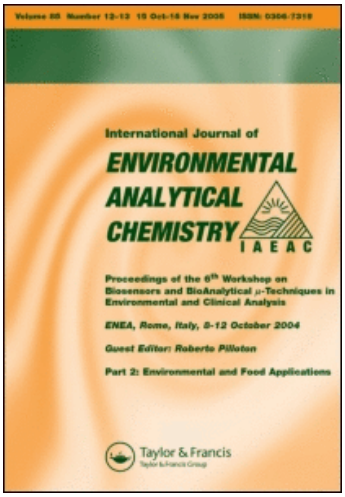

International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Mass Spectrometric Distinction of Free Phenoxy Fatty Acids from Phenols Part I: Application of El-Mass Spectrometry

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To cite this Article Nolte, J. , Paschold, B. and Kettrup, A.(1983) 'Mass Spectrometric Distinction of Free Phenoxy Fatty Acids from Phenols Part I: Application of El-Mass Spectrometry', International Journal of Environmental Analytical Chemistry, 15: 4, 231 — 239
To link to this Article: DOI: 10.1080/03067318308071630
URL: http://dx.doi.org/10.1080/03067318308071630

Intern. J. Environ. Anal. Chem., 1983, 15, pp. 231–239
0306-7319/83/1504-0231 $18.50/0

Printed in Great Britain

Mass Spectrometric Distinction of Free Phenoxy Fatty Acids from Phenols

Part I: Application of EI-Mass Spectrometry

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By comparison of electron impact mass spectra of 16 phenoxy fatty acids with their corresponding phenols, it becomes obvious that the major parts of both spectra are identical.

The dominating signal is the phenol ion. It corresponds to the molecule ion for free phenols and to that fragment for the phenoxy fatty acids which is formed by the loss of the acid moiety under proton migration. As the signals of higher masses than the phenol ions are small in most cases, and as these substances have comparable chromatographic properties, correct identification in mixtures is difficult to achieve. The spectra of both classes of compounds are given to allow the selection of specific signals for the differentiation of fatty acids versus phenols, when this is possible.

KEY WORDS: Phenoxy fatty acids, phenols, mass spectrometry, spectra comparison.

INTRODUCTION

Phenoxy fatty acids are an important group of herbicides.[1] They are used in form of basic material in plant growing, colouring, scenting and pharmaceutical substances.[2] The phenols find an even larger distribution as disinfectants, fungicides and as bases in several industrial processes.[3]

Moreover, they are virtually omnipresent by the degradation of biological materials and by industrial, domestic and clinical refuse.[4, 5] The exact determination of these substances is of great importance, because they can be found metabolized or in their original form in most spheres of the environment.

Caused by their similar physical and chemical properties, both classes of substances are difficult to analyze; e.g. they are enriched and eluted at the same time and their retention behaviour in chromatographic separations is very similar or even identical.[6]

The objective of this study is the use of mass spectrometry for the identification of both at a rather low detection limit. The problems are discussed in the following.

EXPERIMENTAL

The low resolution mass spectra have been recorded with a VARIAN MAT CH7-SS100 system and standard conditions (source temperature: 220°C, electron energy: 70 eV, resolution: 1000, acc. voltage: 3 kV). A home-made TIC-controlled direct probe inlet for complete evaporation was used.

For high resolution accurate mass measurement a MM 7070E (VG Instruments) was used. The conditions were: source temperature 200°C, electron energy 70 eV, resolution ~9000, acc. voltage 6 eV.

RESULTS AND DISCUSSION

In Table I the measured substances are listed. In Figure 1 two spectra are shown to demonstrate that the complete mass spectrum of the respective phenol is the dominating part in the spectrum of the phenoxy fatty acid, even with respect to the distribution of intensities.

