Rev.1-0 s

Technical document 1

MonoTrap™ Guide to proper use

Recommendation of simplified method of analysis after concentration!

(Analysis of aroma components by solvent extraction)

GL Sciences Inc.

Preface

This document provides examples of how to collect samples and extract solvents using the MonoTrap™ and provides the information needed to accomplish these tasks with expertise. Please read this document before using the product.

- Based on Monolithic technologies, Merck KGaA, Darmstadt, Germany.

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Conventional sampling media used for this purpose, including SPME, are in the form of sticks or stirrer bars coated in silicon polymer to a thickness of several microns using a process of chemical bonding. The small surface area and thin coatings have disadvantages that include poor Recovery rate and the need for a long sampling time. The newly released MonoTrap™ is a collector developed using a completely new technique. It has a porous silica surface, which extends the surface area, and contains activated carbon, which provides adsorption capacity. The device can therefore be used as a tool for analysis with a high level of sensitivity that enables good Recovery rate within a short time.

The recommended simplified method of analysis after concentration

○ Is it possible to analyze aroma components after concentration simply and inexpensively?

○ Is it possible to analyze multiple samples after concentration inexpensively?

○ Is it possible to perform analysis after concentration simply, if not as simple as the thermal desorption method?

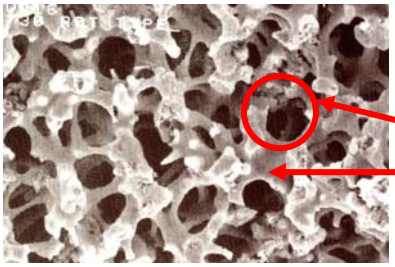
MonoTrap™ has been developed in response to these requirements and offers a simplified method of analysis after concentration.

1.What is MonoTrap™?

MonoTrap™ is an adsorptive made mainly of high-purity silica. The product features a through-pore (due to the monolith structure (Mesopore) of the silica base) and a large surface (due to the pores within the silica frame).

MonoTrap™ is available in two types, one that has the same characteristics as general silica gel and one whose silica frame contains an adsorption medium (activated carbon). The silica frame of both types is linked with ODS groups by chemical bond and is inactivated to become collection medium.

MonoTrap™ can be viewed as a new hybrid adsorptive having a large surface area and possessing the features of silica gel, activated carbon and the ODS group.



MonoTrap™ is available in two configurations, a disk type and a rod type.

Through-pore

Mesopores dotted on the structure

Enlarged view of a section of the MonoTrap™

1-1 Summary of sampling and extraction by MonoTrap™

Most SPME fiber kits currently available on the market contain PDMS (polydimethylsiloxane), PDMS/DVB (divinylbenzene) or carbon.

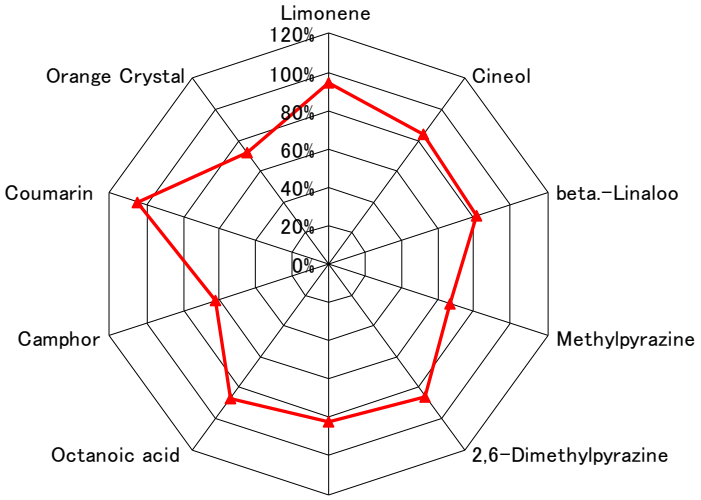
It is reported that these SPME kits have small surface areas and small trapping capacity, with Recovery rate of a few percent to 30 percent. In addition, their thick PDMS coat, which helps in sampling, requires contains considerable time to obtain vapor-liquid equilibrium or liquid-liquid equilibrium, thereby extending the sampling time and causing the efficiency to deteriorate.

Compared with these, MonoTrap™ has higher efficiency as shown below, with high trapping ability, requiring only a short time for sampling (at the time of vapor sampling in a hermetically sealed vial). This high level of efficiency is due to:

1. A large surface area of 150 m^2/g or more, thanks to its monolithic structure;
2. Activated carbon present inside and outside the frame; and
3. ODS groups chemically bonded to its surface.

These factors work in unison to provide a high level of efficiency.

Recovery rate

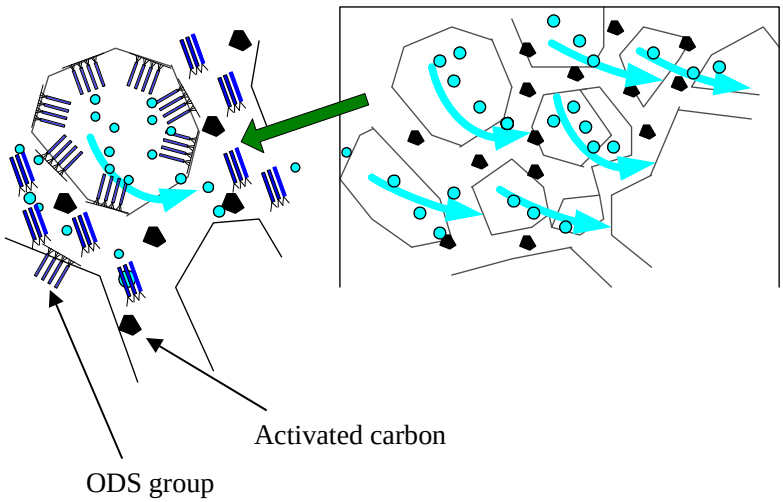


Sampling and extraction by MonoTrap™

When sample passes through the through-pores in a monolithic structure, the sample is trapped by ODS groups chemically bonded to the surface of the silica structure or by activated carbon present inside and outside the structure.

Such trapping is performed all over the large surface area of at least 150 m^2/g, which allows a high level of efficiency.

Illustration of sampling by MonoTrap™



One of the advantages of a monolithic structure is that the through-pores significantly reduce the resistance of the flow path. Therefore, the extraction solvent can be easily diffused throughout the entire structure and can effectively come into contact with ODS groups or activated carbon, so that the sampling and extraction take less time. Moreover, the large surface area ensures the trapping of larger amount of sample, which is another characteristic of MonoTrap™. Therefore, good measurement sensitivity can be obtained despite dilution due to solvent extraction.

→ A significantly large surface area enables efficient trapping.

Extraction (desorption of sample)

Likewise, when extracting the solvent, the full amount of the solvent enters the through-pores and remains in contact with the entire surface to create speedy desorption of the sample. Only a small amount of solvent allows almost complete desorption.

1-2 Types and selection of MonoTrap™

Types of MonoTrap™

cat.No	Product name	Shape	Size	Activated carbon	Functional group
1050-72101	MonoTrap DCC18	Disk	O.D.10mmx thick 1mm	Contained	C18
1050-72201	MonoTrap RCC18	Rod	O.D.2.9 mmxI.D.1mm xHight 5mm	Contained	C18
1050-71101	MonoTrap DSC18	Disk	O.D.10mmx thick 1mm	Not Contained	C18
1050-71201	MonoTrap RSC18	Rod	O.D.2.9 mmxI.D.1mm xHight 5mm	Not Contained	C18

MonoTrap™ DCC18

Disk type with a diameter of approximately 10 mm and a thickness of 1 mm, containing ODS groups and activated carbon; this type has large section area, enabling trapping of a large amount of sample (50 pieces contained in a set).

MonoTrap™ RCC18

Rod type with a diameter of approximately 2.9 mm and a height of 5 mm and with a through hole of 1 mm, containing ODS groups and activated carbon; this type is intended for screening analysis and for a high-concentration sample (50 pieces in a set).

The rod type does not require any dedicated extraction bottle, but the extraction can be performed using an insert (Cat No. 1030-41403) for an automatic sampler.

In the case of an automatic sampler that allows the angle at which the needle is inserted into the vial to be adjusted, the analysis can be performed without changing bottles (50 pieces in a set).

(The angle at which the needle is inserted should be adjusted to at least 10 mm from the lowest position.)

MonoTrap™ DSC18

Disk type with a diameter of approximately 10 mm and a thickness of 1 mm, not containing ODS groups or activated carbon (50 pieces in a set)

MonoTrap™ RCC18

Rod type with a diameter of approximately 2.9 mm and a height of 5 mm and with a through hole of 1 mm, not containing ODS groups or activated carbon (50 pieces in a set)

Selection of MonoTrap™

Selection and applications of MonoTrap™

Shape	Adsorptive	Target concentratio	Example of application
Disk	Not contained	Low concentration	Hydrophobe (medium to high boiling point)
Rod	Not contained	High concentration	Hydrophobe (medium to high boiling point)
Disk	Contained	Low concentration	Polar, hydrophic components, low to medium boiling point
Rod	Contained	High concentration	Polar, hydrophic components, low to medium boiling point

MonoTrap™ has characteristics of mesopores on silica structure, ODS groups on the surface and contained adsorptive. These characteristics exert their effects in a manner that is so complex that the resulting adsorbing property is not uniform. See the table above when selecting the suitable type.

