FOOD FRAUDS

Authenticity and Traceability of Food and Food Flavourings Using a Stable Isotope Approach

Lidija Strojnik, Nives Ogrinc

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10% of the Global Food Supply Affected

40 % of people have confidence that the food products they buy are generally authentic.

EU TrustTracker® study (2020)

Do we really get what we pay for?

1 **Adulteration of natural flavours**

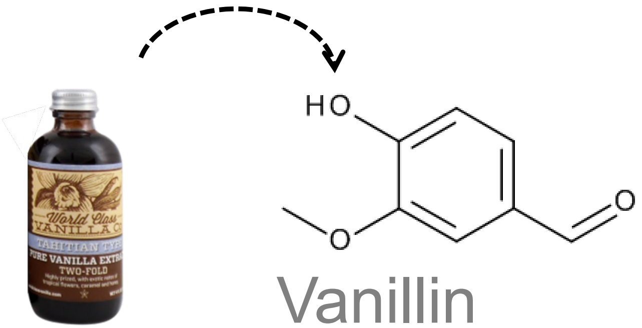
Authenticity of Food Flavourings

2 **Mislabeling of the country of origin**

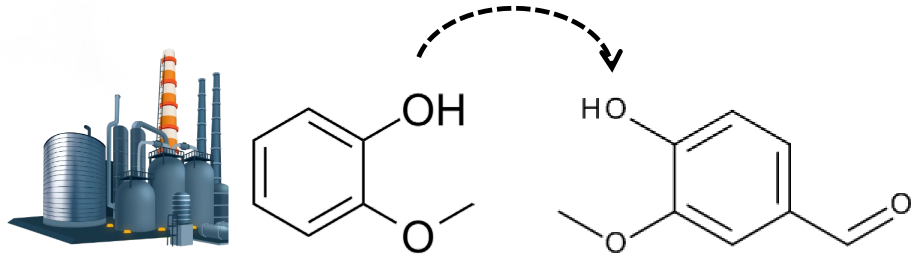
Geographical Origin of Fruits and Vegetables

Regulation (EC) No 1334/2008

Flavouring preparations | **Natural flavouring substances** | **Flavouring substances**



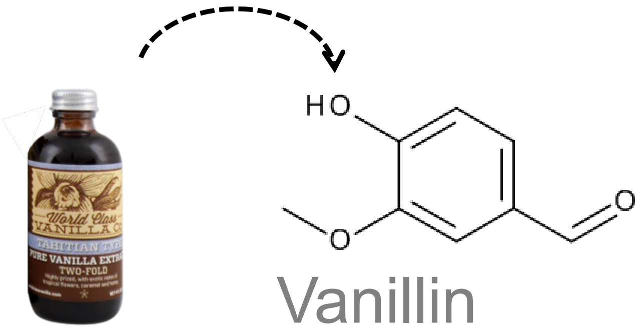
Vanillin

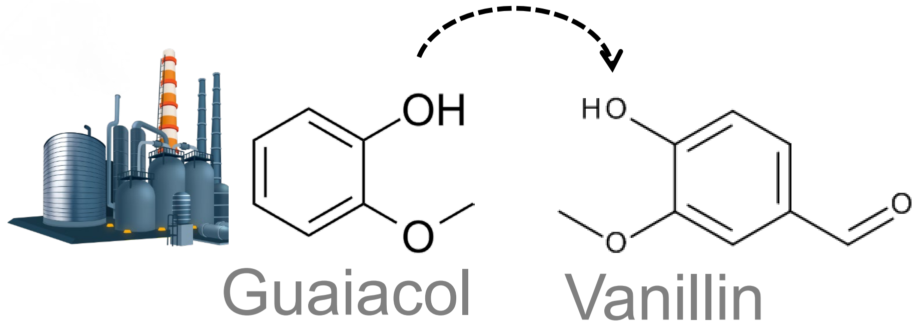


Guaiacol Vanillin

Regulation (EC) No 1334/2008

Flavouring preparations	Natural flavouring substances	Flavouring substances

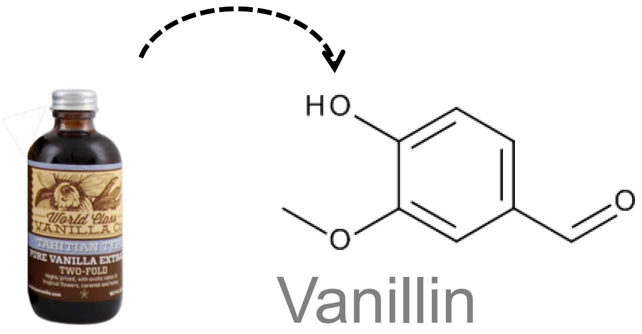


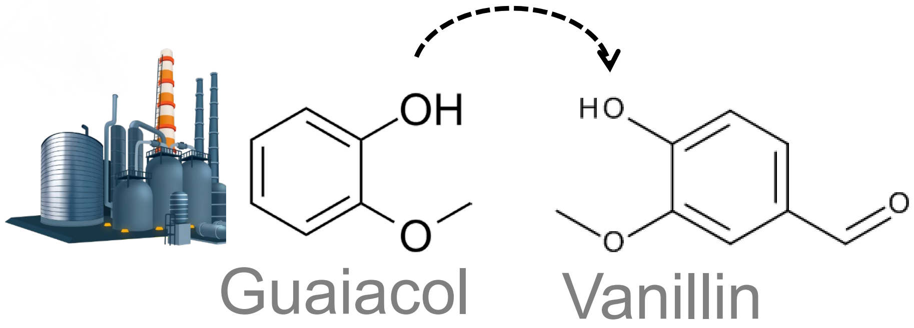


"Natural"

Regulation (EC) No 1334/2008

Flavouring preparations	Natural flavouring substances	Flavouring substances

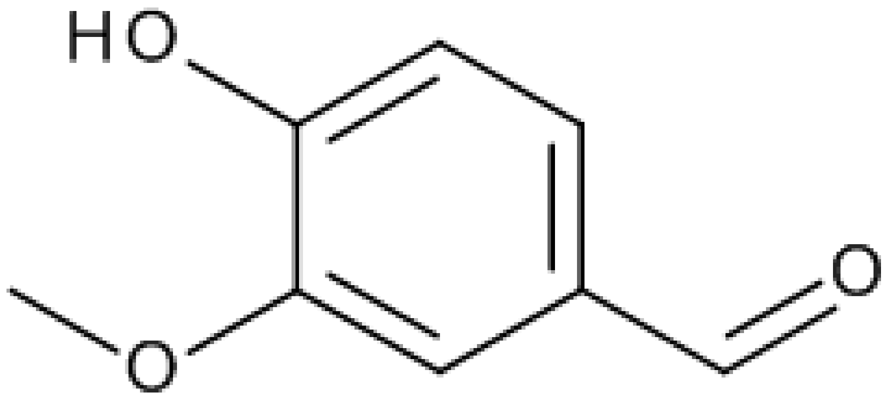




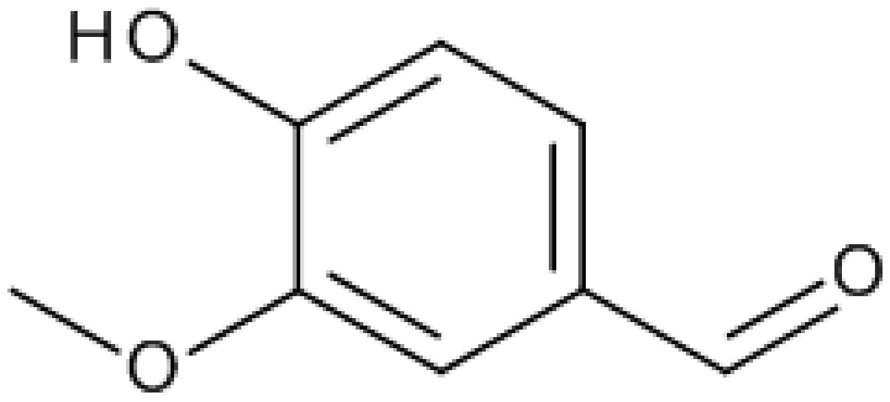
"Natural"

"Synthetic"

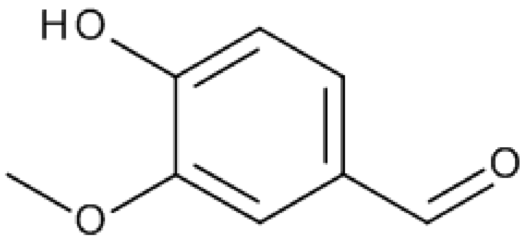
Natural



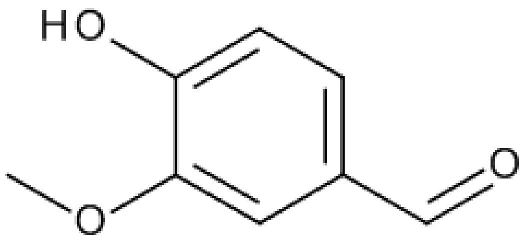
Synthetic



Natural



Synthetic



Fraud risk:

Synthetic flavours are sold as natural!

1 Authenticity of Food Flavourings

Case studies

Fruit flavourings


Fruit flavourings

Price of natural is factor of 10 (or more) higher than the price of synthetic analogues.

Vanillin

1kg pure vanillin = 50 kg of pods

Vanillin

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(1 %) Natural: 120-600 € per kg

Vanillin

1kg pure vanillin = 50 kg of pods

(1 %) Natural: 120-600 € per kg

(99 %) Synthetic: 10-20 € per kg

Truffles

Truffles

Tuber magnatum

3700-6000 € / kg

Tuber melanosporum

880-1200 € / kg

Tuber aestivum

120-220 € / kg

2 Geographical Origin of Fruits and Vegetables

Case studies


















REPUBLIC OF SLOVENIA
MINISTRY OF AGRICULTURE, FORESTRY AND FOOD

THE ADMINISTRATION OF THE REPUBLIC OF SLOVENIA
FOR FOOD SAFETY, VETERINARY AND PLANT PROTECTION

Slovenian origin?



Slovenia

Slovenia

Country with low level of self-sufficiency: fruits (30 %), vegetables (48 %)

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Locally produced food has become more demanded by Slovenian consumer

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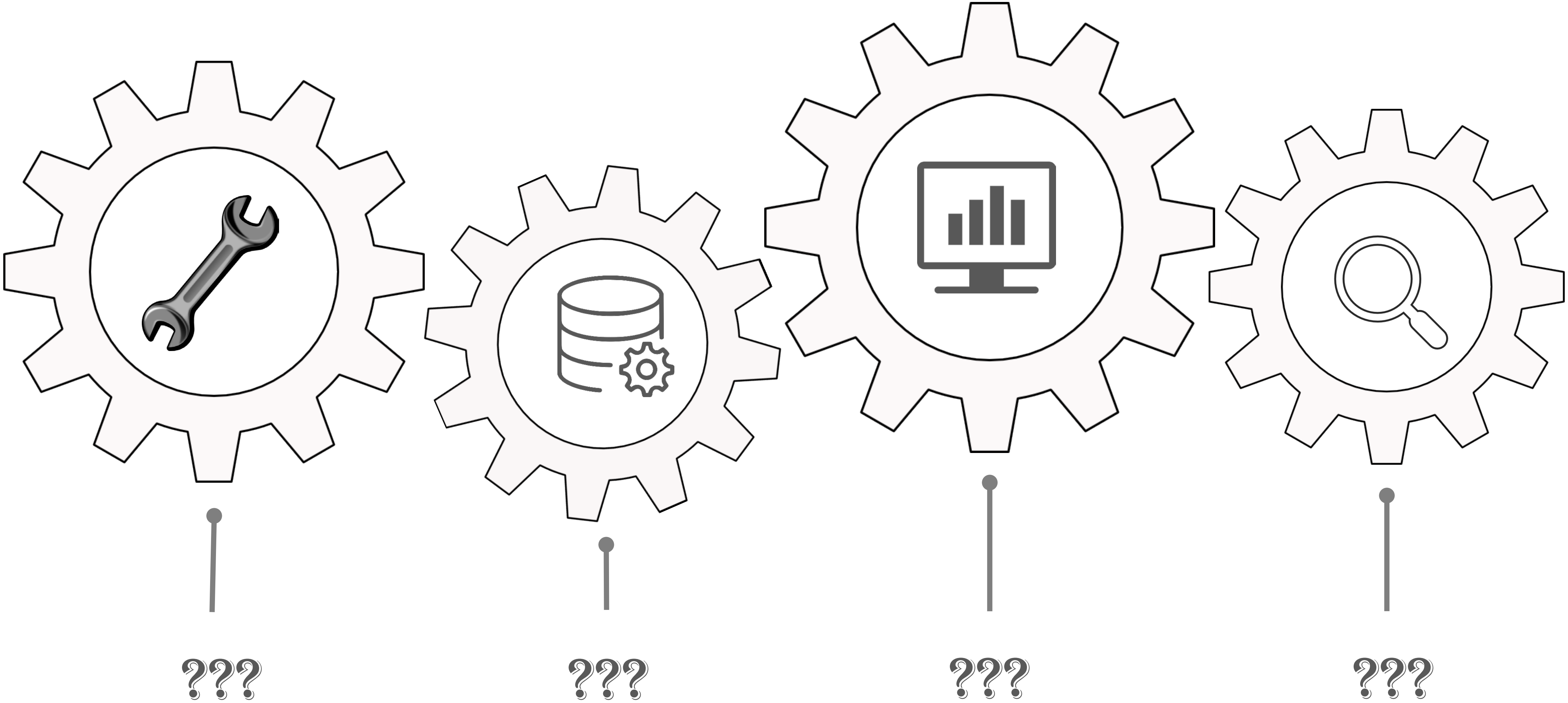
Locally produced food become more demanded by Slovenian consumer

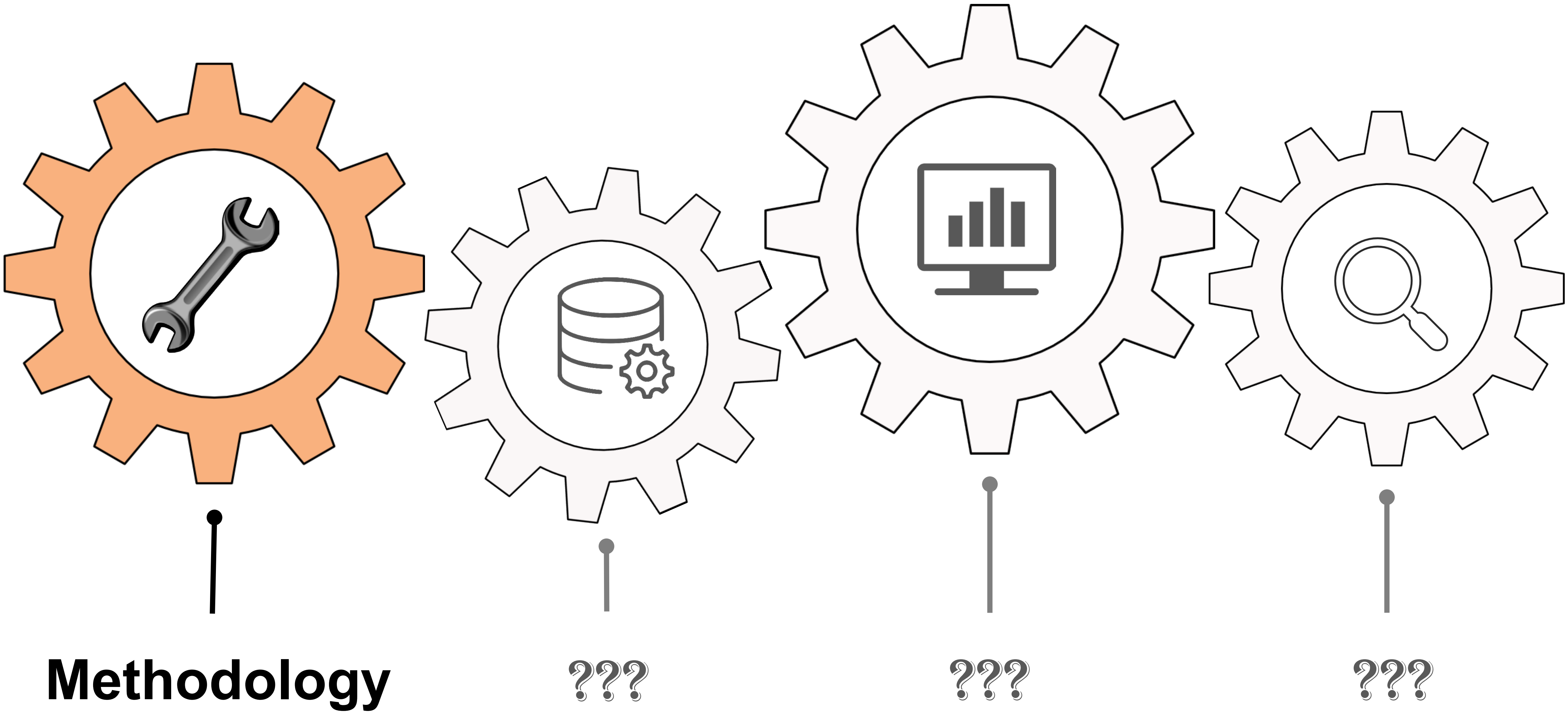
Fraud risk: mislabeling the origin of production!

How can we fight against frauds and be confident that the food we are buying is authentic?

The four gears building trust in our food

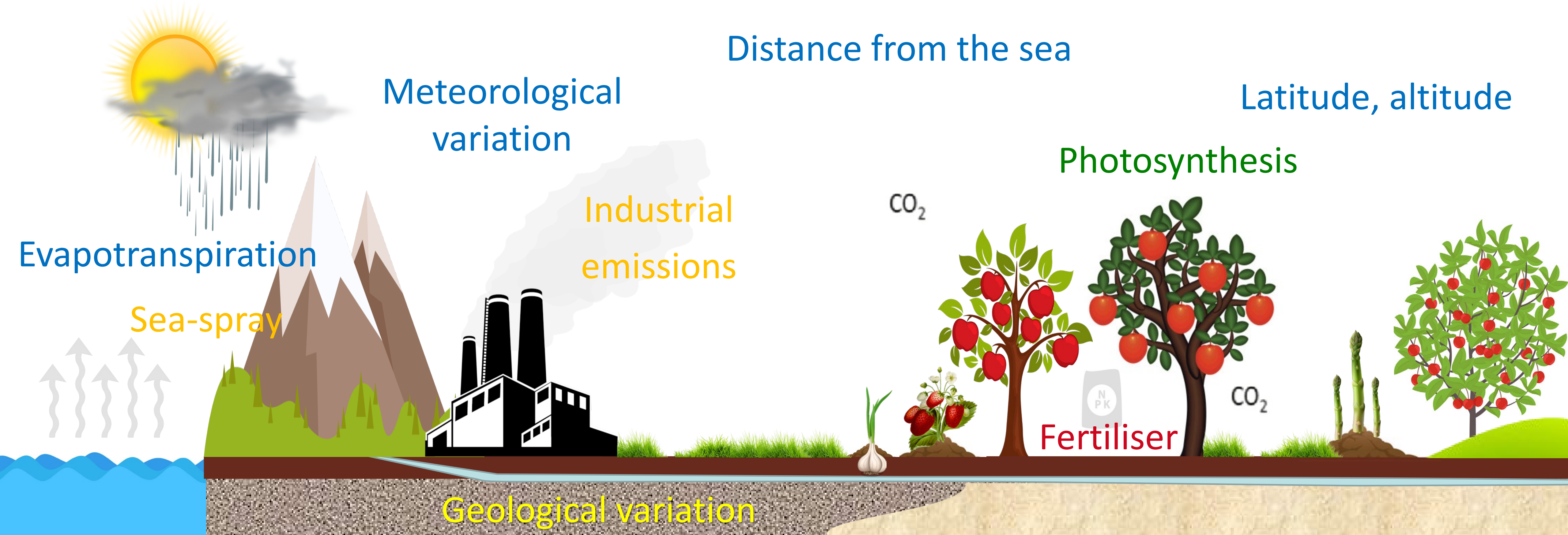


The four gears building trust in our food



Geographical origin of food

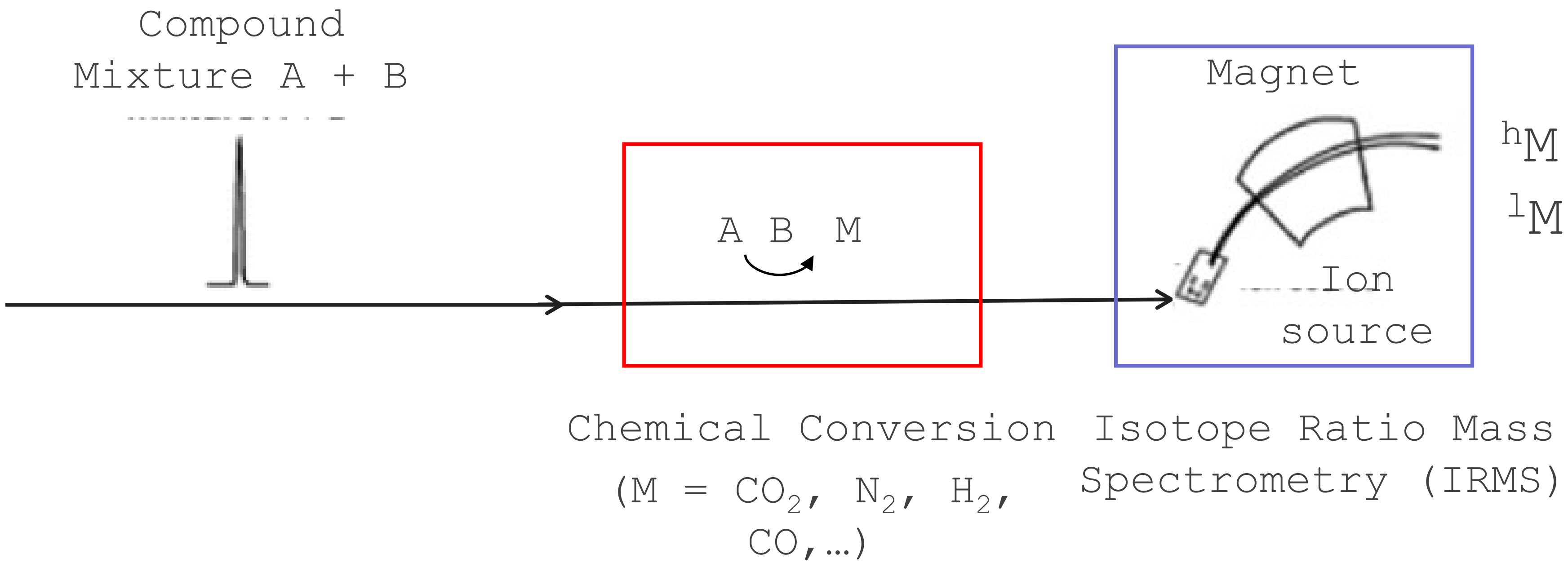
C N O S & elemental composition (ICP-MS)



Geographical origin of food

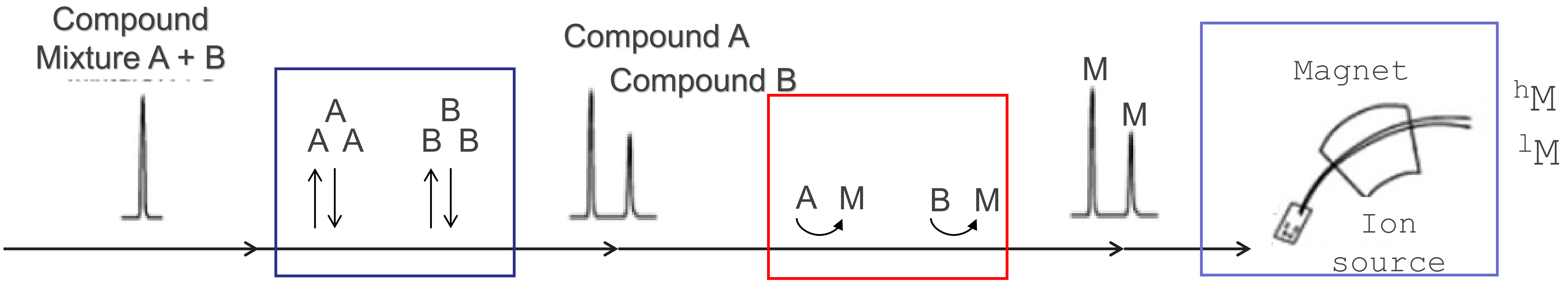
C N O S

"Bulk" EA-IRMS



Authenticity of flavourings

C H "Compound specific" GC-IRMS



Chromatographic Separation
(Gas Chromatography)

Chemical Conversion
($M = CO_2, N_2, H_2, CO,\ldots$)

Isotope Ratio Mass
Spectrometry (IRMS)

Authenticity of flavourings

Solid Phase MicroExtraction (SPME)

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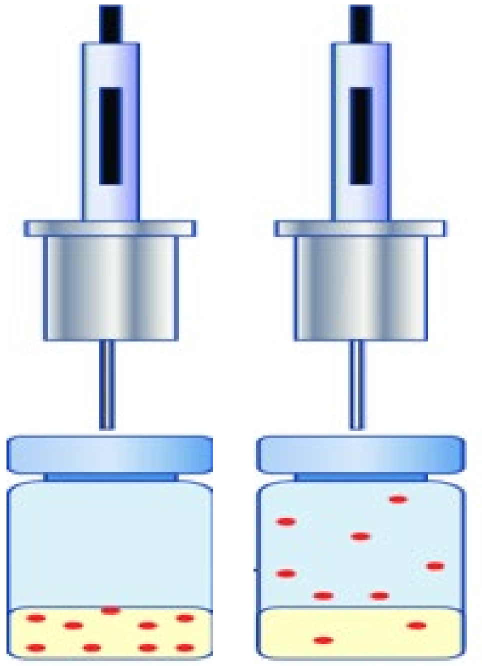
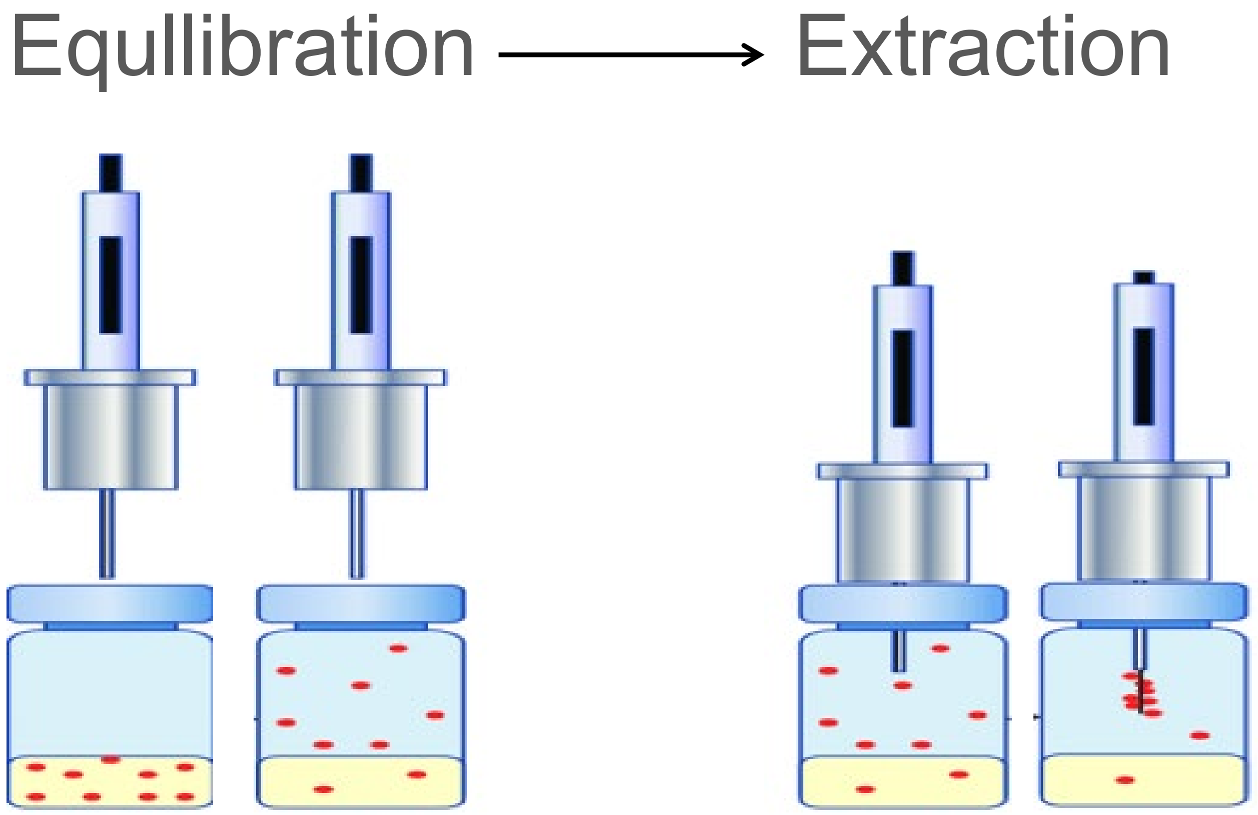
Equllibration



