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Radiofrequency-only daughter scan mode to provide more spectral information in liquid chromatography–thermospray tandem mass spectrometry

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ABSTRACT

A method is presented for increasing the number of specific ions in LC–thermospray mass spectra by means of a quadrupole tandem mass spectrometer (Finnigan TSQ-70) in the radiofrequency-only daughter (RFD) scan mode. The method can be used for screening a large number of compounds eluted from an HPLC system. MS–MS in the usual daughter, parent or neutral loss scan mode (on retention time altered for each eluted compound) in this particular instance is very laborious or even impossible. In the RFD scan mode the first quadrupole is operating as a high-pass mass filter. Only ions with masses equal to or above the arbitrary selected cut-off mass will enter the collision cell. With a low collision offset voltage mainly molecular ions will be present in the third quadrupole, which is acting as a mass analyser in the full-scan mode. With medium and high collision offset voltages, daughter ions are generated in the collision cell. By using two or three different alternating collision offset voltages during one analysis, both molecular and daughter ions can be acquired, increasing the specificity of the mass spectrum. First, data on optimization of the low collision offset voltage and the collision gas (argon) pressure with a mixture of alachlor, atrazine, aldicarb and barban are presented. Next, spectral information and data about the sensitivity of twenty compounds (alachlor, aldicarb, aniline, atrazine, benzothiazole, carbendazim, chloridazon, diazinon, dimethoate, diuron, ethylenethiourea, isocarbamide, isoproturon, metamitron, metolachlor, monolinuron, propachlor, sethoxydim, simazine and warfarin) in the RFD scan mode at three collision offset voltages (−6, −20 and −40 V) are presented and compared with the single-stage Q3MS scan mode. The sensitivity proved to be the same or better at collision offset voltages of −6 and −20 V, partly because adducts and eluent clusters were decreased significantly or even disappeared. At a collision offset of −40 V the sensitivity decreased for many compounds and the more intense ions mainly had low m/z values, which are less specific. The RFD scan mode, using a −6 and −20 V collision offset voltage alternating in each scan, is demonstrated by screening a surface water sample (river Rhine) spiked with ten compounds at a level of 1 μg/l. It resulted in chromatograms with increased spectral information, the same or better signal-to-noise ratios, less eluent clusters and no adducts.

INTRODUCTION

Thermospray is one of the most popular techniques for interfacing HPLC with mass spectrometry. However, compared with GC–MS systems with electron impact ionization there is, in addition to the lower separation power of the HPLC system, a great lack of specific ions. For most compounds only one or two specific ions are generated, mainly with molecular mass information, unless extreme repeller or vaporizer settings are used and a far lower sensitivity is accepted [1,2].

For the unambiguous identification of an analyte by gas chromatography–low resolution mass spectrometry, the European Community recommends that at least four diagnostic ions (including the molecular ion, if possible) should be measured and that the relative abundances of all diagnostic ions should match those of the standard analyte [3]. The US Environmental Protection Agency (EPA) demands at least five

ions for confirmation [4]. These requirements are based on the statistical occurence of mass and abundance values in mass spectra [5] and are much higher than thermospray can give for many compounds.

. The abundant generation of eluent clusters, mainly in the lower mass range, is another disadvantage of the thermospray ion source. They decrease the sensitivity of ions with the same m/z ratio or make it even impossible to analyse such masses [2].

Thermospray MS–MS with parent, daughter and neutral loss scan modes can overcome these problems in many instances. These methods generate additional specific ions, which makes it possible to indentify compounds unambiguously. Thermospray MS–MS, in combination with HPLC separation or with flow-injection analysis (FIA), is now widely accepted [6–9].

In surface water, however, an enormous number of compounds are present. Nearly 40% of the organic compounds in the river Rhine are polar low-molecular-mass substances [7]. Several HPLC methods with UV or MS detection have been reported for the screening of aqueous environmental samples in the presence of 30–80 compounds in one analysis [2,10–12].

MS–MS with parent, daughter or neutral loss scans selected and programmed on retention time, however, is possible with only a limited number of target compounds. A "general" daughter scan mode, selecting each mass in a window of, e.g., m/z 100–500 as parent mass followed by a full range daughter scan of 0.5 s, needs more than 3 min for one complete cycle and is therefore not compatible with HPLC.

To overcome this restriction, the radiofrequency (RF)-only daughter (RFD) scan mode of a triple quadrupole mass spectrometer (Fig. 1) has been investigated [13].

The first quadrupole (Q1) acts as a high-pass mass filter with an arbitrary selected cut-off mass, the second quadrupole (Q2) as a collision cell with a target gas (argon) admitted to the cell and the third quadrupole (Q3) as mass analyser to scan the ions in the full-scan mode. Every ion generated in the thermospray ion source and equal to or above the cut-off mass is allowed to enter the collision cell without the need to select parents for each compound. It can be seen as a
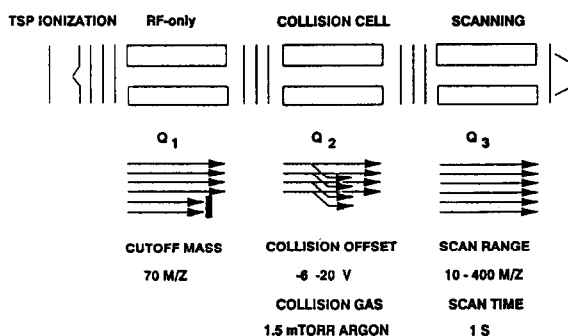

Fig. 1. Triple quadrupole mass spectrometer in the RFD scan mode.

mass spectrometer with separated ionization and fragmentation chambers, compared with electron impact where both actions take place in the ion source.

In the RFD scan mode the collision offset (COFF) voltage can be changed every scan. The chromatographic peak width in LC is generally 20–40 s. Hence, during peak elution, two or three different COFF voltages at a scan time of 0.5–1 s can be applied, to acquire 7–40 scans at each voltage for every peak.

