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GC-MS High Sensitivity Technology Using Overdrive Lens

GC/MS Technical Report No.7

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Abstract

The effects of increased signal intensity and improved signal-to-noise ratio (*S/N*) were investigated by eliminating noise with the installation of an overdrive lens in the GCMS-QP2010 Ultra, and verifying the effectiveness using simulation and experimentation by GC-MS. The results confirmed that *S/N* improved through application of the optimum voltage on the overdrive lens. In addition, it was verified from the results of analysis of 5 ppb chlorpyrifos-methyl by the full-scan method that high-sensitivity analysis is possible using the GCMS-QP2010 Ultra equipped with this technology.

Keywords: GC-MS, Simulation, Surface Charge Method, Overdrive Lens, High-Sensitivity Measurement, *S/N*

Introduction

In addition to the analysis of harmful substances in foods and the environment, the gas chromatograph-mass spectrometer (GC-MS) is being used more and more in a wide range of applications, including metabolite research (metabolomics) in the fields of disease diagnostic markers and functional foods research, and fields that are associated with human health, peace of mind and safety. Measurement of ultra-low concentrations, from nanogram to femtogram levels, is necessary in these fields, and requires a high-sensitivity GC-MS. Thus, one of the important objectives underlying the ongoing development of GC-MS is improvement of sensitivity. Sensitivity is typically expressed as the ratio of signal intensity (S) to noise intensity (N), or *S/N*. One of the factors inhibiting the improvement of *S/N* in GC-MS is the use of He carrier gas, which tends to generate noise. The GCMS-QP2010 Ultra is equipped with 2 electrodes (overdrive lens, Patent No. US6737644)[1] that are installed before the detector, which effectively eliminate noise and, in particular, permit efficient detection of target compound ions. In this report, we introduce the noise elimination effects and improved signal intensity obtained using the overdrive lens, verified through simulation and experimentation. In addition, an explanation of the effectiveness of the overdrive lens is presented.

Introduction of Simulation Software

The optics, charged particles optics, and ultrasonic wave analysis design software Optdesign, originally developed by Shimadzu Corporation, was used for simulation of the signal intensity improvement and noise elimination due to the effect of the overdrive lens (Fig. 1)[2]. Calculation of ion trajectories can be conducted with very high accuracy because Optdesign uses the surface charge method rather than the finite element method. Moreover, calculations were devised to obtain high-accuracy space potential calculations and harmonics (multiple polarizing field development coefficient) calculations.

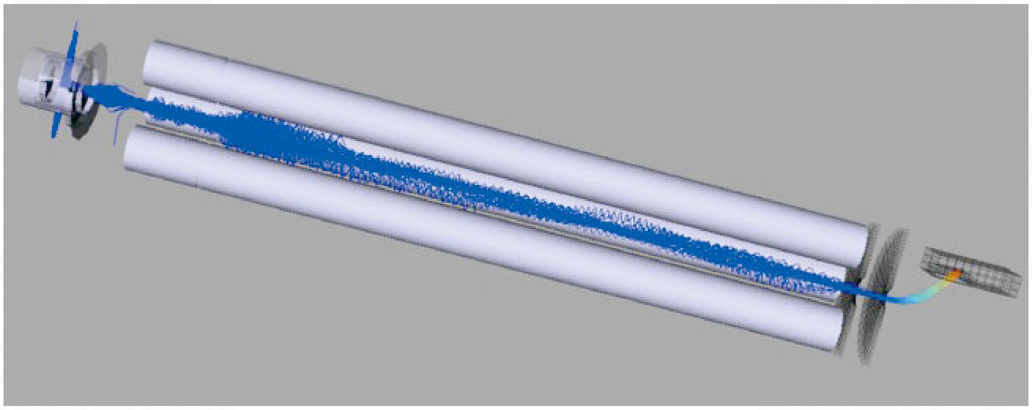


Fig. 1 Calculation of Ion Trajectories Using Optdesign™

Experiments

a. Investigating Signal Intensity and Noise Intensity by Simulation

Fig. 2 shows a cross-sectional diagram of the overdrive lens adopted in the GCMS-QP2010 Ultra. The overdrive lens consists of 2 electrodes. The lens voltage applied to lens electrode 1 is 0 V, and to lens electrode 2, a negative voltage. Using Optdesign, we simulated the lens voltage and signal intensity of the target ion reaching the detector, and the noise intensity changes due to the He ion.

