Sample Extraction Needle

NeedlEx

NeedlEx®
Needle Extraction

Technical Data

Contents

1. About the NeedlEx®

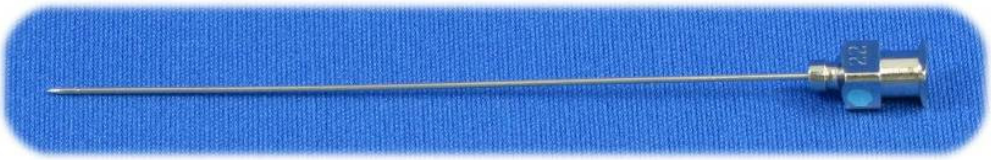
The NeedlEx® is a Luer lock needle designed to concentrate volatile organic compounds present in air.

Conventional methods for concentrating compounds of interest when carrying out offensive odor analyses and working environment measurements include cryofocusing using liquid oxygen, etc., and trapping using adsorbents such as Tenax, activated carbon, and silica gel. However, these concentration methods are complicated and require specialized devices.

After attaching to a gas sampling pump and sampling a fixed volume of sample gas, the NeedlEx® developed by our company is designed to be directly injected into gas chromatograph injection ports.

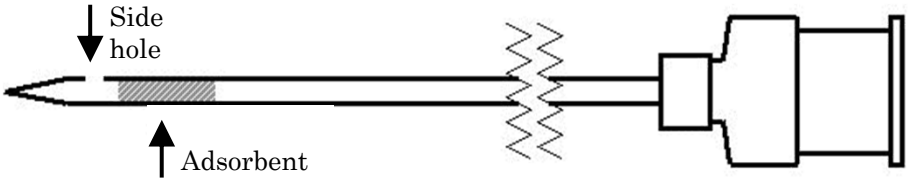
The NeedlEx® contains an adsorbent, and compounds present in gas samples are trapped on this adsorbent when gas passes through the NeedlEx®. The NeedlEx® is then attached to a gas tight syringe, 0.4-1 ml of inert gas is drawn into the syringe, and the NeedlEx® is then inserted into the injection port of a gas chromatograph, after which the trapped compounds are desorbed using the inert gas. The compounds desorbed from the NeedlEx® using the injection port heat are then carried into the column together with the inert gas, where they are separated and subsequently analyzed.

1.1 NeedlEx® structure and specifications



Luer lock needle

Inner diameter: 0.5 mm, outer diameter: 0.7 mm, length: 85 mm



1.2 NeedlEx® types

NeedlEx® needles are available with 4 different types of adsorbents depending on the type of compound to be analyzed.

- Alcohol type

Short chain alcohols including methanol and ethanol, as well as low boiling point compounds such as acetone and acetaldehyde can be concentrated by factors of 50 and greater.

- Organic solvent type

For organic solvents such as ethyl acetate, isobutyl alcohol, methyl isobutyl ketone, toluene, xylene, styrene, etc.

- Fatty acid type

For fatty acids such as n-butyric acid, isobutyric acid, isovaleric acid, and propanoic acid. (The polymer used in this type is a highly heat-resistant polymer selected for its superior fatty acid adsorption and desorption capabilities.)

- Amine type

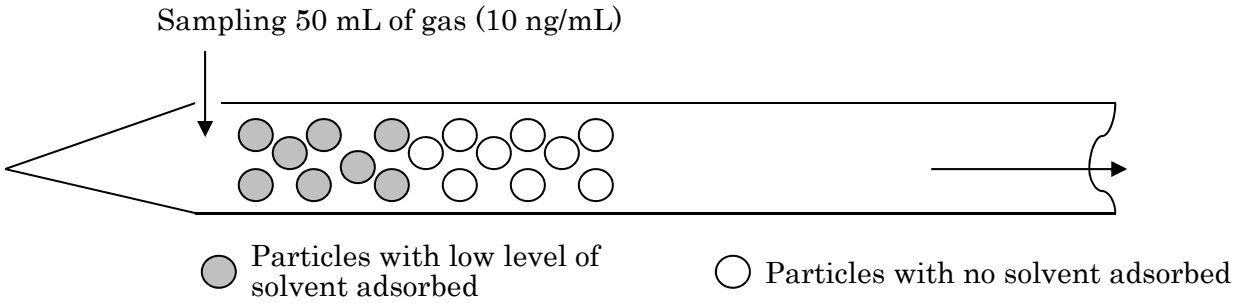
For short chain amines such as trimethylamine.

2. NeedlEx® concentration principles and application examples

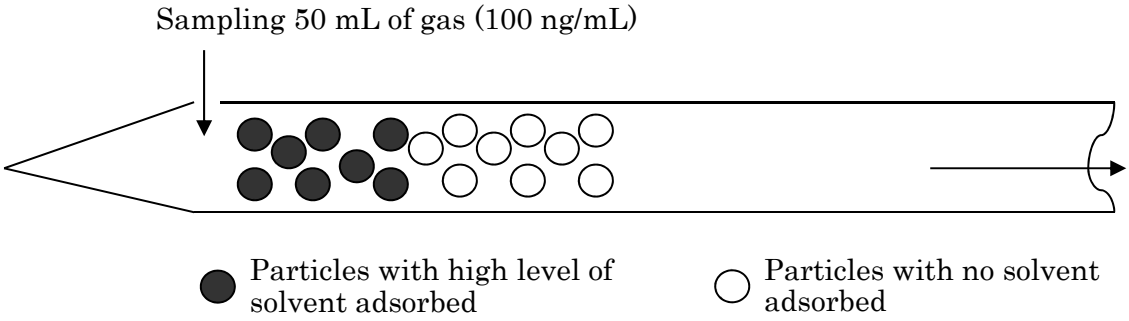
2.1 Concentration principles

Organic solvent NeedlEx®

The polymer particles contained in this needle adsorb compounds contained in sample gases which pass between the particles through the principle of equilibrium. Because sample gases pass through the side hole of the needle and come into contact with particles at the tip of the needle first, particles reach saturation from the tip of the needle upwards. The needle reaches breakthrough point* when all of the particles contained in the needle reach saturation point. Breakthrough capacities differ according to the organic solvent being sampled, but at concentrations below a certain level (100 ng/mL for most solvents), they differ according to the volume of gas sampled rather than the absolute amount of the compound to be analyzed.

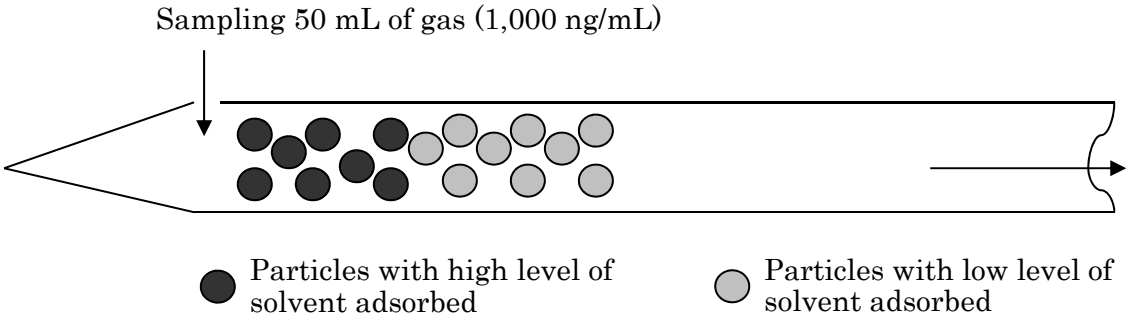


The amount of particles that reach saturation point increases in proportion with the volume of gas sampled. The needle reaches breakthrough point once all of the particles have reached saturation point.

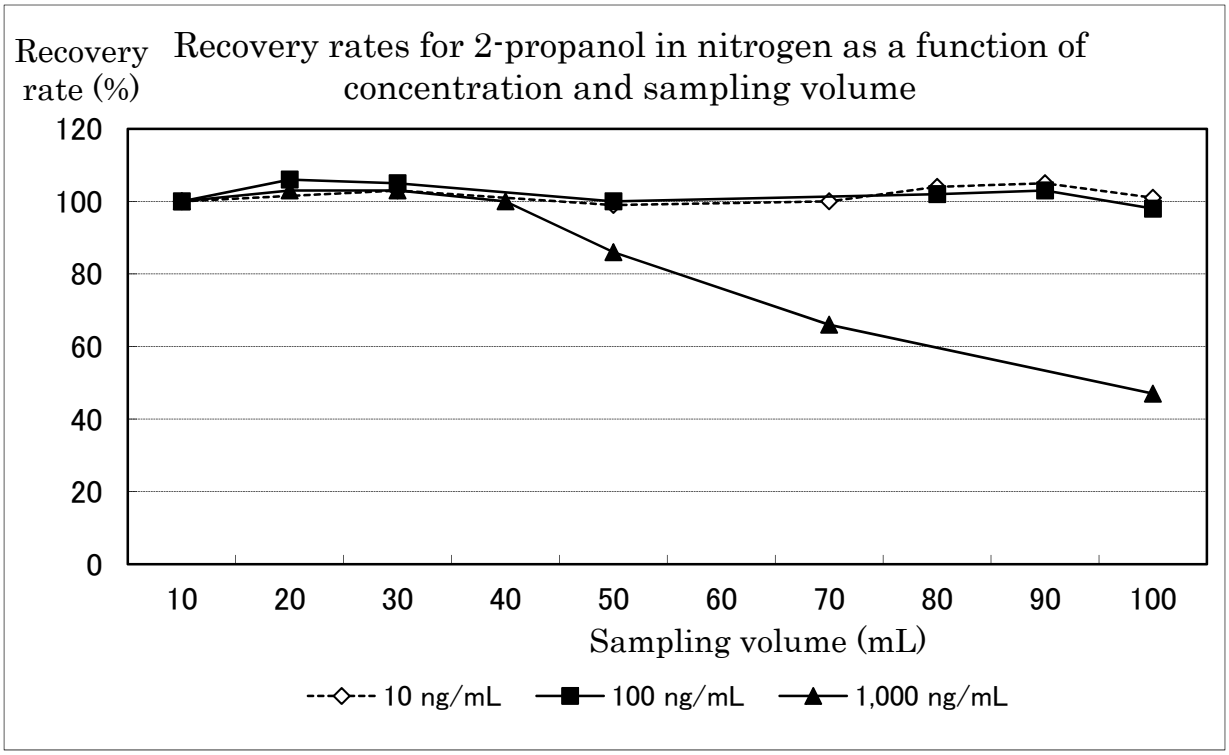


Even if the concentration of the analyte increases, due to the principle of equilibrium, the adsorption capacity of the particles also increases, with the result that the amount of particles that reach saturation point is proportionate to the volume of gas sampled.

*Breakthrough point: The breakthrough point is defined as the point at which a substance to be adsorbed contained in a fluid leaks from a fixed bed after initially flowing the aforementioned fluid through the fixed bed. The volume of fluid that is passed through the fixed bed up to the breakthrough point is referred to as the breakthrough capacity. (See Q&As 12 and 13 on pages 17 and 18 respectively.)



As there is a limit to the adsorption capacity of the particles, breakthrough volumes decrease at extremely high concentrations.



Due to the fact that equilibrium constants differ for different organic solvents, proportions of saturated particles, in other words, breakthrough capacities, will also differ even at the same sampling volumes. In general, breakthrough capacities increase with increases in solvent boiling points.

In addition, solvents with boiling points lower than 100℃ are susceptible to the effects of atmospheric water, with the result that breakthrough capacities for these compounds decrease with increases in humidity.

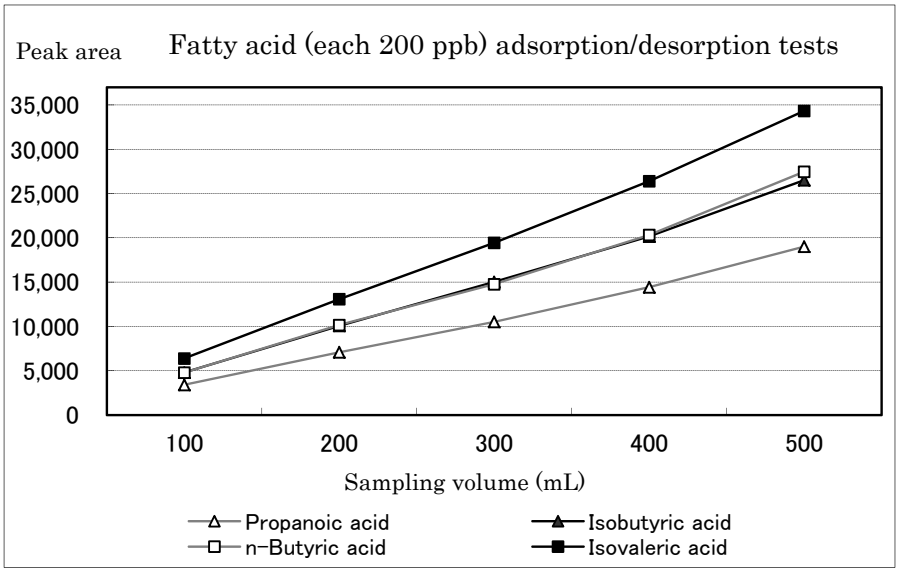
Shown below is a table of sampling volumes for a variety of organic solvents in air at 27℃ and 100% humidity.

Organic solvent	Boiling point (℃)	Sampling volume (mL)	Organic solvent	Boiling point (℃)	Sampling volume (mL)
Methanol	64.5	<10	Tetrachloroethylene	121.2	100
Acetone	56.3	10	Chlorobenzene	132.0	100
2-Propanol	82.4	20	Ethylbenzene	136.2	100
Diethyl ether	34.5	<10	p-Xylene	138.4	100
Methyl acetate	56.3	10	m-Xylene	138.4	100
Dichloromethane	40.0	<10	o-Xylene	144.4	100
trans-1,2-Dichloroethylene	48.0	<10	Isoamyl acetate	142.0	100
cis-1,2-Dichloroethylene	60.3	10	n-Amyl acetate	148.8	100
Methyl ethyl ketone	79.5	50	Cyclohexanol	161.0	100
1-Butanol	117.5	100	Cyclohexanone	156.0	100
2-Butanol	98.5	100	Cellosolve acetate	156.0	100
Isobutanol	108.0	100	Styrene	145.2	100
Ethyl acetate	76.8	50	1,1,2,2-Tetrachloroethane	146.3	100
n-Hexane	68.7	<10	Butyl cellosolve	171.2	100
Chloroform	61.2	10	2-Methylcyclohexanol	167.0	100
Methyl cellosolve	124.3	100	2-Methylcyclohexanone	165.0	100
Tetrahydrofuran	65.0	20	3-Methylcyclohexanol	175.5	100
1,2-Dichloroethane	83.4	30	3-Methylcyclohexanone	169.0	100
1,1,1-Trichloroethane	73.9	10	4-Methylcyclohexanol	174.0	100
Isopropyl acetate	89.4	70	4-Methylcyclohexanone	169.0	100
n-Propyl acetate	101.6	100	m-Dichlorobenzene	172.0	100
Carbon tetrachloride	76.7	<10	p-Dichlorobenzene	174.5	100
1,4-Dioxane	101.0	100	o-Dichlorobenzene	179.2	100
Trichloroethylene	86.6	10	Ethanol	78.3	60
Ethyl cellosolve	135.0	100	o-Cresol	191.0	×
Isoamyl alcohol	132.0	100	p-Cresol	201.9	×
Methyl isobutyl ketone	114.0	100	m-Cresol	202.2	×
Methyl n-butyl ketone	127.2	100			
N,N-Dimethyl formamide	153.0	100			
Isobutyl acetate	118.0	100			
n-Butyl acetate	126.3	100			
Toluene	110.6	100			

*Sampling volume: Maximum sampling volume at which a recovery rate of more than 95% can be achieved at a concentration of 20 ng/mL.
*Sampling volumes of 100 mL indicate that recovery rates have been confirmed up to 100 mL.
*The high boiling points for the cresols mean that desorption of these compounds is incomplete.

