



Food authenticity and adulteration testing using trace elemental and inorganic mass spectrometric techniques

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Overview

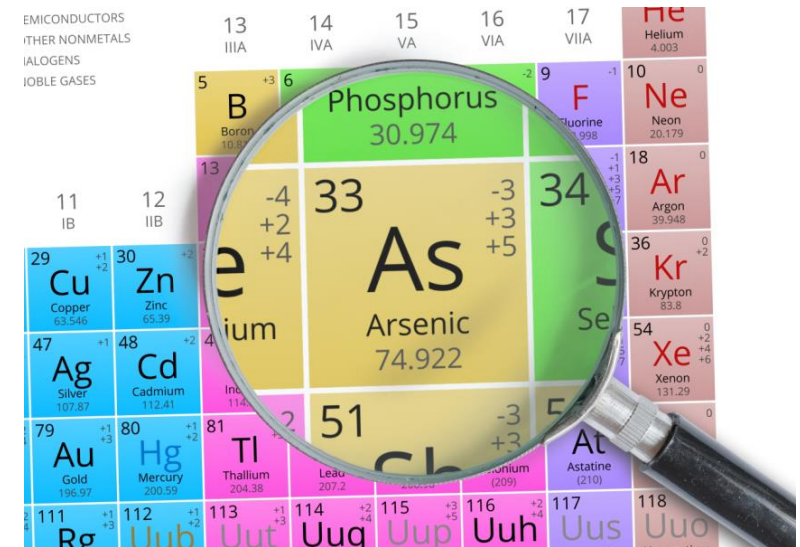
Food authenticity

- What is food authenticity?
- Major food authentication schemes and systems
- Food authentication challenges
- Which techniques can be applied?
- Example applications



Food safety – focus on arsenic and EU 2015/1006

- What is the EU 2015/1006 regulation and how does it impact arsenic measurement in foodstuffs?
- Why has this legislation been developed?
- What levels need to be measured and in what samples?
- Using IC for speciation analysis and automating speciation analysis
- Application examples: Arsenic speciation in organic brown rice syrup and total arsenic quantification in food samples
- Resources available for learning more about As determination



What is food authenticity?

- Food authenticity is about misrepresentation by either mislabeling or by adulterating, usually with lower cost material
- Typical examples:
 - Wine authenticity – illegal sugar addition to grape juice
 - Addition of sugar to honey
 - Addition of hazelnut oil to olive oils
 - Mislabeling geographical origin (wine, olive oil)
 - Mislabeling organic food products
 - Adulteration of meat with cheaper species



Major food authentication schemes and systems

- **Protected Designation of Origin (PDO)**
covers agricultural products and foodstuffs which are produced, processed and prepared in a given geographical area using recognized know-how.
- **Protected Geographical Indication (PGI)**
covers agricultural products and foodstuffs closely linked to the geographical area. At least one of the stages of production, processing or preparation takes place in the area.
- **Traditional Speciality Guaranteed (TSG)**
highlights traditional character
- **DOOR (Database of Origin and Registration) Database**
> 1200 entries for different foods (e.g olive oils, wines, cheeses, honey, beer) from multiple countries



**Council Regulation (EC) No 510/2006
of 20 March 2006**



**Council Regulation (EC) No 509/2006
of 20 March 2006**

See <http://ec.europa.eu/agriculture/quality/> and <http://ec.europa.eu/idabc/en/document/5360/5637.html> for further information

Food authentication challenges

- Chemically identical foods or identical chemical entities
- Unique marker compounds rarely found - more often small analytical differences (isotopic patterns)
- Large natural variability based on climatic conditions, fertilizers used, variety, processing.....
- Techniques must be able to distinguish small differences
- Databases of authentic foods must be available to understand natural variability



Which techniques can be applied?

Technique	Parameters measured
Infrared spectroscopy (NIR, MIR)	Spectral profile, characteristic frequencies
Raman spectroscopy	Spectral profile, characteristic frequencies
Nuclear Magnetic Resonance	Spectral profile, characteristic frequencies
Atomic absorption and emission spectroscopy, ICP/MS	Elemental composition
Mass spectrometry (GC/MS, LC/MS)	Volatile components, phenolic compounds
Chromatography (HPLC/RID)	Amino acids, carbohydrates, phenolic compounds
Isotope Ratio Mass Spectrometry (IRMS)	Isotope Ratios of natural variations

DNA based methods like PCR; used mainly for adulteration of meat based products e.g. addition of chicken and pork meat into minced beef, differentiation of cattle breed, adulteration of foie gras with chicken*

Immunology based approach based on ELISA detection of specific proteins e.g. presence of vegetable proteins in milk or meat, adulteration of sheep/goat milk with cow milk

* *L.M. Reid et al. / Trends in Food Science & Technology 17 (2006) 344–353*

Data analysis: Chemometric approach

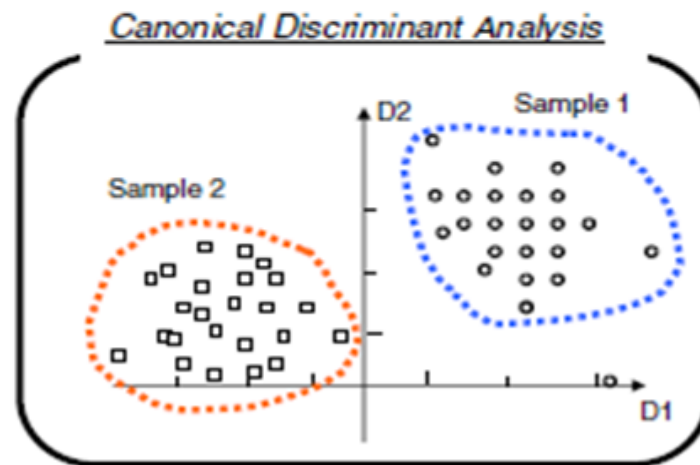
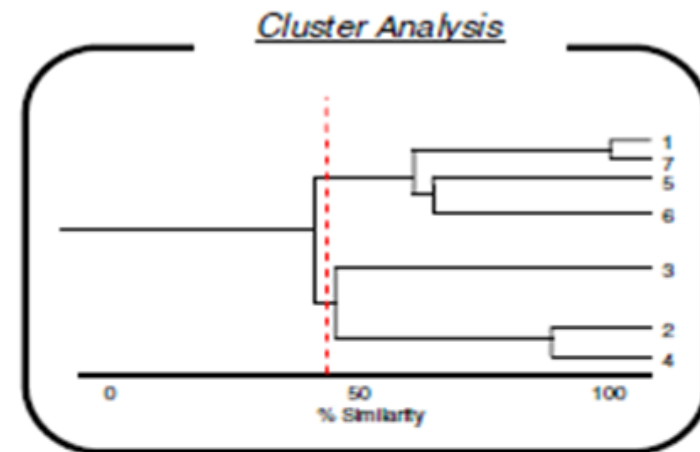
- Large number of variables involved, e.g. delta value, elemental composition, mass spectra, compound concentration etc.
- Multivariate analysis must be applied
- Supervised or unsupervised methods
 - Unsupervised: classification of sample without any knowledge about the origin
 - Supervised: similarity of unknown to authentic material
- Choosing appropriate approach is the key to successful analysis

Unsupervised methods

- ANOVA, MANOVA
- Principal Component Analysis (PCA) - reduces dimensionality
- Cluster Analysis (CA) - grouping of samples based on their similarity

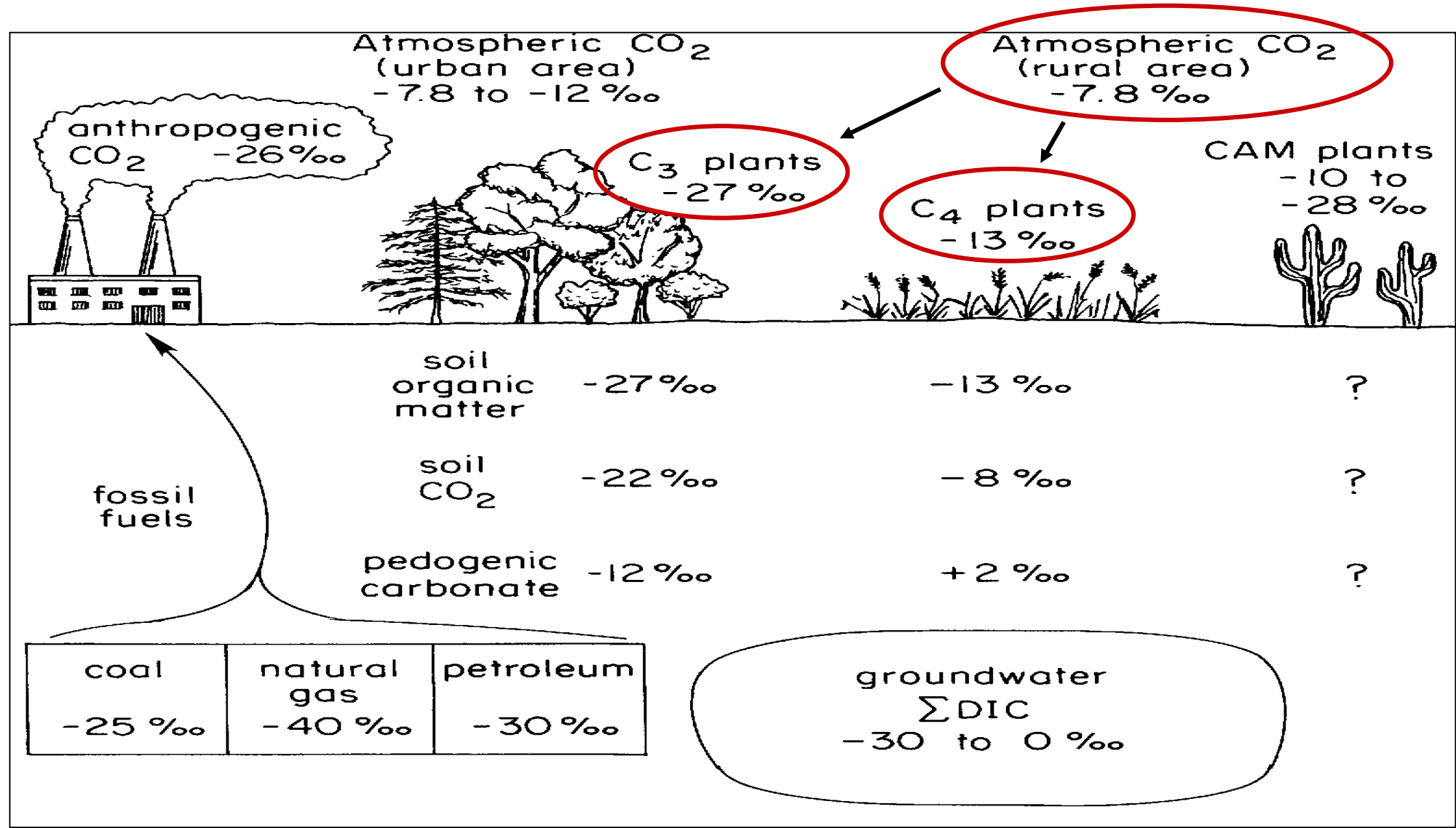
Supervised methods (discriminant techniques)

- Linear discriminant analysis (LDA) - characterize or separate two or more classes
- Partial Least Squares (PLS) - fundamental relations between two matrices
- Artificial Neural Networks (ANN) - complex relationships modelling