Authenticity of flavourings

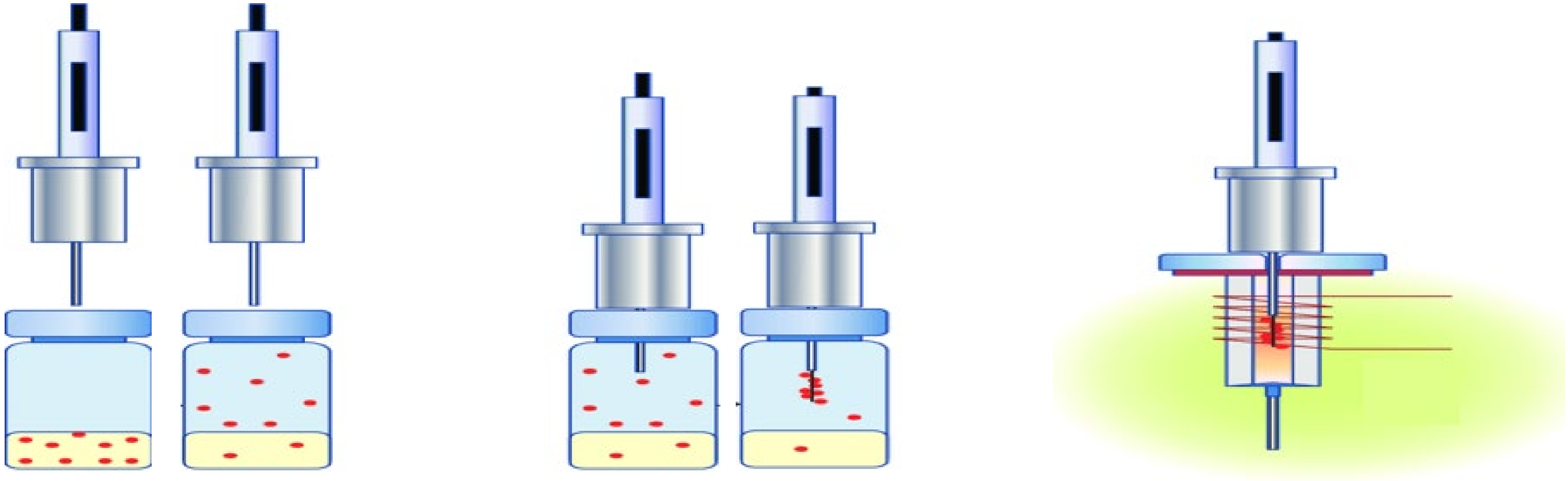
Solid Phase MicroExtraction (SPME)



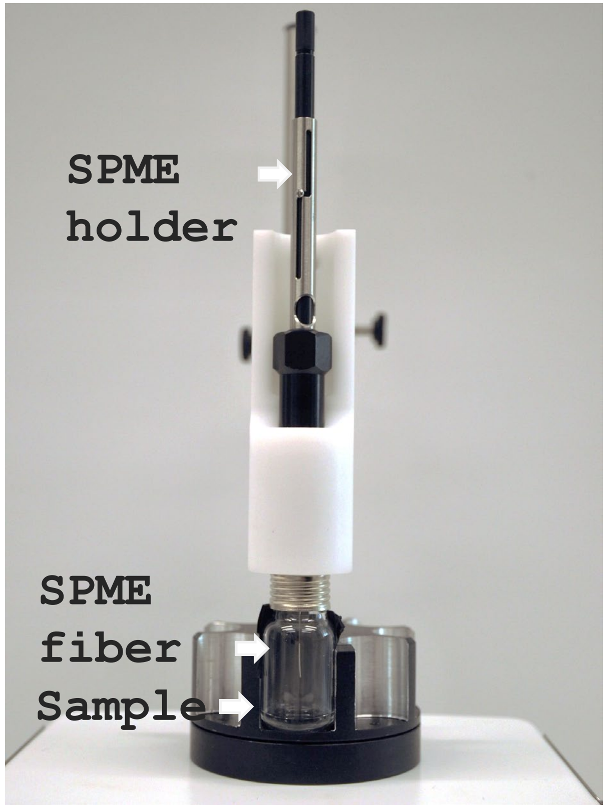
Authenticity of flavourings

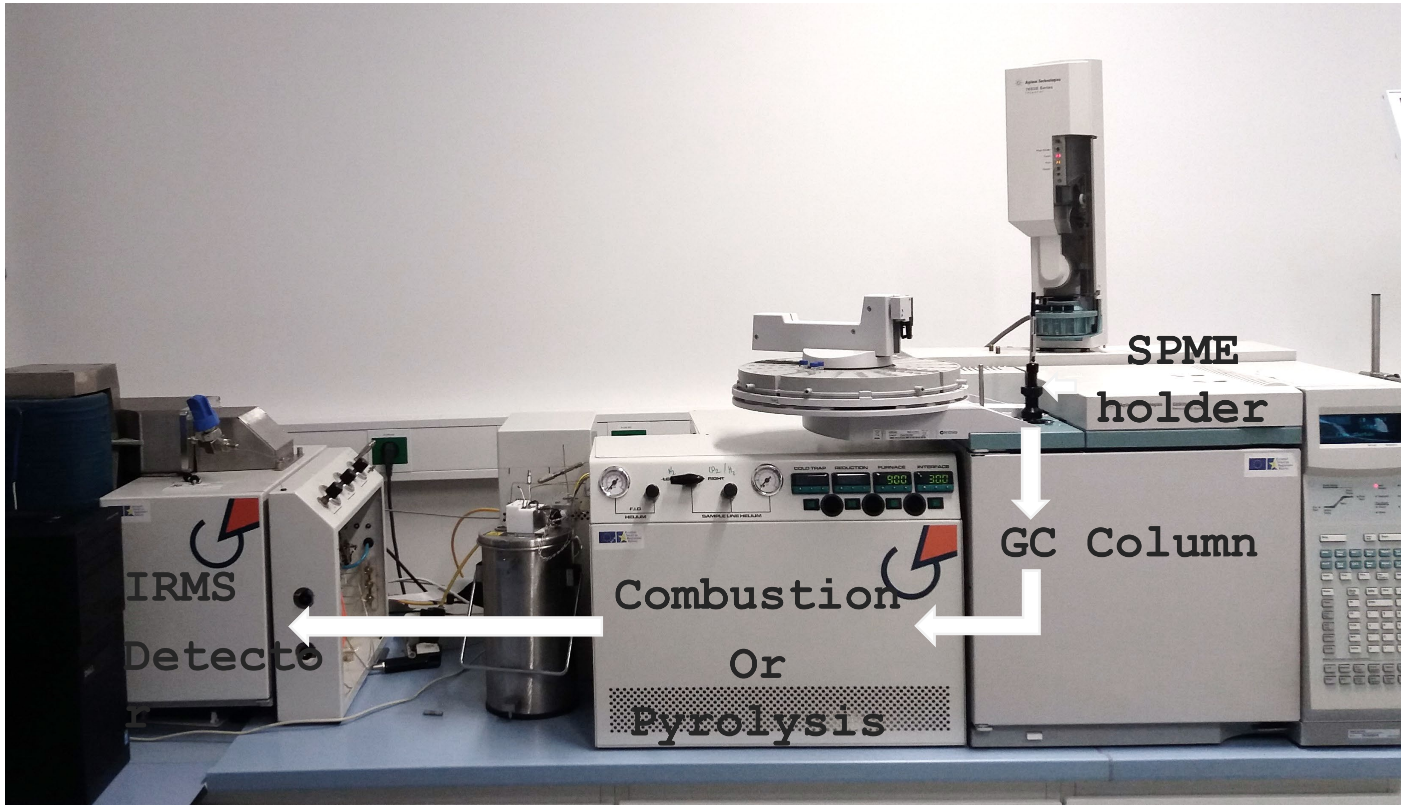
Solid Phase MicroExtraction (SPME)

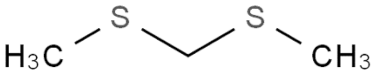
Equllibration → Extraction → Desorption

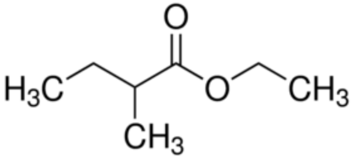


HS-SPME GC-C/P-IRMS ($\delta^{13}C$ or $\delta^{2}H$)

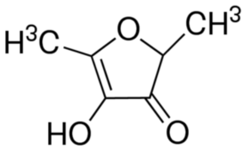




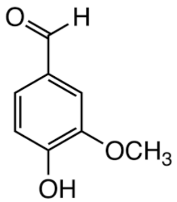




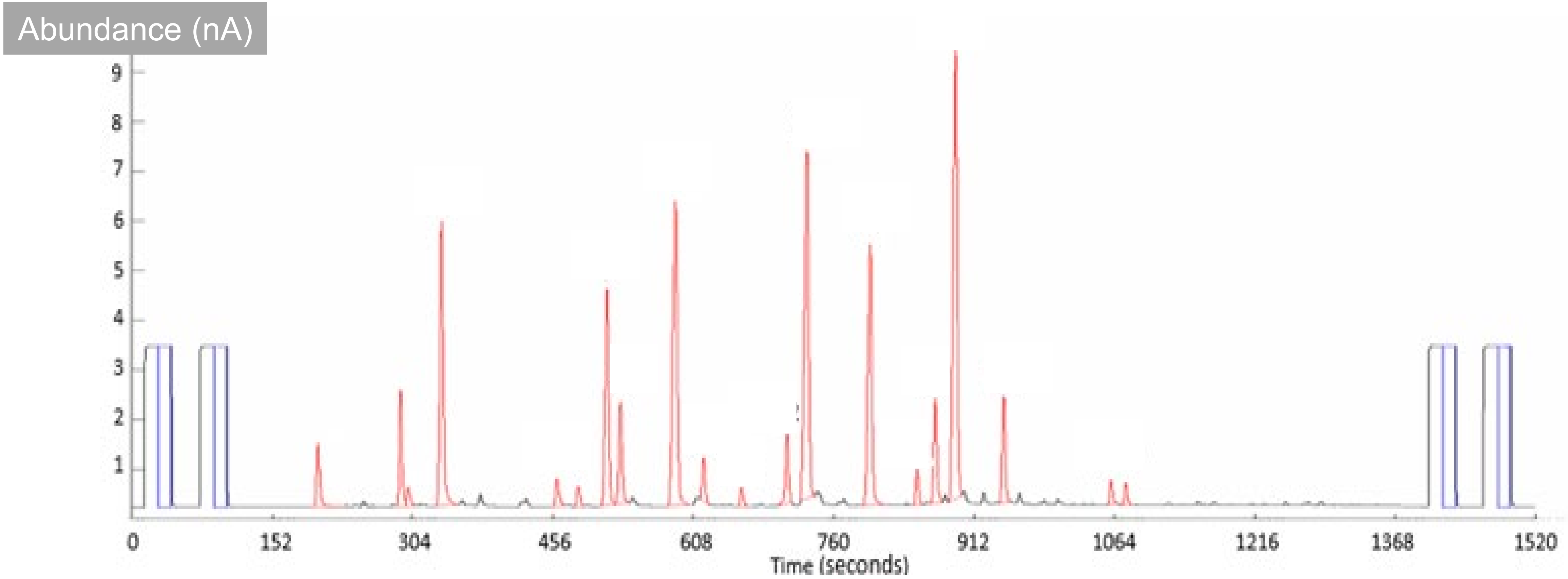






Procedure can be **transferred** to **different flavourings** & it is **suitable** for analysing **complex matrices.**

Many compounds often fall out of the linear range of GC-IRMS instrument



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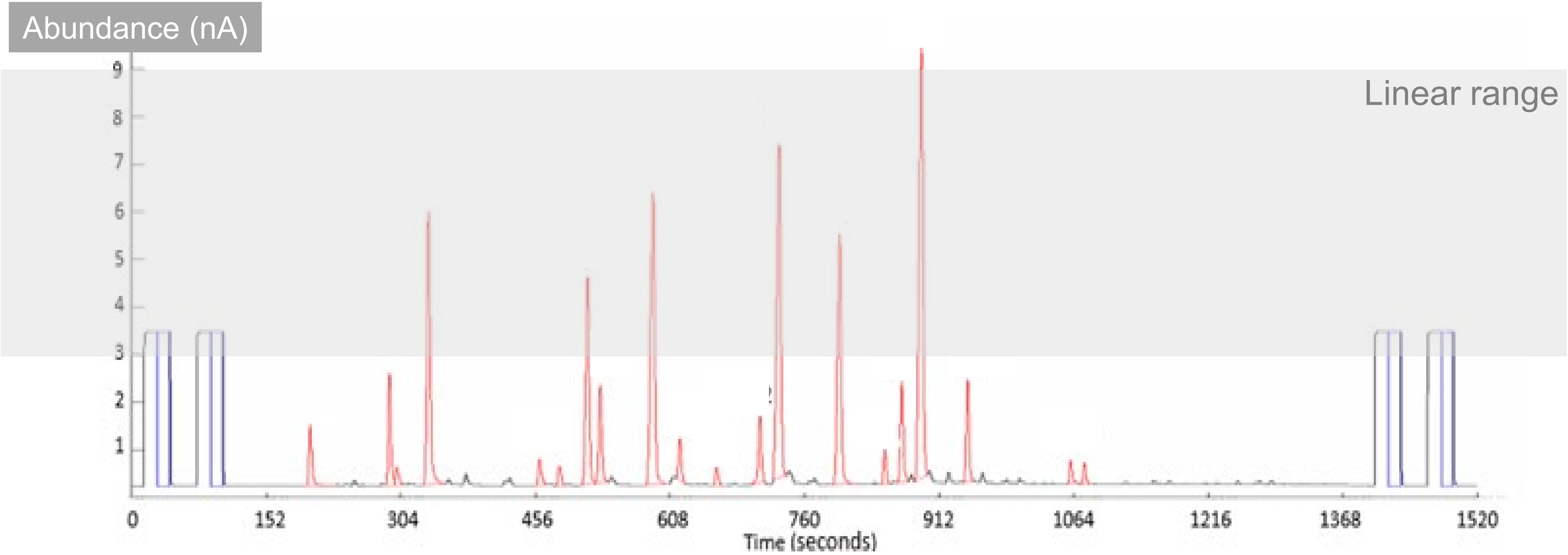
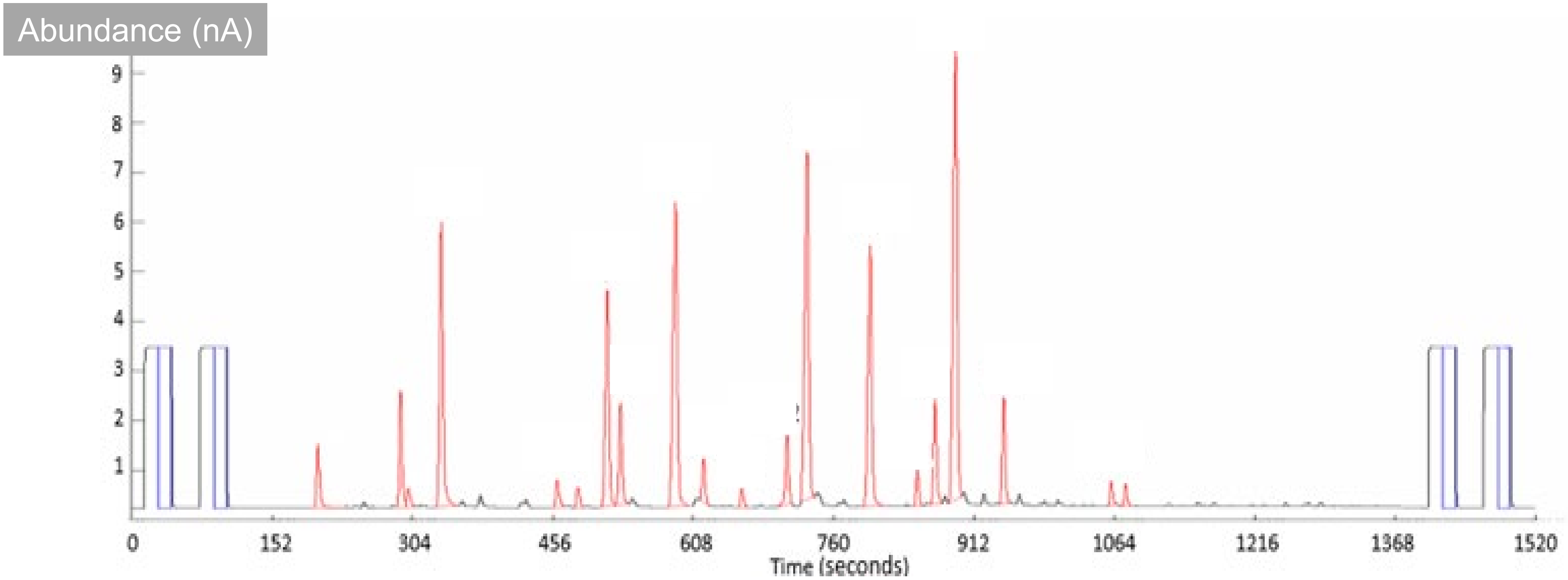
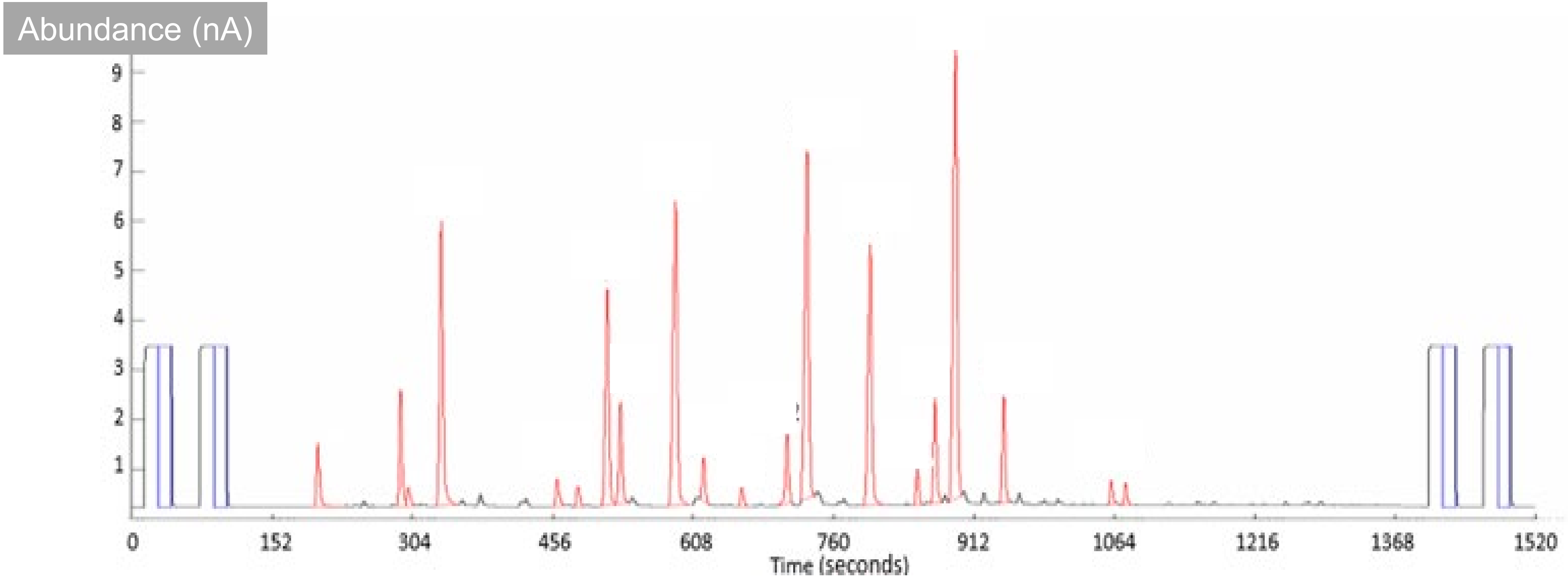


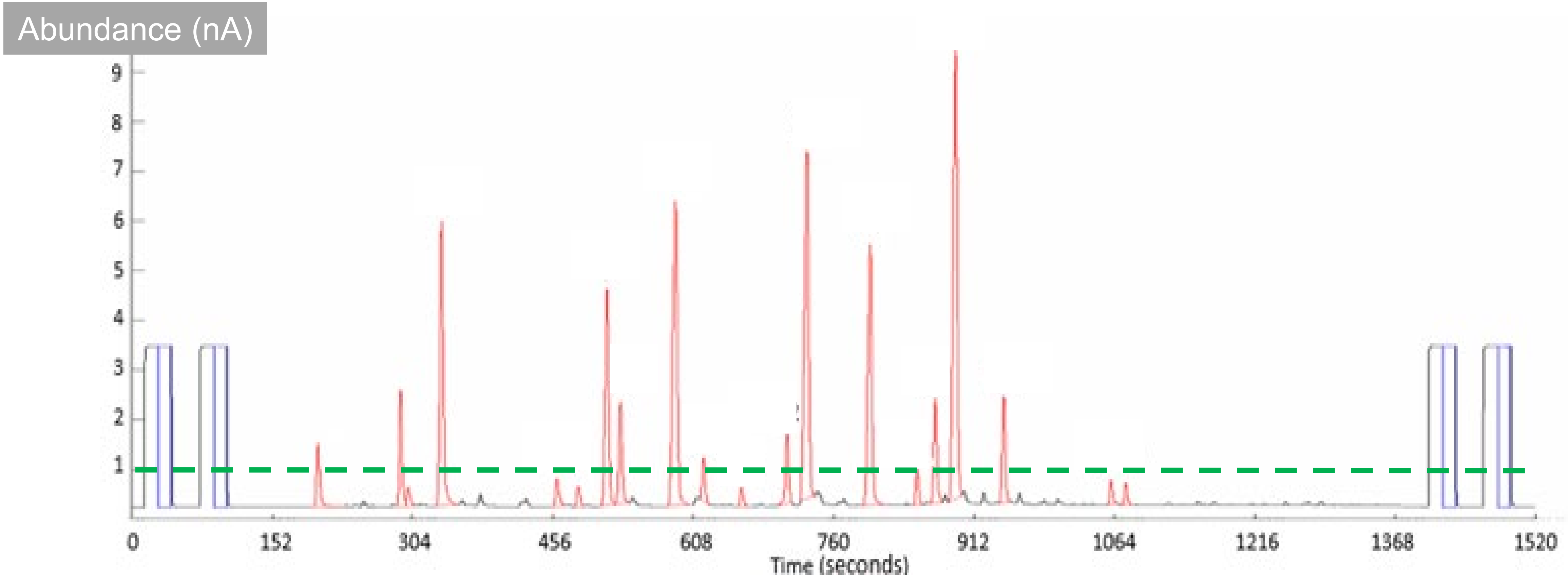

Abundance (nA)
9
8
7
6
5
4
3
2
1
0
152
304
456
608
760
912
1064
1216
1368
1520
Time (seconds)

Peak size / linearity correction



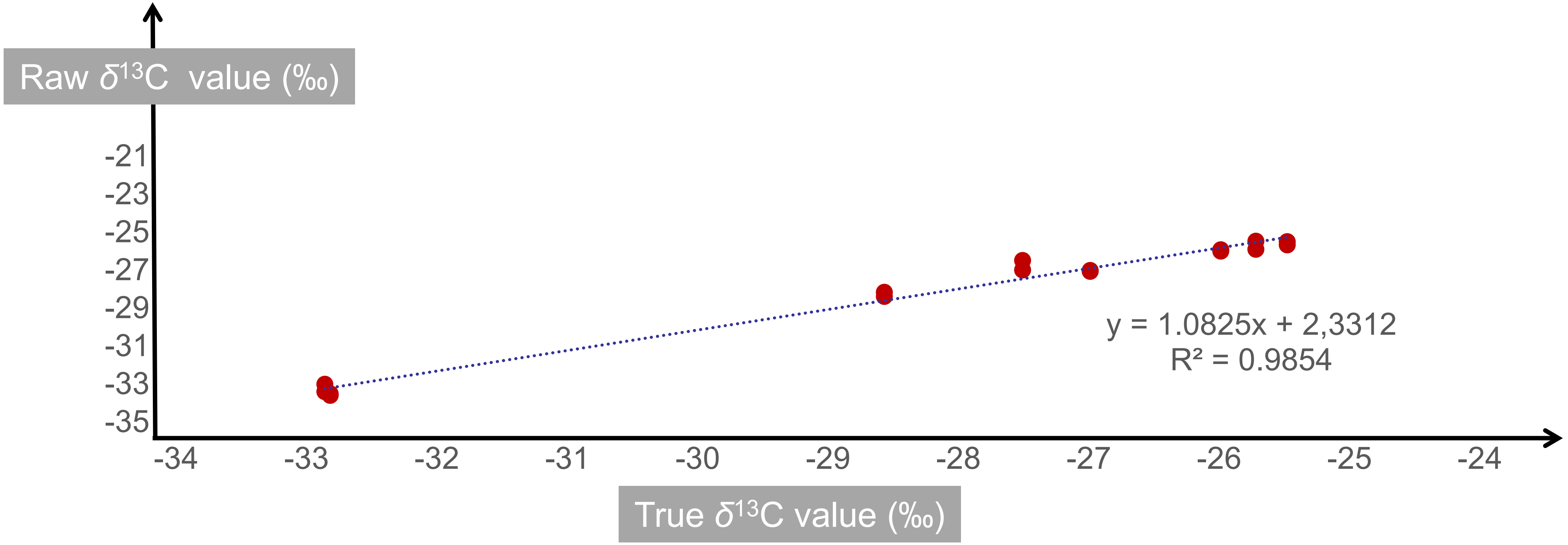
Peak size / linearity correction

Significantly improved the measurement error of small peaks (below 1nA) from 3 ‰ to 0.5 ‰.



Multiple-point isotopic linear normalisation

Reduce the random error associated with the analysis of a reference material used to anchor the linear scale.



