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# Development of Green Technologies in GCMS-QP2010 Ultra

## GC/MS Technical Report No.8

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### Abstract

There has been an increasing interest in reducing running costs and environmental stress in many analytical laboratories using gas chromatograph-mass spectrometers in the fields of food, forensic, life science, environment, and the like. To respond such interest, we have developed two technologies for lower power and carrier gas consumption: "Advanced Scanning Speed Protocol" (ASSP™) necessary for the Fast-GC/MS method and "Ecology Mode" for saving energy in analysis standby mode. The analysis of organic acids in urine for evaluation showed that the use of the Fast-GC/MS with ASSP™ reduced helium gas by 90 percent and power by 66 percent, compared with our previous model, while retaining performance for analysis. An evaluation test in analysis standby mode confirmed that the instrument with the Ecology Mode reduced carrier gas and power consumption, by 60 percent and 36.5 percent, respectively. These results demonstrate that our GCMS-QP2010 Ultra has environmentally friendly features and ensures lower running costs.

Keywords: Ecology mode, Running cost, Fast-GC/MS, High speed scan, GC-MS, Green technologies

### Overview

Gas chromatograph mass spectrometers (GC-MS) are widely used in the fields of food, the environment, forensics, and life science, to name a few. However, there is growing concern regarding operating costs and the environmental burden associated with operating GC-MS systems. In consideration of these social impacts, we have developed technology for reducing carrier gas consumption and electrical power. To address the issue of energy conservation during analysis, we developed the high-speed scanning control technology necessary for the Fast-GC/MS technique which shortens analysis time. Applying this Fast-GC/MS technique using this technology in the analysis of organic acids in urine, we were able to reduce helium gas and power consumption from the existing levels by 90 % and 66 %, respectively, while maintaining the quality of analysis. In addition, we also developed the Ecology Mode, which saves unnecessary electrical power and carrier gas during analysis standby periods, addressing the requirement for energy conservation while the instrument is in the standby mode. This function has been confirmed to reduce carrier gas and power consumption by 60 % and 36.5 %, respectively, during analysis standby.
This report introduces the high-speed scanning control technology and Ecology Mode which achieve significant reductions in operating cost and a reduced environmental burden, and reports on the effects of energy conservation achieved with these technologies.

### Introduction

A gas chromatograph mass spectrometer (GC-MS) consists of gas chromatograph (GC) for separation and a mass spectrometer (MS) for identification; a block diagram of a GC-MS is shown in Figure 1. Samples containing multiple constituents are vaporized at the GC, and the gas-phase sample is channeled through a column for separation of the constituents. Next, the separated components are introduced into the MS, where they are ionized, separated according to mass, and then measured. A GC-MS can measure minute substances from nanogram to femtogram levels, allowing its application over a wide range of fields including the environment, food and chemicals. Quality control in food manufacturing, research and development in the pharmaceutical and chemical industry are examples. In addition to utilizing GC-MS for the measurement of harmful compounds in foods and the environment, applications have widened in recent years to fields associated with human health, assurance and safety, such as metabolite analysis (metabolomics) in the research fields of disease diagnostic markers and functional foods.

GC-MS uses helium as the carrier gas, which offers high chromatographic resolution at a wide range of flow rates. However, helium gas, a non-renewable resource which is in short supply, is becoming more expensive[1)] year by year, and represents the portion of the operating cost that is continually rising. In addition, a great deal of power must be consumed to maintain such functions as heating the GC injector and oven, and maintaining a vacuum in the mass analyzer. Furthermore, since analyte compounds are measured at minute concentrations, the instrument is often kept running even when analysis is not being conducted to ensure that it remains in a state of high stability. Thus, an analysis business model that includes GC-MS operations is typically burdened with significant expenses associated with helium gas and electrical power consumption. On the other hand, limiting the environmental impact is a global issue, even with respect to analytical instruments including GC-MS. There is a demand[2] to support energy conservation as elucidated in the Twelve Principles of Green Chemistry[3]. Taking these social conditions into consideration, the authors developed technologies that achieve reductions in the consumption of helium and electrical power both during analysis as well as in standby periods. Investigating the possibility of using a shorter analysis time as a means of addressing the issue of energy conservation during analysis, we developed the Advanced Scanning Speed Protocol, ASSP™[4]. On the other hand, our approach to achieving energy conservation during analysis standby periods was to automatically turn off power to the GC, MS, and PC, which are unnecessary during standby periods. In addition, we developed a technology (Ecology Mode) for conserving helium gas.

