Ein Meßsystem zur parallelen Isotopenverhältnis- und Elementaranalyse von vier Elementen in Lebensmitteln und anderem biologischen Material

A Measuring System for the Parallel Isotope Ratio and Elemental Analysis of Four Elements in Food Commodities and Other Biological Material

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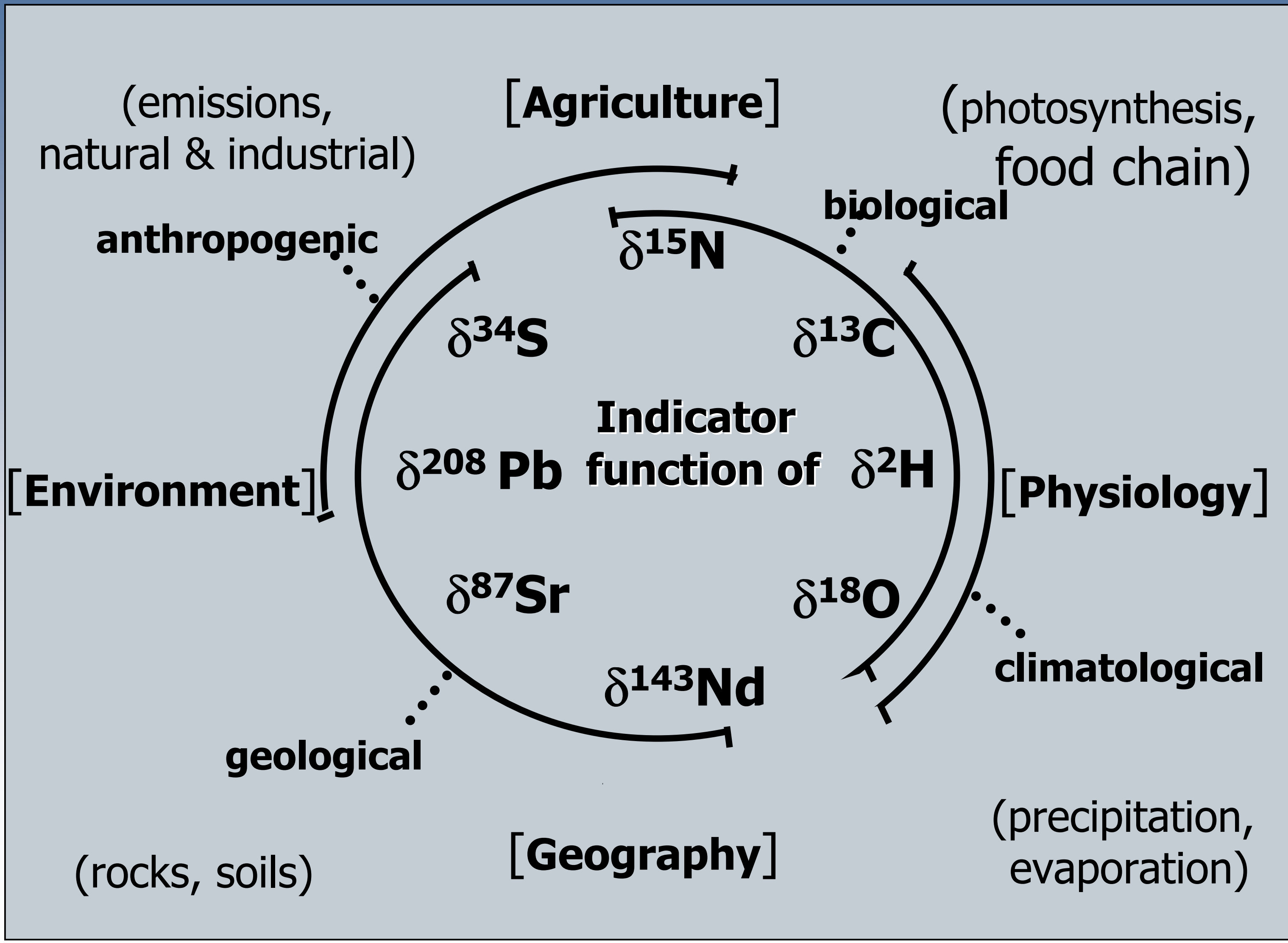
Why Multielement IRMS in

- origin assignment and authenticity check of food,
- discrimination between convential and organic production,
- identification of recent and prehistoric nutrition bases,
- ecological, biological and environmental investigations?