Measurement uncertainty

In-house standard	Reference values (‰)	Combined uncertainty (u_c, k = 1)
ethyl butanoate	-25.7	0.5
hexanal	-25.5	0.3
(E)-hex-2-enal	-27.5	0.8
hexyl acetate	-27.0	0.6
benzaldehyde	-26.0	0.8
ethyl 2-methylbutanoate	-24.7	0.1
2-methylbutyl acetate	-32.9	0.3
ethyl hexanoate	-32.8	0.2
[(z)-hex-3-enyl] acetate	-28.7	0.2

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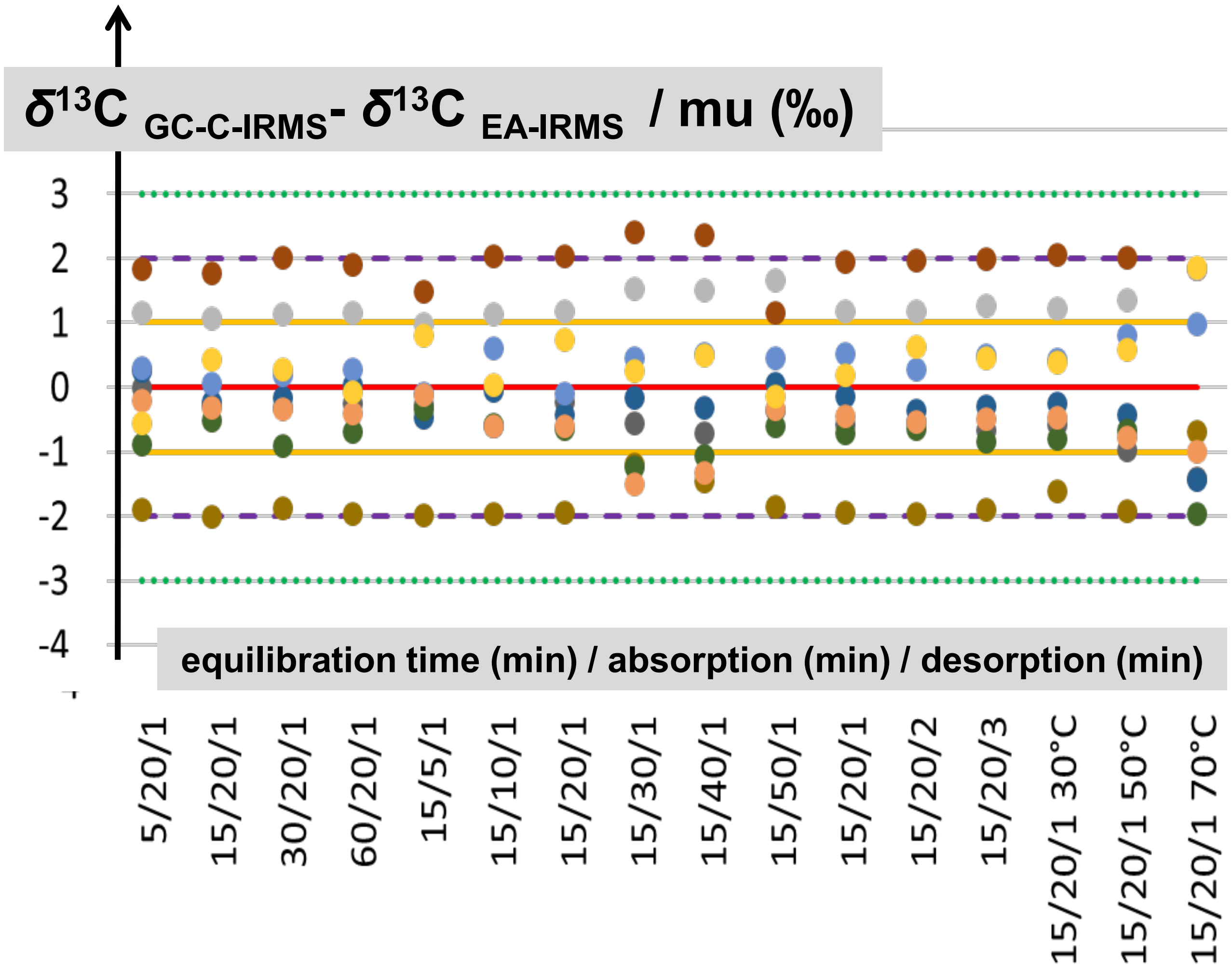
Method		**0.4 ‰**

Perini et al., 2019: 1σ = ± 0.8 ‰ (vanillin)
Hatorri et al., 2010: 1σ = ± 0.4 ‰ (acetic acid)
Schipilliti et al., 2016: 1σ = ± 1.0 ‰ (vanillin)

Compound specific $\delta^{13}C$ measurements

effects of equilibration, adsorption, desorption times and temperatures



Compound specific $\delta^{13}C$ measurements

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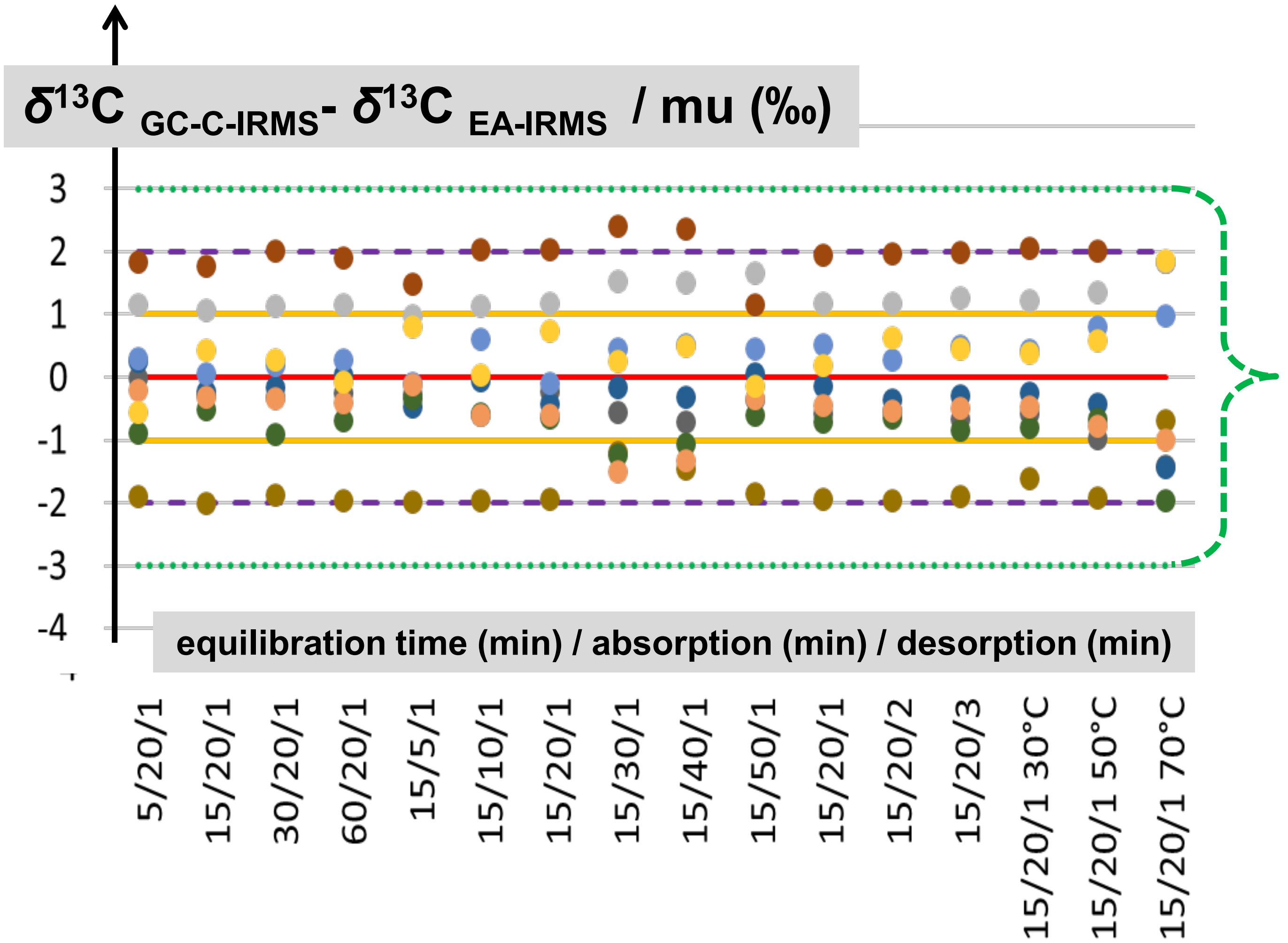
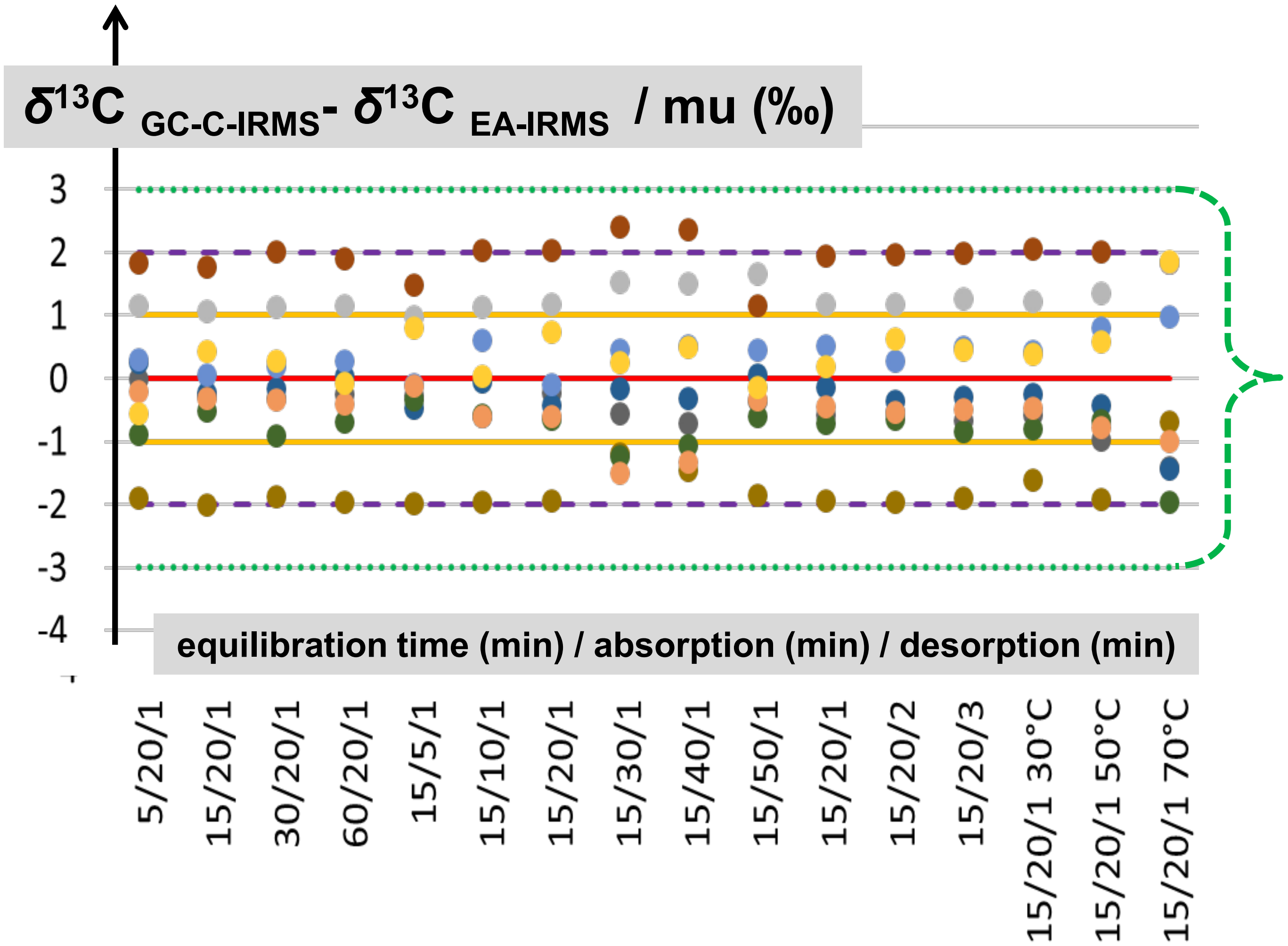


All the $\delta^{13}C$ values were below ± 3*MU.

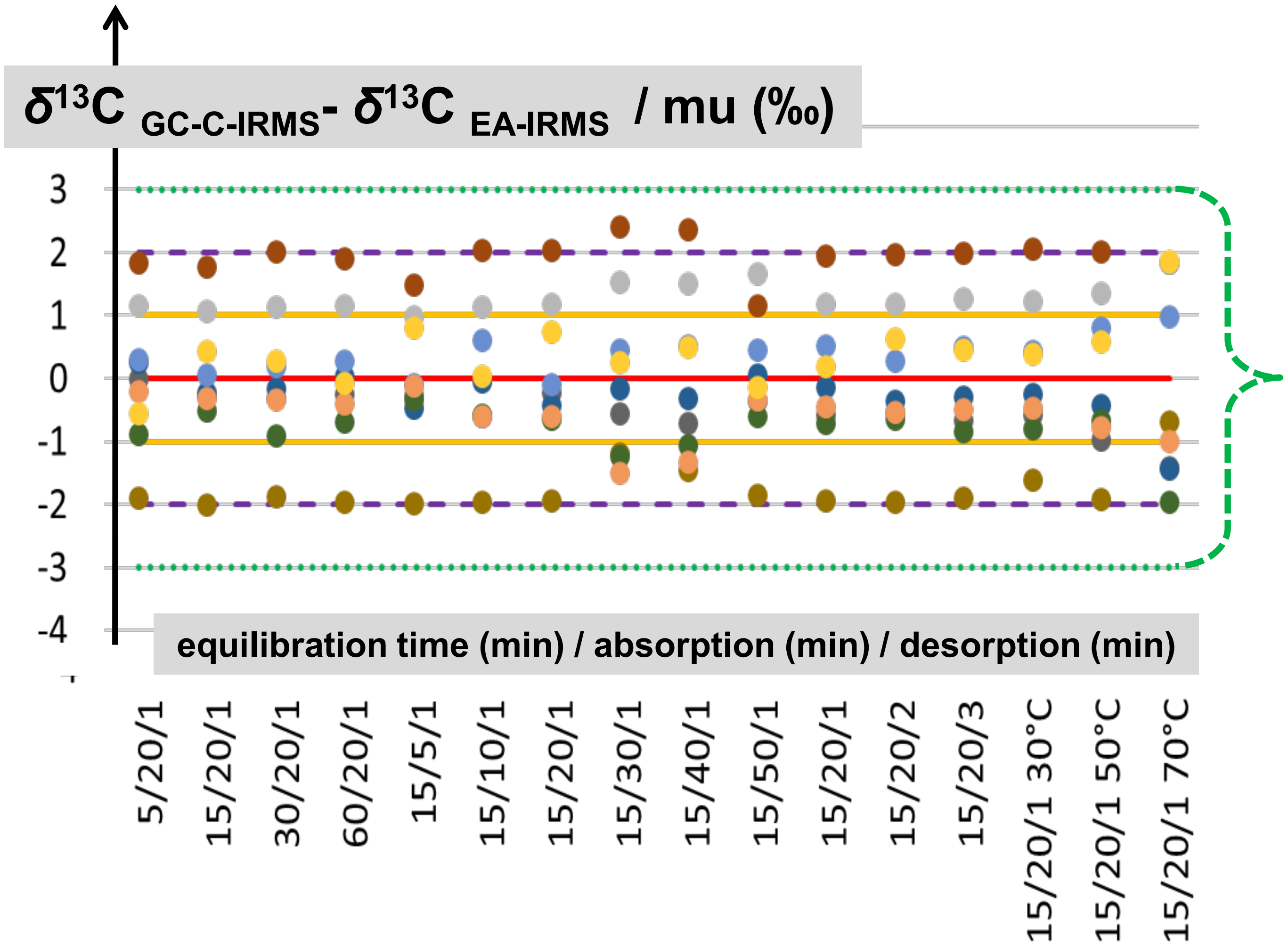
Compound specific $\delta^{13}C$ measurements

effects of equilibration, adsorption, desorption times and temperatures



Compound specific $\delta^{13}C$ measurements

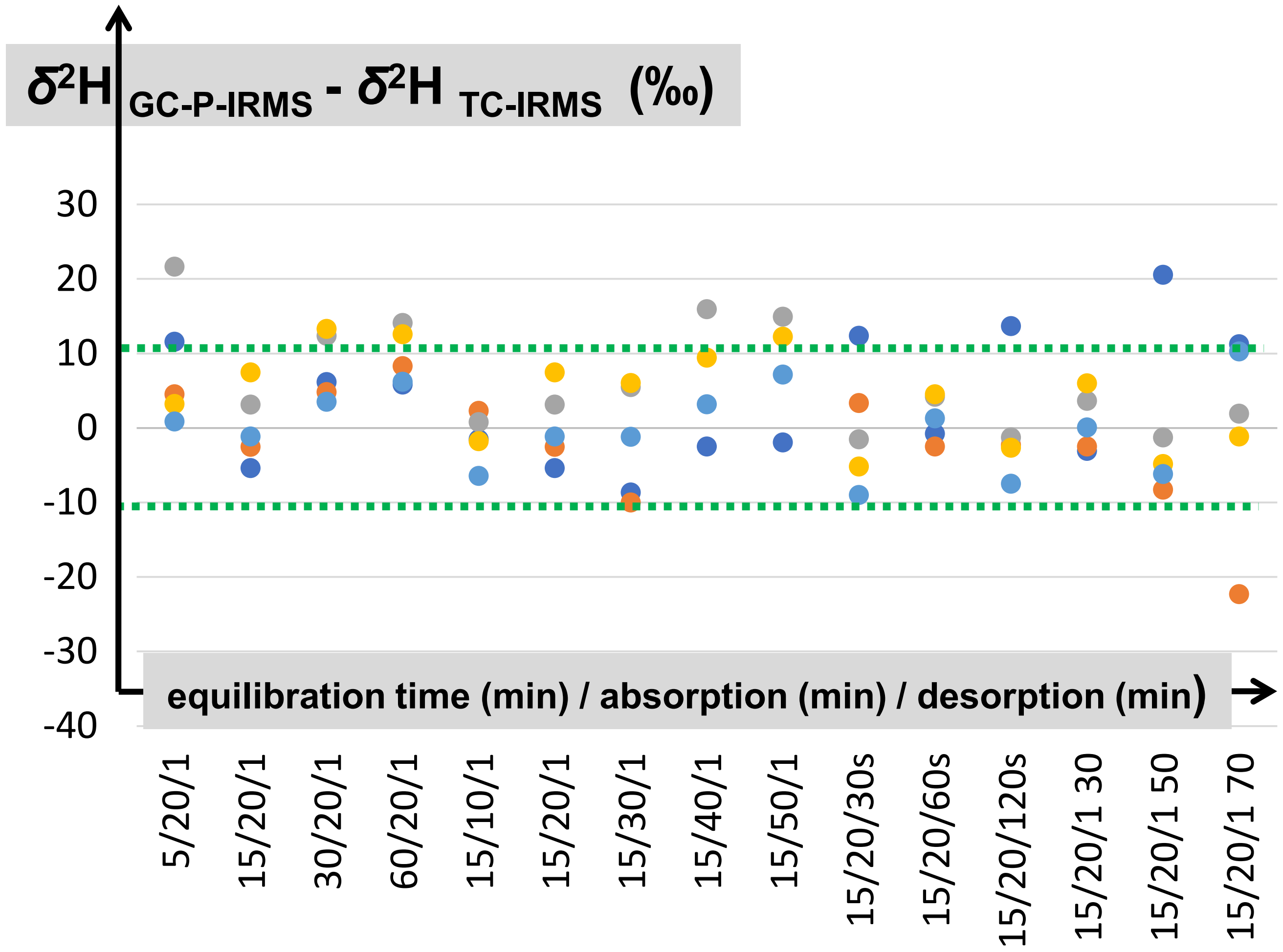
effects of equilibration, adsorption, desorption times and temperatures



No isotopic fractionation was observed.

Compound specific δ²H measurements

effects of equilibration, adsorption, desorption times and temperatures

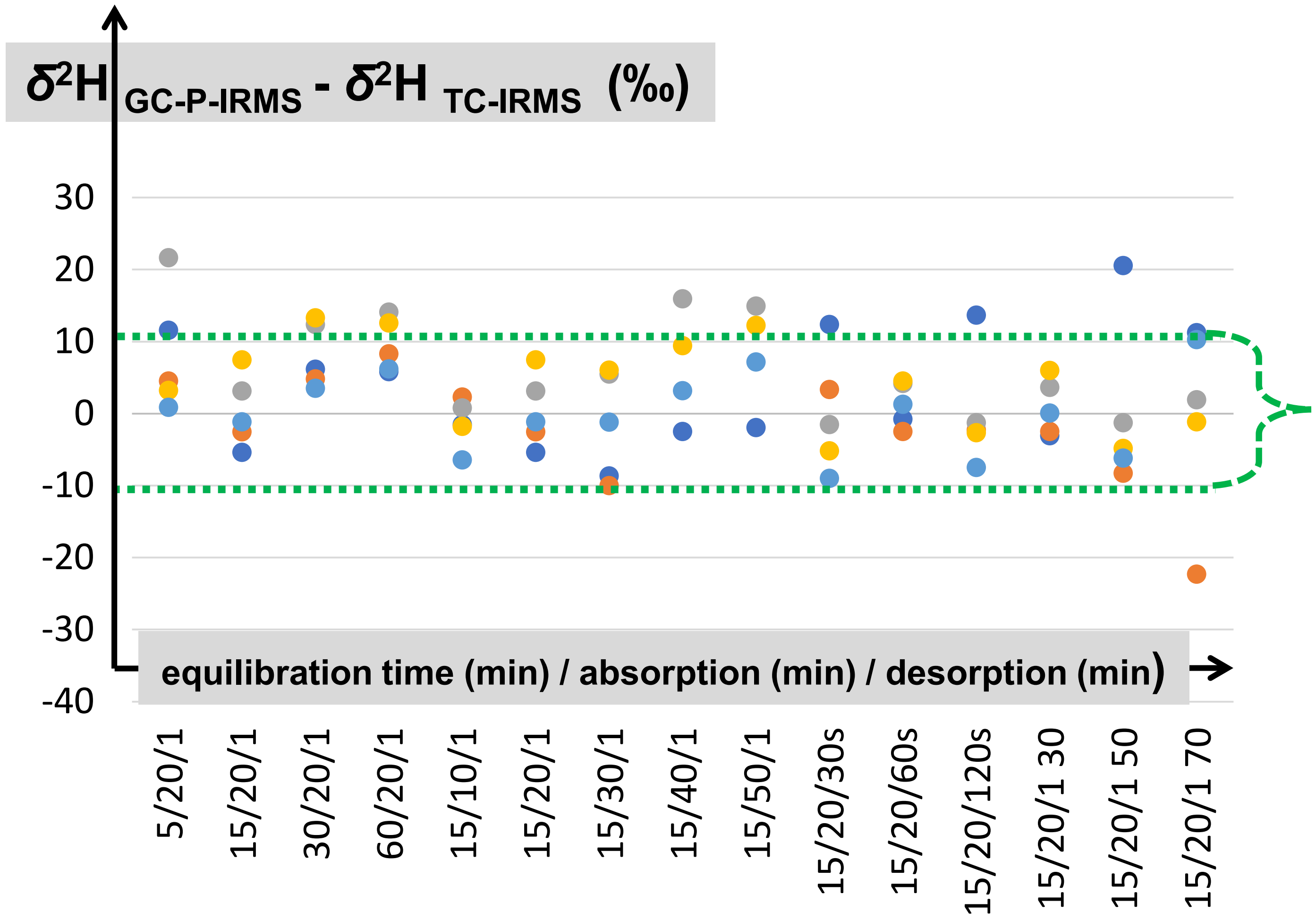


Perini et al., 2019: 1σ = ± 7 ‰ (vanillin)

Hatorri et al., 2010: 1σ = ± 5 ‰ (acetic acid)

Compound specific δ^2H measurements

effects of equilibration, adsorption, desorption times and temperatures



Method error < 10 ‰ can be obtained by optimising measurement conditions.

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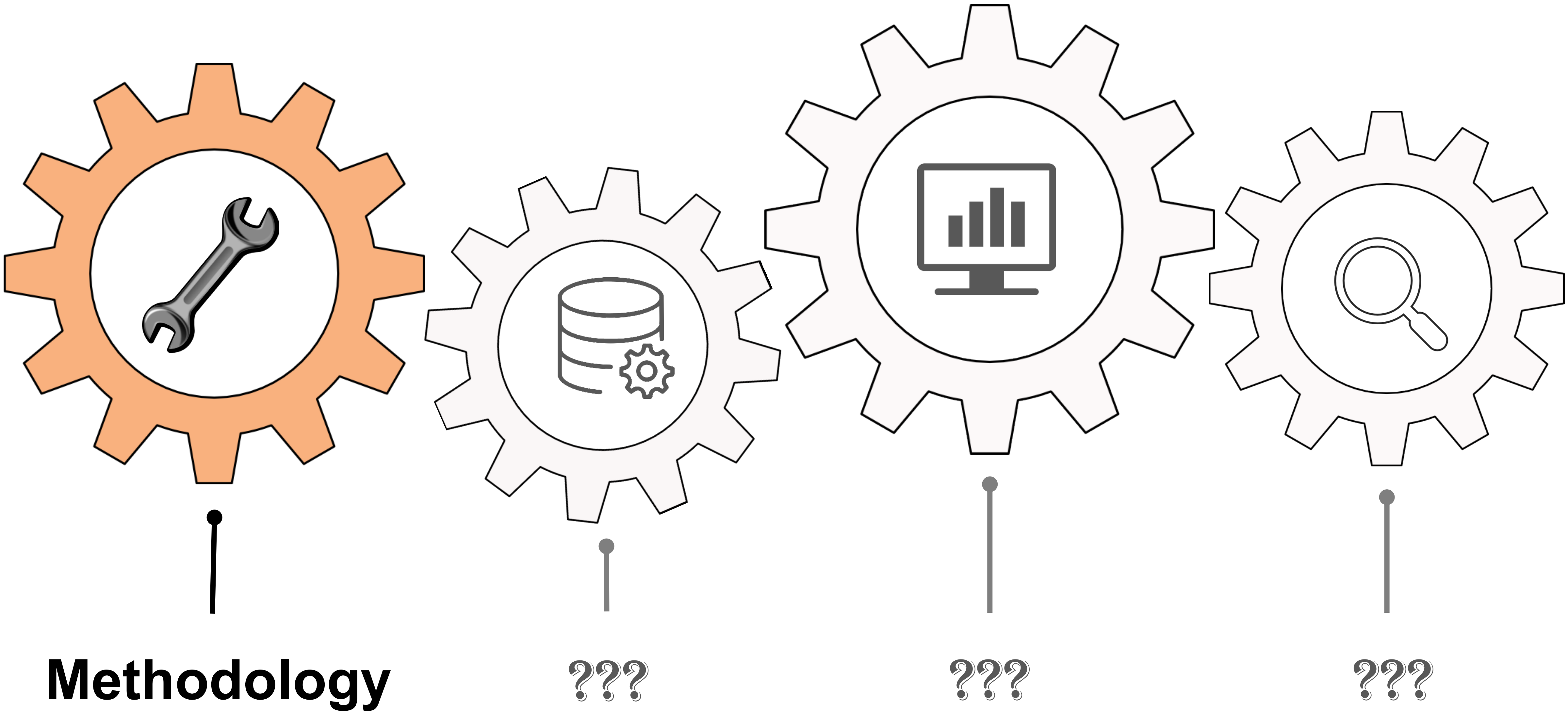
The four gears building trust in our food



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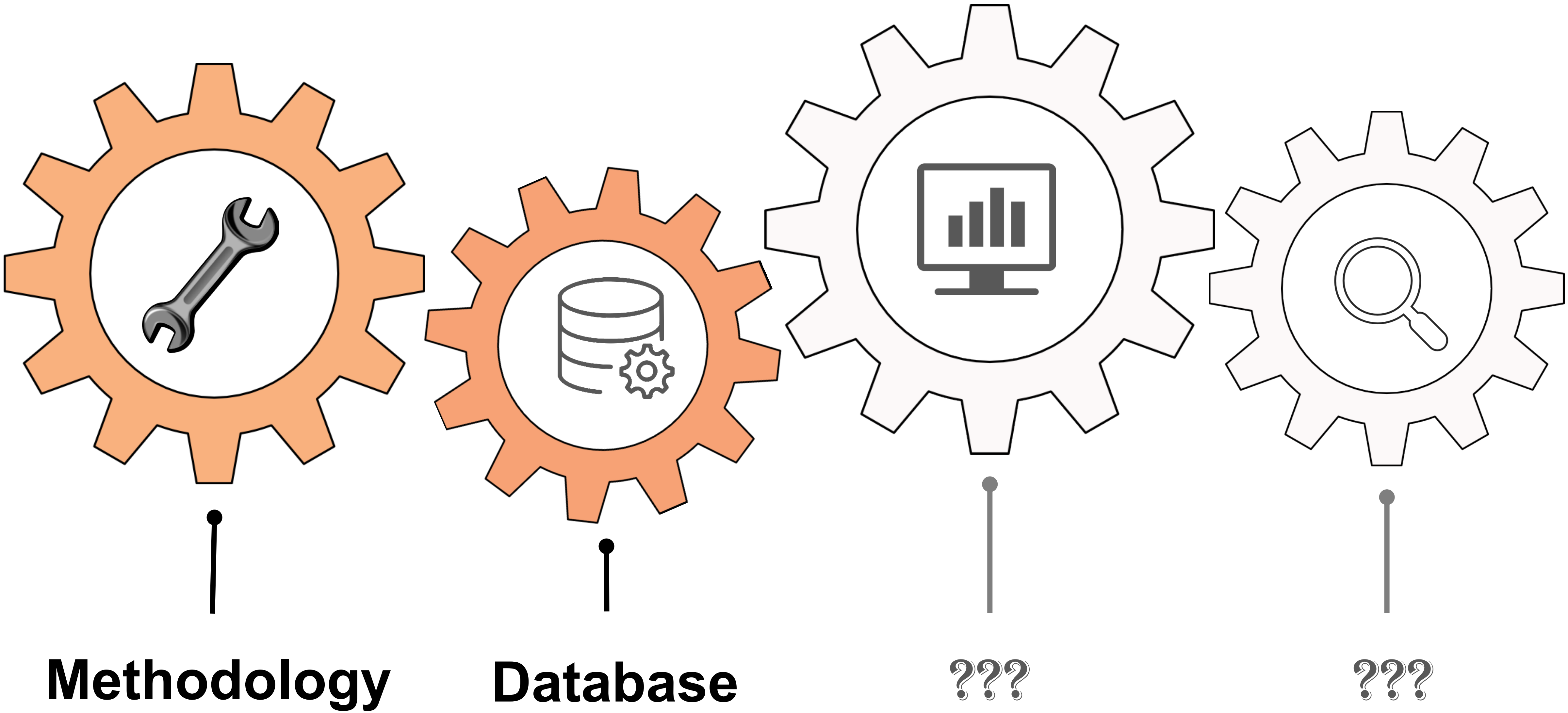

Data interpretation requires extensive reference data set of authentic food samples against which a sample under investigation can be compared.

