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Application Data Sheet

No.126

GC-MS

Gas Chromatograph Mass Spectrometer

Simultaneous Analysis of Pesticides by GC-MS Using Hydrogen Carrier Gas

Helium gas is used as a carrier gas in GC/MS. However, in recent years, the use of hydrogen as an alternative gas has increased due to helium gas supply shortages and soaring prices. There are advantages when hydrogen is used as an alternative gas; for instance, sensitivity is similar to that with helium, and high-speed analysis can be performed. However, caution is necessary in handling hydrogen as it is flammable. Hydrogen is obtained from hydrogen gas generators through the electrolysis of water. As a result, smaller quantities of hydrogen need to be stored, which dramatically improves the degree of safety in comparison to when gas cylinders are used. In addition, there is no need to purchase gas cylinders consecutively, which reduces running costs.
This Data Sheet presents an evaluation of the usefulness of the combination of a hydrogen gas generator with the GCMS-QP2020 for the simultaneous analysis of pesticides. The GCMS-QP2020 is equipped with a new type of turbomolecular pump, and is more than capable of accommodating hydrogen as the carrier gas.

Experiment

Mixed standard solutions were prepared at 0.005 mg/L, 0.01 mg/L, 0.05 mg/L, 0.1 mg/L, and 0.5 mg/L, by diluting a pesticide standard sample containing 59 pesticides. The method was created utilizing the EZGC Method Translator*, which is provided online by Restek Corporation (http://www.restek.com/ezgc-mtfc). For details on EZGC Method Translator*, refer to Application Data Sheet No. 120.

Table 1: Analytical Conditions

GC-MS:	GCMS-QP2020
Hydrogen Gas Generator:	Precision H_2 Trace (PEAK Scientific Corp.)
Column:	SH-Rxi-5MS (20 m long, 0.18 mm I.D., df = 0.36 μm) (P/N: 227-36017-01)
Glass Insert:	Sky Single Taper Inlet Liner w/ Wool (P/N: 23336.5)

GC	
Injection Port Temperature:	250 °C
Column Oven Temperature:	80 °C (1.15 min) → (30.7 °C /min) → 180 °C → (7.1 °C /min) → 280 °C (2.1 min)
Injection Mode:	Splitless
Carrier Gas Control:	Constant linear velocity (75.9 cm/sec)
Injection Volume:	2 μL
Sampling Time:	2 min
High-Voltage Injection:	250 kPa (2.3 min)

MS	
Ionization Mode:	EI
Interface Temperature:	250 °C
Ion Source Temperature:	230 °C
Measurement mode:	SIM mode
Event Time:	0.3 sec
SIM Monitoring m/z:	See below.

Fig. 1: Precision H_2 Trace (PEAK Scientific Corp.) Hydrogen Gas Generator and GCMS-QP2020

Table 2: SIM Monitoring *m/z*

Compound Name	Quantitation m/z	Reference m/z	Compound Name	Quantitation m/z	Reference m/z	Compound Name	Quantitation m/z	Reference m/z
Dichlorvos	185	109.0	Malaoxon	127	99.0, 195.0	Flutolanil	173	281.0
Dichlobenil	171	173.0	Simetryn	213	170.0	Isoprothiolane	189	118.0
Etridiazole	213	211.0	Tolclophos-methyl	265	125.0	Buprofezin	105	175.0
Chloroneb	193	191.0	Alachlor	188	160.0	Mepronil	119	269.0
Isoprocarb	136	121.0	Dithiopyr	354	306.0	Chlornitrofen	319	317.0
Molinate	126	98.0	Fenitrothion	277	260.0	Edifenphos	310	109.0
Fenobucarb	150	121.0	Esprocarb	91	222.0	Propiconazole-1	259	261.0
Trifluralin	306	290.0	Thiobencarb	100	72.0	Endosulfan	272	274.0
Pencycuron	125	180.0	Fenthion	278	125.0, 153.0	Propiconazole-2	259	261.0
Dimethoate	87	125.0	Chlorpyrifos	314	197.0	Thenylchlor	127	288.0
Simazine	201	186.0	Fthalide	243	241.0	Pyributicarb	165	108.0
Atrazine	215	200.0	Dimethametryn	212	255.0	Iprodione	314	316.0
Propyzamide	175	173.0	Pendimethalin	252	281.0	Pyridaphenthion	340	199.0
Pyroquilon	130	173.0	Methyldymron	107	119.0	EPN	157	169.0
Diazinon	304	179.0	Isofenphos	213	185.0	Piperophos	122	140.0
Ethylthiomethon	89	97.0	Captan	79	117.0, 149.0	Anilofos	226	125.0
Chlorothalonil	266	264.0	Phenthoate	274	125.0	Pyriproxyfen	136	226.0
Iprobenfos	204	91.0	Procymidone	96	283.0	Cafenstrole	100	188.0
Bromobutide	120	119.0	Methidathion	145	85.0	Ethofenprox	163	135.0
Terbucarb	220	205.0	Butamifos	286	200.0			

Results

By changing the column length from 30 m to 20 m, and converting the method with EZGC Method Translator*, it became possible to shorten the analysis time from 30 minutes to 20 minutes in comparison with the analytical conditions for helium. The GCMS-QP2020 is equipped with a new type of turbomolecular pump, and was capable of analyzing pesticides with high sensitivity, even in analyses with hydrogen as the carrier gas. Fig. 2 shows the calibration curve and chromatogram for fenitrothion at a concentration of 0.01 mg/L.
Table 3 shows the repeatability (n=5) at a concentration of 0.01 mg/L, and the results for the linearity of the calibration curve. Favorable results were obtained, with the %RSD for almost all components at 10 % max., and the linearity (coefficient of determination: R^2) of the calibration curve for all components at 0.998 min.

