Facing Analytical Challenges of Dithiocarbamate Analysis

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Step-by-Step

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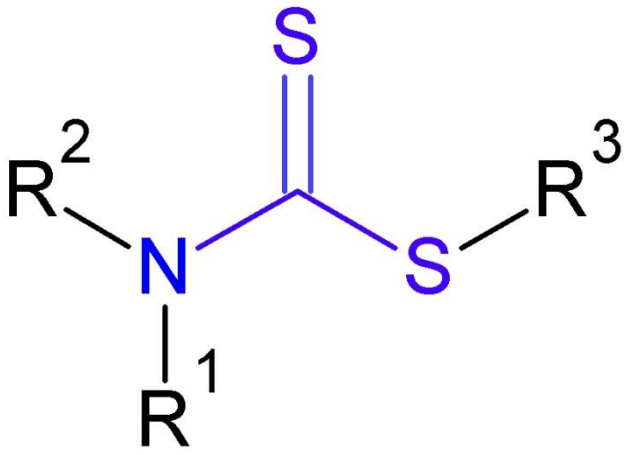
Dithiocarbamate

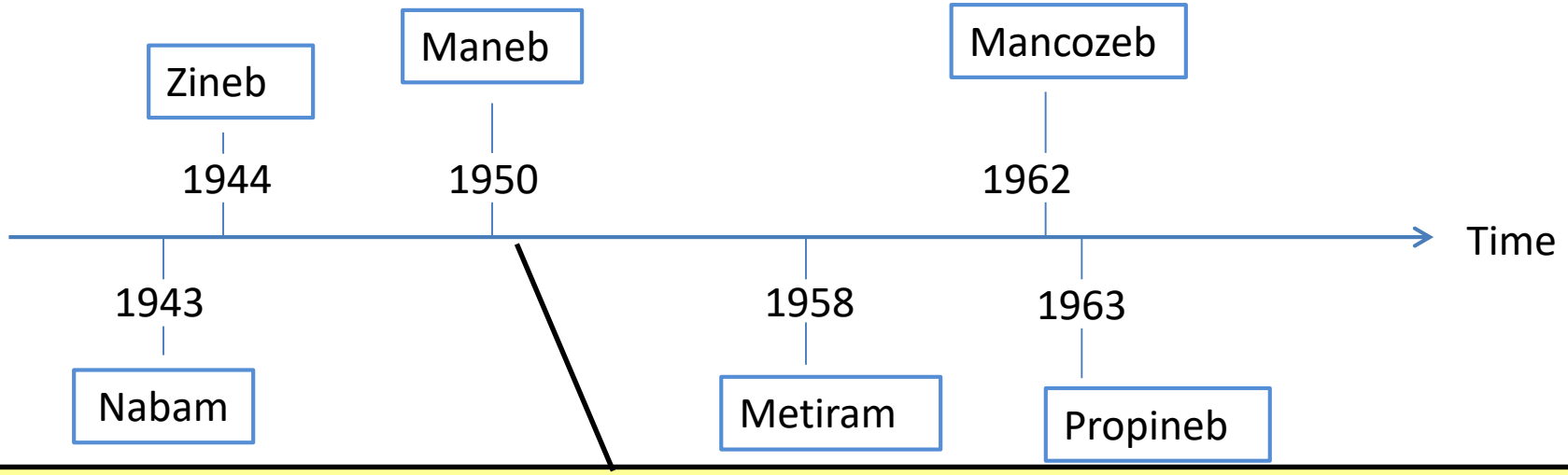
- Dithiocarbamate are esters and salts (or their derivatives) of N-substituted dithiocarbamic acid.



- first reports …
  - Debus, H. Ueber die Verbindungen der Sulfocarbaminsäure. Justus Liebigs Ann. Chem. **1850**, 73, 26–34.
  - Delépine, M. **Metallic salts of dithiocarbamic acids**; preparation of isothiocyanates in the aliphatic series. Compt. Rend. **1907**, 144, 1125–1127

Dithiocarbamate-Fungicides (DTCs) | A Short History

- **Mono Alkylene *bis*-DTCs**



- **1951**: Decomposition of DTCs to CS_2 by mineral acids (e.g. Clarke et al. & Lowen)
- **1969**: Modifikation by Keppel *et al*. (addition of $SnCl_2$ to the sample + boiling with diluted HCl)

→ **official methods for determination of DTC residues**:

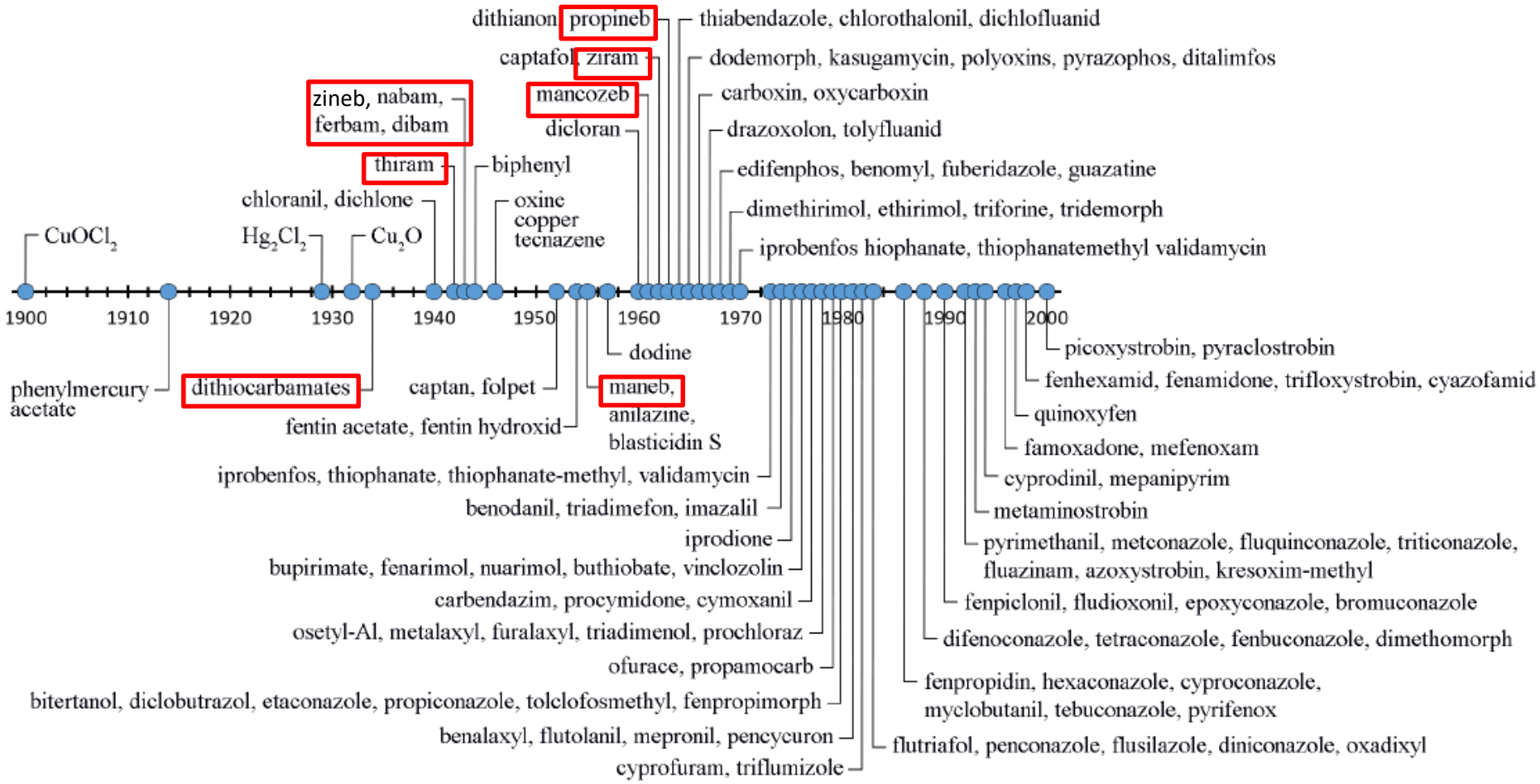
- EN 12396-1: $SnCl_2$/HCl-Cleavage, Cu(II) acetate & DEA spectroph. analysis
- EN 12396-2 type: $SnCl_2$/HCl-Cleavage, headspace SPME, GC-Analysis of CS_2
- EN 12396-3 type: $SnCl_2$/HCl-Cleavage, KOH/MeOH, spectroph. analysis (Xanthogenate mth.)

- **N,N-Dimethyl-DTCs:**

  Thiram -> 1931; Ferbam -> 1948; Ziram -> 1960

DTCs among the first Organic Fungicides

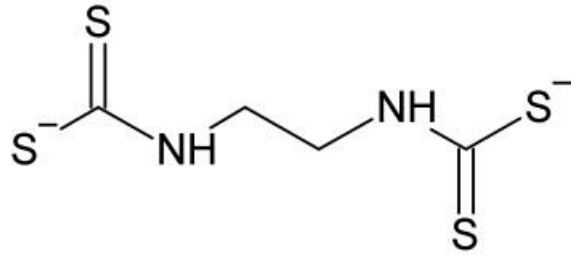
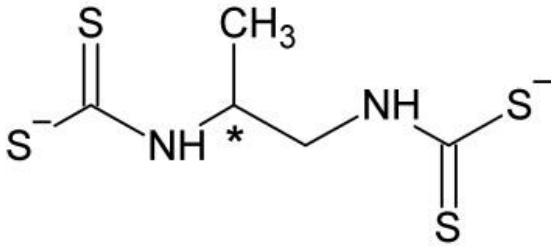
➢ **Timeline of the development of selected fungicides (*):**



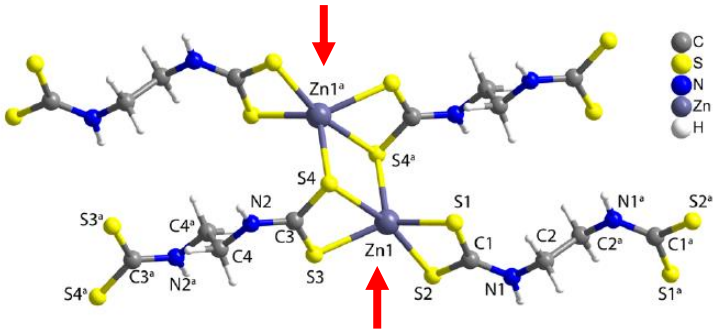
(*) Reproduced from Lefton JB, Pekar KB, Runcevski T. The Crystal Structure of Zineb, 75 years later. ChemRxiv. Cambridge: Cambridge Open Engage; 2019

DTC-Fungicides | Metal-based, polymeric complexes

- **Mono Alkylene *bis*-DTCs**

DTC-Fungicide	Structure: common organosulphur skeleton	Structure: counter ion(s)	Remark	EC 1107/2009 Status
Nabam		$2\ Na^+$	soluble in water, unstable as a solid	not approved
Zineb		Zn^{2+}	Poor or no solubility in water & in commonly used organic solvents	not approved anymore
Maneb		Mn^{2+}		not approved anymore
Mancozeb		Mn^{2+}, Zn^{2+} (94:6)		not approved anymore
Metiram		Zn^{2+}, NH_3		approved
Mancopper		13,7% Mn, 4 % Cu		not approved anymore
Propineb		Zn^{2+}	Poor or no solubility in water & in commonly used organic solvents	not approved anymore

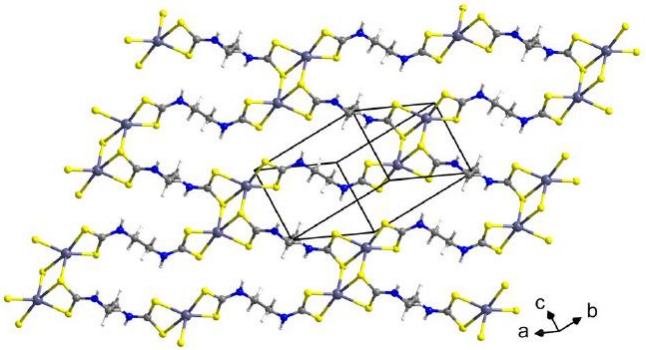
Crystal Structure of Zineb (*)



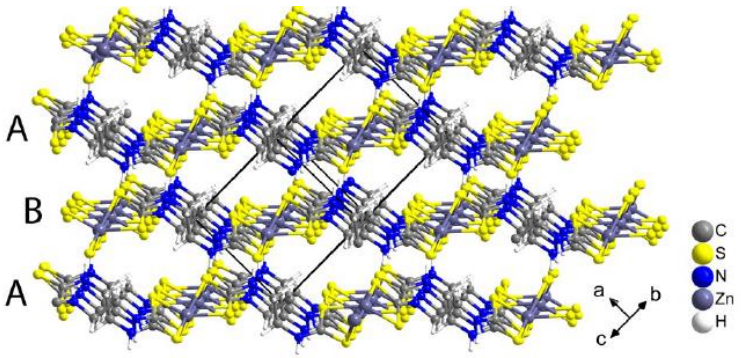
→ Zn^{2+} cations are coordinated by thiocarbamate groups of EBDTC-linkers

→ each Zn^{2+} cations is coordinated by five S-atoms (=> Zn-S-bond)

→ inorganic fragment of structure: Zn_2S_8-cluster

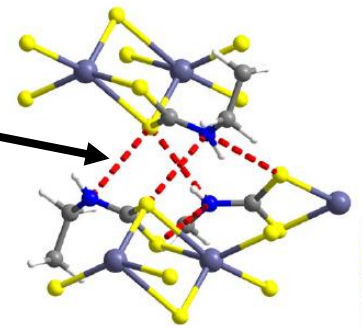


→ Zn^{2+} cations are linked via EBDTC-ligands and form extended, polymeric layers



→ polymeric layers stack one on top of another => layered crystal packing

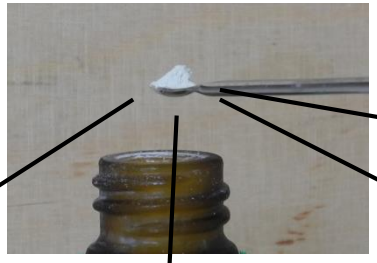
→ layers are held together by hydrogen bonding network (between the amine N-atoms and the thiocarbamate S atoms)



(*) Lefton JB, Pekar KB, Runcevski T. The Crystal Structure of Zineb, 75 years later. ChemRxiv. Cambridge: Cambridge Open Engage; 2019

Microcrystalline powder of Zineb, …| Standard, Food Sample

Hypothesis!