General requirements

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Samples within database are authentic

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Collected from primary producers by impartial collectors

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Adequate number of samples

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Sufficiently representative

General requirements

Samples within database are authentic

Collected from primary producers by impartial collectors

Adequate number of samples

Sufficiently representative

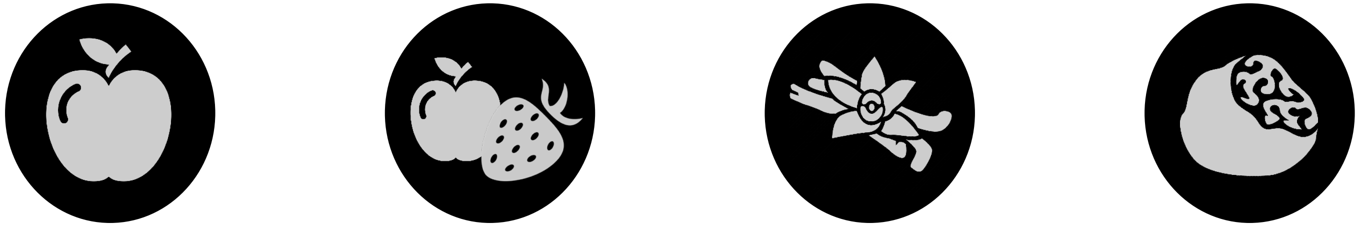
Cover natural variation

10 databases were established

4 within authenticity of flavourings

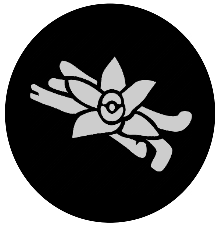
$\delta^{13}C$ ($\delta^{2}H$)

FLAVOURING



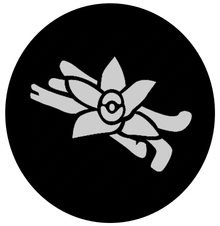
4 within authenticity of flavourings

$\delta^{13}C$ ($\delta^{2}H$)

FLAVOURING				
VOCs	16	39	1	21

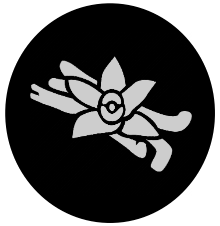
4 within authenticity of flavourings

$\delta^{13}C$ ($\delta^{2}H$)

FLAVOURING				
VOCs	16	39	1	21
NATURAL	34	213	49	87

4 within authenticity of flavourings

$\delta^{13}C$ ($\delta^{2}H$)

FLAVOURING				
VOCs	16	39	1	21
NATURAL	34	213	49	87
SYNTHETIC	16	48	6	13

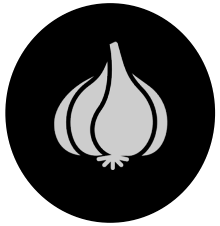
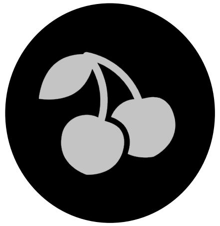
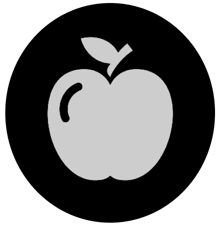
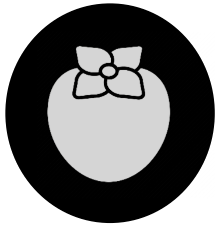
6 within geographical origin of food

$\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O_{w}$, $\delta^{34}S$ and 25 elements

FOOD

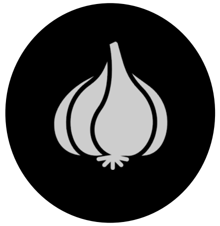
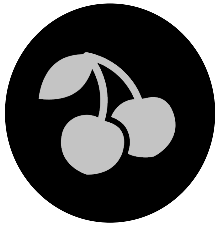
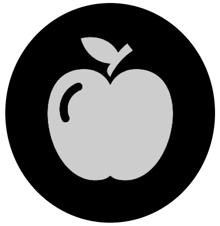
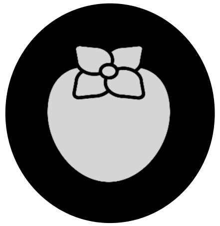
6 within geographical origin of food

$\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O_w$, $\delta^{34}S$ and 25 elements

FOOD						
YEARS	2	3	3	2	1	1

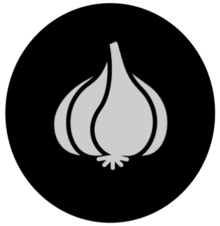
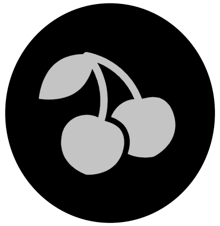
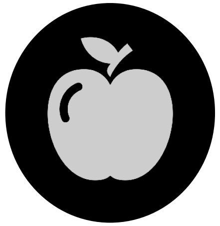
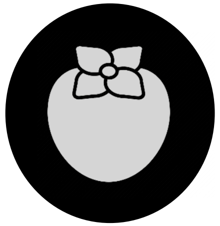
6 within geographical origin of food

$\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O_w$, $\delta^{34}S$ and 25 elements

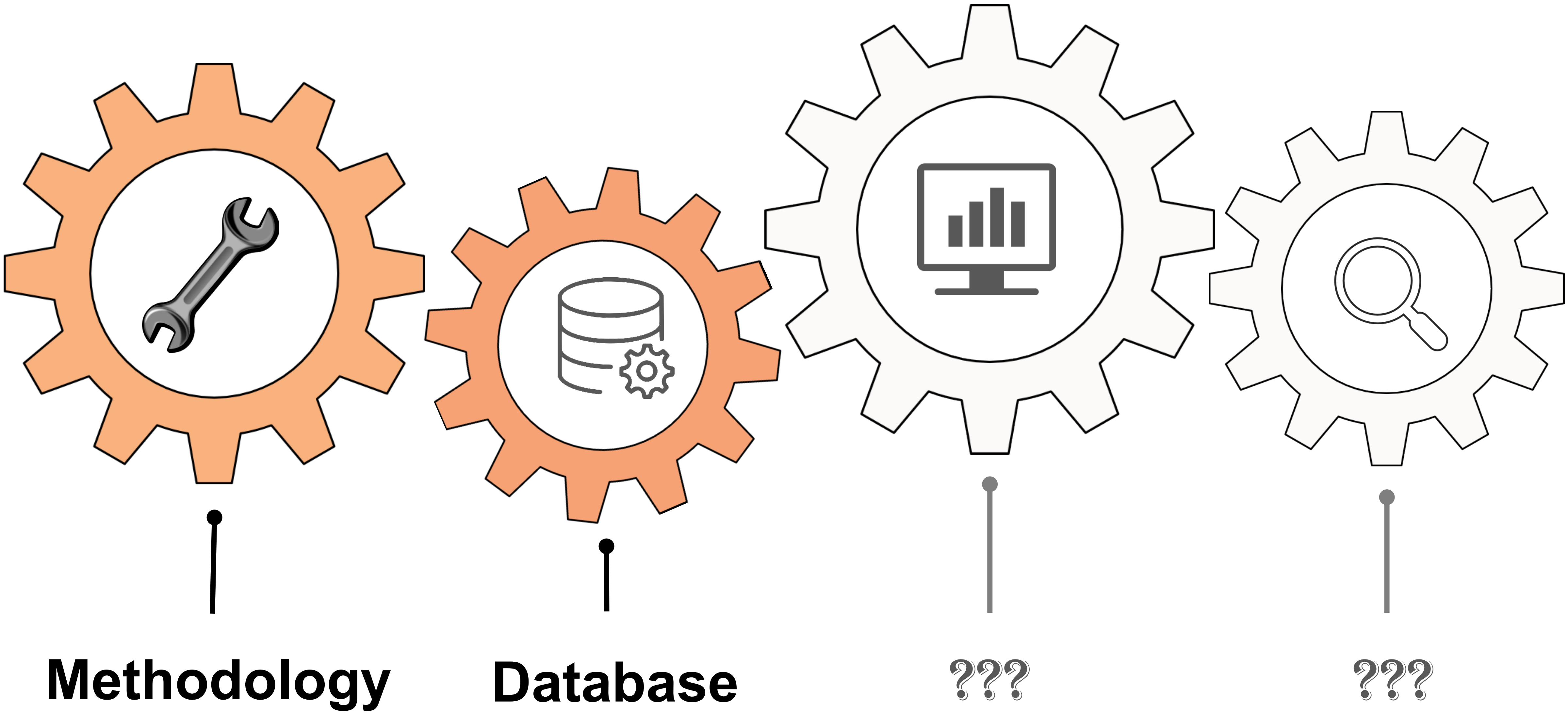
FOOD						
YEARS	2	3	3	2	1	1
AUTHENTIC	52	63	92	54	27	26

6 within geographical origin of food

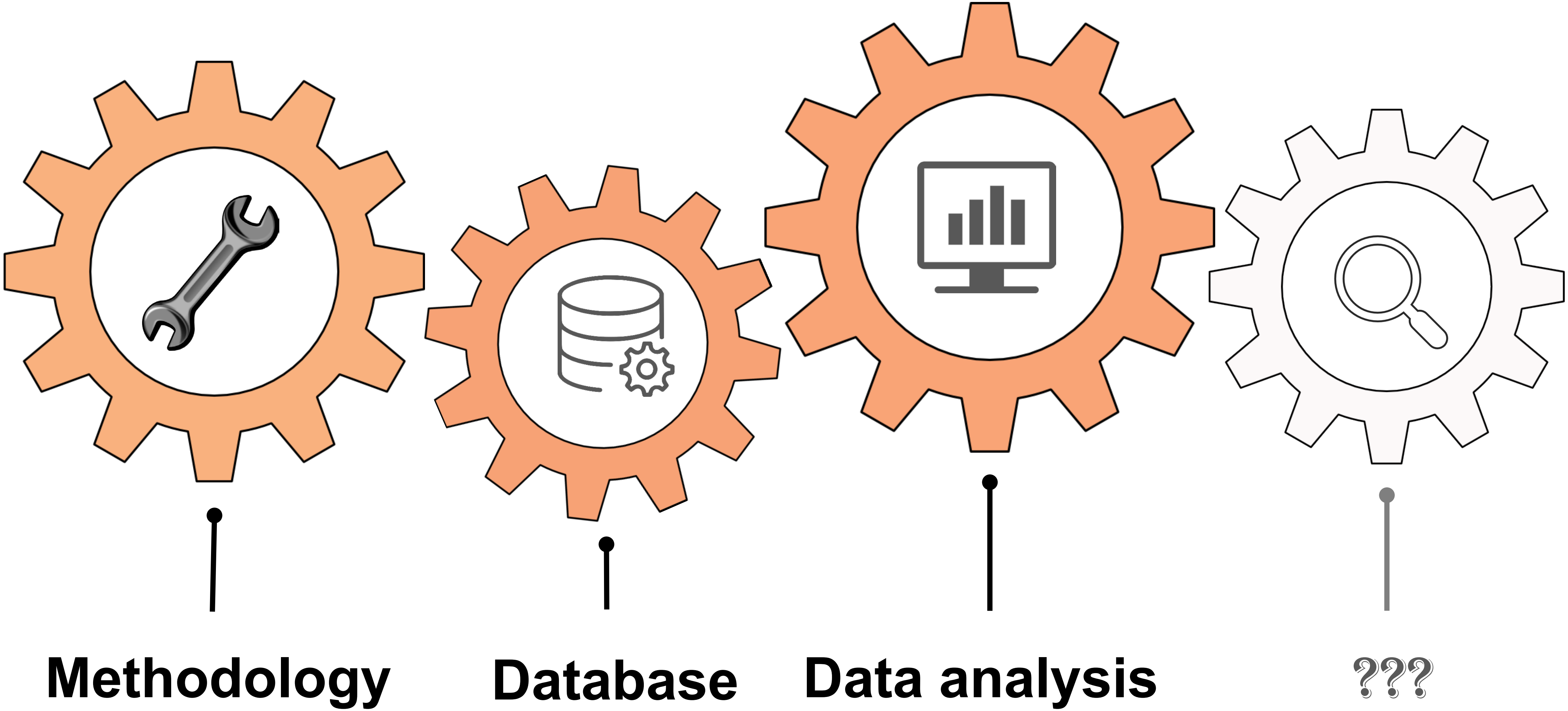
$\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O_w$, $\delta^{34}S$ and 25 elements

FOOD						
YEARS	2	3	3	2	1	1
AUTHENTIC	52	63	92	54	27	26
ABROAD	29	49	32	27	9	14

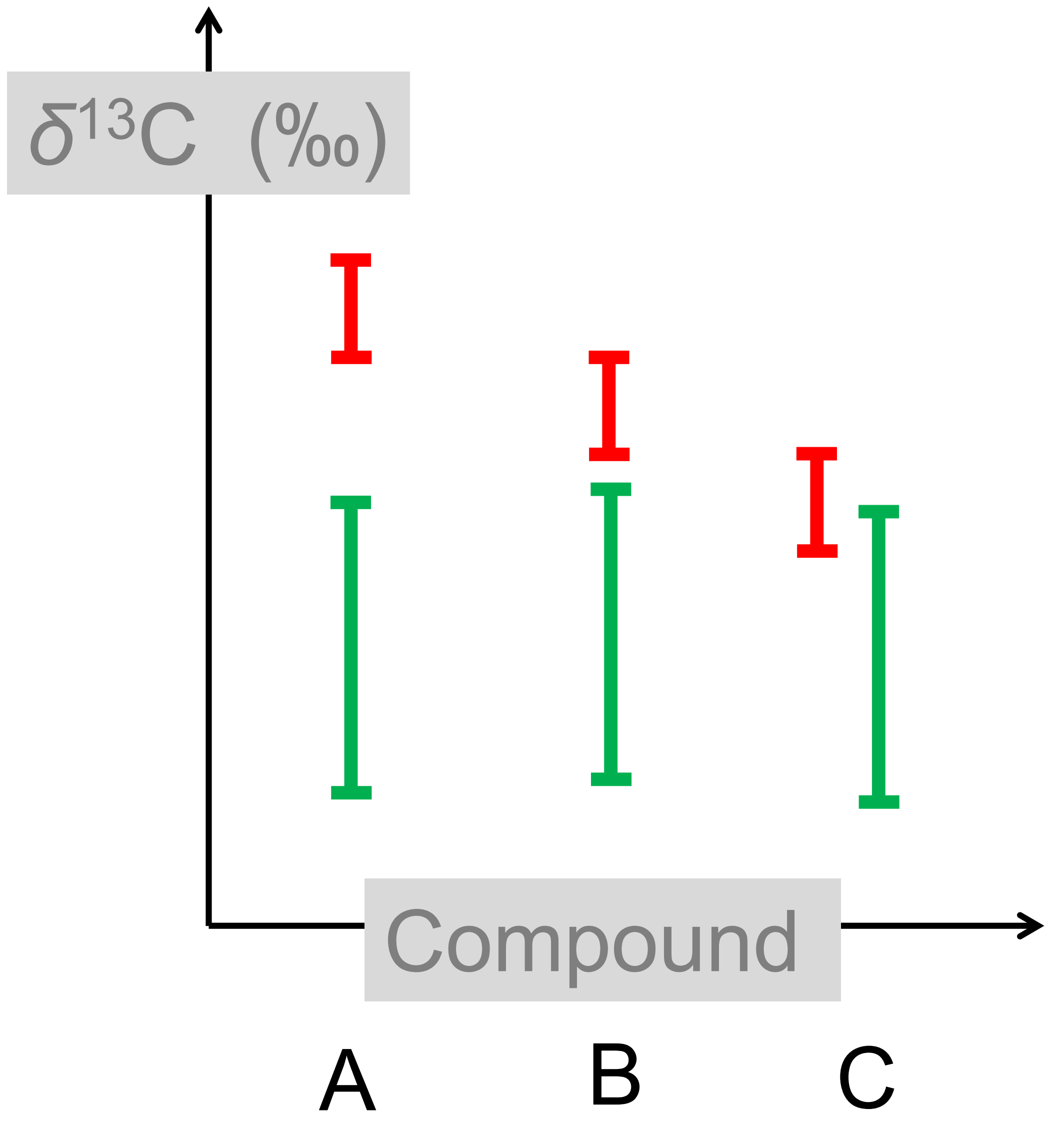
The four gears building trust in our food



The four gears building trust in our food

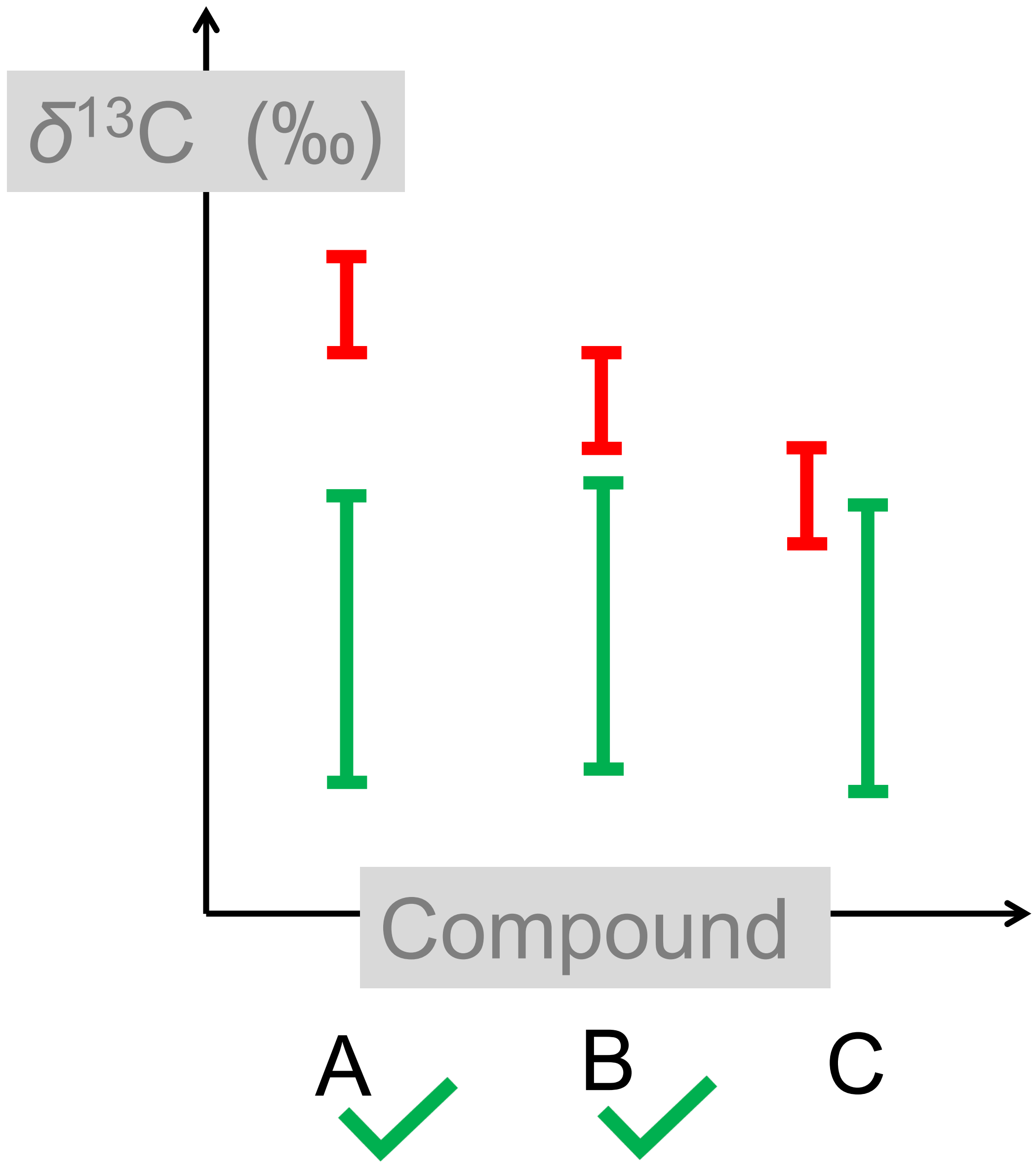


Authenticity of flavourings

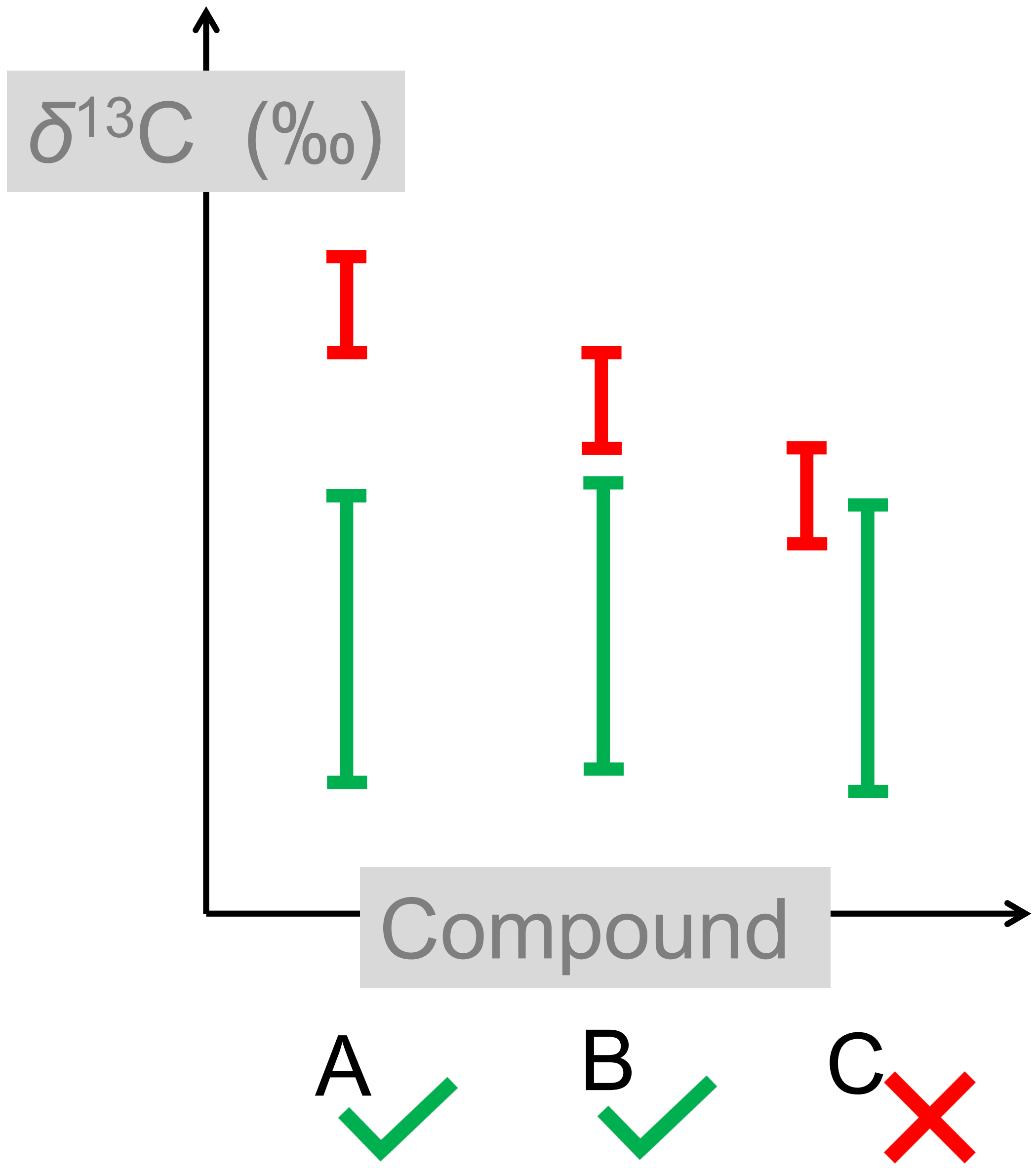


Comparative analysis of natural and synthetic isotope ranges.

Authenticity of flavourings



Comparative analysis of natural and synthetic isotope ranges.