To determine the relationship between the negative voltage (hereafter, lens voltage) applied to lens electrode 2 and the signal intensity, we changed the voltage from 0 to -1000 V in -20 to -200 V steps, and calculated the trajectories under the respective conditions for the *m/z* 69, 264 and 502 ions.

Two factors are known to be associated with the ionization of He carrier gas, a source of noise in GC-MS. One is He ionization due to 70 eV electron flow inside the ion source, and the other is that He in a metastable state (neutral, rather than ionic state) accepts energy through collision with ions to become ionized. In either case, if ionization occurs prior to traversing the quadrupoles, they are eliminated due to the AC and DC voltages applied to the quadrupoles, preventing them from reaching the detector. However, if ionization occurs after traversing the quadrupoles, they are detected as noise. Therefore, simulation of the noise intensity was conducted for He ions that were ionized after traversing the quadrupoles.

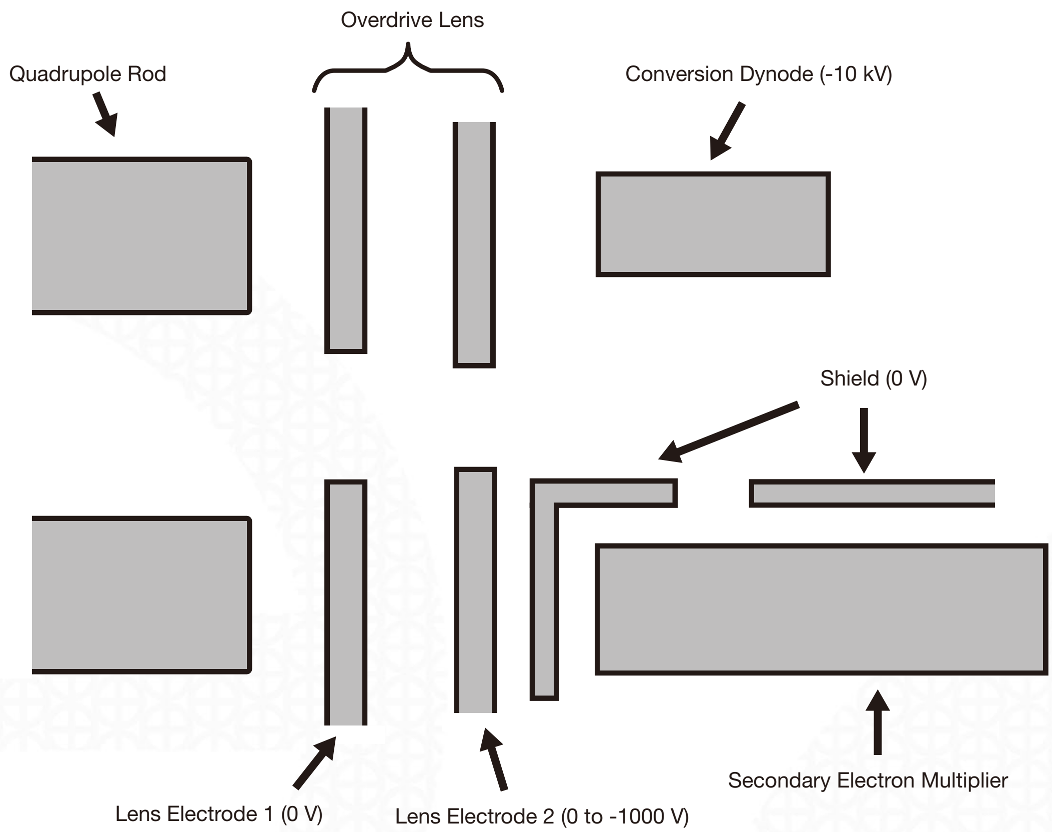


Fig. 2 Cross Sectional Diagram of Detector Vicinity
Overdrive Lens Structure

b. Measurement of Signal Intensity and Noise Intensity Using Instrument at Different Detector Voltages

Using the GCMS-QP2010 Ultra, we measured the observed signal intensity and noise intensity, changing the lens voltage from 0 to -1000 V in -20 to -100 V steps, as in the simulation described above. To investigate the relationship between the signal intensity and lens voltage, we conducted analysis of perfluorotributylamine (PFTBA), a standard substance that can be introduced into the mass spectrometer at a fixed quantity. The intensity fluctuations of PFTBA fragmentation ions, *m/z*: 69, 264, and 502 were subsequently measured. In addition, to investigate the relationship between the noise intensity and lens voltage, a fixed quantity of He carrier gas from the GC was introduced, and the noise intensity was measured.

