COMMUNICATIONS

Identification of Pesticides in Mixtures by High-Resolution Mass Spectrometry

By utilizing the information available from high-resolution mass spectral data of pesticides, it has been possible to identify ions in the spectra of each pesticide whose elemental composition (accurate mass) is unique for that pesticide and can be used to identify the presence of the pesticide in the high-resolution mass spectrum of a pesticide mixture. A number of mixtures containing organophosphorus pesticides and chlorinated hydrocarbons were prepared and mass spectra obtained. All of the pesticide components of the mixtures were identified, using the mass spectral data obtained for the individual pesticides.

A number of investigators have reported the use of mass spectrometry in the study of individual pesticides (Benson and Damico, 1968; Damico, 1966; Damico and Benson, 1965; Damico et al., 1968; Jörg et al., 1966) and for the identification of pesticides in mixtures (Mumma and Kantner, 1966). In the latter case, mass spectrometry was used as a means of identifying pesticide residues as they were isolated and collected by gas chromatographic separation.

Because of its high sensitivity and potential for uniquely identifying organic compounds of known structure, the mass spectrometer appears to be well suited to the identification of pesticides isolated from residues. Also, the recent development of high-resolution mass spectrometry, permitting the precise measurement of the accurate masses of the ions produced in the spectrometer, adds to the technique the potential capability of recognizing the presence of individual pesticides in complex mixtures from mass spectral data without prior separation of the mixtures into their individual components.

In the present investigation, a preliminary study of the use of high-resolution mass spectrometry to identify individual pesticides in a complex mixture is being undertaken, making use of the information available from high-resolution mass spectral data.

EXPERIMENTAL

Chemicals. The samples of pesticides (Table I) used in this investigation were obtained commercially. While the purity of the samples varied (85 to 95%), the small amounts of impurities did not interfere with identification of the major ions in the mass spectra.

Instrumentation. The high-resolution spectra were obtained on a CEC 21-110B mass spectrometer, using photoplate recording of the spectra. The solid samples were introduced through a vacuum lock direct probe

Table I. Pesticides Investigated

Chemical Name	Commercial Name	Molecular Formula
O,O-Diethyl-O-p-nitrophenyl phosphorothioate (I)	Parathion	$C_{10}H_{14}NO_5PS$
O,O-Diethyl-O-(2-isopropyl-4-methyl-6-pyrimidinyl) phosphorothioate (II)	Diazinon	$C_{12}H_{21}N_2O_3PS$
O,O-Dimethyl-S[1,2-di(ethoxycarbonyl)ethyl] phosphorodithioate (III)	Malathion	$C_{10}H_{19}O_6PS_2$
O,O-Diethyl-S-p-chlorophenylthiomethyl phosphorodithioate (IV)	Trithion	$C_{11}H_{16}O_2ClPS_2$
bis(N,N-Dimethylamino)-phosphorous anhydride (V)	Ompa	$C_8H_{24}N_4O_3P_2$
O,O,O',O'-Tetraethyl-S,S'-methylene bisphosphorodithioate (VI)	Ethion	$C_9H_{22}O_4P_2S_4$
1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-endo-exo-5,8-dimethanonaphthalene (VII)	Aldrin	$C_{12}H_8Cl_6$
1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-exo-exo-5,8-dimethanonaphthalene (VIII)	Endrin	$C_{12}H_8Cl_6O$
1,4,5,6,7,8,8-Heptachloro-3a,4,7,7a-tetrahydro-endo-4,7-methanoindene (IX)	Heptachlor	$C_{10}H_5Cl_7$
2,2-bis(p-Chlorophenyl)-1,1,1-trichloroethane (X)	DDT	$C_{14}H_9Cl_5$
2,2-bis(p-Chlorophenyl)-1,1-dichloroethylene (XI)	DDE	$C_{14}H_8Cl_4$
2,2-bis(p-Methoxyphenyl)-1,1,1-trichloroethane (XII)	Methoxychlor	$C_{16}H_{15}O_2Cl_3$

inlet system with variable temperature control, while the liquid samples were introduced through a heated metal oven inlet system (150° C.). The ion source was maintained at 200° C. and the spectra were obtained with an ionizing voltage of 70 e.v. Complete high resolution mass spectra were obtained from the photoplates, using automatic data processing techniques described elsewhere (Biemann and Fennessey, 1967).

