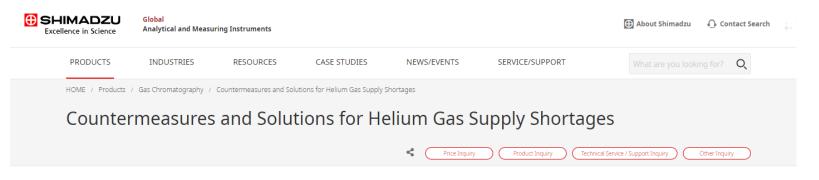


BGAZ-4000-2007

Countermeasures and Solutions for Helium Gas Supply Shortages - GCMS

Analytical & Measuring Instruments Division Shimadzu Corporation

Introduction



Due to helium gas supply shortages, soaring prices, and other factors, reducing the quantity of helium gas consumed and considering alternative carrier gases have become urgent issues. The following describes functionality for reducing helium gas consumption rates and indicates precautions for switching to a different carrier gas.



Reducing Helium Consumption

- <u>Reducing Consumption During Analysis</u>
- Reducing Consumption After Analysis
- Shutting off the Gas Supply After Analysis

Changing the Carrier Gas



Reducing Helium Consumption

- Reducing Consumption During Analysis
- Reducing Consumption During Standby or After Analysis
- Estimating Reductions by Ecology simulation

Changing the Carrier Gas



Because of the challenges seen by our customers, we have created a dedicated page for <u>Countermeasures and Solutions</u> for Helium Gas Supply Shortages

Please scan the above QR code to be taken to the webpage seen here.

Contents

- Approach to Helium Gas Supply Shortages
- Reducing Helium Gas Consumption

• Using an Alternative Carrier Gas

Key Points for Using a Hydrogen Carrier Gas Key Points for Using a Nitrogen Carrier Gas

Countermeasures for Each Sample Introduction System

Contents

- Approach to Helium Gas Supply Shortages
- Reducing Helium Gas Consumption

• Using an Alternative Carrier Gas Key Points for Using a Hydrogen Carrier Gas Key Points for Using a Nitrogen Carrier Gas

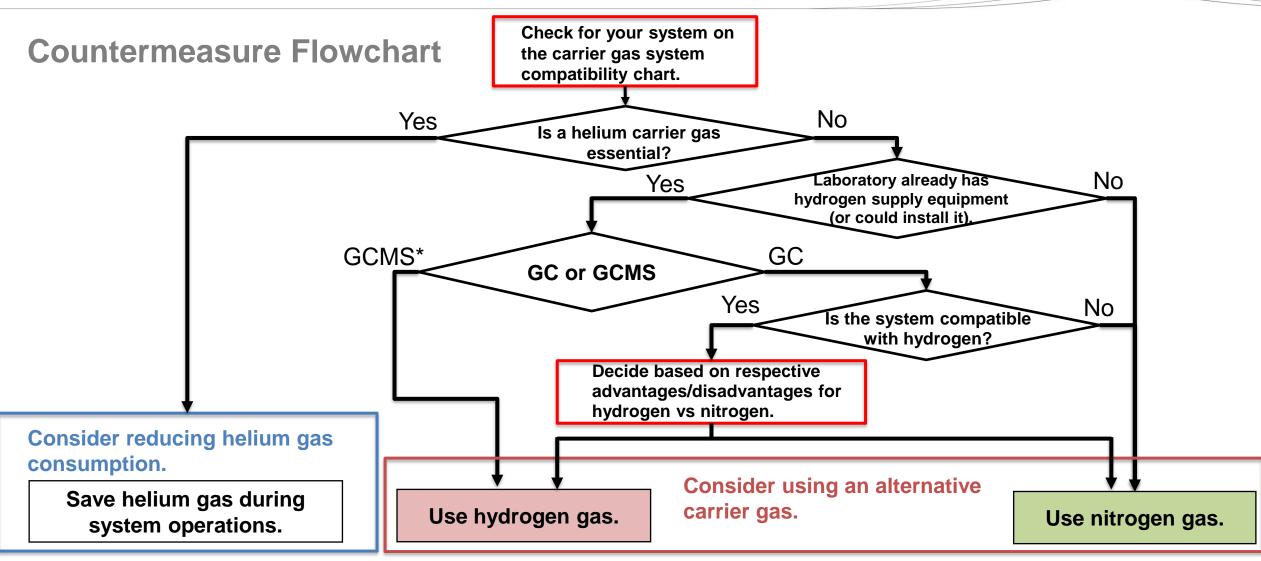
• Countermeasures for Each Sample Introduction System

Approach to Helium Gas Supply Shortages

Reducing Helium Consumption

Changing the Carrier Gas

Introduction



* Nitrogen carrier gas can also be used in GCMS systems.

However, sensitivity will probably decrease to one-tenth or less of normal, so hydrogen is recommended if hydrogen usage is possible.

Contents

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- Using an Alternative Carrier Gas Key Points for Using a Hydrogen Carrier Gas Key Points for Using a Nitrogen Carrier Gas
- Countermeasures for Each Sample Introduction System

Cases where Using an Alternative Carrier Gas would be Difficult



Sensitivity is low near the limit of quantitation (older models, ultra-trace analysis, etc.)

- Alternative carrier gases (hydrogen or nitrogen) generally decrease sensitivity.
- Using alternative gases might be difficult unless S/N is at least 50 to 100 at the limit of quantitation required for using helium.

Database Calibration Curve Customer's GC-MS System is not compatible with alternative carrier gases (certain sample introduction systems,

Pesticide IS (Pesticide-d)

databases, etc.)

- Some sample introduction systems or optional products are not compatible with alternative carrier gases.
- Databases for semi-quantitative analysis cannot be used with alternative carrier gases.

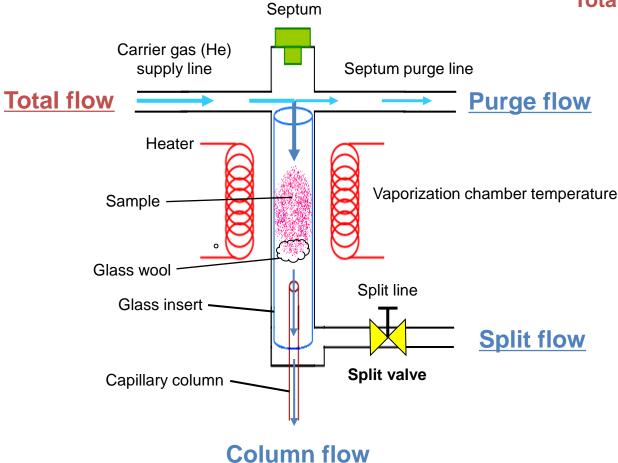
IS (Pesticide-d)

Methods for Reducing Helium Gas Consumption

- 1. Reducing Consumption during Analysis
- Carrier gas saver mode
- 2. Reducing Consumption during Standby or after Analysis
- Ecology mode
- Gas selector (optional)
- 3. Utilization of Correct Purity Gas is Key
- Using a Gas Filter (optional)
- 4. Reducing Consumption by Shutting Off System on Days Not Used
- GCMS systems with quick startup

