Development of an analytical method for volatiles by solid phase adsorption-analytical derivatization-solvent elution technique using online SPE-GC/MS system

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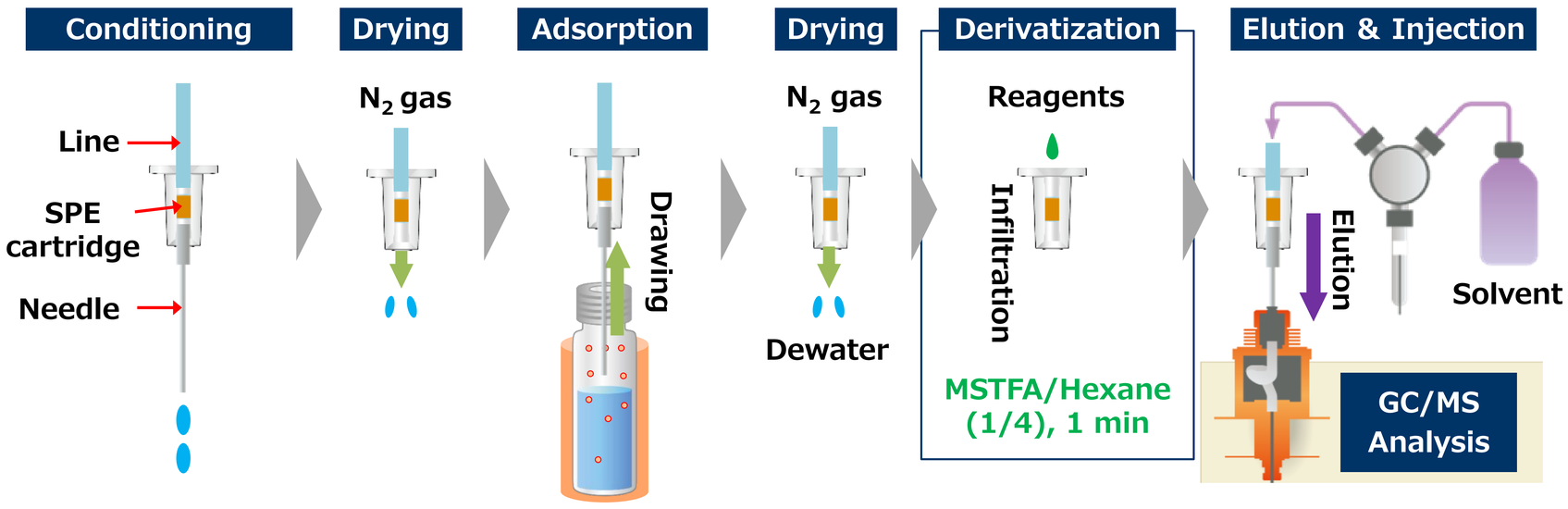
1. Solid phase adsorption-analytical derivatization-solvent elution technique



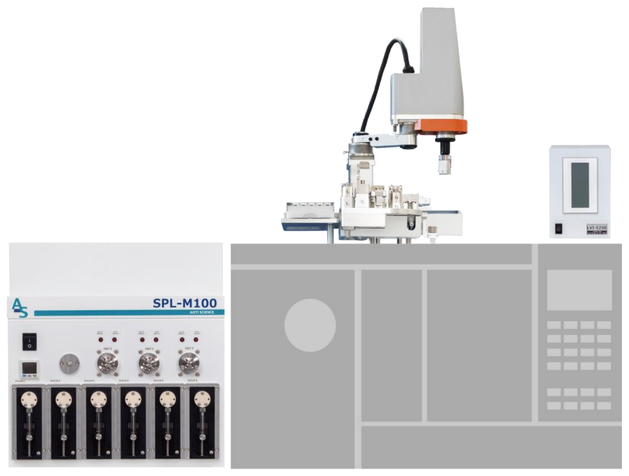


Fig 1. Overview of online SPE-GC/MS system
LVI-S250 and SPL-M100 (AiSTI SCIENCE)

Headspace volatiles are collected and derivatized in a SPE cartridge, the entire eluate is injected into a large volume injection port.