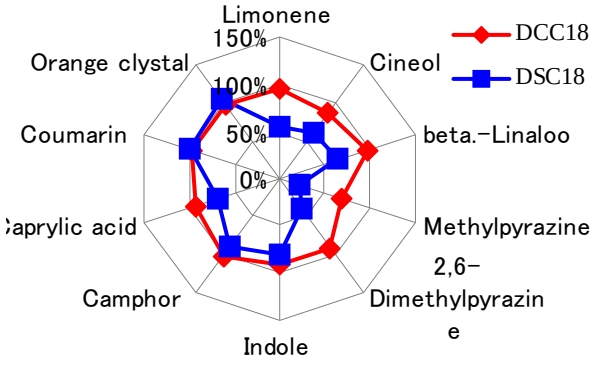
MonoTrap™ DSC18, RSC18 (not containing activated carbon and containing ODS groups)

These types contain ODS groups on the silica structure and are subjected to end cap treatment. The surface of their structure is very hydrophobic, so they can be effectively used for hydrophobic components. Mesopores on the silica frame also contribute to adsorption, so these types are believed to adsorb polar materials and hydrophilic components.

MonoTrap™ DCC18, RCC18 (containing activated carbon and ODS groups)

These types differ from the types above in that they contain activated carbon. The activated carbon is exposed at the surface of the structure. This activated carbon is believed to contribute considerably to the adsoption of polar, low-boiling-point or aromatic components.

The graph below provides a comparison between the Recovery rate of DCC18 (containing activated carbon) and DSC18 (not containing activated carbon) (the Recovery rate is calculated when the standard samples mentioned below are added to a 44-mL vial to which a MonoTrap™ is loaded). Dichloromethane was used as extraction solvent.



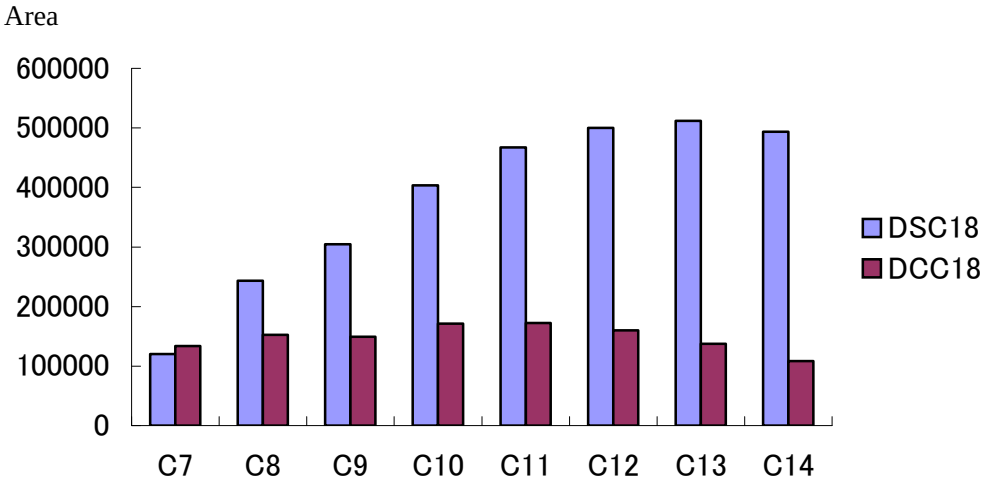
As shown in the graph above, coumarin and orange crystal that are both highly hydrophobic can be collected to a similar degree either by DSC18 (not containing activated carbon) or DCC18

(containing activated carbon). However, polar components are more effectively collected by DCC18 (containing activated carbon). This fact shows that the activated carbon helps a great deal in the collection of polar components and nitrogen-containing components.

<Information Item 1> Comparison of characteristics between DSC18 (not containing activated carbon) and DCC18 (containing activated carbon) in the case of hydrophobic sample

○ Experimental method

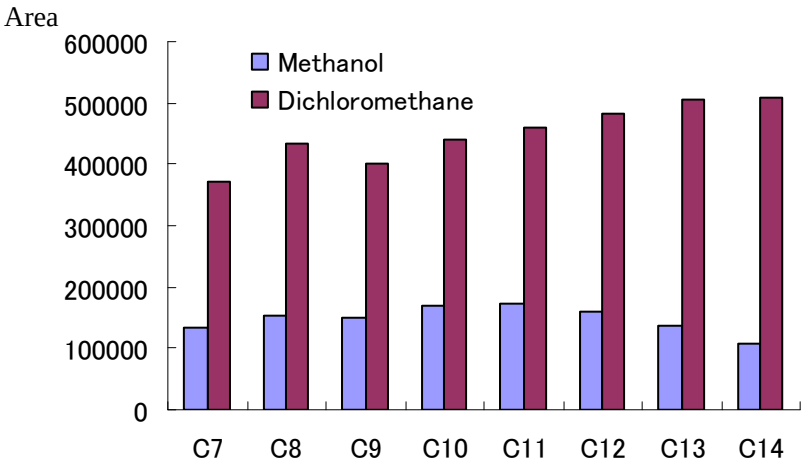
Two microliters of straight-chain hydrocarbons (C5 to C14) in 1 mg/mL were added, as a hydrophobic sample, to 40 mL of 15% NaCl solution (the absolute volume of each sample is 2 μL/40 mL, 50 ppb). The solution was stirred in a constant temperature shaking bath at 60°C, 90 rpm, for 30 minutes. Each hydrocarbon was then extracted with 400 μL of methanol and measured by GC-MS.



DCC18 containing activated carbon shows larger areas on low-boiling-point components, and its areas decrease as the carbon number exceeds C8 (this failure is expected to be corrected by changing the extraction solvent). On the other hand, DSC18 tends to show larger areas as the carbon number increases.

This result indicates that DSC18, which is weak at trapping low-boiling-point compounds and good at extracting of high-boiling-point compounds, is suitable for trapping medium- to high-boiling-point hydrophobic samples.

Concerning DCC18, it can effectively collect low-boiling-point compounds thanks to the adsorbing effect of activated carbon. However, the low Recovery rate of high-boiling-point compounds indicates that it may be weak at extracting high-boiling-point compounds. Therefore, in the case of use of methanol as extraction solvent, DCC18 is suitable for low to medium-boiling-point hydrophobic samples.



In order to improve the extraction capacity, highly solvent dichloromethane may be used as solvent. Extraction effects in case of use of dichloromethane and methanol are shown below. This graph explicitly shows that the tendency of decrease is considerably corrected by use of dichloromethane.

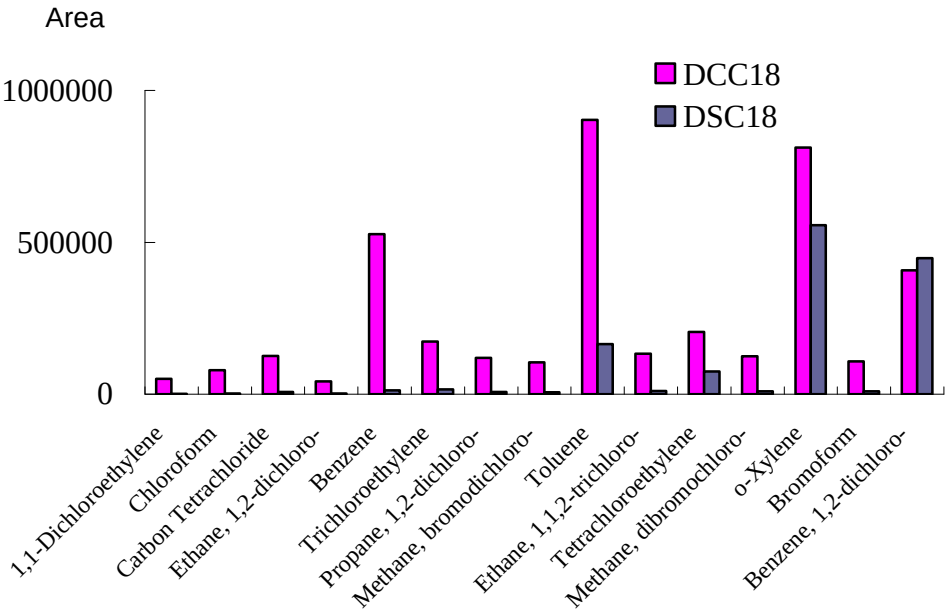
The Recovery rate also depends largely upon selection of extraction solvent.
Especially in case of DCC18, highly solvent chemicals, if used as a solvent, are expected to bring about high efficiency.

<Information Item 2> Comparative experiment between DSC18 and DCC18 in the case of low-boiling-point samples, volatile halogenated hydrocarbons

Experimental method

An amount corresponding to 2 μg of samples mentioned below were added to 40 mL of 15% NaCl solution. The solution was stirred in a constant temperature shaking bath at 60°C, 90 rpm, for 1 hour. Then, each sample was extracted with 400 μL of methanol and measured by GC-MS.

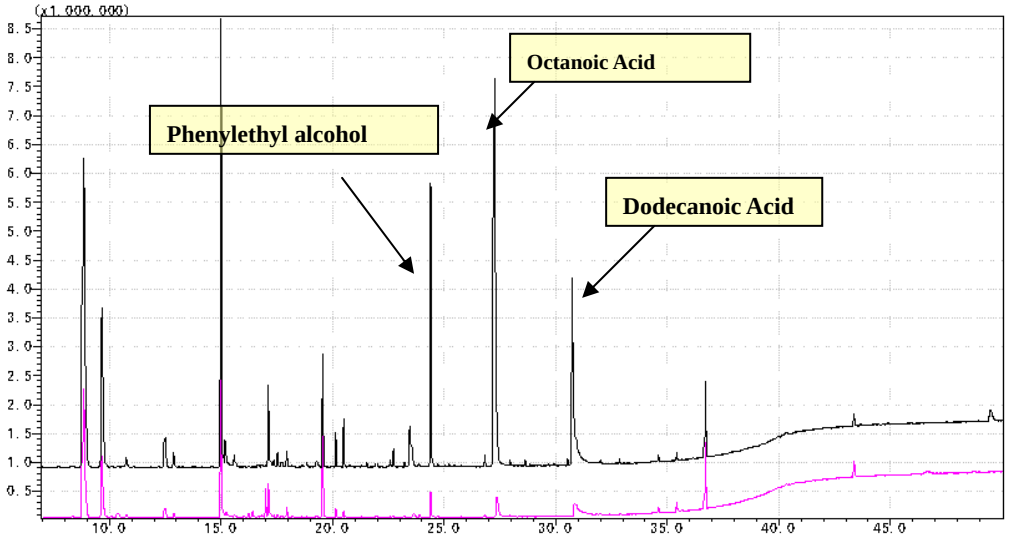
Comparison between DSC18 and DCC18 in case of halogenated hydrocarbons



The result of the experiment shows that DCC18 (containing activated carbon) has apparently higher Recovery rate of low-boiling-point halogenated hydrocarbons than does DSC18 (not containing activated carbon).