Reducing Consumption during Analysis - Carrier Gas Saver

Helium Gas Consumption during Analysis



Total flow = Column flow + Split flow + Purge flow

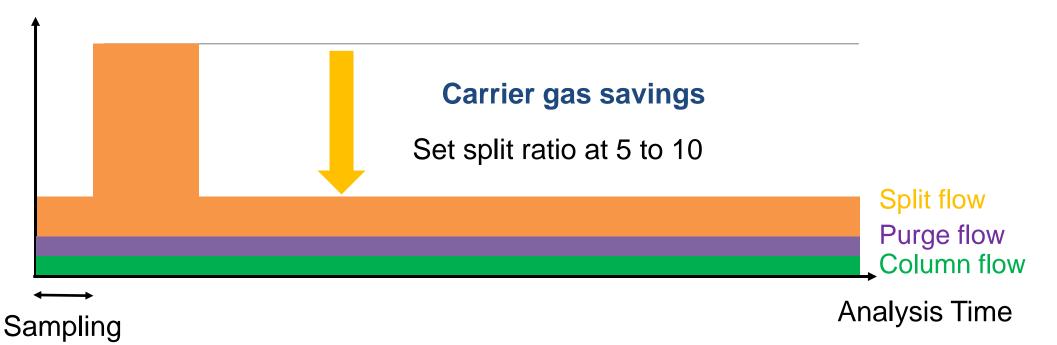
Analysis is normally performed with the split ratio set at 30 to 50 mL/min immediately after injection. However . . .

Required immediately after injection, but not during entire analysis

Reduce split flow rate during analysis. Reduce total carrier gas flow rate.

Reducing Consumption during Analysis - Carrier Gas Saver Mode

Helium gas can be saved during analysis by using the carrier gas saver mode to reduce the split ratio after injection.

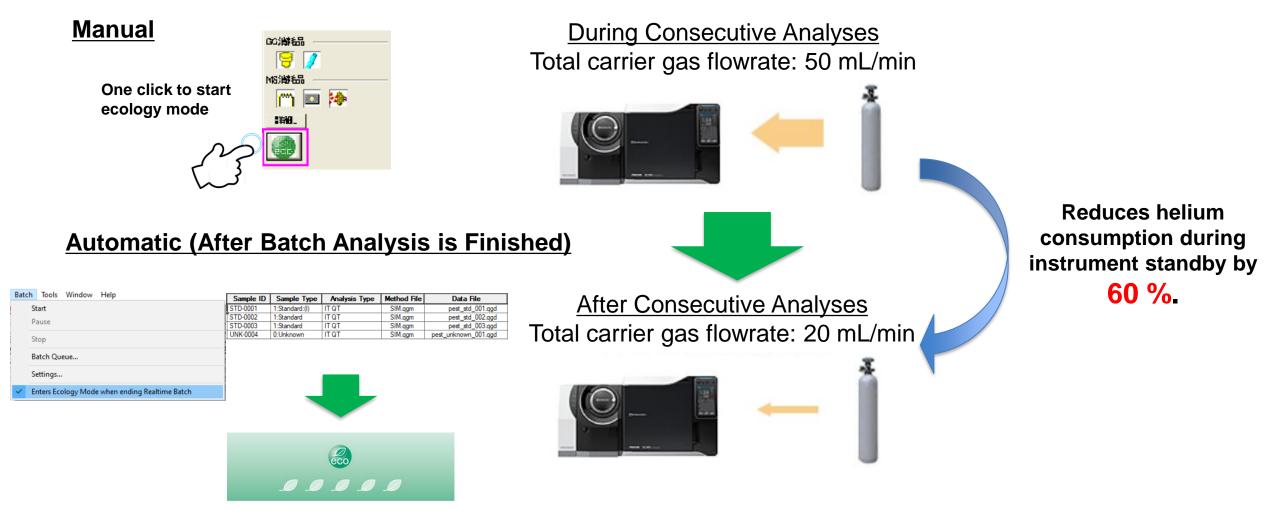


Helium consumption per analysis can be reduced by **74** %.

Simulation Example Analysis time: 30 min Total flow: 50 mL/min

Injection mode: Splitless Split ratio during carrier gas save: 5 Sampling time: 1 min Carrier gas save: 3 min (1455 mL normally, 375 mL during carrier gas save)

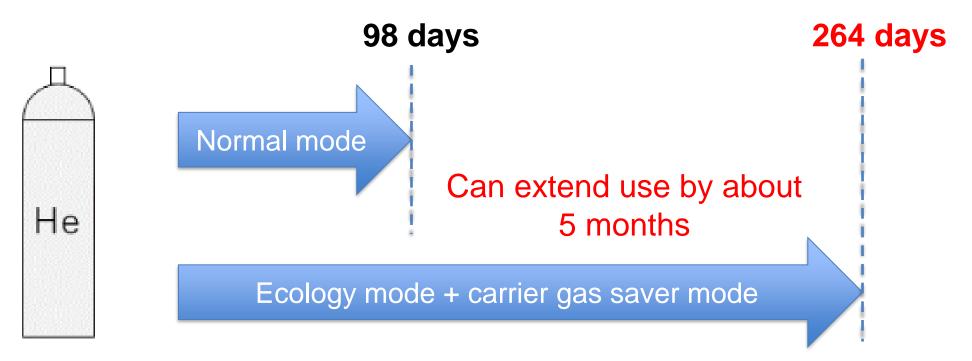
Reducing Consumption during Standby / after Analysis - Ecology Mode



The ecology mode is available on GCMS-QP2010 Ultra or higher-end QP-series models and all TQ-series models. It cannot be used with some pretreatment systems, such as TurboMatrix HS and Optic-4 units. 12

Example of Carrier Gas Savings Using the Ecology and Carrier Gas Saver Modes

Number of days a 7000 L helium gas cylinder can be used*

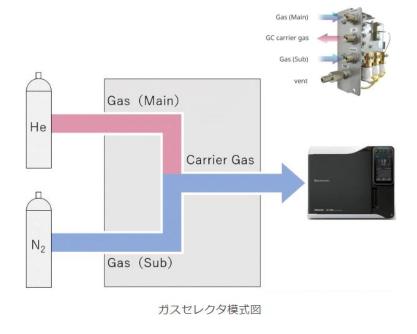


* Simulation Parameters One system connected per helium gas cylinder Per day: 30 min \times 10 analyses (with 5 hrs of analyses and 19 hrs of standby)

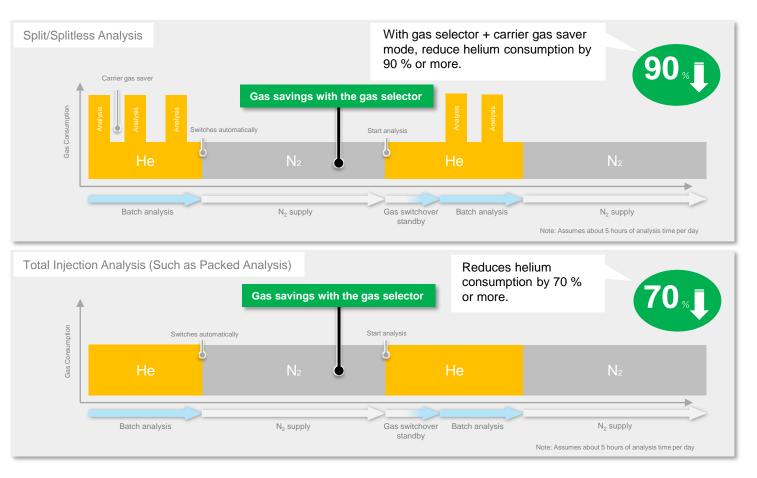
Reducing Consumption during Standby - Gas Selector

Gas Selector

Installing a gas selector in a GCMS-NX series system can significantly reduce helium gas consumption by automatically switching to an alternative gas after analysis.