c. Use of Overdrive Lens in Actual Analysis

Voltages of -10, -100, and -830 V were applied to the GCMS-QP2010 Ultra overdrive lens, and 1 pg of octafluoronaphthalene was analyzed using the scan method to measure the effects of the respective lens voltages. We also conducted scan measurement of a 5 ppb sample of chlorpyrifos-methyl to check the sensitivity of the GCMS-QP2010 Ultra equipped with the overdrive lens.

Experiment Results and Discussion

a. Results of Simulation with Optdesign™

Fig. 3 shows the relationship between the overdrive lens voltage and signal intensity obtained using Optdesign. The signal intensity increases sharply as the lens voltage is increased from 0 V. However, the signal intensity saturates at a certain voltage, and then, as the voltage is further increased, the signal intensity reverses to decrease in minute increments. The results showed that the voltage at which the signal intensity saturates is dependent on the *m/z* value, such that signal intensity saturation of an ion with a small *m/z* value occurs at a relatively small voltage, and for high *m/z* ions, signal intensity continues to increase at higher voltages. Considering the movement of an ion, when a measurement target ion is traversing the quadrupoles, the ion vibrates in a direction that is perpendicular to the direction of travel due to the AC voltage and DC voltage applied to the quadrupoles. It is believed that increasing the lens voltage to a value slightly larger than 0 V causes the ions that had been colliding with the lens electrode due to their vibration to be drawn into the holes of the lens electrode, thereby rapidly increasing the number of ions reaching detector. In addition, if the vibration width of target ions at the quadrupole exit is greater than a certain value, a weak attraction due to a small lens voltage will prevent those ions from reaching the detector.

On the other hand, too large a voltage will create too great an attraction, causing the target ions to collide with the overdrive lens electrode and prevent their detection. Therefore, it is thought that setting the optimum voltage will provide efficient focusing of the ions. Similarly, the relationship between the lens voltage applied to the overdrive lens and the noise intensity obtained using Optdesign is shown in Fig. 4. It is evident that the noise intensity decreases as the voltage is increased. When the lens voltage is 0 V, He ions generated after the quadrupole exit are detected as noise due to the -10 kV applied to the conversion dynode in the detector. But, when the lens voltage is increased, it is evident that the lens voltage has a greater effect on the He ions than the conversion dynode voltage, thereby minimizing the He ion noise factor using the lens. The above simulation results indicate that by applying an appropriate voltage to the overdrive lens, it is possible to increase the signal intensity of the measurement target ion, and, at the same time, eliminate noise from He ions generated from the carrier gas.

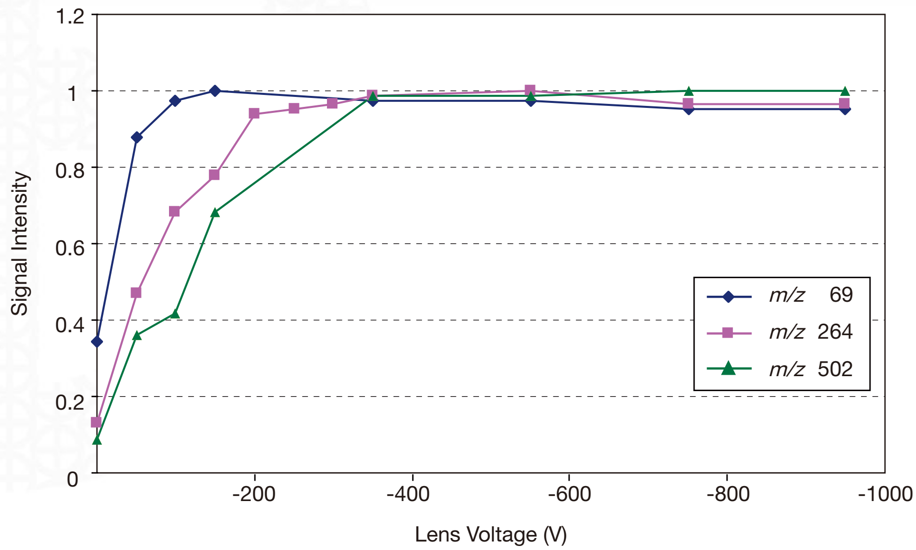


Fig. 3 Changes in Voltage and Signal Intensity Obtained by Simulation
*Y-axis shows normalized maximum signal intensity for each *m/z*

