CHANGES IN THE LIPID AND FLAVOR OF "KATSUOBUSHI" FLESH THROUGH THE SMOKING PROCESS OF THE TRADITIONAL MANUFACTURING METHOD

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1. Katsuobushi processing

Skipjack tuna meat ▶ Boiling ▶ **Drying and Smoking** ▶

- first smoking
- second smoking
- third smoking
- fourth smoking

Molding ▶ **Katsuobushi**

- smoking and molding

➡ the most important steps for the formation of the specific and unique flavor

2. Back ground and purpose

Molding process

- Much research
- to be clarified about the change of flavor and lipids

Smoking process

- Little research
- not to be clarified about the change of flavor and lipids

[Purpose of this study]

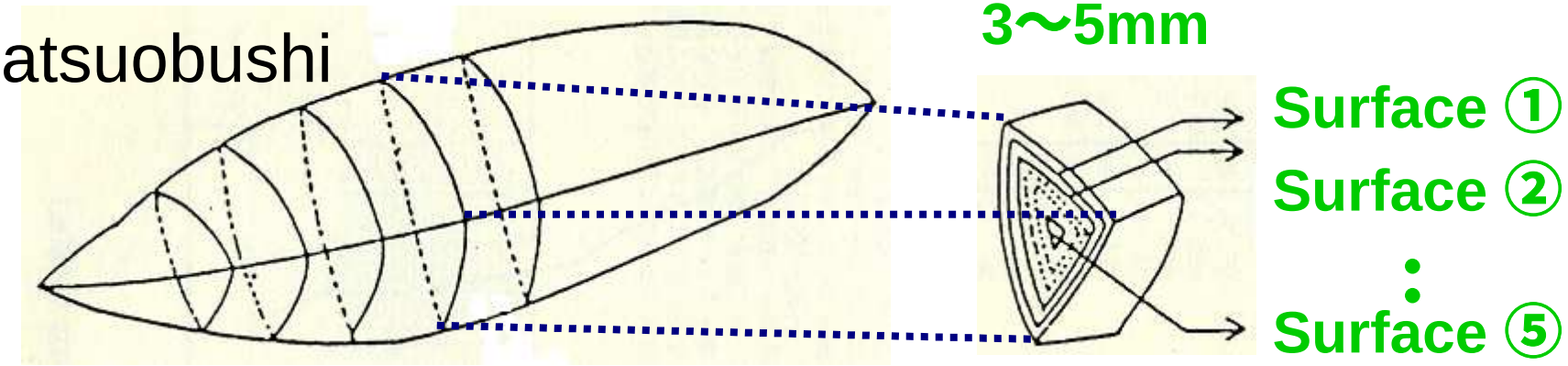
to clarify the change in the flavor and lipid during the smoking at different stages (the first to fourth stages)

3. Materials

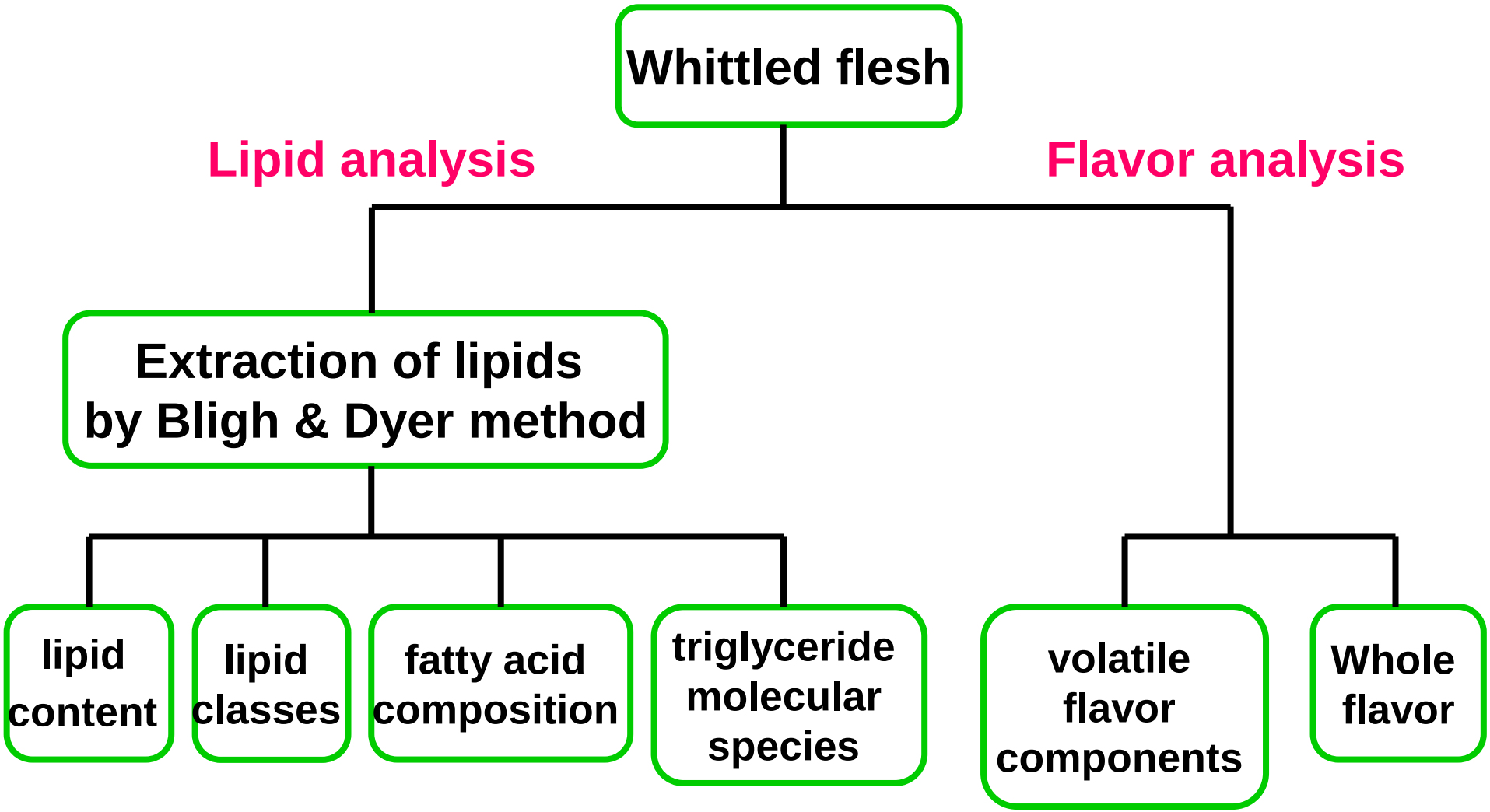
- flesh finished first smoking
- flesh finished second smoking
- flesh finished third smoking
- flesh finished fourth smoking