This is a dedicated option for Nexis GC-2030 and GCMS-NX series.



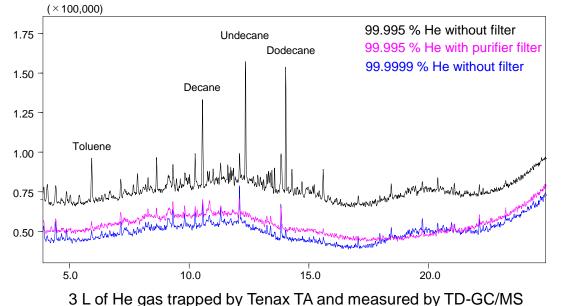
Utilization of Correct Purity is Key

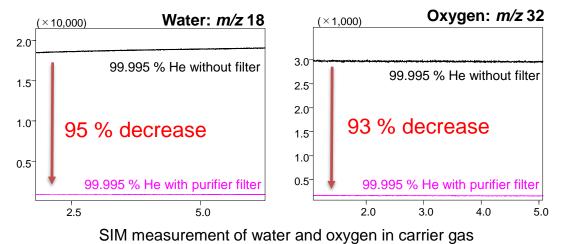
Using a Gas Purifier Filter



• Purifier filter for helium or nitrogen gases Removes moisture, oxygen, and hydrocarbons (replaced about once a year)

Effectiveness of Filtering Out Hydrocarbons





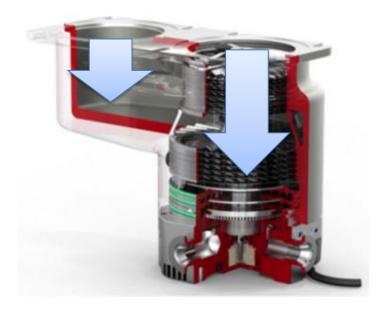
Effectiveness of Filtering Out Water and Oxygen

- By installing a gas purifier filter, 99.995 % helium can be used.
- That also helps reduce costs.
- Gas cylinders are easier to obtain as well.

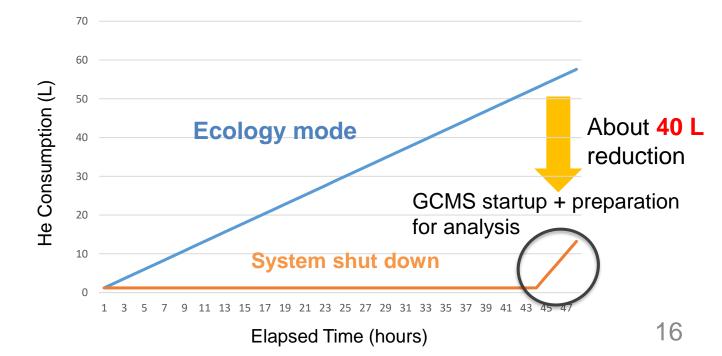
Reducing Consumption by Shutting Off System on Days Not Used

Shutting Off the System on Weekends or Other Days the System is Not Used

Shimadzu's high-end GC-MS model uses a high-capacity differential vacuum pump to achieve extremely fast instrument startup times (about 2 hrs for qualitative analysis or 4 hrs for quantitative analysis).



Comparison of He Consumption Using the Ecology Mode and Shutting Down the System for 48 Hours on Weekends

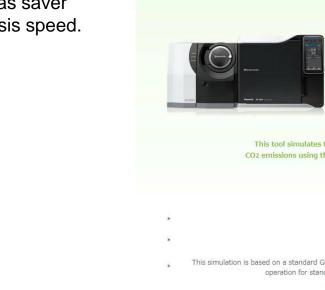


Information on ECO Simulation

Savings during Analysis

ECO Simulation

ECO simulation can simulate the benefits of using the carrier gas saver function and increasing analysis speed.







about 1,048 kg of CO2 and

US\$ 1,121 in running costs per year.



To access the ECO simulation function, use this link.

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Comparison of Various Carrier Gas Properties - GCMS

	Helium	Hydrogen	Nitrogen
Sensitivity	A Suitable for high-sensitivity analysis	B Sensitivity is about 1/3 to 1/5 of helium	C Sensitivity is about 1/10 of helium due to high noise
Price	B Rapidly increasing prices and sometimes long lead times	A Available inexpensively. Installing a hydrogen generator eliminates need to manage gas cylinders.	A Available inexpensively
Safety	A Non-explosive inert gas	B Can explode, but explosion risk is low at volumes used for GC-MS.	A Non-explosive gas with high safety
Column I.D.	A Supported up to 0.53 mm	B 0.18 mm or less recommended	B 0.18 mm or less recommended
Compatible GC/MS Models	All QP and TQ series	All QP except QP2010 SE and TQ series	QP2010 Ultra and QP2020 series (not supported by TQ series)

Note: Argon cannot be used as a GCMS carrier gas.

Alternative Carrier Gas Compatibility Table

GCMS Main Unit	Discontinued Year	Не	H ₂	N ₂	N ₂ (During Standby)
GCMS-QP5050A	2004	\checkmark	—	—	—
GCMS-QP2010	2006	\checkmark	\checkmark		\checkmark
GCMS-QP2010 Plus	2010	\checkmark	\checkmark	_	\checkmark
GCMS-QP2010 Ultra	2015	\checkmark	\checkmark	\checkmark	\checkmark
GCMS-QP2010 SE	Currently available	\checkmark		_	\checkmark
GCMS-QP2020 Series	Currently available	\checkmark	\checkmark	\checkmark	\checkmark
GCMS-TQ Series	Currently available	\checkmark	\checkmark		\checkmark

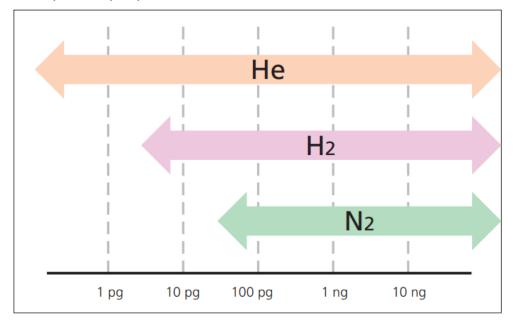
 \checkmark : Indicates supported gas

Sensitivity and Separation with Alternative Carrier Gases

Sensitivity

Approximate Measurement Ranges for Various Carrier Gases (Quantity for SIM and On-Column)

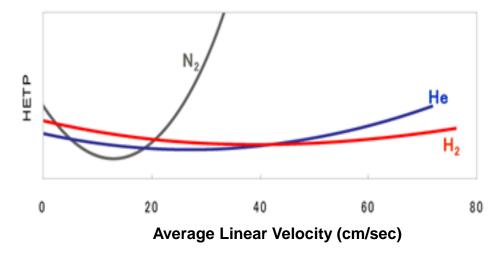
These measurement ranges are only approximate and might not be suitable for some target compounds due to sensitivity or compound properties.



