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A Guide to GCMS Sample Introduction Systems: Choosing the best system for your analysis

Introduction

Gas Chromatography Mass Spectrometry (GC-MS) is a widely-used analytical tool due to its versality and precision in both quantitative analysis and identification of unknown compounds. One of the reasons that GC-MS boasts such excellent versatility is the availability of various sample introduction systems.

Direct injection of a sample into the GC-MS can lead to contamination of the system and poor-quality data. On the other hand, off-line sample preparation can be laborious and time-consuming. Increasingly, automated sample preparation is incorporated directly into the GC-MS system. A good knowledge of sample preparation and injection types is therefore essential for today's lab managers to ensure quality GC-MS data and maintain an efficient workflow.

Shimadzu released its first GC-MS system in 1970, and in the decades since has developed a wide range of GC-MS instruments and accessories, including various autosamplers incorporating different sample introduction techniques.

In this guide, we list the differences and benefits of all the main sample introduction techniques for GC-MS, and explain how to choose the most suitable technique for your analysis. We then introduce Shimadzu autosamplers compatible with these introduction techniques. Finally, we discuss how to configure the overall GC-MS system to optimize your analytical workflow.

We hope you will find this guide useful for your everyday GC/MS analysis.

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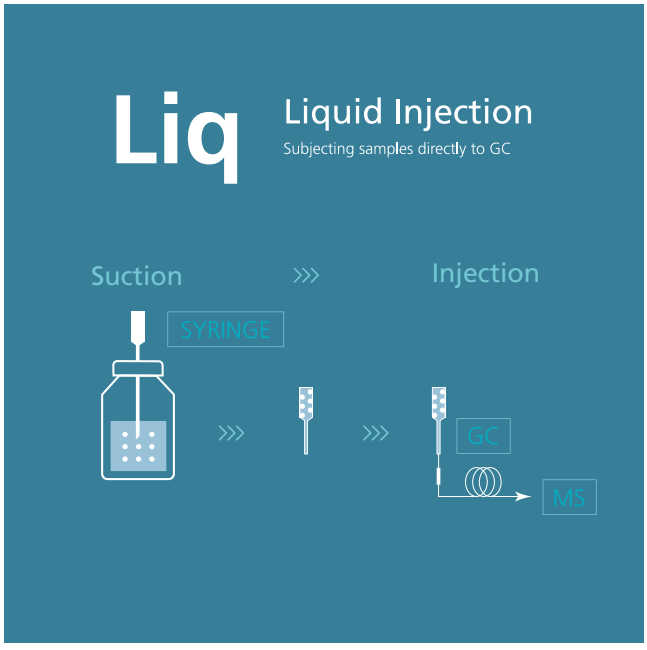
01 CHAPTER Overview of Sample Introduction Techniques

Here we introduce 8 key sample injection techniques for GC-MS. Injection of gaseous samples via gas sampling valves or gas-tight syringes is not included here as it is generally coupled to a GC system rather than GC-MS.

1.1 Liquid injection



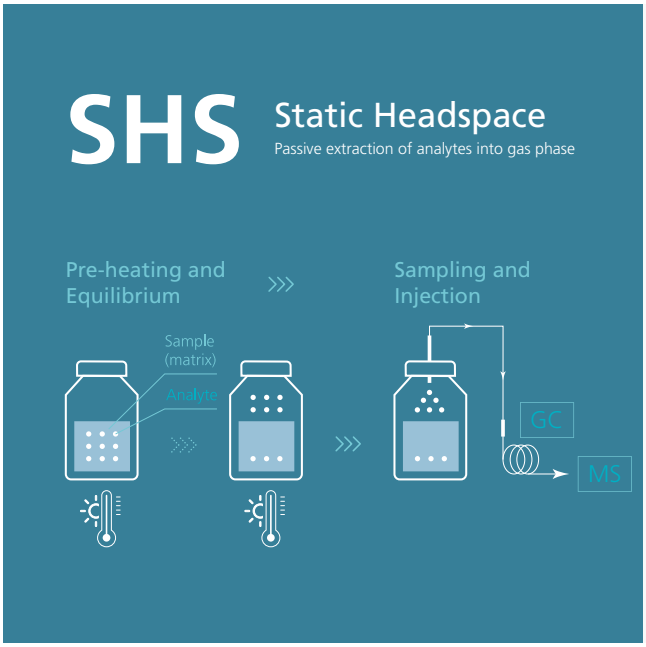
In liquid injection, liquid samples are pipetted directly into GC injection port using a needle. This method is used for volatile and semi-volatile analytes.

The injection port is preheated to the initial column temperature, allowing evaporation of the solvent and dissolved analytes. However, this high temperature can cause deterioration of peaks on the GC. To avoid this problem, the analytes are usually derivatized in order to block hydrophilic functional groups, lowering their boiling point. The sample can therefore be injected with the port at a lower temperature.

Derivatization is a pretreatment procedure to facilitate analysis of thermolabile or less volatile compounds, in which substances contained in a sample are chemically modified to increase volatility and/or thermostability. Derivatization makes analytes more amenable to GC-MS sample introduction and separation and it is employed in many sample introduction techniques.

For accurate analysis, reproducibility of derivatization must be ensured either by optimizing the chemistry to balance reactivity and stability, or by using a robotic GC/GC-MS injector to precisely control the reaction parameters and incubation time.

1.2 | Static headspace

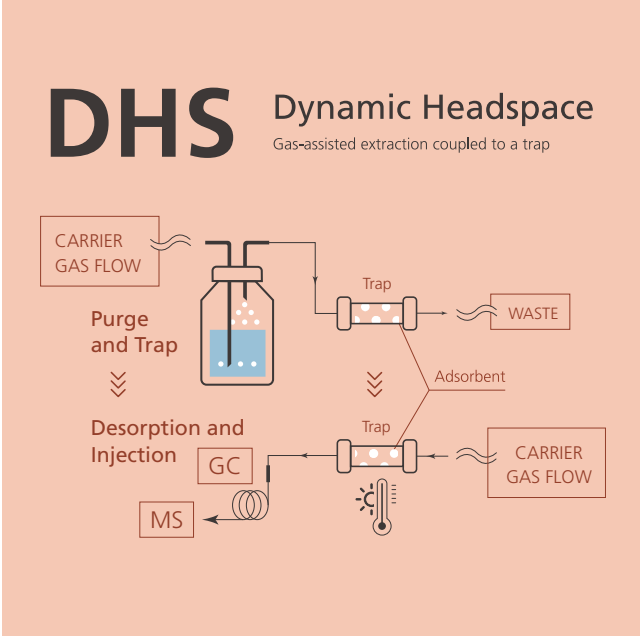


The static headspace method is used for detection of volatile analytes. In this method, liquid samples are pre-heated in an incubating chamber within the autosampler.

This pre-heating causes dissolved components to move freely in equilibrium between the gas headspace and the liquid phase. A higher temperature in the incubation chamber shifts the equilibrium, causing more volatile components to converge in the gas phase. The temperature applied depends on the target analyte.

Headspace gas is then sampled and injected directly into the GC.

1.3 | Dynamic headspace

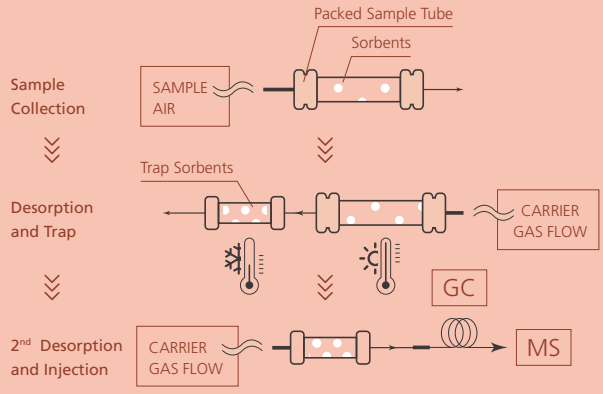


The dynamic headspace method, also known as "purge-and-trap", is a more sophisticated form of headspace injection which can achieve greater accuracy than SHS.

Firstly, a large known volume of inert gas is introduced into the liquid sample, "purging" the sample. The volatile target analytes are swept into an absorbent trap connected to the sample vial.

Then the absorbent trap is heated, releasing the volatile analytes into the GC-MS system.

1.4 | Thermal desorption

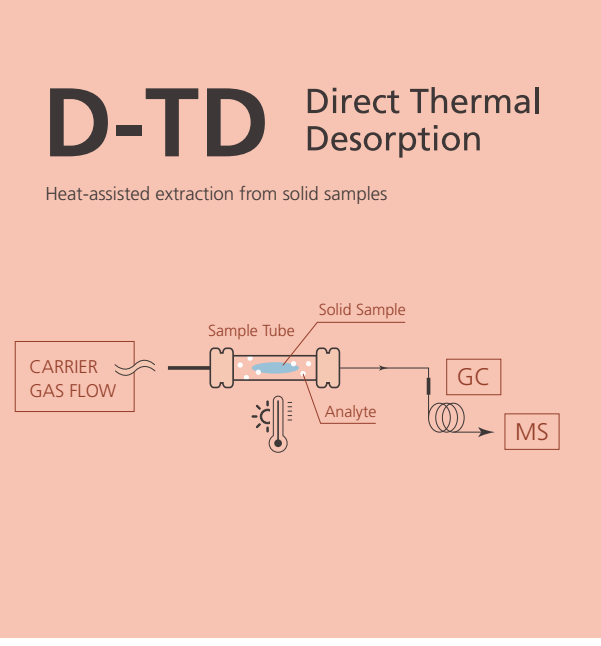


In this method, a portable sampling pump is used for field collection of large volumes of gas in thermal desorption (TD) tubes filled with trap sorbents.

Volatile analytes are released from these tubes into the GC-MS via heat desorption using an adsorbent trap system.

A good trap system has to be able to accommodate a variety of TD tube types while also allowing optimized desorption conditions for each analyte to ensure precise chromatographic data.

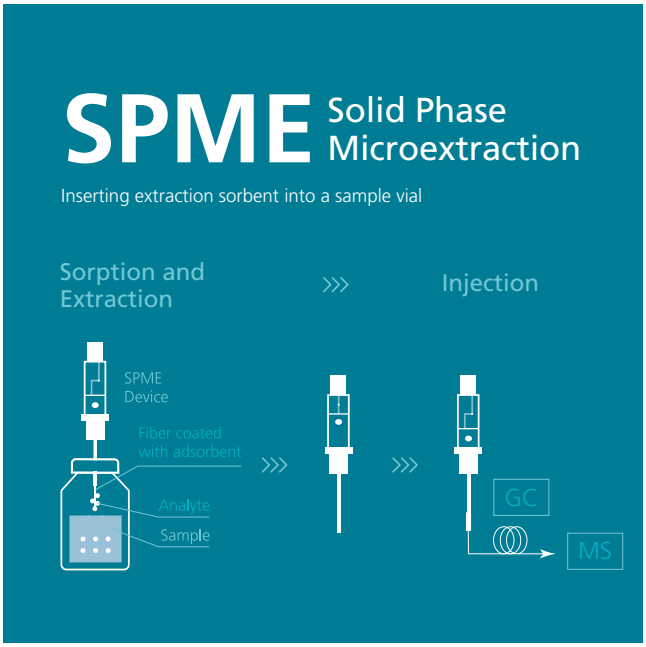
1.5 | Direct thermal desorption



Direct thermal desorption is used for solid samples rather than gaseous samples as in normal TD. The TD tubes are filled directly with the solid material rather than sorbents.

