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Thermogravimetric and FT-IR Analysis of Sulfur Fungicide Products

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Thermogravimetric and FT-IR Analysis of Sulfur Fungicide Products

Introduction

Elemental sulfur is a widely used fungicide product in agriculture. This material is typically sold as a fine powder. Thermogravimetric analysis (TGA) of these products indicates a small percentage (<1.5%) of mass loss during the standard method used by California Department of Pesticide Regulation to determine pesticide volatile emission potential. The TGA test method does not, however, provide information regarding the nature of chemicals lost during heating of the material. This project was designed to determine the identity of volatile chemicals lost during the TGA test of selected sulfur fungicide products by coupling the TGA equipment with a Fourier-Transform Infrared Spectrometer (FTIR). Gases released from the TGA oven were transferred to the FTIR using a heated transfer line. Six fungicide samples were obtained from three companies in California with the assistance of CA DPR.

Methods

TGA Analysis Method

Sulfur fungicide samples were analyzed by TGA following the method defined by the CA Department of Pesticide Regulation Method *:*

> *"Estimation of Volatile Emission Potential of Pesticides by Thermogravimetry"*
> *Method Date: 02/09/2005*

Briefly, using a TA Instruments (New Castle, DE) model Q5000IR thermogravimetric analyzer, platinum weighing pans were conditioned at 125°C for 1 hour and stored in a desiccator prior to their use. Samples (kept in their sealed containers) were equilibrated to room temperature in a desiccator over a drying agent for at least 3 days prior to their testing.

After taring the platinum weighing pan, approximately 10 mg of the pesticide was weighed out and measured by the TGA. The TGA program started at 35°C climbed to 115°C at 5°C/min and held isothermal for a total of 25 minutes (this was sufficient to meet stability criteria listed in CADPR method for all tested fungicides). Pesticide stability at 115°C was previously established.

A heated transfer line (250 ^{o}C) was attached to the outflow from the TGA furnace to transport gases to the FTIR gas cell.

FTIR Analysis Method

Gases emitted from the TGA oven were analyzed using a Nicolet 6700 FTIR. Spectra were collected compared to a background at a similar temperature containing no sample. Spectral range was 4000 cm^{-1} to 400 cm^{-1} and spectral resolution was 1 cm^{-1}. Instrument settings were the same for all samples and are listed on Figures 2-7.

Results

Six sulfur fungicide products were tested using TGA-FT-IR. Results of the TGA tests fell within approximately 0.5% of those values listed in the CA DPR emission potential

database where actual TGA data was submitted (Table 1). Overall the % mass loss ranged from 0.85% for CSC Dusting Sulfur and 1.18%for COCS 15 Sulfur 25 Dust (Figure 1). The major component observed in the FT-IR spectrum for each of these products was water (Figure 2-7). The sharp peaks from 4000 cm^{-1} to 3500 cm^{-1} and from 2000 cm^{-1} to 1300 cm^{-1} are characteristic of H_2O vapor, and the broader peak at 2350 cm^{-1} is from a much smaller amount of CO_2 vapor present. Both H_2O and CO_2 peaks are also present [at lower concentrations] in virtually every background IR spectrum, i.e. of air. Results from this work indicate that no readily detectable volatile organic compounds are released during the application of these particular products and that most of the weight loss from these samples is due to moisture loss. Variations in the TGA values among the different chemicals are probably related to how dry the product material is prior to analysis and will also depend on the physical properties of the samples, e.g. particle size and surface properties. These differences detected are within the precision and accuracy of the method. Other sulfur fungicide products with additional inert or active ingredients will require additional testing to determine VOC emission potential values.

Table 1. Results for sulfur fungicide products tested by TGA-FT-IR.

