

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 or analyzed directly. The purpose of this work was develop a reliable method for identification and quantification of residues.

Methods

Dithiocarbamates were quantitatively converted to carbon disulphide 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 bis(dithiocarbamate) compound 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 mammal toxicity, and low production costs [1]. The dithiocarbamate moiety is highly reactive: it readily chelates most heavy metals, reacts with sulfhydryl 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 estimated by analysing CS₂ as the DTC hydrolysis products by GC-MS.

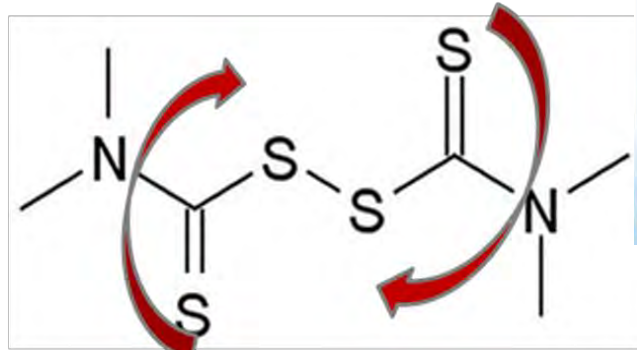


FIGURE 1: Thiram – 1 mole of Thiram generates 2 mole of CS₂



FIGURE 2. ITQ™ 900 GC-MS/MS system with Thermo Scientific TriPlus RSH

Methods

Sample Preparation

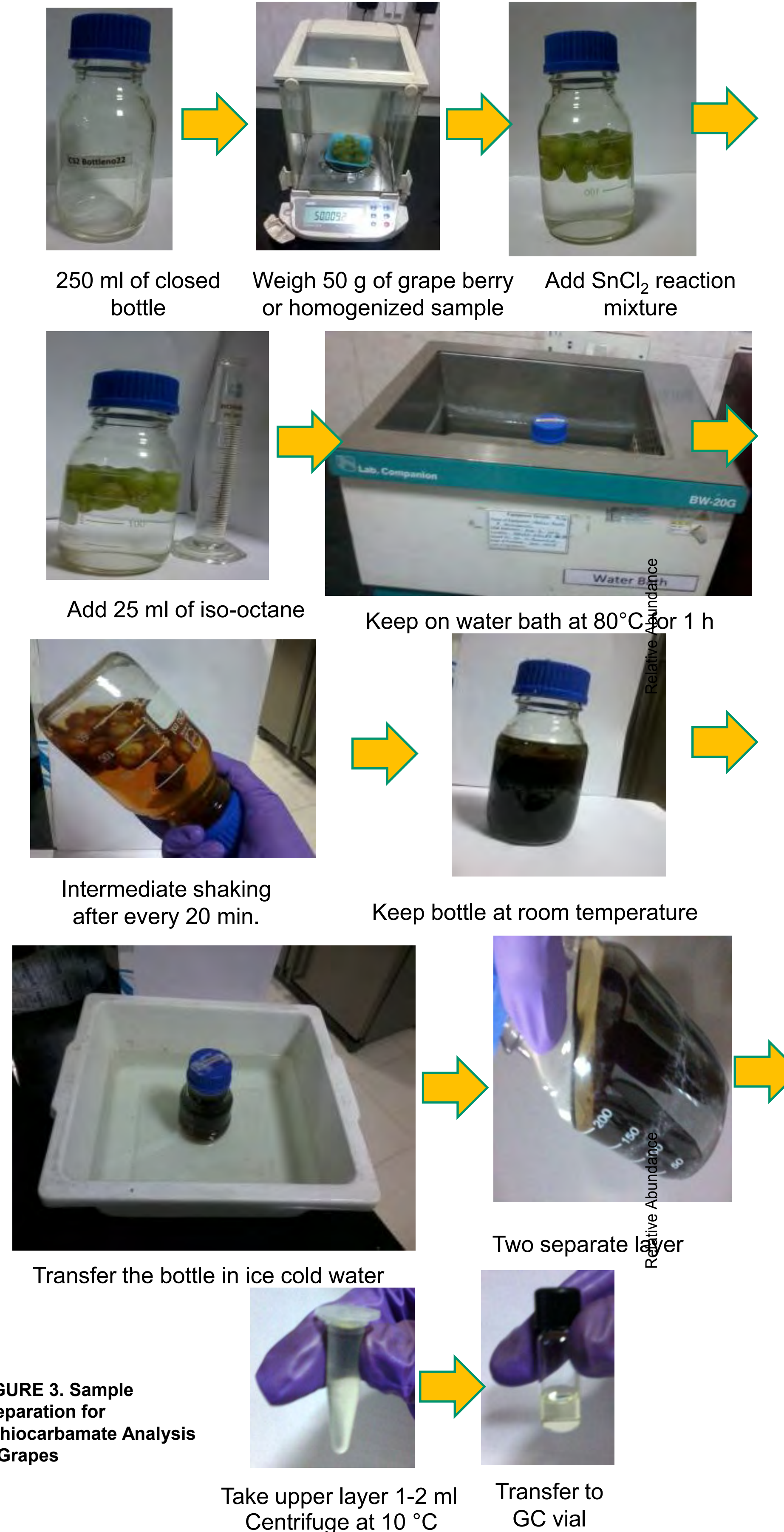


FIGURE 3. Sample Preparation for Dithiocarbamate Analysis in Grapes

A Thermo Scientific™ TRACE GC Ultra™ gas chromatograph equipped with Thermo Scientific™ Triplus™ RSH liquid Autosampler and coupled to a Thermo Scientific™ ITQ™ 900 ion trap mass spectrometer was used for analysis.