Heating the tubes releases volatile analytes via thermal desorption. These analytes may be introduced directly into the GC-MS or pass through a trap sorbent as in the TD system above.

1.6 | Solid phase microextraction

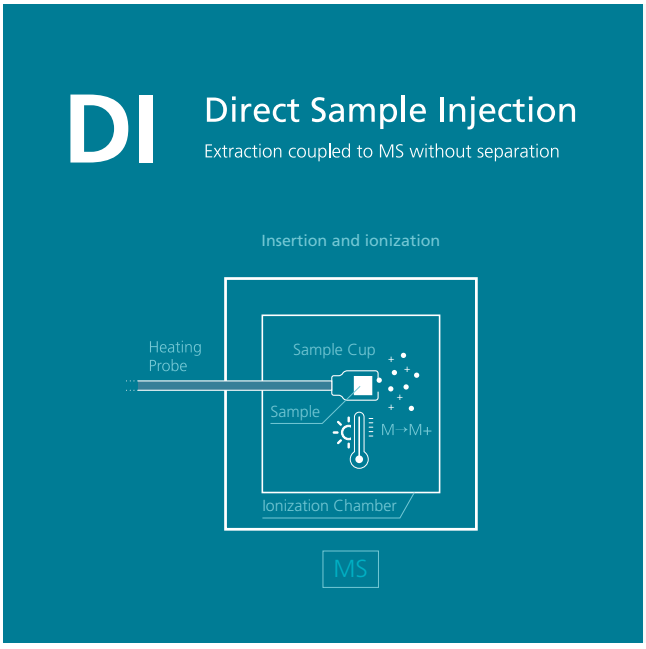


The SPME method is similar to DHS but provides greater flexibility. This method is used for semi-volatile and volatile analytes in liquid or gaseous samples.

The SPME sampling needle consists of a fiber core coated with a polymeric stationary phase. It can be inserted directly into liquid samples or into a sample headspace for adsorption of analytes.

The needle is then inserted into the pre-heated injection port and releases these analytes into the GC-MS system through heat desorption.

1.7 | Direct sample injection

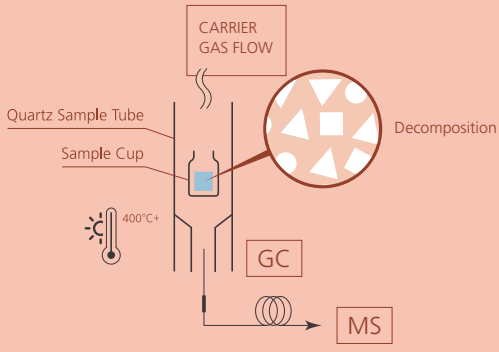


Direct sample injection is used for small solid or liquid samples that can fit into a small sample cup.

The cup is attached to a heating probe and can be inserted directly into the GC-MS ionisation chamber without passing through a GC column. The sample is ionized through heating.

This is a useful option for less volatile or non-volatile analytes that are not suitable for GC separation.

1.8 | Pyrolysis



Pyrolysis is a unique approach to the analysis of less volatile or non-volatile compounds in liquid or solid samples.

The sample is rapidly heated to 600-1000 °C, releasing smaller, more volatile decomposition products that can be separated and analyzed by GC-MS.

The chromatograms/pyrograms obtained in this way can be used as chemical “fingerprints” . Individual mass spectra are used for quality control and component identification.

1.9 | Summary table

Technique	Matrix	Target analytes
Liquid injection	Liquid (no sample prep)	Volatile or semi-volatile
Static headspace	Liquid, (semi-)solid	Volatile
Dynamic headspace	Liquid, (semi-)solid	Volatile
Thermal desorption	Gas, liquid, (semi-)solid	Volatile or semi-volatile
Direct thermal desorption	Liquid, (semi-)solid	Volatile or semi-volatile
Solid phase microextraction	Gas, liquid, (semi-)solid	Volatile or semi-volatile
Direct sample injection	Liquid, (semi-)solid	Less volatile, non-volatile
Pyrolysis	Liquid, (semi-)solid	Less volatile, non-volatile

02 CHAPTER Choosing a Sample Introduction Technique

2.1 | Volatility considerations

Volatility, the tendency of a chemical substance to vaporize, can be described through either vapor pressures or boiling points.

Vapor pressure is a measure of how easily a compound forms a gas at a given temperature, typically 20 °C, taking into account both evaporation (liquid-to-gas) and sublimation (solid-to-gas) phase transitions. The boiling point of a substance is the temperature at which its vapor pressure is equal to the surrounding pressure, and is usually reported with respect to atmospheric pressure. A substance with a high vapor pressure at ambient temperature, or a low boiling point at atmospheric pressure, is considered volatile.

Table 1 | Vapor pressure and boiling points of a range of compounds

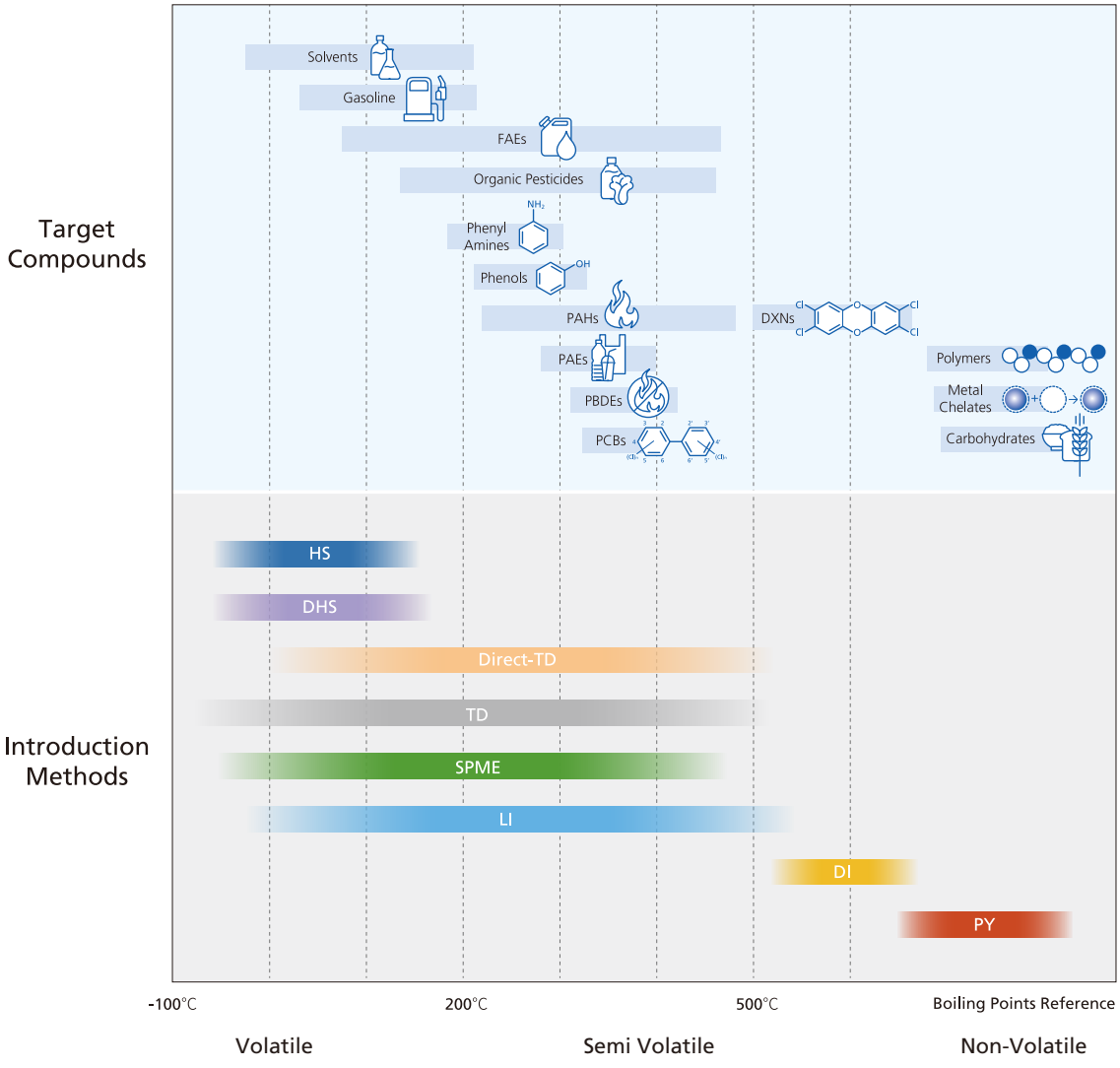
Substance	Vapor pressure at 20°C	Boiling point at 1 atm	Volatility
Polyethylene	$3X10^{-8}$ Pa (25°C)	-	Non-volatile
2,3,7,8-Tetrachlorodibenzodioxin	2×10^{-7} Pa	-	
DINP	6×10^{-5} Pa	403°C	
Glycerol	0.01 Pa (25°C)	290°C	
Ethylene glycol	500 Pa	197°C	
Water (H2O)	2.3 kPa	100°C	
Propanol	2.4 kPa	97°C	
Ethanol	5.83 kPa	78.37°C	
Freon 113	37.9 kPa	47.5°C	
Acetaldehyde	98.7 kPa	20.2°C	
Butane	220 kPa	-1°C	
Formaldehyde	435.7 kPa	-19°C	
Carbon dioxide	5.7 MPa	-78.5°C	Highly volatile

For GC or GC/MS analysis, boiling points are more commonly used. The vapor pressures and boiling points of a selection of compounds are shown in Table 1.

Substances can be broadly classified into non-volatiles, semi-volatiles, or volatiles. Although these is no precise distinction between these categories, it is generally agreed that substances that readily vaporize at ambient temperature and pressure are 'volatiles'; those that vaporize within conditions reached during GC,GC/MS analysis are 'semi-volatiles'; and those with boiling points beyond the scope of GC,GC/MS are 'non-volatiles'.

These classifications are useful in selecting an appropriate sample introduction method. The figure below shows the boiling points of various groups of compounds and the range of volatility over which each of the sample introduction techniques introduced above is effective.

On the next pages, we discuss in more detail the effects of volatility considerations for each sample introduction technique.



Volatility (boiling point) range for compound groups and introduction techniques. Abbreviations: FAEs = fatty acid esters; PAHs = polycyclic aromatic hydrocarbons; PAEs = phthalates; PBDEs = polybrominated diphenyl ethers; PCBs = polychlorinated biphenyls; DXNs = dioxins.

