

● GASCHROMATOGRAPHY MASS SPECTROMETRY

No.M188

Analysis of Pesticides at Golf Courses using GC/MS

In 1990, the Ministry of Health and Welfare and the Environmental Agency designated of pesticides to be used at golf courses and specified guide line values and testing methods for them. Subsequently regulations on water supply and environmental and waste water were further strengthened.

At first the Environmental Agency stipulated the method that each pesticides is analyses individually using GC. However, in April 1998, new pesticides were added for analysis targets, and simultaneous analysis using GC/MS was presented as the analysis method. (Some of the analyses are conducted by HPLC.)

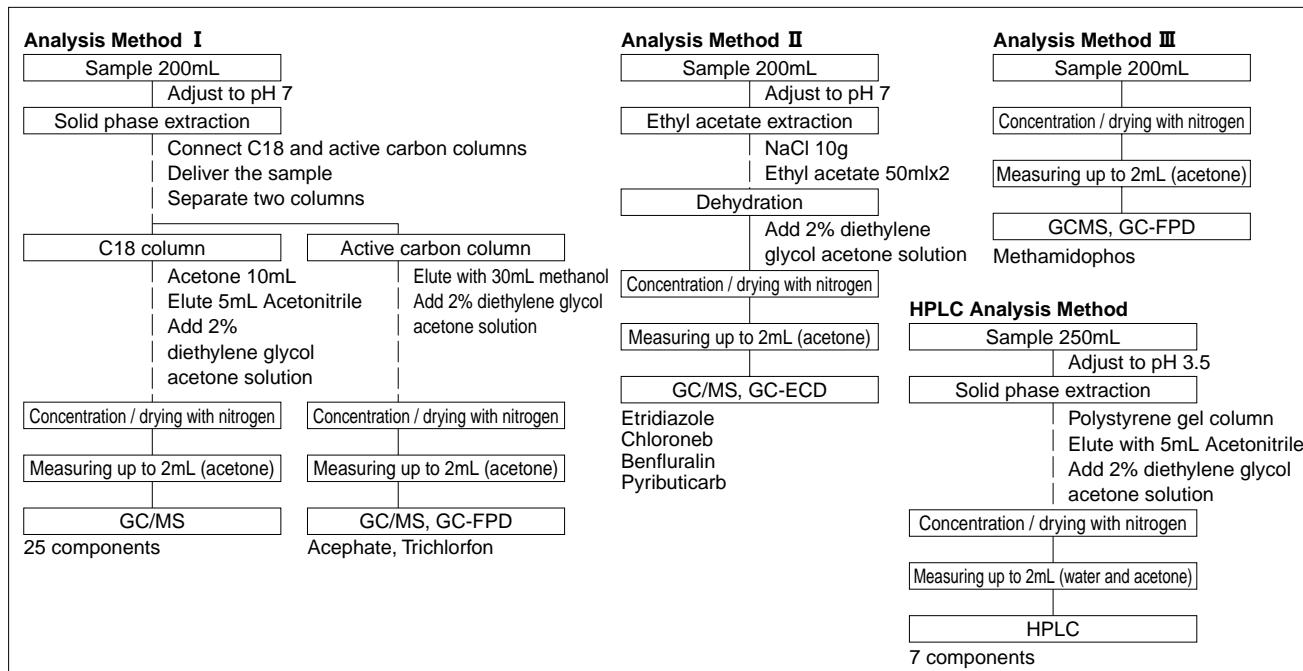
This article introduces examples of measurements by GC/MS, mainly for newly added pesticides acephate, metalaxyl, dithiopyr and pyributicarb.

Table 1 shows the guide line value and analysis method for each pesticides. Table 2 shows the flowchart of the simultaneous analysis. For measurement of pesticides, there are several patterns of analysis method depending on the physical properties of target components. This article presents three sets of measurement data obtained by different analysis methods.

