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Supporting Information

Sulfur-Limonene Polysulfide: A Material Synthesized Entirely from Industrial By-Products and Its Use in Removing Toxic Metals from Water and Soil

*Michael P. Crockett, Austin M. Evans, Max J. H. Worthington, Inês S. Albuquerque, Ashley D. Slattery, Christopher T. Gibson, Jonathan A. Campbell, David A. Lewis, Gonçalo J. L. Bernardes, and Justin M. Chalker**

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General experimental considerations

Proton nuclear magnetic resonance (^{1}H NMR) and proton-decoupled carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a 400 or 600 MHz spectrometer, as indicated. ^{1}H and ^{13}C NMR Spectra were assigned as fully as possible using COSY, HSQC, and DEPT-135 experiments. All chemical shifts are quoted on the δ scale in ppm using residual solvent as the internal standard (^{1}H NMR: $CDCl_3$ $\delta = 7.26$; ^{13}C NMR: $CDCl_3$ $\delta = 77.0$).

Infrared (IR) spectra were recorded on a Fourier Transform spectrophotometer using thin films on NaCl plates. Absorption maxima (υ_{max}) are reported in wavenumbers (cm^{-1}).

Raman spectra were acquired using a Witec alpha300R Raman microscope at an excitation laser wavelength of 532 nm with a 40X objective (numerical aperture 0.60). Typical integration times for the Raman spectra were between 10-20 s for 2-3 accumulations.

Gas chromatography-mass spectrometry (GC-MS) was carried out on a Varian CP-3800 using a Phenomonex Zebron ZB5MS, 5 %-phenyl-Arylene-95 %-dimethylpolysiloxane column (30 m long × 25 mm film thickness × 0.25 mm ID). The injection temperature was set at 220 ºC, the column temperature at 190 ºC, and the gas flow rate 1.2 mL/min. Electron ionization was used to obtained nominal masses.

High resolution mass spectra (HRMS) were recorded on an electrospray ionization mass spectrometer with atmospheric pressure chemical ionization (APCI) capability and an orbitrap mass analyzer. Accurate mass (m/z) values are reported in Daltons.

Simultaneous Thermal Analysis (STA) was carried out on a Perkin Elmer STA8000 simultaneous thermal analyzer (STA). A sample size between 11 and 15 mg was used in each run. The furnace was purged at 20 mL/min with either nitrogen or air, as indicated, and equilibrated for 1 minute at 30 ºC before each run. Heating was carried out up to 700 ºC using either 5 ºC/min or 20 ºC/min heating rates, as indicated. The temperature was held isothermally at 700 ºC at the end of each experiment to oxidize remaining organic matter.

Differential Scanning Calorimetry (DSC) was carried out using a TA Instruments 2930 DSC with nitrogen furnace purge at 50ml/min. Samples were approximately 6 mg and sealed in aluminium hermetic pans. The sample was cooled to -100 ºC at 10 ºC/min, held for 5 minutes, and then heated to 150 ºC at 10 ºC/min.

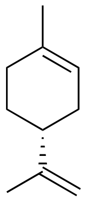
Thin layer chromatography (TLC) was carried out using aluminum backed 200 μm silica plates impregnated with a UV_{254} fluorophore. Visualization of the silica plates was achieved using a UV lamp (λ_{max} = 254 nm), and/or ammonium molybdate (5% in 2M H_2SO_4), and/or potassium permanganate (5% $KMnO_4$ in 1M NaOH with 5% potassium carbonate). All solvents and reagents were used as received from commercial suppliers.

Scanning Electron Microscopy (SEM) images were obtained using an FEI F50 Inspect system, while corresponding EDX spectra were obtained using an EDAX Octane Pro detector.

Size exclusion chromatography (SEC) analysis was carried out by Polymer Solutions Incorporated (Blacksburgh, VA), an ISO-17025 accredited laboratory. A solution of the sample was prepared in THF and filtered into an autosampler vial through a 0.45 μm syringe filter. The sample was then analyzed by size exclusion chromatography using an Agilent Polypore column (300 × 7.5 mm), eluting with THF at a flow rate of 0.8 mL / min. Fractions were detection using a Wyatt Optilab T-rEX refractive index detector. Molar mass averages were calculated relative to polystyrene standards ranging from 162 g/mol to 3,242,000 g/mol.

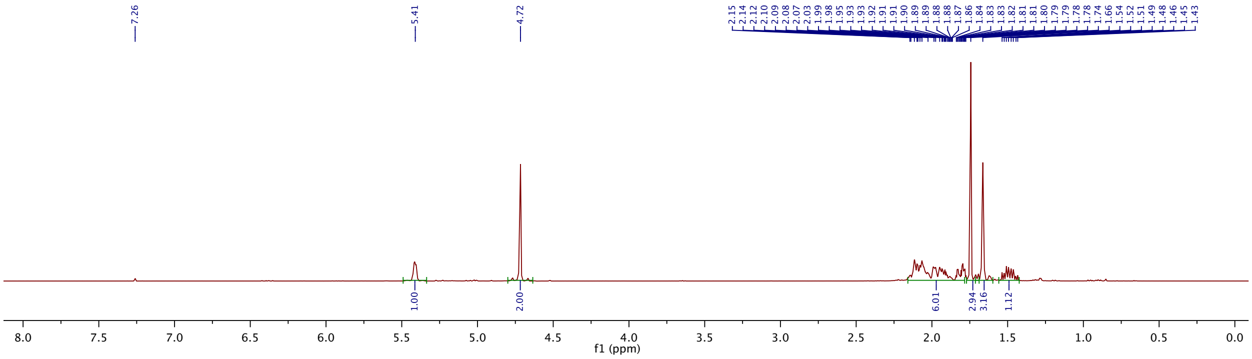
Elemental (combustible) analysis was carried out in duplicate by Micro-Analysis, Inc. (Wilmington, DE). Carbon, hydrogen, nitrogen content (%CHN) was determined by combustible analysis using a thermal conductivity detector. Sulfur (%S) content was determined by combustion ion chromatography.

Cold vapor atomic absorption (CVAA) was used to determine mercury concentration in aqueous samples. CVAA analysis was obtained through Micro-Analysis, Inc. using a Leeman Hydra II Mercury Analyzer with Alfa Aesar Specpure calibration standards.

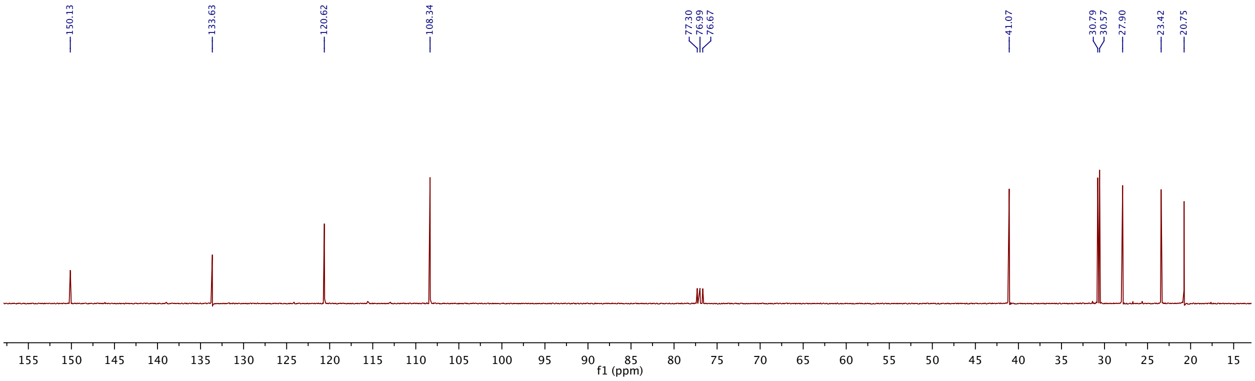


(*R*)-(+)-Limonene
(D-Limonene)

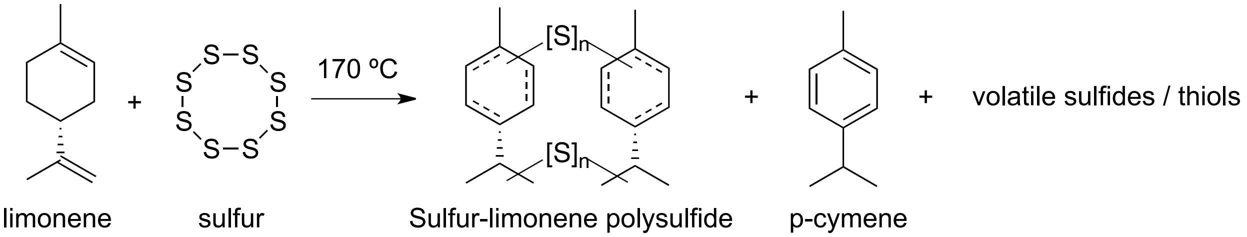
^{1}H NMR for industrial grade D-limonene (400 MHz, $CDCl_3$)



^{13}C NMR for industrial grade D-limonene (100 MHz, $CDCl_3$)

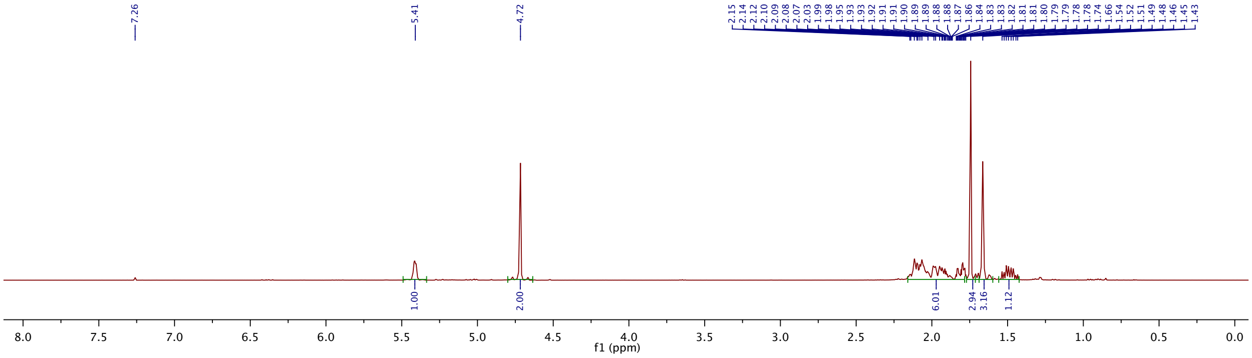


^{1}H NMR analysis of reaction between sulfur and limonene – 100-gram synthesis

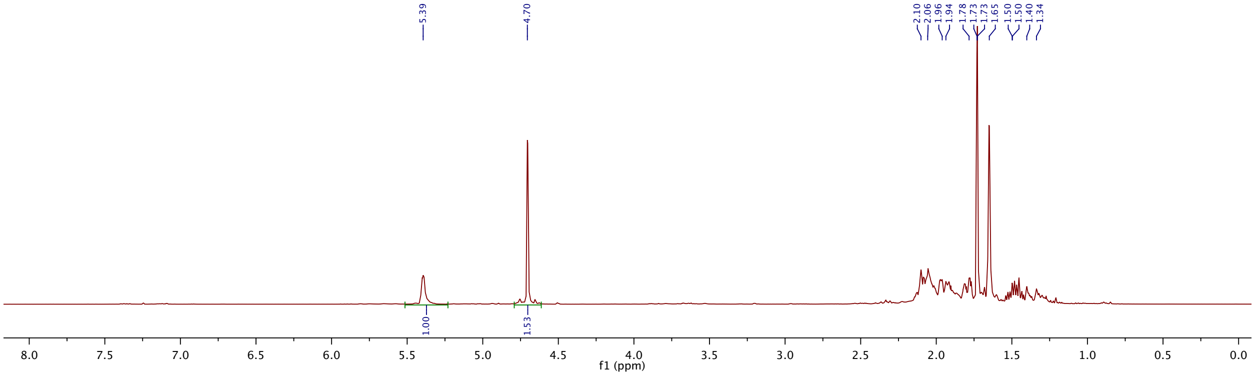


Sulfur (50.0 g, 195 mmol S_8) was added to a 250 mL beaker equipped with a stir bar. The flask was placed in an oil bath pre-heated to 170 ºC and stirred vigorously. The sulfur was observed to melt and change from a yellow liquid to a dark orange liquid over a period of approximately 10 minutes. After this time, limonene (50.0 g, 372 mmol) was added in 5 portions by syringe over a period of approximately 5 minutes. The resulting two-phase mixture was stirred vigorously for 25 minutes, at which time the reaction had merged to one phase. An aliquot (~ 1 g) of the reaction mixture was sampled carefully with a glass vial. Additional samples were collected each hour over the next 5 hours. After each sample cooled, a portion was dissolved in $CDCl_3$ and analyzed by ^{1}H NMR spectroscopy. A time course for the reaction is shown below:

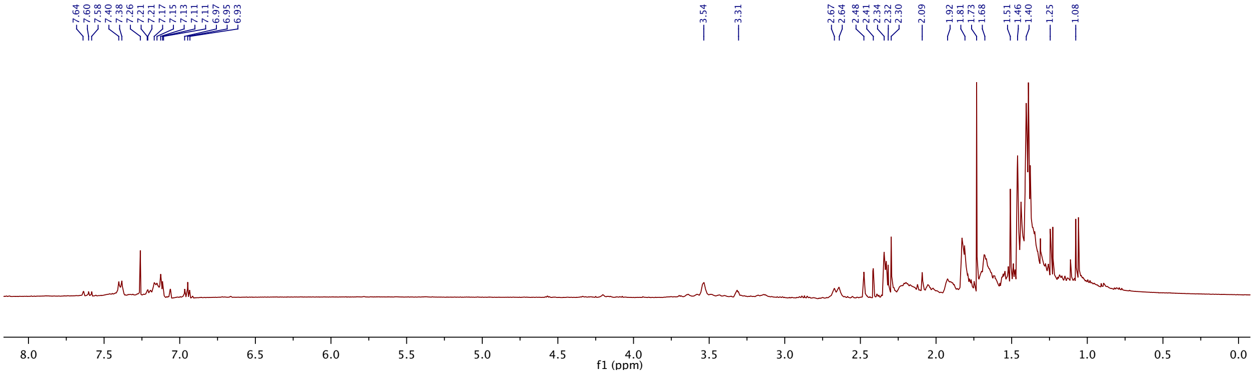
t = 0 (400 MHz, $CDCl_3$)



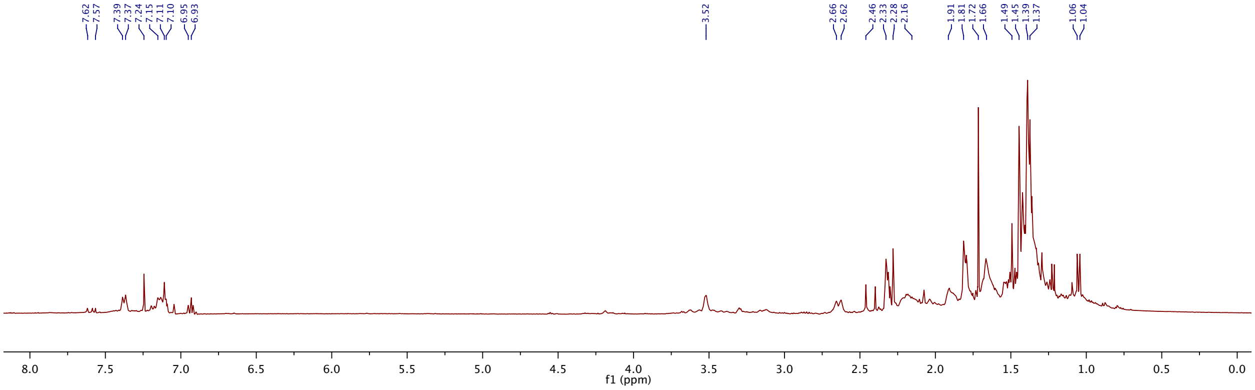
t = 30 minutes (reaction becomes one phase, consumption of alkenes in limonene initiated)



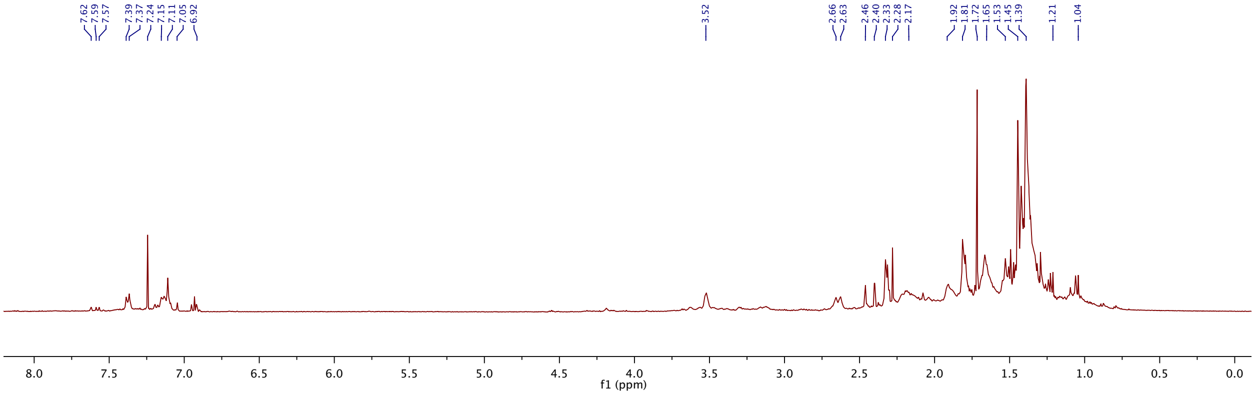
t = 1.5 hours (all limonene consumed – no alkene peaks)



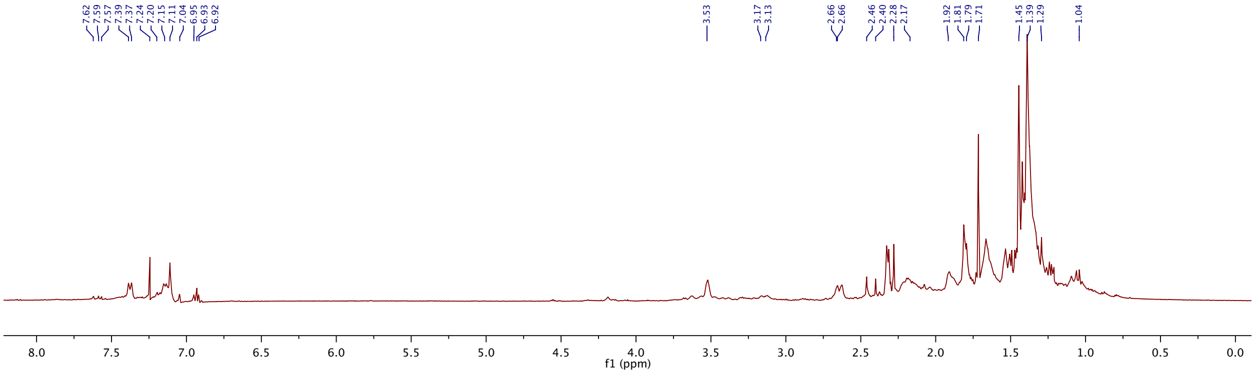
t = 2.5 hours



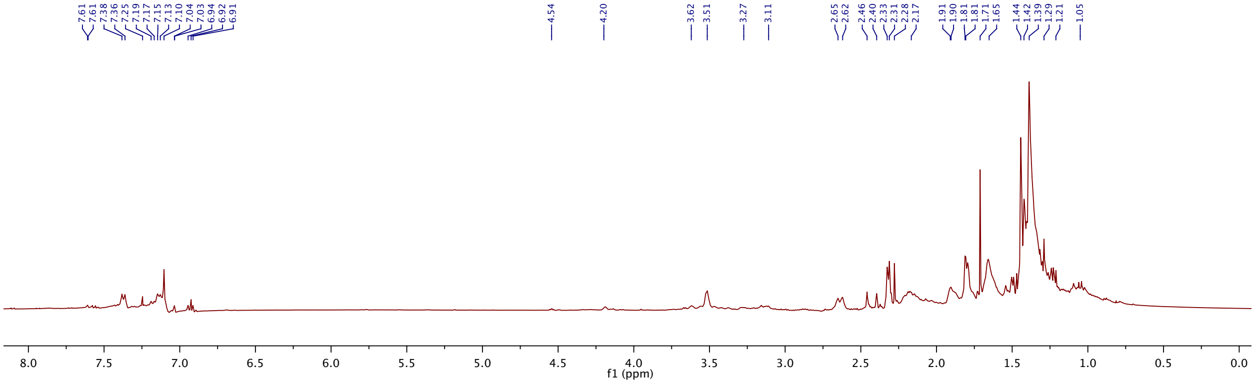
t = 3.5 hours



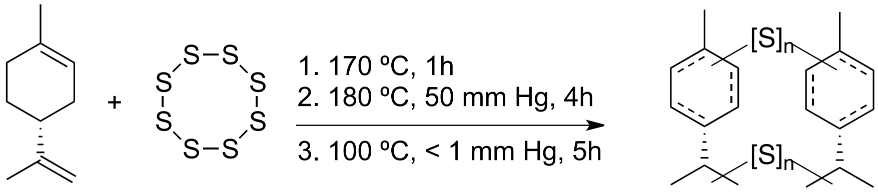
t = 4.5 hours



t = 5.5 hours

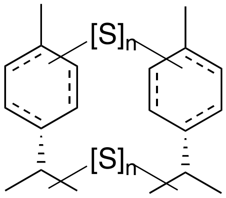


Protocol for 50-gram synthesis of sulfur-limonene polysulfide and removal of volatile byproducts by distillation



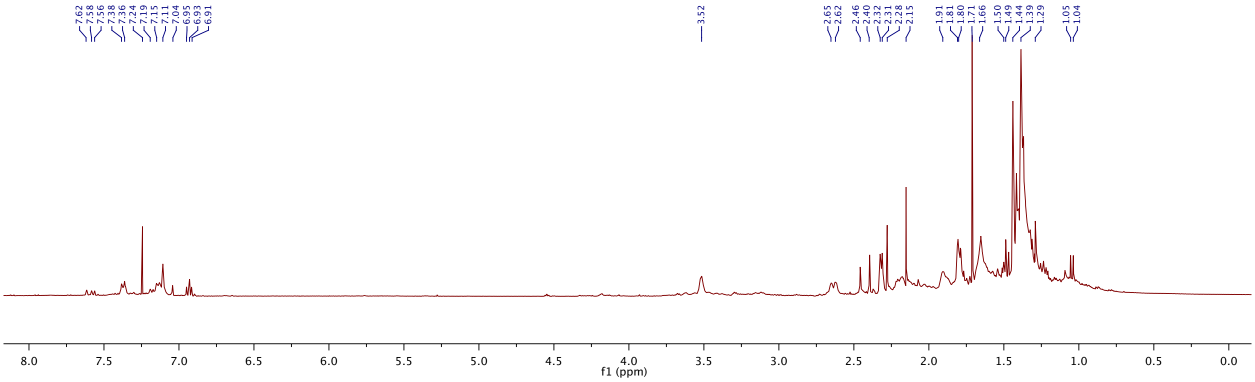
Sulfur-limonene polysulfide, 80% yield

Sulfur (25.0 g, 97.5 mmol S_8) was added to a 100 mL round bottom flask equipped with a stir bar. The flask was then placed in an oil bath pre-heated to 170 ºC and stirred vigorously. The sulfur was observed to melt and change from a yellow liquid to a dark orange liquid over a period of approximately 30 minutes. After this time, limonene (25.0 g, 29.6 mL, 183 mmol) was added to the stirred sulfur over a period of 2 to 5 minutes. After the addition was complete, the flask was equipped with a simple distillation head and condenser. The reaction mixture first appears as two phases with limonene forming the top layer and the sulfur material forming the bottom layer. As the sulfur and limonene react, the mixture gradually forms one phase that appears dark red in color. One phase is typically formed after 30 minutes of vigorous stirring at this scale. After one phase has formed, the reaction was stirred for an additional hour at 170 ºC. After this time, the reaction temperature was increased 180 ºC and volatile material was removed by vacuum distillation (50 mm Hg). The distillate was collected over a period of 4 hours to provide a yellow mixture of *p*-cymene and low molecular weight sulfides. The non-volatile material remaining in the flask was then cooled and dried further under high vacuum (< 1 mm Hg) at 100 ºC for 5 hours. After cooling to room temperature, the final product vitrified and was obtained as a dark red material (39.9 g, 80% yield). ^{1}H, ^{13}C, and HSQC NMR data shown below indicate an aromatic component to the sulfur-limonene backbone. A generic structure of the polysulfide is proposed below that accounts for this feature:

