New approach of simple pretreatment for GCMS analysis by using monolithic material sorptive extraction

Content

- Current sample pretreatment techniques
- Monolithic material sorptive extraction (MMSE)
- PAHs analysis with MMSE in water sample
- Conclusion

Introduction

- Environmental pollutions and food contaminations are biggest social concerns, nowadays. Because of the complex matrices in environmental substances and food stuffs, sample preparations for the quantitative analysis of toxic and hazardous compounds with chromatographic instruments are inevitable in order to obtain reliable results. Gas chromatography mass spectrometry (GCMS) has become the important means in the areas of qualitative and quantitative analysis of environmental monitoring and trace amount of contaminants in food stuffs.
- Although the performances of sensitivity and selectivity of this instrument have rapidly been improved in recent years, the sample pretreatment procedures remain the bottleneck for rapid analysis. Therefore, economical and effective pretreatment methods to eliminate matrix interferences, to achieve high throughout and to enrich the analyte for high sensitive detection are demanded.

Goal for sample pretreatment

There are many types of sample pretreatment techniques. However, most of the goal for sample pretreatment are the same.

- High extraction efficiency
- Removal of potential interferences
- Enrichment of an analyte concentration
- Derivatization of an analyte for better separation and higher sensitivity

Better accuracy and precision must be taken into account in sample pretreatment techniques.

Current sample pretreatment techniques

- Soxhlet extraction
- Liquid-liquid extraction (LLE)
- Ultrasonic extraction
- Solid phase extraction (SPE)
- Solid phase microextraction (SPME)
- Stir-bar sorptive extraction (SBSE)
- Monolithic material sorptive extraction (MMSE)
- Matrix solid-phase dispersion (MSPD)
- Liquid phase microextraction (LPME)
- Supercritical fluid extraction (SFE)
- Pressurized liquid extraction (PLE)
- Microwave-assisted extraction (MASE)
- Superheated water extraction (SWE)

Trends of sample pretreatment

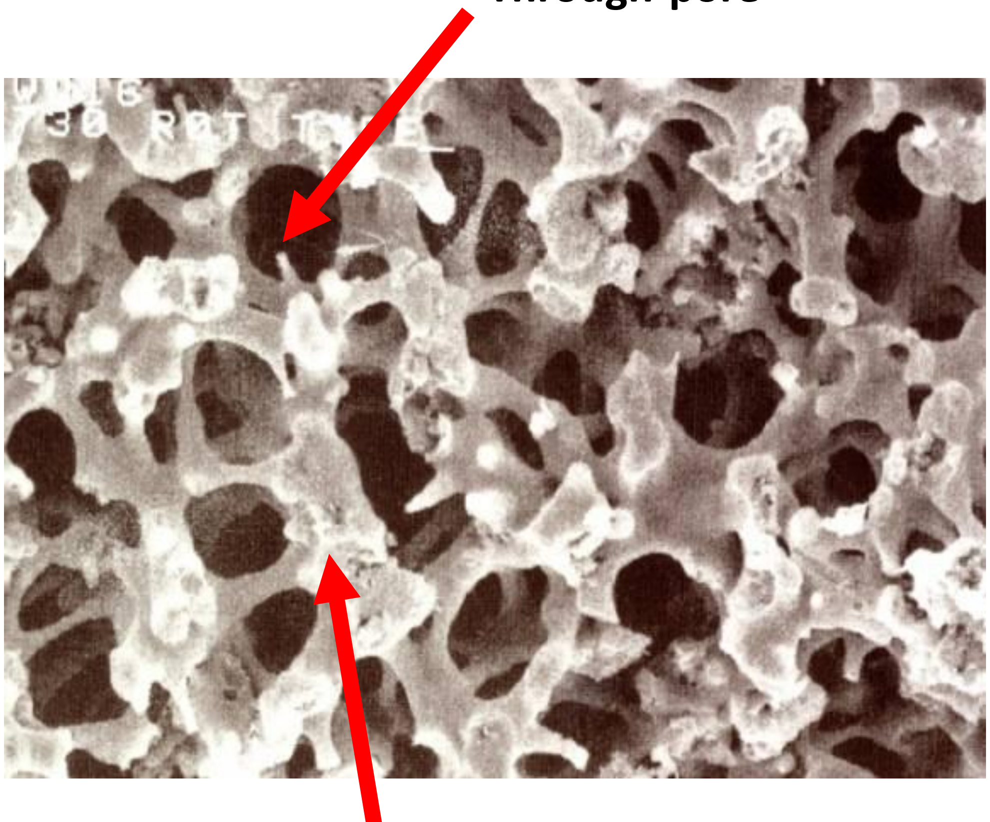
Small initial sample sizes

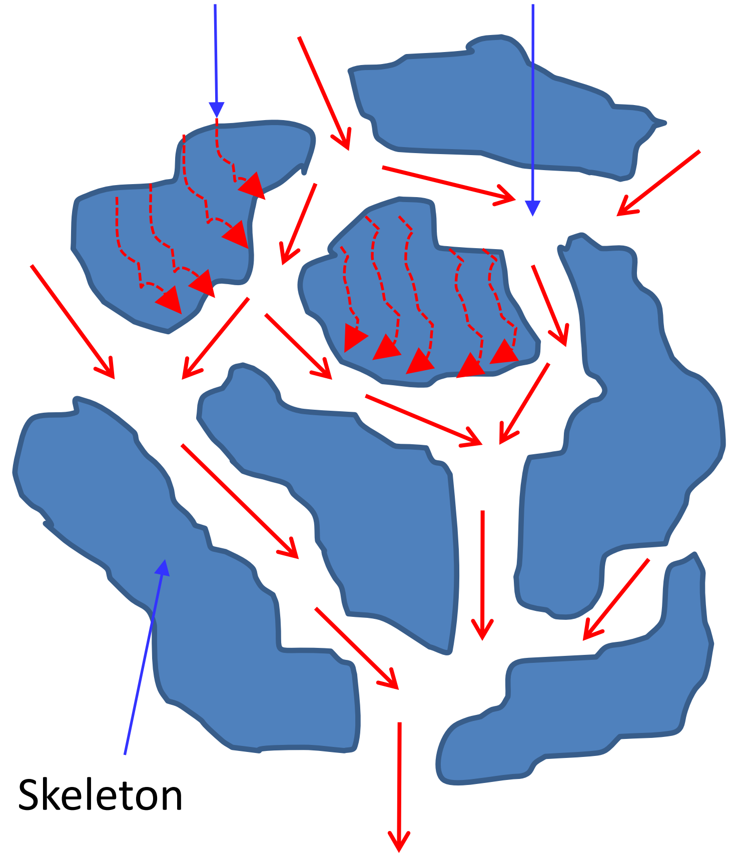
Small preparation volumes

Use of less toxic organic solvents or no organic solvents

Introduction of automation to eliminate human error.

Silica Gel Monolithic Materials

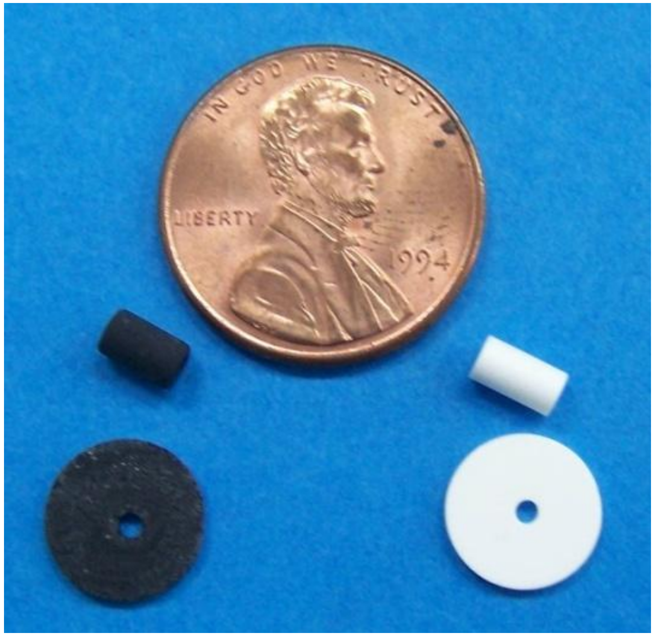




Monolithic Material Sorptive Extraction (MMSE)

Because of through-pore, not only gas substances but also liquid substances are permeable. Meso-pore enlarges the surface area to contact substances. This material can be also used as a sample pretreatment media. This technique may be same as stir bar sorptive extraction (SBSE) and solid-phase microextraction (SPME). However, the difference between MMSE and SBSE/SPME is surface area which will be affected to high extraction efficiency resulting in high sensitivity (Surface area:150 m^2/g).

