

Selective analysis of dithiocarbamates by classes: overview of the French working group project

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Dithiocarbamates (DTC), a class of broad-spectrum fungicides, are among the most frequently detected pesticides in the European Union, often with Maximum Residue Level (MRL) exceedances, due to their extensive use over the past decades. DTC have a polymeric structure composed of one or more metallic cations coordinated to an organic ligand whose structure allow the classification of DTC into three main groups : propylene-bis-dithiocarbamates (*i.e.* propineb), ethylene-bis-dithiocarbamates (*i.e.* maneb, zineb, nabam, metiram, mancozeb) and dimethyl-dithiocarbamates (*i.e.* thiram, ziram, ferbam).

DTC analyses are mostly based on the protocol of the European Reference Laboratory for Single Residue Methods (EURL-SRM, Stuttgart, Germany) which involves the acidic hydrolysis of DTC, resulting in the release of carbon disulfide (CS₂) which is then quantified. However, this method has some limitations since i) naturally sulfur containing commodities (*Brassicaceae*, *Alliaceae*) or commodities subjected to sulfurization as preservative treatments may induce false-positive results or over-estimated results, and ii) this method does not allow the identification of the class of DTC involved in a positive result.

In response to these limitations, some alternative methods, mostly based on the derivatization of DTC, have been published in the past few years. The French National Reference Laboratory for Single Residue Methods set up a working group at the end of 2021 with all the French official laboratories and the competent authority to assess the reliability of a methylation method (1) that should allow the quantification of DTC by classes. This method combines a decomplexation and a S-methylation step to a QuEChERS extraction, and the methylated DTC products corresponding to each of the three classes mentioned above are detected and quantified by reverse-phase LC-MS/MS analysis.

The aim of this work is to investigate the critical points of the methods, from the preparation of the standards to the quantification approach, while optimizing the decomplexation/methylation steps, in order to deliver a reliable method available for controls and risk assessments studies, particularly in the actual MRL revisions context.

Keywords: dithiocarbamates, derivatization, LC-MS/MS analysis, selective analysis

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References

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