Table 1 Temporary guidelines for golf course pesticides (revised in April 24, 1997 by the Environmental Agency)

	Pesticide name	Guide line value (mg/L)	Simultaneous analysis	Individual analysis		Pesticide name	Guide line value (mg/L)	Simultaneous analysis	Individual analysis
Pesticide	Acephate (newly added)	0.8	II	GCMS,GC-FPD	Herbicide	Pencycuron	0.4	I	GC-FTD
	Isoxathion	0.08	I	GC-FTD		Metalaxyl (newly added)	0.5	I	GCMS,GC-FPD,FTD
	Isofenphos	0.01	I	GC-FTD		Mepronil	1	I	GC-FTD
	Chlorpyriphos	0.04	I	GC-FTD		Asulum	2	HPLC	GC-FTD
	Diazinon	0.05	I	GC-FPD		Dithiopyr (newly added)	0.08	I	GCMS,GC-FTD,FPD,ECD
	Trichlorfon (DEP)	0.3	II	GC-FPD		Simazine (CAT)	0.03	I	GC-FTD
	Pyridaphenthion	0.02	I	GC-FPD		Terbucar (MBPMC)	0.2	I	GC-FTD
Fungicide	Fenitrothion (MEP)	0.03	I	GC-FPD	Herbicide	Trichlorpyr	0.06	HPLC	GCMS,HPLC-UV
	Isoprothiolane	0.4	I	GC-ECD		Napropamide	0.3	I	GC-FTD
	Iprodione	3	I	GC-FTD		Pyributicarb (newly added)	0.2	III	GCMS,GC-FTD,FPD
	Etridiazole (echlomezol)	0.04	III	GC-ECD		Butamifos	0.04	I	GC-FPD
	Oxine-copper (organic copper)	0.4	HPLC	HPLC-RF		Propyzamide	0.08	I	GC-ECD
	Captan	3	I	GC-ECD		Bensulide (SAP)	1	I	GC-FTD
	Chlorothalonil (TPM)	0.4	I	GC-ECD		Pendimethalin	0.5	I	GC-FTD
	Chloroneb	0.5	III	GC-ECD		Benfluralin (bethrodine)	0.8	III	GC-ECD
	Thiram	0.06	HPLC	HPLC-UV		Mecoprop (MCPP)	0.05	HPLC	GC-ECD
	Trichlorophos-methyl	0.8	I	GC-FPD		Methyl-dymron	0.3	I	GC-FTD
	Flutolanil	2	I	GC-FTD		Trichlopyr acid, trichlopyrbutoxyethyl			GCMS,HPLC-UV

Table 2 Flowchart scheme of Simultaneous analysis



■ Analysis Method I

Fig. 1 shows the TIC of 28 components, including oxones and those stipulated in Table 1 to be analyzed by Analysis Method I. Table 3 shows the analysis conditions and peak numbers for each component.

Fig. 2 shows the mass spectra of newly added components metalaxyl, dithiopyr, trichlopyr-butoxyethyl and oxones. Fig. 3 shows the SIM chromatograms at 10ppb.