Here we report on the GCMS-QP2010 Ultra (Figure 2), an instrument developed to achieve energy conservation which incorporates the ASSP™ and Ecology Mode technologies, which are designed to reduce the environmental impact of instrument operation.

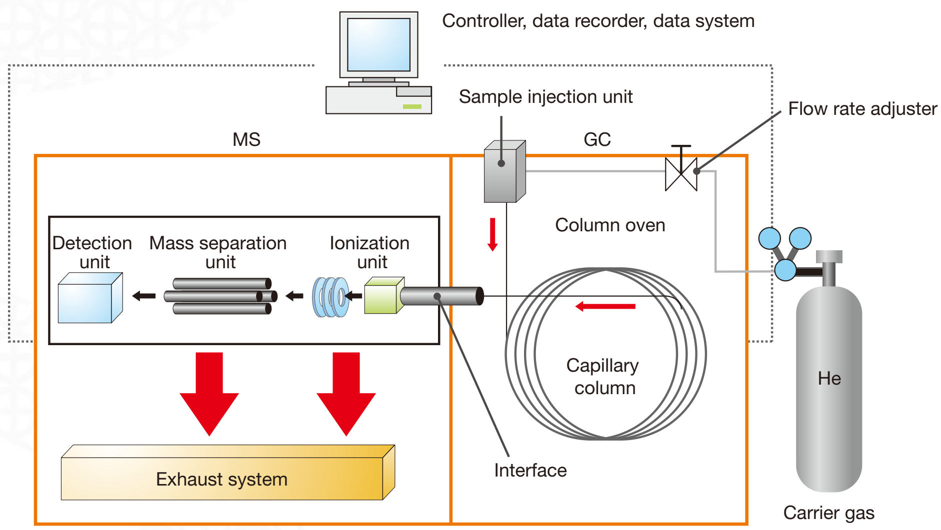


Fig. 1 Principle of Gas Chromatograph Mass Spectrometer

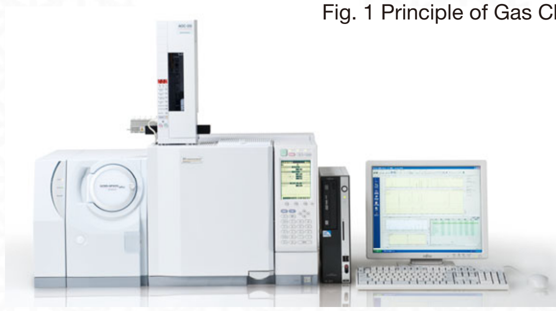

Fig. 2 GCMS-QP2010 Ultra Gas Chromatograph Mass Spectrometer

Table 1 Analysis Times, Peak Widths, and Data Sampling Rates for Conventional and Fast-GC/MS Methods

| | Analysis Time | Peak Width | Sampling Rate[a] |
|---|---|---|---|
| Conventional method | > 10 min | > 4s | > 0.4s |
| Fast-GC/MS method | 1 - 10 min | 0.5 - 3s | 0.05 - 0.3s |

[a] Measurements at 10 points or more per peak are required.

## Technology for Reducing Environmental Burden during Analysis

### a. Fast-GC/MS and Quadrupole Mass Spectrometer

We investigated the possibility of shortening the analysis time as a means of reducing the environmental impact of helium and power consumption. We used Fast-GC/MS[5 to 7] as a means of shortening the analysis time. The Fast-GC/MS technique relies on the use of narrower, shorter columns (for example, length 10 m, diameter 0.1 mm), high carrier gas injection port pressure (greater than several hundred kPa), and rapid heating of column oven (greater than 30 °C/min). Compared to the conventional analysis technique, this technique delivers faster elution and sharper chromatographic peaks, allowing a shorter analysis time (Table 1)[8] without sacrificing chromatographic resolution. However, since the peaks generated with Fast-GC/MS are extremely narrow, measurement at a shorter cycle time than in the conventional method is required to ensure that chromatograms are produced with adequate precision[9]. To illustrate this, Fig. 3 shows the relationship between chromatographic peak width and data sampling rate in conventional and Fast-GC/MS methods.

