

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.

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.

	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
	Isufenphos	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	Terbucarb (MBPMC)	0.2	I	GC-FTD	
	Fenitrothion (MEP)	0.03	I	GC-FPD	Trichlorpyr	0.06	HPLC	GCMS,HPLC-UV	
Isoprothiolane	0.4	I	GC-ECD	Napropamide	0.3	I	GC-FTD		
Fungicide	Iprodione	3	I	GC-FTD	Herbicide	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 (MCP)	0.05	HPLC	GC-ECD
	Trichlorophos-methyl	0.8	I	GC-FPD		Methyl-dymron	0.3	I	GC-FTD
Flutolanil	2	I	GC-FTD	Trichlorpyr acid, trichlorpyrbutoxyethyl			GCMS HPLC-UV		

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graph TD
    subgraph "Analysis Method I"
        A[Sample 200mL] --> B[Adjust to pH 7]
        B --> C[Solid phase extraction]
        C --> D[Connect C18 and active carbon columns  
Deliver the sample  
Separate two columns]
        D --> E[C18 column]
        D --> F[Active carbon column]
        E --> G[Acetone 10mL  
Elute 5mL Acetonitrile  
Add 2% diethylene glycol acetone solution]
        F --> H[Elute with 30mL methanol  
Add 2% diethylene glycol acetone solution]
        G --> I[Concentration / drying with nitrogen]
        H --> J[Concentration / drying with nitrogen]
        I --> K[Measuring up to 2mL (acetone)]
        J --> L[Measuring up to 2mL (acetone)]
        K --> M[GC/MS  
25 components]
        L --> N[GC/MS, GC-FPD  
Acephate, Trichlorfon]
    end

    subgraph "Analysis Method II"
        O[Sample 200mL] --> P[Adjust to pH 7]
        P --> Q[Ethyl acetate extraction]
        Q --> R[NaCl 10g  
Ethyl acetate 50mlx2]
        R --> S[Dehydration]
        S --> T[Add 2% diethylene glycol acetone solution]
        T --> U[Concentration / drying with nitrogen]
        U --> V[Measuring up to 2mL (acetone)]
        V --> W[GC/MS, GC-ECD]
        W --> X[Etridiazole  
Chloroneb  
Benfluralin  
Pyributicarb]
    end

    subgraph "Analysis Method III"
        Y[Sample 200mL] --> Z[Concentration / drying with nitrogen]
        Z --> AA[Measuring up to 2mL (acetone)]
        AA --> AB[GCMS, GC-FPD  
Methamidophos]
    end

    subgraph "HPLC Analysis Method"
        AC[Sample 250mL] --> AD[Adjust to pH 3.5]
        AD --> AE[Solid phase extraction]
        AE --> AF[Polystyrene gel column  
Elute with 5mL Acetonitrile  
Add 2% diethylene glycol acetone solution]
        AF --> AG[Concentration / drying with nitrogen]
        AG --> AH[Measuring up to 2mL (water and acetone)]
        AH --> AI[HPLC  
7 components]
    end
  
```

Analysis Method I

- Sample 200mL
- Adjust to pH 7
- Solid phase extraction
- Connect C18 and active carbon columns
- Deliver the sample
- Separate two columns
- C18 column
 - Acetone 10mL
 - Elute 5mL Acetonitrile
 - Add 2% diethylene glycol acetone solution
 - Concentration / drying with nitrogen
 - Measuring up to 2mL (acetone)
 - GC/MS
 - 25 components
- Active carbon column
 - Elute with 30mL methanol
 - Add 2% diethylene glycol acetone solution
 - Concentration / drying with nitrogen
 - Measuring up to 2mL (acetone)
 - GC/MS, GC-FPD
 - Acephate, Trichlorfon

Analysis Method II

- Sample 200mL
- Adjust to pH 7
- Ethyl acetate extraction
- NaCl 10g
- Ethyl acetate 50mlx2
- Dehydration
- Add 2% diethylene glycol acetone solution
- Concentration / drying with nitrogen
- Measuring up to 2mL (acetone)
- GC/MS, GC-ECD
- Etridiazole
- Chloroneb
- Benfluralin
- Pyributicarb

Analysis Method III

- Sample 200mL
- Concentration / drying with nitrogen
- Measuring up to 2mL (acetone)
- GCMS, GC-FPD
- Methamidophos

HPLC Analysis Method

- Sample 250mL
- Adjust to pH 3.5
- Solid phase extraction
- Polystyrene gel column
- Elute with 5mL Acetonitrile
- Add 2% diethylene glycol acetone solution
- Concentration / drying with nitrogen
- Measuring up to 2mL (water and acetone)
- HPLC
- 7 components

■ 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.