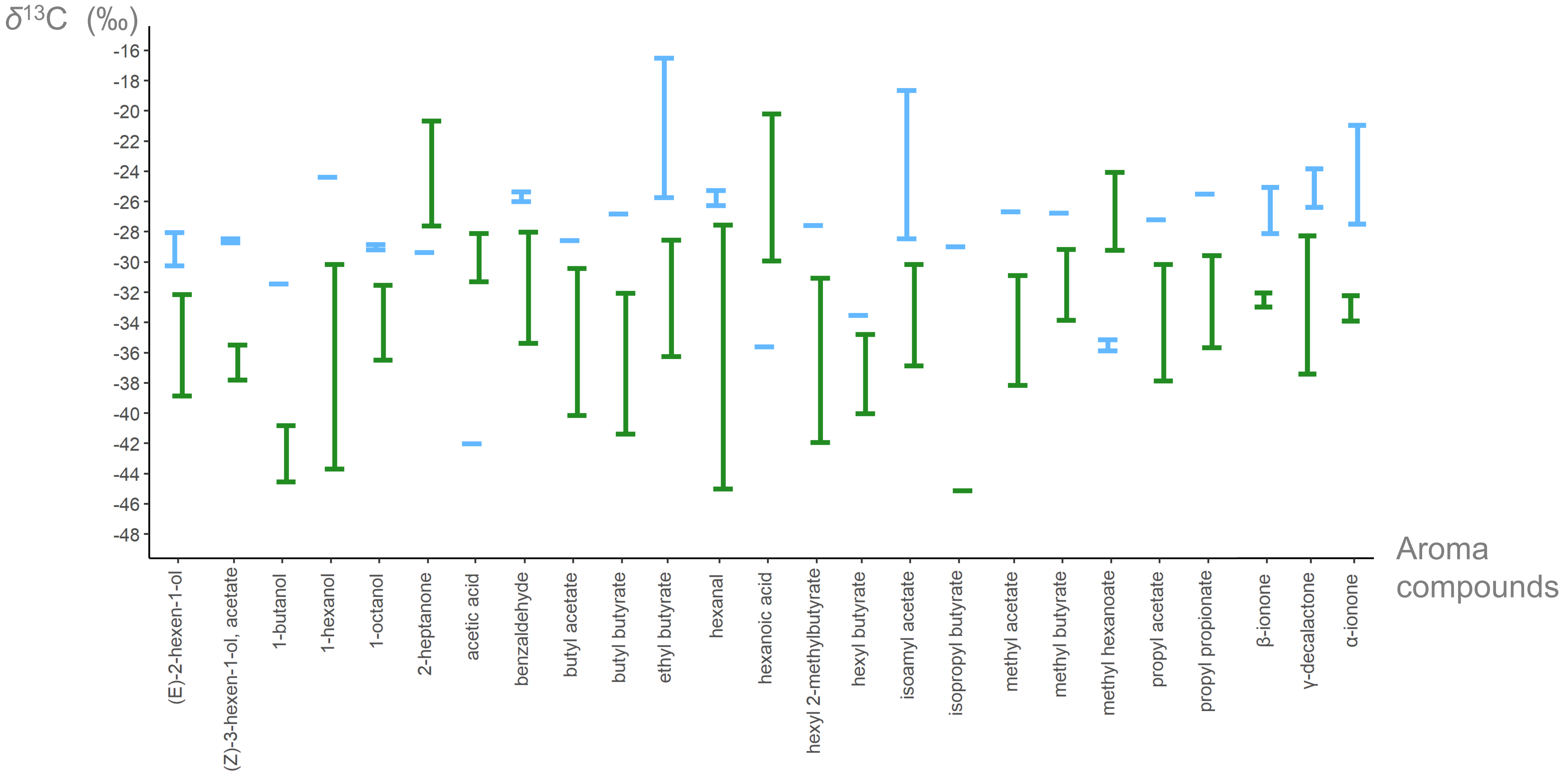


Authenticity of flavourings

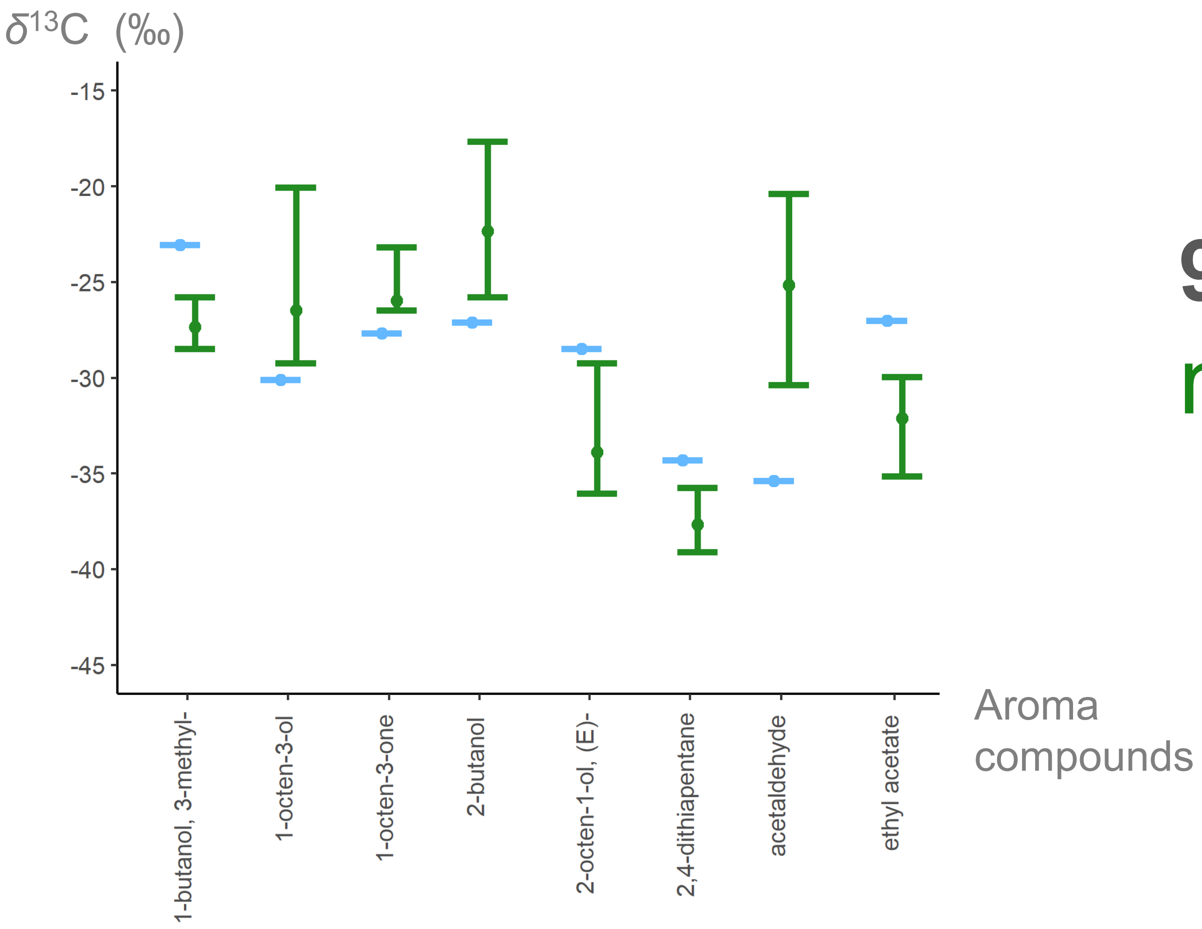
Comparative analysis of natural and synthetic isotope ranges.

Fruits

25 VOCs allow discrimination between natural and synthetic samples

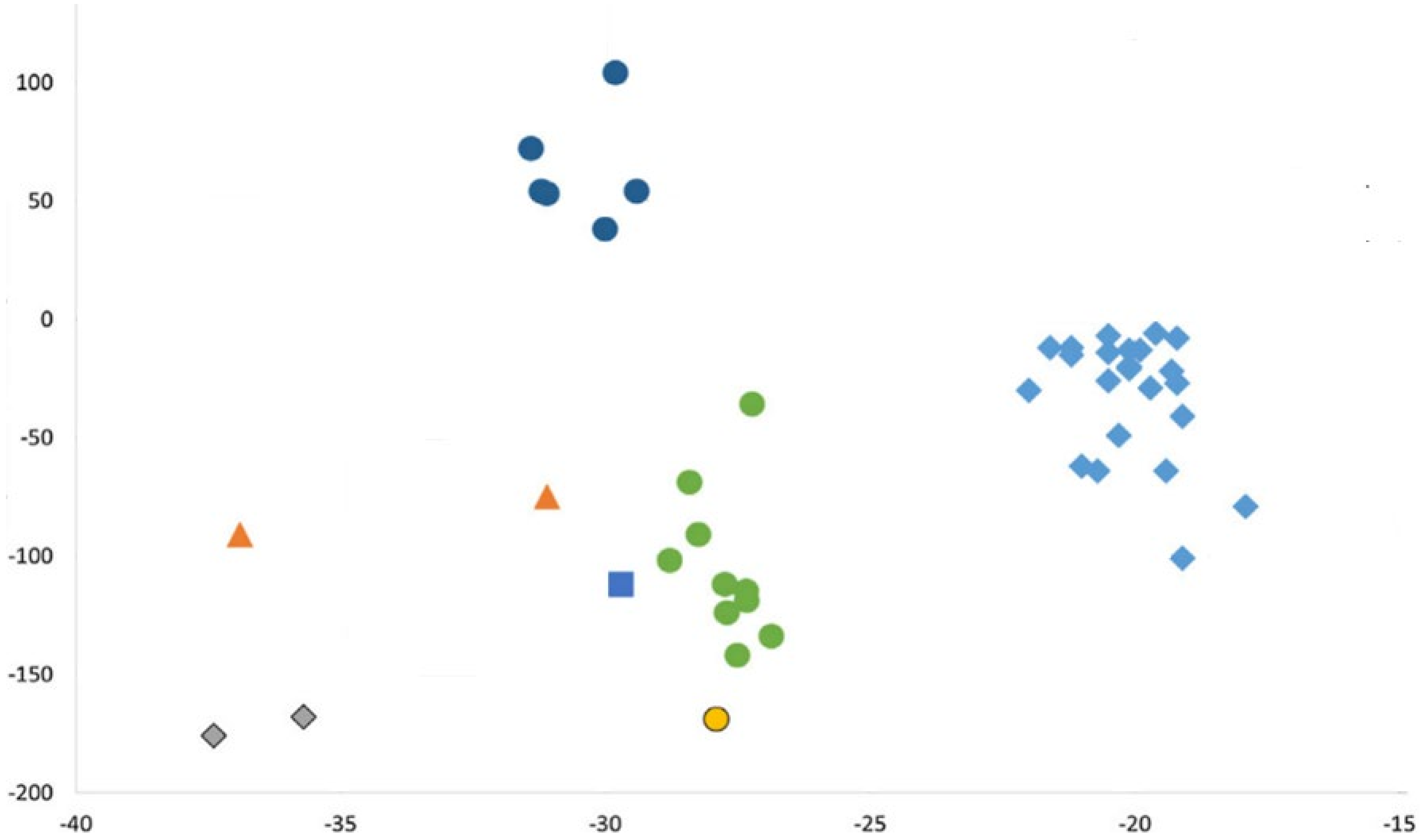


Truffles

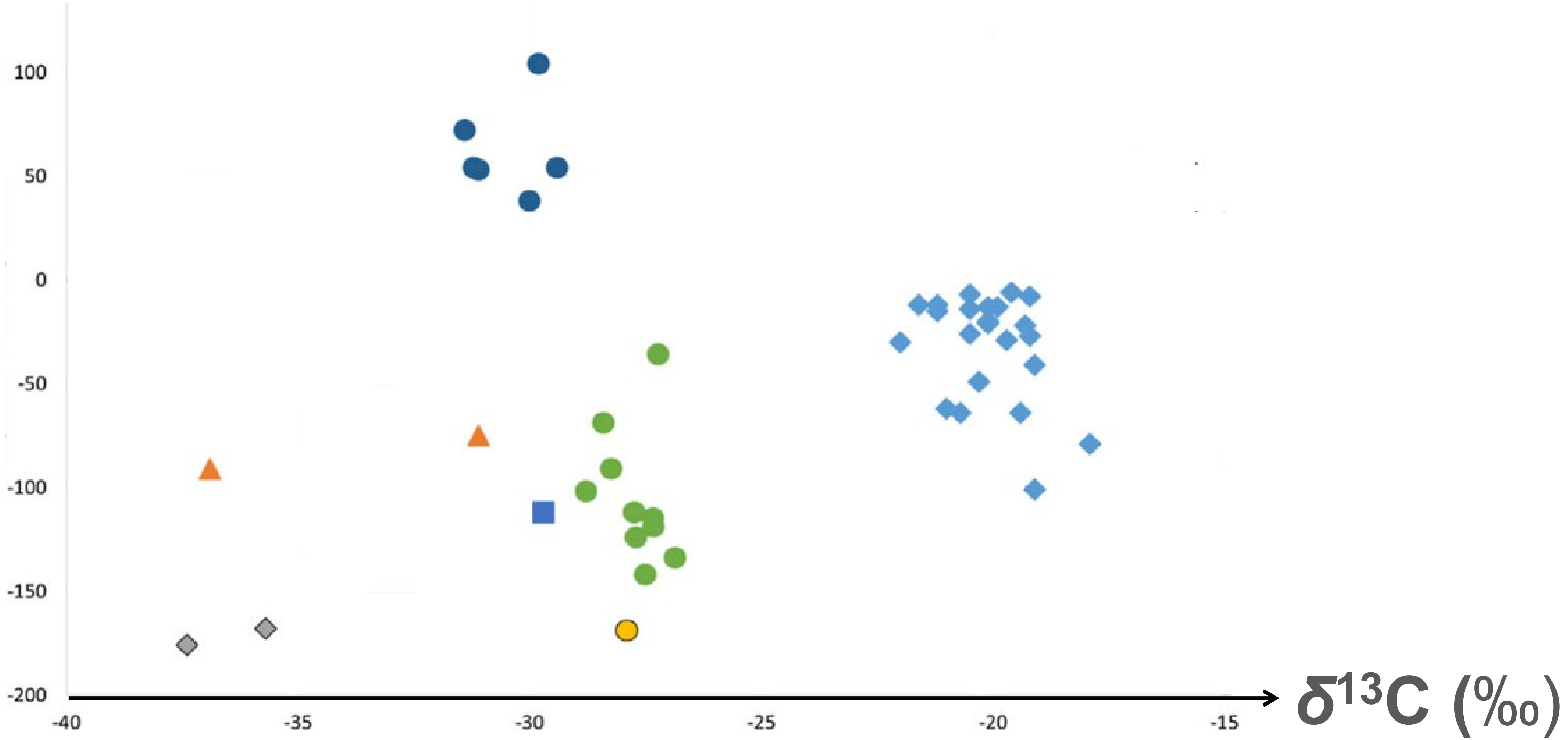


9 VOCs allow discrimination between natural and synthetic samples

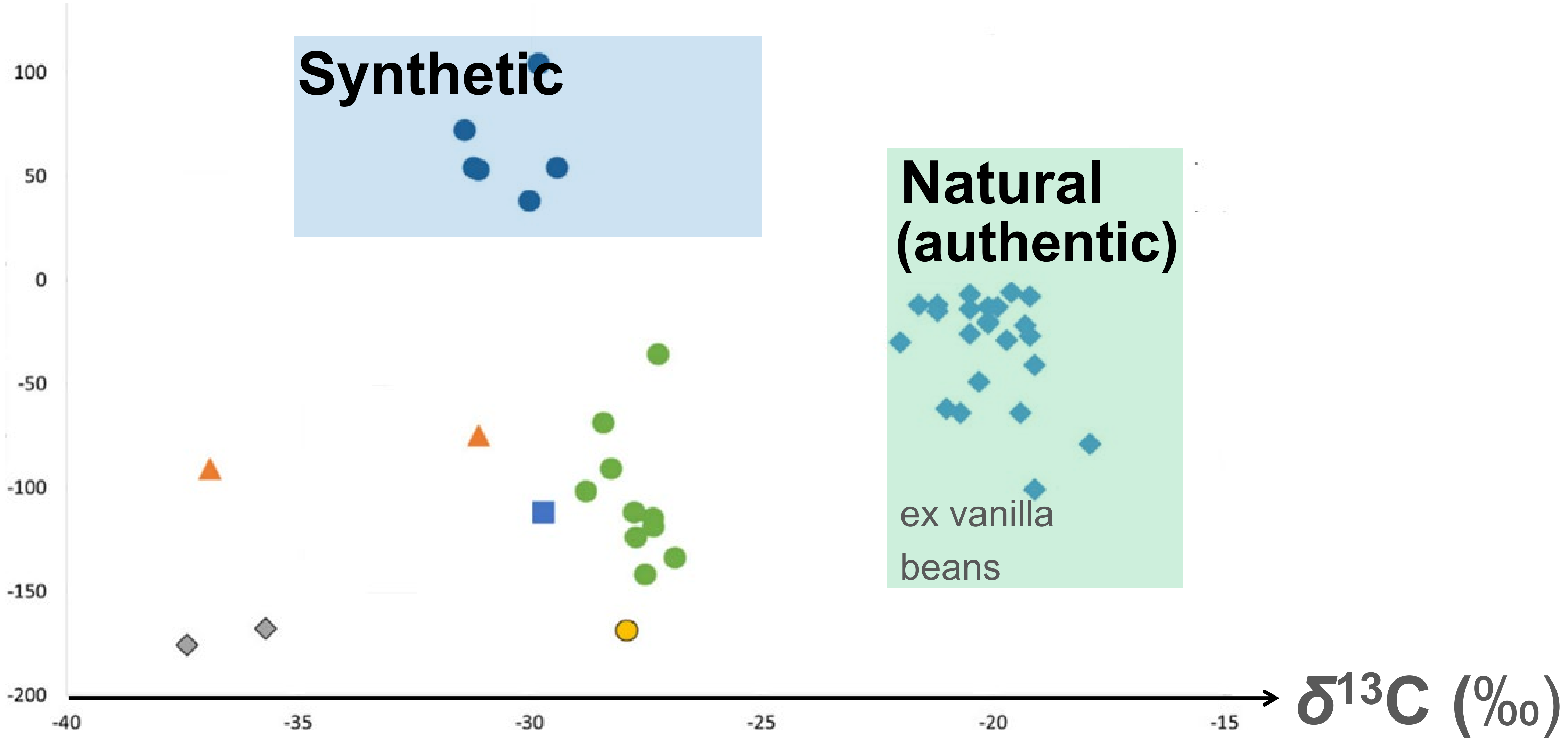
Vanillin



Vanillin

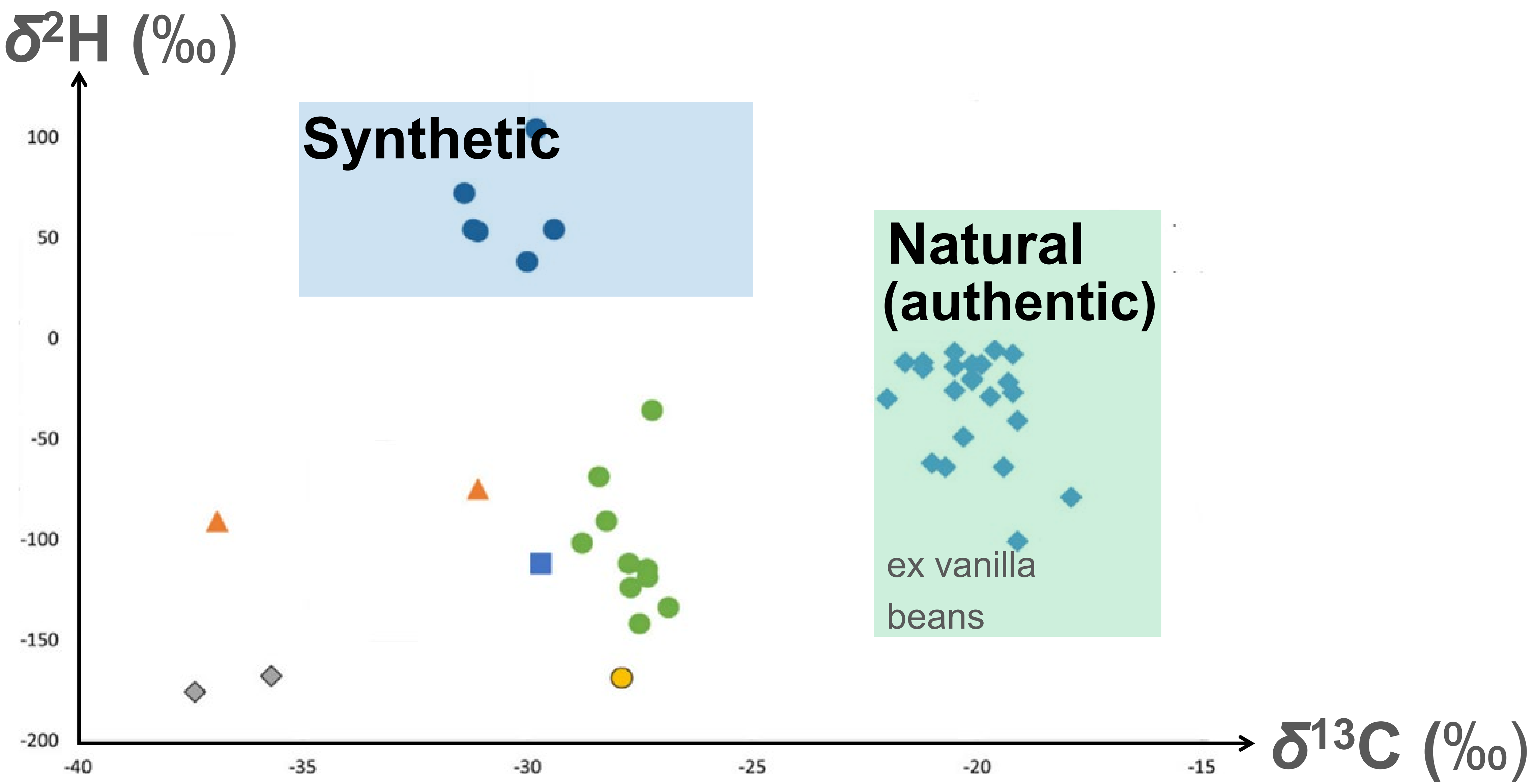


Vanillin



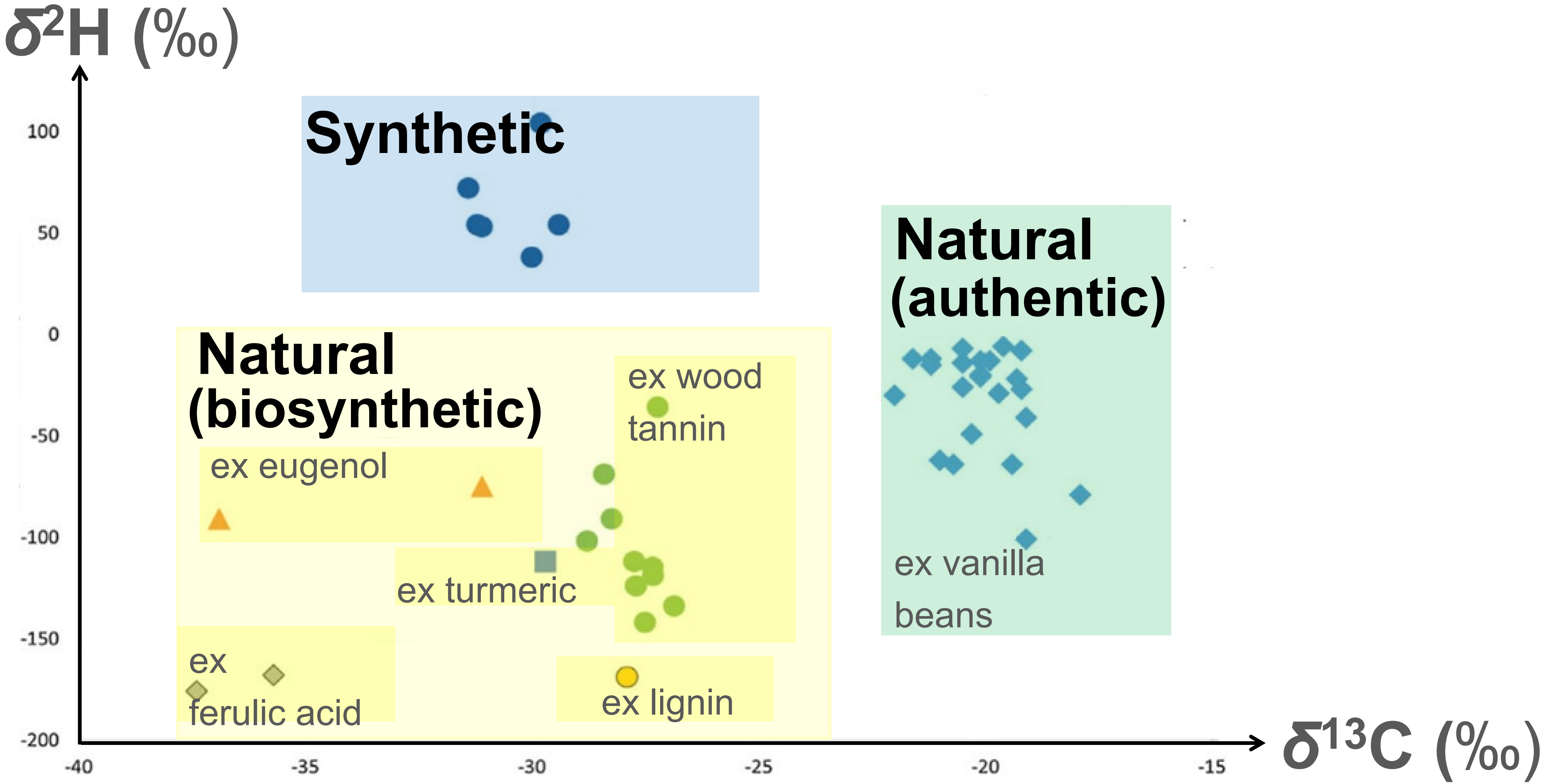
Synthetic
Natural
(authentic)
ex vanilla
beans
100
50
0
-50
-100
-150
-200
-40
-35
-30
-25
-20
-15
δ13C (‰)

Vanillin



δ2H (‰)
Synthetic
Natural
(authentic)
ex vanilla
beans
100
50
0
-50
-100
-150
-200
-40
-35
-30
-25
-20
-15
δ13C (‰)

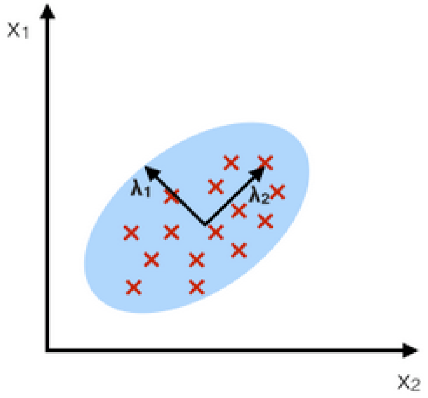
Vanillin


δ²H (‰)
100
50
0
-50
-100
-150
-200
-40
-35
-30
-25
-20
-15
δ¹³C (‰)
Synthetic
Natural (authentic)
Natural (biosynthetic)
ex wood tannin
ex eugenol
ex turmeric
ex ferulic acid
ex lignin
ex vanilla beans

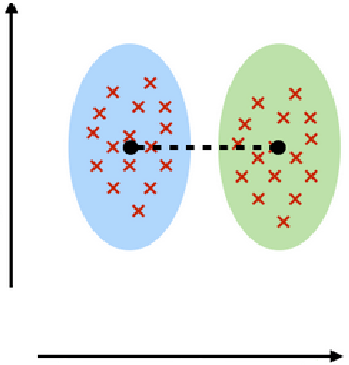
Geographical origin of food

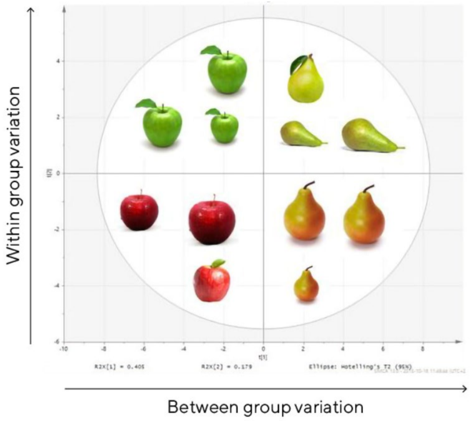
3 general chemometric approaches

Explorative analysis

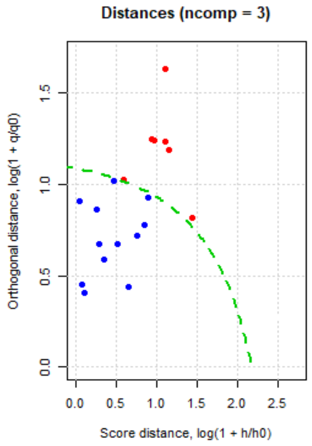


Classification





Class-modelling



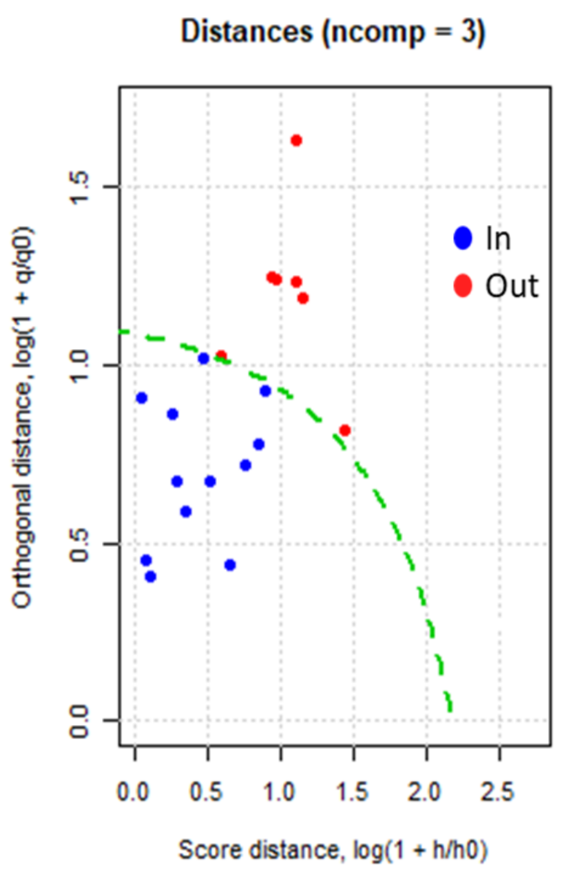
Confirmation that a specific sample originates from a particular country.

Confirmation that a specific sample originates from a particular country.

