

Gas chromatographic system equipped with a mass detector and a selective nitrogen–phosphorous detector operating simultaneously in the analysis of pesticide residues

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Abstract

The possibility to perform gas chromatographic analysis using both a mass detector and a selective nitrogen–phosphorous detector will enable highly sensitive analytical results and an optimal identification reliability. In this work we describe an easily workable technical solution, which has been accomplished in our laboratory and the application of the above system to analytical procedures for the detection and determination of nitrogenous herbicides in drinking water and phosphorylated pesticides in agricultural products is discussed.

Keywords: Detection, GC; Environmental analysis; Pesticides

1. Introduction

In gas chromatographic analysis, several multiple-detection systems have been tested. Some applications utilize simultaneously two identical traditional GC detectors, connected to two columns containing different stationary phases [1]. The flux is divided into the two branches soon after the injector. This allows, with one single introduction of the sample, a sure identification of the detected compounds, through the comparison of the relative retention times (RRT) in the two gas chromatographic branches.

In the same way, applications where the flux of one single column is divided between two different GC detectors may be expected. This allows the quantitative analysis of substances having different

chemical features, while injecting the sample one single time.

The techniques described above do not allow the identification of compounds that are not included in the calibration mixture. In these cases further analyses by GC–MS are necessary.

In the present work we have experimented with the combined use of a traditional GC detector and a mass detector. Utilizing the experimental apparatus described, it is possible to obtain, with one injection, two series of results: the ones obtained with the mass detector that, for reasons explained afterwards, are to be regarded prevalently as qualitative results and the ones obtained with the traditional GC detector, that are quantitative results. This ensures more reliable analyses, while allowing easy search and identification of unknown substances.

The technique has been particularly utilized in the analysis of residues of herbicides in drinking waters

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and of phosphorylated pesticides residues in agricultural products.

These fields of enquiry require even more versatile techniques, as the number of substances authorized by law for agricultural use is steadily increasing [2–5]. Moreover, it is necessary to have a sufficiently sensitive analytical system, as the legal limits for some agricultural products are restrictive (0.01 mg/kg) and the size of the products to be analyzed together with their extraction methodology [2–4] do not allow high concentration of the sample.

Moreover, the analysis of nitrogenous herbicides in drinking water requires extremely sensitive detection, so that the samples can be evaluated within the very restrictive legal limits (0.1 $\mu\text{g/l}$), even if highly enriching methodologies are used [6–9].

2. Experimental

The instrumentation utilized is made up of the following parts: GC–MS Model MD800 Fisons, equipped with body detector and manometer for the make-up gas; nitrogen–phosphorous selective detector NPD40 Fisons; on-column injector; integrator SP4270 Spectra-Physics; column DB5 JW, 30 m \times 0.32 mm I.D., film 0.25 μm (5% phenyl–95% methyl-polysiloxane); column DB5 JW, 30 m \times 0.25 mm I.D., film 0.25 μm (5% phenyl–95% methyl-polysiloxane); fused-silica precolumn, 2 m \times 0.32 mm I.D., ‘Y’ press-fit for columns with 0.32 mm I.D.; linear press-fit for columns with 0.32 mm and 0.25 mm I.D.; carrier gas: He; make-up gas (nitrogen–phosphorus detection, NPD): He; carrier pressure at the top of the column: 55 kPa.

Fig. 1 shows how the system is made up. The flux is divided into two GC branches by means of ‘Y’ press-fit connected to the upstream injector via a 2 m \times 0.32 mm I.D. silica precolumn and downstream to two columns having the same stationary phase, but different inside diameter.