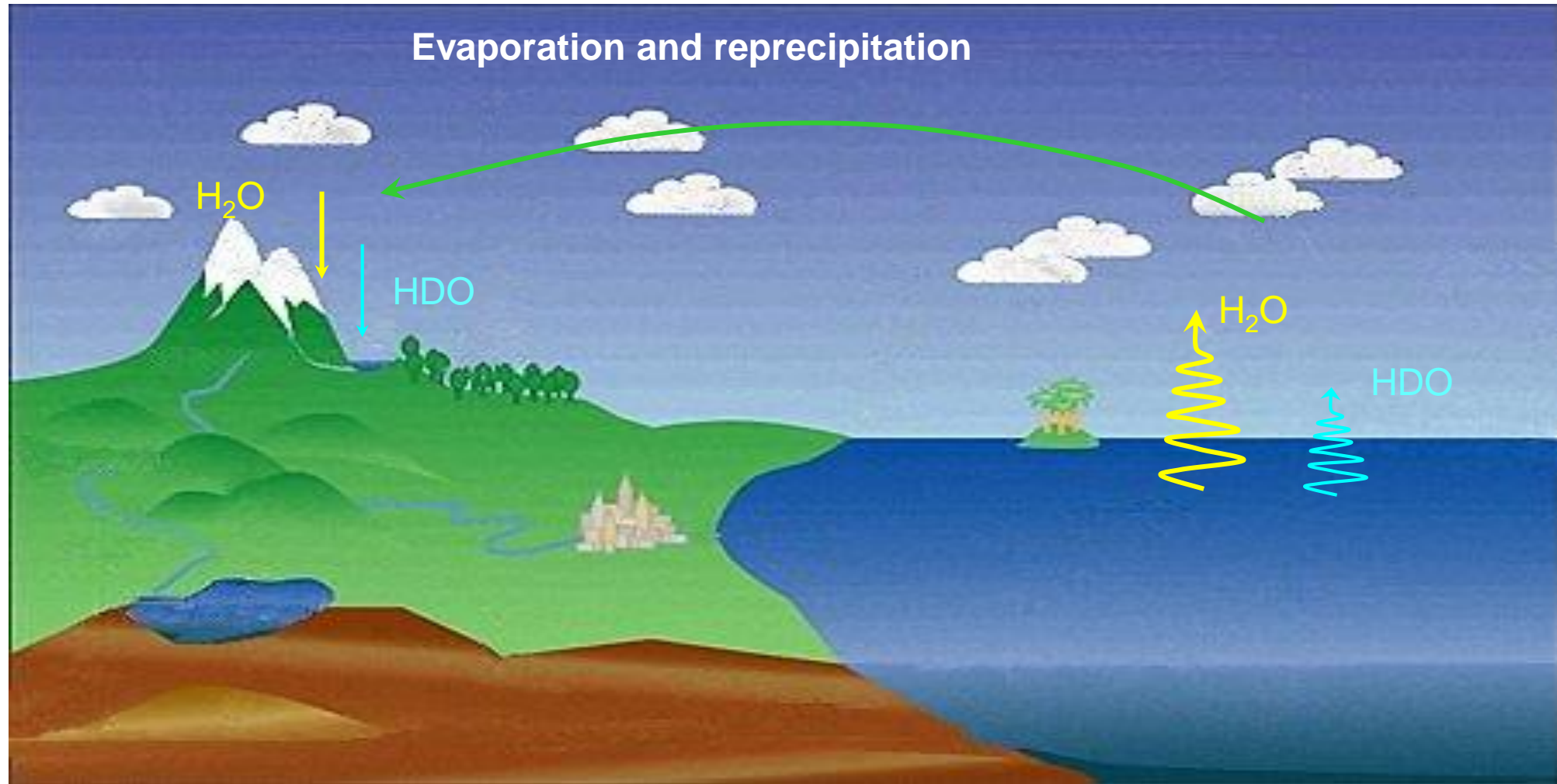


Gonzalves, A, Trends in Analytical Chemistry, Vol. 28, No. 11, 2009

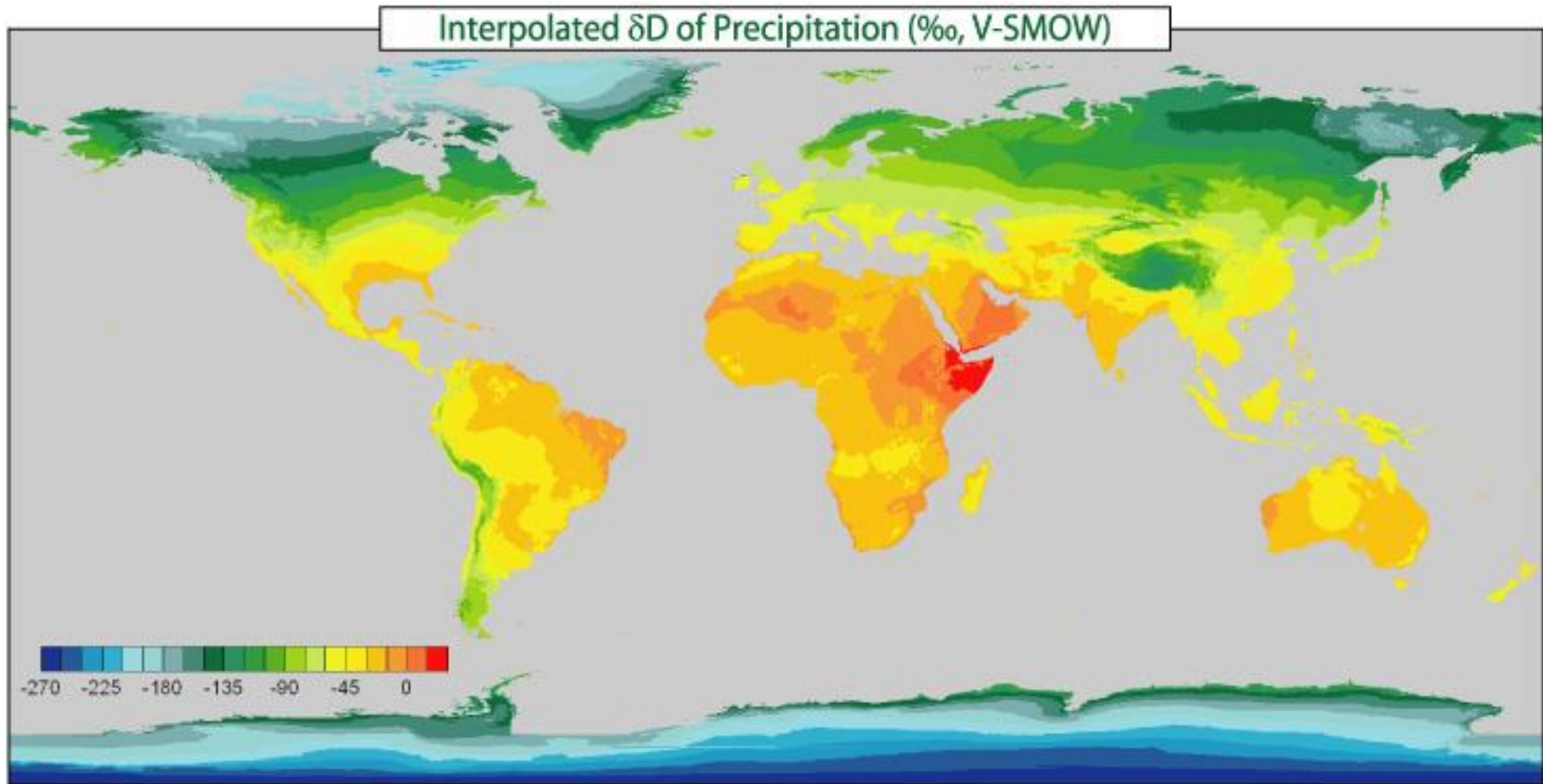
Isotopes - sources of variation



Climatic factors affecting D/H ratio



Interpolated $\delta^2\text{H}$ of precipitation



Produced by James Elhringer (University of Utah)

- Precise isotope ratios of

Element	Minor Isotope	Natural Abundance [%]
Hydrogen	^2H (D)	0.015 57
Carbon	^{13}C	1,111 40
Nitrogen	^{15}N	0.366 30
Oxygen	^{18}O	0.200 04
Sulfur	^{34}S	4.215 00



