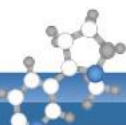


# Current Challenges in the Analysis of Copper Pesticide Residues

E. Eichhorn<sup>1)</sup>, Ann-Kathrin Schäfer<sup>1)</sup>, Susanne Maier<sup>2)</sup>, Jörg Rau<sup>2)</sup>, M. Anastassiades<sup>1)</sup>

1) **European Union Reference Laboratory for Pesticides requiring Single Residue Methods**,  
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Stuttgart, Fellbach, Germany



# Copper Compounds | Introduction

L 95/28

EN

Official Journal of the European Union

4.4.2023

**EU-MACP**

COMMISSION IMPLEMENTING REGULATION (EU) 2023/731

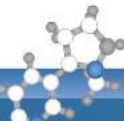
of 3 April 2023

concerning a coordinated multiannual control programme of the Union for 2024, 2025 and 2026 to ensure compliance with maximum residue levels of pesticides and to assess the consumer exposure to pesticide residues in and on food of plant and animal origin and repealing Implementing Regulation (EU) 2022/741

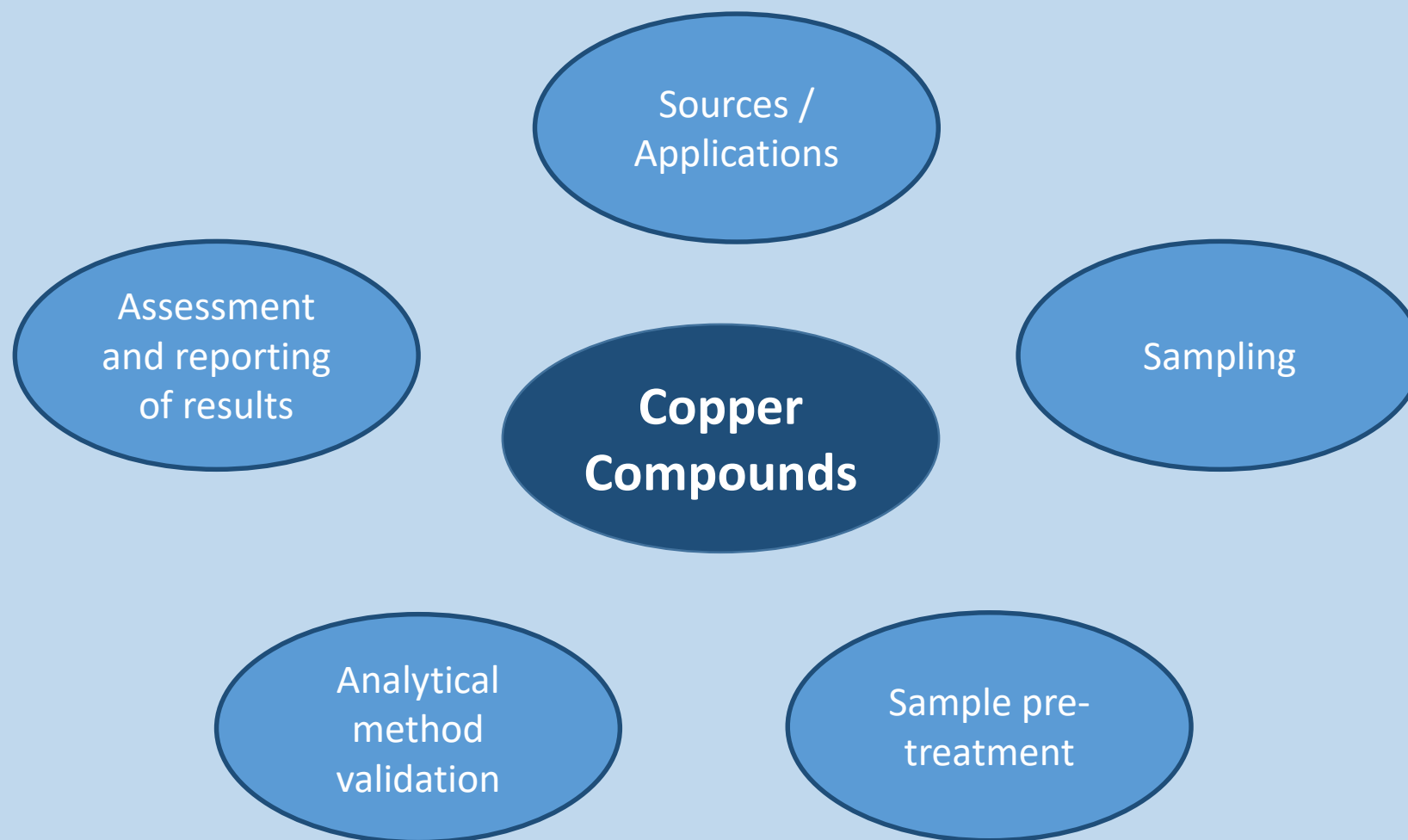
PART C

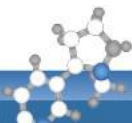
**Pesticide residue/product combinations to be analysed in/on products of plant origin**

	2024	2025	2026	Remarks
Clofentezine	(b)	(c)	(a)	
Clopyralid	(b)	(c)	(a)	
Clothianidin	(b)	(c)	(a)	
Copper compounds	(b)	(c)	(a)	
Cyantraniliprole	(b)	(c)	(a)	
Cyazofamid	(b)	(c)	(a)	
Cyflufenamid	(b)	(c)	(a)	

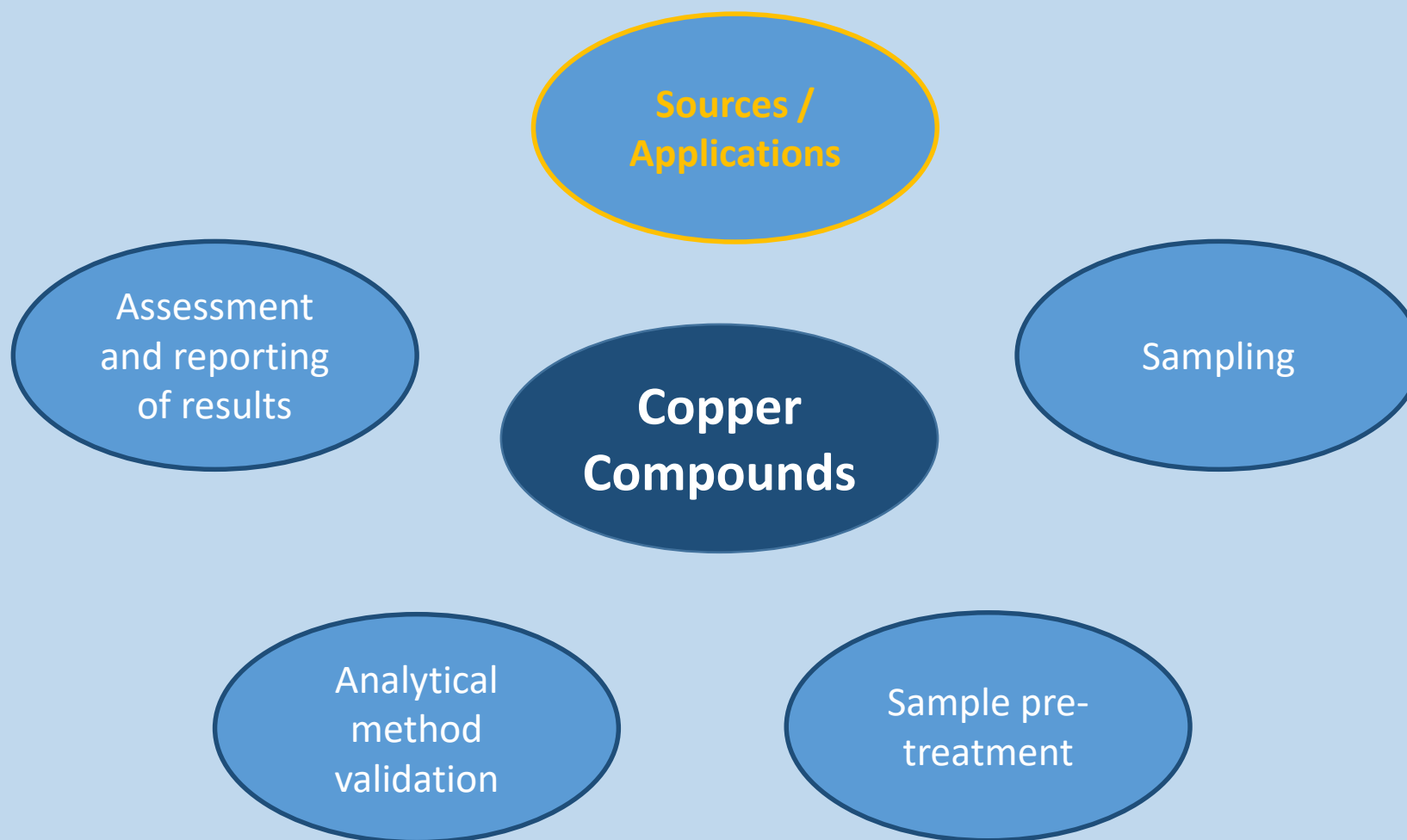


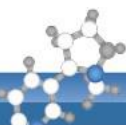
# Copper Compounds | Challenges





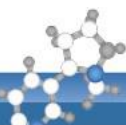
# Copper Compounds | Challenges





# Copper Compounds | Sources and Applications 1

- antimicrobial agent, especially against fungi and bacteria
  - **non-dietary sources**: personal care products, biocides, veterinary medicine,....
  - use as a **pesticide**



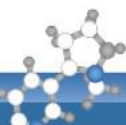
# Copper Compounds | Sources and Applications 2

## USE AS A PESTICIDE:

- approved pesticide active substances according to Reg. (EC) No. 1107/2009
  - Bordeaux mixture\*
  - Copper hydroxide
  - Copper oxide
  - Copper oxychloride
  - Tribasic copper sulphate
- various applications on fruits, vegetables and cereals
- application also approved in organic production according to VO (EU) 2021/1165
- component of other a.s.'s:
  - Mancopper (manganese and copper salt of ethylene-bis-dithiocarbamate)
  - Oxine Copper (Copper salt of 8-Hydroxyquinoline)

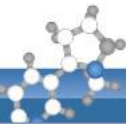
Residue definition according to Reg. (EU) No. 396/2005:  
***Copper Compounds***

\* Bordeaux mixture:  
Mixture of coppersulfate  
& calcium oxide



# Copper Compounds | Sources and Applications 3

- antimicrobial agent, especially against fungi and bacteria
  - **Non-dietary sources:** personal care products, biocides, veterinary medicine,....
  - Use as a **pesticide**
- Essential micro-nutrient for all living organisms as a component of enzymes
  - **feed additive** for all species (Reg. (EC) No. 1334/2003), e.g. 35 mg Cu/kg feeding stuff for bovines
  - **additive in infant and follow-on formulae as well as baby food**
  - **food additives:** component of the pigments Cu-chlorophyll (E 141i) and –chlorophyllin (E 141ii)
  - component in **fertilisers**
    - potential gradual enrichment of copper in the soil and therefore in food crops
    - limitation: Max. 28 kg of copper per hectare over a period of 7 years (as PPP)

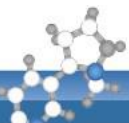


# Copper Compounds | Current practice 1

Finding  
copper?!