The vacuum present in the ionization chamber unbalances the distribution of the flux into the two GC branches, thus necessitating the use of a column with 0.25 mm I.D. connected to the mass detector. The distribution of the flux into the two columns is balanced by means of a 0.32 mm I.D. column to the NPD detector and a 0.25 mm I.D. column to the mass detector, thus allowing, even in trace analyses,

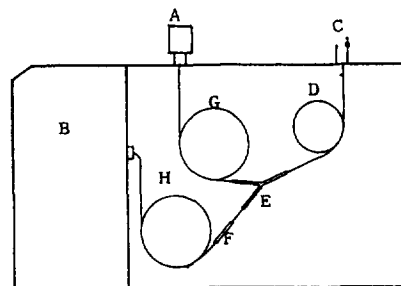


Fig. 1. Analytical system: A, NPD; B, mass detector; C, on-column injector; D, precolumn; E, ‘Y’ press-fit; F, linear press-fit; G, column 0.32 mm I.D.; H, column 0.25 mm I.D.

a fair sensitivity for both detectors, when about 5 μl of sample are injected onto the system. [10].

In the analysis of phosphorylated pesticides the mass detector has been set up in full-scan mode (40–400 u), while in the analysis of nitrogenous herbicides it has been set up in SIR (selected ion recording) mode, selecting three of the most typical and abundant fragments for each of the detected compounds (Table 1).

Quantitative analyses, both for herbicides and pesticides, have been carried out using the internal standard technique.

3. Results

The analytical system studied, besides providing more reliable results, allows an easy search of the substances detected by NPD, but not included in the

Table 1
Abundant and characteristic fragments utilized in the analysis of herbicides with mass detector set in SIR mode

Compound	Mass (u)		
Trifluralin	264	306	186
Simazine	201	186	173
Atrazine	200	215	173
Propazine	241	229	172
Terbumeton	210	169	154
Terbutylazine	214	229	173
Secbumeton	196	225	169
Alachlor	160	188	146
Metolachlor	162	212	238
Cyanazine	212	227	170
Pendimethalin	252	190	124

Table 2
Absolute retention times (min) and relative retention times in NPD and MS-SIR chromatograms of herbicides

Compound	t_R		RRT	
	NPD	MS	NPD	MS
Trifluralin	16.15	16.84	0.689	0.694
Simazine	17.89	18.66	0.763	0.769
Atrazine	18.21	18.97	0.778	0.782
Propazine	18.48	19.25	0.789	0.793
Terbumeton	18.59	19.36	0.793	0.798
Terbuthylazine	19.06	19.85	0.814	0.818
Secbumeton	20.25	21.04	0.864	0.867
Alachlor	23.12	24.00	0.988	0.989
Prometryn (I.S.)	23.41	24.26	1	1
Metolachlor	25.38	26.28	1.084	1.083
Cyanazine	25.69	26.57	1.098	1.095
Pendimethalin	27.69	28.61	1.183	1.179

standard. For the determination of herbicides, even if it is necessary to repeat the analysis with the mass detector set in full-scan mode, the good correspondence of the absolute and relative retention times in the two GC branches (Table 2) allows a quick and reliable identification of the unknown peak, through the recording of its mass spectrum.

Table 3 and Table 4 list the results obtained with both detectors in the analysis of herbicides, carried out by injecting six times the same standard, containing a mixture of eleven substances (the corresponding chromatograms are shown in Fig. 2). The S.D., R.S.D. and relative error values show that the selective NPD produces results more precise and accurate than those provided by the mass detection. In particular, the behaviour of the relative error (%),

Table 3
Average value (\bar{x}), S.D., R.S.D. and relative error obtained injecting six times the same standard of herbicides at the mass detector set in SIR mode

Compound	Mass (u) ^a	Conc. ($\mu\text{g/l}$) ^b	\bar{x} ($\mu\text{g/l}$)	S.D.	R.S.D.	Relative error (%)
Trifluralin	264	198.0	199.9	17.8	8.9	1.0
Simazine	201	100.0	102.2	5.2	5.1	2.2
Atrazine	200	100.0	103.2	6.4	6.2	3.2
Propazine	214	100.0	96.5	2.5	2.6	3.5
Terbumeton	210	100.0	99.5	3.1	3.1	0.5
Terbuthylazine	214	100.0	98.9	3.8	3.8	1.1
Secbumeton	196	100.0	117.8	11.2	9.5	17.8
Alachlor	160	200.0	238.9	35.4	14.8	19.4
Metolachlor	162	200.0	247.7	34.2	13.8	23.8
Cyanazine	212	100.0	96.0	5.7	5.9	4.0
Pendimethalin	252	198.0	221.6	24.8	11.2	11.9
Prometryn (I.S.)	241					

^a Characteristic fragments utilized for quantitative analysis.