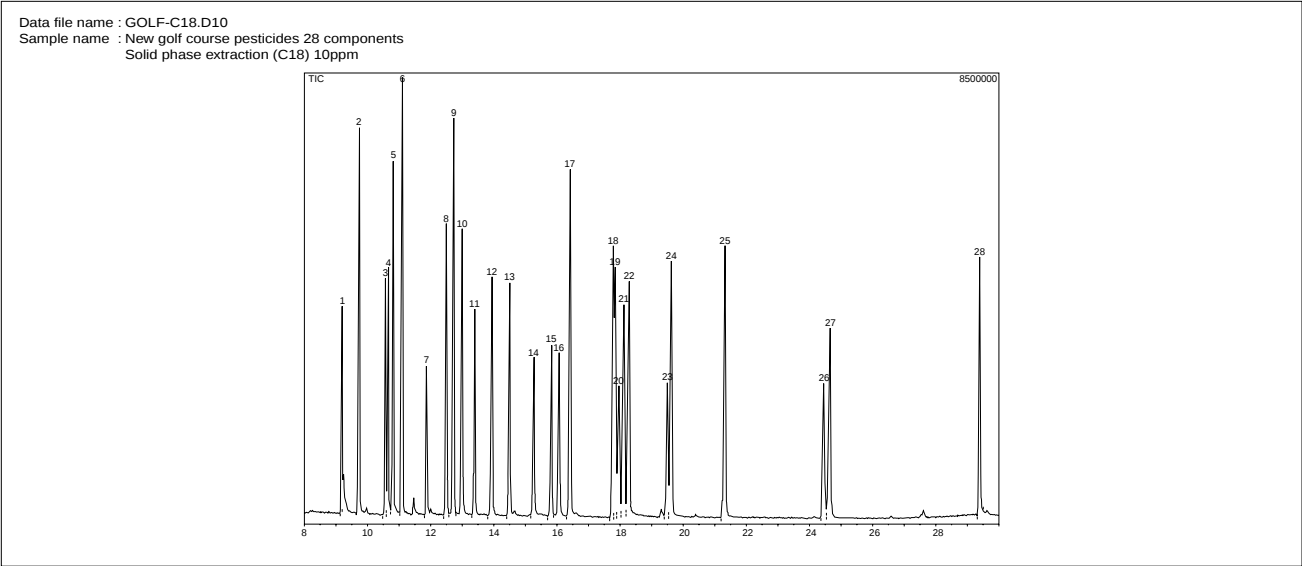


Fig. 1 TIC of Pesticides (Analysis Method I)

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	SIM mass number	Peak number	Component name	SIM mass number
1	Pencycuron	180,109	15	Pendimethalin	252,162
2	Simazine (CAT)	201,186	16	Methyl-dymron	107,119
3	Diazinon oxone	273,137	17	Isofenphos	213,255
4	Chlorothalonil (TPN)	266,264	18	Isoprothiolane	290,162
5	Propyzamide	173,273	19	Napropamide	271,128