TABLE I

Investigated phenoxy fatty acids and their corresponding phenols

No.	Phenoxy fatty acid	Common name	Phenols
1	phenoxyacetic acid	POA	
2	DL-2-phenoxypropionic acid		
3	3-phenoxypropionic acid		phenol
4	4-phenoxybutyric acid		
5	11-phenoxyundecanoic acid		
6	4-chlorophenoxyacetic acid	4-CPA	4-chlorophenol
7	DL-2-(4-chlorophenoxy)-propionic acid		
8	2-(4-chlorophenoxy)-2-methylpropionic acid	Chlorofibrinsäure	
9	2,4-dichlorophenoxyacetic acid	2,4-D; Dichloroprop	2,4-dichlorophenol
10	2-(2,4-dichlorophenoxy)-propionic acid	2,4-DP	
11	4-(2,4-dichlorophenoxy)-butyric acid	2,4-DB	
12	2,4,5-trichlorophenoxyacetic acid	2,4,5-T	2,4,5-trichlorophenol
13	2-(2,4,5-trichlorophenoxy)-propionic acid	2,4,5-TP; Fenoprop	
14	4-chloro-2-methylphenoxyacetic acid	MCPA; Metaxon	4-chloro-2-methyl-phenol
15	2-(4-chloro-2-methylphenoxy)-propionic acid	MCPP; Mecoprop	
16	4-(4-chloro-2-methylphenoxy)-butyric acid	MCPB	

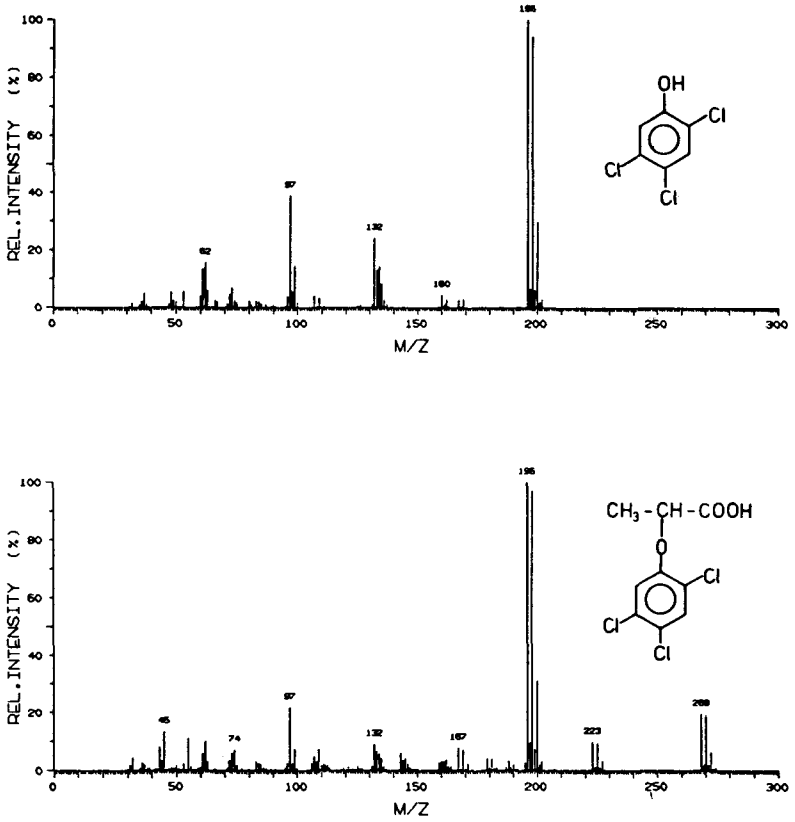

FIGURE 1 The similarity of the mass spectra up to the mass range of the $[C_6H_{6-n}OX_n]^+$ ion is demonstrated with the spectra of 2,4,5-trichlorophenol and 2-(2,4,5-trichlorophenoxy)-propionic acid. (Probe temperature in both cases: 40°C.)

The main fragment $[M-(FA-H)]^+$ is formed by loss of the fatty acids moiety under hydrogen migration. In most cases, that signal is the basic peak of these spectra; exceptions are found in the spectra of components 1, 6 and 14. These findings are contrary to the fragmentation of phenyl alkyl ethers of similar structures,[7-9] but has been rationalized by the transfer of the acid proton to the phenolic oxygen.

