



Direct analysis of dithiocarbamates by DESI-MS/MS

Paul Zomer^{1*}, Hans Mol¹, Tomas Cajka², Jana Hajslova²

¹ RIKILT, Institute of Food Safety, Wageningen University & Research centre, Akkermaalsbos 2, 6708 WB Wageningen, Netherlands; *e-mail: paul.zomer@wur.nl

² Institute of Chemical Technology, Department of Food Chemistry and Analysis, Technická 3, 16628 Prague 6, Czech Republic

Introduction

Dithiocarbamates (DTCs) are a widely used group of fungicides. Due to their physical-chemical properties the analysis has been a problem for a long time. The mostly used method is conversion of the compounds to CS₂, which can then be detected by spectroscopic or GC methods.

Desorption electrospray ionisation (DESI) is a relatively new detection technique where a pneumatically assisted (electro) spray of droplets is aimed at a sample, molecules from the sample are dislodged, ionized and then analyzed by the MS (Figure 1).

Experimental

DESI was coupled to a linear ion trap for MS/MS detection (see Figure 2).

DESI:

- Spray solvent: MeOH:H₂O 1:1 with 10 mM NH₄Formate and 0.1% Formic Acid
- Spray flow: 5 µl/min; Angles: α=55° β=10°
- Gas Pressure: 120 psi
- Scan speed across slide: 250 µm/sec
- Distance: spray tip → sample: ~3 mm
sample → MS inlet: ~0.5 mm
- Sample substrate: HTC printed on glass

MS:

- Spray Voltage: 5 kV
- Temp. Ion Transfer Tube: 50°C
- Fragmentation: m/z 241@CE22 (m/z 196 & 88)

Final Extraction Method Thiram:

- Shake complete fruits (NOT homogenized) gently with acetonitrile, I.S.: Azoxystrobin
- 1 mL acetonitrile / gram sample
- Pipet 1.5 µl extract on HTC spot → let ACN evaporate → DESI

Results

Thiram

By adding Ammonium Formate to the spray solvent [M+Na]⁺ adduct formation was suppressed and [M+H]⁺ was obtained as the most abundant ion with better fragmentation efficiency.

Sensitivity

The absolute response obtained with DESI varies. However, with an internal standard quantitative data can be produced (see Fig. 3). See Fig. 4 for the corresponding extracted ion chromatograms. The LOQ for Thiram in solvent was approx. 0.1 mg/kg.

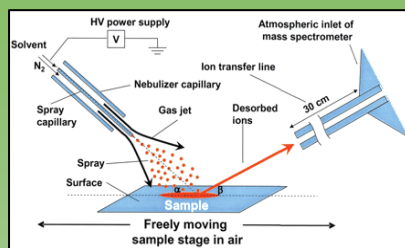


Fig. 1: Schematic description of DESI

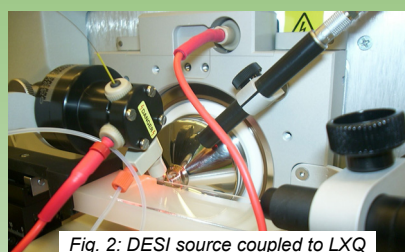


Fig. 2: DESI source coupled to LXQ

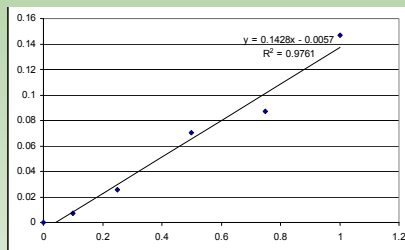


Fig 3: Calibration curve Thiram in Solvent [0-1 g/kg](n=3)

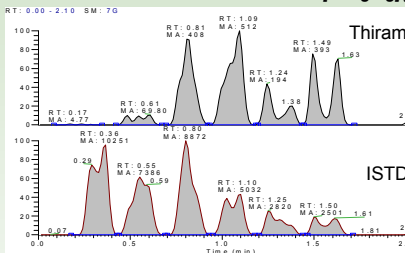


Fig 4: Extracted ion chromatograms. Solvent 0-1 mg/kg



Fig 5: Extraction of whole fruits

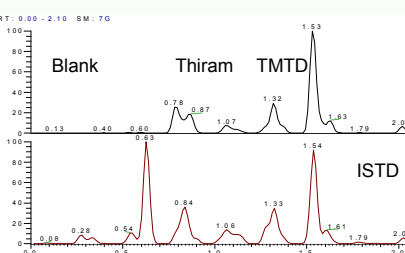


Fig 6: Extracted ion chromatograms. Strawberry 10 mg/kg

Spiked Samples

Thiram can be extracted using QuEChERS type methods. Analyzing these extracts using DESI, an ionization suppression of more than 95% was found and Thiram could not be detected at desired MRL levels.

As an alternative, a similar approach as described by Crnogorac [1] was applied. Using acetonitrile as extraction solvent for the intact fruits (see Fig. 5), it is possible to detect Thiram at relevant levels in various crops (e.g. strawberries, see Fig. 6).

Detection after TMTD application

To test the practical application of the method, samples were also spiked with a commercial plant protection product (TMTD). Thiram could easily be detected on various crops at MRL levels of 1-10 mg/kg. (Fig. 6).

Direct Analysis from leaves

One of the big benefits of DESI compared to conventional MS methods is the ability to detect compounds directly from surfaces. We tried to analyze Thiram directly from leaves from pear trees, but our attempts were unsuccessful so far, in contrast to other pesticide/crop combinations reported by others [2].

Other Dithiocarbamates

Compared to Thiram, other DTCs, e.g. Maneb and Propineb give other analytical challenges. The compounds are polymers which are not soluble in standard organic solvents. Crnogorac [1] described a method where the polymers are broken down to the monomers and these are detected by LC-MSMS. Using direct infusion we were able to replicate those results, but the sensitivity of the compounds using DESI was insufficient for residue analysis.

Conclusions

- Thiram can be rapidly analyzed at relevant levels using DESI-MS/MS.
- Extraction of intact fruits is preferable over extraction of a homogenized sample.
- Using an internal standard, quantitative results can be obtained.
- Analysis of 8 samples takes 2 minutes.
- Attempts to detect Thiram directly from a pear tree leaf surface were unsuccessful.
- More research is required for sensitive detection of other DTCs by DESI.

References

- [1] Crnogorac *et al*, Rap. Comm Mass Spec. 22 (2008) 2539
- [2] Garcia-Reyes *et al*, Anal. Chem. 81 (2009) 820-829