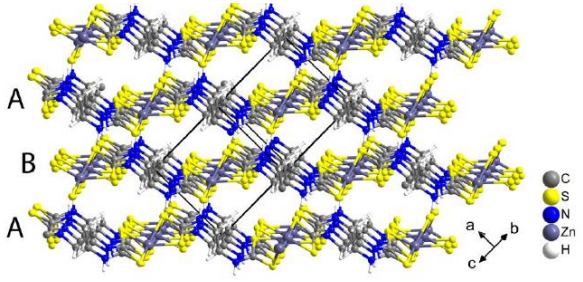


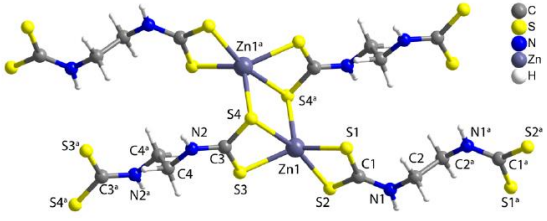
4. degradation products (e.g. ETU, eBIC, …)

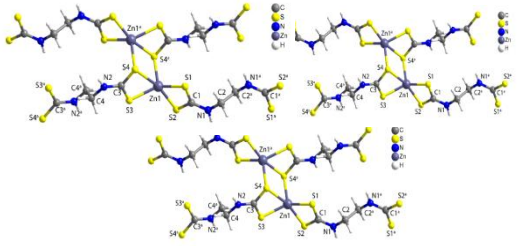
1. polymeric, stacked layers

2. “monomer complexes”

3. “oligomer complexes”



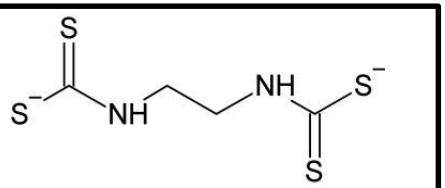




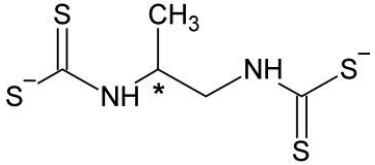
- **stock-/working solutions:**
  - solvent should preserve the complex structure of the DTCs
  - (other aspects: pipette handling, reproducibility, chemical stability, …)
- **quantitative DTC-method:**
  - analytical procedure has to be able to quantitatively disrupt the complex DTC-structures and quantify the analyte (CS_2 or derivatization product or …)

Quantitative DTC-Analysis | Analytical Challenges (among others)

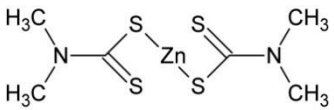
- suitable **solvent for preparation of DTC-stock/working solutions**
- **Quantitative DTC-Analysis:**



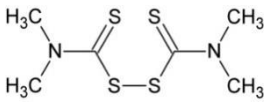
Ethylene *bis*-DTCs



Propylene *bis*-DTCs

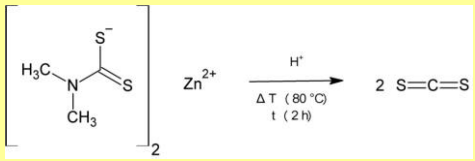


Ziram



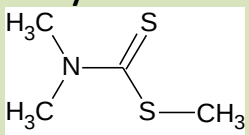
Thiram

Acid decomposition of DTC & release of CS_2

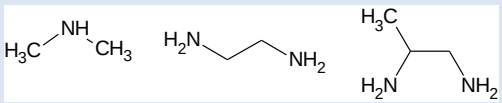


Derivatisation

e.g. methylation



Amine-Moiety



Other methods (see scientific literature)

Single Residue Methods!

???
Is screening for DTCs via multi-residue-methods possible?

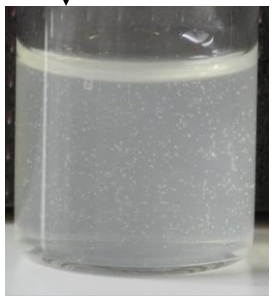
DTC-stock/working solutions | Suitable Solvent?

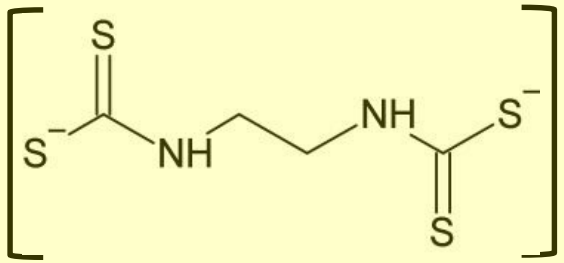
- Most DTCs have low solubility in water and a number of organic solvents (Acetonitrile, Dimethylformamid, Dimethylformamid/Toluol, Tetrahydrofuran)

- **The chelating agent EDTA is often used in aqueous solutions** (e.g. EDTA-4Na (150 µg/ml)/L-cysteine (5 µg/ml);

e.g. mancozeb-susp. (1 mg/ml)

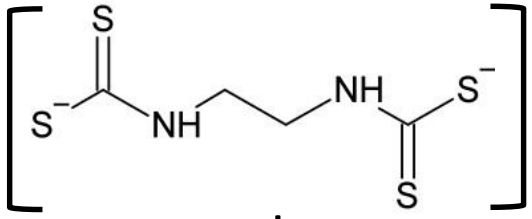
↓ + EDTA





Zn^{2+} zineb
Mn^{2+} maneb
Mn^{2+}/Zn^{2+} mancozeb
Mn^{2+}/NH_3 metiram

Conversion of the water-insoluble DTC (zineb, …) into the soluble sodium salt by means of EDTA

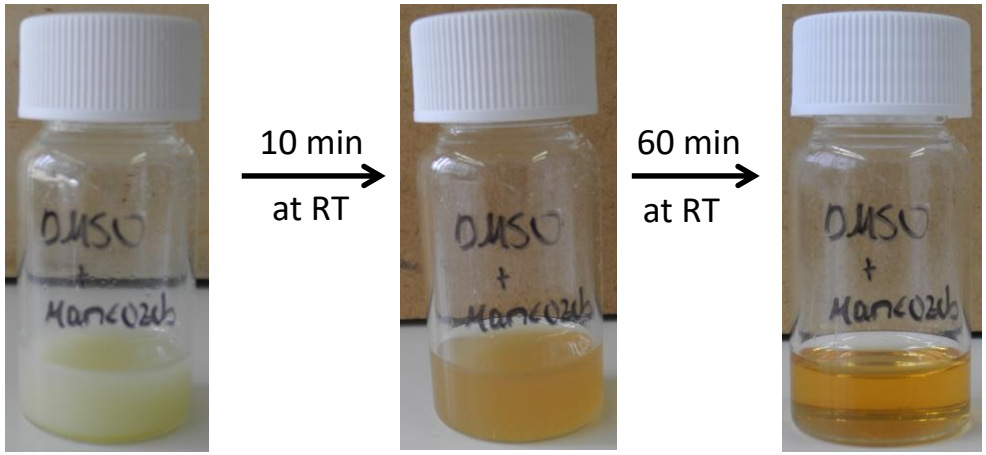


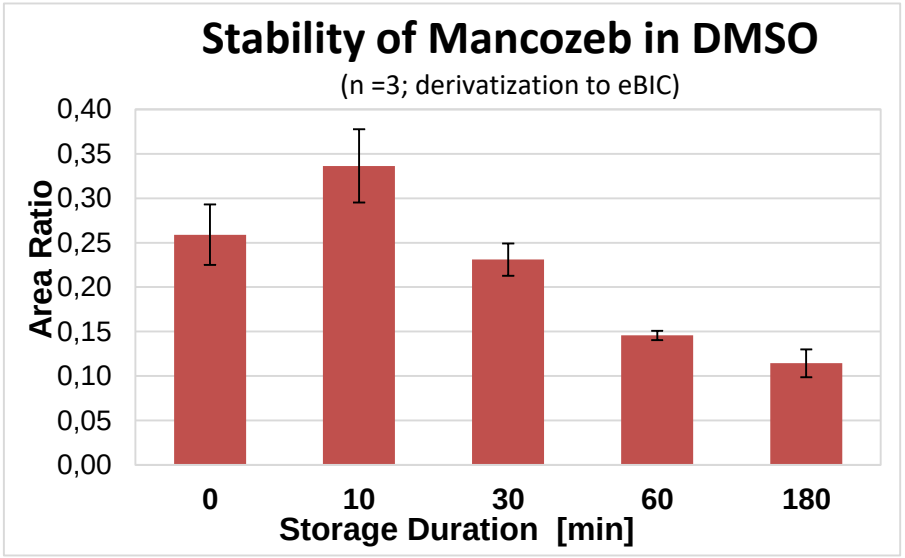
nabam

$2Na^+$ + Me^{2+}-EDTA-complex

DTC-stock/working solutions | Suitable Solvent?

➢ **Dimethyl sulfoxide (DMSO) as solvent for DTCs?**





→ DTCs soluble in DMSO, BUT <u>unstable</u>

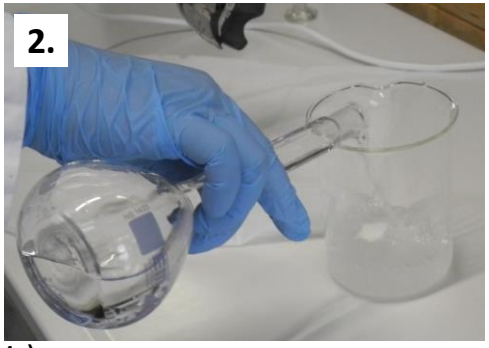
➢ **Glycerin/iso-Propanol 3:1 (v/v)** → stabile DTC-suspension!

challenge: pipette handling!
tip <u>after</u> dispensing movement

Xanthan gum-solution to prepare DTC-suspensions

- **Xanthan gum** (from *Xanthomonas campestris*):
  - used as a thickener, but also as an efficient stabilizer for suspensions, emulsions, foams
  - soluble in both cold and hot water
  - generally not affected by (a) changes in pH value, (b) addition of large amounts of salt

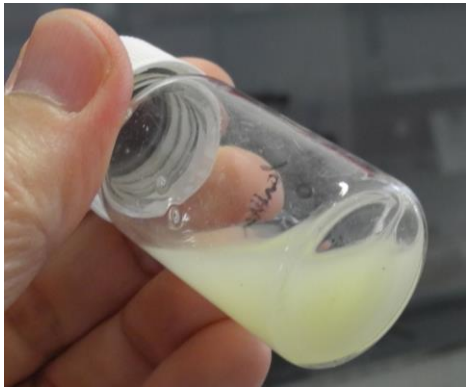
- **Water/acetonitrile/xanthan gum (95/5/0,2 V/V/W):**



a) 0,2 g xanthan gum (from *X. campestris*)
b) 100 ml water/acetonitril-solution 95/5 (V/V)
c) Hand blender

(Air bubbles can be removed with ultrasound.)