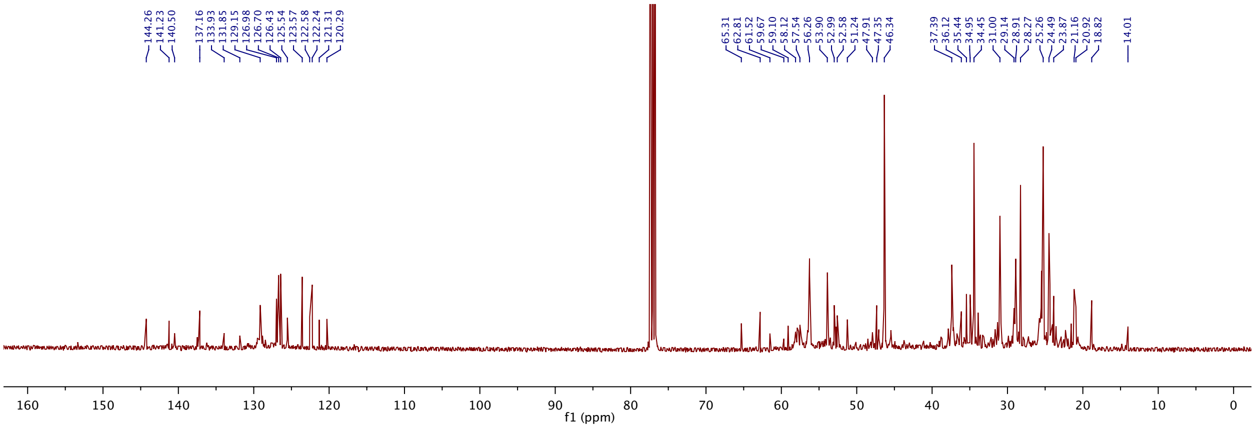


Sulfur-limonene polysulfide

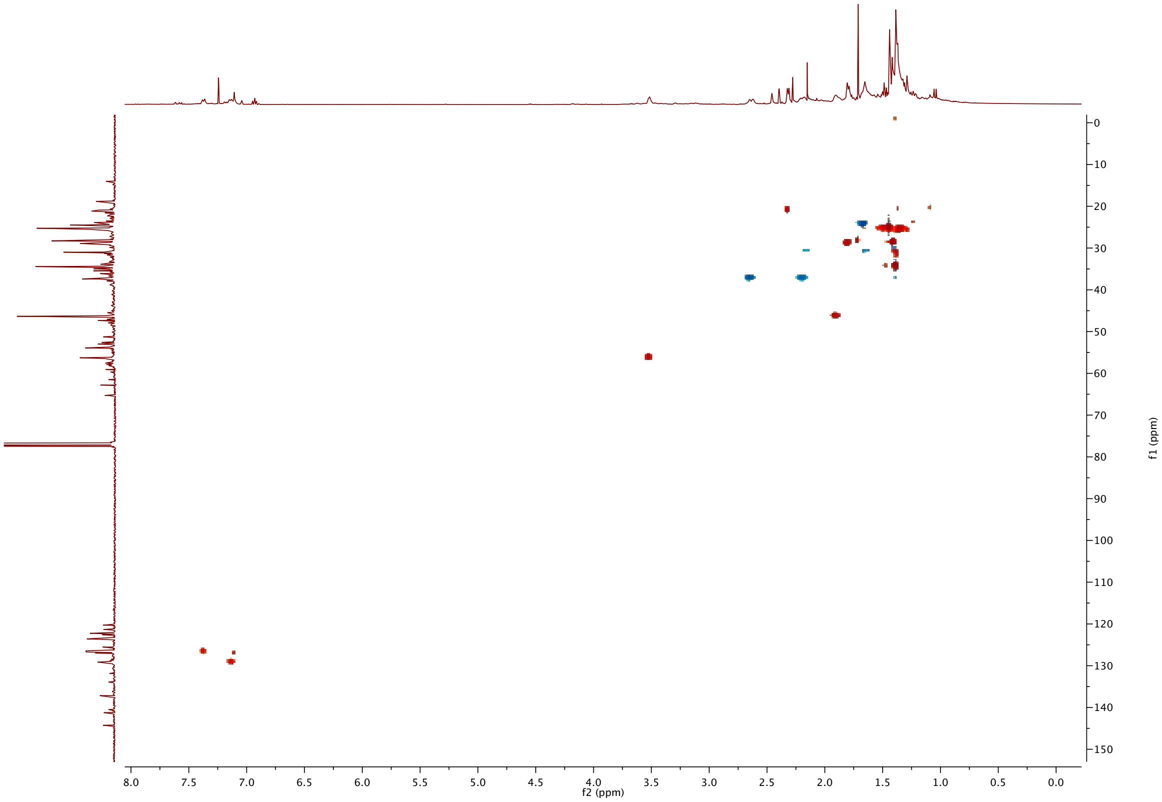
^{1}H NMR for final polysulfide (400 MHz, $CDCl_3$)



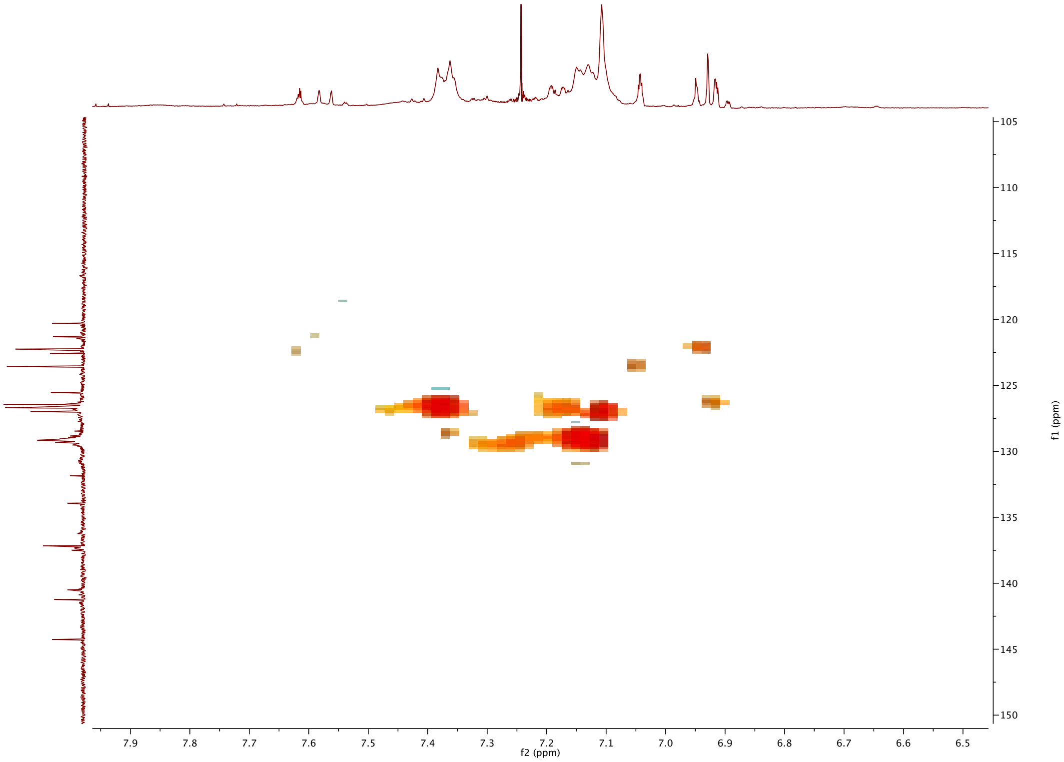
^{13}C NMR for final polysulfide (100 MHz, $CDCl_3$)



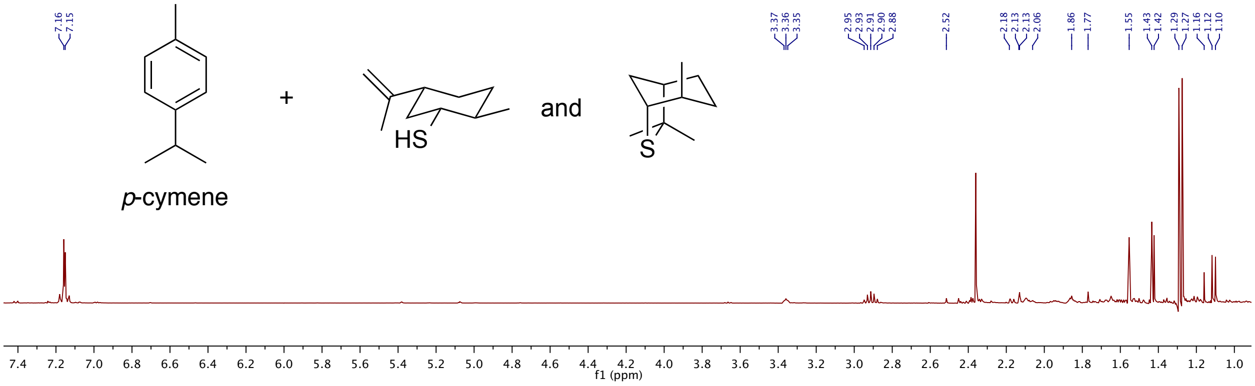
HSQC spectrum for final polysulfide
(Phase editing: blue crosspeak = CH_2; red crosspeak = CH/CH_3)



HSQC spectrum for final polysulfide (aromatic region):

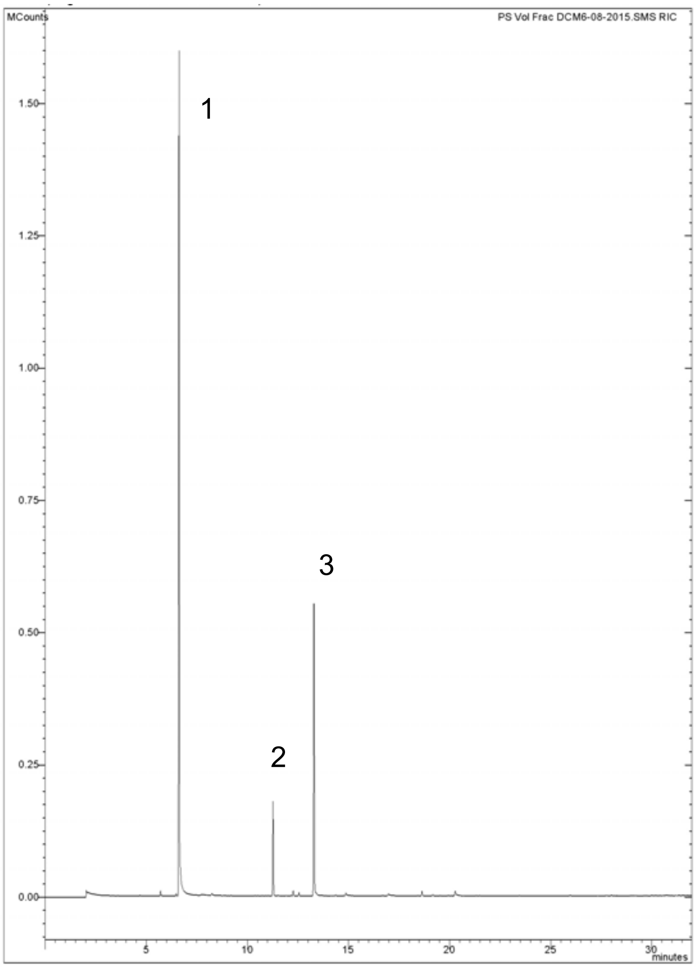


^{1}**H NMR of volatile byproducts** obtained during distillation. Chemical shifts are consistent with that reported in the literature[1] and GC-MS analysis (see next)

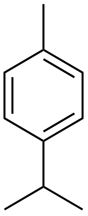


GC-MS analysis of volatile byproducts

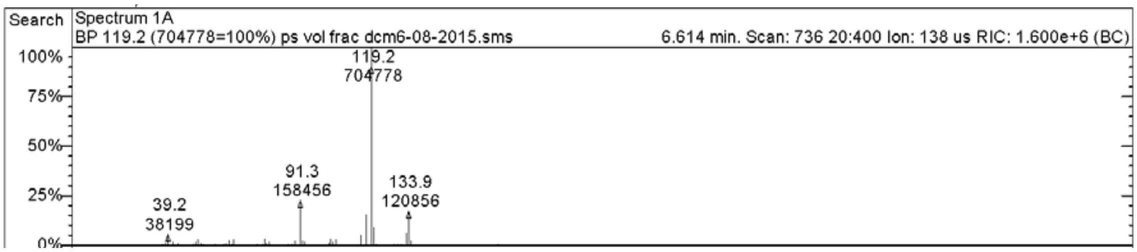
The volatile fraction obtained after the polysulfide synthesis was analyzed by GC-MS using a temperature gradient of 60 ºC to 220 ºC. The chromatogram is shown below. Three major peaks were observed.



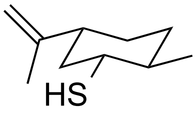
Peak 1 (6.61 min) corresponds to *p*-cymene: m/z = 133.9 $[M]^{\bullet+}$



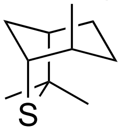
p-cymene calculated m/z = 134.2 for $[M]^{\bullet+}$



Peaks 2 and 3 contain the following thiol and sulfide

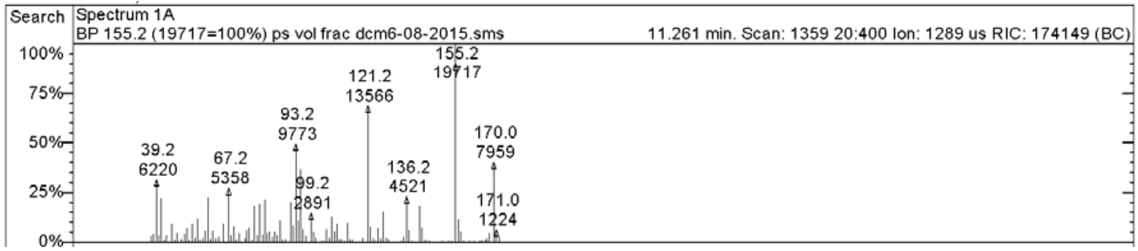


and

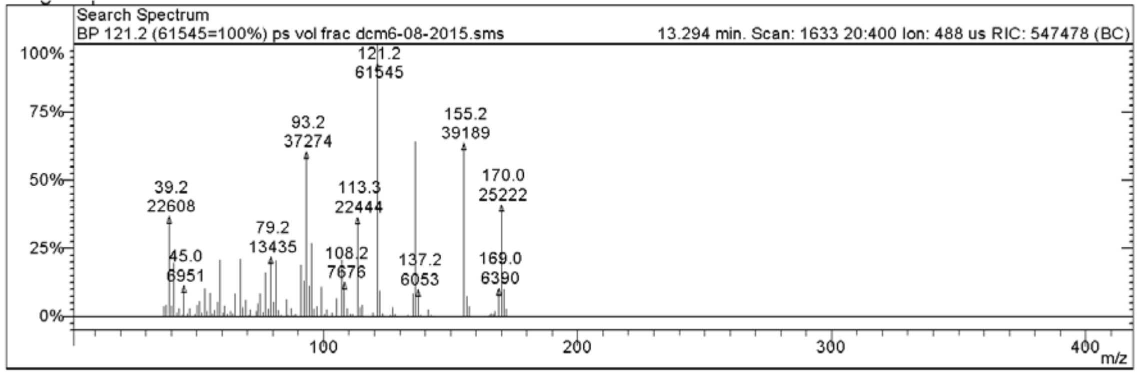


calculated m/z = 170.3 for $[M]^{\bullet+}$

Peak 2 (11.26 min): m/z = 170.0 $[M]^{\bullet+}$

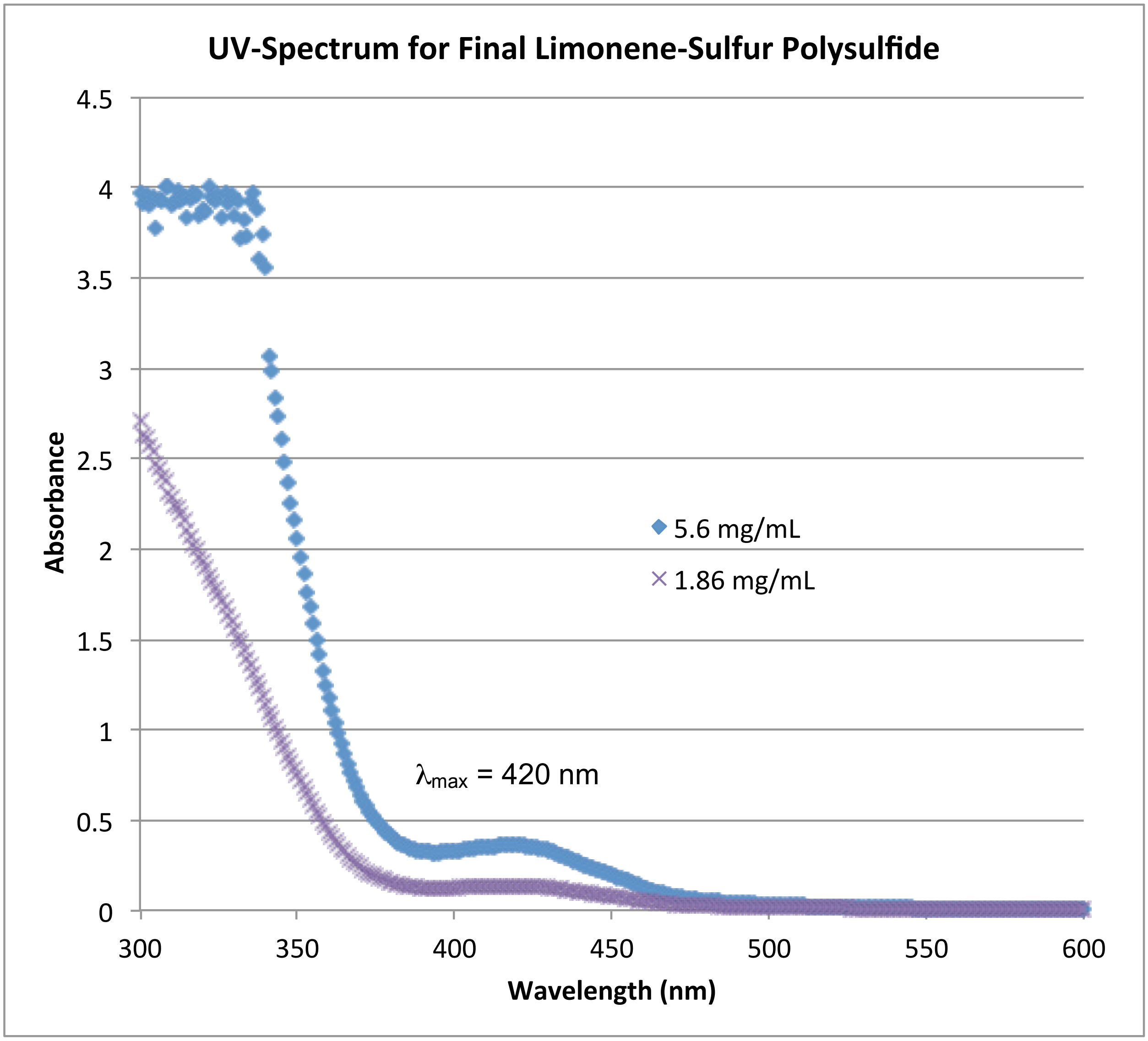


Peak 3 (13.29 min): m/z = 170.0 $[M]^{\bullet+}$



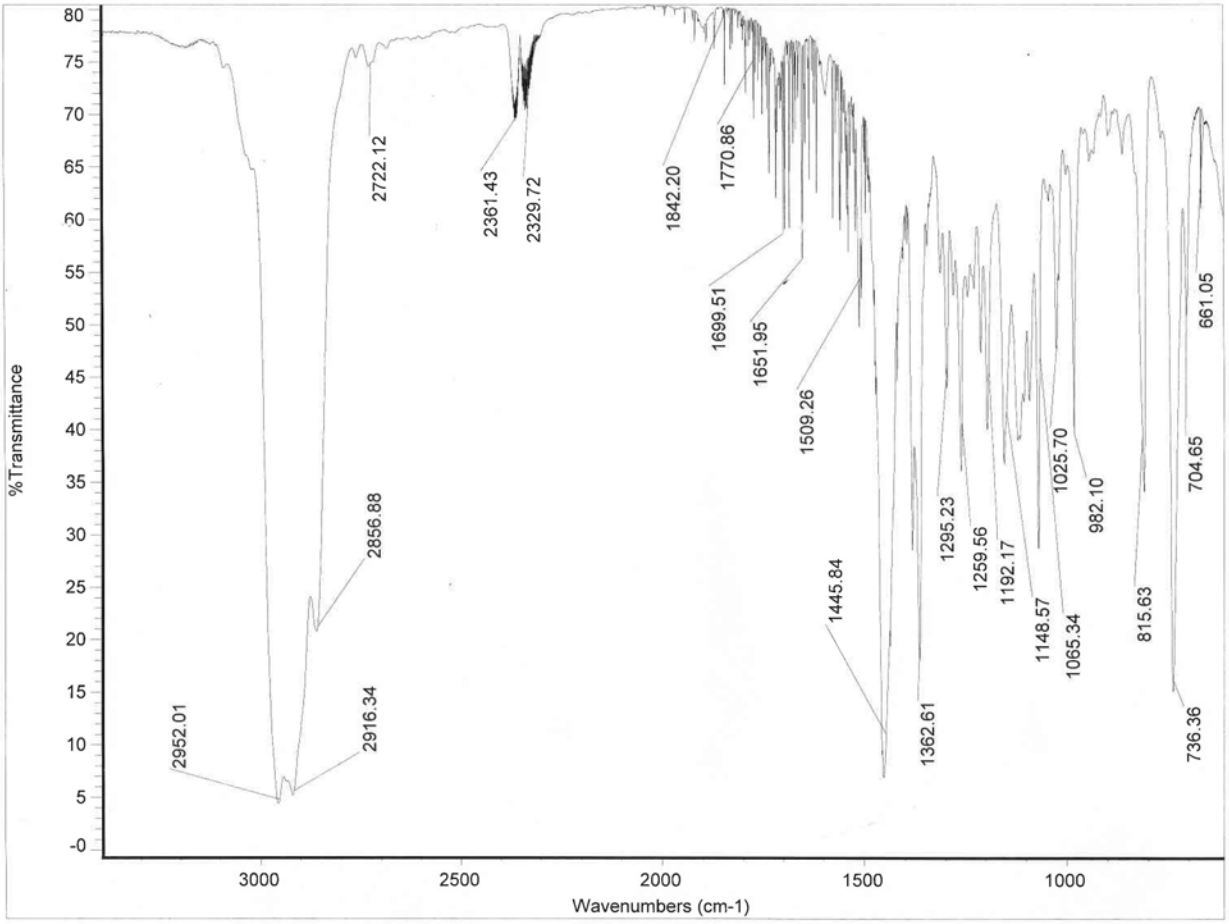
UV-Vis Spectrum of sulfur-limonene polysulfide

A solution of the polysulfide was prepared in CH_2Cl_2 at 5.6 mg/mL and 1.86 mg/mL. The UV-Vis spectrum was acquired in a quartz cuvette. A local absorbance maximum was observed at 420 nm, consistent with the yellow color of the polysulfide solution in CH_2Cl_2.



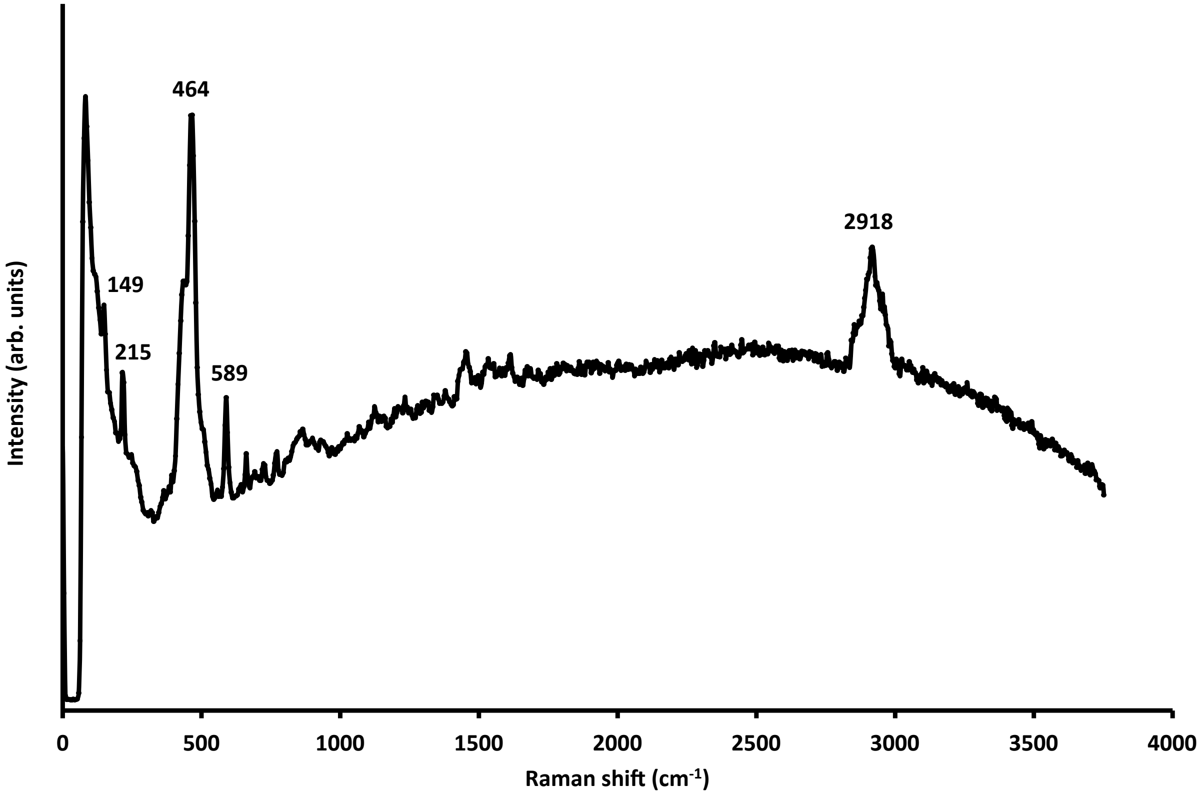
IR spectrum of final sulfur-limonene polysulfide

Several drops of a solution of the polysulfide in CH_2Cl_2 (~ 2 mg / mL) were added to a sodium chloride plate and dried under nitrogen. The resulting thin film was analyzed by FT-IR.



Raman spectrum of final sulfur-limonene polysulfide

A sample of the polysulfide was transferred to a glass microscope slide and analyzed by confocal Raman microscopy. Spectra were acquired using a Witec alpha300R Raman microscope at an excitation laser wavelength of 532 nm with a 40X objective (numerical aperture 0.60). Typical integration times for the Raman spectra were between 10-20 s for 2-3 accumulations. A representative spectrum is shown below. The broad peak at 464 cm^{-1} is consistent with various symmetric and asymmetric stretching modes of S-S bonds, and therefore spectroscopic evidence for the polysulfide structure of the material.[2]



Optical activity of D-limonene monomer and comparison to sulfur-limonene polysulfide

The sulfur-limonene polysulfide was optically active, indicating the stereochemical integrity of at least a portion of the limonene starting material.

Optical activity of sulfur-limonene polysulfide: $[\alpha]_D = -27.3$ (c = 1.0, $CHCl_3$)

Technical grade D-limonene: $[\alpha]_D = +113.5$ (c = 1.1, $CHCl_3$)

Elemental composition of final sulfur-limonene polysulfide:

CHNS composition was analyzed by combustible analysis using thermal conductivity detection for %CHN and ion chromatography for %S. Elemental composition: C, 38.97%; H, 4.97%; N, 0.0%; S, 56.60%.

Given that approximately 4% of the sulfur is free S_8 (see next), the average empirical formula for the sulfur-limonene polysulfide is C_2H_3S.