Type and Dimension of MMSE



Type

(1)ODS (white)

(2)ODS with active carbon (black)

(3)ODS with graphite carbon (gray)

Dimension

Disk type: 10 mmOD x 1 mm thickness

Rod type: 2.9 mmOD x 5 mm height

Selection of MMSE

Thermal Desorption | **Solvent Extraction**

ODS with graphite carbon (gray)

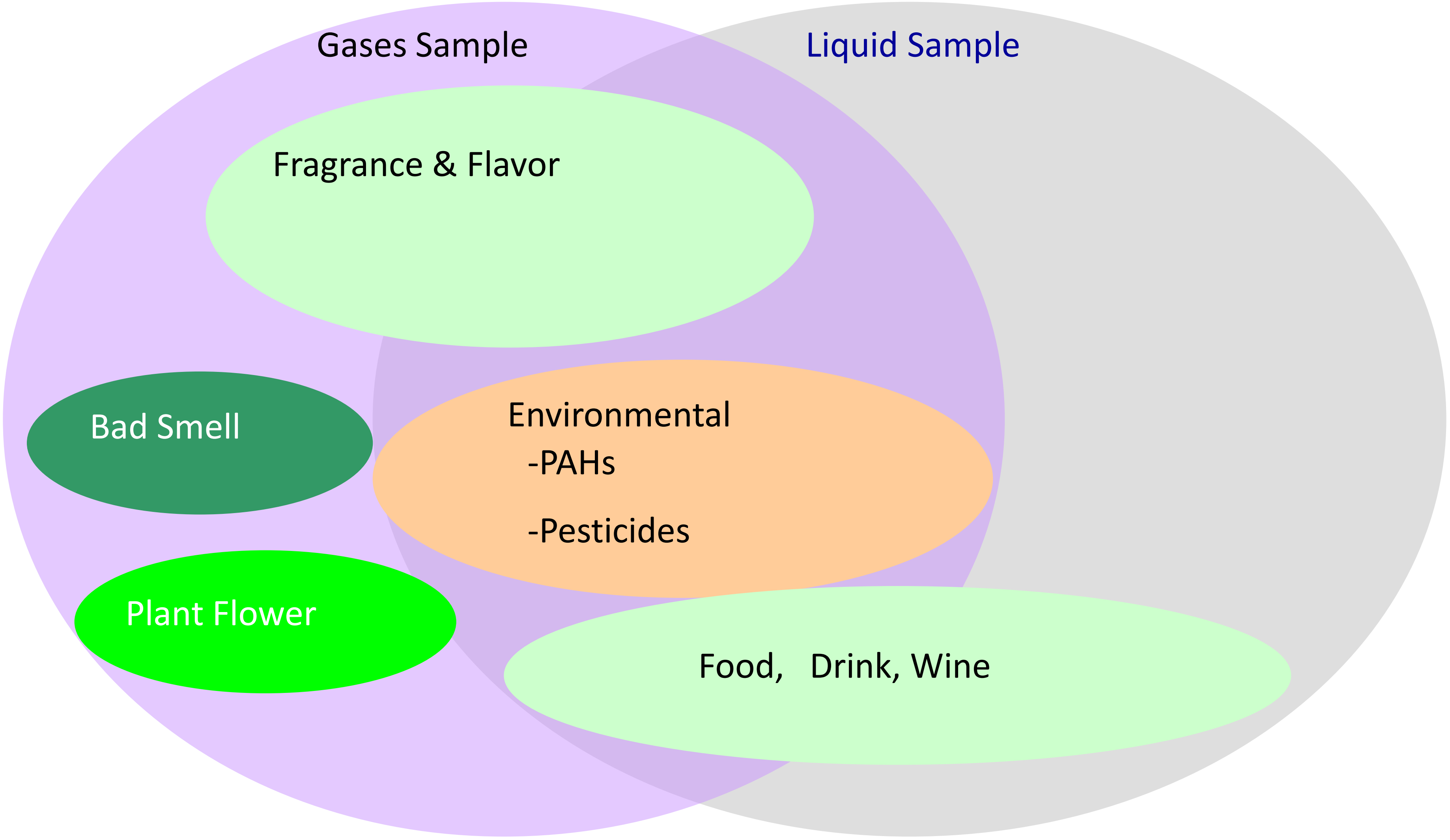
ODS (white)

ODS with active carbon (black)

Adsorption capability →

← **Thermal Desorption capability**

Target Application



Sampling with MMSE

Passive Gas Sampling

Head Space Gas sampling

Agitating Liquid sampling

Agitation for liquid sample

Incubator

Shaker

Desorption from MMSE

- Solvent extraction

Add organic solvent

Very low volume

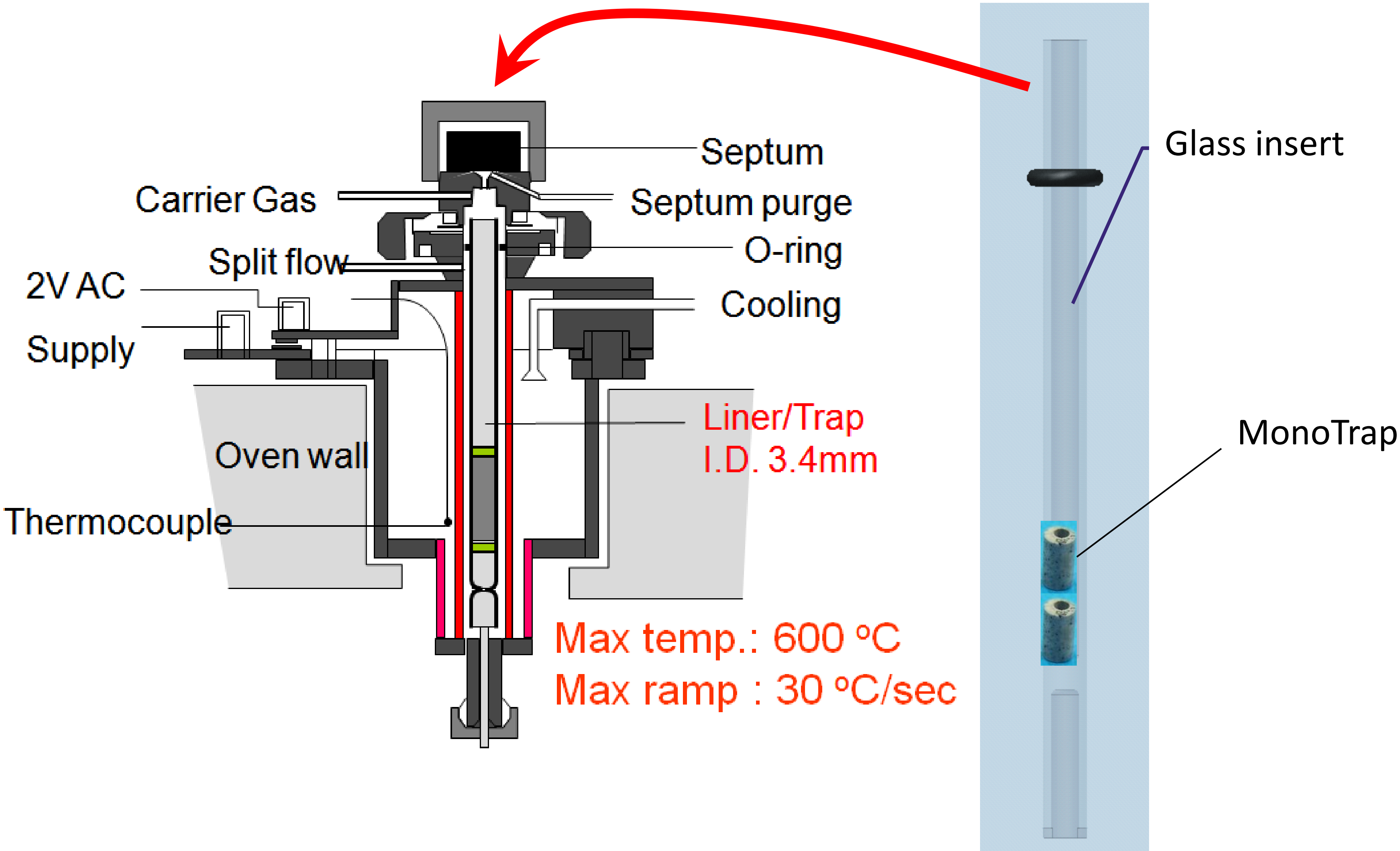
Ultra-sonication for 5 min

- Thermal desorption

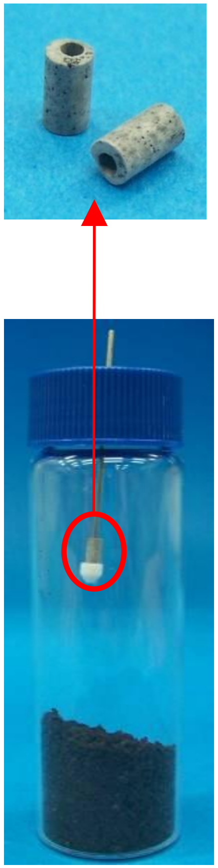
Thermal desorption device for direct injection