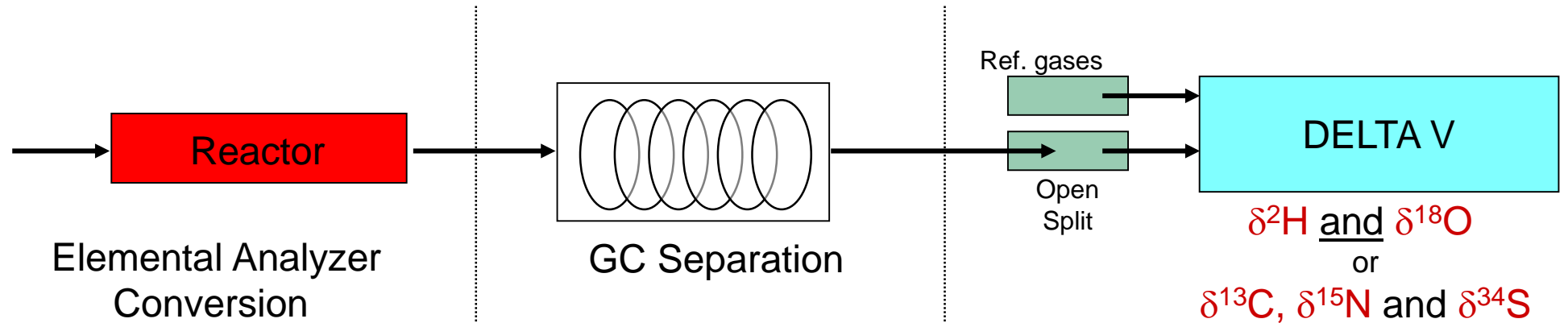
That's where the information is



Different approaches to IRMS

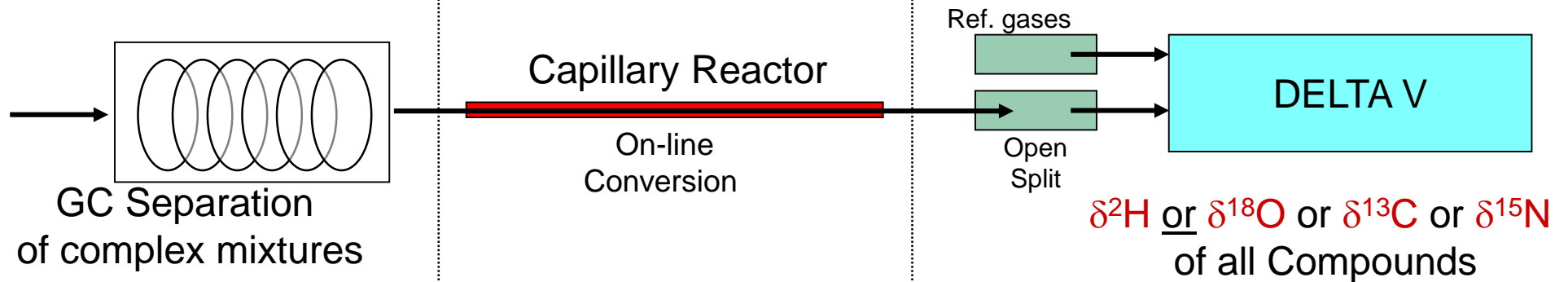
BSIA

Bulk
Stable
Isotope
Analysis



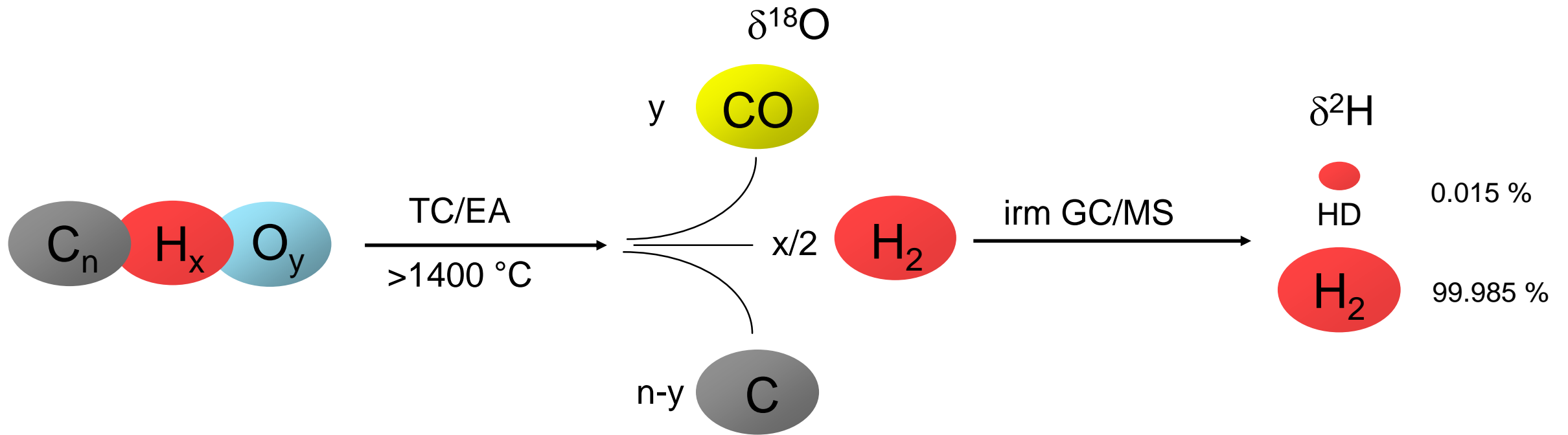
CSIA

Compound
Specific
Isotope
Analysis

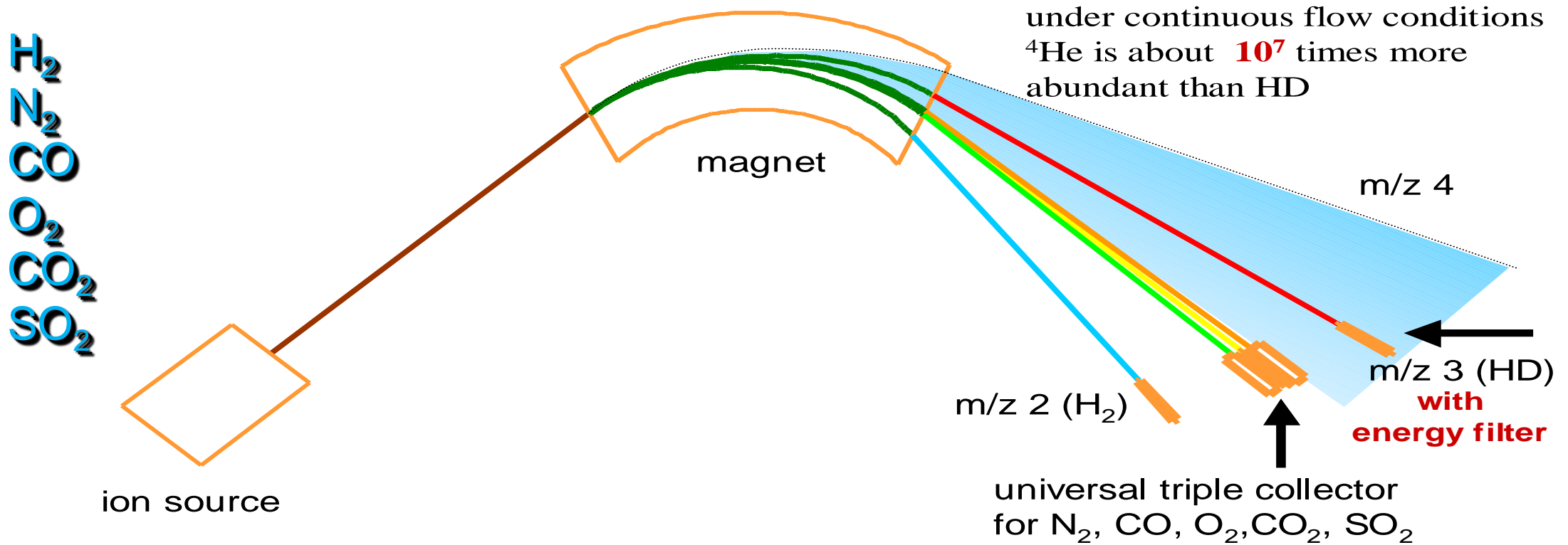


Sample introduction – conversion to simple gases

- BSIA: Dynamic Flash Combustion (EA) for C, N & S → CO₂, SO₂, N₂
- BSIA: High temperature conversion (TC/EA) for O & H → CO, H₂
- CSIA: Combustion (GC/C) for C or N → CO₂, N₂
- CSIA: High temperature conversion (GC/TC) for O or H → CO, H₂



Multi collectors for simultaneous detection



Bulk Stable Isotope Analysis: The Thermo Scientific™ EA IsoLink™ IRMS System

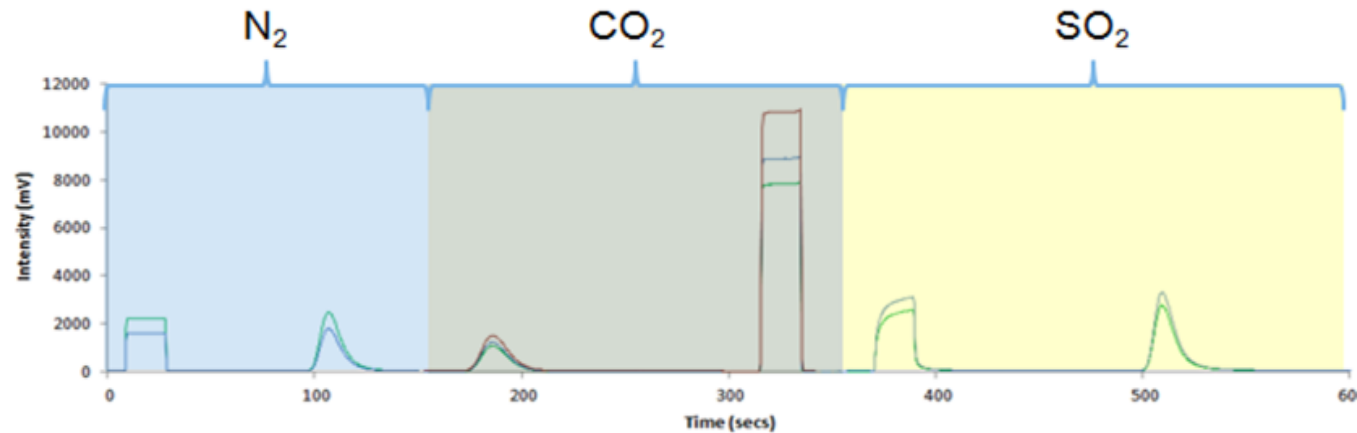
Thermo Scientific™ Flash
IRMS™ Elemental Analyzer

Thermo Scientific™ ConFlo IV™
Universal Interface

Thermo Scientific™ Isotope Ratio
Mass Spectrometer



- Allows simultaneous determination of C, N and S or O and H
- CNS analysis in less than 10 mins, including a very small sample amounts (< 5 µg)
- Provides chromatographic profile of the sample AND isotopic ratio information
- Helium Management (He^M) Module offers > 60% He saving
- All-in-one fully automated, modular EA–IRMS solution for all CNSOH applications

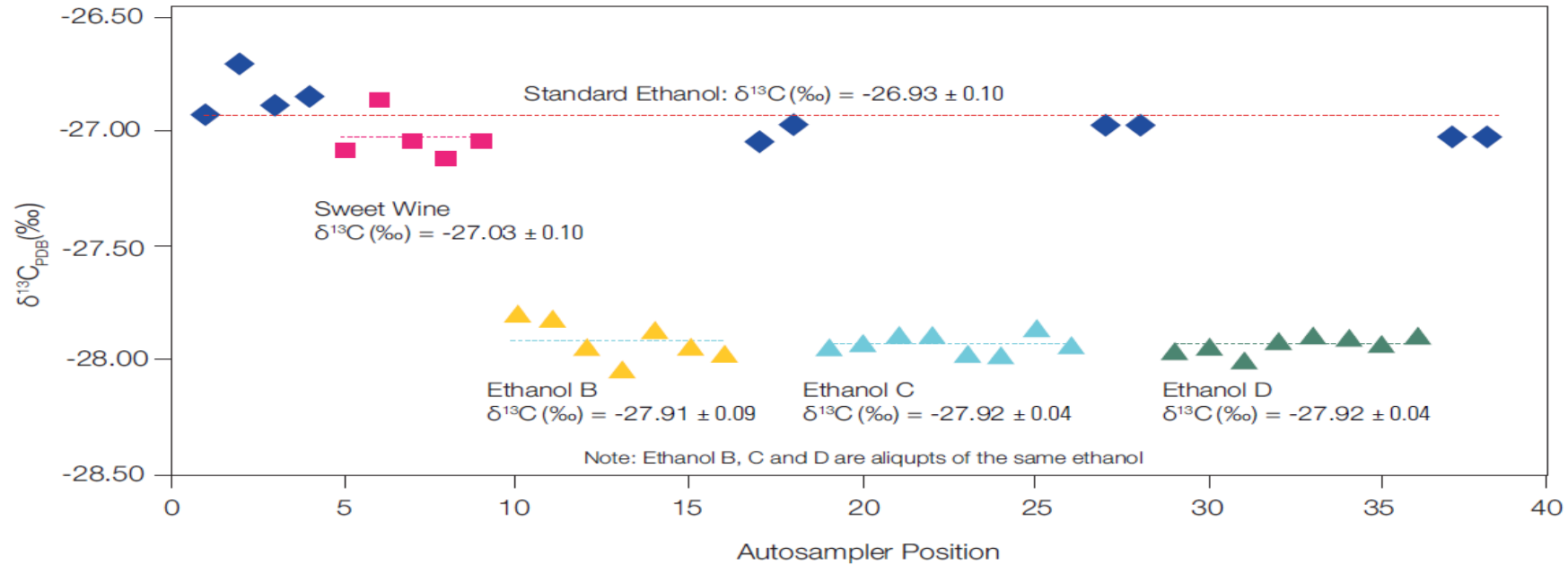


Analysis time: 10 mins
He flow: 100 ml/min
Total He: 1.5 liters per sample

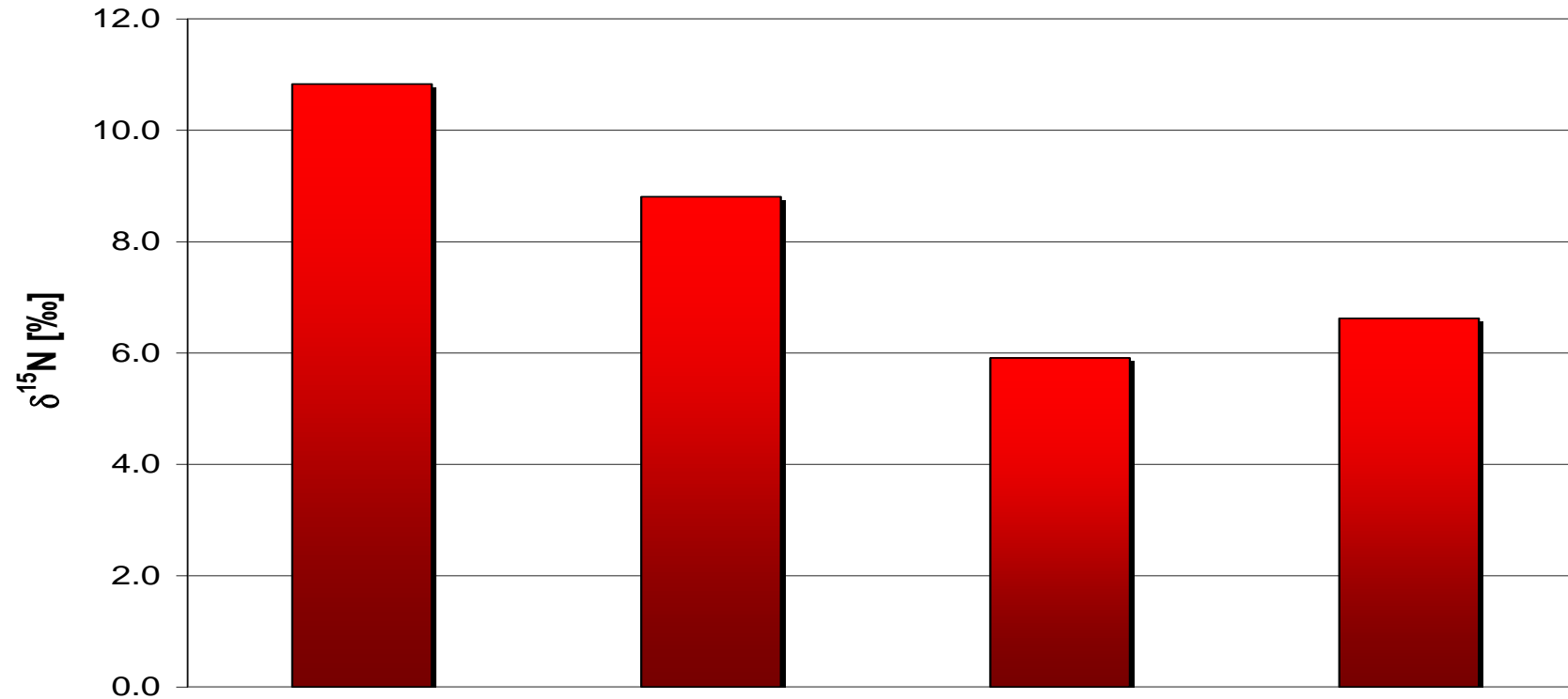
**>60% He saving per
NCS sample**

For further information go to www.thermofisher.com and search for EA IsoLink IRMS