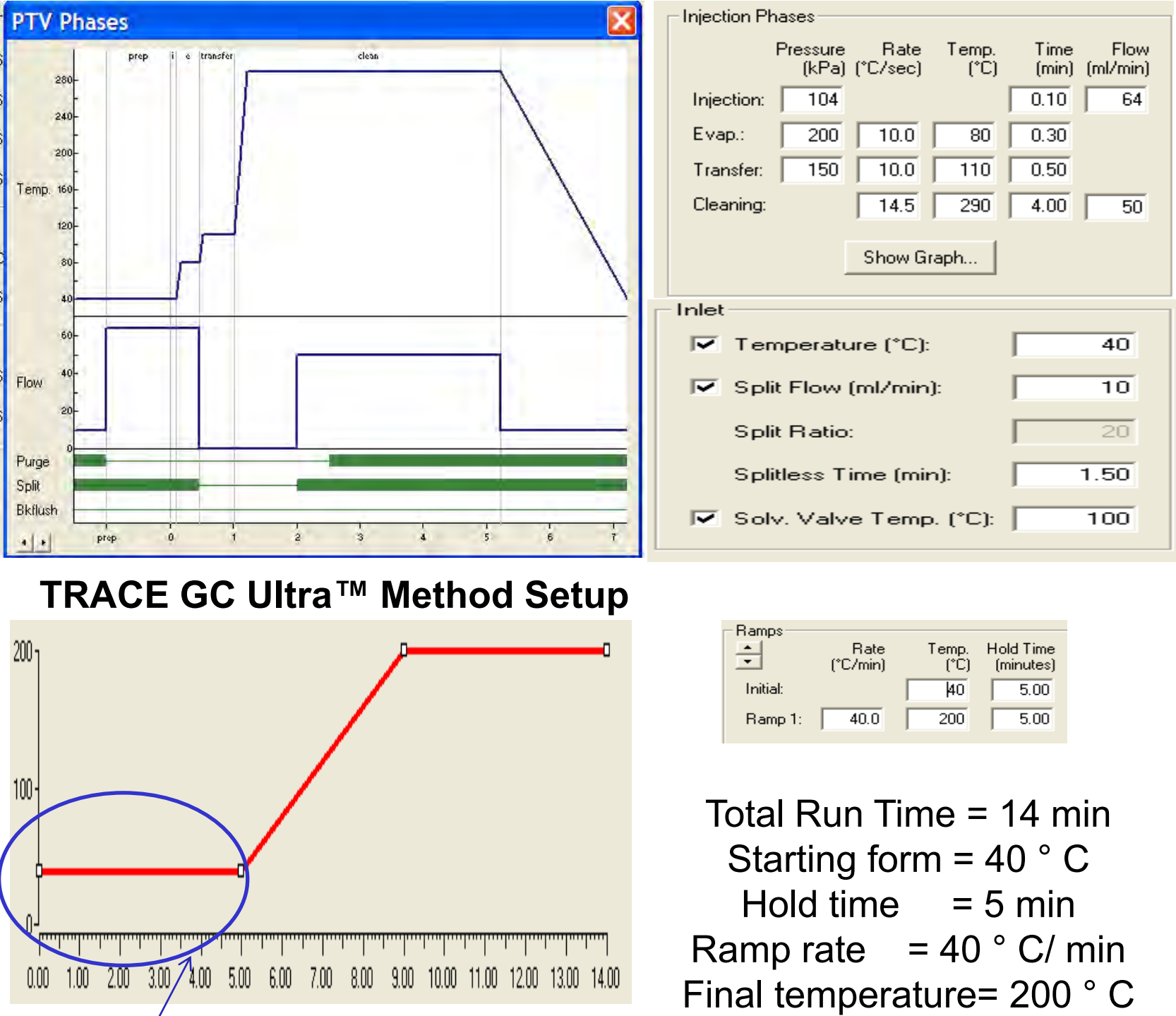


FIGURE 4. Instrument Setup for Dithiocarbamate Analysis

Column : Two GC columns of different polarity, stationary phase, and film thickness have been evaluated.

•6% cyanopropylphenyl/94% dimethyl polysiloxane, 30m x 0.32 mm ID, 1.8 µm film thickness e.g. Thermo Scientific™ TraceGOLD™ TG-624, p/n 26085-3390)

•5% diphenyl/95% dimethylpolysiloxane, 30 m x 0.25 mm ID, 0.25 µm film thickness, e.g. Thermo Scientific™ TraceGOLD™ TG-5MS p/n 26098-1420

ITQ-900 GCMS

Ion source temp :200°C (optimized for CS₂ S/N ratio)

Interface temp :205°C

Acquisition mode :EI

Scan mode, range SIM, m/z 76, 78

Acquisition rate 2 scans/s

Triplus RSH Auto sampler

Injection Volume :4 µL

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 0.005 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.