<Information Item 3> Comparison in the case of polar samples

A comparative test has been conducted between DCC18 and DSC18, using white wine as sample. The result shows that there is a remarkable difference in trapping efficiency of polar components.



1-3 Precautions when using the MonoTrap™

As most of the aroma components are polar, the DCC18 (containing activated carbon) can collect them more effectively than can the DSC18. It is true that DCC18 (containing activated carbon) is so sensitive that it can detect even a very small amount of component, but its high adsorbing capacity may cause it to trap even unnecessary components in a blank test. Moreover, to extract high-boiling-point components or polar components from the activated carbon contained in DCC18, it is necessary to use highly polar solvent. The types of MonoTrap™ or solvent should be carefully selected according to the nature of the sample to be tested or the chemical component to be extracted.

Use of MonoTrap™ enables easy, inexpensive screening. When screening any unknown sample, it is recommended that you conduct screening twice using both the DCC18 and the DSC18 and that you select either result suitable for the purpose.

Storage of MonoTrap™

MonoTrap™ is likely to adsorb components in the ambient atmosphere. Unless properly stored, it may start showing high blank values during storage. Be sure to store it in a clean and hermetically sealed container. After unpacking, it is recommended that you use all the pieces as soon as practicable.

Note: MonoTrap™ is, by its nature, not reusable. It may be repeatedly used for solvent cleaning, aging treatment or conditioning, but its trapping capacity may deteriorate and it becomes less reliable.

2. Comparison of performances with other manufacturer's products

Various performances concerning the sampling have been compared between MonoTrap™ and other products available in the market.

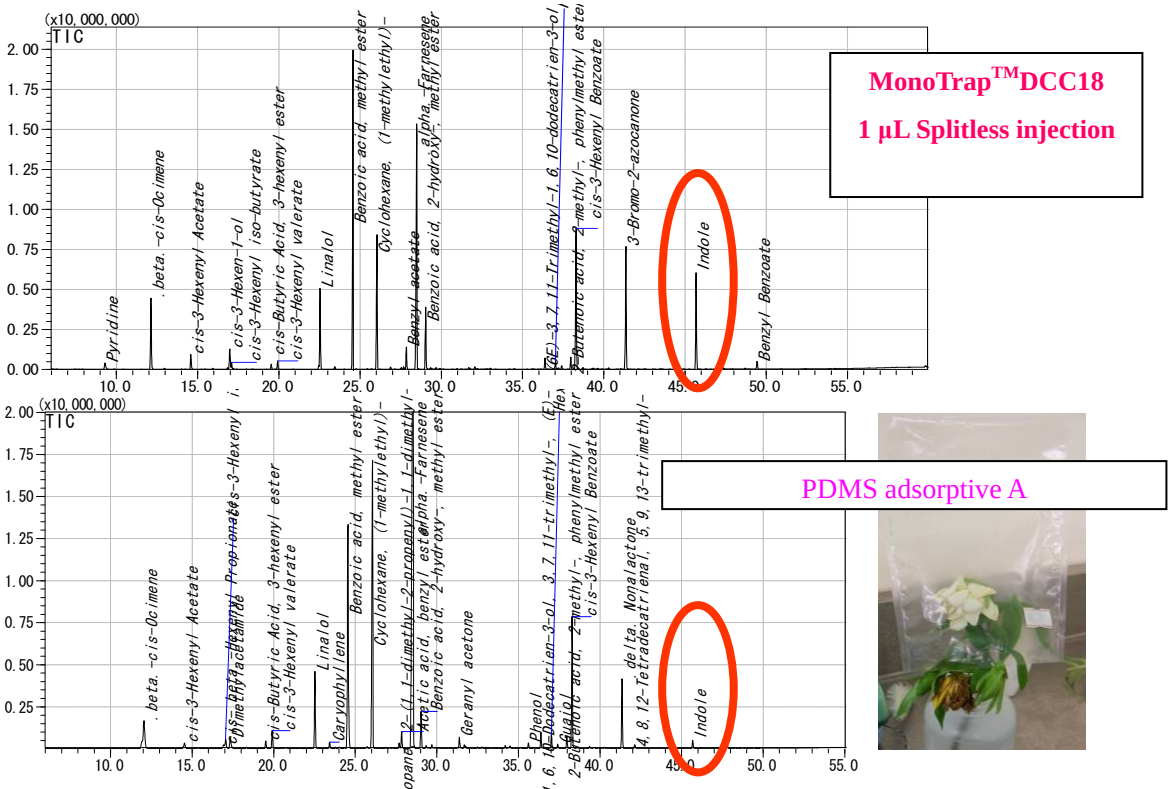
2-1 Comparison of performances in the collection of actual sample (comparison between fiber type and MonoTrap™)

Some gardenia leaves were put in a Tedler Bag. A piece of MonoTrap™ DCC18 and a PDMS adsorptive A were put in the same bag to conduct passive sampling for three hours. After sampling, the MonoTrap™ was subjected to extraction with 1 mL of dichloromethane as solvent, concentrated to a volume of 100 μL, from which 1 μL was inserted into GCMS, while the adsorptive A was directly inserted in GC-MS to be analyzed by thermal desorption.

The result of this experiment shows that its high trapping capacity enables MonoTrap™, even after 100-fold dilution, to obtain sensitivity not less than the thermal desorption with the whole volume injected.

(Note that there is, however, a significant difference observed about the indole.)

In case of the thermal desorption method, redoing the sampling operation for an extended period is required in the event of injection into GC or the failure to satisfy any analysis condition. On the contrary, in the case of the solvent extraction method, there remains part of an extracted sample that facilitates the revision of analysis conditions.



The graphs above are results retrieved from the MS library and not the result of identification using standard samples.

2-2 Comparison with other manufacturer's product in the octanol/water partition coefficient (LogP)

Octanol/water partition coefficient (LogP) represents the ratio of the concentration of a chemical in the n-octanol phase and in the aqueous phase at equilibrium and constitutes an index indicating whether the chemical is hydrophilic or hydrophobic. For example, LogP = 2 means that its concentration in octanol is 100 times higher than that in water. The smaller the value is, the larger its hydrophilicity becomes and the much more difficult it becomes to collect it from the water.

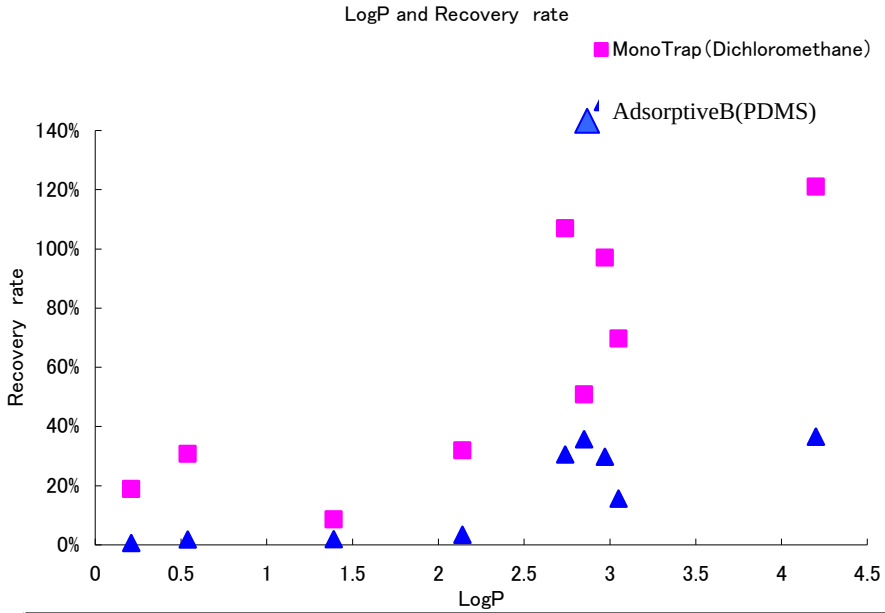
The graph below compares the Recovery rate by MonoTrap with that by another manufacturer, company B's PDMS adsorptive, with the horizontal axis representing the octanol/water partition coefficients (LogP) for the sample mentioned below.

○ Experimental method

Five nanograms of the standard samples mentioned below were added to 20 mL of 15% NaCl solution and the trapping was performed by a piece of MonoTrap™ DCC18 and PDMS adsorptive B. For MonoTrap™ DCC18, the solution was stirred in a constant temperature shaking bath at 60°C, 90 rpm, for 30 minutes. For PDMS adsorptive B, the solution was stirred by means of a magnetic stirrer at 60°C. Then, MonoTrap™ was subjected to the extraction by 200 μL of dichloromethane while PDMS adsorptive B was subjected to the extraction by 200 μL of acetonitrile. Subsequently, the extracted chemicals were measured.