^b Concentration of each herbicide in the standard mixture.

Table 4
Average value (\bar{x}), S.D., R.S.D. and relative error obtained injecting six times the same standard of herbicides at the NPD

Compound	Conc. ($\mu\text{g/l}$) ^a	\bar{x} ($\mu\text{g/l}$)	S.D.	R.S.D.	Relative error (%)
Trifluralin	198	200.3	6.8	3.4	1.2
Simazine	100	97.9	2.0	1.6	2.1
Atrazine	100	97.3	1.6	2.0	2.7
Propazine	100	103.5	2.0	2.0	3.5
Terbumeton	100	96.1	1.9	2.0	3.9
Terbuthylazine	100	98.9	2.3	2.4	1.1
Secbumeton	100	99.3	1.9	1.9	0.7
Alachlor	200	200.2	3.1	1.5	0.1
Metolachlor	200	194.1	4.3	2.2	2.9
Cyanazine	100	100.2	2.0	2.0	0.2
Pendimethalin	198	194.1	5.7	2.9	2.0

^a Concentration of each herbicide in the standard mixture.

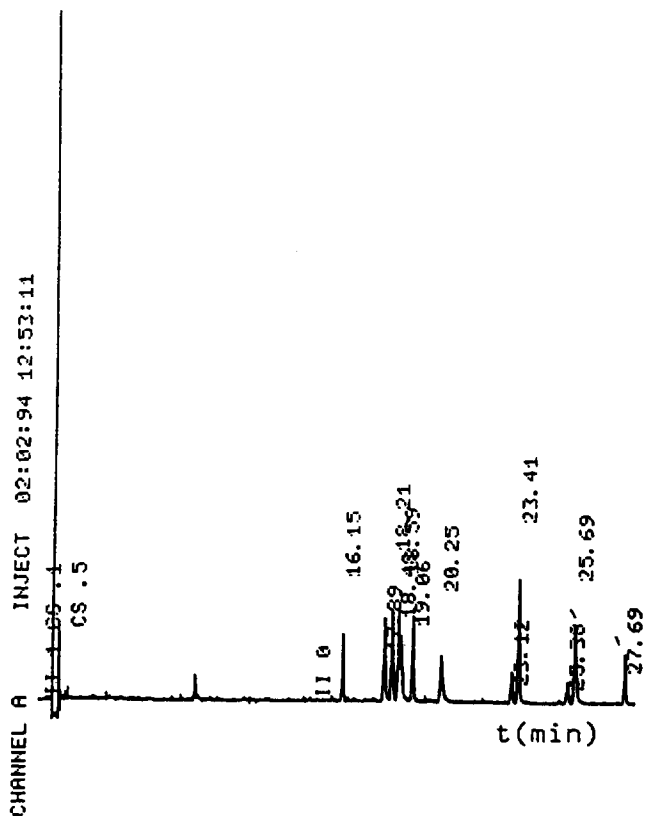
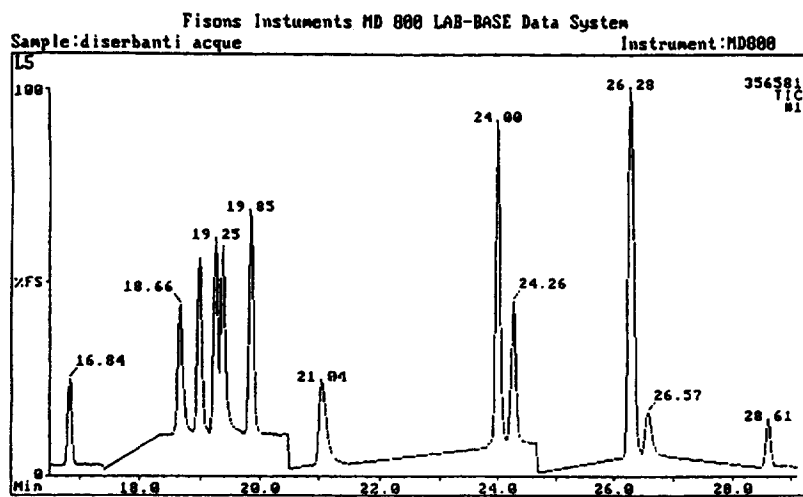


