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Application of spectral libraries for high-performance liquid chromatography–atmospheric pressure ionisation mass spectrometry to the analysis of pesticide and explosive residues in environmental samples

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Abstract

The coupling of high-performance liquid chromatography (HPLC) and atmospheric pressure ionisation mass spectrometry (API-MS) seems to be the method of choice if good separation and selective detection of semi-volatile, thermolabile, and polar substances is required. Libraries of mass spectra will make the identification of unknown substances in complex environmental samples easier and more user-friendly. Unfortunately, existing GC–MS libraries are not applicable to HPLC–API-MS analysis. Thus, new and extensive mass spectral libraries were constructed. Several investigations of chromatographic (composition and salt concentration of the eluent) as well as mass spectrometric (orifice voltage) parameters and a few applications of real environmental samples are used to discuss the possibilities and limits of these libraries.

Keywords: Libraries, MS; Mass spectrometry; Environmental analysis; Explosives; Pesticides

1. Introduction

The coupling of HPLC and atmospheric pressure ionisation (API) MS has become a widely used analytical technique for qualitative and quantitative environmental analysis. In combination with effective enrichment methods HPLC–API-MS is suitable for the investigation of semi-volatile, thermolabile, and polar substances, like various pesticides, explosives, forensic relevant substances etc. in trace levels [1–9].

The general unknown screening (non-target analysis) for pollutants of various substance groups becomes easier and more user-friendly by the use of spectral libraries. Unfortunately, it is impossible to transfer the existing GC–MS libraries (Wiley, National Institute of Standards and Technology, etc.) to HPLC–API-MS. Due to completely different ionisation techniques, like electrospray ionisation (ESI) and atmospheric pressure chemical ionisation (APCI), in contrast to electron impact ionisation (EI), as well as different fragmentation mechanisms, new mass spectral libraries have to be constructed (Fig. 1). Various ion sources, negative and positive ion mode, ion optic voltages, and various compositions of the eluent may influence the structure of the mass spectra. Thus, it is necessary to acquire several spectra of each substance under various conditions, which makes the construction of API-MS libraries extensive.

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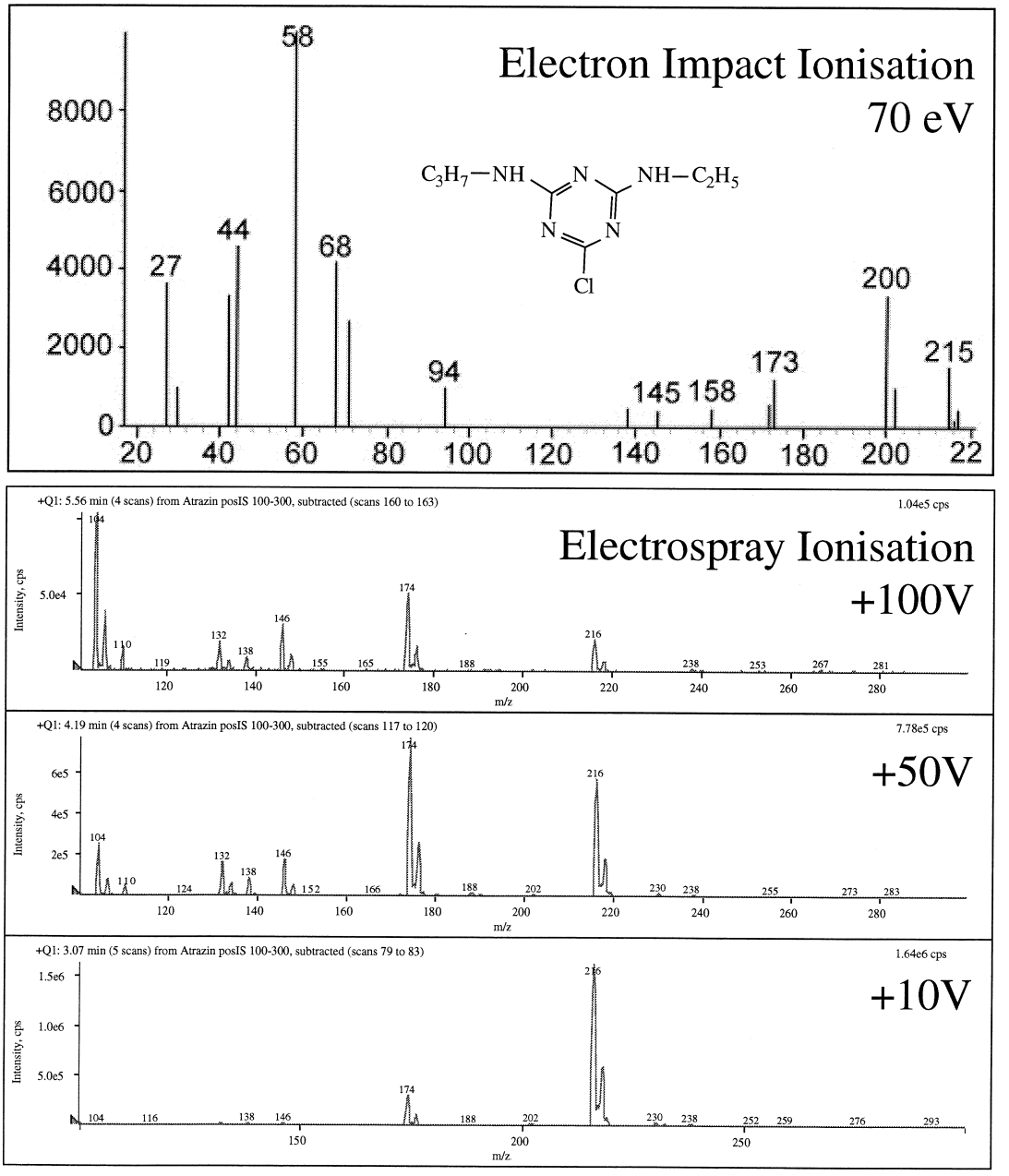

Fig. 1. Comparison of atrazine's EI and three different positive ion mode ESI spectra.

Presently, the usability of such libraries is discussed controversially by manufacturers and users of HPLC–API-MS devices. In this paper the construction of spectral libraries is demonstrated. For that purpose 804 mass spectra of pesticides and explosives were measured. A number of 367 mass spectra of pesticides were integrated into a library 'pesticides' and 188 mass spectra of explosives were integrated into a library 'explosives'.

In the case of HPLC–API-MS, the use of spectral

libraries is successful if the library spectra and the unknown substance are measured under the same mass spectrometric and chromatographic conditions. This fact would reduce the usability of spectral libraries. Thus, several parameters having an influence on the result of the library search were investigated. Finally, a few applications of HPLC–API-MS to environmental samples containing unknown explosives, by-products, metabolites, and pesticides are presented.

