How the screening of marker substances can improve the efficiency in the analysis of ethylene-*bis*-dithiocarbamates via CS_2

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Introduction

Dithiocarbamates, and especially ethylene-*bis*-dithiocarbamates (EBDTCs) are still among the most extensively used organic fungicides in agriculture. The traditional common-moiety approach, involving chemical cleavage to carbon disulfide (CS_2), shows several drawbacks: a) it does not differentiate between specific active substances, not even between DTC groups; b) it does not differentiate CS_2 originating from naturally occurring components of some matrices (e.g. *brassica* and *allium* family); c) the methods are mostly troublesome as the DTCs cleavage is usually conducted at elevated temperatures for several hours; d) high amounts of HCl and $SnCl_2$ are consumed [1].

An information-based two-step-approach for the analysis of DTC-residues is presented, involving judicious selection of the samples worthwhile analyzing further via the common moiety (CS_2) or specific DTC-analysis procedures. The approach involves initial screening for various, carefully chosen, metabolites and/or reaction products of DTCs ("DTC-markers") and a triggered subsequent DTC-analysis.

Analytical Method

CS_2 was analysed using a method involving reductive cleavage with HCl/$SnCl_2$ (SRM-14) [2]. The DTC-markers were analysed using QuPPe and CEN-QuEChERS (EN 15662) combined with LC-MS/MS and GC-MS/MS or GC-Orbitrap (see Fig. 1 and supplemental sheet) [3].

Results

In total, 540 samples were analyzed for CS_2 (sum) and for DTC-markers. These samples were subdivided into two groups:

- „**Untriggered samples**" (N=398), which were analyzed for CS_2 irrespective of any trigger (e.g. monitoring samples);
- „**Triggered samples**" (N=142), which were only analysed for CS_2 after a DTC-marker was encountered.

18.7 % of the „untriggered samples" showed levels of CS_2 (LOQ = 0.01 ppm), of which roughly one third (6.5% overall) concerned matrices, known to naturally generate CS_2 (see Fig. 2).
87.8 % of the „untriggered samples" contained no positive DTC-markers. The vast majority (77.4 %) of these samples had no determinable amounts of CS_2 and were analyzed to no purpose. It should be noted, that about 7 % of „untriggered samples" with no DTC-markers (5.9 % overall) still showed CS_2 levels >0.01 ppm. Nevertheless, only one sample (0.3 % overall) exceeded the MRL for CS_2.

In contrast, 69.7 % of the „triggered samples" contained CS_2 levels >0.01 mg/kg and 10 of these samples (7.0 % overall) contained CS_2 levels exceeding the MRL. **These 10 MRL-violations would have remained unnoticed, if the subsequent CS_2 analyses were not triggered.**

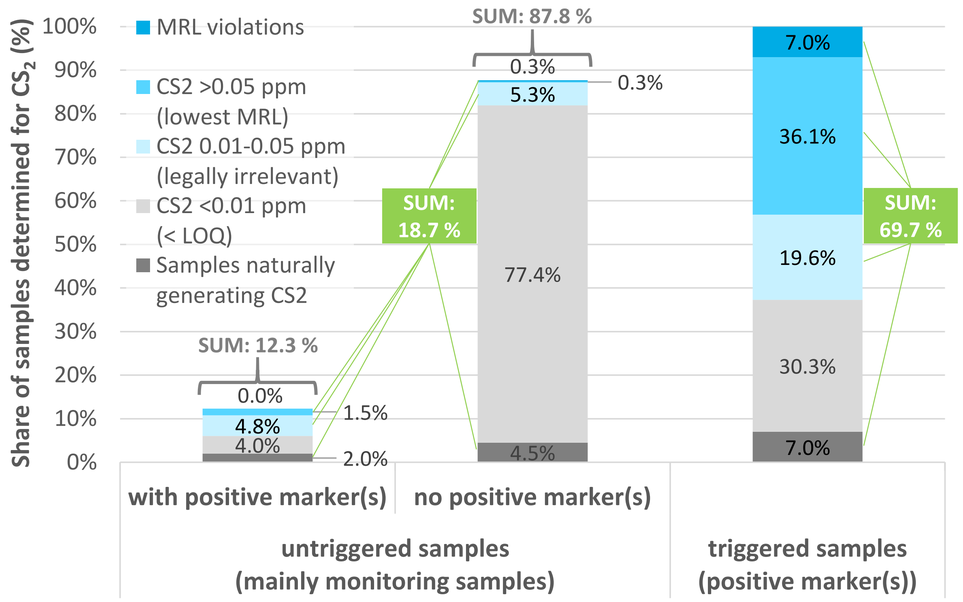

Figure 2: Overview about the share of untriggered samples (in total 398) and triggered samples (in total 142), determined for CS_2 and DTC marker substances.

