Joint EURL Workshop
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Ethylene Oxide Crisis – An Overview of the Crisis

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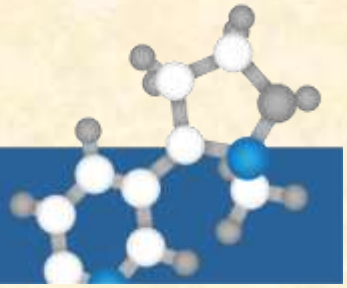
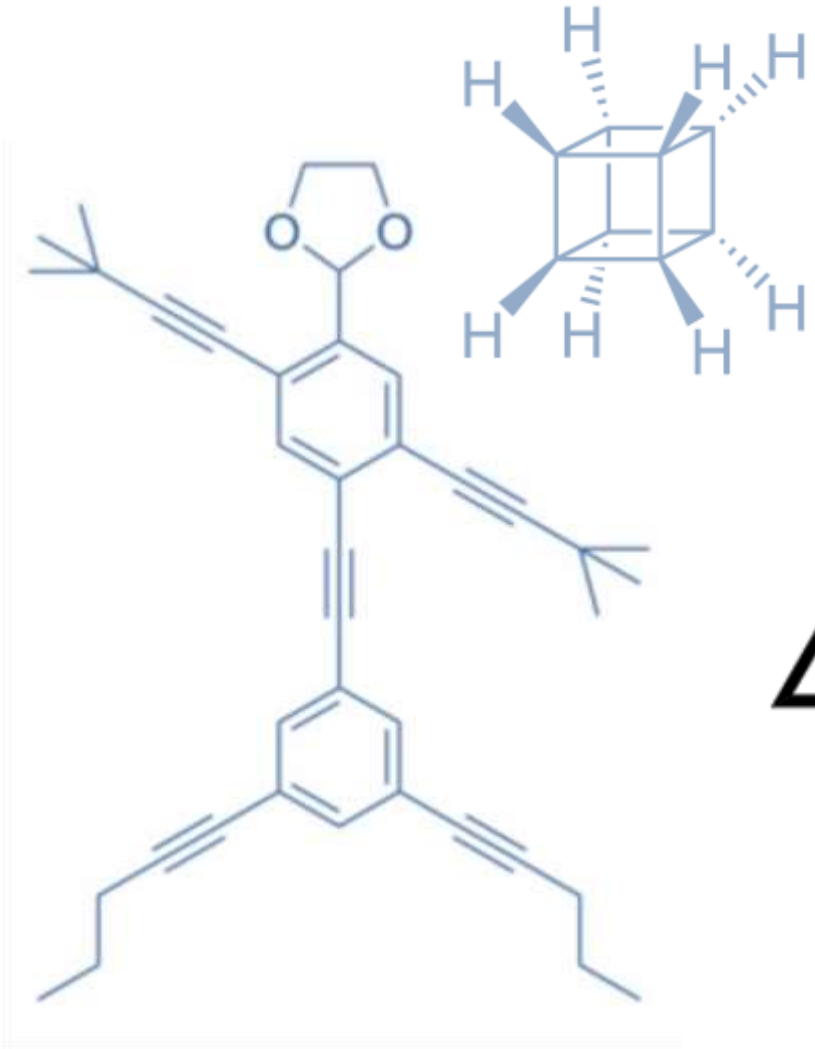
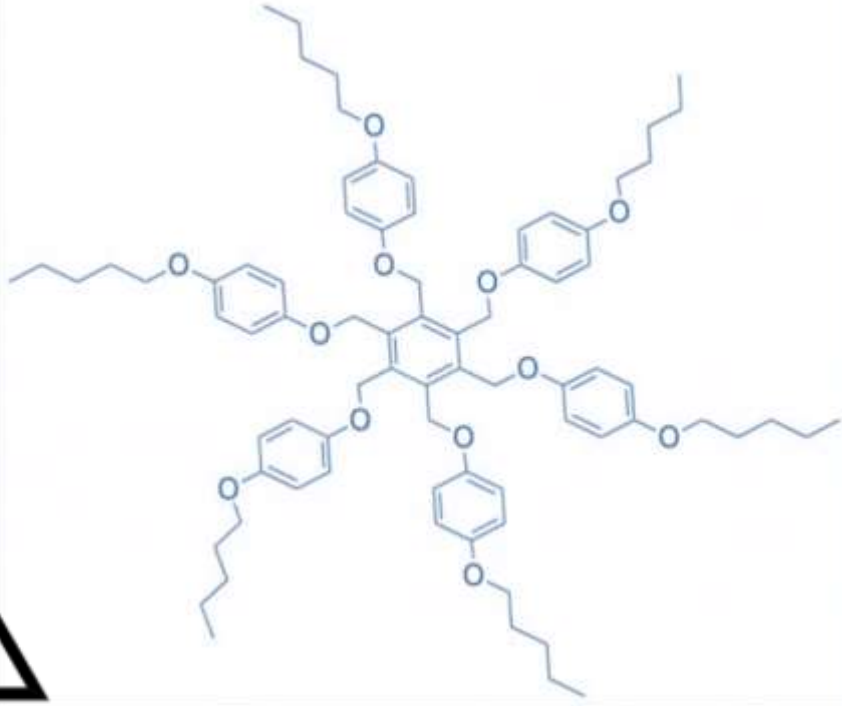
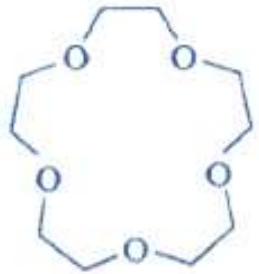
EURL-SRM

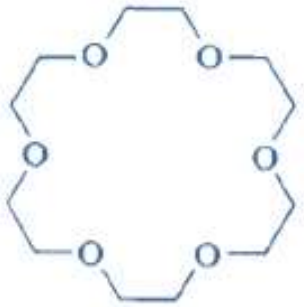


Some molecules look more interesting than others

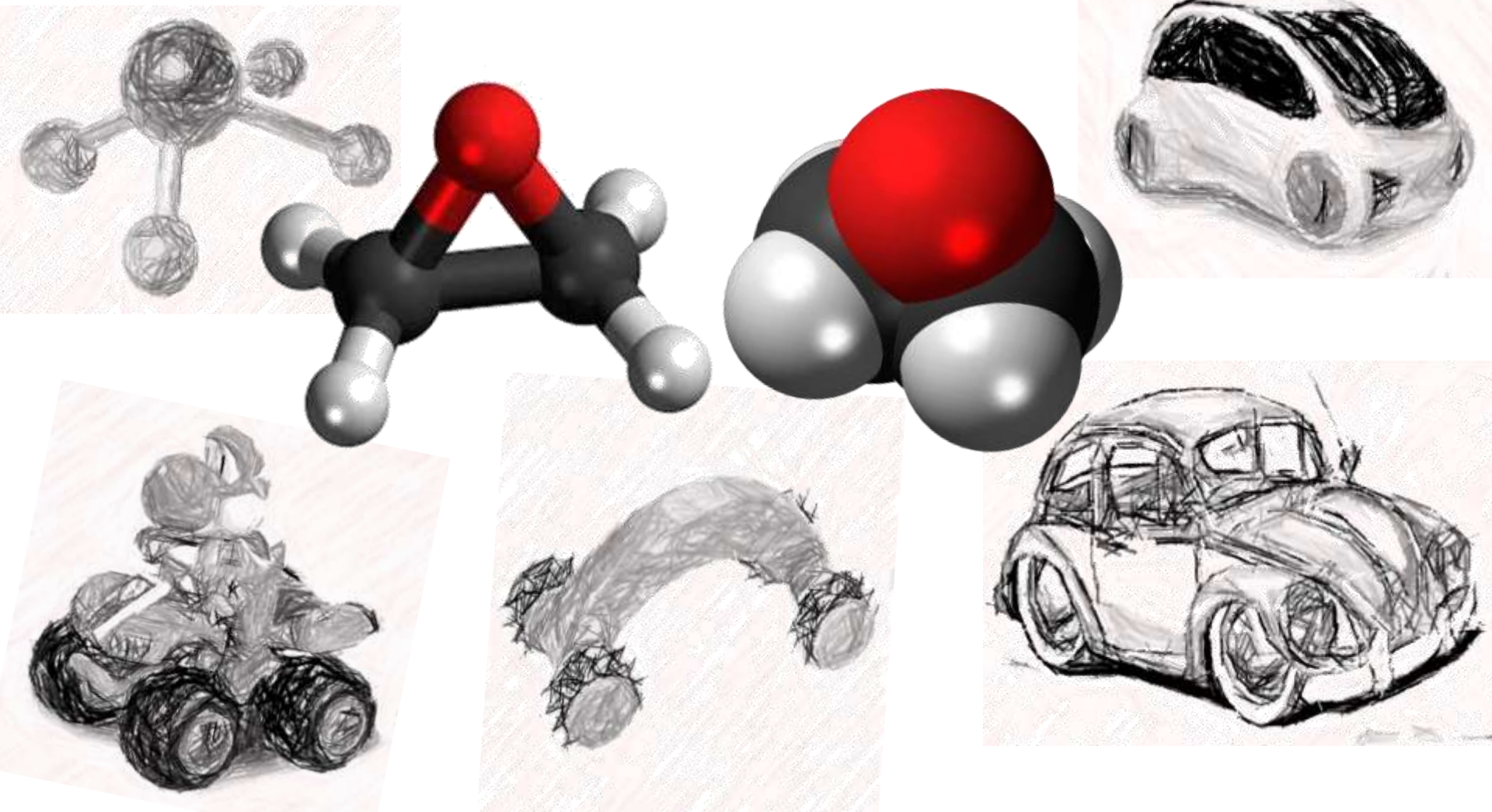








That reminds me of something …



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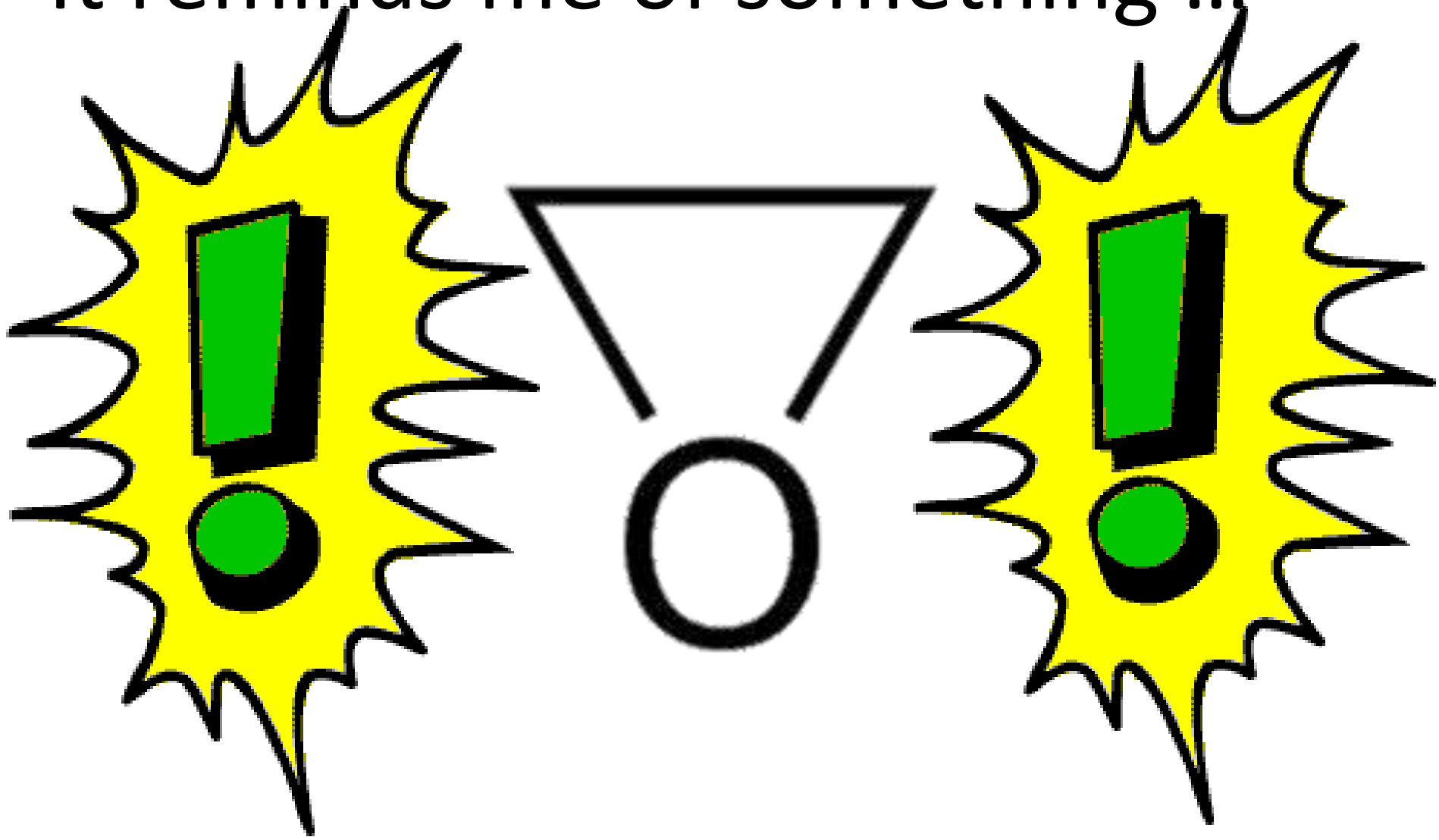


What is Ethylene oxide (EO)?

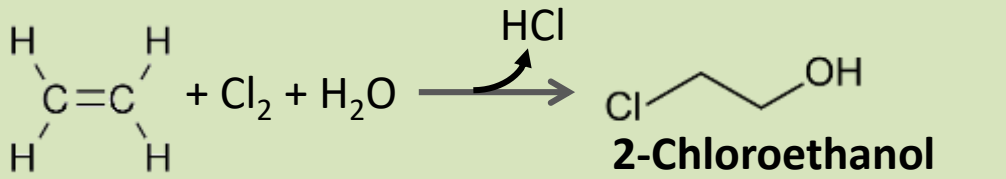
<u>Synonyms</u>:

- Oxirane
- Epoxyethane

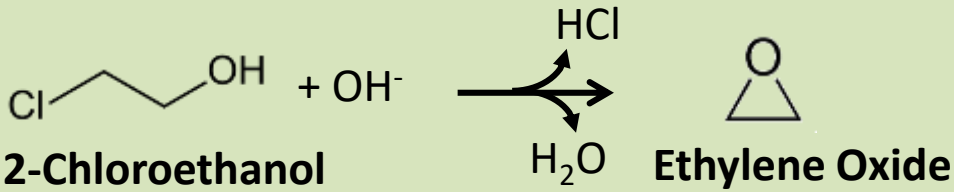
EO-Production

- First synthesized in 1859 (**chlorohydrin process)**
- Industrially produced since 1914 (**chlorohydrin process)**

Chlorohydrin-Process



2-Chloroethanol
(Ethylenechlorohydrin)



2-Chloroethanol **Ethylene Oxide**

- **Nowadays** catalytic (Ag and Al_2O_3) oxidation of $CH_2=CH_2$ (energy consuming)
- **Future** plans → electrochemical production from ethylene

EO-Production

Despite its dangerous nature
EO is one of most important commodity chemicals

EO World Production:
2010->2020: ~20 -> ~30 M t (+50%)

COMPARE:

- **Ethylene:** **~170 M t (PE); (DCE** -> VC -> **PVC); (Styrol** -> **PS**); (**EO** -> next slide); (**2CE -> EO)**
- **MeOH:** **~100 M t (Formaldehyd-> Melamine + other Resins)**
- **Propylene:** **~85 M t (PP)**
- **EG:** **~50 M t (Polyesters)**, Antifreeze, dehydration in petrochem. industry
- **i-Propanol:** **~2 M t (dissinfection)**
- **ACN:** **~0.3 M t**

EO uses

Mainly used as **INTERMEDIATE** for the production of various important chemicals

- **Ethylene glycole** antifreeze agent ➔ **Polyesters** (PET etc.)

- **Di + Triethylene glycole** intermediates ➔ **polyesters , polyurethans**
- **Polyethylene glycols (PEGs)** Dispersant, Lubricant (cosmetics, pharma …)

- **Polyethyleneglycol ethers** non-ionic surfactants *(Brij)* (food+cosmetics)
- **Polyethyleneglycol esters** non-ionic surfactants (food+cosmetics)
- **Polyethoxylated sorbitans (“polysorbitans”)** surfactants *(Tweens)* (food+cosmetics)
- **Ethanolamines (mono-, di- tri)** intermediates an other cosmetics, textiles, waxes

EO-Uses - Food-Additives

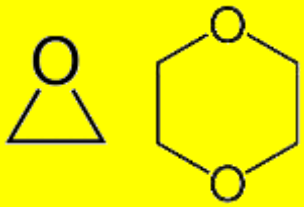
Food additives registered in the EU (Reg 231/2012/EU)

- **Polyoxyethylene sorbitan fatty acids** (E 432, E 433, E 434, E 435, E 436);
- **Polyoxyethylene stearate** (E 431);
- **Polyvinyl alcohol PEG copolymer** (E 1209);
- **PEG** (E 1521).


INGREDIENTS: ICE CREAM - MILK, CREAM, SUGAR SYRUP, CORN SYRUP, HIGH FRUCTOSE CORN SYRUP, WHEY, BUTTERMILK, NATURAL AND ARTIFICAL FLAVORS, CELLULOSE GEL, GUAR GUM, CELLULOSE GUM, MONO- AND DIGLYCERIDES, LOCUST BEAN GUM, POLYSORBATE 80, CARRAGEENAN, ANNATTO (FOR COLOR), CARAMEL FUDGE SYRUP - CORN SYRUP, HIGH FRUCTOSE CORN SYRUP, SUGAR, BUTTERMILK, BUTTER (CREAM, SALT), SKIM MILK, PECTIN, SALT, SODIUM BICARBONATE, SOY LECITHIN, POTASSIUM SORBATE (PRESERVATIVE), SODIUM CITRATE, XANTHAN GUM. PRALINE ALMONDS - SUGAR, ALMONDS, BUTTER (CREAM, SALT), CORN SYRUP, SALT, NATURAL FLAVOR.
CONTAINS: MILK, ALMONDS, SOY

Limits stipulated in Reg. 231/2012/EU

- EO: 0,2 mg/kg
- Dioxane: 5 or 10 mg/kg
- 2CE: no limit !