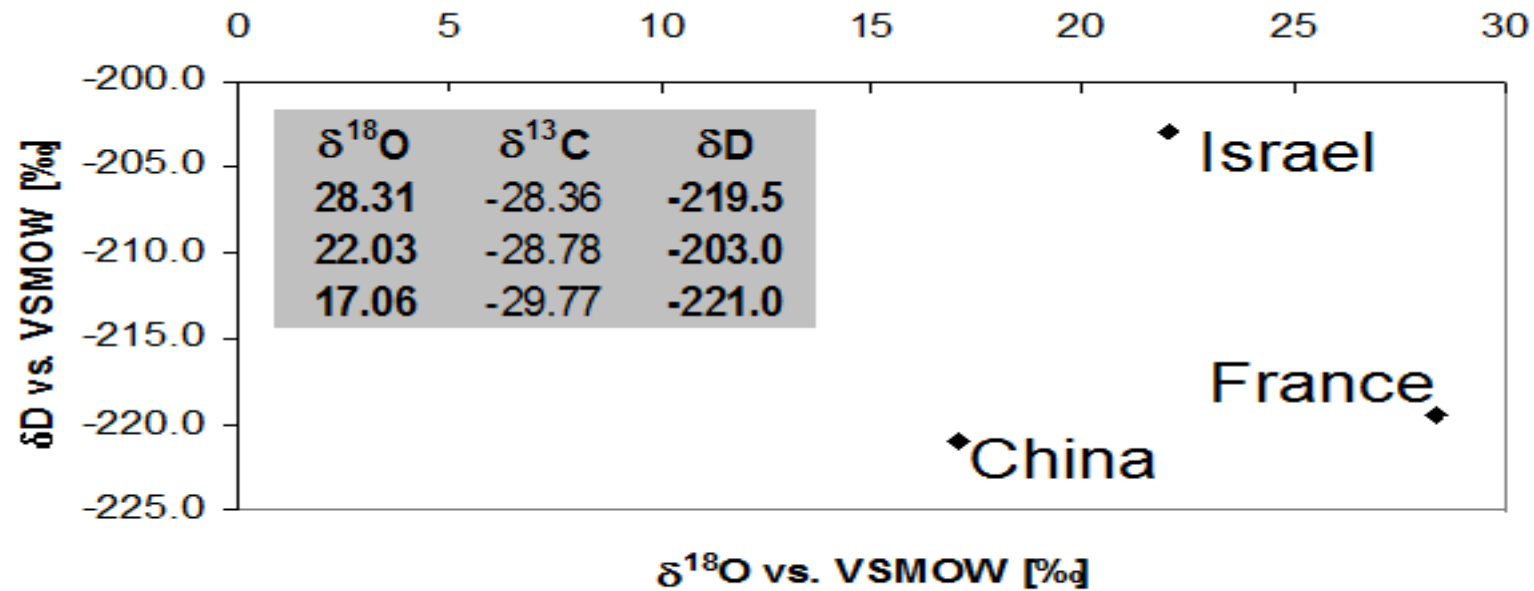
EA-IRMS: C analysis of ethanol



- $\delta^{13}\text{C}$ can be used to determine if wines have been adulterated with sugar
 - See Applications note AN30147



- Depending on the fertilizer the N isotope signature in plants can differ. Mineral fertilizers show low $\delta^{15}\text{N}$ values while organic fertilization by compost results in higher $\delta^{15}\text{N}$ values.
- This allows discrimination of organic from non-organic produced vegetables.



- Edible oils are commonly protected by regional designations (PDO) and subject to strong quality controls. This makes them a target for fraud. The example shows that O and H isotopes can distinguish between oils of different geographical origin.

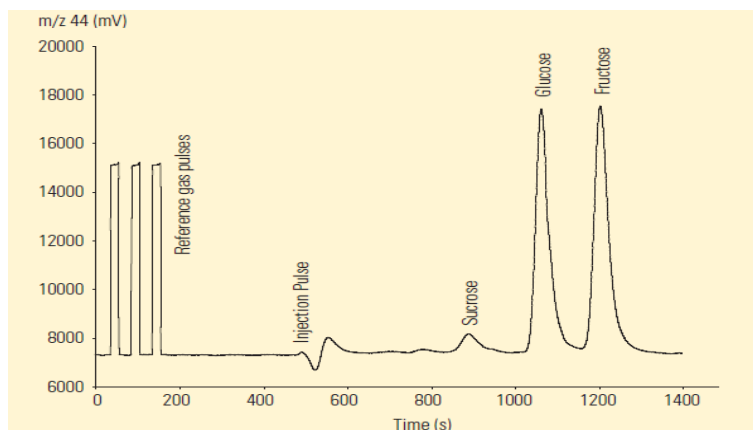
Extending the application of EA-IRMS: Honey adulteration

- Problem: Addition of cheap sugars to honey
- Current analytical approach:
 - EA-IRMS to assess $\delta^{13}\text{C}$ value of honey and its protein fraction (limit of detection $\sim 7\%$ of C4 sugar addition)
 - Low sensitivity for sugars analysis, so need an enhanced approach
- Solution: irm-LC/MS using the LC IsoLink™ interface allows:
 - Comparison of $\delta^{13}\text{C}$ value of different sugars
 - Determination of the sugar pattern
 - Higher sensitivity - 100x more sensitive than direct EA-IRMS
- See our application note AN30024 - Testing honey adulteration by $\delta^{13}\text{C}$ -EA/LC-IRMS for full details

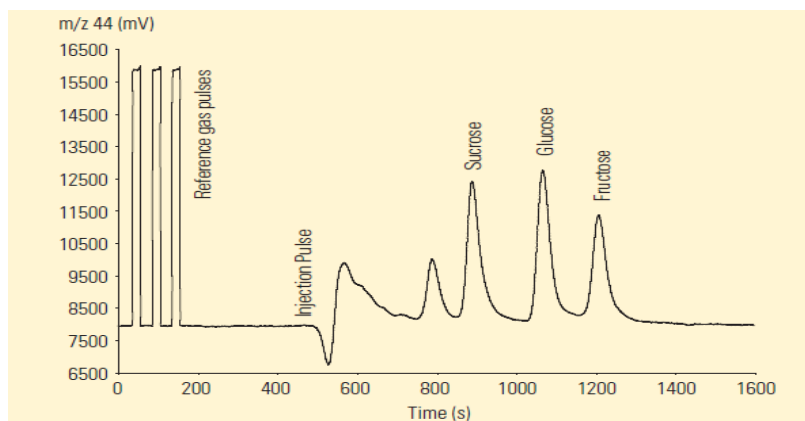


Honey adulteration examples

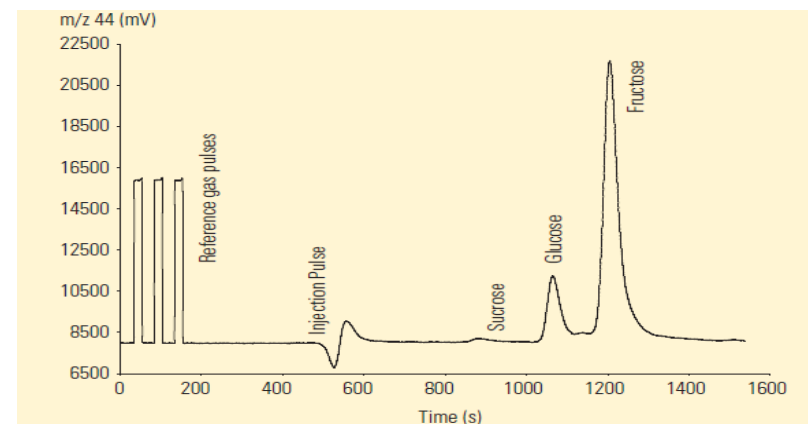
HONEY	SUCROSE ‰	GLUCOSE ‰	FRUCTOSE ‰	FRU/GLU RATIO OF AREAS	EA HONEY(4) ‰	EA PROT.(4) ‰	ADULT.(4) %	
1	-23.3	-23.2	-22.9	1.07	-21.8	-24.2	16.7	adulterated
2	-11.3	-11.2	-13.9	0.65	-11.9	n.a.	n.a.	adulterated
3	-25.3	-24.9	-24.9	1.42	-24.8	-24.8	0.0	
4	-26.4	-26.5	-26.4	0.97	-25.4	-21.6	0.0	
5	n.d.	-26.1	-26.0	4.53	-25.8	-26.1	1.9	adulterated
6	-26.1	-25.0	-25.3	1.62	-24.3	-24.3	0.0	
7	-25.0	-25.2	-25.1	1.16	-24.2	-24.7	3.4	
8	n.d.	-25.1	-26.4	2.17	-24.8	-25.1	1.5	adulterated