(emissions,
natural & industrial)
[Agriculture]
(photosynthesis,
food chain)
biological
anthropogenic
δ15N
δ34S
δ13C
Indicator
function of
δ208 Pb
δ2H
[Environment]
[Physiology]
δ87Sr
δ18O
δ143Nd
climatological
geological
(precipitation,
evaporation)
[Geography]
(rocks, soils)

Isotope Data of Greenhouse Vegetables ($\delta^{18}O$-values of leaf water) from Conventional (c) and Organic (o) Production, Respectively

Products from supermarkets (IL, NL) and local producers (D)					
Plant/Origin	Production	$\delta^{18}O$ $[‰]_{V\text{-}SMOW}$	$\delta^{13}C$ $[‰]_{V\text{-}PDB}$	$\delta^{15}N$ $[‰]_{V\text{-}AIR}$	$\delta^{34}S$ $[‰]_{CDT}$
Paprika/IL	**c**	**0.9**	**-26.5**	**-0.5**	**1.7**
	o	**-0.1**	**-26.9**	**7.9**	**2.6**
Paprika/NL	**c**	**0.8**	**-37.1**	**-2.4**	**7.6**
	c	**2.6**	**-44.1**	**2.2**	**2.5**
Tomato/NL	**c**	**-4.5**	**-36.9**	**-2.4**	**7.5**
Tomato/D	**c**	**-3.2**	**-28.5**	**0**	**4.6**
	o	**-5.3**	**-27.7**	**9.3**	**4.8**

How to Perform Multielement IRMS?

<u>I)   Conventionally:</u> Three samples for the IRMS of four elements

^{13}C, ^{15}N: Combustion, GC separation of N_2 and CO_2; IRMS

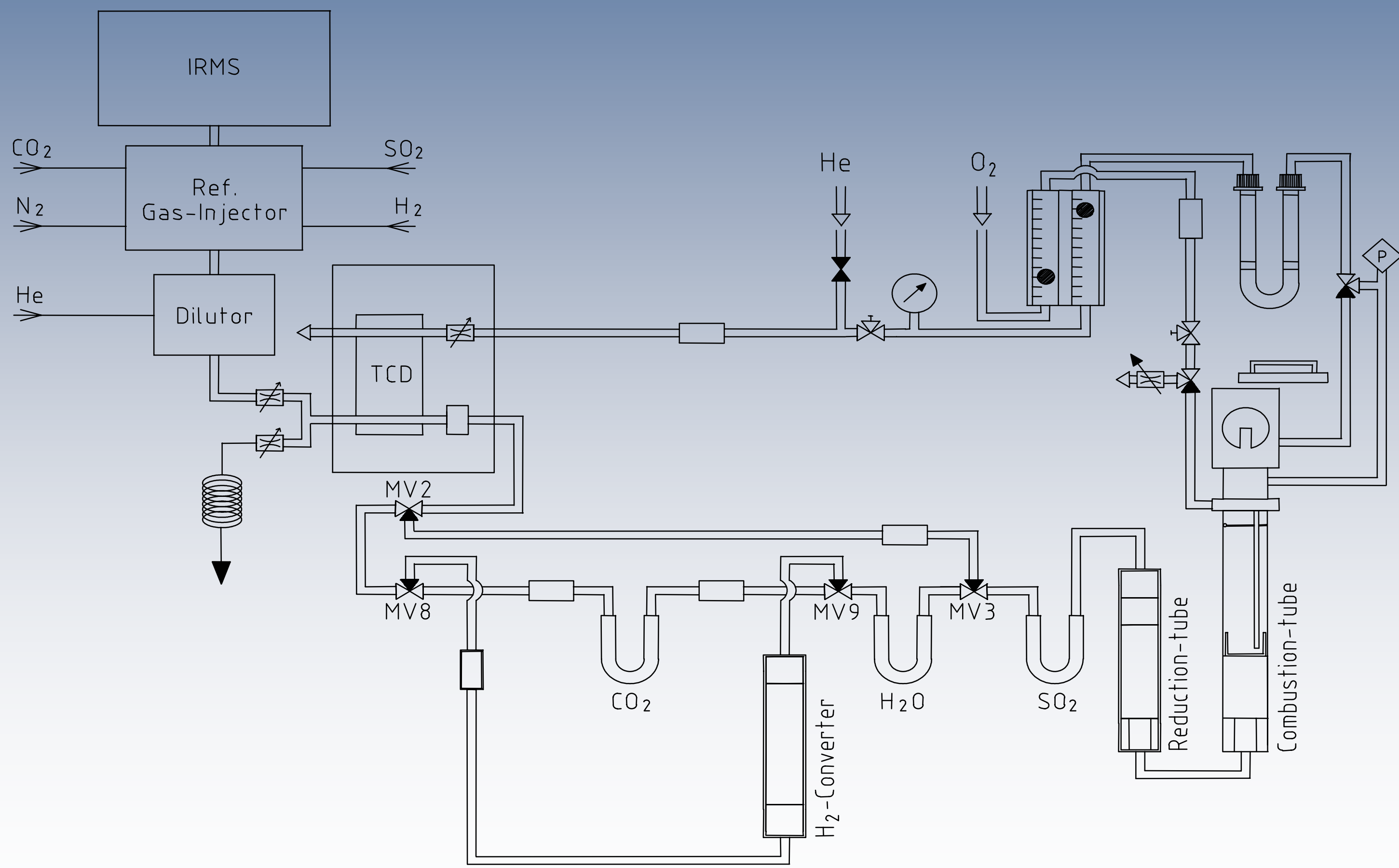
^{2}H, (^{18}O): Pyrolysis, GC separation of H_2 and CO (in absence of N); IRMS

