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Confirmation of Pesticides in Water Samples by Mass Spectrometry

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Mass spectrometry is a highly selective and specific technique broadly applied in environmental analysis. It provides high discriminating power and in combination with high resolution gas chromatography (HRGC), that offers high separating power, it becomes a powerful tool for performing both qualification and quantification of organic pollutants, as pesticides are. GC-MS with electron impact (EI) is the most frequently used MS technique for the analysis of pesticides in water, provided they are thermally stable. Determination of pesticides and their degradation products at the 0.1 μg/L level of the European Union requirement for potable water (Council Directive, 1980) is very difficult, prone to errors and not applicable to all compounds. Determination with EI is often not adequate for determining at these low ppb levels. The sensitivity of GC-MS can be increased by approximately 2 orders of magnitude by monitoring a few selected ions, with the SIM technique.

GC-MS with negative chemical ionization (NCI) with methane is a soft ionization technique with increasing use in environmental analysis of compounds with electron withdrawing groups (Mattina, 1993). It provides increased both selectivity and sensitivity but there are no spectra libraries available, as they are instrument dependent. The limited number of ions formed in the NCI process simplifies the mass spectra and provides greater degree of specificity.

The literature contains many examples of pesticide residues analysis in environmental samples with GC-MS. Review books (Barcelo and Hennion 1997; Vreuls et al 1995) and articles (Benfenati et al 1990; Bangeri et al 1992) have been published describing methods for both EI and NCI applications. Thus, Benfenati et al reported the simultaneous analysis with EI of 50 pesticides of various classes in water samples with 50 ppt sensitivities, while Bagheri et al reported the determination in surface and drinking waters of 12 triazines and found EI more sensitive than NCI for this group of compounds.

The aim of this study was the application of confirmatory GC-MS techniques, employing both EI and NCI, for the identification of 90 pesticides in water samples, and the application of these techniques in the analysis of water samples collected from various districts of Greece.

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MATERIALS AND METHODS

Pesticides analytical standards were provided from various suppliers and agrochemical manufacturers. SPE cartridges (3mL) containing 500mg of endcapped (EC) C-18 sorbent were purchased from Isolute.Solvents methanol and ethyl acetate used were of pesticide residue grade while water was of HPLC grade; all solvents were purchased from Labscan.

Pesticides were extracted from water with solid phase extraction (Miliadis; 1998). The C-18 cartridges were preconditioned by passing, with a syringe, six-cartridge hold up volumes (5 mL) of ethyl acetate, followed by 5 mL methanol and 10 mL of organic-free water. 500 mL of water sample were loaded on the cartridge at 15 mL/min, and air was subsequently sucked for 30 min to dry the cartridge. The trapped pesticides were eluted with 1 mL ethyl acetate and 1 μL of the final extract was injected in the GC-MS system. The recovery test was performed in triplicate, by spiking organic-free water with the target pesticides at various fortification levels.

A Fisons, model Trio 1000, Mass spectrometer associated with a Fisons, model Mega 2, Gas Chromatograph was used. The injector temperature was 230°C. 1 μL volume of sample was injected in the splitless mode with the valve opened at 50 sec. A 30mx0.25mm CP-Sil 8 low blend MS column with 0.25μm film thickness was used with helium as carrier gas. The column temperature was programmed from 70°C (0 min) to 170°C (5 min) at 20°C/min, and to 315°C (20 min) at 5°C/min. The operating conditions of MS were: EI electron energy 70 eV, source at 200°C for EI and 140°C for NCI, trap current 150 μA (for EI), interface at 250°C and source pressure (for NCI) 0.5 mbar.

RESULTS AND DISCUSSION

GC-MS with EI generally gives enough data to reveal structural information, but does not always provide molecular weight. On the contrary the major ion observed with NCI is often the molecular one. This ionization technique was therefore used to provide complementary information to EI. Additionally, the limited number of ions formed with the NCI simplifies the mass spectra and provides greater specificity. The disadvantage of lack of spectra libraries with NCI was overcome by creating our own spectra library. Confirmation of residues in the samples was made by using the general criteria for trace level analysis by MS (Cairnes et al 1989).

Table 1 presents retention time, molecular mass and the main ions with both EI and NCI techniques for the studied pesticides with the described procedure. Ions with m/z>100 and with highest relative abundance were chosen as the main ions in this Table. NCI main ions are not given for all studied pesticides in this Table. This, in some cases, is due to the fact that only highly aromatic and/or halogenated compounds capture electrons and form stable negative ions, while aliphatic or non-electrophilic compounds do not produce ions with the NCI technique.