The cut-off mass can be used to retard at least part of the eluent clusters entering the collision cell. For the experiments m/z 70 is selected to reject the clusters ions of m/z 59 and 60, allowing the lowest molecular ion of the tested compounds (aniline, M_r 93.06) to enter the collision cell.

In the thermospray ion source mainly ions are formed with intact molecules, e.g. $[M+H]^+$, revealing the molecular mass of a compound [2,9]. It is very important to maintain this information, but this aim is contrary to the admittance of a collision gas to the collision cell, necessary for the generation of daughter ions. It is not possible to change the argon pressure in a short time, just as the COFF voltage is changed every scan. Therefore, an argon pressure will be needed, low enough to allow the ions to pass at a low COFF voltage and high enough to generate daughter ions with higher COFF voltages.

First, by altering the COFF voltage and collision gas pressure in the RFD scan mode, the intensities of the molecular ions were optimized at a low COFF voltage range. Second, twenty compounds were tested in the RFD scan mode at the selected and at higher COFF voltages to

establish whether extra ions are generated at the optimized argon pressure without losing the molecular ions.

EXPERIMENTAL

Chemicals

All test compounds were obtained from Riedel-de Haën (Hannover, Germany). Ammonium formate (analytical-reagent grade) was obtained from Sigma (St. Louis, MO, USA), dichloromethane (analytical-reagent grade) from Merck (Darmstadt, Germany), acetonitrile (HPLC grade) from Promochem (Wesel, Germany) and ammonium acetate (analytical-reagent grade), ascorbic acid (analytical-reagent grade), methanol (HPLC grade), HCl (37%) and trifluoroacetic acid (TFA) (>99%) from J.T. Baker (Deventer, Netherlands). Water was purified in a Milli-Q system (Millipore, Bedford, MA, USA) before use.

MS

A Finnigan TSQ-70 mass spectrometer in combination with a TSP-2 thermospray interface (Finnigan Mat, San Jose, CA, USA) equiped with a liquid nitrogen solvent trap was used, with argon (quality 5.0; Hoek Loos, Schiedam, Netherlands) as collision gas. The MS–MS correction factor was set to zero while using the RFD scan mode.

Because a large number of compounds were used in the experiments, a general optimization of the repeller voltage was used each day, based on the intensity of the eluent clusters around m/z 100 [1]. Although in all experiments buffer ionization was applied, an additional discharge voltage was used. From earlier experiments some of the compounds proved to have a better signal-to-noise ratio with buffer ionization in combination with a relative low discharge voltage, without losing the sensitivity for the other compounds.

The vaporizer temperature and source block temperature were kept at 100 and 200°C, respectively, during all experiments except tuning. Tuning was performed on TFA clusters produced by methanol–water–TFA (15:84.5:0.5, v/v/v) containing 0.1 M ammonium acetate [14] delivered at a flow-rate of 1.5 ml/min. Tuning

clusters were m/z 18.0, 78.0, 149.05, 280.07, 542.11 and 804.15 in the positive mode and m/z 31.0, 69.0, 113.0, 227.0, 341.0, 472.1 and 603.2 in the negative mode. The exhaust valve was heated with an heating ribbon to 70°C during the tuning procedure to prevent condensation of ammonium trifluoroacetate in the valve. Tuning the TSQ-70 with a thermospray ion source takes several days for all quadrupoles and lenses in all modes and is only performed after each cleaning of the quadrupoles. The system proved to be very stable for months [15].

FIA–MS

An LKB (Bromma, Sweden) Model 2150 pump was used to deliver the solvent at a flow-rate of 1.5 ml/min. An ASPEC system (Gilson, Villiers Le Bel, France) with a 500-μl loop was used to inject the samples. Each injection was followed by an injection of acetonitrile–water (50:50, v/v) to clean the loop, lines and vaporizer.

HPLC–MS

The HPLC system was connected on-line with an UV detector and the mass spectrometer in series. The LC system consists of a Rheodyne, (Cotati, CA, USA) Model 7125 injection valve (100-μl loop) and a Milton Roy (Riviera Beach, FL, USA) Model CM4000 gradient pump. Separation was carried out on a silica-based C_{18} column (3 mm I.D., 5-μm particles) (Chrompack, Bergen op Zoom, Netherlands) at a flow-rate of 0.6 ml/min and a gradient from 100% A to 100% B in 60 min [A = 0.1 M ammonium acetate (or formate)–acetonitrile (95:5, v/v), B = acetonitrile]. After UV detection at 235 nm (Milton Roy Spectromonitor 3100), the eluent was mixed with a postcolumn flow of 1.2 ml/min (LKB Model 2150) 0.1 M ammonium acetate (or formate) to increase the flow-rate to the vaporizer and to reduce the concentration of the organic modifier.

Sample concentration

The procedure of Di Corcia and Marchetti [11] was used to concentrate surface water samples (river Rhine). Samples of 500 ml were spiked with ten compounds at 1 μg/l and forced by vacuum to pass through ENVI-Carb SPE car-

tridges (6 ml, filled with 250 mg of Carbopack B, 40–100 μm particles) (Supelco, Bellafonte, PA, USA) within 1 h. Each cartridge was conditioned with 5 ml of dichloromethane–methanol (80:20, v/v) followed by 2 ml of methanol and 15 ml of 10 g/l ascorbic acid in HCl-acidified water (pH 2).

After loading with sample, the cartridge was washed with 7 ml of water and dried for several minutes by drawing room air through it. Desorption was performed with 1 ml of methanol followed by 6 ml of dichloromethane–methanol (80:20, v/v). The extract was evaporated with a stream of nitrogen to reduce the volume to 100 μl. Methanol–water (50:50, v/v) was added to adjust the total volume to 500 μl.

RESULTS AND DISCUSSION

Optimization of lower COFF voltage and collision gas pressure

A mixture of alachlor, atrazine, aldicarb and barban (500 ng/ml each) in 0.1 M ammonium acetate in water–acetonitrile (90:10, v/v) was analysed by FIA at different collision gas pressures of argon in the range 0.5–3.5 mTorr (1 Torr = 133.322 Pa). The collision offset voltage was continuously changed (from -2 to -10 V in 2-V steps) from scan to scan. The cut-off mass was m/z 70, the daughter scan range was m/z 10–500 in 0.5 s, the repeller voltage was 160 V and the discharge voltage was 500 V.