Whittled 3～5mm from surface step by step

Katsuobushi



4. Experimental procedure



Lipid analysis

【lipid classes by TLC】

・TLC plate : 5×20cm （Merck）
・The mobile phase ：
petroleum ether / isopropyl ether/ acetic acid (80/20/1, v/v/v)
・Analytical equipment：Image Capture 1D （lyponics)

【fatty acid composition by GC】

・Analytical equipment：GC-14A（SHIMADZU）
・Detector：flame ionization detector (FID)
・Column：SUPERCOWAXTM10 （SUPELCO）
length 30m×inner diameter 0.25nm
film thickness 0.25μm
・The carrier gas：Helium (1mL/min)
・Injection port temperature：250℃
・FID temperature：270℃

Lipid analysis

【triglyceride molecular species by HPLC-ELSD】

Pump : LC-10AD(SHIMADZU)
Detector : ELSD　PL-ELS1000(Polymer Laboratories)
Evaporator temperature : 90 ℃
Nebrizer temperature : 40 ℃
Gas Flow : 1.0 mL/min
Column : DEVELOSIL C30-UG-5　×2(TAS：Nomura chemistry)
250 mm × 4.6 mm i.d., particle size 5 μm, fine pores80 Å
Column temperature：20 ℃
The mobile phase：Acetonitrile / Acetone for the elution solvent in gradient system.

【MS】

MS : Waters Alliance ZMD LC/MS system
Capillary voltage : 4.0 kV
Cone voltage : 40 V
Heater temperature : 400 ℃
Source block temperature : 135 ℃
APCI solvent delay temperature : 400 ℃

Method of flavor analysis

【analysis by GC-MS】

bottle

Whittled flesh 2g

Saturation of flavor

Room temperature 10min

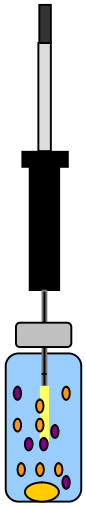
Adsorption of flavor to fiber

40℃ 10min

Desorption of flavor

250 ℃ 4min

GC-MS



【fragrance & flavor analyzer】

Sample bag

Whittled flesh 2g

N_2

Saturation of flavor

Room temperature 1～2h

fragrance & flavor analyzer

Flavor analysis

【volatile flavor components by GCMS-QP5000】

SPME fiber : 65μm PDMS/DVB (SUPELCO)

GC : GC-17A MS : GCMS-QP5050A (SHIMADZU)

Column : HP5(Hewlette Packerd)60m×0.25mm i.d. film thickness 0.25μm

The temperature program : 40℃ for 5min、40-110℃ at 1.5℃/min、
110-160℃ at 3.5℃/min、160-230℃ at 7.0℃/min、
230℃ for 10min

Ionization：EI The carrier gas：Helium (1mL/min)

Injection : splitless Library : NIST107, NIST21

Injection port temperature : 250℃ Detector temperature: 280℃

【whole flavor by fragrance & flavor analyzer】

Analytical equipment：fragrance & flavor analyzer FF-2A(SHIMADZU)

Sensor : oxide semiconductor sensor(10 sensors of different characteristic)

The carrier gas : N2 (G1 grade ＞ 99.9999 vol. %)

Gas of aspiration time ：6s、18s、60s

Collection tube temperature : 40-220 ℃

Data analysis：absolute-value expression analysis
principal component analysis(PCA)