^{34}S: Combustion, GC separation of SO_2; IRMS

<u>II) By our system:</u> One sample for the IRMS and EA of four elements

^{13}C, ^{15}N, ^{2}H, ^{34}S: Combustion, adsorptive separation of all gases; reduction of H_2O; IRMS

Functional Diagram of Simultaneous CHNS Stable Isotope and Elemental Analysis



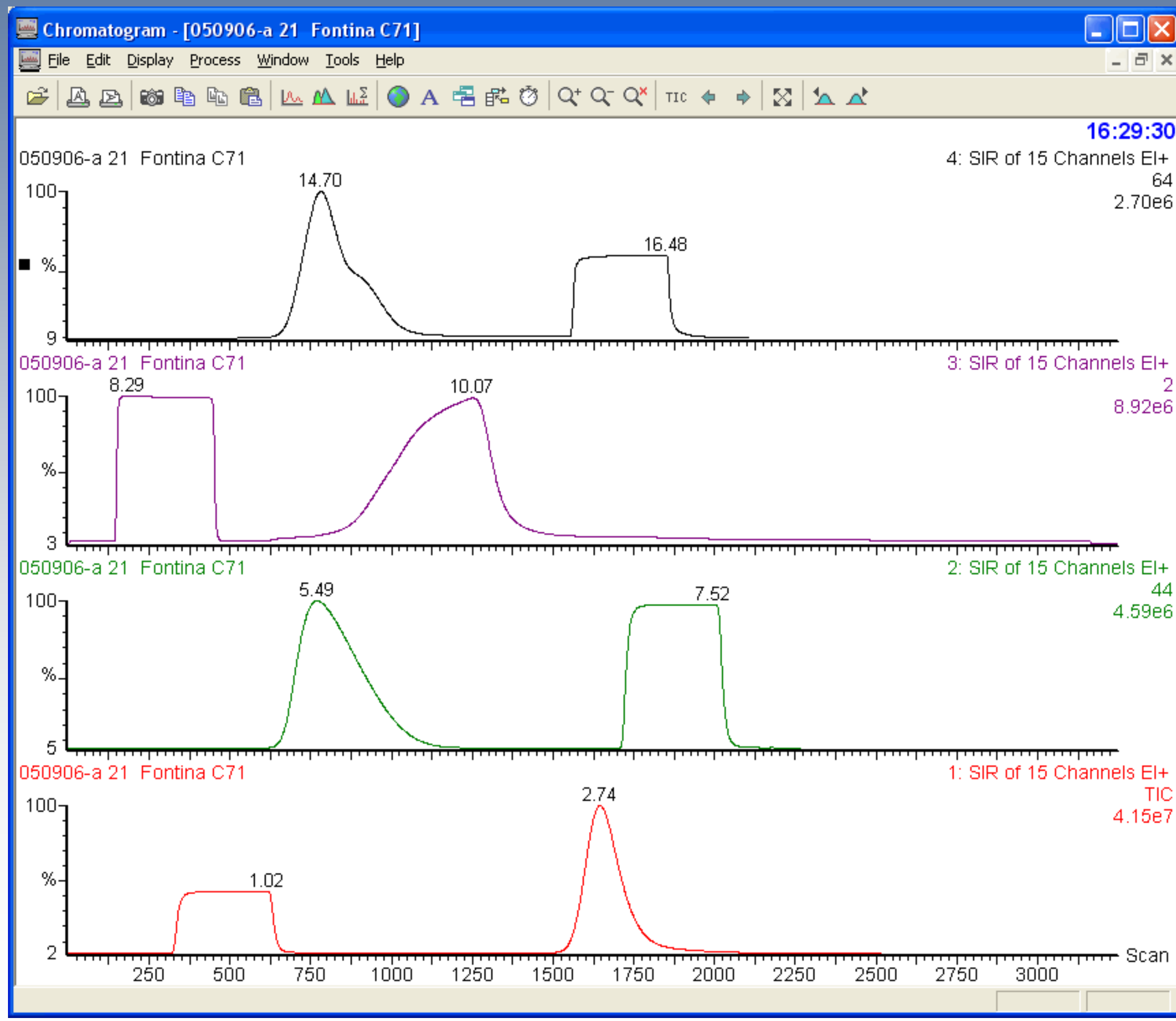
Rel. Mass Traces of NCHS Sample and Reference Gases (from bottom) in min.