2. Analytical devices

Experiments were performed using a PE-Sciex API 100 LC–MS system. A Knauer HPLC 64 pump and a 7125 Rheodyne sampler were used for all flow injection analyses to construct the spectral libraries and to investigate several parameters. Investigations of environmental samples containing explosives were carried out using a Perkin-Elmer series 200 pump. Applications of HPLC–API-MS to analyse pesticides were performed in the Dutch LC–MS laboratory of PE-Biosystems using a PE-Sciex API 365 LC–MS system and a Perkin-Elmer series 200 micro pump system.

Generally, chemicals (solvents and standards) were obtained at the highest available purity.

3. Acquisition of the spectra to construct the mass spectral libraries

3.1. Experimental

Spectra of 42 pesticides[1] and 48 explosives were acquired by flow injection into an eluent consisting of methanol–water (75:25, v/v) and 5 m*M* ammonium acetate (NH_4Ac) at a flow-rate of 0.6 ml min^{-1}. A volume of 20 μl of each standard substance (Table 1) dissolved in the eluent (50 μg ml^{-1}) was injected. Due to the fact that different ionisation techniques yield different mass spectra, IonSpray (ESI) and Heated Nebulizer (APCI) were used as ion sources. Moreover, negative and positive ion mode, and different values of the orifice voltage OR [collision-induced dissociation (CID) fragmentation voltage] yield different mass spectra. Thus, OR was set to ±10 V, ±50 V and ±100 V. A number (12) mass spectra of each substance were measured.

3.2. Results

Due to their different chemical properties, especially the acidity, pesticides are detectable in negative ion mode, positive ion mode, or in both ion modes by means of API-MS (Table 1) [10]. Moreover, the fragmentation is strongly dependent on the orifice voltage. Finally, the kind of ion source has an influence on the structure of the mass spectra. In contrast to ESI, where no thermal treatment of the sample is performed, in the case of APCI much higher fragmentation is observed [11,12]. Thus, 12 mass spectra of each pesticide were measured and all characteristics and sufficient intensive spectra were added to a library ‘pesticides’ using the features of Multi-View 1.3. Substance-name, molecular mass, OR, IUPAC name, and CAS number were simply filed together with the spectrum using an ‘Add Spectrum-Window’.

Due to the electron-withdrawing nitro-group explosives, their by-products and metabolites form anions and thus, the investigation in negative ion mode is preferable. The most detected ion species is the deprotonated molecular ion $[M-H]^-$. Only the nitramines hexogen and octogen form cluster ions with acetate $[M+Ac^-]$ under standard conditions (Fig. 2) [7]. However, the intensity of mass spectrometric signals is strongly dependent on the number and the position of functional groups. Generally, the more nitro-group substances in the same substance group the more intense the detection is. The most important nitro group seems to be the one in the *para*-position. Only a few substances were not detectable by means of API-MS (Table 1). Mass spectra of explosives were measured using ESI and APCI ion sources as well as with different OR. Again all characteristic and sufficient intensive spectra were added to a library ‘explosives’.

[1] All pesticides examined are in the DIN 38407-F12 (German Institute of Standardisation).

Table 1
Investigated pesticides and explosives[a]

Pesticides	CAS	M_r	Explosives	CAS	M_r
Alachlor (+, p)	15972-60-8	269	Nitrobenzene (N.D.)	98-95-3	123
Atrazine (+, p)	1912-24-9	215	1,3-Dinitrobenzene (−)	99-65-0	168
Azinphos-ethyl (+, p)	2642-71-9	345	1,3,5-Trinitrobenzene (−)	99-35-4	213
Bromacil (−/+)	314-40-9	260	3-Nitrotoluene (N.D.)	99-08-1	137
Carbendazim (−/+)	10605-21-7	191	4-Nitrotoluene (N.D.)	99-99-0	137
Carbetamide (−/+, p)	16118-49-3	236	2,4-Dinitrotoluene (−)	121-14-2	182
Chlorfenvinfos (+, p)	470-90-6	358	2,6-Dinitrotoluene (−)	606-20-2	182
Chloridazon (−/+)	1698-60-8	221	3,4-Dinitrotoluene (−)	610-39-9	182
Chlortoluron (−/+, p)	15545-48-9	212	2,4,6-Trinitrotoluene (−)	118-96-7	227
Cyanazine (−/+, p)	21725-46-2	240	Hexogen (−)	121-82-4	222
2,4-D (−, p)	94-75-7	220	Octogen (−)	2691-41-0	296
Desethylatrazine (+)	6190-65-4	187	Tetryl (−)	479-45-8	287
Dichlofluanid (−/+, p)	1085-98-9	332	Hexyl (−)	131-73-7	439
Diuron (−/+, p)	330-54-1	232	2-Nitroaniline (−)	88-74-4	138
Fenuron (+)	101-42-8	164	4-Nitroaniline (−)	100-01-6	138
Hexazinone (+)	51235-04-2	252	3,5-Dinitroaniline (−)	618-87-1	183
Isoproturon (−/+)	34123-59-6	206	2-Amino-3-nitrotoluene (−)	570-24-1	152
Linuron (−/+, p)	330-55-2	248	2-Amino-4-nitrotoluene (−)	99-55-8	152
n-Chloro-2-methylphenoxyacetic acid (−, p)	94-74-6	200	2-Amino-5-nitrotoluene (−)	99-52-5	152
Metamitron (−/+)	41394-05-2	202	2-Amino-6-nitrotoluene (−)	603-83-8	152
Metazachlor (+, p)	67129-08-2	277	2-Amino-4,6-dinitrotoluene (−)	35572-78-2	197
Methabenzthiazuron (−/+)	18691-97-9	221	4-Amino-2,6-dinitrotoluene (−)	19406-51-0	197
Metobromuron (−/+, p)	3060-89-7	258	2,6-Diamino-4-nitrotoluene (−)	59229-75-3	167
Metolachlor (+)	51218-45-2	283	4-Nitro-1-naphtylamine (−)	86-57-7	188
Metoxuron (−/+)	19937-59-8	228	2-Nitrophenol (−)	88-75-5	139
Monolinuron (−/+)	1746-81-2	214	3-Nitrophenol (−)	554-84-7	139
Monuron (−/+)	150-68-5	198	4-Nitrophenol (−)	100-02-7	139
Parathion-ethyl (−/+, p)	56-38-2	291	2,4-Dinitrophenol (−)	51-28-5	184
Pendimethalin (−/+, p)	40487-42-1	281	2,6-Dinitrophenol (−)	573-56-8	184
Phenmedipham (−/+, p)	13684-63-4	300	3,4-Dinitrophenol (−)	577-71-9	184
Prometon (+, p)	1610-18-0	225	3,5-Dinitrophenol (−)	586-118	184
Prometryn (+)	7287-19-6	241	2,4,6-Trinitrophenol (−)	88-89-1	229
Propazine (+, p)	139-40-2	229	3-Methyl-2-nitrophenol (−)	4920-77-8	153
Sebuthylazine (+)	7286-69-3	229	2-Methyl-4,6-dinitrophenol (−)	534-52-1	198
Simazine (+)	122-34-9	201	4-Methyl-2,6-dinitrophenol (−)	609-93-8	198
2,4,5-T (−)	93-76-5	254	2,4-Dinitrobenzoic acid (−)	610-30-3	212
Tebuthiuron (−/+)	34014-18-1	228	3,4-Dinitrobenzoic acid (−)	528-45-0	212
Terbutryn (+)	886-50-0	241	3,5-Dinitrobenzoic acid (−)	99-34-3	212
Terbuthylazine (+)	5915-41-3	229	3-Aminobenzoic acid (—)	99-05-8	137
Thiabendazol (−/+)	148-79-8	201	4-Aminobenzoic acid (−)	150-13-0	137
Trifluralin (−/+)	1582-09-8	335	2,4-Dinitrobenzenesulfonic acid (−)	885-62-1	248
Vinclozolin (−/+)	50471-44-8	285	Nitroglycerin (−)	55-63-0	227
			Nitroguanidine (−)	556-88-7	104
			Diethylene glycol dinitrate (N.D.)	693-21-0	196
			Ethylene glycol dinitrate (N.D.)	628-96-6	152
			Diphenylamine (N.D.)	122-39-4	169