No organic solvents
High recovery, high sensitivity

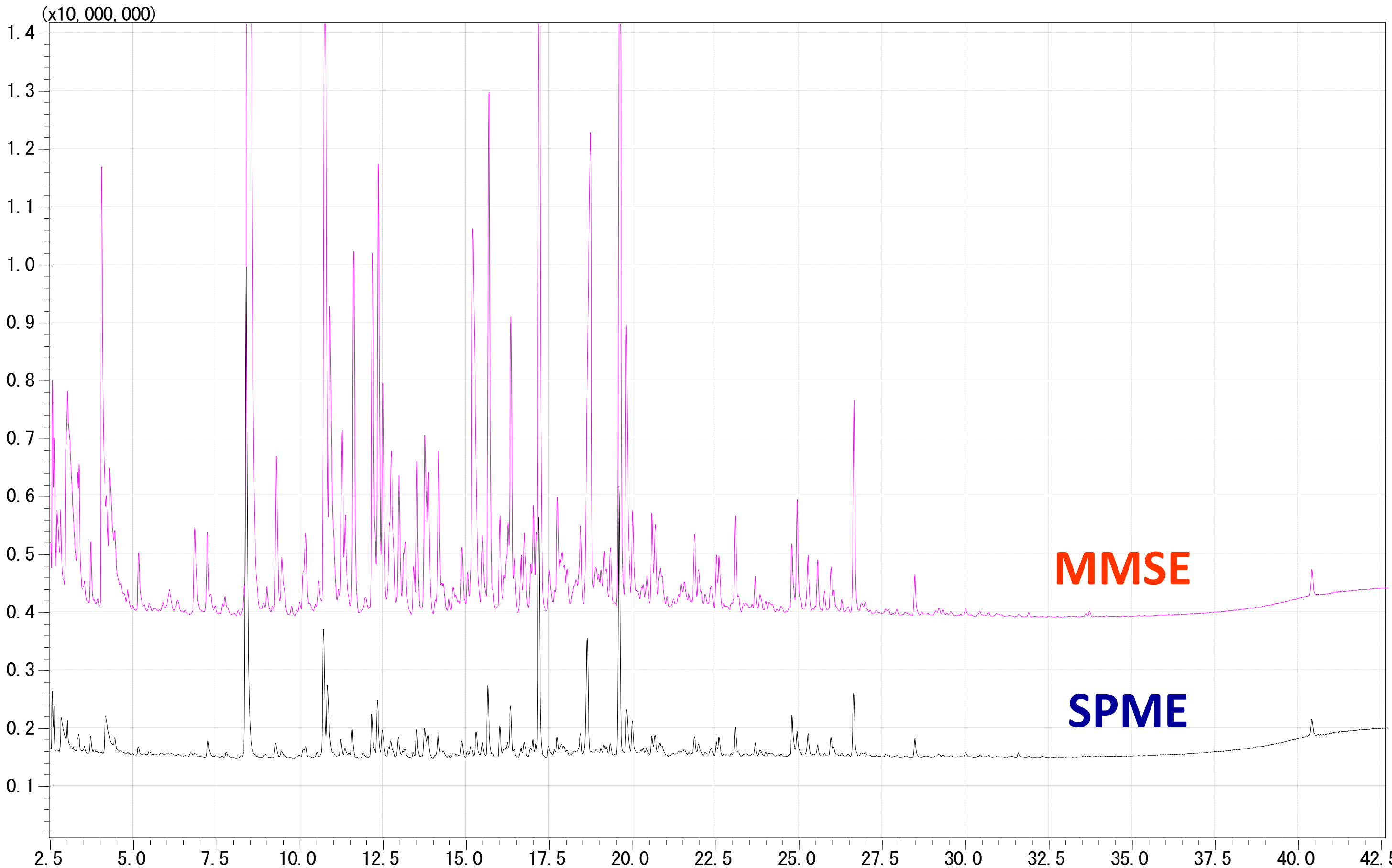
Thermal desorption device for MMSE



Coffee flavor analysis with MMSE vs. SPME



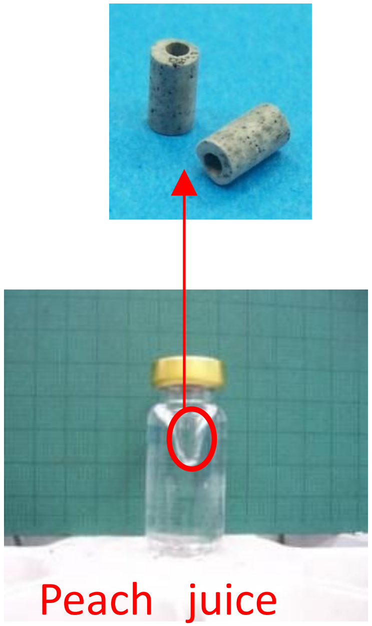
(coffee)