Analysis of Pesticide Mixtures. Mixtures containing two to six pesticides were prepared by mixing samples of the individual pesticides in approximately equal amounts and dissolving the mixture in either acetone or benzene. After removing the solvent, a small portion (10 to 50 μg.) of the resulting homogeneous mixture was transferred to a capillary (0.9 × 15 mm.), which has previously been sealed at one end. Using a microtorch under a 20× power magnifying glass, the open end of the sample capillary was heated slowly with constant rotation until an opening remained which was estimated to be 1 to 2 mils in diameter. The spectra of the mixtures were then recorded by slowly increasing the sample probe temperature, while simultaneously taking rapid successive recordings of the spectra on the photographic plate at the various probe temperatures. This technique permitted partial separation of the mixture by virtue of the differing vapor pressures of the pesticides in the mixture.

RESULTS AND DISCUSSION

Complete high-resolution mass spectral data have been obtained for each of the pesticides listed in Table I. Because the mass spectral behavior of these compounds have been discussed elsewhere (Damico, 1966; Damico et al., 1968), the fragmentation of the compounds will

not be detailed here, except as they relate to the identification of the individual pesticides from their mass spectral data.

By comparing the exact masses of the ions produced in the high resolution mass spectrum of each pesticide with those of each of the other pesticides studied, ions in the spectrum of each pesticide have been identified whose exact masses (elemental compositions) can be used to identify that pesticide uniquely in the spectrum of a mixture of pesticides. These ions are summarized in Table II.

Ions having exact masses unique for the spectra of each pesticide were chosen on the basis of abundance and type of fragment the ions corresponded to. In the spectra of the organophosphorus pesticides, the "molecular ion" in each case was found to have an elemental composition (accurate mass) unique to that pesticide and present in the spectrum in sufficient abundance to be used to identify the pesticide in a mixture. Fragment ions whose compositions were also unique to the spectrum of the individual pesticides were used when available, in addition to the molecular ion, to support the correct identification of the pesticide in the mass spectrum of a mixture. For example, the ion corresponding to the loss of the elements C_2H_5O (Table II) from the molecular ion in the spectrum of malathion(III) is unique to that compound and has been selected as an ion to be used to detect the presence of III in a mixture.

For the identification of the chlorohydrocarbon compounds, as well as for the organophosphorus compounds, extensive use was made of ions containing isotopes of chlorine and/or sulfur present in the pesticide. For example, in the spectrum of aldrin (V), all of the ions except the molecular ion (m/e 361.872:), whose exact

Table II. Composition of Ions Used to Identify Pesticides Listed in Table I from High-Resolution Mass Spectral Data

Pesticide	f_1	f_2	f_3	f_4	f_5	f_6
I	291.0319 ($C_{10}H_{14}NO_5PS$)	293.0308[a]				
II	152.0954 ($C_8H_{12}N_2O$)	216.0489 ($C_8H_{12}N_2OPS$)	248.0391 ($C_8H_{13}N_2O_3PS$)	304.1010 ($C_{12}H_{21}N_2O_3PS$)		
III	173.0817 ($C_8H_{13}O_4$)	283.9943 ($C_8H_{14}O_5PS_2$)	330.0370 ($C_{10}H_{19}O_6PS_2$)			
IV	341.9761 ($C_{11}H_{16}O_2PS_3Cl$)	343.9740[b]	345.9690[b]			
V	152.0709 ($C_4H_{13}N_2O_2P$)	153.0790 ($C_4H_{14}N_2O_2P$)	242.0819 ($C_6H_{18}N_3O_3P_2$)	286.1321 ($C_8H_{24}N_4O_3P_2$)		
VI	337.9992 ($C_8H_{20}O_4P_2S_3$)	338.9544 ($C_7H_{17}O_3P_2S_4$)	383.9869 ($C_9H_{22}O_4P_2S_4$)	385.9840[a]		
VII	328.9008[c]	330.8992[c]	332.8951[c]	361.8721 ($C_{12}H_8Cl_6$)	363.8683[b]	365.8648[b]
VIII	344.8989[d]	346.8961[d]	348.8944[d]	377.8695 ($C_{12}H_9OCl_6$)	379.8661[b]	381.8630[b]
IX	303.8749[e]	305.8718[e]	369.8196 ($C_{10}H_5Cl_9$)	377.8075[b]		
X	351.9145 ($C_{14}H_9Cl_5$)	353.9113[b]	355.9058[b]	357.9063[b]		
XI	315.9356 ($C_{14}H_8Cl_4$)	317.9341[b]	319.9318[b]	321.9290[b]		
XII	225.0906 ($C_{15}H_{13}O_2$)	344.0156 ($C_{16}H_{15}O_2Cl_3$)	346.0119[b]			