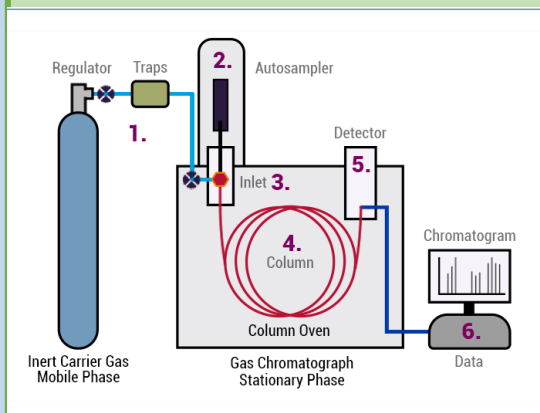




# Copper Compounds| Current practice 1

Finding  
copper?!

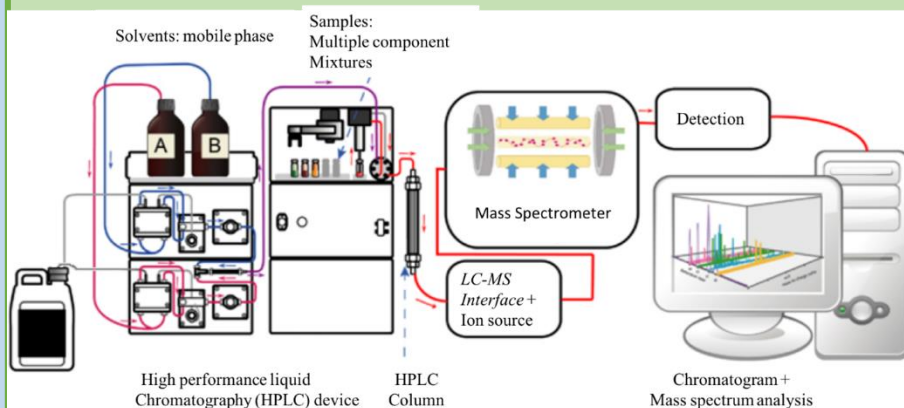
usual analytical equipment  
in a pesticide lab



GC-MS(/MS),  
-HR-MS



<https://blog.perkinelmer.com/posts/gas-chromatography-explained-what-it-is-and-how-it-works/>



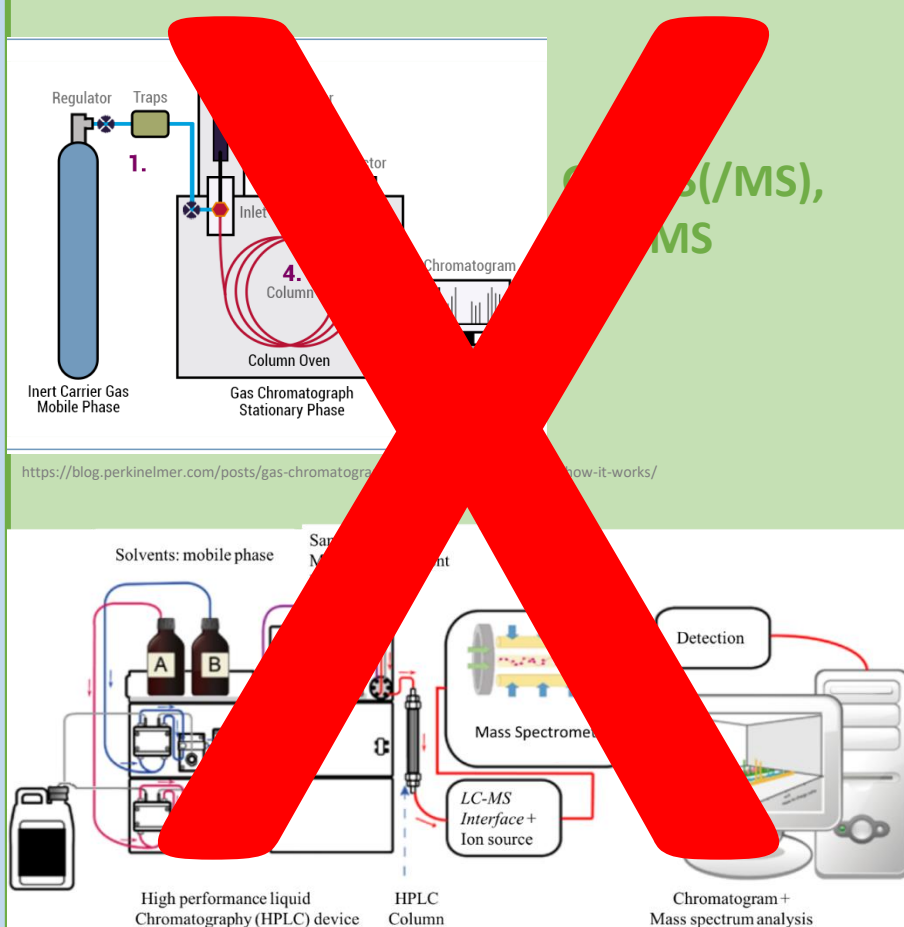
LC-MS/MS,  
-HR-MS

<https://www.technologynetworks.com/analysis/articles/lc-ms-what-is-lc-ms-lc-ms-analysis-and-lc-msms-348238>

# Copper Compounds | Current practice 1

Finding copper?!

usual analytical equipment in a pesticide lab

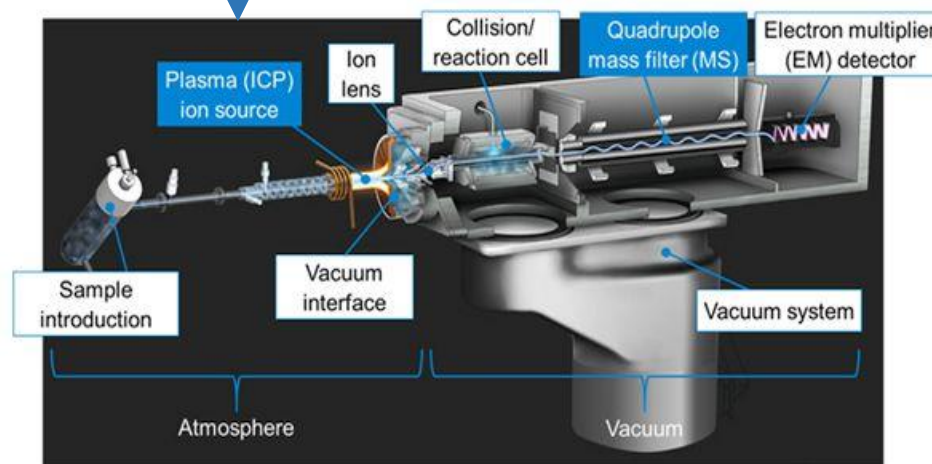


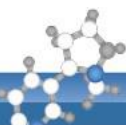
usual analytical equipment in a contaminant/heavy metal lab

Microwave digestion



Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)