SO_2

H_2

CO_2

N_2



Relative Sensitivity for the single elements

	N	C	H	S
Minimum amount [µMol]	50	50	500	30
error range (δ-units)	0.2	0.1	3.0	0.3
Minimum rel. Ratio to C	0.05		0.1	0.005

Standard weight [mg]

Plant dry matter 9-15 mg proteins 2-6 mg

Sugars, carbohydrates 4-5 mg corresp. to 2 mg C

Water Reduction: Memory Effects and Reproducibility (samples 6 µl)

sample type	δ^2H [‰]$_{V\text{-}SMOW}$
Drinking water, Hanau	- 73.7 - 58.6 - 56.9 - 57.7
SLAP	- 352.8 - 414.9 - 418.6 - 420.4 - 419.4
Drinking water, Hanau	- 127.2 - 57.7 - 57.3 - 57.4

Comparison Conventional Method (HT-Pyrolysis) and Simultaneous CHNS Analysis of Ca-Citrate (for detection of citric acid addition to fruit juices)

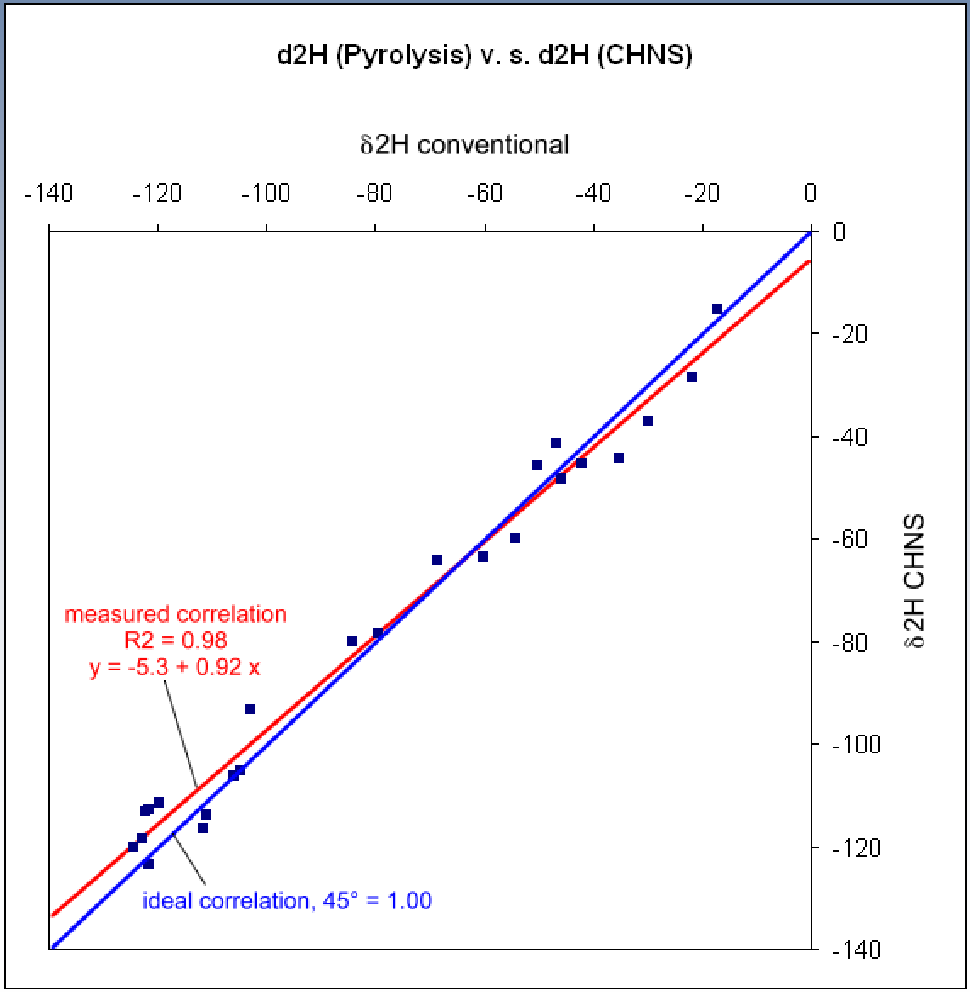
sample type				δ^2H [‰]$_{V\text{-}SMOW}$	$\delta^{13}C$ [‰]$_{V\text{-}PDB}$
synthetic mixture	conv.			-68.7	-16.86
from cane and beet sugars	CHNS			-64.2 ± 3.9	-17.06 ± 0.04
◇ synth. from beet sugar	conv.			-84.3	-24.92
	CHNS			-79.9	-25.22 ± 0.15
◇ synth. from beet sugar	conv.			-79.5	-24.86
	CHNS			-78.3 ± 2.5	-24.91 ± 0.08
⊙ synth./natural mixture	conv.			-46.8	-24.47
	CHNS			-41.5 ± 3.9	-24.38 ± 0.04
⊙ synth./natural mixture	conv.			-50.3	-24.42
	CHNS			-45.6 ± 3.5	-24.33 ± 0.09
natural from orange	conv.			-17.0	-23.99
	CHNS			-15.2 ± 3.6	-23.87 ± 0.06

