Analysis of Propineb as Propylenediamine via LC-MS/MS in Fruit and Vegetables

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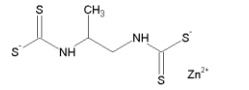
Introduction

Propineb is a foliar-applied dithiocarbamate fungicide with long residual activity which is used on a wide variety of crops for the control of various fungal infections such as blight on potatoes or downy mildew on hops.

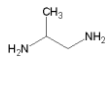
Legal Aspects

Reg. 149/2008/EC establishes the residue definition of "*propineb expressed as propylene-diamine*" with the lowest MRLs being set at 0.05 mg/kg. There are also maximum residue levels set for the whole group of dithiocarbamates whose residues are defined as "*dithiocarbamates expressed as CS_2, including maneb, mancozeb, metiram, propineb, thiram and ziram*".

Propineb



Propylenediamine



Current Approaches

Most labs employ methods by which dithiocarbamates are converted to CS_2 (using HCl and $SnCl_2$). CS_2 is then either analyzed spectrophotometrically following derivatization or directly via GC-MS/-ECD/-NPD. The analysis as CS_2 involves either partitioning to isooctane or headspace sampling. The main handicap of this common moiety approach is that it does not allow for the distinction between different types of dithio-carbamates.

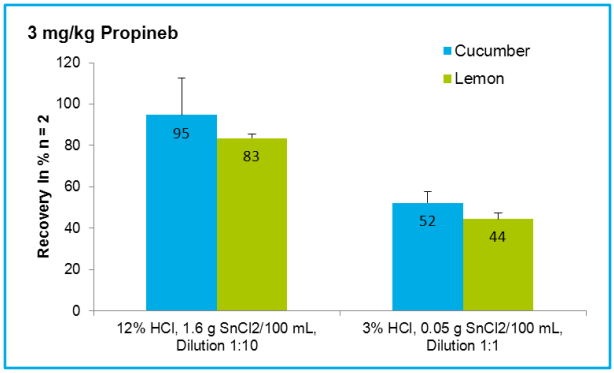
An alternative approach involves superficial extraction of dithiocarbamates using a special solvent containing EDTA and an analysis of the released monomers. This approach is specific for propineb but rarely used by regulatory labs.

Our Approach for Propineb

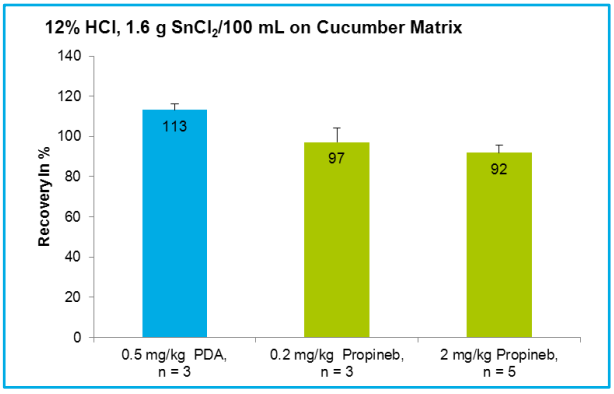
Based on the traditional approach for dithiocarbamates involving hydrolysis to CS_2 and partitioning into isooctane, we developed a method for the analysis of propineb as propylenediamine (PDA). Whereas CS_2 partitions to the isooctane phase, PDA remains in the acidic aqueous phase. The aqueous extract is filtered, diluted and subjected to LC-MS/MS analysis. PDA D6 is employed as ILIS to match for any matrix effects and partitioning losses. CS_2 was analyzed in parallel to check the cleavage rates. The analysis via PDA is specific to propineb and allows for the control of good agriculture practices and a comparison with toxicological thresholds of propineb.

Results

Aiming to reduce the load of matrix and acid applied on the column we tried to reduce the concentrations of HCl and $SnCl_2$. As this had a negative effect on the PDA yields (see graph below) we decided to keep the original hydrolysis conditions (12% HCl and 1.6 mg/100 mL $SnCl_2$).



To better preserve the analytical column, we diluted the extract at various ratios from 1:1 to 1:10. We finally chose 5 fold dilutions as a compromise between sensitivity and chromatographic performance and conducted the validation experiments using this approach. PDA showed a high tendency for interactions within the tubing of the LC-system and the column. Acidity and the presence of matrix in the extract improved chromatographic properties.



Summary

A method is presented which enables the simple and specific analysis of propineb via its degradant propylenediamine (PDA), directly from the aqueous phase of the isooctane-based dithiocarbamate method. PDA D6 was used as ILIS to compensate for all types of errors.

Reference

http://www.fao.org/fileadmin/templates/agphome/documents/Pests_Pesticides/JMPR/Evaluation93/propineb.pdf

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