The results revealed that each compound has its own optimum, which depends on the presence of adduct ions at a COFF of -2 V (aldicarb, alachlor and barban) and/or the presence of fragments or daughter ions at the whole COFF range of -2 to -10 V, but especially at values of -8 and -10 V. High intensities of $[M + H]^+$ ions were obtained in the COFF voltage range -4 to -6 V for most compounds. Both COFF voltages are shown in Fig. 2A and B, with the intensity of the $[M + H]^+$ ions plotted against the collision gas pressure. The optimum pressure is between 1
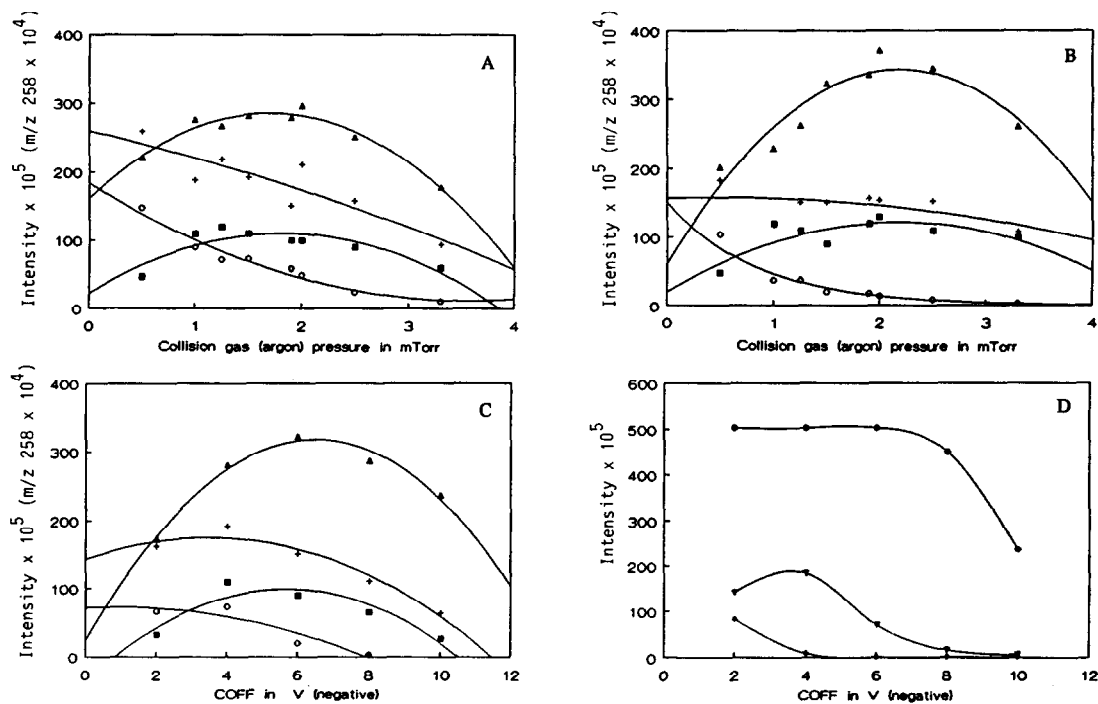
Fig. 2. Optimization of the lower COFF voltage and the collision gas (argon) pressure. Based on the intensities of the molecular ions $[M + H]^+$ of (+) alachlor (m/z 270), ($\blacktriangle$) atrazine (m/z 218; m/z 216 was overloaded), ($\bigcirc$) aldicarb (m/z 191), ($\blacksquare$) barban (m/z 258), and eluent clusters ($\bullet$) m/z 59 saturated between -2 to -6 V, ($\blacktriangledown$) m/z 77 and ($\blacklozenge$) m/z 100, analysed by FIA–RFD. (A) COFF, -4 V; (B) COFF, -6 V; (C) argon, 1.5 mTorr; (D) argon, 1.5 mTorr.

and 2 mTorr at both COFF voltages and therefore 1.5 mTorr of argon was selected for further experiments.

In Fig. 2C the influence of the COFF voltage on the intensity of the $[M + H]^+$ ions is plotted at an argon pressure of 1.5 mTorr and shows an optimum at about −4 to −6 V. In Fig. 2D the intensity of some major eluent clusters (note that m/z 59 is below the cut-off mass and therefore a daughter ion) are plotted against the COFF voltage at a collision gas pressure of 1.5 mTorr. The intensity of these unwanted ions are decreased strongly from −4 to −10 V. From the combined information in Fig. 2C and D a COFF of −6 V was selected and used in further experiments.

Higher COFF voltages

Additional specific ions can be obtained at higher COFF voltages. Therefore, the RFD scan mode was evaluated with three COFF voltages (−6, −20 and −40 V), alternately changed each scan at a collision gas pressure of 1.5 mTorr of argon. For twenty compounds, listed in Table I, flow-injection analyses were performed in the single stage scan mode (Q3MS; scan range m/z 65–500; scan time 0.5 s; electron multiplier voltage 1500 V) and in the RFD scan mode (scan range 10-500 m/z; scan time 0.5 s; cut-off mass m/z 70; electron multiplier voltage 1500 V) with thermospray ionization at a repeller voltage of 160 V and a discharge voltage of 500 V. The sample solution and FIA eluent was 0.1 M ammonium acetate in water–acetonitrile (90:10, v/v). Compounds were separately injected at a concentration of 450 ng/ml.