2. Experimental method

Pretreatment workflow of volatile analysis (trimethylsilylation)

Coffee powder 1 g
- Water 10 mL

80℃, 1000 rpm, 15 min

Extract

20 mL vial
- Extract 2 mL
- Water 6 mL
- NaCl 3 g

Vortex

Setting on the tray

Heat : 80℃, 3 min
Sampling volume: 20 mL
Flow : 150 µL/sec

Conditioning
Acetone/Hexane(1/3)
Drying: N_2 gas

Flash-SPE PBX (SDVB* based polymer)

*SDVB: Stylene divinylbenzene

Drying: N_2 gas

Derivatization: MSTFA/hexane(1/4), 1 min

Elution: Acetone/Hexane(1/3)

Injection (the entire eluate)

Analysis: GC-MS

Automated processing on the system (20 min)

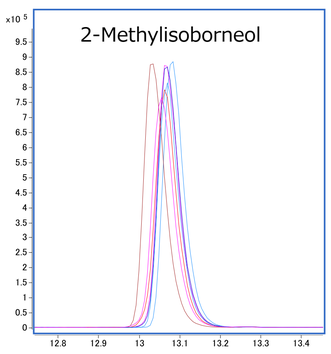
GC-MS condition

Methods	①Volatiles (non-derivatization)	②Volatiles (trimethylsilylation)
PTV Injector	LVI-S250 (AiSTI Science)	LVI-S250 (AiSTI Science)
Injector temp.	70℃(0.3 min)-100℃/min-290℃	150℃(0.5 min)-100℃/min-290℃
GC-MS	7890B + 5977B (Agilent Technologies)	7890B + 5977B (Agilent Technologies)
Split	100 mL/min (70 kPa, 0.3 min) → Splitless (3 min) → 50 mL/min	1:25
Flow mode	Constant flow, 1.4 mL/min	Constant flow, 1.0 mL/min
Pre-column	0.25 mm i.d. × 0.5 m	0.25 mm i.d. × 0.5 m
Column	DB-WAX, 0.25 mm i.d. × 60 m, df=0.25 µm	VF-5ms, 0.25 mm i.d. × 30 m, df=0.25 µm
Oven temp.	40℃ (4 min) - 5℃/min - 230℃ (10 min), **Total 52.5 min**	80℃ (4 min) - 10℃/min - 210℃ - 20℃/min - 310℃ (2 min), **Total 24 min**
Transferline temp.	250℃	290℃
Ion source temp.	260℃	260℃
Acquisition mode	Scan (*m/z* 41-400)	Scan (*m/z* 41-500)

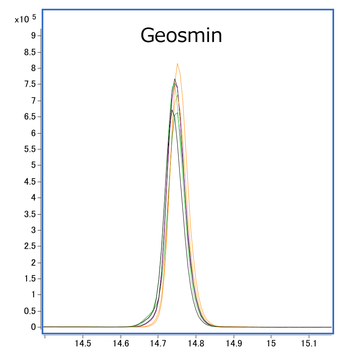
3-1. Repeatability and Linearity by musty odor

Repeatability (**non-derivatization**)

Sample: Spiked ultrapure water
Concentration: 10 µg/L
Sample volume: 5 mL
Additive: NaCl 2 g
Sampling volume: 20 mL
Flow : 150 µL/sec
Injection mode: Large volume injection (①)
GC Oven temp.:
40℃ (4 min) - 20℃/min - 230℃ (10 min)



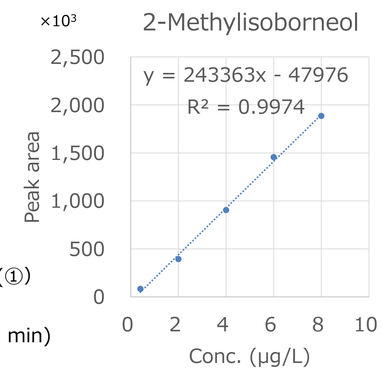
Average: 3,156,403
RSD (n=7): 5.4%

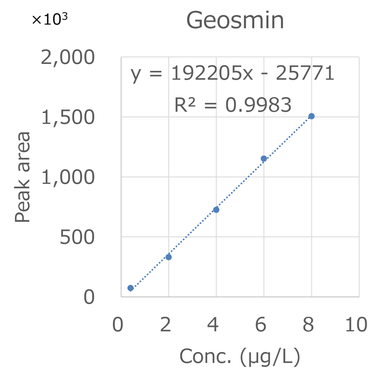


Average: 2,595,621
RSD (n=7): 6.1%

Linearity (**non-derivatization**)