The quadrupole mass spectrometer (hereafter, QMS) that the authors developed is designed so that the ions generated by the ion source resonate in the quadrupole as specific AC and DC voltages are applied, while only ions with specific mass-to-charge ratios (*m/z*) can be transmitted through the quadrupoles to be detected (Fig. 1). Since ions only within a specified *m/z* range are continuously measured in scan mode, the AC voltage and DC voltage applied to the quadrupoles must be continuously changed. Because the data sampling cycle is shorter in Fast-GC/MS, the changes in AC voltage and DC voltage per unit time become faster. Formerly, this caused problems of lower ion transmission rates as well as diminished sensitivity. Therefore, Fast-GC/MS, which requires high-speed scanning, has previously used a time-of-flight mass spectrometer GC-MS[10),11)].

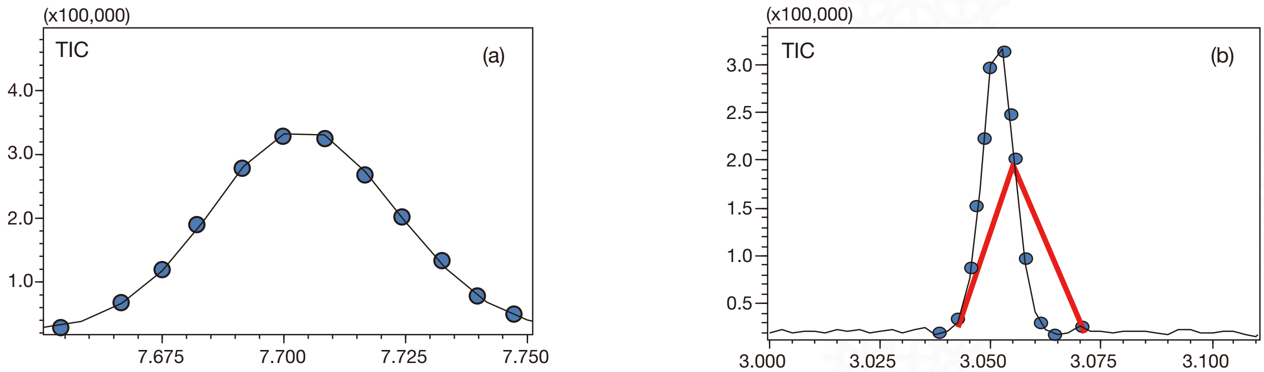


Fig. 3 Data Sampling Rates and Total Ion Chromatograms
a) Conventional method: Peak width 6 s, sampling rate 0.5 s
b) Fast-GC/MS method: Peak width 1.5 s, sampling rate 0.15 s (black), 0.50 s (red)

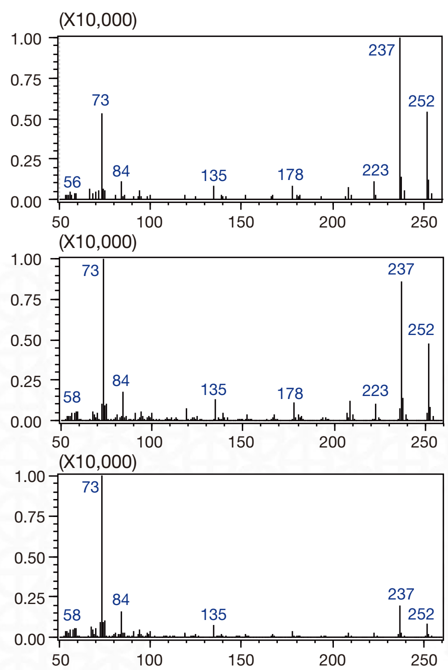


Fig. 4 Mass Spectra of Theophylline-TMS
Upper: NIST mass spectrum
Middle: Mass spectrum with ASSP™
Lower: Mass spectrum without ASSP™

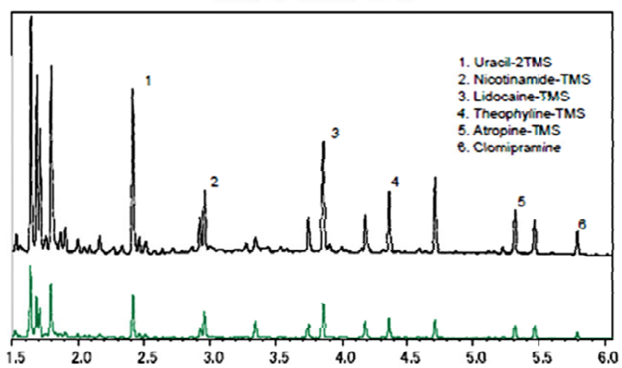


Fig. 5 Analysis of Pharmaceutical Using Fast-GC/MS
Upper: Total ion chromatogram with ASSP™
Lower: Total ion chromatogram without ASSP™