[a] −/+, detectable in negative and/or positive ion mode; N.D., not detected; p, chosen for investigations of several parameters.

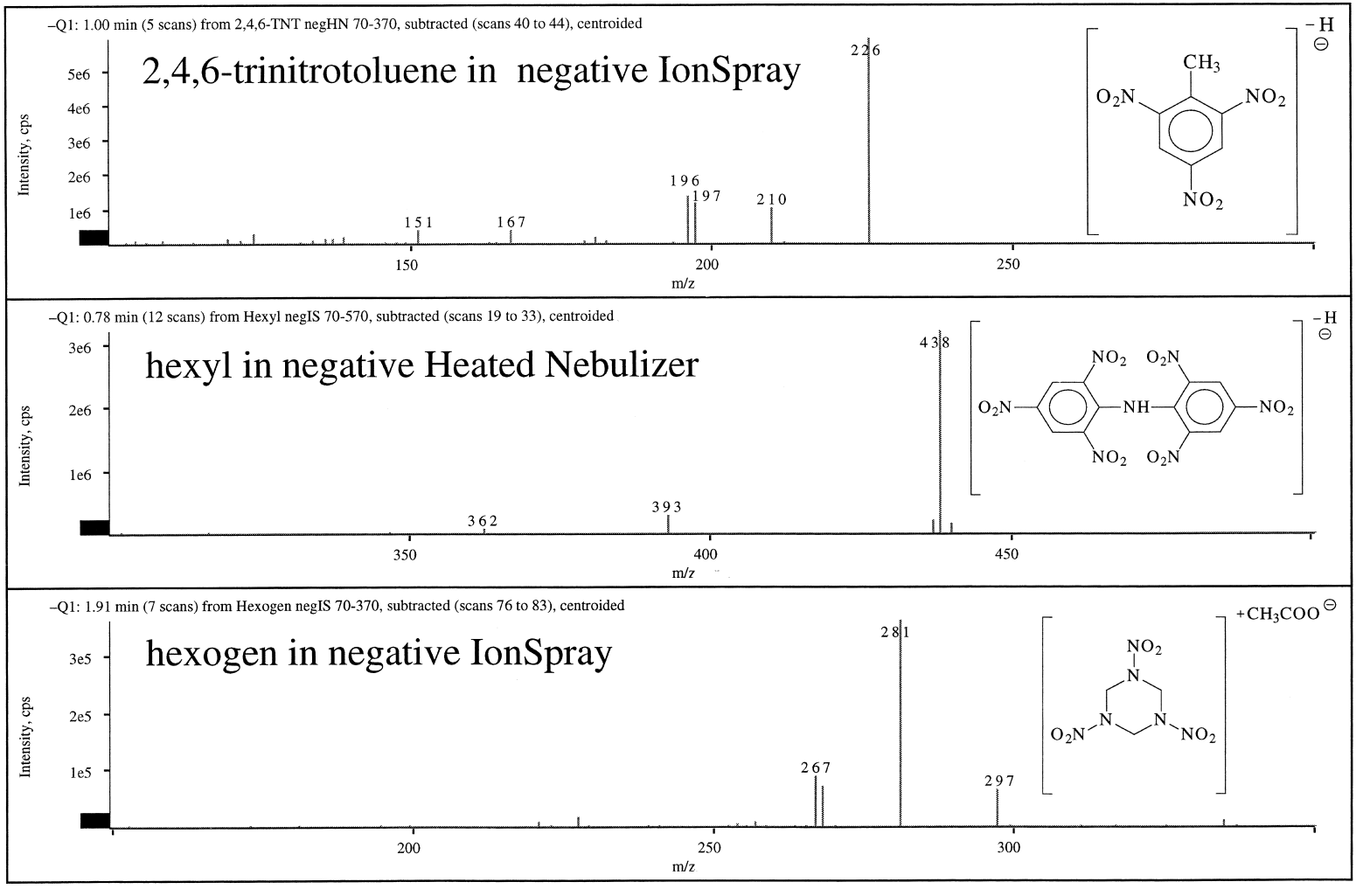

Fig. 2. Negative ion mode mass spectra of three selected explosives.

Table 2
The influence of the composition of the eluent on the intensities and relative intensities of the molecular ion m/z 216, and two fragment ions, m/z 174 and m/z 146, of atrazine

	Methanol–water (plus 5 m*M* NH_4Ac)					Acetonitrile–water (plus 5 m*M* NH_4Ac)				
	90:10	70:30	50:50	30:70	10:90	90:10	70:30	50:50	30:70	10:90
[216]	$1.23\cdot10^7$	$1.37\cdot10^7$	$1.74\cdot10^7$	$1.33\cdot10^7$	$1.95\cdot10^7$	$1.93\cdot10^7$	$1.49\cdot10^7$	$1.05\cdot10^7$	$1.25\cdot10^7$	$1.61\cdot10^7$
[216]/[216]	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
[174]	$9.21\cdot10^5$	$1.29\cdot10^6$	$1.79\cdot10^6$	$1.20\cdot10^6$	$2.08\cdot10^6$	$1.98\cdot10^6$	$1.59\cdot10^6$	$6.87\cdot10^5$	$9.99\cdot10^5$	$1.75\cdot10^6$
[174]/[216]	0.07	0.09	0.10	0.09	0.11	0.10	0.11	0.07	0.08	0.11
[146]	$4.72\cdot10^4$	$7.04\cdot10^4$	$8.72\cdot10^4$	$5.66\cdot10^4$	$8.30\cdot10^4$	$7.22\cdot10^4$	$6.96\cdot10^4$	$4.32\cdot10^4$	$7.60\cdot10^4$	$8.06\cdot10^4$
[146]/[216]	0.004	0.005	0.005	0.004	0.004	0.004	0.005	0.004	0.006	0.005