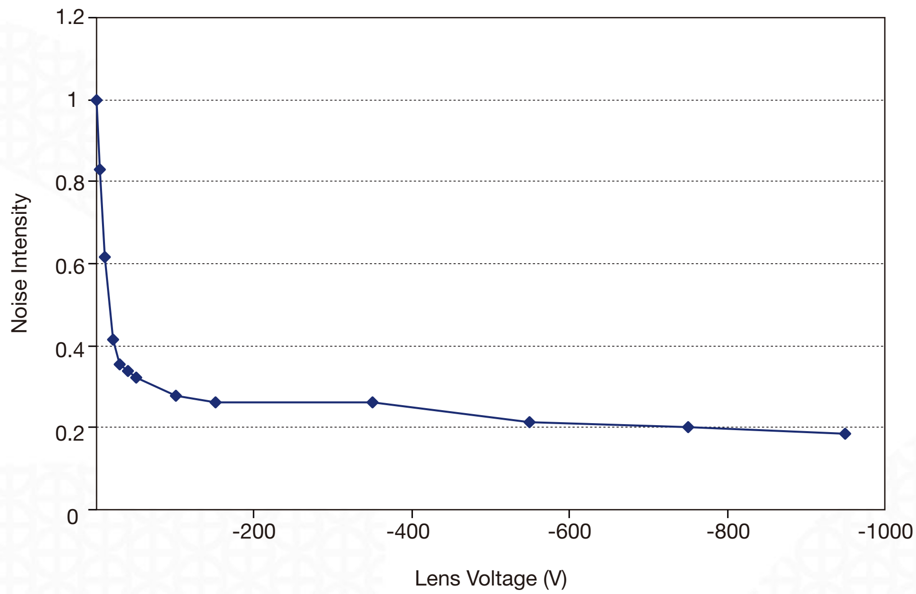


Fig. 4 Changes in Noise Intensity Obtained by Simulation
*Y-axis shows normalized maximum noise intensity

b. Investigating Effectiveness of Overdrive Lens Using GC-MS

The GCMS-QP2010 Ultra was used to measure the relationship between the overdrive lens voltage and the signal intensities of the characteristic fragmentation ions of PFTBA, namely *m/z*: 69, 219, and 502 (Fig. 5). The Y-axis shows the signal intensity of each *m/z* normalized to a maximum signal intensity of 1. The signal intensity increases as the lens voltage increases from 0 V, and the signal intensity saturates when the voltage exceeds a certain value. When the lens voltage is increased further, the signal intensity decreases slightly. Also, the lens voltage at which the signal intensity saturates is dependent on *m/z*, such that the larger the *m/z* value, the higher the voltage at which maximization occurs. Also, with respect to noise, we measured the relationship between the overdrive lens voltage and the noise intensity (Fig. 6). The Y-axis shows the noise intensity normalized to a maximum intensity of 1. The noise intensity is shown to decrease as the lens voltage is set to larger values.

Both the simulation results and experimental results indicate that to increase the *S/N* ratio, the voltage applied to the overdrive lens must be set so that the signal intensity is high and the noise is low over the entire *m/z* region. Based on these results, we determined that a voltage of -830 V should be applied to the overdrive lens considering relationships among the overdrive lens voltage signal and noise intensities at each *m/z* value (Fig. 7).