◇ / ⊙ are blind duplicates

Comparison Conventional Method (HT-Pyrolysis) and Simultaneous CHNS Stable Isotope Analysis (cheese casein from different alpine valleys, Italy)

sample		$\delta^{15}N$ [‰]$_{AIR}$	$\delta^{13}C$ [‰]$_{V\text{-}PDB}$	$\delta^{2}H$ [‰]$_{V\text{-}SMOW}$	$\delta^{34}S$ [‰]$_{V\text{-}CDT}$
Asiago	conv.	4.77	-19.25	-105.9	5.51
	CHNS	4.91 ± 0.03	-19.43 ± 0.02	-106.4 ± 1.5	5.35 ± 0.04
Fontina	conv.	4.68	-22.89	-121.6	4.51
	CHNS	4.93 ± 0.06	-23.20 ± 0.04	-123.4 ± 0.5	4.23 ± 0.17
Montasio	conv.	4.81	-18.55	-104.7	4.53
	CHNS	4.89 ± 0.15	-18.59 ± 0.16	-105.2 ± 1.1	3.15 ± 0.15
Nostr.Castf.	conv.	4.43	-22.10	-122.2	7.04
	CHNS	4.75 ± 0.14	-22.13 ± 0.05	-113.3 ± 0.8	6.63 ± 0.18
Spressa	conv.	4.48	-21.78	-119.6	5.47
	CHNS	4.66 ± 0.05	-21.83 ± 0.06	-116.4 ± 0.7	5.65 ± 0.11
Toma	conv.	5.27	-21.07	-119.6	3.80
	CHNS	5.64 ± 0.31	-21.05 ± 0.04	-111.6 ± 1.3	4.27 ± 0.15
Vezzena	conv.	4.21	-22.13	-110.9	5.21
	CHNS	4.55 ± 0.17	-22.01 ± 011	-113.8 ± 0.9	5.16 ± 0.05