6	Diadinone	304,179	20	Butamifos	286,200
7	MEP oxone	244,109	21	Isoxathion oxone	105,161,254
8	Trichlorophos-methyl	265,267	22	Flutolanil	323,173
9	Terbucarb (MBPMC)	220,205	23	Isoxathion	105,177,313
10	Metalaxyl (newly added)	206,160	24	Trichlopyr-butoxyethyl	210,212,182
11	Fenitrothion (MEP)	277,260	25	Mepronil	119,269
12	Dithiopyr (newly added)	354,306	26	Pyridafenthion	340,199
13	Chlorpyrifos	314,197	27	Iprodione	314,316
14	Captan	79,107,119	28	Bensulide (SAP)	215,131

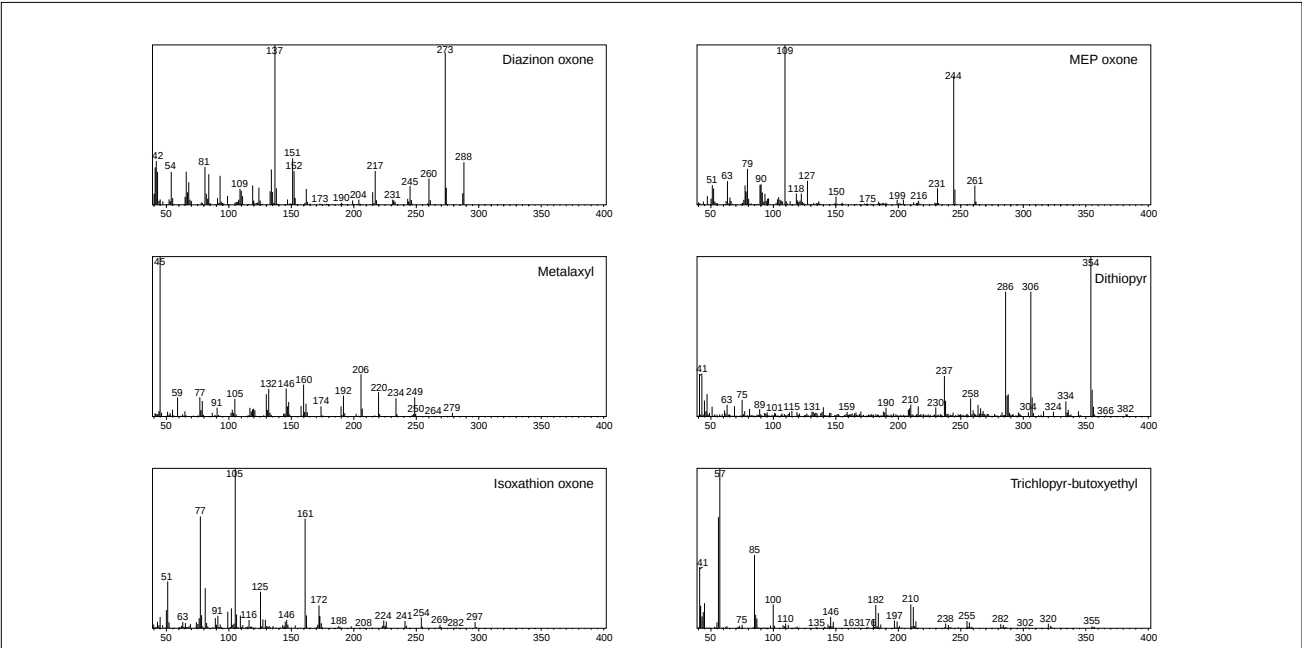


Fig.2 Mass Spectra of Pesticides

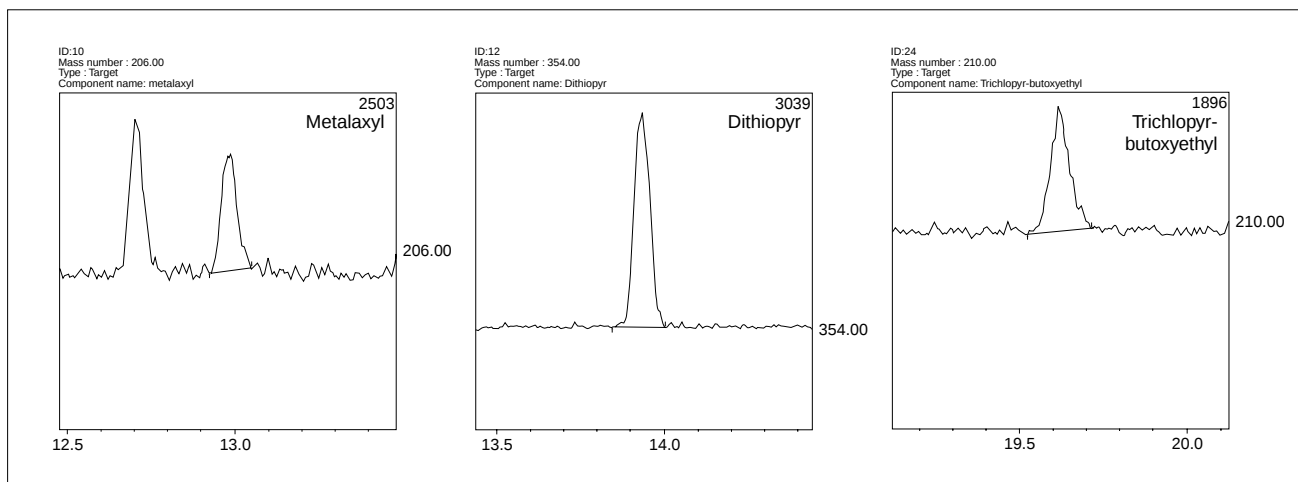


Fig.3 SIM chromatogram (10 ppb)

■ 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.

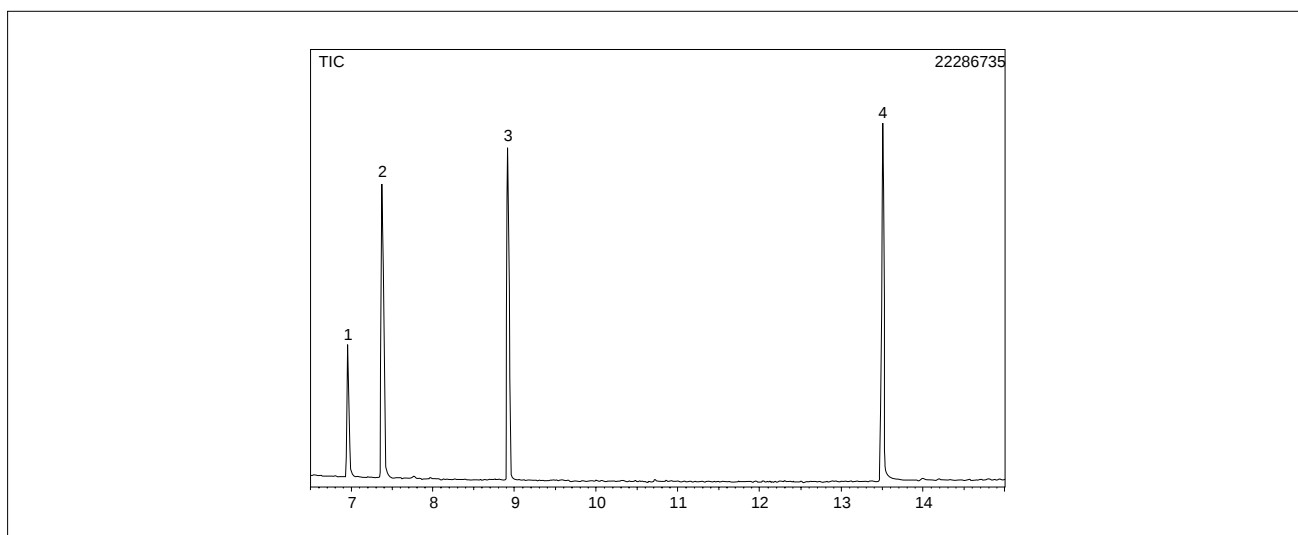


Fig. 4 TIC chromatogram of Pesticides (Analysis Method II)

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

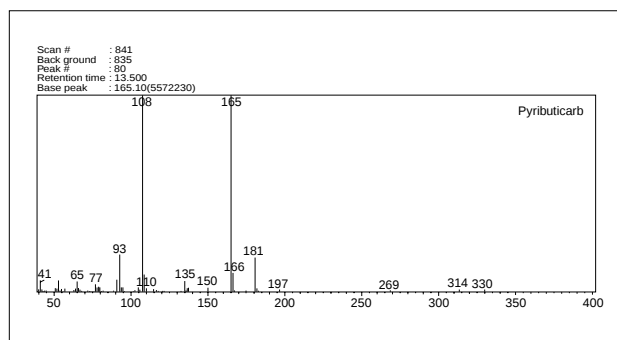


Fig.5 Mass spectrum of Pyributicarb