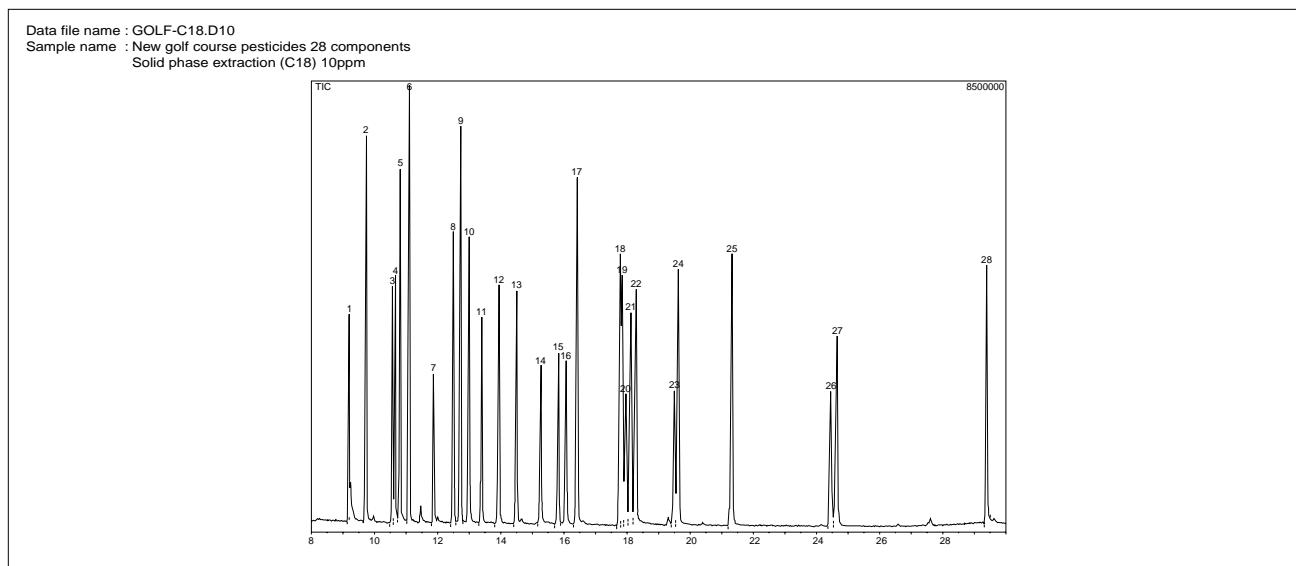


Fig. 1 TIC of Pesticides (Analysis Method I)

Table 3 Analytical Conditions

Instrument: Shimadzu GCMS-QP5050A	Carrier gas: He 40kPa (2min)-2kPa/min-80kPa (16min)
-GC-	Injection method: splitless (sampling time: 2min)
Column: DB-1 (30m × 0.32mm I.D. df=0.25μm)	-MS-
Column temperature: 70°C(2min)-20°C/min-150°C-3°C/min-210°C-10°C/min-300°C(5min)	Interface temperature: 280°C
Injector temperature: 270°C	Mass number range: m/z 35 to 400
Peak number	Component name
1	Pencycuron
2	Simazine (CAT)
3	Diazinon oxone
4	Chlorothalonil (TPN)
5	Propyzamide
6	Diadinone
7	MEP oxone
8	Trichlorophos-methyl
9	Terbucar (MBPMC)
10	Metalaxyl (newly added)
11	Fenitrothion (MEP)
12	Dithiopyr (newly added)
13	Chlorpyrifos
14	Captan
	SIM mass number
1	180,109
2	201,186
3	273,137
4	266,264
5	173,273
6	304,179
7	244,109
8	265,267
9	220,205
10	206,160
11	277,260
12	354,306
13	314,197
14	79,107,119
15	Pendimethalin
16	Methyl-dymron
17	Isofenphos
18	Isoprothiolane
19	Napropamide
20	Butamifos
21	Isoxathion oxone
22	Flutolanil
23	Isoxathion
24	Trichlopyr-butoxyethyl
25	Mepronil
26	Pyridafenthion
27	Iprodione
28	Bensulide (SAP)
	SIM mass number
15	252,162
16	107,119
17	213,255
18	290,162
19	271,128
20	286,200
21	105,161,254
22	323,173
23	105,177,313
24	210,212,182
25	119,269
26	340,199
27	314,316
28	215,131