# Copper Compounds| Current practice 2

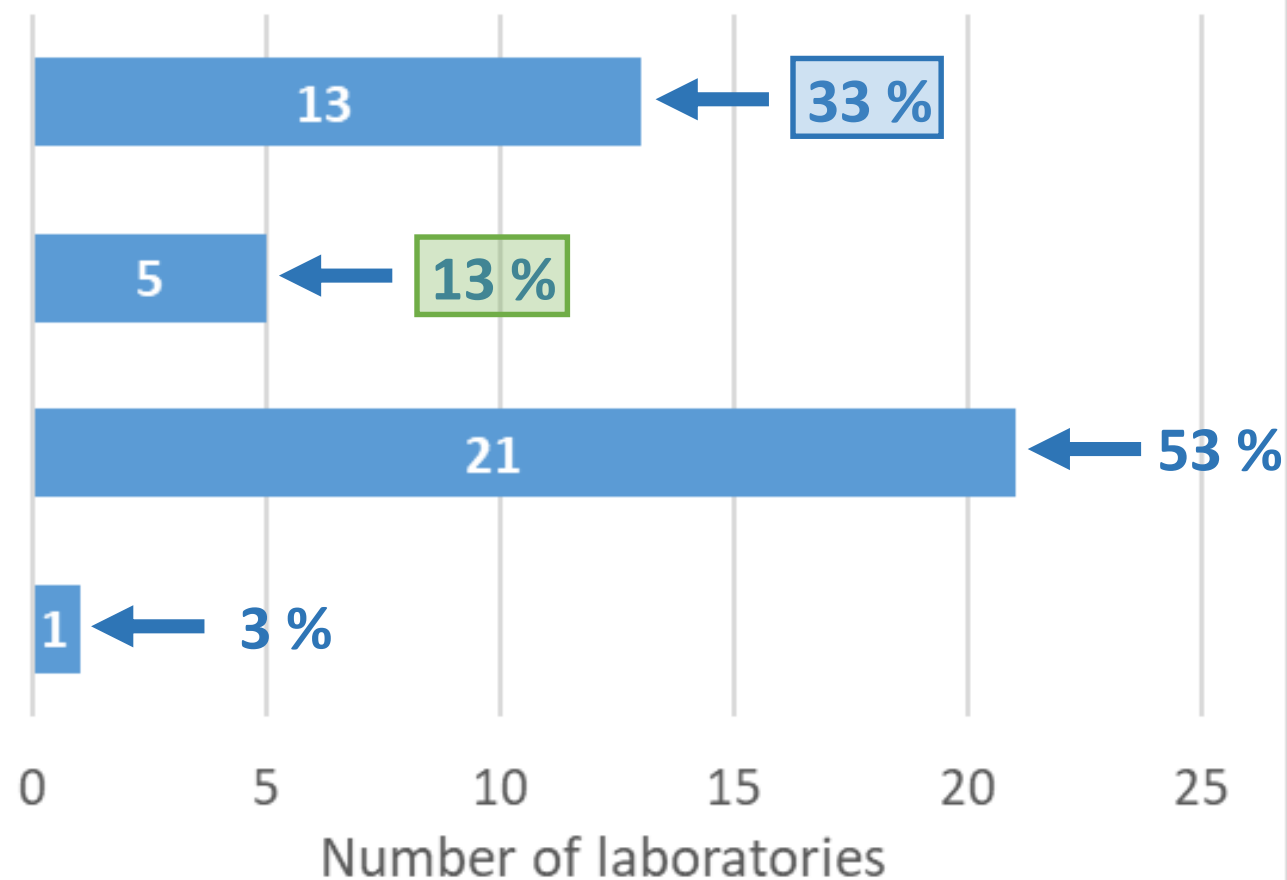
## EU-wide OfL survey, conducted by the EURL-SRM in 2024

ALWAYS sampled and processed as required  
for the analysis of **contaminants**

ALWAYS sampled and processed as required  
for the analysis of **pesticide residues**

DEPENDS on purpose.

Other approach



# Copper Compounds | Current practice 3

**Weigh sample homogenate into a Teflon vessel**

2.0 g (fruit & vegetables)  
0.5 g (dry and high oil content comm.)  
1.0 g (Egg, milk, meat entrails)



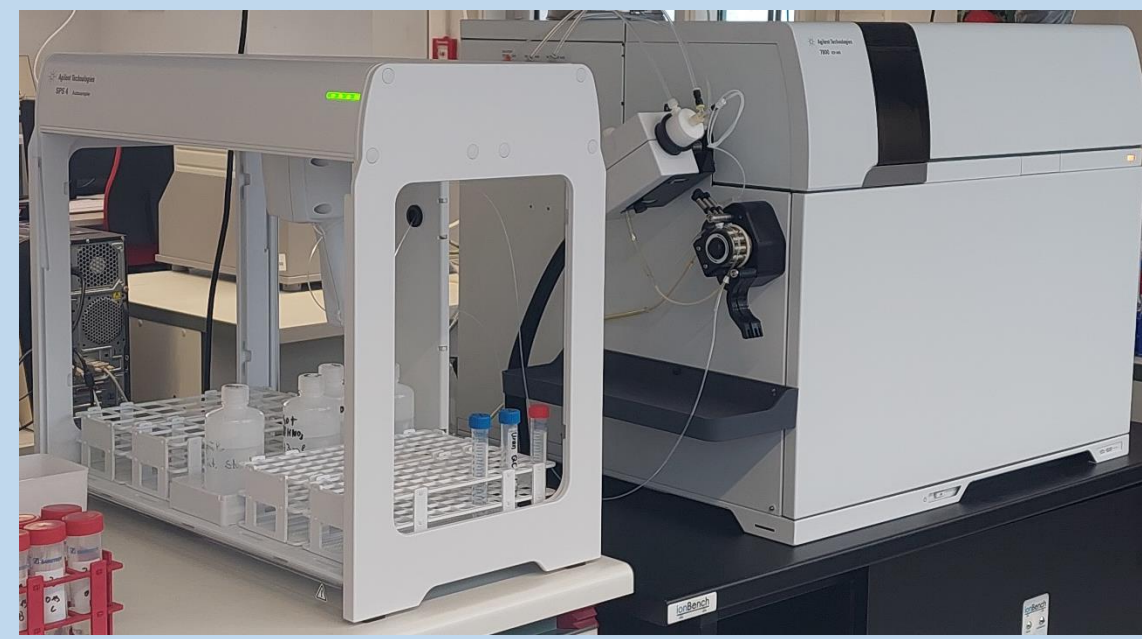
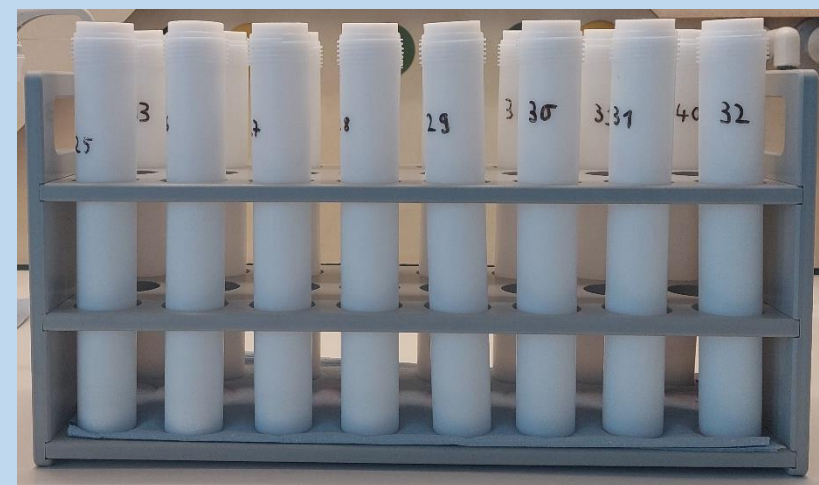
**Addition of acidic solution:  
 $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$**

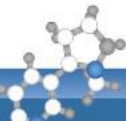


**Microwave digestion**

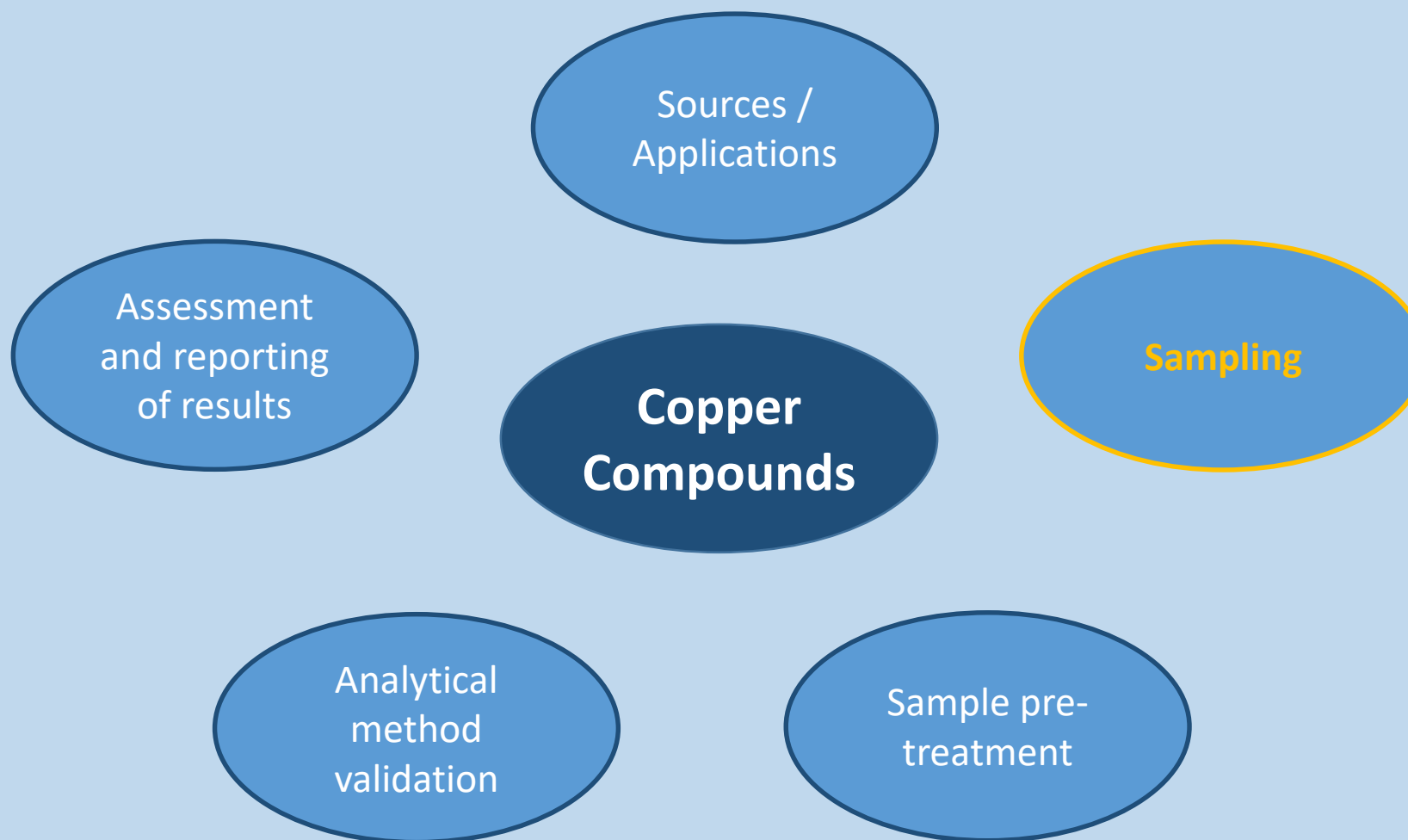


**Measurement with ICP-MS**





# Copper Compounds | Challenges





# Copper Compounds| Sampling

for pesticide analysis

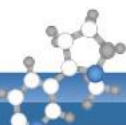
for contaminant analysis

**Dir. 2002/63/EC:**

L 187/30 EN Official Journal of the European Communities 16.7.2002

COMMISSION DIRECTIVE 2002/63/EC  
of 11 July 2002

establishing Community methods of sampling for the official control of pesticide residues in and on products of plant and animal origin and repealing Directive 79/700/EEC