At higher masses, the molecular ions and fragments of the type

TABLE II

Relative intensities of the parent ions and selected key fragments of investigated phenoxy fatty acids

Substance No.	M^+	$[M-COOH]^+$	$[M-(FA-H)]^+$	$[M-FA]^+$	$[M-OFA]^+$
1	61	3	24	2	100
2	37	87	100	14	58
3	20	1	100	2	10
4	3	—	100	42	8
5	5	—	100	1	7
6	92	100	70	25	82
7	33	36	100	9	19
8	6	5	100	2	5
9	43	28	100	29	27
10	23	18	100	14	10
11	4	—	100	3	3
12	55	22	100	18	18
13	19	10	100	3	4
14	89	31	34	100	41
15	44	25	100	45	15
16	10	—	100	7	7

$[M-FA]^+$, $[M-OFA]^+$ and $[M-COOH]^+$ are observed (Table II) with little abundance, though exceptions are the phenoxy acetic acids. The elemental composition of these key fragments have been determined by exact mass measurements. In the spectra of compounds 4, 5, 11 and 16, the loss of the carboxylic moiety cannot be observed. The fragmentation scheme from the literature can be completed and is shown in Figure 2.[10]

In general, it can be stated that the abundance of molecular ions is decreasing with increasing chain length. Fragments of the type $[C_nH_{2n-1}O_2]^+$ or $[C_nH_{2n-1}]^+$ due to the fatty acid chain are of negligible intensity, only m/z 87 $[C_4H_7O_2]^+$ in the butyric acid derivatives is of greater intensity.

The substituents of the aromatic system can be derived from the isotopic pattern and the tropylium or hydroxypropylium ion, but the existence of the fatty acid chain can be overlooked (Tables III–VII).

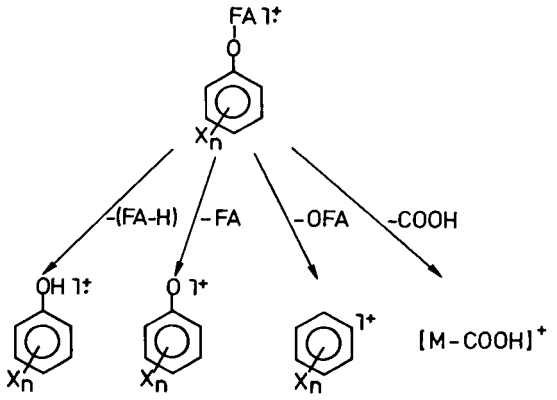

FIGURE 2 Fragmentation pathway for phenoxy fatty acids.

TABLE III

Relative intensities of significant ions of unsubstituted phenoxy fatty acids and phenol (P)

	m/z	51	55	65	66	69	77	83	87	93	94
	P	5	6	20	26	—	—	—	—	—	100[a]
	1	32	2	19	6	—	100	—	—	2	25
	2	28	9	20	20	—	58	—	—	14	100
Substance	3	8	11	14	17	—	10	—	—	2	100
	4	8	6	17	17	4	8	—	8	43	100
	5	2	18	4	3	10	7	5	1	1	100

	m/z	107	109	121	152	166	180	278
	P							
	1	83	7	3	61[a]			
	2	—	—	87	—	37[a]		
Substance	3	3	—	1	—	20[a]		
	4	1	—	—	—	—	3[a]	
	5	2	—	—	—	—	—	5[a]

[a](≙parent ion).

TABLE IV

Relative intensities of significant ions of the 4-chlorophenoxy fatty acids and the 4-chlorophenol (CP)

	m/z	50	51	63	65	73	75	77	91	99	100
	CP	6	3	16	49	9	3	—	—	8	15
Substance	6	26	15	25	10	19	51	28	—	43	6
	7	9	5	12	15	19	21	2	11	13	5
	8	5	3	9	20	6	8	1	1	8	8

	m/z	101	111	113	127	128	129	130	141	143	155
	CP	—	—	—	—	100[a]	7	32			
Substance	6	14	82	46	25	70	13	23	100	32	—
	7	5	19	6	9	100	9	32	—	—	36
	8	3	5	2	2	100	15	34	1	1	1

	m/z	157	169	186	188	200	202	214	216
	CP								
Substance	6	—	—	92[a]	28				
	7	11	—	—	—	33[a]	11		
	8	—	5	—	—	—	—	6[a]	2

[a] (≙ parent ion).