## b. QMS Development for Fast-GC/MS

Since the QMS with energy-saving Fast-GC/MS technology was to be used for analysis, we developed technology that improved the low sensitivity associated with the high-speed data sampling technology and high-speed scanning. High speed data sampling was not possible with the existing technology because of the instrument's slow data processing speed. Also, when conducting high-speed scan measurement, the ion transmission rate through the quadrupoles decreases. In particular, since the transmission rate of large mass ions having slow transmission speeds is dramatically reduced, the relative intensity of large mass ions decreases, which results in an altered mass spectrum (Fig. 4). To resolve these problems, a new high-speed processing platform was developed, capable of a 0.01-second data sampling rate (100 mass spectra per second) and a 20,000 u/sec maximum scan speed, twice that currently possible (world's highest speed for QMS). In addition, to address the problem of reduced sensitivity during high-speed scanning, we developed high-speed scanning control technology (Advanced Scanning Speed Protocol, ASSP™) to accelerate ions that are transmitted through the quadrupoles, thereby improving the ion transmission rate. As a result, sensitivity during high-speed scan measurement improved by greater than five-fold compared with existing instruments (Fig. 5). In particular, this technology remarkably improves the transmission rates of large *m/z* target ions in high-speed scanning, thereby improving mass spectral patterns and elevating the degree of similarity with existing library mass spectra (Fig. 4). These technological advancements have made QMS applicable to Fast-GC/MS.

## c. Energy Conservation in Analysis of Organic Acids in Urine by Fast-GC/MS

The degree to which the environmental impact is reduced using Fast-GC/MS was evaluated in the analysis of organic acids in urine, typically conducted for the diagnosis and biomarker research associated with congenital metabolic disease. The analytical conditions used in the conventional and Fast-GC/MS methods are shown in Table 2, and the respective acquired chromatograms are shown in Fig. 6. Notwithstanding the dramatically shortened analysis time from 60 minutes to 12 minutes using Fast-GC/MS, analysis with similar sensitivity was clearly achieved without any loss of chromatographic resolution. Furthermore, total helium consumption of 1,200 mL per analysis with the conventional method (20 mL/min × 60 min) was reduced to 120 mL using Fast-GC/MS (10 mL/min × 12 min), cutting consumption to one-tenth. On the other hand, electrical power consumption per sample was 945 Wh with the conventional method, and 324 Wh with Fast-GC/MS, realizing a savings of 621 Wh in power consumption per sample.

The above results clearly demonstrate that the Fast-GC/MS technology introduced with the high-speed processing platform and ASSP™ used in the quadrupole GC/MS-QP2010 Ultra permit dramatically reduced consumption of both helium gas and electrical power, while maintaining the expected quality of analysis.

Table 2 Analytical Conditions for Organic Acids in Urine

| | Conventional Method | Fast-GC/MS Method |
|---|---|---|
| Analysis time | 60min | 12min |
| Carrier gas pressure | 83.7kPa | 642.1kPa |
| Total flow rate of carrier gas | 20mL/min | 10mL/min |
| Column oven temperature | 100°C(4min)–4°C/min | 80°C(0min)–30°C/min |
| Program | –280°C(11.0min) | –325°C(3.83min) |
| Data sampling rate | 0.5s | 0.15s |