„EO may not be used for sterilizing food additives.“

Ethylene oxide uses

Hand Creme

=PDMS (-> SPME, GC)
(typical solvent: PEG 10)

SKŁADNIKI / INGREDIENTS / (INCI): Aqua (Water), Paraffinum Liquidum, Urea, Glycerin, Persea Gratissima Oil, Dimethicone, Octyldodecanol, Isopropyl Myristate, Allantoin, Borago Officinalis Leaf Extract, Rosa Canina Seed Extract, PEG-75 Lanolin, Collagen, Tocopheryl Acetate, Lanolin, Panthenol, Sodium Hyaluronate, Linoleic Acid, Hydrolyzed Elastin, Tocopherol, Retinyl Palmitate, Olus Oil, Acrylates/C10-30 Alkyl Acrylate Crosspolymer, Triethanolamine, Sodium Polyacrylate, Parfum (Fragrance), Phenoxyethanol, Methylparaben, Butylparaben, Ethylparaben, Propylparaben, DMDM Hydantoin, Ethylhexylglycerin, Imidazolidinyl Urea, Propylene Glycol, PEG-20 Glyceryl Laurate, Caprylic/Capric Triglyceride, Diethylhexyl Syringylidenemalonate, Polysorbate 20, Disodium EDTA, BHT.

Ethylene oxide - Fumigations

Only 0.05% of global EO production is used for food Fumigations.

For use typically mixed with e.g. CO_2 or N_2

Food types: Grain, Spices, Nuts, Oilseeds, dried Mushrooms, dry Vegetables

Factors: EO-Concentration, Humidity, Temperature, Exposure cycles/time, Aeration cycles/time

➔ Sterilization, Disinfection (e.g. 400-500 g/m^3, 6-24h),

➔ Insect control (e.g. 100 g/m^3, 3h)

Ethylene oxide - Fumigations

EO-Sterilization of food **started in 1930s** and **peaked in 1960s-80s**.
Since the **late 1980s irradiation** has been an alternative (**must be labelled in US + EU!)**

Since ethylene oxide processing does not require labeling in the US, it remains a favoured sanitation agent for a significant number of the country's food processors.

American Spice Trade Association (ASTA):

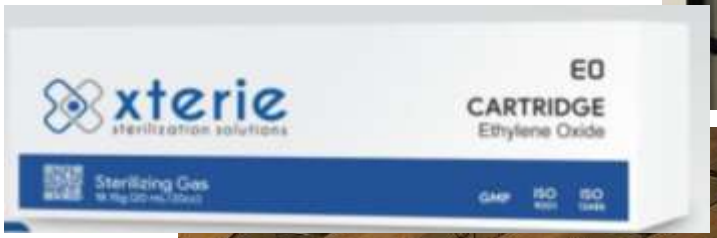
Ethylene Oxide (EtO) is the ***most significant tool available to the U.S. spice industry to prevent human microbial contaminants*** *such as Salmonella and E.coli in spices.*
… it is ***used to treat 40 to 85 percent of spices*** *in the U.S., as well as* ***spice packaging material.***

EU: Banned (in DE banned since 1981): MRLs at the LOQ
US: Still allowed (MRLs: EO 7 ppm; 2CE 970 ppm!!!)

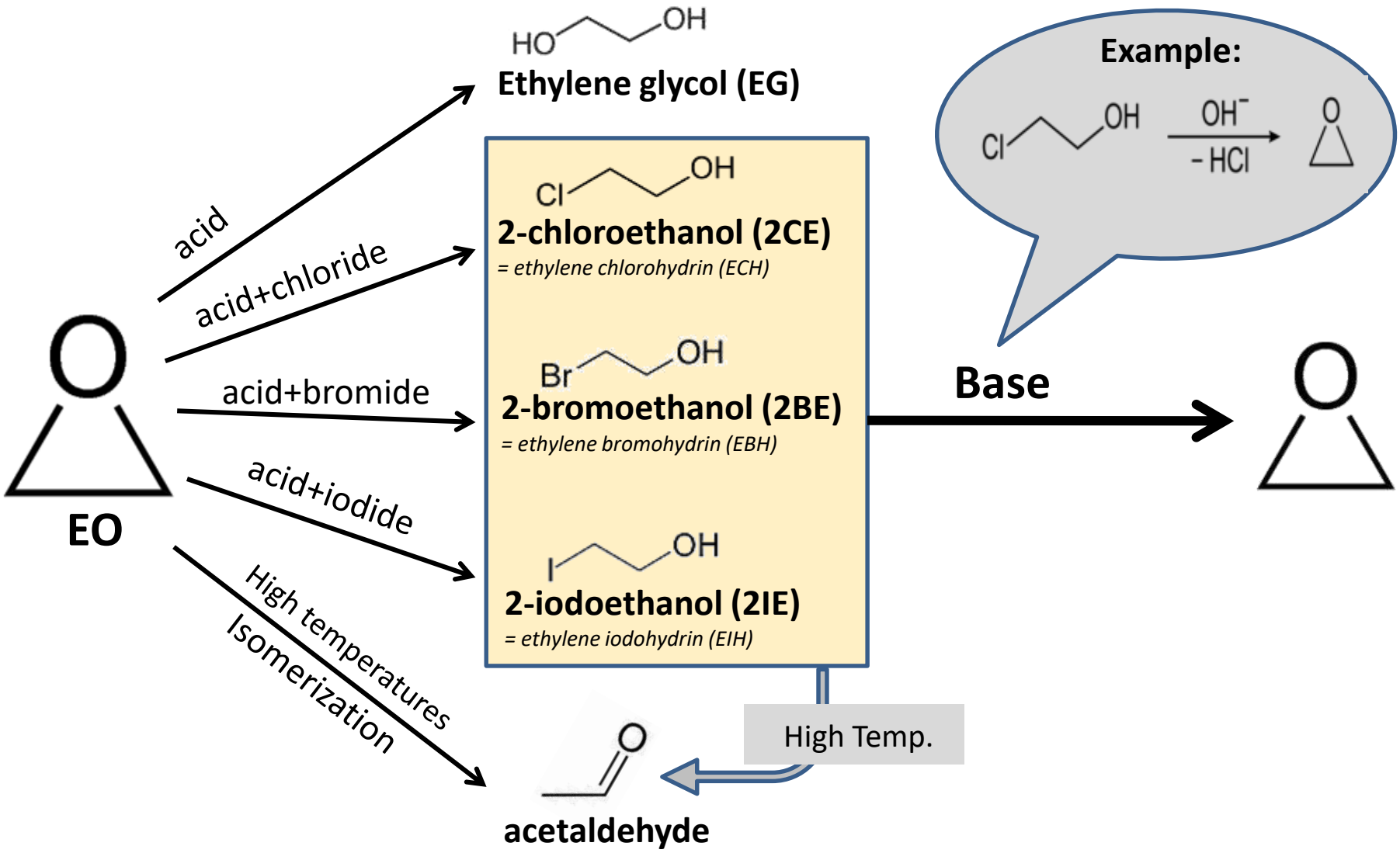
Ethylene oxide - Fumigant

Other applications

- Medical and scientific equipment
- Packaging materials
- Clothing, furs
- Tobacco
- Old documents



Ethylene oxide - Reactions



Ethylene oxide – Residues in Fumigated Food

Residues:

- **EO** (rarely >0.01, depends on aeration and storage time)
- **2CE** (through reaction w. chloride)

} Legally relevant

- **Bromoethanol** (reaction w. bromide; higher if sample previously treated w. MeBr)
- **Ethylene glycol** (non-specific)
- **Hydroxyethyl Adducts** w. matrix components (purines, amino acids, fatty acids …)
- **Conjugated 2CE** (e.g. with Fatty acids)

Residue Definition:

Ethylene oxide (sum of ethylene oxide and 2-chloro-ethanol expressed as ethylene oxide) (F)

MRLs

- Fresh fruits and vegetables 0.02* mg/kg,
- Fungi (fresh) 0.02* mg/kg
- Cereals 0.02* mg/kg
- Pulses 0.02* mg/kg
- Tea, infusions, spices 0.1* mg/kg,
- Nuts and oily seeds 0.05* mg/kg
- AO-products: 0.02* mg/kg

(F) questionable as EO does not bioaccumulate

LogKow EO: -0.3

LogKow 2CE: 0.15

Ethylene oxide – ANALYTICAL STRATEGIES

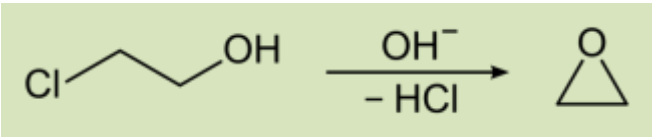
Have a look at the analytes

Compound	LogKow	MW	Vapour pressure at 20 °C	BP
Ethylene oxide	**-0.3**	**44.05**	**1,45 bar**	**10.4 °C**
Acetonitrile	-0.34	41,05	0.1 bar	80.2 °C
Ethanol	-0.3	46,07	0.06 bar	78.5 °C
Water	---	18,02	0.02 bar	100 °C
2-Chloroethanol	**0.14**	**80,52**	**0.007 bar**	**129 °C**

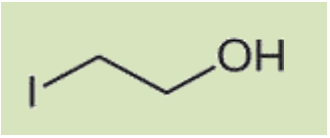
Ethylene oxide – ANALYTICAL STRATEGIES

1) German Official Method (§ 64 LFGB, L53.00-1)

Based on Jensen (1988) further studied by Gilsbach et al. (1999)



1. Sample treated with base 2h (2CE ➔EO)
2. EO purged with N_2 into reservoir with aqueous H_2SO_4 / NaI (EO➔2IE)



3. Partitioning of 2IE into ethyl acetate
4. IE analyzed by GC-ECD or GC-MS(/MS); (LOQs: typically 0.01-0.02)

Analysis of EO levels present in sample as such: ⇨ Skip step 1

EXEMPLARY ANALYTICAL METHODS (from Literture)

- **Analysis of EO**
  - Headspace sampling (e.g. Woodrow et al. (1995); **spices**)
  - Dynamic headspace sampling (e.g. Ramstad et al. (1993); drug)
  - SPME sampling from air (e.g. Shih-Wei Tsai (2003) on-fibre deriv. by HBr ; air samples)
  - SPME direct immersion (e.g. Ayoub et al.(2002); medical devices)
- **Analysis of 2CE**
  - Direct one-phase extraction (Aitkenhead et al (1988); **dried spices**)
- **Analysis of EO+2CE (sum)**
  - Conversion of EO to 2CE followed by Liquid-liquid part. (Tadeo/Bononi (2006); **pepper**)
  - Direct one-phase extraction with MeOH (e.g. Pfeilsticker et al. (1975); **grain**)

EURL-SRM-Approaches Tested

QuEChERS / GC-MS/MS
- EO and 2CE simultaneously
- 2CE individually
- Total 2CE **(following conv. of EO to 2CE w. HCl/NaCl)**
- Total EO **(following conv. of 2CE to EO w. NaOH)**

QuOil / GC-MS/MS
- EO and 2CE simultaneously
- 2CE individually

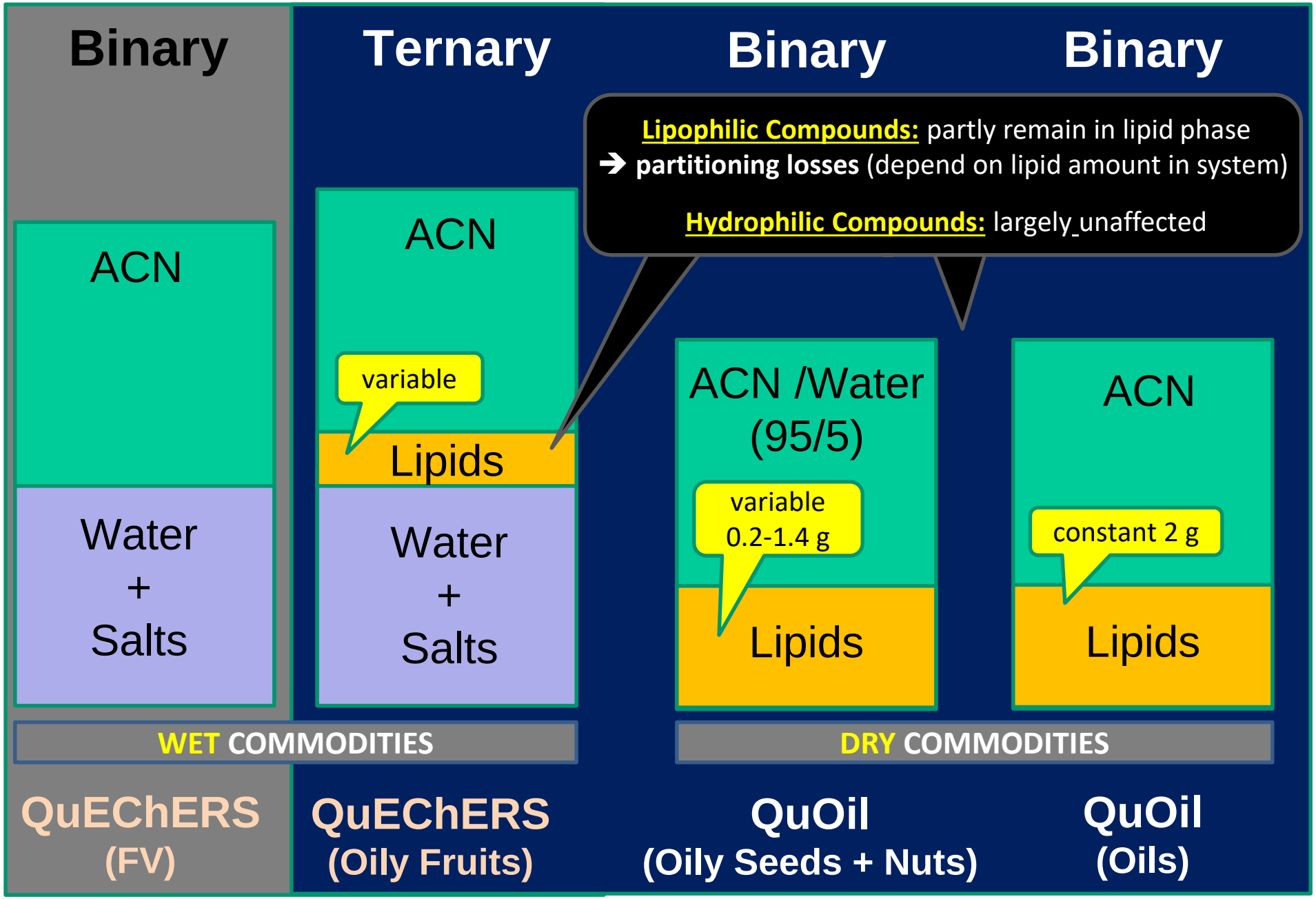
Headspace-SPME / GC-MS
- 2CE individually

Headspace / GC-MS
- EO and 2CE simultaneously
- EO and 2CE separately
- Total EO **(following conv. of 2CE to EO w. NaOH)**
- Total 2CE **(following conv. of EO to 2CE w. HCl/NaCl)**

Impact of various factors on extraction yields:
- **water addition**
- **extraction time**
- **extraction aids**

Methods currently used by CVUA Stuttgart

QuOil and QuEChERS



GC-MS/MS Method Settings

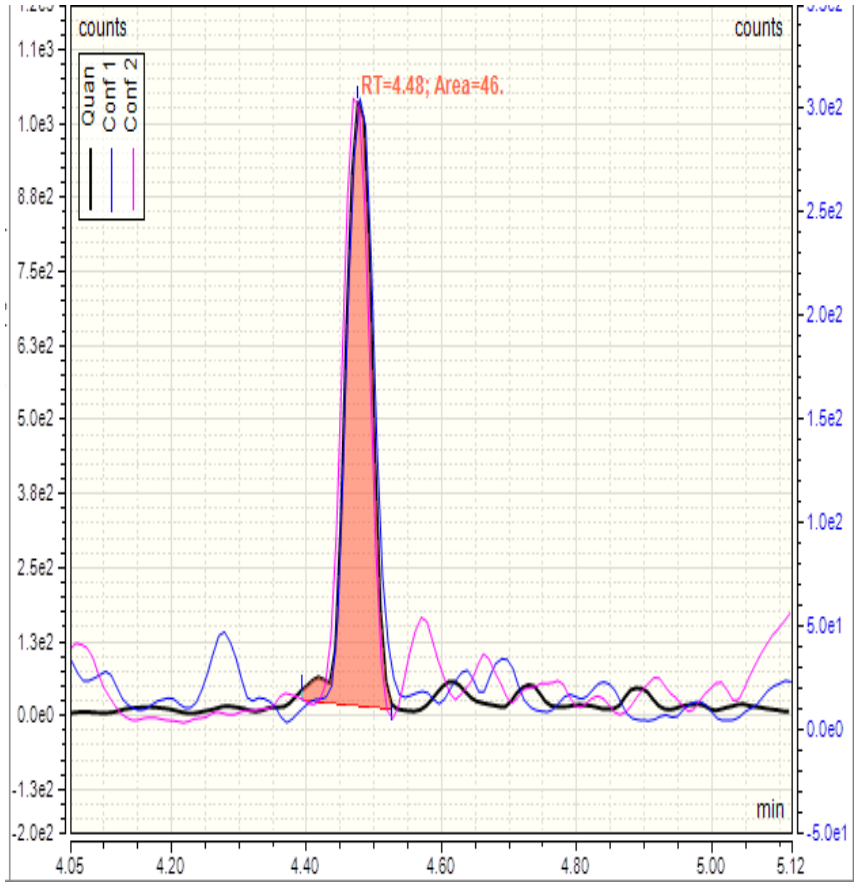
GC-MS/MS Method on HP-VOC Column	
GC	Thermo Trace 1310 with TriPlusRSH Autosampler
Injector	Gerstel KAS 6
MS/MS	Thermo TSQ 8000
Column	HP-VOC; Length: 30 m; Diameter: 0.2 mm (narrowbore); Film thickness: 1.12 µm
Pre-column	Fused Silica Tubing, Deactivated, Diameter: 0.25 mm, Agilent J&W, Length: 3 m
Mobile Phase / Flow	Helium, 1 mL constant flow
Injection mode	Split 1:4
Injection volume	2 µL
injection temp. program	Start temperature 90°C for 0.8 min, with 12°C/s to 250°C, hold 5 min, with 10°C/s to 300°C, hold 5 min
Oven temp. program	Start: 45 °C, hold 2 min, heat to 150°C reached at 4.1 min heat to 280°C reached at 5.1 min, hold 20 min
MS Parameters	Transfer line temperature: 250°C; Ion source temperature: 270°C Ionisation mode: EI; Tune: LowMass
Internal Standards	**Ethylene oxide D4; 2-Chloroethanol D4**
Extract details	QuEChERS or QuOil (cleanup by dSPE, no dilution, AP: Shikimic acid 0.5 mg/mL) (**Note**: ***AP-mix w. ethylglycerol, sorbitol + gulonolactone interfered EO analysis***)