One class classification problem

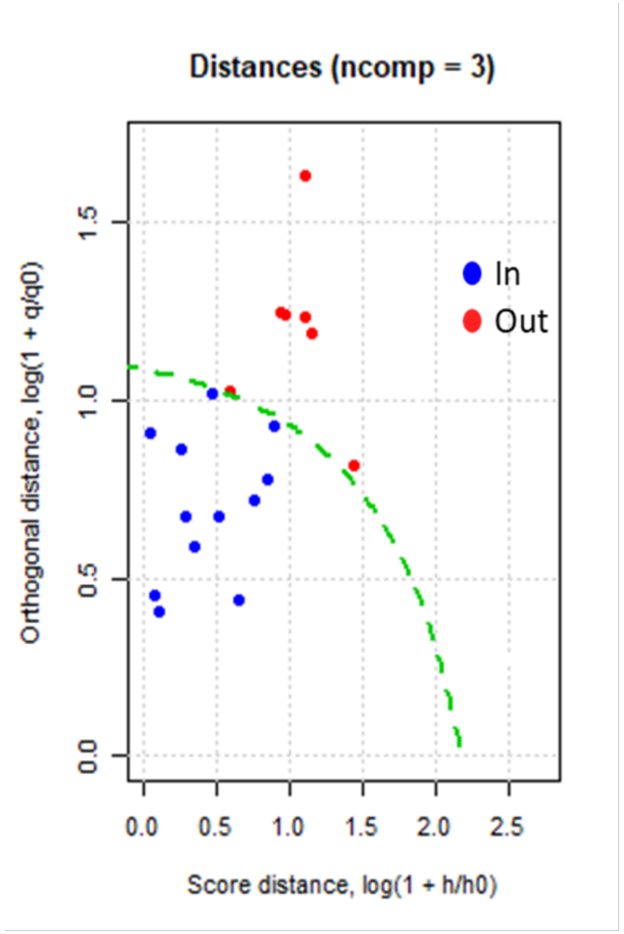
Class-modelling or one-class classifiers

Data Driven Soft Independent Modelling of Class Analogy (DD-SIMCA)



Class-modelling or one-class classifiers

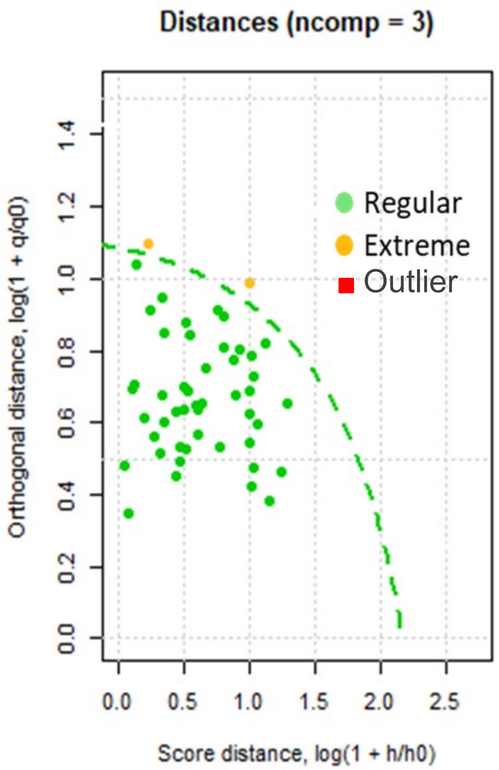
Data Driven Soft Independent Modelling of Class Analogy (DD-SIMCA)



Meant to distinguish objects of one particular class from all other objects and classes.

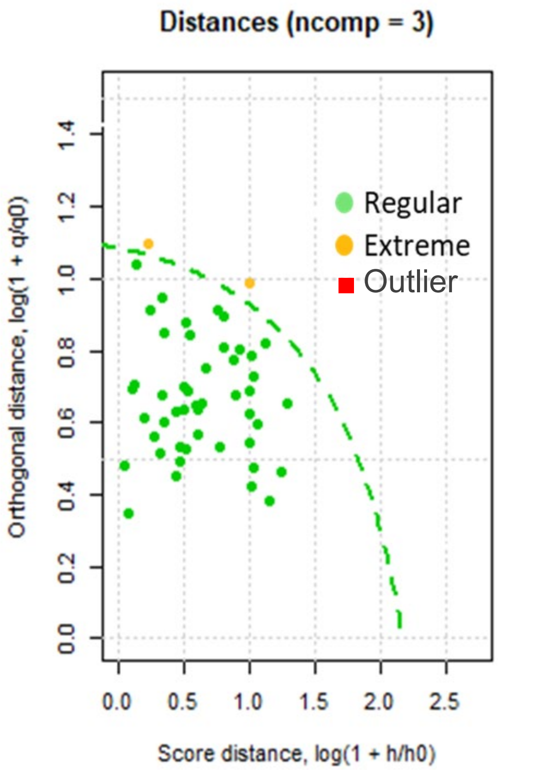
1 Target set

compliant samples



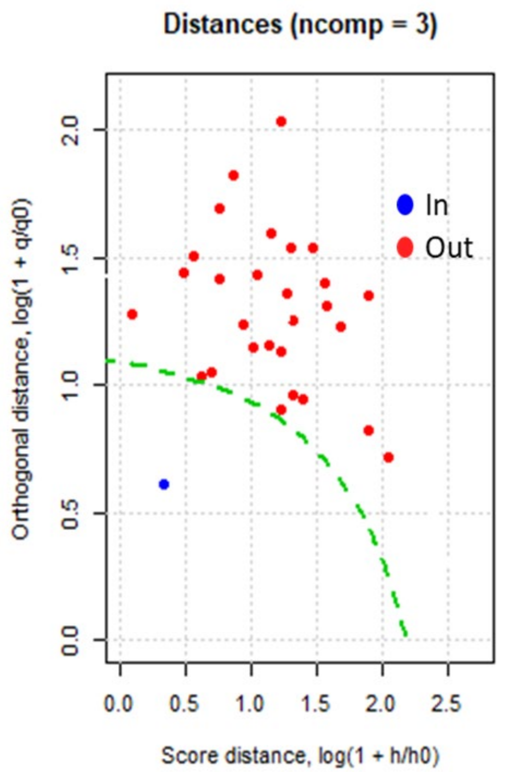
1 Target set

compliant samples



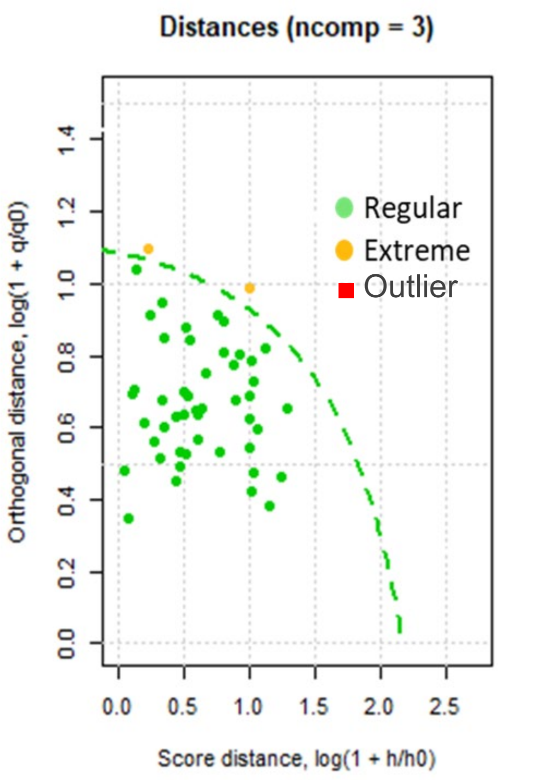
2 Alternative set

non-compliant samples



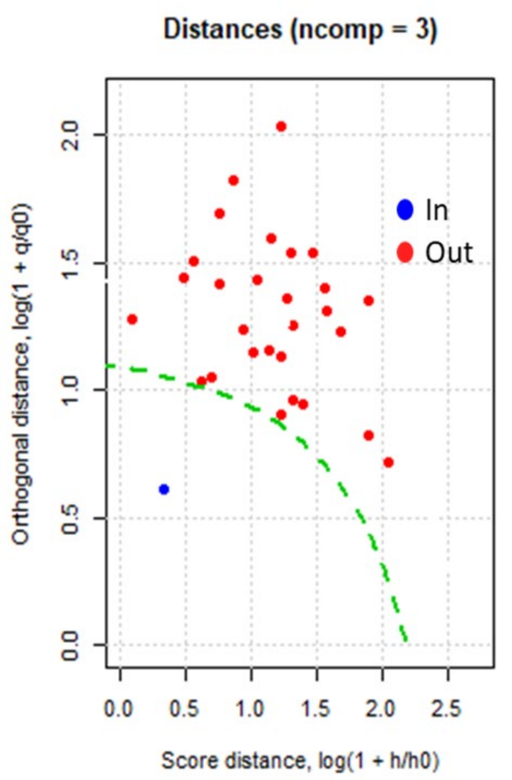
1 Target set

compliant samples



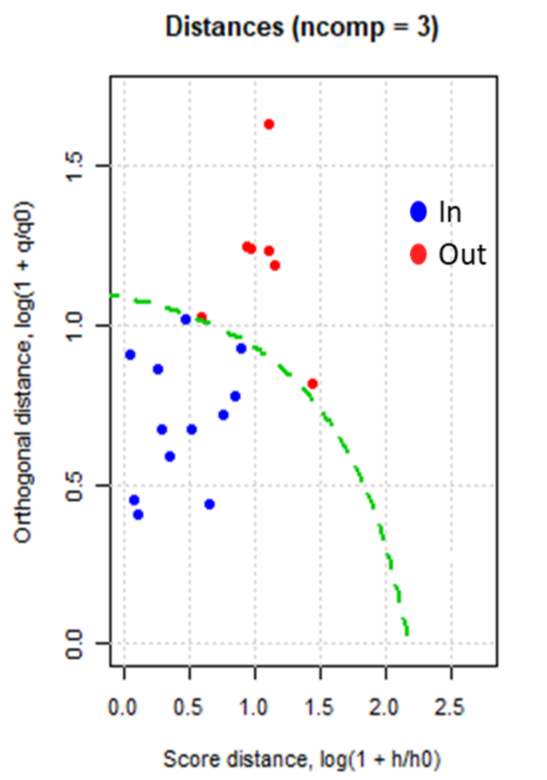
2 Alternative set

non-compliant samples

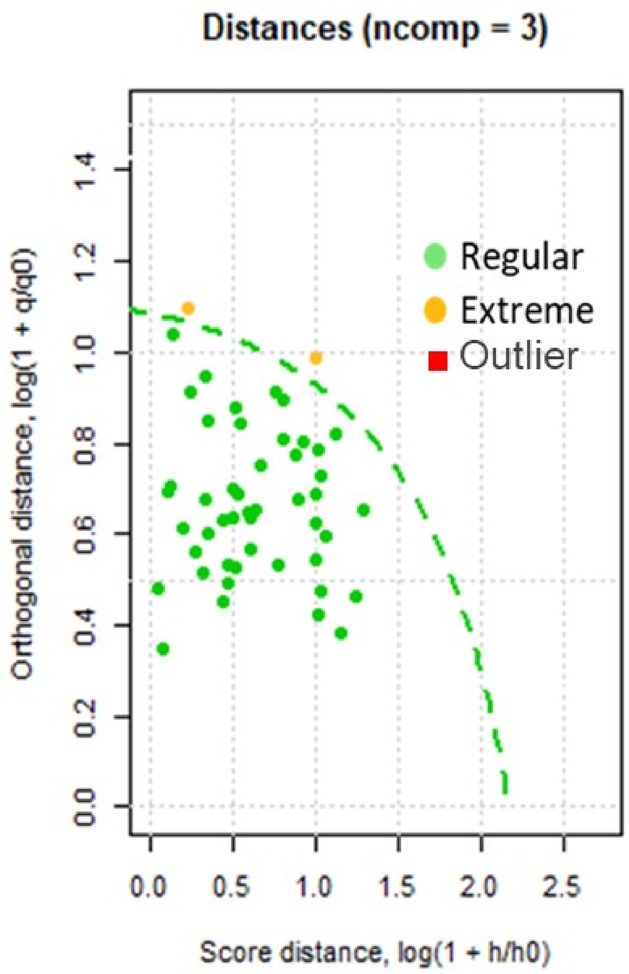


3 Test set

unknown samples



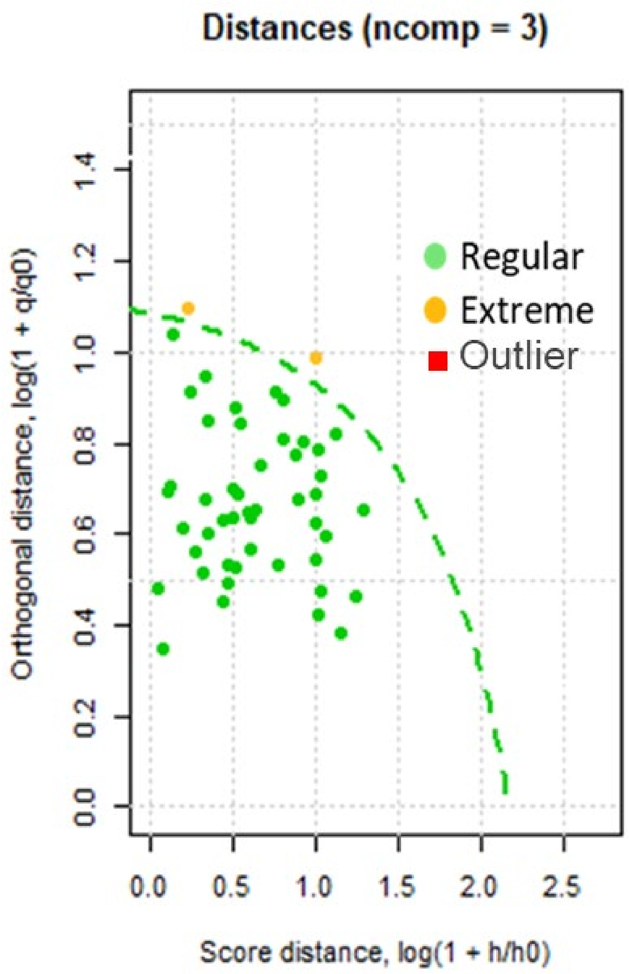
1 Target set (compliant samples)



1 Target set (compliant samples)

70% → Training set

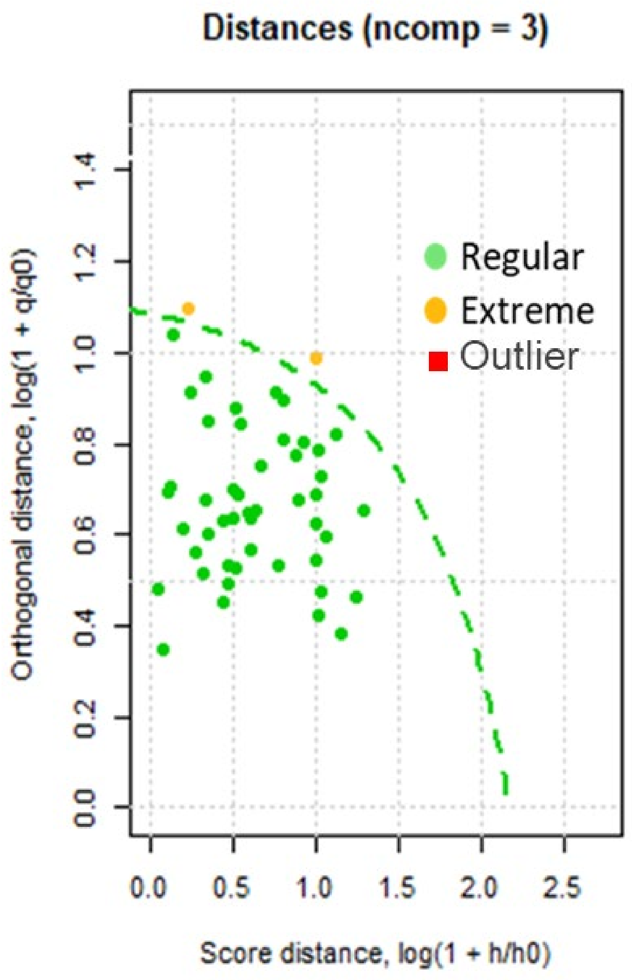
For building the model



1 Target set (compliant samples)

70% → **Training set**
For building the model

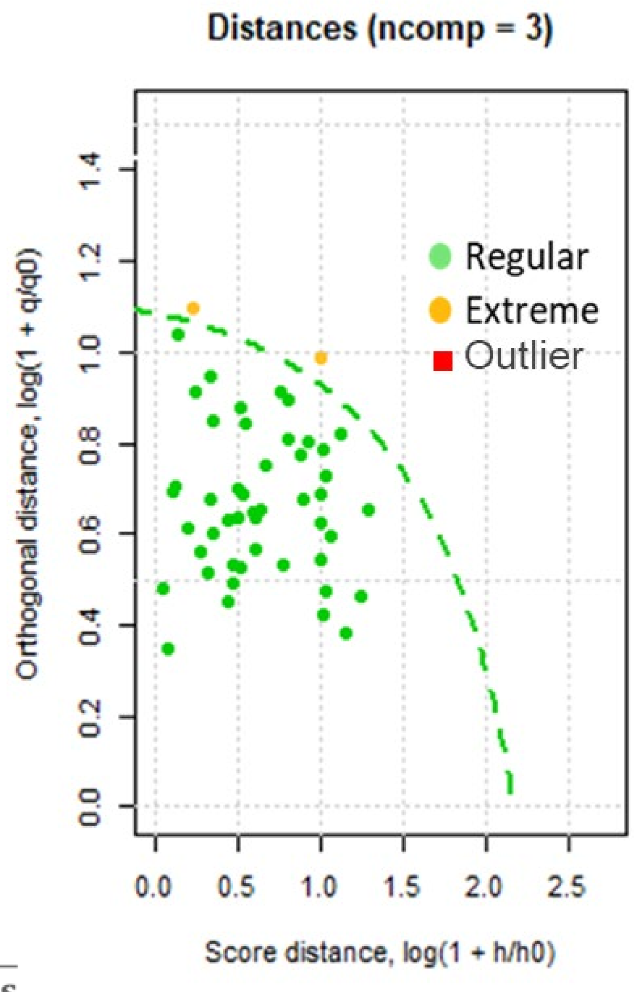
30% → **Test set**
To assess model validity



1 Target set (compliant samples)

70% → **Training set**
For building the model

30% → **Test set**
To assess model validity



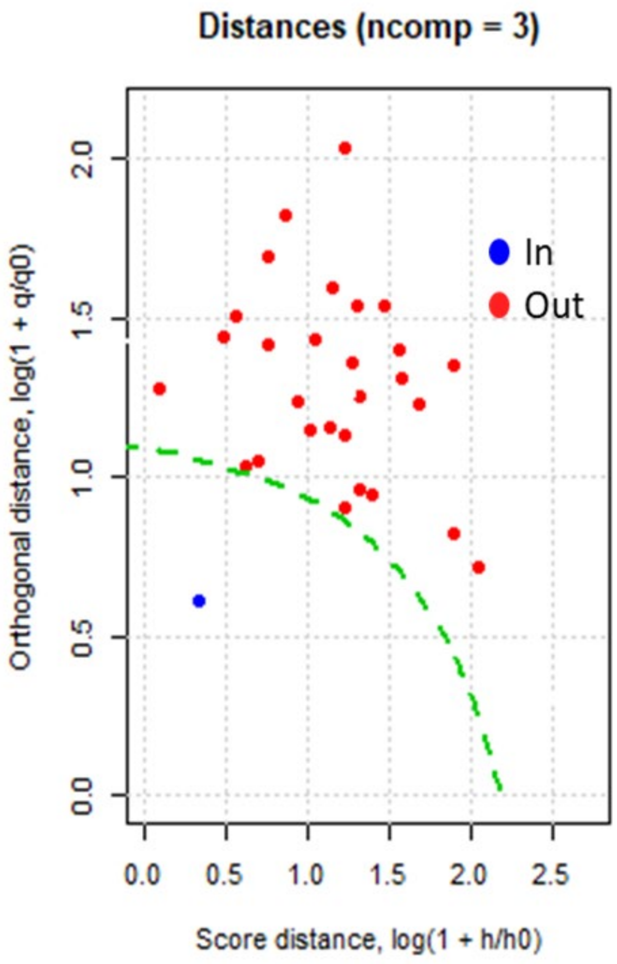
Sensitivity $(\text{type I error } (\alpha)) = \frac{\text{True Positives}}{\text{True Positives} + \text{False Negatives}}$

2 Alternative set (non-compliant samples)

2 Alternative set (non-compliant samples)

Used only to evaluate the model's performance.

Specificity (type II error (β)) = $\frac{\text{True Negatives}}{\text{True Negatives} + \text{False Positives}}$

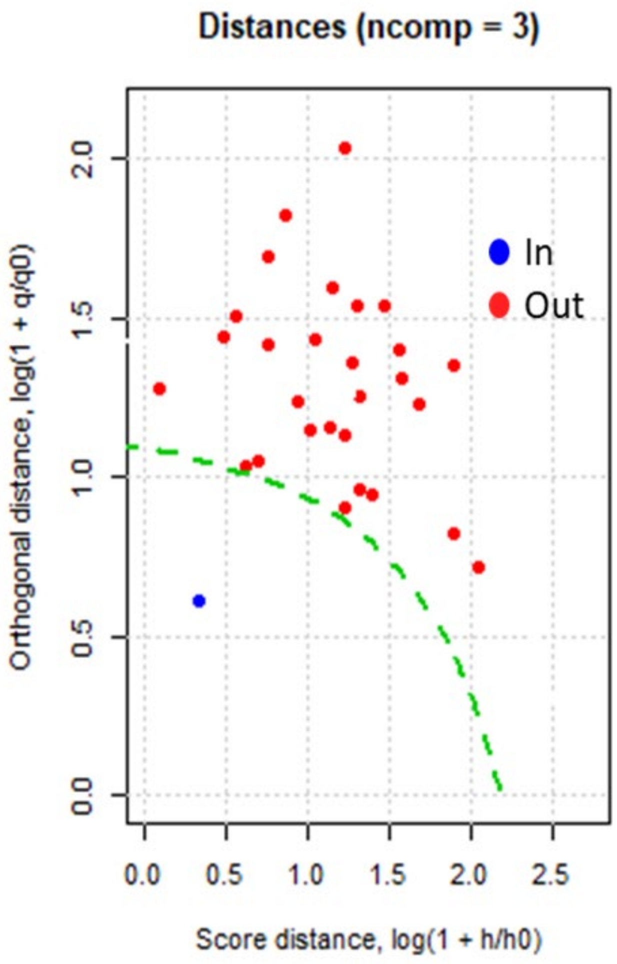


2 Alternative set (non-compliant samples)

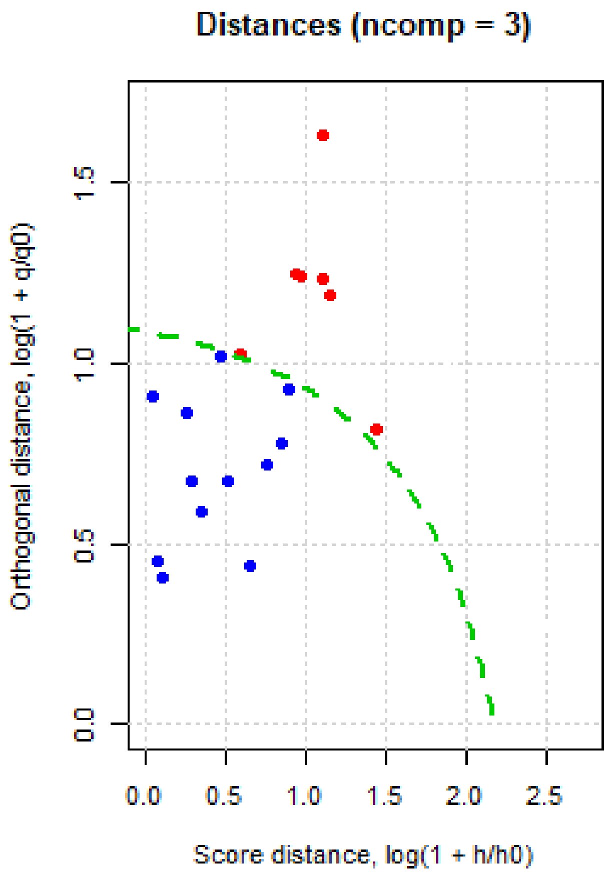
Used only to evaluate the model's performance.

Specificity (type II error (β)) = $\frac{\text{True Negatives}}{\text{True Negatives} + \text{False Positives}}$

Not for building the model!



