

[a] These columns contain the mass spectrum peak heights after correction for naturally occurring isotopes and normalization to a total ionization of 10,000.

[b] After normalizing *m/e* 85 peak to 1·000.

TABLE A-2. CALCULATIONS REQUIRED TO OBTAIN ENHANCEMENT SPECTRA

m/e	Peak height before enhancement	Correction for H loss from 87	Correction for H loss from 86	Correction for H loss from 85	Enhanced data
87	445	—	—	—	= 445
86	188	−(0·341 × 445)			= 36
85	535	−(0·046 × 445)	−(0·341 × 36)		= 503
84	179	−(0·010 × 445)	−(0·046 × 36)	−(0·341 × 503)	= 0
83	22	−(0·004 × 445)	−(0·010 × 36)	−(0·046 × 503)	= −3
82	5	−(0·001 × 445)	−(0·004 × 36)	−(0·010 × 503)	= 0

but greater in mass by two units because of the presence of two deuterium atoms in the ion.

The *m/e* 86 peak of the *n*-decane-2,3-d_2 is corrected by assuming that the hydrogen loss from the fragment peak *m/e* 87 occurs to the same extent as hydrogen loss from the fragment peak *m/e* 85 of *n*-decane. The *m/e* 87 peak height of *n*-decane-2,3-d_2 (445) is multiplied by 0·341 and subtracted from the *m/e* 86 peak height (188) which corrects for the loss of one hydrogen, leaving a residue of 36 units as shown in Table A-1. This is the only correction required for *m/e* 86. Notice in the third row that *m/e* 85 must be corrected for two hydrogen losses from 87 (factor 0·046) and one hydrogen loss from 86 (factor 0·341). By continuing the corrections for each *m/e*, we obtain the final enhanced values shown in column 6 of Table A-2 and column 7, Table A-1.

We recognize that in the example used no correction should be made for the 36 units of *m/e* 86. In a mixture, however, the *m/e* 86 ion is a possible primary fragment. Therefore, for consistency, corrections for the three primary peaks are used throughout.

After enhancement, the sum of the three peaks (85, 86 and 87) are normalized to 1·000. The entire spectrum of each dideuterioalkane is divided into carbon-number regions, and corrections are made as shown in the example. Each region of the appropriate perprotio-*n*-alkane is patterned with *m/e* 57, 71, 85, etc., normalized to 1·000. After each region of a dideuterioalkane is corrected, the sum of the three primary peaks in that region is normalized to 1·000. The resulting data may then be presented as shown in Fig. 2.

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