MS/MS Settings

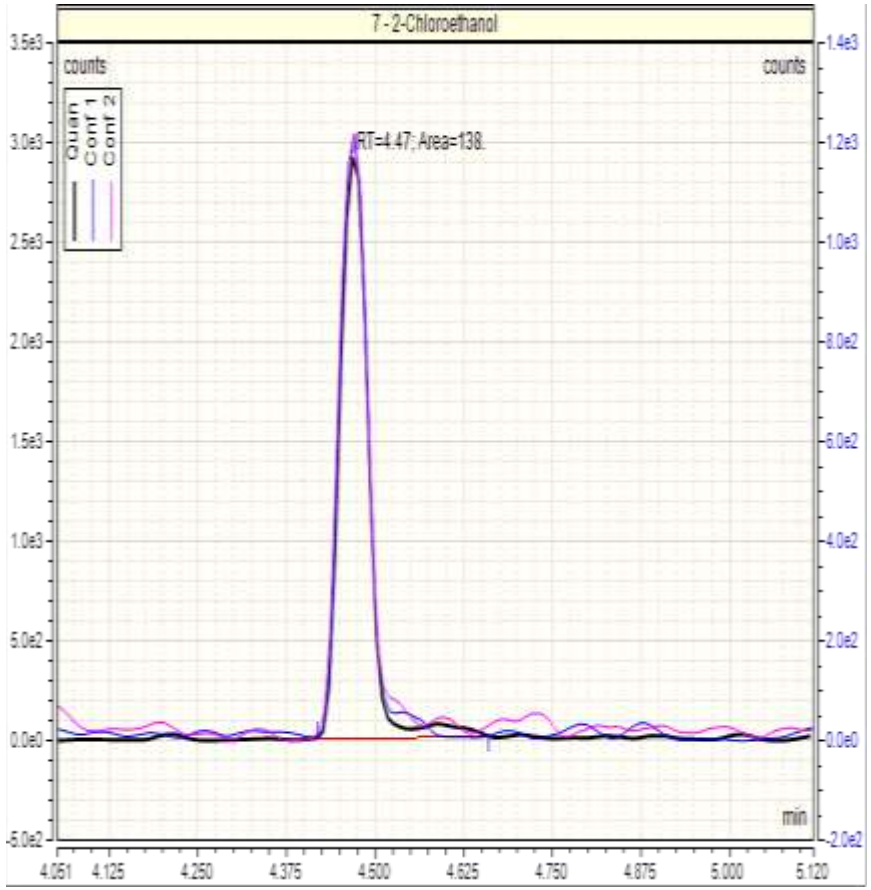
Name of Compound	RT min	Parent mass	Daughter mass	CE
Ethylene oxide	2.57	44 44 44	14 28 29	20 5 5
Ethylene oxide D4	2.57	48 48	16 30	20 5
2-Chloroethanol	4.61	80 80 82	31 43 31	5 5 5
2-Chloroethanol D4	4.61	84 86	33 33	5 5

Exemplary 2-Chloroethanol Peaks

0.005 µg/mL (2 µL inj. vol.)

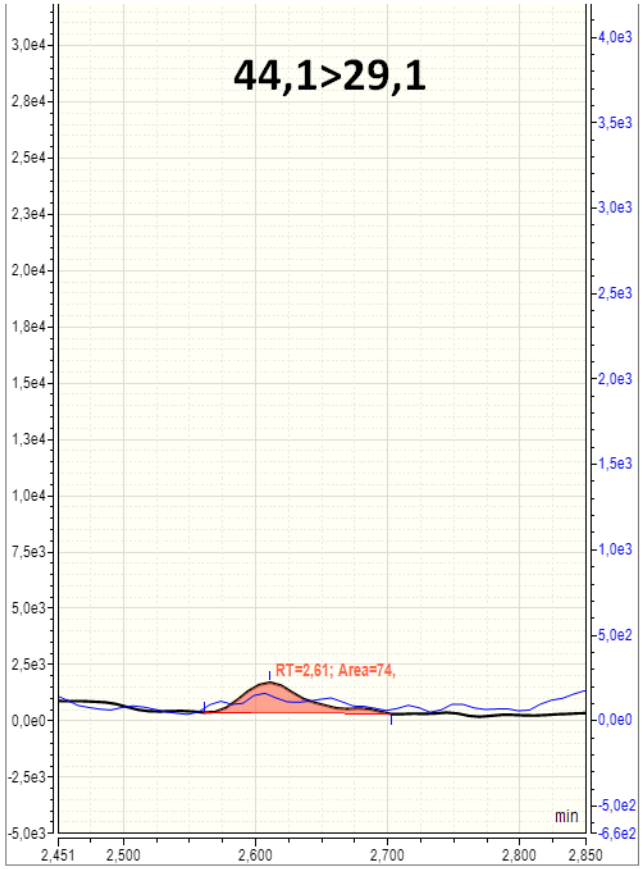


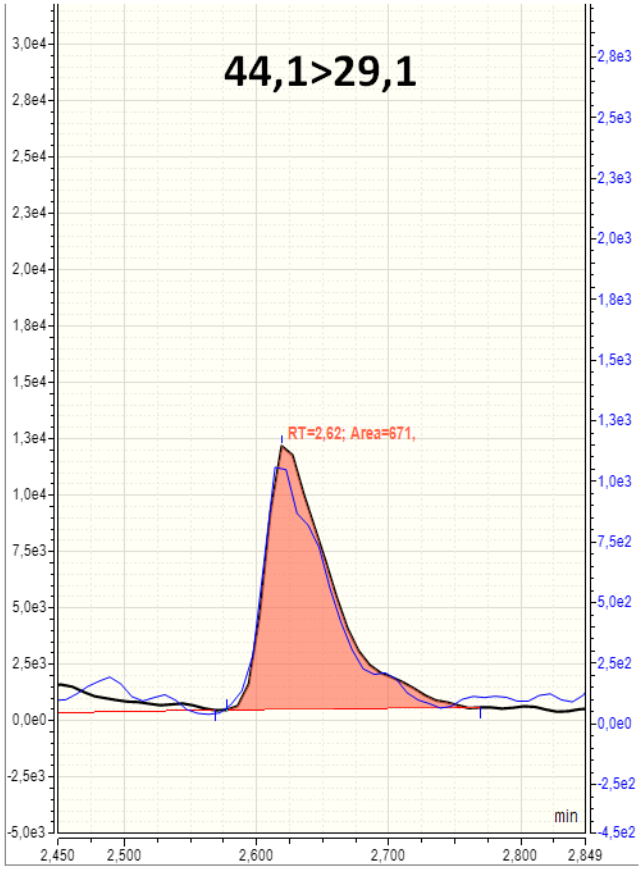
0.2 mg/kg in Cardamom (1µL inj. vol.)

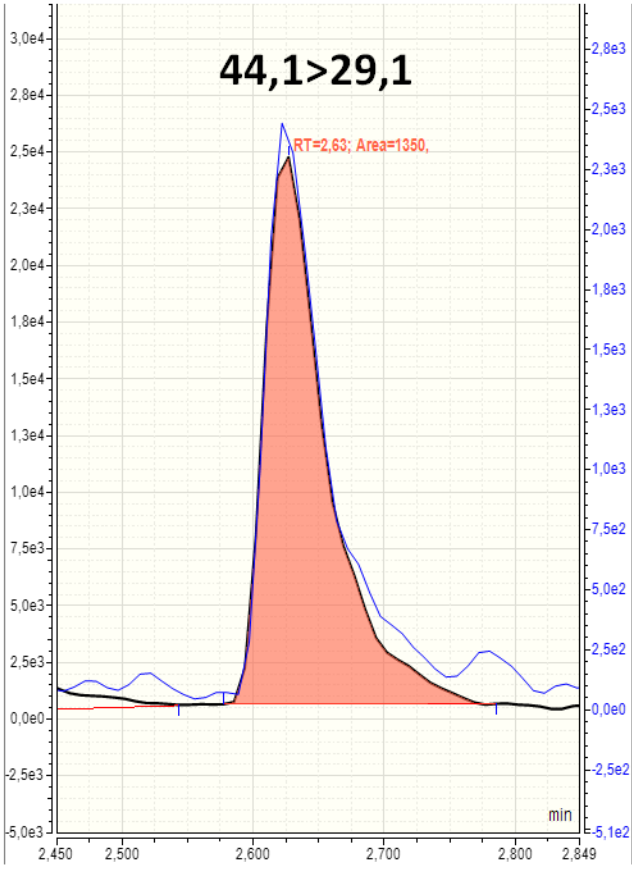


EO in extract of spiked sesame (0.2g/mL)

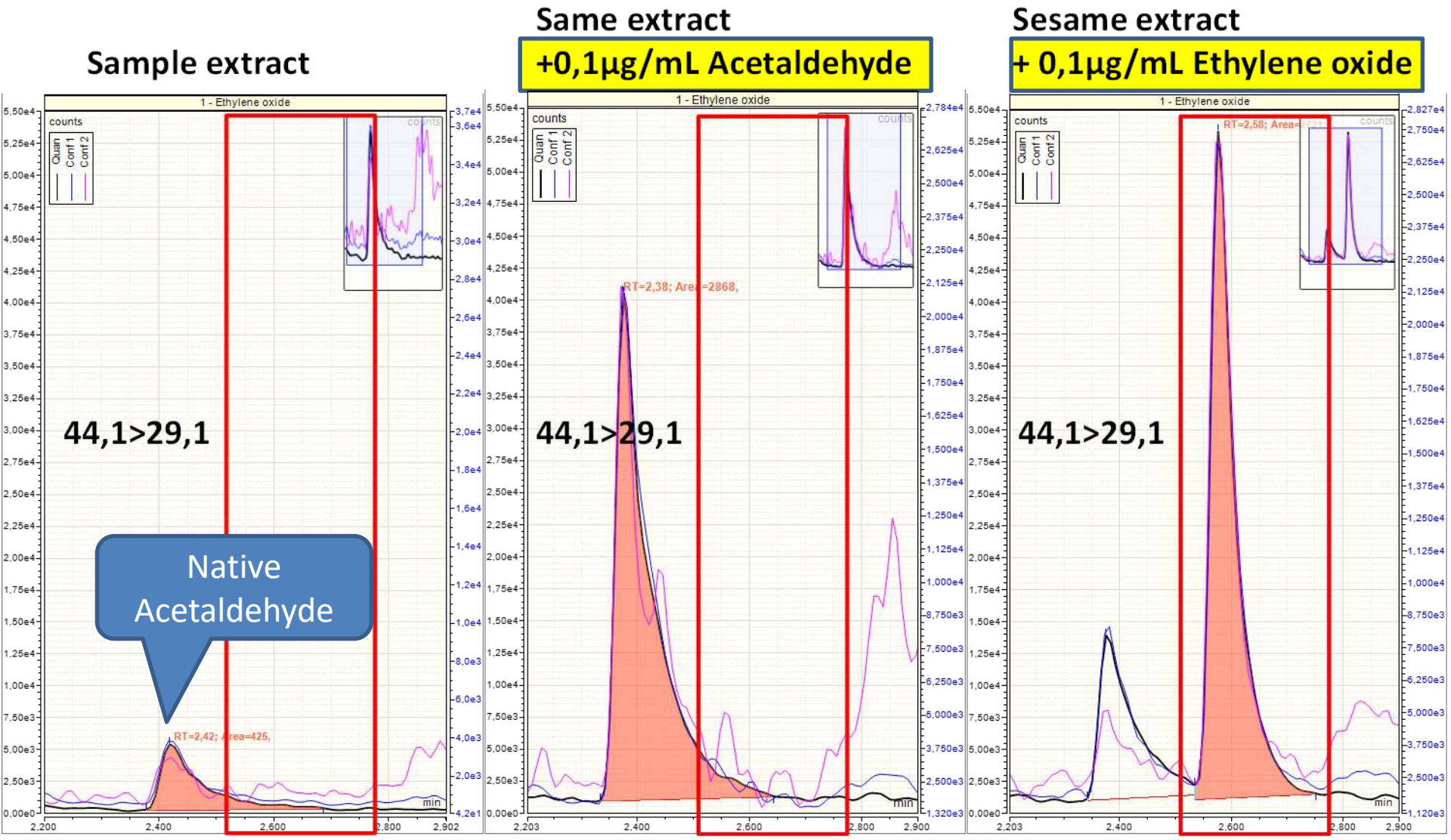
0.005 µg/mL = 0.025 mg/kg **0.05 µg/mL = 0.25 mg/kg** **0.1 µg/mL = 0.5 mg/kg**







Differentiation between EO and acetaldehyd (its isomer) in real sesame samples (0.2g/mL)



GC-MS Method Settings

GC-MS (EI) SIM Method on Carbowax Column

Analyte / m/z acquired	**2-CE:** Target: 49, Qualifiers: 31, 51, 80		
Instrument model	GC 6890N (Agilent); MSD 5973N (Agilent)		
Extraction details	QuEChERS or QuOil following cleanup by dSPE no dilution, no APs		
Int.standard / m/z acquired	**2-Chloropropan-1-ol D6** : 63, 100, 102 **3-Chloroethan-1-ol** : 58; 57, 76, 78		
INSTRUMENT PARAMETERS			
Mode	MSD (EI pos)		
Pre-column / Column	3 m FS, deactiv. (Agilent) / HP-Carbowax 30 m 0.32 mm ID 0.5 µm film		
Run time (min)	39		
Oven Program	**Rate (°C/min)**	**Temp. (°C)**	**Hold Time (min)**
		50	3
	30	150	0
	15	220	20
	Post-run	50	5
Injection details volume (µL),	2 µL; splitless; Baffled Liner		
Injection program	**Rate (°C/min)**	**Temp. (°C)**	**Final Time (min)**
		90	0.8
	720	150	15.8
Carrier gas	Helium, 2.0 mL/min, constant flow		
Transfer-line / source temp. (°C)	220 / 220		
Ionization / Detector	EI-ionization; 70eV,; single quadrupole MSD		

Validation data using QuOil and QuEChERS method

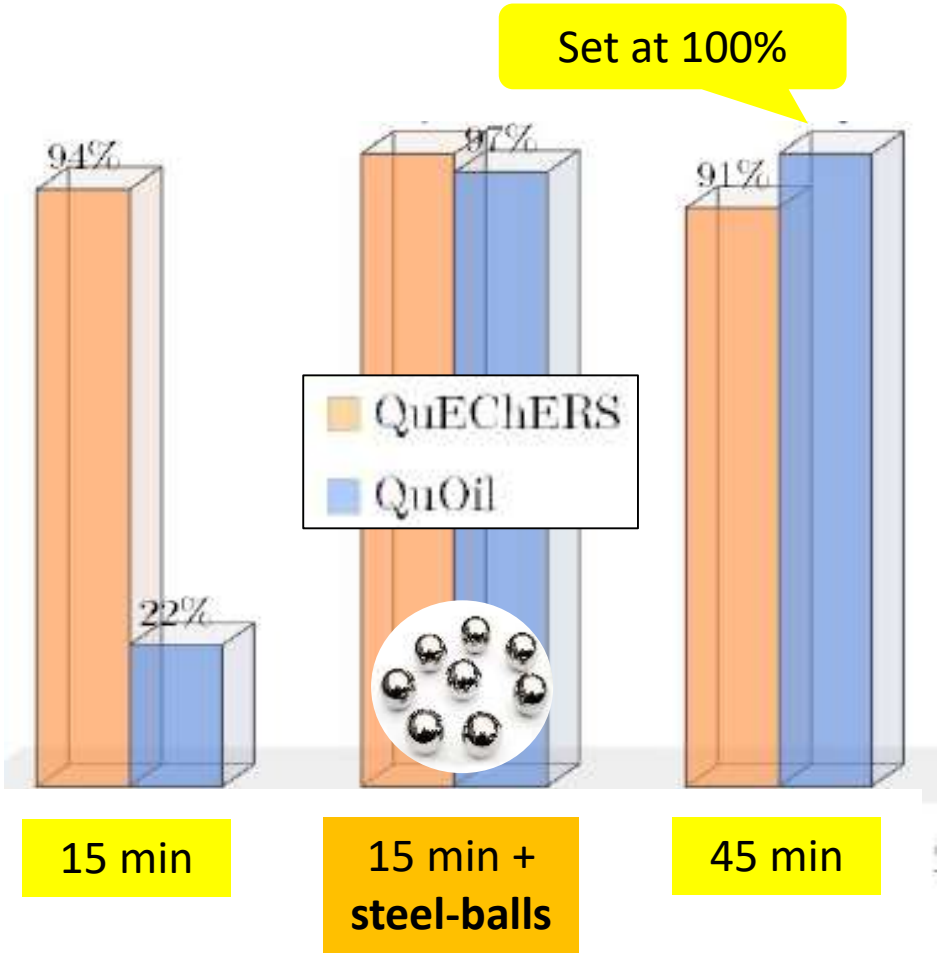
Matrix : Sesame; 2 g portion; Separate experiments for the two analytes

Compound	Mth	n	ILIS	Spiking Level (mg/kg)	Mean Rec. [%]	RSD [%]
Ethylene oxide	QuOil	5	Yes	0.04	90%	12.9%
	QuOil	5	No		92%	8.1%
	QuOil	5	Yes	0.5	94%	3.6%
	QuEChERS	5	No	0.5	83%	7.8%
2-Chloroethanol	QuOil	5	Yes	0.12 (EO: 0.066)	91%	11.5%
	QuOil	5	No	0.12 (EO: 0.066)	93%	9.8%
	QuEChERS/PSA	5	Yes	0.08 (EO: 0.044)	102%	7,4%
	QuEChERS	5	Yes	0.5 (EO: 0.275)	102%	8.1%
	QuEChERS	5	No	0.5 (EO: 0.275)	91%	7.1%

Cleanup with C18/PSA/MgSO4 does not induce any losses

MgSO4 reduces water content in extract and has positive impact on 2CE peak shape

Rel. extraction yields of incurred 2CE from INTACT SESAME SEEDS by QuEChERS and QuOil



OBSERV. 1: QuEChERS more efficient than QuOil

WHY?