For 9 out of the 10 samples exceeding the MRL (6.3% overall), the CS_2 analysis was triggered by EBDTC markers (eBIC, ETU and EU, see Fig. 1 and Fig. 3). **All in all, the detection of these EBDTC markers indicated a high probability for relevant CS_2-findings, especially if two or three of these markers are encountered simultaneously.**

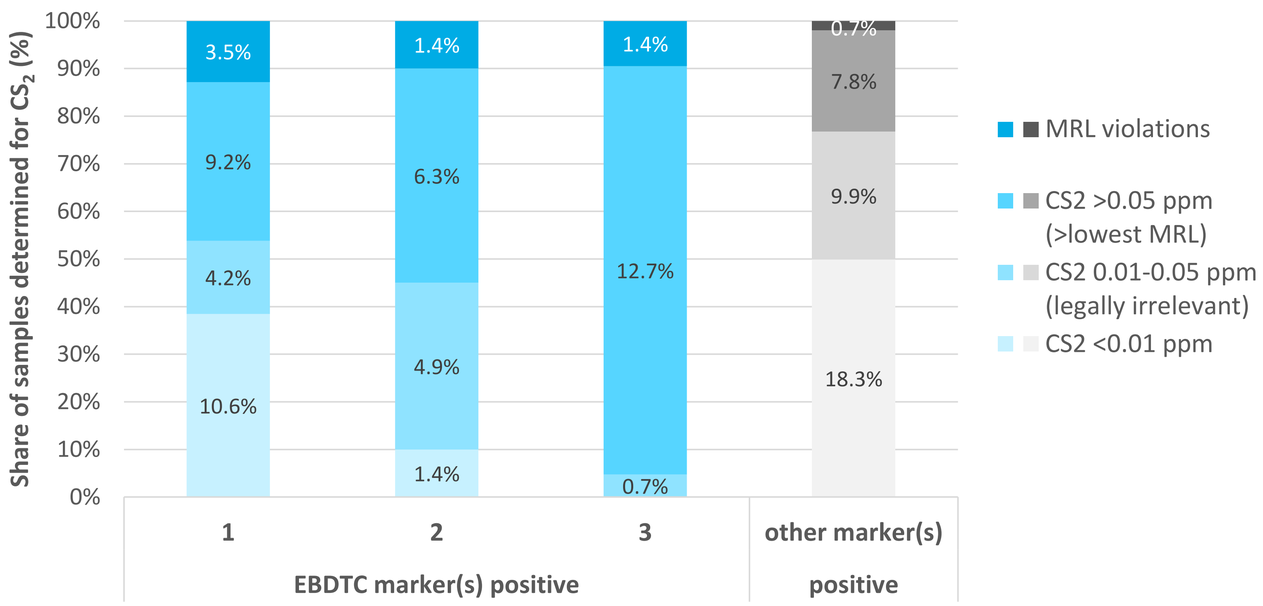

Figure 3: Share of triggered samples depending on the number of EBDTC markers found.

ethylene-*bis*-isothiocyanate (eBIC)
QuEChERS- amenable,
det. with GC-MS/MS or -Orbitrap

ethylene thiourea (ETU)
QuPPe-amenable
det. with LC-MS/MS

ethylene urea (EU)
QuPPe-amenable
det. with LC-MS/MS

Figure 1: Overview of the used EBDTC marker substances.

additional information

Summary

Findings of the EBDTC marker substances ETU, EU and eBIC in samples by using popular multi-residue methods resulted in a high percentage of relevant CS_2-findings. Therefore, the use of the three marker substances as a trigger can highly improve the effort/cost to benefit ratio in the routine analysis of DTCs and significantly lessens unnecessary analyses of CS_2.

Literature
[1] EN 12396-1:1999-1 or EN 12396-2:1998-12
[2] https://www.eurl-pesticides.eu/library/docs/srm/meth_DithiocarbamatesCS2_EurlSrm.PDF
[3] https://www.eurl-pesticides.eu/userfiles/file/EurlSRM/EurlSrm_meth_QuPPe_PO_V12.pdf; latest update: 22.07.2021

LAPRW 2023
M10

Co-funded by the European Union

Baden-Württemberg