Fig. 2. Chromatogram of the standard of herbicides: top, mass detector (SIR); bottom, NPD.

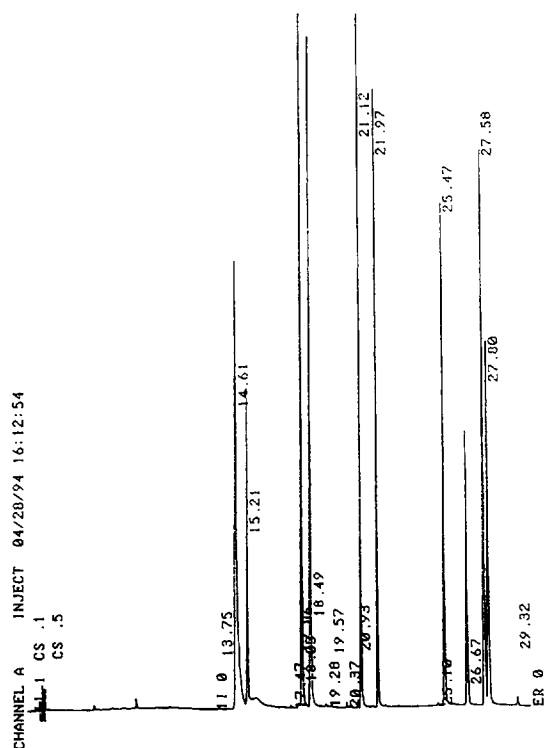


Fig. 3. NPD chromatogram of the standard of phosphorylated pesticides.

calculated for each of the eleven herbicides in each of the six analyses carried out (Table 5 and Table 6), shows that the mass detector produces analytical results that may be affected by considerable errors, so that its use in routine quantitative analysis is to be

Table 5
Relative error (%) for each herbicide in each of the six analyses carried out with the mass detector set in SIR mode

Compound	Analysis					
	1	2	3	4	5	6
Trifluralin	-6.6	-8.3	-6.3	5.9	8.4	12.4
Simazine	-3.3	-3.4	-3.4	4.8	7.8	7.8
Atrazine	-2.0	-4.1	-0.2	6.5	9.8	10.1
Propazine	-3.5	-4.0	7.6	-2.5	-0.1	-3.2
Terbumeton	-1.8	0	-5.5	-0.6	-2.3	-2.8
Terbuthylazine	-3.5	-3.6	-5.4	-0.9	2.7	4.1
Secbumeton	5.4	4.6	18.6	18.0	31.0	29.1
Alachlor	-0.2	1.2	12.6	27.9	32.9	42.5
Metolachlor	3.6	1.4	27.2	34.8	35.9	40.2
Cyanazine	5.0	1.6	-8.6	-7.2	-7.8	-6.3
Pendimethalin	-1.4	1.2	2.7	18.6	22.5	28.9

Table 6
Relative error (%) for each herbicide in each of the six analyses carried out with the NPD