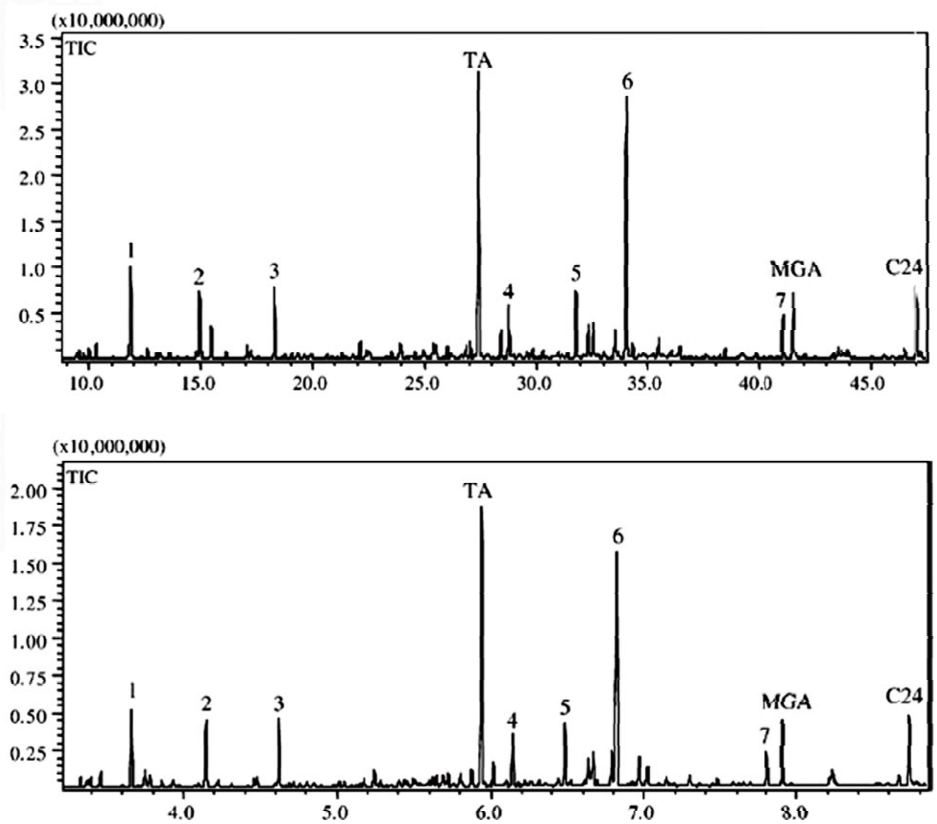


Fig. 6 Total Ion Chromatograms of Organic Acids in Urine
a) Conventional method
b) Fast-GC/MS method

1 = oxalic-2; 2 = methylmalonic-2; 3 = succinic-2; 4 = 4-hydroxyphenylacetic-2; 5 = aconitic-3; 6 = citric-4; 7 = uric-4; TA = tropic-2; MGA = margaric-1; C24 = tetracosane (-1 = -TMS; -2 = -diTMS; -3 = -triTMS; -4 = -tetraTMS)

## Energy Conservation Technology Targeting Periods of Analysis Standby

### a. Ecology Mode

The GC-MS, designed for measurement of substances at micro-level concentrations, must be maintained in a "ready" state prior to the start of analysis to ensure that the instrument is fully stabilized. Therefore, even when the instrument is not being used (on weekends, for example) helium gas continues to flow, and electrical power continues to be consumed to provide for uninterrupted heating of various GC components and maintenance of the MS vacuum. Measures were investigated that could reduce operating costs and minimize the environmental impact by reducing unnecessary consumption of helium gas and electrical power. With conventional instruments, it is up to the analyst to develop and run a special method that reduces the amount of helium gas used and power consumed in the standby mode. However, depending on the column and other analytical conditions used, mishaps such as carrier gas control errors, or introduction of excess helium gas into the mass analyzer can, and do, frequently occur. To resolve these problems, the world's first "Ecology Mode" was developed, which automatically reduces the consumption of helium gas and electrical power, eliminating the need for analysts to be concerned about analytical conditions.

The Ecology Mode function is outlined in the flow chart of Fig. 7. Whenever the instrument is placed in Ecology Mode, the states of the various GC-MS components and the control parameters in force at that time are recorded for re-establishment when the system is switched back into operation mode. Next, the column flow rate is calculated to verify that the column flow introduced into the MS will not exceed the permissible limits. After confirming that an error is not generated, the gas control mode is set to Constant Pressure Mode, and the total flow of carrier gas is reduced to a low flow rate. The temperature of the column oven is cooled to 50 °C after the carrier gas pressure and flow rate of each component reach the set values, and the oven heater and cooling fan are turned off. Finally, the ion gauge, which conducts measurement of the high vacuum of the mass spectrometer, is turned off, and the Ecology Mode state is established (Fig. 8). If the PC's "sleep mode" is to be used in conjunction with these measures, the sleep mode is started when the instrument Ecology Mode is established, allowing further savings of power consumption associated with the electrical power consumption of the PC. When the system is brought out of the Ecology Mode state, the PC is awakened from sleep mode, and the Ecology Mode release button (Fig. 8) is clicked. This initiates the automatic download of the pre-Ecology Mode control parameters to the instrument, re-establishing the instrument's state prior to entering the Ecology Mode. It is also possible for the Ecology Mode to be started automatically following continuous unattended analysis by batch processing.