- 2CE interacts w. matrix (via H-bonds).
- QuOIl solvent (ACN/5% H_2O) **cannot optimally soak into matrix** → **Retarded Extraction**
- **Water helps** to break them up.

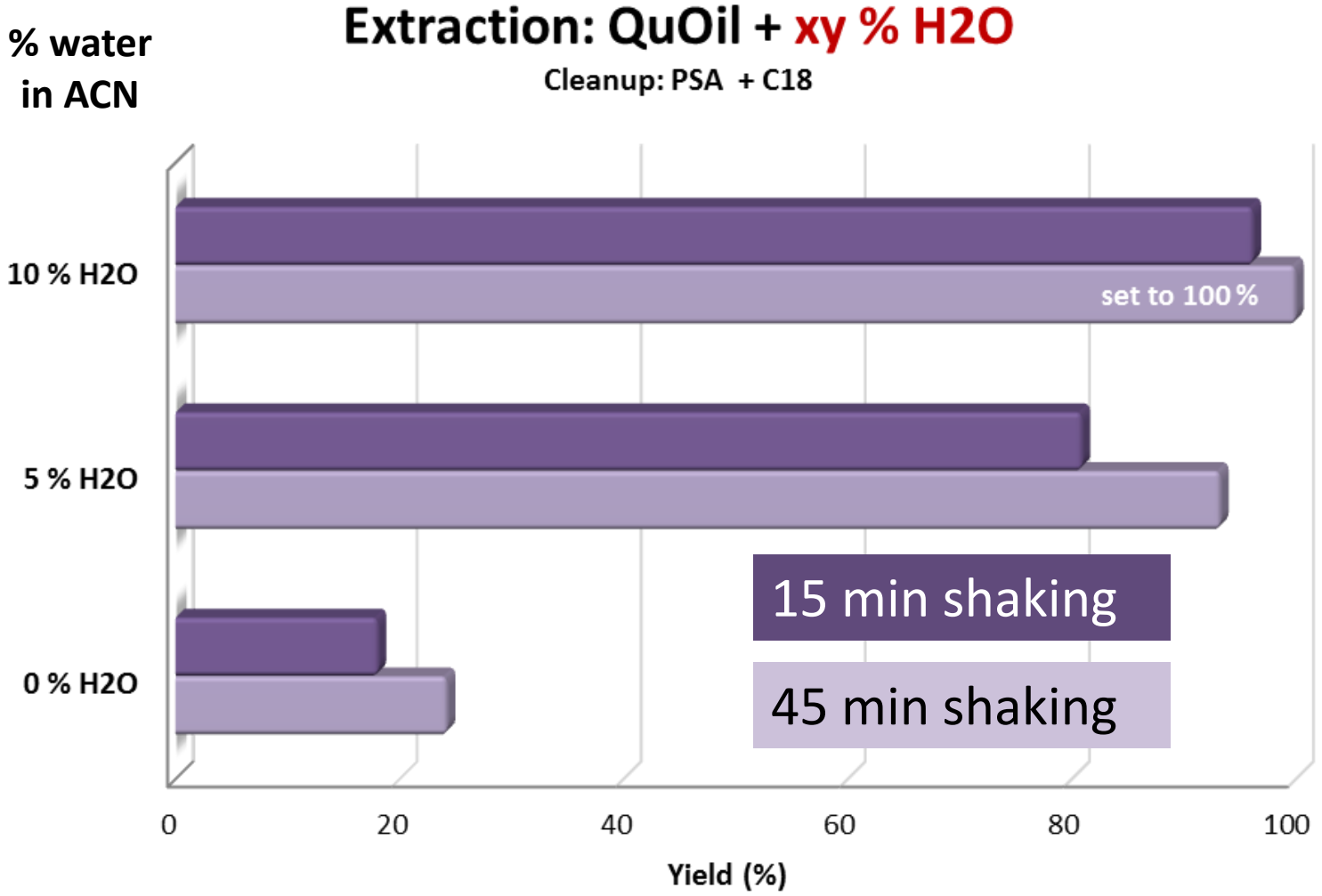
OBSERV 2: Steel balls -> accelerate extraction

WHY?

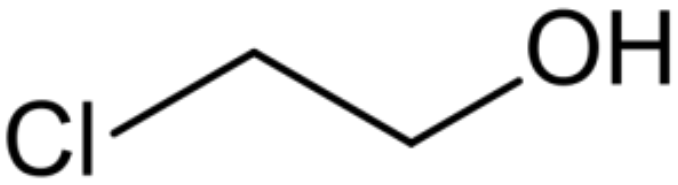
Particle size ↓; Surface area ↑; Temp. ↑

→ **Extraction more efficient**

Impact of WATER on extractability of 2-CE from MILLED sesame



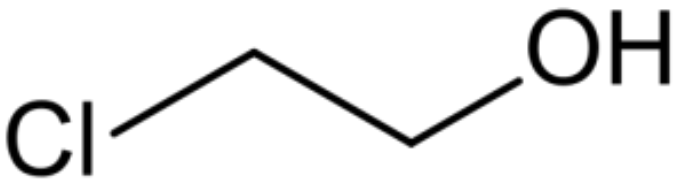
Validations beyond sesame



2-CE

2-Chloroethanol: n=5, ILIS, QuEChERS				
Matrix	**Level (mg/kg)**	**Recovery [%]**	**RSD**	**Analytical portion size**
Ice cream	0.02	90	2	10 g
Carob flour	0.05	94	12	2 g
Guar gum	0.05	108	6	2 g
Xanthan	0.05	120	14	2 g
Infant formula	0.05	91	14	2 g
Instant noodles	0.1	83	15	2 g
Instant noodle seasoning	0.1	87	8	2 g

Validations beyond sesame



2-CE

2-Chloroethanol: n=5, ILIS, QuEChERS				
Matrix	**Level (ppm)**	**Recovery [%]**	**RSD**	**Analytical portion size**
Anise	0.05	113	5	2 g
Lentil	0.05	102	9	2 g
Lentil	0.02	101	12	2 g
Paprika spice	0.05	102	9	2 g
Pepper (spice)	0.05	93	4	2 g
Onion, dried	0.05	101	10	2 g
Okra, dried	0.1	94	10	2 g
Millet	0.02	107	10	5 g

Validations beyond sesame

EO

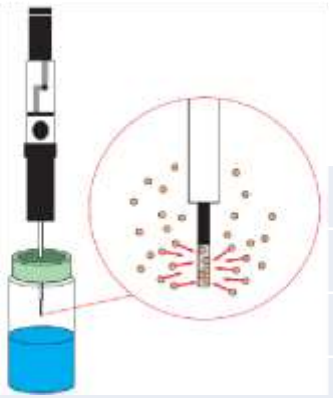
Ethylene oxide: n=5, ILIS, QuEChERS				
Matrix	Level (mg/kg)	Recovery [%]	RSD	Analytical portion size
Ice cream	0.02	92	7	10g
Carob flour	0.05	108	9	2 g
Guar gum	0.05	111	12	2 g
Guar gum	0.05	103	6	1 g
Xanthan	0.05	97	6	2 g
Infant formula	0.05	89	6	2 g

Validations beyond sesame

EO

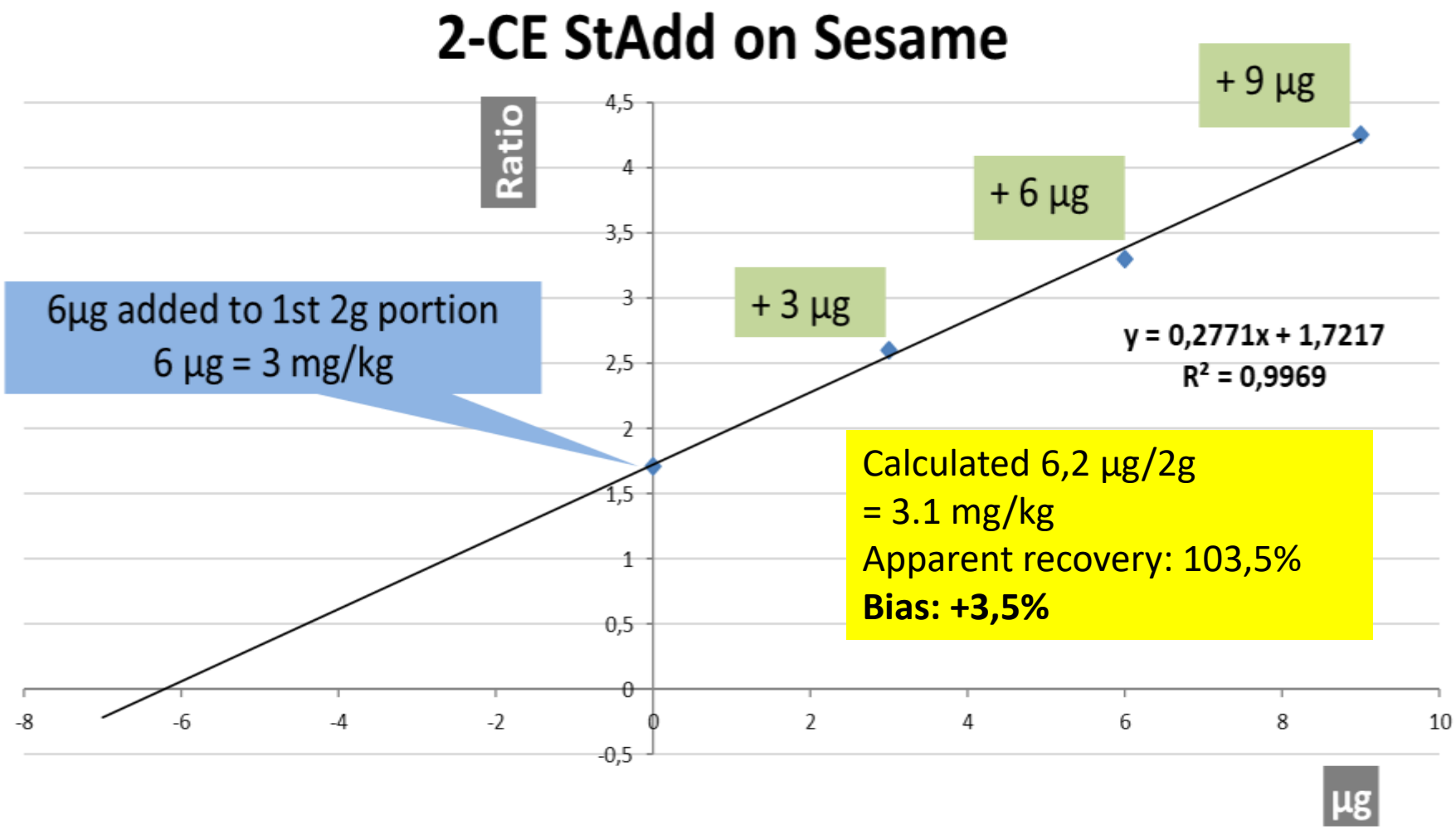
Ethylene oxide: n=5, ILIS, QuEChERS				
Matrix	**Level (ppm)**	**Recovery [%]**	**RSD**	**Analytical portion size**
Lentil	0.025	104	11	5 g
Paprika spice	0.025	108	10	2 g
Pepper (spice)	0.025	95	7	2 g
Onion, dried	0.025	92	12	2 g
Millet	0.01	88	18	5 g

SPME-GC-MS Analysis

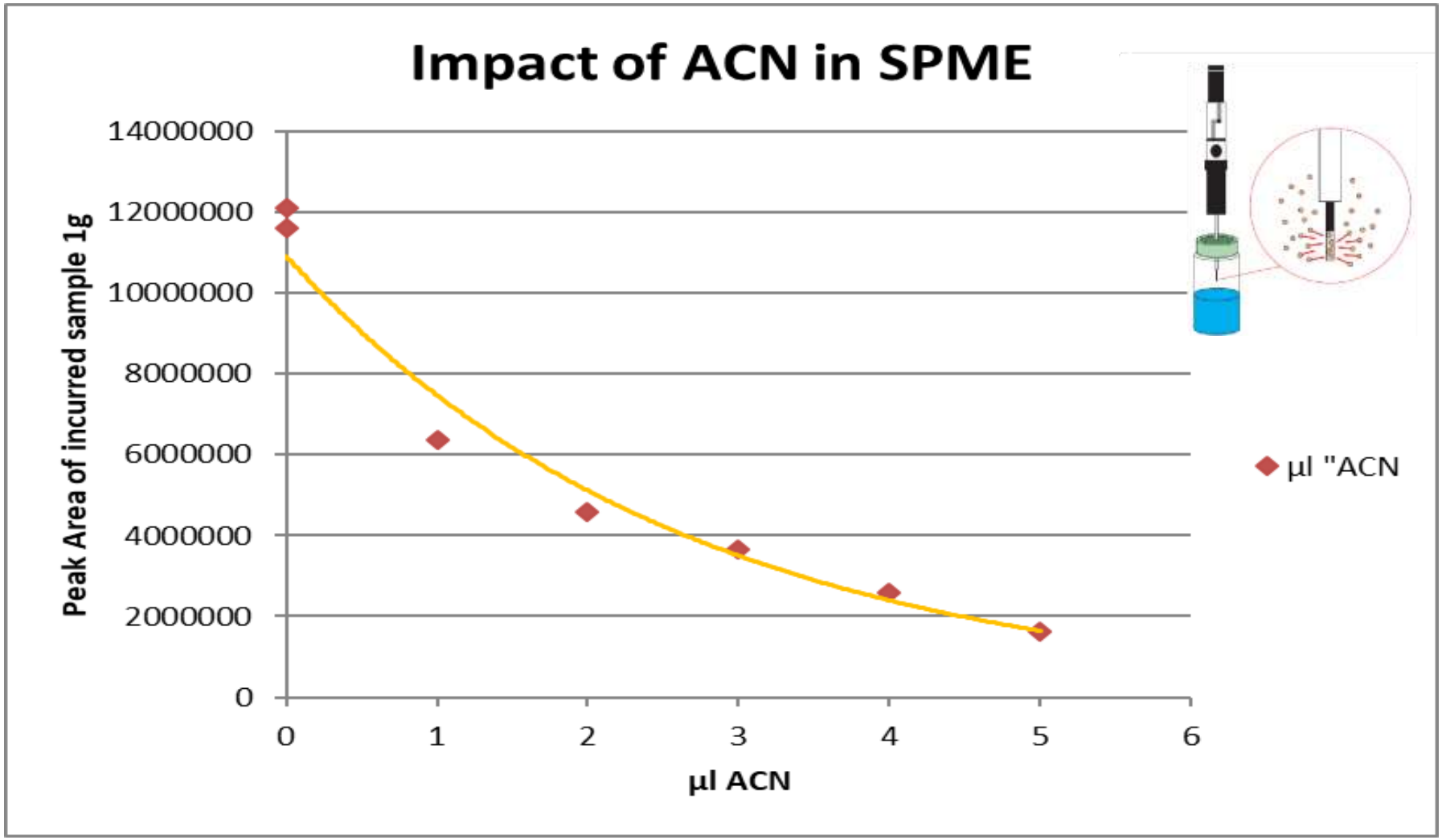


GC	Agilent 7890A			
MSD	Agilent 5975C			
Mode	EI pos			
Sampler	Gerstel MPS			
Column	Restek RTX 1701 60m, 0.25 mm, 1.0 µm (Art.-No.: 12056)			
SPME Fiber	CAR/PDMS (Supelco)			
Inlet	Split 5:1			
Incubation	15 min at 50°C			
Sorption to fiber	20 min at 50°C			
Desorption	150 s with 12°C/s to 275°C, hold 5 min			
GC Oven	#	Rate (°C/min)	Temperature °C	Hold time (min)
	Initial	-	35	5
	1	10°C/min	255	10
Sample weight	0.5 – 2 g, depending on CE concentration			
ILIS	2-CE D4 (with limitations for analysis of small concentrations)			

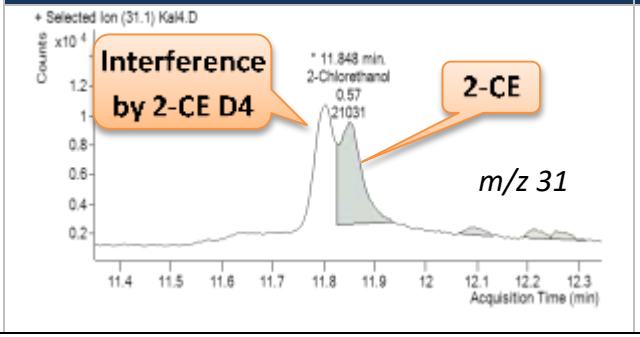
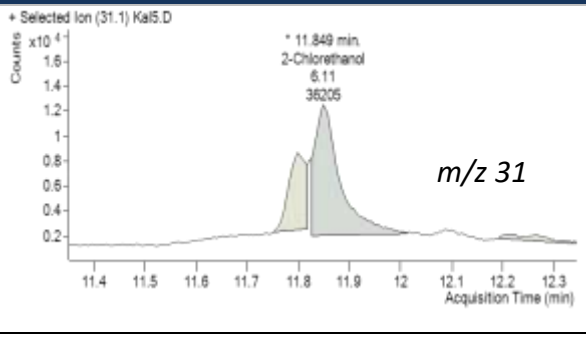
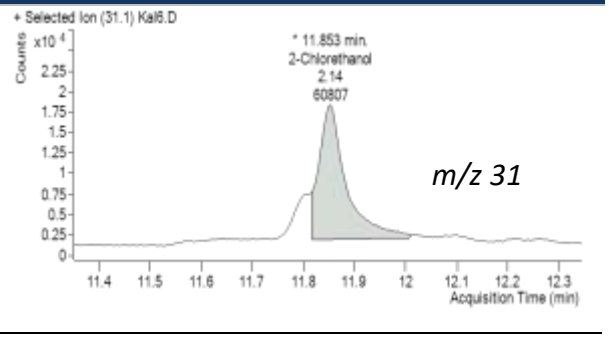
SPME-GC-MS Analysis – Standard Additions