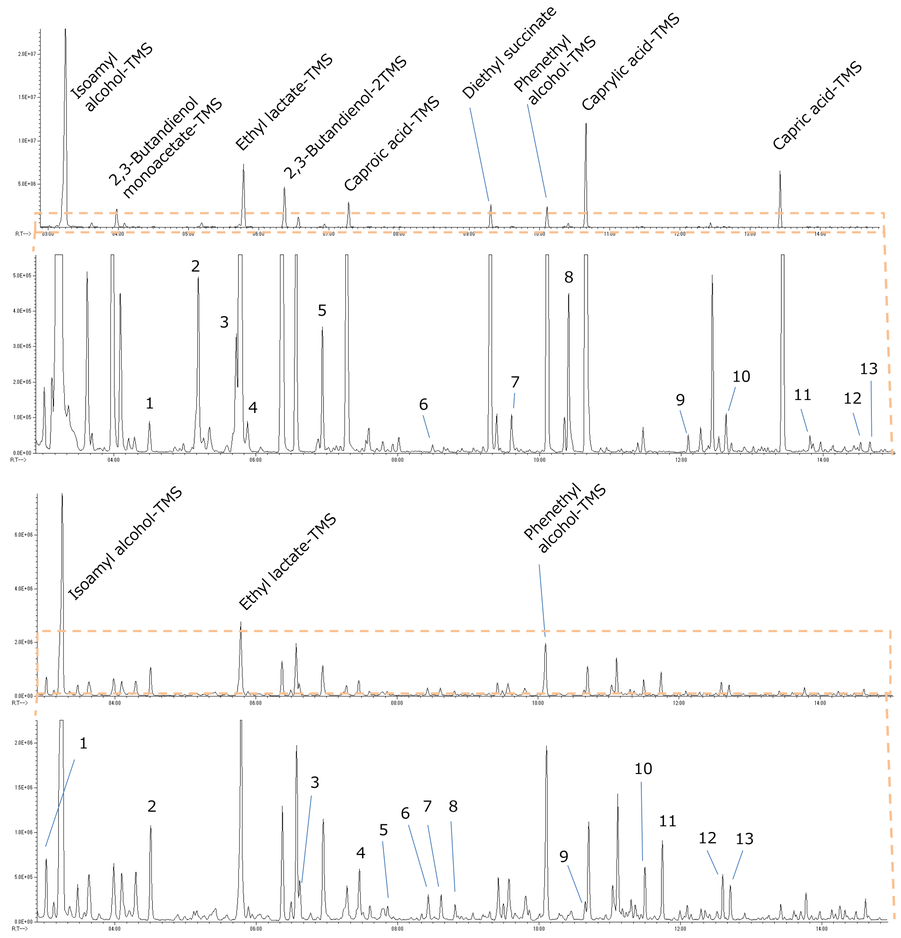
Sample: Spiked ultrapure water
Concentrations: 0.4, 2, 4, 6, 8 µg/L
Sample volume: 5 mL
Additive: NaCl 2 g
Drawing volume: 20 mL
Flow : 150 µL/sec
Injection mode: Large volume injection (①)
GC Oven temp.:
40℃ (4 min) - 20℃/min - 230℃ (10 min)