At a COFF of-6 V in the RFD scan mode the intensities of the base peaks are comparable to those in the Q3MS scan mode (Table I). In MS–MS scan modes in which the first quadrupole is used as a mass filter, the transmission is about 10% relative to a first quadrupole operating in the RF-only mode [13]. However, in both the RFD and Q3MS scan modes the first quadrupole is in the RF-only mode, so the transmission should be equal and a difference in intensity is mainly evoked by the situation in the collision cell. The spectral information regarding

the molecular mass is slightly less in the RFD scan mode, because for none of the compounds were adduct ions acquired. The aim to maintain the molecular $[M + H]^+$ ions is achieved for all analytes, unless they were not present in the single-stage Q3MS scan mode (sethoxydim). The decreased noise level in the RFD scan mode with a COFF of −6 V resulted for many compounds in a better signal-to-noise ratio and lower detection limit.

At a COFF of −20 V the optimized argon pressure of 1.5 mTorr proved to be high enough to generate additional ions for most of the compounds (in Table II the remaining ions besides the base peaks are listed). However, the detection limits shown in Table I are also important. Compared with the Q3MS scan mode, the intensities at a COFF of −20 V are lower (note: values from 10^6 to 10^5), but due to a lower noise level the detection limits are about the same. Compared with −6 V, the detection limit at −20 V is higher. This is mainly caused by the decrease in intensity of the base peak due to the increased fragmentation, rather than by an increased noise level. Hence the generated spectra give more specific information without sacrificing much sensitivity.

At a COFF of −40 V increased fragmentation results in mainly high detection limits and low m/z values. These m/z values are less suitable for diagnostic purposes, *i.e.*, they are less unique. Therefore, the COFF of −40 V was not used in the remaining experiments. If it is nessecary to acquire these masses, *e.g.*, for structural elucidation, it will be better to use the more common MS–MS scan modes. The relationship between a parent ion and low m/z daughter ions is better defined in those modes.

HPLC–MS

The HPLC–RFD method was tested at a collision gas pressure of 1.5 mTorr of argon and with COFF voltages of −6 and −20 V alternating each scan. A cut-off mass of m/z 70 was used. Ammonium acetate and ammonium formate were used separately in the HPLC and post-column eluent. The scan range was m/z 33–400 for the Q3MS mode and m/z 10–400 for the RFD mode. For both modes the scan time was 1

TABLE I

INTENSITY OF BASE PEAKS AND NOISE WITH FIA ANALYSES IN Q3MS AND RFD SCAN MODES

DL = Detection limit (signal-to-noise ratio = 5) in ng calculated on the base peak. Peak width is 20–30 s, comparable to HPLC-MS.

Compound	M_r	Q3 MS			RFD, COFF −6V			RFD, COFF −20V			RFD, COFF −40V		
		Base peak			Base peak			Base peak			Base peak		
		m/z	$(\times 10^6)$	Noise intensity $(\times 10^4)$	DL (ng)	m/z	$(\times 10^6)$	Noise intensity $(\times 10^4)$	DL (ng)	m/z	$(\times 10^5)$	Noise intensity $(\times 10^3)$	DL (ng)	m/z	$(\times 10^5)$	Noise intensity $(\times 10^3)$	DL (ng)

Note: The header structure above is: Compound, M_r, then four groups (Q3 MS; RFD, COFF −6V; RFD, COFF −20V; RFD, COFF −40V) each with Base peak (m/z and intensity), Noise intensity, and DL (ng).

Compound	M_r	Q3 MS m/z	Q3 MS $(\times 10^6)$	Q3 MS Noise $(\times 10^4)$	Q3 MS DL (ng)	−6V m/z	−6V $(\times 10^6)$	−6V Noise $(\times 10^4)$	−6V DL (ng)	−20V m/z	−20V $(\times 10^5)$	−20V Noise $(\times 10^3)$	−20V DL (ng)	−40V m/z	−40V $(\times 10^5)$	−40V Noise $(\times 10^3)$	−40V DL (ng)
Alachlor	269.12	270	2	1.6	2.3	238	2.2	0.35	0.4	162	7	3	1.2	147	2.4	1.4	1.6
Aldicarb	190.08	208	1.3	0.64	1.4	116	1.6	0.9	1.6	89	5	7	3.9	89[a]	0.75	2	7.5
Aniline	93.06	135	0.1	0.7	20	94	0.2	0.25	3.5	94	0.6	2	9.4	51	0.18	2	31
Atrazine	215.09	216	4.7	0.5	0.3	216	4	0.28	0.2	174	7	2	0.8	68	2.4	3	3.5
Benzothiazole	135.01	136	0.5	3	17	136	0.56	0.24	1.2	136	2.3	3	3.7	65	0.4	10	70
Carbendazim	191.07	192	3.2	0.5	0.4	192	2.4	0.5	0.6	160	9.5	2.5	0.7	160	0.9	1	3.2
Chloridazon	221.04	222	4	1	0.7	222	2.7	0.5	0.5	222	6.5	2.5	1.1	77	3	30	28
Diazinon	304.10	305[a]	3.2	2.5	2.2	305	2.6	2	2.2	153	7.5	5	1.9	97	2.4	10	12
Dimethoate	229.00	230	11	1	0.3	230	7.5	1.5	0.6	125	16	9	1.6	125[a]	3.2	4	3.5
Diuron	232.02	233[a]	1	1	2.8	233	0.73	0.9	3.5	46	6.4	5	2.2	72	1.6	5	8.8
Ethylenethiourea	102.02	103	13	3	0.6	103	9.4	2	0.6	103[a]	9	10	3.1	103[a]	1	8	23
Isocarbamide	185.12	186	15	6	1.1	186	13	5	1.1	87	40	10	0.7	87[a]	5	4	2.3
Isoproturon	206.14	179	6.7	3	1.3	179	6	2	0.9	137[a]	7	13	5.2	72[a]	1.7	6	10
Metamitron	202.09	203	13	10	2.2	203	9	3	0.9	203	4	15	10	104[a]	1.1	5	13
Metolachlor	283.13	284	16	3	0.5	284	10	2	0.6	252	43	5	0.3	133	4	6	4.2
Monolinuron	214.05	215	4	1.4	1.0	215	3.2	0.9	0.8	126	7	4	1.6	127[a]	1	2	5.6
Propachlor	211.05	212	9	2	0.6	212	10	1	0.3	170	24	4	0.5	94[a]	8	3	1.1
Sethoxydim	327.19	282	15	3	0.6	282	12	1	0.2	178	13	3	0.6	107	4	7	4.9
Simazine	201.08	202	13	4	0.9	202	11	2.5	0.6	132[a]	10	3	0.8	68	8	5	1.8
Warfarin	308.11	309	6	3	1.4	309	3.5	1.5	1.2	251	8	5	1.8	163[a]	0.7	3	12

[a] No base peak, but more specific and/or lower DL.