Hydrogen and nitrogen have lower ionization energies than helium, which tends to increase noise.

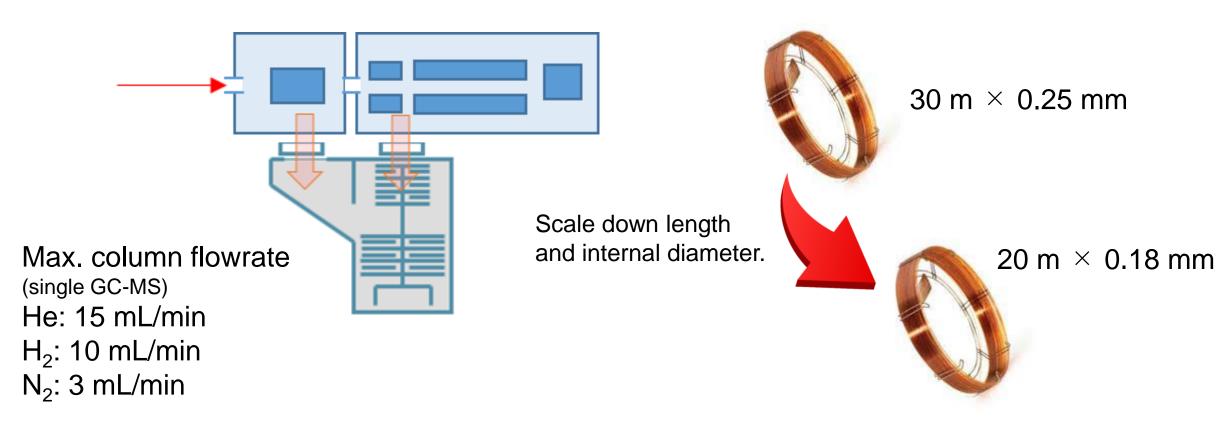
GC Separation

Separation Performance for Various Carrier Gases



- The smaller the height equivalent to Height equivalent to a theoretical plate (HETP), the better the separation.
- Hydrogen provides good separation even at higher linear velocities, which means analysis times can be shortened.
- Nitrogen has a steeper HETP curve, which results in a tendency for separation to become worse.

Column Selection for Alternative Carrier Gases



- Maximum column flowrate is lower for hydrogen or nitrogen, because the MS vacuum level decreases.
- For nitrogen, scaling down the column length and internal diameter is recommended due to the 3 mL/min maximum column flowrate.

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Key Points for Using a Nitrogen Carrier Gas

• Countermeasures for Each Sample Introduction System

Using a Hydrogen Carrier Gas

Hydrogen Gas Cylinder



Note: Order gas cylinders from a gas supplier.

Hydrogen Generator



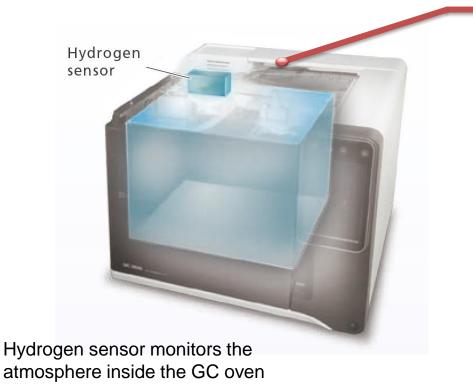
- Contact a Shimadzu sales representative before changing the carrier gas.
- Using dichloromethane or carbon disulfide as a solvent could generate hazardous gases.
 Prepare a suitable exhaust ventilation system in advance.

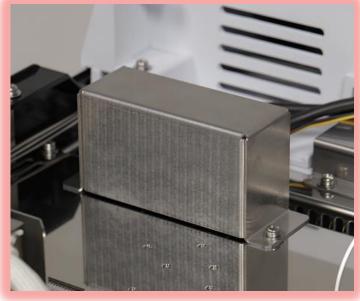
Hydrogen Safety Measures – Optional GC Accessory

Using Hydrogen Safely—Optional GC Safety Countermeasures

Hydrogen Sensor Helps Ensure Hydrogen Carrier Gas is Used Safely

Shimadzu GC's newly designed hydrogen sensor monitors the hydrogen concentration in the GC oven and can detect potential leaks early. When leaks has been detected, it lowers the temperature and automatically switches to a safe standby mode. If the hydrogen concentration rises continueously, the main power is turned off to prevent accidents. (This is an option for Nexis GC-2030)





External Appearance of Hydrogen Sensor

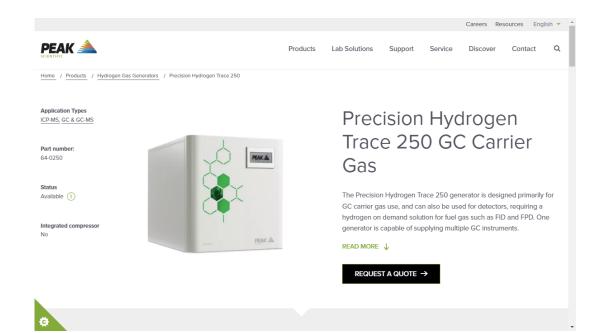
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Safety Countermeasures Using a Hydrogen Gas Generator

Using an Alternative Carrier Gas—Precautions for Using Hydrogen

A hydrogen gas generator can be a good choice when installing a hydrogen cylinder is difficult. For more details, refer to the following link.

https://www.peakscientific.com/products/hydrogen/





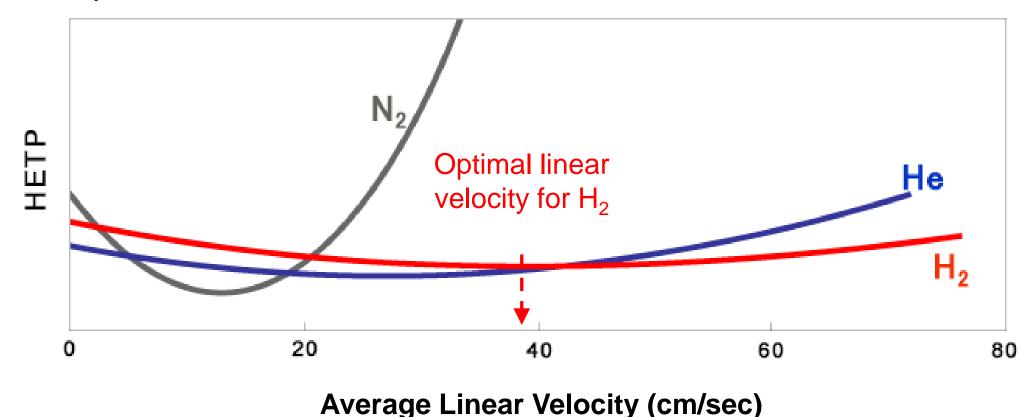
Features

- Suitable for flame gas and carrier gas at trace detection limits
- 99.99999%* Purity
- Internal leak detection with automatic shutdown features
- Proven PEM technology to generate hydrogen safely and reliably
- Regenerative PSA dryers to ensure highest level of purity
- Automatic loading pump as standard
- Maintenance limited to replacing de-ionizer cartridge
- Compact, space-saving modular design
- Creates hydrogen on demand, minimal storage of hydrogen in the system
- Combine multiple units for higher flow requirements
- GC in-oven hydrogen leak detector available as an optional extra
- Peak offers a 3 year cell warranty with this generator as standard.