Pesticides with very similar retention times coelute and present overlapping peaks. Such cases can be encountered with the reconstructed ion chromatogram

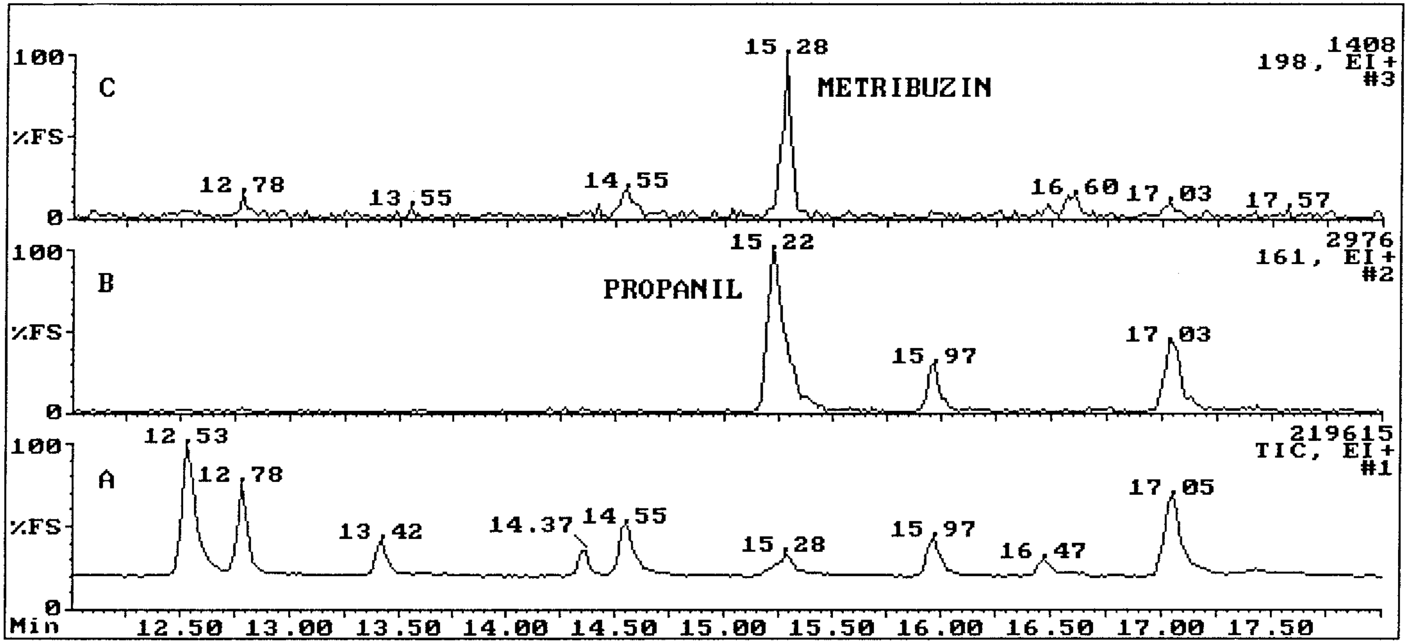

Figure 1. GC-MS with EI chromatogram of an extract of spiked water sample with various pesticides at the 2 μg/L level. (A) : Total ion current (B) : Reconstructed chromatogram for the ion 161 (C) : Reconstructed chromatogram for the ion 198.