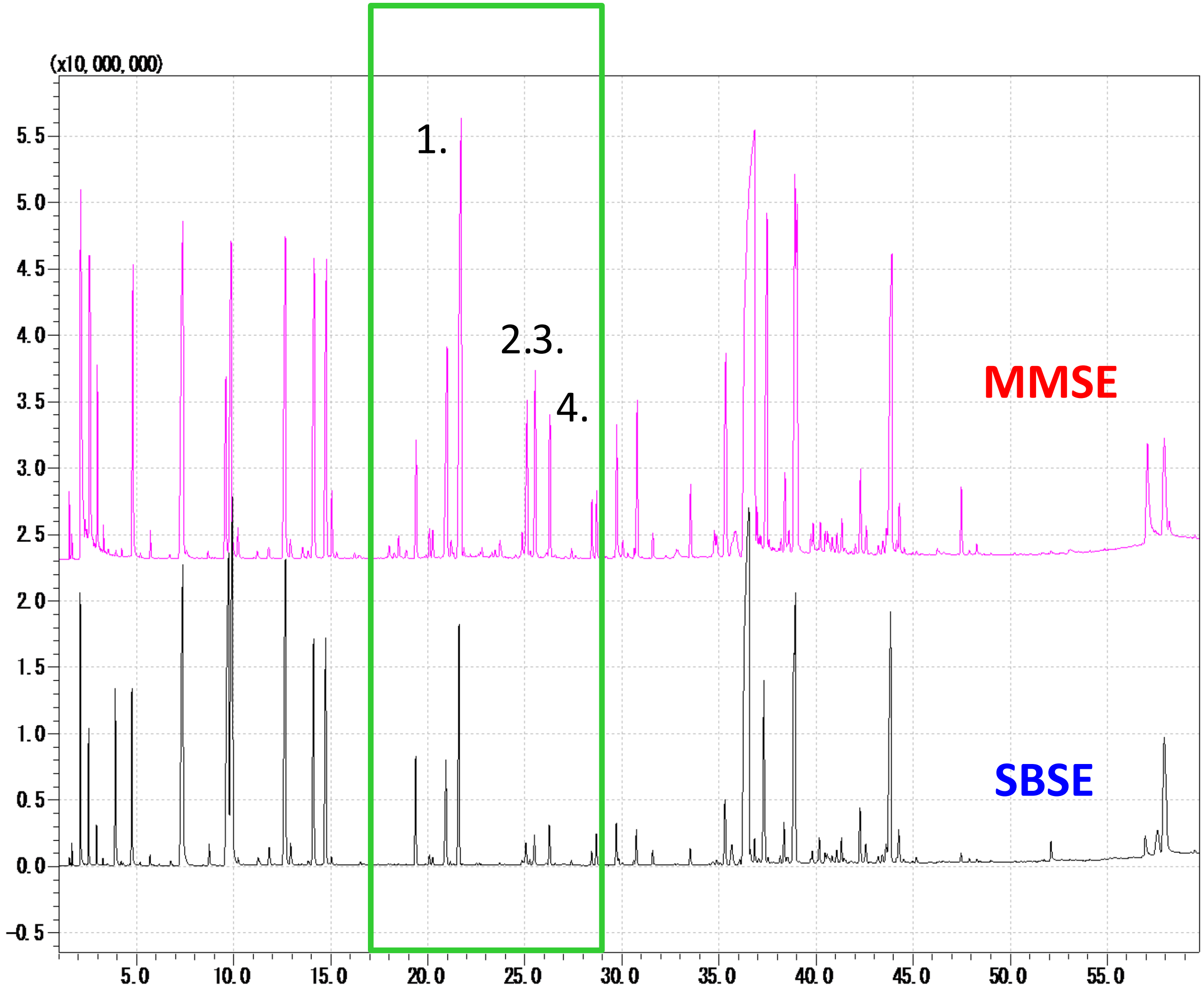


Thermal desorption for MMSE

Peach juice analysis with MMSE vs. SBSE

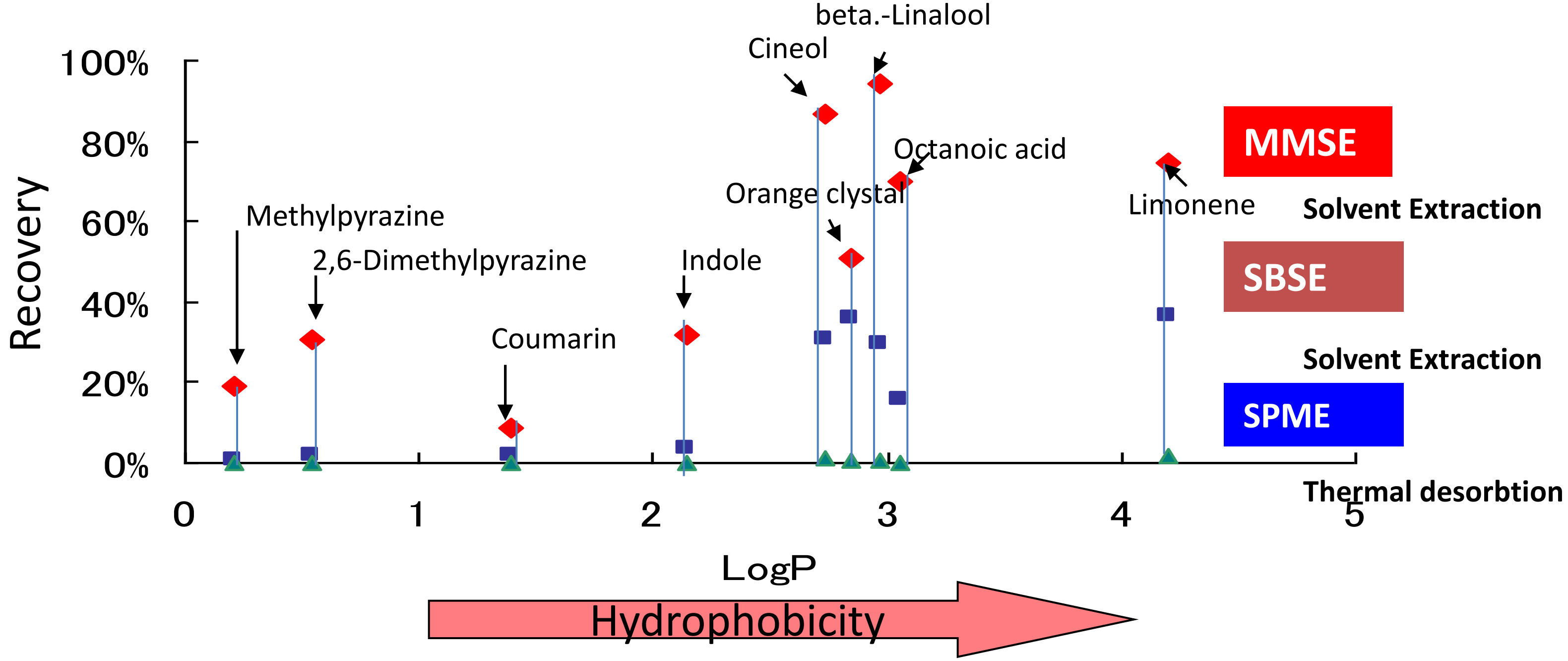
(SBSE:Stir-Bar Sorptive Extraction)



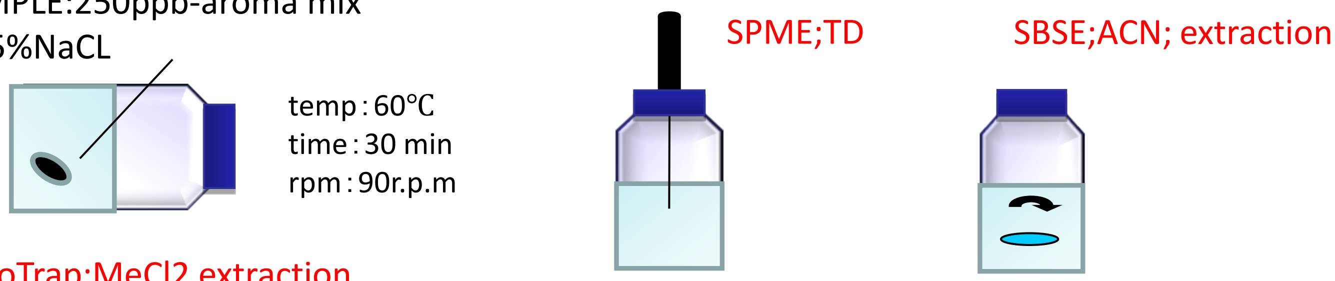


#1;beta-Linalool
#2;gamma-Caprolactone
#3;alpha-Terpineol
#4;Benzyl acetate

Comparison of MMSE, SBSE and SPME - Log P and Recovery -



SAMPLE:250ppb-aroma mix in15%NaCL



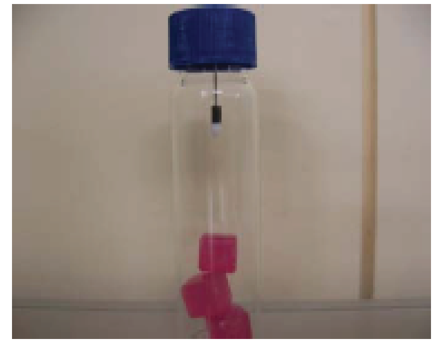
MonoTrap;MeCl2 extraction

Flavor analysis in candy

Sample

→ Three pieces of candy

Head Space Sampling



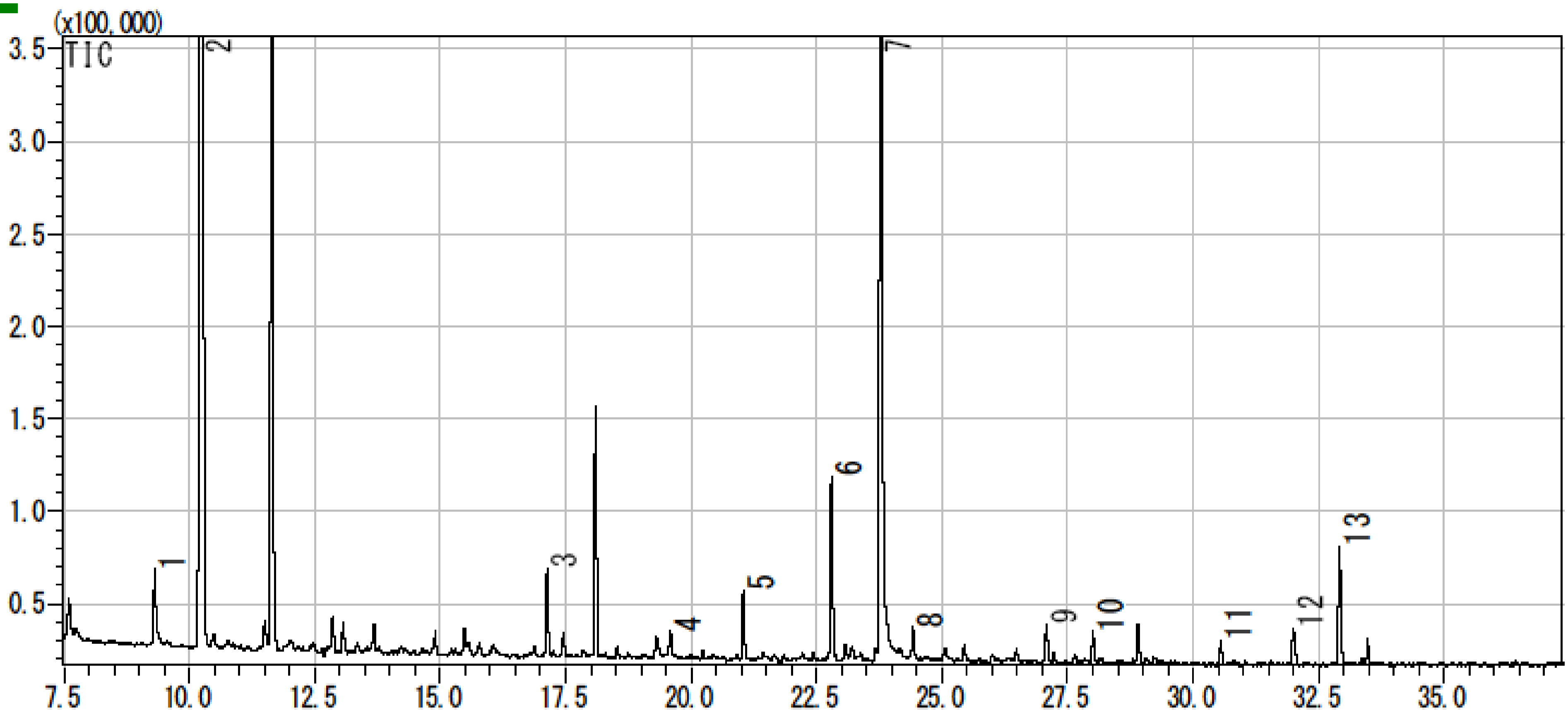
→ Leave the sample with a piece of MonoTrap RCC18 at 60° C for 1 hours for sampling.