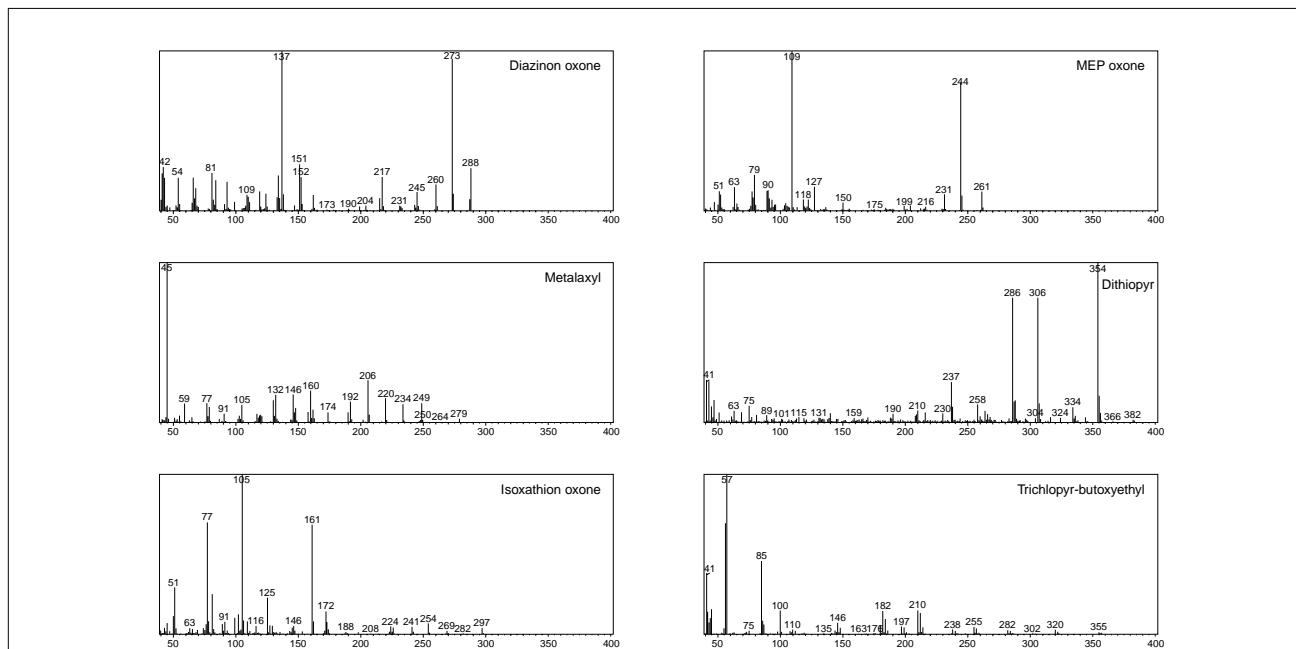


Fig.2 Mass Spectra of Pesticides

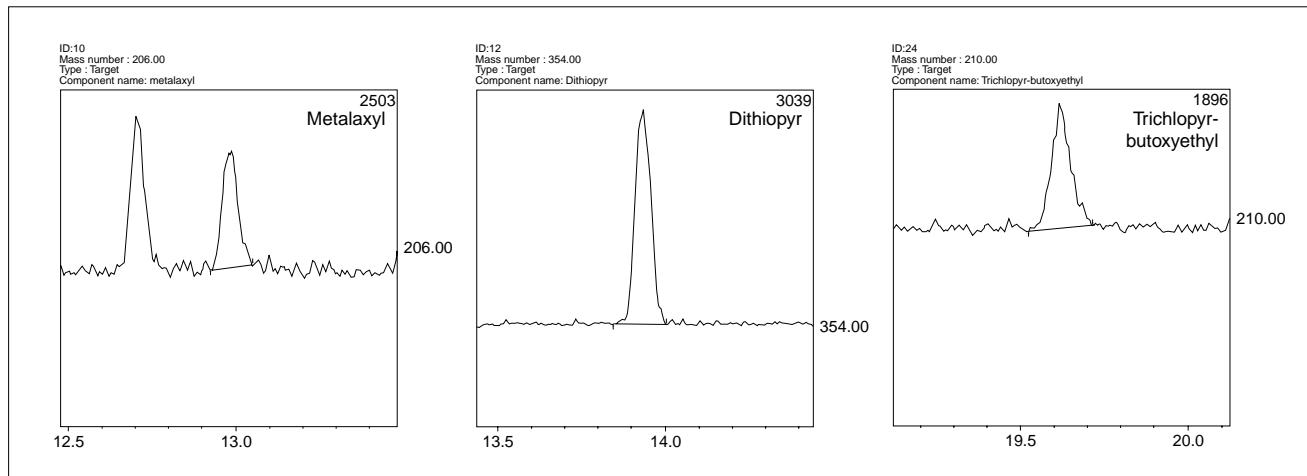


Fig.3 SIM chromatogram (10 ppb)

■ Analysis Method II

Fig.4 shows the TIC of the components stipulated in Table 1 to be analyzed by Analysis Method II. Table 4 shows the analysis conditions and peak numbers for

each component. Fig.5 shows the mass spectrum of pyributicarb, a newly added component. Fig.6 shows the SIM chromatogram at 10ppb.