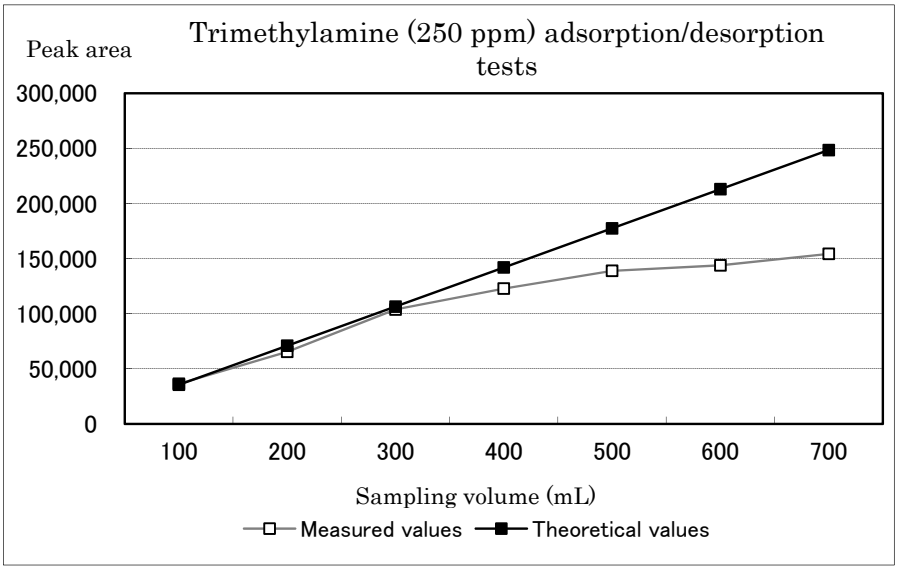
Fatty acid NeedlEx®

Because the packing material used in this variety of NeedlEx® consists of a basic polymer, the adsorption mechanism is believed to differ from that of the organic solvent NeedlEx®. As shown in the graph below (y-axis: peak area on desorption), at a concentration of 200 ppb for each fatty acid, increases in peak areas were found to be linear even at sampling volumes of 500 mL.



Amine NeedlEx®

Because the packing material used in this variety of NeedlEx® consists of an acidic partitioning agent, the adsorption mechanism is believed to involve ionic bonding in the same manner as that for the fatty acid NeedlEx®. As shown in the graph below, sampling is possible up to 300 mL.



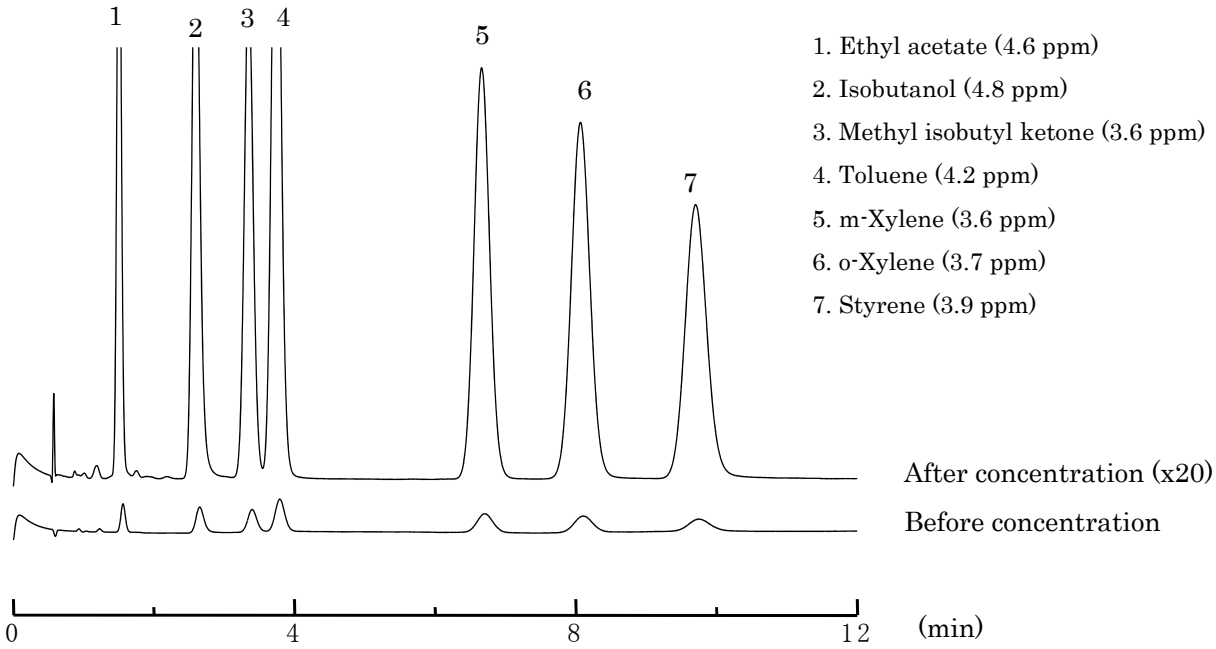
Alcohol NeedlEx®

This NeedlEx® is capable of concentrating methanol (the most difficult to concentrate organic solvent) by a factor of 50, and is also capable of concentrating low boiling point compounds such as acetone and acetaldehyde, as well as the gases propane and butane by factors of more than a 100.

2.2 Application examples

Organic solvent NeedlEx®

Shown below is an analysis of a standard gas sample containing ethyl acetate, isobutanol, methyl isobutyl ketone, toluene, m-xylene, o-xylene, and styrene. 20 mL of this gas was sampled using an organic solvent NeedlEx®. The adsorbed compounds were then thermally desorbed and analyzed. All peaks were found to have areas approximately 20 times those of peaks obtained from direct analysis of the standard gas sample.



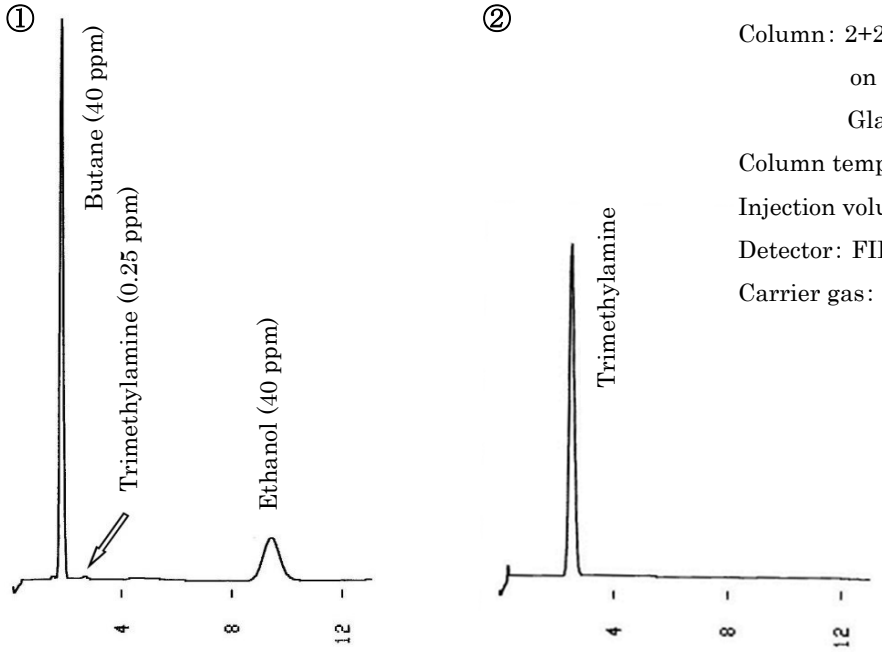
Column: 12% SBS-120 on SHINCARBON A 80/100 mesh
Glass 3.0 m x 3.0 mm I.D.
Column temp.: 120℃
Injection volume: 1 mL (200℃)
Detector: FID (200℃)
Carrier gas: N_2, 50 mL/min

Comparison of peak areas before and after concentration

Compound	Peak area before concentration	Peak area after concentration
Ethyl acetate	5,873	133,335
Isobutanol	9,715	217,474
Methyl isobutyl ketone	9,376	201,866
Toluene	15,100	315,345
m-Xylene	13,474	299,383
o-Xylene	14,580	305,031
Styrene	12,565	277,204

Amine NeedlEx®

① below shows a direct analysis of 1 mL of a standard gas sample containing trimethylamine (250 ppb), butane (40 ppm), and ethanol (40 ppm). Due to the very low concentration for trimethylamine, this compound was not detected.
② below shows an analysis of the same standard gas sample after sampling 300 mL of the gas using an amine NeedlEx® and thermal desorption. As the packing material used in this NeedlEx® is highly selective, only amines are adsorbed; with the result that butane and ethanol were not detected.

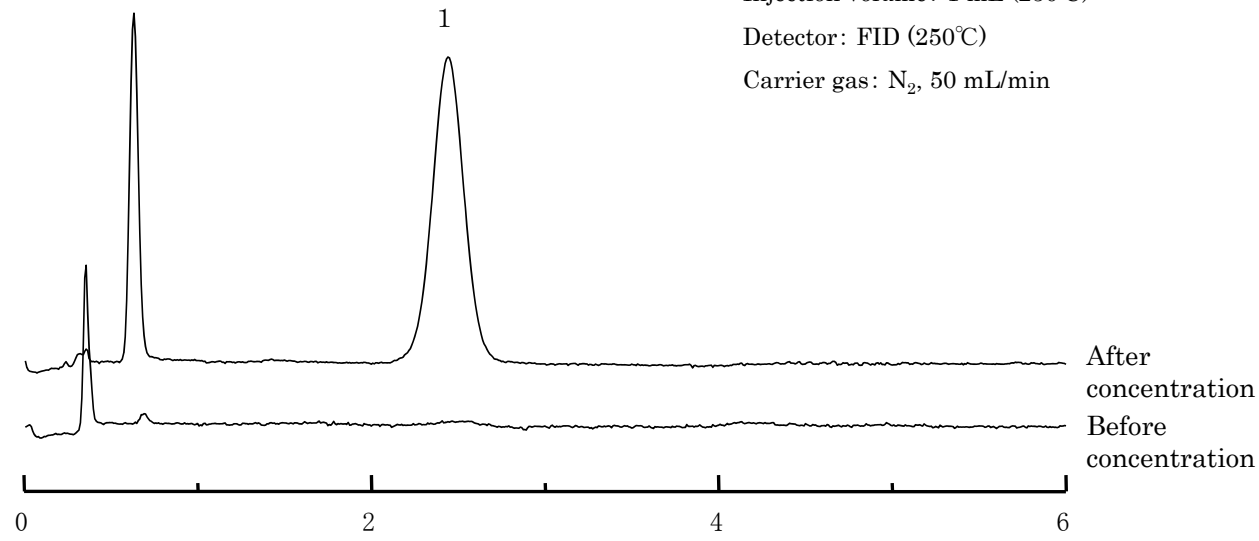


Column: 2+2% Thermon-3000+KOH
on Sunpak-N 60/100 mesh
Glass 2.0 m x 3.0 mm I.D.
Column temp.: 150℃
Injection volume: 1 mL (250℃)
Detector: FID (250℃)
Carrier gas: N_2, 50 mL/min

Headspace gas of dry chicken manure (100 mL sample)

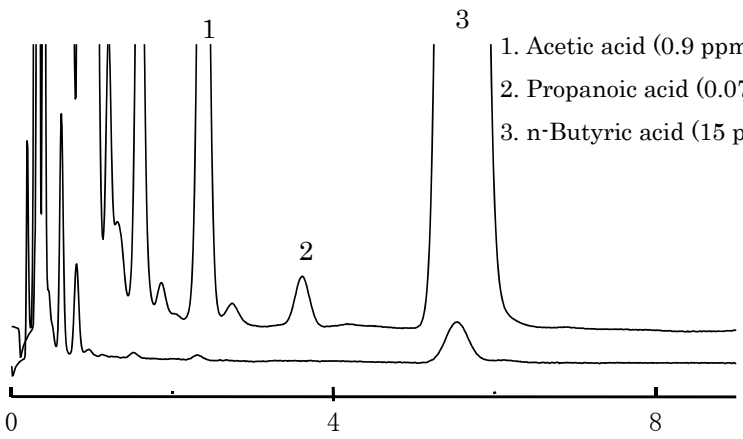
1. Trimethylamine (0.3 ppm)

Column: 2+2% Thermon-3000+KOH
on Sunpak-N 60/100 mesh
Glass 2.0 m x 3.0 mm I.D.
Column temp.: 150℃
Injection volume: 1 mL (250℃)
Detector: FID (250℃)
Carrier gas: N_2, 50 mL/min



Fatty acid NeedlEx®

Ginkgo nut headspace gas (100 mL)

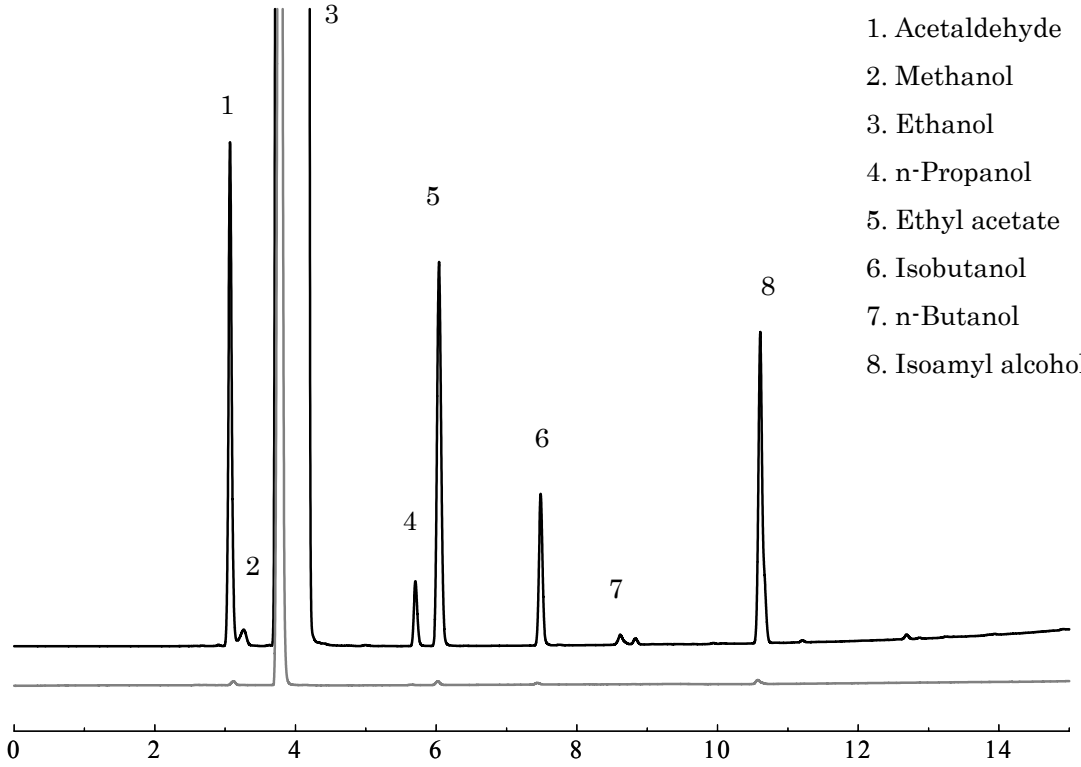


1. Acetic acid (0.9 ppm)
2. Propanoic acid (0.07 ppm)
3. n-Butyric acid (15 ppm)

After concentration
Before concentration

Column: 5% Thermon-3000 on SHINCARBON A 60/80 mesh Glass 1.5 m x 3.0 mm I.D.
Column temp.: 120℃
Injection volume: 1 mL (250℃)
Detector: FID (250℃)
Carrier gas: N_2, 60 mL/min