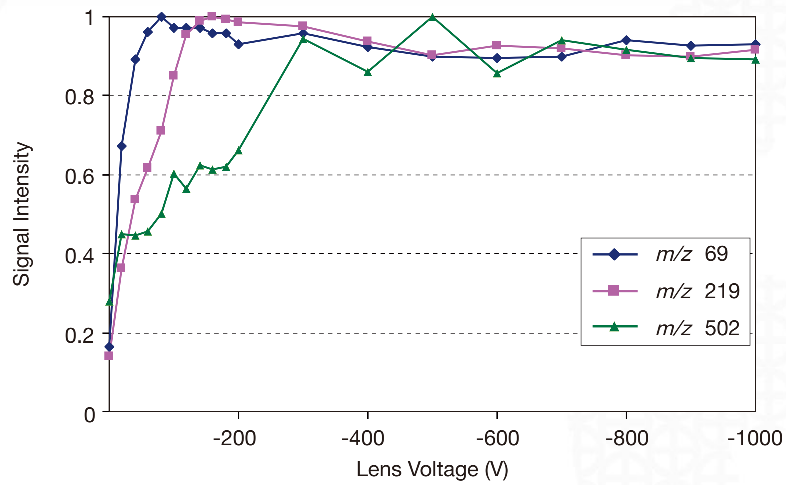


Fig. 5 Voltage and Signal Intensity Experiment Results Obtained by GC-MS
*Y-axis shows normalized maximum signal intensity for each *m/z*

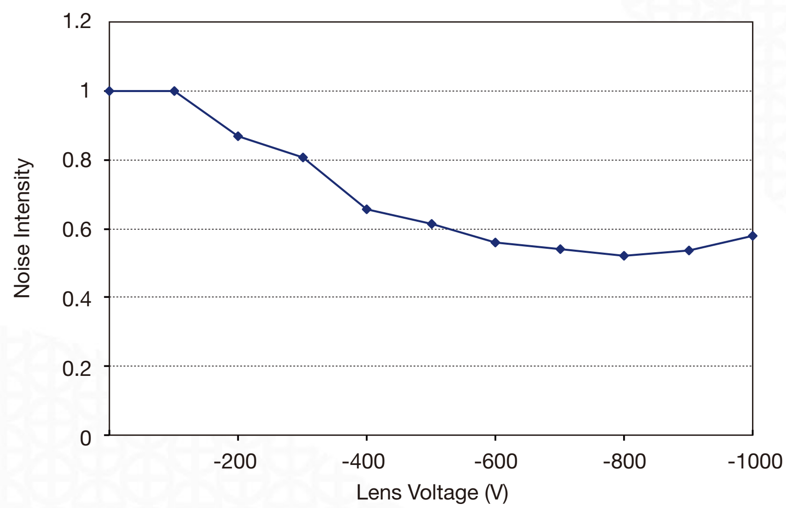


Fig. 6 Lens Voltage and Noise Intensity Experiment Results by GC-MS
*Y-axis shows normalized maximum noise intensity

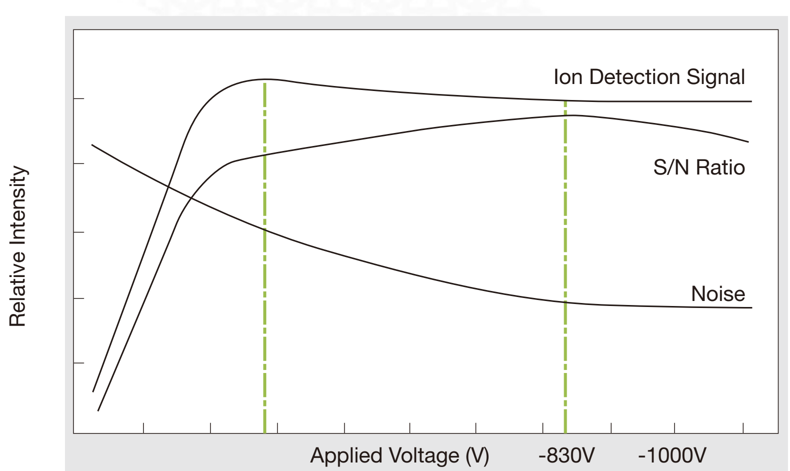


Fig. 7 Concept Diagram of Voltage and Signal Intensity, Noise Intensity, and *S/N* Changes

c. Effect of Overdrive Lens Use in Actual Analysis

To verify the effect of the overdrive lens in actual analysis, we conducted analyses of 1 pg of OFN in the full-scan mode using overdrive lens voltages of 0, -10, and -830 V. The experimental results are shown in Fig. 8. Use of a higher lens voltage had the effect of increasing the signal intensity, and decreasing the noise, thus improving the *S/N* ratio. Using a GCMS-QP2010 Ultra equipped with an overdrive lens, the results of analysis of 5 ppb chlorpyrifos-methyl using the full-scan mode are shown in Fig. 9. High-sensitivity measurement was achieved even with a trace-level sample.