# Copper Compounds | Sampling

for pesticide analysis

for contaminant analysis

Dir. 2002/63/EC:

Table 4

Plant products: description of primary samples and minimum size of laboratory samples

	Commodity classification (1)	Examples	Nature of primary sample to be taken	Minimum size of each laboratory sample
Primary food commodities of plant origin				
1.	All fresh fruits			
	All fresh vegetables including potatoes and sugar beets and excluding herbs			
1.1.	Small sized fresh products units generally < 25 g	Berries, peas, olives	Whole units, or packages, or units taken with a sampling device	1 kg
1.2.	Medium sized fresh products, units generally 25 to 250 g	Apples, oranges	Whole units	1 kg (at least 10 units)
1.3.	Large sized fresh products, units generally > 250 g	Cabbages, cucum- bers, grapes (bunches)	Whole unit(s)	2 kg (at least 5 units)

# Copper Compounds| Sampling: **Example avocados in a retail store**


for pesticide analysis

for contaminant analysis

Dir. 2002/63/EC:


Table 4

Plant products: description of primary samples and minimum size of laboratory samples

	Commodity classification (*)	Examples	Nature of primary sample to be taken	Minimum size of each laboratory sample
				
1.2.	Medium sized fresh products, units generally 25 to 250 g	Apples, oranges	Whole units	1 kg (at least 10 units)
1.3.	Large sized fresh products, units generally > 250 g	Cabbages, cucumbers, grapes (bunches)	Whole unit(s)	2 kg (at least 5 units)



# Copper Compounds| Sampling: **Example avocados in a retail store**

for pesticide analysis					for contaminant analysis				
Dir. 2002/63/EC:					Reg. (EC) No. 333/2007:				
Table 4					29.3.2007    EN    Official Journal of the European Union    L 88/29				
Plant products: description of primary samples and minimum size of laboratory samples					COMMISSION REGULATION (EC) No 333/2007				
					of 28 March 2007				
					laying down the methods of sampling and analysis for the official control of the levels of lead, cadmium, mercury, inorganic tin, 3-MCPD and benzo(a)pyrene in foodstuffs				
									
1.2.	Medium sized fresh products, units generally 25 to 250 g	Apples, oranges	Whole units	1 kg (at least 10 units)					
1.3.	Large sized fresh products, units generally > 250 g	Cabbages, cucumbers, grapes (bunches)	Whole unit(s)	2 kg (at least 5 units)					

# Copper Compounds| Sampling: **Example avocados in a retail store**


## for pesticide analysis

## for contaminant analysis

**Dir. 2002/63/EC:**

Table 4

Plant products: description of primary samples and minimum size of laboratory samples

	Commodity classification (*)	Examples	Nature of primary sample to be taken	Minimum size of each laboratory sample
				
1.2.	Medium sized fresh products, units generally 25 to 250 g	Apples, oranges	Whole units	1 kg (at least 10 units)
1.3.	Large sized fresh products, units generally > 250 g	Cabbages, cucumbers, grapes (bunches)	Whole unit(s)	2 kg (at least 5 units)

**Reg. (EC) No. 333/2007:**

### B.2.2. Number of incremental samples

For food, other than food supplements, dried spices or herbs, dried fungi, algae or lichen, the aggregate sample shall be at least 1 kilogram or 1 litre, except where it is not possible, e.g. when the sample consists of 1 package or unit.

For food, other than food supplements, the minimum number of incremental samples to be taken from the lot or subplot shall be in accordance with Table 3.

Table 3

Minimum number of incremental samples to be taken from the lot or subplot of food, other than food supplements

Weight or volume of lot/sublot (in kilogram or litre)	Minimum number of incremental samples to be taken
< 50	3
≥ 50 and ≤ 500	5
> 500	10



# Copper Compounds| Sampling: **Example avocados in a retail store**


## for pesticide analysis

## for contaminant analysis

Dir. 2002/63/EC:

Table 4

Plant products: description of primary samples and minimum size of laboratory samples

	Commodity classification (1)	Examples	Nature of primary sample to be taken	Minimum size of each laboratory sample
				
1.2.	Medium sized fresh products, units generally 25 to 250 g	Apples, oranges	Whole units	1 kg (at least 10 units)
1.3.	Large sized fresh products, units generally > 250 g	Cabbages, cucumbers, grapes (bunches)	Whole unit(s)	2 kg (at least 5 units)

Reg. (EC) No. 333/2007:

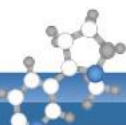
B.2.2. Number of incremental samples

For food, other than food supplements, dried spices or herbs, dried fungi, algae or lichen, the aggregate sample shall be **at least 1 kilogram** or 1 litre, except where it is not possible, e.g. when the sample consists of 1 package or unit.

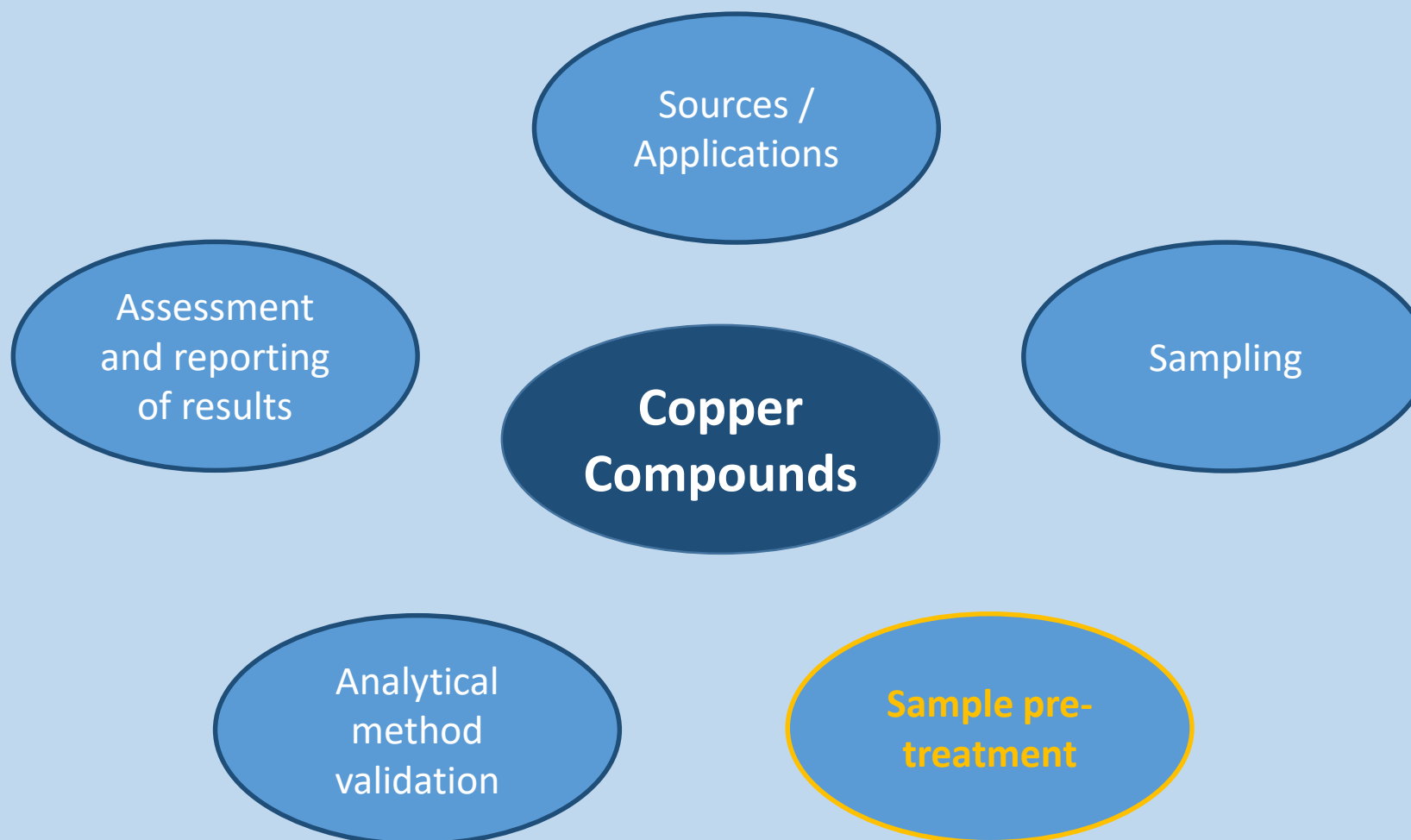
For food, other than food supplements, the minimum number of incremental samples to be taken from the lot shall be in accordance with the following table:

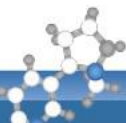


Weight or volume of lot/sublot (in kilogram or litre)	Minimum number of incremental samples to be taken
< 50	3
≥ 50 and ≤ 500	5
> 500	10



# Copper Compounds | Challenges





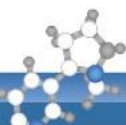
# Copper Compounds | Sample pre-treatment