Product	**EPA Reg. No.**	**CADPR EP**	**% Mass Loss This Study***	**Major Volatile Component**
CSC Dusting Sulfur	55429-3-AA	0.32‡	0.85	Water
Yellow Jacket Special Dusting Sulfur	6325-17-AA	0.6†	0.95	Water
COCS 15 Sulfur 25 Dust	34704-393-ZA	1.53§	1.18	Water
Wilbur-Ellis Dusting Sulfur	2935-48-ZA	0.6‡	0.94	Water
Dusting Sulfur Fungicide	34704-724-ZA	0.6†	1.09	Water
Special Electric Dusting Sulfur	2935- 503-AA	0.47‡	0.96	Water

* Calculated 15 minutes beyond initial 5 min rate stabilization as per CADPR Method (total time of isothermal at 115 ºC = 20 min)
† Special Default value
‡ TGA analysis
§ Formulation Class Default

Figure 1. Combined % mass loss trace for sulfur fungicide products and TGA temperature program.

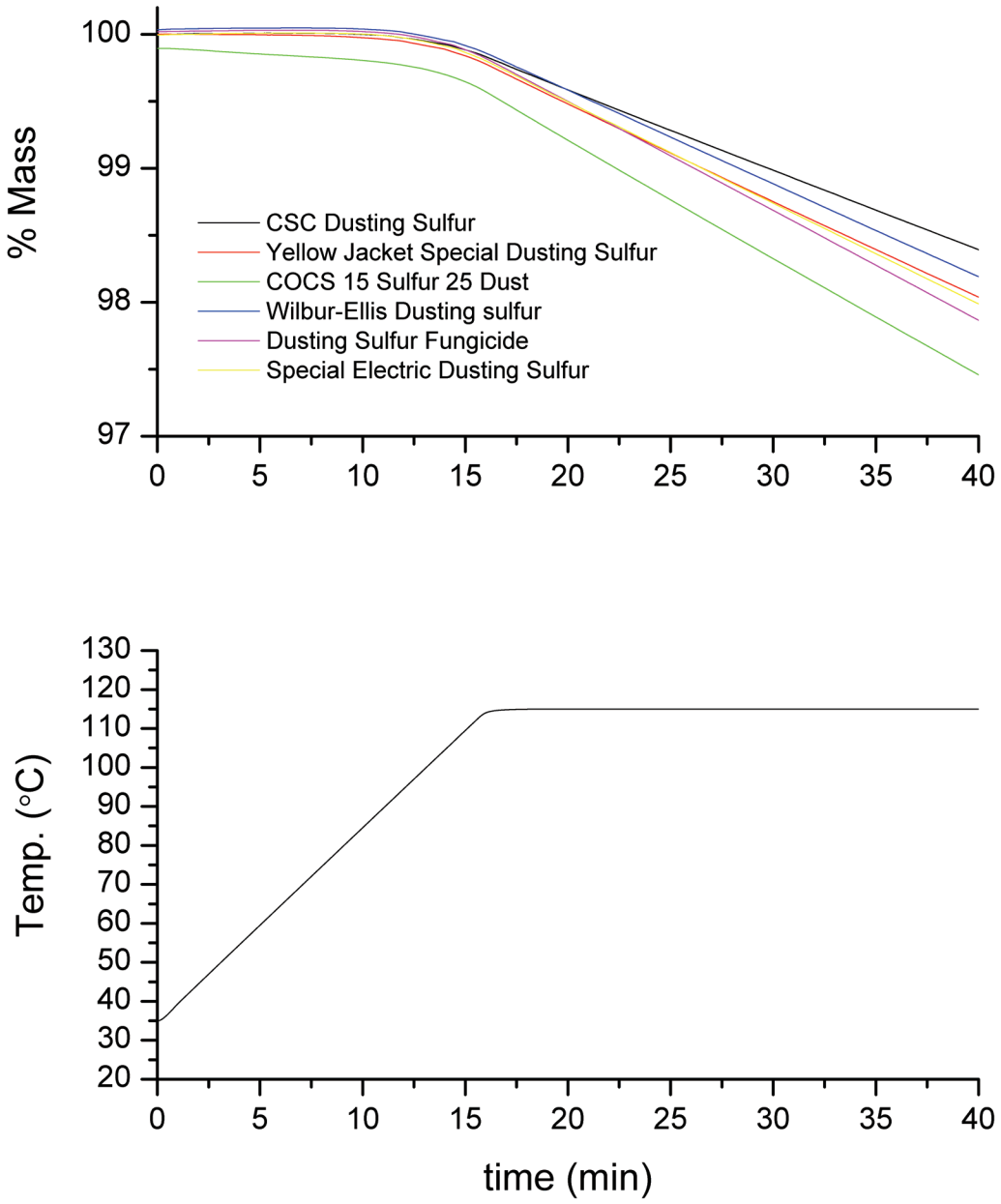


Figure 2. FTIR spectra of CSC Dusting Sulfur

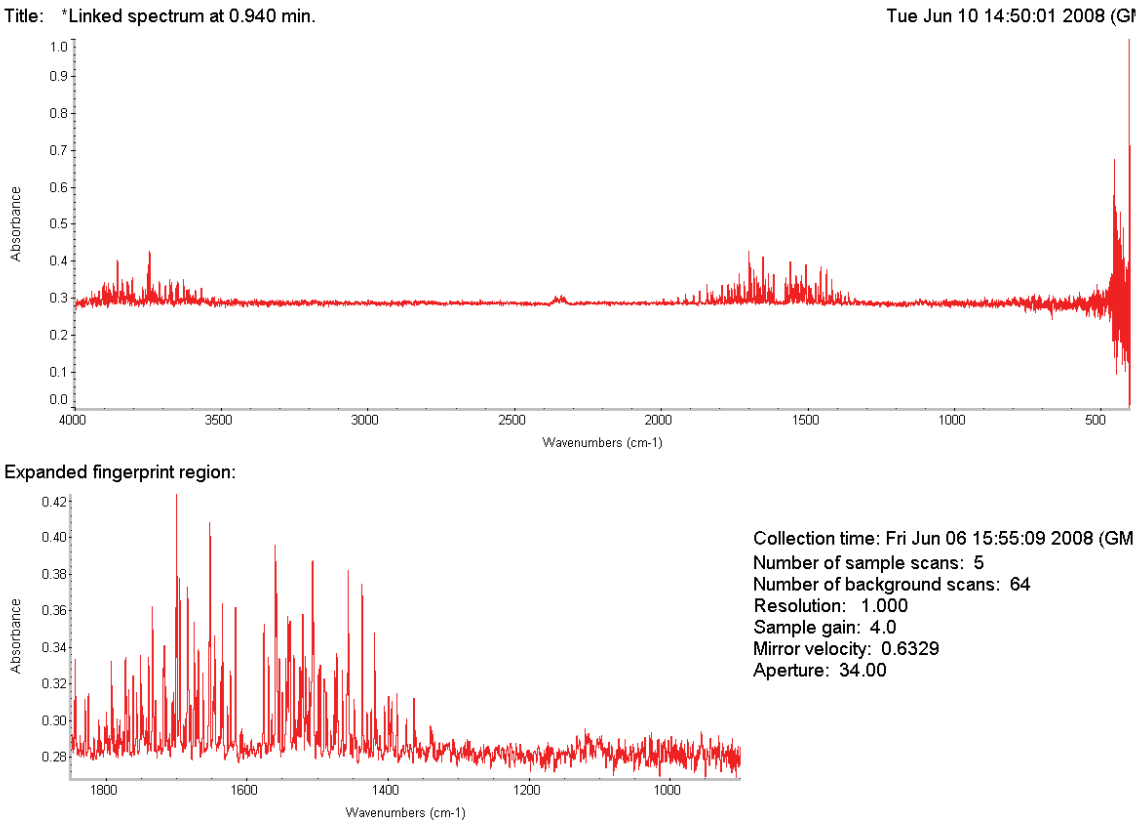