With this function, the operator no longer need be concerned about how to reduce consumption of gas and electrical power during analysis standby periods, regardless of the column and other analytical conditions used for analysis.

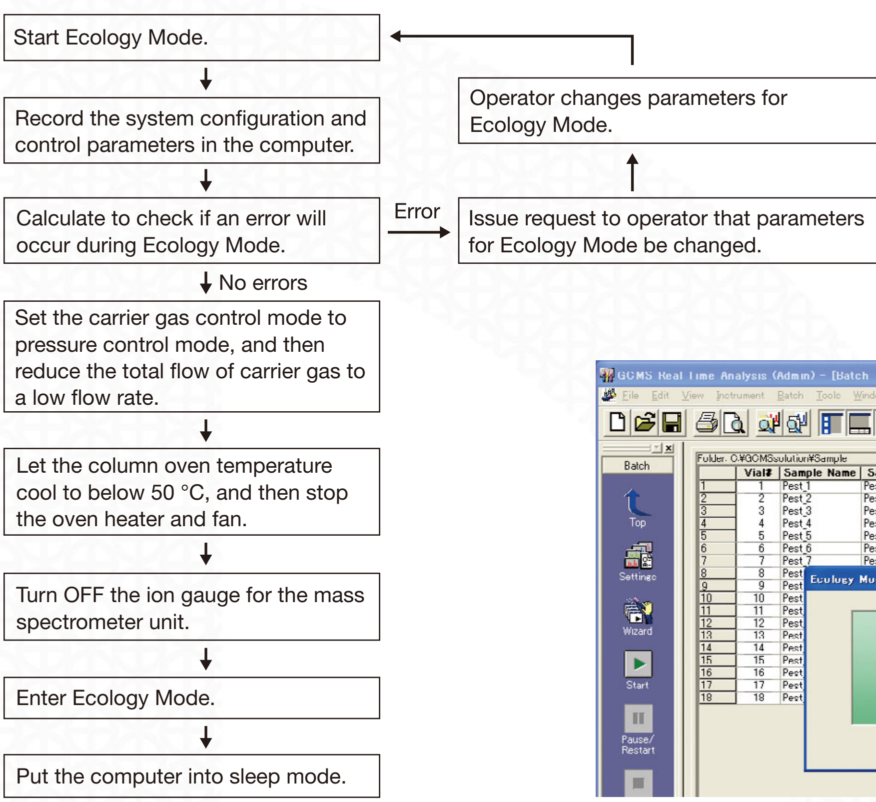


Fig. 7 Flowchart of Ecology Mode

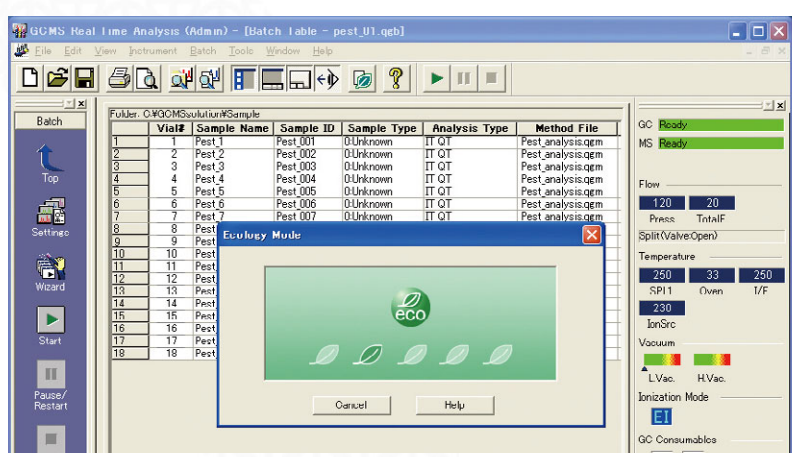


Fig. 8 Screen Display in Ecology Mode

## b. Effectiveness of Energy Conservation Measures in Ecology Mode

Table 3 shows a comparison of power consumption in the analysis standby mode using the conventional method and Ecology Mode. With Ecology Mode, the conventional analysis standby power requirement of 760 W was successfully reduced to 483 W. The breakdown of the 277 W of electrical power saved is 200 W allocated to switching off the GC oven heater and cooling fan, 20 W for switching off the MS ion gauge, and 57 W for placing of the PC into sleep mode. Furthermore, carrier gas consumption during analysis standby is unchanged from that in force during analysis under the previous set of analytical conditions in a conventional system. The carrier gas flow rate in analysis using a typical column, split line and purge line is 30 to 100 mL/min, a rate of consumption which is more than that required to ensure column protection. Using the Ecology Mode, the total carrier gas flow rate during analysis standby can be lowered to less than 20 mL/min (depending on the column length and instrument configuration).

Next, the effectiveness of the Ecology Mode in reducing operating costs and the environmental impact was investigated on the basis of yearly consumption. For the GC-MS operating conditions, it was assumed that analysis is conducted 20 days a month, with the instrument in analysis standby mode the remaining 10 days. In addition, analysis was assumed to occupy 6 hours per day, with the instrument in analysis standby mode the remaining 18 hours. Carrier gas (helium) consumption was assumed to be 50 mL/min during analysis, and 50 mL/min (with a conventional system) or 20 mL/min (in Ecology Mode) during analysis standby. Power consumption was taken as 1.5 kW during analysis, and as indicated in Table 3 during analysis standby. Based on the above conditions, the helium gas consumption, electrical power consumption, and the $CO_2$ emissions as a result of that power consumption are expressed in Table 4. The 25,926 L yearly consumption of helium is reduced to 12,963 L by using Ecology Mode, for a reduction of 12,963 L. This reduction is equivalent to about 1.85 gas cylinders with a capacity of 7 $m^3$, an