[a] Sulfur (^{34}S) isotope peak.
[b] Chlorine (^{37}Cl) isotope peak.
[c] Chlorine (^{37}Cl) isotope peak of 326.9020 ($C_{12}H_6Cl_6$).
[d] Chlorine (^{37}Cl) isotope peak of 342.9005 ($C_{12}H_7OCl_6$).
[e] Chlorine (^{37}Cl) isotope peak of 299.8805 ($C_{10}H_5Cl_8$).

Table III. Partial Listing of Intensities and Accurate Masses Calculated from High-Resolution Mass Spectrum of Mixture of Chlorohydrocarbons

Mixture A

Int.	m/e	Int.	m/e	Int.	m/e	Int.	m/e	Int.	m/e	Int.	m/e
2	159.9653	0	159.9788	17	160.0080	0	160.4668	2	160.9736	2	161.0138
1	161.0396	2	162.0044	0	162.0232	1	162.0469	0	162.9702	30	163.0556
1	164.0567	19	164.0626	0	164.9950	1	165.0645	44	165.0707	22	166.0749
0	166.9658	1	167.0780	0	167.9579	1	168.9611	0	169.0671	23	169.9694
11	170.9763	1	171.0015	17	171.9670	2	171.9850	1	172.0084	3	172.9739
0	172.9897	0	172.9996	2	173.0175	1	173.0410	1	173.9637	1	173.9824
0	174.0070	0	174.0212	30	174.0485	0	174.9706	1	175.0128	36	175.0544
0	175.9791	1	176.0554	60	176.0632	30	177.0677	1	178.0732	9	178.0787
1	179.0819	0	181.0666	0	181.9684	1	182.9770	0	183.0627	0	183.9661
1	184.9740	2	185.0157	1	186.0050	2	186.0231	0	186.9721	1	187.0127
0	187.0270	1	188.0207	0	188.9680	0	189.8324	0	190.6948	1	192.9368
1	193.9683	1	194.9344	0	195.0829	0	195.9649	0	195.9843	0	196.0888
0	196.9827	1	197.0163	1	198.0228	0	199.0139	30	199.0321	22	200.0373
10	201.0289	2	201.0451	2	202.0347	0	202.0503	1	203.0427	1	203.9928
0	204.9366	0	205.0080	2	205.9468	0	206.2613	0	206.2785	0	206.9348
0	206.9507	1	206.9766	2	207.9433	1	208.0098	0	208.9473	0	208.9747
1	209.0154	1	209.9403	0	210.0055	32	210.0237	0	211.0123	19	211.0285
15	212.0210	28	212.0380	2	213.0254	2	213.0428	12	214.0361	1	215.0272
1	215.0405	1	216.0347	1	217.0242	0	218.0305	0	218.9334	1	219.0400
0	220.9890	0	221.0350	2	221.9834	0	222.2199	1	222.2415	24	227.1072
2	228.1112	0	230.0300	39	232.9953	2	233.9978	2	234.9895	362	235.0059
42	236.0092	2	236.9888	300	237.0032	37	238.0069	56	239.0024	2	240.0053
26	244.9946	1	245.9828	208	245.9991	2	246.9865	46	247.0017	698	247.9959
1	248.0151	174	249.9933	243	250.0976	6	252.0039	42	252.9975	1	253.9929
2	254.0007	1	254.9977	0	256.0009	0	265.9915	1	269.9804	1	270.9674
0	272.9237	0	272.9655	0	274.0781	14	279.9631	2	280.9697	17	281.9618
51	281.9799	41	282.9682	2	283.9591	25	283.9749	2	284.9654	1	284.9792
6	285.9763	0	286.9778	0	296.9563	0	308.0365	0	310.0326	0	313.9904
238	315.9373 a	34	316.9403	782	317.9351 a	2	317.9520	53	318.9378	700	319.9338 a
5	319.9496	40	320.9356	1	320.9540	135	321.9285 a	4	321.9429	4	322.9334
0	322.9504	2	323.9265	1	323.9418	1	344.0148 c	1	346.0108 c	0	349.9792
2	351.9138 b	0	352.9193	5	353.9119 b	1	354.9153	2	355.9085 b	0	356.9133
1	357.9057 b	0	369.9073	0	370.0032	2	370.0858	2	370.1477	1	370.1586