Compound	Analysis					
	1°	2°	3°	4°	5°	6°
Trifluralin	-3.2	4.3	6.1	0.9	-1.1	0.1
Simazine	-6.0	-0.9	-2.4	-1.0	-1.7	-0.4
Atrazine	-4.6	-1.1	-0.6	-3.6	-3.6	-2.6
Propazine	-5.9	0.4	-0.7	1.3	-2.0	-4.9
Terbumeton	0	3.5	5.6	3.9	2.8	5.3
Terbuthylazine	-6.4	-3.3	-3.3	-5.0	-4.5	-0.9
Secbumeton	-4.2	-2.6	0.1	-2.3	0.6	2.0
Alachlor	-2.0	0.2	1.2	-1.0	-3.7	1.0
Metolachlor	0.1	1.6	1.6	0.4	-2.3	-1.0
Cyanazine	-1.5	-2.2	-3.1	-0.1	-5.6	-5.2
Pendimethalin	-2.4	2.9	1.5	-0.6	-1.4	1.0

regarded with caution. Fig. 5 and Fig. 6 show the dispersion of the relative error for each compound, respectively for the NPD and for the mass detection.

For these reasons, in the analyses of herbicides, the selective NPD gives quantitative results, while the mass detection gives a qualitative confirmation of the detected compounds.

The lower reproducibility of the mass detector may be due to its complex structure: the components of the source, such as the lens, the collector, etc., undergo a progressive deterioration caused by the deposition of various substances during each analysis. In this way, the working conditions of the mass detector are never the same from one analysis to the other. Since in the analysis of herbicides the mass detector is set in SIR mode, to have high sensitivity, it is easy to understand how little variations of the source conditions may produce great variations in the analytical results.

The analysis of pesticides has been carried out injecting seven times a standard mixture, containing nine substances.

Table 7 and Table 8 show that the average values obtained with the two detectors do not sensitively diverge from the real values, with the exception of dimethoate at NPD, with an error of 10.1%, and azinphos methyl and azinphos ethyl at the mass detector, with an error of, respectively, 14.4% and 12.1%. In the whole, the analytical results obtained with NPD are more precise, because the S.D. and R.S.D. values are lower. This is clearly shown in Fig.