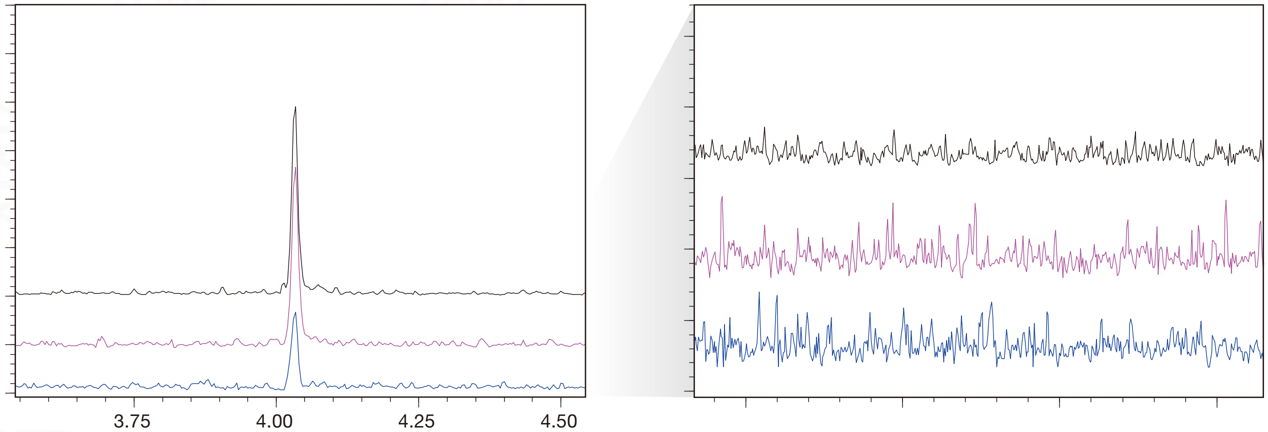


Fig. 8 Lens Voltages and OFN Mass Chromatograms (*m/z* : 272)
Black: -830 V, Pink: -100 V, Blue: -10 V
Figure at right is magnified portion of baselines

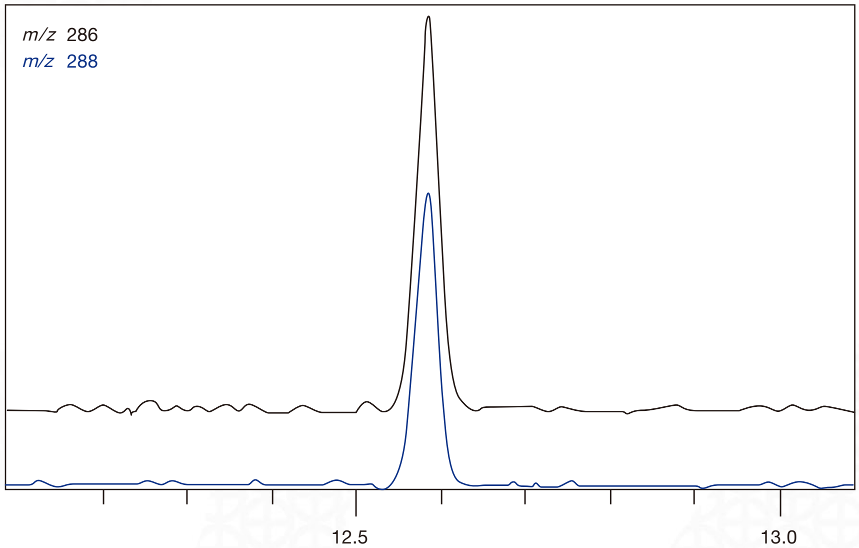


Fig. 9 High-Sensitivity Data by Scan Measurement
Chlorpyrifos-methyl (5 ppb)