Mixture B

Int.	m/e	Int.	m/e	Int.	m/e	Int.	m/e	Int.	m/e	Int.	m/e
1	252.8709	42	252.8948	2	252.9131	4	253.8421	218	253.8806	8	253.9020
1	254.8500	8	254.8833	23	254.8909	1	254.9111	10	254.9527	141	255.8781
2	255.8978	8	255.9613	24	256.8829	2	256.8900	1	256.9082	11	256.9493
1	256.9680	37	257.8747	9	257.9577	1	258.8781	1	258.8868	2	258.9458
2	258.9646	3	259.8720	1	259.9545	74	260.8600	18	261.8660	162	262.8581
27	263.8620	34	263.9068	118	264.8544	34	264.9143	17	265.8595	48	265.9038
2	265.9177	25	266.8514	39	266.9104	2	266.9292	2	267.8565	25	267.9015
7	267.9157	2	268.8474	23	268.9068	3	268.9271	0	268.9460	322	269.8137
2	269.8979	1	269.9112	20	270.8170	1	270.9042	1	270.9234	1	270.9432
643	271.8104	50	272.8132	0	272.8596	0	272.9402	20	273.7973	222	273.8083
1	273.8673	31	274.8112	1	274.8565	2	274.8741	225	275.8042	2	275.8648
14	276.8077	7	276.8718	1	276.9149	44	277.8004	1	277.8611	0	277.9217
1	278.8037	2	278.8691	2	278.9108	3	278.9292	5	279.7976	1	279.8995
1	279.9180	0	280.8641	1	280.9080	5	280.9265	1	281.8977	1	282.9050
1	282.9236	0	283.8938	0	284.8173	1	286.8313	0	286.8548	1	286.8741
96	287.8595	1	288.8293	21	288.8674	169	289.8569	22	290.8614	25	290.9294
147	291.8533	2	291.9336	11	292.8581	33	292.9271	42	293.8504	5	293.9300
2	294.8535	20	294.9227	19	295.8271	15	295.8465	1	295.9256	2	296.9202
35	297.8234	1	297.8416	1	298.8267	13	298.8731	30	299.8215	1	299.8616
4	299.8812	0	300.8237	18	300.8713	16	300.8889	14	301.8194	13	301.8792
1	301.8938	13	302.8694	22	302.8873	7	302.9053	1	303.8167	9	303.8764 f
2	303.8940	1	304.7807	1	304.8657	19	304.8835	12	304.9023	1	305.8738 f
2	305.8903	0	305.9091	11	306.7771	2	306.8811	6	306.8988	10	308.7743
0	308.8959	1	308.9186	2	310.7723	0	312.7693	1	314.8698	0	314.8894
10	314.9073	2	316.8679	0	316.8833	15	316.9038	1	317.9055	1	318.8650
7	318.9010	1	320.8969	1	325.8991	7	326.9063	2	327.8953	13	328.9035 d
1	329.8923	7	330.9008 d	1	332.8958 d	61	334.8512	21	335.8581	137	336.8492
16	336.8651	0	337.4779	37	337.8564	134	338.8473	26	338.8630	38	339.8525
1	339.8706	41	340.8433	24	340.8605	14	341.8483	1	341.8636	10	342.8393
9	342.8576	4	342.9009	1	343.8466	0	344.8380	1	344.8550	14	344.8996 e
0	345.9030	4	346.8956 e	0	348.8673	0	348.8932 e	62	350.8471	1	350.8641
2	351.8521	1	351.8714	98	352.8448	12	353.8479	75	354.8424	4	355.8444
28	356.8393	1	357.8413	8	358.8350	0	360.8278	5	361.8746 d	14	363.8726 d
0	364.8747	11	365.8697 d	1	366.8739	1	367.8658	34	369.8211 f	26	370.8279
104	371.8171	6	371.8265	57	372.8249	128	373.8161	70	374.8226	82	375.8140
37	376.8177	24	377.8072 f	2	377.8212	1	377.8685 e	9	378.8152	1	379.8037
6	379.8662 e	0	380.8134	4	381.8630 e	1	383.8593	2	385.8155	12	387.8113