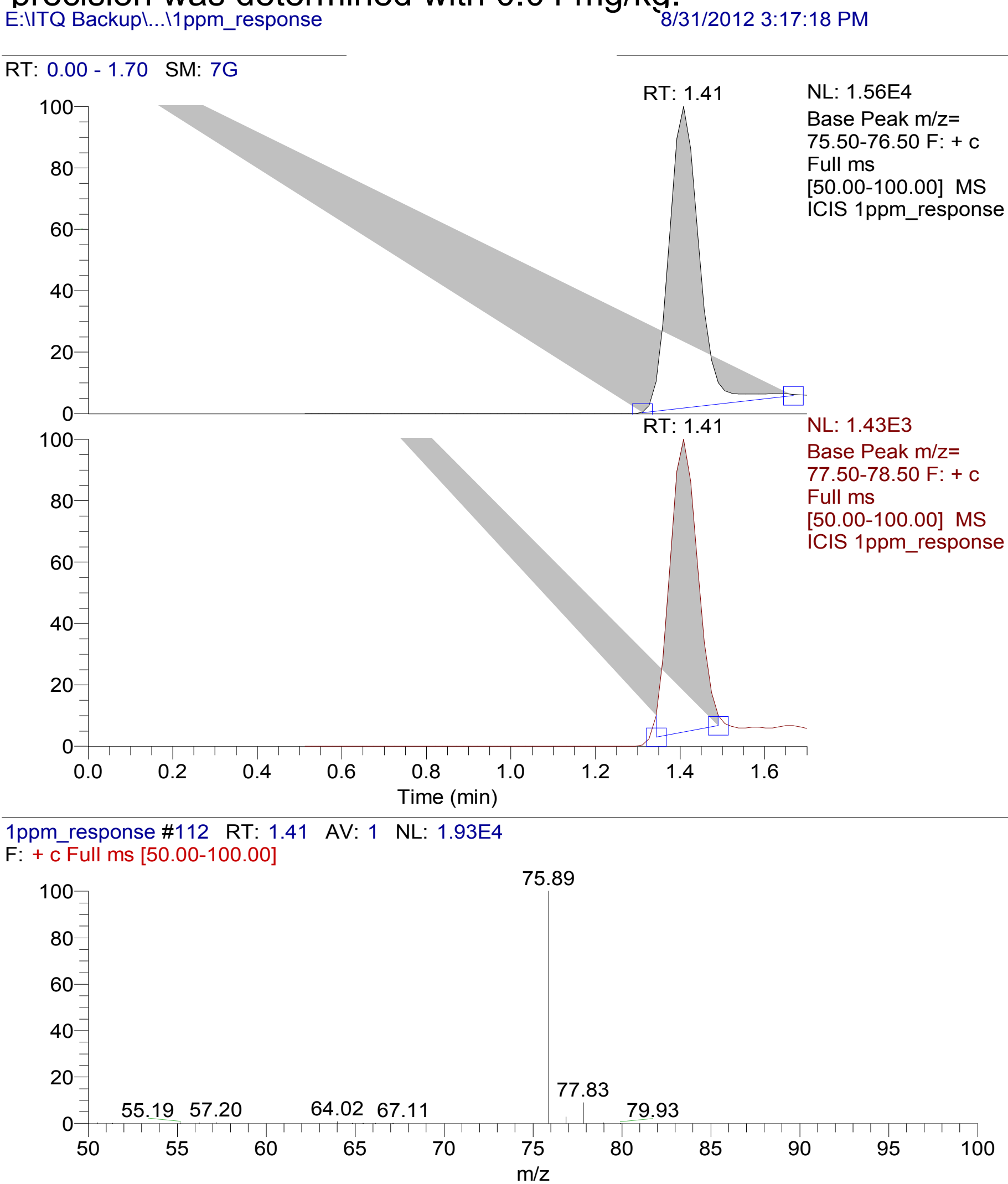