Honey 1



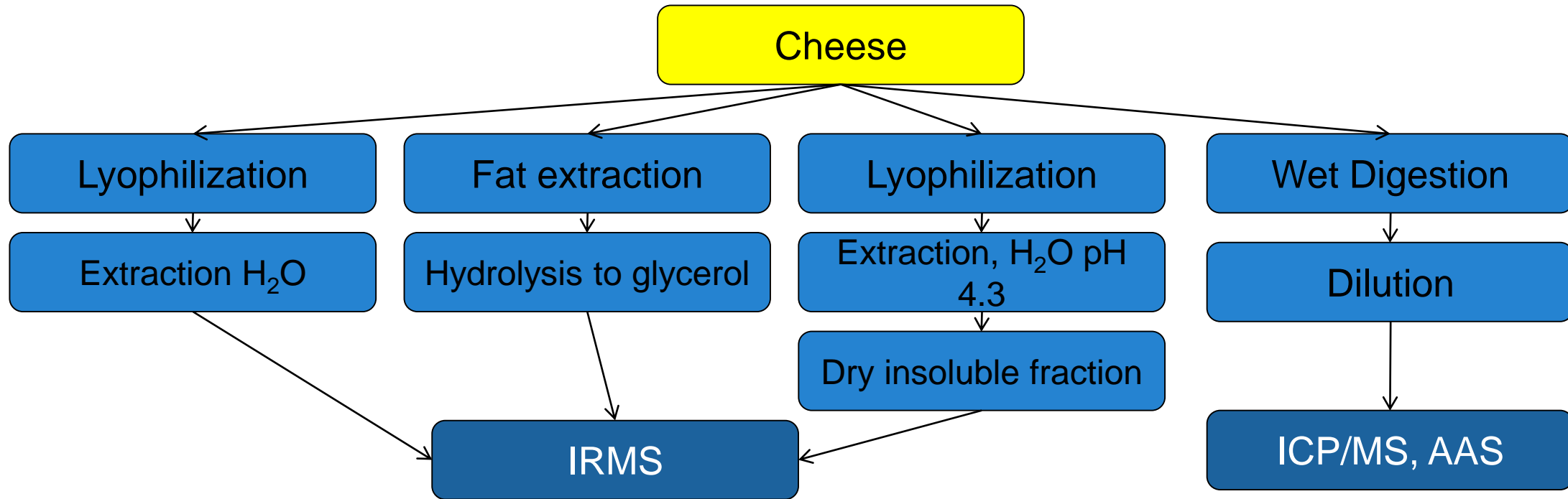
Honey 2



Honey 5

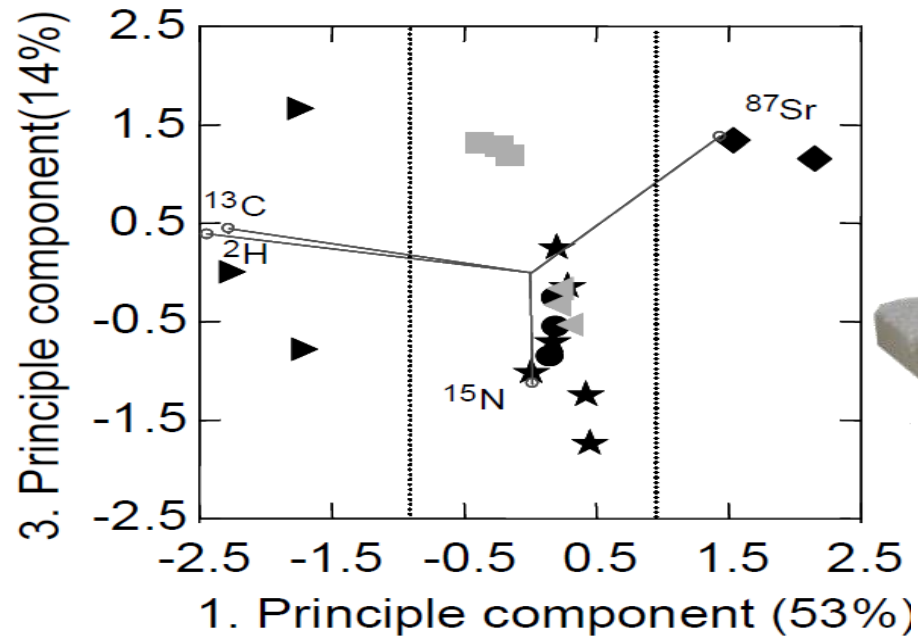
Assessing the origin of European cheeses

- Measurands taken: Stable isotope ratios, major, trace and radioactive elements
- Techniques used: IRMS, AAS, ICP-MS

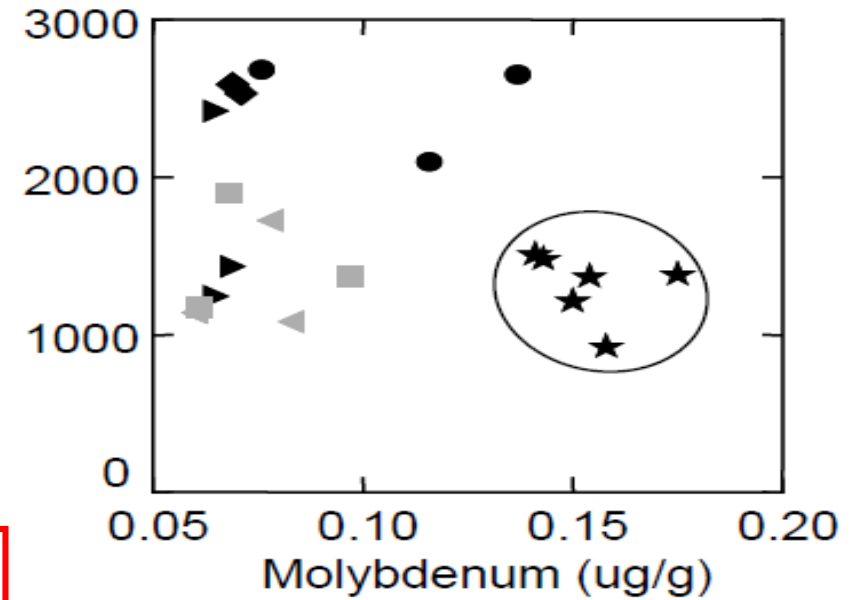


Pillonel L et al, Lebensm.-Wiss. u.-Technol. 36 (2003) 615–623.

Assessing the cheese origin in Europe



Sodium (ug/g)



- Region**
- Allgäu (D)
 - ▶ Bretagne (F)
 - ◆ Finland
 - Savoie (F)
 - ★ Switzerland
 - ◀ Vorarlberg (A)



Pillonel L et al, *Lebensm.-Wiss. u.-Technol.* 36 (2003) 615–623.

Infrared spectroscopy

- Benefits:
 - Ease of use
 - Fast response
 - No or limited sample preparation
 - Low price
- Limitations:
 - Lower sensitivity
 - Small spectral differences
- Typical examples: Near Infrared Spectroscopy (NIR, FT-NIR)
- Different Sampling accessories:
 - Sample cup spinner – heterogeneous materials
 - SabIR Fiber Optic Probe – material identification
 - Viscous Liquid Sampler – syrups, suspensions
 - Softgel detector (Gum)
 - Fiber Optic probes – in-process testing of solids and liquids



FT-NIR to assess geographic origin of olive oils

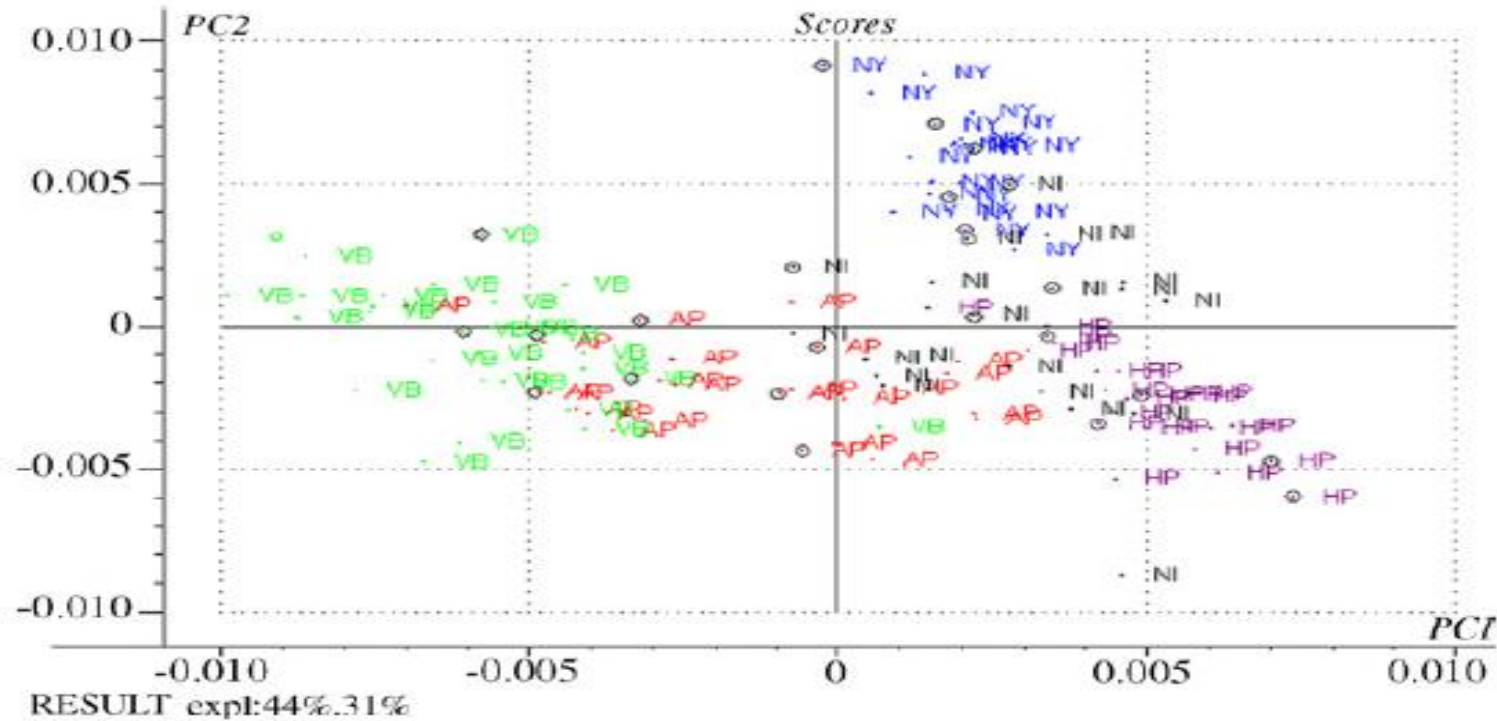
- Antaris FT-NIR with sample cup spinner
- Direct measurement in 2mm path length cell
- 4 cm^{-1} resolution
- Spectral range - 10000 and 4500 cm^{-1}



O. Galtier et al.; Analytica Chimica Acta 595 (2007) 136–144.

FT-NIR to assess geographic origin of olive oils

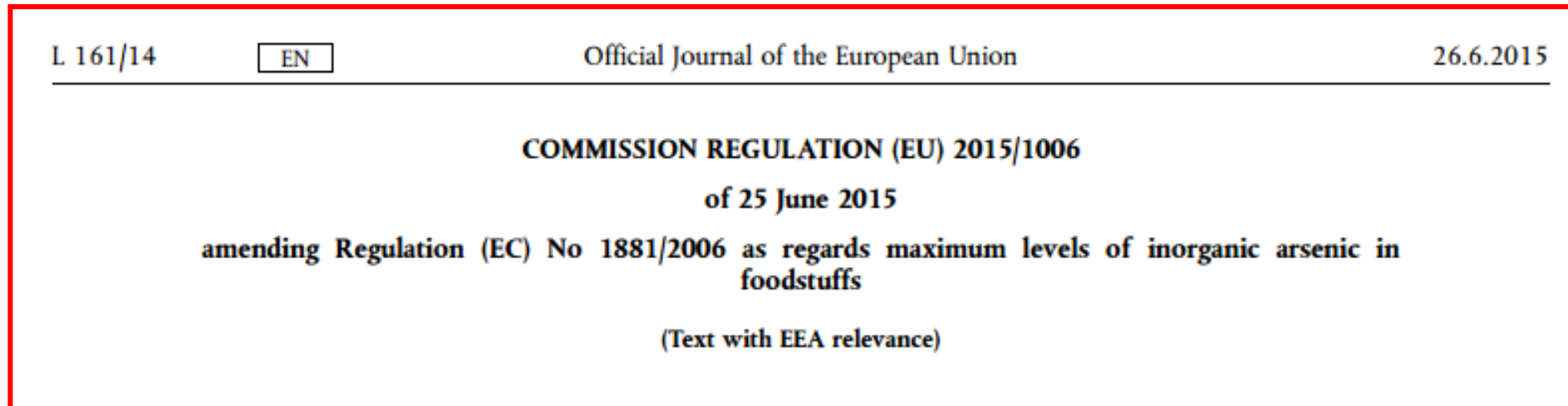
- Quantification of fatty acids and triglycerols
- Classification in registered designation origin



O. Galtier et al.; *Analytica Chimica Acta* 595 (2007) 136–144.

What is the EU 2015/1006 regulation and how does it impact arsenic measurement in foods?