a Fragments due to DDE. b Fragments due to DDT. c Fragments due to methoxychlor. d Fragments due to aldrin. e Fragments due to endrin. f Fragments due to heptachlor.

Table IV. Partial Listing of Intensities and Accurate Masses Calculated from High-Resolution Mass Spectrum of Mixture of Organophosphorus Pesticides

Int.	m/e	Int.	m/e	Int.	m/e	Int.	m/e	Int.	m/e	Int.	m/e
17	140.0023	7	140.0311	41	140.9600	1	140.9787	7	141.9621	53	141.9672
28	141.9851	17	142.9385	0	142.9557	58	142.9723	2	143.0160	1	143.0337
6	143.9470	13	143.9639	117	143.9812	1	144.0241	34	144.9688	41	144.9875
22	145.0494	0	145.0862	0	145.9421	65	145.9753	1	146.0399	2	146.9802
14	146.9940	1	147.9716	1	148.1239	2	149.0462	14	150.0547	25	151.0617
12	151.0850	2	151.9710	53	152.0704[a]	30	152.0937[b]	1	152.9822	139	153.0125
0	153.0587	110	153.0780[a]	12	153.1018	0	153.9667	3	153.9822	2	153.9892
10	154.0145	55	154.0196	3	154.0655	3	154.0812	14	154.9730	68	155.0043
7	155.0279	2	155.9451	1	155.9623	28	155.9814	2	156.0049	61	156.9534
111	156.9866	1	156.9980	3	157.9562	90	157.9629	3	157.9880	57	157.9946
3	158.9505	49	158.9681	1	158.9969	20	159.0107	43	159.9571	2	159.9863
3	160.0180	1	160.9649	2	160.9809	3	161.0277	1	162.1158	1	162.9653
2	163.1242	1	164.1319	2	167.0651	1	168.0727	0	169.9618	15	170.0171
30	170.9701	12	171.0257	34	171.9776	41	172.0118	1	172.9678	1	172.9822
1	173.0142	74	173.0812[c]	1	173.9734	1	174.0088	36	174.0848	12	174.9102
3	174.9445	1	174.9639	1	175.0878	0	175.9510	1	176.9402	30	179.1169
1	180.1024	1	180.1224	1	181.9616	1	182.9677	26	183.9755	0	184.0298
30	184.9836	1	185.0218	3	186.9423	3	187.9506	18	187.9681	12	187.9881
1	188.0498	0	188.9380	11	188.9573	1	189.0562	1	189.9324	1	189.9477
6	189.9654	0	189.9830	2	190.9552	3	191.9564	0	193.9514	39	196.1201
1	196.9834	1	197.0224	1	197.1257	1	198.0314	2	198.0483	68	199.0393
16	199.0630	50	200.0480	1	201.0515	1	201.9901	5	202.0031	3	202.9431
1	203.9840	1	206.0615	18	210.9663	1	212.9618	36	214.0261	2	215.0304
1	215.0605	1	216.0210	2	216.0503[b]	1	216.9602	18	217.9681	0	226.9607
4	227.0960	1	229.9689	50	230.9783	0	231.0381	17	231.9806	28	232.9719
3	234.9667	9	234.9720	2	237.9535	29	242.0831[a]	35	243.0898	1	244.0942
2	245.9997	1	247.0310	3	248.0395[b]	1	254.9560	28	255.9970	2	260.0742
1	264.0001	0	264.0070	3	268.9896	3	276.0708	8	283.9938[c]	28	285.0015
1	286.0043	47	286.1319[a]	6	287.1354	0	289.0728	1	289.0773	53	291.0321[d]
7	292.0366	2	293.0308[d]	1	295.9872	24	304.1021[b]	1	305.1059	11	330.0367[e]
1	337.9996[e]	45	341.9738[f]	50	343.9729[f]	2	344.9751	1	345.9669[f]	1	366.9703
0	382.9819	43	383.9860[c]	2	384.9897	2	386.9803	0	390.9750	0	397.2418