TABLE V

Relative intensities of significant ions of 2,4-dichlorophenoxy fatty acids and 2,4-dichlorophenol (DCP)

	m/z	63	73	74	75	87	98	109	111	126	133	135
	DCP	44	9	3	3	—	35	—	—	15	3	2
Substance	9	35	16	21	23	—	13	23	23	—	32	21
	10	25	9	10	12	—	15	12	—	—	16	—
	11	15	6	—	5	32	9	4	3	—	6	3

	m/z	145	147	149	161	162	163	164	165	166	175	177
	DCP	—	—	—	—	100[a]	7	63	4	10		
Substance	9	27[b]	20	7	29[c]	100[d]	25	63	8	13	28[e]	17
	10	10	—	—	14	100	12	63	13	14	—	—
	11	3	2	—	3	100	8	63	3	11	—	—

	m/z	189	191	220	222	224	234	236	238	248	250
	DCP										
Substance	9	—	—	44[af]	28	6					
	10	18	12	—	—	—	23[a]	17	3		
	11	—	—	—	—	—	—	—	—	4[a]	2

[a] (≙ parent ion).

[b–f] One example for precise mass determination (found/calculated):

$C_6H_3Cl_2^+$ (144,9639/144,9612)

$C_6H_3OCl_2^+$ (160,9458/160,9560)

$C_6H_4OCl_2^+$ (161,9637/161,9639)

$C_7H_5OCl_2$ (174,9864/174,9717)

$C_8H_6O_3Cl_2^+$ (219,9652/219,9693)

TABLE VI

Relative intensities of significant ions of the 2,4,5-trichlorophenoxy fatty acids and 2,4,5-trichlorophenol (TCP)

	m/z	61	62	73	74	97	99	107	132	133	134	135
	TCP	18	24	10	4	56	22	6	33	19	20	12
Substance	12	12	17	10	19	29	10	19	7	5	5	2
	13	6	10	6	7	22	7	7	9	6	6	4
	m/z	145	167	169	179	181	195	196	197	198	199	200
	TCP	—	4	4	—	—	—	100[a]	7	96	6	31
Substance	12	18	27	25	18	20	18	100	24	96	12	31
	13	4	8	7	4	4	3	100	10	97	7	31
	m/z	202	209	211	213	223	225	227	254	256	258	260
	TCP	4	—									
Substance	12	4	22	21	7	1	—	—	55[a]	52	17	2
	13	3	—	—	—	10	9	3	—	—	—	—
	m/z	268	270	272	274							
	TCP											
Substance	12											
	13	19	19	6	1							

[a](≙ parent ion).

TABLE VII

Relative intensities of significant ions of 4-chloro-2-methylphenoxy fatty acids and 4-chloro-2-methylphenol (CMP)

	m/z	51	62	63	77	78	79	87	89	90	91
	CMP	20	4	7	47	9	20	2	12	—	—
Substance	14	34	10	23	80	19	6	6	29	10	15
	15	27	4	15	59	13	8	2	21	6	4
	16	17	3	7	30	7	6	28	11	4	—
	m/z	99	101	107	113	125	141	142	143	144	155
	CMP	—	—	100	4	2	13	83[a]	10	26	
Substance	14	12	6	23	16	41	100	34	37	11	31
	15	6	3	55	7	15	45	100	21	32	1
	16	4	1	47	4	7	7	100	11	34	3
	m/z	157	169	171	200	202	214	216	228	230	
	CMP										
Substance	14	12	—	—	89[a]	31					
	15	—	25	8	—	—	44[a]	17			
	16	—	—	—	—	—	—	—	10[a]	3	

[a](≙ parent ion).

In conclusion it becomes evident that the differentiation between phenoxy fatty acids in mixtures with their respective phenols by EI-MS or even by GC/MS in EI-mode is ambiguous. To overcome that problem the use of Chemical Ionization (NH_3 or isobutane) should be recommended, as will be shown in a subsequent paper.

Acknowledgements

The authors wish to thank Mr. M. Linscheid for the helpful discussion. For their financial support, the authors thank the Bundesministerium für Forschung und Technologie as well as the Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen.

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