TABLE II

REMAINING IONS HIGHER THAN 10% OF THE BASE PEAK (% OF THE BASE PEAK)

Compound	M_r	m/z (relative intensity, %)		
		Q3 MS	RFD, COFF −6V	RFD, COFF −20V
Alachlor	269.12	226 (12); 238 (37); 240 (12); 271 (14); 272 (31); 287 (25)[a]	226 (14); 239 (14); 240 (30); 270 (45); 272 (16)	90 (13); 238 (50); 240 (19)
Aldicarb	190.08	116 (13); 191 (80)	191 (13)	41 (16); 70 (22); 116 (16)
Aniline	93.06	94 (13)	–	–
Atrazine	215.09	218 (33)	218 (33)	96 (25); 132 (12); 146 (11); 176 (33); 216 (40); 218 (12)
Benzothiazole	135.01	177 (28)[a]	–	–
Carbendazim	191.07	134 (14); 193 (10)	134 (20); 193 (10)	134 (17)
Chloridazon	221.04	224 (33)	224 (33)	92 (12); 104 (20); 224 (33);
Diazinon	304.10	153 (110); 306 (13)	153 (113); 306 (13)	84 (19); 93 (21); 97 (15); 125 (16); 169 (70); 249 (17)
Dimethoate	229.00	–	199 (40)	88 (31); 171 (35); 199 (17)
Diuron	232.02	87 (212)[a]; 205 (36); 207 (24); 222 (23); 224 (12); 235 (61); 250 (12)[a]	46 (123); 205 (57); 207 (38); 235 (67)	72 (42)
Ethylenethiourea	102.02	–	–	44 (177); 86 (19)
Isocarbamide	185.12	–	–	–
Isoproturon	206.14	87 (33)[a]; 196 (12); 207 (41)	46 (15); 207 (37)	46 (117); 72 (69); 94 (87); 120 (12); 179 (20)
Metamitron	202.09	204 (11)	204 (11)	31 (21); 77 (37); 79 (19); 104 (95); 106 (16); 145 (17); 174 (47); 175 (76)
Metolachlor	283.13	285 (17); 286 (33)	252 (35); 254 (11); 285 (17); 286 (33)	176 (43); 253 (16); 254 (33)
Monolinuron	214.05	171 (16); 217 (33); 232 (35)[a]; 234 (11)[a]	171 (21); 217 (33)	62 (23); 93 (11); 128 (33); 148 (66)
Propachlor	211.05	213 (12); 214 (33); 229 (22)[a]	213 (12); 214 (33)	94 (40); 106 (24); 172 (32);
Sethoxydim	327.19	283 (18)	283 (18)	107 (91); 108 (20); 150 (15); 151 (12); 176 (82); 220 (45); 282 (47);
Simazine	201.08	204 (33)	204 (33)	68 (29); 71 (44); 96 (87); 104 (48); 106 (16); 124 (110); 134 (33); 174 (13); 202 (61); 204 (20)
Warfarin	308.11	310 (20)	310 (20)	45 (24); 147 (21); 163 (97); 252 (15)

[a] Adductions.

s, electron multiplier voltage 1500 V, repeller voltage 100 V and discharge voltage 500 V.

A Q3MS and an RFD analysis of a concentrated (on Carbopack B) Rhine water sample spiked at 1 μg/l are shown in Fig. 3. The RFD chromatogram (Fig. 3B) looks "strange" owing to the different noise and ion intensity levels at a COFF voltage of −6 and −20 V and is difficult to interpret both manually as automatically. Therefore, the scans were copied alternately to different files (Fig. 3C and D). The retention time was copied together with each scan, so the resulting chromatograms can be compared (same compound, different spectra) and interpreted as usual.

In Fig. 4 background spectra from chromatograms of a standard mixture (ten compounds, listed in Fig. 3, in methanol–water (50:50, v/v) at a concentration of 1 μg/ml) are shown. In the Q3MS scan mode it is difficult to analyse below m/z 143 because of the eluent clusters generated with both ammonium acetate and ammonium formate as ionization buffers. In the RFD scan mode with a cut-off mass of m/z 70 this value is decreased to m/z 78 (COFF −6 V) and m/z 62 (COFF −20V). Remaining ions such as those of m/z 227 and 243 in the formate spectra are probaly due to the chemical background.