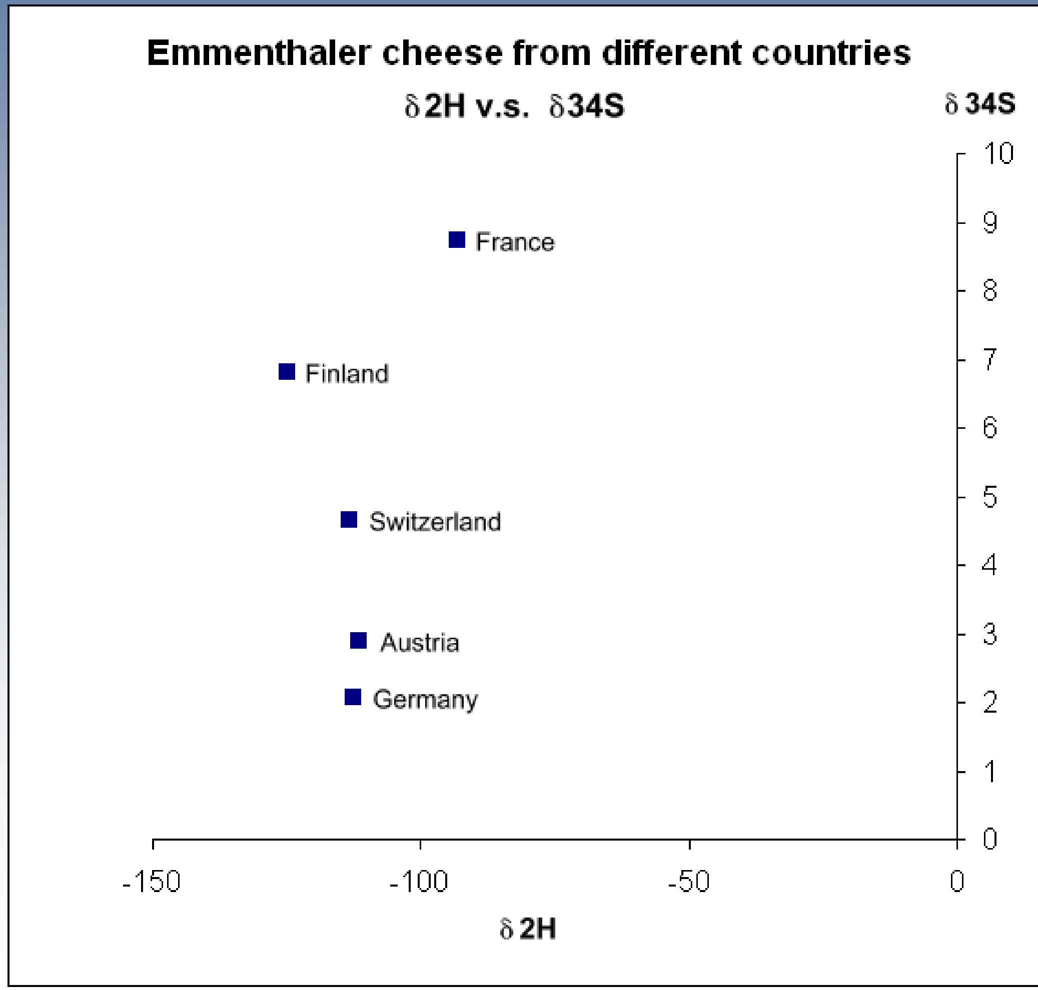
Comparison of δ²H-Values: Conventional Method (HT-Pyrolysis) and Simultaneous CHNS Isotope Ratio Analysis



Hydrogen and Carbon Isotopic Ratios of Wines from Different Geographical Origin

Sample type	δ^2H [‰]$_{V\text{-}SMOW}$	$\delta^{13}C$ [‰]$_{V\text{-}PDB}$
Pinot Noir 2003 Eastern France West of Rhine River	- 6.1 ± 0.7	- 25.96 ± 0.04
Merlot 2003 Western Germany East of Rhine River	- 5.3 ± 0.9	- 25.88 ± 0.05
Grenache 2002 Bordeaux France	+ 2.0 ± 1.7	- 26.72 ± 0.04
Sangiovese 2003 Italy Isle of Sicily	+ 10.0 ± 1.4	- 24.88 ± 0.09