Alcohol NeedlEx®



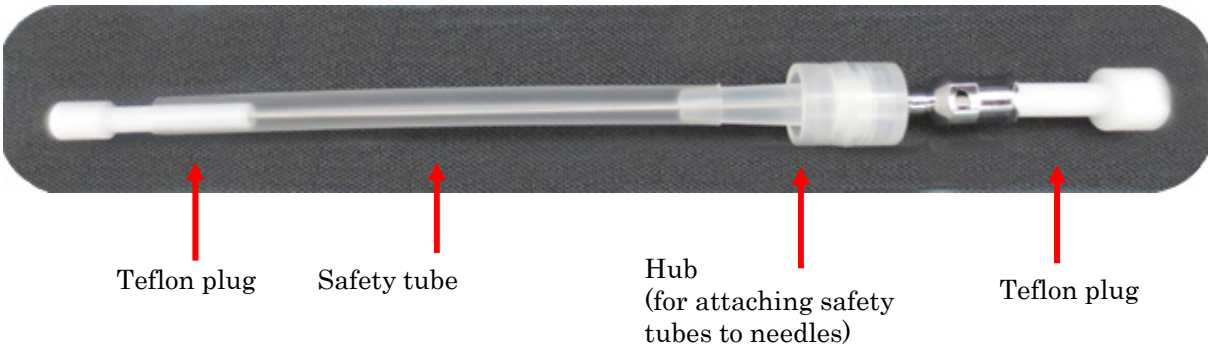
1. Acetaldehyde
2. Methanol
3. Ethanol
4. n-Propanol
5. Ethyl acetate
6. Isobutanol
7. n-Butanol
8. Isoamyl alcohol

After concentration
Before concentration

Column: ULBON HR-1701, 30 m x 0.32 mm I.D. df. = 0.25 µm
Column temp.: 50℃ (2 min hold) – 250℃ Program rate 10℃/min
Injection volume: 0.3 mL (250℃)
Detector: FID (250℃)
Carrier gas: He, 1.7 mL/min
Split ratio: 10:1

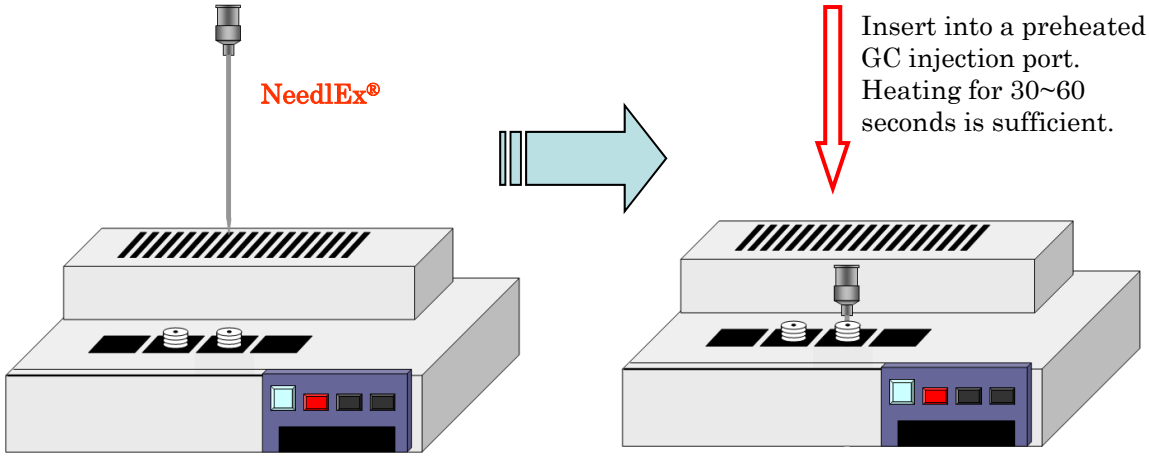
3. How to use the NeedlEx®

Fig. 1 The NeedlEx® after removal from its case



3.1 Cleaning

Needles are cleaned before use in order to prevent carryover.
Although needles are cleaned before shipment, it is necessary to clean needles if they have been stored for extended periods of time after purchase or after they were previously used.



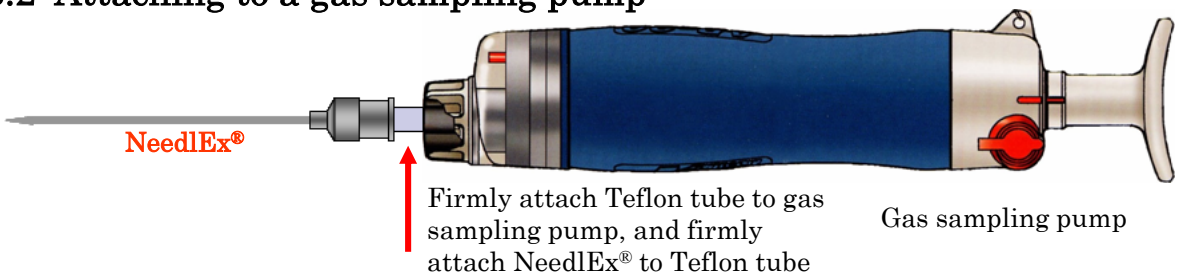
Remove the NeedlEx® from its box and remove all the attachments from the needle. Next, insert the NeedlEx® into a GC injection port set to the appropriate temperature for the type of NeedlEx® to be used. Before cleaning needles, attach a column to the injection port, and set the injection port pressure to 100 kPa (G).

GC injection port heat is used to clean needles. An insertion time of 30~60 seconds is sufficient to clean needles in most cases. After cleaning, remove the NeedlEx® from the injection port and firmly attach the Teflon plugs included with the NeedlEx® to both ends of the needle.

Avoid setting the GC injection port temperature above the appropriate temperature for the type of NeedlEx® to be used.

The NeedlEx® is then attached to a gas sampling pump using the Teflon tube included with the NeedlEx®.

3.2 Attaching to a gas sampling pump



3.3 Sampling and concentrating gas samples

A fixed volume of gas is sampled at room temperature. During sampling, the compounds of interest are completely adsorbed onto the adsorbent contained inside the needle.

When carrying out sampling, attach the safety tube to the NeedlEx® (Fig. 2) in order to avoid injuries from the needle tip. Remove the safety tube from the needle when the needle is to be directly injected into a sample container such as a Tedlar bag.

Fig. 2

Examples of Tedlar bag sampling and headspace sampling of liquids are shown in figures 3 and 4 respectively.

Firmly hold the gas sampling pump, and pull the pump handle until it locks in place at the desired volume. Please refer to the gas sampling pump instruction manual for details regarding the sampling of gases.

Fig. 3

Fig. 4

Sampling volumes differ according to the type of compound to be sampled. Refer to the table on page 5 for sampling volumes. Approximately 10~15 minutes is required to sample 100 ml of gas. Carry out sampling at a temperature of 30℃ or below, and a relative humidity of 80% or below. In addition, when not performing analyses immediately after sampling, firmly attach the Teflon plugs to both ends of the NeedlEx® in order to prevent sample loss. Samples can be stored for approximately 10 days by storing in a cool, dark location.

Note: The AP-20N Kitagawa gas sampling pump is required when sampling volumes of 10 ml. Both the AP-20N and AP-20 Kitagawa gas sampling pumps can be used to sample volumes of 50 and 100 ml.

The completion of sampling is indicated by the red indicator on the gas sampling pump. Read the gas sampling pump instruction manual before using the sampling pump.
Shown below is an example of use of the Kitagawa gas sampling pump.

Sampling pump indicator

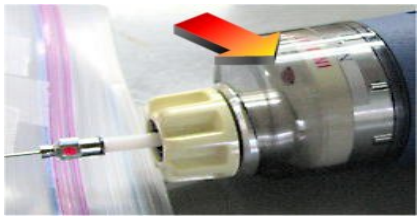
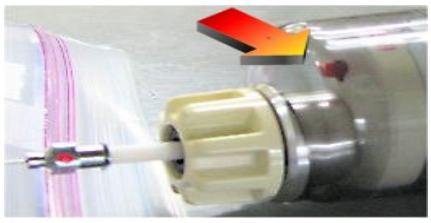
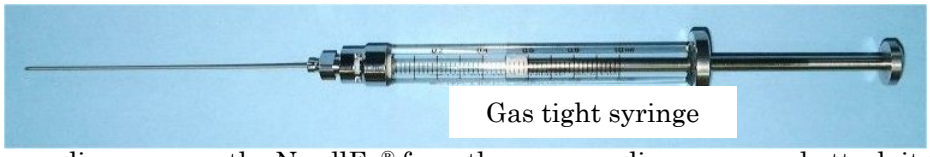
Fig. 5 

Fig. 6 

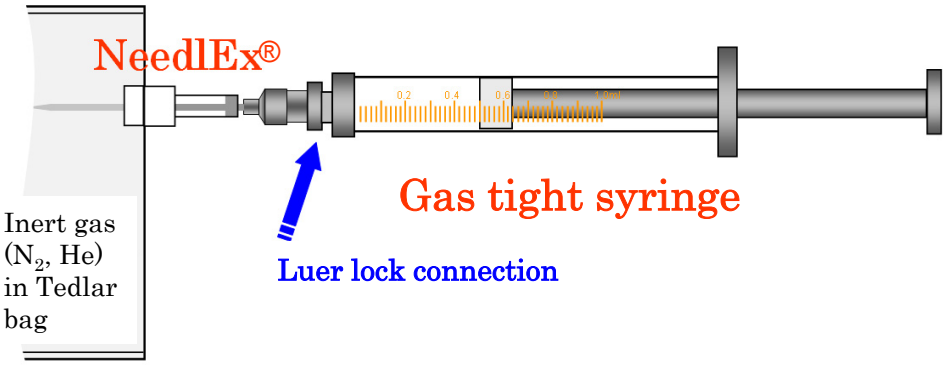
As shown in figure 5, the red indicator is withdrawn during sampling. As shown in figure 6, the red indicator pops out when sampling is finished.

3.4 Preparing to inject into a GC

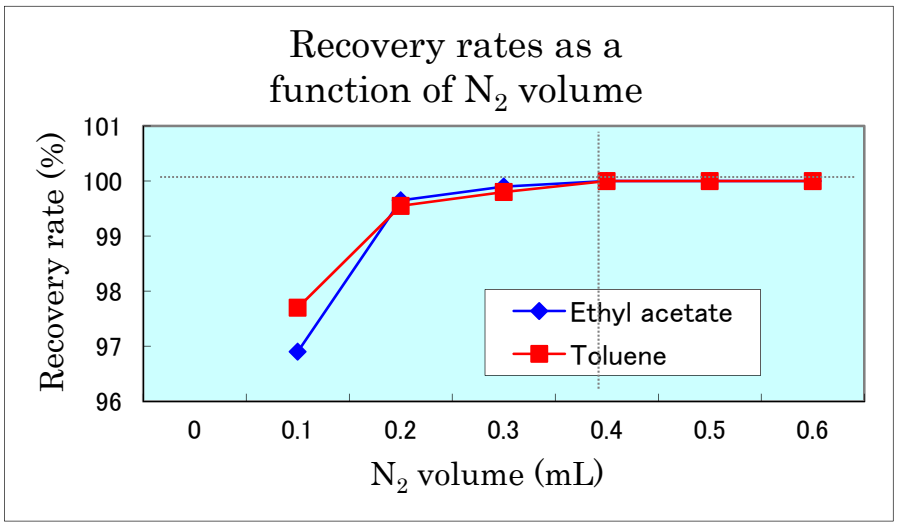
NeedlEx® needle attached to a gas tight syringe



After sampling, remove the NeedlEx® from the gas sampling pump and attach it to a 1 ml gas tight syringe. Next, draw 0.4~1 ml of inert gas from a Tedlar bag. After drawing the inert gas from the Tedlar bag, immediately insert the NeedlEx® into the injection port of a gas chromatograph.



Shown below is a graph indicating the recovery rates for two compounds as a function of the volume of inert gas used for desorption. As can be seen, recovery rates of almost 100% can be achieved using gas volumes of 0.4 ml and above.

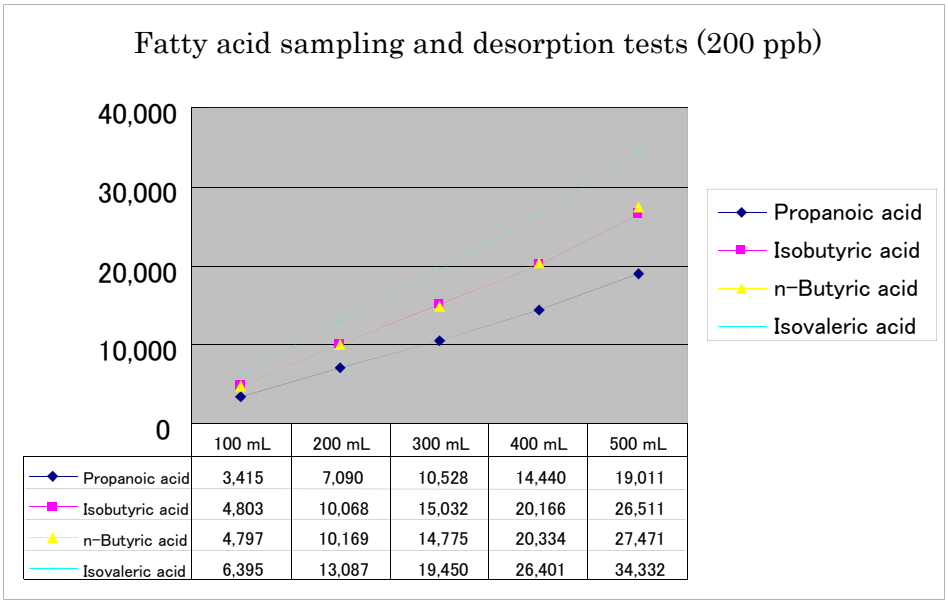


4. NeedlEx® Q & A

Q1 What is the lower limit of detection when using the NeedlEx®?

Due to the need to determine breakthrough points for a variety of compounds, we have carried out numerous tests for compounds at high concentrations. However, we have yet to perform tests at low concentrations for a large number of compounds. With regard to general organic solvents, it is possible to concentrate these compounds by a factor of 100. Using an FID, this means that these compounds can be detected down to levels of approximately 30 ppb. With regard to fatty acids, concentration tests were carried out for a number of compounds at concentrations of 200 ppb. As shown in the table below, the results of these tests indicated excellent linearity even at sampling volumes of 500 ml.

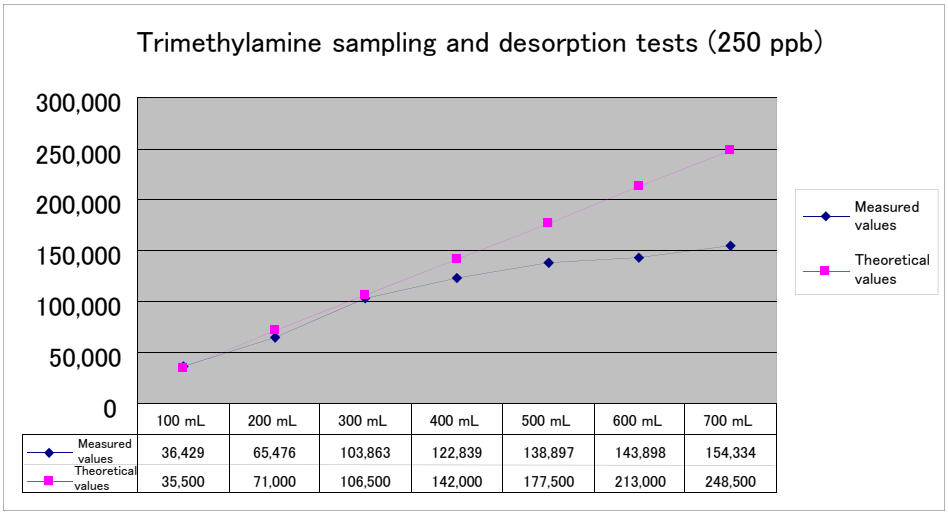
Table 1 Peak area as a function of sampling volume for four fatty acids (each 200 ppb)



	100 mL	200 mL	300 mL	400 mL	500 mL
Propanoic acid	3,415	7,090	10,528	14,440	19,011
Isobutyric acid	4,803	10,068	15,032	20,166	26,511
n-Butyric acid	4,797	10,169	14,775	20,334	27,471
Isovaleric acid	6,395	13,087	19,450	26,401	34,332

The same test was performed for trimethylamine at a concentration of 250 ppb. As shown in Table 2 below, sampling was possible up to 300 ml. The peak area values for trimethylamine are one digit larger than those for the fatty acids above due to the use of different gas chromatograph ranges (10^2 for fatty acids and 10^1 for trimethylamine).

