# 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).
12.3 % of the „untriggered samples“ contained at least one DTC-marker with about two thirds of them also containing $CS_2$ levels >0.01 mg/kg.
87.8 % of the „untriggered samples“ contained no relevant levels of DTC-markers. It should be noted, that about 7 % of these samples (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, 62.7 % 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.**

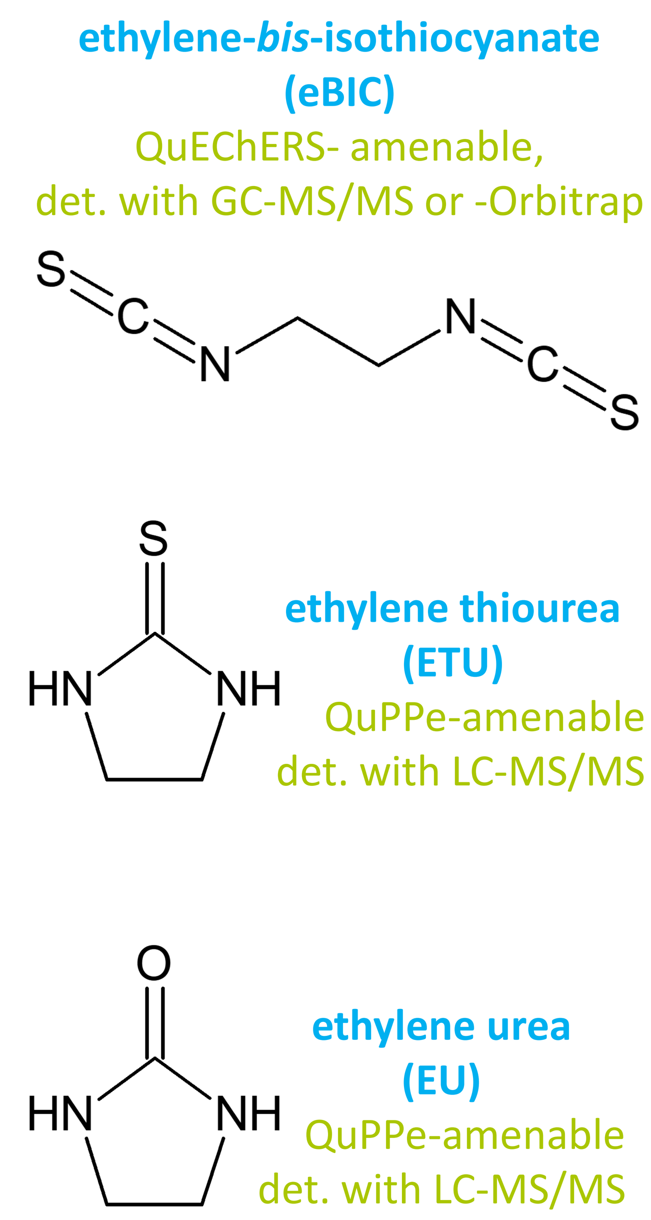