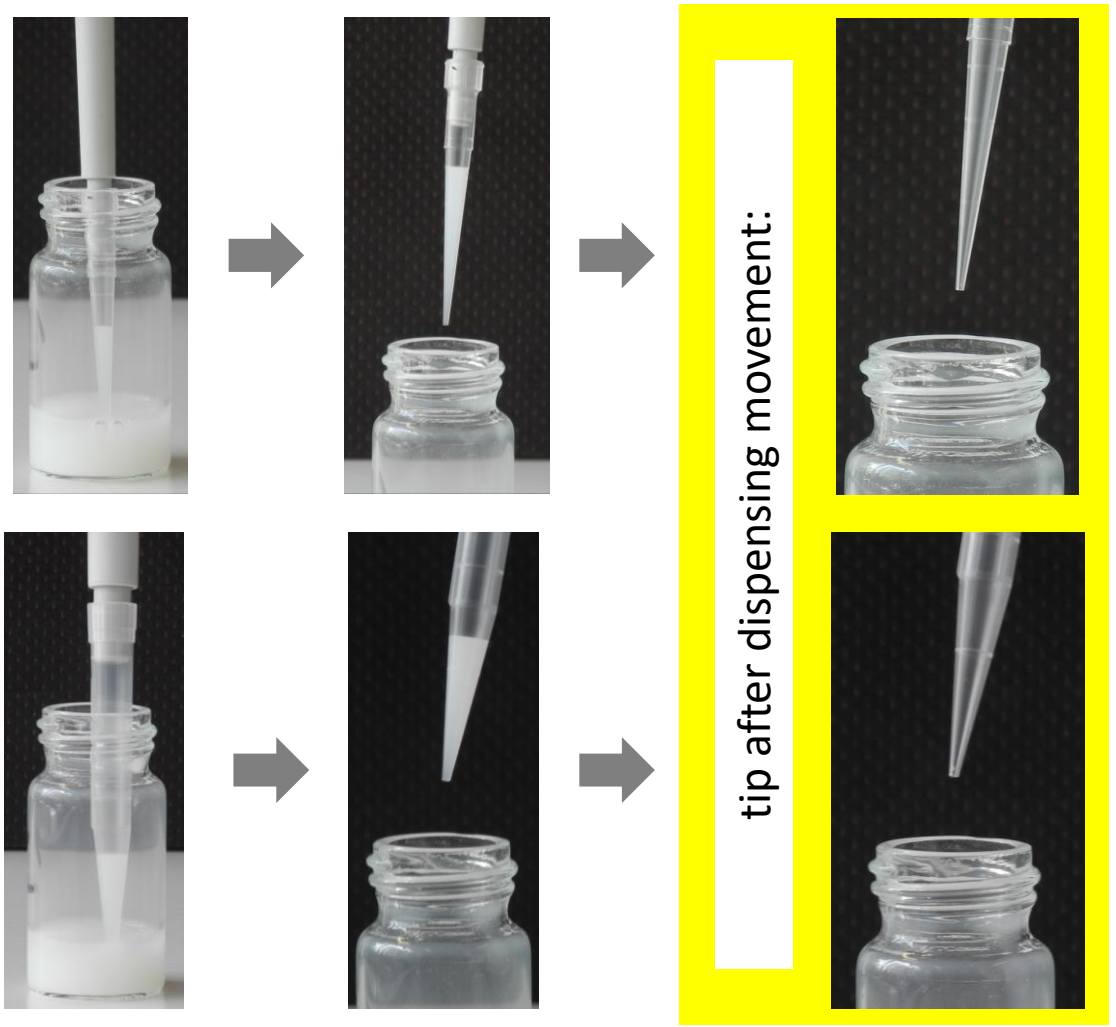
+ DTC-standard



- Stabile & homogeneous suspension of DTC (up to 60 min)
- Hypothesis: DTC complexes & polymeric DTC structure remain intact
- Chemical stability of DTC in xanthan gum solution???

DTC-Xanthan Gum Suspension | Pipette Handling

100 µl-Pipette (*):



1000 µl-Pipette (*):

[(*) propineb-stock-suspension (1 mg/ml) used for this demo; similar pipetting behavior was observed for other DTCs.]

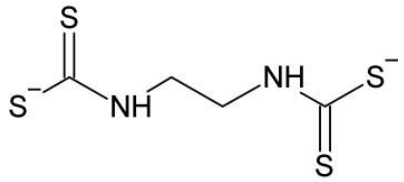
Only very minor residues of DTC-stock-suspension remain in tip after dispensing movement.

=> minimal losses of standard during pipetting (e.g. diluting, spiking)

DTC-Suspensions used for spiking procedures | Recovery Studies

Mancozeb

organosulphur skeleton

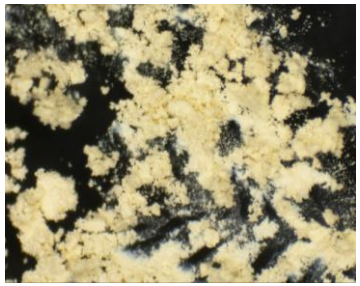
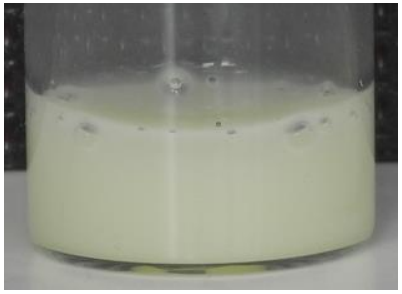
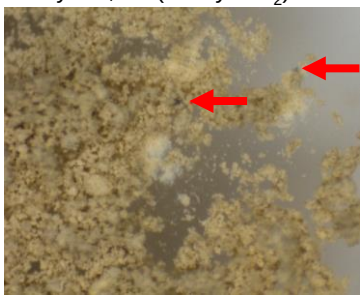
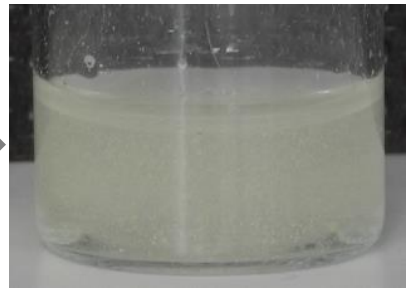


counter ion(s)

Mn^{2+}, Zn^{2+} (94:6)

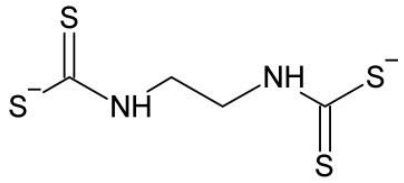
experimental conditions

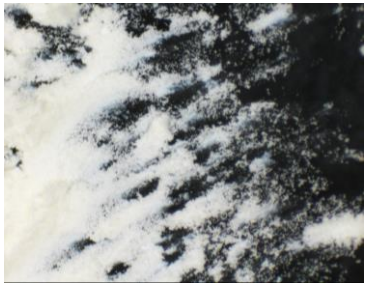
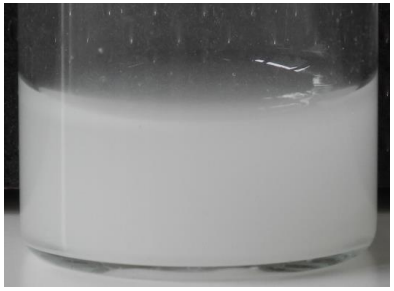
- Solvent of Suspension: Water/ACN/Xanthan (95/5/0,2 % V/V/W)
- Recovery Study: **spiking level: 0,5 ppm**; matrix: tomato; SnCl2/HCl-Hydrolysis (80°C, 2h); CS_2-Detection: GC-MS/MS

Supplier	Stock Suspension (1 mg/ml)	Storage time	Recovery via CS_2 (calc. as mancozeb) [%] 1	2	3	4	5	Mean Rec [%]	RSD [%]
Supplier I Purity: 99,6% (assay: HPLC/UV-VIS)  Exp. date: 31.01.23		0 min	89	90,1	81,5	86,5	68,7*	**86,8**	**3,8**
		4 h	75,8	69,4	69,8	70,1	67,3	**70,5**	**4,0**
Supplier II Purity: 99,3% (assay: CS_2)  Exp. date: 01.09.24		0 min	38,1	24,9	59,5	60,5	35,2	**43,6**	**32,2**
		4 h	26,3	32,0	30,3	38,8	33,8	**32,3**	**12,7**

*: identified as outlier

DTC-Suspensions used for spiking procedures | Recovery Studies

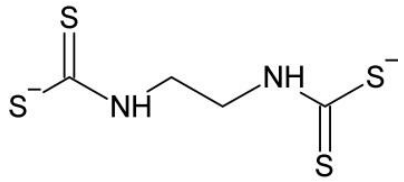
Zineb	organosulphur skeleton	counter ion(s)	experimental conditions
		Zn^{2+}	• Solvent of Suspension: Water/ACN/Xanthan (95/5/0,2 % V/V/W) • Recovery Study: **spiking level: 0,2 ppm**; matrix: tomato; SnCl2/HCl-Hydrolysis (80°C, 2h); CS_2-Detection: GC-MS/MS

Supplier	Stock Suspension (1 mg/ml)	Storage time	Recovery via CS_2 (calc. as zineb) [%] 1	2	3	4	5	Mean Rec [%]	RSD [%]
Supplier I Purity: 98,2% (assay: EDTA-titration)	 Exp. date: 01.02.23		0 min	78,0	97,1	105,2	84,4	111,6	**95,2**	**13,2**
		30 min	135,2	117,0	123,4	110,7	137,9	**124,8**	**8,3**
Supplier II Purity: 95,2% (assay: qNMR)	 Exp. date: 01.05.26		0 min	93,6	99,1	84,9	88,2	81,3	**89,4**	**7,1**
		30 min	80,2	74,4	84,5	81,6	86,4	**81,4**	**5,1**

DTC-Suspensions used for spiking procedures | Recovery Studies

Metiram

organosulphur skeleton

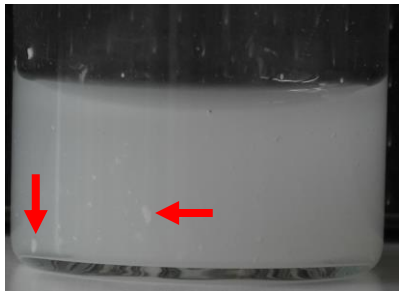
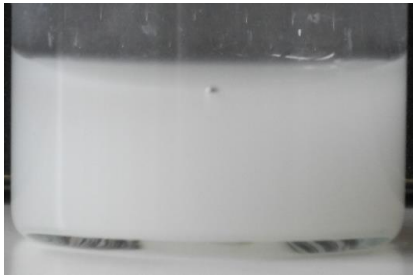


counter ion(s)

$Zn2^{+}$, NH_3

experimental conditions

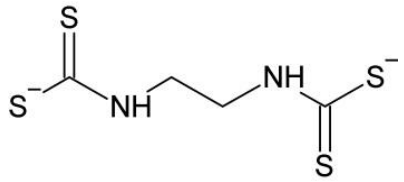
- Solvent of Suspension: Water/ACN/Xanthan (95/5/0,2 % V/V/W)
- Recovery Study: **spiking level: 0,2 ppm**; matrix: tomato; SnCl2/HCl-Hydrolysis (80°C, 2h); CS_2-Detection: GC-MS/MS

Supplier	Stock Suspension (1 mg/ml)	Storage time	Recovery via CS_2 (calc. as metiram) [%] 1	2	3	4	5	Mean Rec [%]	RSD [%]
Supplier III									
Purity: 84,3% (assay: elemental anal.)									
 Exp. date: 19.03.24		0 min	82,4	79,7	72,5	77,9	81,5	**78,9**	**4,4**
		30 min	77,9	66,3	81,5	80,1	83,3	**77,8**	**7,8**
Ultrasonication of stock suspension (7 min)									
		0 min	62,7	53,8	53,8	63,6	55,5	**57,8**	**7,6**
		30 min	71,6	77,9	49,2	52,8	43,9	**59,1**	**22,4**

DTC-Suspensions used for spiking procedures | Recovery Studies

Metiram

organosulphur skeleton

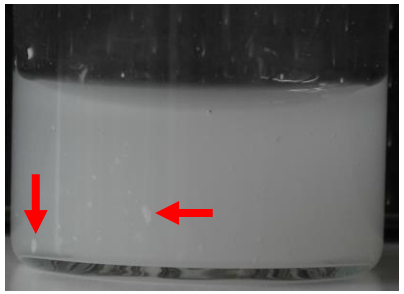


counter ion(s)