The system repeatability and sampling linearity were confirmed

3-2. Applicability and annotated volatiles



Wine

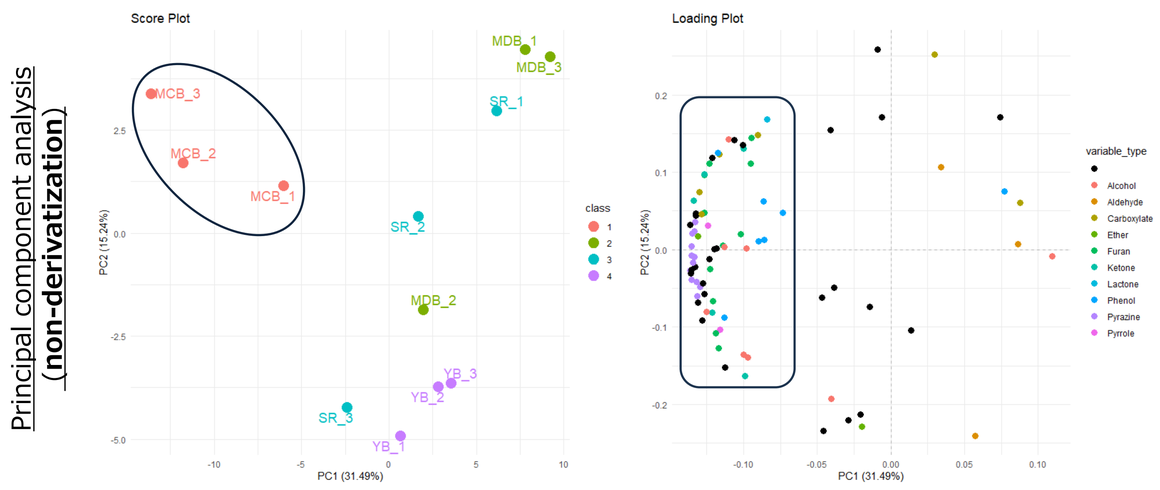
1. Isovareric acid-TMS
2. 3-Ethoxypropanol-TMS
3. Propylene glycol-2TMS
4. Ethyl glycolate-TMS
5. Lactic acid-TMS
6. 2-Furonic acid-TMS
7. Ethyl caprylate
8. Monoethyl succinate-TMS
9. Nonanoic acid-TMS
10. Ethyl caprate
11. Diethyl 2-hydroxyglutarate-TMS
12. Ethyl 3-phenyllactate-TMS
13. Diethyl tartarate-2TMS

Dashi-soysauce

1. Butyric acid-TMS
2. Isovareric acid-TMS
3. Isocaproic acid-TMS
4. 1-Octen-3-ol-TMS
5. 2-Ethylhexanol-TMS
6. *o*-Cresol-TMS
7. *m*-Cresol-TMS
8. *p*-Cresol-TMS
9. Caprylic acid-TMS
10. 4-vinylguaiacol-TMS
11. Hydroxystylene-TMS?
12. Vanillin-TMS?
13. Syringol-TMS

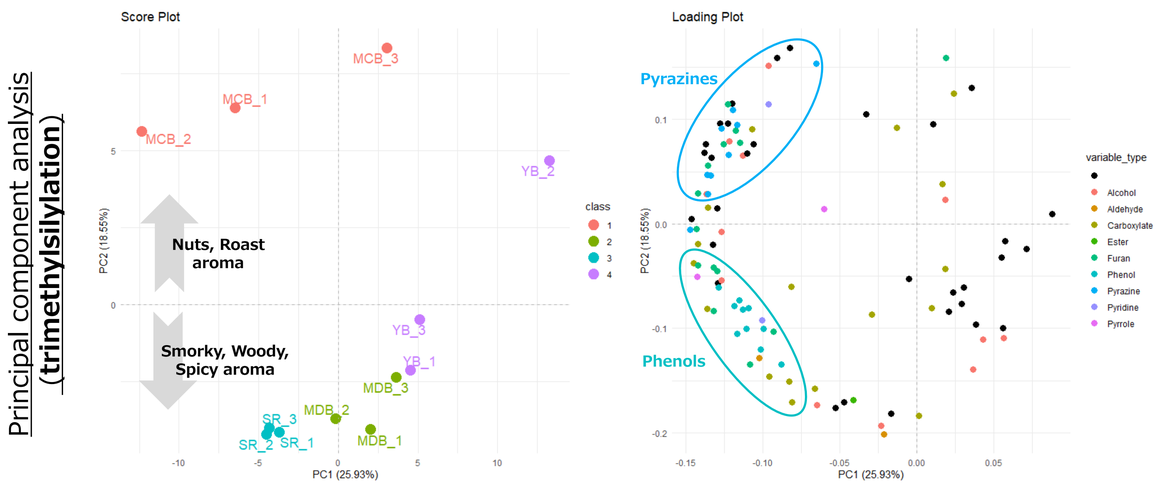
3-3. Discrimination test by coffee samples

Principal component analysis (**non-derivatization**)



In non-derivatization method, only MCB showed characteristic group of compounds

Principal component analysis (**trimethylsilylation**)



Derivatization method showed that pyradines and phenols contributed

4. Discussions and Conclusion

Advantages of the derivatization method

- Analysis can be performed using the same configuration for metabolome analysis
- Shorter analysis time and high-throughput

Disadvantages of the derivatization method

- Detection of >C3 components is difficult (elution is faster than reagent)
- Sensitivity is lower compared to the non-derivatization method + large-volume injection

Future issues

- Establishment of a database of derivatized volatiles
- Simultaneous analysis with taste components (amino acids, organic acids, sugars, etc.)

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