Solvent Extraction

→ 200 μL of Dichloromethane,5 minutes of exposure to ultrasound

GC/MS

Chromatogram of Candy flavor



1	β-Myrcene	8	Ethyl laevulinate
2	Limonene	9	α-Terpineol
3	cis-3-Hexenol	10	Citral
4	Furfural	11	β-Damascenone
5	Decanal	12	Benzyl Alcohol
6	β-Linalool	13	Phenylethyl Alcohol
7	Propylene Glycol		

※Identified with spectral libraries

Red characters ･･･Identified with standard sample

Flavor analysis in Japanese red wine

Sample

↓ ← 20ml of Japanese red wine

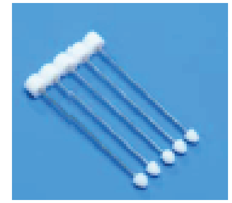
Head Space Sampling

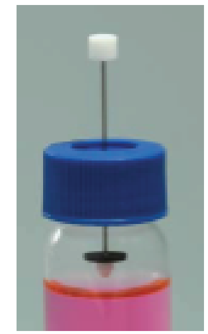
↓ ← Leave the sample with a piece of MonoTrap DCC18 at 60° C for 30 minutes for sampling.

Solvent extraction

↓ ← 300 μ L of Dichloromethane,5 minutes of exposure to ultrasound

GC/MS





③MT Extract Cup with Vial

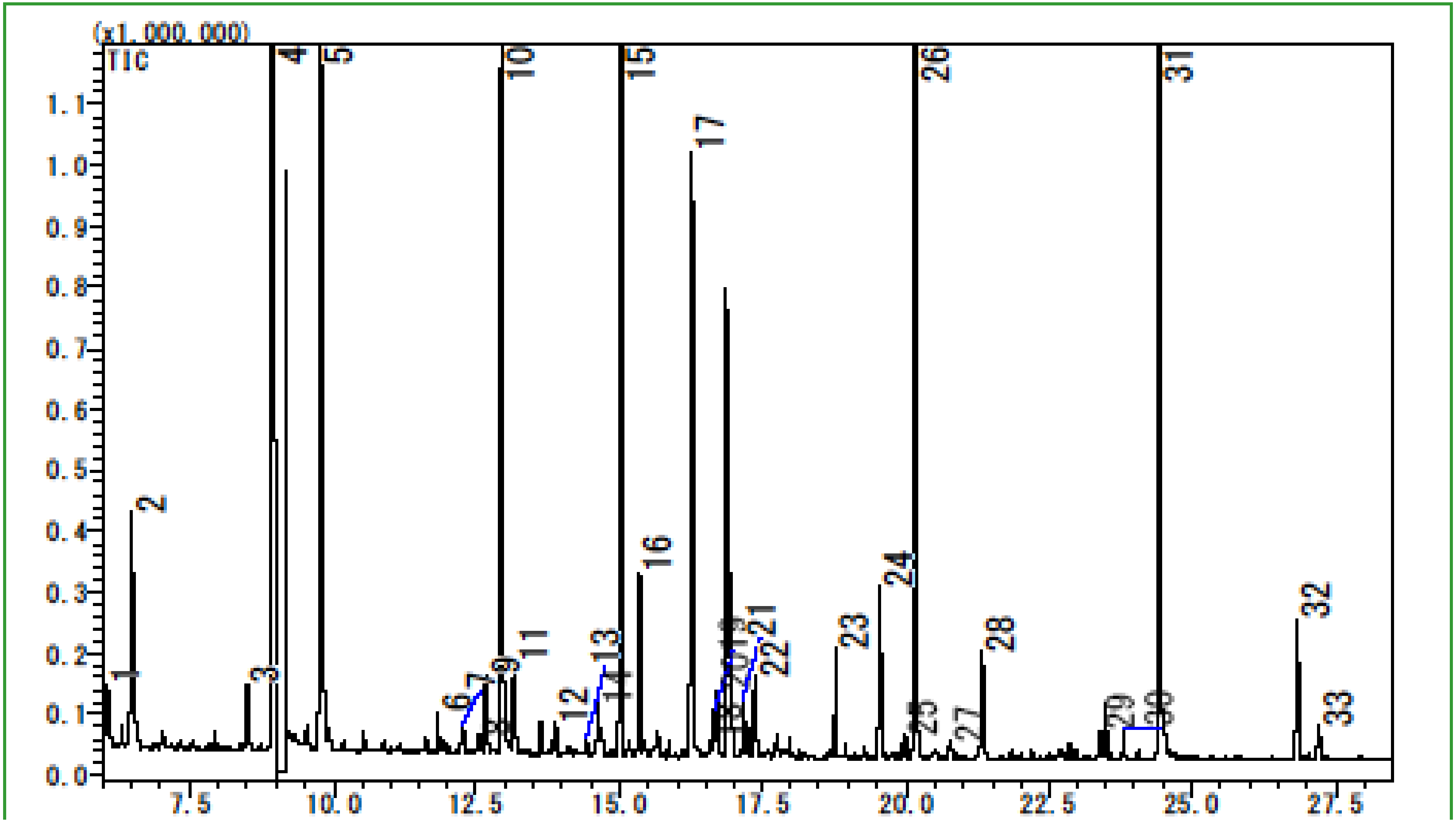
(Start UP-Kit)

GCMS Analytical Conditions

GC/MS analysis

System	:SHIMADZU GC-2010、GCMS-QP2010
Column	:InertCap Pure-WAX(Cat.1010-68142)New!!
	0.25mmI.D.×30m df=0.25μm
Column Temp	:40℃(5min)→6℃/min→250℃(5min)
Carrier Gas	:He 95kPa
Injection	:Split /Splitless,1uL
	250℃
Detection	:MS Scan (m/z;55-400)

Chromatogram of Japanese red wine flavor



Identification of compounds in Japanese red wine

1	2,2,6-Trimethyl-6-vinyltetrahydropyran
2	Isoamyl acetate
3	Limonene
4	1-Pentanol
5	Ethyl hexanoate
6	Maleic anhydride
7	3-Methylpentanol
8	1,1-Dimethoxy-2-propanol
9	Ethyl 2-hexenoate
10	1-Hexanol
11	cis-3-Hexen-1-ol
12	Nonanal
13	cis-2-Hexen-1-ol
14	Ethyl 2-hydroxy-3-methylbutanoate
15	Ethyl octanoate
16	Furfural
17	2-Ethyl-1-hexanol
18	Benzaldehyde
19	3-Ethyl-4-methylpentanol
20	2-Bornene
21	n-Propyl propionate
22	Ethyl dl-2-hydroxycaproate
23	β-Cyclocitral
24	Ethyl decanoate
25	α-D-Galactopyranose methyl glycoside
26	Diethyl succinate
27	3-(Methylthio)-1-propanol
28	1,5,8-Trimethyl-1,2-dihydronaphthalene
29	Hexanoic acid
30	Benzyl Alcohol
31	Phenylethyl Alcohol
32	Diethyl dl-malate
33	Octanoic Acid

※Identified with spectral libraries

Red characters ･･･Referred to Japan Perfumery & Flavoring Association Encyclopedia of Flavor[food]

Analytical conditions for PAHs analysis

Thermal desorption device :ATAS-GL OPTIC3 Linex

Desorption Temperature :250 ^{o}C, Time 10min

Injection Temperature:250 ^{o}C

Split ratio :1:10

Carrier Gas :He (1 mL/min)