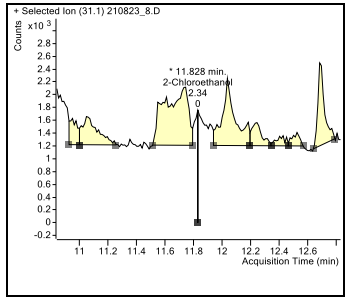
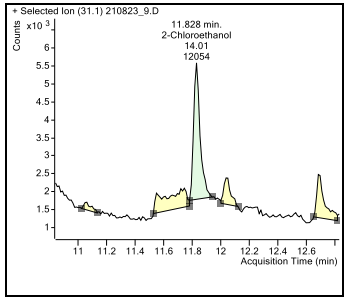
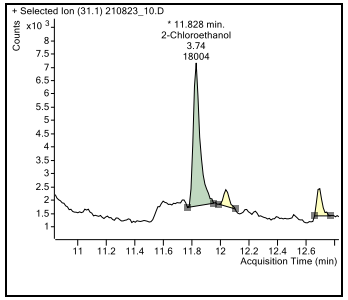
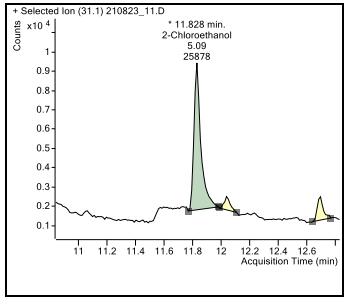
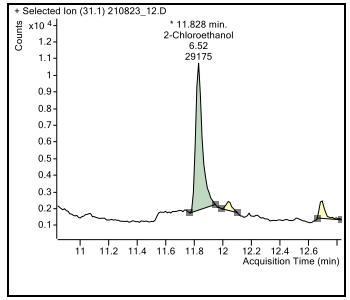
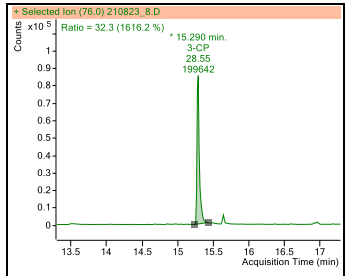
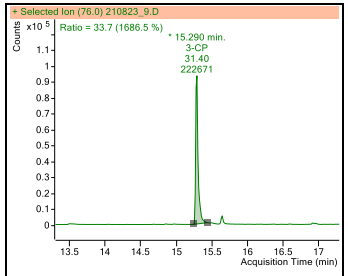
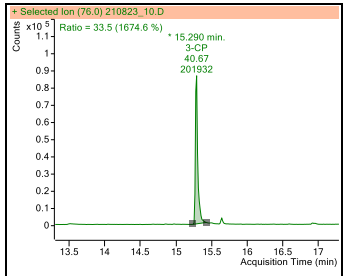
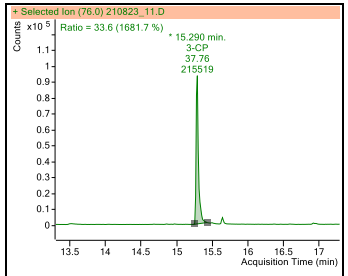
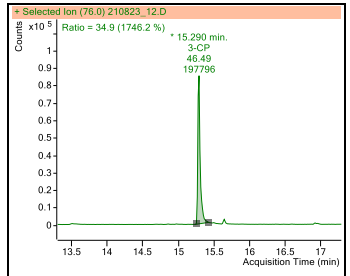


SPME Analysis – Impact of ACN on Signals



Problems with interferences caused by 2-CE-D_4 3-CP as an alternative IS

0.05 mg/kg 2-CE	0.1 mg/kg 2-CE	0.2 mg/kg 2-CE
		

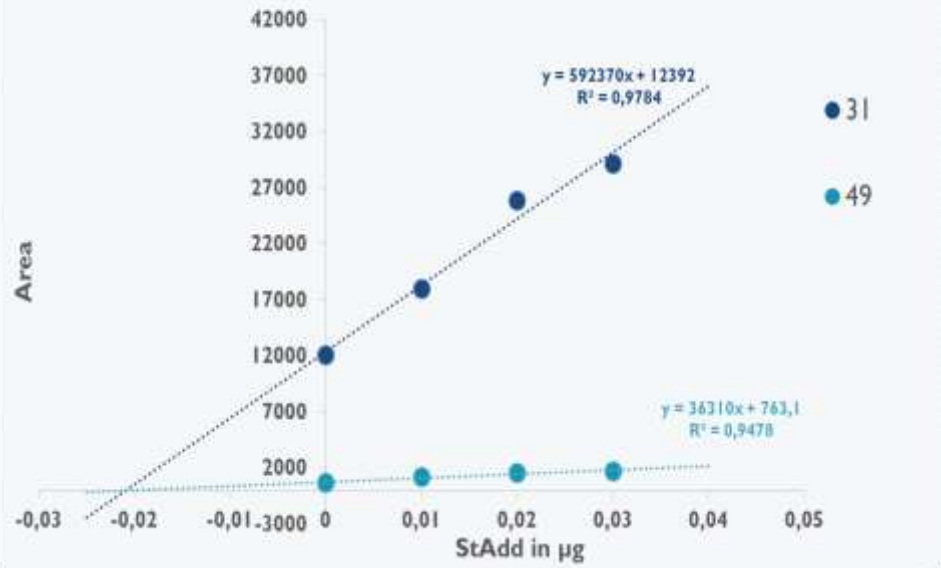
	Psyllium husks 1g	Psyllium husks 1g (+0.02 µg 2-CE)	Psyllium husks 1g (+0.04 µg 2-CE)	Psyllium husks 1g (+0.06 µg 2-CE)	Psyllium husks 1g (+0.08 µg 2-CE)
2-CE (m/z 31)					
IS 3-CP (m/Z 76)					

Simulated Std Add. on Psyllium husks

Impact of 3-CP (3-chloropropanol) as IS

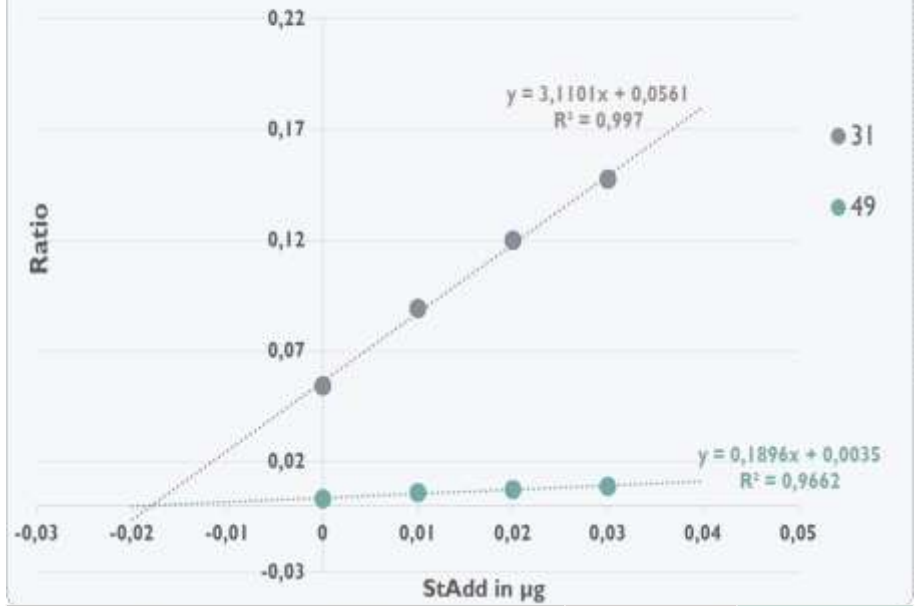
ACN vol. equalized

Via Peak Area of 2-CE



m/z	31	49
Calc. conc. (mg/kg)	0.021	0.021
„Apparent Recovery“	105%	105%
Trueness (bias)	+5%	+5%

Via Area Ratio against 3-CP, (m/z 76)



m/z	31	49
Calc. conc. (mg/kg)	0.018	0.018
„Apparent Recovery“	90%	92
Trueness (bias)	-10%	-8%

European Commission
EURL-SRM
EU Reference Laboratories for Residues of Pesticides
Single Residue Methods

EURL-SRM - Analytical Observations Report

Concerning the following…

- **Compound(s)**: Ethylene oxide (EO), 2-Chloroethanol (2CE)
- **Commodities**: Sesame seeds
- **Extraction Method(s)**: QuOil, QuECHERS
- **Instrumental analysis**: GC-MS/MS

Analysis of Ethylene Oxide and its Metabolite 2-Chloroethanol by the QuOil or the QuEChERS Method and GC-MS/MS

Version 1.1 (December 2020)

EURL-SRM

EU Reference Laboratories for Residues of Pesticides

Single Residue Methods

ANALYSIS OF SAMPLES FROM THE MARKET

Sesame Opened the Door!!

Sesame Production

Top producers in 2019

Rang	Land	Menge (in t)
1	Sudan	1.210.000
2	Myanmar	744.498
3	Indien	689.310
4	Tansania	680.000
5	Nigeria	480.000
6	Volksrepublik China	467.000
7	Burkina Faso	374.703
8	Äthiopien	262.654
9	Südsudan	208.109
10	Tschad	170.000

India:

- ~1.5 Mio people involved in sesame industry
- Import of sesame from other countries (Africa, Myanmar…)
  → processed, partly re-exported.

Annual Consumption of Sesame Seeds in EU and elsewhere

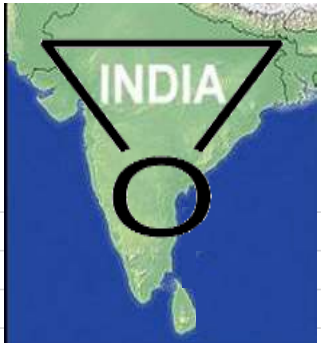
Country	kg/person annually
CY	1.7
GR	1.7
DE	0.3
MT	0.3
NL	0.3
PL	0.3
CH	0.3
LU	0.2
DK	0.2
AT	0.2
SI	0.2
NO	0.2
All other MS	≤ 0.1

Country	kg/person annually
Lebanon	5
Israel	5
Syria	3
Turkey	1.3
Tunisia	1.1
Egypt	0.7
China	0.7
India	0.3
Kenya	0.3
Morocco	0.2
Algeria	0.1

Some consumer groups may phase higher risk and may need to be protected

Source: https://app.indexbox.io/table/120740/0/

RASFF-Notifications related to the use of ETHYLENE OXIDE (Sept 2020 – Mid-Oct 2021)



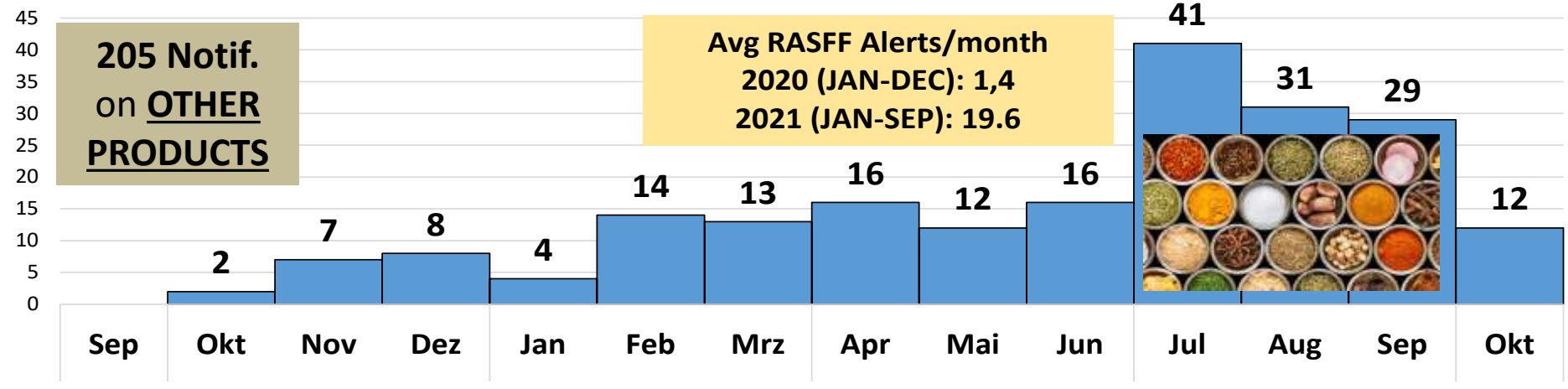
INDIA most often named as origin

525 Notif. on SESAME PRODUCTS

Avg RASFF Alerts/month
2020 (JAN-DEC): 33.2
2021 (JAN-SEP): 14.0
2021 (APR-SEP): 1.6

205 Notif. on OTHER PRODUCTS

Avg RASFF Alerts/month
2020 (JAN-DEC): 1,4
2021 (JAN-SEP): 19.6

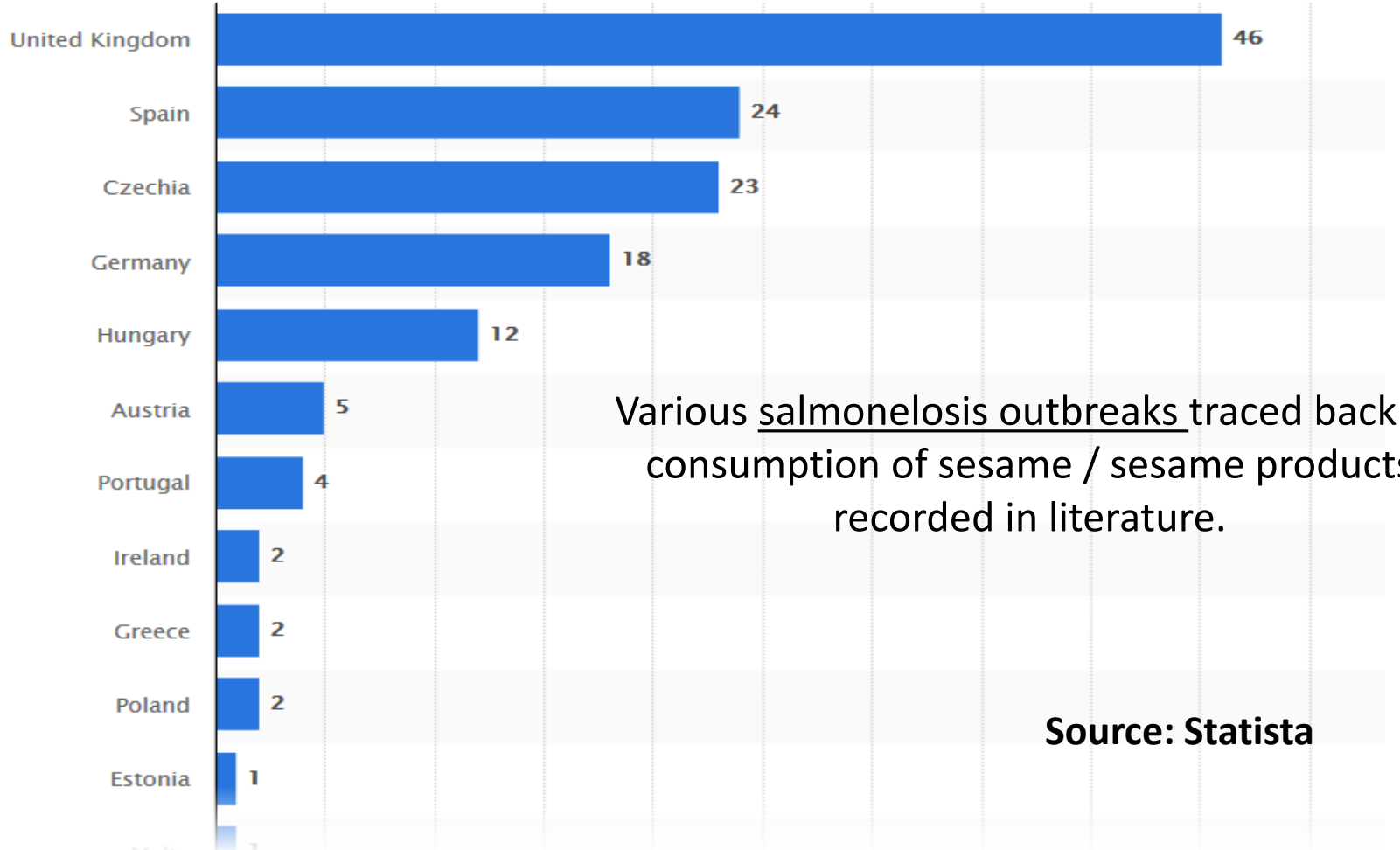


RASFF-Notifications related to the use of ETHYLENE OXIDE (Sept 2020 – Today)

Conventional vs. Organic

Problems with Salmonella contamination

Number of deaths caused by salmonellosis confirmed in Europe in 2019, by country



Various salmonelosis outbreaks traced back to consumption of sesame / sesame products recorded in literature.