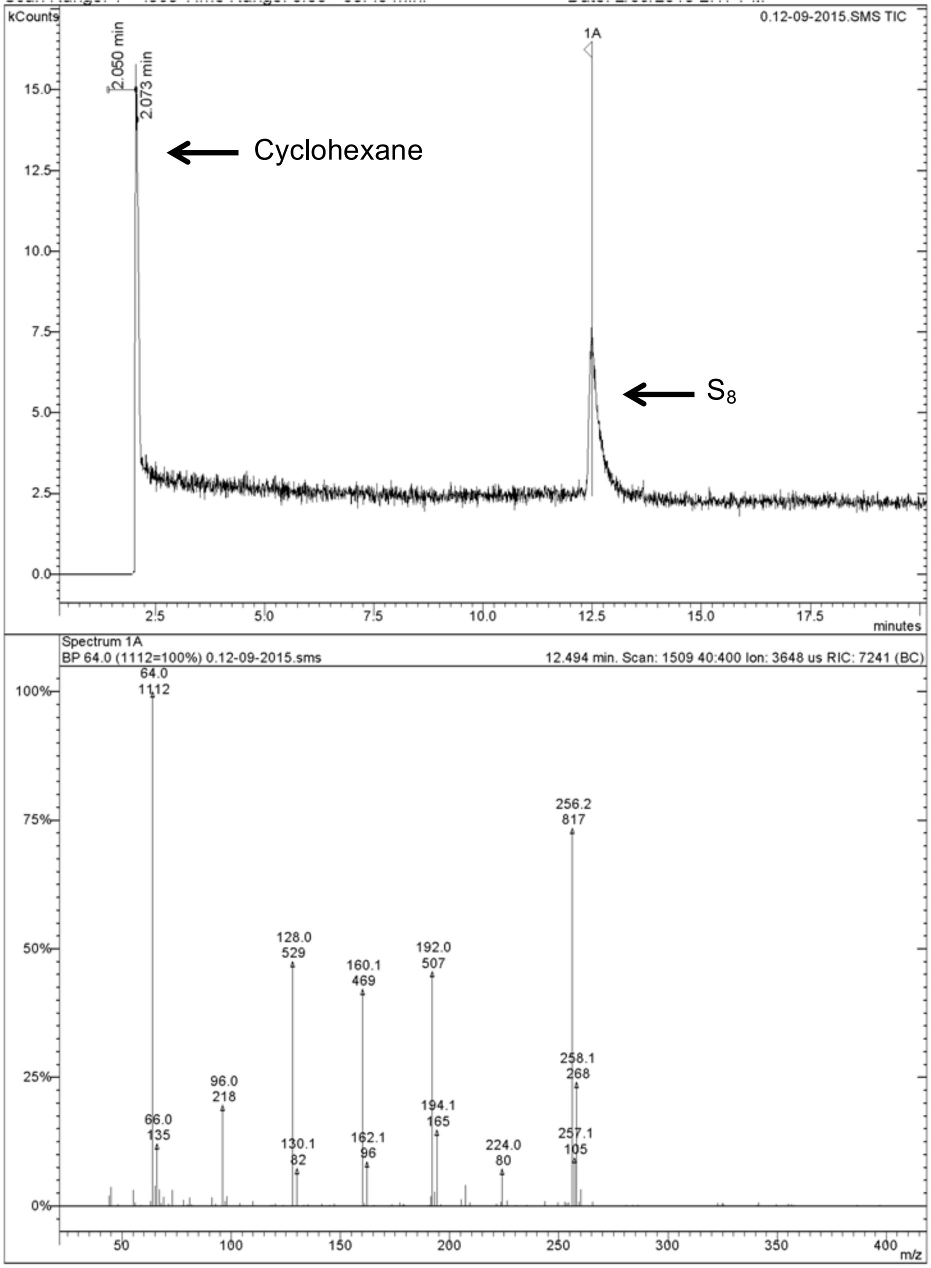
GC-MS of sulfur-limonene polysulfide to quantify free S_8

This series of experiments was adapted from a previously published method for quantifying elemental sulfur by gas chromatography.[3]

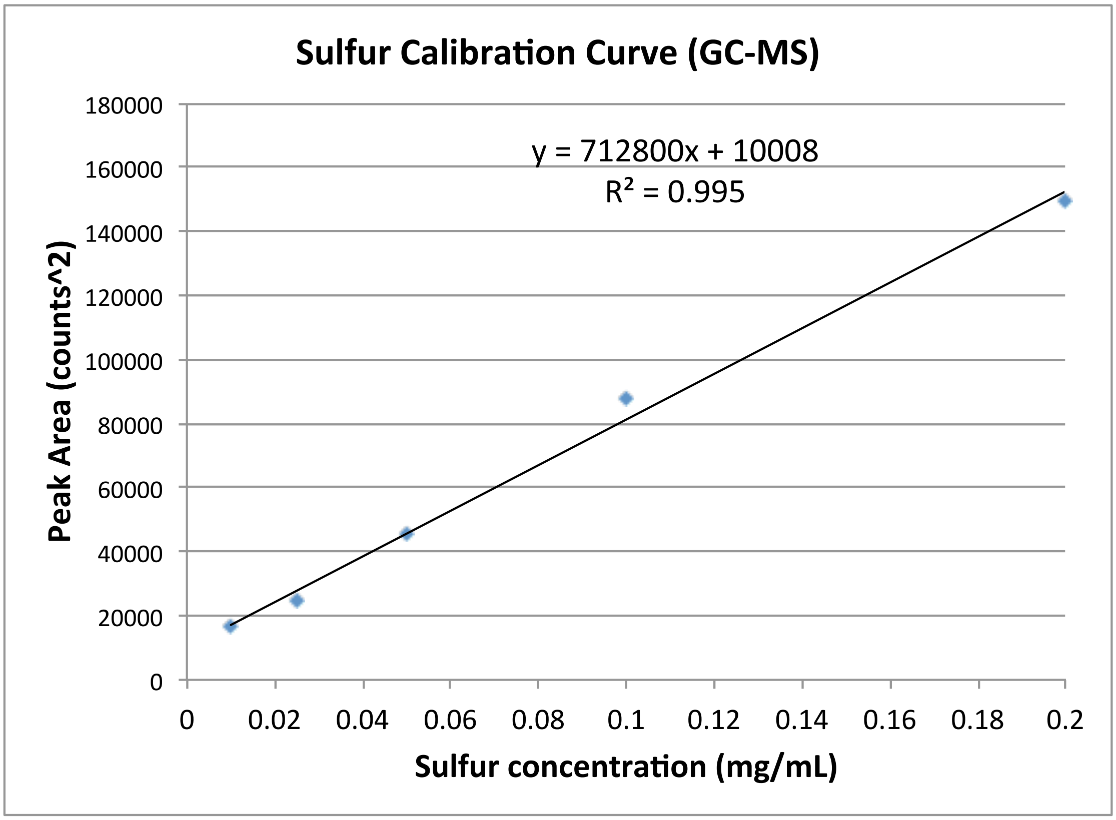
Calibration curve: GC-MS analysis of elemental sulfur in cyclohexane

Solutions of elemental sulfur (S_8) were prepared in cyclohexane at concentrations of 0.010, 0.025, 0.050, 0.10, and 0.20 mg/mL. Each sample was analyzed by GC-MS using the conditions described above. Sulfur eluted at approximately 12.5 minutes in all cases and displayed a mass corresponding to S_8 (m/z calculated: 256.5 $[M]^{\bullet+}$, 256.2 observed). A representative GC-MS trace for 0.1 mg/mL S_8 is shown below. A calibration curve was constructed, plotting the area under the curve vs. concentration of sulfur.

Representative GC-MS of sulfur in cyclohexane (0.1 mg/mL):



Calibration curve:

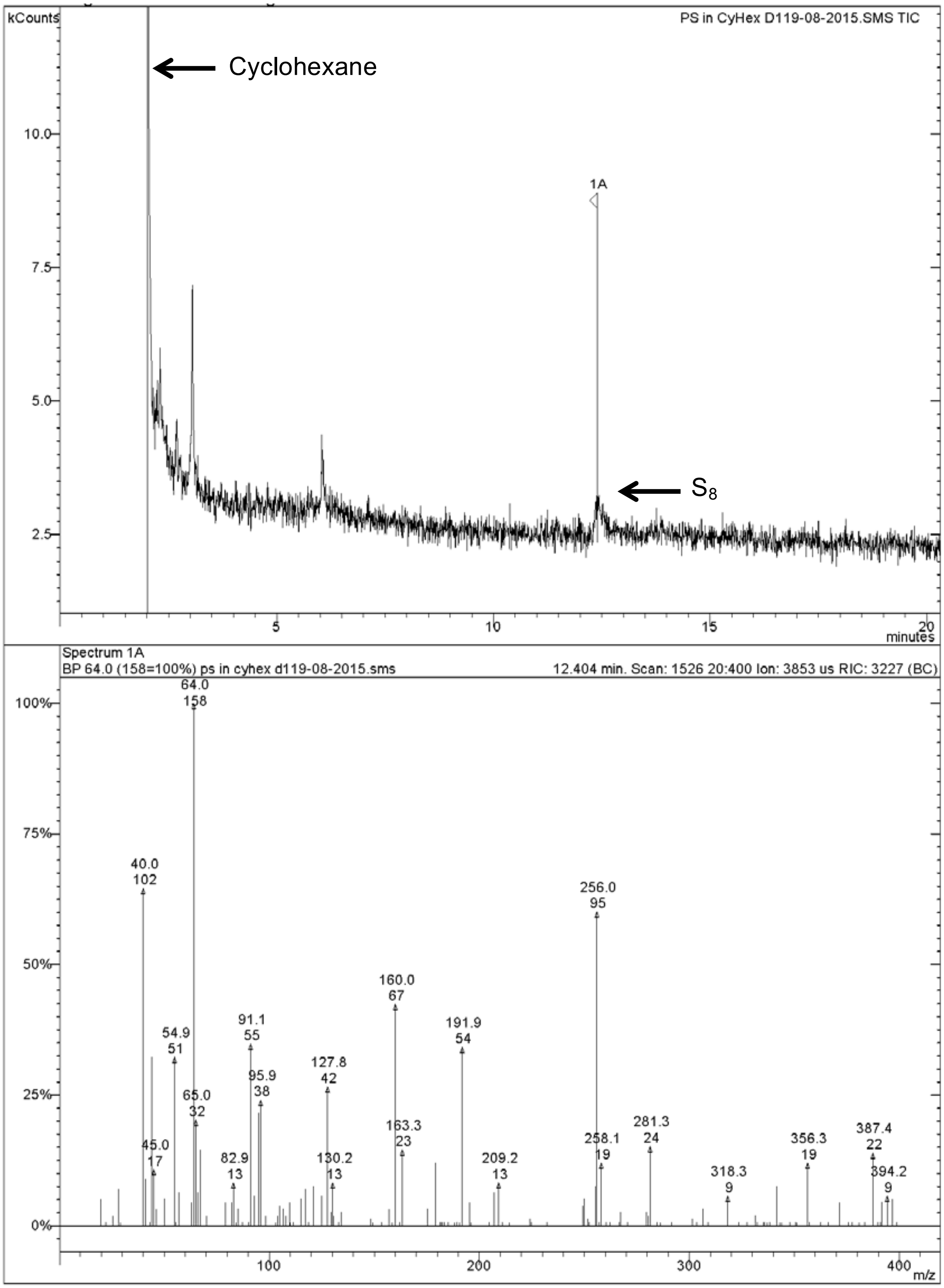


Analysis of elemental sulfur in the sulfur-limonene polysulfide.

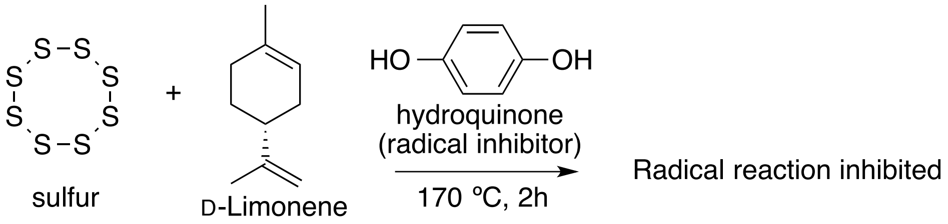
A sample of the sulfur-limonene polysulfide was prepared at 0.1 mg/mL in cyclohexane. The sample was analyzed directly by GC-MS using the sample parameters as described above. Peaks from the polysulfide were observed at 3.0 min (m/z = 196, 181, 148) and 6.0 min (m/z = 232, 283, 341). These peaks were not assigned as the polysulfide may not move efficiently on the GC column and may decompose at the column temperature. This experiment was used primarily to identify if free sulfur was present, as the previous experiments demonstrated that S_8 can be readily detected by GC-MS under these conditions. Accordingly, a minor peak at 12.4 minutes was observed with $[M]^{\bullet+} = 256$. This peak corresponds to sulfur (S_8). Using the calibration curve shown above, the amount of sulfur (S_8) in the sulfur-limonene polysulfide was calculated to be approximately 0.004 mg/mL or 4% free sulfur by weight with respect to the sulfur-limonene polysulfide. We note that this constitutes an upper limit of free S_8 present in the sulfur-limonene polysulfide, as S_8 could potentially form through decomposition of the polysulfide on the column (the column temperature is sufficient to break sulfur-sulfur bonds of a polysulfide). The GC-MS of the sulfur-limonene polysulfide is shown on the following page.

GC-MS, 0.1 mg/mL sulfur-limonene polysulfide in cyclohexane

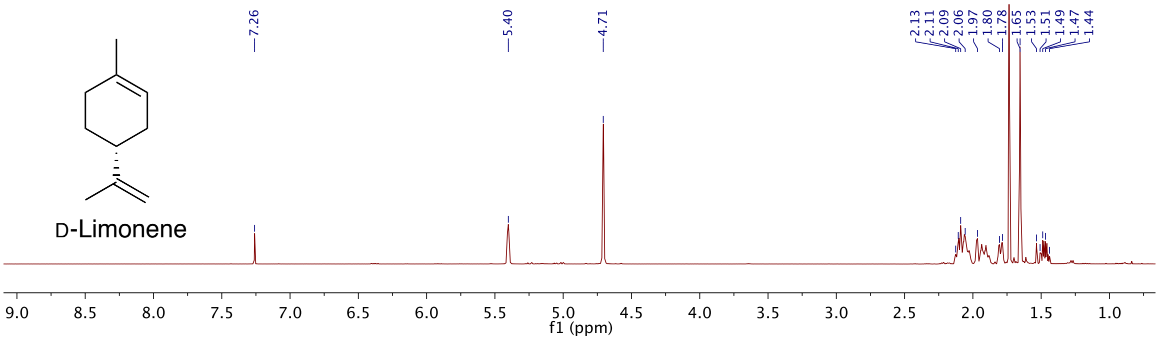
Less than 4 wt% S_8 was detected in the sulfur-limonene polysulfide

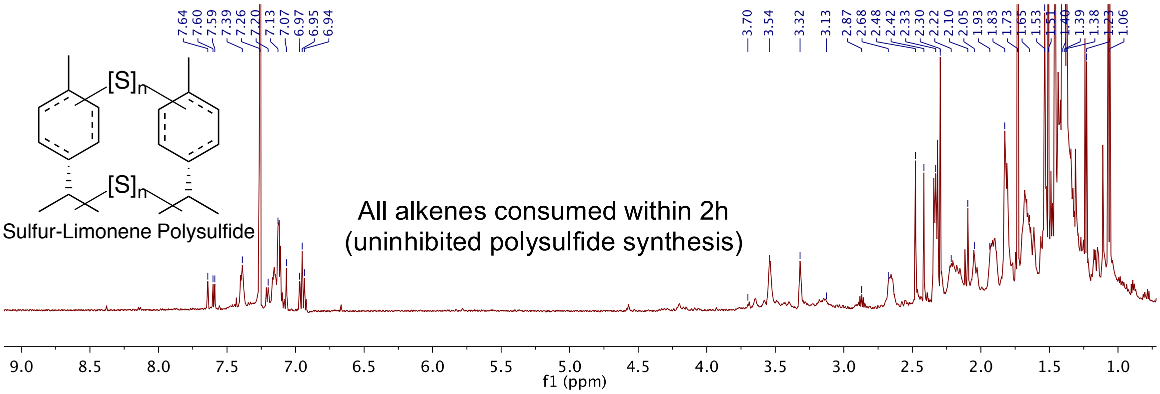


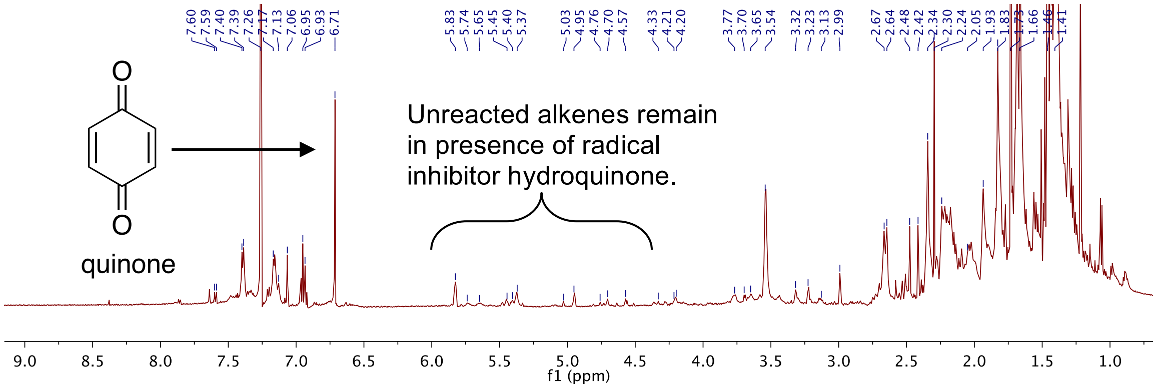
Reaction of sulfur and limonene in presence of a radical inhibitor



Sulfur (500 mg) was added to a 25 mL round bottom flask and heated to 170 ºC. Hydroquinone (a hydrogen atom donor and radical inhibitor) (50 mg, 0.45 mmol) was added to the molten sulfur, followed by limonene (500 mg). The reaction was then stoppered loosely and stirred at 170 ºC for 15 minutes. After this time, another portion of the hydroquinone radical inhibitor was added (50 mg, 0.45 mmol). The reaction was stirred an additional 1hr 45 minutes at 170 ºC. After this time, the reaction was cooled to room temperature and dissolved in $CDCl_3$ (~ 5 mL). The solution was then analyzed by ^{1}H NMR (600 MHz). Alkene peaks were observed along with *p*-benzoquinone. The alkene peaks correspond to partially reacted limonene. The formation of *p*-benzoquinone is consistent with hydroquinone reacting as an H-atom donor (and terminating radical intermediates). This result is consistent with other reports in the literature that suggest the thermal initiated reaction between sulfur and alkenes can proceed through a radical mechanism.[1,4] NMR data for limonene and the standard polysulfide are provided for comparison on the next page.


7.26
5.40
4.71
2.13
2.11
2.09
2.06
1.97
1.80
1.78
1.65
1.53
1.51
1.49
1.47
1.44
D-Limonene
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)


7.64
7.60
7.59
7.39
7.26
7.20
7.13
7.07
6.97
6.95
6.94
3.70
3.54
3.32
3.13
2.87
2.68
2.48
2.42
2.33
2.30
2.22
2.10
2.05
1.93
1.83
1.73
1.65
1.53
1.51
1.40
1.39
1.38
1.23
1.06
[S]n
[S]n
Sulfur-Limonene Polysulfide
All alkenes consumed within 2h
(uninhibited polysulfide synthesis)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)


7.60
7.59
7.40
7.39
7.26
7.17
7.13
7.06
6.95
6.93
6.71
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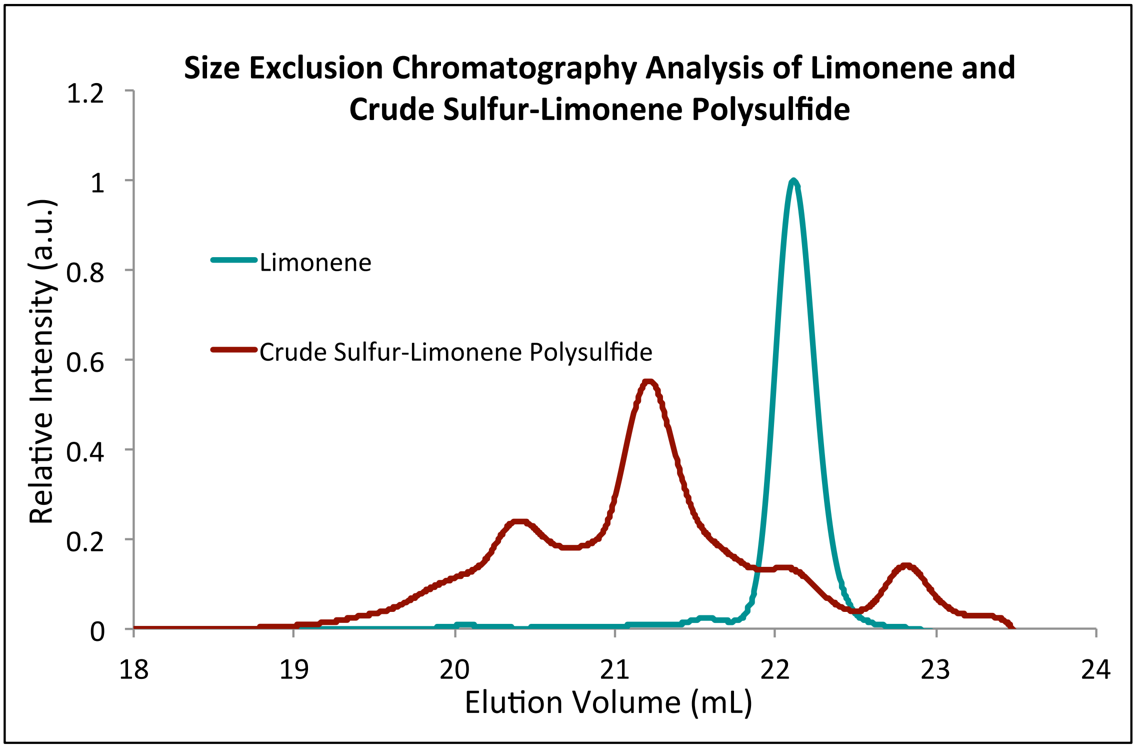
5.65
5.45
5.40
5.37
5.03
4.95
4.76
4.70
4.57
4.33
4.21
4.20
3.77
3.70
3.65
3.54
3.32
3.23
3.13
2.99
2.67
2.64
2.48
2.42
2.34
2.30
2.24
2.05
1.93
1.83
1.73
1.66
1.46
1.41
O
O
quinone
Unreacted alkenes remain
in presence of radical
inhibitor hydroquinone.
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)

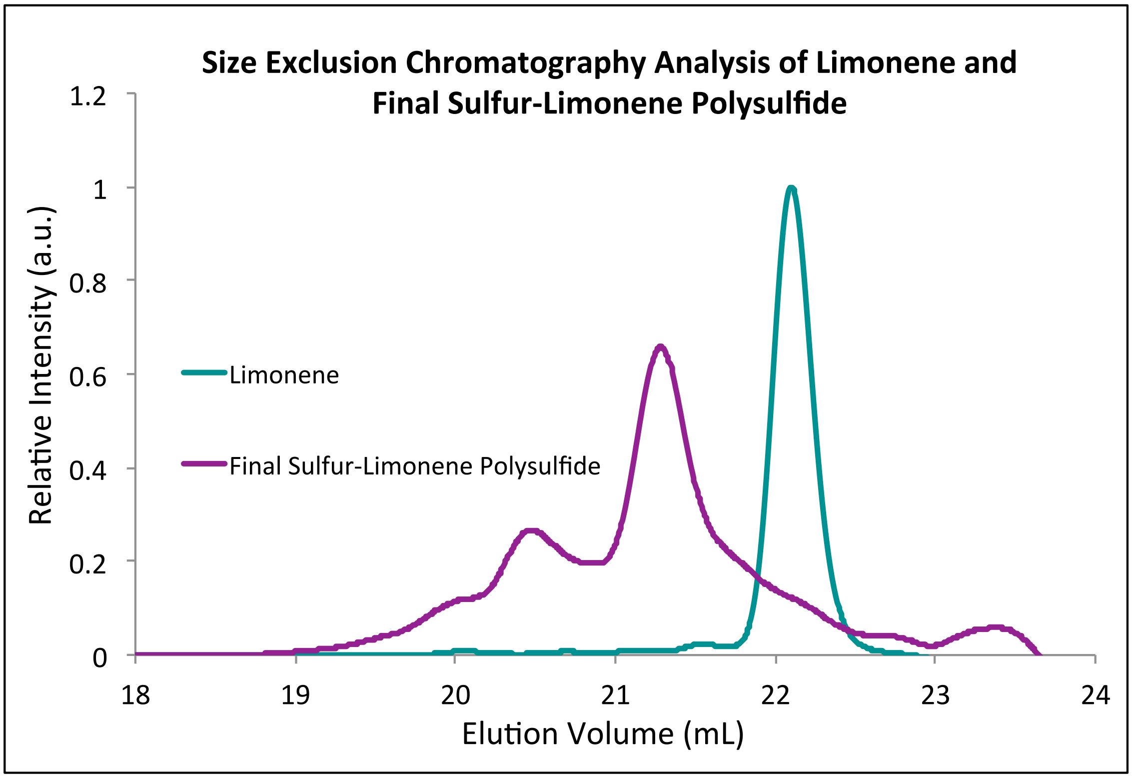
Size Exclusion Chromatography (SEC) analysis of sulfur-limonene polysulfide

Refractive index chromatograms are shown below for both the polysulfide and the limonene starting material. The decreased retention time for the reaction mixture (red trace) is consistent with higher molecular weight products formed by reaction of limonene and sulfur. The lower molecular weight products formed (peak at elution volume of 22.8 mL) are consistent with the cymene byproduct formed during the reaction.



Size Exclusion Chromatography (SEC) analysis of sulfur-limonene polysulfide after removal of volatile materials by distillation

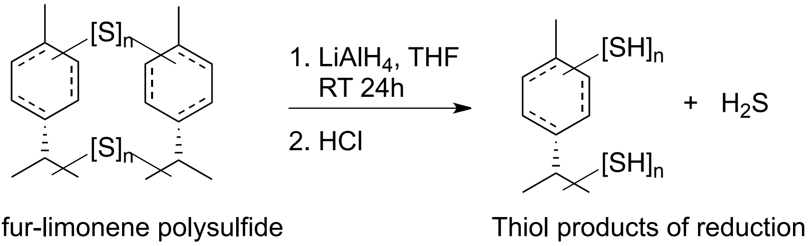
Refractive index chromatograms are shown below for both the final sulfur-limonene polysulfide and the limonene starting material. The lower retention time for the polysulfide is consistent with a higher molecular weight product formed from the reaction between sulfur and limonene. The lower molecular weight compounds (*p*-cymene and volatile thiols and sulfides) were no longer present in the polysulfide sample after they were removed by distillation.