GC/MS instrument :Shimadzu GCMS-QP2010 Plus

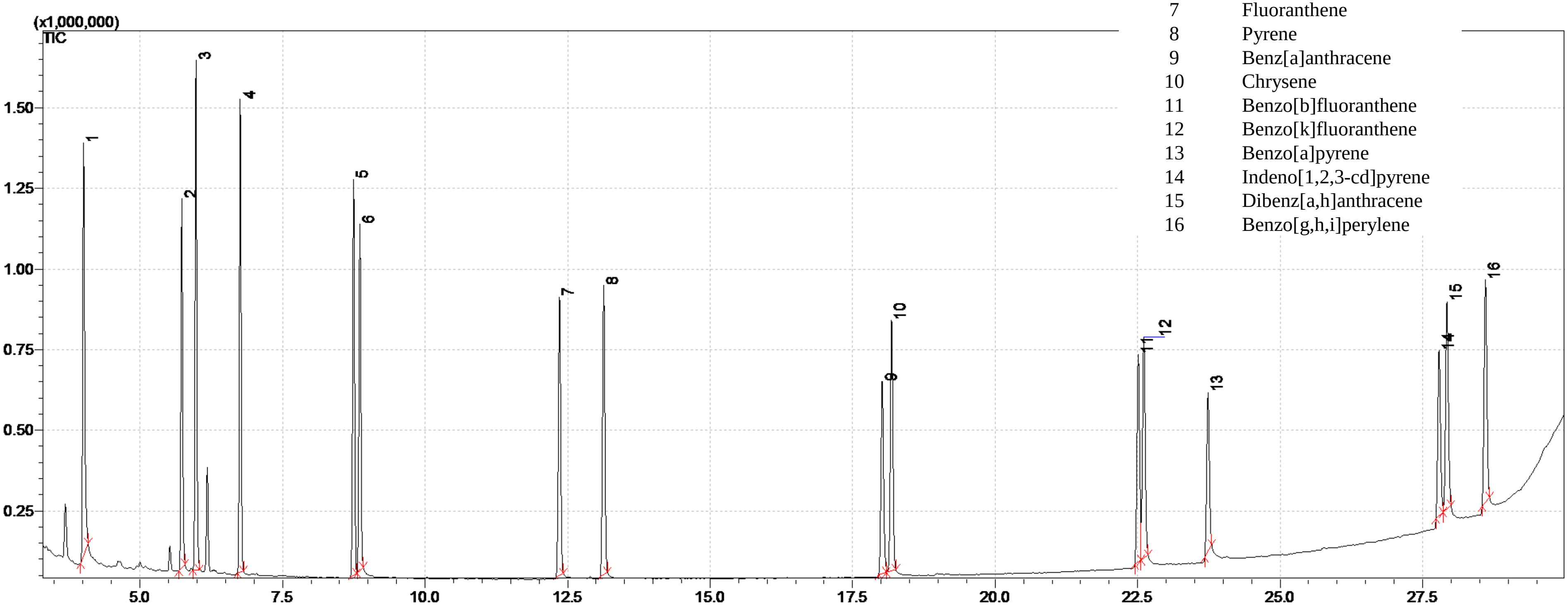
Column :InertCap Pesticide 0.25 mmIDx30 m

Column Temperature :50 ^{o}C(3 min)→10 ^{o}C/min→310 ^{o}C

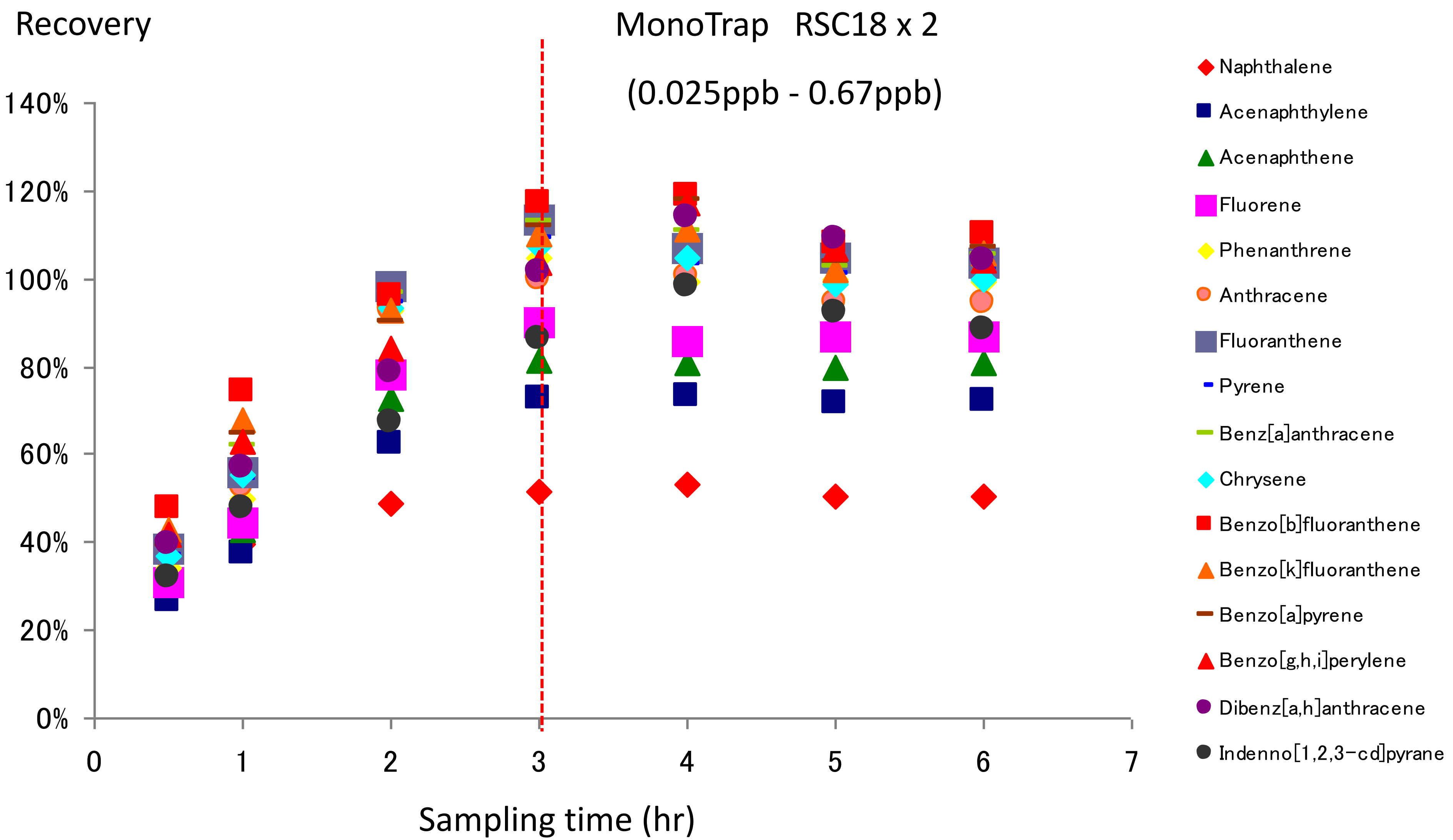
Detection :SIMmode (I.F.;340 ^{o}C,I.S.;230 ^{o}C)

Chromatogram of STD PAHs

Peak #	Name
1	Naphthalene
2	Acenaphthylene
3	Acenaphthene
4	Fluorene
5	Phenanthrene
6	Anthracene
7	Fluoranthene
8	Pyrene
9	Benz[a]anthracene
10	Chrysene
11	Benzo[b]fluoranthene
12	Benzo[k]fluoranthene
13	Benzo[a]pyrene
14	Indeno[1,2,3-cd]pyrene
15	Dibenz[a,h]anthracene
16	Benzo[g,h,i]perylene



Evaluation of sampling time for PAHs analysis



Recovery result

	1 Rod	2 Rods
Naphthalene	30%	51%
Acenaphthylene	51%	72%
Acenaphthene	65%	81%
Fluorene	70%	90%
Phenanthrene	79%	105%
Anthracene	84%	100%
Fluoranthene	84%	113%
Pyrene	81%	109%
Benz[a]anthracene	86%	113%
Chrysene	87%	108%
Benzo[b]fluoranthene	88%	117%
Benzo[k]fluoranthene	86%	110%
Benzo[a]pyrene	82%	112%
Benzo[g,h,i]perylene	85%	104%
Dibenz[a,h]anthracene	87%	102%
Indenno[1,2,3-	73%	87%

Sampling time : 3 hr

Repeatability (0.25 ppb)

PAHs	n1	n2	n3	Ave	RSD
Naphthalene	214862	249466	248469	237599.0	8.3%
Acenaphthylene	232528	257623	280506	256885.7	9.3%
Acenaphthene	181728	200323	215534	199195.0	8.5%
Fluorene	200912	215331	229094	215112.3	6.6%
Phenanthrene	290295	309267	318268	305943.3	4.7%
Anthracene-d10(IS)	21452	21926	23885	22421.0	5.8%
Anthracene	274284	266254	254799	265112.3	3.7%
Fluoranthene	287263	302767	307833	299287.7	3.6%
Pyrene	286815	298771	310061	298549.0	3.9%
Benz[a]anthracene	214072	207132	197872	206358.7	3.9%
Chrysene-d12(IS)	20330	19863	23610	21267.7	9.6%
Chrysene	213968	209389	190320	204559.0	6.1%
Benzo[b]fluoranthene	226864	211373	205630	214622.3	5.1%
Benzo[k]fluoranthene	226928	215212	192301	211480.3	8.3%
Benzo[a]pyrene	157758	148425	143156	149779.7	4.9%
Benzo[g,h,i]perylene	187547	176735	168432	177571.3	5.4%
Dibenz[a,h]anthracene	192653	187190	171664	183835.7	5.9%
Indenno[1,2,3-cd]pyrane	188182	186530	175394	183368.7	3.8%