Source: Statista

Problems with Salmonella contamination in Sesame

RASFF Notifications on Salmonella and other enterobacteria in Sesame:

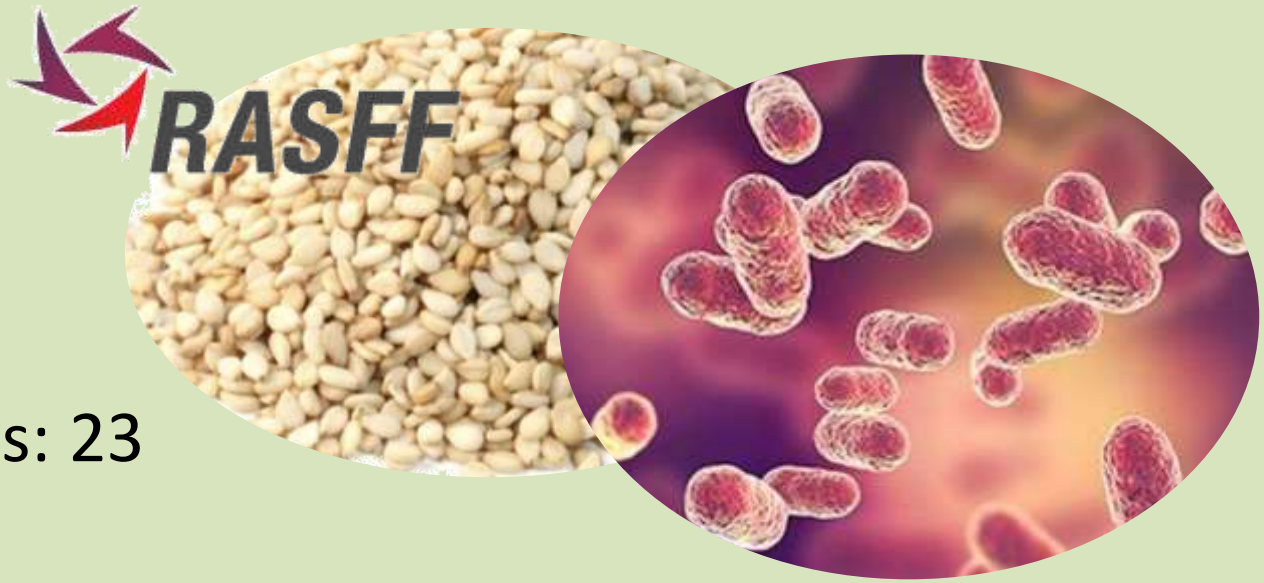
First **notification**: Germany (2001 3x).

First **Border rejection**: Greece (2007).

RASFF Notifications on Salmonella in Sesame since 2001

- Greece: 60
- Italy: 45
- Poland: 45
- Germany: 34
- The Netherlands: 23

…



Problems with Salmonella contamination

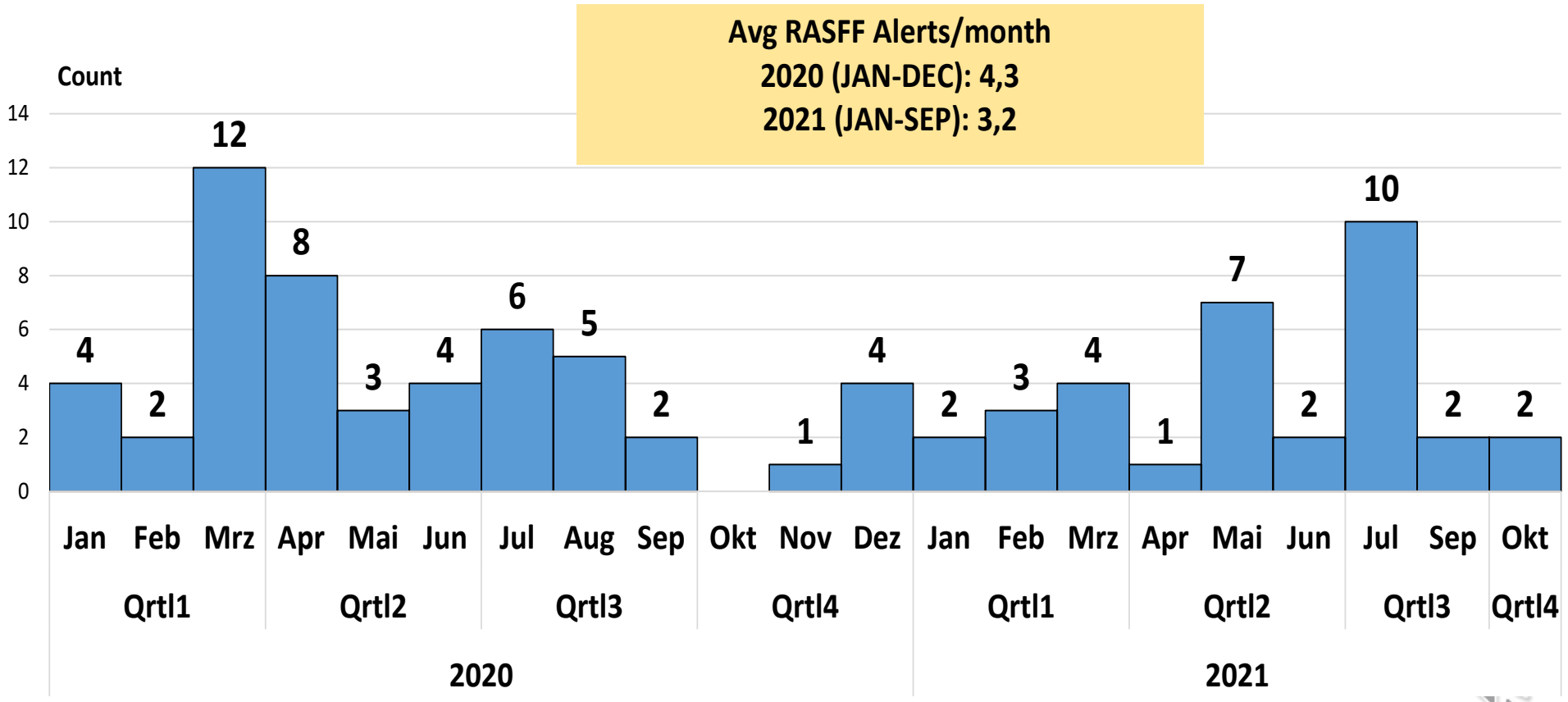
Reg. 669/2009/EC: Increased Border Controls

Increased level of import controls on sesame seeds to be checked for salmonella

- **Oct. 2014: India (20% of lots)**
- **Dec. 2016 : Uganda (50% of lots)**
- **Feb. 2017:** Health Certificate + laboratory report verifying absence of Salmonella spp. shall accompany each consignment of sesame seeds
- **Jun. 2017: Nigeria and Sudan (50%). Outbreaks in GR, DE, CZ, LU, UK**
- **Jan 2019: Ethiopia (50%)**

RASFF

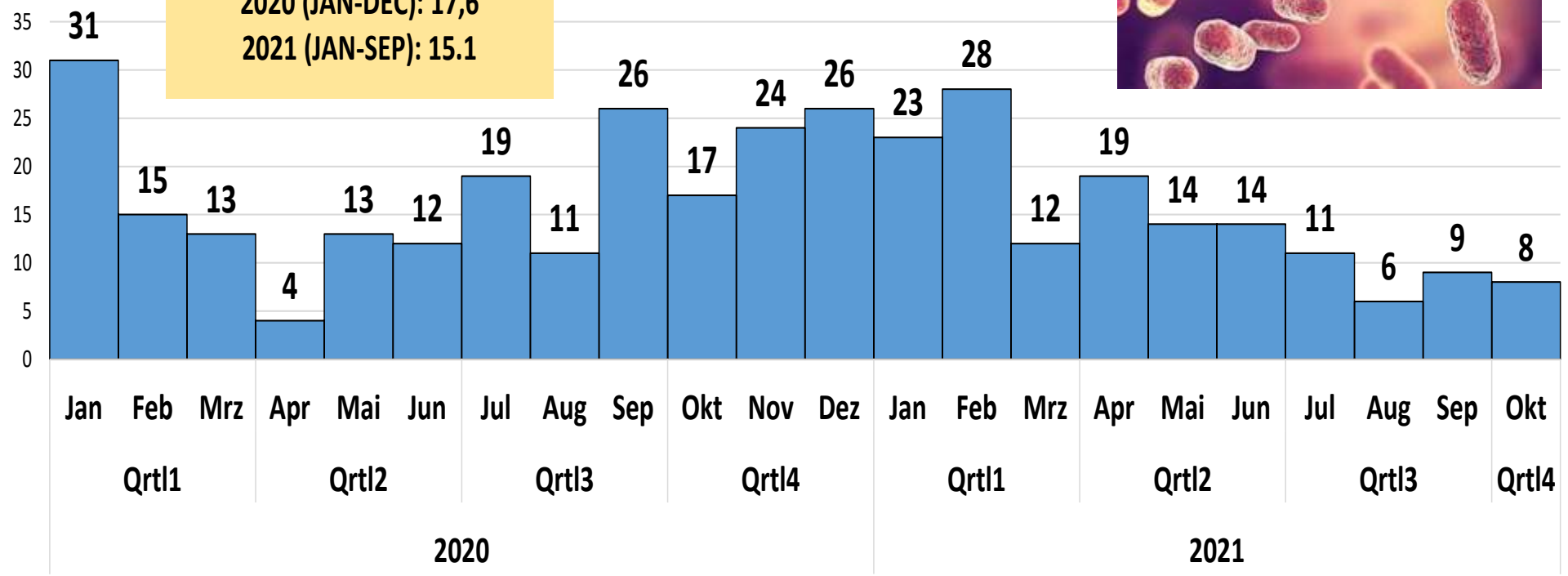
RASFF-Notifications related to Enterobacteria in SESAME PRODUCTS (Jan 2020 – mid-Oct 2021)



RASFF-Notifications related to Enterobacteria in OTHER DRY PRODUCTS (Jan 2020 – Today)

Avg RASFF Alerts/month
2020 (JAN-DEC): 17,6
2021 (JAN-SEP): 15.1

1 out of 3 concerning pepper from Brasil




WORSE
BAD

Overview of RASFF-Notifications (Jan2020-Oct2021

Matrix Group	Ethylene Oxide (2CE)	Enterobacteria
Sesame and products thereof	525	84
Thikeners	44	
Spices	44	136
Food Supplements	27	1
Cereals/Pseudocereals + products	25	4
Various superfood	20	7
Plant Extracts	11	
Instant Noodles	10	
Other nuts and oilseeds	9	25
Dried fruit and Veg	7	3
CaCO3	3	
Sausages	2	
Herbs, dried	1	5

SPICES: RASFF-Notifications (Jan2020-Oct2021

Matrix Group	Ethylene Oxide (2CE)	Enterobacteria
Spice blend (incl. Curry)	16	5
Curcuma	8	1
Paprika/Chili dried	7	14
Ginger	5	1
Pepper (spice)	2	110
Coriander seeds	1	1
Fenugreek	1	1
Celery seeds	1	
Sumac	1	
Ajowan caraway	1	
Isabgol seeds	1	
Nigella seeds		1
Cumin		1
Nutmeg		
Spice mix		1
Mustard seed		1
Overall	**44**	**136**

Overview of EO findings at EURL-SRM/CVUA Stuttgart

Zeilenbeschriftungen	TOTAL Analyzed	<0,02	0,02-MRL	>MRL (numerical)	>MRL (consid. MU)	Total >MRL %
Sesame + Products	**115**	89	7	2	17	17%
Spices and Herbs	**111**	68	27	11	5	14%
Capsules/Tablets	**92**	70			8 (+ 14)	9%
Dried vegies + mushr.	**22**	18	1	2	1	14%
Nuts	**20**	19	1			0%
Superfood	**14**	12			2	14%
Oily seeds, other	**13**	10	3			0%
Pulses	**11**	11				0%
Dried seafood + algae	**11**	11				0%
Dried Fruits	**10**	5	4		1	10%
Teas and infusions	**5**	5				0%
Guar gum + products	**5**	3			2	*(40%)*
Pseudocereals	**3**	2			1	*(33%)*
TOTAL	**432**	**323**	**43**	**15**	**37+14**	12%

EO Residues in Food Supplements

	Analyzed	<LOQ	> Food MRL	with EO
Capsules/Tablets	**92**	**70**	**8**	**14**
Capsules with content	45	33	8	4
Capsules empty	17	15		2
Tablets	30	22		8

Capsules mostly composed of Semisynthetic polymer **Hypromelose** (Hydroxypropylmethylcellulose = E464)

Often other components are added such as **Carrageen** and **PEG**

EO Residues in FOOD SUPPLEMENTS (only positive samples)

Type	Description	Notes	ORG	Conc. EO (sum)
CAPSULES	Moringa powder	Industry feedback: entire capsule >820; powder not analyzed; capsule (gelatine-based) 0.14 (-> concl: **Moringa was contaminated**)		2210
	Prickly pear flower powder 1	Same as ..2 but other LOT, cellulose-based capsule		146
	Extract of plants, minerals, vitamins	Powder alone 164 (2CE); emptied capsule 372		108
	Prickly pear flower powder 2	Capsule emptied in lab 480; powder alone 49.7		79
	Extract of plants, vitamins, minerals	Powder alone 8,7 mg/kg; emptied capsule: 739 mg/kg (both 2CE)		62
	Barleygrass, powder	Industry feedback: entire capsule 86; powder 0.017; originally empty capsule 88; (-> concl: **Capsule was contaminated**)		17,5
	Mix of plants for Women	Powder alone:0.81; Shatavari roots powder; sage extract; Ashwagandha roots powder, curcuma powder, Aloe Vera, Algae; Champignons, Spirulina (Arthrospira olatensis), ginger	Organic	1,8
	Vitamins, minerals, bact. cultures			1,3
	Peruvian ginseng (red Maca)			0,821
	Milk thistle powder	Capsule emptied in lab: 6.9; powder alone 0.11 mg/kg 2CE	Organic	0,711
	Curcuma, powder	Capsule emptied in lab: 2.4	Organic	0,219
	Lactose	Capsule emptied in lab and analyzed separately: 0.55		0,090
EMPTY CAPSULES				295
				0,18
TABLETS	Vitamin K2 and D3	cellulose-based coating		14,0
	Vitamin D3			12,0
	Vitamin K2 and D3	Different badge 17.3		10,8
	Magnesium	cellulose-based coating		8,70
	Vitamin D3	cellulose-based coating		7,06
	Magnesium, Calcium, Vitamin D3	analysis of different badge: 4.25		5,80
	Ginger, elderberry, Vitamins …2	same as …1 but other LOT, cellulose-based coating		4,92
	Ginger, elderberry, Vitamins …1	cellulose-based coating		3,94

Risk Asessment of 2-CE Levels

EO is a potent **carcinogen**
→ Risk assessment NOT according to ARfD / ADI
Instead use of „**Benchmark-Approach**“
BMDL10 (Benchmark dose lower confidence limit 10%) = 370 µg/kg BW
+ **margin of exposure of 10,000** to minimize cancer risk to 1:100,000)

→ Tolerable intake of reduced concern by adults : 0,037 µg/kg BW per day

2-CE possibly cancerogen and mutagen.
Available tox. data insufficient → **precautionary principle**

↓

apply toxicological threshold of EO

www.bfr.bund.de

BfR
Bundesinstitut für Risikobewertung

DOI 10.17590/20201223-111442

Gesundheitliche Bewertung von Ethylenoxid-Rückständen in Sesamsamen

Aktualisierte Stellungnahme Nr. 024/2021 des BfR vom 01. September 2021*

Judgement of residue levels in Food Supplements

BfR

Tolerable intake by adults : 0,037 µg/kg BW per day

Erzeugnis	2-Chlorethanol in mg/kg (Ethylenoxid Äquivalente)	Empfohlene Verzehrmenge pro Tag (laut Verpackung)	Aufnahmemenge für Erwachsene (76,37 kg mittl. KG)
Gerstengras-Kapseln	96,8	12 Kapseln (0,552 g/Kapsel)	**8,4 µg/kg KG**
Moringa-Kapseln	2035	9 Kapseln (0,604 g/Kapsel)	**145 µg/kg KG**
Rote Maca-Kapseln	0,93	4 Kapseln (0,626 g/Kapsel)	0,0305 µg/kg KG
Pukka-Frauenglück-Kapseln	1,8	2 Kapseln (0,67 g/Kapsel)	0,0316 µg/kg KG
Mariendistel-Kapseln	0,71	2 Kapseln (0,4 g/Kapsel)	0,0074 µg/kg KG
Kaktusfeige-Kapseln	79,2	3 Kapseln (0,5 g/Kapsel)	**1,556 µg/kg KG**
Vitamin-D-Tabletten	12	1 Tablette (0,407 g Tablette)	**0,064 µg/kg KG**
Vitamin K2, Vitamin D3 Tabletten	9,5 10,8	1 Tablette (0,43 g Tablette)	**0,053 µg/kg KG** **0,057 µg/kg KG**
Magnesium, Calcium, Vitamin-D3-Tabletten	3,2 5,9	1 Tablette (2,06 g Tablette)	**0,086 µg/kg KG** **0,159 µg/kg KG**


Apply Precautionary Approach (BfR-model) on sesame w. 2CE @ US MRL (940 mg/kg):
Tolerable daily consumption of sesame: 3.6 mg = 1 seed!


Guess what this is ?

In Memoriam

Momofuku Ando (1910-2007)

Pioneer, Procrastinator, Inventor of the Instant Ramen Noodle

"Peace will come to the world when all its people have enough to eat."

TAIWANESE-BORN MOMOFUKU ANDO INVENTED THE INSTANT NOODLE AT THE AGE OF 48 AS A RESPONSE TO THE FOOD SHORTAGES IN POST-WWII JAPAN.

ORIGINALLY A NOVELTY FOOD ITEM, HIS TECHNIQUE OF FLASH-FRYING NOODLES FOUNDED AN EMPIRE THAT SELLS OVER 86 BILLION SERVINGS A YEAR TO FAST-PACED WORKERS AND LAZY ACADEMICS.

HE DIED TODAY AT THE AGE OF 96 (WHO SAID RAMEN NOODLES ARE BAD FOR YOU?)