SHS

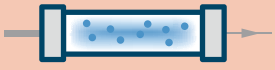
DHS

In static and dynamic headspace sampling, the recovery rate for injection depends strongly on the volatility of the sample, because only substances that equilibrate with the gas phase (headspace) are introduced into the GC-MS.

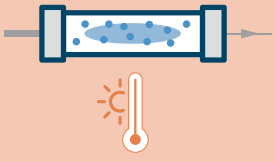
Even after incubation, the majority of semi-volatile components remain liquid. SHS/DHS are therefore suited for relatively volatile analytes with boiling points below 200 °C.

Example applications: Lower halohydrocarbons, residual solvents, monomers, blood alcohol, flavors and fragrances.

TD



D-TD



Thermal desorption methods are based on heat extraction of analytes from a solid phase that can tolerate the high temperatures required for extraction of semi-volatiles. This makes TD and D-TD suitable for a wide range of analytes with boiling points up to 525 °C.

Moreover, the sorbent in the TD tubes can be selected for specific chemical properties that provide better selectivity for the analyte of interest. For example, a strong absorptive sorbent improves sensitivity in the analysis of highly-volatile, gaseous analytes.

Example applications: Lower hydrocarbons, residual monomers, flavors and fragrances, phthalate esters, brominated flame retardants.

SPME

SPME offers two possible extraction modes, headspace mode (HS-SPME) or direct immersion mode (DI-SPME). DISPME allows analysis of less volatile polar compounds that do not readily transfer to headspace. SPME is therefore compatible with a wide range of volatiles and semi-volatiles.

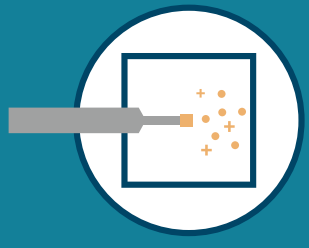
Example applications: Polar airborne organic compounds, flavors and fragrances, pesticides, polycyclic aromatic hydrocarbons, phthalates.

Liq

Of all the introduction techniques listed here, liquid injection is compatible with the widest range of volatility. It can be combined with various derivatization methods to enable vaporization of otherwise non-volatile compounds.

Example applications: Dioxins, residual pesticides, petroleum hydrocarbons, aliphatic esters.

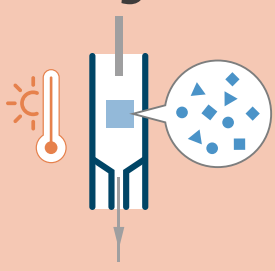
DI



Direct injection is useful for low-volatility compounds susceptible to thermal decomposition during GC separation, as the sample is ionized by the GCMS ion source. DI can be used with other types of ion source (chemical/electron ionization, etc.) for rapid qualitative analysis.

Example applications: refractory organics and thermolabile compounds, chelating agents, reserpine, antibiotics.

Py



Pyrolysis is used particularly for analysis of non-volatile compounds with high molecular weights that cannot be vaporized easily. Most non-volatiles will decompose between 400-1000 °C, and the decomposed fragments enter the GC-MS system for analysis. The original analytes are identified via these fragments.

Example applications: natural and synthetic polymers, microplastics, polysaccharides, proteins.

2.2 | Recovery of target analytes

Another factor in selecting a sample introduction method is the type and concentration of target compounds to be analyzed.

The sensitivity of each introduction technique determines the concentration range of target analytes that can be detected. Table 2 shows the approximate sensitivity of each technique; however, there are a number of other factors that affect overall sensitivity including the specific analyte to be measured and the sample matrix.

Table 2 | General sensitivity range for different sample introduction techniques

Sample Introduction Technique	Sensitivity (GC-MS)	Extraction Mode
SHS	ppb~ppm level	Static equilibrium gas extraction
DHS	ppt~ppb level	Dynamic non-equilibrium gas extraction
SPME	ppt~ppb level	Sorptive extraction
TD	ppt~ppb level	Sorptive extraction
Direct-TD	ppt~ppm level	Direct thermal extraction
Liq	ppb level	-
Py	µg level	Destructive thermal decomposition
DI	ng level	-

All of these techniques can be used for trace level analysis when coupled with a highly-sensitive MS detector. The following points should be noted when selecting a technique:

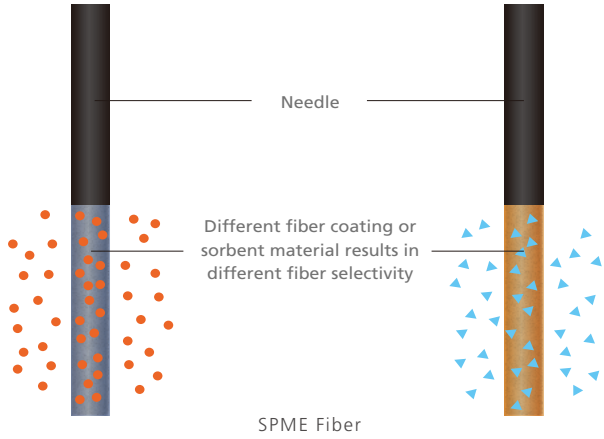
- In general, SHS is limited in sensitivity and DHS is a better choice for low-concentration volatiles.
- The purge and trap (P&T) technique is the most widely-used form of DHS, but is not suitable for analytes present in high concentrations (>1 ppm) because of possible system contamination.
- DI is more suitable for analysis of pure compounds. The sensitivity of DI is based on the sensitivity of the MS detector. Introducing too large a sample may contaminate the ion source.

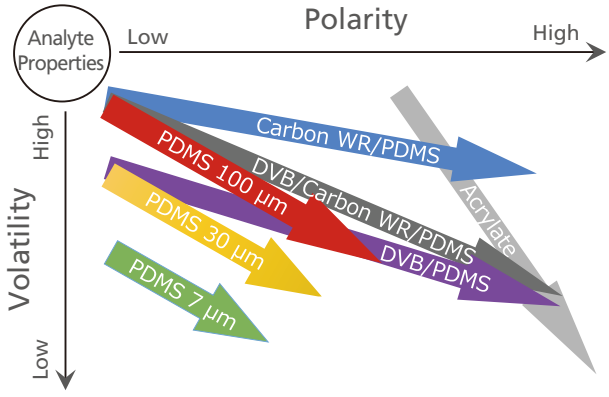
If the range of target analytes is limited to a certain class of compounds, more efficient analysis can be achieved through the use of enrichment techniques.

The selectivity of SPME is dependent on the coating of the SPME needle. For TD and DHS, the type of sorbents used can impact selectivity.

SPME needle coating

When the SPME needle is inserted into a vial, the fiber coating (outermost layer) interacts with the headspace gas or solvent. The selectivity of the needle, that is, which molecules are adsorbed onto the needle, depends on the properties and thickness of the coating. Thus, selection of an optimum SPME fiber requires prior knowledge of polarity and molecular weight of the target analytes.





The coating should therefore be chosen based on the target analytes. The graph shows the approximate compatibility of different coatings with analyte volatility and polarity. A thin coating e.g. 7 µm is suitable for relatively large molecules, whereas a thick coating is required for small, gaseous substances. The arrows point to the bottom-right because polar substances tend to be less volatile for the same molecular weight.

Compatibility of SPME fiber coatings with analyte properties
(PDMS = polydimethylsiloxane, DVB = divinylbenzene, Carbon WR = Carbon Wide Range)

Sorbent materials for TD and DHS

Sorbent or trap materials for these techniques must be sufficiently strong to retain the compounds of interest during sampling/trapping, but weak enough to release them efficiently during the thermal desorption process.

There are three main types of sorbent materials: porous organic polymers, carbon-based materials, and inorganic sorbents. Porous organic polymers are the most commonly used due to their large sample capacity, inertness, and hydrophobic properties. Carbon-based materials, such as graphite or carbonized molecular sieves, are more suitable for trapping highly-volatile compounds. Inorganic sorbents are used for more specific purposes, e.g. hydrophilic silica gel for trapping polar compounds. These sorbents tend to trap moisture, interfering with GC/MS analysis, so cannot be used more widely.

Different sorbent materials can also be used in combination for sampling and trapping to further enhance selectivity.

2.3 | Sample Matrices

The sample matrix significantly affects the sample pretreatment. The volatility of the sample matrix determines which sample introduction techniques can be applied, and matrix interferences also need to be considered to ensure accurate results.

The table below shows common matrix interferences for gas, liquid, semi-solid and solid samples.

Real-life samples often include a large number of non-target analytes. In general, the more similar the properties of these non-target compounds are to those of the target, the more difficult it will be to perform an analysis.

Some relatively pure gas or liquid samples can be injected into the GC directly or after simple dilution (e.g. solvents, perfumes, essential oils). However, solid samples and mixtures always require some pretreatment, for which we must consider the compatibility of the injection method.

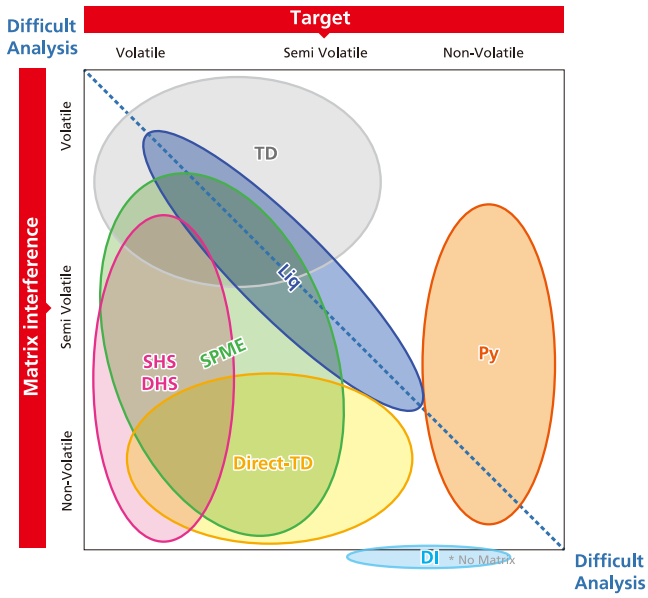
Table 3 | Examples of sample types and common matrix interferences

Sample Type	Examples	Possible Matrix Interferences
Gas	Environmental air, exhaled breath	Volatiles, semi-volatiles
Liquid	Perfume, gasoline, paint thinner,mouthwash, drinking/waste water,wine, blood, urine, milk	Volatiles, semi-volatiles, non-volatiles
Semi-solid	Oil paint, shampoo, shower gel,toothpaste	Volatiles, semi-volatiles, non-volatiles
Solid	Soil, plastic, rubber, leaves, textiles, soap, meat, vegetables, coffee beans,tablets	Volatiles, semi-volatiles, non-volatiles

Previously we looked at the choice of a sample introduction technique based on the volatility of the target analytes. However, the volatility of the matrix must also be taken into account. The figure below shows the most appropriate technique taking into account both sample and matrix volatility.