**Figure 1:** Overview of the used EBDTC marker substances.

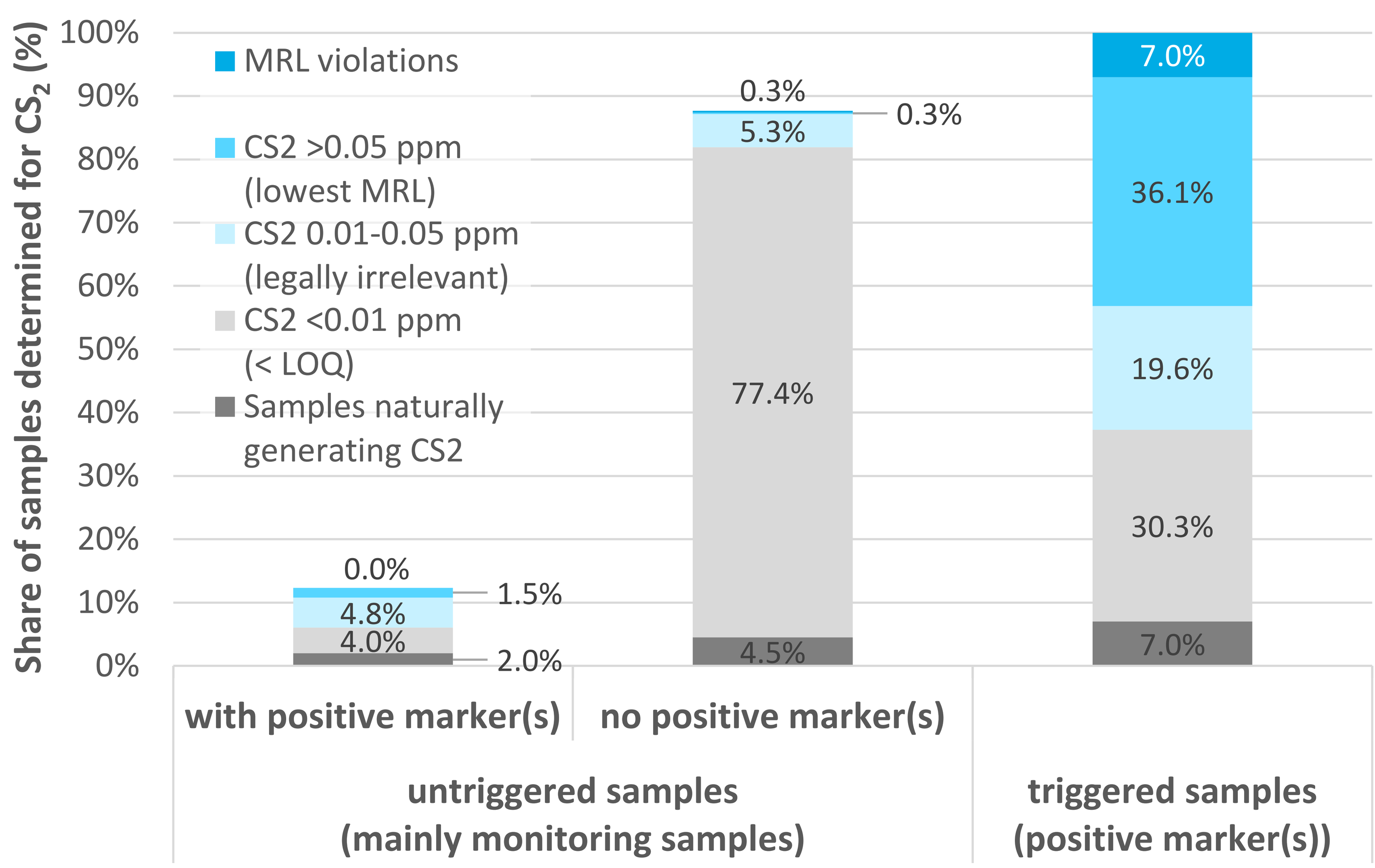


**Figure 2:** Overview about the share of untriggered samples (in total 398) and triggered samples (in total 142), determined for $CS_2$ and DTC marker substances.

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.**

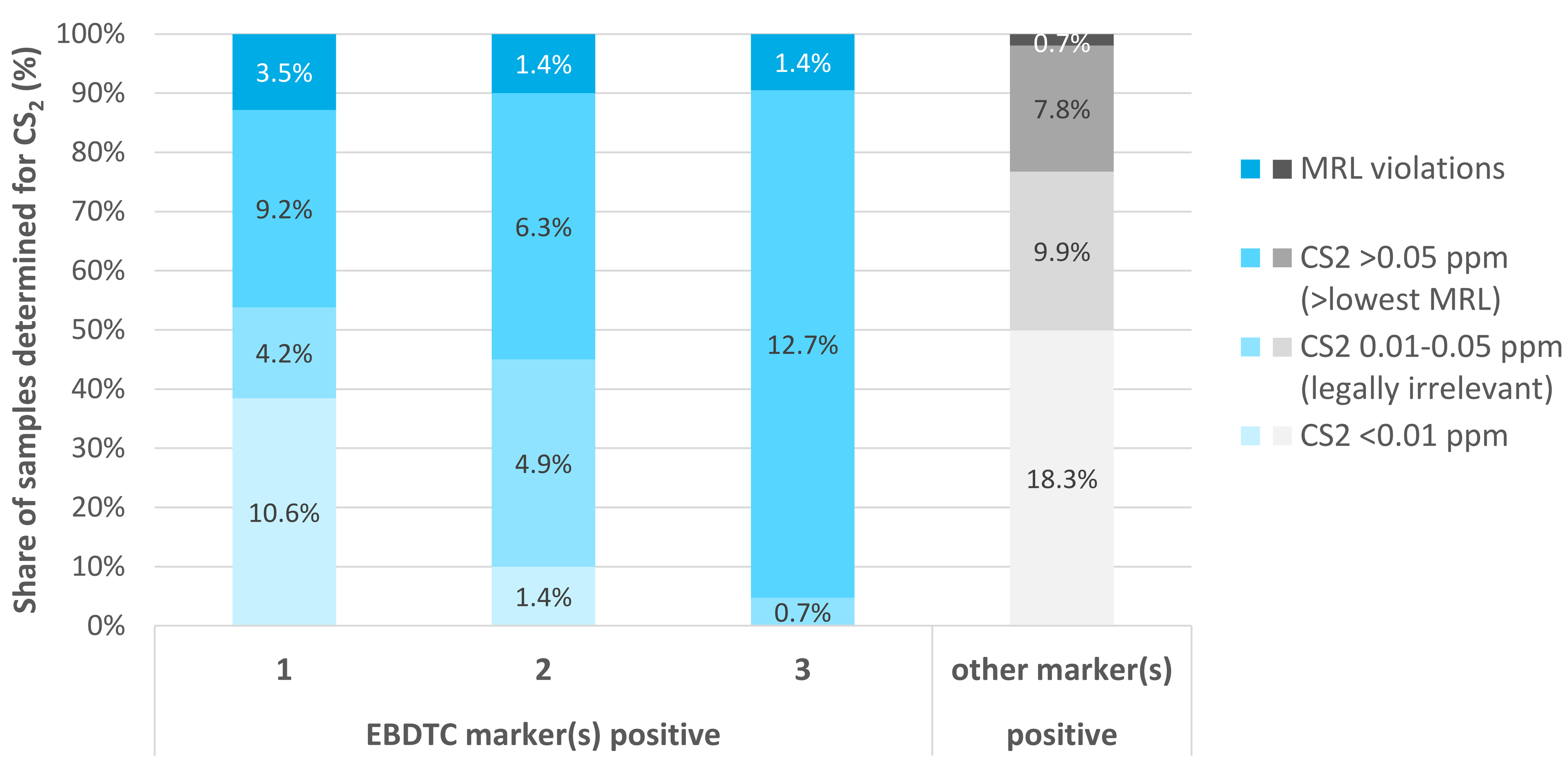


**Figure 3:** Share of triggered samples depending on the number of EBDTC markers found.

## 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

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