4. Investigations of parameters having an influence on the structure of mass spectra, and thus on the library search

4.1. Experimental

A number of 19 pesticides (Table 1) of various substance groups were injected into the appropriate eluent (20 μl of 5 $\mu g\,ml^{-1}$) at a flow-rate of 0.6 $ml\,min^{-1}$. A Heated Nebulizer ion source was chosen because a bigger influence, in contrast to IonSpray, of investigated parameters can be expected. For these experiments only a single parameter was changed without varying other parameters. Eluents of different composition (CH_3OH–water and CH_3CN–water, 10:90 to 90:10, v/v) and various concentrations of NH_4Ac (0–20 m*M*) were investigated using an OR of ±10 V. Furthermore, the structure of the mass spectra and dependence on the

Table 3
The influence of the concentration of ammonium acetate in the eluent on the intensities and relative intensities of the molecular ion m/z 216, and two fragment ions, m/z 174 and m/z 146, of atrazine

	Methanol–water plus				
	0 m*M* NH_4Ac	2.5 m*M* NH_4Ac	5 m*M* NH_4Ac	10 m*M* NH_4Ac	20 m*M* NH_4Ac
[216]	$1.81\cdot10^7$	$1.87\cdot10^7$	$1.74\cdot10^7$	$1.36\cdot10^7$	$1.06\cdot10^7$
[216]/[216]	1.00	1.00	1.00	1.00	1.00
[174]	$1.22\cdot10^6$	$1.82\cdot10^6$	$1.79\cdot10^6$	$8.01\cdot10^5$	$1.15\cdot10^6$
[174]/[216]	0.07	0.10	0.10	0.06	0.11
[146]	$7.18\cdot10^4$	$6.80\cdot10^4$	$8.72\cdot10^4$	$3.82\cdot10^4$	$3.53\cdot10^4$
[146]/[216]	0.004	0.004	0.005	0.003	0.003

Table 4
The influence of the CID-fragmentation voltage (orifice voltage) on the intensities and relative intensities of the molecular ion m/z 216, and two fragment ions, m/z 174 and m/z 146, of atrazine

	OR (V)						
	10	20	30	40	50	60	70
[216]	$1.70\cdot10^7$	$1.85\cdot10^7$	$1.56\cdot10^7$	$1.08\cdot10^7$	$4.96\cdot10^6$	$1.84\cdot10^6$	$6.00\cdot10^5$
[216]/[216]	1.00	1.00	1.00	1.00	1.00	1.00	1.00
[174]	$1.54\cdot10^6$	$5.57\cdot10^6$	$1.12\cdot10^7$	$1.17\cdot10^7$	$9.23\cdot10^6$	$6.92\cdot10^6$	$3.41\cdot10^6$
[174]/[216]	0.09	0.30	0.72	1.08	1.86	3.75	5.68
[146]	$4.98\cdot10^4$	$3.77\cdot10^5$	$9.53\cdot10^5$	$1.47\cdot10^6$	$2.16\cdot10^6$	$2.04\cdot10^6$	$1.41\cdot10^6$
[146]/[216]	0.00	0.02	0.06	0.14	0.44	1.10	2.35

OR (±10 V to ±70 V) was investigated (Tables 2–4). Finally, 588 mass spectra of 19 pesticides under various conditions were acquired and interpreted.

4.2. Results and discussion

Spectra measured under various conditions were compared with the library spectrum. In Tables 2–4 these intensities are very well demonstrated using the protonated molecular ion m/z 216, and the two dealkylated ions, m/z 174 and m/z 146, of atrazine. The comparison of mass intensities and relative mass intensities is quite difficult to assess, thus the PURITY FIT was chosen as a measure of the spectra's agreement. The averages of the probabilities from

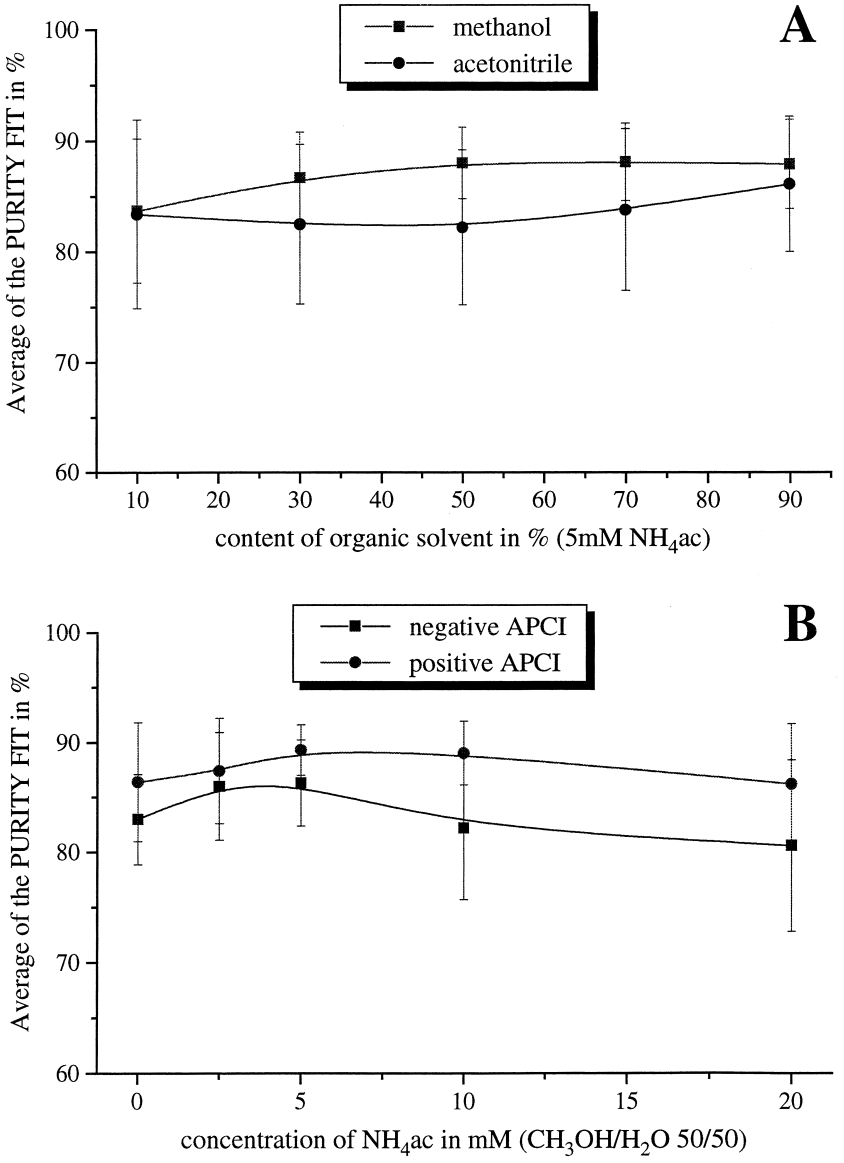

Fig. 3. Influence of chromatographic parameters on the library search of 19 pesticides.

the library search of all 19 pesticides are discussed and the dependence on the changed parameter.