In addition, the following points should be taken into account:

- Direct injection is more suitable for pure compounds or simple samples without matrix interferences.
- Liquid injection can be combined with various sample pretreatment methods to be applied to all types and sizes of samples, e.g. for complex samples with similar properties to the target analytes, pretreatment methods such as solid phase extraction (SPE) can be effective.
- Semi-solid or solid samples should be dissolved in a solvent when using direct immersion SPME for analysis of semi-volatiles.
- For any of these techniques, matrix interferences can be further reduced by multidimensional chromatography techniques or tandem MS configurations (see Section 4 below).



Quick reference chart

Liquid/(semi-)solid samples

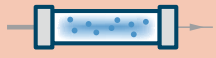
SHS/DHS

Ideal for analysis of volatiles in less or non-volatile matrix

SPME

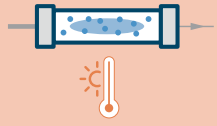
Ideal for analysis of volatiles in less to non-volatile matrix

TD



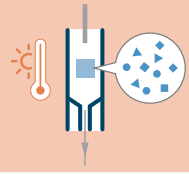
TD can be expanded to liquid and(semi-)solid analysis

Direct-TD



Good for(semi-)solid with high sensitivity and minor sample pretreatment

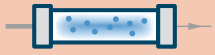
Py



Suitable for small samples (100s of µg) and complex matrices

Gaseous Samples

TD



Best choice for analysis of large volume sample

SPME

More suitable for in field and in vivo or vitro analysis

2.4 Application examples

This table shows real application examples of the introduction techniques we have discussed.

Technique	Main Fields	Applications	
		Target	Matrix
SHS	Foods & Agricultures	Flavors Discriminant markers	Flours Coffee brew
	Materials & Chemicals	Volatiles Volatiles	Mattress fabric Electronic cigarette liquids
	Environmental	Pollutants	Soil
	Life Science	Biomarkers	Blood
DHS	Foods & Agricultures	Flavors Odors	Tomato juice Fish
	Environment	Off-flavor Pollutants	Environmental water Drinking/Surface water
	Life Science	Pollutants	Animal secretions
SPME	Foods & Agricultures	Contaminations Contaminations Volatile profile Discriminant markers Flavors	Seaweeds Fruit & meat Juice Rice Tea
	Environment	Pollutants Pollutants Pollutants	Soils Waters Sewage
	Life Science	VOCs profiling Metabolites of aroma compounds Odor	Cell Saliva Leaves
	Pharmaceuticals	Quality evaluation of active components	Cannabis
TD	Life Science	Volatile biomarkers Volatile biomarkers	Exhaled breath Exhaled breath
	Environment	Sorbent materials	Outdoor air
	Pharmaceuticals	Leachables	Drug products
	Foods & Agricultures	Odor-Spoilage markers	Chicken breast
Direct-TD	Materials	Additives	Polymer materials
	Forensics	Volatiles Ethylene gylcon	Fire debris Blood
	Pharmaceuticals	Residual solvents	Drug
Py	Environment/ Materials	Microplastic	Sea water, beach sediments, bivalves
	Biomass	Catalyst (pine wood)	-
	Forensics	Volatiles profiles of Paper	-
DI	Pharmaceuticals	Synthetics	-
	Chemicals	Synthetics	-

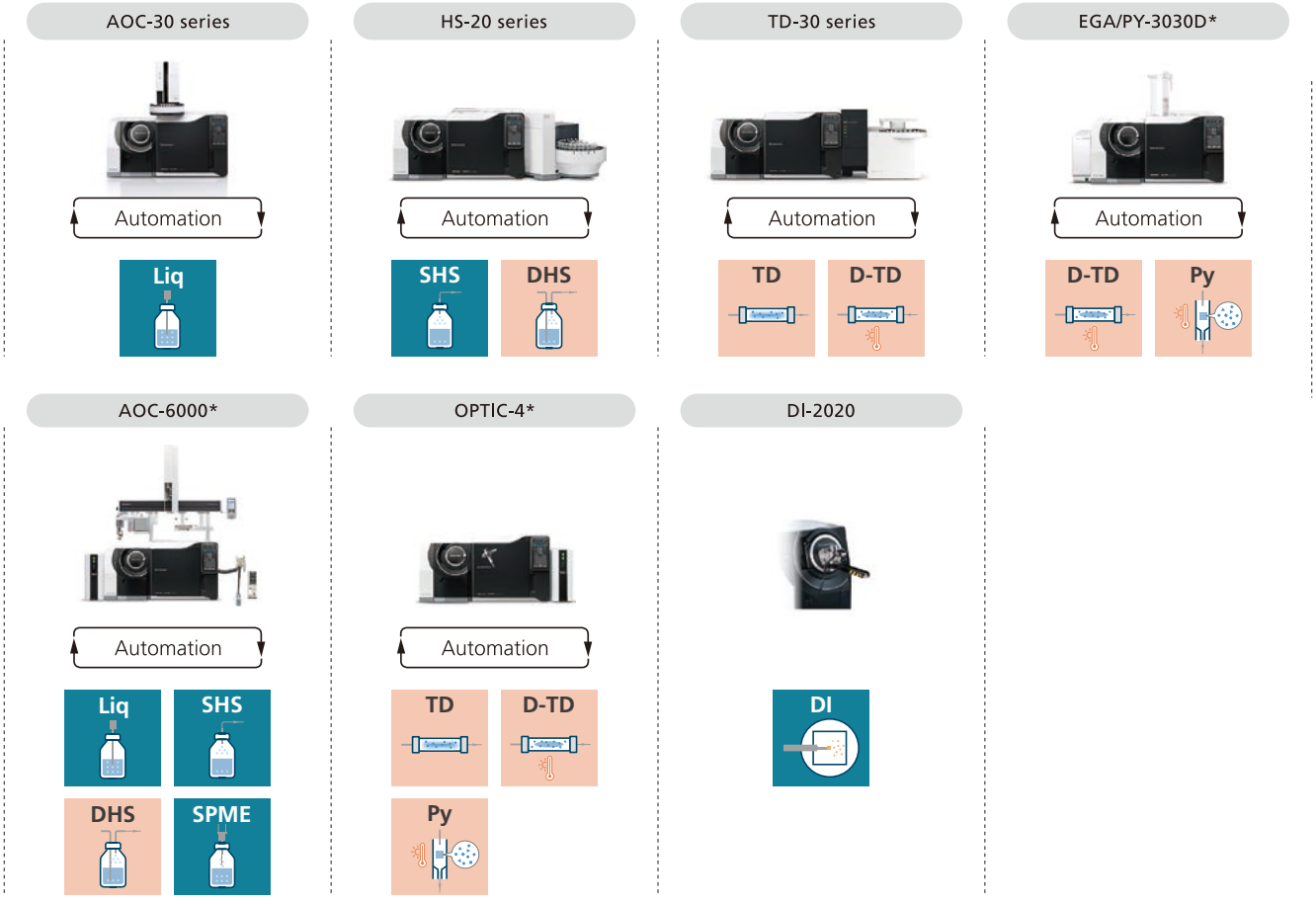
03 CHAPTER Shimadzu's Autosampler Lineup

3.1 | Overview

Shimadzu provides a range of autosamplers and accessories compatible with the sample introduction techniques we have discussed. The correct equipment will simplify pretreatment, increase overall workflow efficiency and help you to attain quality data every time.

The table below is quick reference guide to the introduction techniques available for each Shimadzu autosampler or accessory.

Various Sample Introduction Techniques for each of Shimadzu's GCMS Accessories



Visit Shimadzu's website to learn more on the functions of these GCMS accessories.

* The combination of OPTIC-4 and AOC-6000 allows the automation of sample introduction.

Link

Click here >

3.2 | AOC-30 series

The AOC-30 series comprises the most basic autosampler models offered by Shimadzu. Simple and cost-effective, the AOC-30 series are nonetheless equipped with multifunctional robotics to improve the reliability and productivity of GC/MS analysis.

Features

- Reliable automatic operation for liquid injection and automation of pretreatments such as the addition of internal standards (IS) and derivatization
- Space-saving design and easy expansion to sampler system and dual tower
- Equipped with a Sampler Navigator that provides optimal conditions such as low carryover
- Supports programmed temperature vaporization (PTV) for large-volume samples

Usability enhancements

- Simple and cost-effective GC-MS configuration
- Routine procedures are easy to program
- 30 samples capacity and up to 150 samples with sampler system

Optional extras

- MEPS syringes (MicroExtraction by Packed Sorbent)

Recommended for

- Established workflows
- Minimizing installation and running costs

Featured Application: Streamlining Sample Analysis Using Automated Injection of Internal Standards

By selecting the Co-injection preset menu in the Sampler Navigator, anyone can set the recommended conditions for IS automatic injection with one click.

Link

Click here >

Featured System: On-Column Derivatization System

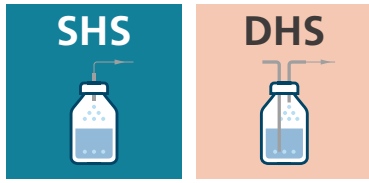
This system offers an established protocol for high-sensitivity detection of amphetamine, methamphetamine and analogues in urine samples.
Derivatization with trifluoacetic anhydride is automated for more efficient analysis.

Link

Click here >

3.3 | HS-20 series

The HS-20 series are valve-loop headspace systems with fixed sample volumes, short transfer lines and dynamic headspace mode option. Its minimal carryover and excellent cost-performance make it a reliable choice for headspace sampling.