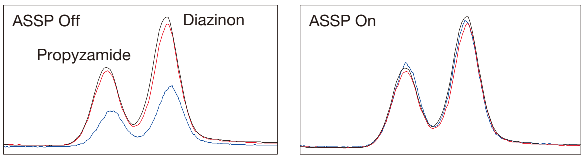
Summary

To determine the effect of using the overdrive lens (Patent: US6737644) installed in the GCMS-QP2010 Ultra for improvement of the *S/N* ratio (by increasing signal intensity and eliminating noise), we conducted simulations using Optdesign and actual analysis by GC MS.
The results indicated a relationship between the voltage applied to the overdrive lens and the signal intensity; when a negative voltage was applied from a starting voltage of 0 V, the greater the voltage applied, the greater became the signal intensity, until the signal maximized at a certain voltage. Further increasing the applied voltage resulted in a very slight decrease in signal intensity. In addition, the relationship between the voltage applied to the overdrive lens and the noise intensity was such that when a negative voltage was applied from a starting voltage of 0 V, the greater the voltage applied, the greater the decrease in noise intensity. From the above results, it was verified that applying an optimum overdrive lens voltage of -830 V significantly improves the *S/N* ratio. Furthermore, using the GCMS-QP2010 Ultra with the overdrive lens installed to increase signal intensity and eliminate noise, we conducted analysis of chlorpyrifos-methyl at a trace-level concentration of 5 ppb, in the full-scan mode and confirmed that high-sensitivity analysis is enhanced through the use of the overdrive lens.

[1] H. Itoi, Quadrupole Mass Spectrometer, U.S. Patent 6737644, 2004-05-18.
[2] Masahiro Takabe, Yoshihiro Ueno, Akira Sato, Makoto Fujita, Junichi Taniguchi, Akihiko Iwata, Shinji Miyauchi, Kenji Yamada, Sumio Kumashiro; Optics, Charged Particle Optics, and Ultrasonic Wave Analysis Design Software "Optdesign" Development, Shimadzu Review, 1998 55[1] 83 to 91

Ultra Fast Equipped with High-Speed Data Acquisition Processing Via the Newly Developed ASSP Function

A newly developed quadrupole mass spectrometry technology has been developed which allows us to increase the scan speed of our GC-MS system. This technology, Advanced Scanning Speed Protocol (ASSP), is the key to faster data acquisition.
Incorporated in the new GCMS-QP2010 Ultra, it is a firmware protocol that optimizes the ion transmission hardware parameters combined with a highly efficient data collection algorithm allowing acquisition speeds of 20,000 u/sec and 100 Hz. ASSP provides the added benefit of maintaining system sensitivity at the elevated scan speeds and virtually eliminates mass pattern skewing. (Patent: US6610979)

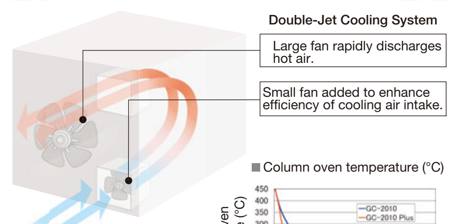


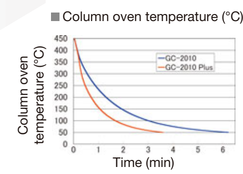
Variation of chromatogram intensity at each scan speed

ASSP optimizes the ion transmission optics to maintain ion signal intensity across the entire mass range as the scan speed of the system increases.

Variety of Functions for Enhanced Productivity in the Laboratory

The GC is able to cool from 350°C to 50°C in approximately 2.7 minutes using a newly developed "double-jet cooling system".
Imagine your VOC analysis cycle time being cut in half. The GCMS-QP2010 Ultra makes this a reality by combining Fast GC technology with rapid oven cool-down, effectively increasing sample throughput in your lab! Many applications require that the injection port undergoes maintenance on a frequent basis. With the GCMS-QP2010 Ultra, maintenance is possible without venting the MS so downtime is minimized. In addition,the GCMS-QP2010 Ultra is capable of accepting installation of two narrow-bore capillary columns into the MS simultaneously. This allows you to switch applications without physically modifying the column installation.

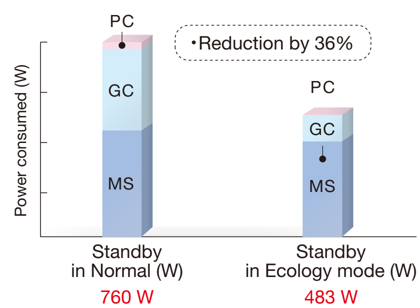




Eco-Friendly Design for Lower Running Costs in the Laboratory

When Ecology mode is entered, unnecessary power consumption by the GC, MS, and PC is automatically eliminated. The consumption of carrier gas is also automatically reduced. Furthermore, the Ecology mode can be entered automatically after continuous analysis so power and carrier gas can be saved automatically after the completion of nighttime analysis.

Ecology mode software window



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