3 Test set (unknown samples)



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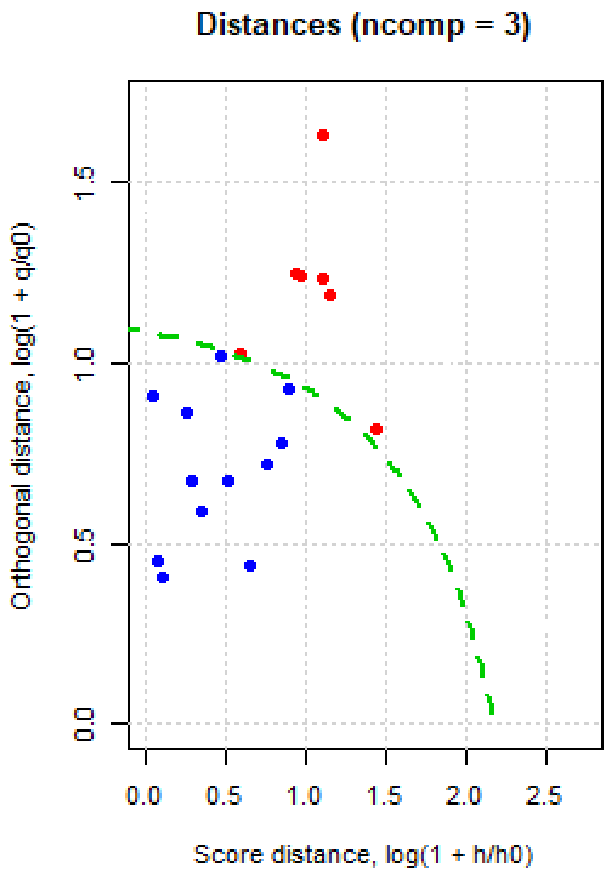

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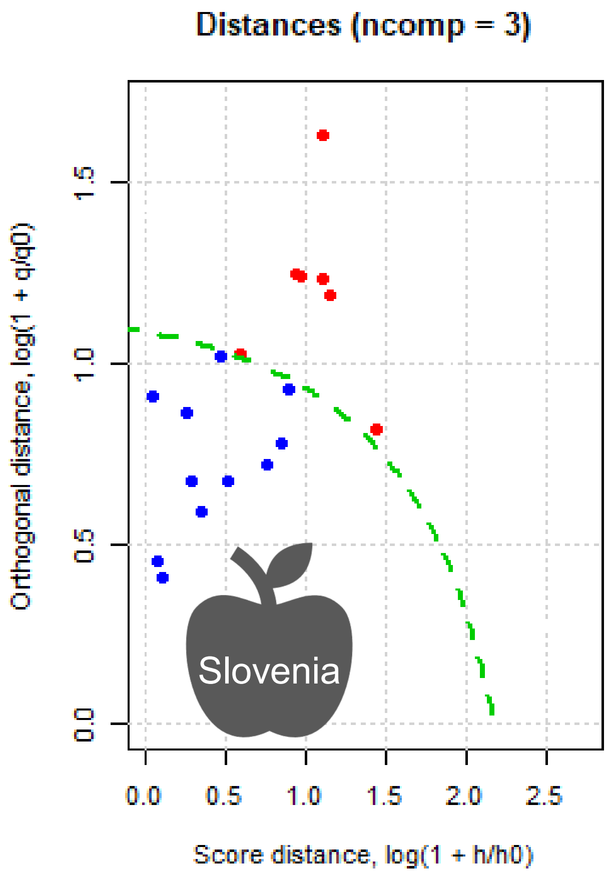
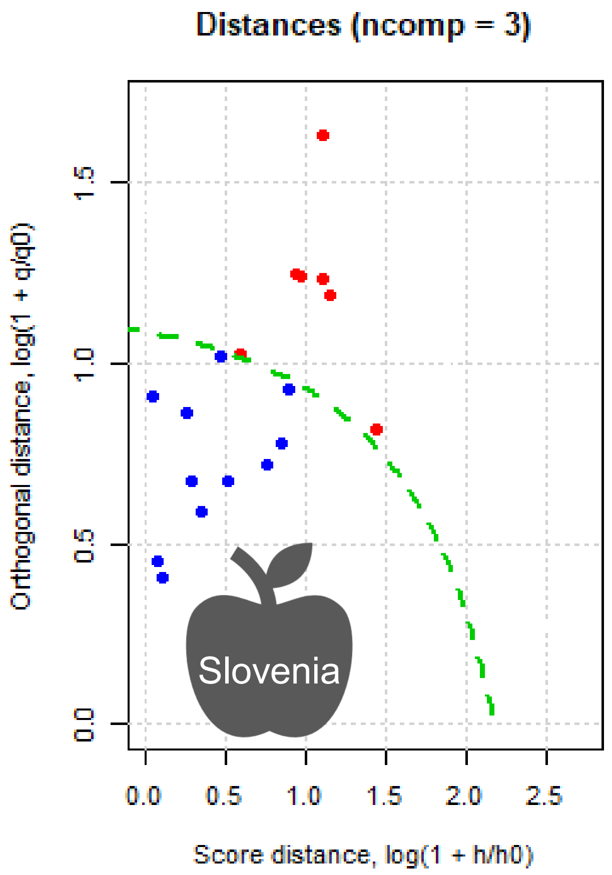
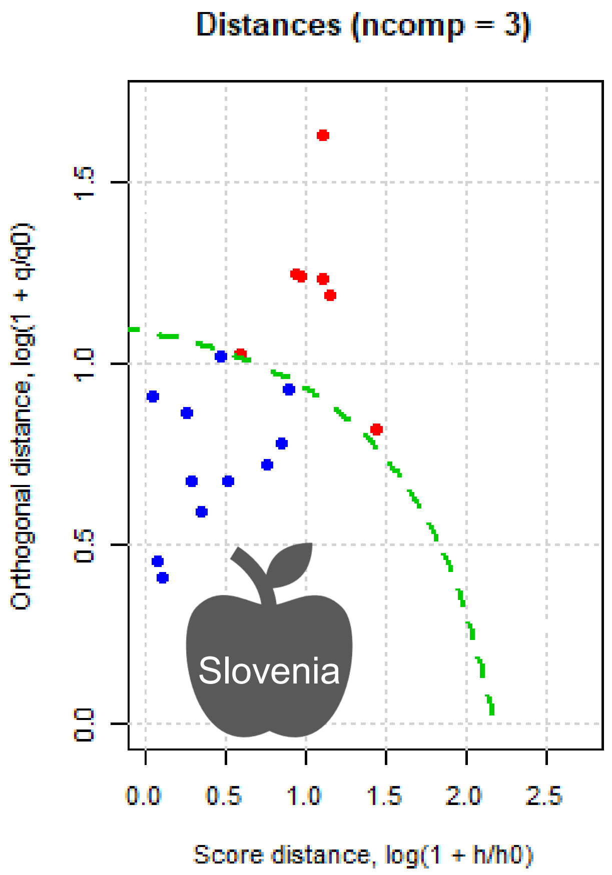


3 Test set (unknown samples)



IN: object is similar to the other objects in a class

3 Test set (unknown samples)



IN: object is similar to the other objects in a class

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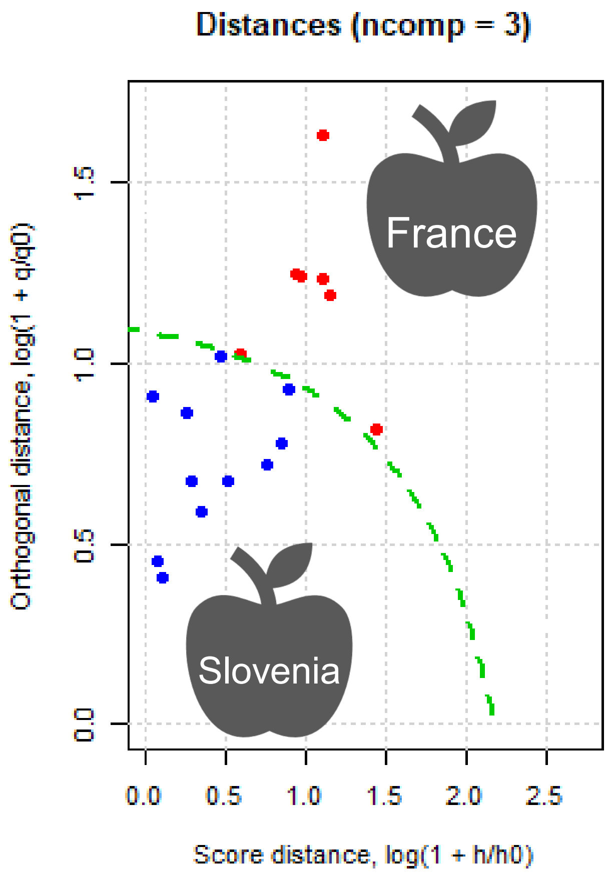
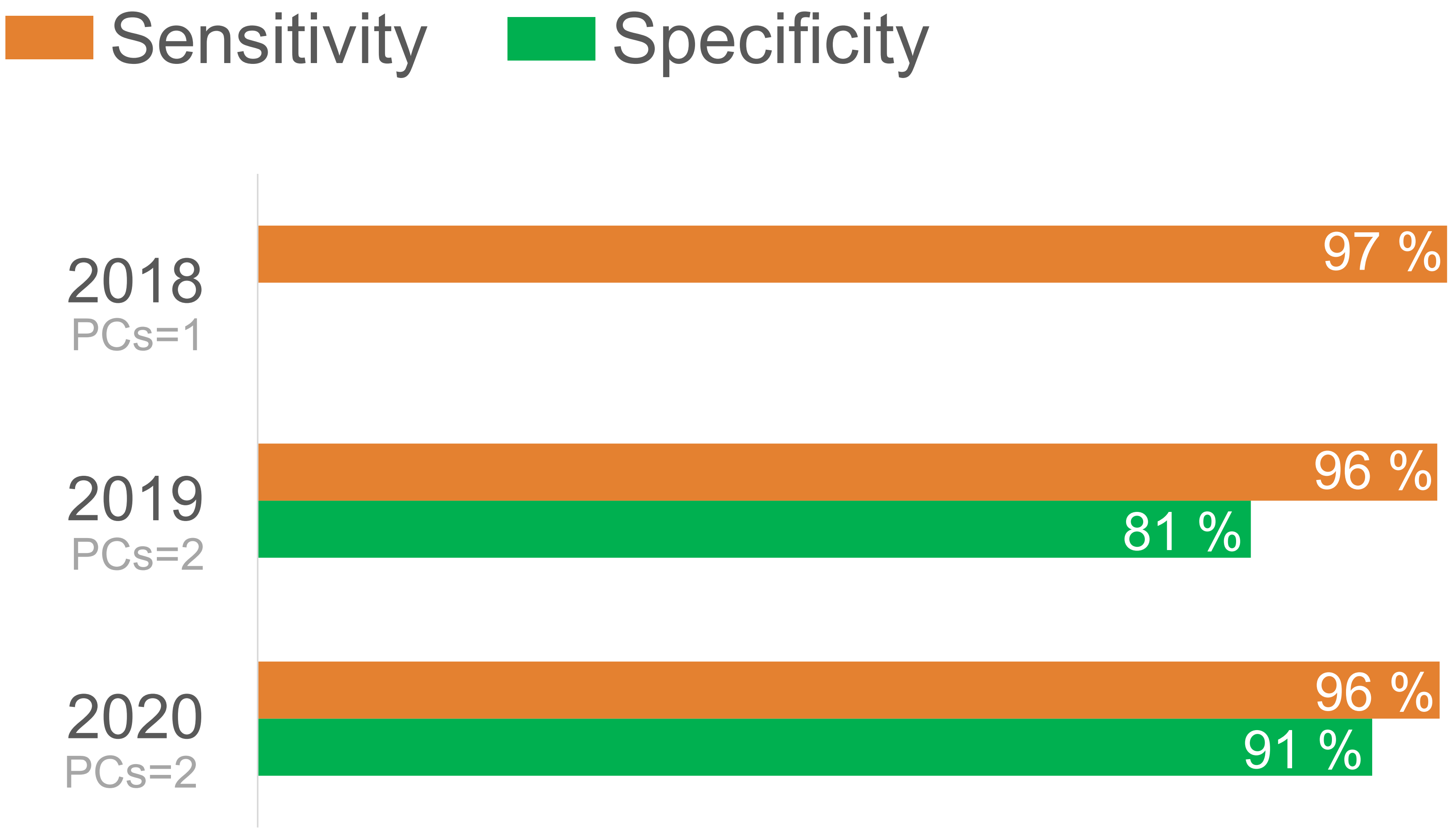


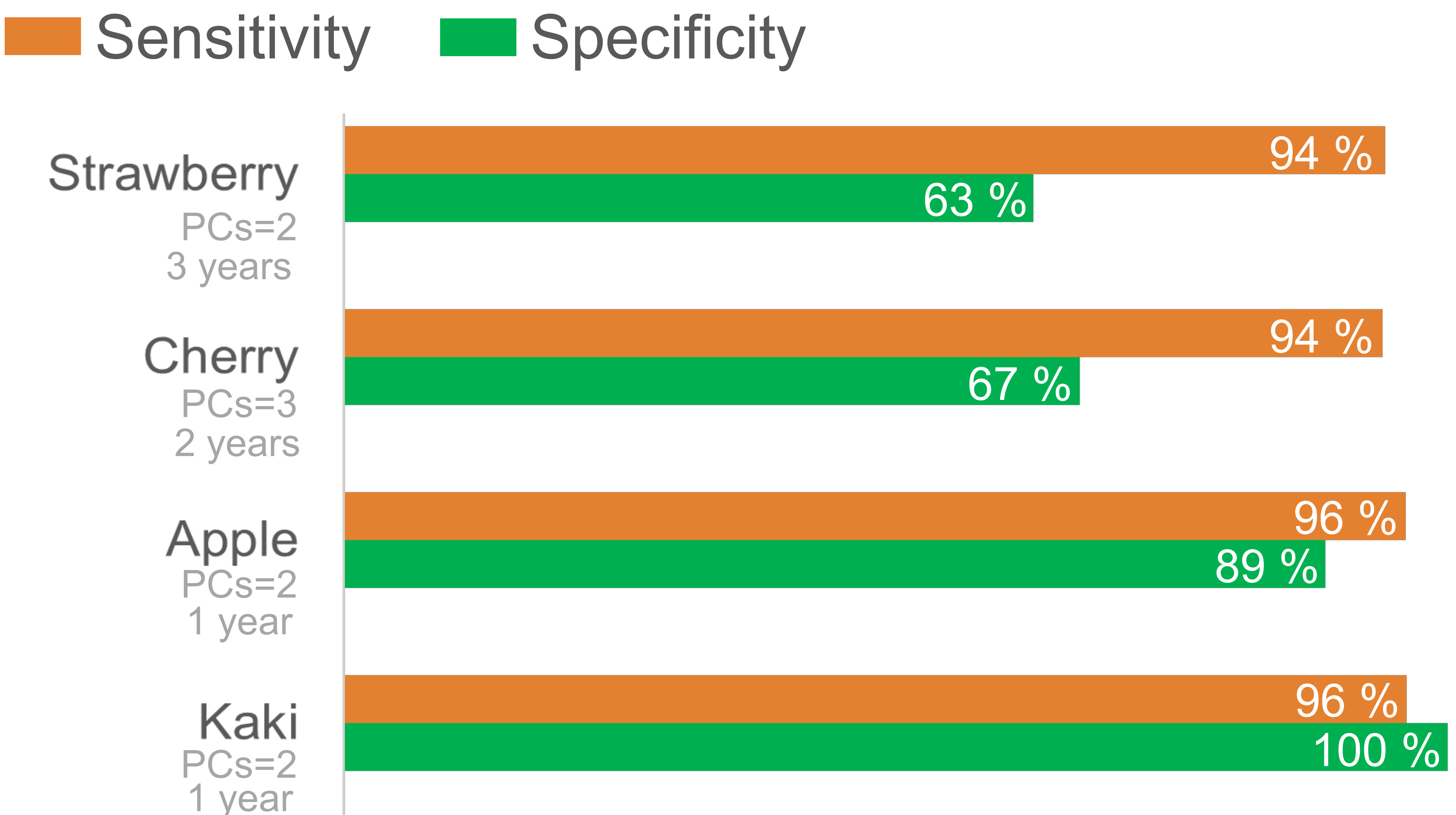
IN: object is similar to the other objects in a class

OUT: sample is either outlier or belongs to a class that is not represented in the data set

Excellent year to year DD-SIMCA models

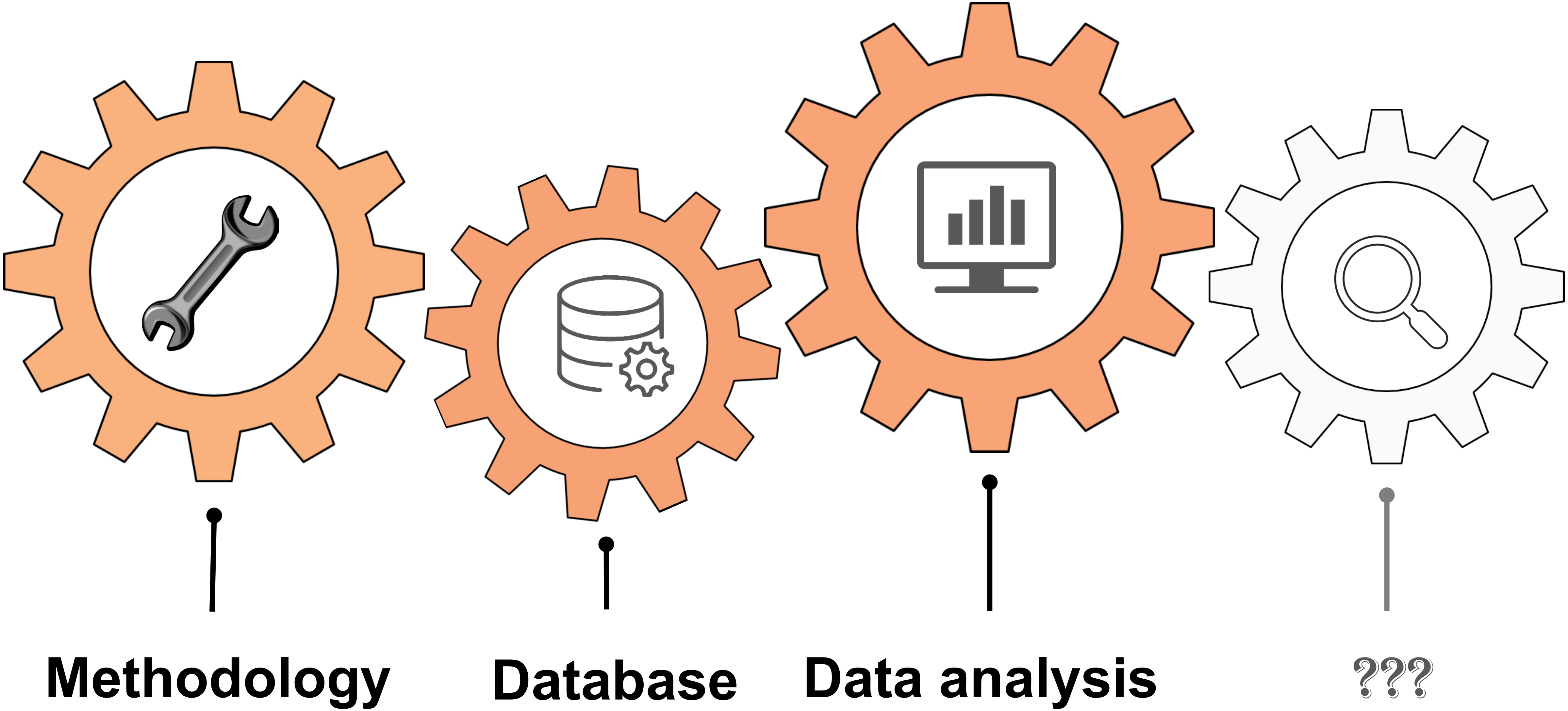


Significant year to year variation

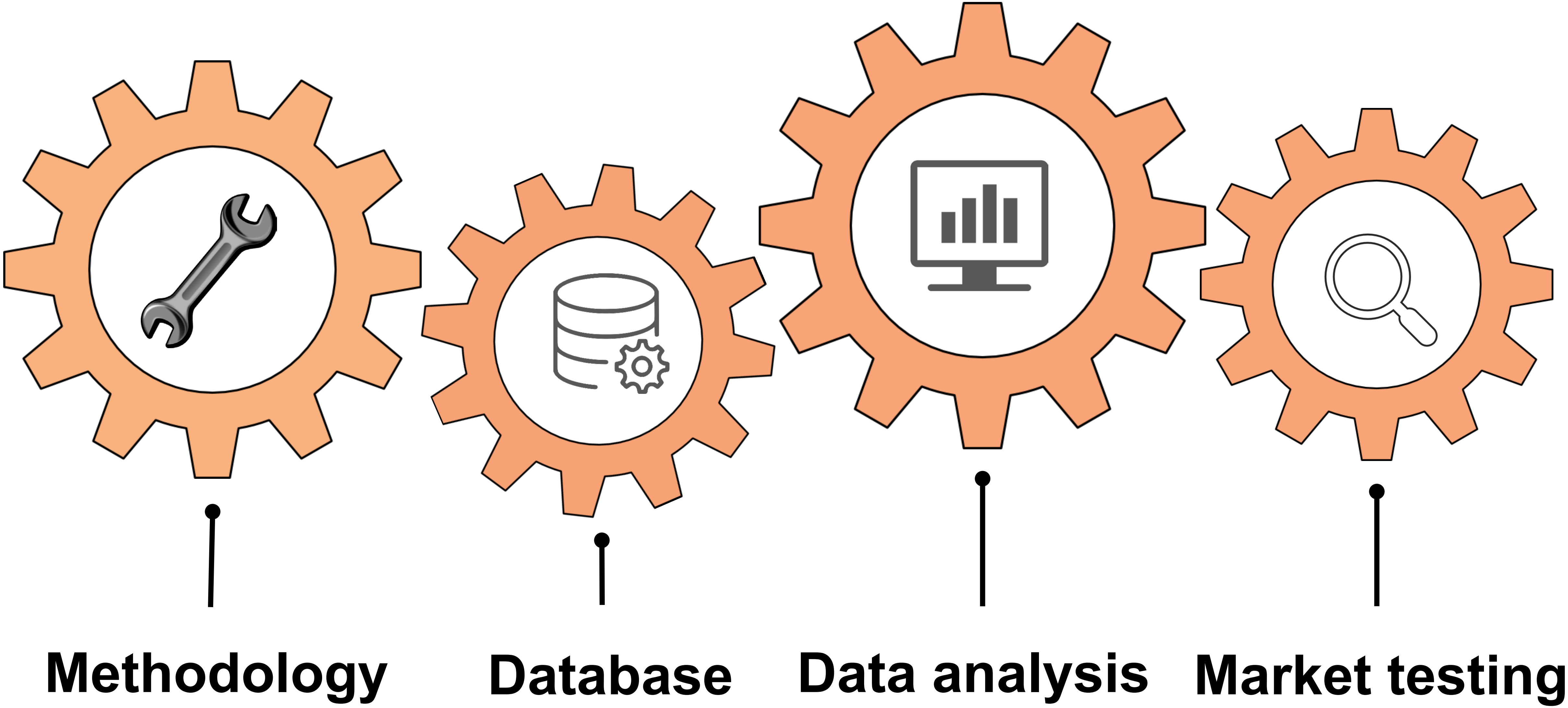


Robust general DD-SIMCA model for &

The four gears building trust in our food



The four gears building trust in our food



Authenticity of Food Flavourings

Number of commercial samples

Number of commercial samples

33

Fruit flavourings

Apple, strawberry, banana, blueberry, peach, grape, pear, kiwi, raspberry, blackberry, plum and sour cherry

Number of commercial samples

33 Fruit flavourings

Apple, strawberry, banana, blueberry, peach, grape, pear, kiwi, raspberry, blackberry, plum and sour cherry

4 Vanilla flavourings

Yoghurt, ice cream, pudding and tea

Number of commercial samples

33 **Fruit flavourings**

Apple, strawberry, banana, blueberry, peach, grape, pear, kiwi, raspberry, blackberry, plum and sour cherry

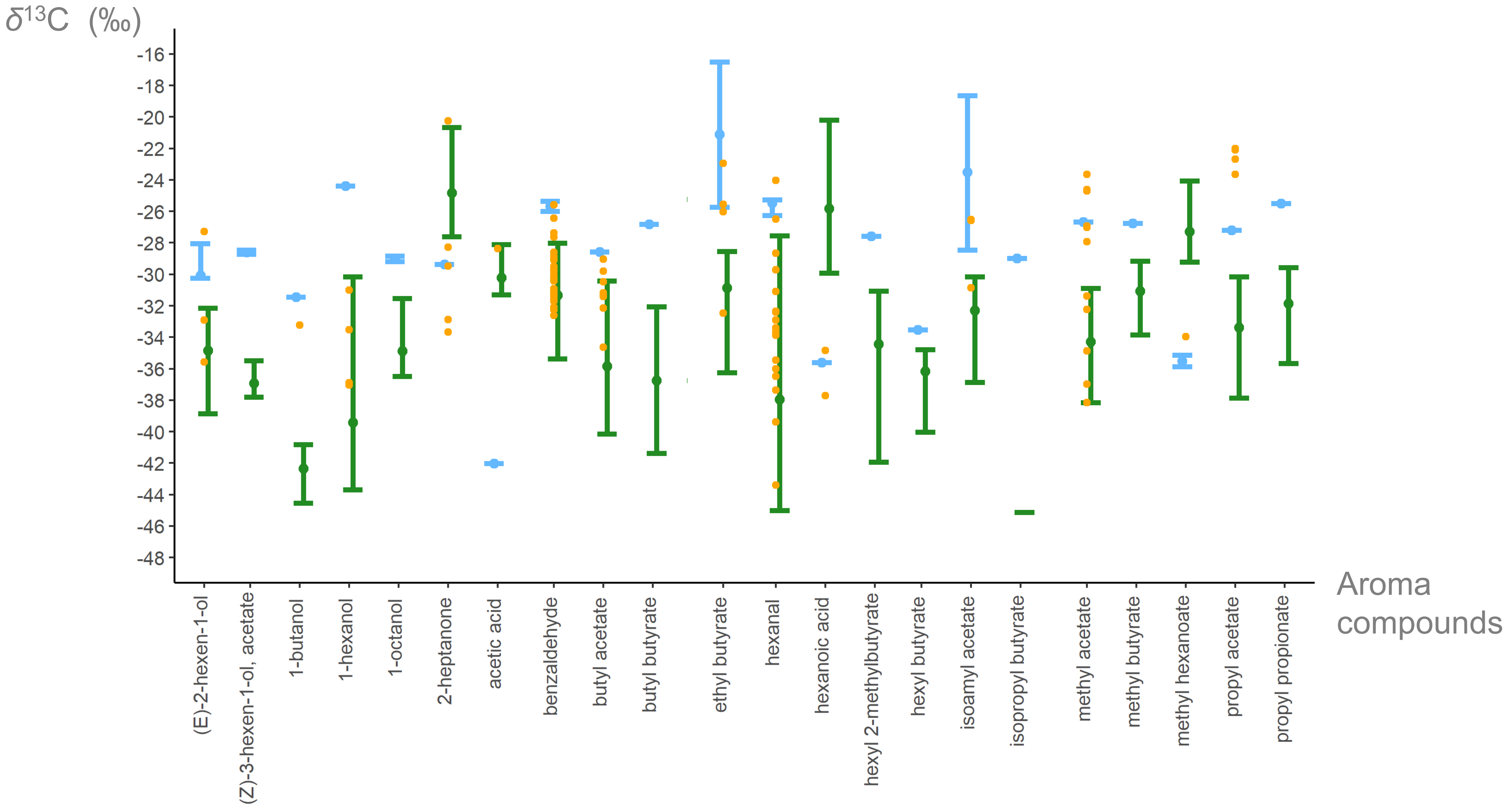
4 **Vanilla flavourings**

Yoghurt, ice cream, pudding and tea

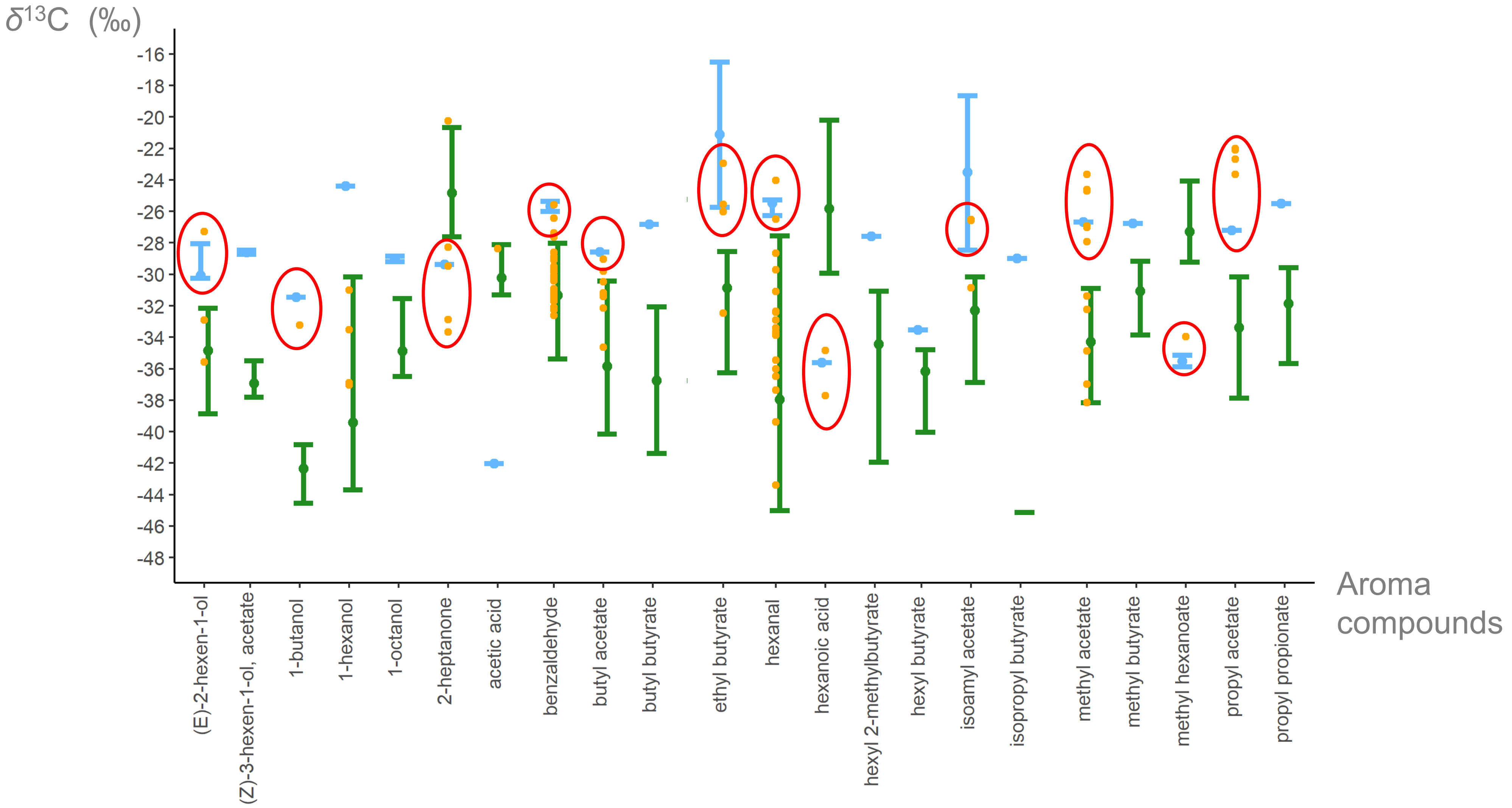
11 **Truffle flavourings**

Olive oils, sauces, fish spread, *T. magnatum*, *T. aestivum*

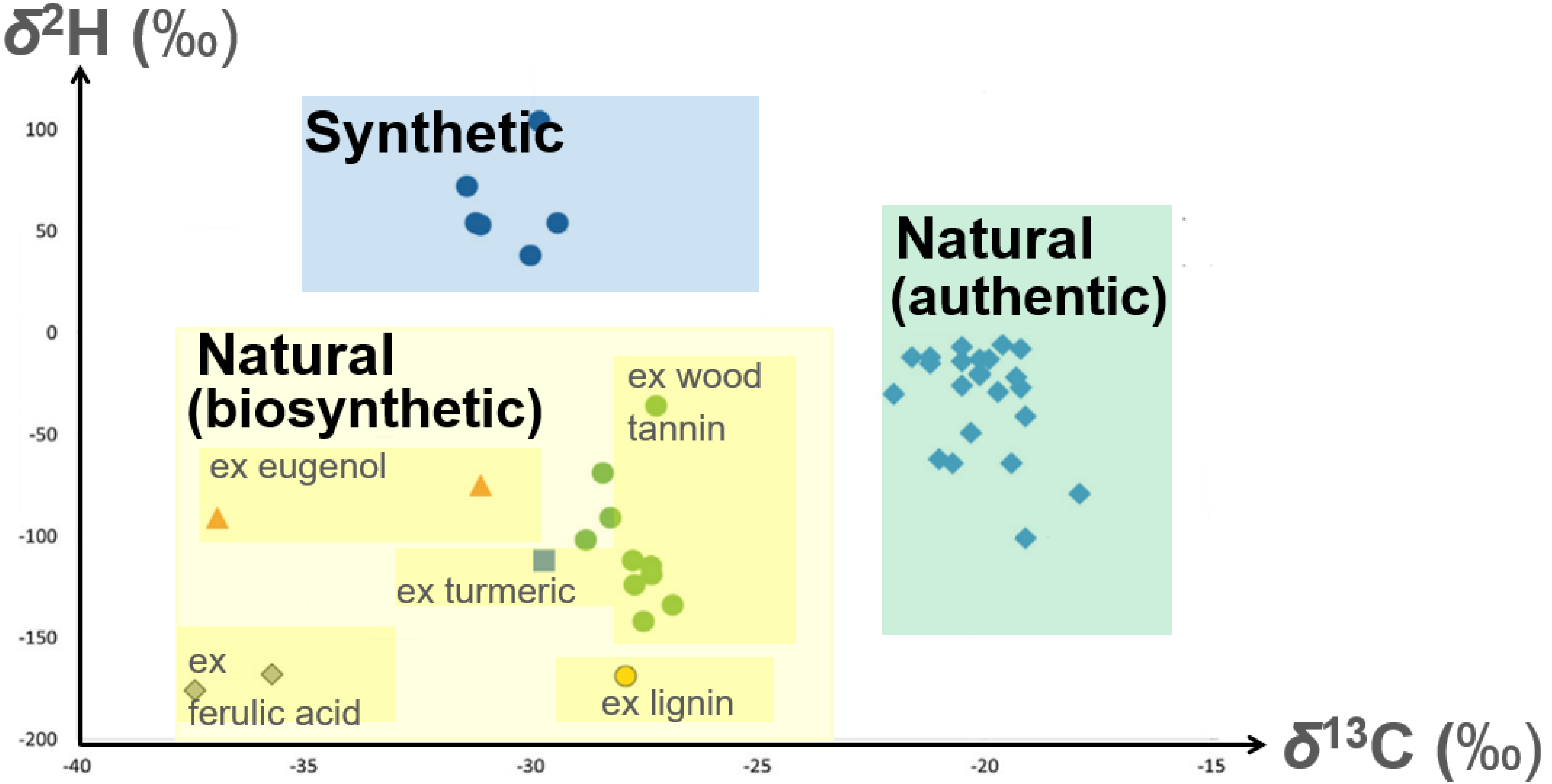
Fruit flavourings on the market can be questioned