Features

- AFC system for reproducible flow control
- Covered sample chamber keeps temperature stable
- Short transfer line minimizes carryover
- Oven temp. up to 300 °C

Optional extras

- Trap model for enhanced sensitivity
- Barcode reader

Usability enhancements

- Easy maintenance
- User-friendly sample tray stores 90 vials
- Overlapping pretreatment

Recommended for

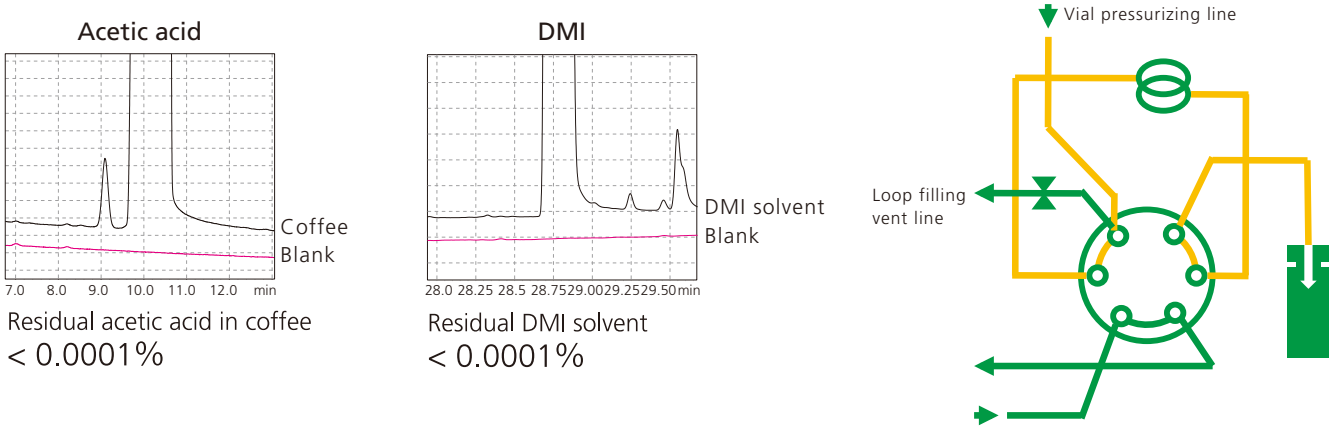
- Replacing conventional HS-GC-MS system to improve reliability
- Cost-effective alternative to a fully-robotic DHS injector

HS-20

Click here ›

Unique to Shimadzu:
Extremely low carryover

The very short headspace transfer line (30 cm), high loop and transfer line temperature (300 °C), and special deactivated inert sample line contribute to extremely low carryover. A high degree of reliability is achieved even for polar compounds. (US Patent No. 8584507)



Featured Application:
Trap-cooling unit for high-sensitivity quantitation

The HS-20Trap model is equipped with a cooling trap unit, which can cool the headspace gas to as low as -30 °C, increasing the quantity of low-abundance volatiles in samples.

This application demonstrates the use of this injector system for high-sensitivity quantitation of 2,4,6-trichloroanisole in wine. Using the most affordable GCMS model, the calibration curve ranged from 1-100 ppt, and a 3 ppt spiked in wine sample was quantitated at <5% precision.

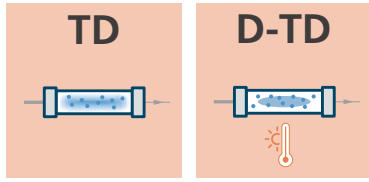
Application Data Sheet:
High-Sensitivity Analysis of 2,4,6-Trichloroanisole in Wine Using Headspace-Trap GC/MS

Link

Click here >

3.4 | TD-30 series

The TD-30 series autosampler is a two-stage thermal desorber with a trap to refocus target analytes and sharpen chromatogram peaks. It is compatible with a wide variety of applications and provides excellent processing speed.



Features

- Excellent sensitivity for analytes with high boiling points
- Co-injection of internal standard
- Compatible with high temperatures

Optional extras

- Efficient reanalysis with the Restore function
- Barcode reader

Usability enhancements

- Easy maintenance
- Stores up to 120 samples
- Built-in sensor to protect tubes
- Overlapping pretreatment

Recommended for

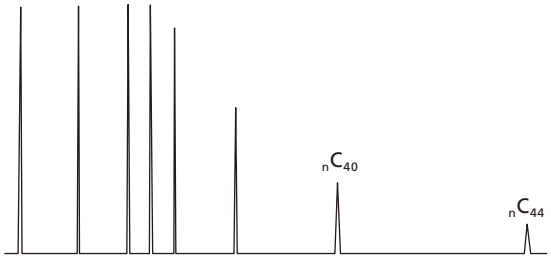
- Analysis of volatile pollutants and biomarkers
- Analysis of gases sampled in the field

TD-30

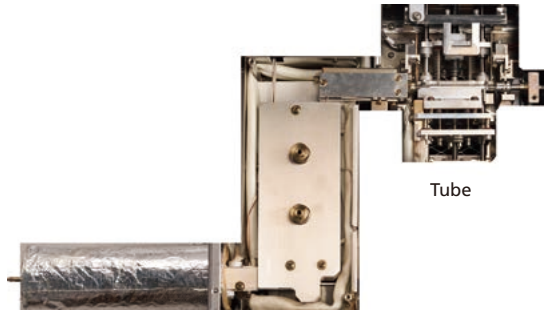
Click here ›

Featured Application 1: Short transfer line heated evenly for direct TD

The entire sample transfer line is heated without cold points, and its short length minimizes the dead volume. This allows even highly adsorbent components and high boiling point components to be analyzed with high sensitivity and low carryover. In this application, VOC and SVOC emissions are analyzed using direct thermal desorption.



Analysis of High Boiling Point Hydrocarbons



Transfer Line Trap

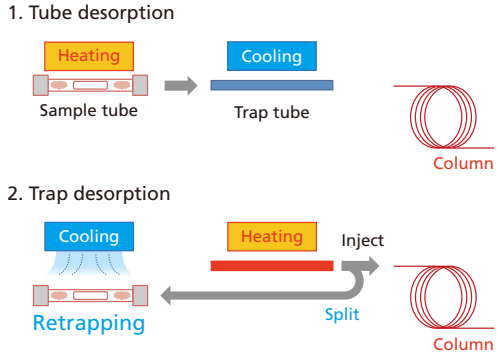
Application Data Sheet:
Analysis of VOC and SVOC Emissions from Automotive Interior Materials in Accordance with VDA278 Using the Thermal Desorption Method

Link

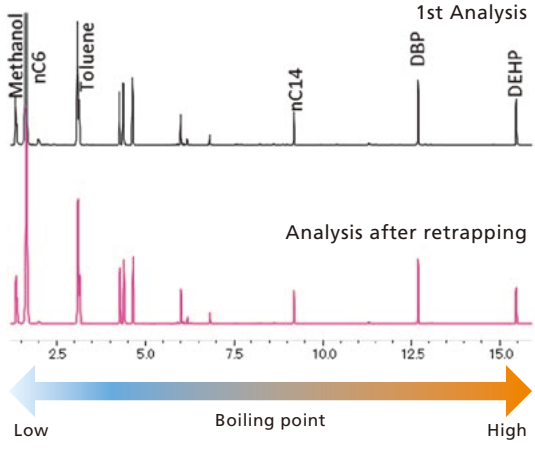
Click here

Featured Application 2: Restore function avoids repeated sample collection

The Restore function allows samples to be reanalyzed easily. In addition, since the tube is cooled quickly after desorption, the loss of low boiling point components is minimized.



Thermal desorption system achieves sharp peaks by heating sample tube and trapping condensed sample in trap tube. Retrapping function of TD-30R traps split samples, which saves precious samples.



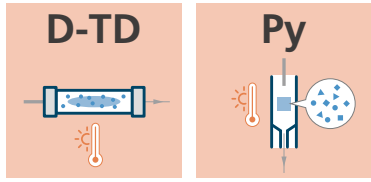
Technical Report:
Analysis of Volatile Organic Compounds in the Environment Using the Restore Function of TD-GC/MS

Link

Click here

3.5 | EGA/PY-3030D

This pyrolyzer is a versatile sample introduction device that allows qualitative and quantitative analysis of samples with little to no preparation. The simplicity of this system makes it an ideal instrument for many fields including plastics testing, cannabis testing, food, and more.



Features

- High-temperature pyrolysis up to 1050 °C
- Precise temperature control
- Small dead volumes
- Developed by Frontier Laboratories Ltd.

Usability enhancements

- Flexible configuration with various accessories

Optional extras

- Auto-shot sampler with 48 sample cups
- Cryo-trap (vent-free GC-MS adaptor)
- Carrier gas selector
- Capillary columns for high temperatures

Recommended for

- RoHS compliance testing (with Py-Screener)
- Investigation of unknown solid samples

EGA/
PY-3030D

Click here >

Featured Application 1:
Evolved Gas Analysis (EGA) for planning qualitative analysis

In EGA, samples are gradually heated with precise temperature control, and the evolved gases are introduced directly into an MS. Data is recorded as thermograms rather than chromatograms. These thermograms indicate the decomposition profiles of the samples. From this, the user can decide whether to carry out qualitative analysis with TD-GC/MS, Py-GC/MS or both, as well as choosing an appropriate temperature range.

This application walks the reader through the EGA process and data interpretation for polyethylene terephthalate.

Paper:
Qualitative Profiling of Co-polymer Polyethylene Terephthalate through Multifunctional Pyrolyzer-GC/MS by various Thermal Treatment Techniques

Link

Click here >

Featured Application 2:
Using nitrogen carrier gas to reduce running costs

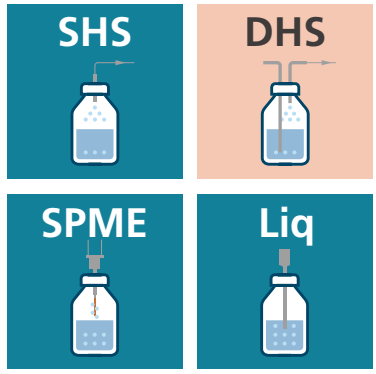
If analytes are present on the order of ppm, switching the carrier gas from helium to nitrogen may reduce the costs of analysis. This application demonstrates the conversion of an existing helium-based method to nitrogen with negligible impact on the chromatographic profile.

Application Data Sheet:
Py-GC/MS Analysis of Electronic Circuit Board Parts Using Nitrogen Carrier Gas

Link

Click here >

3.6 AOC-6000 Plus Multifunctional Autosampler



The AOC-6000 Plus is a multi-functional autosampler that dramatically increases everyday analysis productivity. In addition to its complex liquid-handling capabilities for liquid injection, headspace and SPME pretreatment, the AOC-6000 Plus can accommodate extensions such as ITEX and SPME Arrow to meet the needs of more specialist research.

Features

- Automation of complex sample pretreatment improve sreproducibility for derivatization, dilution, and liquid injection
- Automation of multiple introduction techniques on one sample

Recommended for

- Labs where one GC-MS instrument is used for multiple types of analysis
- Advanced research using the latest concentration technologies

Usability enhancements

- Fully-integrated with Shimadzu software
- Routine procedures are easy to program
- Overlapping pretreatment

Optional extras

- ITEX DHS
- SPME Arrow
- OPTIC-4 (see next section)

AOC-6000 Plus

Click here ›

Optional Accessory 1: SPME Arrow

The main drawbacks of SPME are the lack of mechanical stability and the small phase volumes of the SPME fibers. The new SPME Arrow is a fiber with thicker coating and larger sorption phase surface and volume, making it more durable and sensitive. In the below example, the SPME Arrow achieved three times the sensitivity of a conventional SPME fiber.