- It is an amendment to COMMISSION REGULATION (EC) No 1881/2006, which covers setting maximum levels for certain contaminants in foodstuffs
- REGULATION (EC) 1881/2006 includes inorganic Pb, Cd, Hg and Sn
- REGULATION (EU) 2015/1006 is the addition of inorganic As to the above list
- It's been developed because:
 - Inorganic arsenic shown to cause cancer (lung, bladder and skin) at exposures levels lower than previously thought
 - High consumers of rice most exposed to inorganic arsenic dietary exposure
 - Dietary exposure for children < 3 years old from rice-based foods is estimated to be about 2 to 3x that of adults



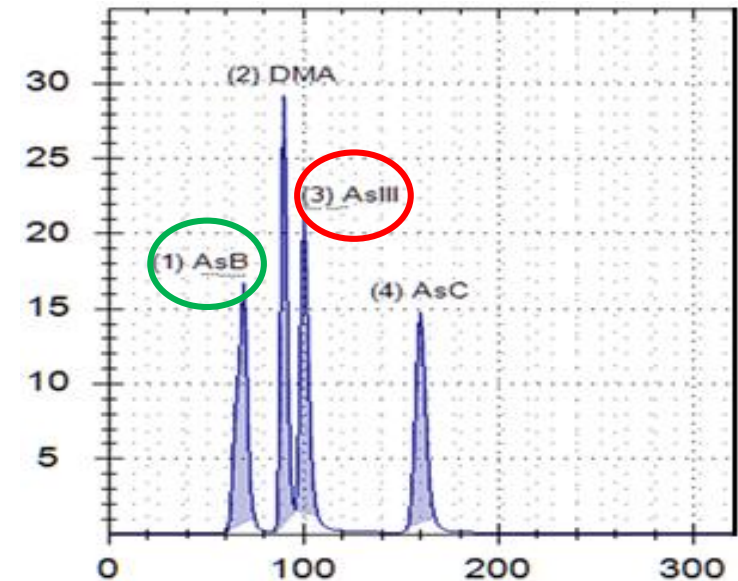
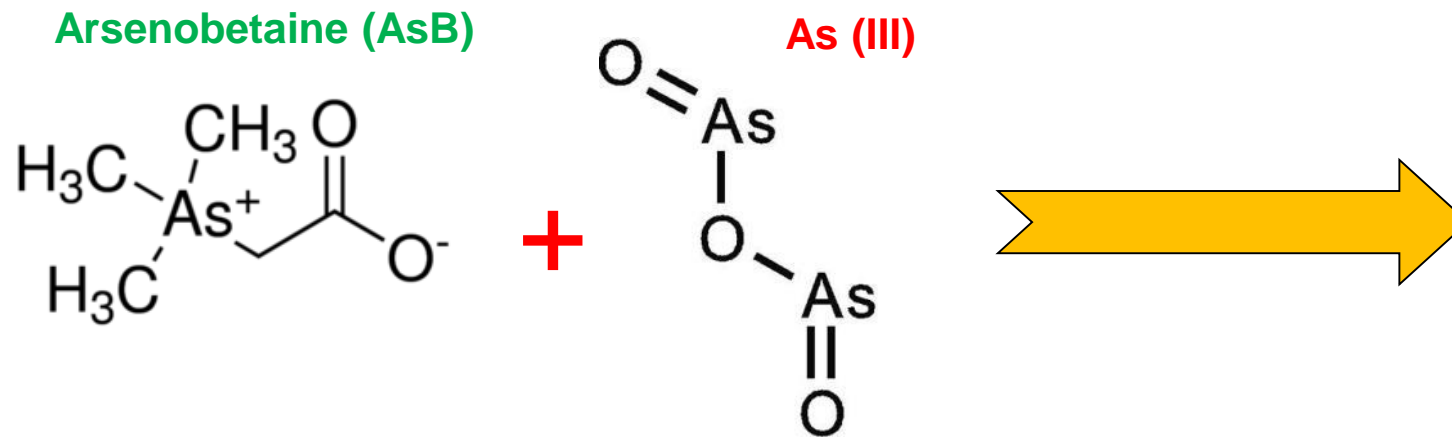
What levels of inorganic arsenic need to be measured and in what samples?

Arsenic (inorganic) ⁽⁵⁰⁾ ⁽⁵¹⁾	Maximum levels (mg/kg wet weight)
Non-parboiled milled rice (polished or white rice)	0,20
Parboiled rice and husked rice	0,25
Rice waffles, rice wafers, rice crackers and rice cakes	0,30
Rice destined for the production of food for infants and young children ⁽³⁾	0,10

- The maximum levels of arsenic specified above apply from 1 January 2016
- The question is, if arsenic is present in your food, how much of it is actually inorganic arsenic?
 - **Just measuring total arsenic could give a false answer; food could be wasted that is actually safe to consume**
- How can you separate inorganic arsenic (As (III) and As (V)) from other arsenic species in the sample?
 - **By applying speciation using ion chromatography coupled to ICP-MS**

What is speciation?

- **Definition** - 'the analytical activity of identifying and/or measuring the quantities of one or more individual chemical species in a sample' **IUPAC**
- **That means** – chemical species of an element are determined rather than the total element concentration
- **Example** – Arsenobetaine and As (III) species separated by ion chromatography (IC) and detected by ICP-MS



Dimethylarsinic acid (DMA) and arsenocholine (AC) peaks also shown

- **Speciation analysis is important as it reveals valuable information about elemental bioavailability, mobility, metabolism and toxicity**

Speciation analysis using IC-ICP-MS

- Fully integrated hardware and software system:
 - Thermo Scientific™ Qtegra™ ISDS drives the whole system and includes:
 - Thermo Scientific Chromeleon™ plug-in drivers to control IC or HPLC
- Single control software
 - One software interface controls both the ICS and the ICP-MS
 - Includes all required functionality for fully automated data collection, calibration, quantitation and results reporting
 - Simple hardware connection – inert, metal free tubing connection from IC output to ICP-MS nebuliser



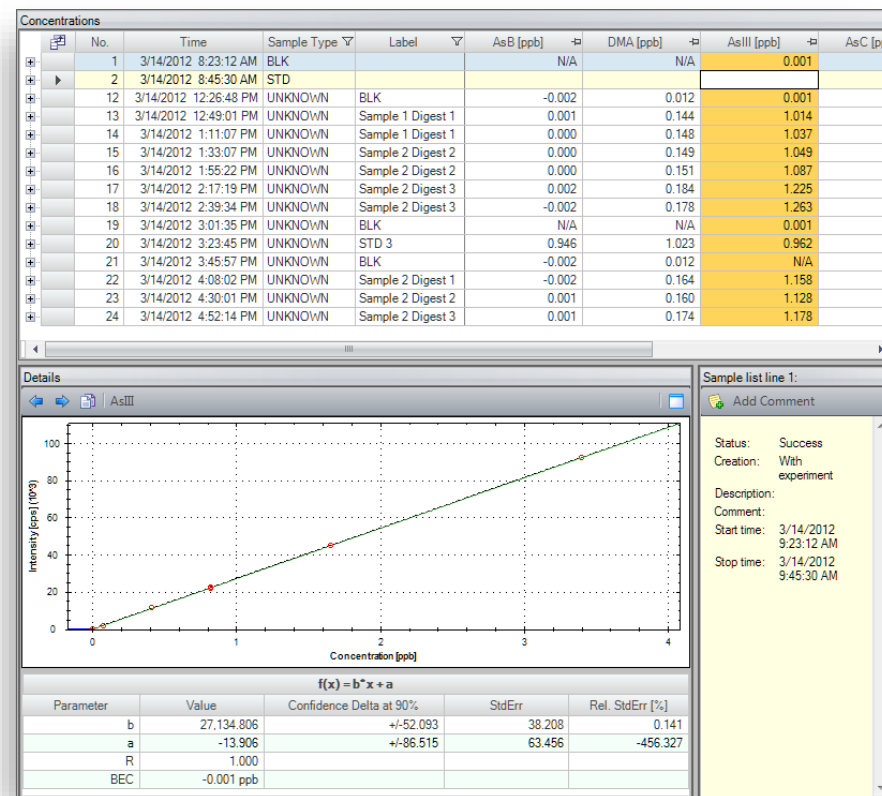
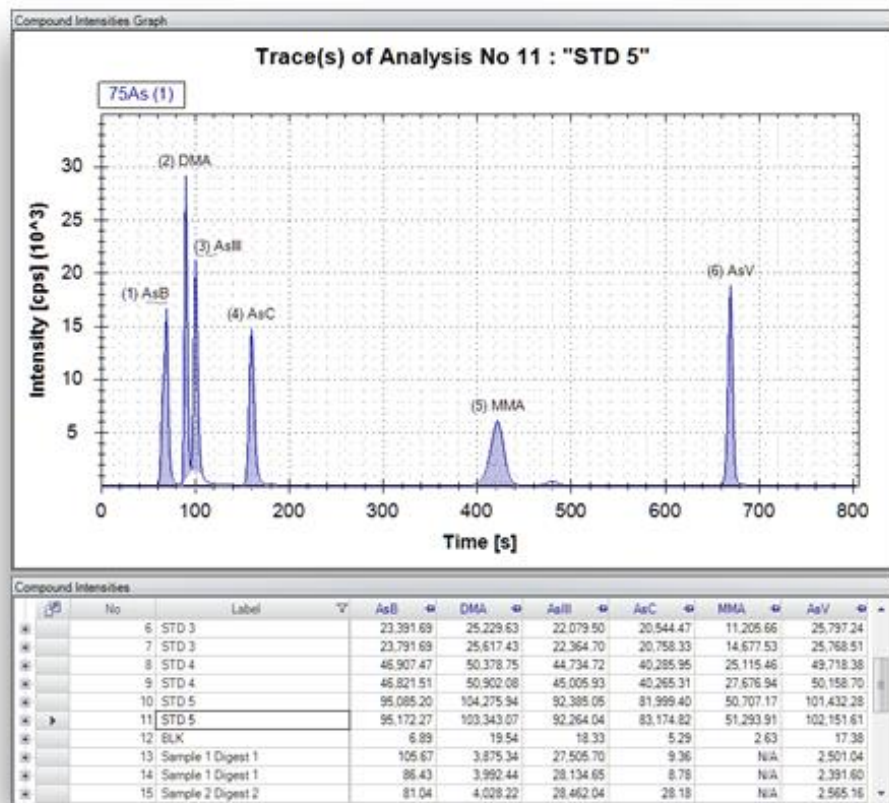
**Thermo Scientific™
Dionex™ ICS-5000+**



**Thermo Scientific™
iCAP™ RQ**

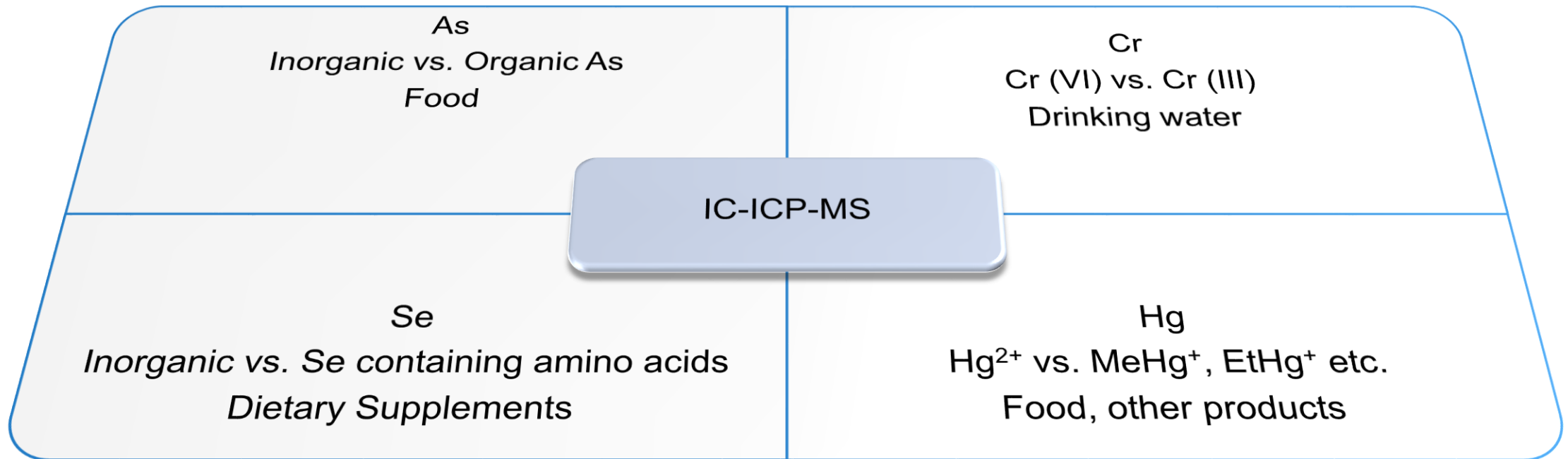
IC-ICP-MS is ideally suited to trace elemental speciation