Generally, MonoTrap™ presents higher Recovery rate than other manufacturer's products, even in the case of hydrophilic samples. Concerning adsorptive B, whose PDMS phase is vulnerable to damage, only the acetonitrile can be used as an extraction solvent. Highly solvent chemicals such as dichloromethane cannot be used as solvents.

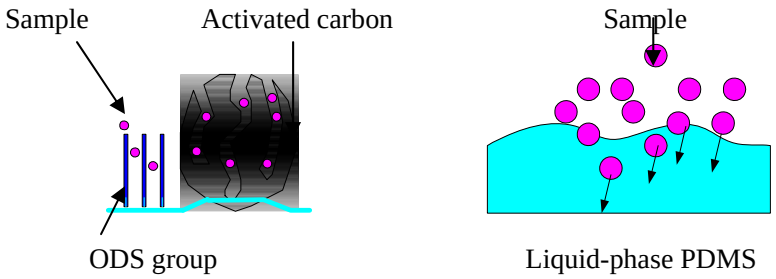
In the case of MonoTrap™, however, which is composed of silica gel and modified by ODS groups, such chemicals can be also used as solvent. Therefore, you can select suitable solvent according to the sample to be tested.



	LogP	MonoTrap	Adsorptive B(PDMS)
Methylpyrazine	0.21	18.8%	0.6%
2,6-Dimethylpyrazine	0.54	30.7%	1.8%
Indole	2.14	32.0%	3.5%
Cineol	2.74	107.0%	30.5%
Linalool	2.97	97.0%	29.8%

3. Collection of a gaseous sample

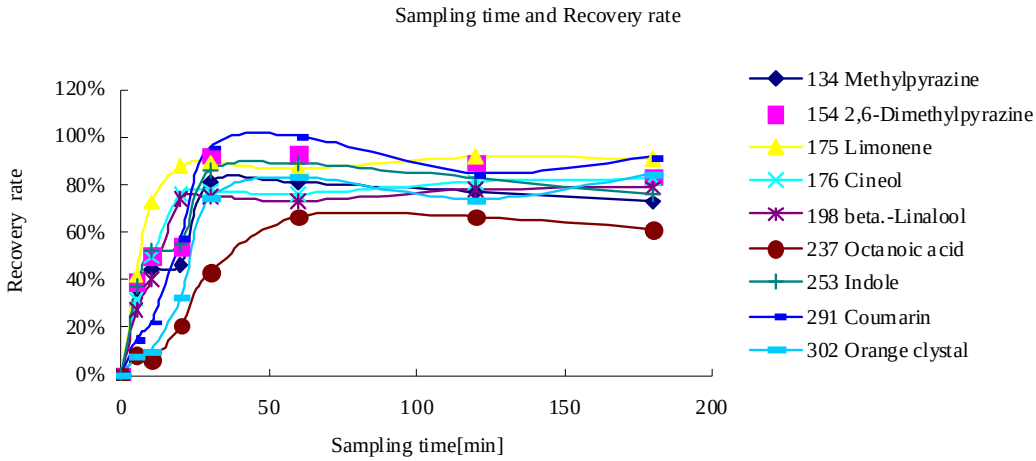
While sampling with PDMS needs considerable time to obtain vapor-liquid equilibrium, MonoTrap™ can perform sampling within a shorter time period because the sample is trapped by ODS groups chemically bonded to the silica structure surface and because the activated carbon exerts the adsorbing effect.



3-1 Sampling time and Recovery rate of gaseous sample

○ Experimental method

The standard samples in the amount corresponding to 125 ppb of concentration in ambient atmosphere were added to a hermetically sealed vial (with a capacity of 40 mL). They were then subjected to sampling (at 60°C) by means of a piece of MonoTrap™ DCC18, solvent extraction and measurement.The sampling time and Recovery rate were calculated for each compound (Recovery rate calculated assuming that all samples have been vaporized).

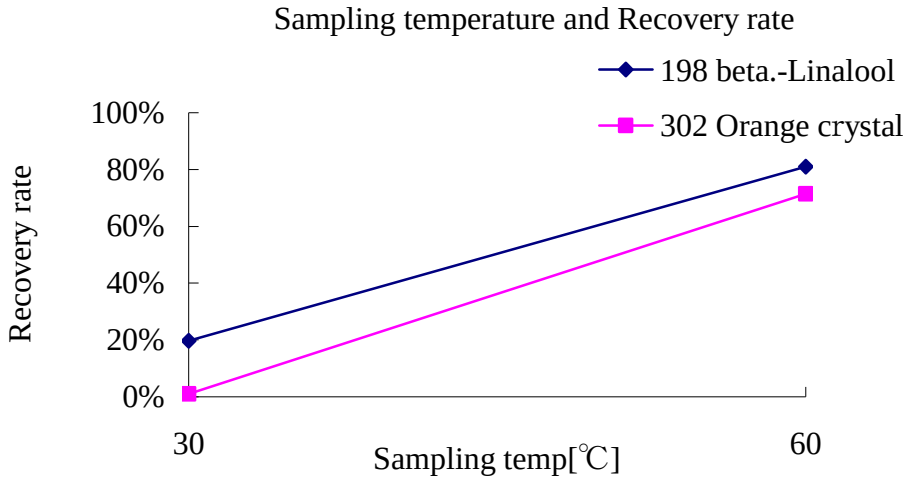


In the case of polar samples such as acidic compounds or basic compounds, it is recommended that around 60 minutes be planned as the sampling time in order to obtain sufficient Recovery rate despite the influence of water vapor or adsorption on the vial.The trapping efficiency of other less adsorbing samples is believed to depend on the boiling point. Heating the sample as indicated above helps shorten the sampling time. For example, the orange crystal (b.p. 302°C) has been collected with satisfactory efficiency after 30 minutes of sampling time.

3-2 Sampling temperature and Recovery rate of gaseous samples

The collection efficiencies in 30°C and in 60°C were compared with each other according to the experimental method mentioned above (the sampling time fixed to thirty minutes).

Since the diffusion coefficient of a vapor depends on the temperature, the sampling time can be shortened by heating. The graph at the right provides an example, illustrating the result of an experiment where linalool and orange crystal, which are relatively non-reactive, are used. It is confirmed that the Recovery rate increases in proportion to the temperature.



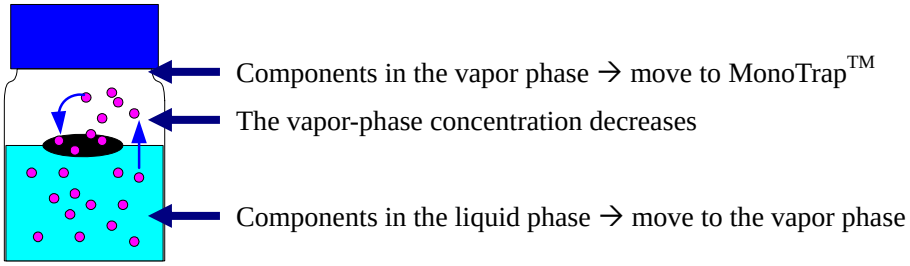
For the effective collection of gaseous samples

In the case of gaseous samples, sufficient efficiency can be obtained with a sampling time of around 20 to 30 minutes.

Aside from the differences caused by the boiling point, it is recommended that the sample be heated to approximately 60°C for shortening the sampling time.

4. Sampling of water-soluble samples

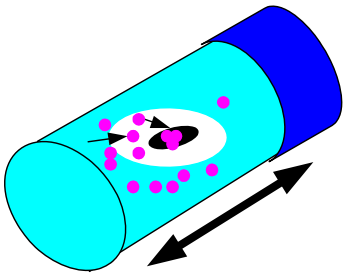
In a vial to which liquid samples are added, the components will move according to the vapor-liquid partition coefficient until equilibrium is attained. MonoTrap™, whose surface is highly hydrophobic due to bonded ODS groups and end-cap treatment, floats on the surface of the liquid. As MonoTrap adsorbs the components from the vapor phase, the low-boiling-point components move to the vapor phase, increasing the concentration at the vapor phase, which accelerates the sampling, until equilibrium is attained. The hydrophilic components in the liquid are directly adsorbed by the activated carbon layer of MonoTrap.



4-1 Principles of sampling water-soluble samples

As described above, components move among three phases, namely the liquid phase, vapor phase (at the head space) and MonoTrap™ to finally be trapped by MonoTrap™.

As the move between the liquid and vapor phases depends upon the partition coefficient, treatments such as salting-out or pH control can be performed as in the case of solvent extraction or solid-phase extraction. This feature is expected to effectively shorten the sampling time or increase the Recovery rate.