expense reduction of 74,074 yen (assuming 40,000 yen per cylinder). Regarding the power consumption over a year, 7,639 kWh is reduced to 5,638 kWh, for a power saving of 2,001 kWh. This amounts to a reduction equivalent to 46,037 yen (assuming 23 yen per kWh). Furthermore, the 2,001 kWh power consumption reduction is equivalent to 1,123 kg of $CO_2$ emissions (equivalent to 0.561 kg $CO_2$ / kWh)[12]. From the above results, not only is it clear that the Ecology Mode contributes to reduction of the environmental impact, it is also effective for reducing operating costs.

Table 3 Power Consumption in Analysis Standby Mode

| | GC Unit[a] | MS Unit | PC | Total |
|---|---|---|---|---|
| Conventional method (W) | 300 | 400 | 60 | 760 |
| Ecology mode (W) | 100 | 380 | 3 | 483 |

[a] Injection port temp.: 250 °C; Interface temp.: 250 °C; Oven temp.: 100 °C

Table 4 Power and Carrier Gas Consumption in One Year

| | Conventional Method | Ecology Mode | Reduced by |
|---|---|---|---|
| Carrier gas consumption (L) | 25,926 | 12,963 | 12,963 |
| Power consumption (kWh) | 7,639 | 5,638 | 2,001 |
| $CO_2$ emissions (kg) [a] | 4,286 | 3,163 | 1,123 |

[a] $CO_2$ emissions are calculated based on power consumption.

## c. Environmentally-Friendly Approach to GC-MS Manufacturing

The GC-MS, which is used for measurement of trace organic substances, requires internal cleaning when making adjustments and inspections during the production process, requiring that the instrument remain running in the analysis standby state. Thus, large amounts of helium gas and electrical power are consumed during the production process. To reduce the environmental impact during production, a production process which utilizes the Ecology Mode of the GCMS-QP2010 Ultra was implemented. We thereby succeeded in reducing the amount of helium gas and electrical power required per unit instrument produced by 50 % and 30 %, respectively, thus establishing an environmentally friendly manufacturing system.

## Conclusion

Here we reported on the effectiveness of technology implemented in the GCMS-2010 Ultra in reducing operating costs and the environmental impact through dramatic reductions in helium gas and electrical power consumption. With the aim of achieving low energy analysis using Fast-GC/MS, a high-speed processing platform and ASSP™ high-speed scanning technology were developed. We demonstrated that these technologies could shorten analysis time without sacrificing data quality and that helium gas and power consumption could be reduced by 90 % and 66 %, respectively.