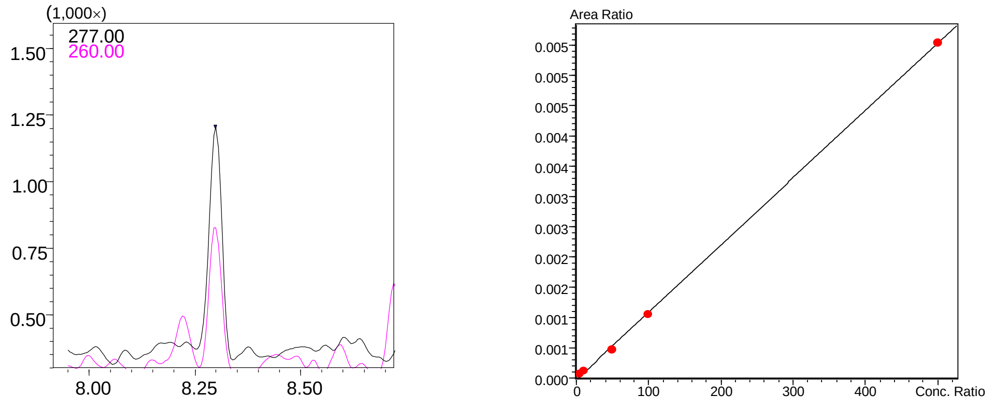

Fig. 2: 0.01 mg/L Fenitrothion Chromatogram (Left) and Calibration Curve (Right)

Table 3: Area Repeatability (n=5, 0.01 mg/L) and Calibration Curve Linearity (R^2)

Compound Name	%RSD	R^2
Dichlorvos	7.3	0.9993
Dichlobenil	3.7	0.9993
Etridiazole	4.9	0.9996
Chloroneb	2.8	0.9996
Isoprocarb	3.9	0.9994
Molinate	4.2	0.9980
Fenobucarb	4.5	0.9993
Trifluralin	4.7	0.9998
Pencycuron	5.2	0.9973
Dimethoate	6.6	0.9997
Simazine	4.6	0.9988
Atrazine	7.4	0.9984
Propyzamide	6.7	0.9976
Pyroquilon	2.4	0.9966
Diazinon	9.3	0.9996
Ethylthiomethon	7.3	0.9994
Chlorothalonil	4.6	0.9983
Iprobenfos	4.9	0.9992
Bromobutide	4.7	0.9969
Terbucarb	5.8	0.9987

Compound Name	%RSD	R^2
Malaoxon	8.2	0.9987
Simetryn	4.7	0.9987
Tolclophos-methyl	4.2	0.9991
Alachlor	10.0	0.9994
Dithiopyr	5.0	0.9982
Fenitrothion	4.1	0.9996
Esprocarb	2.0	0.9998
Thiobencarb	2.4	0.9985
Fenthion	7.7	0.9991
Chlorpyrifos	6.7	0.9996
Fthalide	3.0	0.9990
Dimethametryn	5.6	0.9998
Pendimethalin	5.6	0.9992
Methyldymron	8.3	1.0000
Isofenphos	11.2	0.9995
Captan	7.8	0.9999
Phenthoate	3.2	0.9994
Procymidone	3.7	0.9985
Methidathion	3.3	0.9990
Butamifos	5.3	0.9991

Compound Name	%RSD	R^2
Flutolanil	1.0	0.9996
Isoprothiolane	8.5	0.9997
Buprofezin	8.1	1.0000
Mepronil	5.3	0.9992
Chlornitrofen	5.5	0.9988
Edifenphos	9.8	0.9994
Propiconazole-1	7.6	0.9993
Endosulfan	3.5	0.9988
Propiconazole-2	7.8	0.9989
Thenylchlor	3.6	0.9976
Pyributicarb	4.9	0.9997
Iprodione	6.5	0.9989
Pyridaphenthion	7.3	0.9987
EPN	6.8	0.9990
Piperophos	8.3	0.9994
Anilofos	9.5	0.9992
Pyriproxyfen	4.5	0.9990
Cafenstrole	2.2	1.0000
Ethofenprox	4.4	0.9978

Conclusions

Using the GCMS-QP2020, a simultaneous analysis of 59 pesticides was performed, with hydrogen produced by a hydrogen generator as the carrier gas. From the results, it is evident that the analysis time was shortened, and that the pesticides were analyzed with high sensitivity. The hydrogen gas generator works well as a hydrogen gas supply source both in terms of safety and cost. It demonstrates peak performance in combination with the GCMS-QP2020, in which a large-capacity exhaust system has been adopted for vacuum exhaust. Note that if you are using hydrogen gas as a replacement, first confirm that the required sensitivity and quantitative performance can be obtained.
The Precision H2 Trace from PEAK Scientific Corporation can supply ultrapure hydrogen suitable for GC/MS. In addition, as a safety countermeasure, a leak detection function is provided inside the instrument. Further, a hydrogen detector (optional) can be connected inside the GC oven. Accordingly, even if a hydrogen gas leak occurs, the system as a whole, including the GCMS, will stop automatically, ensuring safe operation.

For cautions related to the handling of hydrogen gas, check the Shimadzu website.
http://www.shimadzu.com/an/gcms/gcmssolution/2.html

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