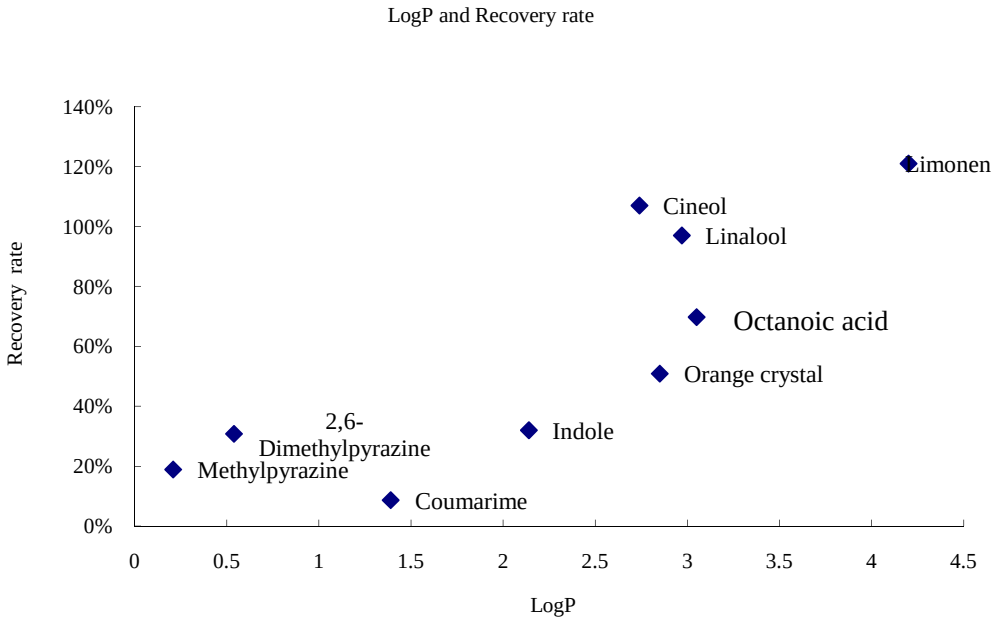
When used for the water sample, MonoTrap™ whose surface is highly hydrophobic due to bonded ODS groups and end-cap treatment, does not sink but floats on the surface of the liquid. If the vial is shaken during sampling, MonoTrap™ sways with the vapor phase inside the vial and the liquid phase itself also is agitated. Accordingly, movement of the components to MonoTrap™ is accelerated, reducing the sampling time. Because of the hydrophobicity of the whole surface and the through-pore frame (with an inner diameter of approximately 3 to 5 μm), the liquid is in contact only with the surface of MonoTrap™ and does not penetrate inside. Therefore, after sampling, the tube can be easily dry-purged.

(Hydrophobic liquids or organic solvents can penetrate MonoTrap™, causing it to sink. MonoTrap™ is not suited for treating these liquids or solvents.)

4-2 Water-octanol partition coefficient of sample and Recovery rate

○ Experimental method

25 μL of the standard samples mentioned below (200 μg/mL) were added to 20 mL of 15% NaCl solution. The solution was stirred with a piece of MonoTrap™ (DCC18 containing activated carbon, in a shape of a disk) in a constant temperature shaking bath at 60°C, at 90 rpm, for 30 minutes. Then, the samples were extracted with dichloromethane and measured.The graph below indicates the relationship between LogP and the Recovery rate of each sample. High collection efficiencies not less than 19% were obtained even in the case of hydrophilic samples whose LogP is lower than 1. MonoTrap™ thus recorded high collection efficiencies for a wide variety of samples.



4-3 Comparison of sampling methods of samples in water

For the sampling of water samples using MonoTrap™, there are various methods, including the Head Space (HS) method, the stirring method and the floating method. The collection efficiencies in these methods have been compared.

○ Experimental method

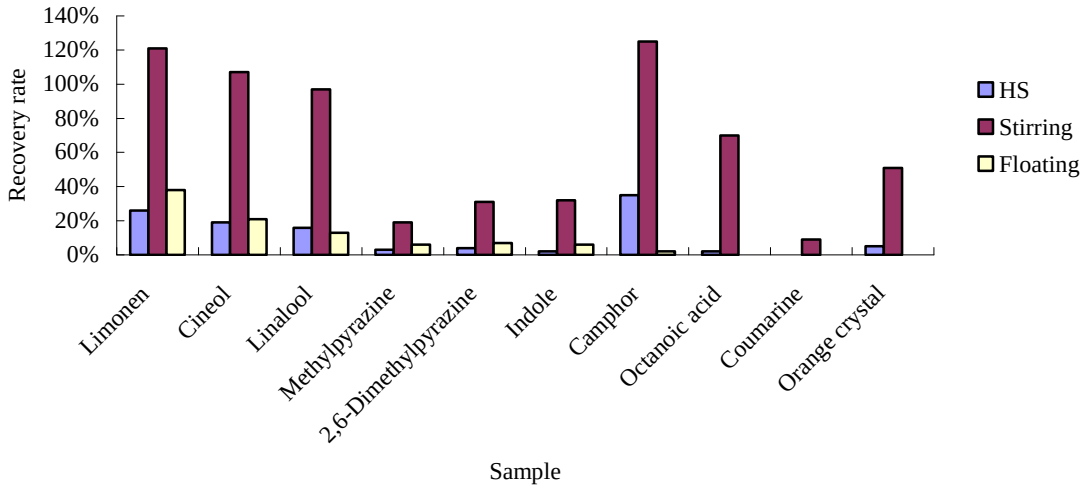
Twenty-five microliters of the standard samples mentioned above (200 μg/mL) were added to 40 mL of 15% NaCl solution. The samples were collected by means of a piece of MonoTrap™ DCC18.

- Head Space method → The solution was left untouched at 60°C for 30 minutes.
- Stirring method → The sample bottle with a piece of MonoTrap™ inside was stirred at a constant-temperature agitation bath at 60°C, at 90 rpm, for 30 minutes.
- Floating method → A piece of MonoTrap™ was put on the surface of the sample liquid and the sample was left untouched in a constant temperature bath at 60°C for 30 minutes.

Each sample was extracted with the solvent and measured. (The Recovery rate was calculated taking as reference the added volume.)

The result of this experiment shows that stirring generally helps improve the Recovery rate. Further improvement can be expected from other treatments, such as salting-out or pH control, conducted in addition to stirring.

Comparison of recovery rate obtained by different sampling methods



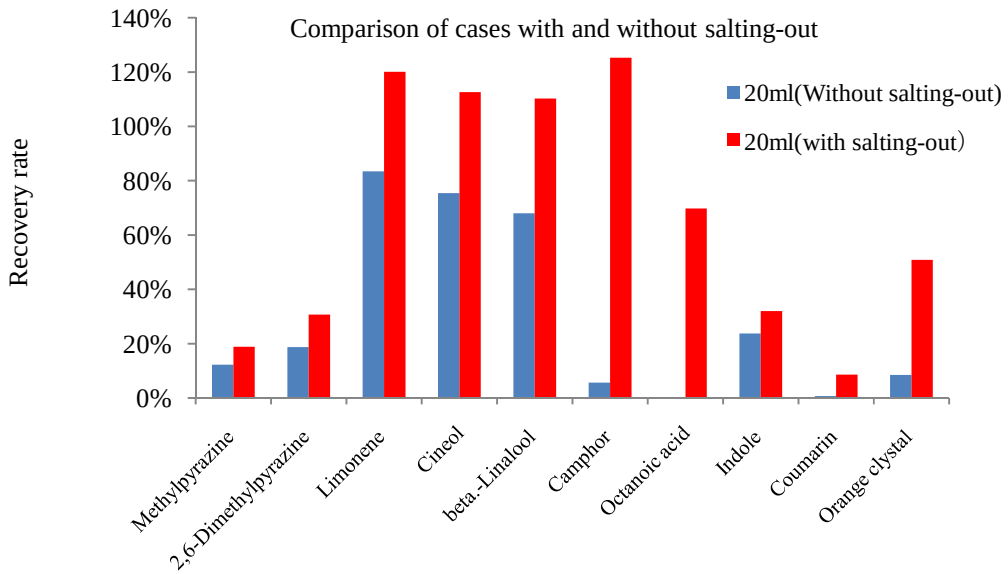
4-3-1 Consequences of salting-out of water samples

The most effective method, that is to say, the stirring method was adopted for this experiment.

○ Experimental method

Twenty-five microliters of the standard samples mentioned above (200 μg/mL) were added to 20 mL of 15% NaCl solution. The solution was stirred with a piece of MonoTrap™ (DCC18 containing activated carbon, in the shape of a disk) in a constant-temperature agitation bath at 60°C, at 90 rpm, for 30 minutes. Then, samples were extracted with dichloromethane.

As shown below, salting-out generally improves the Recovery rate. In addition to salting-out, it is also recommended that the pH of the sample solution be controlled as necessary in order to improve the partition coefficient.