Table 2 Peak area as a function of sampling volume for trimethylamine



	100 mL	200 mL	300 mL	400 mL	500 mL	600 mL	700 mL
Measured values	36,429	65,476	103,863	122,839	138,897	143,898	154,334
Theoretical values	35,500	71,000	106,500	142,000	177,500	213,000	248,500

Q2 Are FIDs the only detectors that can be used with NeedlEx® needles?

There are no limitations with regard to the type of detector that can be used with NeedlEx® needles. NeedlEx® needles can be used with devices including TCDs, ECDs, FPDs, and GC/MS.

Q3 Is the NeedlEx® compatible with official methods?

The NeedlEx® is not currently compatible with official methods. We are aware that this is an extremely important issue, and as such, intend to carry out comparisons between the NeedlEx® and official methods, and release this data as soon as possible.

Q4 Can the NeedlEx® be used in combination with GC/MS devices?

Yes it can. However, the dimensions of injection ports need to be investigated in advance, and helium is used for the desorption gas rather than nitrogen.

Q5 I want to prepare a calibration curve. Is there an easy way of doing this?

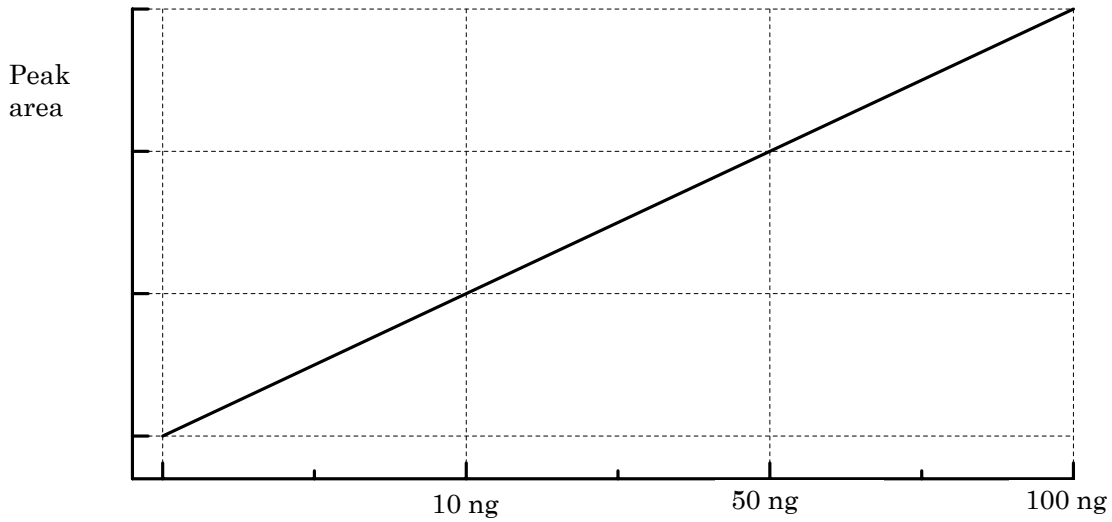
As the preparation of standard gas samples with accurate concentrations is difficult due to difficulties in measuring gas volumes and the adsorption of analytes on sample container walls, etc., use liquid samples to prepare calibration curves. For example, when preparing a calibration curve for toluene, inject 1 µl of each of 10, 50, and 100 ng/µl of toluene in hexane into a GC, and obtain the peak areas. Next, prepare a calibration curve with the absolute weight of toluene (ng) as the x axis, and peak area as the y axis. Then, obtain the absolute amount of toluene in your sample using the peak area obtained from analysis of the NeedlEx® used to obtain your sample as well as this calibration curve. Finally, calculate the concentration of toluene using the volume of gas sampled using the NeedlEx® and the absolute amount of toluene.

Shown below is an example of the preparation of a calibration curve.

First, prepare liquid solutions in order to plot your calibration curve.

10, 50, 100 ng/µl (1 ng/µl = 1 ppm)

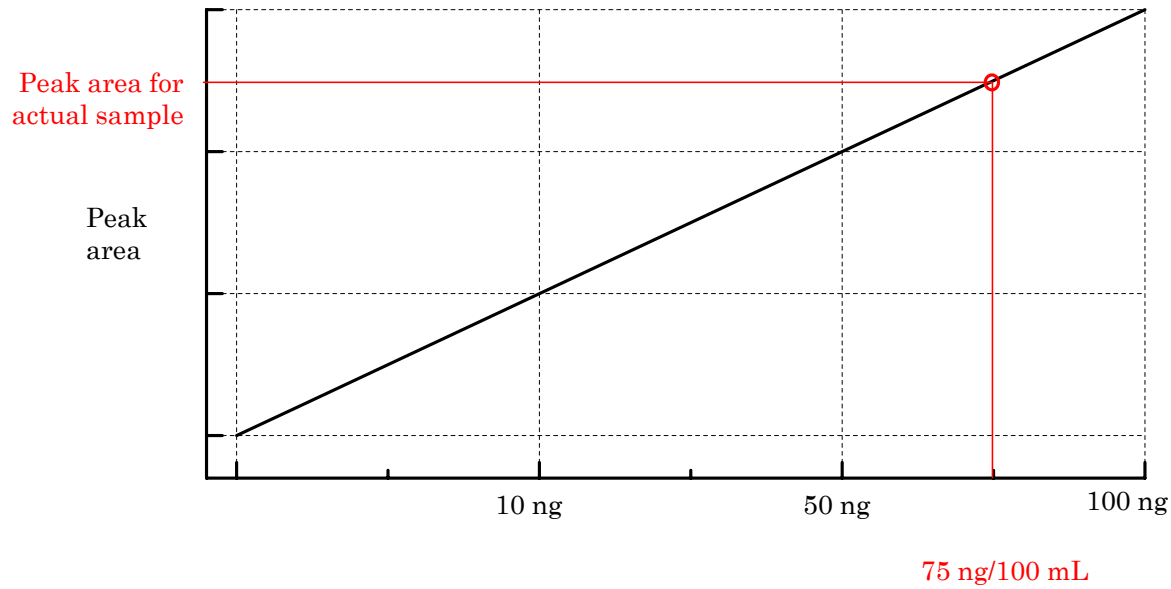
The calibration curve created using the above solutions is shown below.



Next, sample and analyze an actual sample.

E.g.: Sample 100 ml using a gas sampling pump ⇒ Analyze using a GC

Analysis results are shown in the figure below.



Results

The concentration of toluene in the actual sample is:

75 ng/100ml = 0.75 ng/ml

Because calculations for converting ng/ml concentrations to concentrations in ppm are complex due to differing volumes when different compounds are vaporized, the following simplified method is used to calculate ppm concentrations.

Toluene concentration from calibration curve: 0.75 ng/ml

At room temperature (no correction made for atmospheric pressure)

$$\text{Concentration} = 0.75\ \text{ng/ml} \div \underset{(*1)}{92.14} \times \underset{(*2)}{22.4} \times \underset{(*3)}{\frac{298}{273}}$$

$$= 0.20\ \text{ppm}$$

*1: Molecular weight of toluene (g/mol)
*2: Volume when 1 mole of substance turns into a gas (l/mol)
*3: Temperature correction
0℃ = 273K
25℃ = 298K

Q6 Is it possible to concentrate sulfur compounds using the NeedlEx®?

It is not currently possible to concentrate sulfur compounds using the NeedlEx®. As these are common causes of bad odors, we are currently in the process of developing an appropriate adsorbent.

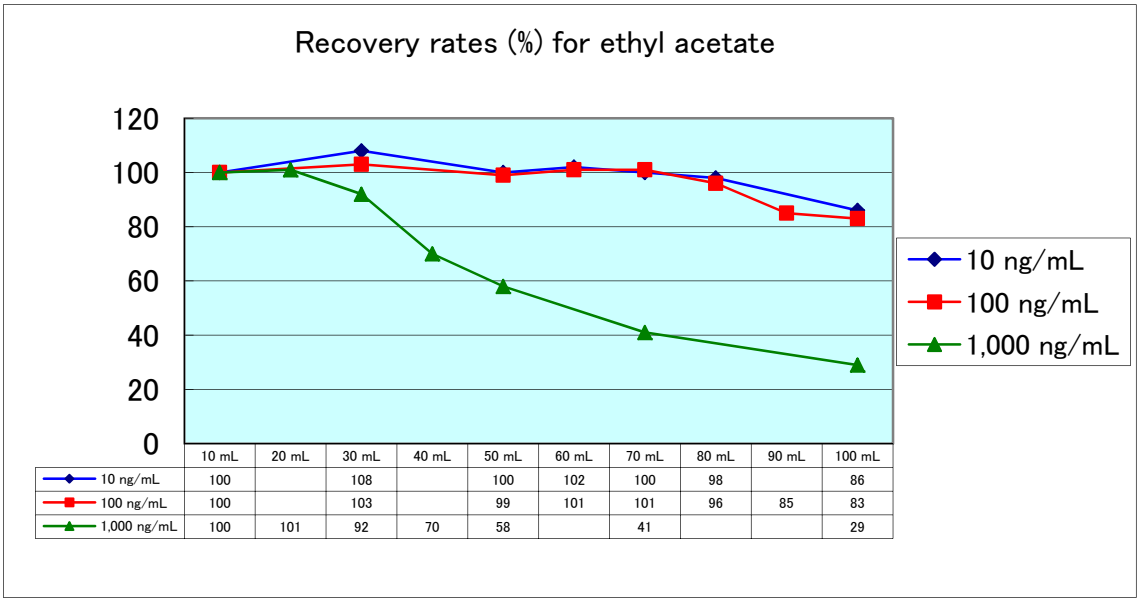
Q7 Can hydrogen sulfide be measured using the NeedlEx®?

As mentioned above, we do not currently have a needle available that is capable of adsorbing hydrogen sulfide.

Q8 Depending on the type of compound being analyzed, sampling volumes can range from 10, 50 to 100 ml. What is the reasoning behind these sampling volumes? How are sampling volumes determined?

Table 3 below shows the relationship between concentration, sampling volume, and recovery rate for ethyl acetate. In this case, recovery rates of almost 100% were obtained up to sampling volumes of 80 ml at concentrations of 10 and 100 ng/ml. In other words, the breakthrough volume for ethyl acetate is 80 ml. Breakthrough volumes for a variety of other organic solvents have also been measured in the same manner. The 50 and 100 ml sampling volumes shown in the NeedlEx® instruction manual are based on the results of these measurements. As in the case of ethyl acetate, compounds with breakthrough volumes greater than 50 and less than 100 ml are listed in the instruction manual with maximum sampling volumes of 50 ml.

Table 3 Relationship between concentration, sampling volume, and recovery rate for ethyl acetate



	10 mL	20 mL	30 mL	40 mL	50 mL	60 mL	70 mL	80 mL	90 mL	100 mL
10 ng/mL	100		108		100	102	100	98		86
100 ng/mL	100		103		99	101	101	96	85	83
1,000 ng/mL	100	101	92	70	58		41			29

Q9 Because sampling volumes differ according to the type of compound being analyzed, what would be an appropriate sampling volume for a sample containing two compounds one of which requires a sampling volume of 100 ml for example, and the other for which a volume of 10 ml is sufficient?

For example, when analyzing a sample containing a mixture of toluene and methanol, because the breakthrough points for methanol and toluene are 10 ml and greater than 100 ml respectively; when methanol needs to be analyzed, the sampling volume needs to be set at 10 ml. If only toluene needs to be analyzed, the sampling volume can be set to 100 ml. When sampling gases, always set the sampling volume in accordance with the compound with the lowest breakthrough volume.

Q10 When analyzing 10 ml of a gas sample for which 50 ml would normally be sampled, would the result for the 10 ml analysis multiplied by five be the same as that obtained if 50 ml was sampled?

As long as the NeedlEx does not reach its breakthrough point, peak area increases in proportion to the sampling volume. Therefore, the result described in the question above would be obtained.

Q11 What sampling volumes should I use when sampling organic solvents that are not shown in the sampling volume table in the NeedlEx® instruction manual?

As a guideline, compounds with boiling points higher than 100℃ can be sampled up to 100 ml. However, desorption rates for solvents with boiling points higher than 200℃ decrease. When analyzing solvents with boiling points lower than 100℃ and higher than 200℃, use alcohol and fatty acid type NeedlEx® needles respectively.

Q12 How do you determine when a NeedlEx® has reached its breakthrough point?

The breakthrough sampling volumes for ethyl acetate shown in the table in Q8 above are 20 ml at a concentration of 1,000 ng/ml, and 80 ml at concentrations of 10 and 100 ng/ml. The absolute amounts of ethyl acetate adsorbed on NeedlEx® needles at each of these concentrations are:

At 1,000 ng/ml: 1,000 ng/ml x 20 ml = 20 μg
At 100 ng/ml: 100 ng/ml x 80 ml = 8 μg
At 10 ng/ml: 10 ng/ml x 80 ml = 0.8 μg

As can be seen, breakthrough points cannot be expressed in terms of absolute amounts. In addition, breakthrough sampling volumes also differ according to concentration. However, as a result of carrying out the same test for a wide variety of other organic solvents, we have found that they display the same tendency as ethyl acetate. In other words, at concentrations of both 10 and 100 ng/ml, these compounds display the same breakthrough sampling volumes. This means that at concentrations of 100 ng/ml and less, breakthrough points are determined by sampling volumes.

Of course, it is impossible to tell if concentrations of compounds are less than 100 ng/ml when performing working environment measurements. Although there is some variation depending on molecular weight, because concentrations of general organic solvents of 100 ng/ml are equivalent to concentrations of approximately 30 ppm, these compounds can be detected to some extent using smell. In addition, 100 ng of a compound is sufficient to perform accurate detection using a GC FID. At concentrations of 100 ng/ml it is not necessary to concentrate compounds. Instead, analyses can be performed by simply injecting 1 ml of air containing the compound in question into a GC, etc.

The NeedlEx® was developed in order to concentrate and accurately analyze solvents present at extremely low concentrations of less than 10 ng/ml (a few ppm). As such, set sampling volumes as low as possible when there is a possibility that the compound to be sampled is present at a high concentration.

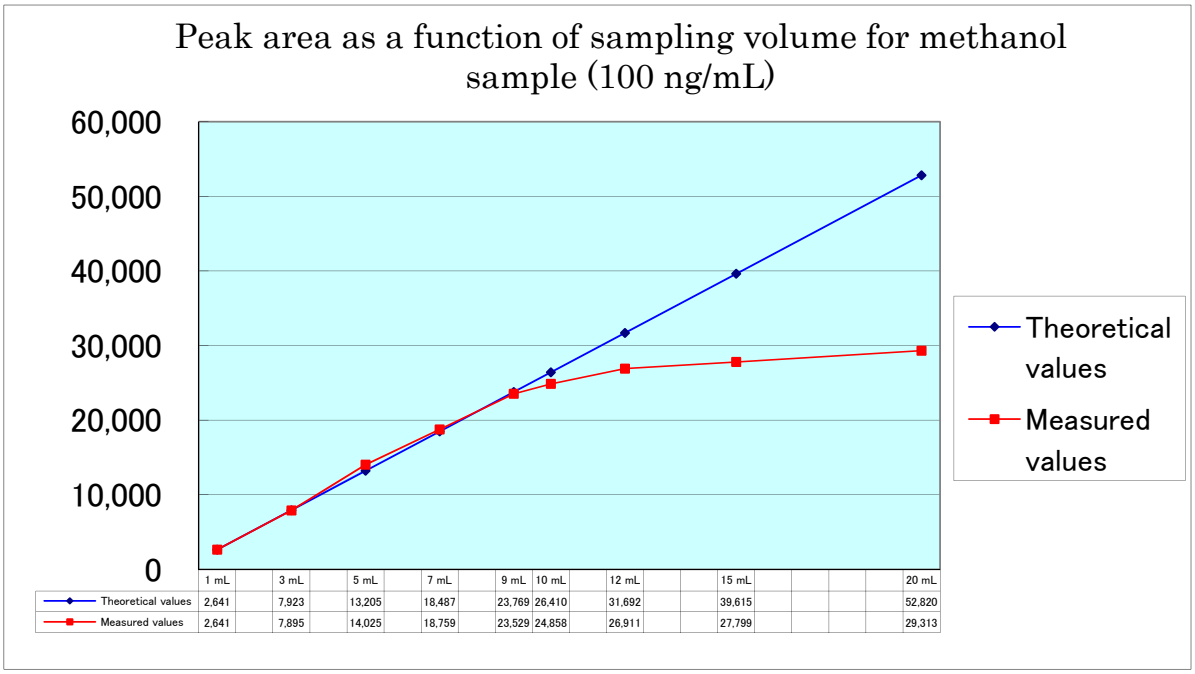
Although NeedlEx® needles are not damaged when they reach their breakthrough points, measured concentrations of compounds will be lower than actual concentrations. Although somewhat time-consuming, the most reliable method of determining breakthrough sample volumes is to sample 10, 50, and 100 ml of air from the same site, analyze the samples, and determine whether or not peak area increases in proportion to sampling volume. For example, if the peak area for a particular compound is 1,000 on sampling 10 ml, then the peak areas should be 5,000 and 10,000 on sampling 50 and 100 ml respectively. If results similar to these are obtained, then the NeedlEx® has not reached its breakthrough point. However, if, for example, the peak value is approximately 5,000 on sampling 50 ml, but is approximately 8,000 on sampling 100 ml, then the NeedlEx® has reached its breakthrough point somewhere between 50 and 100 ml.