Generally, an influence of the eluent's composition on the mass intensities is observable (Table 2). The reason for the strange decreasing and increasing of the atrazine's intensity is not known. Due to the fact that relative intensities are nearly invariable, the PURITY FIT is nearly independent on this parameter [Fig. 3(A)]. Therefore, problems in using the library are not expected in the case of gradient elution. However, it has to be mentioned that a higher content of water complicates the evaporation of droplets, and thus the base line is much noisier.

Fig. 3(B) demonstrates that a library search with high probability is possible over a wide range of the concentration of NH_4Ac. The optimal concentration

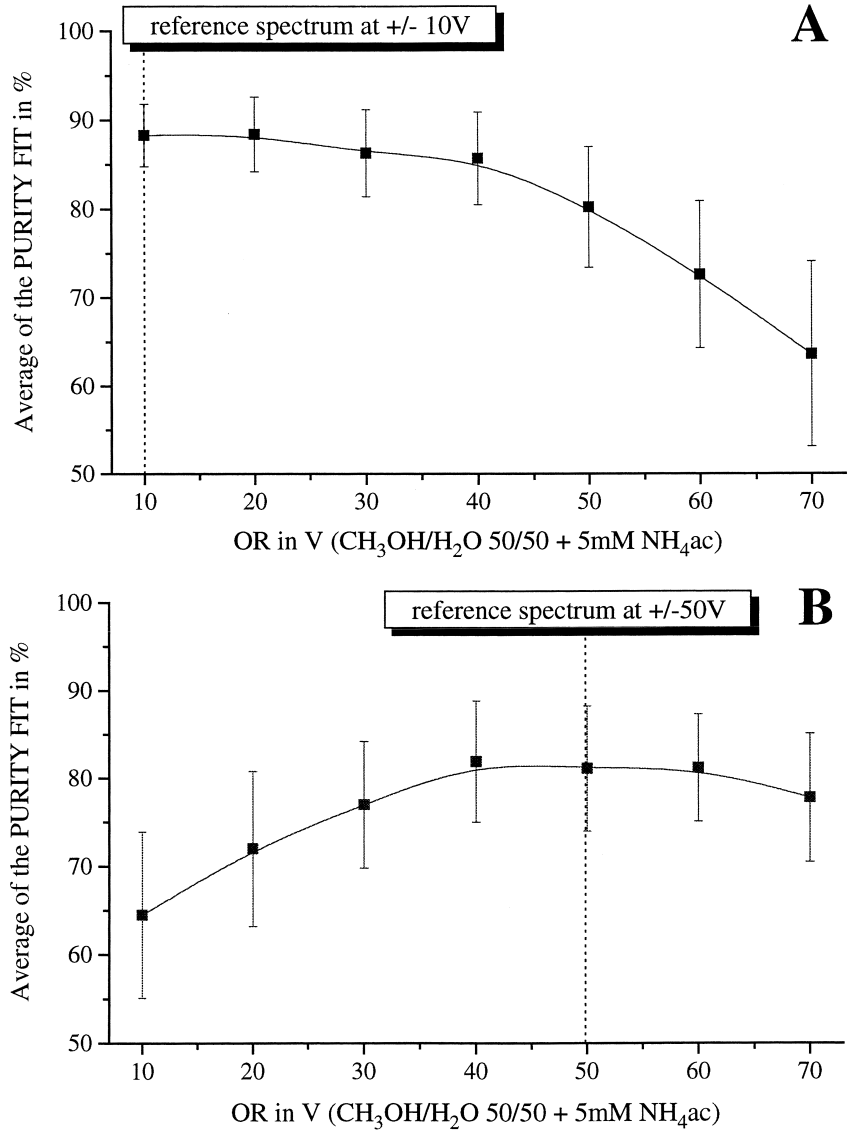

Fig. 4. Influence of the CID-fragmentation voltage (OR) on the library search of 19 pesticides.