5. Result and Discussion

5-1. Lipid content

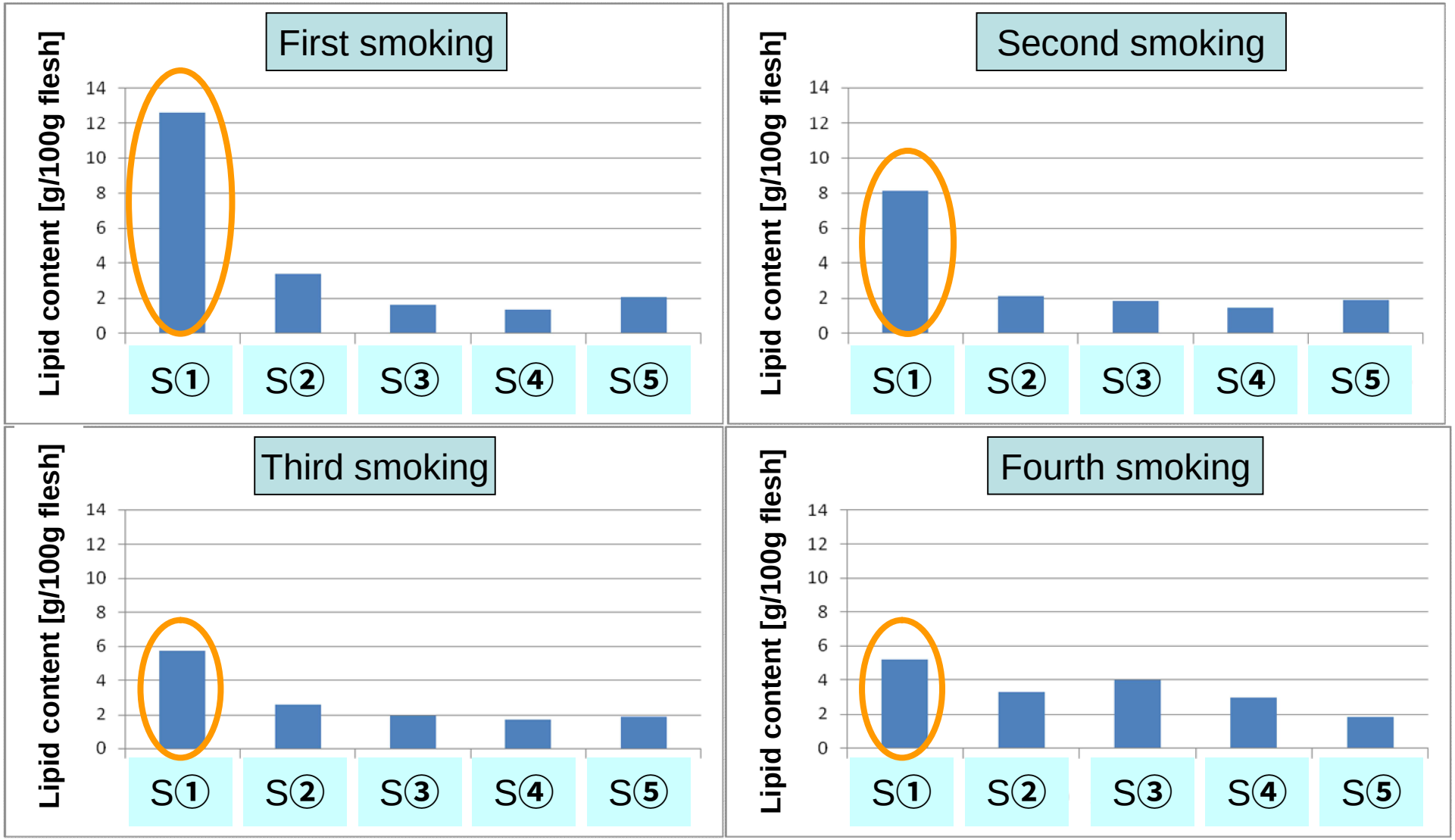


Fig.1 Lipid content

※S : surface

5-2. Lipid classes

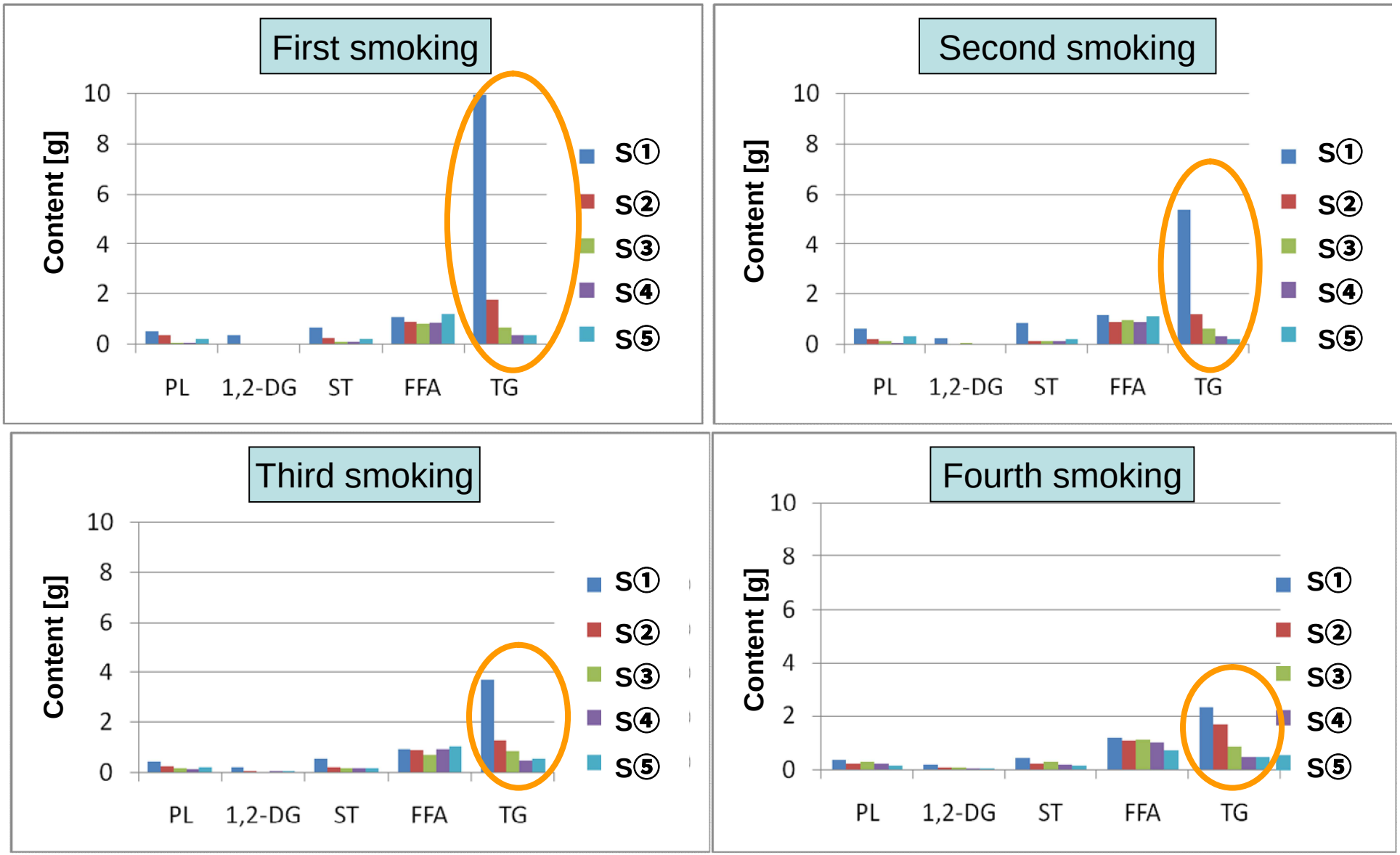


Fig.2 Lipid classes

※S : surface

TG was mainly decreased