## for pesticide analysis

## for contaminant analysis

### Dir. 2002/63/EC: Chapter 4.7

- „[...] *The part of the commodity to be analysed (1), (2), [...] should be prepared as soon as practicable.*
- *Where the residue level must be calculated to include parts which are not analysed, the weights of the separated parts must be recorded.“*



# Copper Compounds| Sample pre-treatment

for pesticide analysis

for contaminant analysis

**Dir. 2002/63/EC: Chapter 4.7**

- „[...] *The part of the commodity to be analysed (1), (2), [...] should be prepared as soon as practicable.*
- *Where the residue level must be calculated to include parts which are not analysed, the weights of the separated parts must be recorded.“*

**(1), (2) → Reg. (EU) No. 396/2005 Annex I:**

## PART A

Products of plant and animal origin referred to in Article 2(1) to which MRLs apply

Code number	Category	Group	Main product of the group or subgroup (°)	Part of the product to which MRLs apply
		subgroup		
0160000		Miscellaneous fruits with		Whole product after removal of stems (except pineapples)
0163000		(c) inedible peel, large		
0163010			Avocados	

# Copper Compounds| Sample pre-treatment

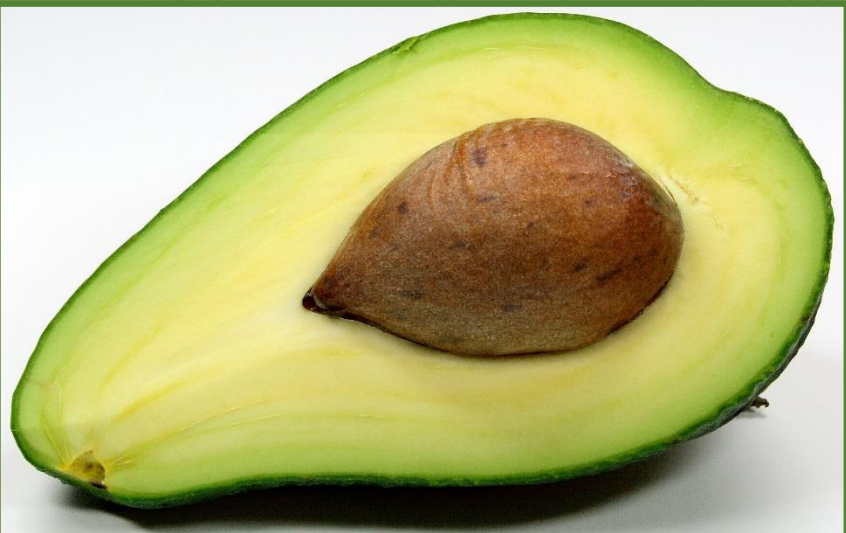
for pesticide analysis

for contaminant analysis

Dir. 2002/63/EC: Chapter 4.7

- „[...] The [...] should [...]
- Where [...] parts v [...] separa [...]

(1), (2) →



Code number	Category	subgroup	Main product of the group or subgroup (1)	Part of the product to which MRLs apply
0160000		Miscellaneous fruits with		Whole product after removal of stems (except pineapples)
0163000		(c) inedible peel, large		
0163010			Avocados	



## 2.4 Procedures for sample preparation



# Copper Compounds| Sample pre-treatment

for pesticide analysis

Dir. 2002/63/EC: Chapter 4.7

- „[...] The sample should be prepared in a way that the results are representative of the whole product, (2), [...] include
- Where parts of the product are separated, (1), (2) →



apply

Code number	Category	subgroup	Main product of the group or subgroup (°)	Part of the product to which MRLs apply
0160000		Miscellaneous fruits with		Whole product after removal of stems (except pineapples)
0163000		(c) inedible peel, large		
0163010			Avocados	

for contaminant analysis

Reg. (EC) No. 333/2007 → EN 13804:2013:  
2.4 Procedures for sample preparation

- „[...] of results
- „Parts should
- „Surface removal
- „Please count

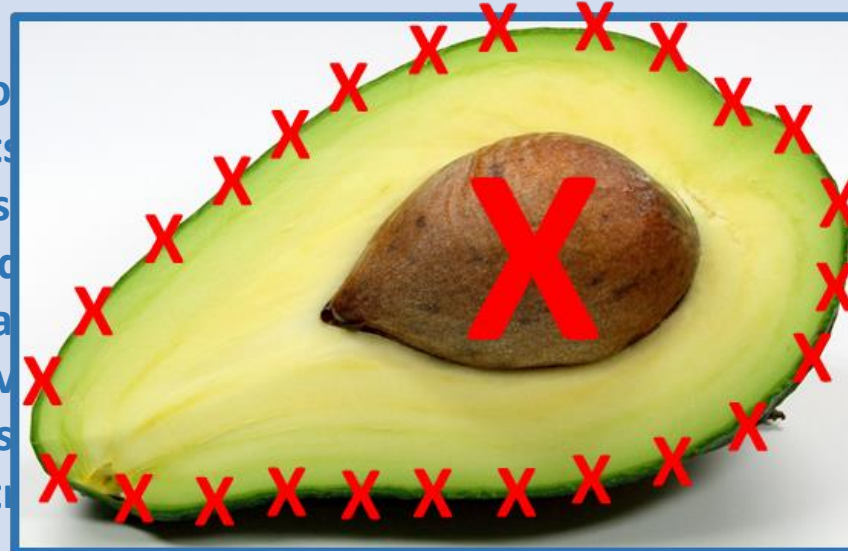


Table 2 — Examples of sample preparation procedures for some foodstuffs

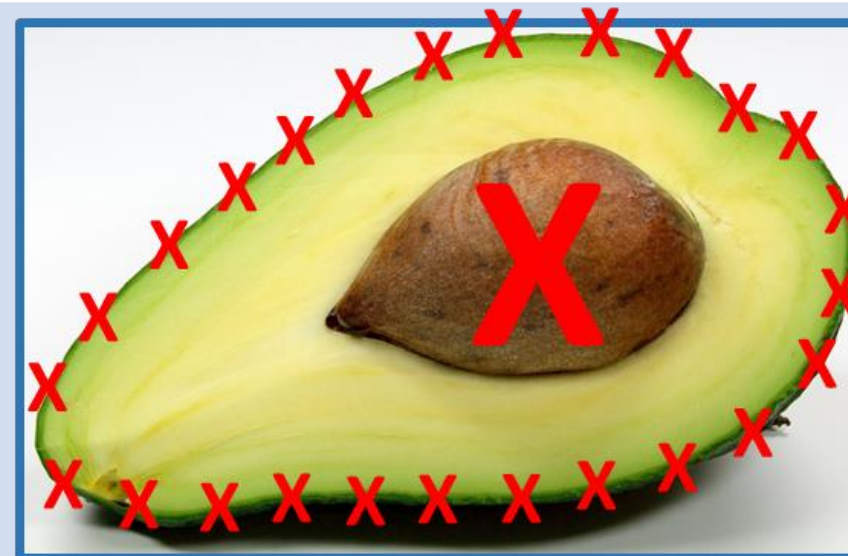
Fruit and fruiting vegetables	Remove stalks, sepals, petals, dirty and rotten parts. Rinse the sample and remove the seeds if necessary. Fruits which are not intended for eating with peel should not be rinsed but peeled and the seeds should be removed (e.g. pumpkin, melon).
-------------------------------	--

# Copper Compounds | Sample pre-treatment

for pesticide analysis

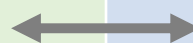


for contaminant analysis

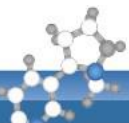


Avocados are the perfect example of the two different main goals of both approaches:

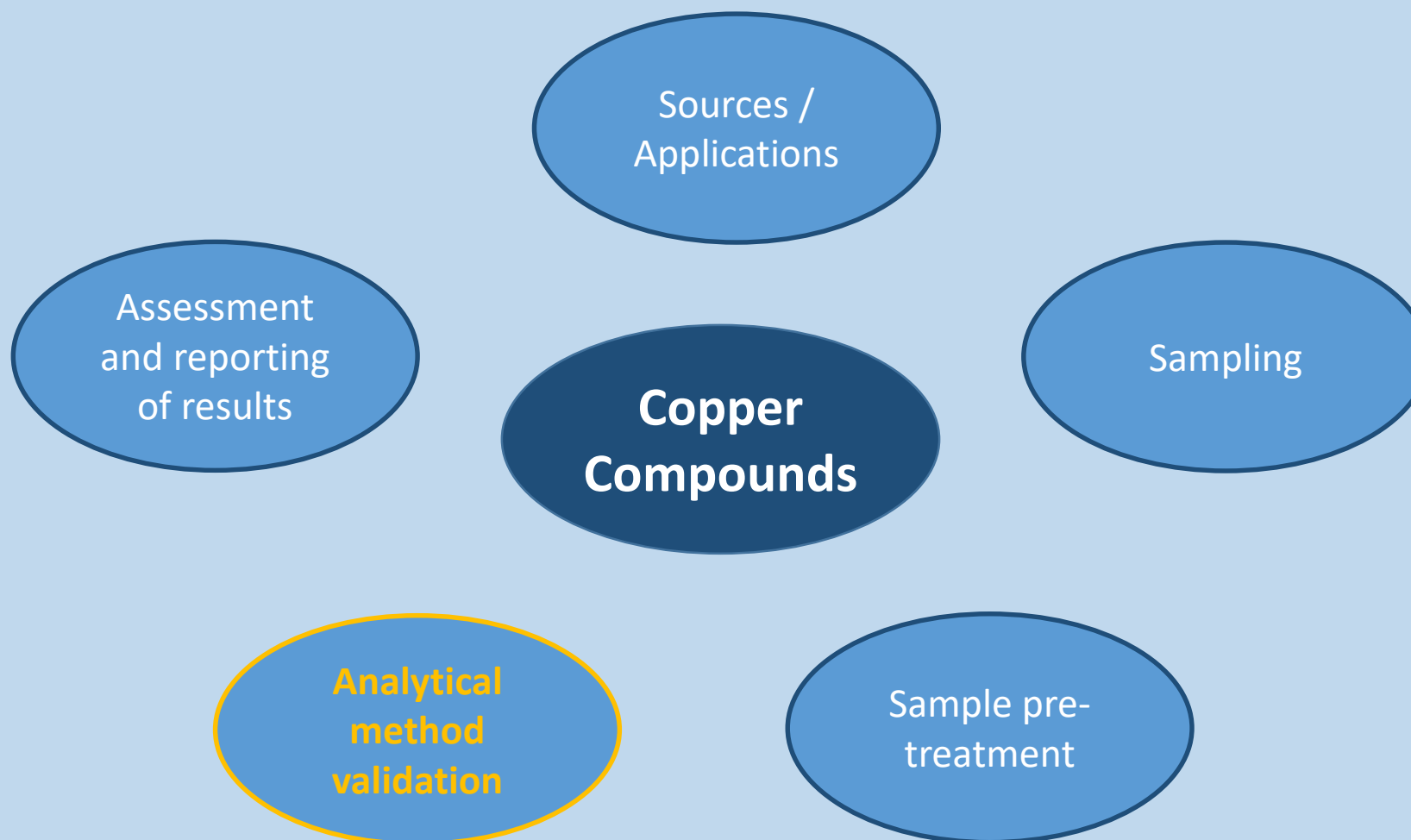
Control of the Good Agricultural Practice