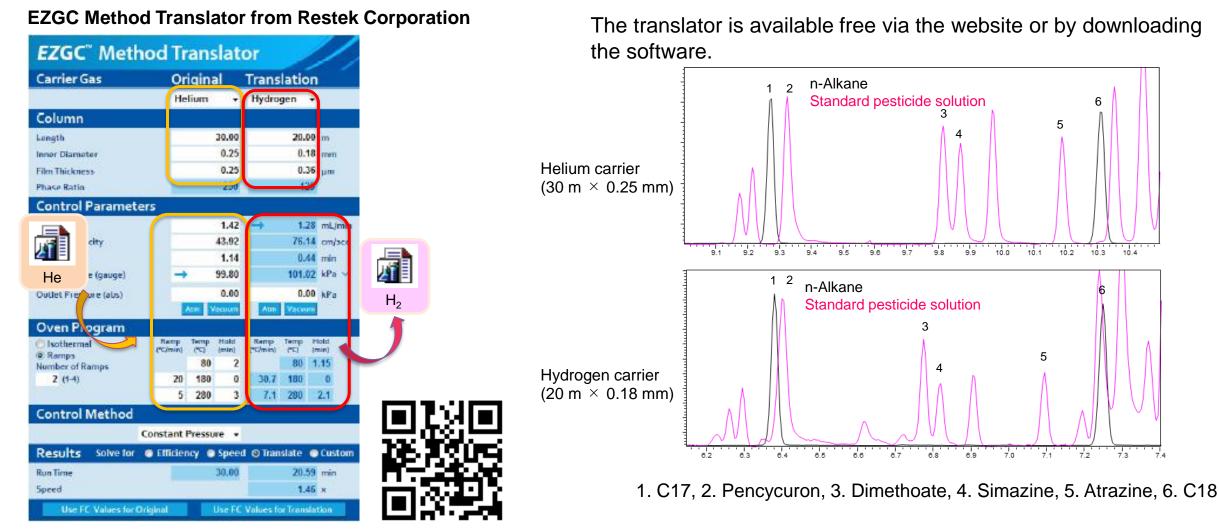
*based on O2 content independently verifled by National Physical Laboratory, UK

Separation Using a Hydrogen Carrier Gas

The optimal linear velocity for hydrogen carrier gas is about the same as for helium carrier gas. With hydrogen, separation does not worsen if the linear velocity is increased, which enables high-speed analysis.



Converting Analytical Conditions for a Hydrogen Carrier Gas

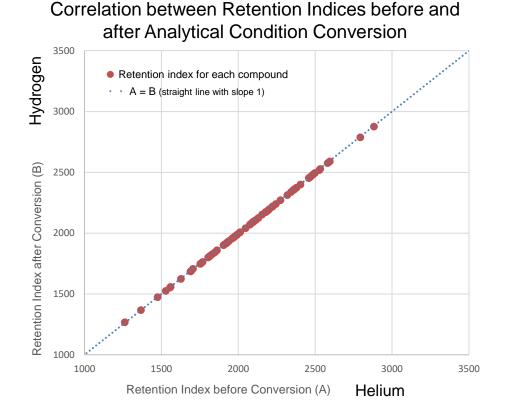


Note: For more information, refer to the Restek Corporation website. http://www.restek.com/ezgc-mtfc Elution patterns similar to using helium can be obtained.

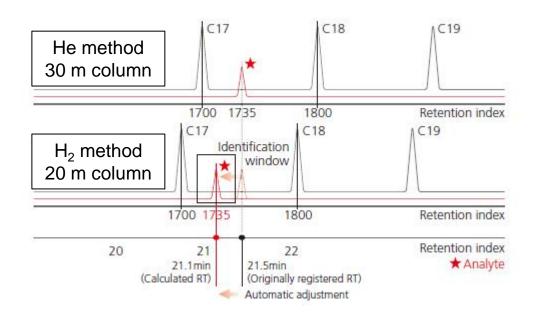
Converting Analytical Conditions for a Hydrogen Carrier Gas

Retention Indices can be Used Even if the Carrier Gas is Switched to Hydrogen

By using hydrogen in combination with the Automatic Adjustment of Retention Time (AART) function, retention times for target compounds in databases and existing methods can be adjusted to support identification.



Using AART Function to Automatically Adjust Retention Times

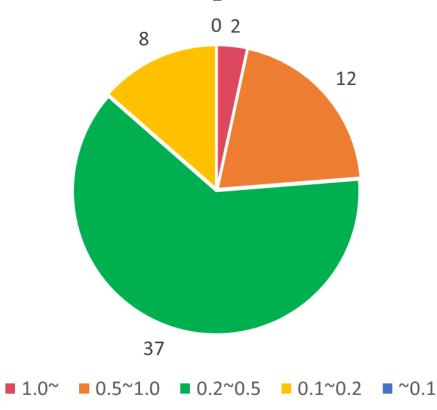


Sensitivity Using a Hydrogen Carrier Gas

Name of	S/N Ratio	Name of	S/N Ratio	Name of	S/N Ratio
Compound	(H ₂ /He)	Compound	(H ₂ /He)	Compound	(H ₂ /He)
Dichlorvos	0.16	Malaoxon	0.18	Flutolanil	0.29
Dichlobenil	0.68	Simetryn	0.18	Isoprothiolane	0.15
Etridiazol	0.22	Tolclofos-methyl	0.40	Buprofezin	0.35
Chloroneb	1.80	Alachlor	0.23	Mepronil	0.26
Isoprocarb	0.84	Dithiopyr	0.44	Chlornitrofen	0.82
Molinate	1.41	Fenitrothion	0.39	Edifenphos	0.29
Fenobcarb	0.32	Esprocarb	0.35	Propiconazole-1	0.37
Trifluralin	0.39	Thiobencarb	0.48	Endosulfate	0.76
Pencycuron	0.47	Fenthion	0.27	Propiconazole-2	0.40
Dimethoate	0.53	Chlorpyrifos	0.45	Thenylchlor	0.51
Simazine	0.30	Fthalide	0.47	Pyributicarb	0.37
Atrazine	0.18	Dimethametryn	0.24	Iprodione	0.90
Propyzamide	0.65	Pendimethalin	0.31	Pyridafenthion	0.45
Pyroquilone	0.27	Methyl daimuron	0.46	EPN	0.60
Diazinon	0.19	Isofenphos	0.20	Piperophos	0.34
Ethylthiometon	0.17	Captan	0.37	Anilofos	0.32
Chlorothalonil	0.70	Phenthoate	0.39	Pyriproxyfen	0.43
Iprobenfos	0.16	Procymidone	0.65	Cafenstrole	0.32
Bromobutide	0.36	Methidathion	0.21	Ethofenprox	0.31
Terbucarb	0.47	Butamifos	0.56	Mean: 0.	43