5-3. Fatty acid composition

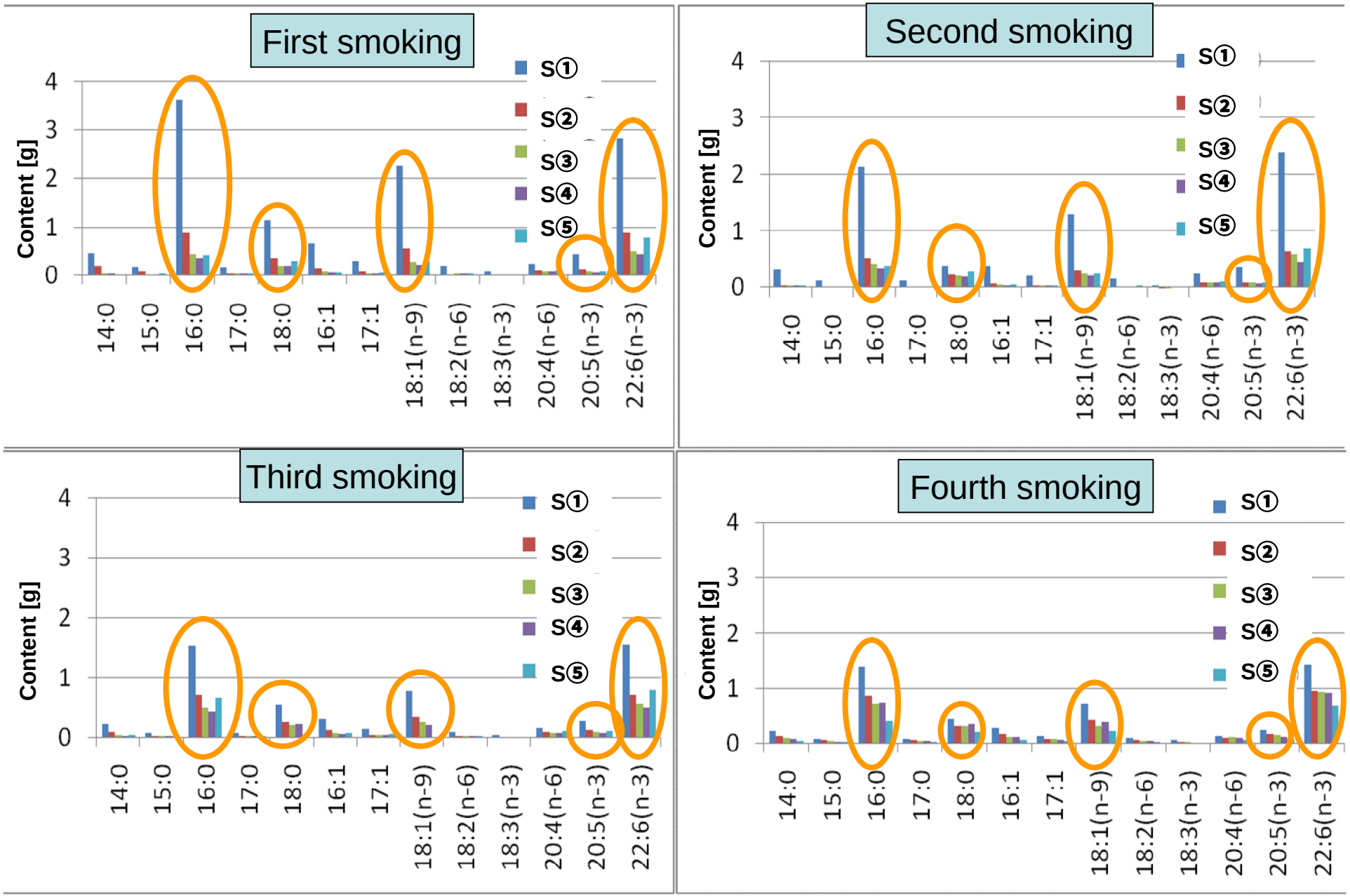


Fig.3-1 Fatty acid composition

※S : surface

5-3. Fatty acid composition

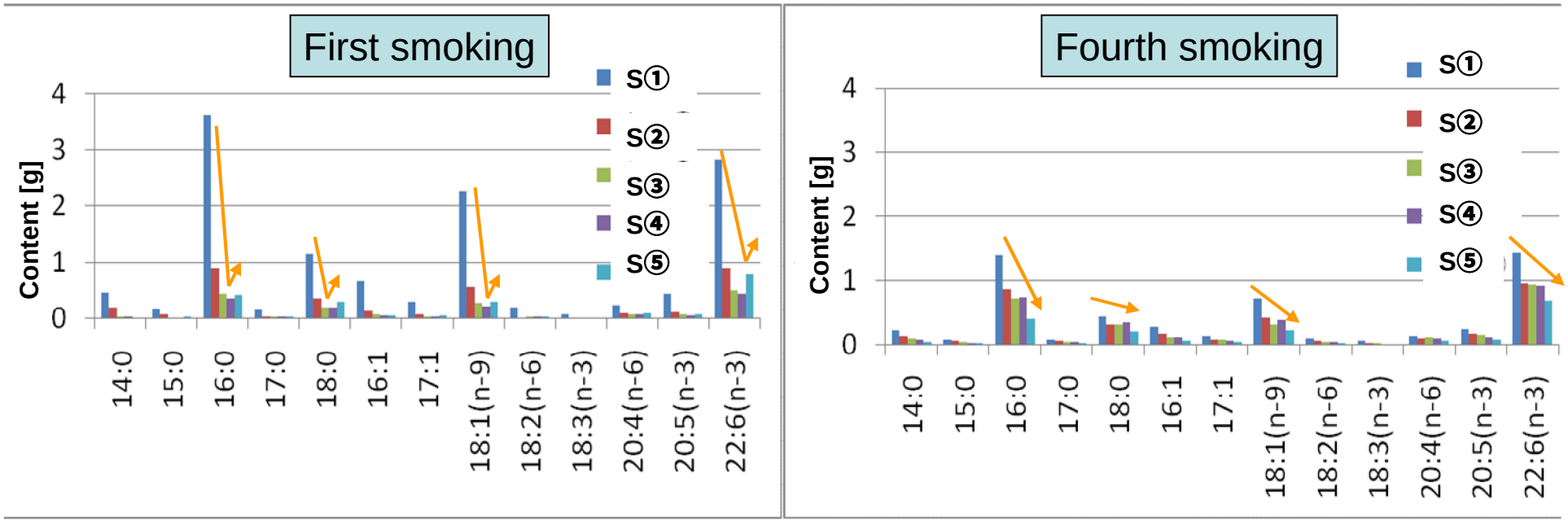
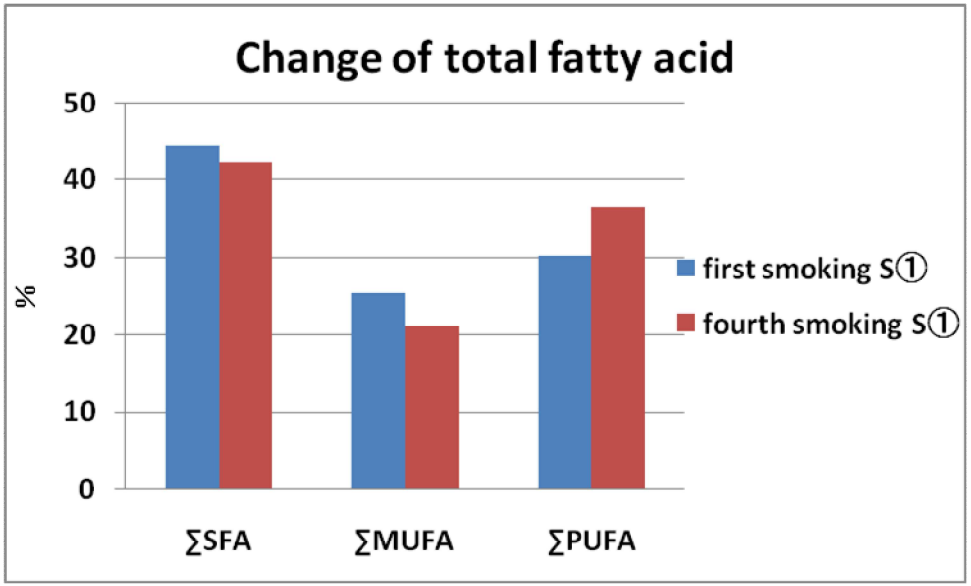