If multiple compounds are contained in the same sample, not all compounds will reach breakthrough point at the same sampling volume. For example, if a sample containing methanol, acetone, and toluene is sampled using an organic solvent NeedlEx®; methanol and acetone will reach their breakthrough points at 10 and 50 ml respectively, but toluene may not reach breakthrough even after sampling 100 ml. In this case, if 100 ml is sampled, the concentration value for toluene will be correct, but those for methanol and acetone will be significantly lower than actual values. Consequently, in cases such this, use the sampling volume for methanol (10 ml), which is the smallest sampling volume.

Q13 How do you determine when a NeedlEx® has reached its breakthrough point?

When a NeedlEx® reaches its breakthrough point, peak areas will remain unchanged even if the sampling volume is increased. For example, Table 4 below shows the relationship between sampling volume and peak area for a gas sample containing methanol at a concentration of 100 ng/ml. On surpassing the breakthrough volume for methanol (10 ml), peak area values flatten out.

Table 4 Peak area as a function of sampling volume for methanol



Q14 Why is it not possible to sample gases at temperatures higher than 30℃? If gases are sampled at temperatures higher than 30℃, what will happen to the NeedlEx®?

At temperatures higher than 30℃, adsorption may not take place completely. The NeedlEx® adsorbent will not degrade at temperatures above 30℃, but we recommend the use of needles at temperatures below 30℃.

Q15 Is it possible to use the NeedlEx® to concentrate compounds with boiling points higher than 200℃?

In general, the higher the boiling point of a compound, the more easily it is adsorbed onto the adsorbent contained in the NeedlEx®. Consequently, although the breakthrough capacity will also increase, it will become increasingly difficult to desorb the compound from the adsorbent. The fatty acid NeedlEx® can be used for compounds with boiling points from 200 to 300℃.

Q16 Are desorption rates for alcohol, organic solvent, amine, and fatty acid NeedlEx® needles all greater than 95%? Do desorption rates differ according to the type of compound being analyzed?

All varieties of NeedlEx® display almost complete adsorption up to their breakthrough points. However, desorption in GC injection ports is not 100% complete. Desorption rates for a wide variety of common organic solvents except the cresols were found to be greater than 95%. Desorption rates for fatty acids and trimethylamine were also found to be greater than 95%. The most important factor in desorption is the GC injection port temperature. Injection port temperatures for amine, organic solvent, fatty acid, and alcohol NeedlEx needles are 200℃ (amine and organic solvent needles), 250℃, and 300℃ respectively. Temperatures lower than these result in decreases in desorption rates. Higher temperatures result in acceleration of the deterioration of needle adsorbents.
In the case of the organic solvent NeedlEx®, desorption rates are approximately 80% for compounds with boiling points higher than 200℃, such as the cresols.

Q17 If the NeedlEx® continues to be used for more than 30 times, what will eventually happen to the NeedlEx®? Will the NeedlEx® become unable to adsorb compounds, or will it become impossible to desorb compounds?

30 times is the number of analyses per NeedlEx® that is guaranteed by our company. The performance of needles will not immediately deteriorate when this figure is surpassed; however, because needles may be used in harsh environments, we have established a safety margin. When needles do eventually degrade, adsorption performance, rather than desorption, worsens.

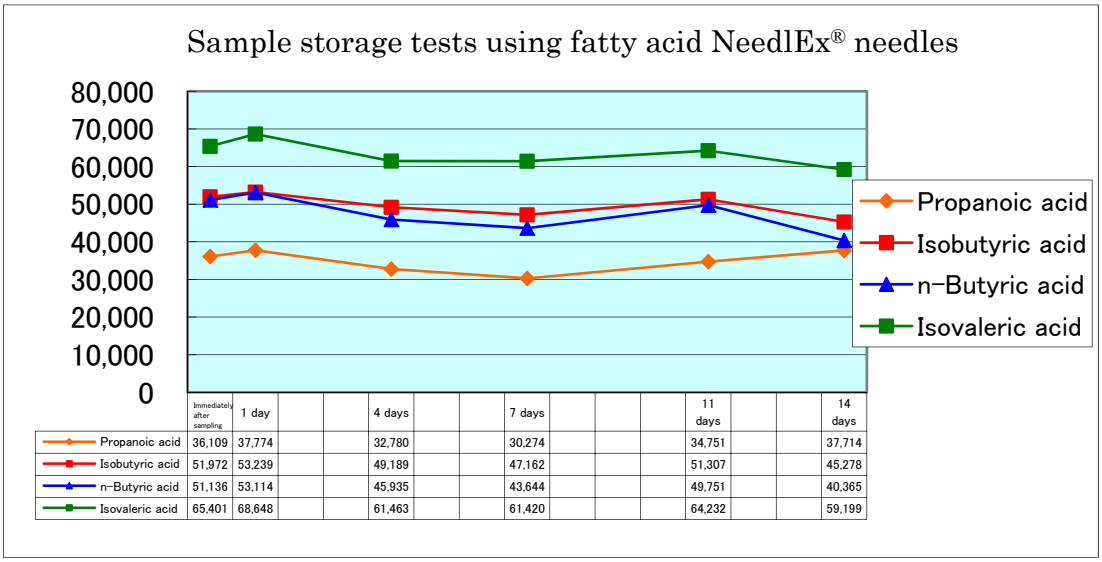
Q18 After carrying out analyses of compounds that have been sampled in harsh environments, is it possible to completely remove remaining trace amounts of gases by cleaning in an injection port before using needles again? Are mist and other contaminants adsorbed inside needles?

As described in the NeedlEx® instruction manual, volatile compounds can be completely removed from needles by cleaning in an injection port for 30 seconds. However, when mist and other contaminants are adsorbed during sampling in harsh environments, the original performance of needles cannot be restored by cleaning.

Q19 How stable is the NeedlEx®? I understand that analyses must be performed within 10 days of sampling. What happens when analyses are performed more than 10 days after sampling?

Table 5 below shows the results of measurements of four fatty acids at varying intervals after sampling. 200 ppb samples of each compound were prepared, and 100 ml of each sample were sampled using 6 NeedlEx® needles. The needles were immediately sealed using Teflon plugs, and then analyzed at varying intervals after sampling.

Table 5 Sample storage tests using fatty acid NeedlEx® needles

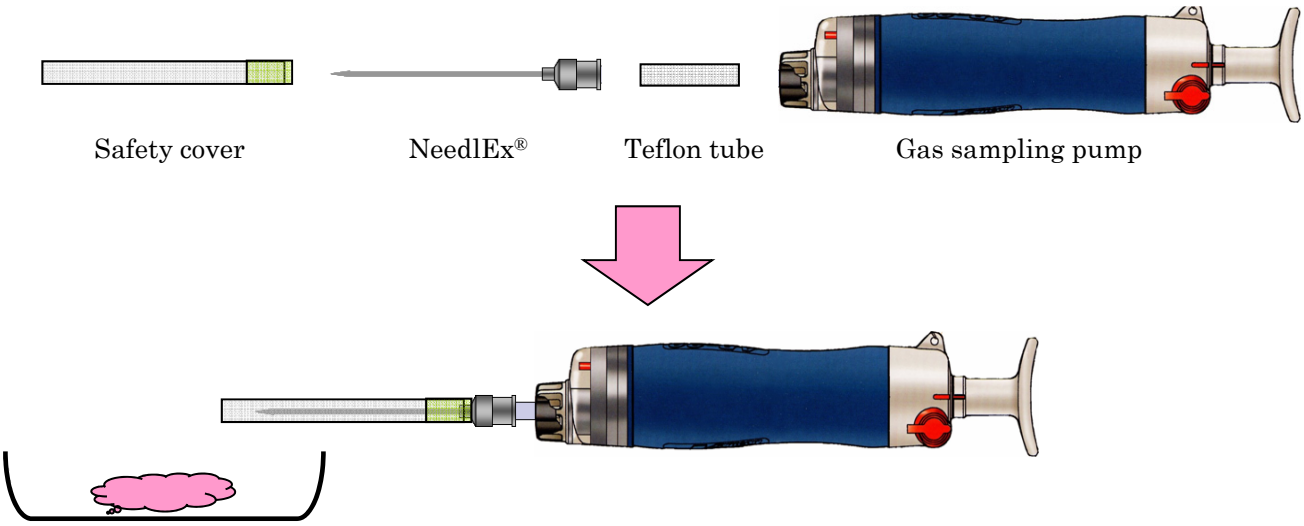


	Immediately after sampling	1 day			4 days			7 days			11 days			14 days
Propanoic acid	36,109	37,774			32,780			30,274			34,751			37,714
Isobutyric acid	51,972	53,239			49,189			47,162			51,307			45,278
n-Butyric acid	51,136	53,114			45,935			43,644			49,751			40,365
Isovaleric acid	65,401	68,648			61,463			61,420			64,232			59,199

The same test was performed using organic solvent and amine NeedlEx® needles. Both types of NeedlEx® were found to be capable of storing samples without significant loss for at least 10 days. Although sample storage capabilities do not immediately deteriorate after 10 days, we have established 10 days as the maximum guaranteed storage period after sampling.

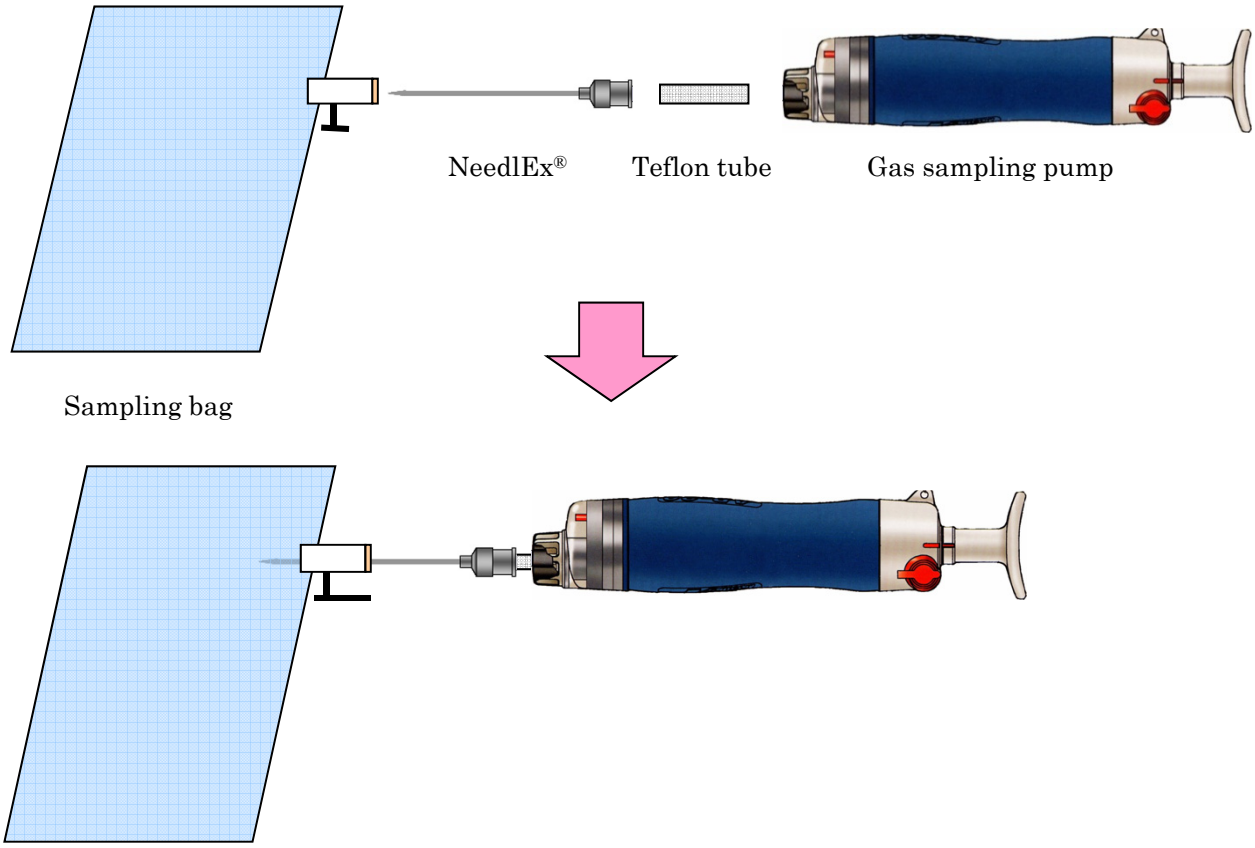
5.NeedlEx® usage examples

5.1 Direct sampling method



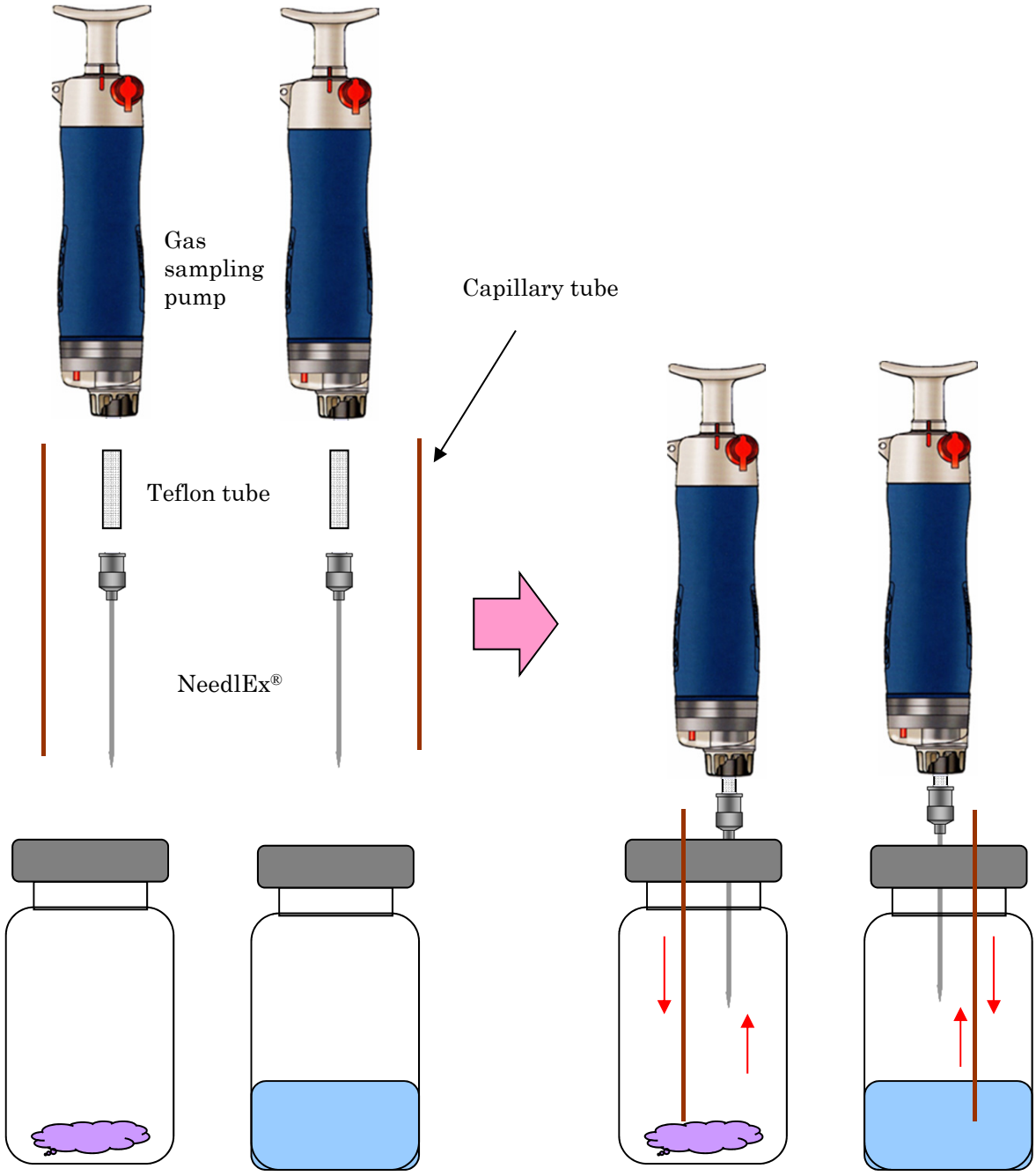
Attach a NeedlEx® needle with a safety cover to a gas sampling pump, and directly sample the gaseous compounds above a sample (solid or liquid).