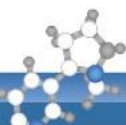


Monitoring of the actual consumer intake



# Copper Compounds | Challenges





# Copper Compounds | Analytical method validation

## for pesticide analysis

## for contaminant analysis

### Document N° SANTE/11312/2021v2

A typical example of the experimental set up of a validation is:

#### Instrumental sample sequence:

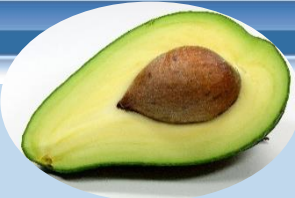
- Conditioning blanks in GC
- Calibration standards\*
- Reagent blank
- Blank sample
- 5 spiked samples at target LOQ
- 5 spiked samples at 2-10 x target LOQ
- Calibration standards\*

\* e.g. involving bracketing calibration using 60 %- and 120 %-levels

**Table 4.** Validation parameters and criteria

Parameter	What/how	Criterion
LOQ	Lowest spike level meeting the identification and method performance criteria for recovery and precision	$\leq$ MRL
Specificity	Response in reagent blank and blank control samples	$\leq$ 30 % of RL
Recovery	Average recovery for each spike level tested	70-120 %
Precision (RSD <sub>r</sub> )	Repeatability RSD <sub>r</sub> for each spike level tested	$\leq$ 20 %





# Copper Compounds| Analytical method validation

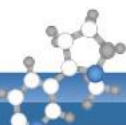
for pesticide analysis

Document Nº SANTE/11312/2021v2

Validation experiment results: 10 mg/kg

	ICP-MS signal (Counts)									
Mass trace	Blank	Matrix Calib. 60 %	Matrix Calib. 120 %	Rec. 1	Rec. 2	Rec. 3	Rec. 4	Rec. 5	Matrix Calib. 60 %	Matrix Calib. 120 %
Lutetium m/z 175 (ISTD)	8.23E+05	8.03E+05	7.90E+05	8.13E+05	8.23E+05	8.32E+05	8.35E+05	8.48E+05	8.26E+05	8.10E+05
Copper m/z 63	4.30E+05	9.98E+05	1.87E+06	1.57E+06	1.64E+06	1.66E+06	1.62E+06	1.62E+06	1.02E+06	1.86E+06
Recovery (%)				98.1	101.3	101.5	98.8	97.0		
Average Recovery (%)				99.3 (%)					criteria fulfilled	
Relative standard deviation (±%)				2.0					criteria fulfilled	

for contaminant analysis



# Copper Compounds | Analytical method validation

for pesticide analysis

for contaminant analysis

Document N° SANTE/11312/2021v2

Validation experiment results: 10 mg/kg

ICP-MS signal (Counts)

Mass trace	Blank	Matrix Calib. 60 %	Matrix Calib. 120 %	Rec. 1	Rec. 2	Rec. 3	Rec. 4	Rec. 5	Matrix Calib. 60 %	Matrix Calib. 120 %
Lutetium m/z 175 (ISTD)	8.23E+05	8.03E+05	7.90E+05	8.13E+05	8.23E+05	8.32E+05	8.35E+05	8.48E+05	8.26E+05	8.10E+05
Copper m/z 63	4.30E+05	9.98E+05	1.87E+06	1.57E+06	1.64E+06	1.66E+06	1.62E+06	1.62E+06	1.02E+06	1.86E+06
Recovery (%)				98.1	101.3	101.5	98.8	97.0		
Average Recovery (%)				99.3 (%)					criteria fulfilled	
Relative standard deviation (±%)				2.0					criteria fulfilled	
Signal in Blank				26 % (of the avg. signal in recovery samples)					criteria fulfilled	

- natural content in avocado: approx. 2.8 mg/kg in average  
(based on CVUA data from 2019, n = 5)
- validation at lower levels virtually impossible
- lowest successfully validated level = MRL = legal **LOQ: 10 mg/kg**

# Copper Compounds | Analytical method validation



for pesticide analysis

for contaminant analysis

Document N° SANTE/11312/2021v2

EN 13804:2013 → DIN 32645:2008-11

Validation experiment results: 10 mg/kg

a) direct calibration curve method:

- standard deviation (SD) of a **number ≥20 of blank measurements**

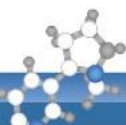
b) indirect calibration curve method:

- **spike** the analyte free sample at **10 equidistant concentrations** of the expected LOD up to 10x of the LOD
- alternative: **four spiking levels in triplicate**
- SD is derived from the interceptions of the calibration curves

	ICP-MS signal (Counts)									
Mass trace	Blank	Matrix Calib. 60 %	Matrix Calib. 120 %	Rec. 1	Rec. 2	Rec. 3	Rec. 4	Rec. 5	Matrix Calib. 60 %	Matrix Calib. 120 %
Lutetium m/z 175 (ISTD)	8.23E+05	8.03E+05	7.90E+05	8.13E+05	8.23E+05	8.32E+05	8.35E+05	8.48E+05	8.26E+05	8.10E+05
Copper m/z 63	4.30E+05	9.98E+05	1.87E+06	1.57E+06	1.64E+06	1.66E+06	1.62E+06	1.62E+06	1.02E+06	1.86E+06
Recovery (%)				98.1	101.3	101.5	98.8	97.0		
Average Recovery (%)				99.3 (%)					criteria fulfilled	
Relative standard deviation (±%)				2.0					criteria fulfilled	
Signal in Blank				26 % (of the avg. signal in recovery samples)					criteria fulfilled	

- natural content in avocado: approx. 2.8 mg/kg in average (based on CVUA data from 2019, n = 5)
- validation at lower levels virtually impossible
- lowest successfully validated level = MRL = legal **LOQ: 10 mg/kg**

- Detection limit: 3x SD
- Limit of quantitation: 10x SD



# Copper Compounds | Analytical method validation

for pesticide analysis

Document N° SANTE/11312/2021v2

Validation experiment results: 10 mg/kg

ICP-MS signal (Counts)

Mass trace	Blank	Matrix Calib. 60 %	Matrix Calib. 120 %	Rec. 1	Rec. 2	Rec. 3	Rec. 4	Rec. 5	Matrix Calib. 60 %	Matrix Calib. 120 %
Lutetium m/z 175 (ISTD)	8.23E+05	8.03E+05	7.90E+05	8.13E+05	8.23E+05	8.32E+05	8.35E+05	8.48E+05	8.26E+05	8.10E+05
Copper m/z 63	4.30E+05	9.98E+05	1.87E+06	1.57E+06	1.64E+06	1.66E+06	1.62E+06	1.62E+06	1.02E+06	1.86E+06
Recovery (%)				98.1	101.3	101.5	98.8	97.0		
Average Recovery (%)				99.3 (%)					criteria fulfilled	
Relative standard deviation (±%)				2.0					criteria fulfilled	
Signal in Blank				26 % (of the avg. signal in recovery samples)					criteria fulfilled	

- natural content in avocado: approx. 2.8 mg/kg in average (based on CVUA data from 2019, n = 5)
- validation at lower levels virtually impossible
- lowest successfully validated level = MRL = legal **LOQ: 10 mg/kg**

for contaminant analysis

EN 13804:2013 → DIN 32645:2008-11

a) direct calibration curve method:

- standard deviation (SD) of a number  $\geq 20$  of blank measurements

b) indirect calibration curve method:

- spike the analyte free sample at **10 equidistant concentrations** of the expected LOD up to 10x of the LOD
- alternative: **four spiking levels in triplicate**
- SD is derived from the interceptions of the calibration curves