$Zn2^{+}$, NH_3

experimental conditions

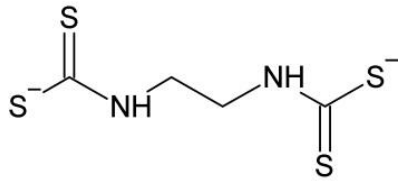
- Solvent of Suspension: Water/ACN/Xanthan (95/5/0,2 % V/V/W)
- Recovery Study: **spiking level: 0,2 ppm**; matrix: tomato; SnCl2/HCl-Hydrolysis (80°C, 2h); CS_2-Detection: GC-MS/MS

Supplier	Stock Suspension (1 mg/ml)	Storage time	Recovery via CS_2 (calc. as metiram) [%] 1	2	3	4	5	Mean Rec [%]	RSD [%]
Supplier III									
Purity: 84,3% (assay: elemental anal.)									
 Exp. date: 19.03.24		0 min	82,4	79,7	72,5	77,9	81,5	**78,9**	**4,4**
		30 min	77,9	66,3	81,5	80,1	83,3	**77,8**	**7,8**
	+ 0,1 M NaCl								
		0 min	n. d.						
		30 min							

DTC-Suspensions used for spiking procedures | Recovery Studies

Maneb

organosulphur skeleton

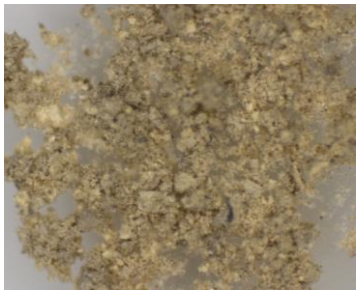
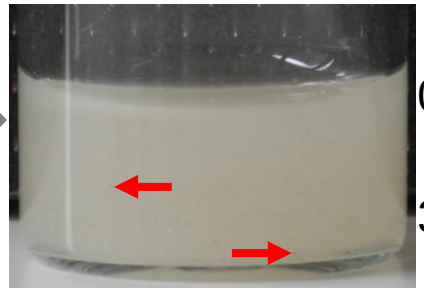
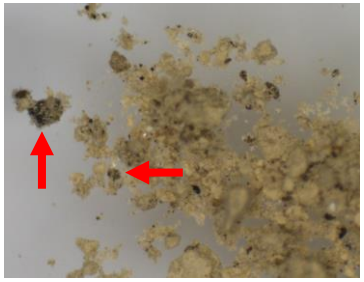
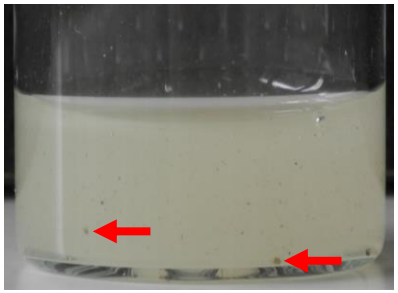


counter ion(s)

Mn^{2+}

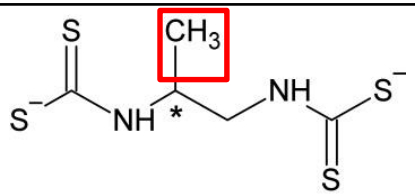
experimental conditions

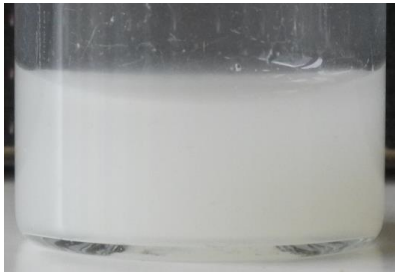
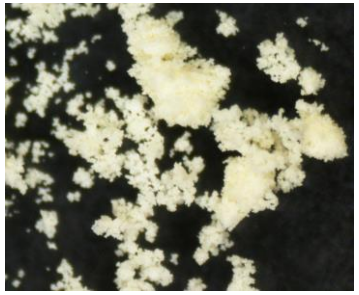
- Solvent of Suspension: Water/ACN/Xanthan (95/5/0,2 % V/V/W)
- Recovery Study: **spiking level: 0,2 ppm**; matrix: tomato; SnCl2/HCl-Hydrolysis (80°C, 2h); CS_2-Detection: GC-MS/MS

Supplier	Stock Suspension (1 mg/ml)	Storage time	Recovery via CS_2 (calc. as maneb) [%] 1	2	3	4	5	Mean Rec [%]	RSD [%]
Supplier I Purity: 85,7% (assay: N/A)	 Exp. date: 01.02.26		0 min	25,7*	45,0	38,6	40,4	35,8	**40,0**	**8,4**
			30 min	68,0*	37,7	37,7	38,6	36,7	**37,7**	**1,7**
Supplier II Purity: 95,0% (assay: CS_2)	 Exp. date: 01.09.24		0 min	71,6	83,8	74,2	50,6	50,6	**66,2**	**20,1**
			30 min	50,6	58,5	55,9	61,1	32,3*	**56,5**	**6,9**

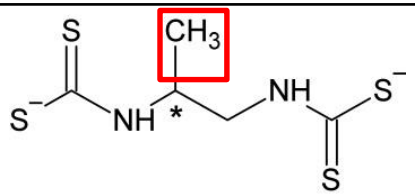
*: identified as outlier

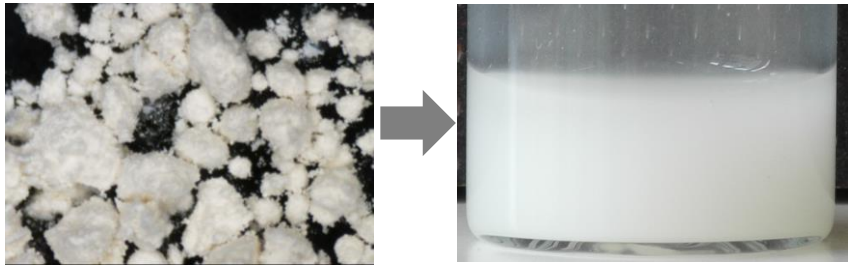
DTC-Suspensions used for spiking procedures | Recovery Studies

Propineb	organosulphur skeleton	counter ion(s)	experimental conditions
		Zn^{2+}	• Solvent of Suspension: Water/ACN/Xanthan (95/5/0,2 % V/V/W) • Recovery Study: **spiking level: 0,2 ppm**; matrix: tomato; SnCl2/HCl-Hydrolysis (80°C, 2h); CS_2-Detection: GC-MS/MS

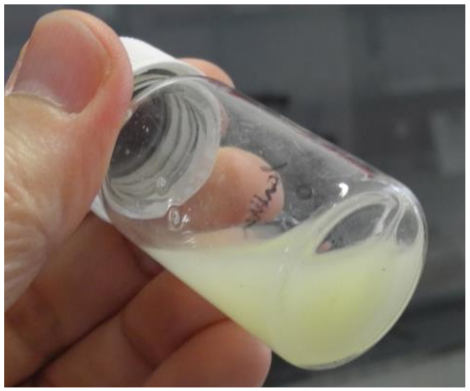
Supplier	Stock Suspension (1 mg/ml)	Storage time	Recovery via CS_2 (calc. as propineb) [%] 1	2	3	4	5	Mean Rec [%]	RSD [%]
Supplier I Purity: 17,7% (assay: EDTA-titration)	 Exp. date: 30.06.23		0 min	164,9	138,2	147,8	144,9	148,7	**148,9**	**5,9**
		30 min				n.d.			
Supplier II Purity: 94,1% (assay: CS_2)	 Exp. date: 01.03.23		0 min	6,7	5,7	4,8	6,7	6,7	**6,1**	**12,5**
		30 min	6,7	5,7	6,7	8,6	5,7	**6,7**	**15,6**

DTC-Suspensions used for spiking procedures | Recovery Studies

Propineb	organosulphur skeleton	counter ion(s)	experimental conditions
		Zn^{2+}	• Solvent of Suspension: Water/ACN/Xanthan (95/5/0,2 % V/V/W) • Recovery Study: **spiking level: 0,2 ppm**; matrix: tomato; SnCl2/HCl-Hydrolysis (80°C, 2h); CS_2-Detection: GC-MS/MS

Supplier	Stock Suspension (1 mg/ml)	Storage time	Recovery via CS_2 (calc. as propineb) [%] 1	2	3	4	5	Mean Rec [%]	RSD [%]
Supplier IV Purity: 71,5% Exp. date: N/A									
		1. Experiment							
		0 min	94,4	86,7	93,4	95,3	88,7	**91,7**	**3,7**
		30 min	93,4	94,3	86,7	95,3	90,6	**92,1**	**3,4**
		2. Experiment (another person, another day)							
		0 min	89,6	86,7	79,1	75,3	80,1	**82,2**	**6,4**
		30 min	83,9	85,8	86,7	80,1	98,2	**86,9**	**7,0**

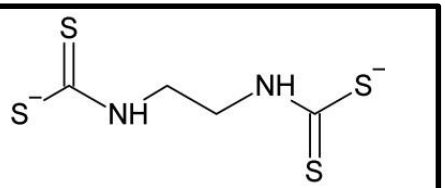
DTC-Xanthan Gum Suspension



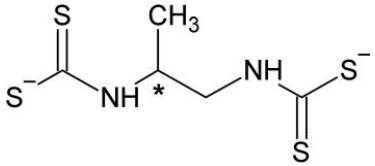
- In case you intend to use this **suspension for validation studies with DTCs**, please **send us your experiences/feedback/results: eurl-srm@cvuas.bwl.de**

Quantitative DTC-Analysis | Analytical Challenges (among others)

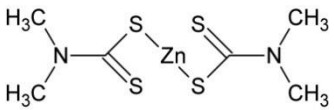
- suitable **solvent for preparation of DTC-stock/working solutions**
- **Quantitative DTC-Analysis:**



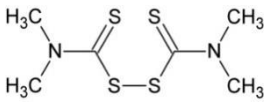
Ethylene *bis*-DTCs



Propylene *bis*-DTCs

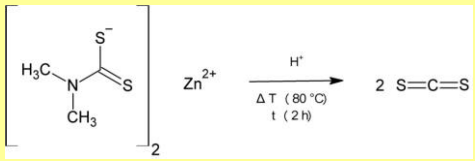


Ziram



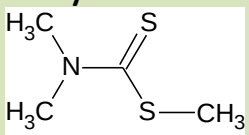
Thiram

Acid decomposition of DTC & release of CS_2

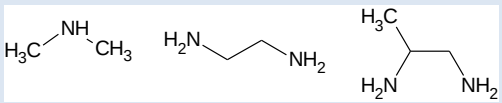


Derivatisation

e.g. methylation



Amine-Moiety



Other methods (see scientific literature)

Single Residue Methods!

???

qualitative method that enables the **screening for characteristic decomposition products** of

- ethylene-DTCs (e.g. maneb)
- propylene-DTC (propineb)
- N,N-dimethyl DTCs (e.g. ziram)

in QuEChERS-extracts by routine MS-techniques

DTC-Decomposition Products as Screening-Marker

- **Mono Alkylene *bis*-DTCs**

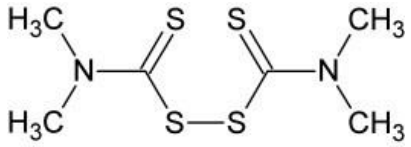
DTC	Suitable screening-marker for DTCs	Remark
Nabam, Zineb, Maneb, Mancozeb, Metiram, Mancopper	✓ Ethylene-bis-isothiocyanate (eBIC)	QuEChERS, GC-amenable
	✓ ETU	QuPPe, LC-MS/MS (*)
	(other screening-marker see previous presentation)	
Propineb	✓ Propylene-bis-isothiocyanate (pBIC)	QuEChERS, GC-amenable
	✓ PTU	QuPPe, LC-MS/MS (*)
	(other screening-marker see previous presentation)	

(*) https://www.eurl-pesticides.eu/docs/public/tmplt_article.asp?CntID=887&LabID=200&Lang=EN

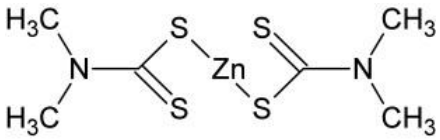
DTC-Decomposition Products as Screening-Marker

DTC	Suitable screening-marker for N,N- dimethyl DTCs	Remark
Ziram, Thiram	? Dimethyldithiocarbamate-Methyl (DiMeDTC-Me) ? Dimethyldithiocarbamoyl-chloride (DMTCC) (other screening-marker see previous presentation)	QuEChERS, GC-amenable, (false positive (-> GC-vial caps)!)