CUPNOODLES MUSEUM

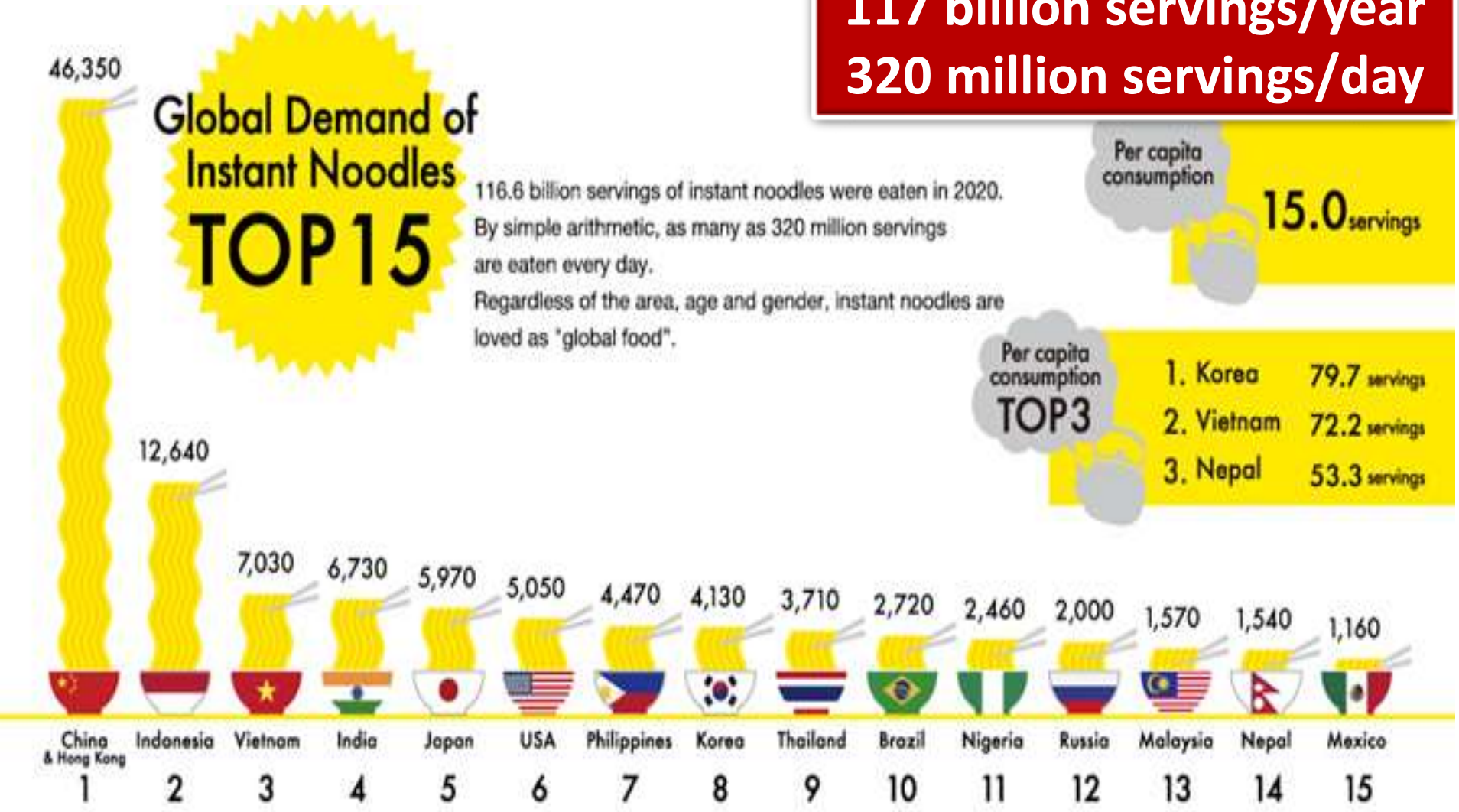
安藤百福発明記念館

OSAKA IKEDA


WINA
World Instant Noodles Assosiation

Instant Noddles - Consumption

117 billion servings/year
320 million servings/day

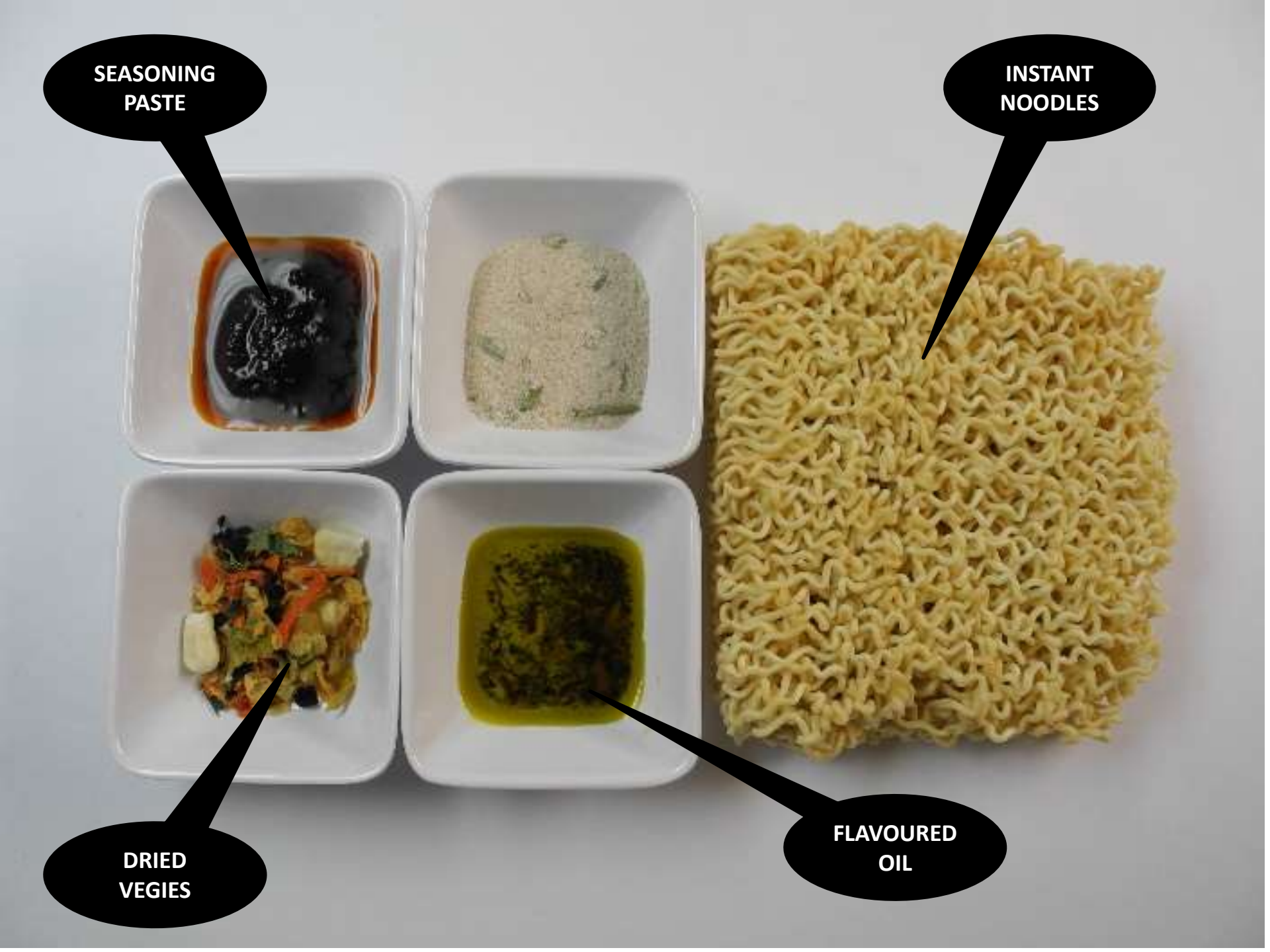


10 countries out of 15 are from Asia, where more than 80% of instant noodles are consumed. Korea leads per capita consumption by far.
The Koreans like instant noodles so much that they are served even at restaurants and stalls there.
In Vietnam and Nepal, instant noodles are popular for breakfast and night snacks.

https://instantnoodles.org/en/noodles/report.html

EO- PILOT MONITORING

13 samples


SEASONING PASTE
INSTANT NOODLES
DRIED VEGIES
FLAVOURED OIL

Analysis of Instant Noodle Soups

Residues in various components of Asia Noddles



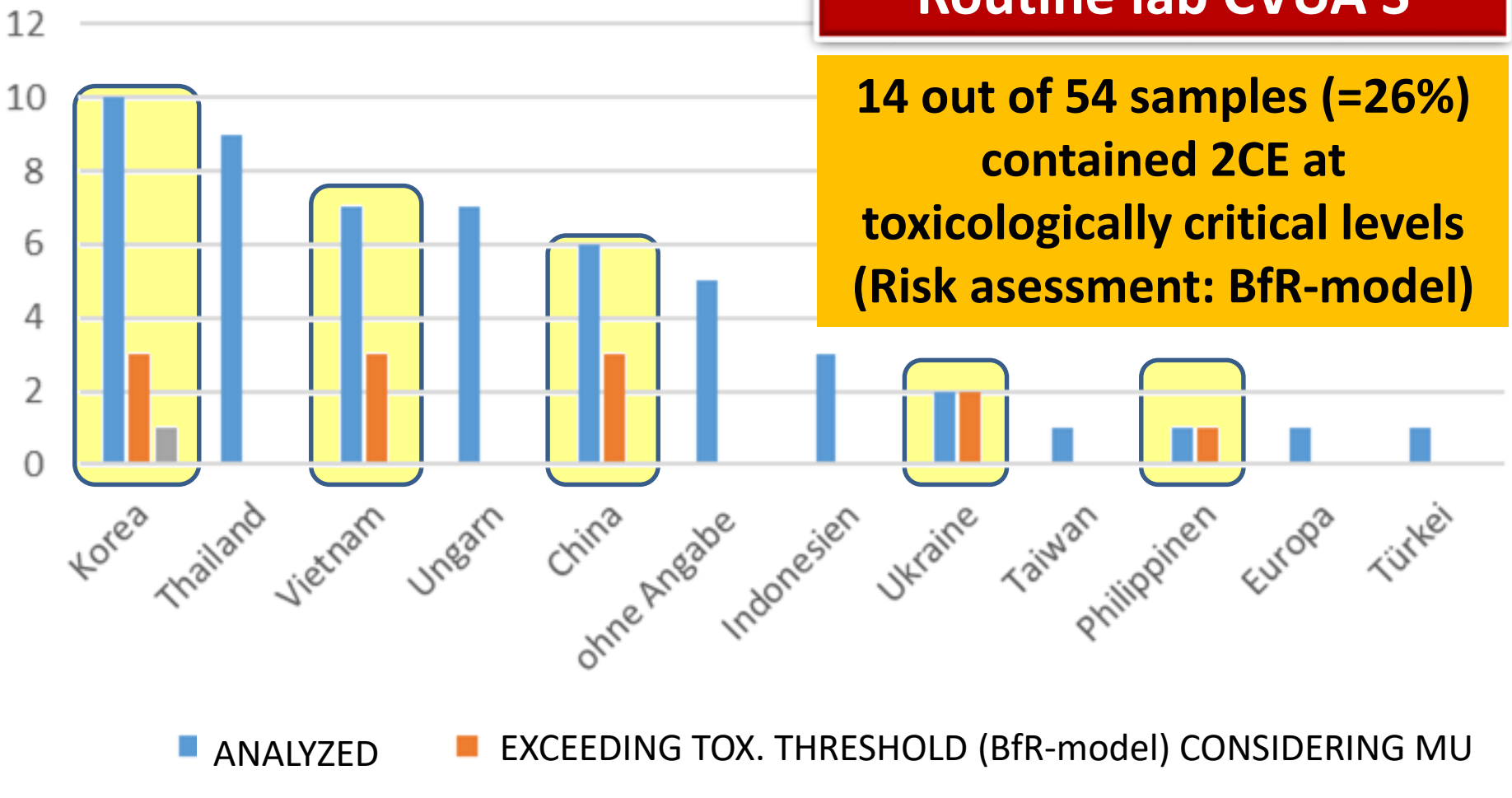
EO- PILOT MONITORING

Origin	Noodles	Dried vegetables/ herbs	Seasoning paste	Soy sauce	Seasoning powder (Soup base)	Seasoning Oil	Dried Chili
China	n.d.		n.d.	n.d.	n.d.		
China	n.d.	n.d.	n.d.		n.d.		
China	1.4	320	1.5				
Hungary/Thailand	n.d.		n.d.		n.d.		n.d.
Indonesia	n.d.	n.d.		n.d.	n.d.	n.d.	n/a
Indonesia	n.d.				n.d.	n.d.	
Indonesia	n.d.				n.d.		n.d.
Korea	0.12	8.8	n.d.				
Taiwan	n.d.		n.d.		n.d.		
Thailand	n.d.				n.d.	n/a	n.d.
Thailand	n.d.			0.28	n.d.	n.d.	
Vietnam	n.d.	0.3	n.d.			n.d.	n.d.
Vietnam	7	180			146		

Additional Noodle Products Analyzed

Routine lab CVUA S

14 out of 54 samples (=26%) contained 2CE at toxicologically critical levels (Risk asessment: BfR-model)



Cross-contamination of 2-CE

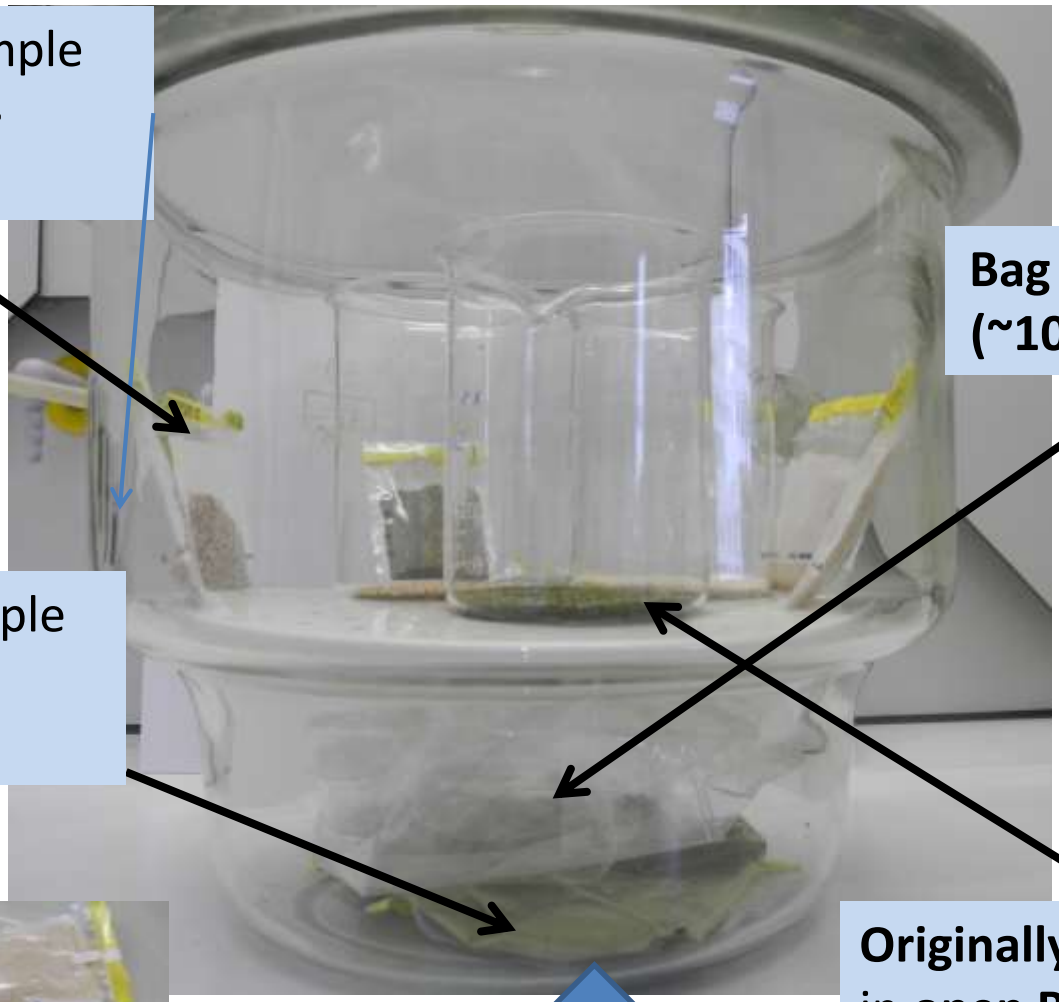
2CE-containing Moringa (75 g) in **KNOTTED** plastic bag

2CE-containing Moringa (75 g) in **OPEN** plastic bag

Originally Blank sample in **closed WhirlPak -** ~10 cm distance

Bag with Moringa (~1000 ppm 2-CE)

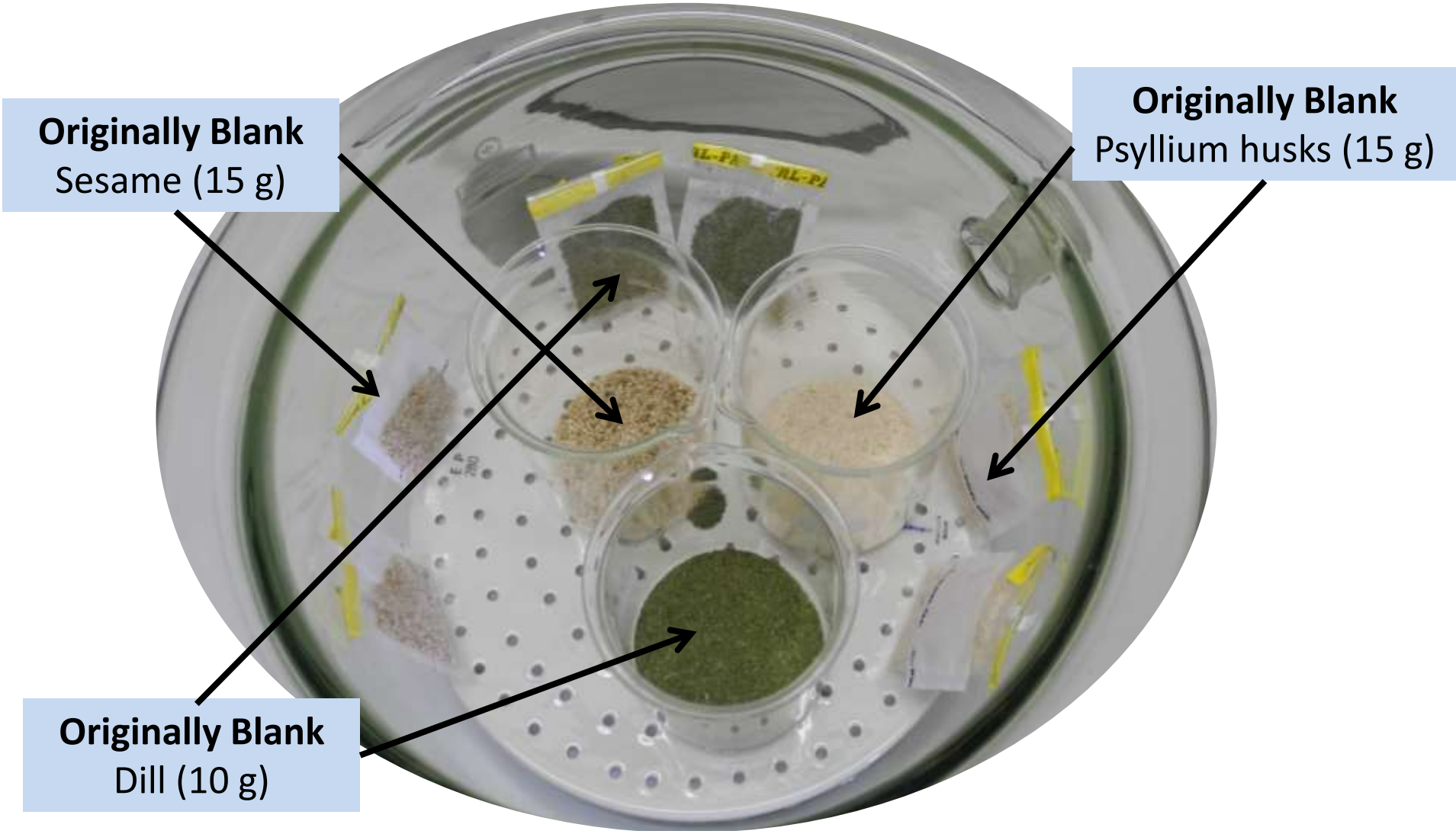
Originally Blank sample in **closed WhirlPak - No distance**