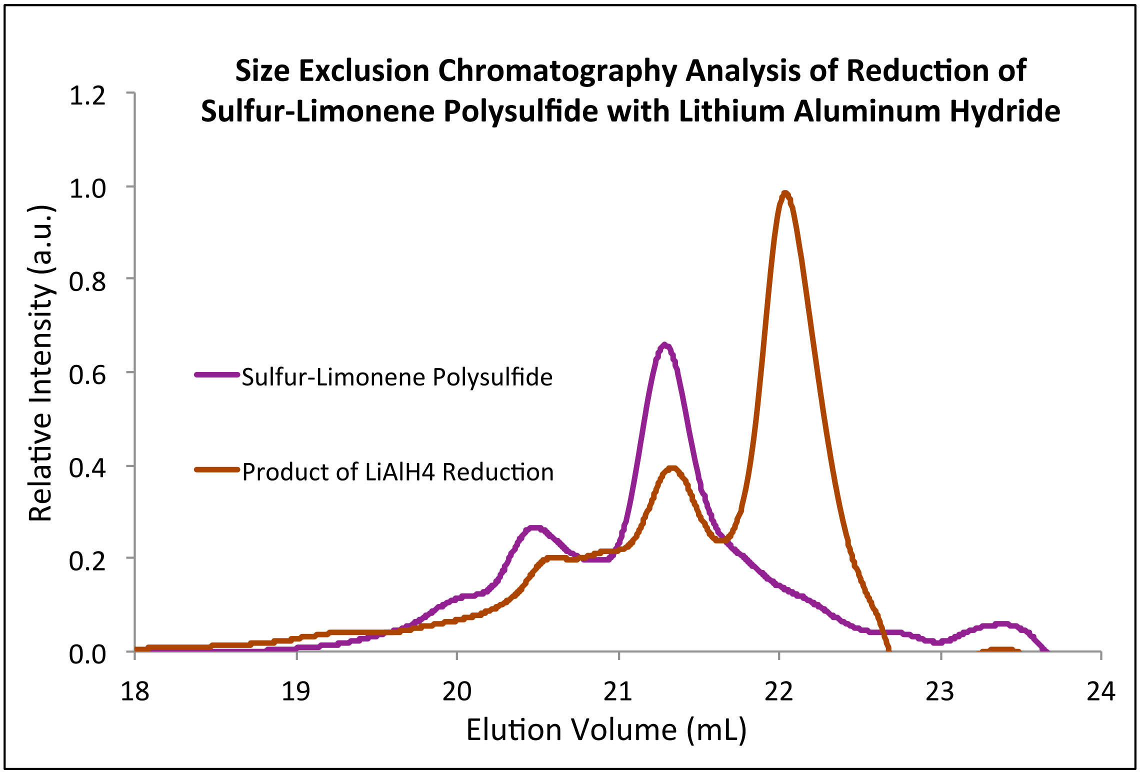
Relative to polystyrene standards (see general experimental details), the following molar mass averages (g/mol) and polydispersity were calculated:
$M_n = 210$
$M_w = 242$
$M_z = 292$
Polydispersity = $(M_w / M_n) = 1.16$

We note that the mass averages obtained in this analysis are only apparent and should be used primarily to quantify dispersity. Absolute molar mass averages cannot be obtained using this method because the sulfur-limonene polysulfide may not be a linear construct like the polystyrene standards. It should also be noted that while lower retention time is indicative of higher molecular weight, previous reports have shown that polysulfides typically require longer elution times than polystyrene of the same molar mass (leading to a lower apparent molar mass, as calculated from the SEC).[4]

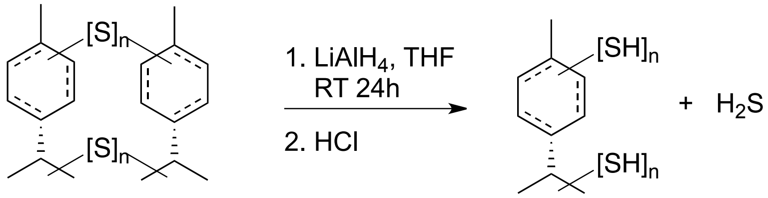
Reduction of sulfur-limonene polysulfide with $LiAlH_4$ and analysis by Size Exclusion Chromatography (SEC)



The sulfur-limonene polysulfide (66 mg) was added to a 25 mL round bottom flask equipped with a stir bar and placed under an atmosphere of nitrogen. A solution of $LiAlH_4$ (4.4 mL of 1.0 M in THF) was added to the polysulfide at room temperature. The polysulfide dissolved over a period of approximately 5 minutes. The resulting solution was stirred at room temperature for 24 hours. After this time, the reaction was cooled to 0 ºC and quenched by the dropwise addition of 1.0 M HCl (10 mL). The mixture was then diluted with diethyl ether (20 mL) and transferred to a separatory funnel. The organic layer was isolated and then dried with $MgSO_4$, filtered and concentrated under a stream of nitrogen. The resulting residue (22 mg) was then analyzed by size exclusion chromatography using the same method described above. A higher retention time was observed, consistent with a lower molecular weight product of reduction. This experimental result is consistent with the polysulfide linkage formed during the reaction between sulfur and limonene. It also demonstrates that the sulfur-limonene polysulfide can be broken down with reducing agents.



Reduction of sulfur-limonene polysulfide with $LiAlH_4$ and analysis by GC-MS

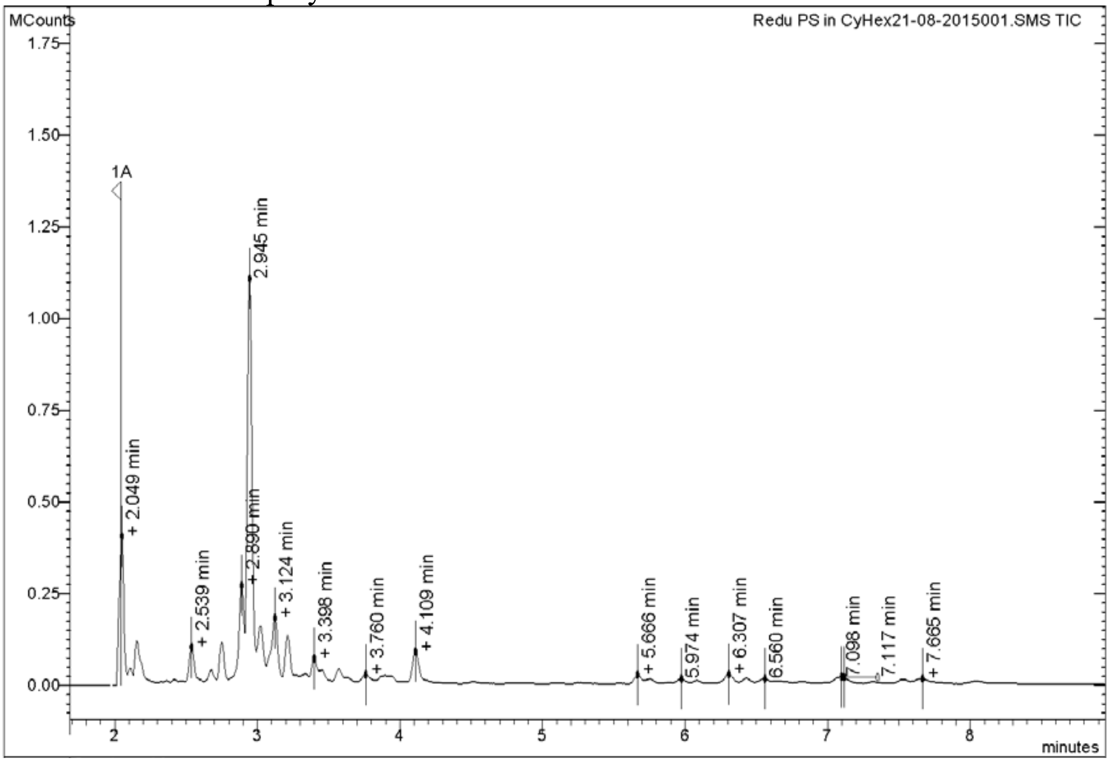


Sulfur-limonene polysulfide

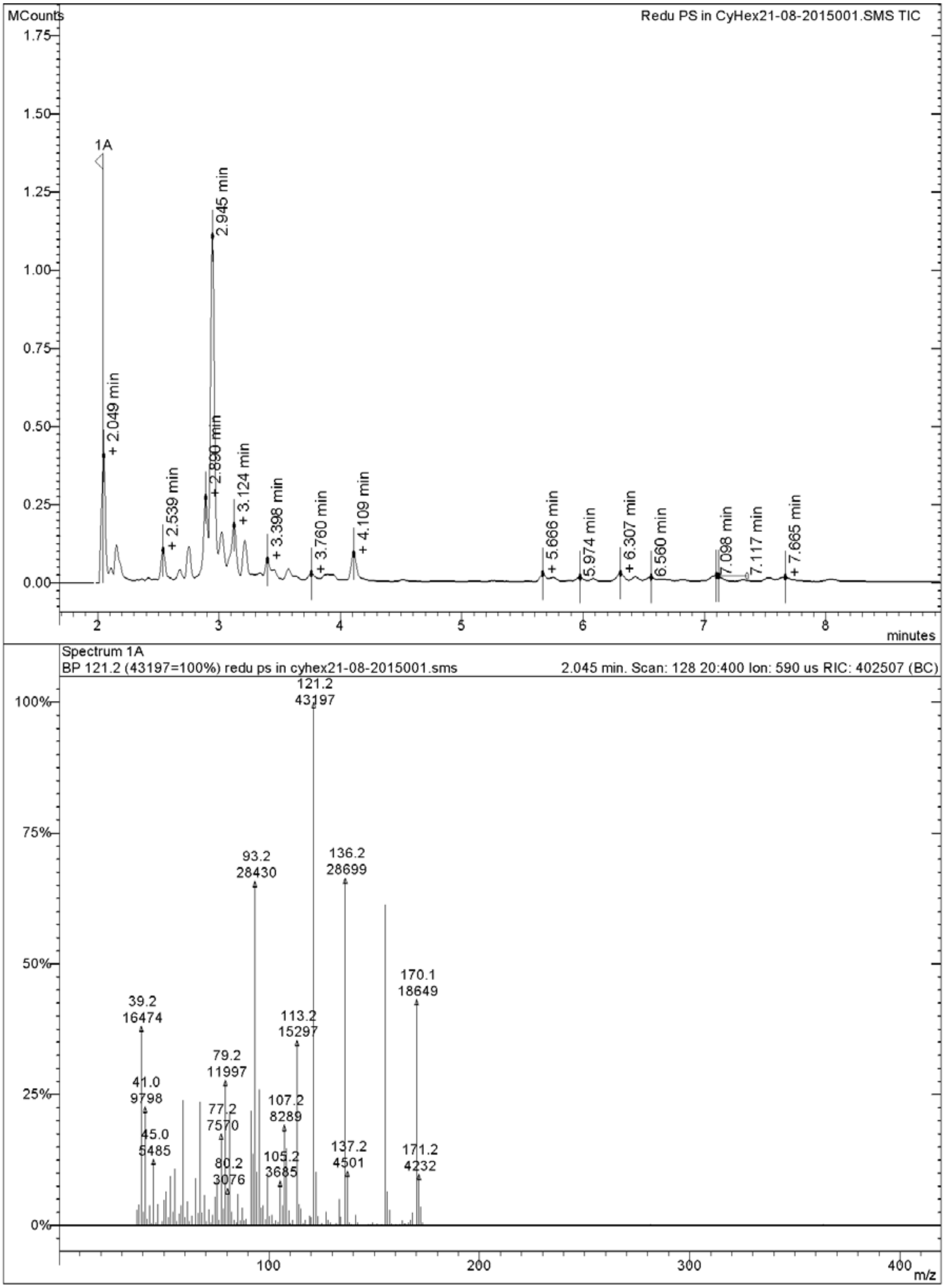
Thiol products of reduction

The sulphur-limonene polysulfide (33 mg) was added to a 25 mL round bottom flask and placed under an atmosphere of nitrogen. A solution of $LiAlH_4$ (2.2 mL, 1M in THF, 2.2 mmol) was added to the polysulfide and the resulting reaction mixture was stirred at room temperature for 24 hours. After this time, the reaction flask was cooled to 0 ºC and quenched slowly with 1M HCl (5.0 mL). The mixture was kept under nitrogen while cyclohexane (5 mL) was added to the mixture. This mixture was stirred vigorously for 1 hour to extract the organic material. An aliquot of the cyclohexane layer was then analyzed directly by GC-MS (same conditions as described in the general experimental considerations). Several products were observed, all eluting in less than 10 minutes. All observed masses were less than m/z = 220, consistent with reduction of the polysulfide to lower molecular weight components composed of a single limonene unit with no more than two sulfur atoms. Representative GC-MS data are shown below.

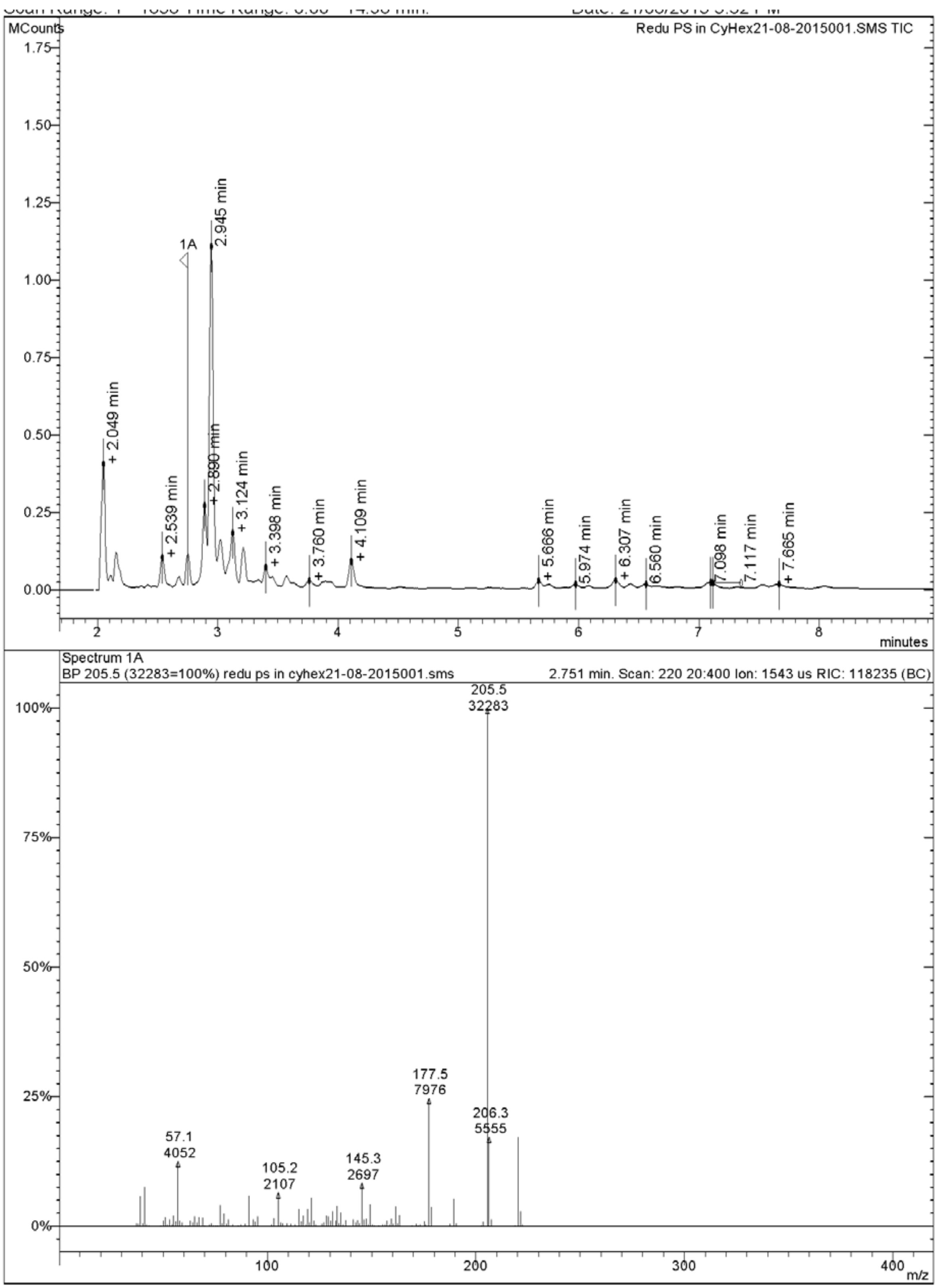
GC trace of reduced polysulfide:



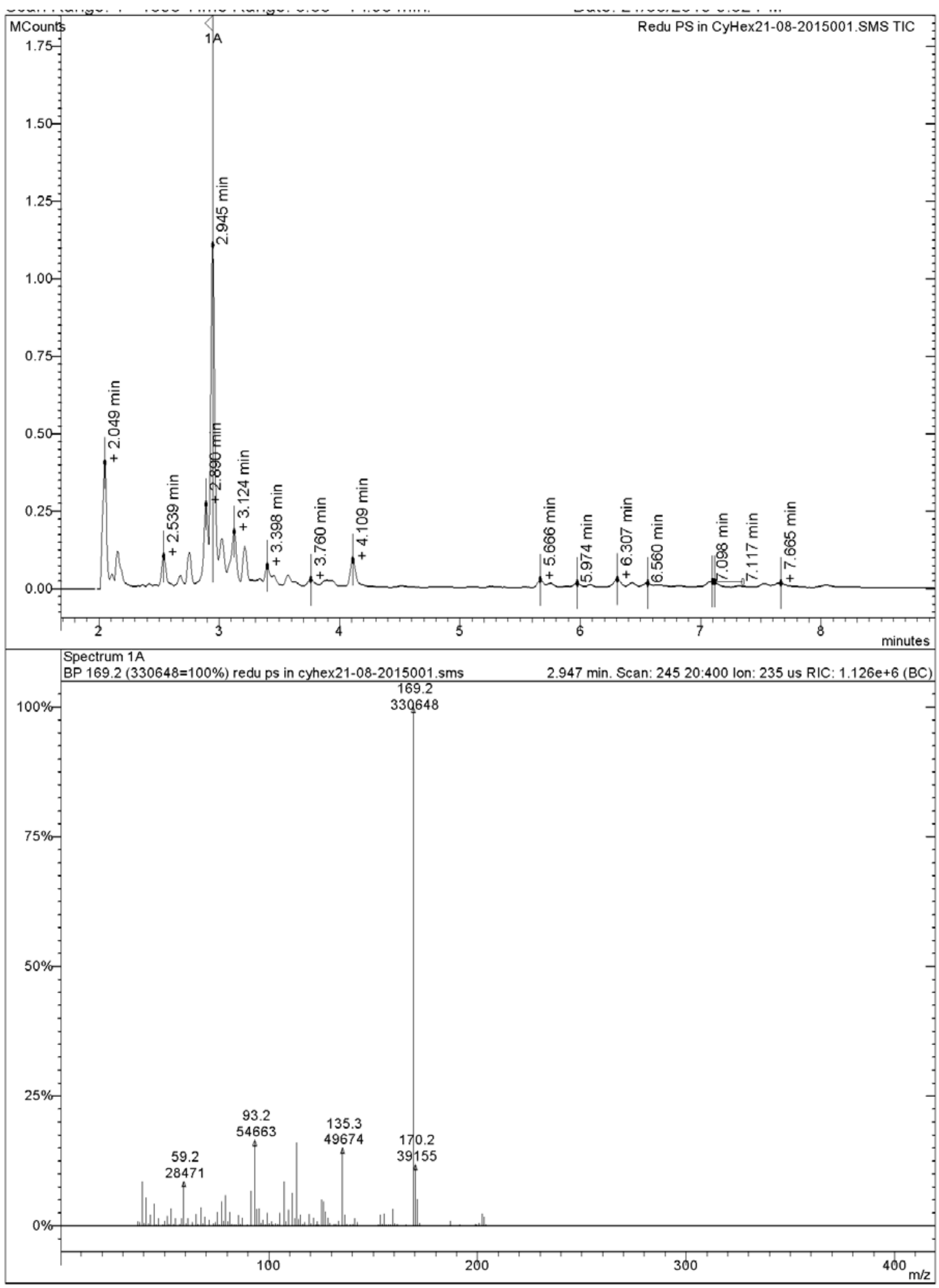
GC-MS of reduced polysulfide (2.05 min, m/z = 170).



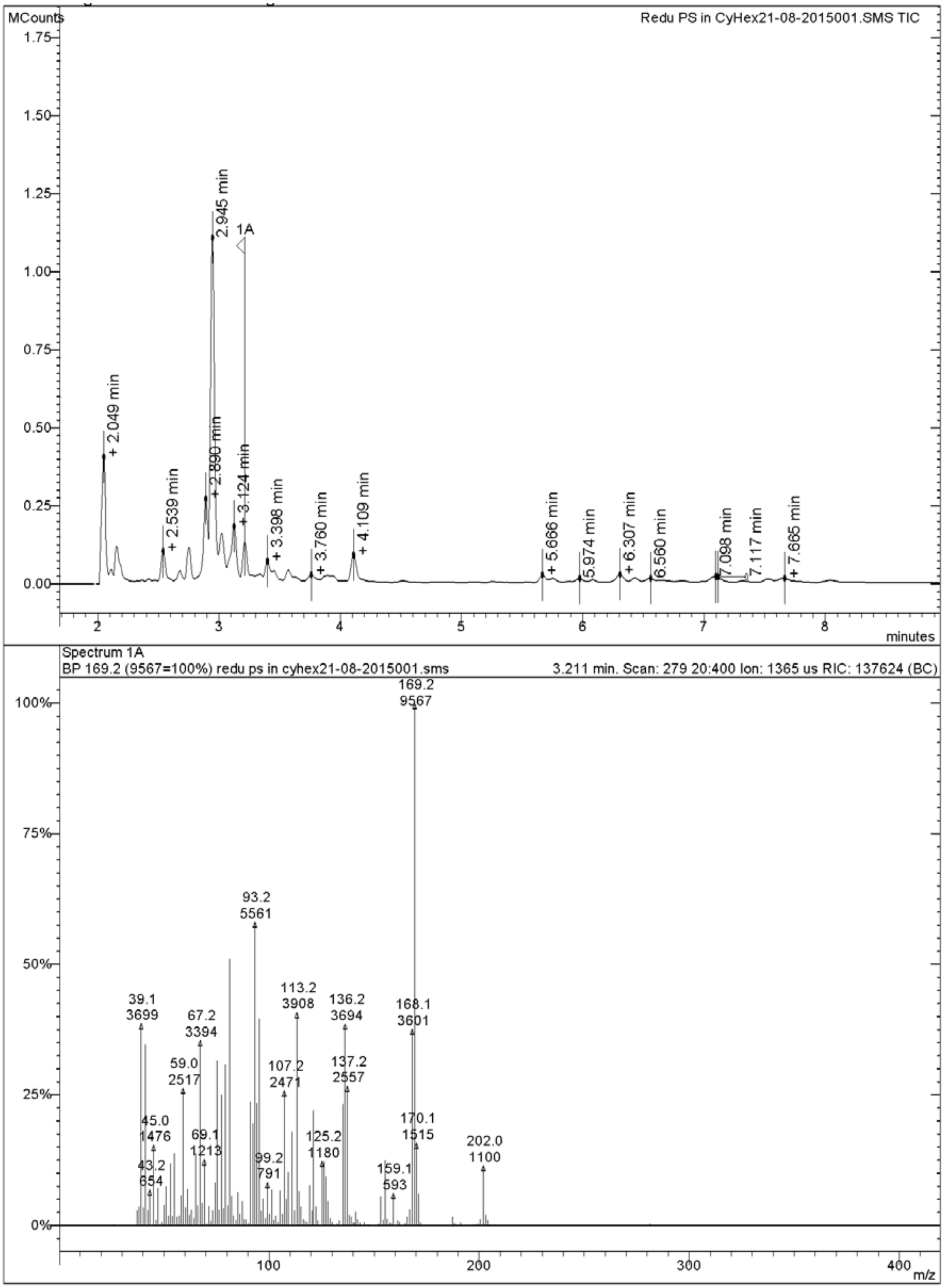
GC-MS of reduced polysulfide (2.75 min, m/z = 205).



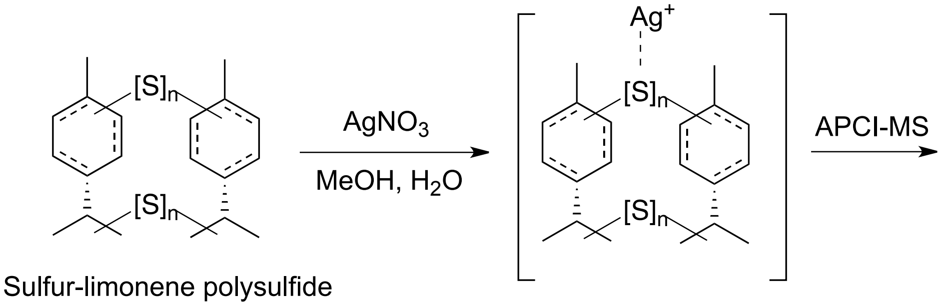
GC-MS of reduced polysulfide (2.95 min, m/z = 169).



GC-MS of reduced polysulfide (3.21 min, m/z = 202, 169).