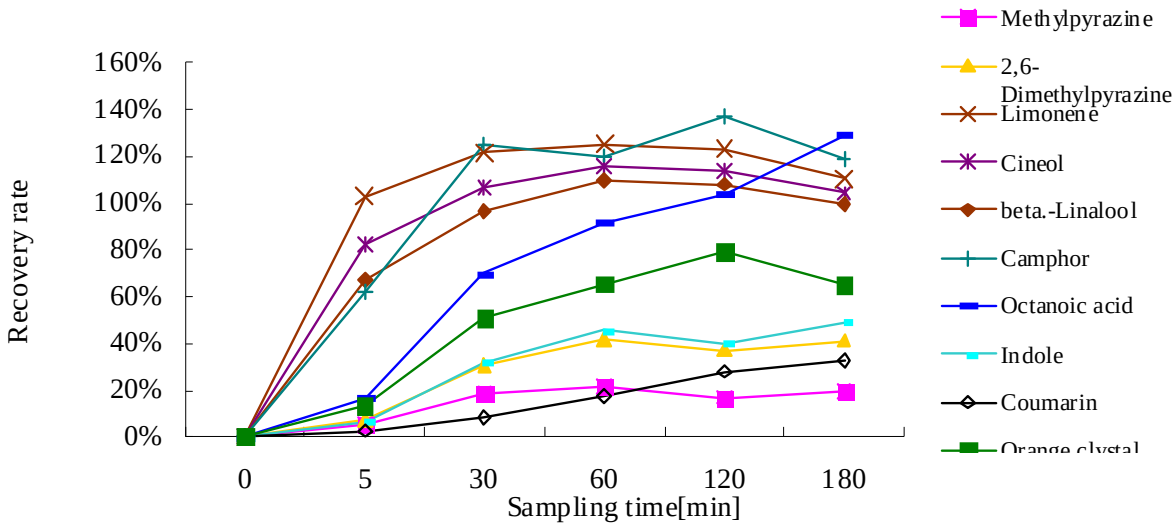


4-3-2 Consequences of difference in sampling time of water samples

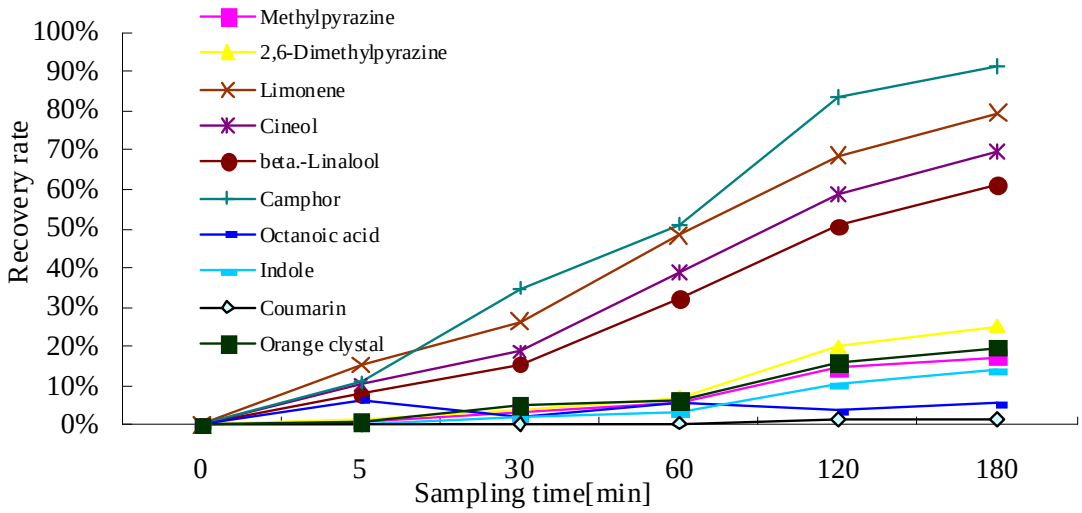
○ Experimental method

Twenty-five microliters of the standard samples mentioned above (200 μg/mL) were added to 20 mL of 15% NaCl solution. The samples were collected by means of a piece of MonoTrap™ (DCC18 containing activated carbon, in the shape of a disk).- Shaking method The sample bottle was stirred in a constant-temperature agitation bath at 60°C, at 90 rpm, for different sampling times.- Head Space method The solution was heated to 60°C and left untouched for different sampling times.In the case of water samples, the components move between the solvent and HS area only by diffusion before being trapped by MonoTrap™, so a long time is required before the sample concentration reaches equilibrium.If the liquid is stirred, equilibrium is generally attained in approximately 30 minutes. However, in the case of an acidic sample, octanoic acid, approximately 60 minutes is required.

Comparison of collection efficiencies using the stirring method with salting-out according to different sampling times



Comparison of collection efficiencies using the HS method with salting-out according to different sampling times



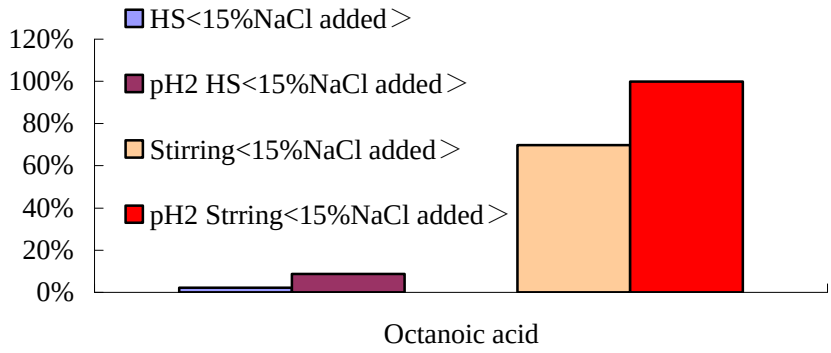
4-3-3 Consequences of pH control

○ Experimental method

Twenty-five microliters of the standard samples (200 μg/mL) were added to 20 mL of 15% NaCl solution (adjusted to pH2 by 1M phosphoric acid). The samples were collected by means of a piece of MonoTrap™ DCC18.

- Shaking method The sample bottle was stirred in a constant-temperature agitation bath at 60°C, at 90 rpm, for 30 minutes.

- Head Space method The solution was heated to 60°C and left untouched for 30 minutes.



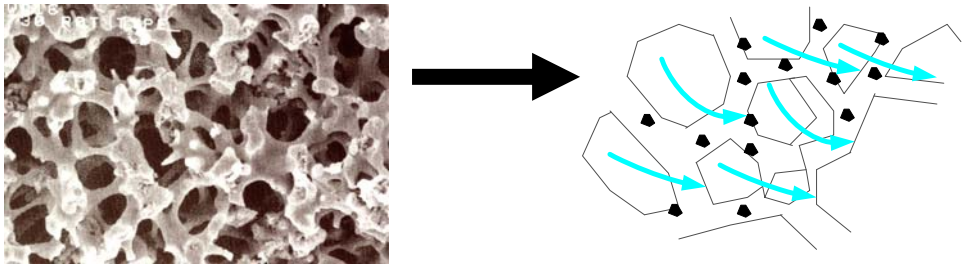
As shown above, pH control and salting-out improve the Recovery rate of the acid sample almost to 100%. Salting-out is useful for sampling of water samples, but pH control, used together with salting-out, further improves the Recovery rate. The stirring method is considered to be more effective than the HS method.

MonoTrap™ itself has advantages, such as high trapping capacity and short extraction time. However, in the case of liquid samples, the sampling efficiency or extraction efficiency largely depends upon the nature of the samples and the matrix effects. It is recommended that salting-out or pH control be adopted as necessary in order to improve the Recovery rate of the target samples.

5. Analysis operation after sampling

Desorption factor

The through-pore in monolithic structure allows the extraction solvent to come into contact with the entire surface, largely facilitating the desorption of samples. MonoTrap™ can be used for both the solvent extraction and the thermal desorption. The disk type in particular is suitable for the solvent extraction and the rod type for the thermal desorption.



5-1 The most suitable method of solvent extraction

The samples trapped by MonoTrap™ can be extracted by a small amount of solvent within a short time.

At least 200 μL of extraction solvent is required for the extraction of samples for the purpose of screening analysis, and at least 500 μL is required for the purpose of quantitative analysis.

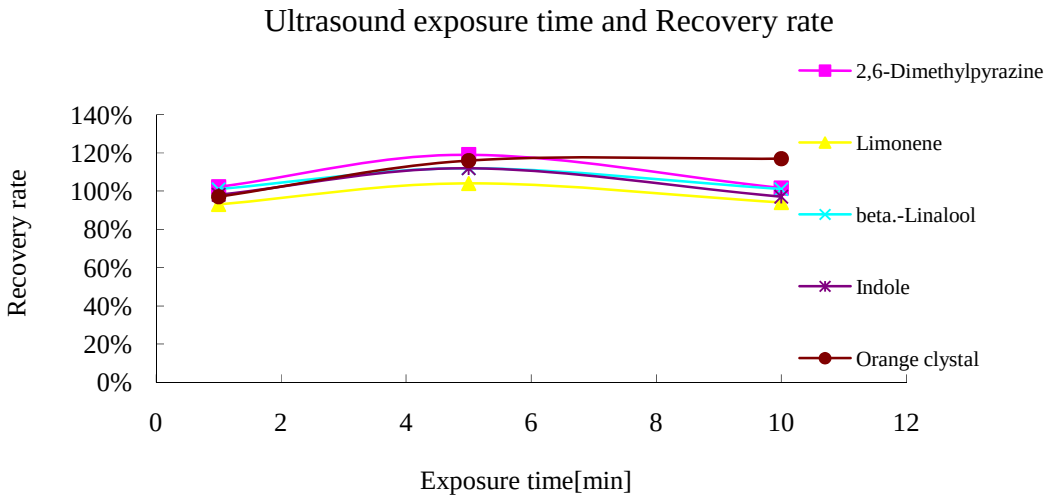
Depending upon the target sample concentration, the concentrating operation, such as nitrogen gas purge, may be desirable to improve the sensitivity. In this case, due attention should be paid to the loss of volatile components to be extracted. It is recommended that the vial be exposed to ultrasound for a short time during extraction.

5-1-1 Extraction time

The graph below shows the variation of the Recovery rate of the extraction with 500 μL of dichloromethane according to the time of exposure to ultrasound. It suggests that an exposure to ultrasound for around one minute allows sufficient Recovery rate to be attained.

○ Experimental method

The standard samples in the amount corresponding to 125 ppb of concentration in ambient atmosphere were added to a hermetically sealed vial (with a capacity of 40 mL). They were then subjected to sampling (at 60°C) by means of a piece of MonoTrap™ DCC18, changing the ultrasound exposure time during extraction. Subsequently, the Recovery rate was measured.

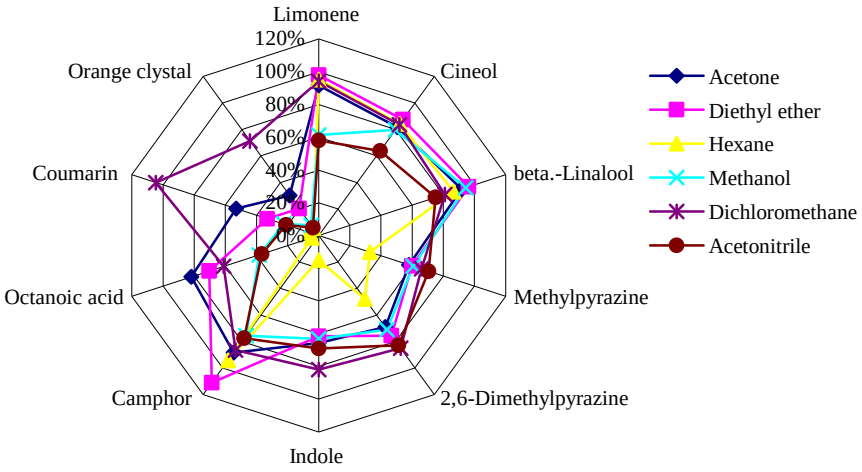


Please note, however, that exposing the vial to ultrasound for too long a time may cause it to be heated and the solvent to be volatilized. (As a guide, the effect of exposure is reduced when the time exceeds five minutes.)