Linearity result

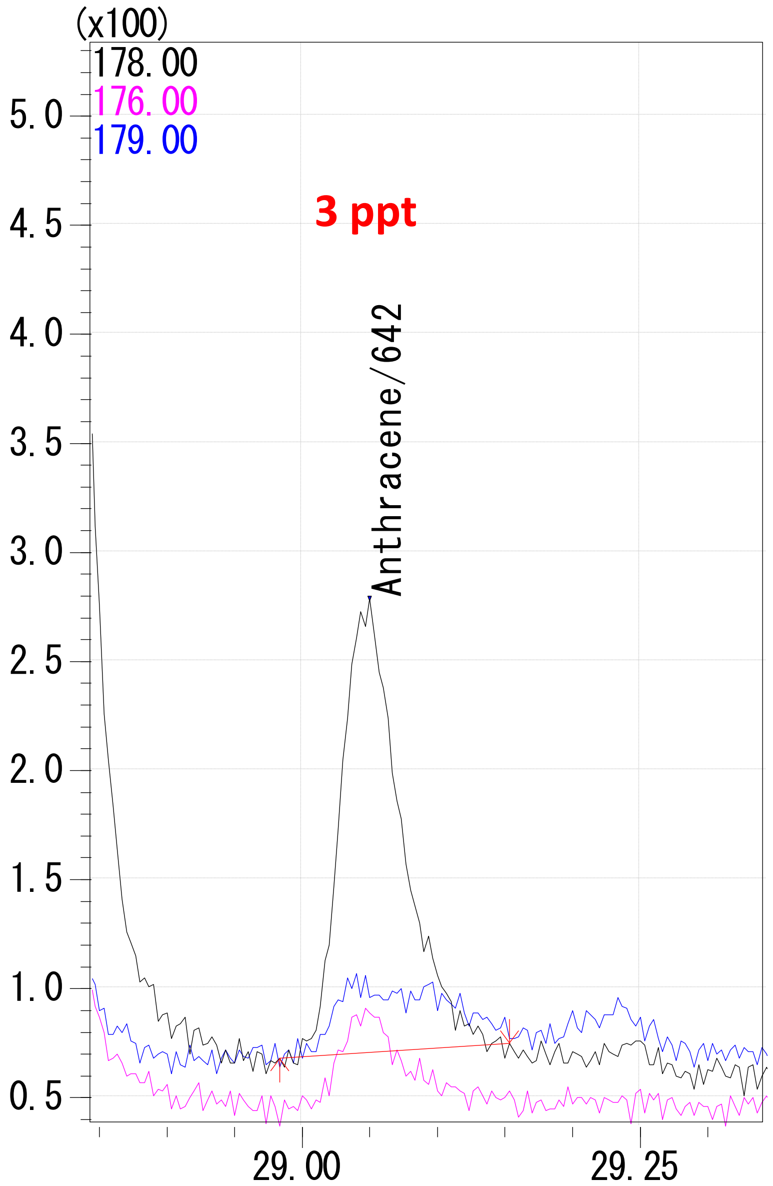
Concentration (ppb)	0.1	1	10	100	r^2
Naphthalene	8810	85133	908151	5548551	0.9961
Acenaphthylene	7848	76464	872538	6703493	0.9991
Acenaphthene	10529	103589	1107188	7337325	0.9975
Fluorene	2776	25793	272269	2365694	0.9998
Phenanthrene	4257	32143	305547	2496179	0.9996
Anthracene	625	7815	66312	597123	0.9999
Fluoranthene	7315	79293	778395	5450872	0.9983
Pyrene	8362	92965	919141	6139653	0.9977
Benz[a]anthracene	2773	36124	403727	3024379	0.9989
Chrysene	2697	35329	366602	2605325	0.9984
Benzo[b]fluoranthene	2718	38055	416201	3132210	0.9990
Benzo[k]fluoranthene	3457	47304	494551	3577392	0.9986
Benzo[a]pyrene	2962	37944	441353	3505523	0.9993
Benzo[g,h,i]perylene	1682	31334	392890	2991132	0.9990
Dibenz[a,h]anthracene	1852	26736	324509	1520019	0.9872
Indenno[1,2,3-cd]pyrane	1757	30934	352939	2091641	0.9954

Limit of Quantitation (LOQ)

PAHs	LOQ (ppb)	PAHs	LOQ (ppb)
Naphthalene	0.065	Benz[a]anthracene	0.013
Acenaphthylene	0.050	Chrysene	0.012
Acenaphthene	0.067	Benzo[b]fluoranthene	0.013
Fluorene	0.015	Benzo[k]fluoranthene	0.015
Phenanthrene	0.011	Benzo[a]pyrene	0.016
Anthracene	0.003	Benzo[g,h,i]perylene	0.014
Fluoranthene	0.025	Dibenz[a,h]anthracene	0.011
Pyrene	0.027	Indenno[1,2,3-cd]pyrane	0.012

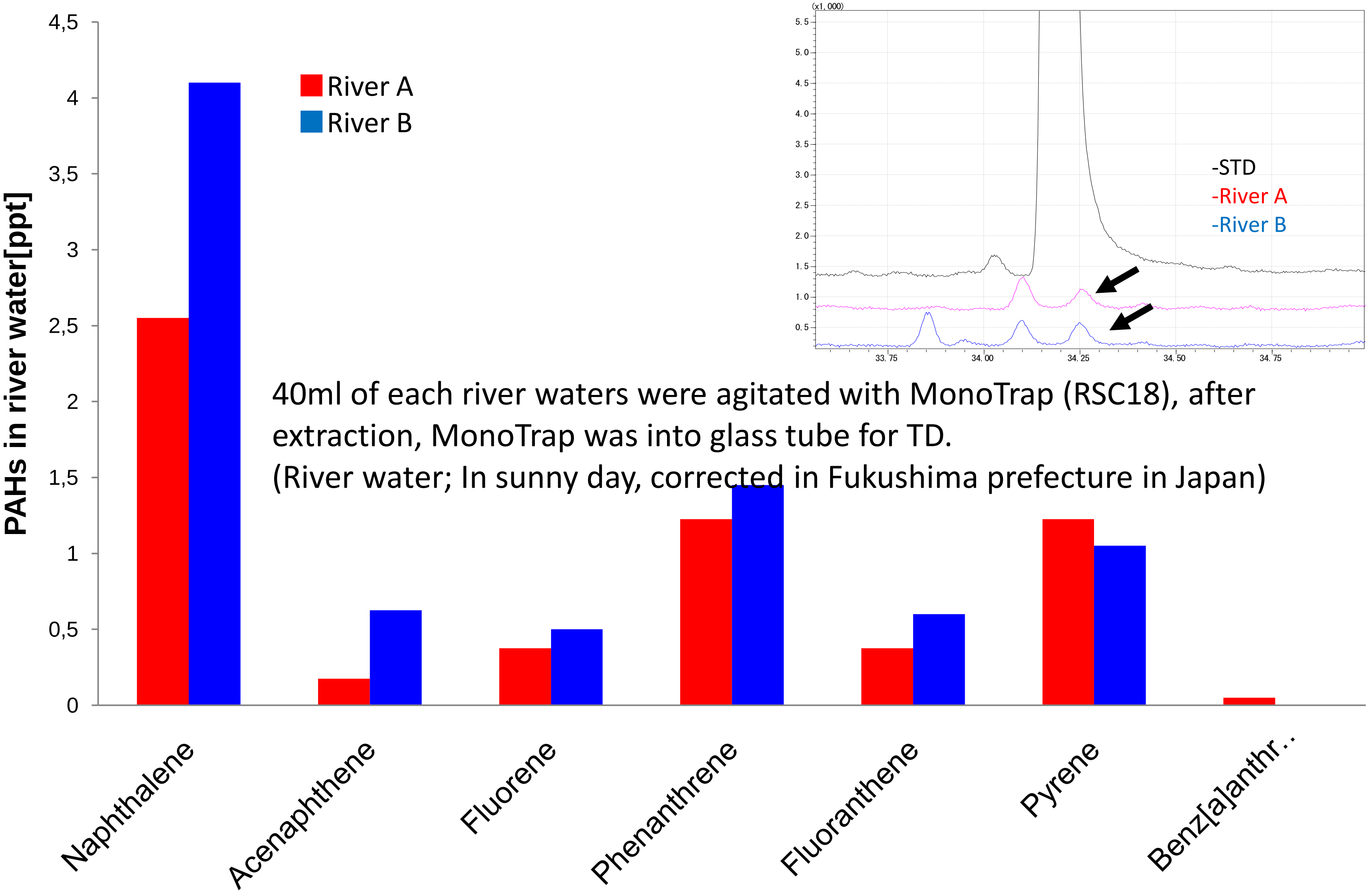
(LOQ: S/N=10)