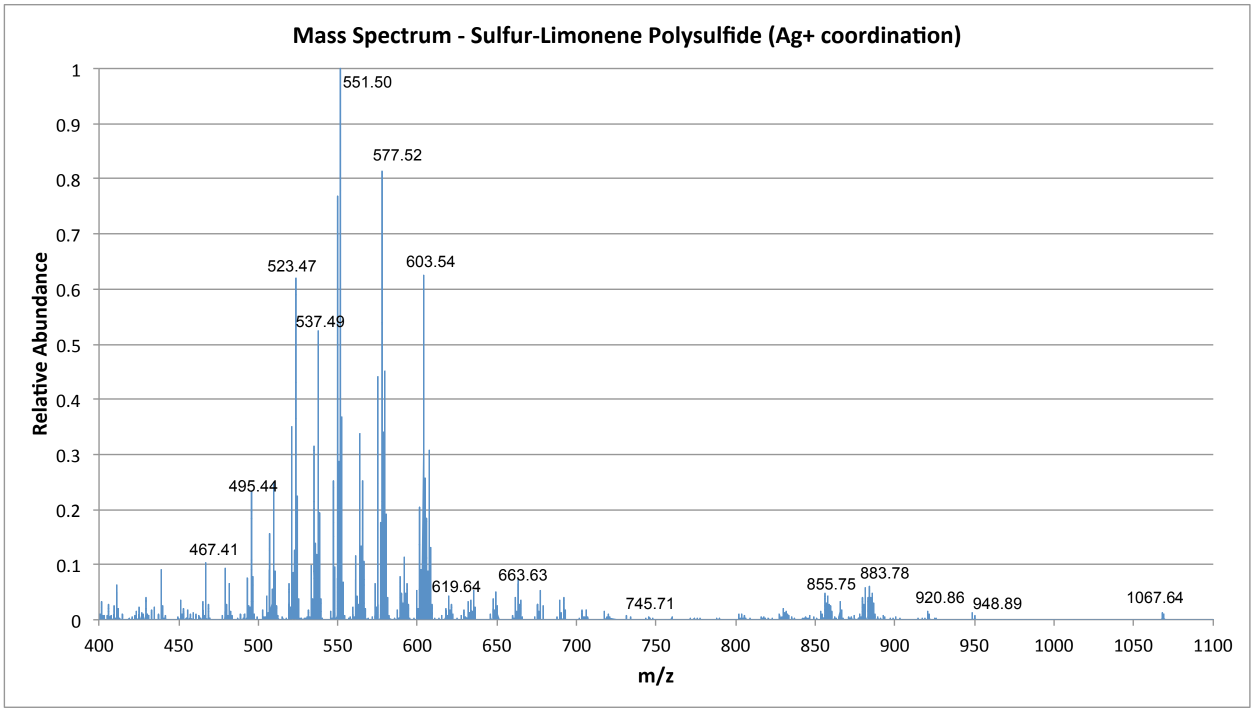


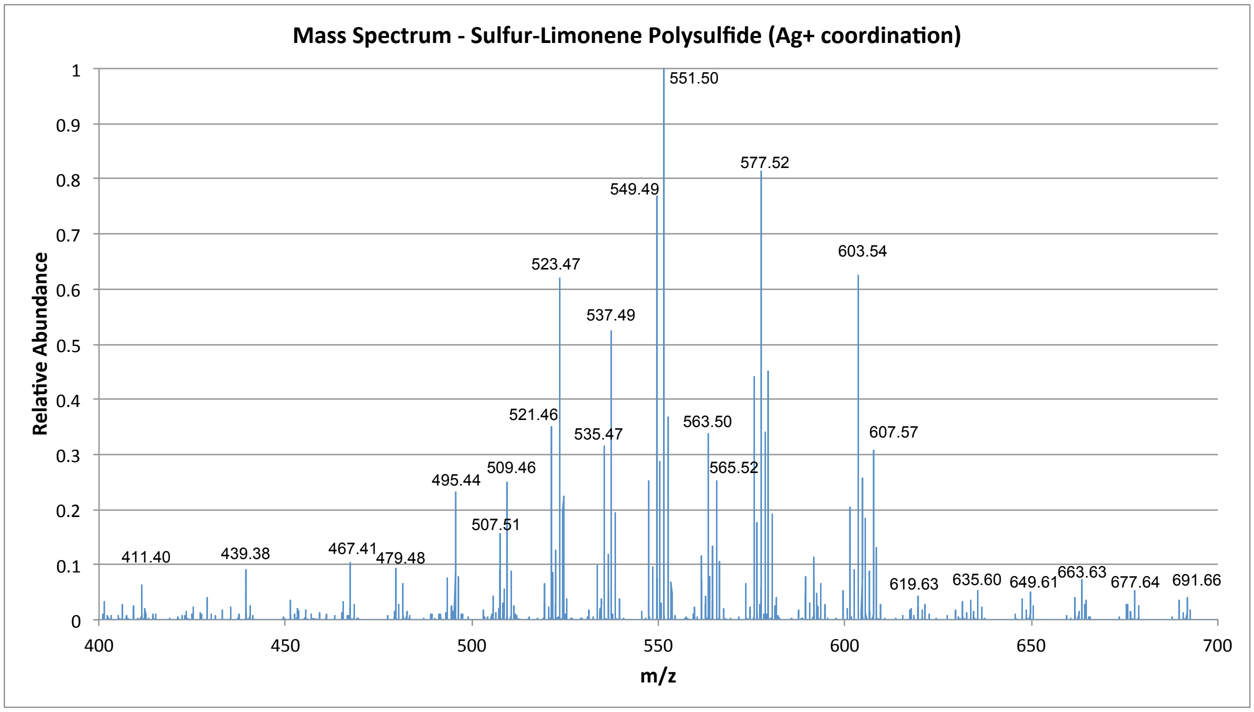
Mass Spectrometry using Ag^+ coordination

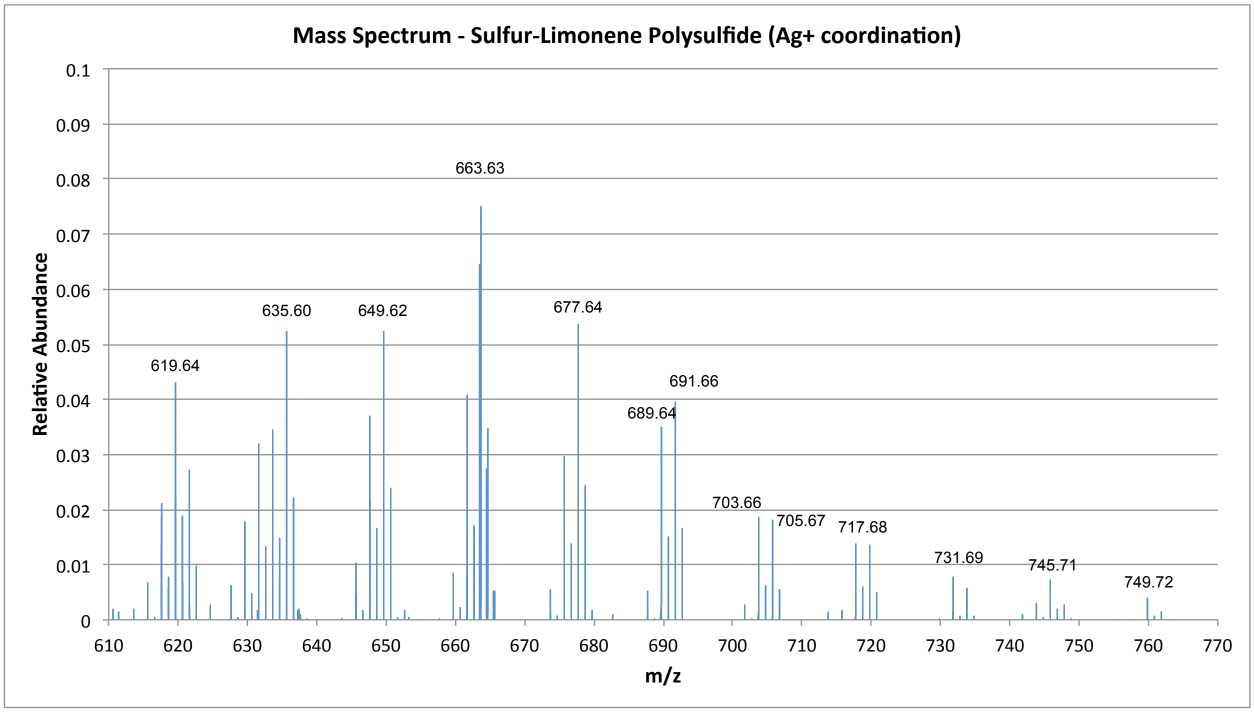


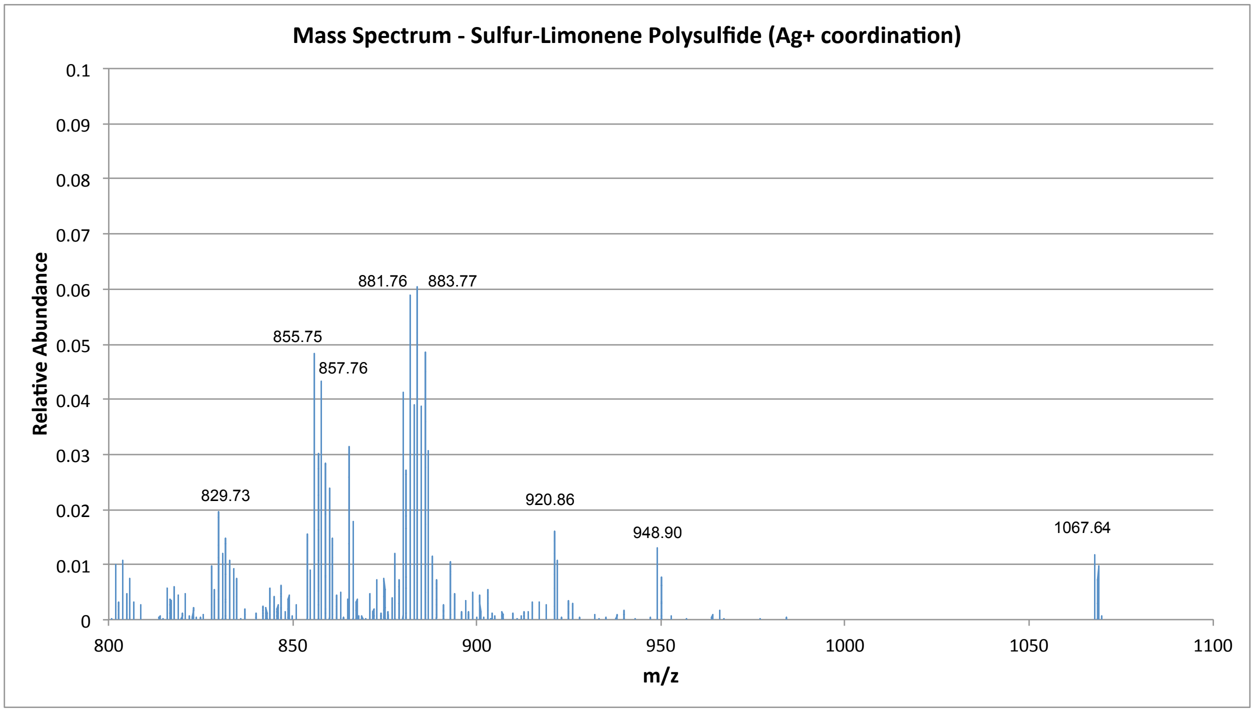
A solution of $AgNO_3$ in H_2O was prepared at 0.5 mg/mL. This solution was mixed with methanol in a 9:1 ratio by volume to provide the mass spectrometry infusion solution. Next, the sulfur-limonene polymer (20 mg) was prepared as a saturated mixture in the $MeOH/H_2O/Ag^+$ infusion solution. From this mixture, a 100 microliter aliquot was taken and then diluted further to 1.0 mL with the $MeOH/H_2O/Ag^+$ infusion solution. This solution was injected by direct infusion to the mass spectrometer using atmospheric pressure chemical ionization with operation in positive mode. Signals were detected between $m/z = 495$ and 886 that contained doublets separated by two mass units. These signals are proposed to correspond to the components of the sulfur-limonene polysulfide coordinated to Ag^+. In a control experiment without silver nitrate, a sample prepared by the same method gave no signal in the mass spectrometer. The doublets are a consequence of the two abundant isotopes of Ag (106.9 and 108.9 Da). As such, we propose that the components of the sulfur-limonene polysulfide that can be detected by Ag^+ coordination mass spectrometry vary between 386 and 777 Da. Assuming that only whole limonene units are incorporated into the polysulfide and linked together with at least two sulfur atoms, the polysulfide could, in principle, be comprised of a mixture of compounds each containing 1-3 limonene units and up to 19 atoms of sulfur. Considering that combustible analysis revealed an average empirical formula of C_2H_3S, the average composition of the polysulfide consistent with the detected m/z values is two limonene units (C_{20}) and ten sulfur atoms (S_{10}). It should be pointed out that we do not assume the relative abundance in the mass spectrum necessarily reflects the molar ratio of each component, as each component in the mixture may ionize with different efficiency and some components may not be detected. Furthermore, even though this is a soft ionization technique, some of the polysulfide may still decompose through S-S scission during MS analysis. Overall, the purpose of this experiment was to obtain an estimate, however crude, of the mass distribution of the products formed in the reaction between limonene and sulfur. It has also been noted in the literature that mass spectrometry of polysulfides is notoriously challenging due to low and variable ionization efficiency and instability of these analytes.[4]

The mass spectra are shown on the following pages


Mass Spectrum - Sulfur-Limonene Polysulfide (Ag+ coordination)
Relative Abundance
m/z
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
400
450
500
550
600
650
700
750
800
850
900
950
1000
1050
1100
551.50
577.52
523.47
603.54
537.49
495.44
467.41
619.64
663.63
745.71
855.75
883.78
920.86
948.89
1067.64


Mass Spectrum - Sulfur-Limonene Polysulfide (Ag+ coordination)
Relative Abundance
m/z
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
400
450
500
550
600
650
700
551.50
577.52
549.49
523.47
603.54
537.49
521.46
563.50
535.47
607.57
565.52
495.44
509.46
507.51
411.40
439.38
467.41
479.48
619.63
635.60
649.61
663.63
677.64
691.66


Mass Spectrum - Sulfur-Limonene Polysulfide (Ag+ coordination)
Relative Abundance
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
619.64
635.60
649.62
663.63
677.64
689.64
691.66
703.66
705.67
717.68
731.69
745.71
749.72
610
620
630
640
650
660
670
680
690
700
710
720
730
740
750
760
770
m/z


Mass Spectrum - Sulfur-Limonene Polysulfide (Ag+ coordination)
Relative Abundance
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
829.73
855.75
857.76
881.76
883.77
920.86
948.90
1067.64
800
850
900
950
1000
1050
1100
m/z

Simultaneous Thermal Analysis (STA) of the Sulfur-Limonene Polysulfide

The sulfur-limonene polysulfide was tested using a Perkin Elmer STA8000 simultaneous thermal analyzer (STA). A sample size between 11 and 15 mg was used in each run. The furnace was purged at 20 mL/min with either nitrogen or air and equilibrated for 1 minute at 30 ºC before each run. A heating rate of 20 ºC/min up to 700 ºC was used for these experiments. An additional heating experiment was run at 5 ºC/min to 400 ºC to determine the effect of slower heating rate on char formation. An identical experiment with no sample was run to form a baseline, which was then subtracted from each series of data.

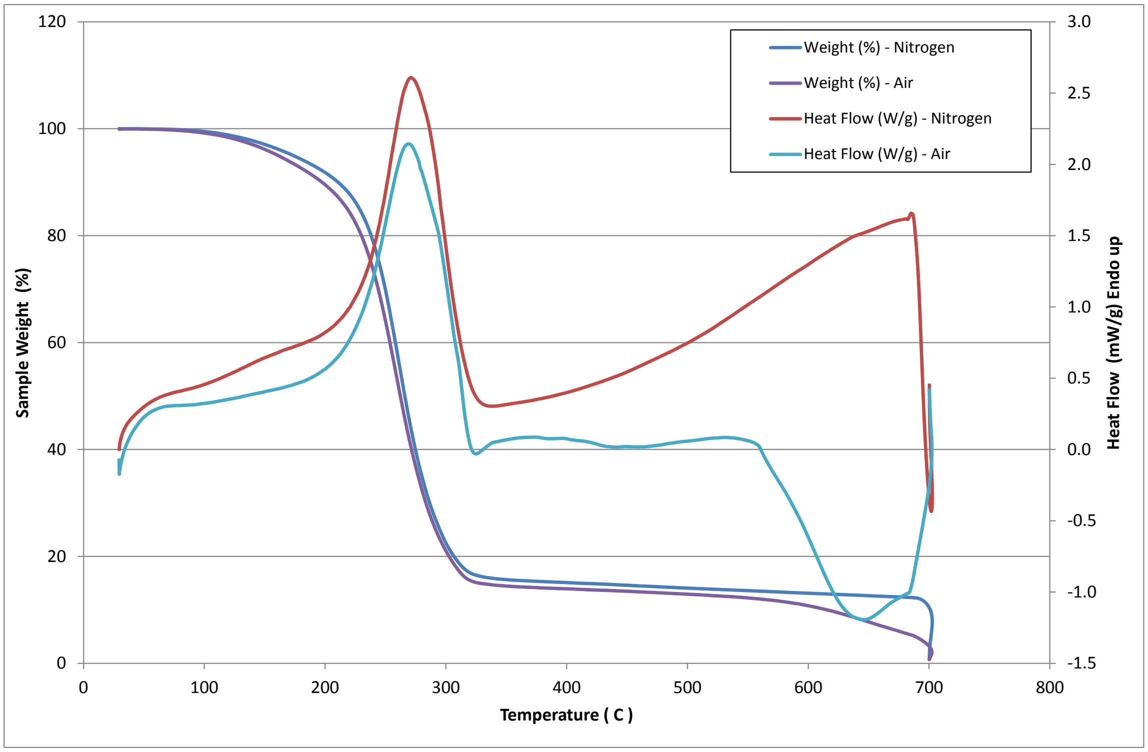
Results and Discussion of STA (see plots on next 2 pages):

- The sulfur-limonene polysulfide degrades between 100 ºC and 300 ºC, with a significant mass loss above 200 ºC (**STA Plot 1**). This degradation profile in this temperature region is similar in both nitrogen and air atmospheres, indicating polysulfide degradation is not an oxidative process. The degradation may therefore be a depolymerization process (S-S bond cleavage), which is supported by the endothermic peak in the heat flow data.

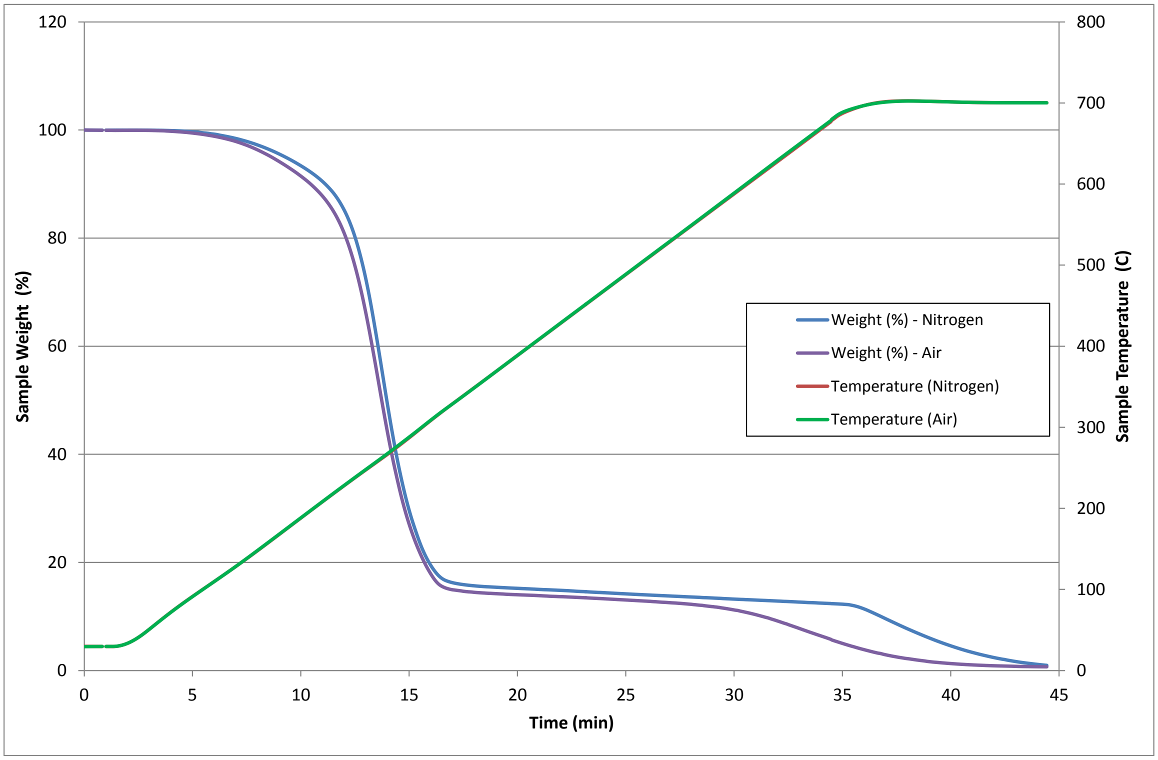
- At temperatures above 350 ºC, the behavior is quite different in each of the two atmospheres, with heat flow becoming more endothermic in nitrogen (an indication of a sublimation-like process) or exothermic in air (an indication of an oxidative degradation process).

- A char consisting of approximately 15% of the initial mass is formed, and is stable up to 700 ºC in nitrogen, but this material partially oxidizes in an air atmosphere. This char is degraded by oxidation during i) the isothermal heating step at 700 ºC (after heating in nitrogen), or ii) above ~550 ºC when heating in air (**STA Plot 2**).

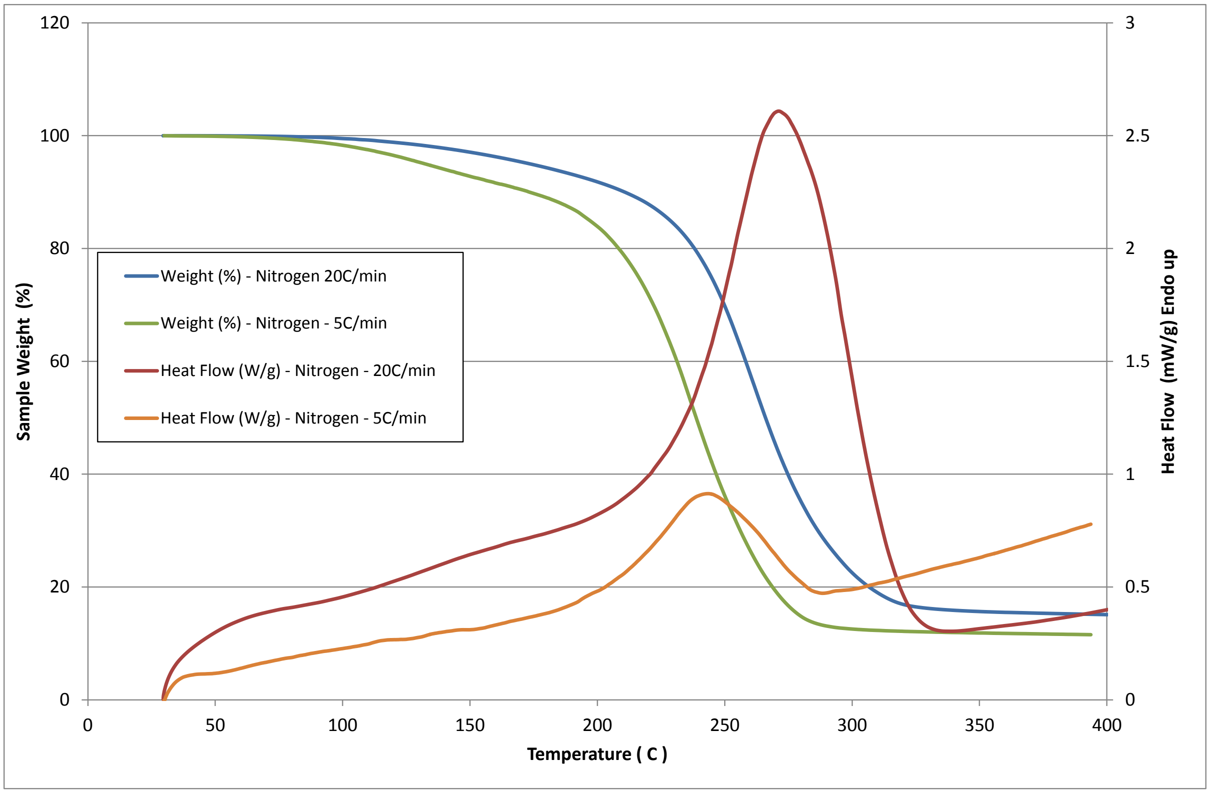
- Scanning at a slower heating rate (5 ºC/min) was used to determine if the faster heating rates caused char formation. There was slightly less char formed at 400 ºC when heating at the slower rate, but it was not avoided all together, indicating that the formation of char is an inherent part of the degradation process of this material. The char formed was black, consistent with the formation of carbonaceous material (**STA Plot 3**).



STA Plot 1. STA analysis of the sulfur-limonene polysulfide in nitrogen and air atmospheres – showing weight loss and heat flow.



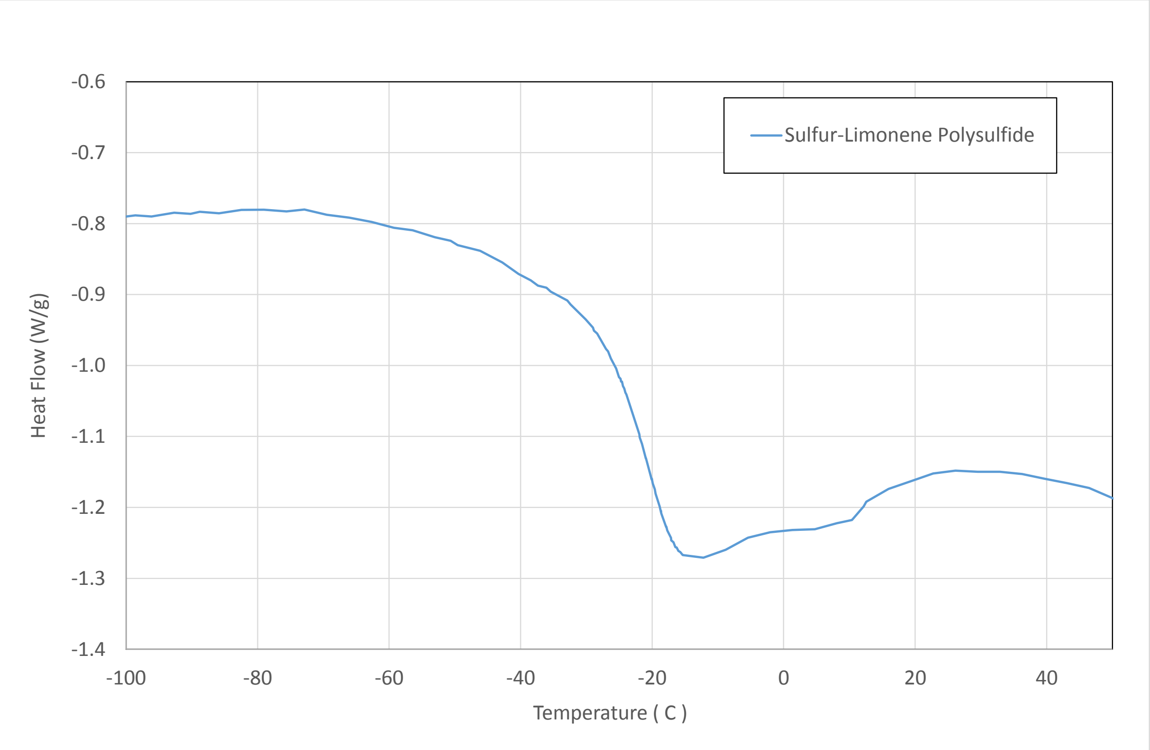
STA Plot 2. STA analysis of the sulfur-limonene polysulfide in nitrogen and air atmospheres (with time) – showing weight loss and temperature.