Qtegra ISDS: Full feature set for chromatography



Definition of compounds, retention times with automated peak detection.
 Compound specific calibration graphs generated using the same workflow used in total element determinations

Overview of the range of IC-ICP-MS applications



Applications covered in this presentation:-

- Arsenic speciation in organic brown rice syrup
- Total arsenic quantification in food samples

Example application 2: Arsenic in organic brown rice syrup (OBRS)

- Rice is well known to accumulate As and can contain high amounts of this element
- Organic brown rice syrup is commonly used as a sweetener for toddler formulas and cereals
 - Healthier alternative to fructose containing corn syrups
- OBRS is also used in cereal bars and energy products for endurance athletes



Example application 2: Arsenic in organic brown rice syrup (OBRS) - results

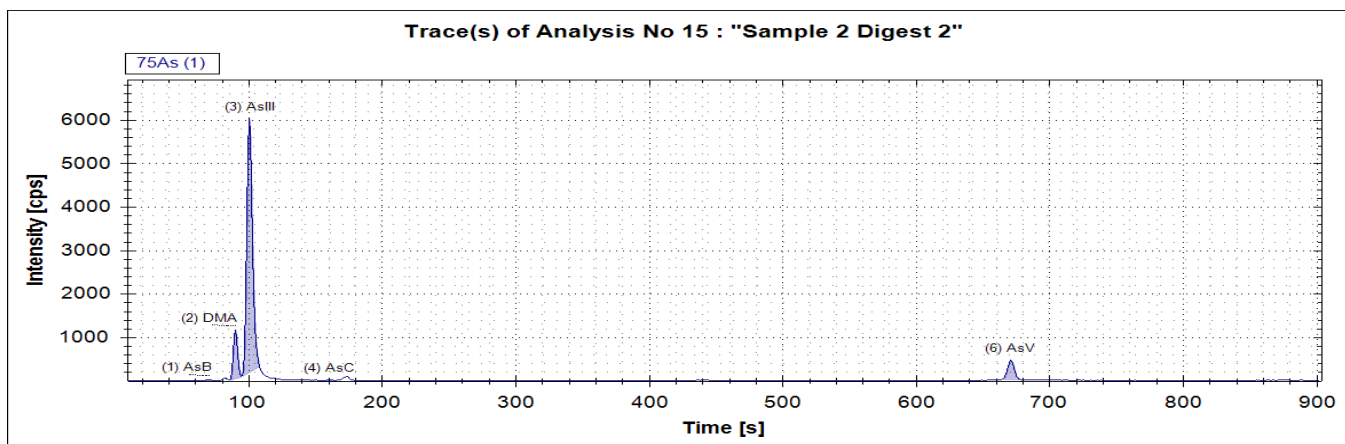
- Three different samples were sourced in Germany
- Total As determination: Closed vessel microwave digestion¹
 - 0.5 g sample + 4 mL of 50% HNO₃, 10 minutes @ 180°C
 - Dilution to 20 mL total volume
 - Further dilution prior to measurement
- All samples contained $\geq 100 \mu\text{g kg}^{-1}$ As (which is the maximum level allowed in EU 2015/1006 for rice products for young children)
 - Sample 1: $118 \pm 7 \mu\text{g kg}^{-1}$
 - Sample 2: $136 \pm 7 \mu\text{g kg}^{-1}$
 - Sample 3: $107 \pm 11 \mu\text{g kg}^{-1}$
- Other studies have indicated that even higher As levels can be found in OBRS (between 80 - 400 $\mu\text{g kg}^{-1}$)
- Speciation analysis was then conducted for all samples



1: Jackson, B. P. et al., Environmental Health Perspective, doi 10.1289/ehp.1104619

Example application 2: Arsenic in organic brown rice syrup (OBRS) - results

- Species extraction: Open vessel extraction²
 - 1.5 g sample + 15mL of 1% HNO₃, 90 minutes under reflux
 - Centrifugation + filtration
 - Dilution to 20 mL total volume + further dilution prior to measurement



Species distribution %	DMA	As III	As V	Sum
Sample 1	12%	82%	6%	100%
	12%	82%	6%	100%
	12%	81%	7%	100%
Sample 2	12%	83%	5%	100%
	12%	83%	5%	100%
	12%	82%	6%	100%
Sample 3	10%	84%	6%	100%
	10%	87%	3%	100%
	11%	86%	3%	100%

- Most abundant species was As (III), but As (V) was also present
- Most abundant organic As species was DMA
- Arsenobetaine was also detected
- Extraction efficiency was determined to be 74-78%

2: Huang et al., J. Anal. At. Spectrom. **25** (2010), 800-802

Example application 2: Total arsenic quantification in food samples

- Rice flour and chicken reference materials selected for this analysis
 - Rice Flour IRMM-804 and Chicken NCS ZC73016
- Multi-element determination, including As
 - Closed vessel microwave digestion
 - 0.5g of sample acid digested using a mixture of HNO_3 and HCl
- Reference materials analysed 5 times each during an extended run of 80 other digested food samples to test analysis repeatability
- Samples analysed using a Thermo Scientific™ iCAP™ RQ ICP-MS



Example application 3: Rice Flour IRMM-804 results

Isotope	Measured	Certified
^{55}Mn	35800 ± 470	34200 ± 2300
^{65}Cu	2650 ± 30	2740 ± 240
^{66}Zn	23100 ± 270	23100 ± 1900
^{75}As	52.3 ± 0.8	49 ± 4
^{78}Se	35.1 ± 1.0	38 (Reference value)
^{111}Cd	1620 ± 9	1610 ± 70
^{208}Pb	460 ± 8	420 ± 70



Example application 3: Chicken NCS ZC73016 results

Isotope	Measured	Certified
⁷ Li	28 ± 1	34 ± 7
¹¹ B	730 ± 23	760 ± 130
²³ Na (ppm)	1310 ± 25	1440 ± 90
²⁵ Mg (ppm)	1200 ± 22	1280 ± 100
³¹ P (ppm)	8950 ± 220	9600 ± 800
³⁴ S (ppm)	8310 ± 220	8600 ± 500
³⁹ K (ppm)	14000 ± 480	14600 ± 700
⁴⁴ Ca (ppm)	200 ± 4	220 ± 20
⁵² Cr	450 ± 10	590 ± 110
⁵⁵ Mn	1640 ± 20	1650 ± 70

Isotope	Measured	Certified
⁵⁶ Fe	32700 ± 260	31300 ± 3000
⁶⁰ Ni	153 ± 2	150 ± 30
⁶⁵ Cu	1350 ± 11	1460 ± 120
⁶⁶ Zn	25300 ± 220	26000 ± 1000
⁷⁵ As	115 ± 1	109 ± 13
⁷⁸ Se	549 ± 11	490 ± 60
⁸⁸ Sr	611 ± 11	640 ± 80
⁹⁸ Mo	112 ± 1	110 ± 10
¹³⁸ Ba	1610 ± 16	1500 ± 400
²⁰⁸ Pb	90.7 ± 2.0	110 ± 20



Example application 3: Rice Flour IRMM-804 results – precision during the run (n=5)

Isotope	Mean	Standard deviation	% RSD
⁵⁵ Mn	35500	170	0.5
⁶⁵ Cu	2670	11	0.4
⁶⁶ Zn	23400	170	0.7
⁷⁵ As	52.7	0.7	1.4
⁷⁸ Se	34.7	0.5	1.3
¹¹¹ Cd	1630	11	0.7
²⁰⁸ Pb	490	3.9	0.8



Example application 3: Chicken NCS ZC73016 results – precision during the run (n=5)

Isotope	Mean	Standard deviation	% RSD
⁷ Li	29	0.6	1.9
¹¹ B	720	14	1.9
²³ Na (ppm)	1380	18	1.3
²⁵ Mg (ppm)	1170	13	1.1
³¹ P (ppm)	8700	150	1.7
³⁴ S (ppm)	8230	150	1.9
³⁹ K (ppm)	13800	240	1.8
⁴⁴ Ca (ppm)	196	3.3	1.7
⁵² Cr	440	4.2	0.9
⁵⁵ Mn	1630	13	0.8



Isotope	Mean	Standard deviation	% RSD
⁵⁶ Fe	32600	225	0.7
⁶⁰ Ni	149	1.2	0.8
⁶⁵ Cu	1330	9	0.7
⁶⁶ Zn	25200	150	0.6
⁷⁵ As	114	1.0	0.9
⁷⁸ Se	550	8.9	1.6
⁸⁸ Sr	616	9.7	1.6
⁹⁸ Mo	113	2.1	1.9
¹³⁸ Ba	1620	23	1.4
²⁰⁸ Pb	89.8	0.9	1.0



Summary and conclusions

- Isotope Ratio Mass Spectrometry shown to be an ideal approach for food authenticity testing
 - Provides high isotope ratio accuracy and precision enabling clear identification of adulteration or provenance of food products
 - Covers a wide range of isotope groups – C, H, N, S and O
- Elemental analysis can provide additional information to IRMS
- Hyphenation of ion chromatography with ICP-Q-MS shown to be effective for speciation analysis of As in rice product samples
 - Excellent MDL obtained due to high sensitivity of iCAP Q
 - Narrow chromatographic peaks improve detection sensitivity
 - Low flow rates reduce sample- and mobile phase consumption
 - Ideal technique for meeting the demands of the EU COMMISSION REGULATION (EU) 2015/1006 relating to inorganic As in rice products
- Total arsenic quantification in food samples using ICP-MS demonstrated
 - Single analysis mode (He gas with kinetic energy discrimination) for multi-element analysis including As
 - Accurate and precise results obtained, with good internal standard robustness throughout the run

Available IC-ICP-MS application notes

Determination of Inorganic Arsenic in Rice using IC-ICP-MS

Andreas Flaab', Shona McSheehy Duoss', Thermo Fisher Scientific, Bremen

Key Words: Arsenic, Codex Alimentarius, Rice, ICP-MS

Goal: Demonstrate how the coupling of IC with ICP-MS meets the requirements in the field of arsenic detection.

Introduction: The ability of rice to accumulate quantities of arsenic compounds, like arsenite, in rice grain, contains dimethylarsinic acid (DMA), in rare cases of tetramethylarsenic, and the speciation and growth cycle in North America have often no origin in rice, making it important to make an informed decision regarding legislation in rice (and other) for variable health effects. Whereas inorganic arsenic is far less toxic compared to fully arsenated, legislation therefore requires the quantification of arsenic in rice potentially dozens of times more than the detection systems. The combination of arsenic detection systems for separation with ICP-MS.

Key Words: Bromide, Drinking Water, EPA 321.8, Inductively Coupled Plasma Mass Spectrometry, Ion Chromatography, Speciation

Goal: Speciate and quantify bromine (Br) species in ion chromatography (IC) coupled with Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Applying the EPA method 321.8 for bromate detection in drinking water.

Introduction: Bromine speciation in drinking water is a major regulatory lead (MCL) of 10 mg/L in water and in the EU of 3 mg/L and spring water treated by ozonation. As a common water disinfectant formed by the oxidation of bromide, whereas bromine is toxic and carcinogenic. Differentiating bromate from bromide is due to the toxicity difference. Bromine analysis with IC-ICP-MS has the lowest sensitivity in ICP-MS. The United States Environmental Protection Agency (EPA) has developed several methods for bromate detection in drinking water (EPA 816-0104-4 and 15041) all Thermo Scientific™ Dionex AN10A, AN11, AN15A Thermo Scientific™ Dionex AS10A, AS11, AS15A. The EPA Method 321.8 for bromate detection in drinking water (EPA 816-0104-4 and 15041) is the only method that uses IC-ICP-MS. Various methods for bromate detection in drinking water (EPA 816-0104-4 and 15041) are the only methods that use IC-ICP-MS.

Speciation of Bromine Compounds in Ozonated Drinking Water using Ion Chromatography and Inductively Coupled Plasma Mass Spectrometry

Antonia Guzman', Shona McSheehy Duoss', Daniel Kutscher', Carl Fisher', Thermo Fisher Scientific, Bremen, Germany, Thermo Fisher Scientific, Sunnyvale, CA, USA

Key Words: Bromine, Ion Chromatography (IC), Speciation, Toxins

Goal: To answer the need for trace level determination of several elements and hazardous chromium that migrates from toy materials at limits outlined in EU directive 2009/48/EC.