Figure 3. Yellow Jacket Special Dusting Sulfur

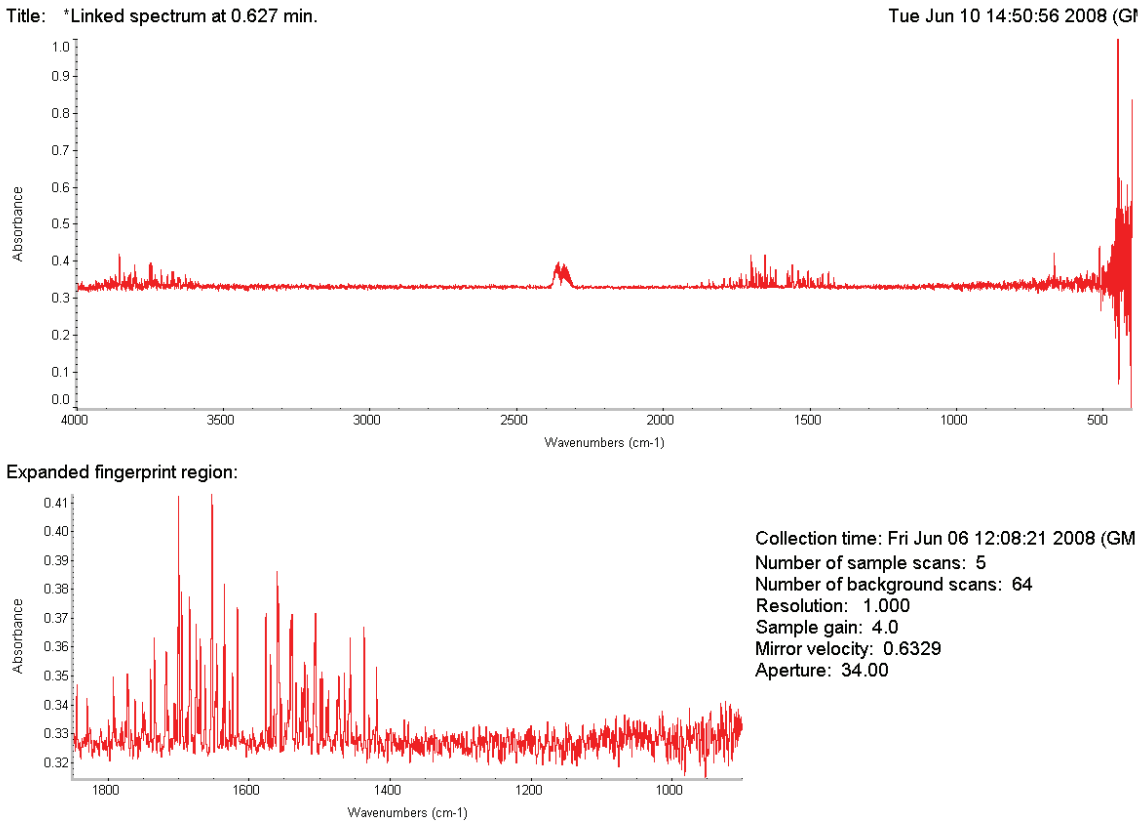


Figure 4. COCS 15 Sulfur 25 Dust

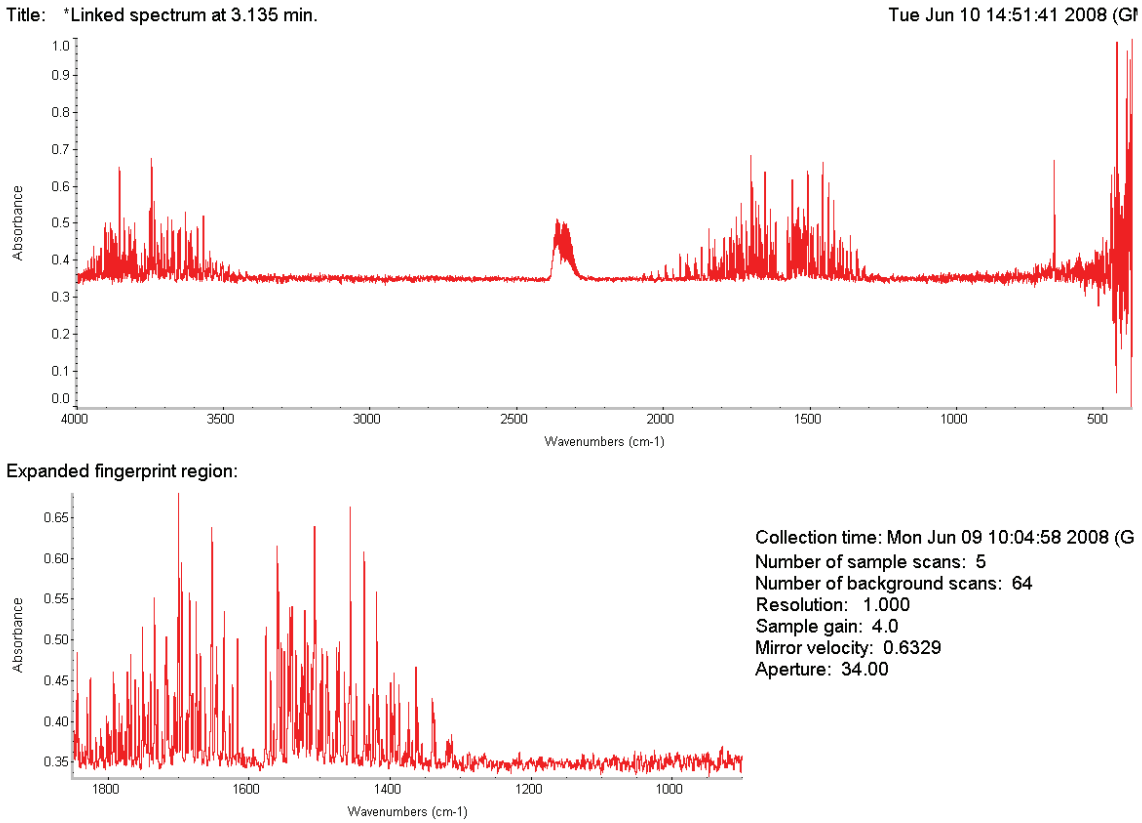


Figure 5. Wilbur-Ellis Dusting Sulfur

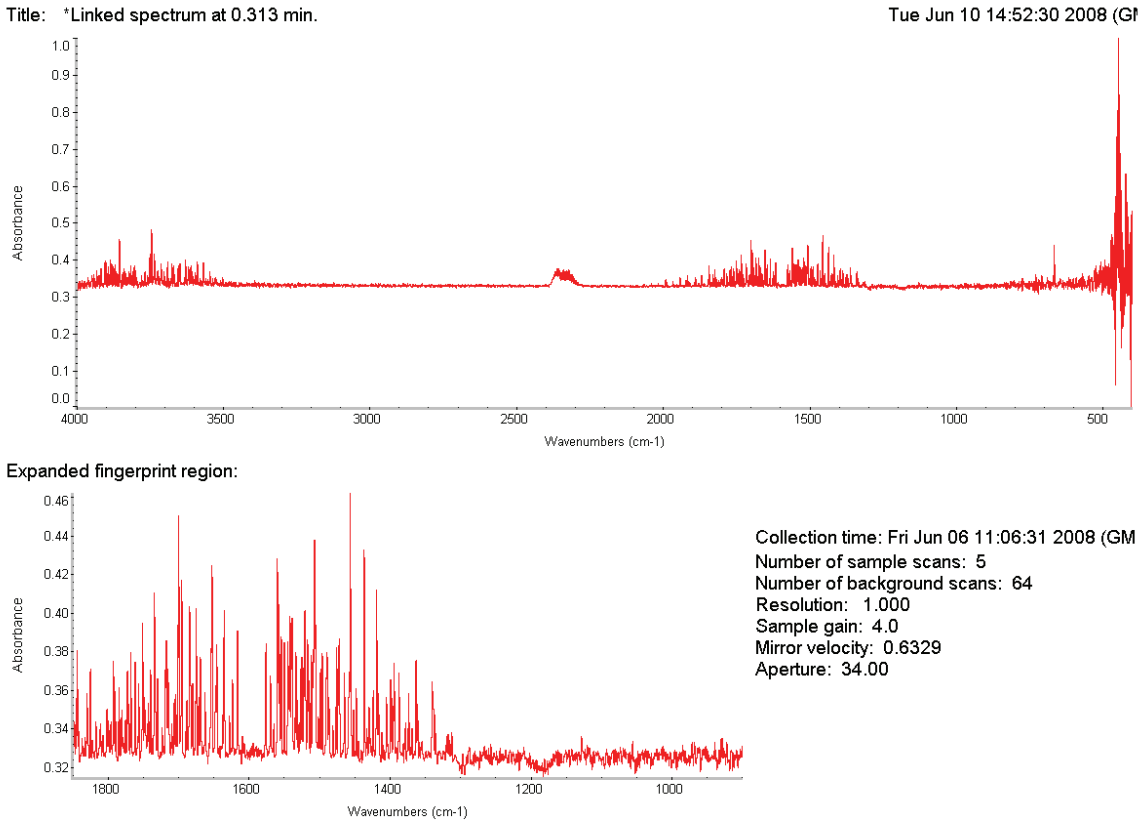


Figure 6. Dusting sulfur Fungicide:

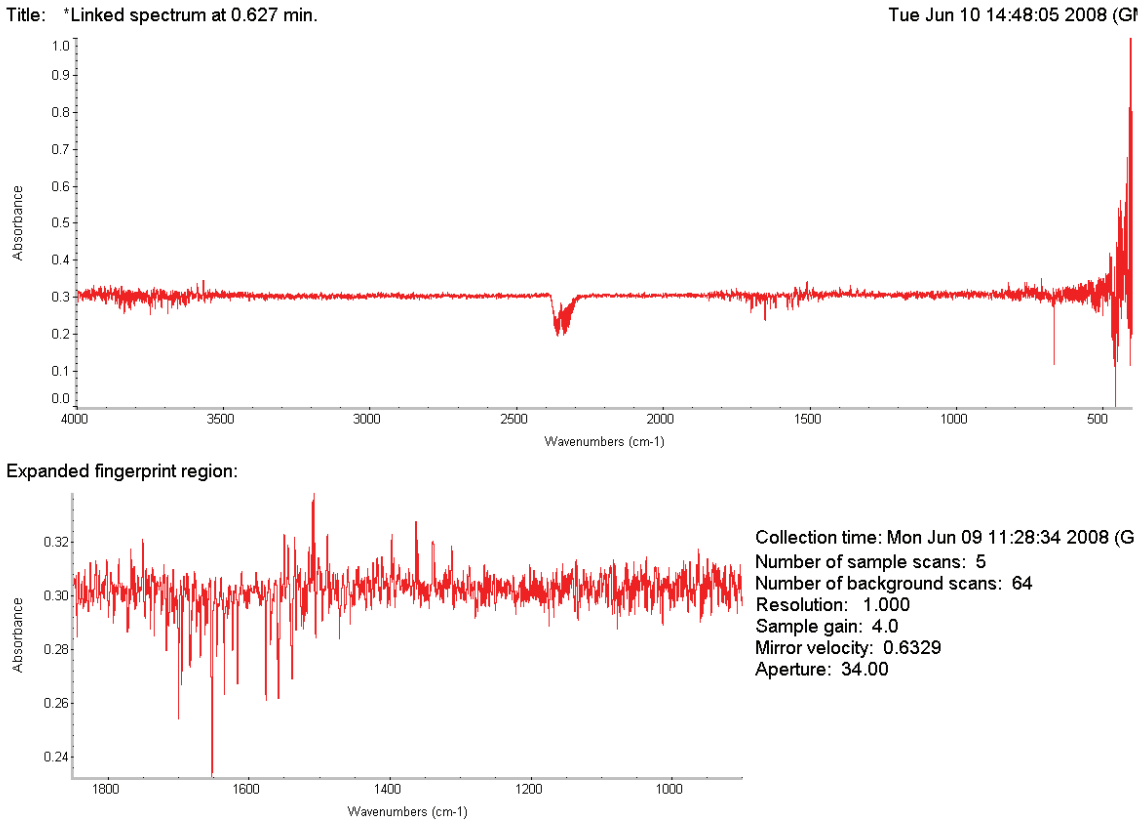
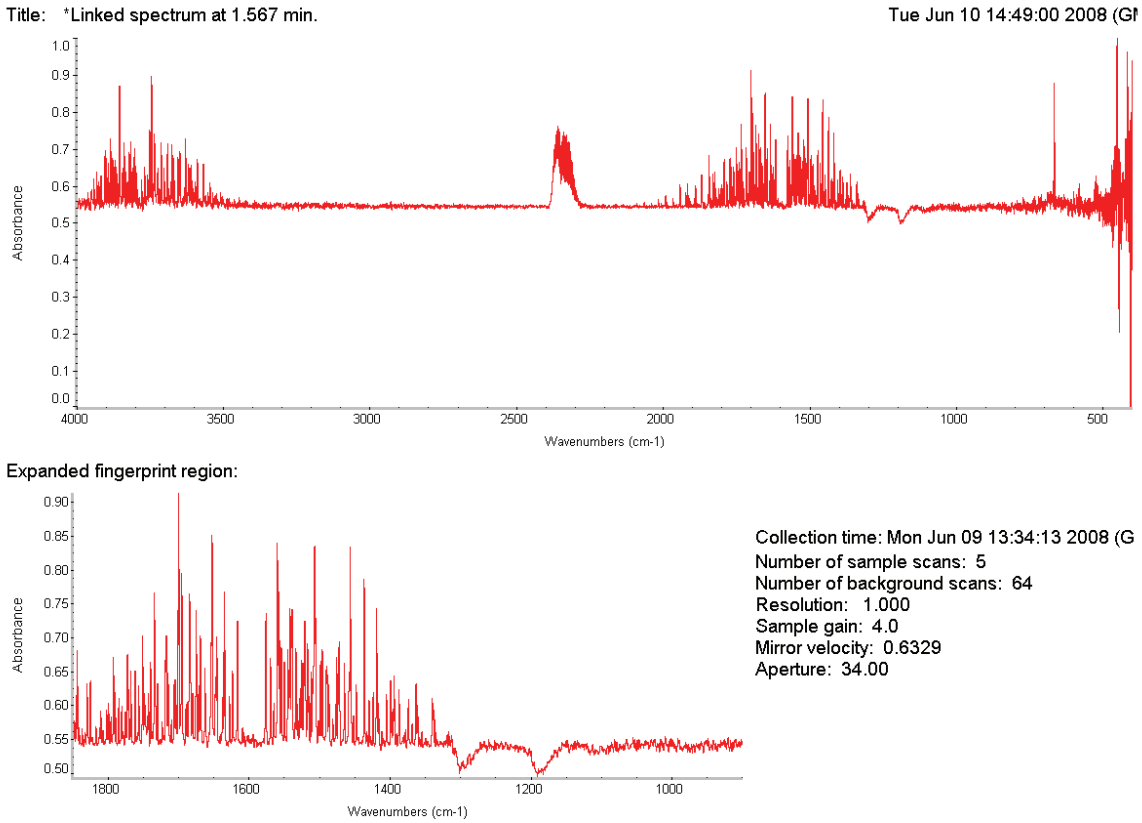


Figure 7. Special Electric Dusting Sulfur



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