Fig.3-2 Fatty acid composition

- The lipid content remained
  in outer part of the flesh ＞ in the inner part of the flesh.

⇒ the diffusion and decomposition of the lipid occurred during the fourth smoking process

Change of total fatty acid at surface①



SFA and MUFA

⇨ decrease

PUFA

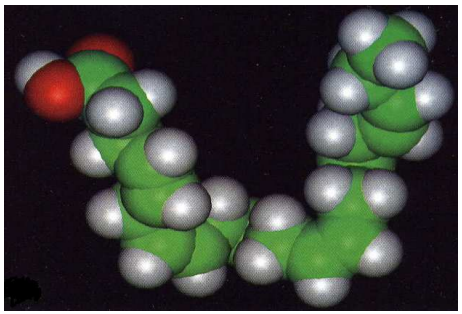
⇨ increase

Fig.4 Change of total fatty acid

- Antioxidant action by phenol adherent derivative from smoke
- Physical structure

Structure of SFA

Structure of MUFA



Structure of PUFA

5-4. Triglyceride molecular species

PDD : SFA-PUFA-PUFA (palmitic acid-DHA-DHA)

PSD : SFA-SFA-PUFA (palmitic acid-stearic acid-DHA)

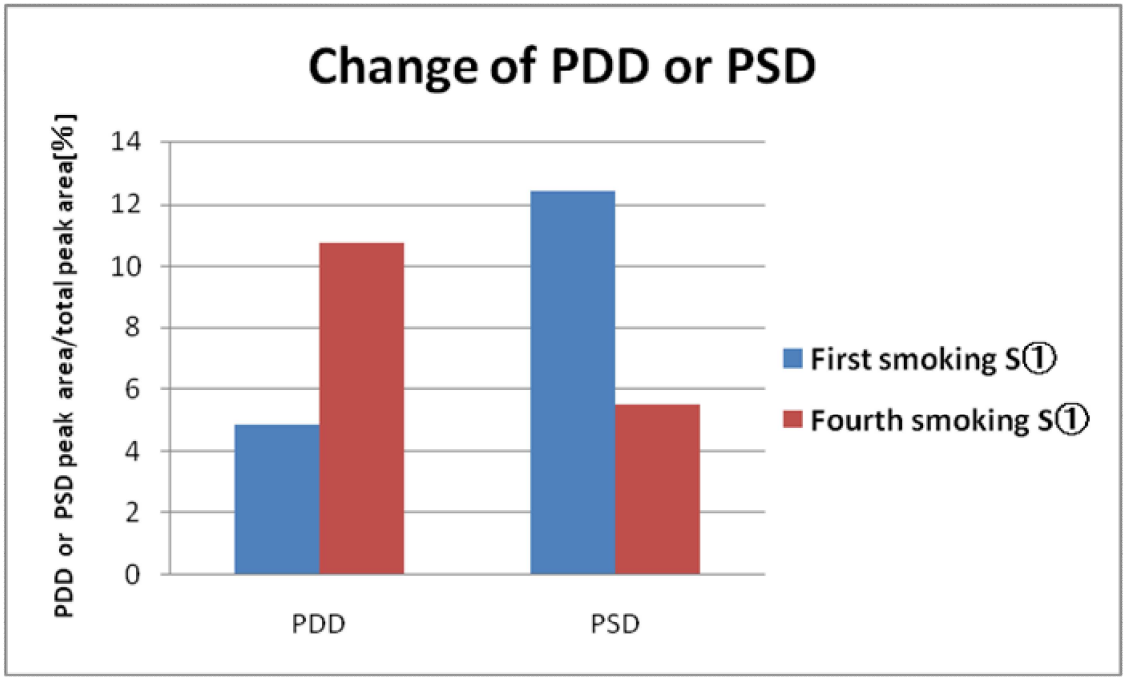


Fig.5 Change of PDD or PSD

SFA-rich TG might be decreased rather than PUFA-rich TG

5-5. Volatile flavor components

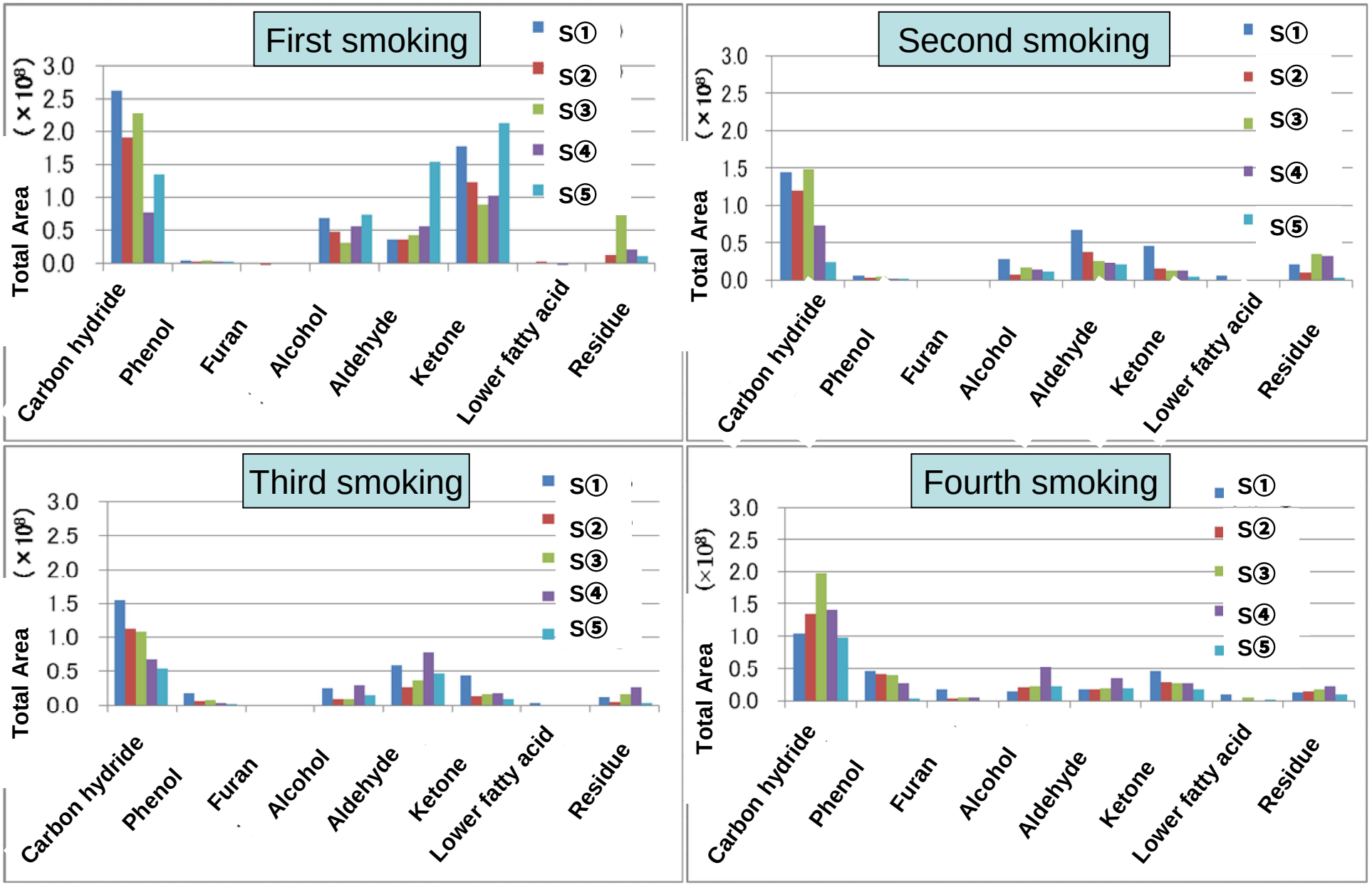


Fig.6 Volatile flavor components

Phenols

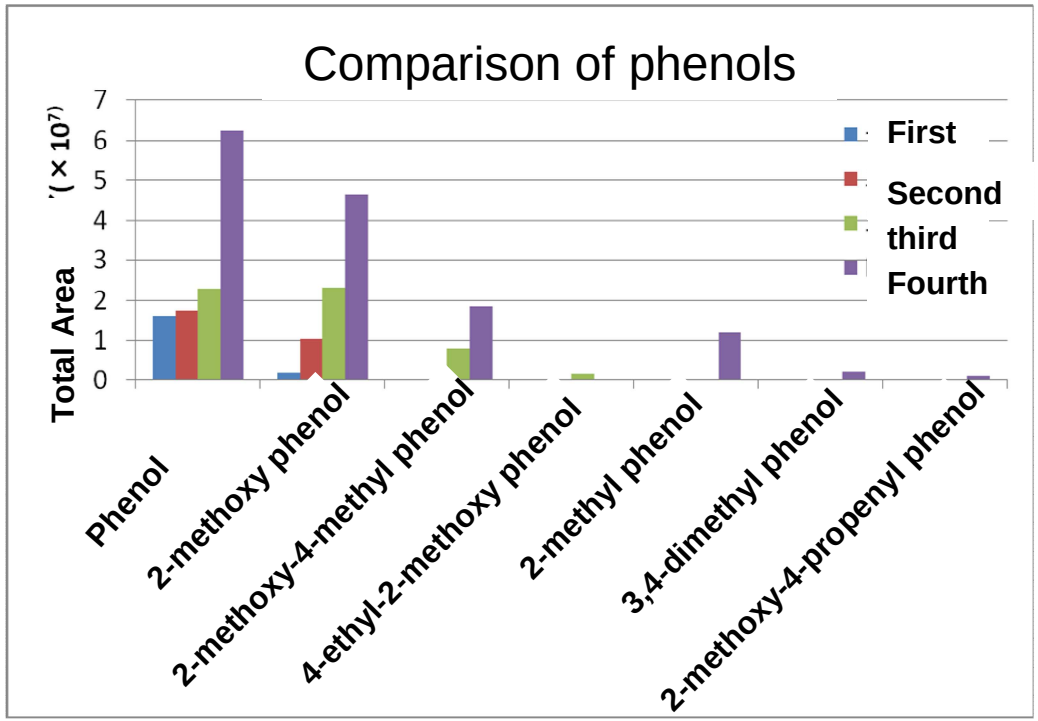


Fig.7 Comparison of phenols

Total Area of phenols

Fourth smoking flesh

∨

Third smoking flesh

∨

Second smoking flesh

∨

First smoking flesh

- Phenols : much presence in smoke
  - ⇒ Derivation from smoke
- Furans , Pyrazines : less presence in smoke
  - ⇒ Generation by Maillard reaction