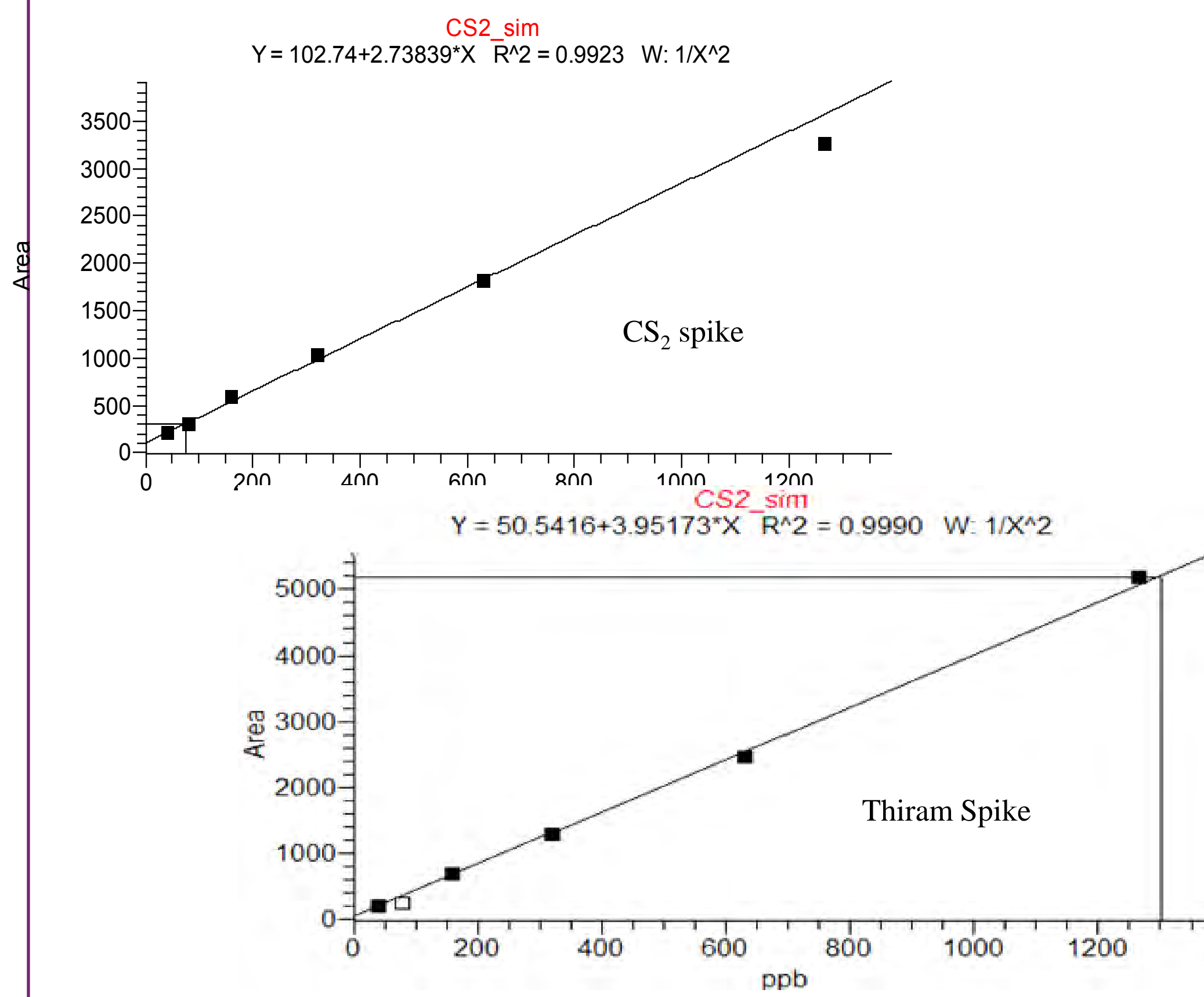