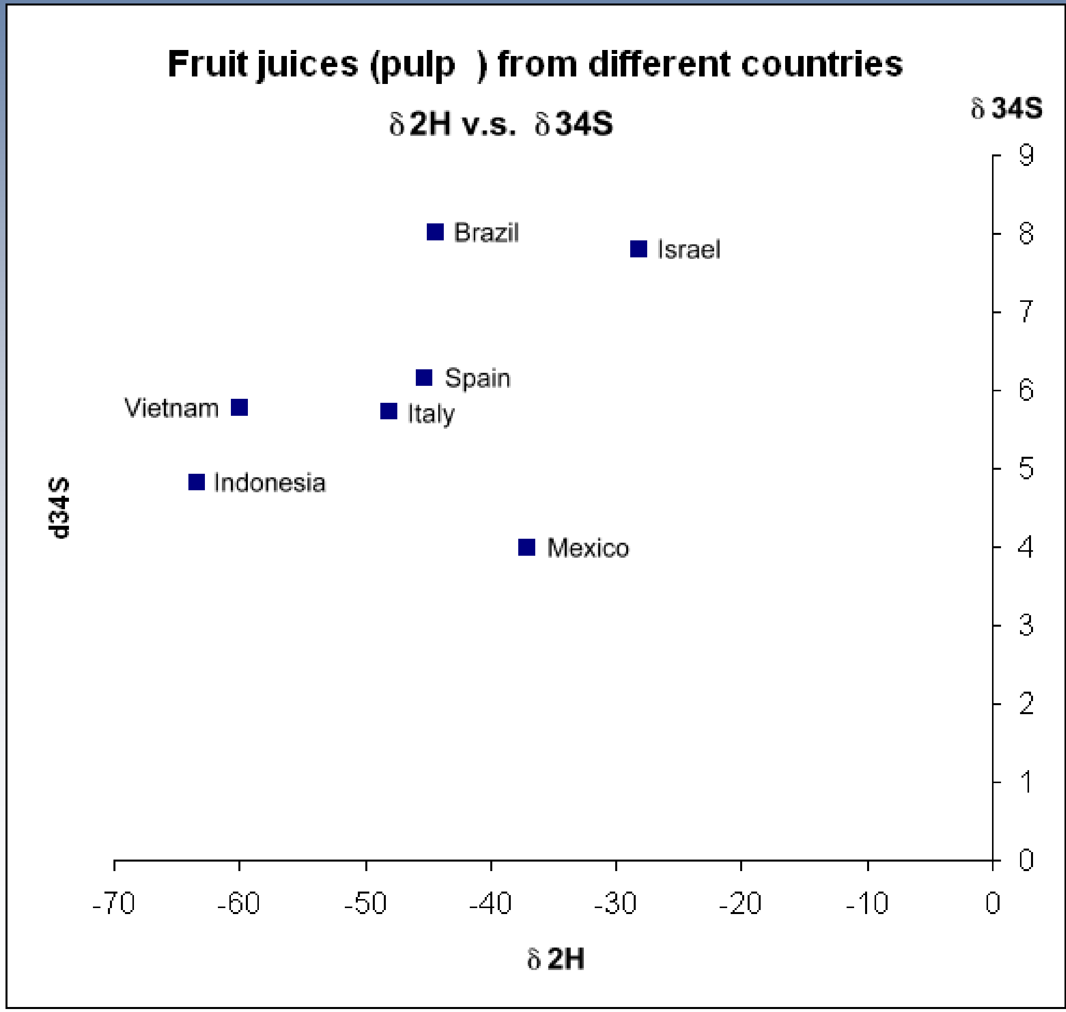
CHNS Simultaneous Stable Isotope Ratio Analysis of Emmenthaler Cheese from Different Countries



CHNS Simultaneous Stable Isotope Analysis of Fruit Juice Pulp from Different Countries

sample	$\delta^{15}N$ [‰]$_{AIR}$	$\delta^{13}C$ [‰]$_{V\text{-}PDB}$	$\delta^{2}H$ [‰]$_{V\text{-}SMOW}$	$\delta^{34}S$ [‰]$_{V\text{-}CDT}$
Pineapple / Indonesia	1.17 ± 0.17	-13.69 ± 0.25	-63.4 ± 1.8	4.84 ± 0.10
Grapefruit / Israel	6.11 ± 0.02	-25.69 ± 0.13	-28.3 ± 0.9	7.82 ± 0.25
Pineapple / Vietnam	4.89 ± 0.03	-13.27 ± 0.07	-60.0 ± 1.8	5.79 ± 0.25
Orange / Mexico	5.77 ± 0.03	-25.96 ± 0.11	-37.2 ± 1.1	3.99 ± 0.11
Orange / Spain	5.57 ± 0.03	-25.38 ± 0.11	-45.3 ± 0.8	6.16 ± 0.25
Orange / Italy (Isle of Sicily)	5.54 ± 0.11	-24.80 ± 0.12	-48.2 ± 1.2	5.73 ± 0.08
Orange / Brazil	6.09 ± 0.09	-25.75 ± 0.25	-44.5 ± 1.3	8.02 ± 0.35