5-6. Whole flavor

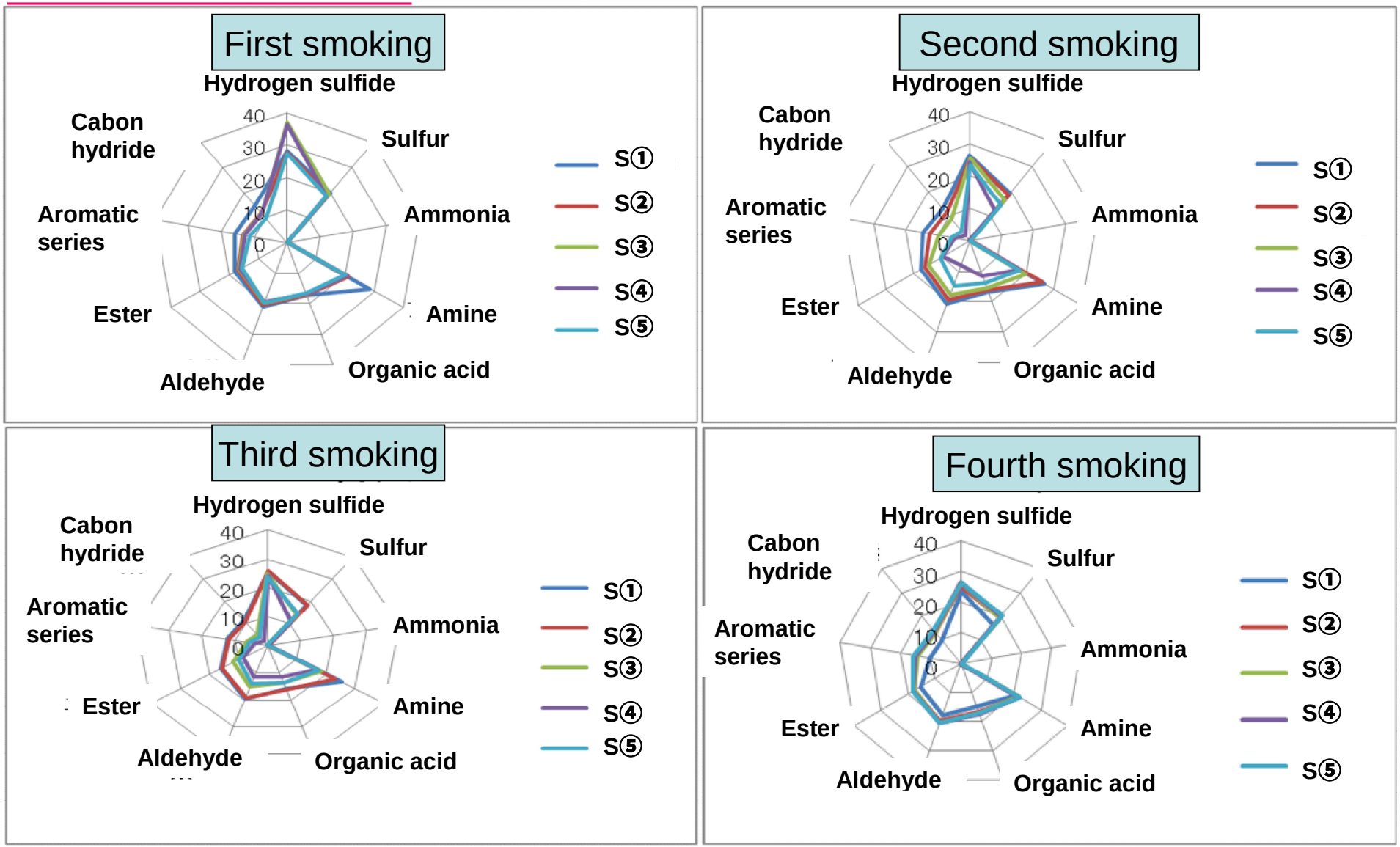


Fig.8 flavor contribution

● Flavor intensity

The outer part ＞ The inner part (Only fourth smoking)