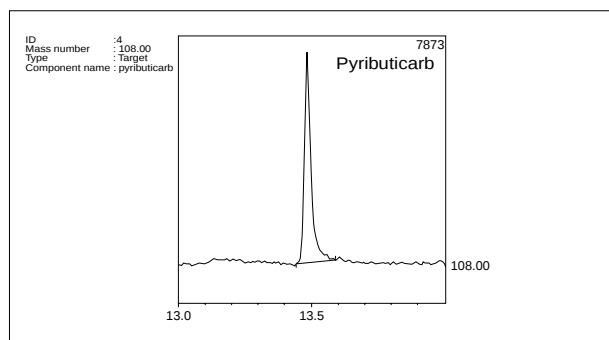


Fig.6 SIM chromatogram (10 ppb)

■ 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

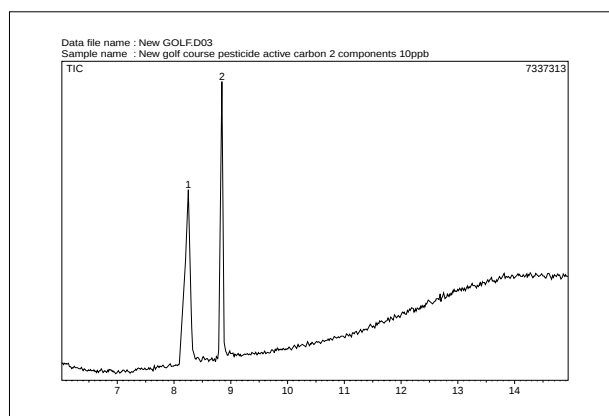


Fig. 7 TIC of Pesticides (Analysis Method I separate extraction)

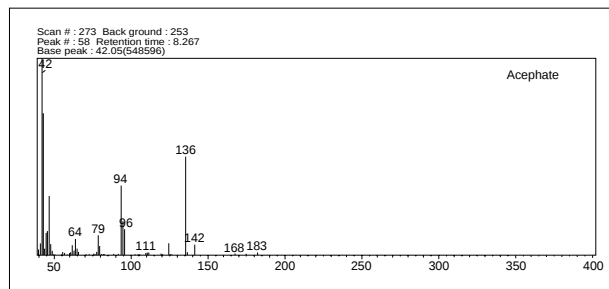


Fig.8 Mass spectrum of Acephate

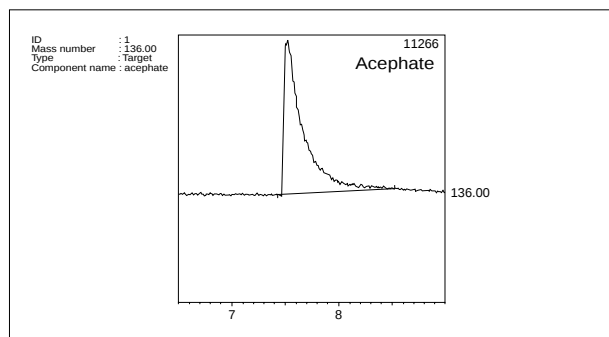


Fig.9 SIM chromatogram (500 ppb)



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