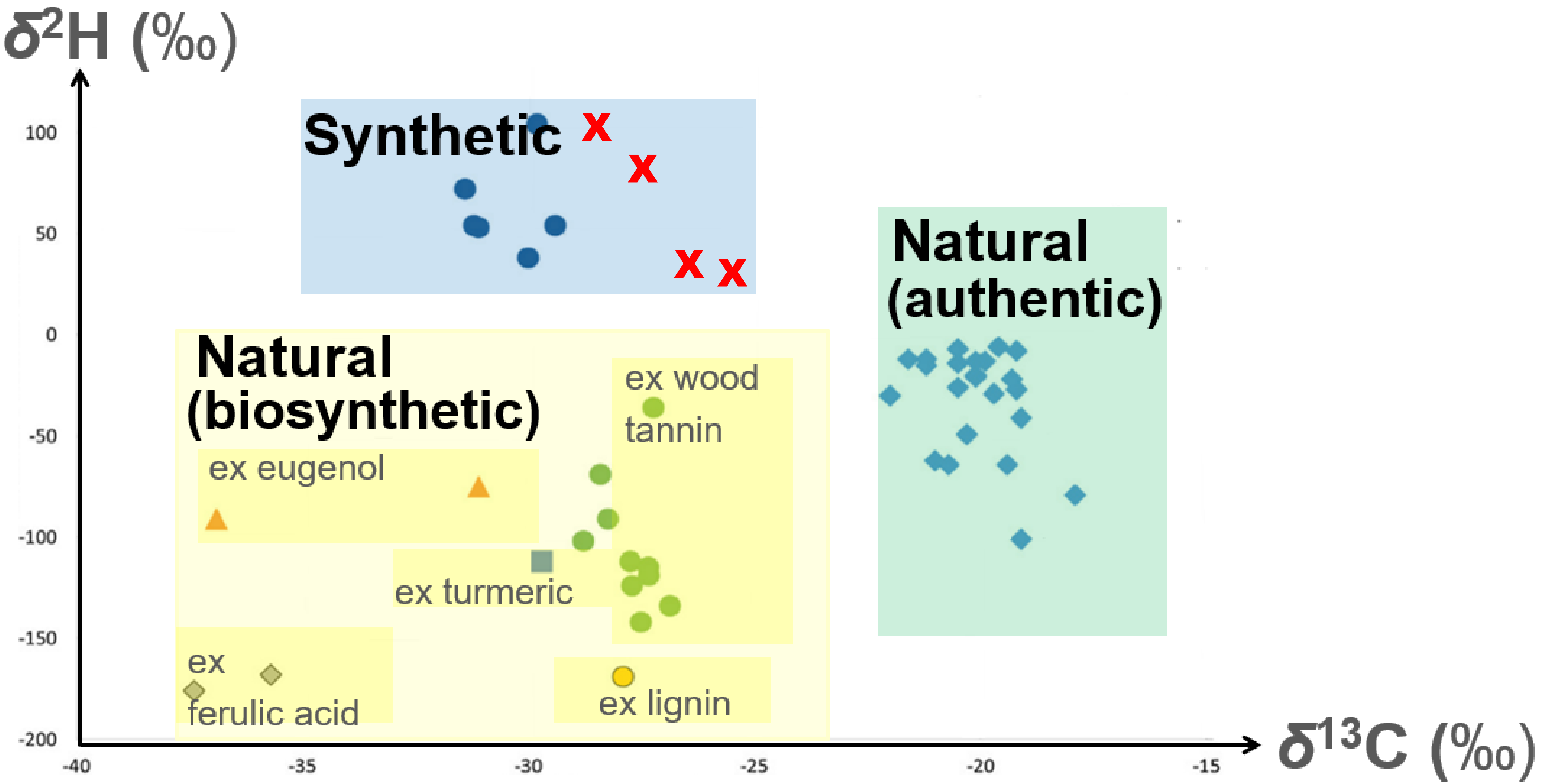
Fruit flavourings on the market can be questioned



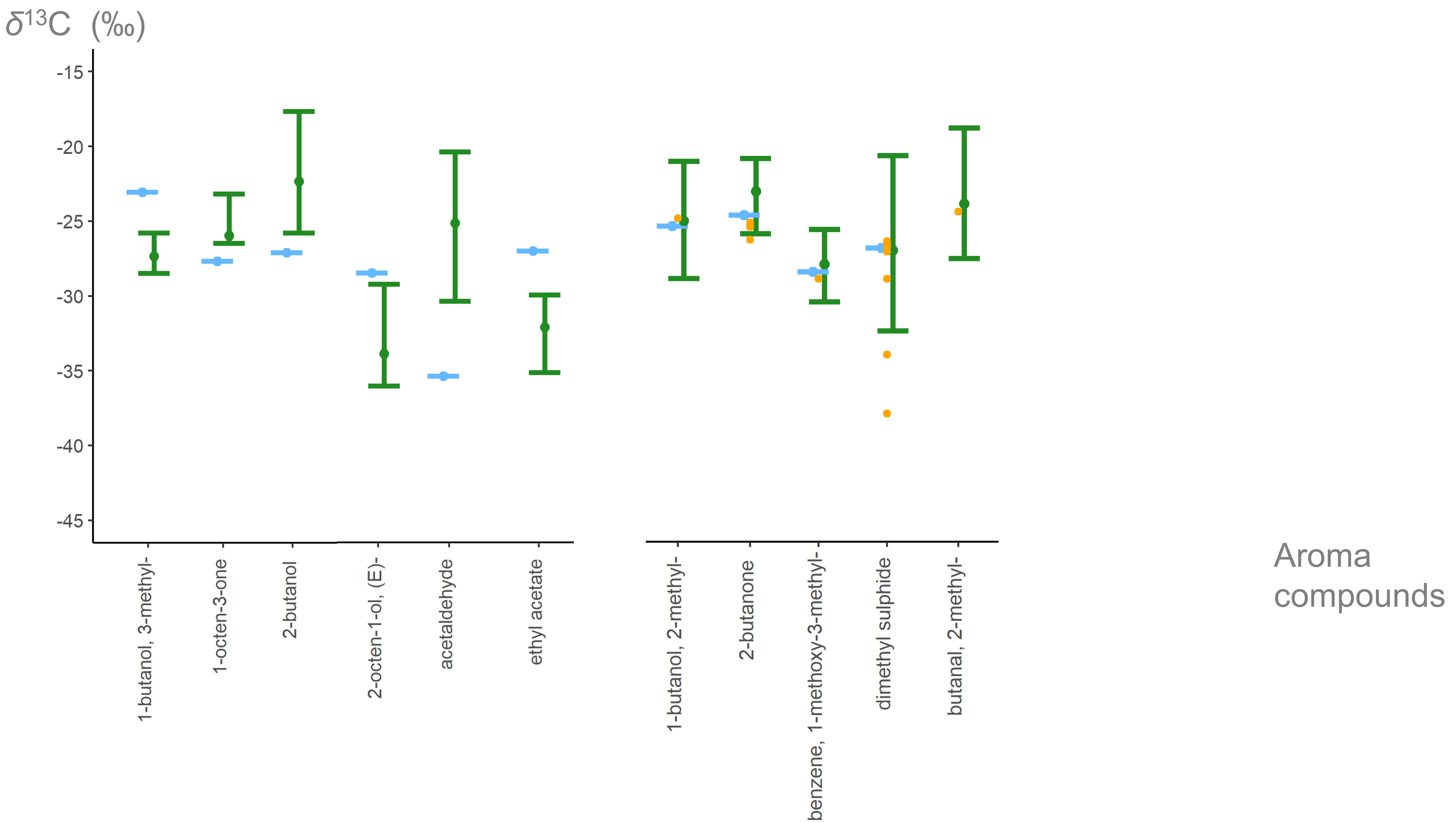
All 4 samples contain synthetic vanillin



All 4 samples contain synthetic vanillin



2 compounds indicate presence of synthetic flavour in truffle samples



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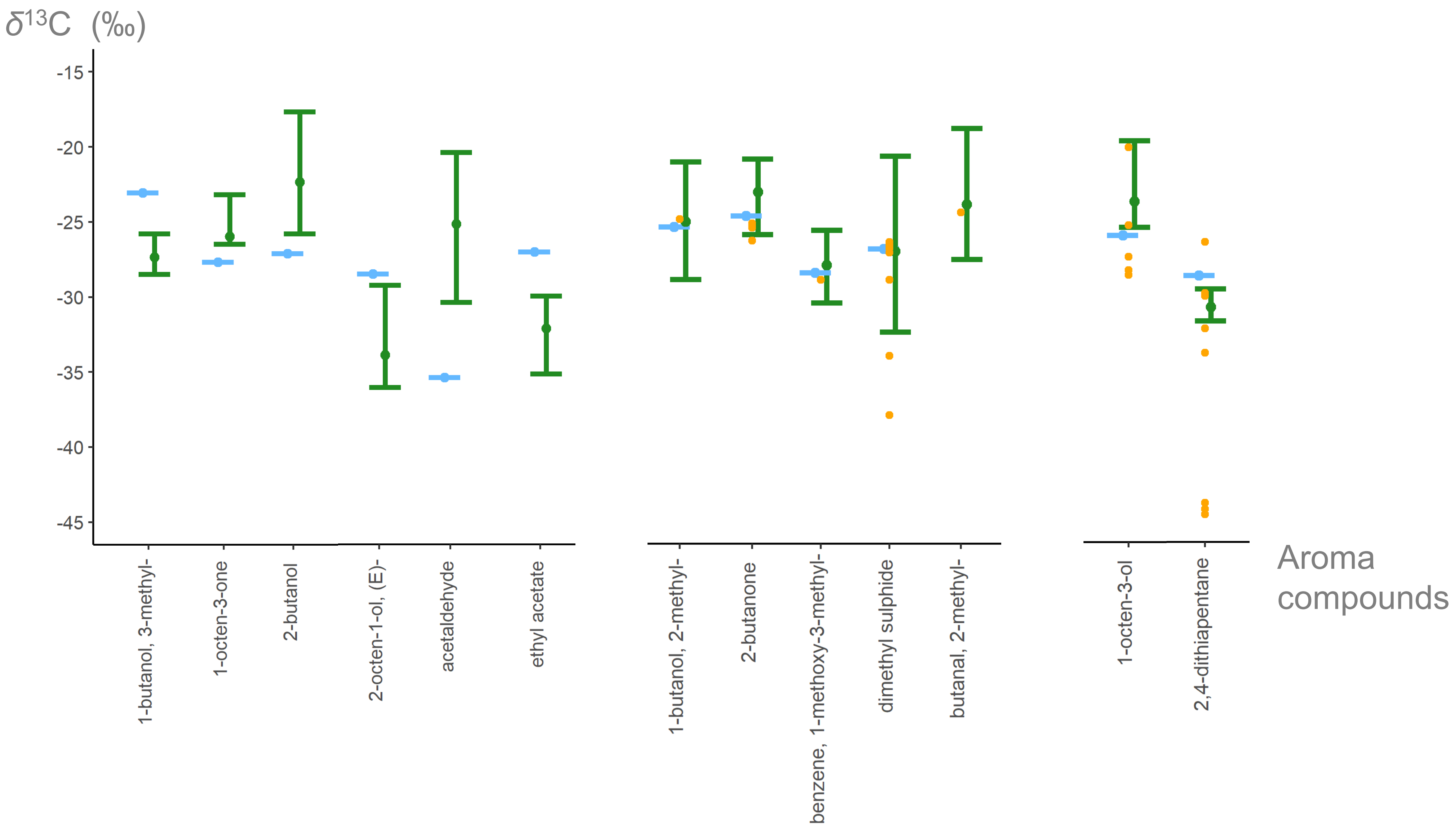
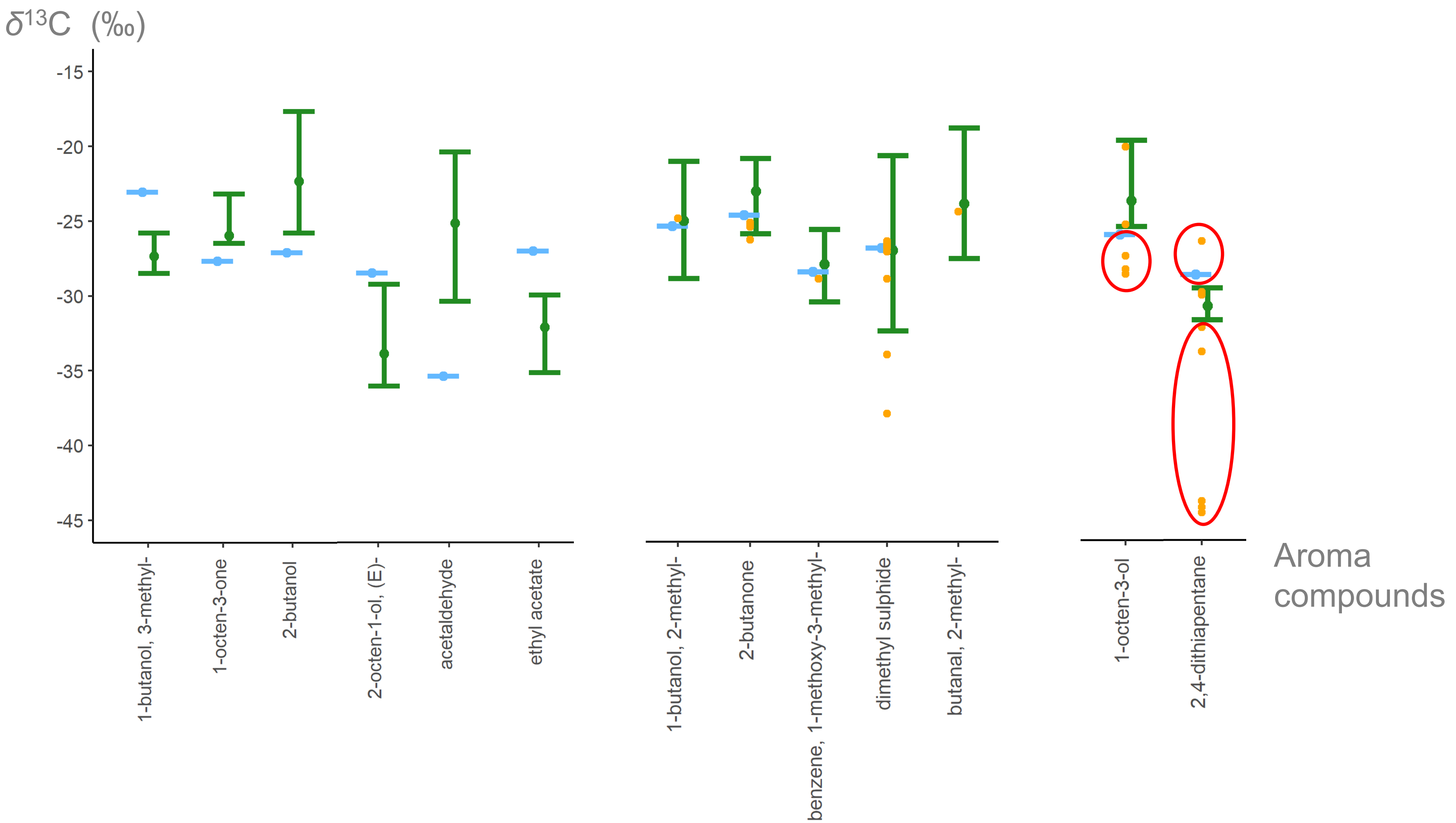
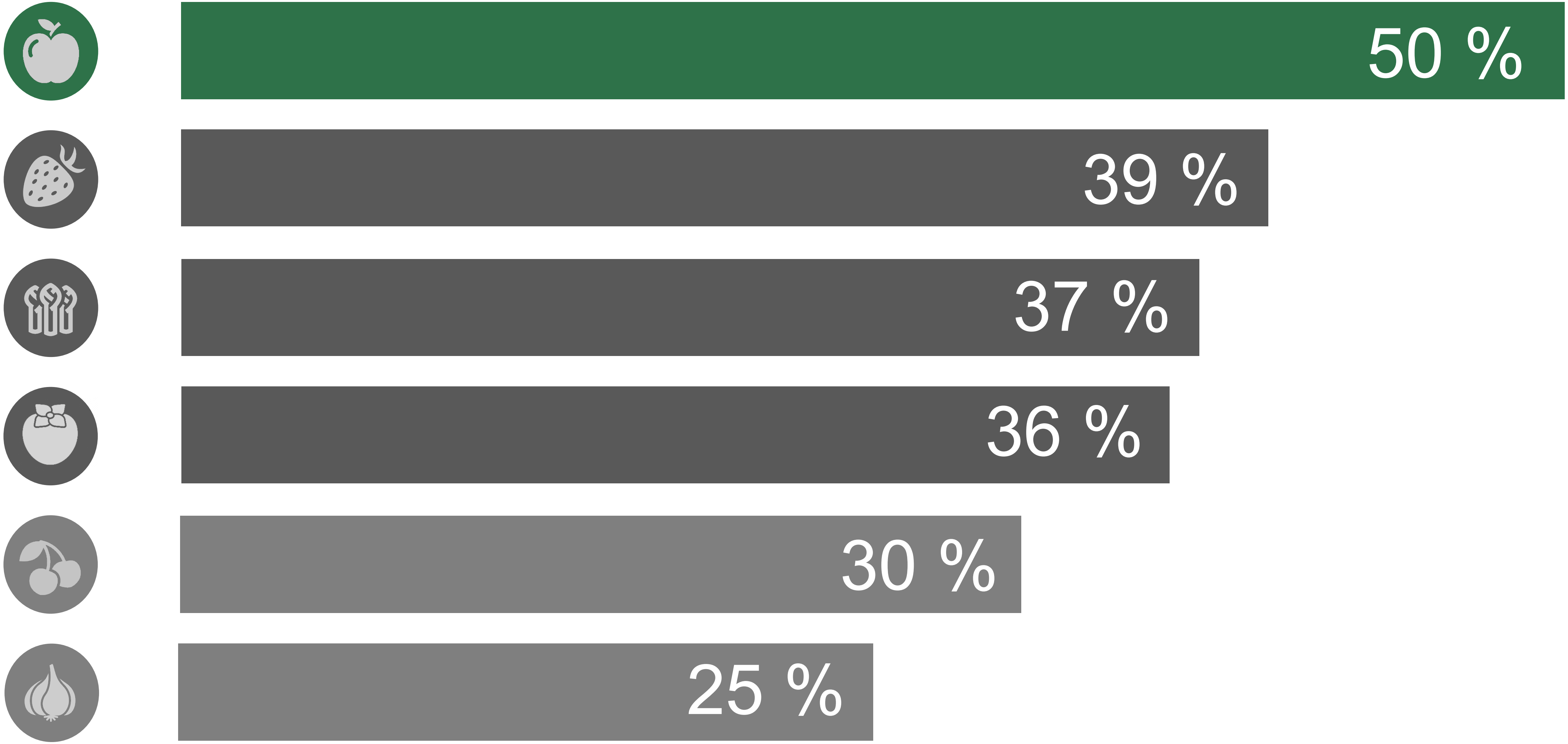


2 compounds indicate presence of synthetic flavour in truffle samples



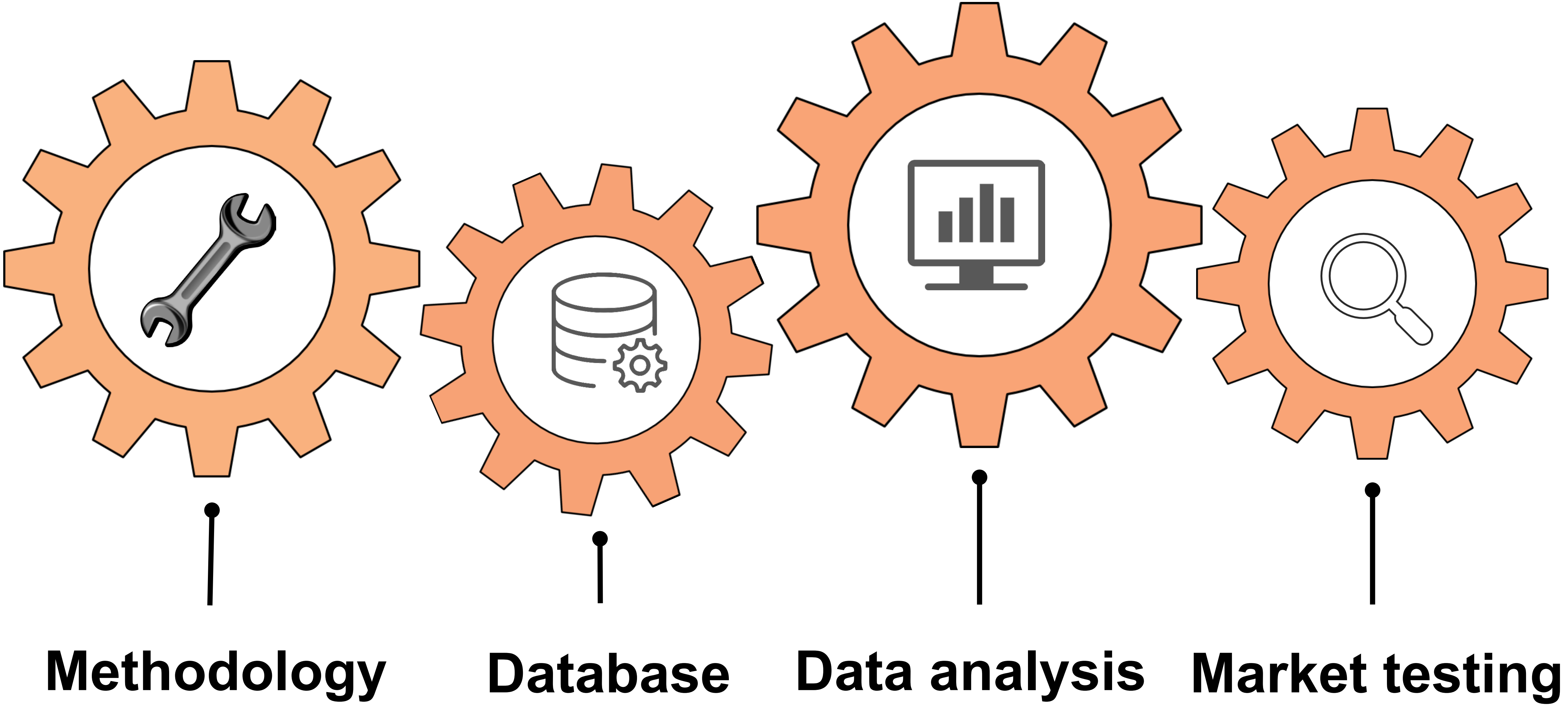
Geographical origin of Fruits and Vegetables

% of samples non compliant with declaration



Conclusions

The four gears building trust in our food



1 Methodology

Developed HS-SPME GC-C/P-IRMS ($\delta^{13}C$ / $\delta^{2}H$) method opens up new possibilities for its application.

2 Database

10 extensive databases are of significant importance for producers or enforcement agencies.

3 Data analysis

Utilisation of DD-SIMCA for geographical traceability can be transferred to any food commodity or country.

4 Market testing

Insight into potential mislabeling and adulteration benefiting producers and enhancing consumer trust.

Acknowledgements

Implementation of research

REPUBLIKA SLOVENIJA
MINISTRSTVO ZA IZOBRAŽEVANJE, ZNANOST IN ŠPORT

EVROPSKA UNIJA
EVROPSKI SKLAD ZA REGIONALNI RAZVOJ
NALOŽBA V VAŠO PRIHODNOST

REPUBLIC OF SLOVENIA
MINISTRY OF AGRICULTURE, FORESTRY AND FOOD
THE ADMINISTRATION OF THE REPUBLIC OF SLOVENIA FOR FOOD SAFETY, VETERINARY AND PLANT PROTECTION

FOOD 4 FUTURE

REAL Med

ISO Fd Food ERA Chair
Safety Quality Traceability

mass twin

Samples

FRUTAROM
FOUNDED 1933
etol
since 1924

University of Ljubljana
Biotechnical Faculty

Kmetijski inštitut Slovenije
Agricultural Institute of Slovenia

GOZDARSKI INŠTITUT SLOVENIJE
SLOVENIAN FORESTRY INSTITUTE

THANK YOU

Any questions?

lidija.strojnik@ijs.si

Lidija Strojnik, Nives Ogrinc

ISO-FOOD Symposium, April 24^{th}, 2023