Comparison of Carrier Gas Sensitivity for 59 Pesticides at 10 ppb

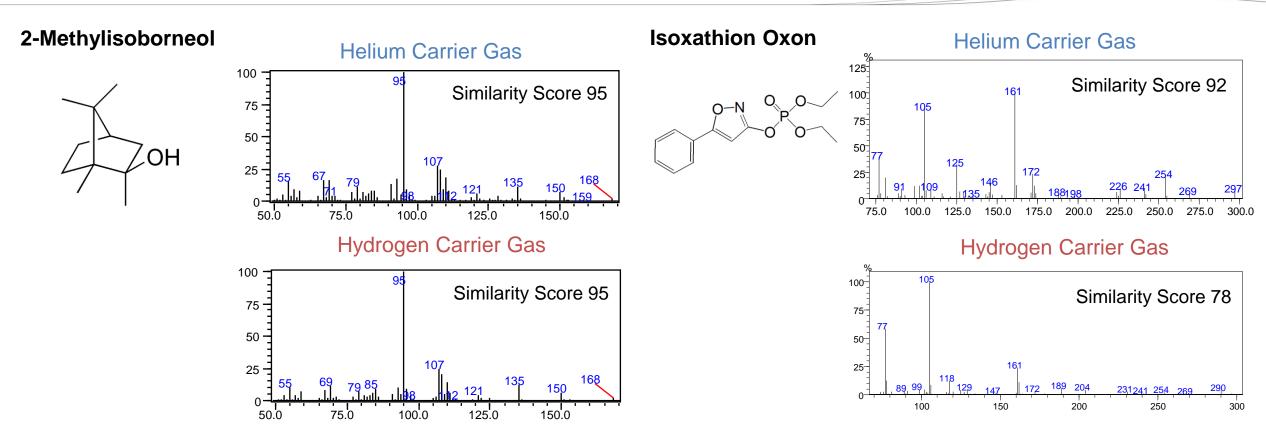
Distribution of H₂/He S/N Ratios



- Reproducibility is 10 % or lower for all compounds.
- For most compounds, sensitivity is about 1/3 to 1/5 as high as using helium.

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Mass Spectra Using a Hydrogen Carrier Gas



- Though an existing mass spectral library can be used, similarity scores in library search results might be about 10 to 20 lower depending on the compound.
- For more accurate identification, measuring a standard sample to check quantitation values and reference ions in mass spectra or to check retention times is recommended.

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- Approach to Helium Gas Supply Shortages
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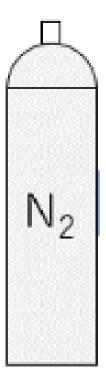
Key Points for Using a Hydrogen Carrier Gas

Key Points for Using a Nitrogen Carrier Gas

• Countermeasures for Each Sample Introduction System

Using a Nitrogen Carrier Gas

Nitrogen Gas Cylinder



Nitrogen Gas Generator



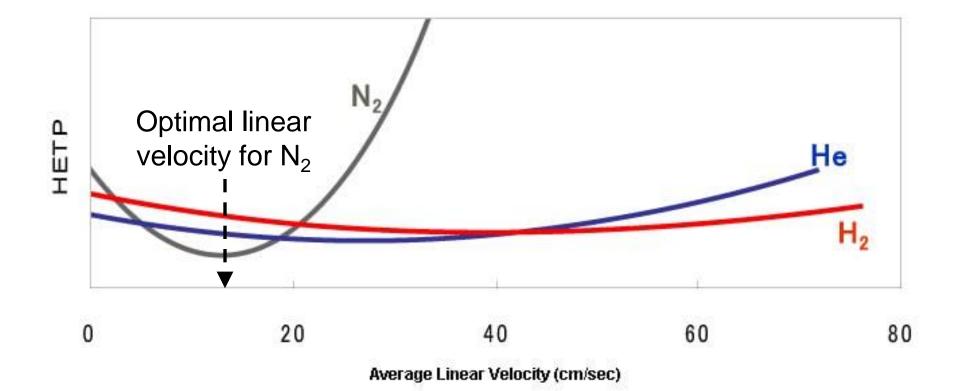
Nitrogen generators designed for LC-MS cannot be used as GC-MS carrier gas because the purity is too low (99.0 % or less). Be sure to prepare a nitrogen gas cylinder.

Caution: Nitrogen leakage cannot be checked with a peak monitor. Use a leak detector or Snoop solution to check for leaks.

Separation Using a Nitrogen Carrier Gas

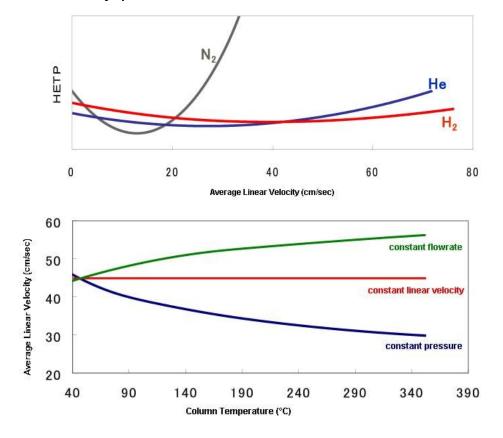
With a nitrogen carrier gas, separation is best at a low linear velocity so prioritizing separation will result in long analysis times.

Also, the range of linear velocities that result in good separation is narrow, so the nitrogen carrier gas is not suitable for conditions that cause linear velocity variation.



Converting Analytical Conditions for a Nitrogen Carrier Gas

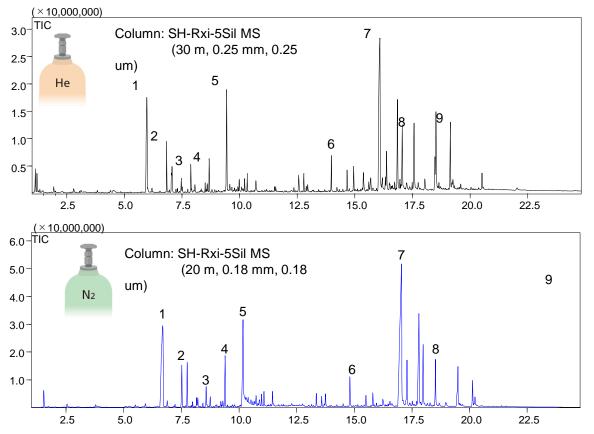
- If constant pressure or constant flowrate control is used for a temperature-programmed analysis, the column linear velocity will vary.
- Because nitrogen has a narrower range of linear velocities that result in optimal separation than helium or hydrogen, constant linear velocity control may provide the best results.



Carrier Gas	Original	Translation		
	Helium	✓ Nitrogen ✓		
Column				
Length	30.(20.00	m	
Inner Diameter	0.2	25 0.18	mm	
Film Thickness	0.2	25 0.18	μm	
Phase Ratio	25	50 250		
Control Paramete	rs			
Outlet Flow	→ 1.4	40 → 0.32	mL/min	
Average Velocity	43.5	26.56	cm/sec	
Holdup Time	1.1	1.25	min	
Inlet Pressure (gauge)	98.0	40.49	kPa 🗸	
Outlet Pressure (abs)	0.0	0.00	kPa	
	Atm Vacuu	m Atm Vacuum	N2	
gram				
	Ramp Temp Hol (°C/min) (°C) (mir		Hold T	
He Notifier of Kamps	80		2.2	
1 (1-4)	10 300	5 9.2 300 5	5.45	
Control Method				
Constar	nt Linear Velocity	Consta	ant linear velo	С
Results Solve for	Efficiency OSpe	eed O Translate	Custom	
Run Time	29.0			
Speed		0.92	×	