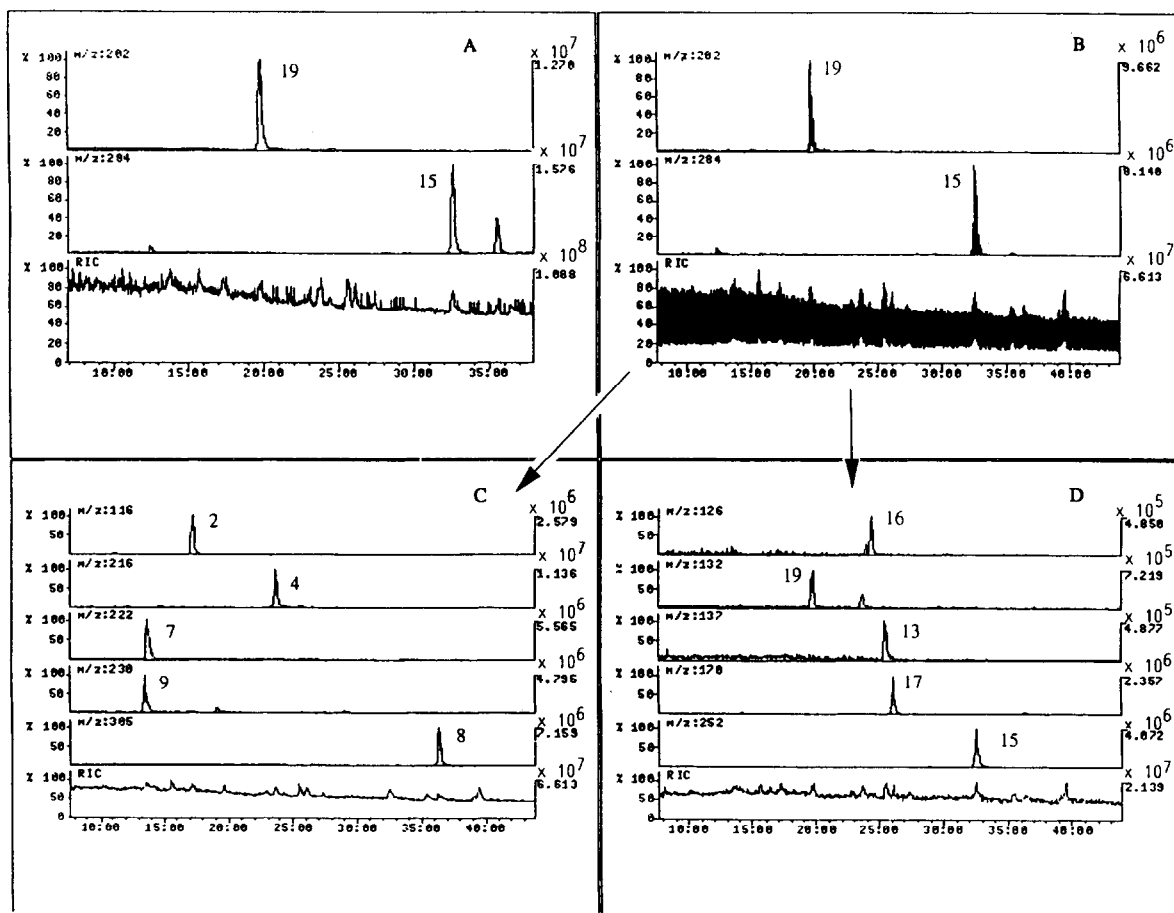Fig. 5 shows the spectra of dimethoate and metolachlor in a spiked Rhine water sample after

Fig. 3. Chromatograms of Rhine water spiked with ten compounds at 1 μg/l. Injected amount after concentration, ca. 100 ng. Ionization buffer with ammonium formate. (A) Q3MS; (B) RFD with COFF of −6 and −20 V alternately; (C) RFD with COFF of −6 V, copied from (B); (D) RFD with COFF of −20 V, copied from (B). Peaks: 2 = aldicarb; 4 = atrazine; 7 = chloridazon; 8 = diazinon; 9 = dimethoate; 13 = isoproturon; 15 = metolachlor; 16 = monolinuron; 17 = propachlor; 19 = simazine.
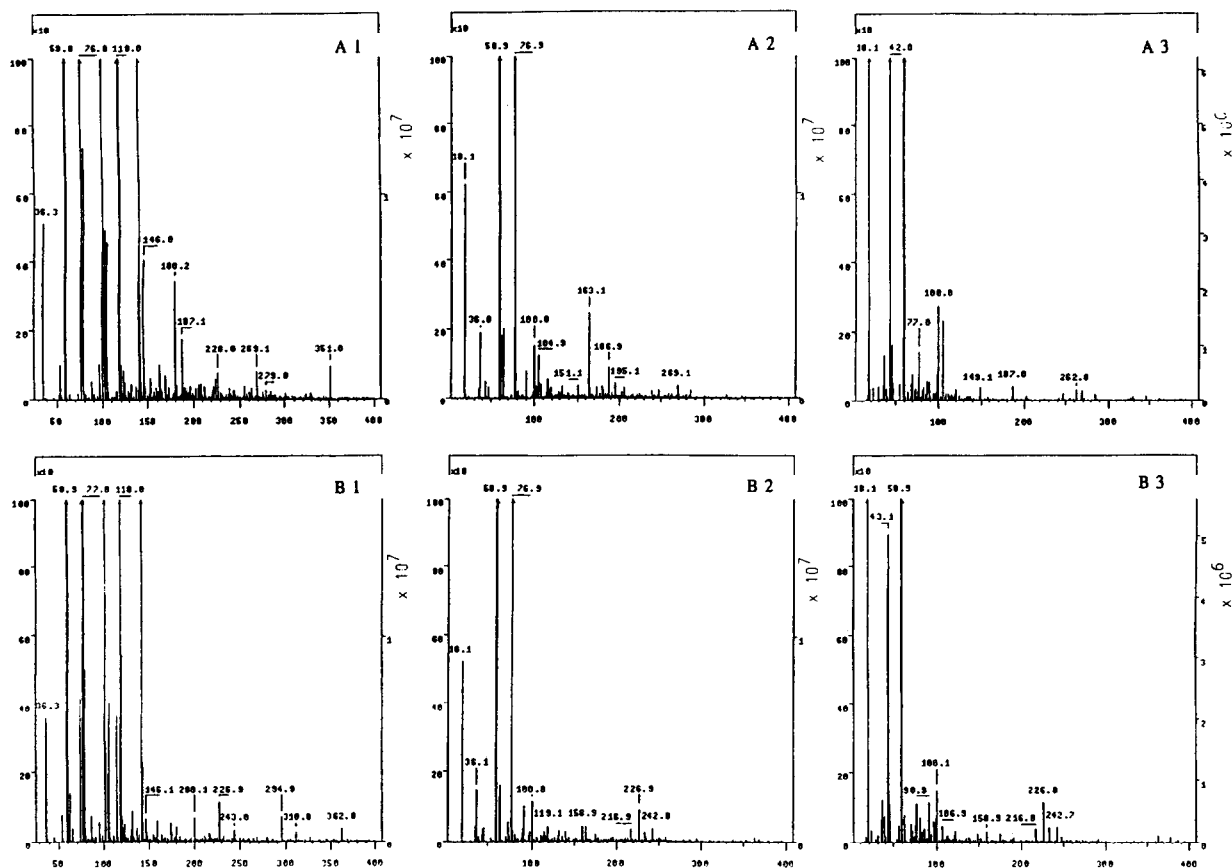
Fig. 4. Background spectra of 0.1 M ammonium acetate (or formate)–acetonitrile (*ca.* 90:10) in the Q3MS and RFD scan modes. (A) Acetate; (B) formate; 1 = Q3MS; 2 = RFD, −6 V; 3 = RFD, −20 V. Blow-up factor = 10 for all spectra.