PLACE ON BOTTOM

Originally Blank sample in **open Beaker -** ~10 cm distance

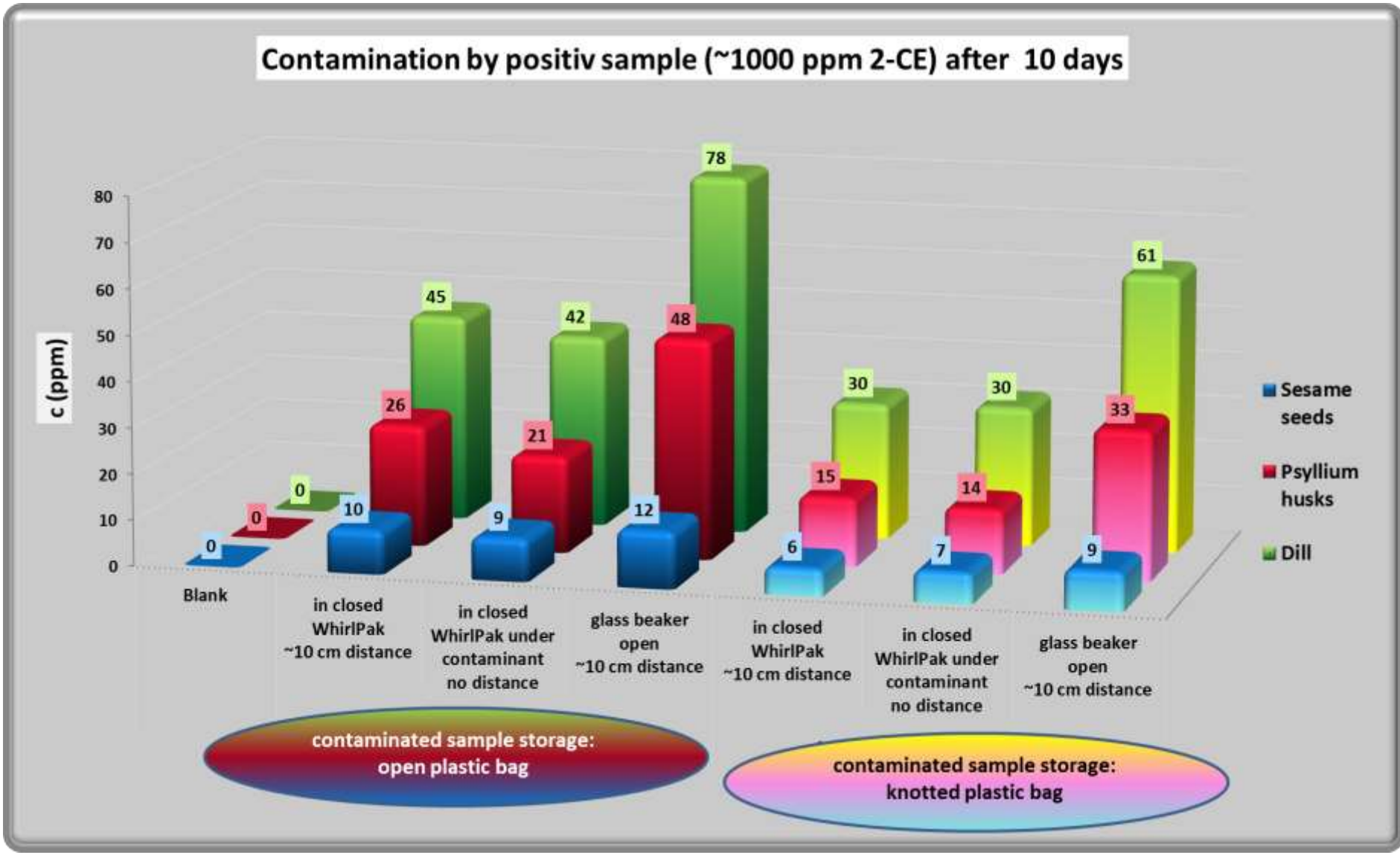
Experiment setup for cross-contamination of 2-CE



Whirl-Paks (bags in different sizes, designed for sampling)

Checked for presence of 2CE or EO (direct extraction) -> ND
Checked for migration of EO or 2CE with dill -> ND

Results


Contamination by positiv sample (~1000 ppm 2-CE) after 10 days
c (ppm)
80
70
60
50
40
30
20
10
0
0
0
0
10
26
45
9
21
42
12
48
78
6
15
30
7
14
30
9
33
61
Blank
in closed WhirlPak ~10 cm distance
in closed WhirlPak under contaminant no distance
glass beaker open ~10 cm distance
in closed WhirlPak ~10 cm distance
in closed WhirlPak under contaminant no distance
glass beaker open ~10 cm distance
Sesame seeds
Psyllium husks
Dill
contaminated sample storage: open plastic bag
contaminated sample storage: knotted plastic bag

PROFICIENCY TESTS

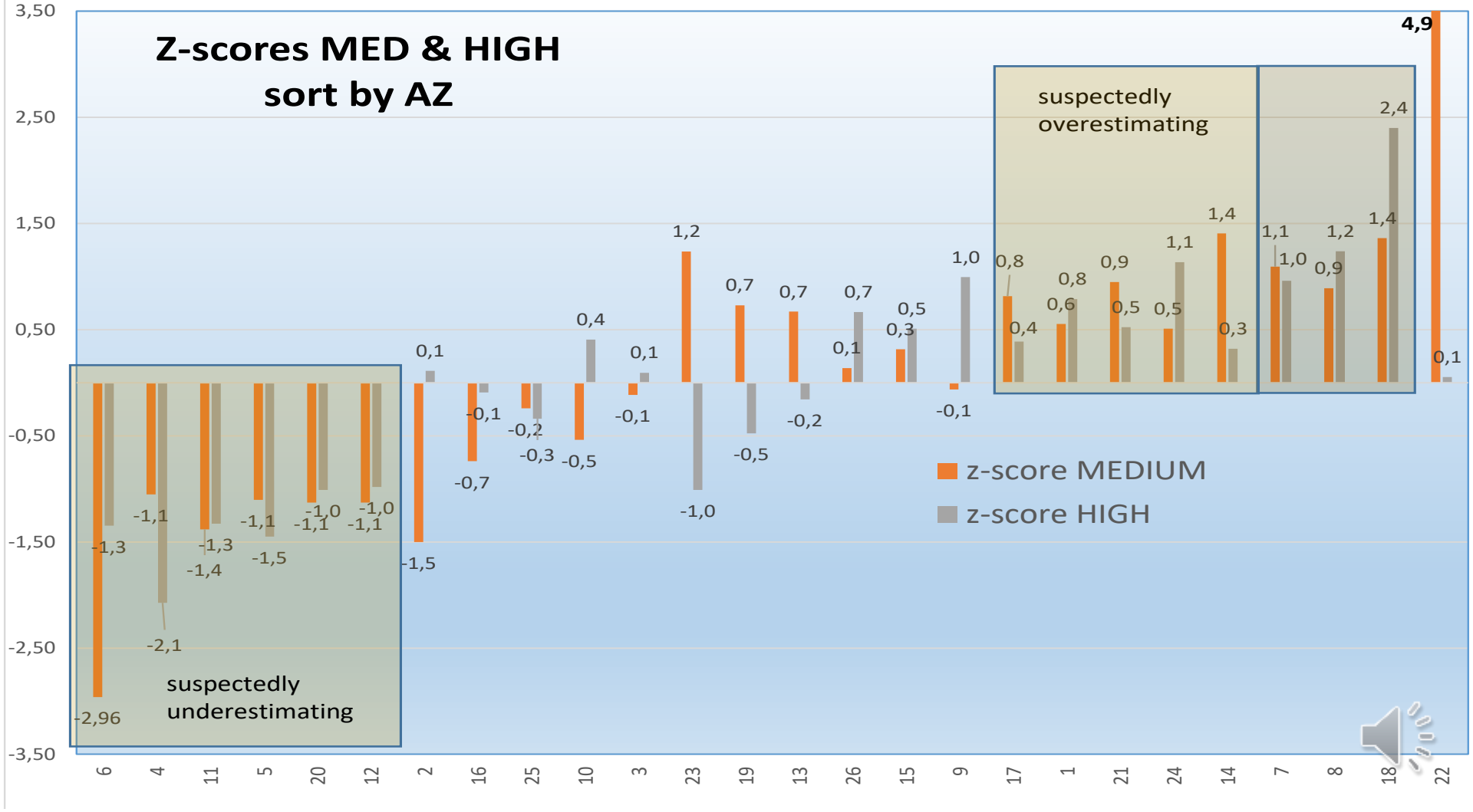
1) AdHoc PT (in collaboration w. Eurofins-DE)

- December 2020
- 3 sesame samples w. incurred 2CE
- 26 2CE results (7 countries; 5x IN)

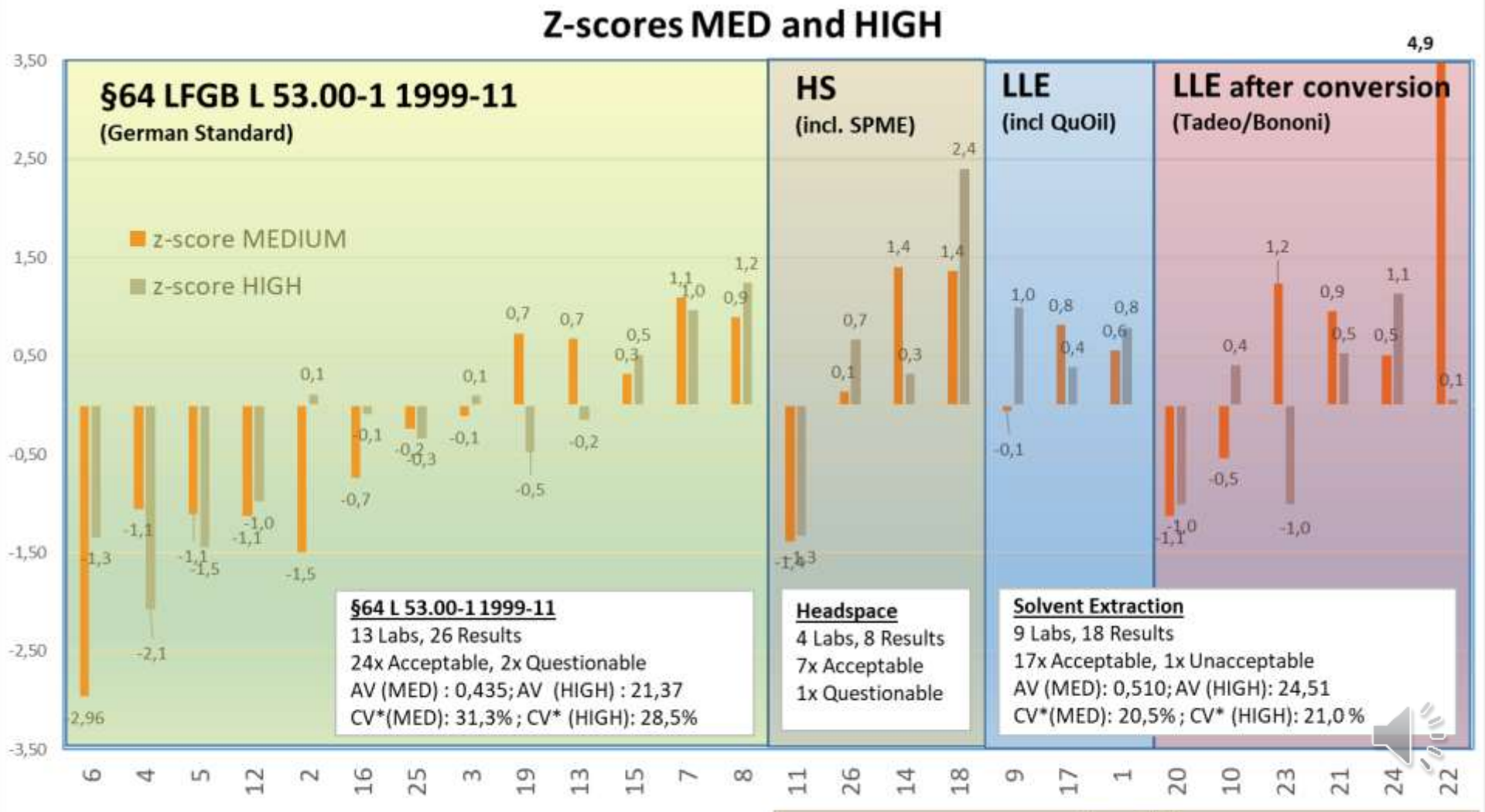
2) Regular EUPT-SRM (in collaboration with COOP-CH)

- March-April 2021
- 1 sesame sample w. incurred 2CE (+ other SRM-analytes)
- 52 2CE results (8x IN)

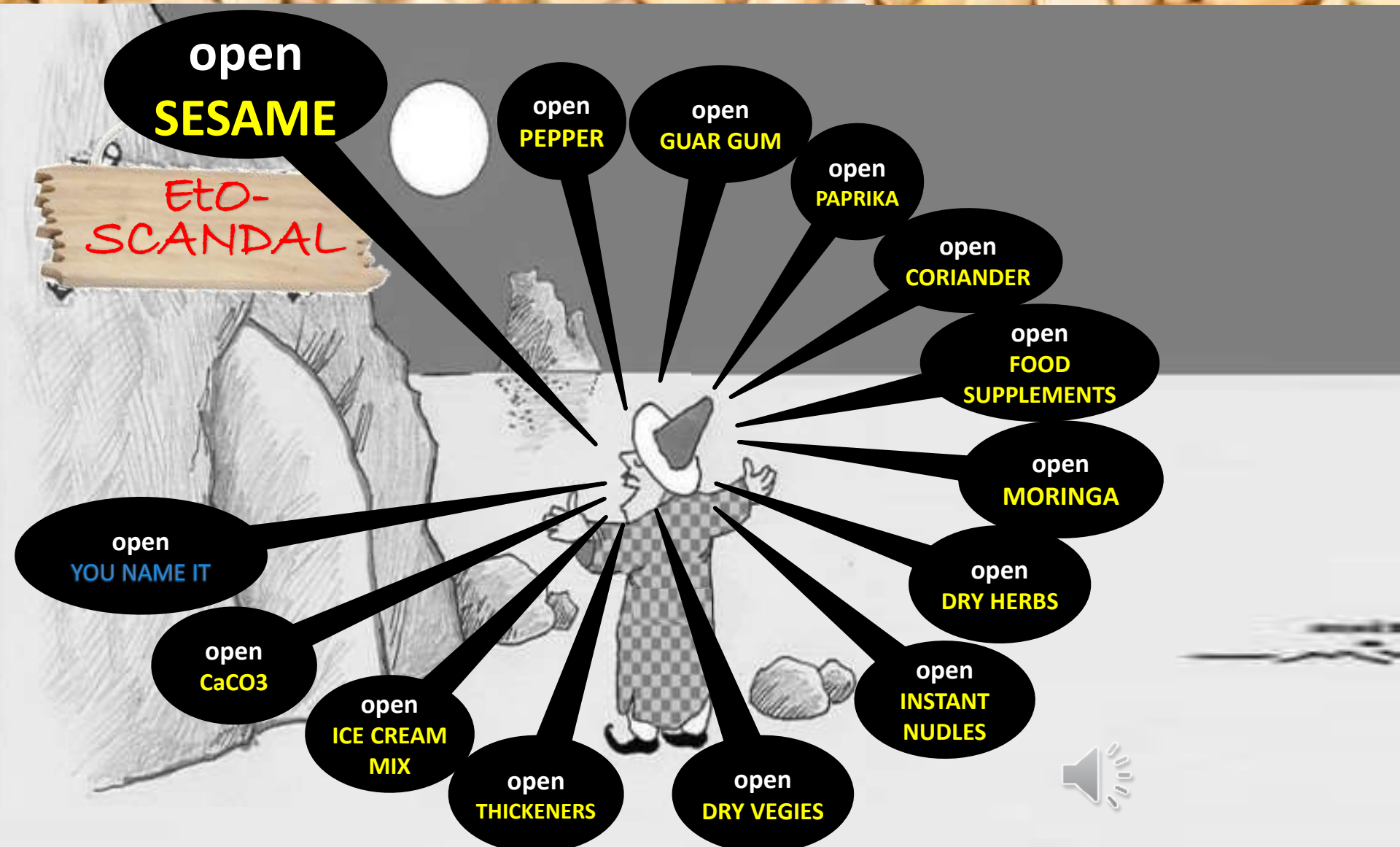
Z-scores of labs ranked by the AZ-score (Average of z-scores) of MED and HIGH samples



Comparison of results obtained by different methods (only MED and HIGH levels shown)



What's Next?


open SESAME
EtO-SCANDAL
open PEPPER
open GUAR GUM
open PAPRIKA
open CORIANDER
open FOOD SUPPLEMENTS
open MORINGA
open DRY HERBS
open INSTANT NUDLES
open DRY VEGIES
open THICKENERS
open ICE CREAM MIX
open CaCO3
open YOU NAME IT

Thank You
for Your Attention

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