STA Plot 3. STA analysis of the sulfur-limonene polysulfide in nitrogen at 20 ºC/min and 5 ºC/min heating rates – showing weight loss and heat flow.

Differential Scanning Calorimetry (DSC)
The sulfur-limonene polysulfide was analyzed using a TA Instruments 2930 DSC with nitrogen furnace purge at 50ml/min. Samples were approximately 6 mg and sealed in aluminium hermetic pans. The sample was cooled to -100 ºC at 10 ºC/min, held for 5 minutes, and then heated to 150 ºC at 10 ºC/min.

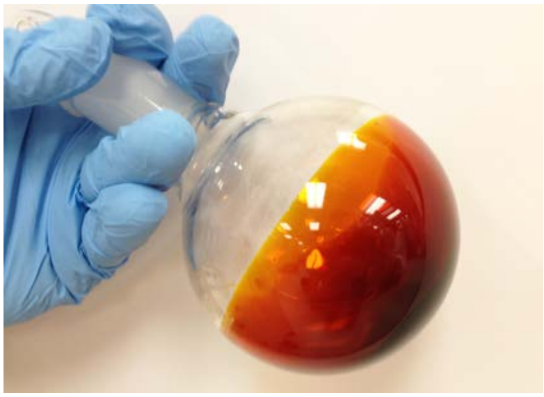
Results and Discussion of DSC (exotherm up):
The figure below shows the heat flow data from the heating step, revealing a step change characteristic of a glass transition temperature, with midpoint at -21 ºC. The transition is quite broad, which is due to the low molecular weight nature of the compound.



General procedures for molding and processing the sulfur-limonene polysulfide

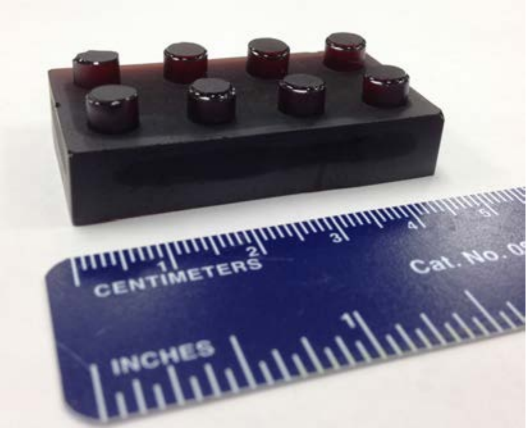
Using the sulfur-limonene polysulfide as a coating

The sulfur-limonene polysulfide was synthesized according to the general procedure, except no distillation was carried out. Accordingly, after 5 hours of reaction time at 170 ºC, the resulting mixture was used directly as a polysulfide coating in which the *p*-cymene and volatile products served as a solvent for the sulfur-limonene polysulfide. This solution can be applied to various non-metal surfaces and dried under vacuum or a stream of nitrogen. To transfer the coating, the polysulfide solution was typically heated to >100 ºC and decanted to a desired application device. For example, 10 g of the polysulfide solution was transferred to a 250 mL round bottom flask. The interior of the flask was then spin-coated using a rotary evaporator operating with a 70 ºC water bath (no vacuum was applied). After the flask was evenly coated it was removed and cooled at 0 ºC to fix the polysulfide coating. The coated flask was stored at room temperature.



Casting the sulfur-limonene polysulfide in a silicone mold

The sulfur-limonene polysulfide was synthesized according to the general procedure in which the volatile material was removed by distillation and high vacuum. The polysulfide was then poured into a silicone mold by heating the material to >100 ºC. This is conveniently executed by gentle heating with a heat gun while pouring into the mold. After the molten polysulfide was cast in the mold, it was cooled to room temperature and then incubated further at 4 ºC for 12 hours. After this time, the polysulfide was removed from the mold and stored at room temperature. A picture of the molded polysulfide is shown below.



Casting the sulfur-limonene polysulfide in a glass dish

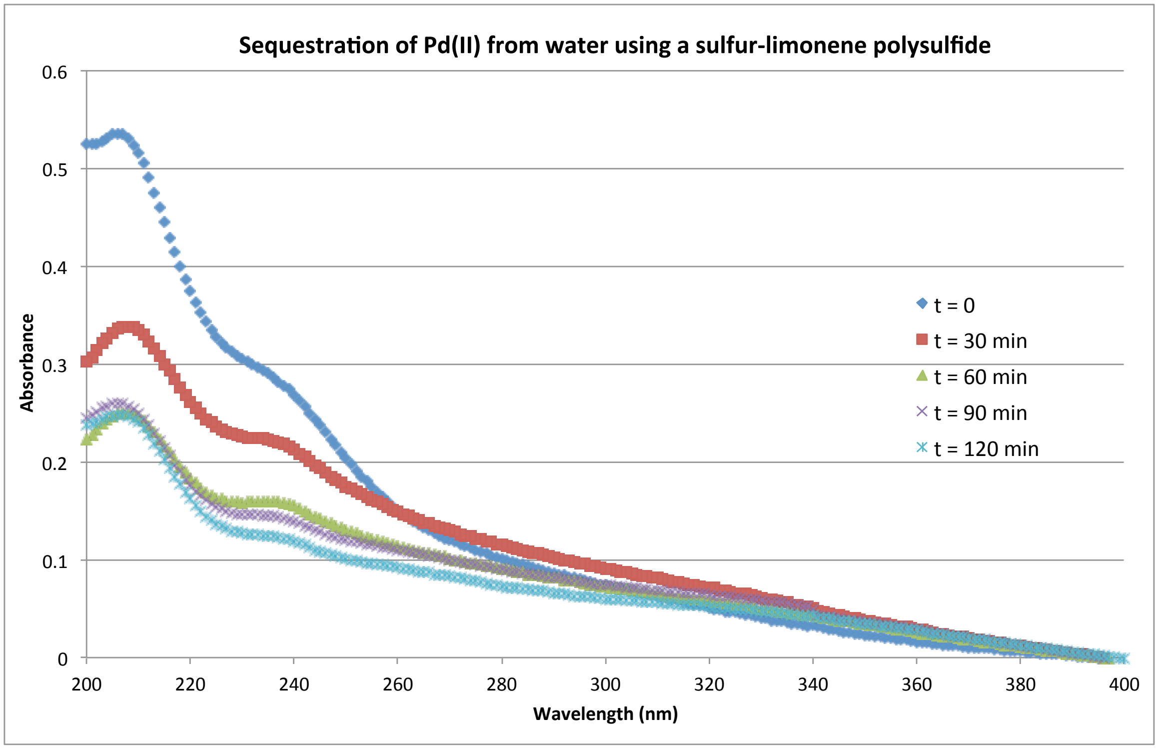
The sulfur-limonene polysulfide was synthesized according to the general procedure in which the volatile material was removed by distillation and high vacuum. The polysulfide was then heated to > 100 ºC and then poured into a glass petri dish (6 cm diameter). This transfer is conveniently executed by gentle heating with a heat gun while pouring into the petri dish. After the molten polysulfide is cast in the dish it was cooled to room temperature. A picture of the molded polysulfide is shown below. At a thickness of 3 mm, the polysulfide is red, but optically transparent such that an image can be viewed through the plate (see printed star on paper below plate).

Sequestration of palladium salts from aqueous solution using the sulfur-limonene polysulfide

Preparation of an aqueous Na_2PdCl_4 solution:
Palladium chloride (3.1 mg, 0.017 mmol) was added to a 50 mL volumetric flask along with sodium chloride (5.2 mg, 0.088 mmol) followed by 5 mL deionized water. The resulting mixture was dissolved by incubation in an ultrasonication bath for 10 minutes at room temperature. The resulting solution was then diluted to 50 mL with deionized water to provide a 0.35 mM aqueous solution of Na_2PdCl_4.

Palladium sequestration experiment:
A 10 mL aliquot of the Na_2PdCl_4 solution (0.35 mM in Pd) was added to a sulfur-limonene polysulfide plate (prepared in 6 cm glass petri dishes as described above). The solution was incubated at room temperature on the plates and the UV-Vis spectrum was measured every 30 minutes for 2 hours. In this measurement, an aliquot of the solution was transferred to a quartz cuvette and the UV-Vis spectrum was obtained before returning the solution to the plate. A clean cuvette was used for each measurement. UV-Vis spectra are shown on the following page.

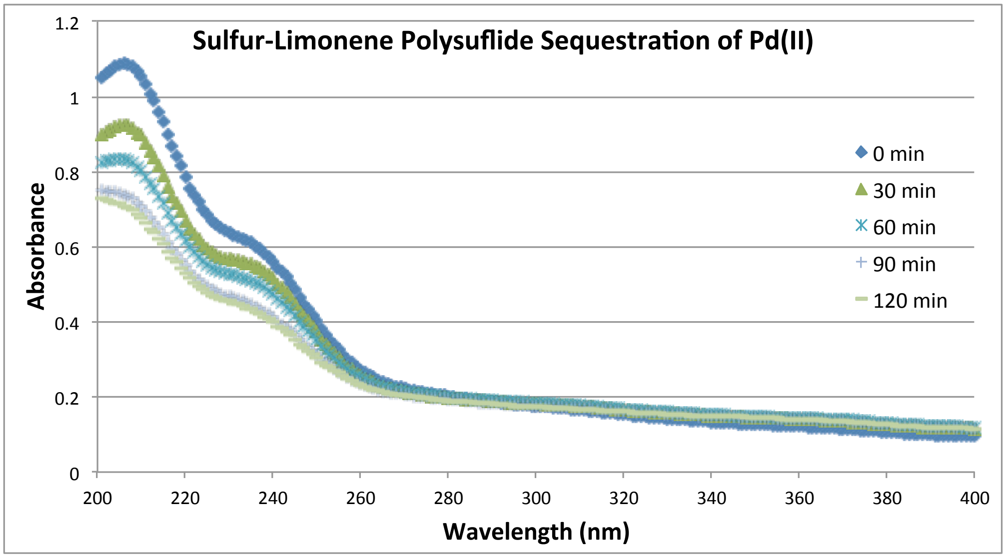
UV-Spectrum of Na_2PdCl_4 solution after incubation with sulfur-limonene polysulfide:

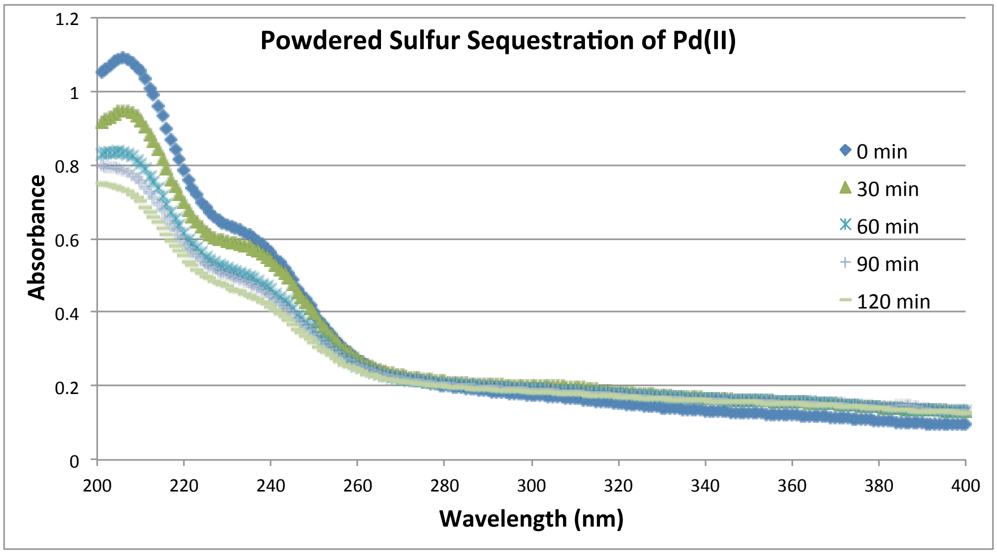


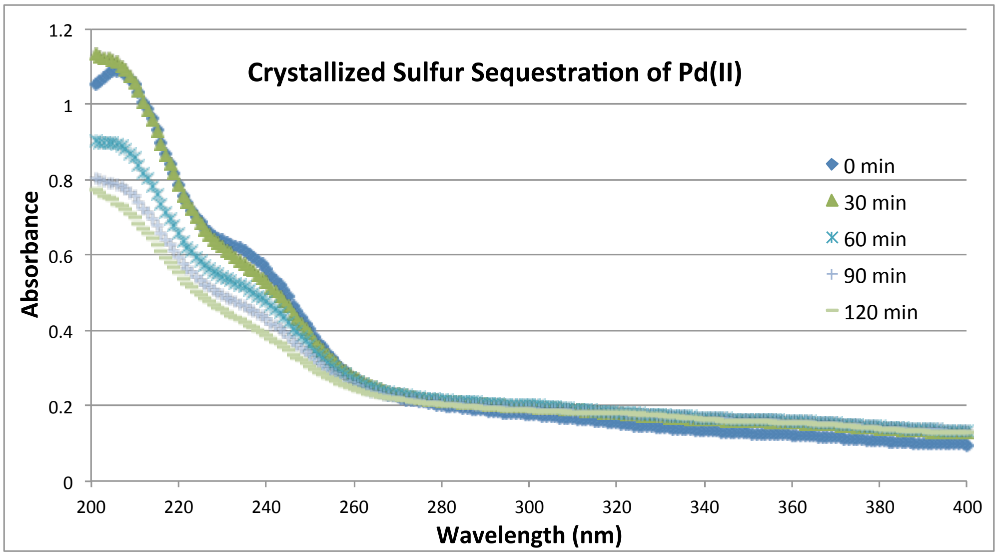
A decrease in absorbance at λ = 236 nm indicates removal of Na_2PdCl_4 from water. When the palladium solution was incubated in the absence of the polysulfide, no change in absorbance was observed. Based on a calibration curve constructed from absorbance values for known concentrations of Na_2PdCl_4, approximately 42% of the palladium was removed from the water.

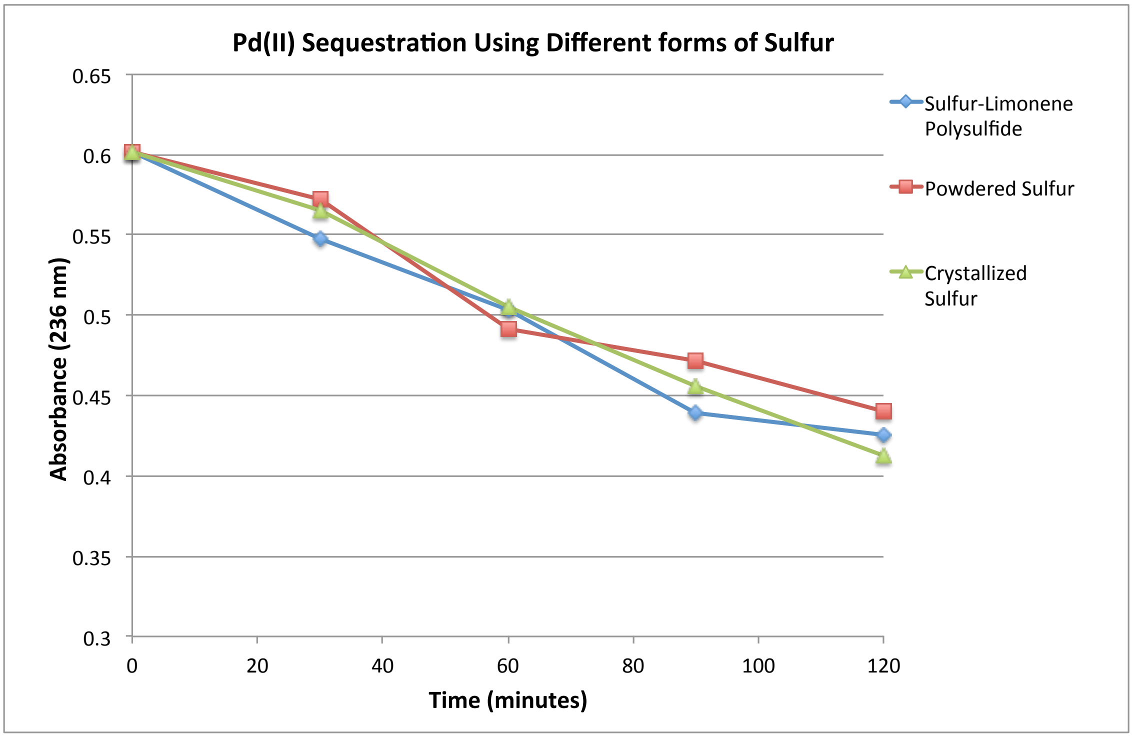
Direct comparison of Pd(II) sequestration for sulfur-limonene polysulfide, elemental sulfur (powdered) and elemental sulfur (crystalized).

Three separate 6 cm petri dishes were prepared. The first dish contained enough sulfur-limonene polysulfide to cover the bottom surface (5.5 g). The second dish contained elemental sulfur to cover the bottom surface when melted (9.0 g). This surface appears highly crystalline. The third dish contained elemental sulfur in powdered form (9.0 g). Next, an aqueous solution of Na_2PdCl_4 was prepared so that its absorbance at 236 nm was 0.6 absorbance units. A 12.0 mL aliquot of this solution was added to each of the petri dishes and incubated for 2 hours, while monitoring by the absorbance of this solution every 30 minutes by UV-Vis at 236 nm. The amount of Pd(II) in the water (inferred by its absorbance at λ_{max} = 236 nm) was reduced in all cases, with a comparable rate and sequestration between all samples over this time (the palladium was reduced by about 30% over this time for all samples). This experiment demonstrates that the sulfur-limonene polysulfide is as least as effective as elemental sulfur in removing palladium from water. The advantage of the sulfur-limonene polysulfide is its processibility (it can be a coating or molded), while elemental sulfur is brittle and highly crystalline under the same conditions. On the following two pages, a plot of how the absorbance due to Pd(II) changes over time is shown, along with UV-Vis spectra.


Sulfur-Limonene Polysuflide Sequestration of Pd(II)
Absorbance
1.2
1
0.8
0.6
0.4
0.2
0
200
220
240
260
280
300
320
340
360
380
400
Wavelength (nm)
0 min
30 min
60 min
90 min
120 min


Powdered Sulfur Sequestration of Pd(II)
Absorbance
1.2
1
0.8
0.6
0.4
0.2
0
200
220
240
260
280
300
320
340
360
380
400
Wavelength (nm)
0 min
30 min
60 min
90 min
120 min


Crystallized Sulfur Sequestration of Pd(II)
Absorbance
1.2
1
0.8
0.6
0.4
0.2
0
200
220
240
260
280
300
320
340
360
380
400
Wavelength (nm)
0 min
30 min
60 min
90 min
120 min


Pd(II) Sequestration Using Different forms of Sulfur
Absorbance (236 nm)
0.65
0.6
0.55
0.5
0.45
0.4
0.35
0.3
0
20
40
60
80
100
120
Time (minutes)
Sulfur-Limonene Polysulfide
Powdered Sulfur
Crystallized Sulfur

Sequestration of mercury(II) chloride from an aqueous solution using the sulfur-limonene polysulfide

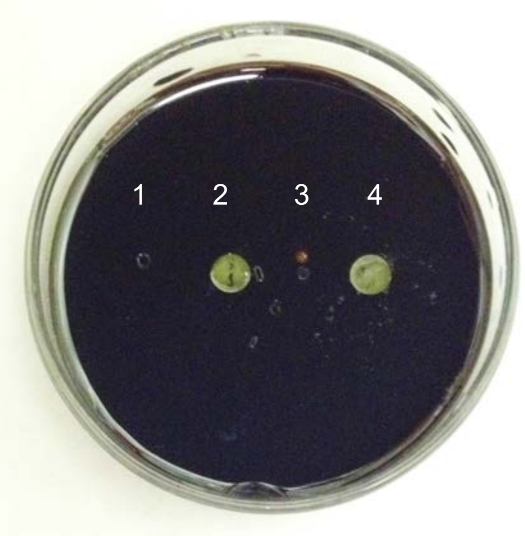
A stock solution of $HgCl_2$ was prepared by dissolving 36.0 mg $HgCl_2$ (133 mmol) in a total volume of 600 μL deionized water. A 0.3 μL aliquot of the stock solution was then diluted to 10.0 mL total volume in water to provide an aqueous solution that is 2000 ppb $HgCl_2$. All 10 mL of this solution was then added to the petri dish containing the sulfur-limonene polysulfide mold. The solution was covered and incubated for 24 hours at room temperature. After this time, the solution was removed from the plate and analyzed by cold vapor atomic absorption spectroscopy. The concentration of mercury(II) was measured to be 910 ppb. This experiment shows that a single incubation on a 28 cm^2 polysulfide plate results in removal of 55% of the mercury.

Detection of mercury(II) chloride in water and river water

A 2 μL aliquot of an aqueous $HgCl_2$ stock solution (60 mg/mL $HgCl_2$) was diluted to a total volume of 60 μL with deionized water (sample A) and 60 μL of Arkansas River water (sample B). 30 μL aliquots of these solutions (2 mg/mL $HgCl_2$) were then added to the surface of the polysulfide. The samples were incubated on the polysulfide mold for 24 hours at room temperature. A yellow deposit was visible in the samples containing mercury after less than 30 minutes of incubation. Control drops of deionized water (30 μL) or Arkansas River water (30 μL) did not produce any change in color. After 24 hours of incubation, the drops were removed by micropipette and the polysulfide surface was washed with deionized water (3 × 10 mL). The yellow deposits were not removed during the washing. This experiment demonstrates that mercury binding to the sulfur-limonene polysulfide can be visualized at certain concentrations and that the inorganic mercury adheres to the polysulfide. Notably, elemental sulfur (S_8) does not change color when exposed to $HgCl_2$ (see next page).

t = 0

t = 24 h, post-wash

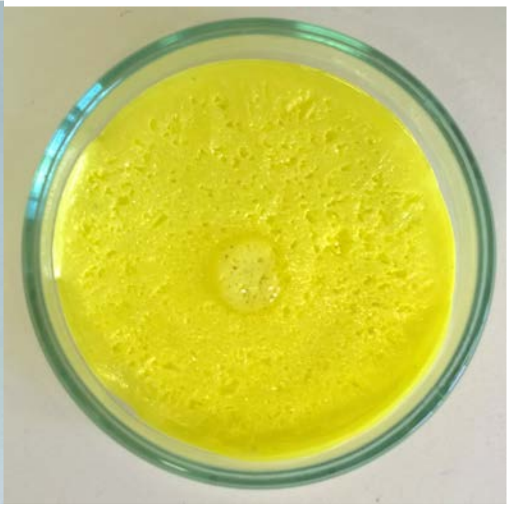


1 = DI H_2O
2 = $HgCl_2$ in H_2O (2 mg/mL)
3 = Arkansas River water
4 = $HgCl_2$ spiked Arkansas River water (2 mg/mL)

Sulfur does not change color when exposed to $HgCl_2$

Sulfur (~15 g) was added to a round bottom flask and melted. The molten sulfur was then poured in a 6 cm diameter petri dish and allowed to crystallize. To the crystallized sulfur was then added 200 μL of $HgCl_2$ (100 mM in H_2O). The sample was incubated for 24 hours. No color change was observed. This experiment illustrates an advantage of the sulfur-limonene polysulfide over elemental sulfur: the former changes color when exposed to 100 mM $HgCl_2$ while elemental sulfur is not an indicator (it does not change color).

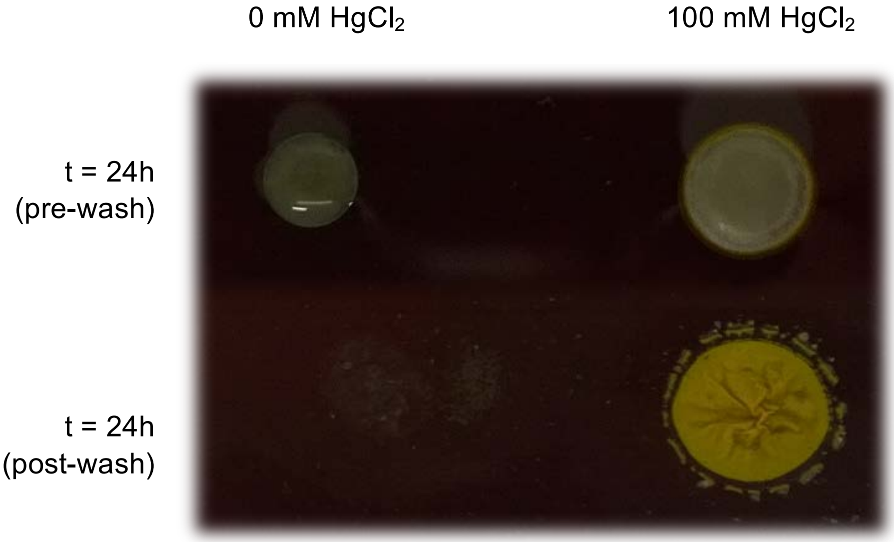
T = 0 ($HgCl_2$ Applied)



T = 24 hr (no color change)

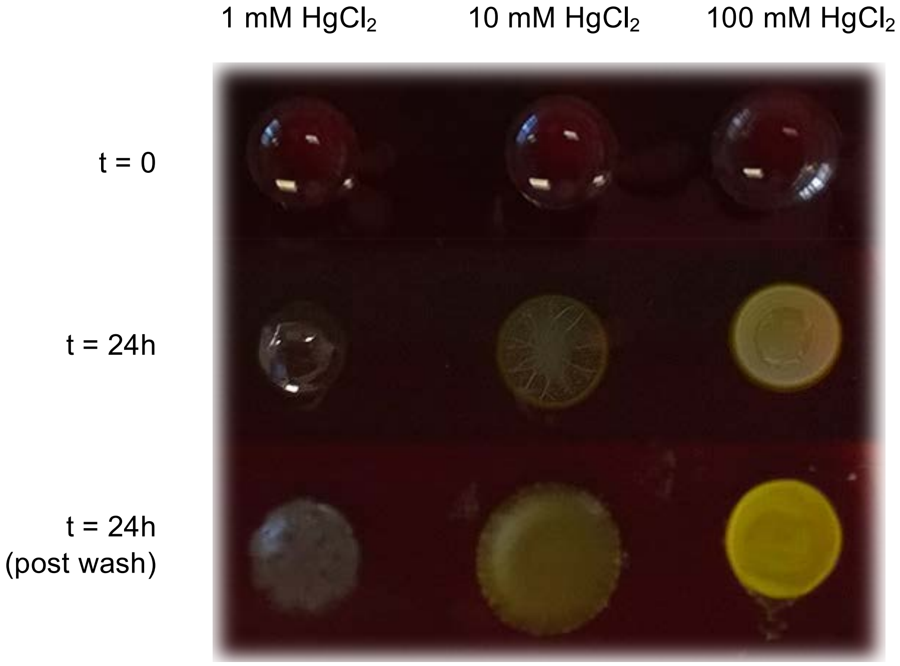
Detection of mercury in contaminated soil using the sulfur-limonene polysulfide

Pond mud and silt (~100 g) was obtained from the bank of the Flinders University Lake and suspended in 250 mL of water from the lake. Before the soil settled, an aliquot of the soil suspension was spiked with $HgCl_2$ so that the final concentration was 100 mM mercury(II). Two samples were then applied in 100 μL aliquots to a polysulfide plate: a 100 μL aliquot of mercury-free suspension of pond silt and a 100 μL aliquot of the pond silt suspension that had been spiked with 100 mM $HgCl_2$. The petri dish was covered and incubated for 24 hours at room temperature. After this time, both spots appear colored due to the presence of silt and mud (top of image t = 24h). However, after washing the plate with deionized water (3 × 10 mL) the sand and mud were removed. No residue remained on the mercury-free sample. A yellow deposit remained on the sample that contained mercury(II) (bottom of image, post-washing). This experiment indicates that inorganic mercury present in suspensions of mud or soil can bind to the polysulfide. Washing removes the soil and mud, while leaving the mercury deposit on the polysulfide.