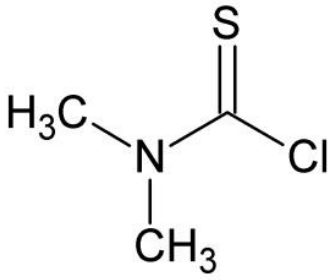
Thiram



Ziram



QuEChERS

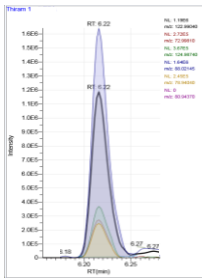


Dimethyl-thiocarbamoylchlorid (DMTCC)

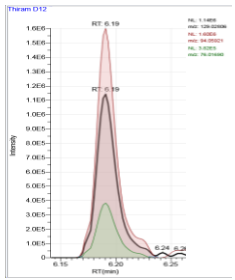
- ***very labile!***
- *false positives (e.g. Vial Caps)*

- DMTCC is being formed during QuEChERS procedure:
  - Conversion of D_{12}-Thiram / D_{12}-Ziram to D_6-DMTCC

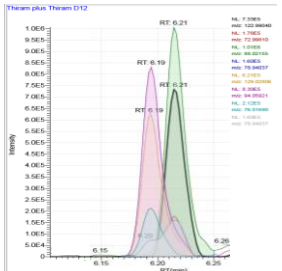
Thiram:



D_{12}-Thiram:



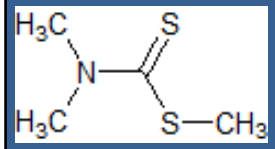
Thiram + D_{12}-Thiram:

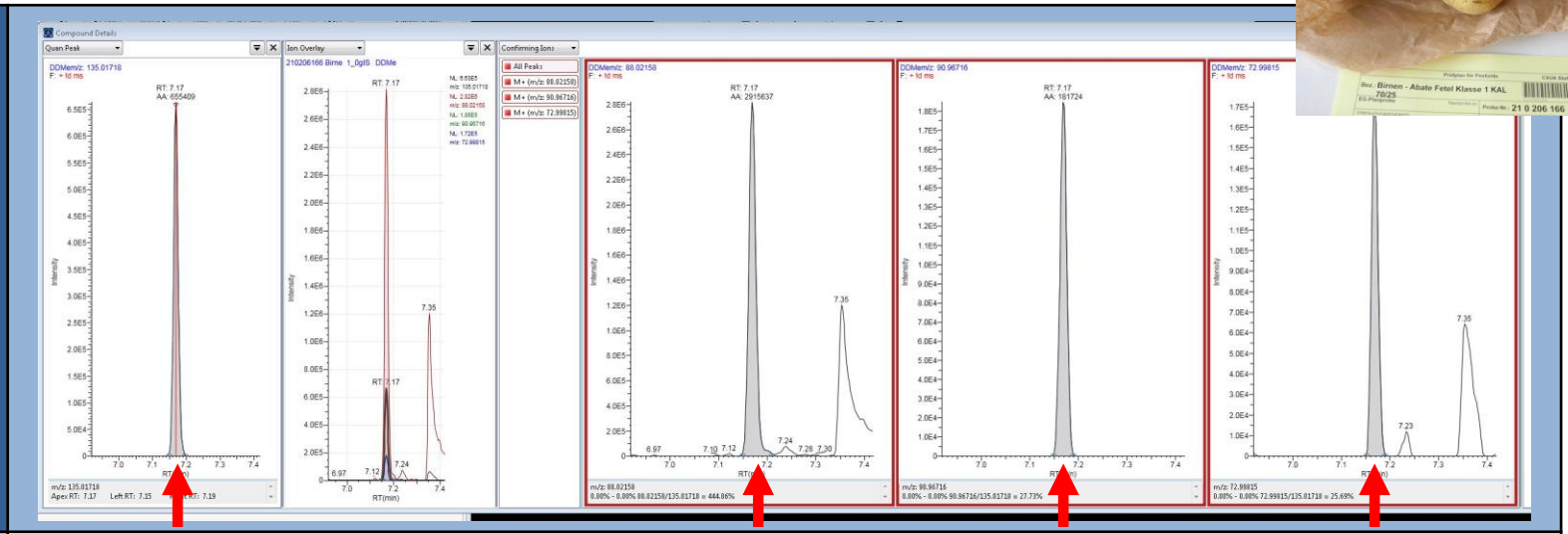


DMTCC / DiMeDTC as Screening Marker?

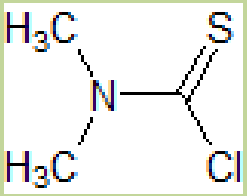
- **Example: Pear (Italy), QuEChERS extract;**
  GC-Orbitrap (PTV injector)**:**

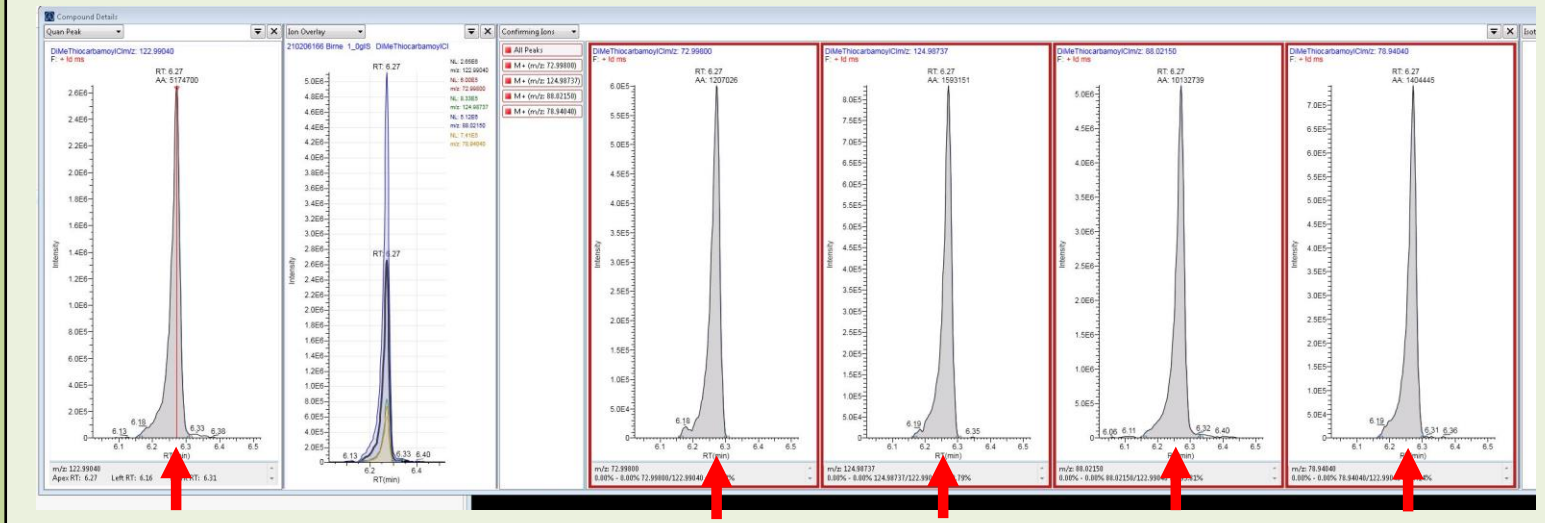
DiMeDTC-Me





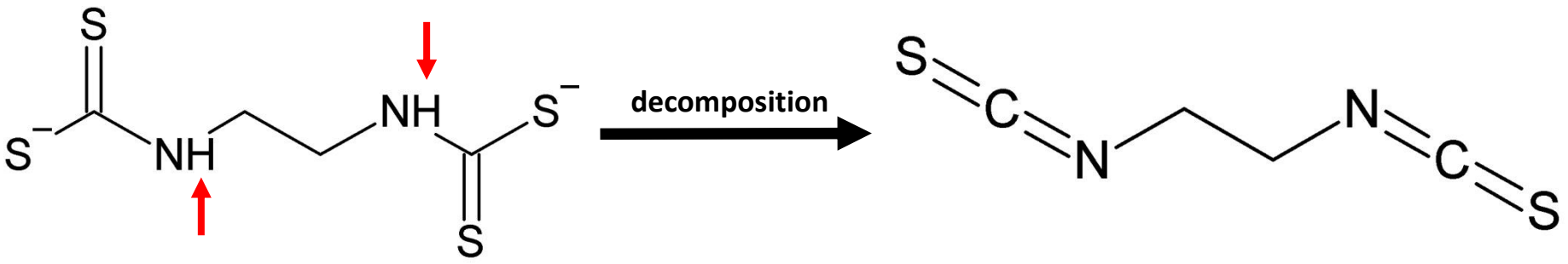
DMTCC





- CS_2-finding: 0,61 mg/kg

Decomposition of Ethylene-bis-DTCs to eBIC



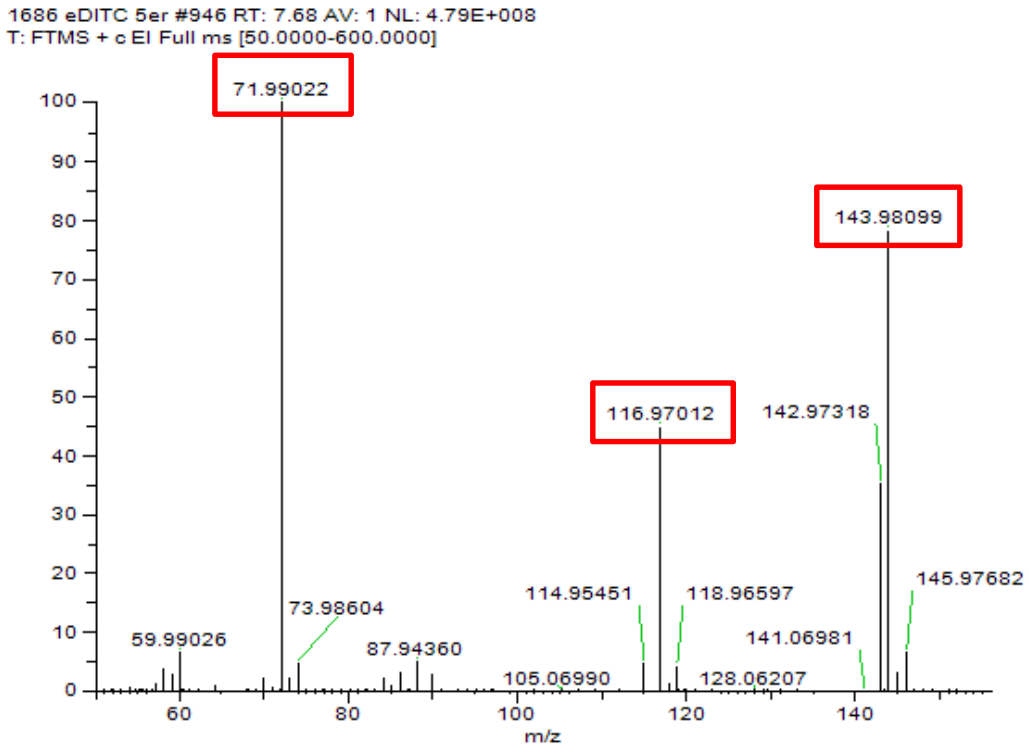
Ethylene-*bis*-DTC

Ethylene-*bis*-isothiocyanate (eBIC)

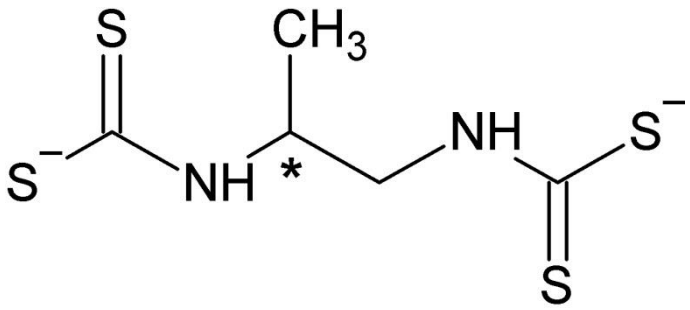
- see metabolic pathways of ethylene-*bis*-DTC
- **GC-amenable**
- NOT LC-MS (ESI pos/neg) amenable
- calculated LogP = 2,0
- standard not stable!