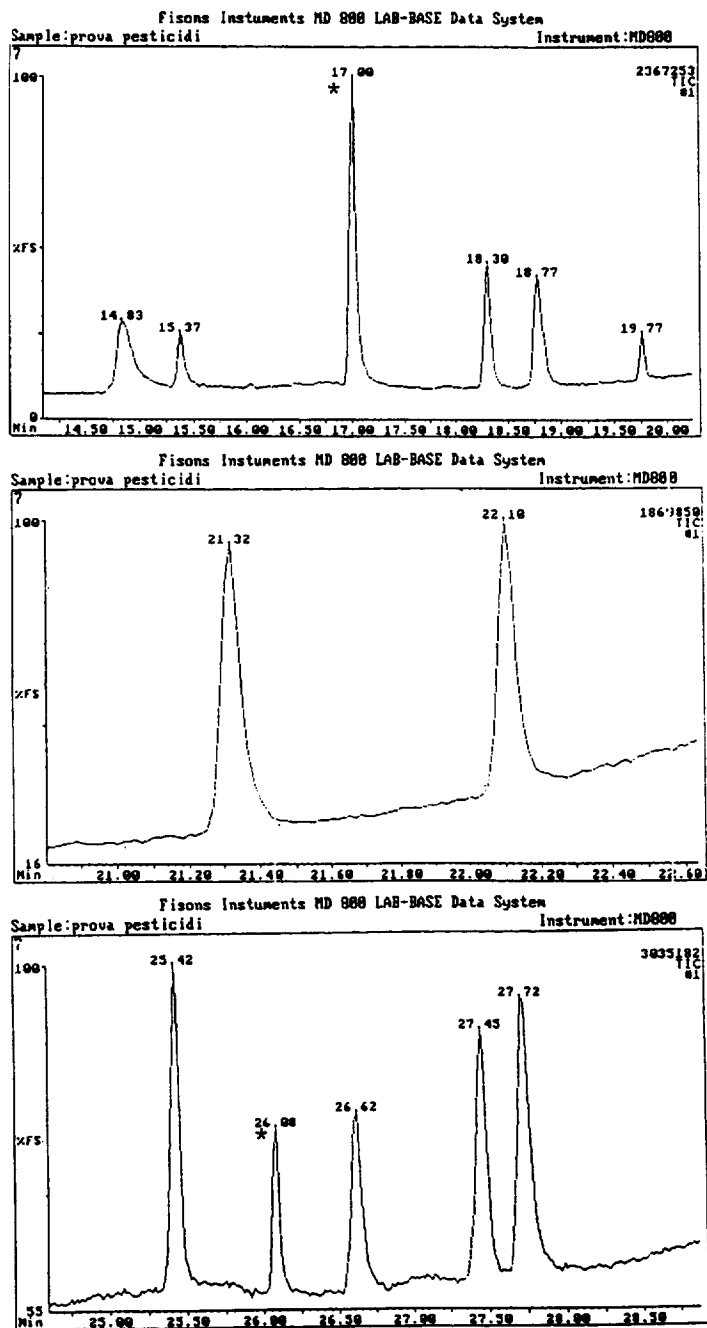


Fig. 4. Mass detector (full scan) chromatogram of the standard of phosphorylated pesticides. * Phthalate, contaminant compound.

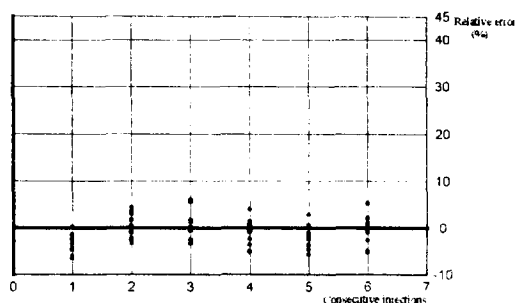


Fig. 5. Behaviour of relative error (%) calculated for six consecutive injections of the same standard of herbicides (NPD). Each point represents one single compound.

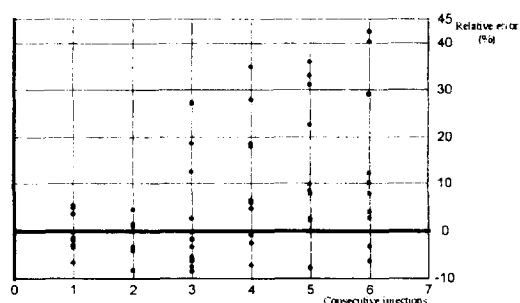


Fig. 6. Behaviour of relative error (%) calculated for six consecutive injections of the same standard of herbicides (mass detector). Each point represents one single compound.

Table 7

Average value (\bar{x}), S.D., R.S.D., and relative error obtained injecting seven times the same standard of pesticides at the NPD

Compound	Conc. ($\mu\text{g/l}$) ^a	\bar{x} ($\mu\text{g/l}$)	S.D.	R.S.D.	Relative error (%)
Dimethoate	1015	1118	13.7	1.2	10.1
Dioxathion	1002	1075	11.0	1.0	-7.3
Fenitrothion	998	1058	18.2	1.7	-6.0
Methidathion	998	1044	11.2	1.1	-4.6
Profenofos	994	1038	13.9	1.3	-4.4
Phosmet	1028	1061	15.9	1.5	-3.2
Azinphos methyl	1046	1014	27.1	2.7	3.1
Pyrazophos	1004	1034	18.6	1.8	-3.0
Azinphos ethyl	1023	1053	19.4	1.8	-2.9

^a Concentration of each pesticide in the standard mixture.