Sensitivity assay in the colorimetric indication of mercury(II) binding to the polysulfide

To the surface of the polysulfide were added four solutions of aqueous $HgCl_2$: a 30 μL drop of 0.1 mM $HgCl_2$, a 30 μL drop of 1 mM $HgCl_2$, a 30 μL drop of 10 mM $HgCl_2$, and a 30 μL drop of 100 mM $HgCl_2$. The petri dish was covered and the drops were monitored over 24 hours. No color change was observed for the 0.1 mM $HgCl_2$. However, a visible deposit was observed for the 1 mM, 10 mM and 100 mM $HgCl_2$ samples (see figure below). After 24 hours, the plate was washed with deionized water (3 × 10 mL). The yellow deposits were not removed during the washing. This experiment demonstrates that mercury binding to the sulfur-limonene polysulfide can be visualized at as low as 1 mM $HgCl_2$ and that the inorganic mercury adheres to the polysulfide even after washing. The three samples that resulted in a color change are shown below. The same drop is shown for t = 0, t = 24 hours, and after washing.



Selectivity assay in the detection of mercury(II) chloride in water using the sulfur-limonene polysulfide

Stock solutions were prepared at 10 mM in H_2O for the following inorganic salts: $HgCl_2$, LiCl, $FeCl_3$, $CaCl_2$, $CuSO_4$, $PbCl_2$, $MgCl_2$, $ZnCl_2$, $NiCl_2$, KCl, and $MnCl_2$. A 30 μL aliquot of each solution was placed on a limonene-polysulfide plate and incubated for 24 hours. After 30 minutes of incubation, a yellow deposit from $HgCl_2$ sample was visible. No visible deposit was formed from any salts other than inorganic mercury. After 24 hours of incubation, the drops were removed by micropipette and the polysulfide surface was washed with deionized water (3 × 10 mL). The yellow deposits from the $HgCl_2$ sample were not removed during the washing. This experiment demonstrates that the color change is selective for $HgCl_2$.


t = 0

t = 24 h, post-wash

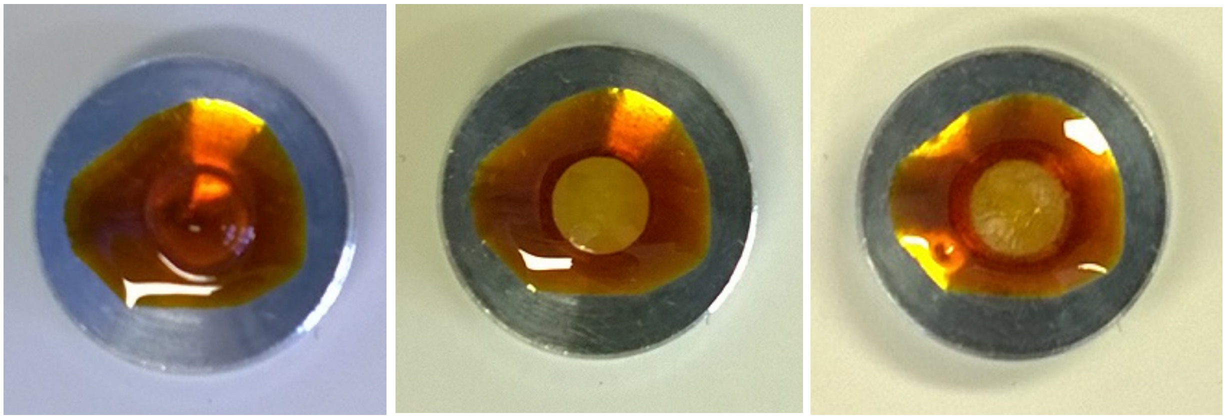
Key:
A1 = $HgCl_2$ B1 = LiCl C1 = $FeCl_3$ D1 = $CaCl_2$

A2 = $CuSO_4$ B2 = $PbCl_2$ C2 = $MgCl_2$ D2 = $ZnCl_2$

A3 = $NiCl_2$ B3 = KCl C3 = $MnCl_2$ D3 = H_2O only

SEM and EDX analysis of polysulfide after mercury(II) exposure

General protocol for preparing samples for SEM and EDX analysis: A sample of the polysulfide was transferred to a 12.7 mm aluminum SEM pin mount. Next, a 10 μL aliquot of 100 mM $HgCl_2$ was added (t = 0 in figure below). The sample was incubated at room temperature for 24 hours. Over this time, the area exposed to the mercury solution turned yellow (t = 24 hours in figure below). Next, water remaining from the mercury solution was then carefully removed by micropipette. Then, the area exposed to mercury was washed by applying 15 μL of deionized water onto the surface, incubating for 1 minute, and then removing by micropipette. This washing procedure was repeated a total of three times. The yellow deposit remained in tact during the washing (right image in figure below). Care was taken not to transfer any of the wash water to other regions of the sample.



t = 0
$HgCl_2$ solution applied

t = 24 hours
Yellow deposit formed

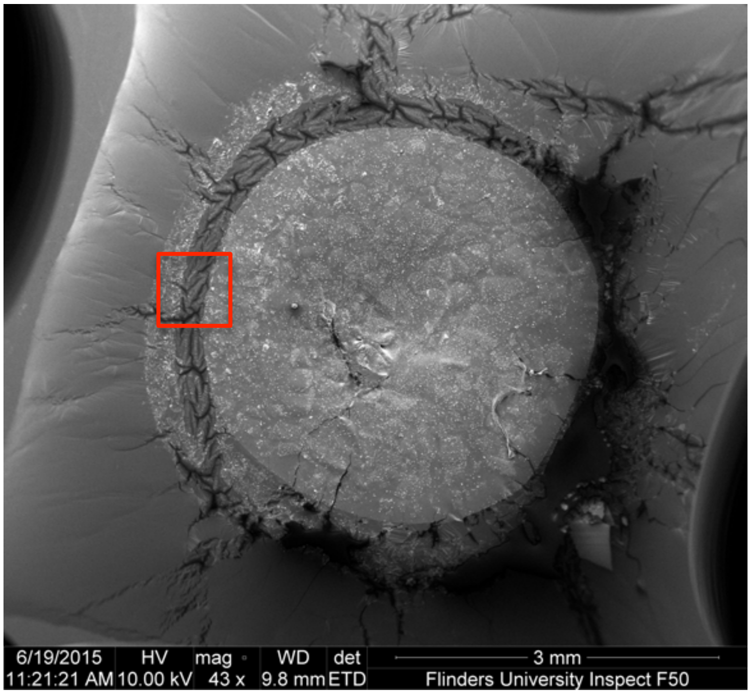
Sample after washing

The sample was then analyzed further by SEM and EDX to assess the surface morphology and elemental composition at various regions of the sample. The main goals in this assessment were to verify that the yellow deposit did indeed contain mercury and to study the morphology of the polysulfide in the mercury-free and mercury-treated regions.

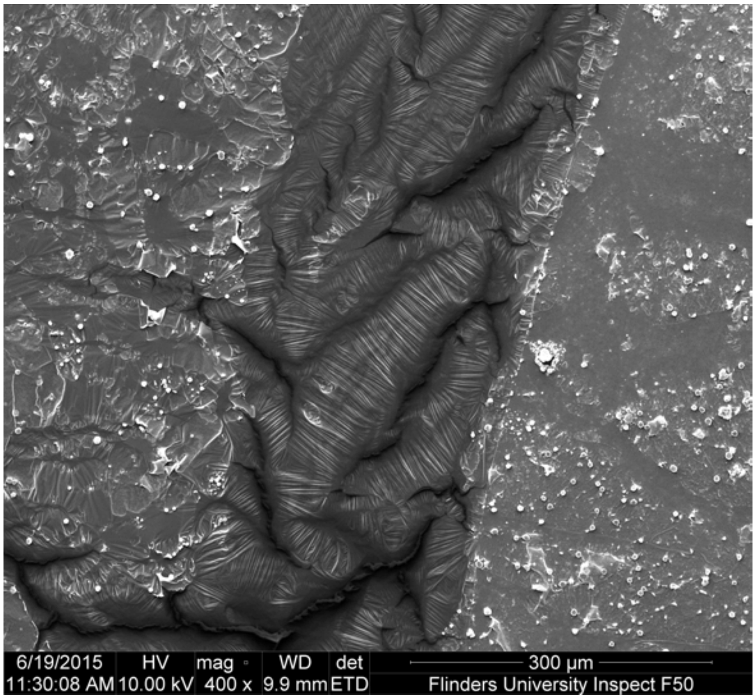
The sample was prepared by coating with 5 nm of platinum (99.99%, Proscitech) using a Quorumtech Q300T-D sputter coater. SEM and EDX analysis was then performed at a 10 kV accelerating voltage and spectra were acquired using 30 second integration time. Key SEM images are shown on the next two pages. EDX analysis is shown on pages S28-S41.

SEM Analysis

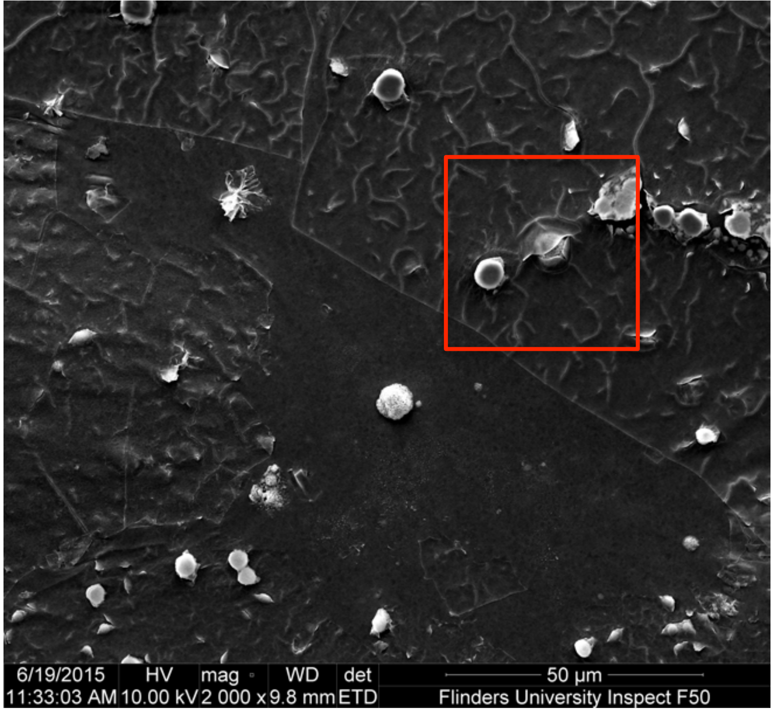
The first image is the full view of the yellow deposit formed upon exposure to $HgCl_2$. The smooth regions at the perimeter are areas that were not exposed to $HgCl_2$. The circular region was exposed to the $HgCl_2$ solution.



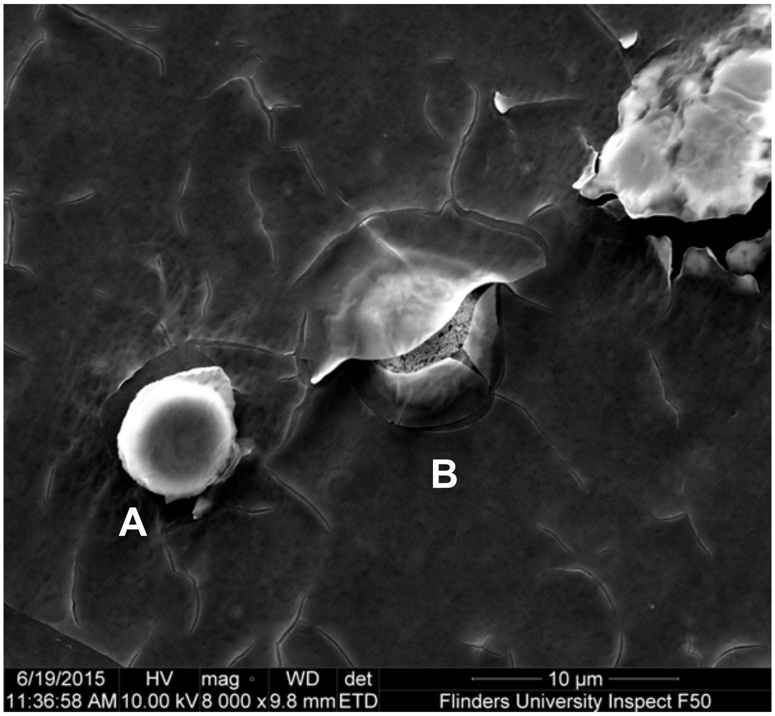
Magnfied SEM image for region indicated in the red box. This image shows the outer boundary of the region exposed to $HgCl_2$.



SEM image of region exposed to $HgCl_2$ solution (50 μm scale bar for top image; 10 μm scale bar bottom image). Exposure to $HgCl_2$ results in the formation of nano- and microstructures that contain mercury (see EDX analysis next). The surface of the polysulfide also appears to form ripples, ridges and other features upon exposure to $HgCl_2$.

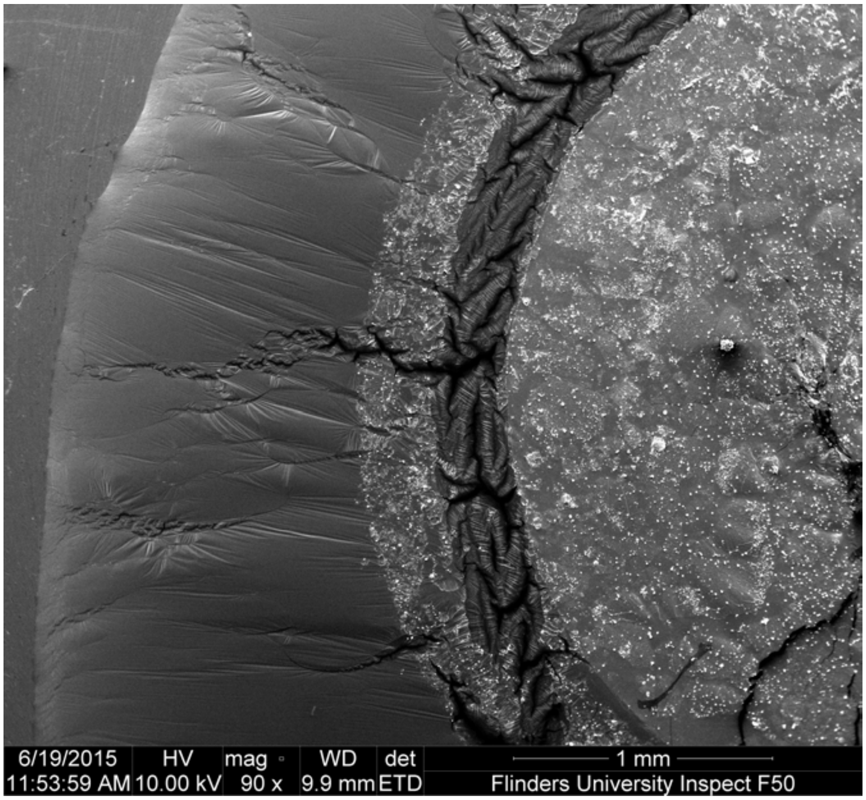


SEM image for region in the red box shown above. The mercury-containing particles (EDX – see next) were both bound to the surface of the polysulfide (A) and enveloped in the material (B).

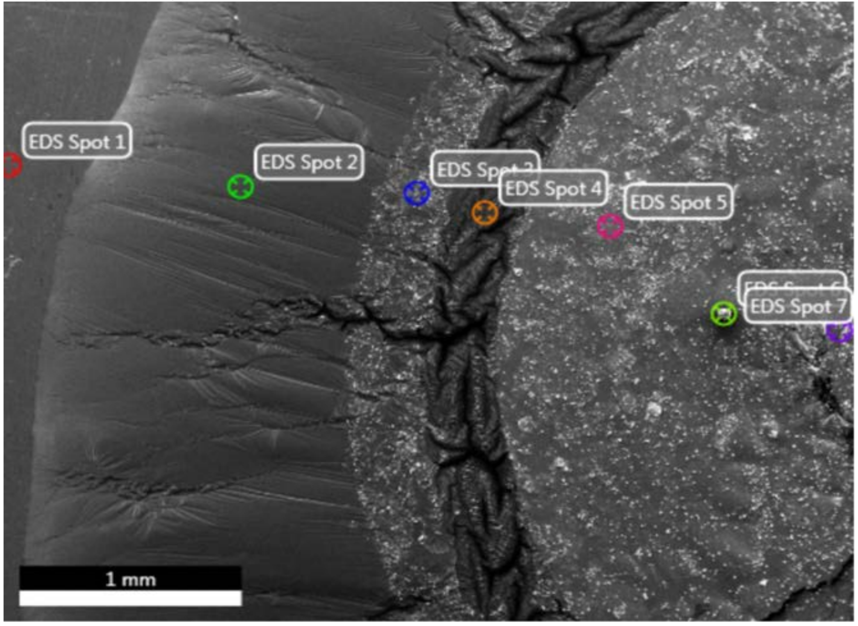


EDX Analysis I: survey of various regions of the polysulfide after exposure to $HgCl_2$.

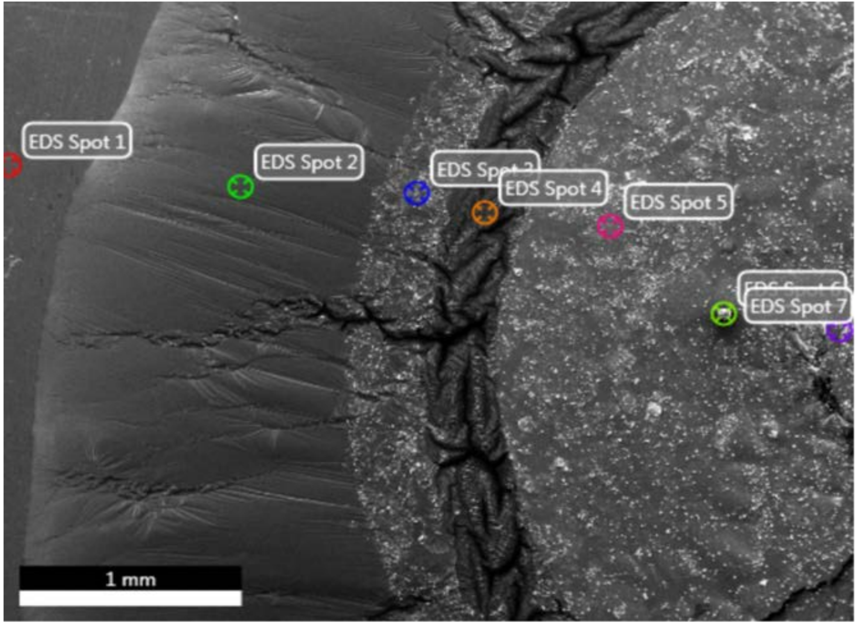
Reference SEM:



Regions analyzed by EDX (EDS Spots 1-7):

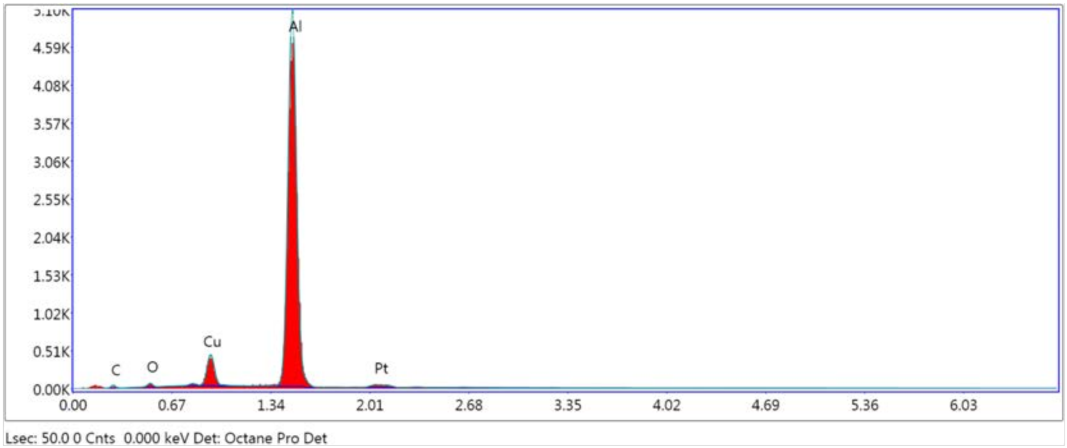


EDX Analysis I (EDS Spot 1) – Control analysis on region of aluminum SEM pin mount that was not exposed to the polysulfide. EDX analysis revealed a strong signal for Al.



kV: 10 Mag: 82 Takeoff: 33.9 Live Time(s): 50 Amp Time(μs): 1.92 Resolution:(eV) 122.7

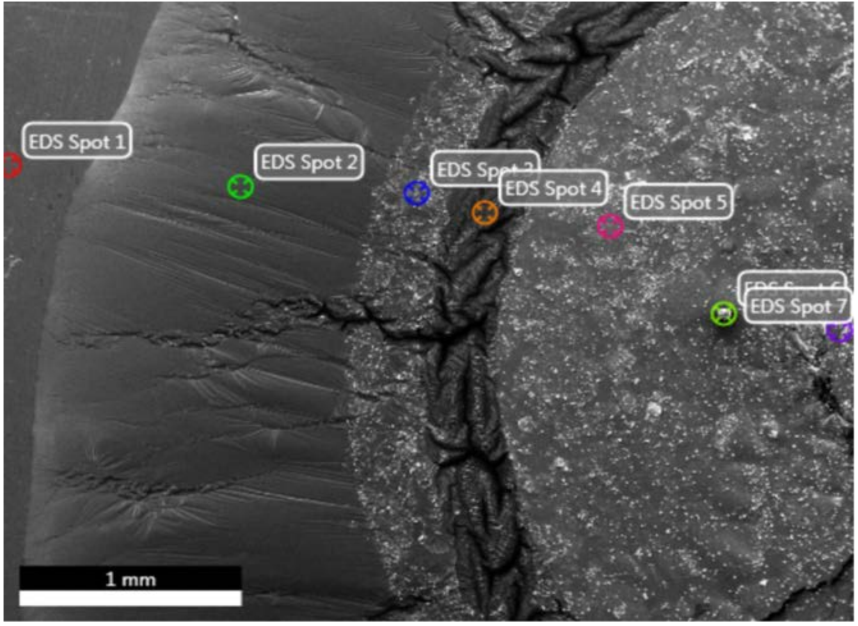
EDS Spot 1



eZAF Smart Quant Results

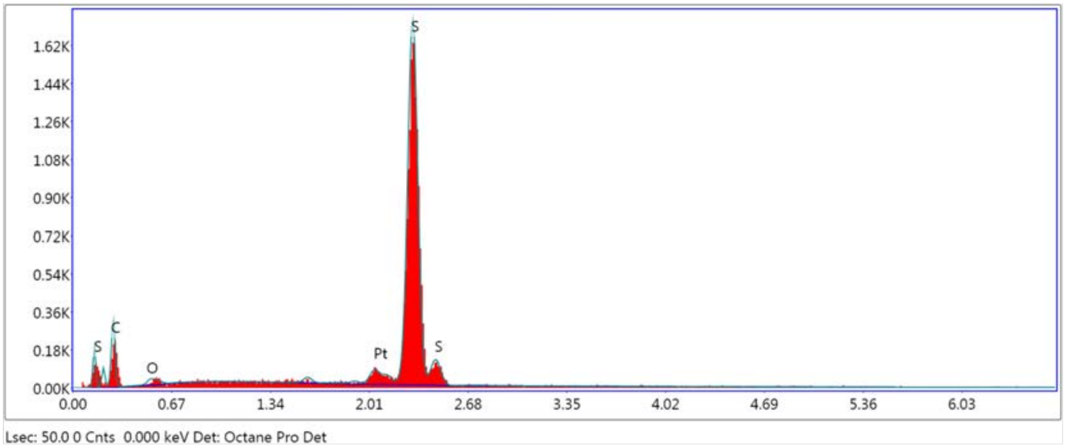
Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	R	A	F
C K	2.90	6.72	2.49	28.71	0.01	1.23	0.92	0.15	1
O K	0.86	1.49	3.65	25.98	0.00	1.17	0.95	0.49	1
CuL	8.09	3.54	34.78	7.44	0.08	0.84	1.11	1.13	1.06
AlK	85.14	87.82	670.39	3.21	0.81	1.02	0.99	0.94	1
PtM	3.01	0.43	5.48	23.74	0.02	0.62	1.31	0.99	1

EDX Analysis I (EDS Spot 2) – This is the region of the polysulfide that was not exposed to $HgCl_2$. This region showed the expected EDX signals for sulfur and carbon.



kV: 10 Mag: 82 Takeoff: 33.9 Live Time(s): 50 Amp Time(μs): 1.92 Resolution:(eV) 122.7