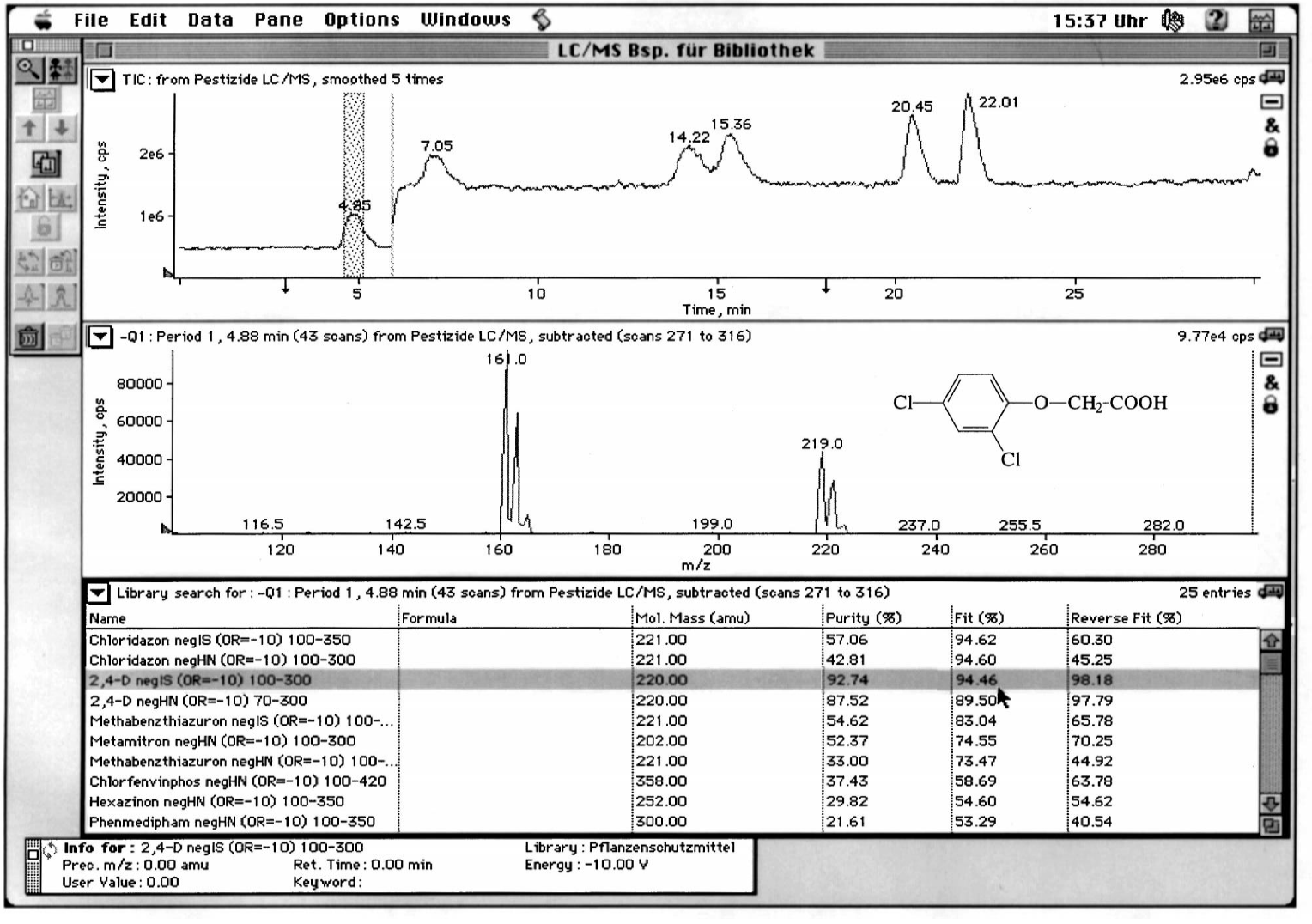

Fig. 5. Result of the library search for an unknown substance.

is approximately 2.5 m*M*. This corresponds to the value of the highest intensity of API-MS signals of these pesticides (Table 3). Smaller concentrations of NH_4Ac result in lower ion formation, and higher concentrations yield an increasing intensity of cluster ion signals $[M+Ac^-]$ and $[M+NH_4^+]$, respectively.

The probabilities in Fig. 4(A) and (B) were obtained by comparing the reference spectra of ±10 V and ±50 V, respectively, and the spectra of 19 pesticides measured with various orifice voltages. The relative mass intensities as well as the average of the PURITY FIT decreases with an increasing OR difference between both spectra (Table 4). A good library search is possible if the OR difference is not larger than 10–20 V. Nevertheless, the more experienced the user of the HPLC–API-MS technique is, the better he is able to interpret the result of the library search [13].

Further investigations show that the pH value has an influence on the intensity of mass signals [8] but not on the library search and the temperature of the nebulizer gas has no significant influence on the PURITY FIT in the range 300–400°C.

Weinmann et al. obtained similar results by investigating forensic relevant substances. They showed that the use of different PE-Sciex devices (API 150, API 365) equipped with different ion sources yield negligible differences in intensity and structure of mass spectra. The pharmacological agent haloperidol was used to characterise the OR-dependent fragmentation behaviour and to optimise the parameters of the ion sources [14].

5. Use of mass spectral libraries

After zooming out and subtracting the baseline from the total ion current (TIC) it is possible to start the library search. Several parameters, like intensity factor, OR, and/or molecular mass can be inserted in a 'Search Options-Window' to specify the library search. An INCOS algorithm leads to three probabilities (Fig. 5). The FIT is a measure of finding the signals of the reference spectrum in the unknown spectrum. The REVERSE FIT gives information about finding the unknown spectrum in the reference spectrum. Both values are combined in the PURITY FIT [15].

6. Investigation of a real sample containing explosives

6.1. Experimental

A drainage water extract from the former ammunition plant Elsnig (Saxony, Germany) was analysed using an RP-18 column (Ultrasep ES; 250×4 mm; 5 μm) from Sepserv (Berlin, Germany) and an isocratic eluent at a flow-rate of 0.6 ml min^{-1} consisting of CH_3OH–water (41:59; v/v) and 5 m*M* NH_4Ac. The pH value of 5.0 was adjusted using acetic acid. TurboIonSpray (thermally assisted IonSpray) was used as the ion source. OR was set to –10 V.

6.2. Results

The TIC and several mass spectra of the drainage water extract investigated using the TurboIonSpray are shown in Fig. 6. Several explosives, by-products, and metabolites were identified using the spectral library (Table 5). However, it has to be mentioned that the identification of isomeric substances is a tricky problem with a mass spectral library. Thus, knowledge about the retention behaviour is necessary.

7. Investigations of samples containing pesticides

7.1. Experimental

Several samples containing pesticides were investigated using a conventional RP column and a gradient eluent (water–CH_3CN, 90:10 to 10:90, v/v, in 23 min) at a flow-rate of 1.0 ml min^{-1}. A PE-Sciex API 365 LC/MS system equipped with a Heated Nebulizer ion source was used.

7.2. Results

Generally, these samples were analysed several years ago without knowing something about a future mass spectral library. Chromatographic and spectrometric conditions of analysing these samples completely differ from the conditions of constructing the library. Thus, the application of the library