5.2 Sampling bag sampling method



Attach a NeedlEx® needle to a gas sampling pump, and sample gaseous compounds gathered using a sampling bag.

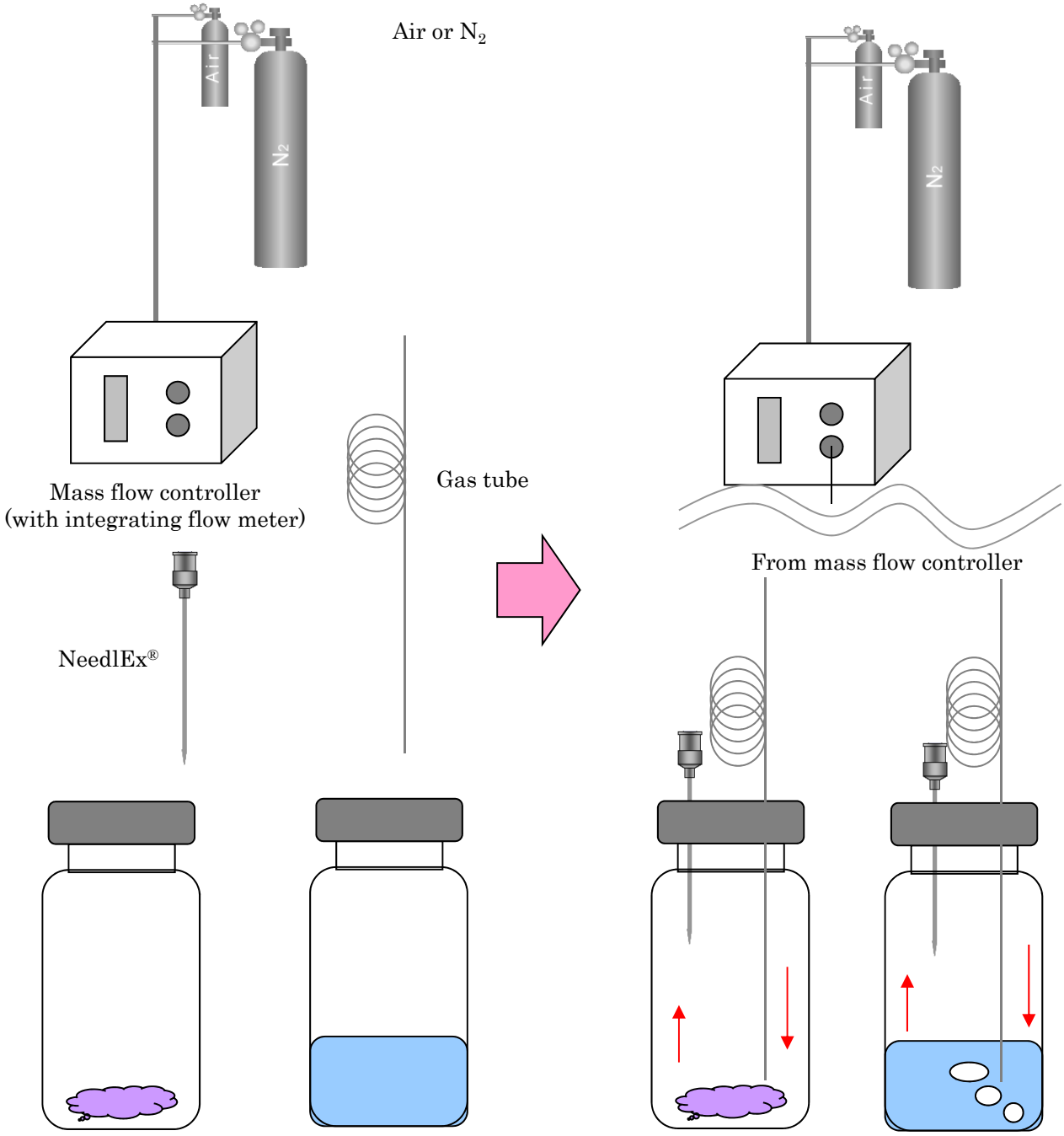
5.3 Headspace sampling method (1)



Attach a NeedlEx® needle to a gas sampling pump, and sample the gas above a solid sample placed in a headspace vial. Alternatively, for liquid samples, more efficient sampling is possible by placing the tip of an air intake capillary tube below the surface of a liquid sample, and simultaneously sampling headspace gas and intaking air.

NeedlEx® breakthrough volumes significantly decrease when sample temperatures are raised. When heating samples, cool samples to room temperature before carrying out sampling.

5.4 Headspace sampling method (2)



Sample sampling method using a mass flow controller. Place a solid sample in a headspace vial, and sample the gas above the sample. Alternatively, for liquid samples, more efficient sampling is possible by bubbling gas through the sample and sampling gas above the sample.

As sudden increases in gas flow rates can result in destruction of vials and emissions of adsorbents packed inside NeedlEx® needles, set gas flow rates to 50 ml/min or less (the differential pressure for NeedlEx® needles at 50 ml/min is 100 kPa).

6. NeedlEx® selection guide

Compounds shown in alphabetical order

Compound name	Boiling point (℃)	For alcohols	For organic solvents	For fatty acids	For amines
Acetic acid	118.0	◎	○	◎	–
Acetoaldehyde	20.2	◎	–	–	–
Acetone	56.5	◎	×	–	–
Acetonitrile	82.0	◎	×	×	–
Acrolein	53.0	◎	×	×	–
Acrylic acid	139.0	–	◎	◎	–
Acrylonitrile	77.0	◎	×	×	–
Allyl alcohol	97.0	◎	○	△	–
Ammonia	-33.3	–	–	–	◎
iso-Amyl acetate	142.0	–	◎	◎	–
n-Amyl acetate	149.0	–	◎	◎	–
iso-Amyl alcohol	130.0	◎	◎	◎	–
n-Amyl alcohol	137.5	◎	◎	◎	–
Benzene	80.0	◎	×	×	–
Benzyl alcohol	205.0	–	–	◎	–
1,3-Butadiene	-4.4	◎	–	–	–
iso-Butane	-12.0	◎	–	–	–
n-Butane	-0.5	◎	–	–	–
2-Butanol	99.0	◎	◎	○	–
iso-Butanol	108.0	◎	◎	◎	–
1-Butanol	117.0	◎	◎	◎	–
iso-Butene	-6.9	◎	–	–	–
1-Butene	-6.3	◎	–	–	–
trans-2-Butene	0.9	◎	–	–	–
cis-2-Butene	3.7	◎	–	–	–
iso-Butyl acetate	118.0	◎	◎	◎	–
n-Butyl acetate	126.0	◎	◎	◎	–
iso-Butyl aldehyde	62.0	◎	△	△	–
n-Butyl aldehyde	85.0	◎	○	○	–
Butyl cellosolve	172.0	–	◎	◎	–
iso-Butyric acid	154.0	–	–	◎	–
n-Butyric acid	164.0	–	–	◎	–
iso-Caproic acid	199.0	–	–	◎	–
n-Caproic acid	205.0	–	–	◎	–
Carbon tetracloride	76.8	◎	–	–	–
Cellosolve	135.0	◎	◎	◎	–
Cellosolve acetate	156.0	–	◎	◎	–
Chlorobenzene	131.0	–	◎	◎	–
Chloroform	61.2	◎	×	×	–
o-Cresol	191.0	–	–	◎	–
p-Cresol	202.0	–	–	◎	–
m-Cresol	202.0	–	–	◎	–

Concentration ratios: ◎ Greater than 100 times, ○ 50 to 100 times, △ 20 to 50 times, × 10 to 20 times,
– less than ten times or not confirmed
Colored cells represent NeedlEx® types particularly recommended.

Compound name	Boiling point (℃)	For alcohols	For organic solvents	For fatty acids	For amines
Crotonaldehyde	100.0	◎	○	○	—
Cyclohexane	81.0	◎	×	×	—
Cyclohexanol	161.0	—	◎	◎	—
Cyclohexanone	155.7	—	◎	◎	—
Cyclohexene	83.0	◎	×	×	—
Cyclopentane	49.3	◎	—	—	—
n-Decane	174.2	—	◎	◎	—
m-Dichlorobenzene	173.0	—	◎	◎	—
p-Dichlorobenzene	174.0	—	◎	◎	—
o-Dichlorobenzene	180.5	—	◎	◎	—
1,1-Dichloroethane	57.0	◎	×	×	—
1,2-Dichloroethane	84.0	◎	△	△	—
1,1-Dichloroethylene	32.0	◎	—	—	—
trans-1,2-Dichloroethylene	48.0	◎	—	—	—
cis-1,2-Dichloroethylene	61.0	◎	×	×	—
Dichloromethane	40.0	◎	—	—	—
Diethyl ether	35.0	◎	—	—	—
Diisopropyl ether	69.0	◎	△	△	—
Dimethyl ether	-23.6	◎	—	—	—
N,N-Dimethyl formamide	153.0	—	◎	—	—
Dimethylamine	6.9	×	○	—	◎
1,4-Dioxane	101.0	◎	◎	○	—
Ethane	-89.0	—	—	—	—
Ethanol	78.4	◎	○	△	—
Ethyl acetate	77.1	◎	○	×	—
Ethyl acrylate	99.0	◎	○	○	—
Ethyl cellosolve	124.5	◎	◎	◎	—
Ethyl tert-butyl ether	73.0	◎	△	△	—
Ethylbenzene	136.0	◎	◎	◎	—
Ethylene	-104.0	—	—	—	—
Ethylene oxide	10.7	◎	—	—	—
Formaldehyde	-19.3	○	—	—	—
Formic acid	100.7	◎	○	◎	—
Furfural	161.7	—	◎	◎	—
Glycidol	167.0	—	◎	◎	—
n-Heptane	98.0	◎	×	△	—
n-Hexane	69.0	◎	—	×	—
Isoprene	34.0	◎	—	—	—
Methacrolein	69.0	◎	△	△	—
Methacrylic acid	159.0	—	◎	◎	—
Methane	-161.6	—	—	—	—
Methanol	64.7	○	—	—	—
Methyl acetate	56.9	◎	×	—	—
Methyl acrylate	80.0	◎	△	△	—
Methyl ethyl ketone	79.5	◎	○	△	—

Concentration ratios: ◎ Greater than 100 times, ○ 50 to 100 times, △ 20 to 50 times, × 10 to 20 times,
— less than ten times or not confirmed
Colored cells represent NeedlEx® types particularly recommended.

Compound name	Boiling point (℃)	For alcohols	For organic solvents	For fatty acids	For amines
Methyl formate	32.0	◎	—	—	—
Methyl iso-butyl ketone	116.0	◎	◎	◎	—
Methyl methacrylate	101.0	◎	○	○	—
Methyl n-butyl ketone	127.0	◎	◎	◎	—
Methyl tert-butyl ether	55.2	◎	×	×	—
Methylamine	-6.0	×	○	—	◎
Methylcyclohexane	101.0	◎	◎	◎	—
2-Methylcyclohexanol	167.0	—	◎	—	—
4-Methylcyclohexanol	174.0	—	◎	—	—
3-Methylcyclohexanol	175.0	—	◎	—	—
2-Methylcyclohexanone	165.0	—	◎	—	—
3-Methylcyclohexanone	169.0	—	◎	—	—
4-Methylcyclohexanone	169.0	—	◎	—	—
n-Nonane	150.0	—	◎	◎	—
n-Octane	125.0	—	◎	◎	—
iso-Pentane	28.0	◎	—	—	—
n-Pentane	36.0	◎	—	—	—
Phenol	181.7	—	—	◎	—
Propane	-42.0	◎	—	—	—
2-Propanol	82.4	◎	△	△	—
1-Propanol	97.2	◎	○	△	—
Propionaldehyde	48.0	◎	×	×	—
Propionic acid	141.0	—	—	◎	—
Propionitrile	96.0	◎	△	△	—
iso-Propyl acetate	89.0	◎	○	○	—
n-Propyl acetate	96.6	◎	◎	○	—
Propylene	-47.4	◎	—	—	—
Propylene oxide	34.0	◎	—	—	—
Styrene	145.0	◎	◎	◎	—
tert-Butanol	82.0	◎	○	△	—
1,1,2,2-Tetrachloroethane	147.0	—	◎	◎	—
Tetrachloroethylene	121.0	◎	◎	◎	—
Tetrahydrofuran	72.0	◎	△	△	—
Toluene	110.6	◎	◎	◎	—
1,1,1-Trichloroethane	74.0	◎	×	×	—
Trichloroethylene	87.0	◎	×	×	—
Trimethylamine	2.9	△	○	—	◎
iso-Valeric acid	175.0	—	—	◎	—
n-Valeric acid	186.0	—	—	◎	—
Vinyl acetate	72.0	◎	△	×	—
Vinyl chloride	-13.0	◎	—	—	—
Water	100.0	○	—	—	×
p-Xylene	138.0	◎	◎	◎	—
m-Xylene	139.0	◎	◎	◎	—
o-Xylene	144.0	◎	◎	◎	—

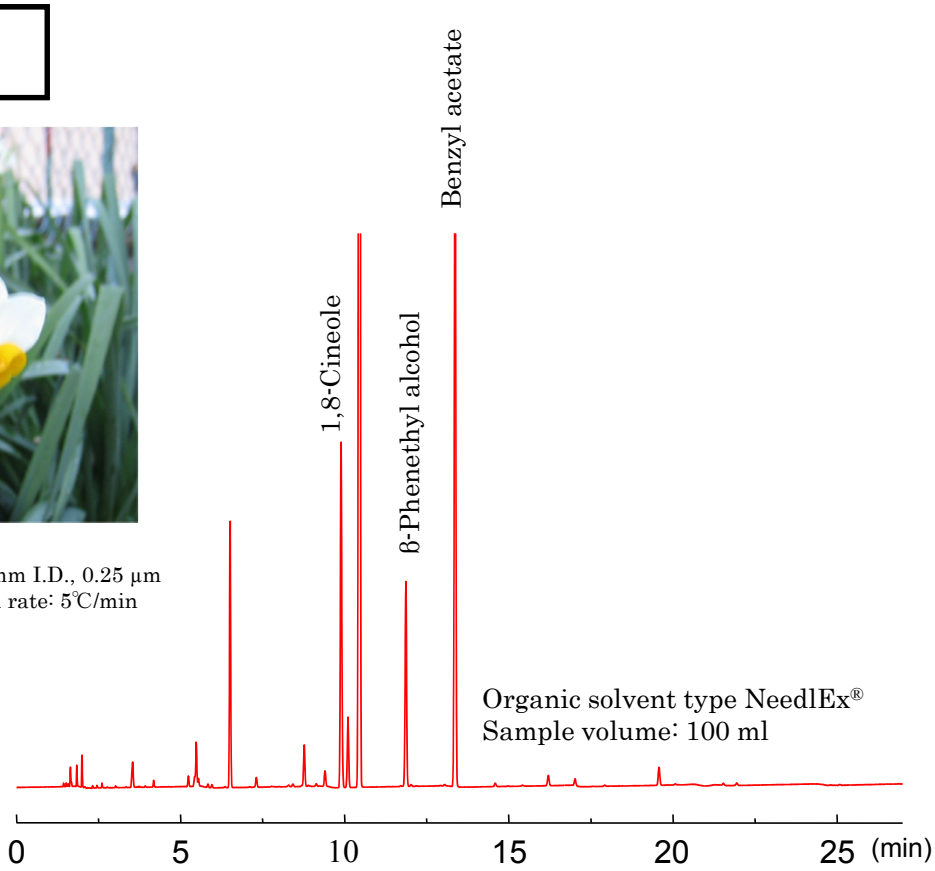
Concentration ratios: ◎ Greater than 100 times, ○ 50 to 100 times, △ 20 to 50 times, × 10 to 20 times, — less than ten times or not confirmed

Colored cells represent NeedlEx® types particularly recommended.