background subtraction in both the Q3MS and RFD scan modes. On going from the Q3MS to the RFD scan mode with a COFF voltage of −6 V, the NH_4^+ adduct of dimethoate (m/z 247) disappears, but molecular information for both compounds is retained. At a COFF voltage of −20 V extra ions are acquired. By combining the information from both COFF voltages for both compounds at least five diagnostic ions are obtained. A problem is how to deal with the ions with the same m/z ratio in both spectra (COFF −6 and −20 V). In fact, they are the result of different collisionally activated decomposition processes. The ratio between them depends on the stability of the ion and is therefore additional information. How far this ratio is stable between the standard analyte and the analyte in a sample and whether it can be used for confirmation will be investigated in future work.

One of the chromatograms of the standard mixture was acquired with a cut-off mass of m/z 105 to remove the intense eluent clusters around m/z 77 and 100 generated in the thermospray ion source, to test the stability of the spectra in the RFD scan mode. With a cut-off mass of m/z 70, ions from the eluent are still entering the collision cell together with an analyte. Using a cut-off mass of m/z 105 the number of eluent ions is decreased strongly, which may influence the collision and fragmentation process. Fig. 6 shows the spectra of simazine with cut-off values of m/z 70 (Fig. 6A and C) and m/z 105 (Fig. 6B and D). The spectra show a further decrease in the intensity of the remaining eluent clusters (*e.g.*, m/z 59, Fig. 6A and B). Subtraction of the background results in comparable spectra (Fig. 6C and D) indicating that the number of ions entering the collision cell together with the
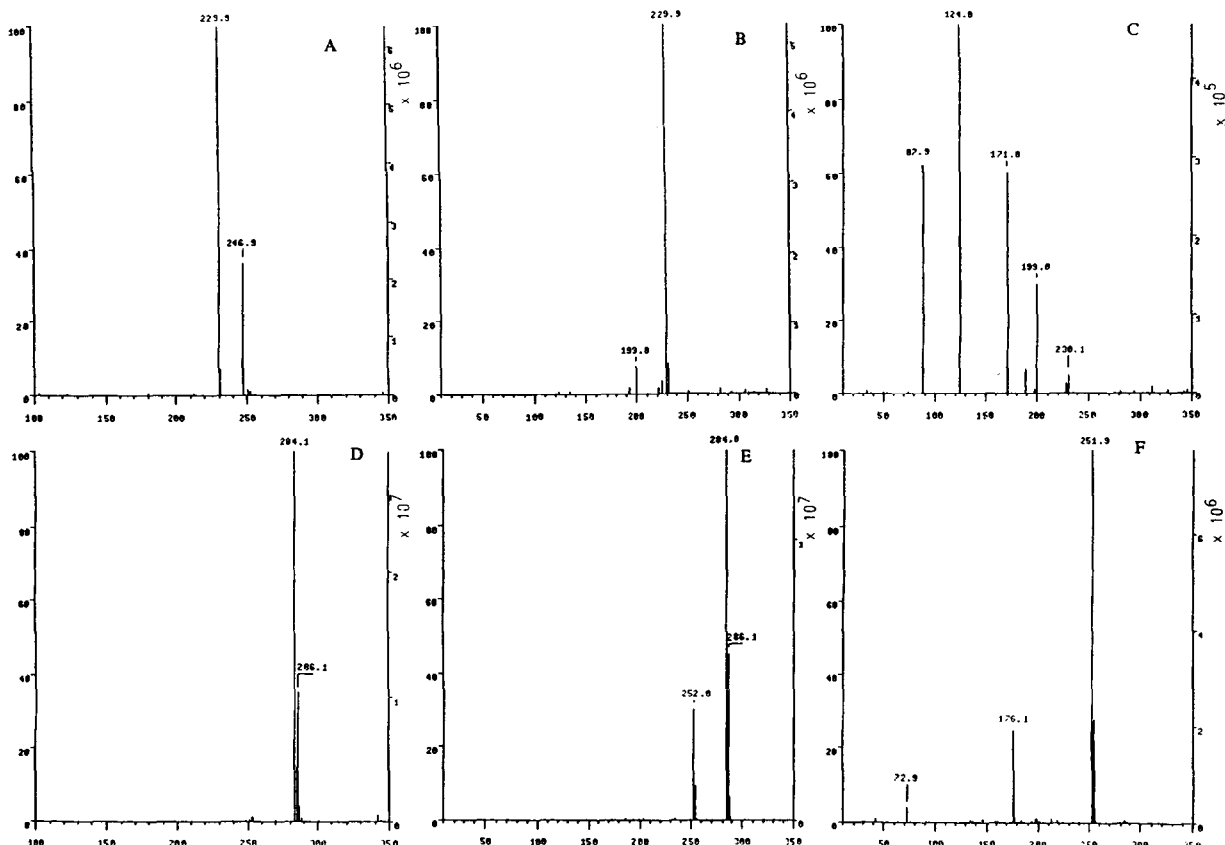
Fig. 5. Spectra of (A–C) dimethoate and (D–F) metolachlor from chromatograms in Fig. 3 after background subtraction. (A, D) Q3MS; (B, E) RFD with −6 V; (C, F) RFD with −20 V.

analyte is not very critical. In what way the optimization of the argon pressure at a relatively low cut-off mass has influenced this stability has not been investigated.