Chromatogram of Anthracene



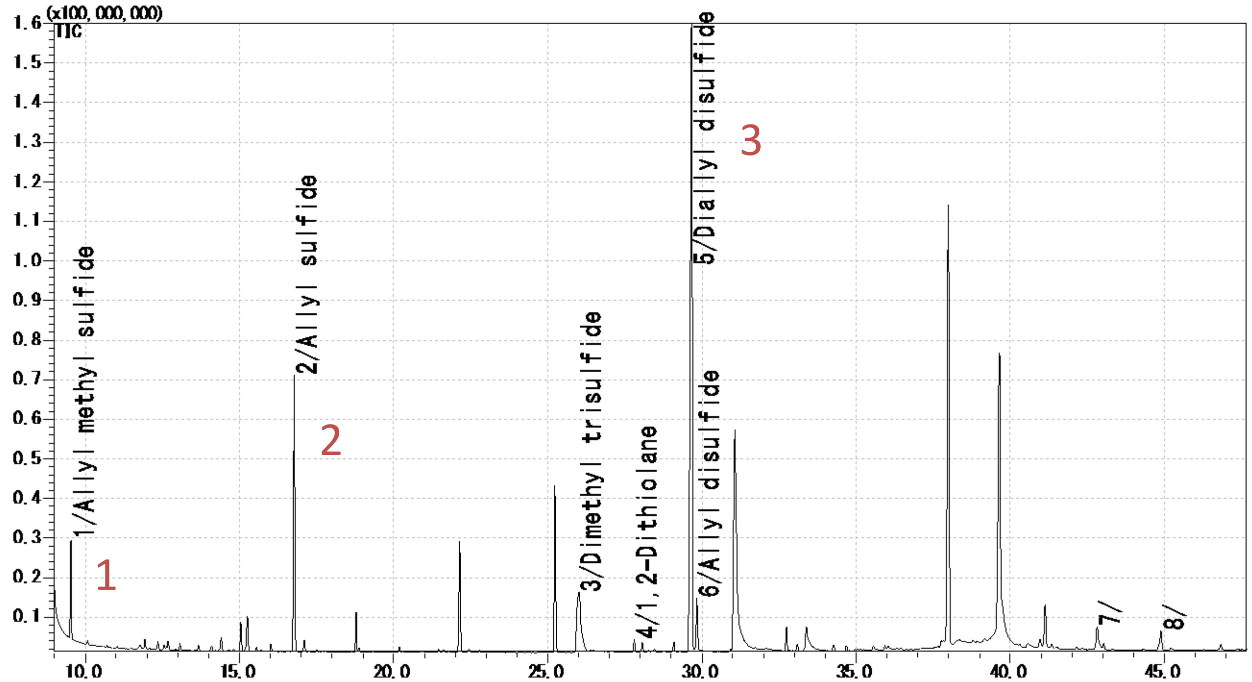
Measurement of PAHs in river water by MMSE

Selected ion monitoring chromatogram of *Fluoranthene*



40ml of each river waters were agitated with MonoTrap (RSC18), after extraction, MonoTrap was into glass tube for TD.
(River water; In sunny day, corrected in Fukushima prefecture in Japan)

Analysis of the bad breath after eating a garlic



GC/MS

System : SHIMADZU GC-2010、GCMS-QP2010

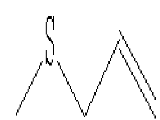
Column : InertCap Pure-WAX
0.25mmI.D. × 60m df=0.25µm

Column Temp : 35℃(5min)→4℃/min→250℃(10min)

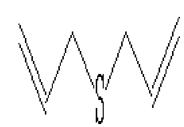
Carrier Gas : He 120kPa

Injection : Split less、1µL 250℃

Detection : MS Scan (m/z;35-500)



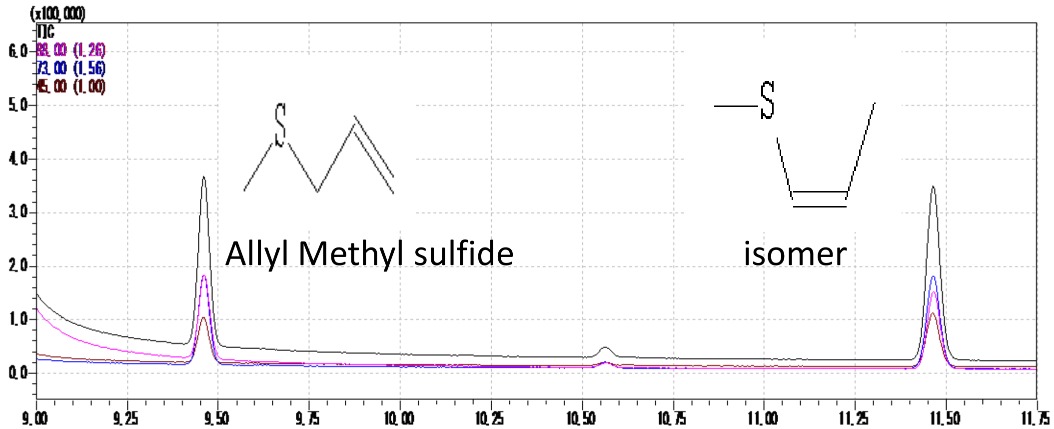
1,Allyl Methyl sulfide

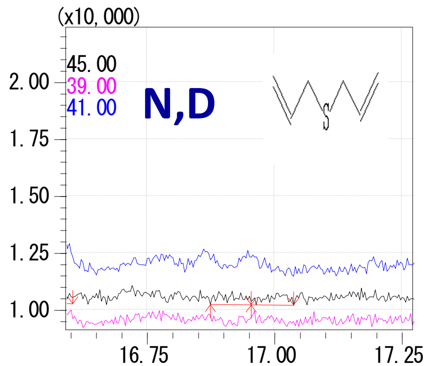


2,Allyl sulfide

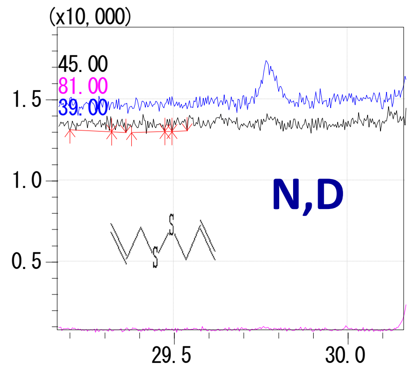
3,Diallyl disulfide

Result of breath analysis





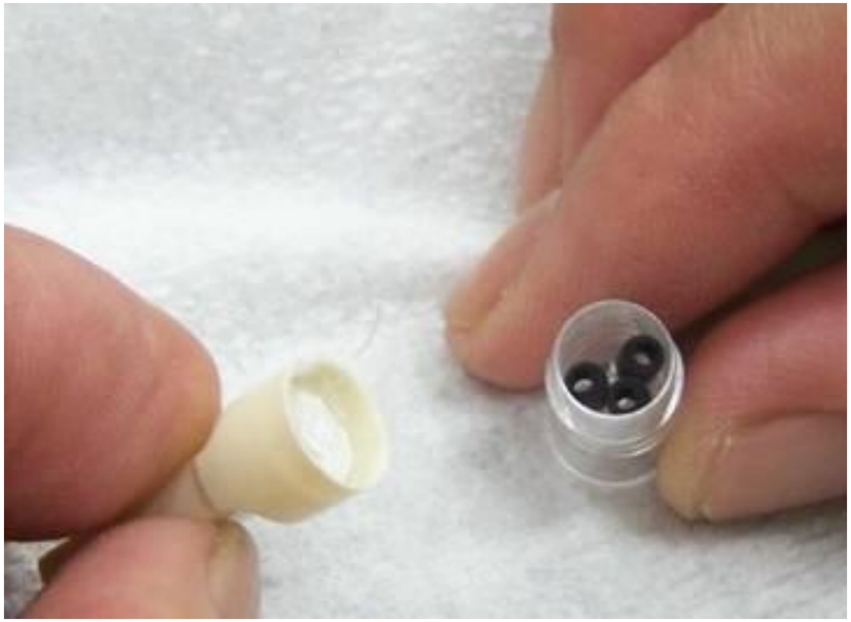
Allyl sulfide



Diallyl disulfide

The main aroma compound of a raw garlic are almost decomposed or metabolized in a body, and are considered that allyl methyl sulfide is generated.

Breath analysis with MMSE



Breath can indicate some of symptoms of diseases.
Collecting the breath with MMSE is extremely simple and the thermal desorption GCMS technique can easily determine organic substances as a maker of health conditions.

Conclusions

- MMSE can be used for simple pretreatment of the sample as a qualitative and quantitative analysis for gases and liquid samples.
- Small quantity of organic solvent is required for organic solvent desorption from monolithic materials.
- No organic solvent is required for thermal desorption from monolithic materials.
- Thermal desorption GCMS combined with MMSE has been confirmed as a simple pretreatment method for determination of 16 PAHs with acceptable analytical performances.
- As compared to SBSE and SMPE, MMSE had better sensitivity because of higher recovery.