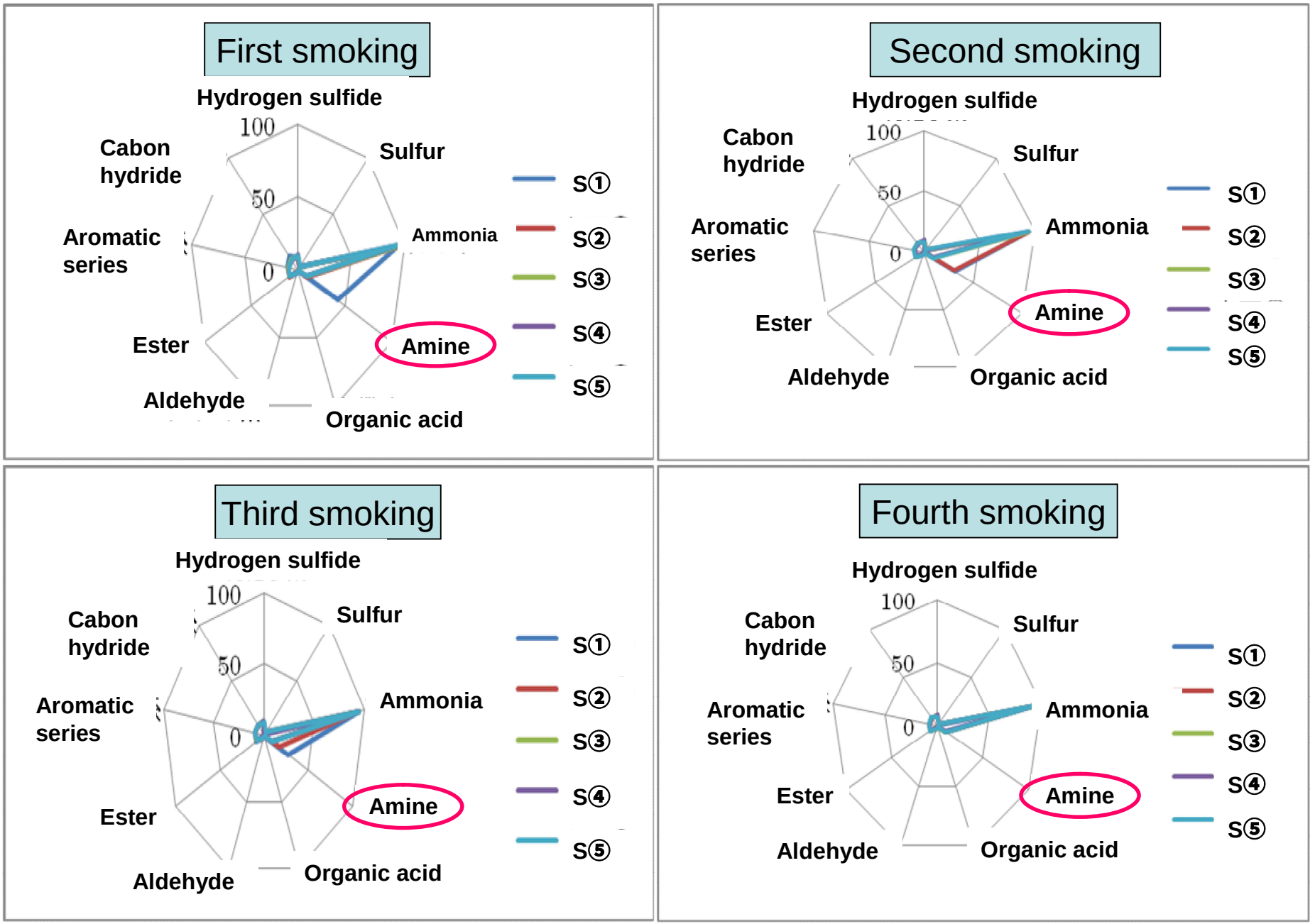


Fig.9 Degree of similarity

Decrease raw fishy flavor such as amines through each stage of the smoking process

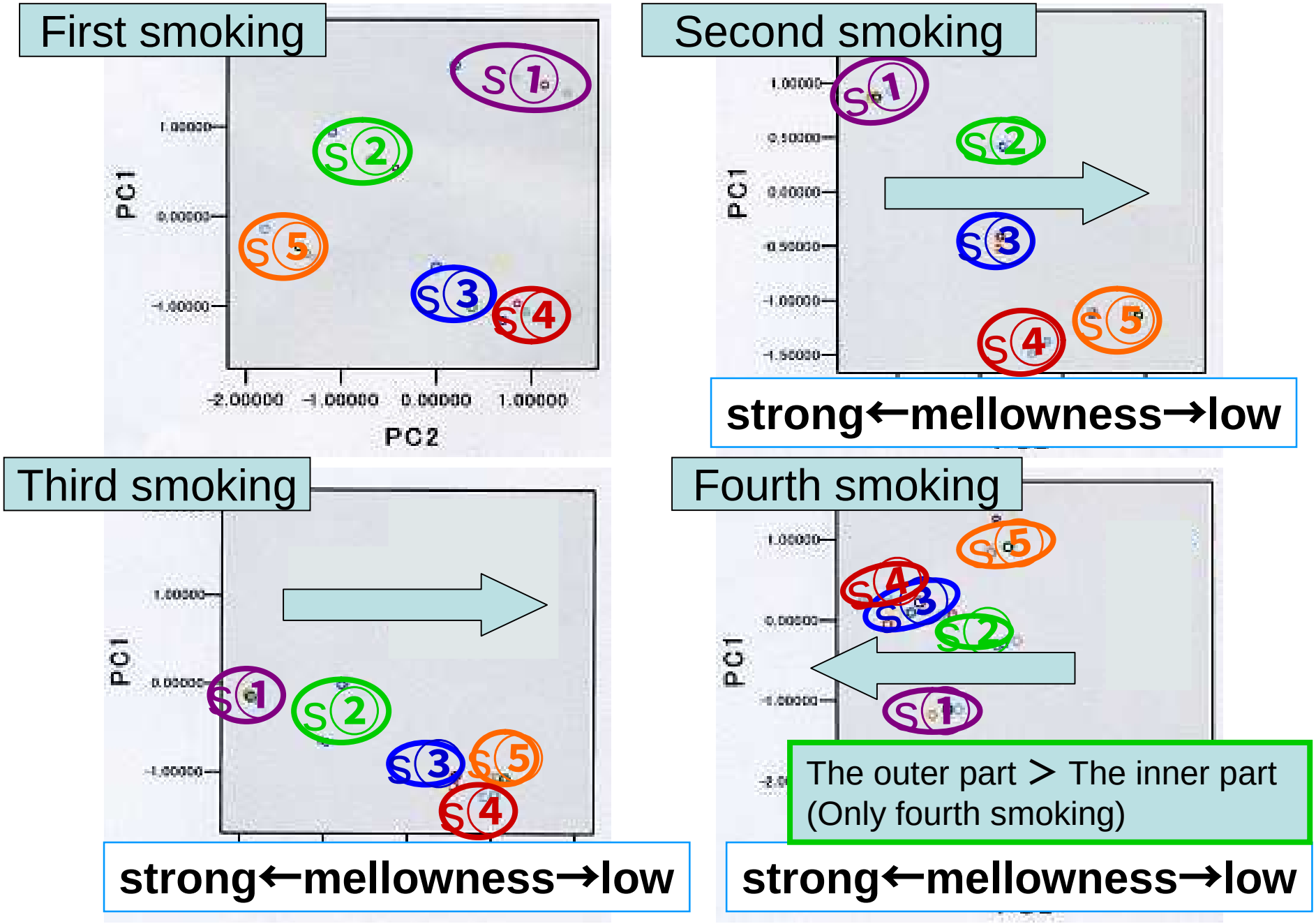


Fig.10 principal component analysis

6. Conclusion

[Lipid analysis]

- The lipid and TG contents decreased
- TG was mainly decreased
  by saturated and monounsaturated fatty acids.

  → ∗Antioxidant action by phenol related compounds and derivatives from smoke
  ∗Physical structure

- The lipid content remained in outer part of
  the flesh rather than in the inner part of the flesh.

  → the diffusion and decomposition of the lipid occurred during the fourth smoking process.

6. Conclusion

[Flavor analysis]

- Several phenols, furans, and pyrazines through each stage of the smoking process.

- The final high quality flavor was produced in the inside of the flesh after the fourth stage of the smoking.

⇨ the raw fishy flavor such as amines diminished in the dried flesh during the fourth stage of the smoking process compared to the first to third ones.

Repeating the process of smoking by the traditional method is very important to establish the high quality of the “Katsuobushi” flavor formation.