- for qualitative screening-purposes: extraktion of eBIC of e.g mancozeb-standard with acetonitrile

GC-EI spectrum of eBIC:

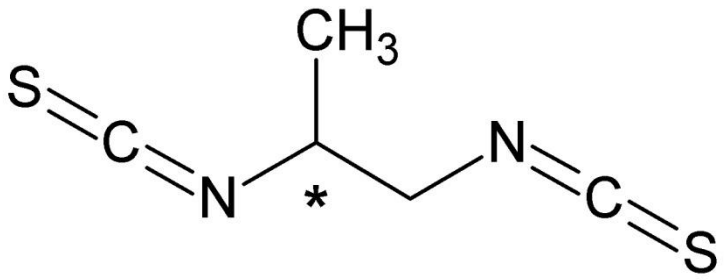


Decompositioin of Propylene-*bis*-DTCs to pBIC



Propylene-*bis*-DTC

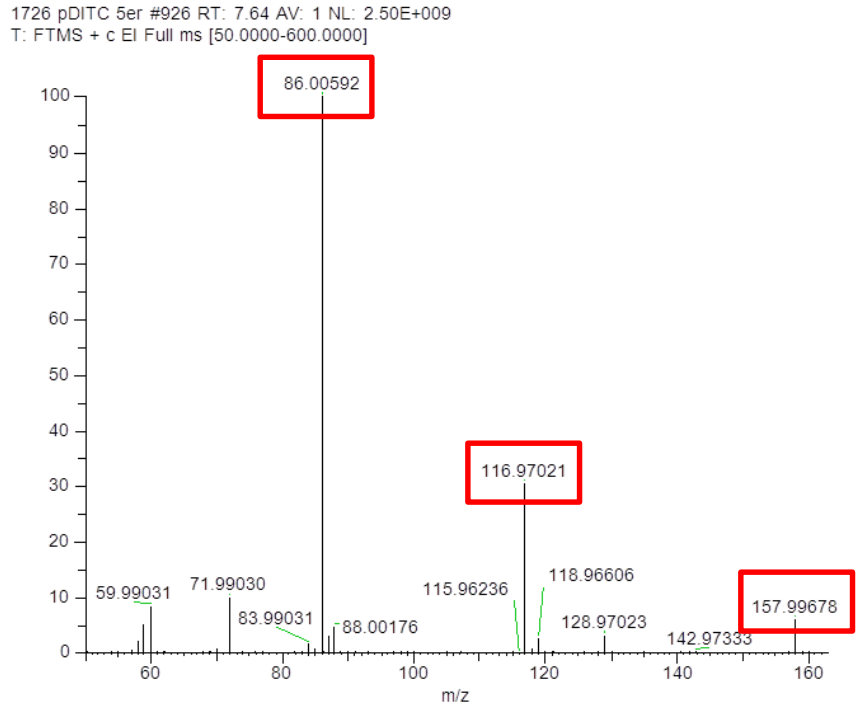
decomposition



Propylene-*bis*-isothiocyanate (pBIC)

- see metabolic pathways of Propylene-*bis*-DTC
- **GC-amenabe**
- NOT LC-MS (ESI pos/neg) amenable
- calculated logP = 2,3
- standard commercially available

GC-EI spectrum of pBIC:



Screening Detection Limits (SDL) according to SANTE/11813/2017

GC-MS/MS:

- 2 (or more) transitions

	eBIC	pBIC
Quantifier	144 > 72	158 > 86
Q1	72 > 45	86 > 60
Q2	144 > 88	117 > 88

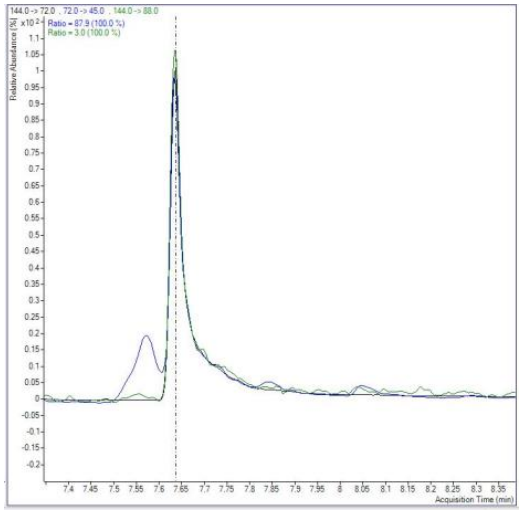
→ **SDL:**

5 ppb eBIC

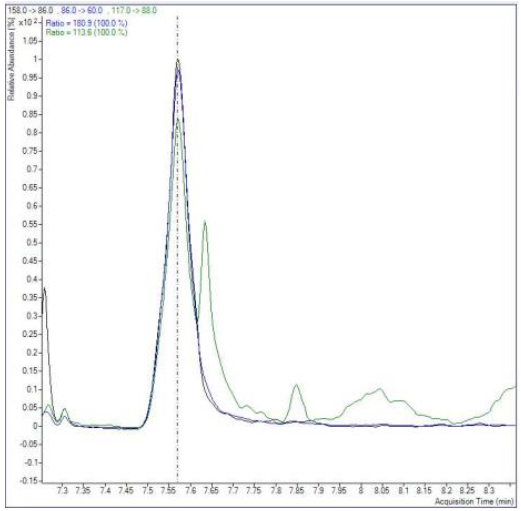
5 ppb pBIC

- Ion ratio within ±30% (relative) of average of calibration standards from same sequence

eBIC – Apple (QuEChERS-extract) – 5 ppb



pBIC – Apple (QuEChERS-extract) – 5 ppb



BIC Screening | Achievements: more CS_2-findings

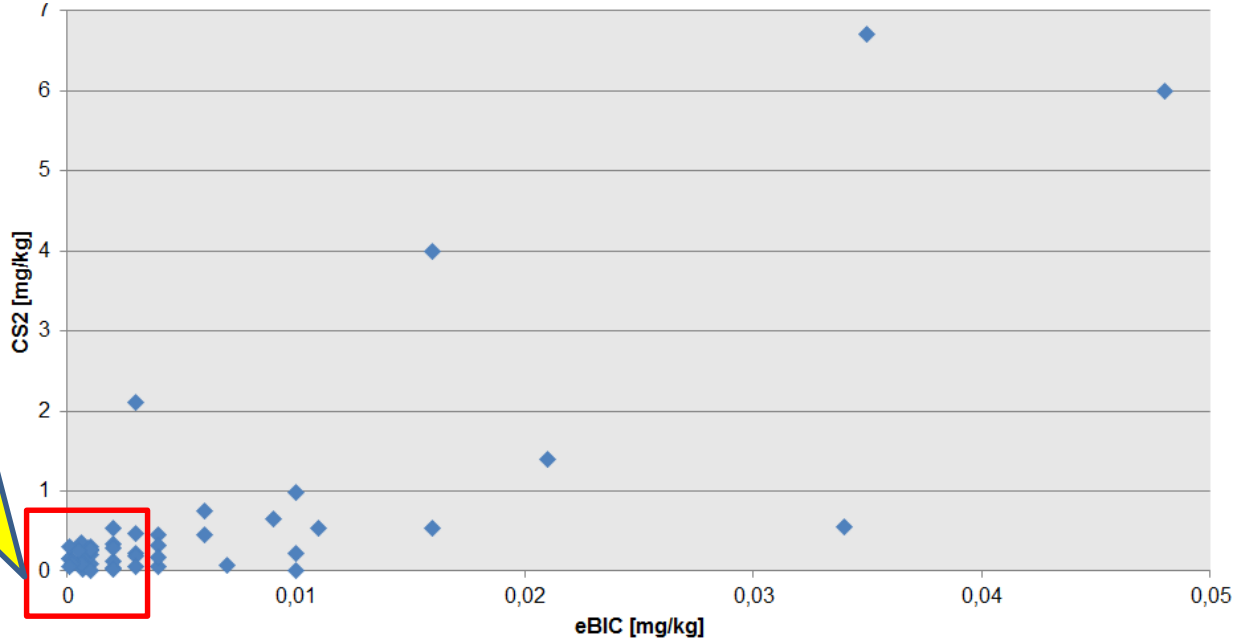
- Good correlation of eBIC/ETU-positives and CS2-results (DTC-cleavage to CS2):

Matrix	# of samples screened	# of positive eBIC-findings		# of ETU-findings (QuPPe, LC-MS/MS)	CS_2-Results	
		GC-MS/MS	GC-Orbitrap		# of samples	[mg/kg]
Pear	27	3	5	3	5	0,031 – 0,61
Zucchini	56	3	3	3	3	0,02 – 0,041
Parsley	16	2	2	2	2	1,6 – 1,7

data from 2021; LOQ for CS_2 (GC-MS/MS): 0,01 mg/kg

- BUT: no correlation of eBIC- or pBIC-concentration and CS_2-concentration

Samples were positive for CS_2 (chemical cleavage of DTCs), although eBIC-values were below SDL! CS_2-values as screening detection limits reflect the situation better than eBIC-SDL and pBIC-SDL in this case.



BIC Screening | Achievements: more MRL-violations

- Identification of EU-MRL violations by BIC Screening:

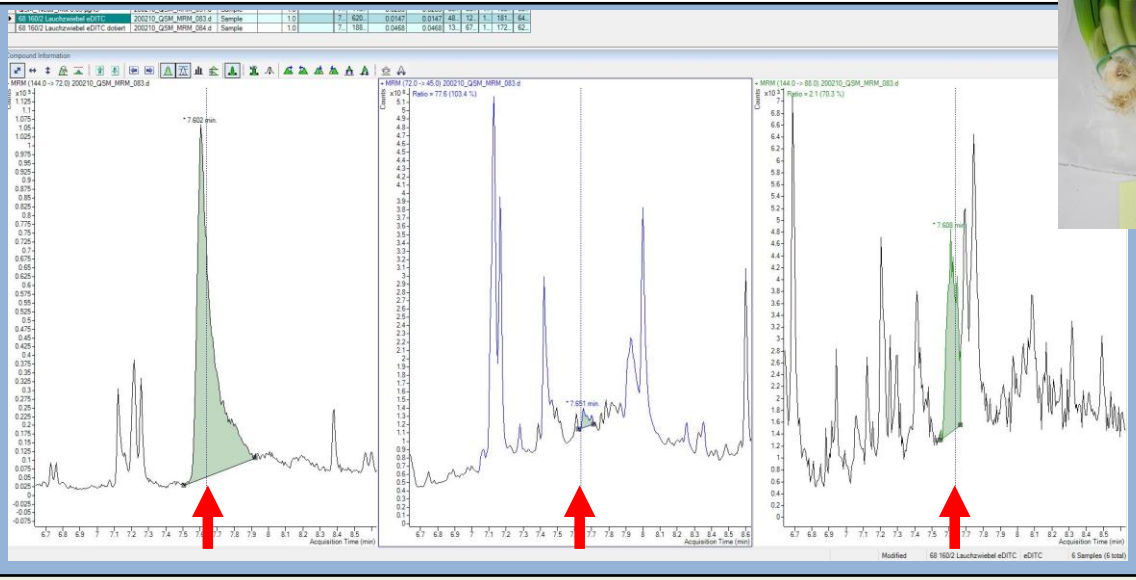
Matrix	Screening	CS_2-Befund [mg/kg]	EU-HM CS_2 [mg/kg]
> MRL (non compliant)			
Figs	eBIC / ETU	4,0	0,05
Raspberry (frozen)	eBIC	0,3	0,05
Parsley	eBIC / ETU	24,5	5,0
Sugar pea	pBIC / PTU	0,3	0,05
> MRL, but compliant due to uncertainty interval			
Basil	eBIC / ETU	6,0	5,0
Head lettuce	eBIC / ETU	5,6	5,0
Basil	eBIC / ETU	7,2	5,0

➢ Samples were analyzed for CS_2 by chemical cleavage of DTCs **because of positive BIC screening.**

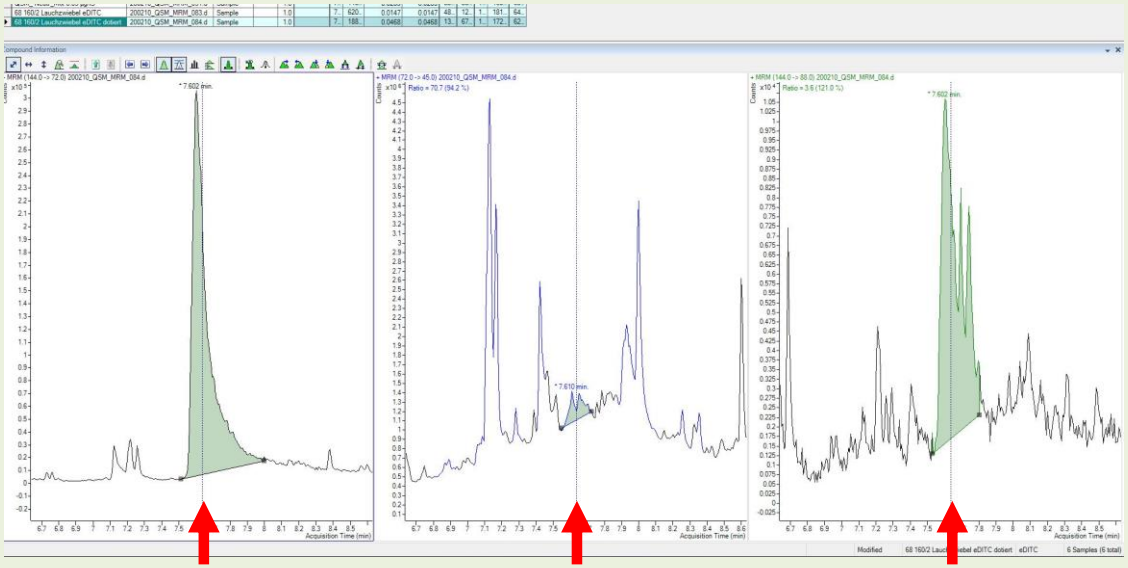
1. Example | Spring onion: eBIC

- **QuEChERS extract; GC-MS/MS chromatogram:**

eBIC (~0,016 ppm)