On the other hand, by developing the Ecology Mode which effectively cuts the consumption of helium gas and electrical power during standby periods, helium usage and power consumption were reduced by 60 % and 36.5 %, respectively. Using Ecology Mode, it was demonstrated that under typical operating conditions, yearly helium consumption could be reduced by 12,963 L (equivalent to 1.85 cylinders, each with capacity of 7 $m^3$), and yearly power consumption by 2,001 kWh (equivalent to 1,123 kg of $CO_2$ emissions).

Following is a link to our web site which is available to easily estimate the yearly GC-MS operational consumption of helium gas and electrical power, in addition to the associated $CO_2$ emissions (http://www.shimadzu.com/eco-sim/eco.htm).

Recently, a Fast-GC/MS technique using hydrogen gas rather than helium is receiving much attention due to the superior chromatographic resolution that can be achieved, along with a shorter analysis time and lower price per unit volume compared to helium[13),14)]. Thus, hydrogen not only contributes to shorter analysis time, it is expected to become an analytical technique with few adverse environmental consequences since it is a resource that can be regenerated from water.

We intend to begin development of a Fast-GC/MS method using the GCMS-QP2010 Ultra with hydrogen as the carrier gas, and to investigate ways to even further decrease operating costs and reduce the environmental impact of GCMS operation.

Finally, we wish to express our appreciation to all the members who were involved in development of the GCMS-QP2010 Ultra.

## Reference


1) Japan Association for Trade with Russia & NIS: Japan-Russia technology newsletter, No.3 (6) (2008)

2) P.T. Anastas and J.C. Warner: Green Chemistry: Theory and Practice, Oxford University Press, New York, USA (1998)

3) Pat Sandra, Koen Sandra, Alberto Pereira, Gerd Vanhoenacker and Frank David: Green Chromatography, LCGC Europe, 23 (5), 242–259 (2010)

4) S. Harada: QUADRUPOLE MASS SPECTROMETER, U.S. Patent 6,610,979 (2003)

5) Kateřina Maštovská, Steven J. Lehotay: Practical approaches to fast gas chromatography-mass spectrometry, J. Chromatogr. A 1000, 153–180 (2003)

6) Luigi Mondello, Alessandro Casilli, Peter Quinto Tranchida, Rosaria Costa, Biagina Chiofalo, Paola Dugo, Giovanni Dugo: Evalua tion of fast gas chromatography and gas chromatography-mass spectrometry in the analysis of lipids, J. Chromatogr. A 1035, 237–247 (2004)

7) Michal Kirchner, Eva Matisová, Robert Otrekal, Andrea Hercegová, Jaap de Zeeuw: Search on ruggedness of fast gas chromatography-mass spectrometry in pesticide residues analysis, J. Chromatogr. A 1084, 63–70 (2005)

8) E. Matisová, M. Dömötörová: Fast gas chromatography and its use in trace analysis, J. Chromatogr. A, 1000, 199–221 (2003)

9) Jens Dallüge, René J.J. Vreuls, Dick J. van Iperen, Martijin van Rijn, Udo A. Th. Brinkman: Resistively heated gas chromatography coupled to quadrupole mass spectrometry, J. Sep. Sci., 25, 608–614 (2002)

10) René J.J. Vreuls, Jens Dallüge, Udo A. Th. Brinkman: Gas chromatography-time-of-flight mass spectrometry for sensitive determination of organic micro contaminants, J. Microcolumn Separations, 11 (9), 663–675 (1999)

11) R. Hirsch, T.A. Ternes, I. Bobeldijk, R.A. Weck: Determination of Environmentally Relevant Compounds Using Fast GC/TOF, Chimia 55, 19–22 (2001)

12) Japan's Ministry of the Environment: $CO_2$ emission coefficient by electricity business (result of 2009) http://www.env.go.jp/earth/ghg-santeikohyo/material/denkihaishutu/list_ef_eps.pdf

13) T. Veriotti, R. Sacks: High-speed GC and GC/MS with a series-coupled column ensemble using stop-flow operation, Anal. Chem., 73, 3045–3050 (2001)

14) Rana, Sumandeep, Urarlets, Victor P. Ross, Wayne: A New Method for Simultaneous Determination of Cyclic Antidepressants and their Metabolites in Urine Using Enzymatic Hydrolysis and Fast GC-MS, Journal of Analytical Toxicology, Volume 32, (5), 355–363 (2008)

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