Table 8

Average value (\bar{x}), S.D., R.S.D. and relative error obtained injecting seven times the same standard of pesticides at the mass detector set in full scan mode

Compound	Mass (u) ^a	Conc ($\mu\text{g/l}$) ^b	\bar{x} ($\mu\text{g/l}$)	S.D.	R.S.D.	Relative error (%)
Dimethoate	87	1015	960	57.8	6.0	5.4
Dioxathion	97	1002	999	44.2	4.4	0.3
Fenitrothion	109	998	959	47.2	4.9	3.9
Methidathion	85	988	1037	54.3	5.2	-3.9
Profenofos	139	994	994	25.3	2.5	0
Phosmet	160	1028	971	34.8	3.6	5.5
Azinphos methyl	160	1046	895	58.2	6.5	14.4
Pyrazophos	221	1004	1008	54.9	5.4	-0.4
Azinphos ethyl	132	1023	899	181.4	20.2	12.1
Fenchlorphos (I.S.)	125					

^a Characteristic fragments utilized for quantitative analysis.

^b Concentration of each pesticide in the standard mixture.

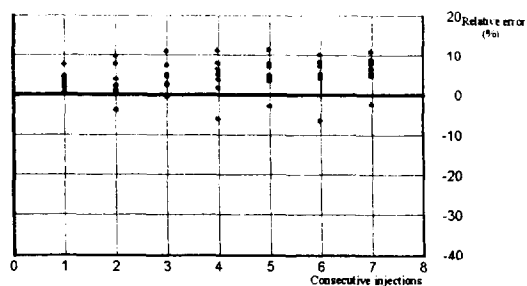


Fig. 7. Behaviour of relative error (%) calculated for seven consecutive injections of the same standard of pesticides (NPD). Each point represents one single compound.

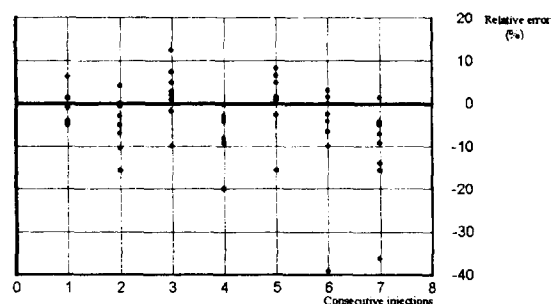


Fig. 8. Behaviour of relative error (%) calculated for seven consecutive injections of the same standard of pesticides (mass detector). Each point represents one single compound.

7 and Fig. 8, where the dispersion of the relative error (%) is wider for the results obtained with the mass detector. Table 9 shows the absolute retention times in NPD and MS-full scan chromatograms of phosphorylated pesticides. From Fig. 7 and Fig. 8, as

well as from Table 10 and Table 11, it can also be seen that the relative error (%) has a random behaviour for the results obtained with the mass detector, while it has a systematic behaviour for those of NPD.

Table 9

Absolute retention times (min) and relative retention times in NPD and MS full-scan chromatograms of phosphorylated pesticides

Compound	t_R (NPD)	t_R (MS)	RRT (NPD)	RRT (MS)
Dimethoate	14.51	14.83	0.809	0.810
Dioxathion	15.12	15.37	0.843	0.840
Fenchlorphos(I.S.)	17.94	18.30	1	1
Fenitrothion	18.39	18.77	1.025	1.026
Methidathion	21.03	21.32	1.172	1.165
Profenofos	21.90	22.10	1.221	1.208
Phosmet	25.37	25.42	1.414	1.389
Azinphos methyl	26.56	26.62	1.480	1.455
Pyrazophos	27.46	27.45	1.531	1.500
Azinphos ethyl	27.68	27.72	1.543	1.515

Table 10

Relative error (%) for each pesticide in each of the seven analyses carried out with NPD

Compound	Analysis						
	1	2	3	4	5	6	7
Dimethoate	7.5	9.6	10.9	11.1	11.3	10.0	10.8
Dioxathion	4.9	7.7	7.3	8.0	7.0	8.1	7.8
Fenitrothion	3.8	4.0	5.1	6.1	7.6	7.1	8.6
Methidathion	4.3	2.2	5.2	5.2	4.4	5.4	5.2
Profenofos	3.2	2.4	4.8	3.9	4.8	5.3	6.5
Phosmet	2.4	1.2	3.0	1.6	5.0	4.2	4.9
Azinphos methyl	0.5	-3.7	-0.6	-6.0	-2.8	-6.4	-2.3
Pyrazophos	1.7	0.5	2.9	1.7	4.3	4.6	5.6
Azinphos ethyl	1.6	0.7	2.5	1.7	3.6	4.9	5.9

Table 11
Relative error (%) for each pesticide in each of the seven analyses carried out with the mass detector set in full scan mode.