FIGURE 5. Full Scan Spectrum of 1 ppm CS₂



LOQ = 40 ppb

LOD = 10 ppb

FIGURE 6. Calibration Curve of CS₂ and Thiram Spike

Recovery

The recovery experiments were carried out on fresh untreated potato, tomato, eggplant, green chili, and grapes by fortifying 25 g of the samples with Thiram solution at 0.04, 0.16, and 1.30 µg/g levels in six replicates. The control samples of each of the tested commodities were obtained from an organic farm near Pune, India, and screened for absence of DTC residues before spiking. The spiked the samples were extracted using the sample preparation method described above. The quantitation of the residues was performed using matrix matched standards.

Table 1. Recoveries from different foods

Spike level in ppb	Grapes	Chilly	Potato	Egg plant	Tomato
1300	96 (±4)	81 (±10)	90 (±9)	90(±5)	81 (±4)
160	94 (±10)	80 (±13)	94 (±10)	92 (±8)	85 (±10)
40	104 (±15)	79 (±9)	104 (±15)	86 (±10)	96(±15)

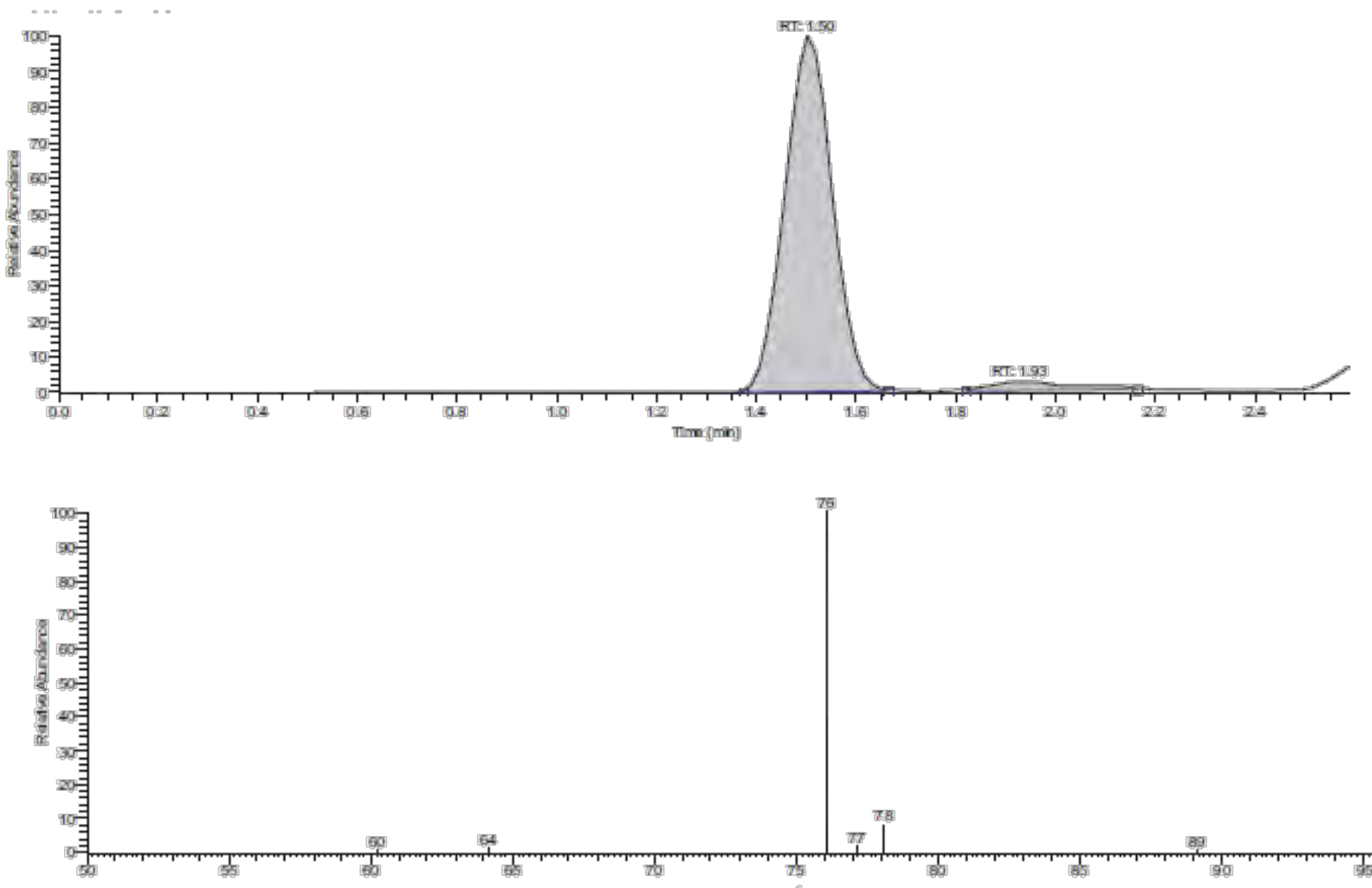


FIGURE 7. Chili sample analysis with confirming CS₂ ion ratio 100:10 for m/z 76:78

Conclusions

A reliable routine method for the analysis of dithiocarbamates with high precision in different vegetable and fruits has been developed. The method allows a wide calibration range of 0.04 – 1.300 µg/mL Thiram. The LOQ has been determined as 0.04 µg/mL. The extraction uses a SnCl₂/HCl acid-hydrolysis with isooctane as solvent to form CS₂ which finally gets quantified by GC-MS. The recovery from different food commodities has been shown to be very high with 79 to 104%.

This method has been developed initially for the ITQ ion trap mass spectrometer, but the same parameter setup is suitable for the Thermo Scientific™ ISQ™ series single quadrupole or Thermo Scientific™ TSQ™ Quantum XLS Ultra or Thermo Scientific™ TSQ 8000™ triple quadrupole mass spectrometers, as well.

References

- Crnogorac, G., Schwack, W., Residue analysis of dithiocarbamate fungicides, Trends in Analytical Chemistry, Vol. 28, No. 1, 2009.

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