7. NeedlEx® application examples

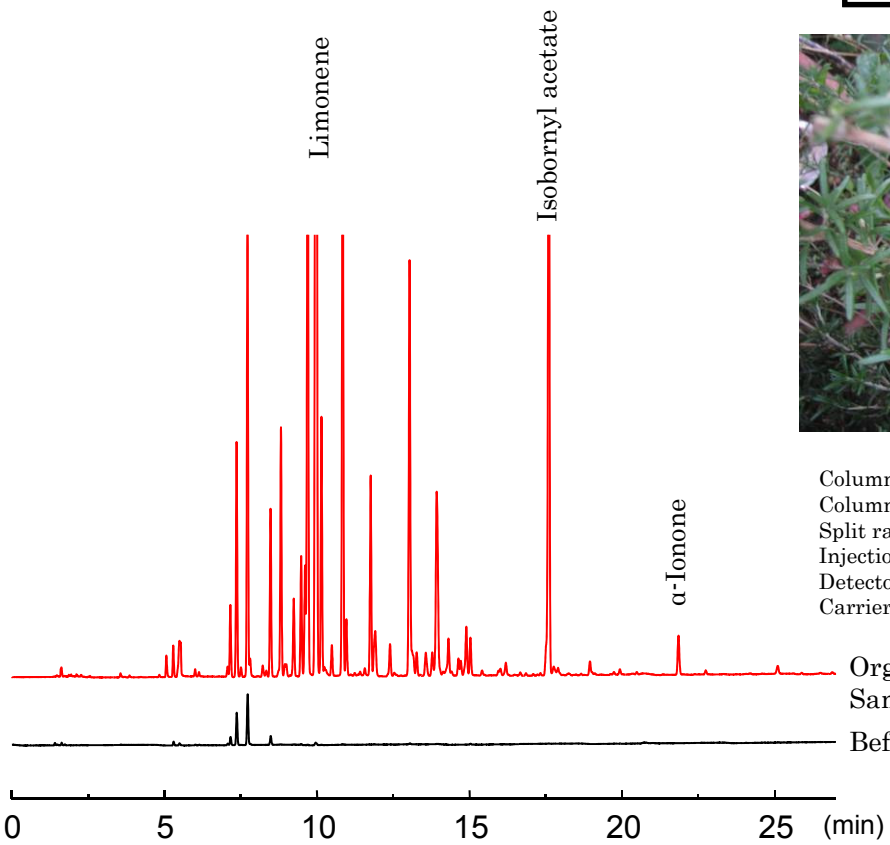
Daffodil fragrance

Column: ULBON HR-1, 30 m x 0.32 mm I.D., 0.25 µm
Column temp.: 50℃～200℃, Program rate: 5℃/min
Split ratio: 10:1
Injection port temp.: 200℃
Detector: FID (250℃)
Carrier gas: He, 2.4 mL/min

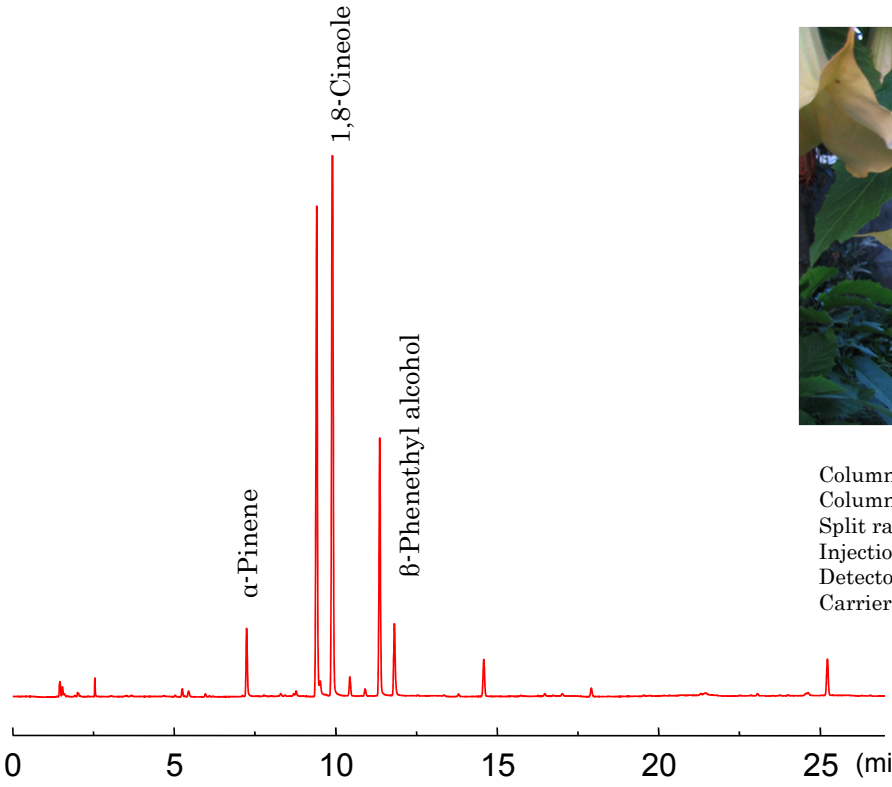


Rosemary fragrance

Column: ULBON HR-1, 30 m x 0.32 mm I.D., 0.25 µm
Column temp.: 50℃～200℃, Program rate: 5℃/min
Split ratio: 10:1
Injection port temp.: 200℃
Detector: FID (250℃)
Carrier gas: He, 2.4 mL/min



Angel's trumpet fragrance

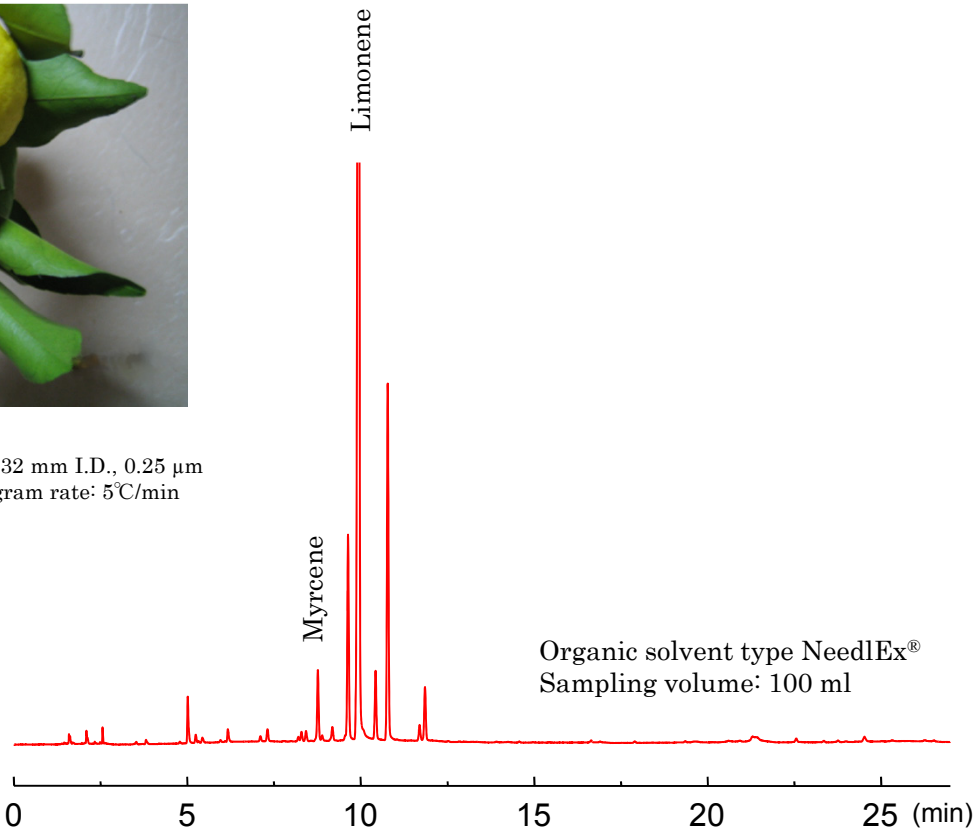


Column: ULBON HR-1, 30 m x 0.32 mm I.D., 0.25 µm
Column temp.: 50℃～200℃, Program rate: 5℃/min
Split ratio: 10:1
Injection port temperature: 200℃
Detector: FID (250℃)
Carrier gas: He, 2.4 mL/min

Organic solvent type NeedlEx®
Sampling volume: 100 ml

Citron fragrance

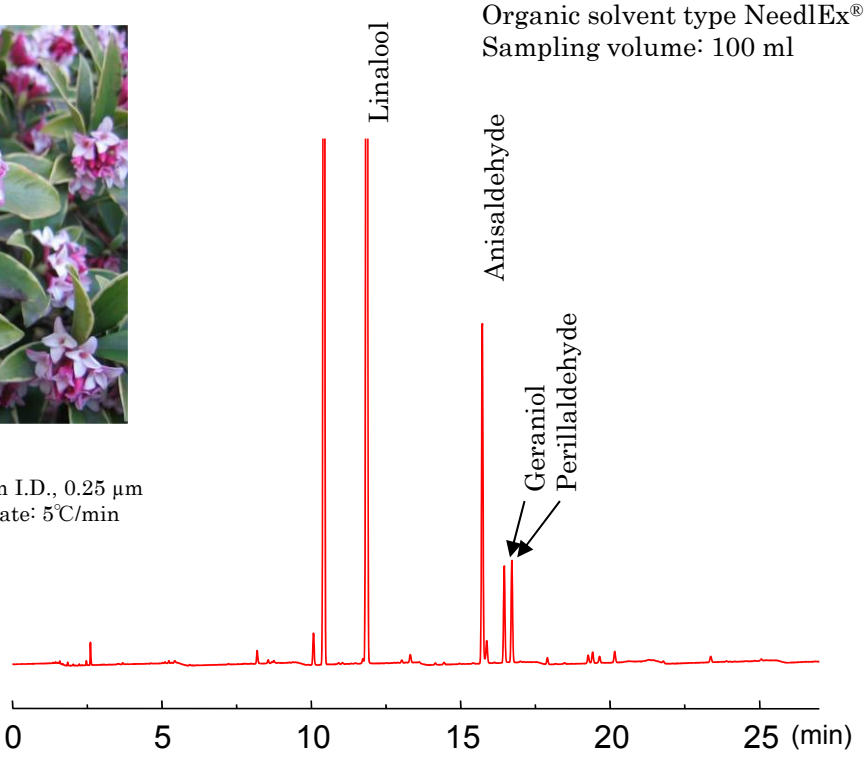
Column: ULBON HR-1, 30 m x 0.32 mm I.D., 0.25 µm
Column temp.: 50℃～200℃, Program rate: 5℃/min
Split ratio: 10:1
Injection port temp.: 200℃
Detector: FID (250℃)
Carrier gas: He, 2.4 mL/min



Organic solvent type NeedlEx®
Sampling volume: 100 ml

Daphne fragrance

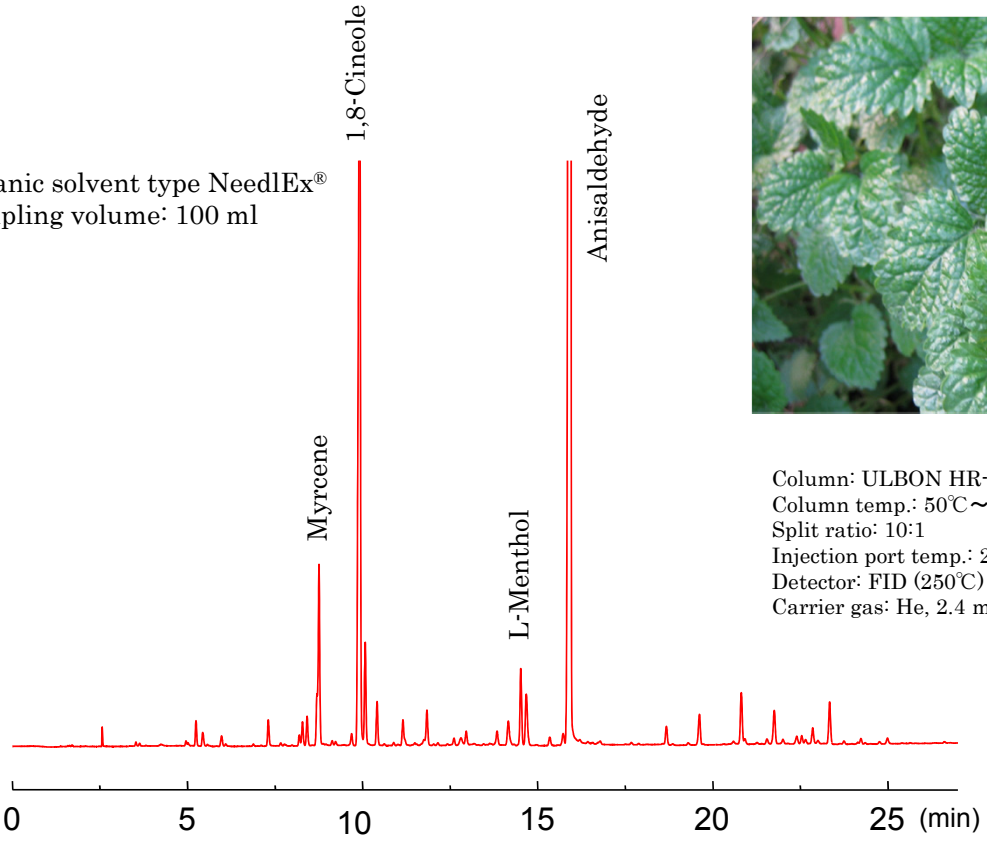
Organic solvent type NeedlEx®
Sampling volume: 100 ml



Column: ULBON HR-1, 30 m x 0.32 mm I.D., 0.25 µm
Column temp.: 50℃～200℃, Program rate: 5℃/min
Split ratio: 10:1
Injection port temp.: 200℃
Detector: FID (250℃)
Carrier gas: He, 2.4 mL/min