Compound	Analysis						
	1	2	3	4	5	6	7
Dimethoate	n.d.	-5.2	1.0	-8.2	0.7	-6.5	-14.1
Dioxathion	1.2	0.0	4.8	-3.6	4.8	-2.4	-7.2
Fenitrothion	-1.0	7.1	2.0	-9.2	1.0	-4.1	-9.2
Methidathion	6.2	4.1	12.5	-0.3	6.5	3.0	-4.6
Profenofos	1.4	-2.8	2.8	-4.1	1.4	0.0	1.4
Phosmet	-4.0	-10.4	-1.7	-9.4	-2.6	-6.7	-4.1
Azinphos methyl	-4.4	-15.6	-10.0	-20.0	-15.6	-10.0	-10.0
Pyrazophos	-5.1	-0.7	7.3	-2.9	8.1	1.5	-5.1
Azinphos ethyl	-4.4	-4.9	2.0	-3.4	1.5	-39.2	-36.3

n.d.: not determined.

The above observations suggest to make a different use of the two detectors, even in the analysis of pesticides: to use the chromatograms obtained with NPD for quantitative analysis and to use the mass detector for qualitative analysis, as a means of confirmation of the calibrated substances and, at the same time, as a means of identification of other substances, that may be present in the injected samples. In the latter case, as the mass detector is already set in full-scan mode, it is not necessary to repeat the analysis to identify the unknown peaks detected by NPD; moreover, the good correspondence of the relative retention times in the two GC branches (Table 9; Fig. 3 and Fig. 4) makes this operation easier.

A system with such features lends itself for the analysis of complex matrices, which undergo various contaminations. Moreover, giving results with very low standard deviations, this technique is particularly useful in routine work, where it is impossible to repeat the same analysis enough times to obtain an accurate average value.

In our laboratory the system described above has been utilized for some years, with good results, for routine analysis of nitrogenous herbicides residues in drinking waters.

Different fields of applications can be seen of this

technique. The NPD-MS combination is only one of the many possible ones. It is certainly possible to use different detectors (flame ionization, electro-capture, flame photometric) for analysing other compounds with different characteristics.

References

- [1] M. Morello, C. Rubatti, V. Guelpa and P. Minoglio, *Boll. Chim. Igien.*, 43 (1992) 163.
- [2] P. Branca and P. Quaglino, *Boll. Chim. Igien.*, 41 (1989) 71.
- [3] M. Baldi, S. Coppi, M.C. Cristofori, M.L. Davi, S. Benedetti, L. Penassi and M.P. Previati, *Boll. Chim. Igien.*, 41 (1990) 295.
- [4] P. Quaglino and P. Branca, *Boll. Chim. Igien.*, 43 (1992) 399.
- [5] L. Dagna, C. Gasparini, M.L. Icardi and E. Sesia, *Boll. Chim. Igien.*, 44 (1993) 383.
- [6] S. Galassi, N. Boniardi and A. De Paolis, *Boll. Chim. Igien.*, 41 (1990) 405.
- [7] M. Morello, C. Rubatti, V. Guelpa, P. Minoglio, A. Delaini and R. Cavicchioli, *Boll. Chim. Igien.*, 42 (1991) 665.
- [8] J.C. Moltò, Y. Picò, G. Font and J. Manes, *J. Chromatogr.*, 472 (1989) 365.
- [9] J. Manes Vinuesa, J.C. Moltò Cortès, C. Igualda Canas and G. Font Perez, *J. Chromatogr.*, 555 (1991) 137.
- [10] K. Grob, *On-Column Injection in Capillary Gas chromatography*, Hüthig, NY, 1987.