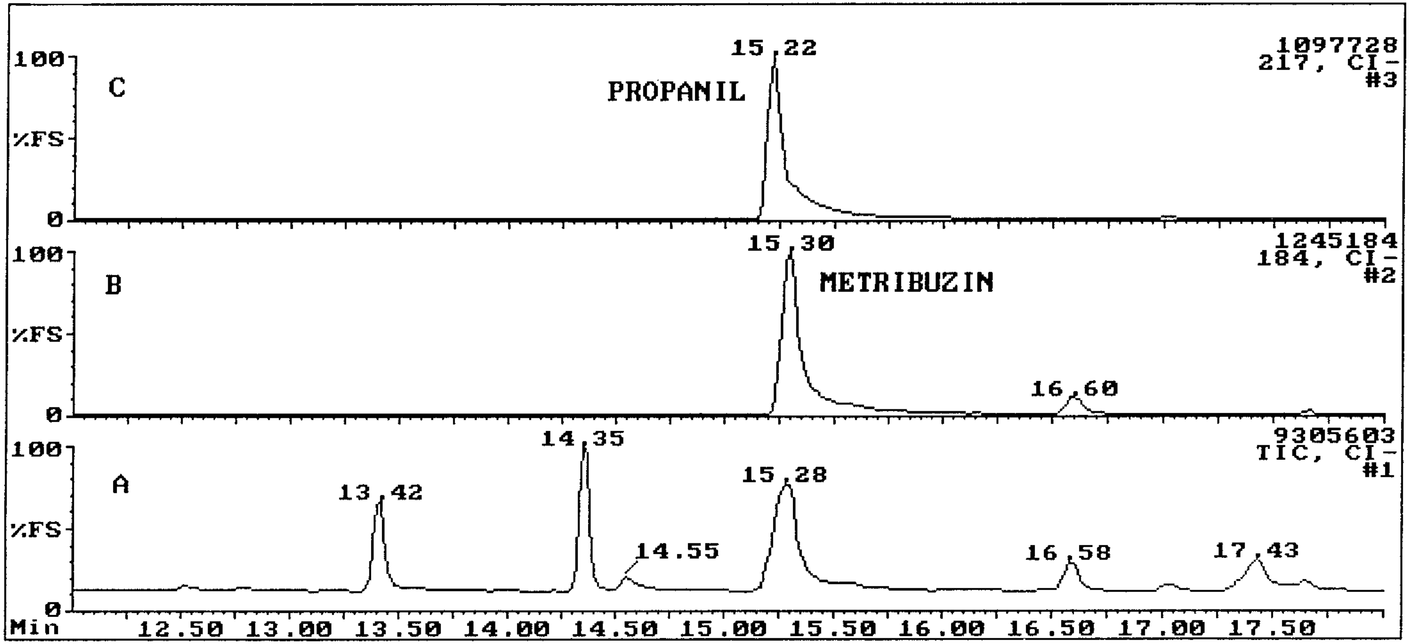

Figure 2. GC-MS with NCI chromatogram of an extract of spiked water sample with various pesticides at the 2 µg/L level. (A) : Total ion current (B) : Reconstructed chromatogram for the ion 184 (C) : Reconstructed chromatogram for the ion 217.

Table 1. Retention time (RT), molecular mass (MM) and main ions by both EI and NCI techniques for the studied pesticides. The ions are placed in order of significance. I.S. = internal standard

Compound	RT(min)	MM	Main ions	
			EI	NCI
acephate	6.45	183	136, 94	
alachlor	15.56	269	160, 188, 224	35, 37
aldrin	17.40	362	263, 261, 265	330, 332, 328
atrazine	12.25	215	200, 215, 173	
azinphos methyl	28.30	317	105, 132, 160	133, 157, 147
benalaxyl	24.25	325	148, 91, 206	
α-BHC	11.18	288	181, 217, 109	255, 253, 257
β-BHC	12.32	288	181, 217, 109	255, 253, 257
γ-BHC (lindane)	12.65	288	181, 217, 109	255, 253, 257
binapacryl	22.33	322	83	
butylate	6.43	217	146, 156, 174	
cadusafos	10.66	270	270	213
captafol	25.88	347	79, 92, 151	217, 198, 150
chlormephos	6.60	234	121, 97, 234	
chlorothalonil	12.92	264	264, 266, 268	266, 264, 268
chlorpropham	10.07	213	153, 127, 171	
chlorpyriphos ethyl	17.33	349	97, 314, 195	
Chlorpyriphos methyl	15.27	321	125, 286, 109	
cycloate	9.67	215	83, 154	
λ-cyhalothrin	28.92	449	181, 197, 208	
Cypermethrin I II III IV	32.34 32.57 32.67 32.77	415	163, 165, 181	
o,p DDD	21.92	318	235, 237, 165	
p,p DDD	23.88	318	235, 237, 165	
p,p DDE	21.66	316	246, 318, 176	
o,p DDT	23.42	352	235, 237, 165	
p,p DDT	24.87	352	235, 237, 165	
deltamethrine	35.74	503	209, 181,198	
demeton-S-methyl	9.32	230	88, 109	
demeton-S-methyl sulfone	16.35	262	92, 109, 169	
diazinon	13,15	304	137, 179, 199	169, 170, 171
dibutyl phthalate	16.87	258	149, 205, 223	
dichlofluanid	16.93	332	123, 167, 224	
dicloran	11.78	206	124, 176, 206	
o,p dicofol	16.63	368	139, 111, 141	214, 216, 250
p,p dicofol	18.05	368	139, 111, 141	250, 252, 251
dieldrin	21.75	378	79, 237, 277	
dimethoate	11.70	229	87, 93, 125	
diphenylamine (DPA)	9.47	169	169, 168, 170	
disulfoton	13.52	274	88, 97, 125	
α-endosulfan	20.63	404	339, 195, 341	406, 372, 338
β-endosulfan	23.12	404	337, 339, 341	
endosulfan sulfate	24.68	420	272, 422, 387	
endrin	22.67	378	317, 281, 263	