SHIMADZU Converting Analytical Conditions for a Nitrogen Carrier Gas

Example of Using Py-GC/MS for Instantaneous Pyrolysis of a Circuit Board



Library Search Results for Identifiable Peaks

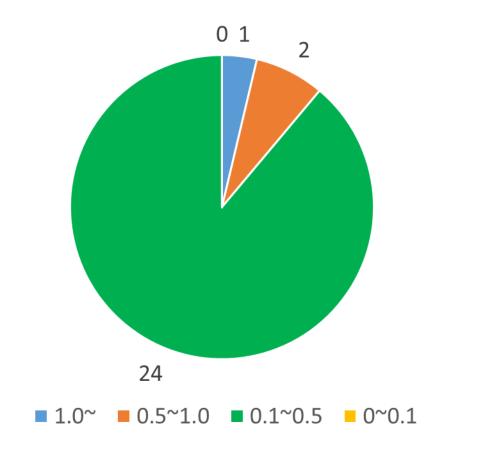
	Name of Compound	He	N ₂	
ID		Similarity Score	Similarity Score	
1	Phenol	99	98	
2	2-Methylphenol	98	98	
3	Dimethylphenol	97	97	
4	MethylethylPhenol	95	97	
5	p-lsopropenylphenol	95	95	
6	p-Cumylphenol	93	93	
7	Biphenol A	95	96	
8	Dibromobisphenol A	83	89	
9	Tribromobisphenol A	83	87	

Mass spectral patterns obtained with a nitrogen carrier gas tend to be almost equivalent to those with helium.

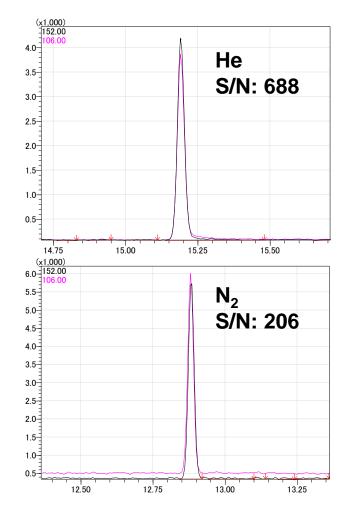
EZGC Method Translator can be used to align chromatogram patterns to some extent.

Sensitivity Using a Nitrogen Carrier Gas

S/N Ratio Comparison Using Helium and Nitrogen Carrier Gases (27 Azo Compounds at 1 ppm)



1 ppm 2-methyl-5-nitroaniline



For most compounds, sensitivity was about 1/10 as high as using helium.

Application Examples

Using Alternative Carrier Gases

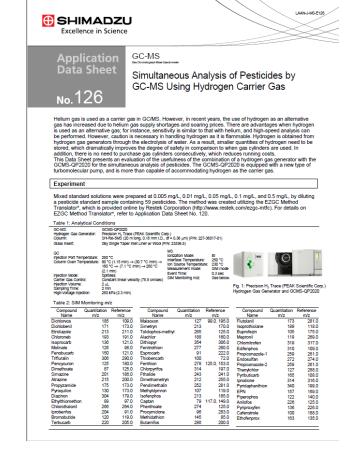
Examples of applications using alternative carrier gases are posted on the Shimadzu website. Please refer to it.

https://www.shimadzu.com/an/service-support/technical-support/technical-information/gaschromatograph-mass-spectrometry/mesure/top/index.html#applihe



Application

- > Measurement of VOCs in Vehicle Interiors Using Thermal Desorption GC-MS with Nitrogen as the Carrier Gas NEW
- > Py-GC/MS Analysis of Electronic Circuit Board Parts Using Nitrogen Carrier Gas
- > High-Sensitivity Analysis of Phenols in Drinking Water Using Nitrogen Carrier Gas
- Simultaneous Analysis of Pesticides by GC-MS Using Hydrogen Carrier Gas
- > Using a Method Translator Program for GC-MS Analysis with a Hydrogen Carrier Gas
- > Simultaneous Analysis of 66 Pesticides by GC-MS Using Hydrogen Carrier Gas
- > Analysis of Di(2-ethylhexyl)phthalate by GC-MS Using Hydrogen Carrier Gas



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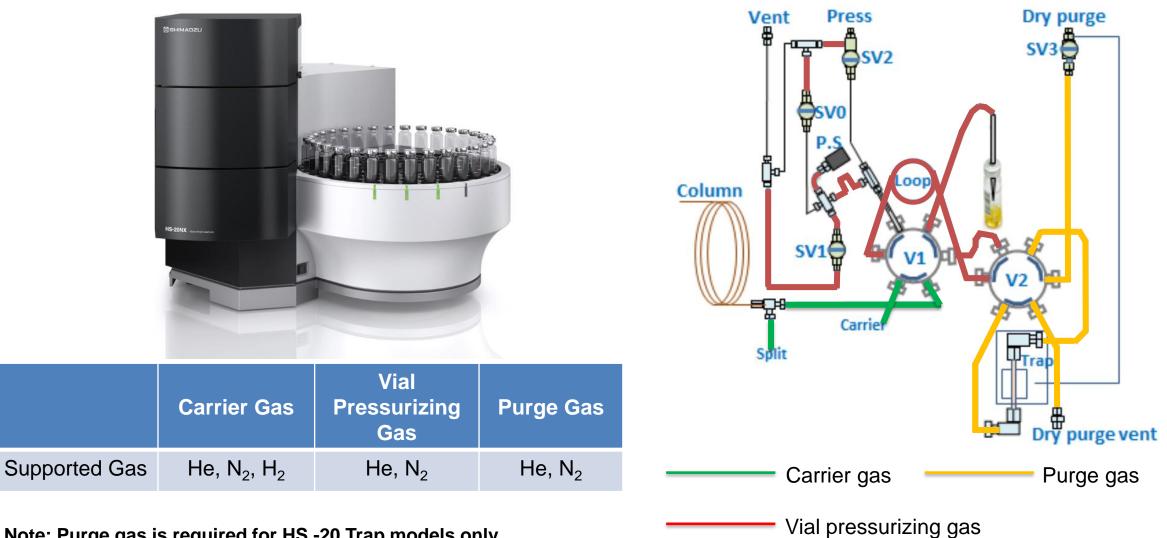
- Approach to Helium Gas Supply Shortages
- Reducing Helium Gas Consumption

• Using an Alternative Carrier Gas Key Points for Using a Hydrogen Carrier Gas Key Points for Using a Nitrogen Carrier Gas

Countermeasures for Each Sample Introduction System

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HS-20 NX Headspace Sampler



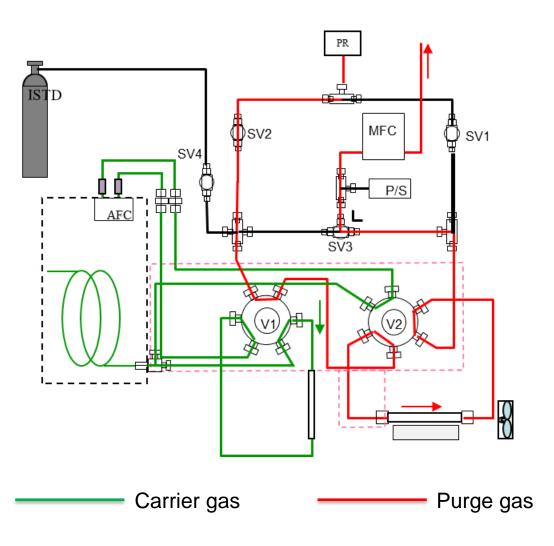
Note: Purge gas is required for HS -20 Trap models only.