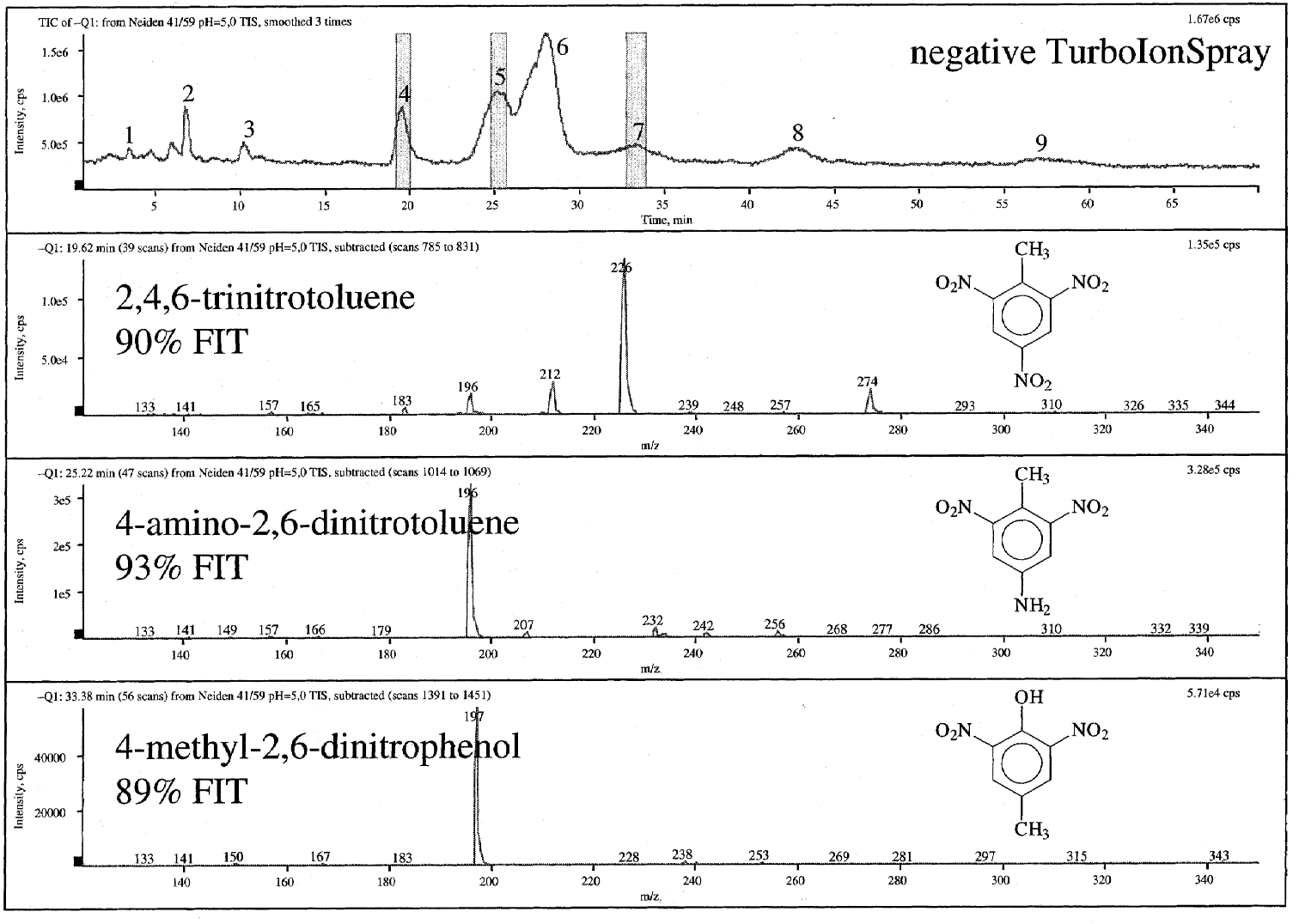

Fig. 6. Identification of several explosives in a real sample of a former ammunition plant by means of HPLC–API-MS in negative ion mode.

Table 5
Identification of explosives in a sample of a former ammunition plant using HPLC–API-MS in negative ion mode and the library 'explosives'

No.	Retention time (min)	Explosive	FIT (%)
1	3.5	Octogen	55
2	6.8	Hexogen	79
3	10.3	1,3,5-Trinitrobenzene	93
4	19.5	2,4,6-Trinitrotoluene	90
5	25.3	4-Amino-2,6-dinitrotoluene	93
6	27.9	2-Amino-4,6-dinitrotoluene	92
7	33.4	4-Methyl-2,6-dinitrophenol	89
8	42.8	2-Methyl-4,6-dinitrophenol	92
9	57.4	Unknown substance	–

'pesticides' should represent an excellent test of the library's suitability. Two selected examples are chosen to demonstrate the possibilities of the library.

Fig. 7 shows the negative and the positive TIC of a sample containing unknown pesticides as well as the mass spectra of the peak at 5.4 min. The mass spectra in the positive ion mode contains signals of desethylatrazine m/z 188, m/z 146 as well as of chloridazon m/z 222, and thus good probabilities for both pesticides are obtained. Due to the fact that chloridazon form negative as well as positive ions, whereas desethylatrazine is detectable only in positive ion mode, these substances are distinguishable without doubt using the spectral library on the spectra of both ion modes in a coeluting peak. Finally, all identified pesticides are represented in Table 6.

The unknown substance in Fig. 8 ($t_R = 7.7$ min) was investigated using an OR of +30 V. The reference spectra in the library were measured with +10 V and +50 V, respectively. However, the identification of bromacil by performing a library search is not problematic. Furthermore, both latter applications show the possibility of using the libraries constructed on a PE-Sciex API 100 LC–MS system on other API-MS devices of PE-Sciex.

8. Conclusion

In contrast to GC–MS, libraries for the identification of unknown substances separated using HPLC and detected by means of API-MS are not available. Mass spectral libraries for the analysis of samples containing explosives as well as pesticides were constructed and successfully applied on real environmental samples. Investigations of several chromatographic and mass spectrometric parameters show that a library constructed once for all produces correct and reproducible results of the library search. The composition of eluents normally used for HPLC–API-MS has no significant effect on the structure of the mass spectra, and thus no effect on the results of the library search. Nevertheless, knowledge about the ionisation and fragmentation behaviour of the analytes makes the assessment of the library search easier.

Public and widespread use requires reliable and user-friendly functioning. Thus, these mass spectral libraries for environmental and forensic analysis are available via the Internet [16].

Table 6
Identified and non-identified pesticides in an unknown sample, determined using negative and positive ion mode and the library 'pesticides'

No.	Retention time (min)	Ion mode	Pesticide	FIT (%)
1	2.1	Negative	2,4-D	91
2	2.9	Negative	DNOC	96
4	5.4	Positive	Desethylatrazine	75
4	5.4	Negative/positive	Chloridazon	96/89
5	6.1	Negative	2,4,5-T	93
6	7.7	Negative/positive	Bromacil	97/97
9	9.3	Negative/positive	Methabenzthiazuron	84/99
10	9.4	Negative/positive	Chlortoluron	95/99
11	10.0	Positive	Carbendazim	88
12	10.2	Negative/positive	Diuron	97/97
3, 7, 8, 13–20	–	Negative/positive	Unidentified substances	–