- Detection limit: 3x SD
- Limit of quantitation: 10x SD



# Copper Compounds | Analytical method validation



for pesticide analysis

for contaminant analysis

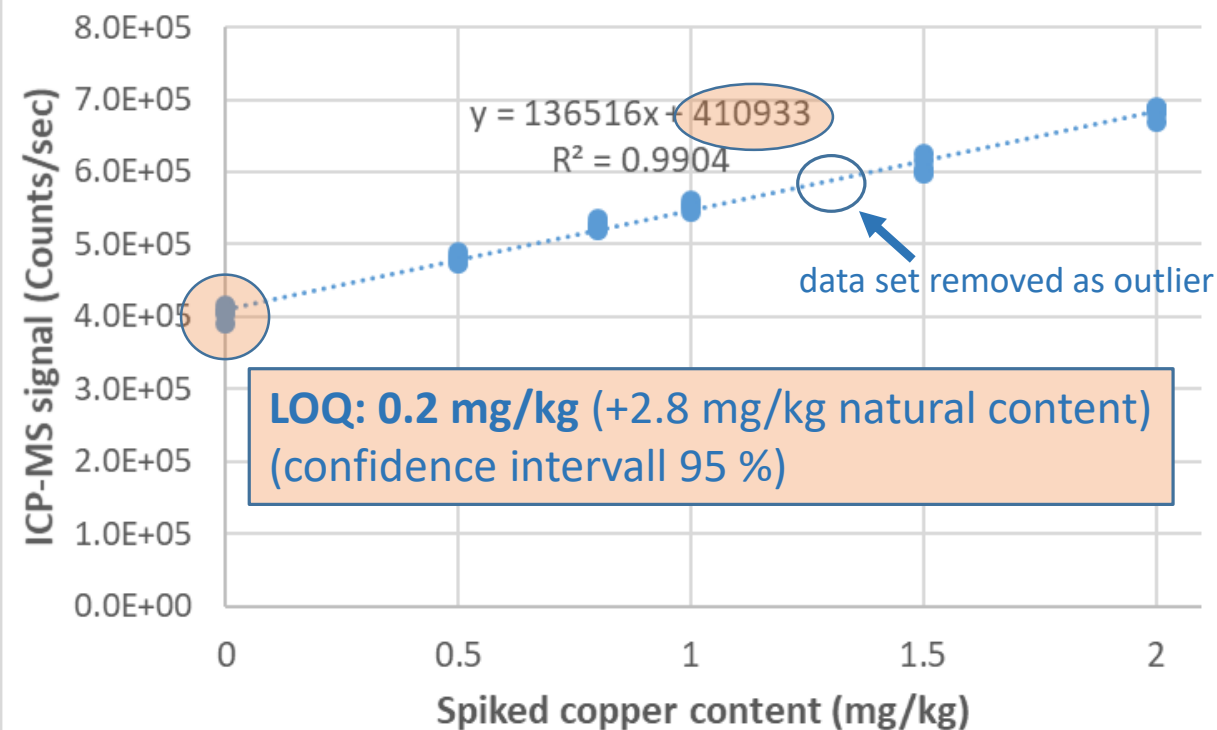
Document N° SANTE/11312/2021v2

EN 13804:2013 → DIN 32645:2008-11

Validation experiment results: 10 mg/kg

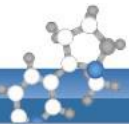
Validation experiments using 7 spiking levels, each n = 5

	ICP-MS signal (Counts)									
Mass trace	Blank	Matrix Calib. 60 %	Matrix Calib. 120 %	Rec. 1	Rec. 2	Rec. 3	Rec. 4	Rec. 5	Matrix Calib. 60 %	Matrix Calib. 120 %
Lutetium m/z 175 (ISTD)	8.23E+05	8.03E+05	7.90E+05	8.13E+05	8.23E+05	8.32E+05	8.35E+05	8.48E+05	8.26E+05	8.10E+05
Copper m/z 63	4.30E+05	9.98E+05	1.87E+06	1.57E+06	1.64E+06	1.66E+06	1.62E+06	1.62E+06	1.02E+06	1.86E+06
Recovery (%)				98.1	101.3	101.5	98.8	97.0		
Average Recovery (%)				99.3 (%)					criteria fulfilled	
Relative standard deviation (±%)				2.0					criteria fulfilled	
Signal in Blank				26 % (of the avg. signal in recovery samples)					criteria fulfilled	

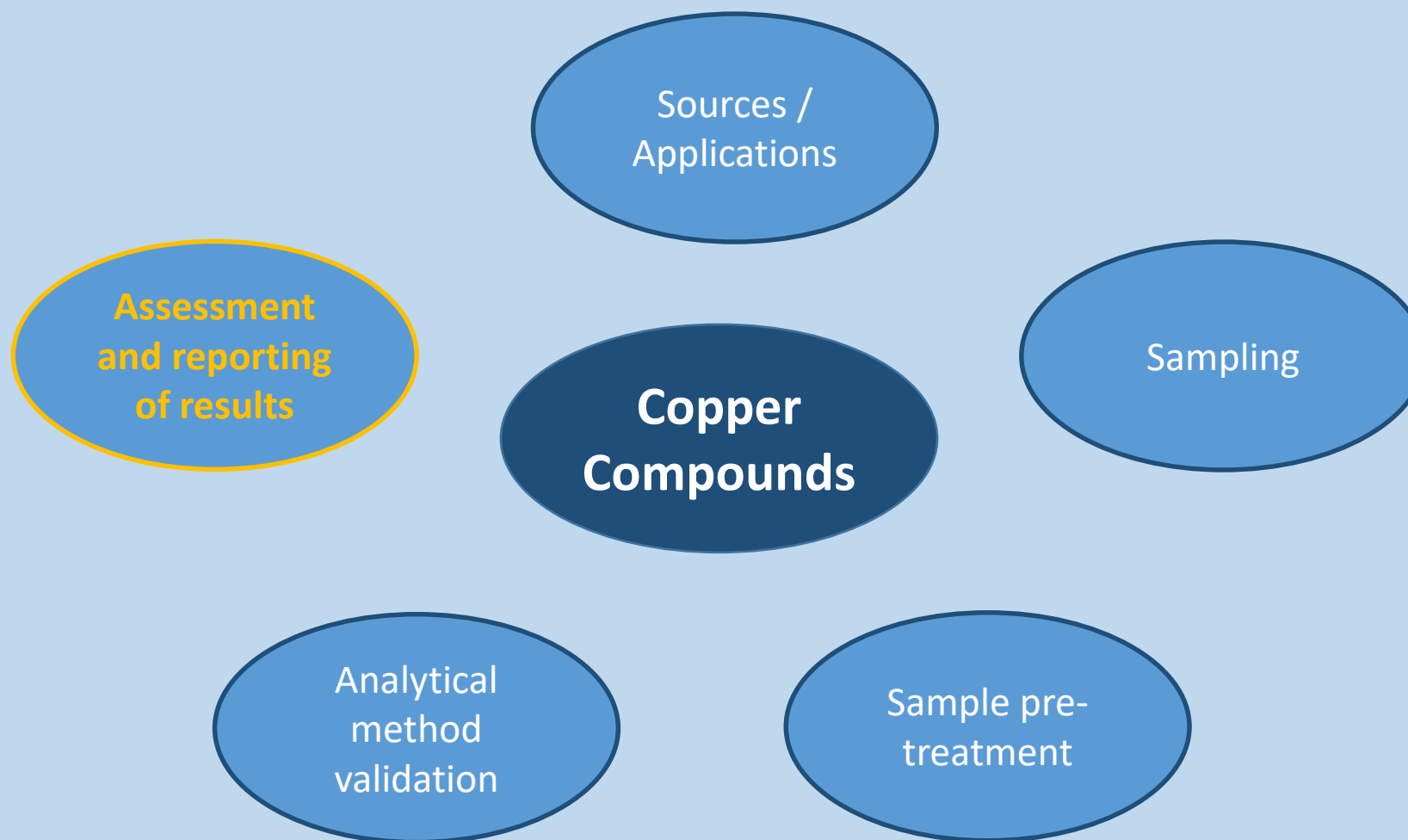


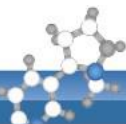
- natural content in avocado: approx. 2.8 mg/kg in average (based on CVUA data from 2019, n = 5)
- validation at lower levels virtually impossible
- lowest successfully validated level = MRL = legal **LOQ: 10 mg/kg**

Data based on validation experiments by the elemental analysis laboratory of the CVUA Stuttgart, 06/2024



# Copper Compounds | Challenges





# Copper Compounds | Assessment and reporting of results

for pesticide analysis

for contaminant analysis

**Document N° SANTE/11312/2021v2:**

**Default Expanded Measurement uncertainty:  $\pm 50\%$ \***

\*with the prerequisite that the laboratory must demonstrate that its own expanded MU is less than 50 %, e.g. by the participation in PTs