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TD-30/20 Thermal Desorption Systems



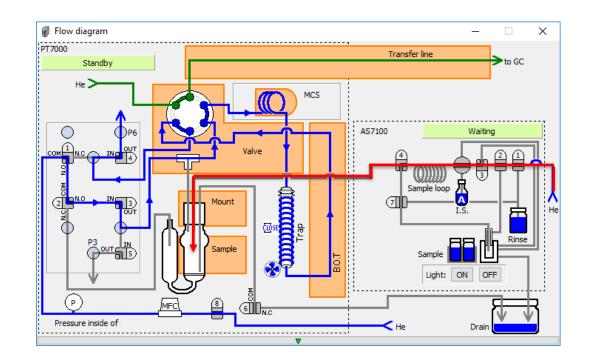
	Carrier Gas	Purge Gas
Supported Gas	He, N ₂	He, N ₂



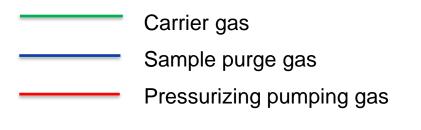
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PT7000/Aqua PT6000 Purge & Trap System

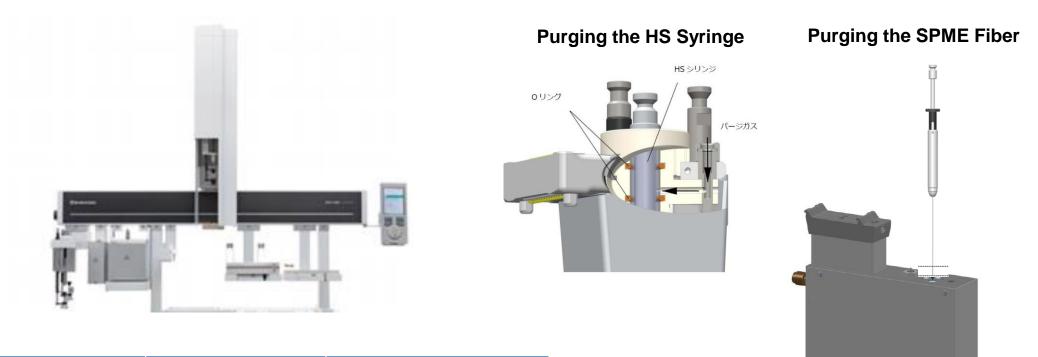




	Carrier Gas	Sample Purge Gas	Pressurizing Pumping Gas
Supported Gas (PT7000)	He, N ₂ , H ₂	He, N ₂	He, N ₂
Supported Gas (Aqua PT6000)	He, N_2	He, N ₂	He, N ₂



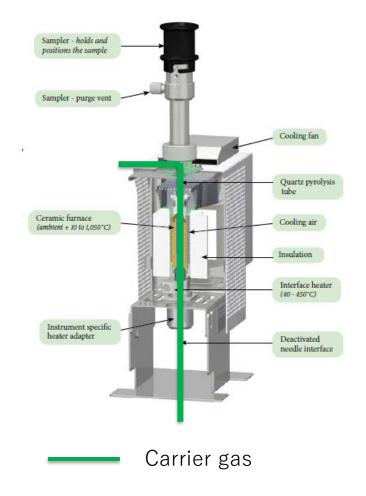
AOC-6000/5000 Series Multi-Functional Autosamplers



	Carrier Gas	Purge Gas for HS and SPME
Supported Gas	He, N_2 , H_2	He, N ₂

PY-3030D/PY-2020iD Multi-Shot Pyrolyzer





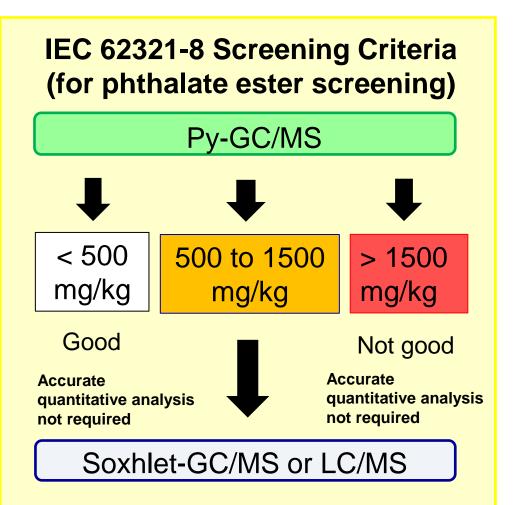
SHIMADZU

Measures for Using Py-Screener

Py-Screener Ver. 2 Phthalate Ester and Brominated Flame Retardant Screening System

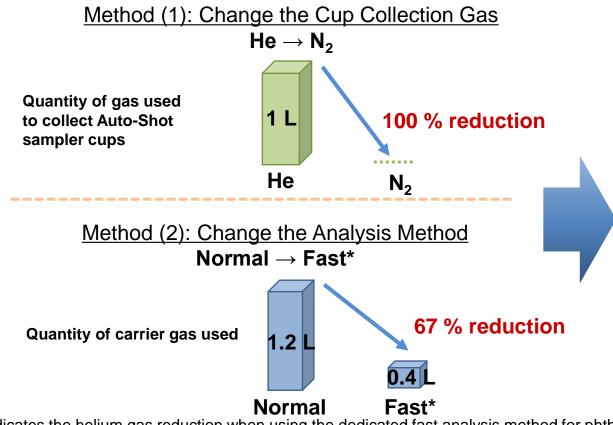


Note: Identical as when using Py-Screener Ver. 1



Measures for Using Py-Screener

- IEC standards specify using helium, so measures involve reducing helium consumption.
- Additional helium gas reductions can be achieved by the following measures.



Cup Collection Gas	Не	N ₂	N ₂			
Method	Normal	Normal	Fast*			
Total He Reduction	_	36 %	73 %			
Quantity of gas used to collect Auto-Shot sampler cups						
Quantity of carrier gas used	2 L 1	.4 L*	0 L 0.6 L*			

* If the cup collection gas is changed to N₂, change the Auto-Shot sampler purge time to 3 minutes. Consequently, 0.2 L more helium will be used for Py-GCMS than when using helium.

* Indicates the helium gas reduction when using the dedicated fast analysis method for phthalate esters. The helium gas reduction rate will be almost equivalent when the fast analysis method for simultaneous analysis of phthalate esters and brominated flame retardants.

Summary

Countermeasures-1: Reduce helium gas consumption

- Use the carrier gas saver mode and ecology mode.
- Use a gas selector.
- Use purity gas filter.
- Shut off the system if not being used for 2 to 3 days.

Countermeasures-2: Use an alternative carrier gas

- Alternative carrier gas choices differ depending on the system and options used.
- As a first choice, consider using hydrogen as an alternative carrier gas.
- Implement safety measures whenever hydrogen is used.

Be sure to read "Gas Chromatograph Hydrogen Gas Safety" on the Shimadzu website before using hydrogen. <u>https://www.shimadzu.com/an/service-support/technical-support/handling-precautions/gas-</u> <u>chromatography/index.html</u>



Thank you for your attention.

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