5-1-2 Comparison of recovery rate by different solvents

The solvent to be used for extraction should be selected according to the samples to be extracted. Dichloromethane, acetone, methanol, ethanol, hexane or other solvents can be used for MonoTrap™. The Recovery rate may differ depending on the selected solvent, so please select the one that is suitable for your purpose.

○ Experimental method: standard samples in the amount corresponding to 100 ppb of concentration in an ambient atmosphere were added to a hermetically sealed vial (with a capacity of 40 mL). They were then subjected to sampling (at 60°C) by means of a piece of MonoTrap™ DCC18, and extracted with 500 μL of the solvent indicated below.



In this experiment, samples were extracted most effectively when dichloromethane was used. For DCC18 used here, which includes activated carbon on its frame, it is recommended to use highly solvent dichloromethane or acetone. Concerning DSC18, which does not have an adsorptive capacity supplied by activated carbon, only a small difference in extraction efficiency is caused by the different solvents.

5-2 Reproducibility and quantitativeness of extraction efficiency (linearity)

Highly reproducible data can be obtained by a simply designed concentration analysis method using MonoTrap™.

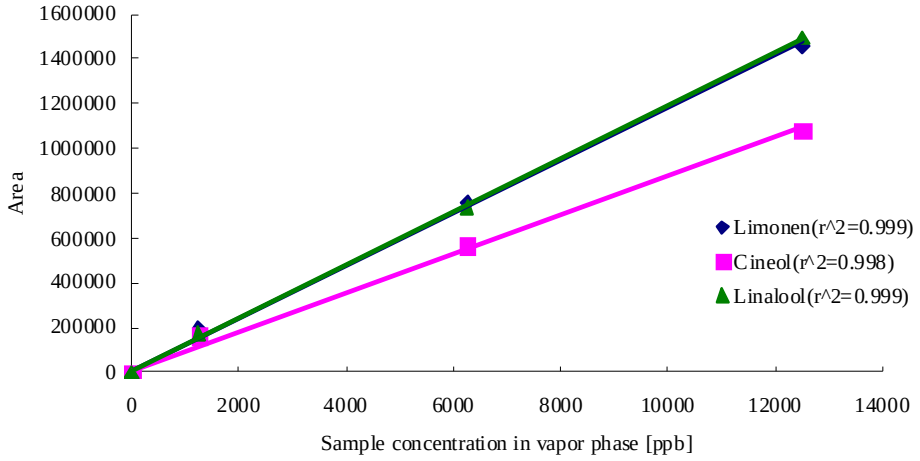
○ Experimental method: standard samples in the amount corresponding to 100 ppb of concentration in ambient atmosphere were added to a hermetically sealed vial (with a capacity of 40 mL). They were then subjected to sampling (at 60°C) by means of a piece of MonoTrap™ DCC18, and extracted with 500 μL of solvent.

Reproducibility of recovery rate

		n1	n2	n3	n4	n5	Cv
Terpene alcohol	Limonene	494006	485681	496876	536678	445839	7%
	Cineol	466202	462056	467971	503924	414963	7%
	beta.-Linaloo	374763	376581	379221	409548	344641	6%
Nitrogen compounds	Methylpyrazine	475084	495867	400198	444554	478906	8%
	2,6-Dimethylpyrazine	600413	615705	515633	551620	587695	7%
	Indole	933392	943024	799651	865060	902124	7%
ketone carbonyl	Camphor	392101	416782	352397	401182	382398	6%
	Caprylic acid	222252	249125	189229	208219	181751	13%
	Coumarin	406345	433194	346172	405409	383219	8%
	Orange clystal	435164	456385	339972	436287	433021	11%

Check of linearity

○ Experimental method: standard samples were directly added to a hermetically sealed vial in amounts that were appropriate to obtain each concentration in a vapor phase, and heated to 60°C, then subjected to sampling by means of a piece of MonoTrap™ DCC18. They were then extracted with 500 μL of dichloromethane while being exposed to ultrasound and measured.



As shown above, almost complete linearity, that is to say, quantitativeness was confirmed.
The values of linearity may vary depending upon the adsorptive characteristics of the samples.

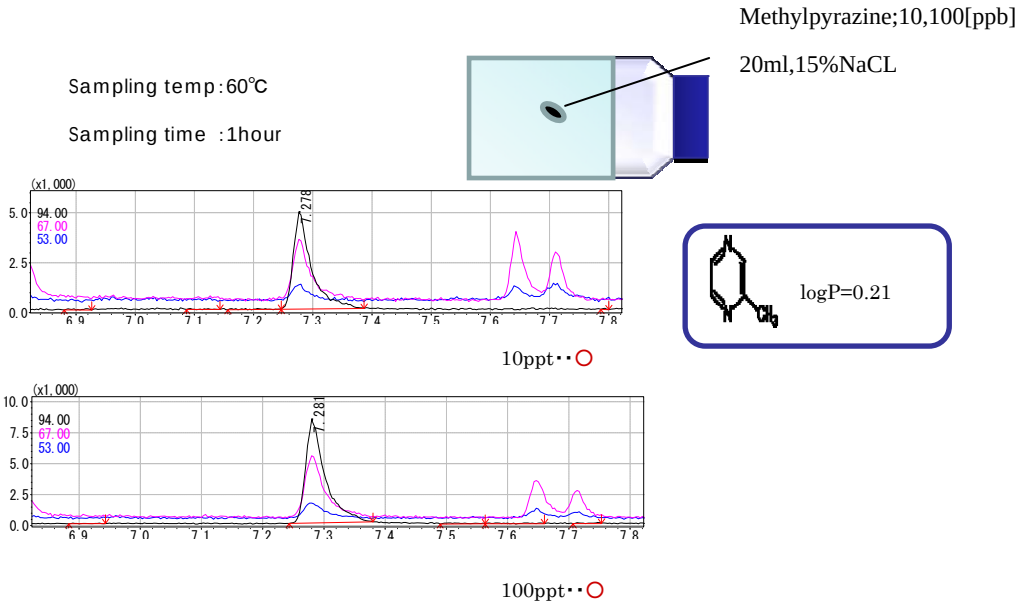
5-3 Detection limit

The detection limit of the methylpyridine whose LogP is small has been measured as described below.

Experimental method: a certain amount of standard samples were added to 20 mL of 15% NaCl solution and then subjected to sampling by means of a piece of MonoTrap™ DCC18. The solution was stirred in a constant-temperature agitation bath at 60°C, at 90 rpm, for 30 minutes. Samples were extracted with 200 μL of dichloromethane and measured in the GC-MS SIM mode and Splitless mode.

The absolute volume of methylpyradine in solution of sample concentration of 100 ppb is 2 ng, and that in the case of 10 ppb is 0.2 ng. If 100% of the sample is collected and extracted, as 200 mL of solvent is used, the absolute volume collected is 10 pg and 1 pg respectively.

In this experiment, the sample, even after being diluted 200 times in the course of the solvent extraction, could be collected from solution of such low concentration as 10 ppt. Even higher sensitivity can be expected when using some other methods, such as the thermal desorption method in which the whole volume is inserted into the analysis device. Higher sensitivity can be also expected to be obtained by increasing the volume of the samples.



6. Analysis method using peripheral accessories

Accessories are available such as holders and fittings for the MonoTrap™ for sampling. These accessories greatly help in the sampling operations. We recommend you use them for effective sampling.

6-1 Introduction to useful peripheral accessories

1. HS-MT-Sampling Kit (1050-79002)

This kit enables processes from sampling to extraction using the HS method without the need to directly touch the MonoTrap™ and is supposed to reduce contamination and improve reproducibility.

MT Stand **MT Holder (1)** **(2)** **(3)**





Place the MT Holder so that it stands on the MT Stand.

(1) Graps the MonoTrap™ with tweezers and insert the holder into the hole on the MonoTrap™.

(2) Hold MT Holder with pliers whose ends have been cleaned and pass it through the septum. Put a cap on top of the Holder.

(3) Tighten the septum on the vial.

MT Extract Cup with Vial


(1) Fill the MT Extract Cup with the extraction solvent and tighten the septum.

(2) Put the vial in an ultrasonic cleaner and expose it to ultrasound to accelerate the extraction.

2. MonoTrap Start-Up Kit (1050-79001)

This kit includes: MT Stand × 1, MT Holder × 5, MT Extract Cup with Vial × 5, Clean Pin Hole Septum with vial × 5, 200-µL glass insert (flat bottom) × 40 and 4 types of MonoTrap × 20 each.

All the necessary tools are included in each set.

Shaker

If stirring is required, it is recommended that you use the constant-temperature agitation bath shown below.

6-2 Measurement of procedural blank

Measurement of procedural blank level

Measure the procedural blank level at first.

As both the DCC18 and DSC18 are high-efficiency adsorptive devices, they also adsorb components in the ambient air during the procedures. Therefore, it is important to measure and ascertain the procedural blank level before sampling.

Step 1

Put MonoTrap™ into the vial to be used for sampling (use MonoTrap™ of the same quantity as used for sampling).

Leave the vial untouched in the same temperature for the same time as in the case of sampling of liquid samples according to the HS method.