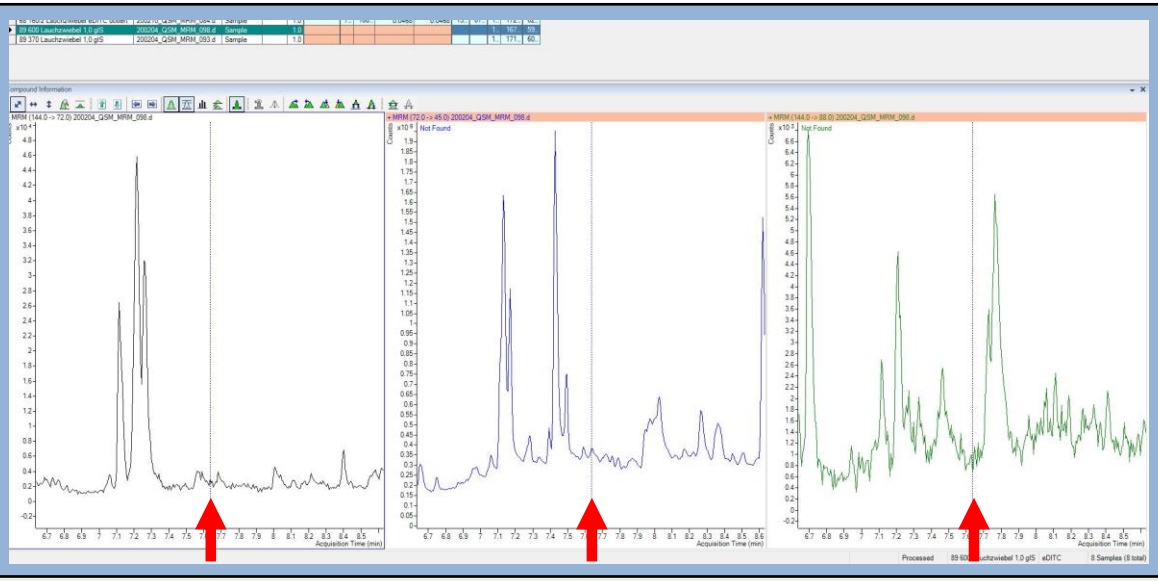
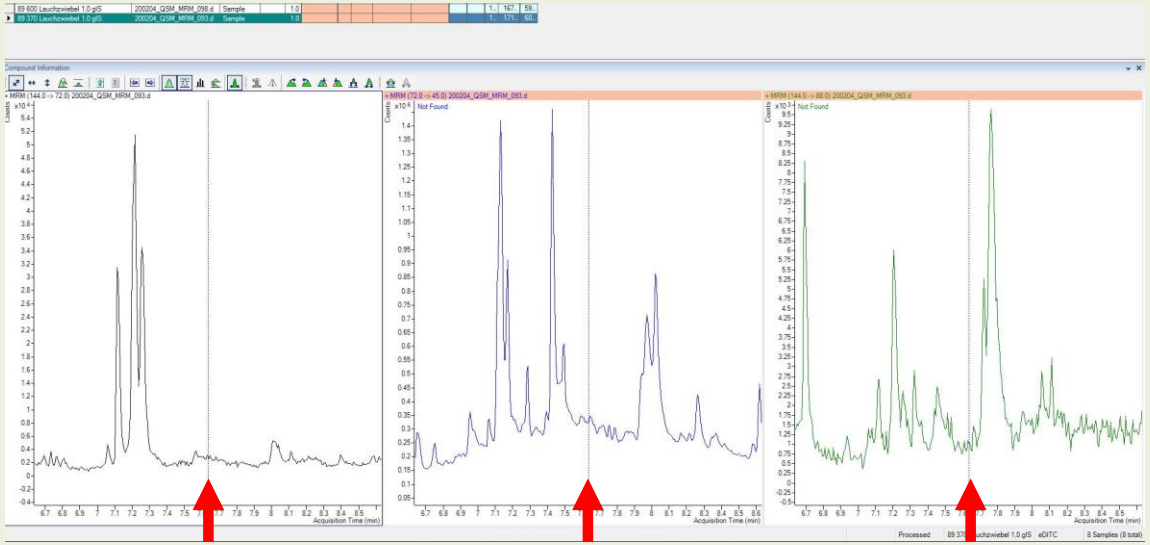


eBIC spiked

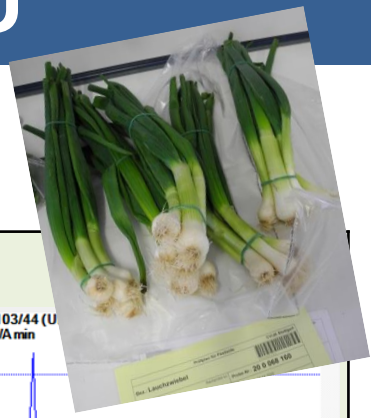


1. Example | Spring onion: control samples

- **QuEChERS extract; GC-MS/MS chromatogram:**

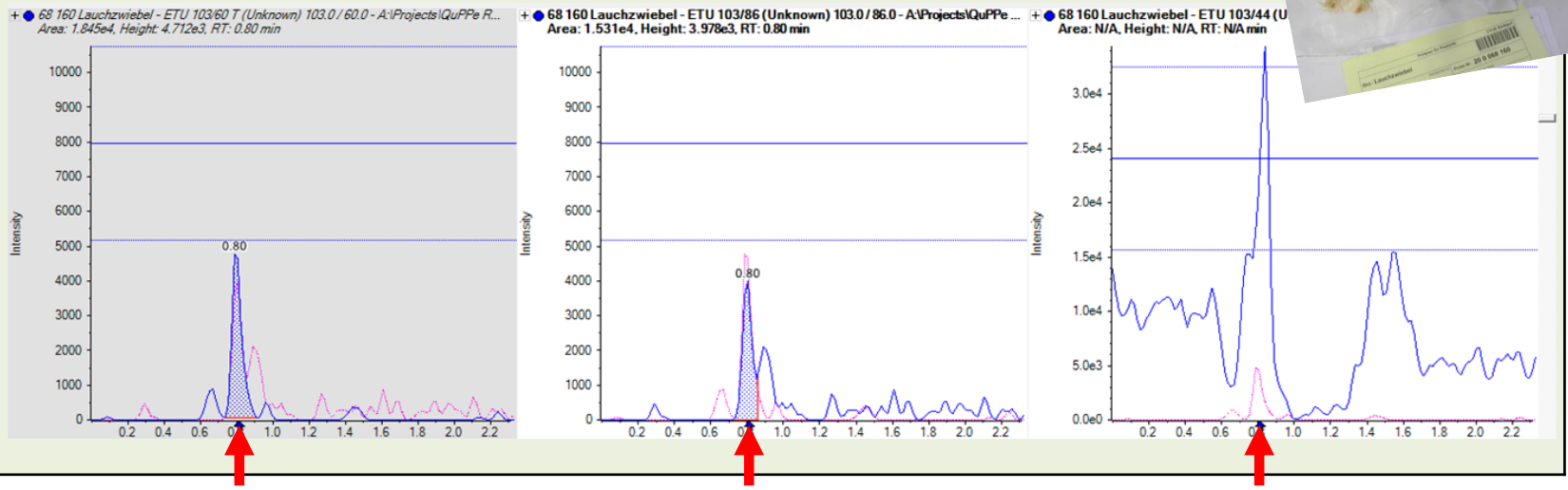
Control 1	
Control 2	

1. Example | Spring onion: ETU



- **QuPPE extract; LC-MS/MS Chromatogram:**

ETU
(~0,005 ppm)



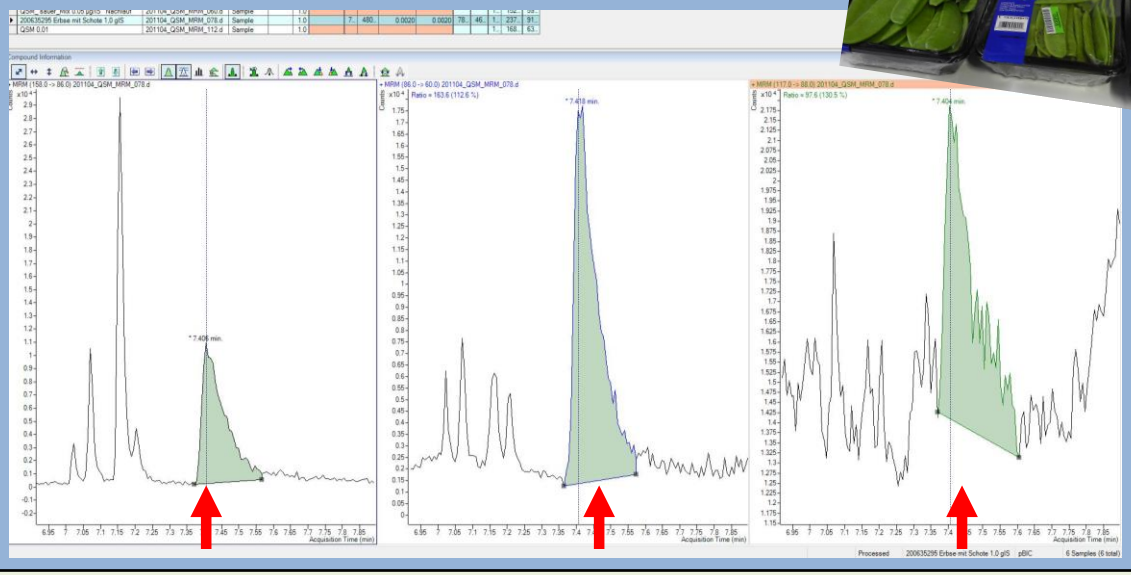
	Result [mg/kg]	EU-MRL [mg/kg]
Dithiocarbamates (dithiocarbamates expressed as CS2, including maneb, mancozeb, metiram, propineb, thiram and ziram)	**0,99**	1,0

- Alliaceae naturally contain compounds (e.g. mustard oil glycosides) that can transform to intermediates (e.g. isothiocyanates) which can release CS2 when applying the the acidic digestion/hydrolysis method => background CS2-levels

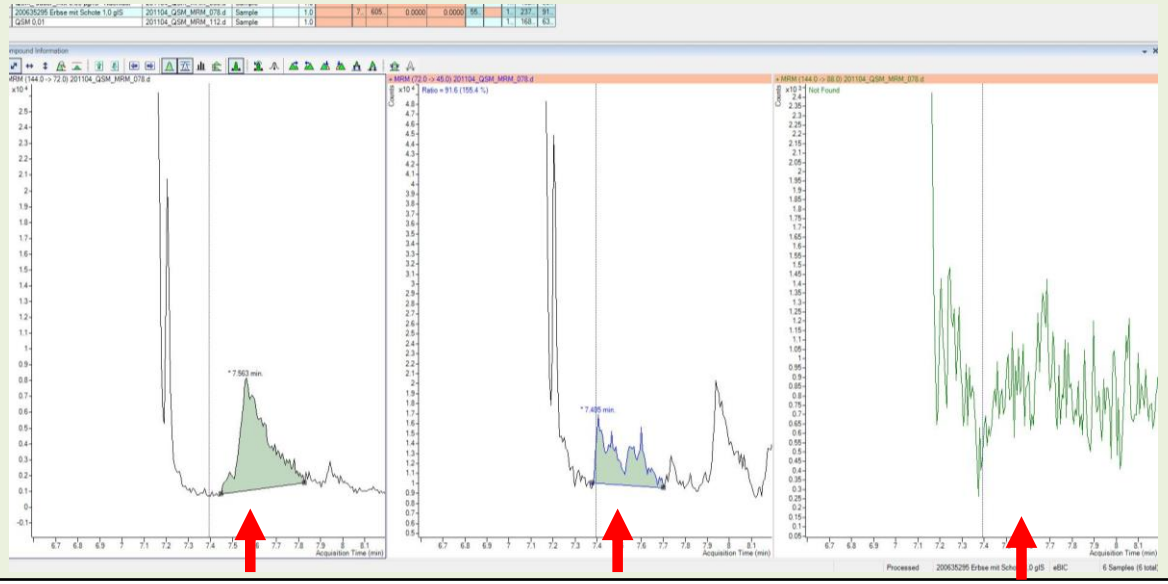
2. Example | Sugar peas (Kenya): pBIC, eBIC