**for pesticide analysis**

**for contaminant analysis**

38% 44% 47%



# Copper Compounds | Assessment and reporting of results

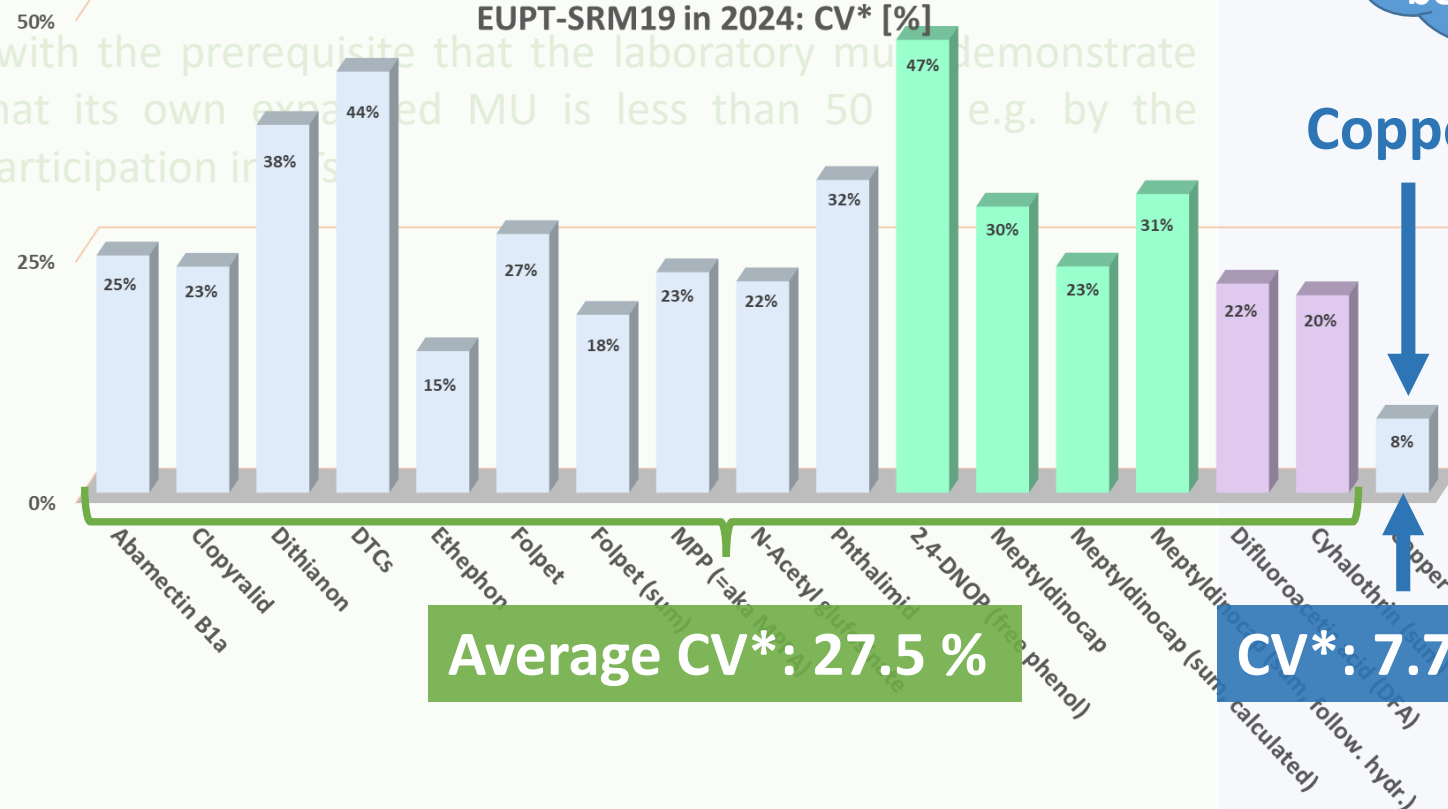
for pesticide analysis

for contaminant analysis

Document N° SANTE/11312/2021v2:

Default Expanded Measurement uncertainty:  $\pm 50\%$ \*

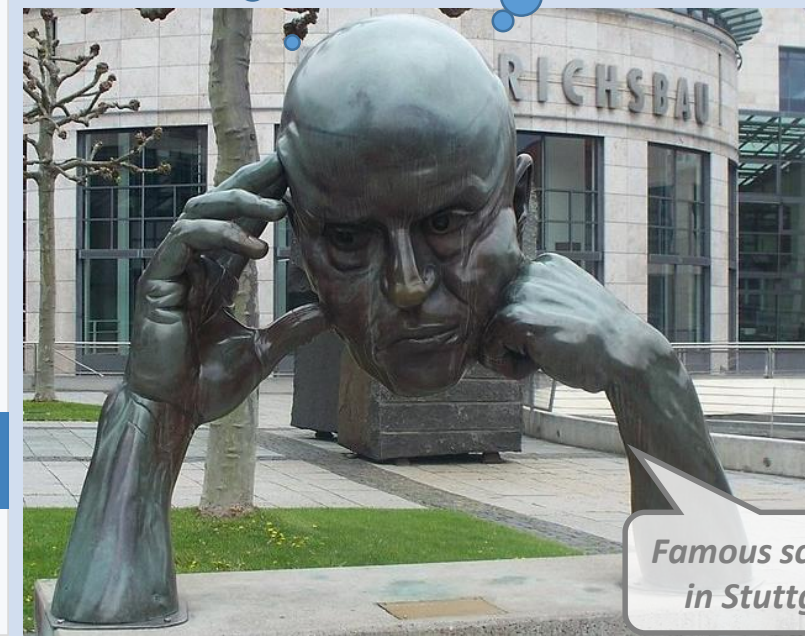
EUPT-SRM19 in 2024: CV\* [%]



The MU for metal elements seems to be much smaller....

Should and/or can the default expanded MU of  $\pm 50\%$  applying for pesticides be used?

Copper



Famous sculpture in Stuttgart...

# Copper Compounds | Assessment and reporting of results

for pesticide analysis

for contaminant analysis

[https://food.ec.europa.eu/plants/pesticides/eu-pesticides-database\\_en](https://food.ec.europa.eu/plants/pesticides/eu-pesticides-database_en)



EN English

Search

Pesticide residue(s) and maximum residue levels (mg/kg)

Code	Products to which MRLs apply	Copper compounds (Copper) Reg. (EC) No 149/2008 applicable
010000	FRUITS, FRESH or FROZEN; TREE NUTS	
011000		20
011010		20
011020	Oranges	20
011030	Lemons	20
011040	Limes	20
011050	Mandarins	20
011090	Others (2)	20

The MRLs only apply if the provisions regarding sampling and sample pre-treatment FOR PESTICIDES were followed!



# Copper Compounds | Assessment and reporting of results

## for pesticide analysis

[https://food.ec.europa.eu/plants/pesticides/eu-pesticides-database\\_en](https://food.ec.europa.eu/plants/pesticides/eu-pesticides-database_en)



EN English

Search

Search

Pesticide residue(s) and maximum residue levels (mg/kg)

Code Products to which MRLs apply

0100000 FRUITS, FRESH or FROZEN; TREE NUTS

0110000 20

0110010 20

0110020 Oranges 20

0110030 Lemons 20

0110040 Limes 20

0110050 Mandarins 20

0110990 Others (2) 20

Copper compounds  
(Copper)   
Reg. (EC) No  
149/2008  
applicable

The MRLs only apply if the provisions regarding sampling and sample pre-treatment FOR PESTICIDES were followed!

## for contaminant analysis

5.5.2023

EN

Official Journal of the European Union

L 119/103

COMMISSION REGULATION (EU) 2023/915

of 2 April 2023

on maximum levels for certain contaminants in food and repealing Regulation (EC) No 1881/2006

- No maximum limits for copper in the contaminant law!
- toxicological assessment possible:  
health-based guidance value of 0.07 mg/kg bw per day

## SCIENTIFIC OPINION

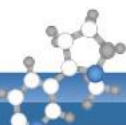
EFSA JOURNAL

ADOPTED: 16 November 2022

doi: 10.2903/j.efsa.2023.7728

## Re-evaluation of the existing health-based guidance values for copper and exposure assessment from all sources

EFSA Scientific Committee,  
Simon John More, Vasileios Bampidis, Diane Benford, Claude Bragard,  
Thorhallur Ingi Halldorsson, Antonio F Hernández-Jerez, Susanne Hougaard Bennekou,  
Kostas Koutsoumanis, Claude Lambré, Kyriaki Machera, Ewen Mullins, Søren Saxmose Nielsen,  
Josef R Schlatter, Dieter Schrenk, Dominique Turck, Maged Younes, Polly Boon,  
Gordon AA Ferns, Oliver Lindtner, Erik Smolders, Martin Wilks, Maria Bastaki,  
Agnès de Sesmaisons-Lecarré, Lucien Ferreira, Luna Greco, George E N Kass,  
Francesca Riolo and Jean-Charles Leblanc















# Copper Compounds | Chia seeds



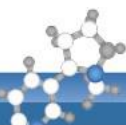
Data from CVUA Stuttgart 2017-22	No. of samples	Mean	Median	Min	Max
Total	18	16.1	16.0	11.5	21.8
thereof from conventional production	1	14.2	-	-	-
thereof from organic production	17	16.2	16.0	11.5	21.8

➤ The **use** is rather analogous to **oilseeds** (especially linseeds) but the **MRL** for **pseudo-cereals** applies

Code	Products to which MRLs apply	Copper compounds (Copper)  Reg. (EC) No 149/2008 applicable
0400000	 OILSEEDS AND OIL FRUITS	
0401000	 Oilseeds	
0401010	 Linseeds	30
0401020	 Peanuts/groundnuts	30
0401030	 Poppy seeds	30

Code	Products to which MRLs apply	Copper compounds (Copper)  Reg. (EC) No 149/2008 applicable
0500000	 CEREALS	10
0500010	 Barley	10
0500020	 Buckwheat and other pseudocereals	10
0500030	 Maize/corn	10
0500040	 Common millet/proso millet	10

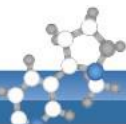




# Copper Compounds | Bovine liver

Data from CVUA Stuttgart and Freiburg 2010-22	No. of samples	Mean	Median	Min	Max	MRL
<b>Bovine liver</b>	113	<b>56</b>	<b>45</b>	1.4	255	<b>30</b>
<b>Calf liver</b>	22	<b>112</b>	<b>117</b>	1.4	330	
Chicken liver	55	3.3	3.1	1.8	4.8	
Swine liver	75	10	8.5	4.8	36	

- **Ruminants**, including bovines, **have genetic disadvantages** when it comes to copper retention in the liver (target organ)
  - Resorption rate of approx. 20 %
  - **ACCUMULATION** (EFSA 2023)
- **Possible sources:**
  - **! Feeding stuff: additive!**, natural content, pesticide application,...
  - veterinary medicine,...

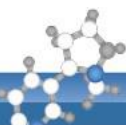


# Copper Compounds | Summary

There are **DISCREPANCIES** between the field of pesticides and the field heavy metals/contaminants, regarding....

- analytical instruments used
- sampling
- sample pre-treatment
- analytical method validation and LOQ determination
- expression of results in regards to applying measurement uncertainty
- assessment of results - **do NOT mix the data of copper contents in samples** – otherwise....
  - wrong natural background assessments
  - wrong intake calculations
  - wrong conclusions as regards to MRL conformity

➤ **There is a need of EU-wide consolidation!**



# Thank you for your attention!

**Questions to:**

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**Benedikt  
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**Cristin  
Wildgrube**



**Doro  
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**Dorota  
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**Heike  
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**Hubert  
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**Leonie  
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**Irina  
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**Rebekka  
Lötterle**



**Sahra  
Fieberg**



**Sigrid  
Schüler**



**Silvia  
Zechmann**



**Florian  
Hägele**

## Pesticide team of the CVUA Stuttgart

## Elemental Analysis team of the CVUA Stuttgart