Peppermint fragrance

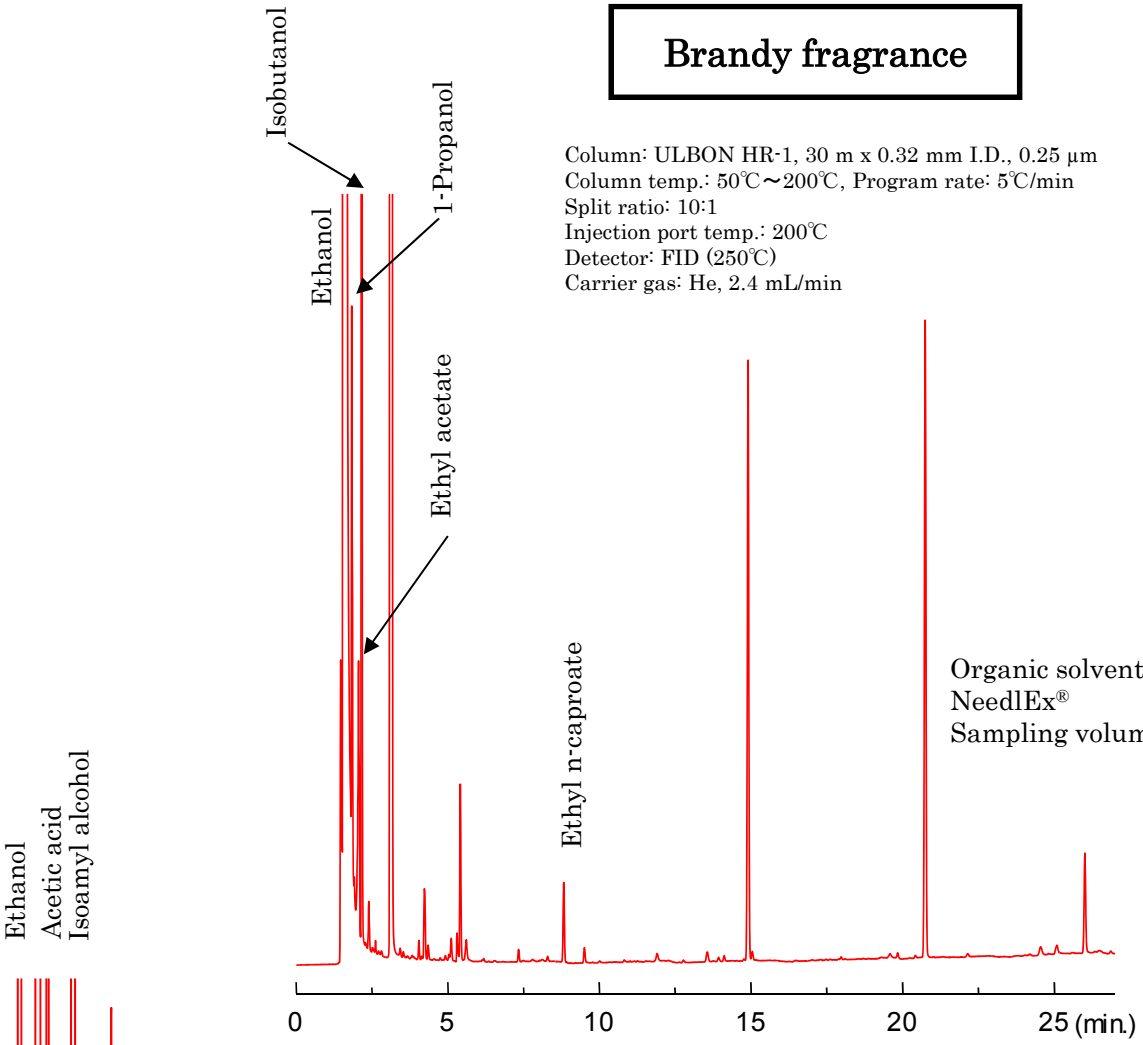
Organic solvent type NeedlEx®
Sampling volume: 100 ml



Column: ULBON HR-1, 30 m x 0.32 mm I.D., 0.25 µm
Column temp.: 50℃～200℃, Program rate: 5℃/min
Split ratio: 10:1
Injection port temp.: 200℃
Detector: FID (250℃)
Carrier gas: He, 2.4 mL/min

Brandy fragrance

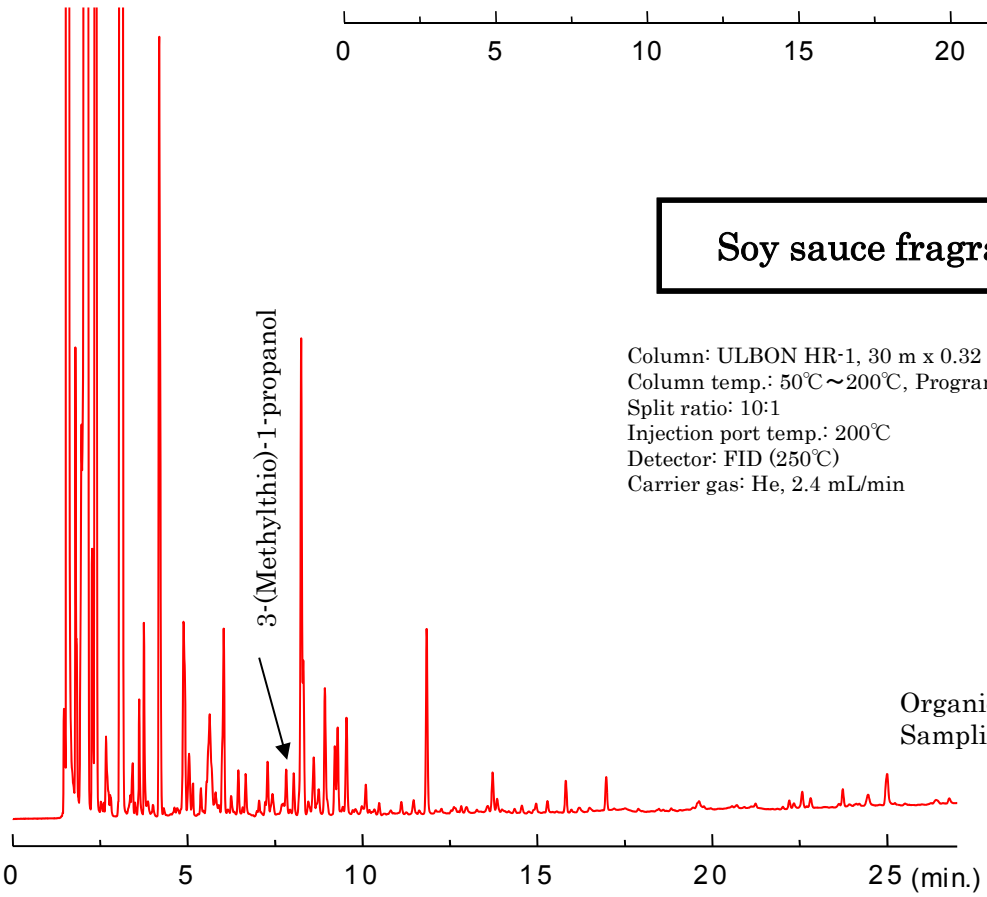
Column: ULBON HR-1, 30 m x 0.32 mm I.D., 0.25 µm
Column temp.: 50℃～200℃, Program rate: 5℃/min
Split ratio: 10:1
Injection port temp.: 200℃
Detector: FID (250℃)
Carrier gas: He, 2.4 mL/min



Organic solvent type
NeedlEx®
Sampling volume: 100 ml

Soy sauce fragrance

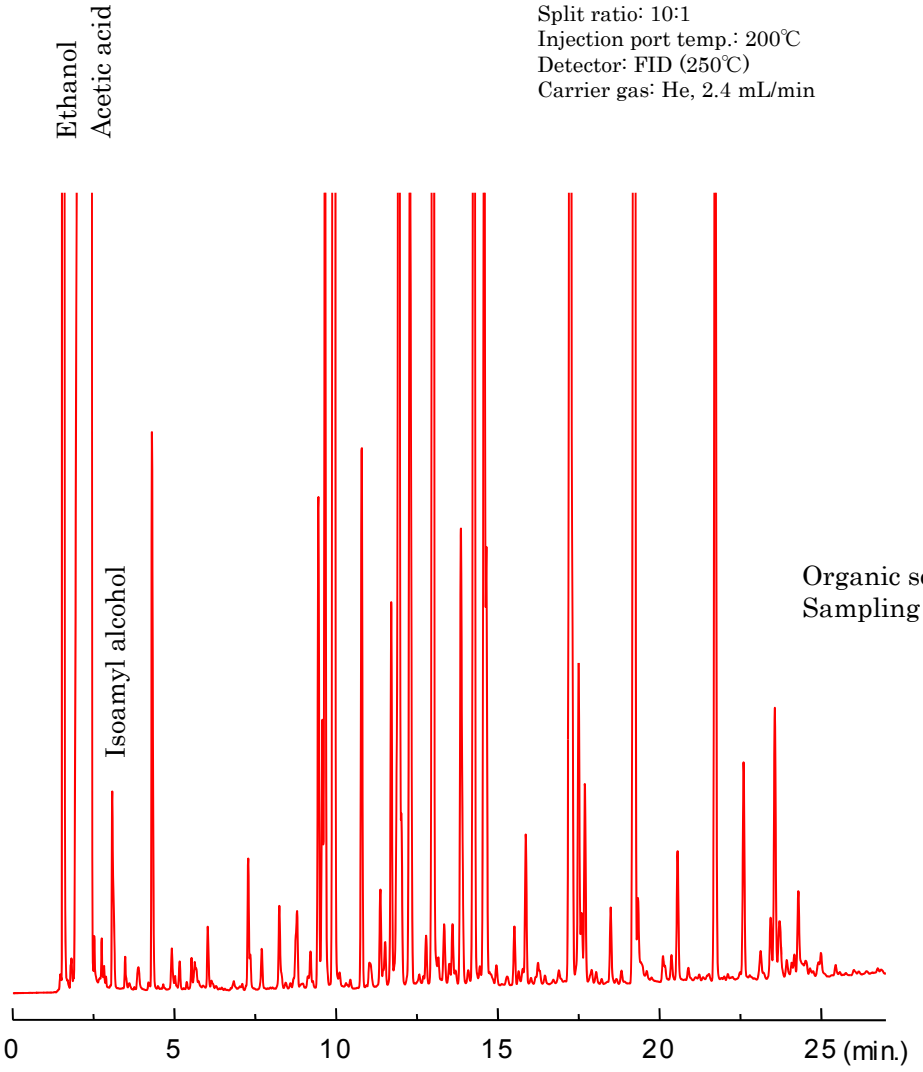
Column: ULBON HR-1, 30 m x 0.32 mm I.D., 0.25 µm
Column temp.: 50℃～200℃, Program rate: 5℃/min
Split ratio: 10:1
Injection port temp.: 200℃
Detector: FID (250℃)
Carrier gas: He, 2.4 mL/min



Organic solvent type NeedlEx®
Sampling volume: 100 ml

Worcestershire sauce fragrance

Column: ULBON HR-1, 30 m x 0.32 mm I.D., 0.25 μm
Column temp.: 50℃～200℃, Program rate: 5℃/min
Split ratio: 10:1
Injection port temp.: 200℃
Detector: FID (250℃)
Carrier gas: He, 2.4 mL/min



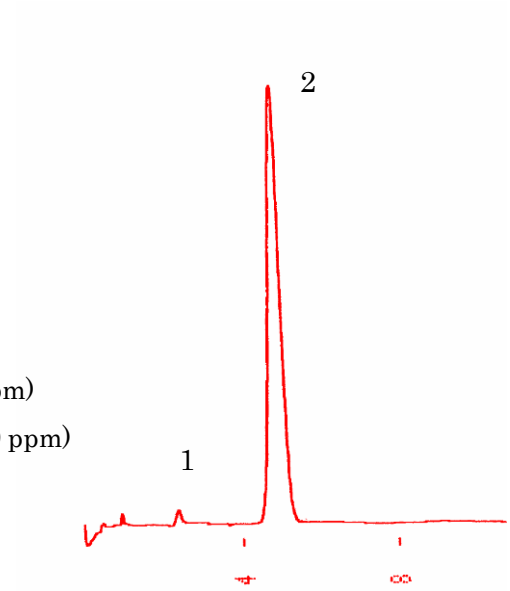
Organic solvent type NeedlEx®
Sampling volume: 100 ml

Seafood putrefaction odor

Column: 2 + 2% Thermon-3000 + KOH Sunpak-N 2.1 m x 3.2 mm
Column temp: 120℃
Injection port temp.: 250℃
Detector: FID (250℃)
Carrier gas: N_2, 50 mL/min
Range: 10^1 x ATT 3

Amine type NeedlEx®
Sampling volume: 100 ml

1. Methylamine (0.02 ppm)
2. Trimethylamine (0.49 ppm)



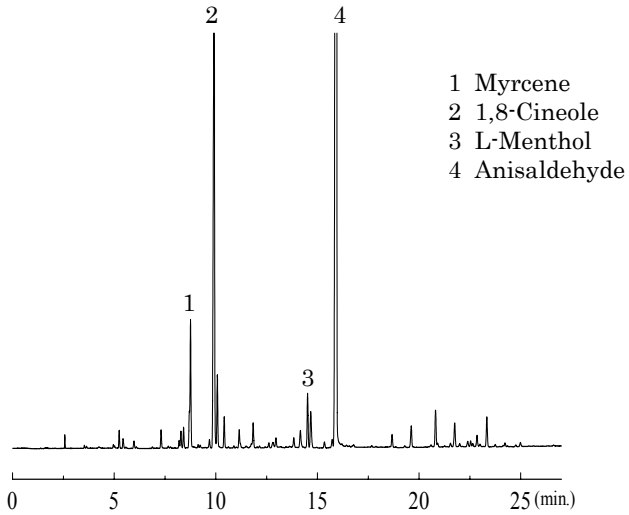
8. Comparison with solvent extraction method

Solvent extraction and steam distillation are two methods commonly used as pretreatment methods in quantitative analyses of the aroma components of flowers and herbs. Below is a comparison of the results of two analyses of the aroma components of peppermint carried out using solvent extraction and headspace sampling employing a NeedlEx®.

On comparison of the chromatograms below, it was found that the peak area ratios for anisaldehyde (b.p.: 247℃), the main fragrance constituent of peppermint which appears at approximately 16 minutes, were approximately 67% and 93% for the headspace and solvent extraction methods respectively. This result is due to the fact that when using the solvent extraction method, not only compounds naturally emitted from peppermint leaves, but also all lipid-soluble substances contained in peppermint leaves including compounds present in cells and high boiling point compounds, are extracted and detected as peaks. The same reasoning can also be used to explain the two peaks that appear at approximately five minutes in the solvent extraction method chromatogram.

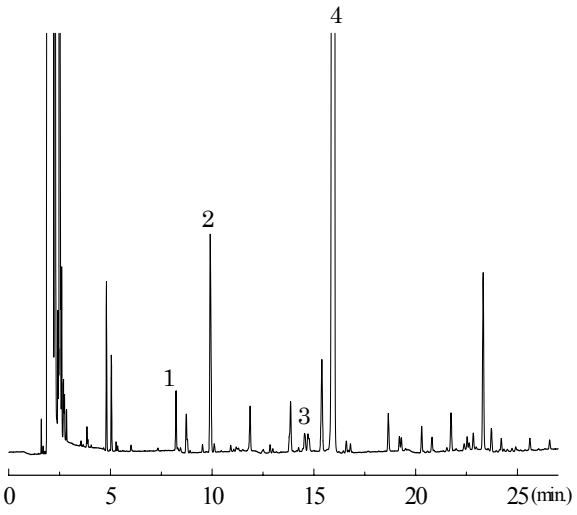
From this comparison it can be said that headspace sampling using the NeedlEx® is an effective method for measuring aroma constituents that can be detected using the sense of smell.

Headspace analysis using the NeedlEx®



Organic solvent type NeedlEx®
(sampling volume: 100 ml)

Solvent extraction analysis



Extraction from 100 g of peppermint leaves using 20 ml of hexane

Column: ULBON HR-1, 30 m x 0.32 mm I.D., 0.25 μm
Column temp.: 50℃～200℃, Program rate: 5℃/min
Split ratio: 10:1
Injection port temp.: 200℃
Detector: FID (250℃)
Carrier gas: He, 2.4 mL/min

Distributed by:

EURO-GAS MANAGEMENT SERVICES LTD
Churston House, Bascombe Road,
Churston Ferrers, Devon, TQ5 0JJ, UK
Tel: +44 (0)1803 844414
Website: www.euro-gasman.com
Email: sales@euro-gasman.com

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1-8-28 Shimonoge, Takatsu-Ku,
Kawasaki-City, Kanagawa, 213-0006, Japan
Tel: +81-44-833-8911
Website: www.komyokk.co.jp/english/
Email: qa@komyokk.co.jp