- **QuEChERS extract; GC-MS/MS Chromatogram:**

pBIC (~0,002 ppm)



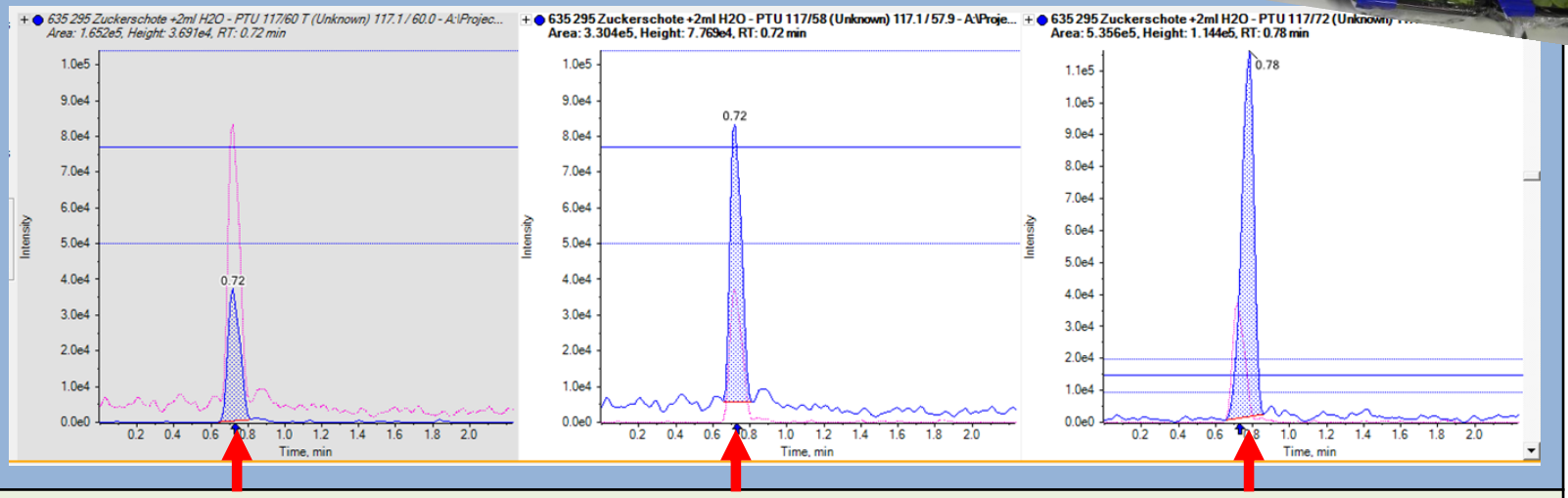
eBIC (~0,001 ppm)



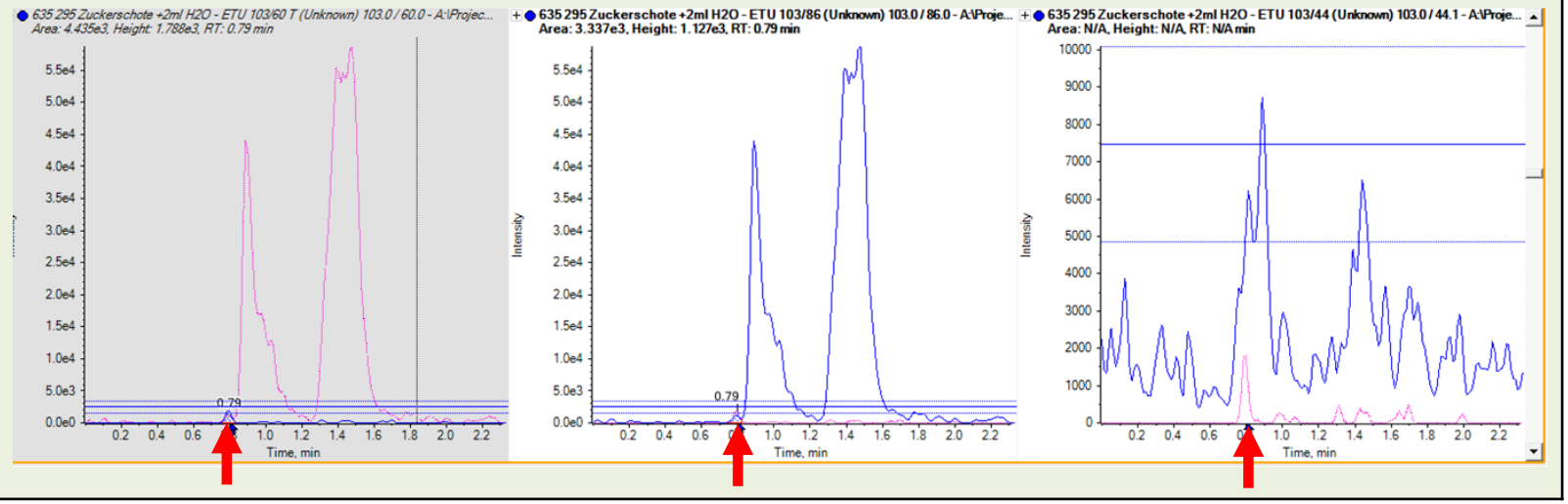
2. Example | Sugar peas (Kenya): PTU, ETU

- **QuPPe extract; LC-MS/MS Chromatogram:**

PTU (~0,005 ppm)



ETU (~0,0008 ppm)



2. Example | Sugar peas (Kenya)

- **EU MRL residue definitions for propineb**:
  - Dithiocarbamates (dithiocarbamates **expressed as CS_2**, including maneb, mancozeb, metiram, **propineb**, thiram and ziram)
  - **Propineb, expressed as propilendiamine** (SANTE/12108/2020; Reg. (EC) No 149/2008)

- Quantification of propineb in sugar pea-sample via derivatization to pBIC (standard addition (spiking of test portions), GC-MS/MS)

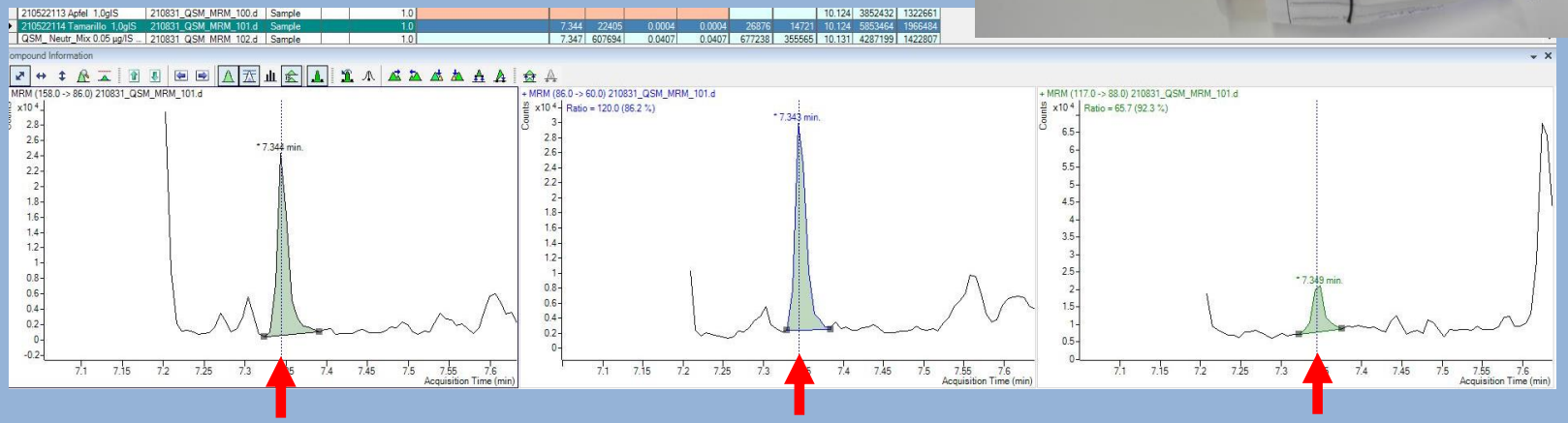
	Result [mg/kg]	EU-MRL [mg/kg]
Propineb (expressed as propilendiamine)	**0,30**	0,05
Dithiocarbamates (dithiocarbamates expressed as CS_2, including maneb, mancozeb, metiram, propineb, thiram and ziram)	(0,62*)	1,0

*<u>theoretical</u> CS_2-result (calculated on basis of propineb-finding)

3. Example | Tamarillo (Colombia): Propineb

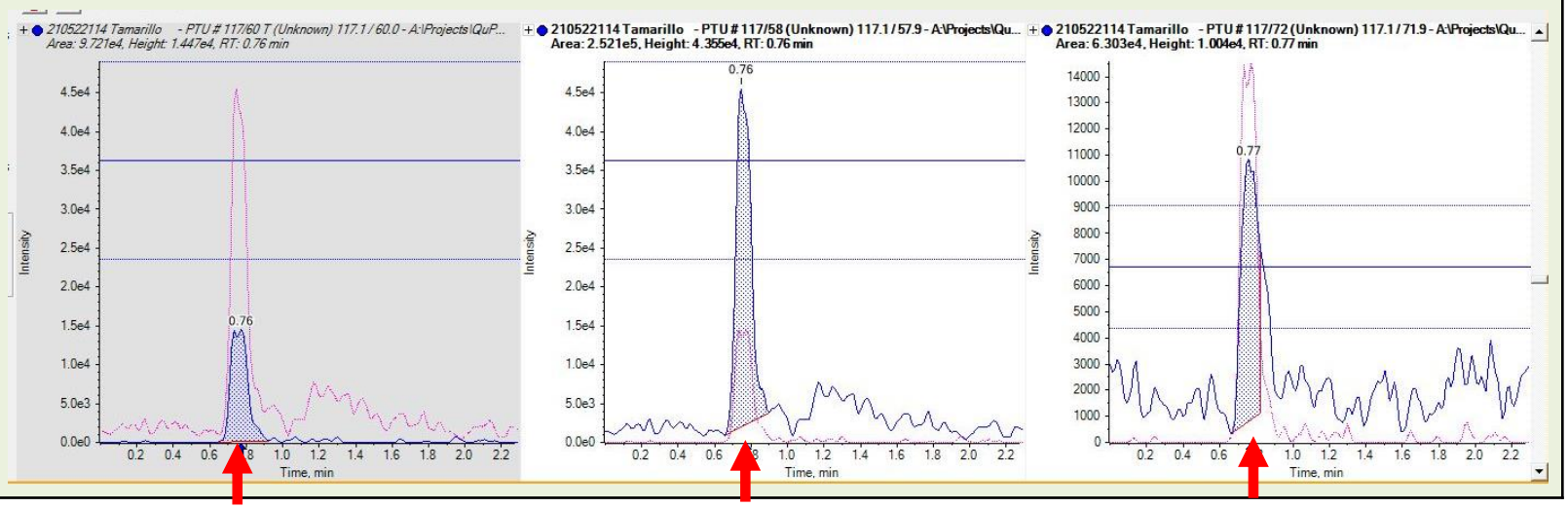
pBIC
(~0,0004 ppm)

QuEChERS; GC-MS/MS Chromatogramm:



PTU
(~0,003 ppm)

QuPPE; LC-MS/MS Chromatogramm:



3. Example | Tamarillo (Colombia): Propineb

EU Pesticides Database:

Code number	Products to which	Dithiocarbamates (dithiocarbamates expressed as CS2, including maneb, mancozeb, metiram, propineb, thiram and ziram) (O)	Propineb (expressed as propilendiamine) (O)
		Reg. (EU) 2017/171	Reg. (EC) No 149/2008
		applicable	applicable
0163040	Papayas	7	0.05*

Scientific name(s):
Carica papaya

Other products names or synonyms:
Akee apples
Feijoas/pineapple guavas
Langsats/lanzones/longkongs
Mangosteens
Naranjillas/lulos
Paw paws
Tamarillos

Category | Group | Sub-grou | Clickable footnotes | * Indicates lower limit of analytical determination

- CS_2-finding: <u>0,039 mg/kg</u>

Summary

- Xanthan gum-solvent is suitable to prepare DTC-suspensions; only usage of freshly prepared suspensions is recommended
- Quality of DTC-standards varies
- Screening for mono alkylene *bis*-DTCs via eBIC/pBIC and/or ETU/PTU is a CHANCE (more CS_2-findings, more MRL-violations)!

What‘s next?

- Enhance chemical stability of DTC-xanthan gum-suspensions
- Check for other DTC-screening marker (especially for N,N-dimethyl-DTCs)
- Development of a group-specific DTC-method
- Survey on DTC-methods (in cooperation with French NRL)

Our Pesticide-Team