Application News:
High Sensitivity Analysis of Coffee Aroma Components Using the SPME Arrow

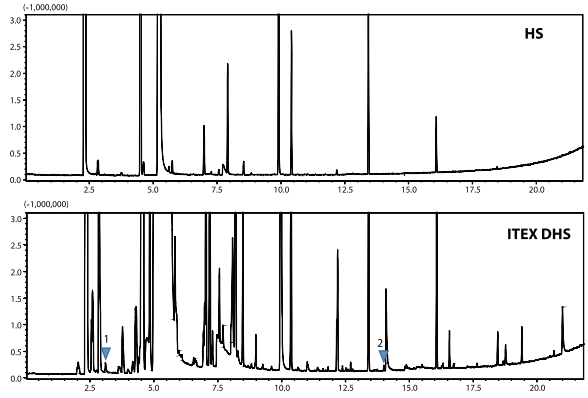
Link

Click here

Optional Accessory 2: ITEX-DHS

ITEX-DHS stands for In-Tube Extraction Dynamic Headspace. It uses a syringe with a trap to concentrate samples multiple times, achieving greater sensitivity than static headspace. It requires lower sample volumes than a conventional purge and trap system, and in addition is less prone to contamination and easier to maintain.

In this analysis of VOCs in white wine, dimethyl disulfide and furfral were detected with 10 times higher sensitivity compared to a conventional headspace method.



Analysis results comparison of HS and ITEX DHS in white wine

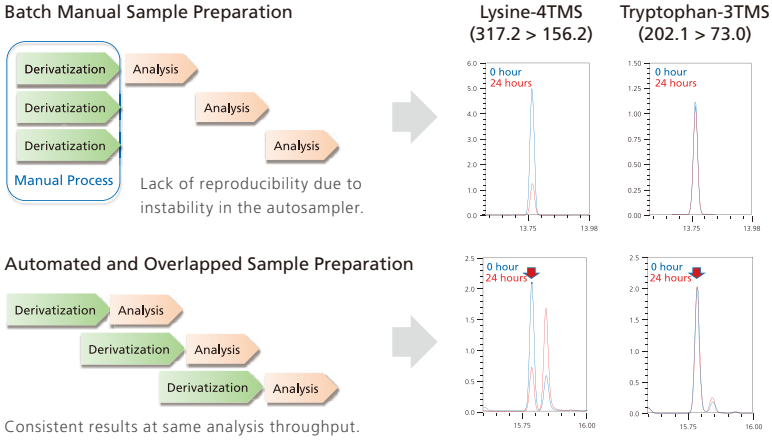
Application News:
High Sensitivity Analysis of White Wine Aroma Components Using ITEX DHS

Link

Click here

Featured Application: Liquid injection for analysis of plasma metabolites

The Automated TMS Derivatization GC-MS/MS System was developed for analysis of metabolites in human plasma. This system ensures that signal intensities for easily degradable compounds are not compromised even with inconsistent time before analysis.



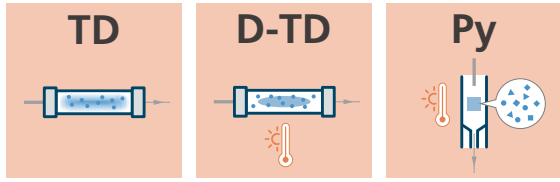
Paper:
Analysis of Plasma Metabolites Using Gas-Chromatography Tandem Mass Spectrometry System with Automated TMS Derivatization

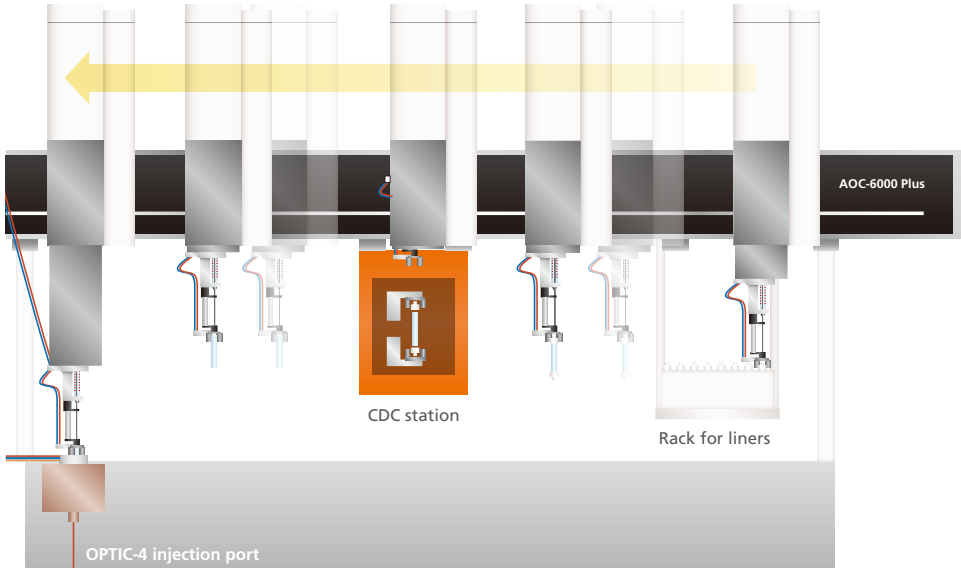
Link

Click here

3.7 | OPTIC-4 Multimode Inlet

OPTIC-4 is an inlet extension for the AOC-6000 Plus (see previous pages) to support high-temperature extraction methods including TD, D-TD and pyrolysis.





Features

- Rapid heating (60 °C/s) provides greater resolution
- Short inlet path (1 cm) prevents adsorption and degradation

Recommended for

- Expanding the types of analysis that can be carried out on one GC-MS instrument

Usability enhancements

- Various options for sample holders to accommodate different samples
- Overlapping pretreatment

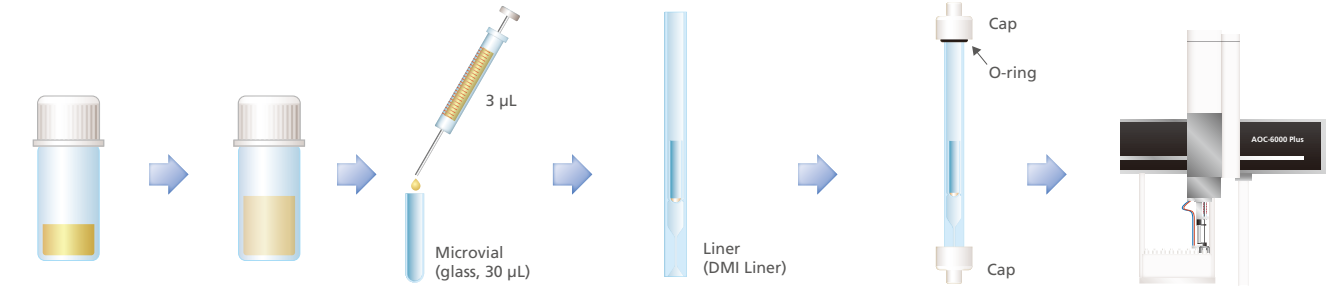
OPTIC-4

Click here ›

Featured Application 1: DMI mode for analyzing volatiles in a complex matrix

DMI (Difficult Matrix Introduction) mode allows relatively impure or raw samples to be introduced directly into the GC-MS with a minimal amount of pretreatment. Samples are placed in disposable microvials, and by adjusting the inlet temperature, non-volatile components are retained in the microvial.

In this case, DMI-GC/MS was used for analysis of 1,4-dioxins in shampoo without introducing any contaminants into the column.



Measure out 1 g of shampoo.

Add 1,4-dioxane-d8 to 1 g of ultrapure water and then agitate.

Place 3 µL in the microvial.

Insert the microvial in the liner.

Attach an O-ring to the upper part of the liner, then cap both top and bottom.

Place it in the AOC-6000 Plus rack, then start the analysis.

Application Data Sheet:

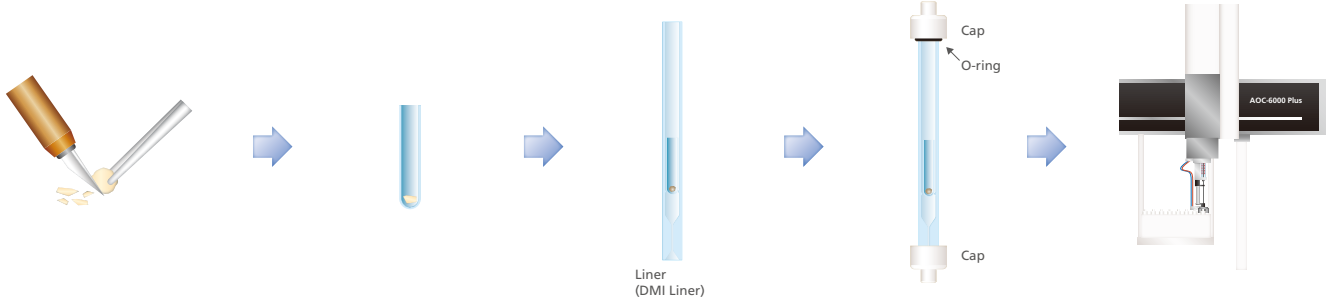
Determination of 1,4-Dioxane in Shampoo Using the OPTIC-4 Multimode Inlet

Link

Click here >

Featured Application 2: Pyrolysis mode for less volatile or non-volatile components

OPTIC-4 can heat up to 600 oC at a rapid rate, meaning it can provide data equivalent to that of instantaneous-heating pyrolyzers. Using this pyrolysis mode, numerous phenolic compounds, including bisphenol A, were detected in polycarbonate resins.



Cut out a small piece of sample using a cutter or file.

Place a small piece (several tens of µg or less) of the sample in the microvial.

Insert the microvial in the liner.

Attach an O-ring to the upper part of the liner, then cap both top and bottom.

Place it in the AOC-6000 Plus rack and start analysis

Application Data Sheet:

Analysis of Resin Using the OPTIC-4 Multimode Inlet in Pyrolysis Mode

Link

Click here >

3.8 | DI-2010

The DI-2010 is a heating probe for injecting samples directly into the GC ion source. It is useful for analysis of thermally unstable compounds that cannot be separated by GC.

The DI-2010 is compatible with all models in Shimadzu's GCMS-QP and GCMS-TQ series. It is especially recommended for use in conjunction with the Smart EI/CI Ion Source, which generates both fragmented and molecular ions with high efficiency.