[a] Fragments due to ompa.
[b] Fragments due to diazinon.
[c] Fragments due to malathion.
[d] Fragments due to parathion.
[e] Fragments due to ethion.
[f] Fragments due to trithion.

masses were unique to that spectrum, are chlorine isotope peaks of other ions. The isotope peaks, while not indicative of structural characteristics, were chosen because the combination of atoms in the ions were unique for the pesticide in which they occurred. For example, the ion of mass 361.8721 ($C_{12}H_8Cl_6$) and its corresponding isotope peaks at m/e 363.8683 and 365.8648 in the spectrum of aldrin will successfully identify the presence of aldrin in a mixture of other chlorohydrocarbons, as long as none of the other components in the mixture produce ions of exactly the same accurate mass (elemental composition). The possibility of this type of interference is eliminated by comparing the spectra of the individual pesticides and finding exact masses, including isotope peaks in the spectrum of each, which do not occur in the spectra of the others. Obviously, as the library of spectra increases, the successful identification of masses unique for each spectrum will become an enormous task and can only be done by computer techniques. A computer program is presently being written for this purpose.

To investigate further the utility of identifying individual components of pesticide mixtures by this method, the high-resolution spectra of three pesticide mixtures were obtained. The high mass portion of the spectra of these mixtures are shown in Tables III and IV. From the spectrum of a mixture containing parathion (I), malathion (III), trithion (IV), diazinon (II), ethion (VI), and Ompa (V), the ions listed in Table II for these pesticides were identified in sufficient abundance and their exact masses were sufficiently separated from the masses of other ions in the spectrum to permit their accurate measurement and identification. These ions are underlined in Table IV. Two mixtures of chlorinated hydrocarbons (A and B), one containing endrin (VIII), aldrin (VII), and heptachlor (IX), and the other containing DDT (X), DDE (XI), and methoxychlor (XII), were also submitted to high-resolution mass spectral analysis and, as in the case of the mixtures of organophosphorus pesticides, the ions in Table II selected for the identification of these pesticides were present in large abundance in the spectra of the mixtures. The spectra of these mixtures are tabulated in Table III and the ions used to identify the pesticides are labeled.

In the high-resolution mass spectra of the pesticides used in this investigation there are ions produced by each pesticide whose elemental compositions (accurate mass) are unique to that pesticide and which may be used successfully to identify the presence of that pesticide in a mixture. The method is presently limited to distinguishing between two species of differing elemental composition and cannot differentiate between two structurally isomeric pesticides of identical elemental composition, such as dieldrin and endrin or p,p,-DDT and o,p-DDT. However, the mass spectra of isomeric compounds such as these do differ in the relative intensities of the ions in the spectra, and on this basis further work is under way to expand this approach to include

the identification of these and other pesticides by adding to the technique the accurate measurement of the relative intensities of these exact masses, thereby providing sufficient data to distinguish the isomeric pesticides in mixtures. Application of the techniques to the identification of pesticide residues in extracts of food and soil samples is also being investigated.