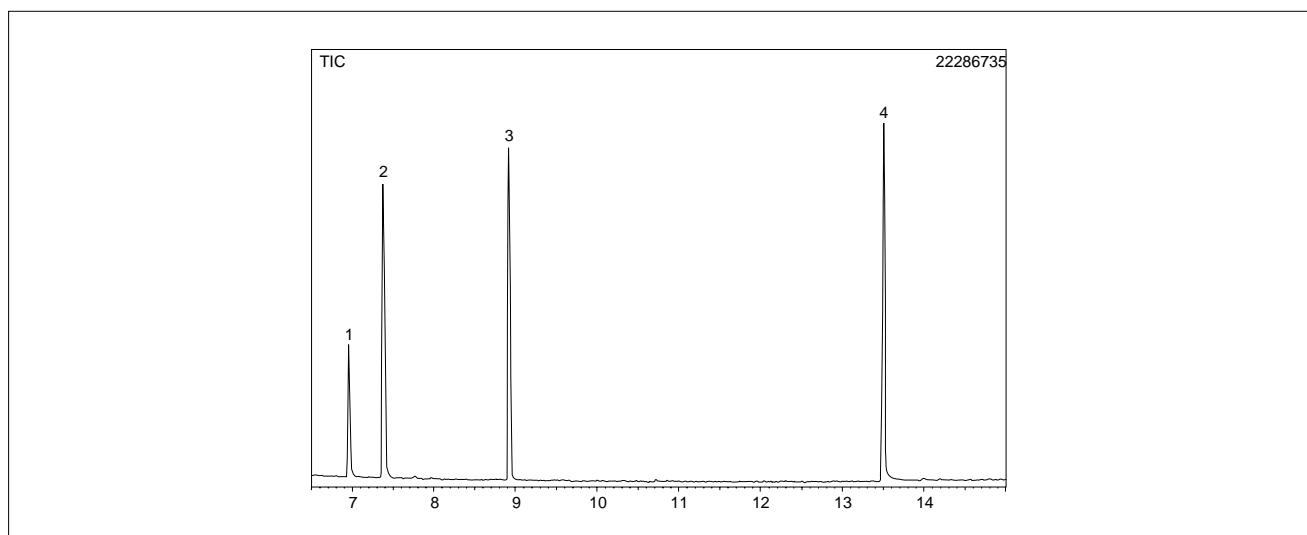


Fig. 4 TIC chromatogram of Pesticides (Analysis Method II)

Table 4 Analytical Conditions

Instrument: Shimadzu GCMS-QP5050A		
-GC-		
Column: DB-1 (30m × 0.32mm I.D. df=0.25μm)		
Column Temperature: 70°C(2min)-20°C/min-100°C-15°C/min-300°C(5min)		
Injector temperature: 270°C		
Carrier gas: He 40kPa (2min)-3kP/min-80kPa (6min)		
Injection method: splitless (sampling time: 2min)		
-MS-		
Interface temperature: 280°C		
Mass number range: m/z 35 to 400		
Peak number	Component name	SIM mass number
1	Echlomezol	211,183,213
2	Chloroneb	191,193,206
3	Benfluralin	292,264,335
4	Pyributicarb	108,165,181

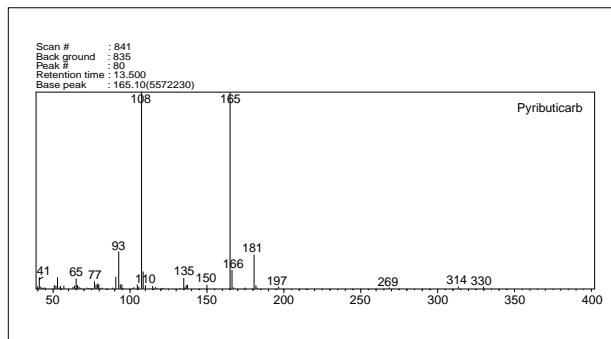


Fig.5 Mass spectrum of Pyributicarb

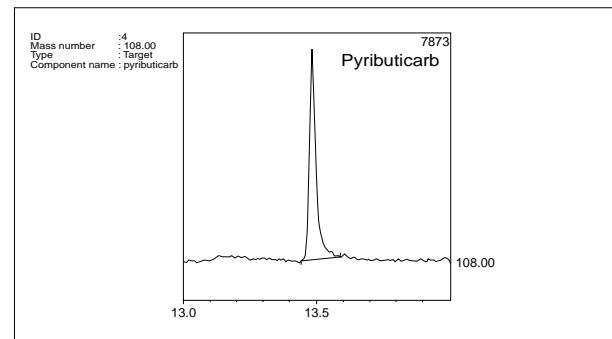


Fig.6 SIM chromatogram (10 ppb)