Introduction: Hexavalent chromium (Cr (VI)) is highly toxic and classified as a carcinogen. Trivalent chromium (Cr (III)), however, is essential for enzymatic function in human metabolism. The distinction between the oxidation states is therefore essential for an accurate risk assessment of chromium in materials we are exposed to.

The European Union directive for toy safety (2009/48/EC) is currently under revision, and the proposed limits for Cr (VI) content are analytically challenging with commonly used methods. For example, High Pressure Liquid Chromatography (HPLC) coupled to Inductively Coupled Plasma Mass Spectrometry (ICP-MS) may not be suitable as high elemental chromium backgrounds push detection limits above the directive specified values. In this paper, the use of Ion Chromatography (IC) is shown to be a powerful alternative to HPLC, allowing the analysis of both Cr species in the low ng L⁻¹ range. Although IC-ICP-MS chromatographic separation of the two species is simple, sample preparation plays an important role. Depending on sample conditions (e.g. pH), inter-species conversion may occur prior to quantification producing inaccurate species distribution. In this application note, we present a method for total elemental quantification (TEQ) and for stabilization and quantification of Cr (VI) after migration from toy material and its sensitive detection at the 2009/48/EC directive required levels.

Sample and Calibration Solution Preparation: Three different samples were analyzed: finger paint, pen ink and a titanium dioxide (TiO₂) raw material that is commonly used as a white pigment in many different toy products.

To evaluate the method for the determination of total elemental concentrations, each element outlined in the EU directive was spiked into the finger paint sample at different concentrations and analyzed by ICP-MS. All samples were subjected to the migration process as described in the European Standard EN 71-3:2012-3. This Standard Operating Procedure (SOP) has been recently updated and as the time of publication of this application note has not been officially released to the public. In the migration solution, Cr (VI) is prone to slow reduction in the acidic environment and a stabilization step is necessary after migration is completed to maintain the original species distribution.

The Migration of Elements from Toys and Speciation of Chromium (VI) in Toy Material Using a IC-ICP-MS Solution

Daniel Kutscher, Shona McSheehy Duoss, Lutz Patzmann, Thermo Fisher Scientific, Germany

Key Words: Chromium, Ion Chromatography (IC), Speciation, Toxins

Goal: To answer the need for trace level determination of several elements and hazardous chromium that migrates from toy materials at limits outlined in EU directive 2009/48/EC.

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IC-ICP-MS speciation analysis of As in apple juice using the Thermo Scientific iCAP Q ICP-MS

Daniel Kutscher, Shona McSheehy, Julian Willis, Thermo Fisher Scientific, Germany, Dorel Jensen, Thermo Fisher Scientific, Switzerland

Key Words: Arsenic, Apple Juice, ICP-MS, Speciation

Goal: Demonstrate the use of IC-ICP-MS for the speciation of arsenic in apple juice.

Introduction: Arsenic is a naturally occurring element found in various forms in the environment. Inorganic arsenic is highly toxic and is classified as a carcinogen. Organic arsenic species, such as dimethylarsinic acid (DMA) and trimethylarsinic acid (TMA), are less toxic and are not classified as carcinogens. The speciation of arsenic is important for risk assessment and regulatory compliance. The Thermo Scientific iCAP Q ICP-MS is a high-resolution ICP-MS that is capable of speciating arsenic in complex matrices like apple juice. The use of IC-ICP-MS allows for the separation of arsenic species before detection, ensuring accurate and sensitive results.

IC-ICP-MS speciation analysis of As in Organic Brown Rice Syrup (OBRs) using the Thermo Scientific iCAP Q ICP-MS

Daniel Kutscher, Julian Willis and Lutz Patzmann, Thermo Fisher Scientific, Germany and Dorel Jensen, Thermo Fisher Scientific, Switzerland

Key Words: Arsenic, Organic Brown Rice Syrup, ICP-MS, Speciation

Goal: Demonstrate the use of IC-ICP-MS for the speciation of arsenic in organic brown rice syrup.

Introduction: Arsenic is a naturally occurring element found in various forms in the environment. Inorganic arsenic is highly toxic and is classified as a carcinogen. Organic arsenic species, such as dimethylarsinic acid (DMA) and trimethylarsinic acid (TMA), are less toxic and are not classified as carcinogens. The speciation of arsenic is important for risk assessment and regulatory compliance. The Thermo Scientific iCAP Q ICP-MS is a high-resolution ICP-MS that is capable of speciating arsenic in complex matrices like organic brown rice syrup. The use of IC-ICP-MS allows for the separation of arsenic species before detection, ensuring accurate and sensitive results.

Speciation analysis of Cr (III) and Cr (VI) in drinking waters using anion exchange chromatography coupled to the Thermo Scientific iCAP Q ICP-MS

Daniel Kutscher, Shona McSheehy, Julian Willis, Thermo Fisher Scientific, Germany, Dorel Jensen, Thermo Fisher Scientific, Switzerland

Key Words: Chromium, Ion Chromatography, Drinking water, ICP-MS

Goal: To develop a sensitive, robust and high throughput method for the trace level analysis of Cr (III) and Cr (VI) species in natural waters using IC-ICP-MS.

Introduction: Due to its widespread use in industrial applications such as chromium plating, the manufacturing and preservation of wood and leather materials, chromium concentrations in environmental samples are monitored on a routine basis. Both the United States EPA and the European Union have specified maximum admissible chromium concentrations in their respective drinking water directives. As with many other trace elements, chromium (Cr) is typically found in more than one chemical form, each of which with different chemical properties and behavior, such as bioavailability and toxicity. For chromium, Cr (III) is essential to human beings and involved in different processes in the body while Cr (VI) is highly toxic. Total Cr content therefore is, for example, a drinking water sample does not provide sufficient information to evaluate potential hazards to populations exposed to it. In order to provide this critical information a supporting speciation analysis is required to determine the amounts of the different Cr species in the sample. The speciation analysis of Cr however is a challenging task, since the stability of different Cr species is easily affected by conditions during sample collection and treatment. For example, low pH values may lead to the degradation of Cr (VI) to Cr (III) due to the increased redox potential, while high pH values may lead to the precipitation of Cr (III) as Cr(OH)₃. An additional difficulty in the accurate speciation analysis of Cr by ICP-MS are the numerous spectral interferences (e.g. ¹⁰²Sn⁺ or ¹⁰²Ag⁺) on the most abundant chromium isotope, ⁵²Cr.

IC-ICP-MS speciation analysis of As in apple juice using the Thermo Scientific iCAP Q ICP-MS

Daniel Kutscher, Shona McSheehy, Julian Willis, Thermo Fisher Scientific, Germany, Dorel Jensen, Thermo Fisher Scientific, Switzerland

Key Words: Arsenic, Apple Juice, ICP-MS, Speciation

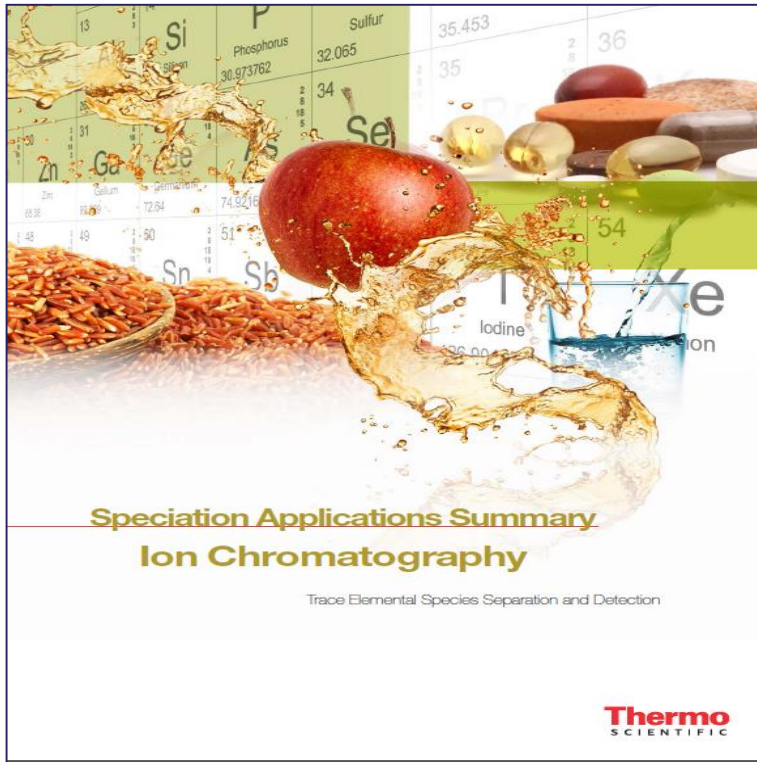
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These notes and other useful information can be accessed by searching for 'iCAP RQ (or iCAP Q) applications notes' at thermofisher.com

Other resources

- AN 70590 Ion Chromatography Speciation Applications Summary
- PO 64596 TEA Speciation Poster



A Guide to Trace Elemental Speciation

What is elemental speciation?
IUPAC Definition – "the analytical activity of identifying and/or measuring the quantities of one or more individual chemical species in a sample"
That means – chemical species of an element are determined rather than the total element concentration
Examples – Methylmercury, tributyltin, arsenobetaine

Why is speciation important?
Elemental speciation data can reveal valuable information in addition to total element concentrations such as:

- Environmental Fate
- Bioavailability
- Mobility
- Reactivity
- Toxicity
- Process Control Chemistry

What sample types is speciation analysis applied to?
Speciation analysis is useful for a wide range of sample types, including foodstuffs and beverages, environmental samples, biological specimens and even petrochemicals. Key applications include As in rice and fruit juice and Cr in potable water.

What instrumentation is used for elemental speciation?
Liquid chromatography (either HPLC or IC) connected to ICP-MS
Used for e.g. As, Cr, Se and I speciation
Gas chromatography connected to ICP-MS
Used for e.g. Hg, S and Sn speciation

What steps make up the speciation analysis workflow?

Extraction	Separation	Detection
Sample containing various compounds Need to preserve original species composition, so require pH control and mild extraction conditions to ensure non-destructive, quantitative extraction	Different separation mechanisms Ion chromatography (IC) High performance liquid chromatography (HPLC) Gas chromatography (GC)	ICP-MS detects the primary element in the species Allows quantification of different compounds containing the same element e.g. As, Cr, Hg, Sn

Speciation analysis performed together with total element concentration measurement – as a rule, the sum of the species should match this concentration

Using IC-ICP-MS for elemental speciation

- Metal-free PEEK systems – lower backgrounds and better detection limits especially for Cr
- Sharp, well resolved peaks with short run times
- Reproducible and sensitive
- Reagent-Free Ion Chromatography Eluent Generation (RFIC-EG) – the ion chromatograph electrolytically creates the eluents and regenerants required for IC applications, as required

Automating speciation analysis using IC-ICP-MS

Requires fully integrated hardware and software system:
Thermo Scientific™ Omega™ ICS drives the whole system and includes:
Thermo Scientific™ Dionex™ Chromelcon™ plug-in drivers to control the IC or HPLC.

Single control software
One software interface controls both the IC and the ICP-MS
Simple hardware connection – inert tubing connection from the IC directly to the ICP-MS nebuliser

Transient chromatographic peaks captured by the Omega software

Peak search and integration capabilities allow species specific calibrations to be generated and concentrations of unknowns to be calculated

Speciation resources

- www.thermoscientific.com/dramatic – ICAP Q Resource Centre
- www.thermoscientific.com/HPC – High Pressure Ion Chromatography
- For more information on speciation analysis in general, visit The European Virtual Institute for Speciation Analysis (EVISA) web site at: <http://www.speciation.net>
- Commission Regulation (EU) 2015/1006 regarding maximum levels of inorganic arsenic in foodstuffs

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- Analyte Guru blog on the new EU legislation on arsenic in rice by Paul Dewsbury:

<http://analyteguru.com/arsenic-in-rice-new-legislation-comes-to-the-boil/>