LITERATURE CITED

Benson, W. R., Damico, J. N., *J. Assoc. Offi. Anal. Chem.* **51**, 347 (1968).
Biemann, K., Fennessey, P. V., *Chimia* **21**, 226 (1967).
Damico, J. N., *J. Assoc. Offic. Anal. Chem.* **49**, 1027 (1966).
Damico, J. N., Barron, R. P., Ruth, J. M., *Org. Mass Spectrom.* **1**, 331 (1968).
Damico, J. N., Benson, W. R., *J. Assoc. Offic. Anal. Chem.* **48**, 344 (1965).
Jorg, J., Houriet, R., Spiteller, G., *Monatsh. Chem.* **97**, 1064 (1966).
Mumma, R. O., Kantner, T. R., *J. Econ. Entomol.* **59**, 491 (1966).

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An Empirical Relationship between Chemical Structure and the Sorption of Some Herbicides by Soils

A factor given by (parachor–45N), where N is the number of sites in a molecule which can participate in the formation of a hydrogen bond, is shown to be correlated with log Freundlich k value for the adsorption of 29 aromatic herbicides by two soils. This empirical relationship may be useful for prediction of the approximate extent of adsorption of such herbicides by soils in which the organic matter is the dominant adsorbing constituent.

L ambert (1967) has proposed a relationship between the parachor of an organic molecule and its sorption by soil of the form log $k_\alpha P$, where k is the adsorption equilibrium constant and P is the parachor. This relationship is subject to the conditions that the molecule is un-ionized and that no appreciable hydrogen bonding occurs. For compounds capable of significant hydrogen bonding an additional term is required, as such materials might be expected to show a greater interaction with water and hence be less extensively absorbed in soil-water systems than the relationship would predict. Since most soil-applied herbicides contain groups which can form hydrogen bonds, it is of interest to estimate the approximate magnitude of the additional term, so that the applicability of this relationship to these compounds may be tested.

Since the nature and energy relationships of all the possible solute-water, solute-soil, and water-soil interactions have not yet been evaluated, it is not possible to predict on theoretical grounds the contribution of hydrogen bonding to the distribution of an organic solute between water and a soil surface. It is, however, possible to ascribe an empirical value to the effect of hydrogen bonding based on experimental observations of the adsorption of organic molecules by soil. This exercise has been attempted using data previously reported (Hance, 1967) for the adsorption of 29 compounds by two soils. The compounds included ureas, 1,3,5-triazines, carbamates, and uracils. The figures were in the form of Freundlich k values. As Lambert has observed, this constant is not ideal on theoretical

grounds and is not strictly valid as a comparative measurement if the value of $1/n$ in the Freundlich equation is not 1. In the present case, only six compounds gave values of $1/n$ which were not 1 and these all gave values between 0.85 and 0.99. It was therefore decided that for the purposes of this study the Freundlich k value gives a useful measure of adsorption.

Simple correlation coefficients and the magnitude of the correction factor were determined for the relation between log Freundlich k and the figure given by parachor—(a correction factor $\times N$). Parachors were calculated from the table of group and bond contributions given by Quayle (1953). The value of N was given by the number of proton- or electron donating sites on the molecule which could conceivably participate in hydrogen bond formation. The following groups in this category occurred in the compounds studied: primary, secondary, and tertiary amino, carbonyl, heterocyclic nitrogen, and ether oxygen. Thus N for diuron (N'-3,4-dichlorophenyl-N,N-dimethylurea) is 3 because of the presence of one secondary and one tertiary amino group and a carbonyl group. Similarly, N for simazine (2-chloro-4,6-bisethylamino-1,3,5-triazine) is 5, as it contains three heterocyclic nitrogen atoms and two secondary amino groups. Possible interactions between adjacent groups such as internal hydrogen bonding or the effects of steric hindrance were ignored.

Using this process, a value of 45 for the correction factor gave the best fit. Correlation coefficients were 0.79 for a chalky boulder clay and 0.67 for a gray sandy loam. Values of k were also calculated con-