### Analysis of Dithiocarbamate Pesticides by GC-MS

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#### Overview

**Purpose**

Analysis of dithiocarbamate pesticides (DTCs) using an optimized GC-MS method is described. DTCs are not stable and cannot be extracted and analyzed directly. The purpose of this work was to develop a reliable method for identification and quantification of residues.

**Methods**

Dithiocarbamates were quantitatively converted to carbon disulfide by reaction with tin(II)chloride in aqueous HCl (1:1) in a closed bottle at 80 °C. The CS₂ gas produced is absorbed into iso-octane and measured by GC-MS. The analysis of DTCs for this application follows the acid-hydrolysis method using SnCl₂·HCl. For method validation of the DTC pesticides, Thiram (99.5% purity) was used as representative b/c(dithiocarbamate) compounds considering its simple structure (1 mole of Thiram = 2 mole of CS₂ = 1 mg of Thiram theoretically generates 0.6333 mg CS₂). This is a non-specific DTC sum method that does not distinguish between the different species of DTCs in the sample.

**Results**

The results show good correlation factors with satisfactory recoveries. Real life samples were analyzed demonstrating the robustness and productivity of the applied method.

#### Introduction

The class of dithiocarbamate fungicides (DTCs) is widely used in agriculture. They are non-systemic and both the formulation and their break-down products typically remain at the site of application. DTCs are characterized by a broad spectrum of activity against various plant pathogens, low acute mammalian toxicity, and low production costs [1]. The dithiocarbamate moiety is highly reactive: it readily chelates most heavy metals, reacts with sulphydryl groups of proteins, rendering itself neurotoxic, teratogenic, and cytotoxic.

It is not possible to homogenize plant samples and extract DTCs by organic solvents, as it is, for instance, with the QuEChERS standard procedure in pesticide-residue analyses. The analysis of DTCs for this application follows the acid-hydrolysis method using SnCl₂·HCl. The total DTC residues were extracted by analyzing CS₂, as the DTC hydrolysis products by GC-MS.

#### Methods

**Sample Preparation**

250 ml of closed bottle
- Weigh 50 g of grape berry or homogenized sample
- Add SnCl₂ reaction mixture

Add 25 ml of iso-octane
- Keep on water bath at 80 °C for 1 h
- Intermediate shaking after every 20 min.
- Keep bottle at room temperature
- Transfer the bottle in ice cold water
- Two separate layer
- Take upper layer 1:2 ml
- Centrifuge at 10 °C

#### Data Analysis

The data processing and reporting was done using the XCalibur™ quantitation and reporting software suite.

**Results**

**Sensitivity**

The sensitivity of the method was evaluated in terms of the limit of detection (LOD) and limit of quantification (LOQ) which were respectively 0.055 and 0.04 μg/mL. The LOD is the concentration at which the signal to noise ratio (S/N) for the quantifier ion is ≥ 3, whereas LOQ is the concentration for which the S/N is ≥ 10.

**Precision**

The precision of repeatability was determined by three analysts preparing six samples each on a single day. The intermediate precision was determined by the same analysts with six samples each on six different days. The method precision was determined with 0.04 mg/kg.