Step 2

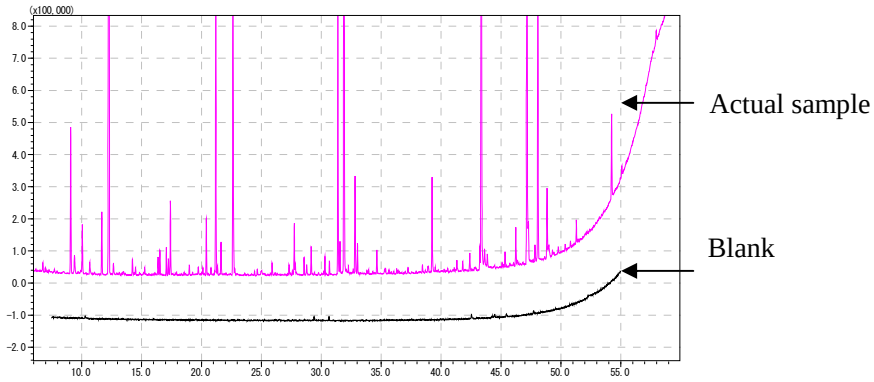
Take MonoTrap™ out of the vial and subject it to extraction with a solvent.

Step 3

Analyze the blank components under the same conditions as those for the analysis of actual samples.

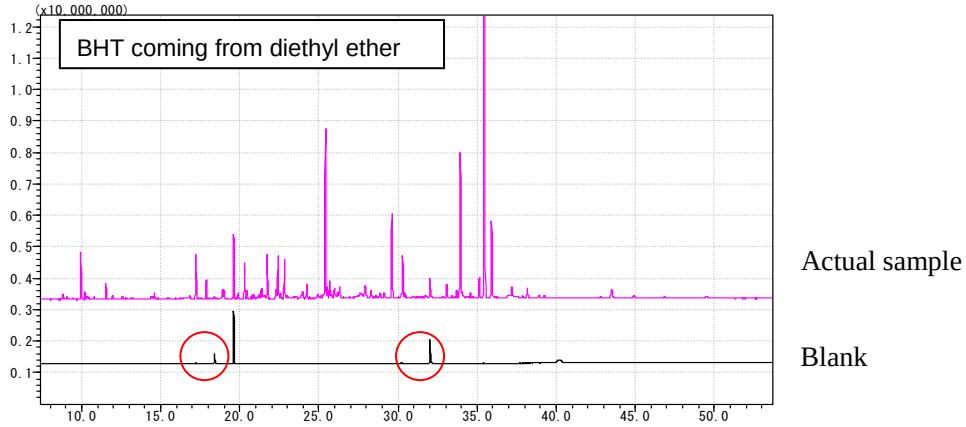
This measurement is intended to ascertain the extent to which the blank level in the ambient air and the conditions from sampling to extraction of the actual samples has consequences over the sampling and extraction. Note that the components detected in the blank test include those coming from the bottle used for sampling, from ambient air or from contamination caused when concentrating the solvent. Some components coming from MonoTrap™ itself are also detected.

Comparison of blank level with sweet potato-based distilled liquor (without concentration)



The graph shown above provides a comparison of the chromatograph obtained by analysis using GC-MS of sweet potato-based distilled liquor sampled using the stirring method and the one obtained by blank test using MonoTrap™ (DCC18) subjected to solvent extraction. In the experiment, 200 μL of solvent is used. The graph shows that a small amount of the components have been detected by the blank test.

Comparison of the blank level with lily petals (after approximately concentration by 1000 times)



The graph shown above provides a comparison of the chromatograph obtained by analysis using GC-MS of lily petals sampled by the passive method and the one obtained by blank test using MonoTrap™ (DCC18) subjected to solvent extraction. In the experiment, both of the actual sample and the blank were extracted with 1000 μL of solvent and concentrated to a few microns. As shown in this case, if concentration is performed by 1000 times, some components (mainly coming from the

base material of MonoTrap™) are observed in the blank test. Therefore, if you want to subject MonoTrap™ to a high concentration, it is recommended that you conduct a blank test before sampling the actual sample to ascertain the procedural blank level and to compare it with the actual sample.

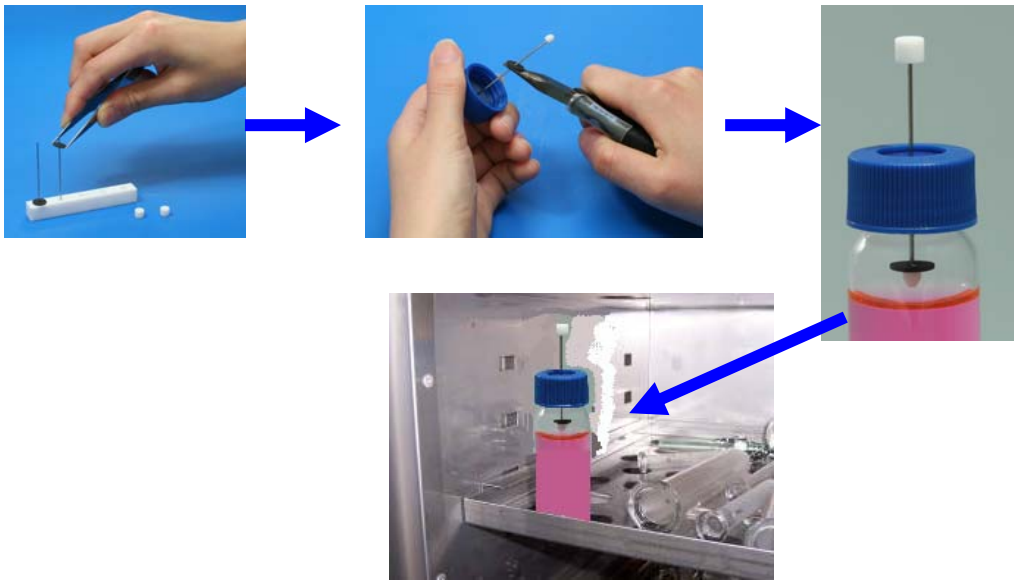
Three sampling methods are described below.

6-3 Head space sampling

For sampling using the head space method, please use the HS-MT-Sampling Kit, which allows easy and accurate sampling.

○ Grasp MonoTrap™ with (cleaned) tweezers and insert it into the septum from the rear side. Adjust the position as shown in the figure at the lower left. Heat it to approximately 60°C and leave it untouched for 20 minutes or more.

In the case of a solid sample, MonoTrap™ may be put directly on the sample. In the case of a liquid sample using the head space method, the Recovery rate is expected to be improved through salting-out and pH control.



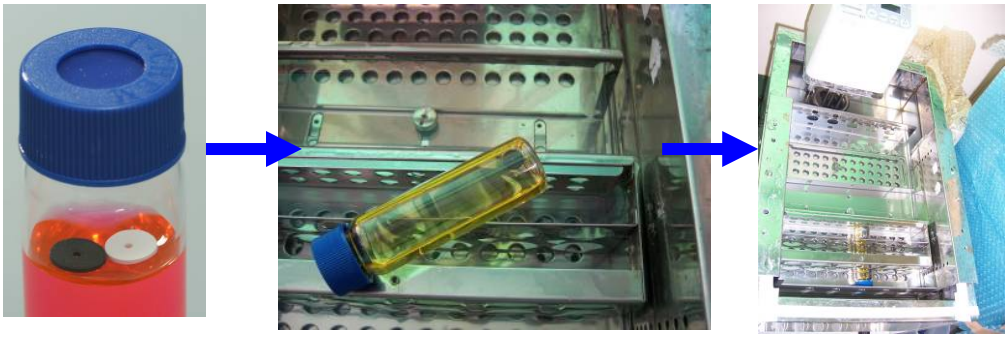
6-4 Stirring sampling

This method is very useful for low-viscosity liquid samples at low concentration.

The hydrophobicity of MonoTrap™ allows it to trap samples while floating on the surface of the liquid. Stirring the liquid sample with MonoTrap™ accelerates the movement of components contained by the solution to shorten the time required to attain vapor-liquid equilibrium.

The stirring method described below is useful for sampling low-viscosity liquid samples at low concentration. When using this method for high-viscosity liquid samples, dilute the sample with pure water or suchlike before sampling.

Stir the sample at approximately 90 rpm while heating it to 60°C for 20 minutes or more. As in the case of the head space method for liquid samples, the Recovery rate can be improved through salting-out and pH control.



6-5 Passive sampling

This method is useful for sampling the aroma components of flowers in their natural state.

Cut off one end of a Tedler Bag to create a sack and cover the flower with it from above. Put MonoTrap™ inside the sack and leave it untouched for three hours or more. If the concentration is supposed to be low, increase the number of pieces of MonoTrap™ inside to improve the sensitivity. As the efficiency depends on the room temperature, it is recommended that you use a long sampling time.

(As a guide, about 24 hours is required for a low-concentration sample.)

6-6 Solvent extraction

- In the case of head space sampling 40 mL vial (made by I-CHEM) and the vial for MT Extract Cup have the same diameter. Therefore, fill the MT Extract Cup directly with extraction solvent and tighten the cup on the vial and expose the vial to ultrasound. (200 mL or more of solvent should be used for each piece of MonoTrap™.)
- In case of stirring sampling Take MonoTrap™ out of the vial and wipe the liquid from its surface with cloth such as KimWipes. Then put the MonoTrap™ into MT Extract Cup to extract the solvent and fill the cup with solvent. Hermetically seal the cup and expose it to ultrasound (for five minutes maximum).

Note: if the cup is exposed to ultrasound in an ultrasonic cleaner, add pure water to the vial until its surface comes close to the cup. The exposure time should be five minutes maximum.

In case of Rod type

Put the rod type MonoTrap™ in an insert for the automatic sampler (Cat No. 1030-41403) and add 200 mL of solvent to the vial. Close the cap and expose the vial to ultrasound in an ultrasonic cleaner for five minutes.