Features

- Heats up to 500 °C at 5 possible heating rates

Usability enhancements

- Insertion of probe does not interfere with GC oven
- Can use in conjunction with EI, CI/NCI and Smart EI/CI ion sources

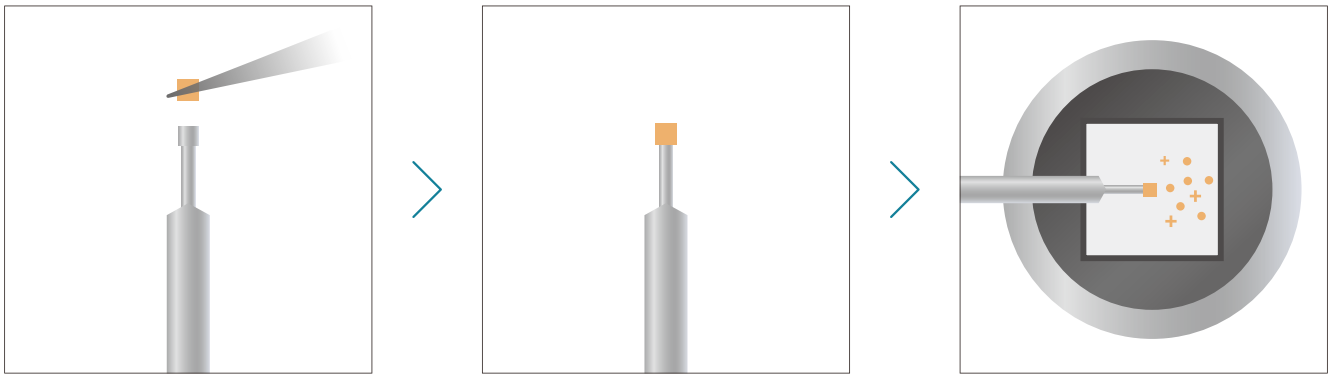
Recommended for

- An extra analysis option for labs processing unknown samples
- Troubleshooting if an analysis fails

DI-2010

Click here >

Simple sample introduction



Step 1 | Place solid sample on sample cup

Step 2 | Sample on end of probe

Step 3 | Insert probe and begin data acquisition

Application Data Sheet:
Analysis of Chelate Compounds Through Direct Sample Introduction

Link

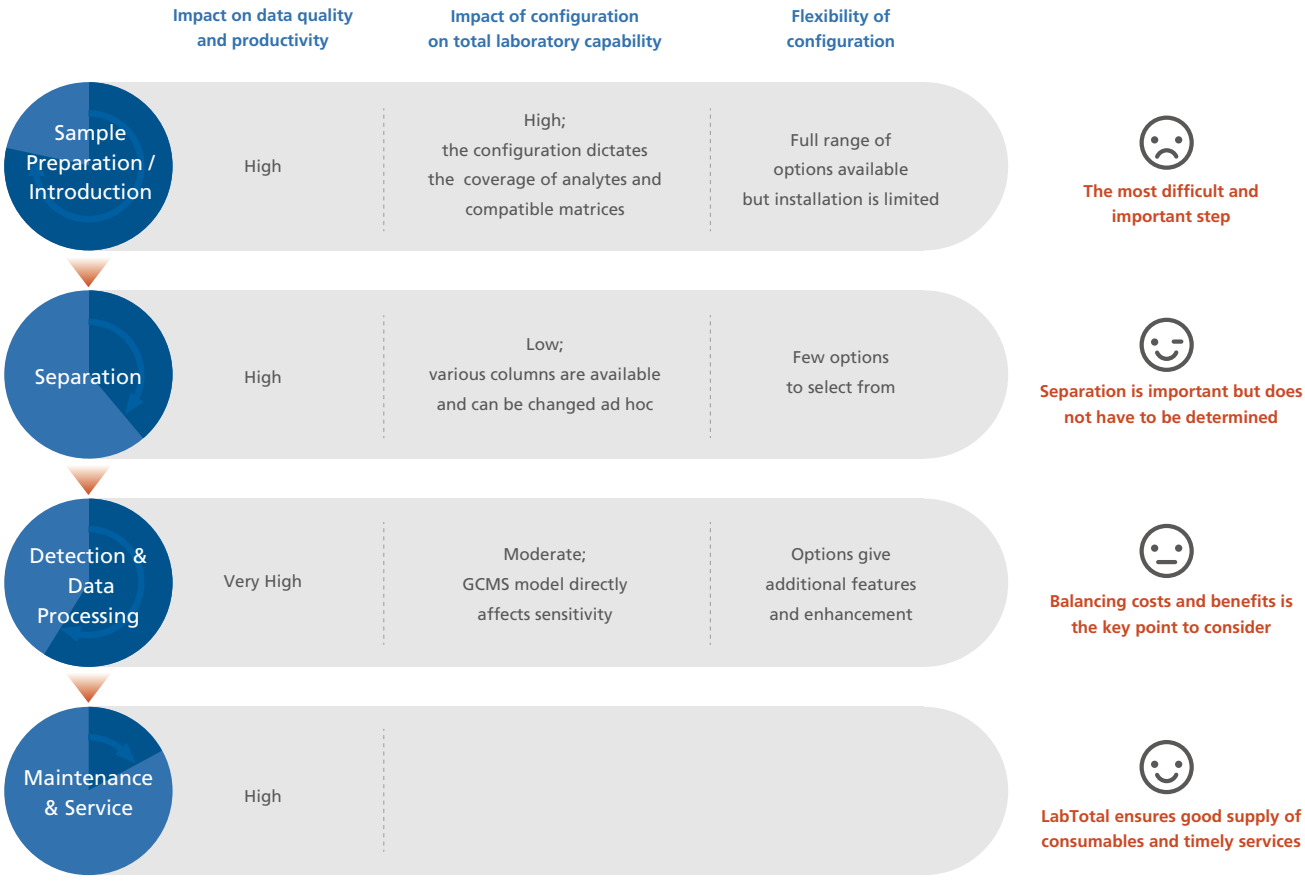
Click here >

04 CHAPTER Improving Overall GC-MS Workflow

4.1 | Planning GC-MS configuration

So far we have considered the impact of sample preparation and introduction on the efficiency and accuracy of GC/MS analysis. As we have discussed, there is great flexibility in possible setups. The sample introduction system must be chosen with care as multiple inlet devices cannot be installed on one GC-MS instrument.

However, when optimizing overall workflow, we must take other key steps into consideration, namely GC separation; MS detection and data processing; and general maintenance. All these factors have an impact on productivity and data quality. This section evaluates options available for these other aspects of the workflow and presents some of Shimadzu' s recommended configurations.

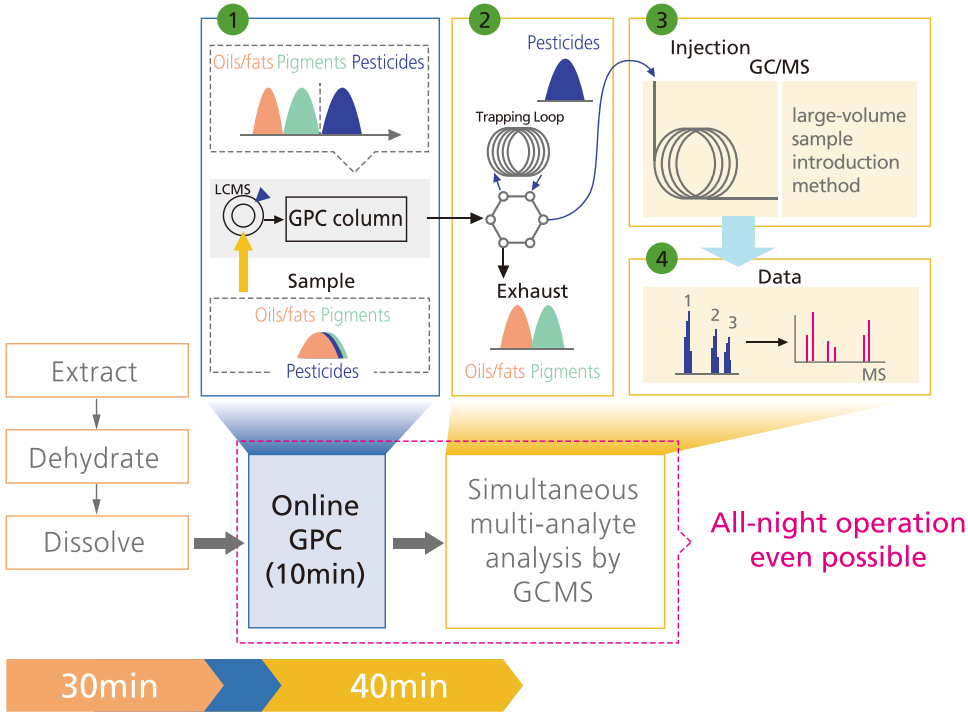


4.2 Shimadzu's proprietary configuration for liquid injection (GPC-GC/MS)

This unique configuration invented by Shimadzu uses chromatography as the selectivity mechanism for sample introduction, rather than temperature change or adsorption as in the techniques we have discussed.

The Online GPC-GC/MS System introduces the eluate of gel permeation chromatography (GPC) into the GC-MS via large-volume liquid injection with programmable temperature variation (PTV). GPC is an ideal method for enrichment of low-molecular-weight compounds such as pesticides. It removes biological macromolecules and semimacromolecules that cause both matrix interference and GC-MS contamination. Efficient cleanup means that crude samples (typically QuEChERS extracts) may also be analyzed.

Online GPC-GC/MS Method



Features

- High recovery rates
- Reduced matrix effects
- Significantly less matrix interference in peaks gives closer library matches

Usability enhancements

- All processes are online and automated
- Long column lifetime and infrequent GC-MS cleaning
- Greatly reduces consumable costs compared to batch purification

Recommended for

- Pesticide analysis in foods with difficult matrices e.g. oranges
- Dedicated GC-MS system for one application

4.3 | Shimadzu's configurations for GC separation

Appropriate sample introduction techniques and autosamplers can greatly simplify sample preparation. However, samples with complex matrices or multiple isomers generally require a further clean-up or separation stage. Extensive sample cleanup can be difficult to implement, and increasing GC separation capabilities is often a more efficient and straightforward alternative.

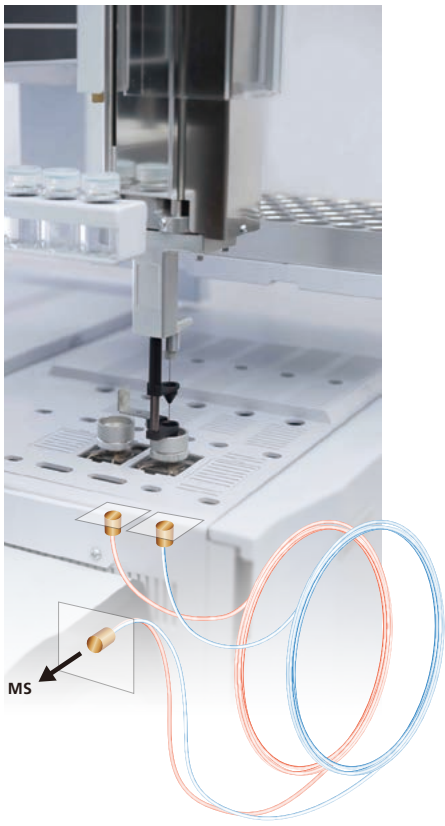
Shimadzu offers three specific GC-MS configurations to improve separation capabilities, and their features are summarized in the table below.

Table 3 | Shimadzu's recommended GC-MS configurations for optimizing separation

	Twin Line MS System	MDGC-MS (Multi-Dimensional GC-MS)	GC×GC-MS
Mechanism	Enables seamless and sequential GC-MS analyses using two columns with different selectivities. Unclear results from one column can come out more accurately on the other.	A limited range of partially or completely co-eluted components in the first column are selected by a modulator ("heart-cut") to introduce to a second, different column.	All effluents from the first column are diverted to the second short column via a thermal modulator.
Peak Capacity	N1 (line 1) or N2 (line 2)	N1 (1st dim) + N2 (2nd dim)	N1 (1st dim) × N2 (2nd dim)
Advantages	High chance of overall target coverage. No manual effort or MS vents are required to switch the columns.	Highly accurate separation of target components from a complex matrix in the first column	Comprehensive separation of all components.