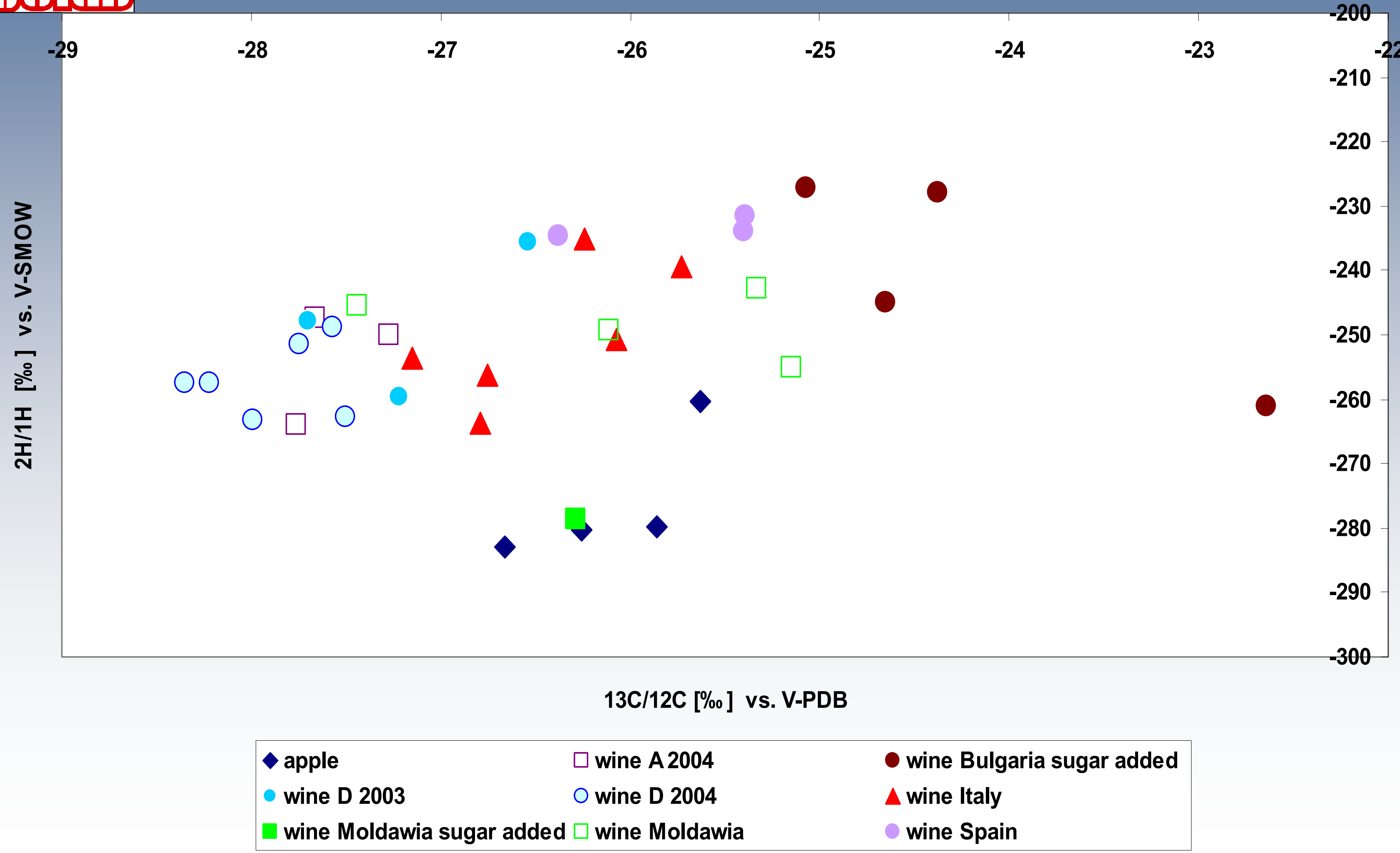
CHNS Simultaneous Stable Isotope Ratio Analysis of Fruit Juice Pulps from Different Countries



CHNS Simultaneous Stable Isotope Analysis of Emmenthaler Cheese Casein from Different Countries

sample	$\delta^{15}N$ [‰]$_{AIR}$	$\delta^{13}C$ [‰]$_{V\text{-}PDB}$	$\delta^{2}H$ [‰]$_{V\text{-}SMOW}$	$\delta^{34}S$ [‰]$_{V\text{-}CDT}$
Germany (Allgäu)	5.40 ± 0.06	-25.18 ± 0.08	-112.7 ± 0.2	2.08 ± 0.17
France (Bretagne)	6.00 ± 0.05	-16.67 ± 0.05	-93.4 ± 2.1	8.75 ± 0.16
Finland	6.21 ± 0.08	-26.05 ± 0.02	-124.9 ± 1.8	6.84 ± 0.13
Switzerland (St. Gallen)	7.14 ± 0.10	-25.21 ± 0.04	-113.5 ± 1.3	4.67 ± 0.09
Austria (Vorarlberg)	5.04 ± 0.07	-24.78 ± 0.02	-111.8 ± 1.3	2.91 ± 0.13

Hydrogen and Carbon isotopic ratios of ethanol from various origin



Conclusion

With the combination of the elemental analyser vario EL III of Elementar Analysensysteme GmbH and a suitable MS, the multielement IRMS and EA of the elements H, C, N and S can be performed with satisfactory sensitivity, reproducibility and accuracy on a sole sample within 20 min. The system is also suitable for the independent ^{2}H and ^{18}O IRMS by pyrolytic sample preparation. Its capacity for the combustion of samples up to 100 mg provides the possibility to analyse material with very low element concentrations and extreme elemental ratios.