Compound	RT(min)	MM	Main ions	
			EI	NCI
EPTC	5.73	189	128, 132, 189	
ethion	23.40	384	231, 153, 121	
ethoprop	9.58	242	97, 158, 150	
fenitrothion	16.67	277	125, 109, 277	168, 277, 278
fenthion	17.57	278	278, 109, 125	
fenthion sulfoxide	23.10	294	278, 109, 125	
fenoxon	16.15	262	262, 247, 109	
fenoxon sulfoxide	21.75	278	109, 262	
Fenvalerate I " II	34.14 34.57	419	125, 167, 181	
folpet	19.80	295	104, 114, 147	146, 147
formothion	14.52	257	125, 131, 207	
heptaclor	15.88	370	100, 272, 135	35, 37, 71, 73
heptachlor epoxide	19.10	386	351, 353, 355	318, 282, 388
hexachlorobenzene	11.33	282	284, 249, 142	
imazalil	21.20	296	215, 173, 137	35, 37
iprodione	26.52	329	70, 187, 314	
linuron	16.88	248	187, 189, 124	
malathion	17.06	330	173, 125, 158	
malaoxon	15.42	314	127, 99, 109	
mecarbam	19.35	329	131, 97, 159	
metalaxyl	15.88	279	206, 160, 146	
methamidophos	4.67	141	94, 95, 141	
metribuzin	15.28	214	198, 144, 171	198, 199, 184
mevinphos (cis&trans)	6.33	224	127, 109, 192	
monolinuron	12.53	214	127, 153, 214	
myclobutanil	21.82	288	179, 206, 245	288, 289, 290
omethoate	8.74	213	110, 156	
oxydemeton-methyl	4.05	246		
parathion methyl	15.55	263	109, 125, 263	263, 154
parathion ethyl	17.70	291	97, 109, 139	291
paraoxon	16.10	275	109, 139, 149	
pendimethalin	18.79	281		281, 251, 282
permethrin I " II	30.52 30.80	390	183, 163, 165	
phorate	10.92	260	75, 121, 97	
phorate oxon	9.20	244		
phorate sulfoxide	17.10	276	97, 153, 199	
phosalone	28.15	367	182, 121, 111	
phosmet	26.70	317		161, 157, 175
phosphamidon (E) " (Z)	13.08 14.82	299	127, 138, 264	
pirimiphos methyl	16.55	305	290, 276, 307	
procymidone	19.70	283	96, 283, 285	
prometryn	16.10	241	184, 226, 199	
propachlor	9.07	211	120, 176, 77	
propargite	25.53	350	135, 107, 215	
propanil	15.22	217	161, 163, 217	217, 219, 221
propyzamide	12.96	256	145, 173, 255	255, 257, 259
pyrazophos	29.27	372		373, 169, 374
quintozene	12.47	293	142, 265, 295	
simazine	12.07	201	201, 186, 173	

Compound	RT(min)	MM	Main ions	
			EI	NCI
terbuthylazine	12.73	229	214, 229, 173	
triadimefon	17.83	293	57, 128, 208	127, 166, 129
triadimenol A " B	19.62 19.95	295	112, 128, 168	
trifluralin	10.05	335		335, 305, 336
Triphenyl phosp(IS)	25.62	326	94, 325, 326	
vinclozolin	15.43	285	285, 212, 198	241, 243

technique. Figure 1A is an EI chromatogram of a water sample, fortified with various pesticides at the 2 ppb level, in which metribuzin and propanil coelute at 15.28 min. However by reconstructing the chromatogram for the ions 161 and 198 the individual determination of propanil and metribuzin is attained (figures 1B and 1C respectively). The NCI chromatogram of the same spiked water sample is shown in figure 2A. By reconstructing this chromatogram for the ions 184 and 217 the individual determination of metribuzin and propanil is attained (figures 2B and 2C respectively).

The extraction method has been validated by fortifying HPLC grade water with pesticides (Miliadis and Malatou,1997; Miliadis 1998). Recovery values were >80% for most analytes. The detection limits, set at a signal-to noise ratio no less than 3:1, were 1-10 µg/L for the full scan mode and 0.01-0.1 µg/L for the SIM mode, making the method at the SIM mode sensitive for the E.U. requirements. Quantitation limits, when required, should be performed at a signal to noise ratio no less than 10:1.

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