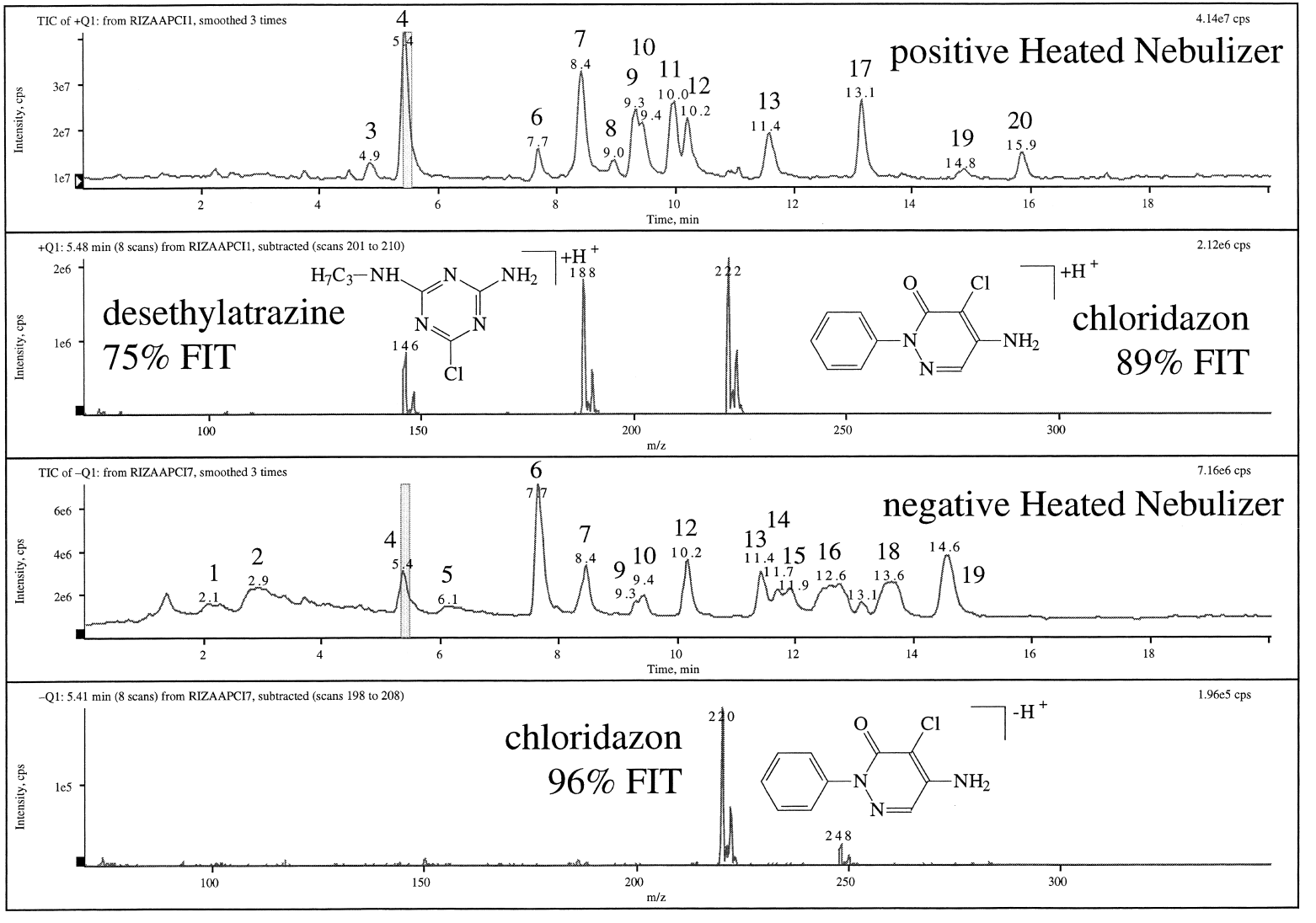

Fig. 7. Identification of two pesticides in a coeluting peak using negative and positive ion mode.

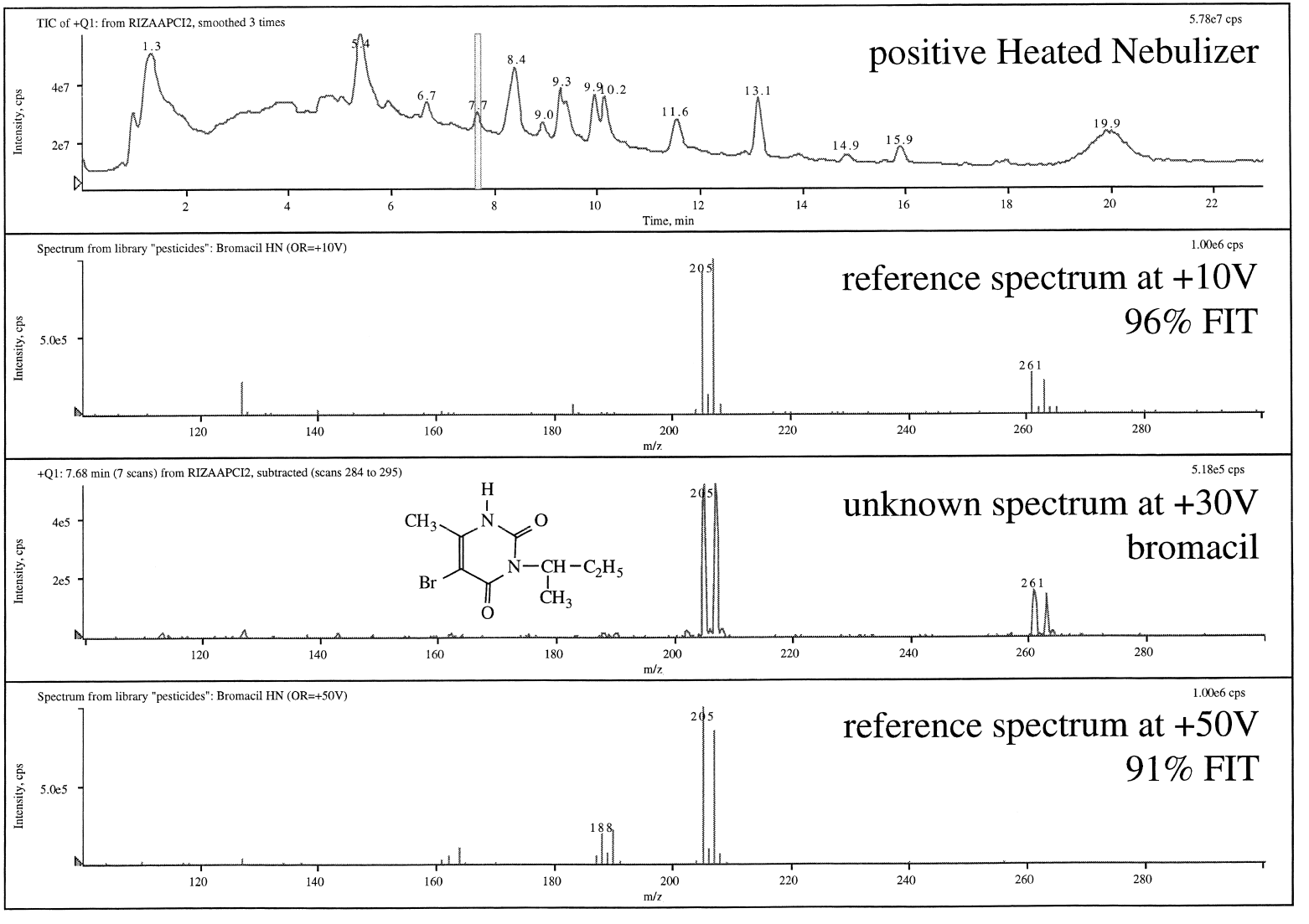

Fig. 8. Identification of a pesticide using the reference spectra acquired at various orifice voltages.

Furthermore, the possibility of transferring the libraries on HPLC–API-MS devices of other manufacturers has to be investigated.

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