■ Analysis Method I (separate extraction)

Fig.7 shows the TIC of acephate and trichlorfon (DEP). Table 5 shows the analysis conditions. Because DEP decomposes if being exposed to a high temperature at the injection port, the measurement must be performed at a low temperature or by on-column injection. Here, to analyze DEP, the temperature at the injection port was kept low. Although DEP does not decompose under these conditions, the sensitivity for acephate decreases. Fig.8 shows the mass spectrum and Fig.9 shows the SIM chromatogram at 500ppb.

Table 5 Analytical Conditions

Instrument: Shimadzu GCMS-QP5050A		
-GC-		
Column: DB-1 (30m × 0.32mm I.D. df=0.25μm)		
Column Temperature: 100°C (4min)-7°C/min-150°C-15°C/min-280°C (3min)		
On-column injector temperature: 70°C (0.5min)-100°C/min-300°C (22min)		
Carrier gas: He 50kPa (pressure control)		
Injection method: on-column injection		
-MS-		
Interface temperature: 230°C		
Mass number range: m/z 35 to 400		
Peak number	Component name	SIM mass number
1	Acephate	136,94,183
2	Trichlorfon (DEP)	79,109,145

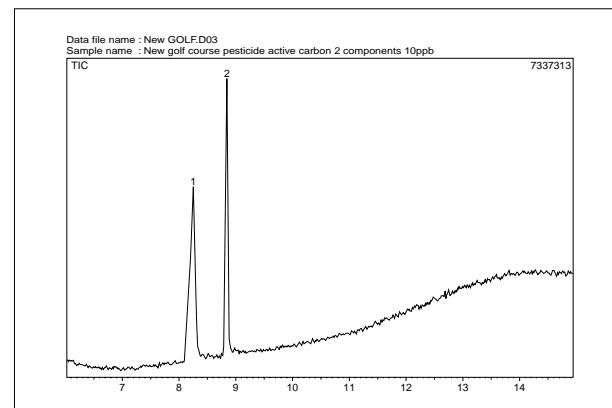


Fig.7 TIC of Pesticides (Analysis Method I separate extraction)

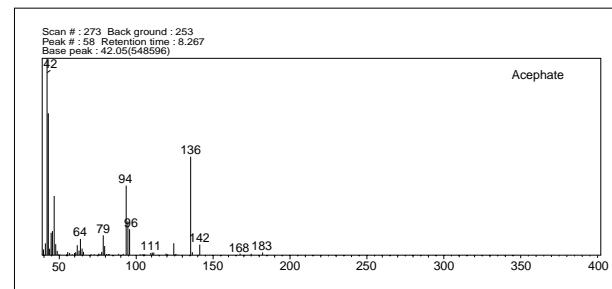


Fig.8 Mass spectrum of Acephate

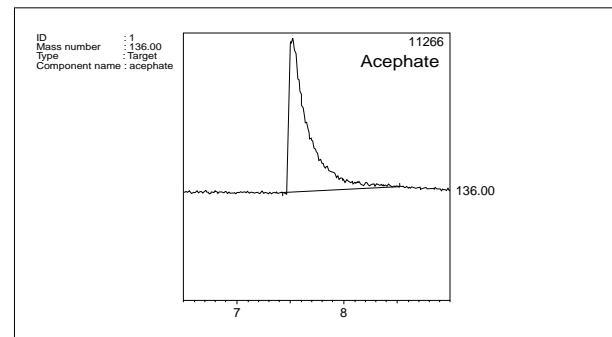


Fig.9 SIM chromatogram (500 ppb)