Even in cases where matrix effects are not a concern, the Twin Line MS configuration is still recommended as the most versatile system for simple switching between applications. The same sample can be analyzed with two different columns simultaneously e.g. for SVOC and VOC components.

Featured Application: Pesticide analysis with the Twin-Line MS system



*Do note that Twin Line does not support simultaneous analysis of the two lines

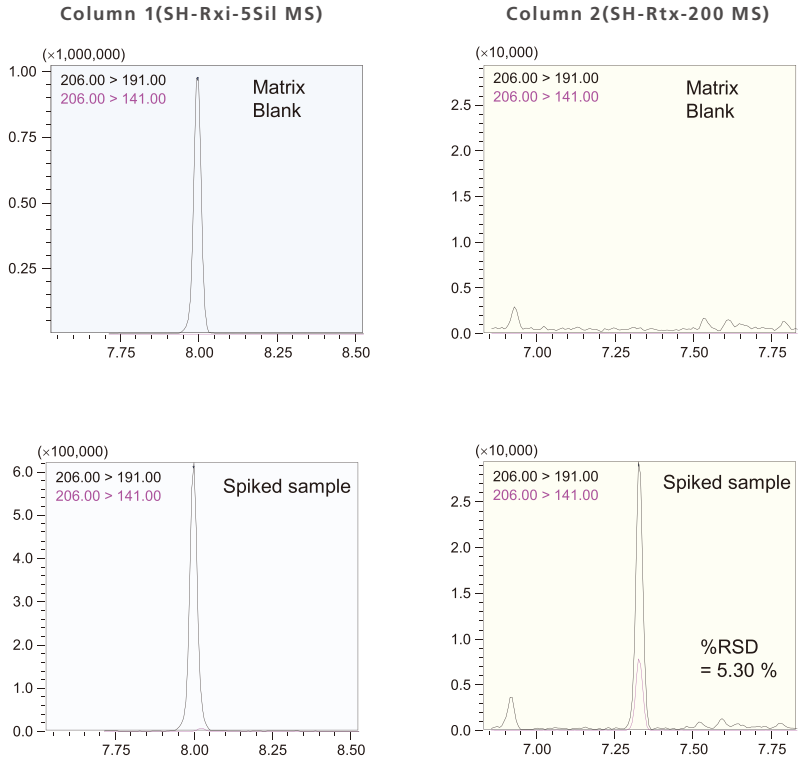


Fig. 2: MRM Chromatograms of Chloroneb in a Soy Bean Sample Using Column 1 (left) and Column 2 (right)

Application Data Sheet:

Simultaneous Analysis of 477 Residual Pesticides in Agricultural Crops Using GC-MS/MS - Part 2

Link

Click here >

4.4 MS detection and data processing

Here we introduce Shimadzu solutions for improving the detection stage in specific types of analysis.

Triple quadrupole MS

Using a triple instead of a single quadrupole MS can improve the sensitivity and selectivity of GC-MS analysis. MRM mode can be used to separate co-eluting peaks or eliminate background matrix interference.

Application News:
Ultra-Fast Analysis of Volatile Organic Compounds in Water By Headspace-GC/MS/MS

Link

Click here >

Analysis applications with the Py-Screener

Py-Screener is a total solution for phthalate ester screening using the thermal desorption mode of EGA/PY-3030D.

• Phthalate ester screening system

The use of phthalate esters is restricted in toys and food packaging, which are expected to be classified as restricted substances in the RoHS(II) directives. This system is simple to operate, even for novices. It consists of special software to support a series of procedures from sample preparation to data acquisition, data analysis and maintenance, as well as special standard samples and a sampling toolkit.

Application Data Sheet:
Analysis of Phthalate Esters Using the Py-Screener (1)

Link

Click here >

• Simultaneous screening of phthalate esters and brominated flame retardants

Brominated flame retardants are also restricted as hazardous substances. With the Py-Screener method package, they can be screened for simultaneously with phthalate esters.

Application Data Sheet:
Analysis of Phthalate Esters Using the Py-Screener (2)

Link

Click here >

• Simultaneous analysis of additives in medical supplies

This application uses Py-Screener to analyze various medical supplies. A simultaneous Scan/SIM analysis method was paired with Py-Screener's high-speed scanning mode to perform both a highly sensitive screening analysis for phthalate esters using SIM and a simultaneous qualitative analysis of other additives based on Scan information.

Application Data Sheet:
Screening Analysis of Phthalate Esters and Qualitative Analysis of Other Additives in Medical Supplies Using the Py-GC/MS Screening System

Link

Click here

Shimadzu databases and libraries

4.5 Maintenance and consumable supplies

Equipment maintenance and uninterrupted operation are fundamental to achieving greater reliability and productivity. Shimadzu instruments are designed for superior ease-ofmaintenance, and professional service engineers are available to assist with any maintenance questions or issues in a timely manner.

Reliable supply of consumables is also necessary to avoid excess downtime. Shimadzu provides various consumables to enhance your GC-MS analysis.

Syringes

Shimadzu syringes for liquid injection, headspace sampling, etc. offer excellent solvent
resistance and are compatible with a wide range of temperatures.

Link

Click here

Sample injection tools

Various tools are available to enhance the reliability of your analysis:

- Septa
- Inlet liners
- Ferrules

Link

Click here

Xtra life micrsyringe

Xtra life inlet septum

Gas filter

The Super-Clean Gas Filter removes impurities from the gas line, outputting 99.9999% purity gas. This both reduces column degradation and prevents ghost peaks and detector noise. The filter is quick and easy to replace without the need for tools.

Link

Click here

Sample vials and tubes

A wide array of sample vials and tubes are available for different autosamplers.

Link

Click here

LabTotal Vial

Headspace Vial

Sample Tubes for TD

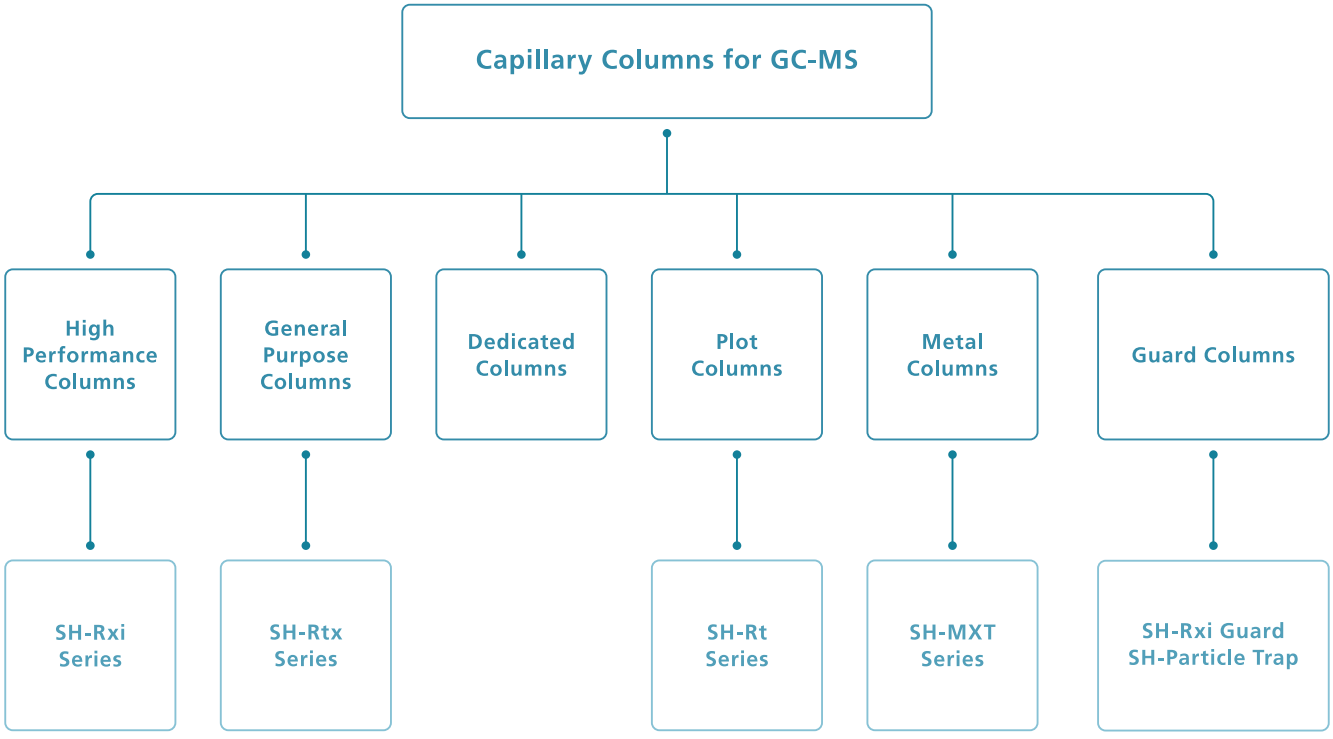
Columns

Columns are provided for analysis of a wide range of compounds and sample loads. Shimadzu columns ensure high resolution and are ultra-low bleed for high sensitivity and MS integrity.

Link

Click here >

Column types:



Appendix | List of Abbreviations

CI	Chemical Ionization
DHS	Dynamic Headspace
DI	Direct Sample Injection
DINP	Diisononyl Phthalate
DXNs	Dioxins
Direct-TD	Direct Thermal Desorption
EI	Electron Ionization
FAEs	Fatty Acid Esters
GC	Gas Chromatography
GCMS	Gas Chromatography Mass Spectrometry
GC×GC	Comprehensive Two-Dimensional Gas Chromatography
GPC	Gel Permeation Chromatography
ITEX DHS	In-tube Extraction Dynamic Headspace
Liq:	Liquid Injection
MDGCMS	Multi-dimensional GCMS
MMSE	Monolithic Material Sorptive Extraction
NCI	Negative Chemical Ionization
PAEs	Phthalates
PAHs	Polycyclic Aromatic Hydrocarbons
PBBs	Polybrominated Biphenyls
PBDEs	Polybrominated Diphenyl Ethers
PCBs	Polychlorinated Biphenyls
PPM	Parts per million
PPB	Parts per billion
PPT	Parts per trillion
PTV	Programmable Temperature Vaporization
P&T	Purge and Trap
Py	Pyrolysis
RoHS	Restriction of Hazardous Substances
SBSE	Stir Bar Sorptive Extraction
SHS	Static Headspace
SPME	Solid Phase Microextraction
SVOCs	Semi-Volatile Organic Compounds
TD	Thermal Desorption
VDA	European Automotive Industry
VOCs	Volatile Organic Compounds

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