CONCLUSIONS

The RFD scan mode of a triple quadrupole mass spectrometer has been used to generate additional ions for twenty pesticides. The results indicate that, for most of the compounds, spectra with more ions are acquired with the same or better base peak signal-to-noise ratios compared with the single-stage Q3MS scan mode. The number of ions depends on the stability of a compound; e.g., aniline and benzothiazole did not generate extra ions at a COFF voltage of

−20 V, but even the fact that a compound does not break down at a medium COFF voltage is already extra information. By combining the diagnostic ions with different m/z values at both COFF voltages, at least four ions, with an intensity of more than 10% of the base peak at each COFF voltage, are available for sixteen of the twenty compounds.

The aim of not to lose molecular mass information was achieved. All compounds tested (Table I) have spectra with intense $[M + H]^+$ ions in the RFD scan mode with a COFF voltage of −6 V, unless they were not present in the single-stage MS mode (sethoxydim).

Adduct ions of the tested compounds disappear in the RFD mode. The importance of adducts is twofold. In many instances they are useful to trace the molecular mass of a com-
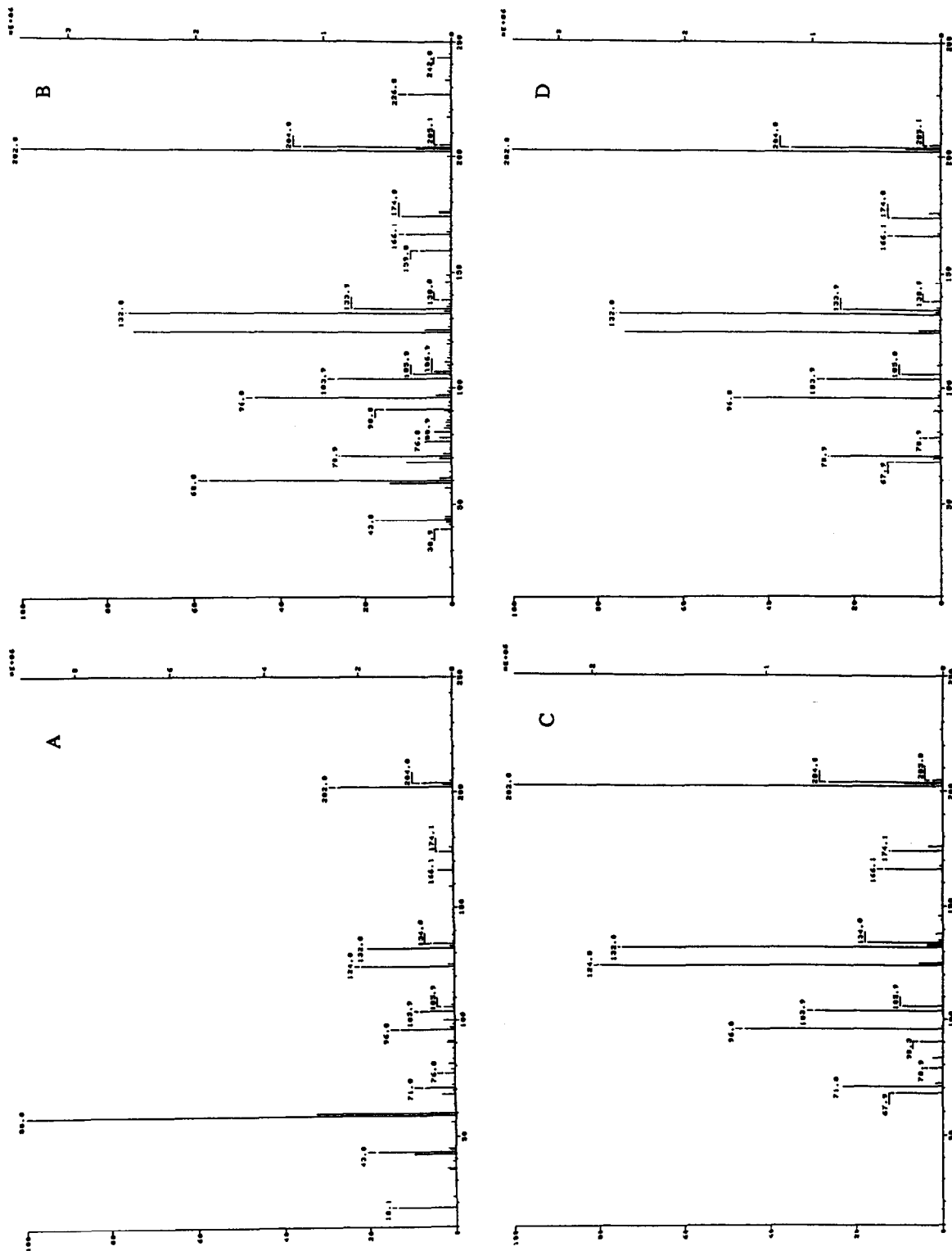
Fig. 6. Spectra of simazine at a COFF voltage of −20 V (A, B) without and (C, D) with background subtraction and a cut-off mass of (A, C) m/z 70 and (B, D) m/z 105. Analysis of a standard of 1 μg/ml (100 ng injected) with ammonium formate-assisted ionization.

pound, but they are also not very specific, matrix and source dependent and sometimes rather confusing if an adduct represents the base peak (aniline).

Eluent clusters are strongly decreased compared with the single-stage Q3MS scan mode. With a cut-off mass of m/z 105 spectra can be acquired in the whole mass range down to m/z 10 with only a few masses from eluent clusters with medium intensities (compare Fig. 6B and D).

The method was used to analyse a Rhine water sample spiked at 1 μg/l with ten compounds. Owing to the different noise levels at both COFF voltages the chromatograms look "strange", but after separation of the scans the resulting chromatograms can be evaluated as usual.

The principle of the RFD scan mode is not restricted to positive ionization. Preliminary investigations with phenoxyacid herbicides in the negative mode revealed that optimization of the argon pressure and the COFF voltage in relation to the intensity of the molecular ions $[M - H]^-$ resulted in values of 1.5 mTorr and +6 V, respectively. At a COFF of +20 V extra ions could be acquired. The RFD scan mode acted in the same way as the positive mode.

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