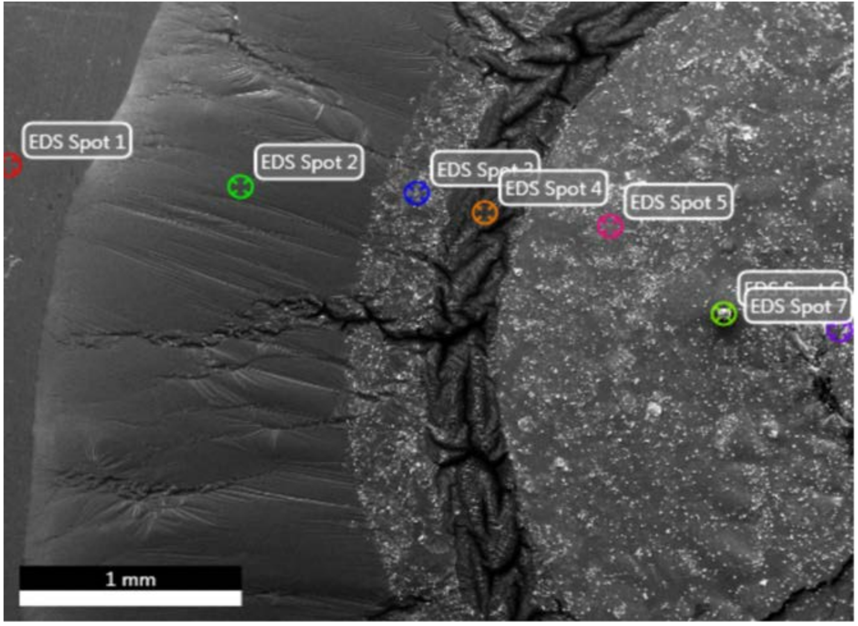
EDS Spot 2



eZAF Smart Quant Results

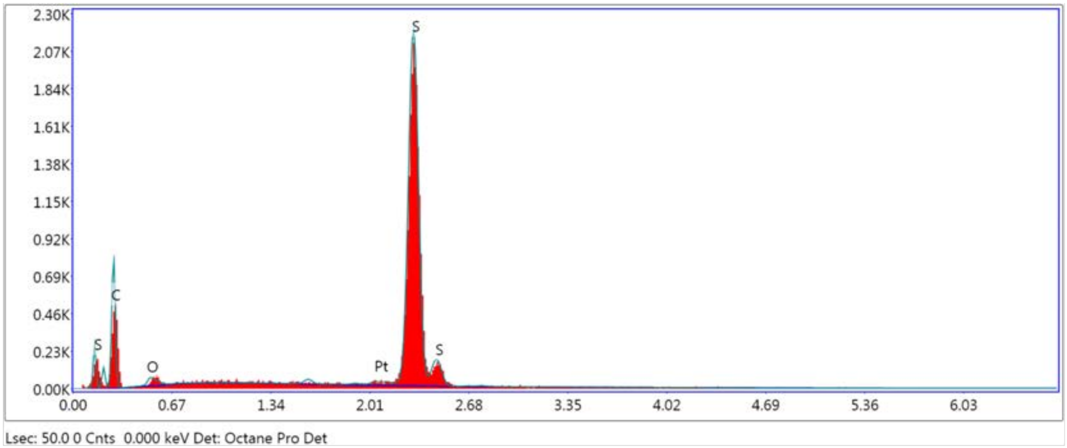
Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	R	A	F
C K	32.24	57.34	19.38	14.51	0.04	1.16	0.93	0.12	1
O K	0.40	0.53	0.88	99.99	0.00	1.09	0.96	0.29	1
PtM	4.94	0.54	10.13	18.60	0.04	0.58	1.32	1.2	1.06
S K	62.42	41.59	283.12	3.28	0.58	0.95	1.01	0.99	1

EDX Analysis I (EDS Spot 3) – This region is on the perimeter of the area of the polysulfide exposed to $HgCl_2$. While defects in the surface were observed, this area did not contain mercury.



kV: 10 Mag: 82 Takeoff: 33.9 Live Time(s): 50 Amp Time(μs): 1.92 Resolution:(eV) 122.7

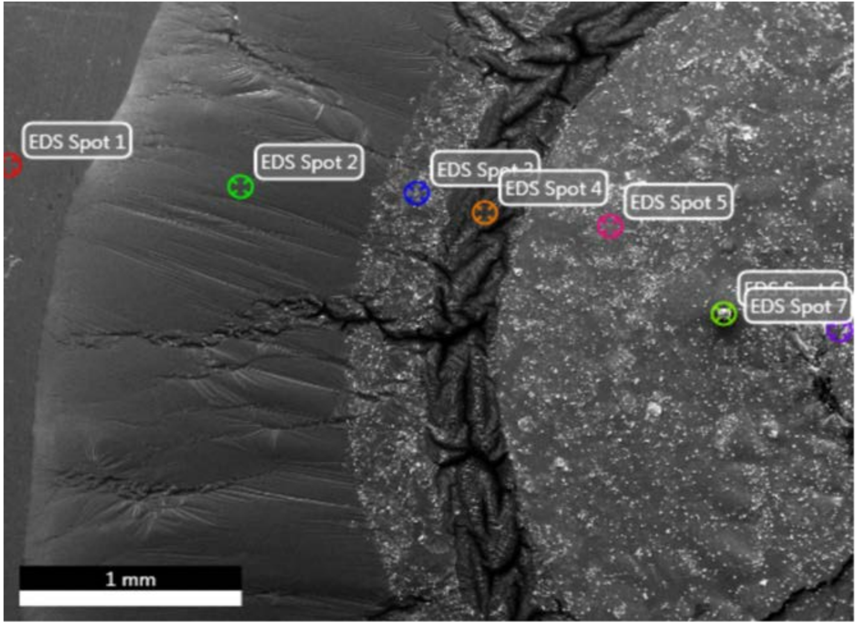
EDS Spot 3



eZAF Smart Quant Results

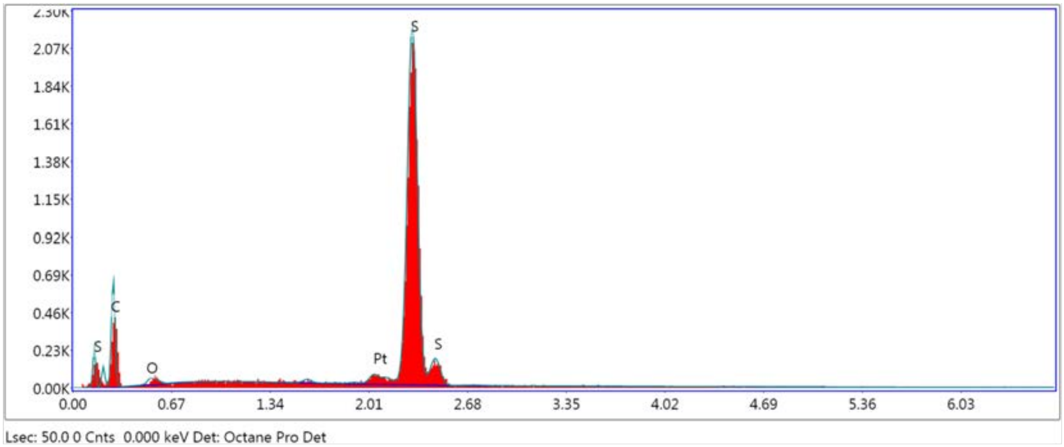
Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	R	A	F
C K	45.24	68.81	47.42	12.80	0.07	1.11	0.95	0.14	1
O K	0.80	0.92	2.53	40.31	0.00	1.05	0.97	0.28	1
PtM	0.99	0.09	3.03	30.12	0.01	0.55	1.34	1.21	1.07
S K	52.97	30.18	358.02	3.04	0.48	0.91	1.03	1	1

EDX Analysis I (EDS Spot 4) – This region is on the perimeter of the area of the polysulfide exposed to $HgCl_2$. While defects in the surface were observed, this area did not contain mercury.



kV: 10 Mag: 82 Takeoff: 33.9 Live Time(s): 50 Amp Time(μs): 1.92 Resolution:(eV) 122.7

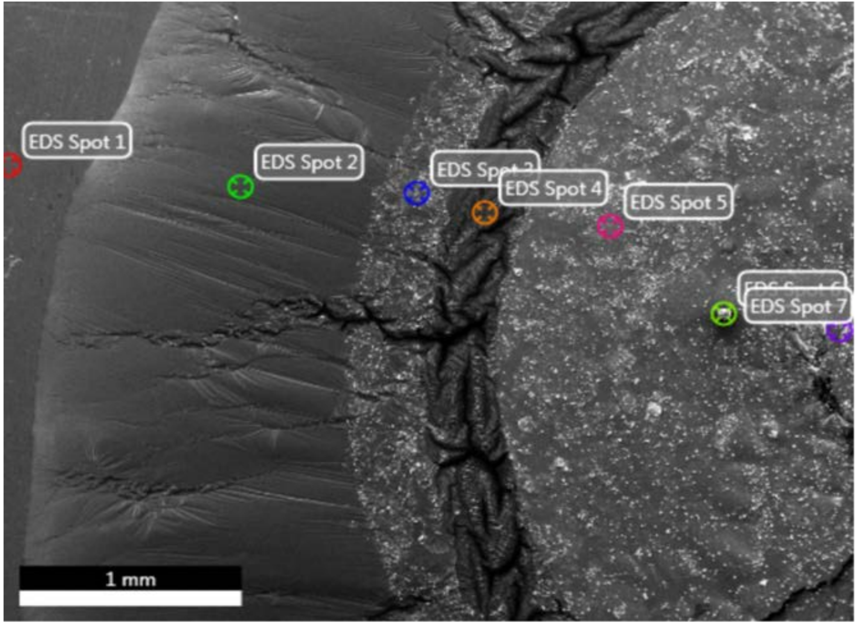
EDS Spot 4



eZAF Smart Quant Results

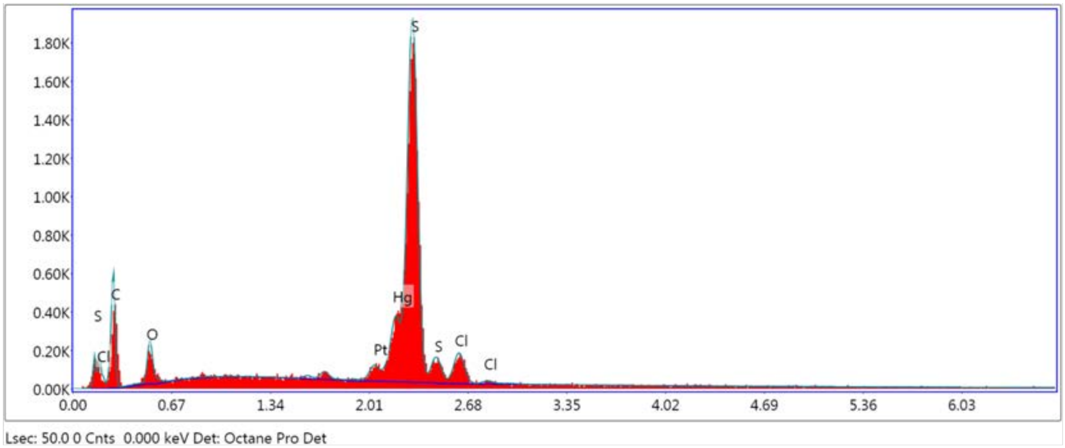
Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	R	A	F
C K	40.86	65.65	39.09	13.16	0.06	1.13	0.94	0.13	1
O K	0.49	0.59	1.49	67.59	0.00	1.07	0.97	0.29	1
PtM	3.08	0.30	8.99	19.33	0.02	0.56	1.33	1.21	1.06
S K	55.57	33.45	358.55	3.13	0.51	0.93	1.02	0.99	1

EDX Analysis I (EDS Spot 5) – This region of the polysulfide was exposed to the $HgCl_2$ solution. A clear signal for mercury was observed by EDX.



kV: 10 Mag: 82 Takeoff: 33.9 Live Time(s): 50 Amp Time(μs): 1.92 Resolution:(eV) 122.7

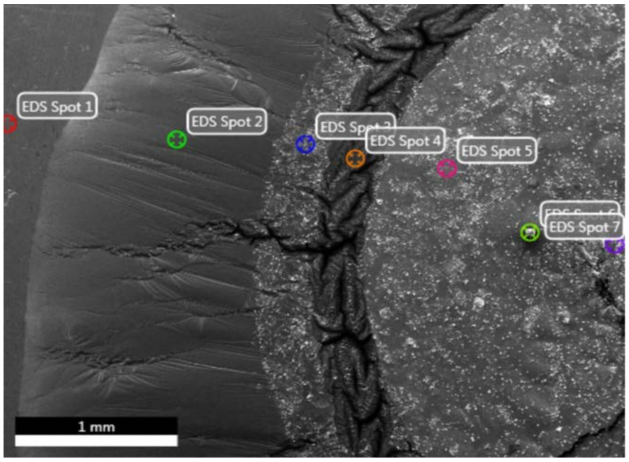
EDS Spot 5

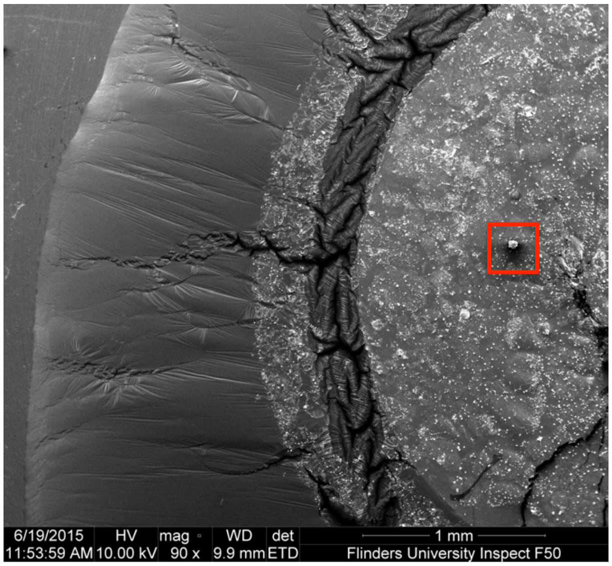


eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	R	A	F
C K	27.86	56.14	33.73	13.15	0.05	1.24	0.9	0.15	1
O K	4.41	6.66	16.14	14.73	0.02	1.17	0.92	0.31	1
PtM	3.74	0.46	11.57	19.06	0.03	0.62	1.28	1.18	1.03
HgM	17.62	2.13	50.61	9.09	0.13	0.62	1.29	1.15	1.02
S K	40.92	30.89	288.47	3.56	0.40	1.02	0.99	0.96	1
ClK	5.45	3.72	27.76	12.10	0.05	0.97	0.99	0.86	1

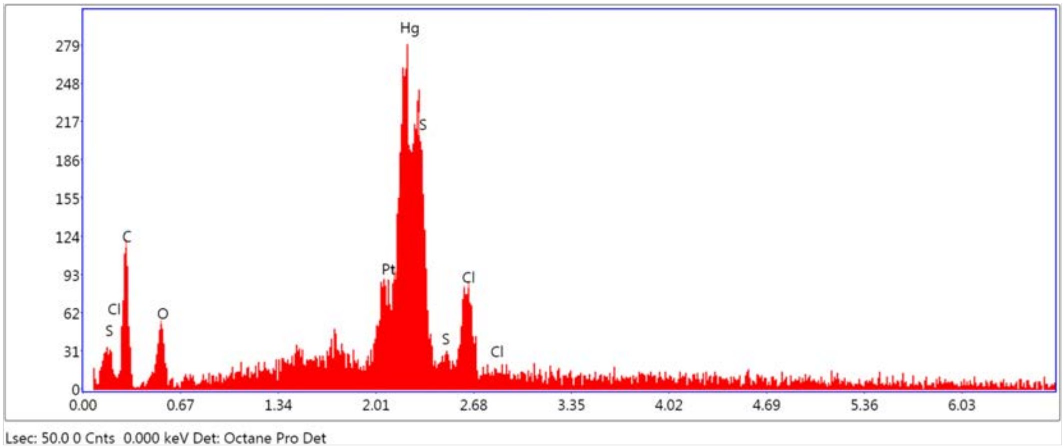
EDX Analysis I (EDS Spot 6) – This region of the polysulfide contains a microparticle (red box, right image) that was produced upon exposure to the $HgCl_2$ solution. EDX revealed this particle to contain high levels of mercury, sulfur and carbon.





kV: 10 Mag: 82 Takeoff: 33.9 Live Time(s): 50 Amp Time(µs): 1.92 Resolution:(eV) 122.7

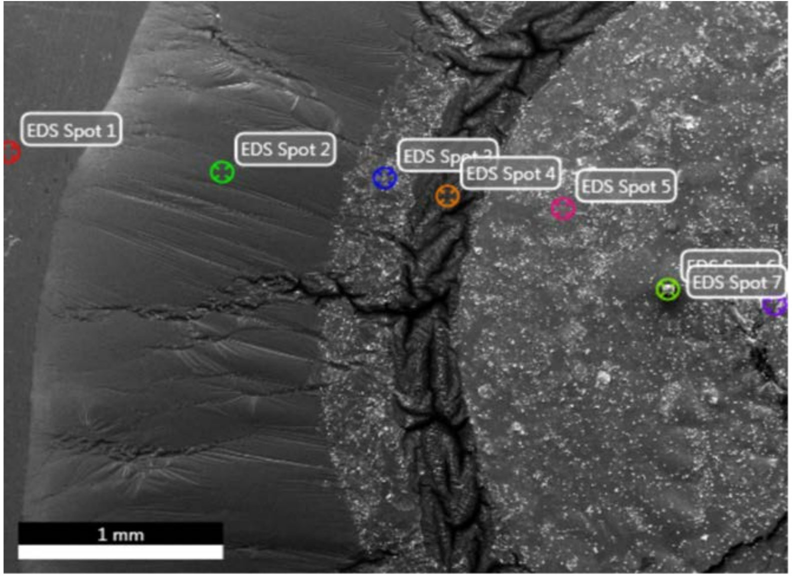
EDS Spot 6



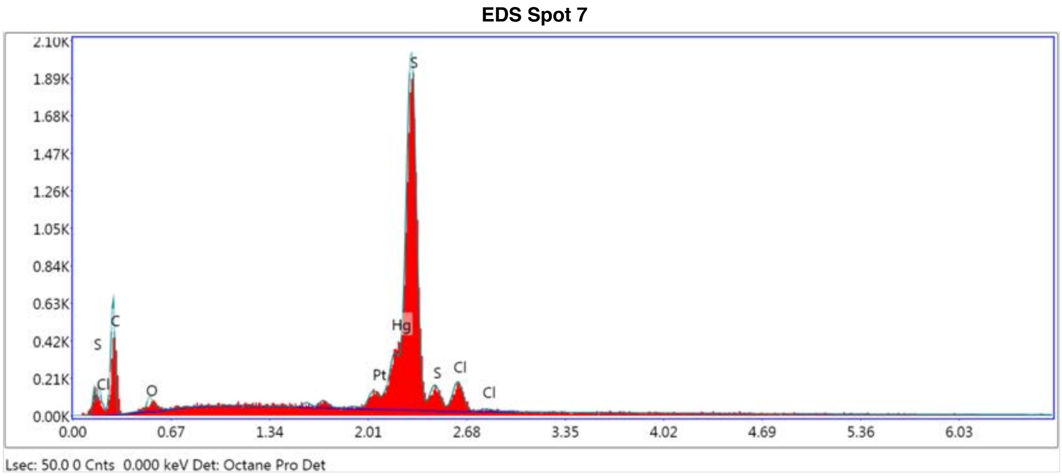
eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	R	A	F
C K	15.83	54.26	8.55	15.32	0.06	1.52	0.79	0.23	1
O K	3.93	10.11	4.21	21.90	0.02	1.45	0.81	0.31	1
PtM	11.32	2.39	9.30	14.85	0.10	0.78	1.16	1.1	1.01
HgM	50.20	10.30	38.36	8.07	0.41	0.77	1.17	1.07	1
S K	9.79	12.57	18.33	11.34	0.11	1.28	0.9	0.88	1.01
ClK	8.93	10.37	12.36	13.30	0.09	1.22	0.9	0.8	1

EDX Analysis I (EDS Spot 7) – This region of the polysulfide was exposed to the $HgCl_2$ solution. A clear signal for mercury was observed by EDX.



kV: 10 Mag: 82 Takeoff: 33.9 Live Time(s): 50 Amp Time(μs): 1.92 Resolution:(eV) 122.7

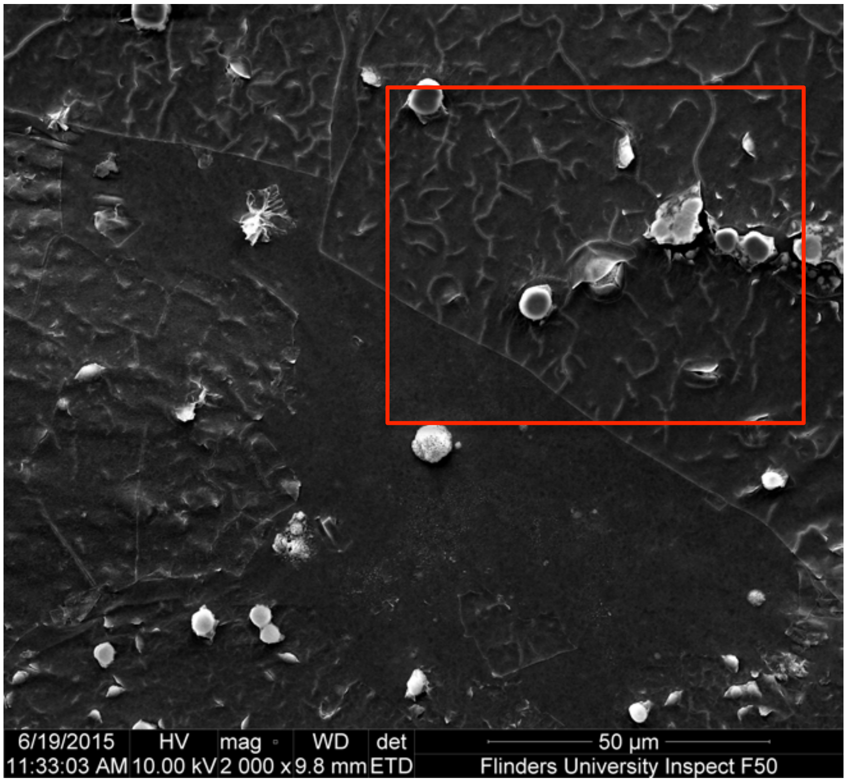


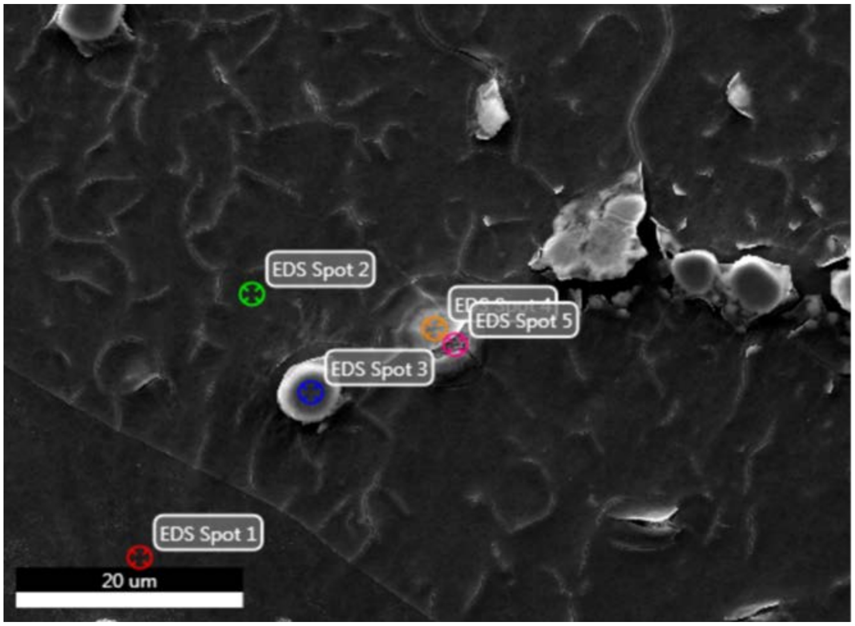
<u>eZAF Smart Quant Results</u>

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	R	A	F
C K	30.14	60.24	36.55	13.06	0.05	1.23	0.9	0.15	1
O K	1.18	1.78	4.32	25.88	0.00	1.17	0.92	0.3	1
PtM	4.54	0.56	14.48	16.70	0.03	0.62	1.29	1.18	1.03
HgM	16.23	1.94	47.95	9.26	0.12	0.61	1.29	1.15	1.02
S K	42.38	31.74	307.10	3.52	0.42	1.02	0.99	0.96	1
ClK	5.52	3.74	28.87	11.63	0.05	0.97	0.99	0.85	1

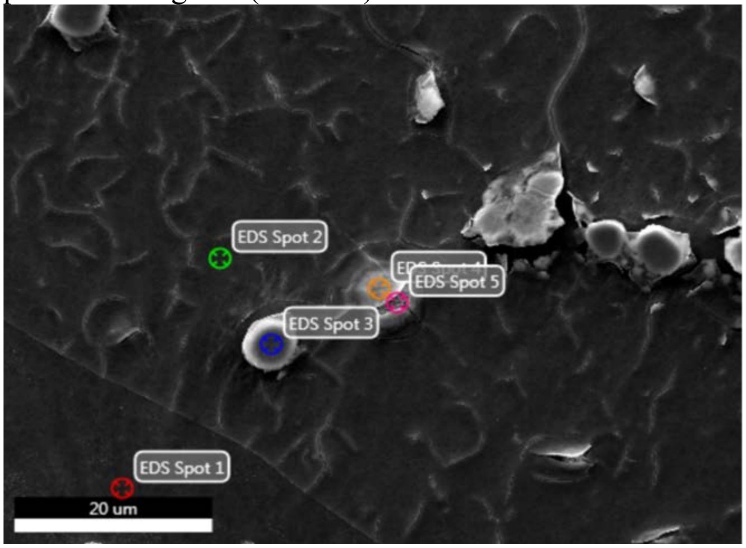
EDX Analysis II: Region of polysulfide where Hg particles are formed.

The region indicated below in the red box was analyzed by EDX. This region was exposed to the $HgCl_2$ solution. In this analysis, a comparison was made between the smooth regions and the regions containing particles. All regions contained mercury, but the particles contained a far higher amount of mercury (% weight and % atom) than the smooth regions.



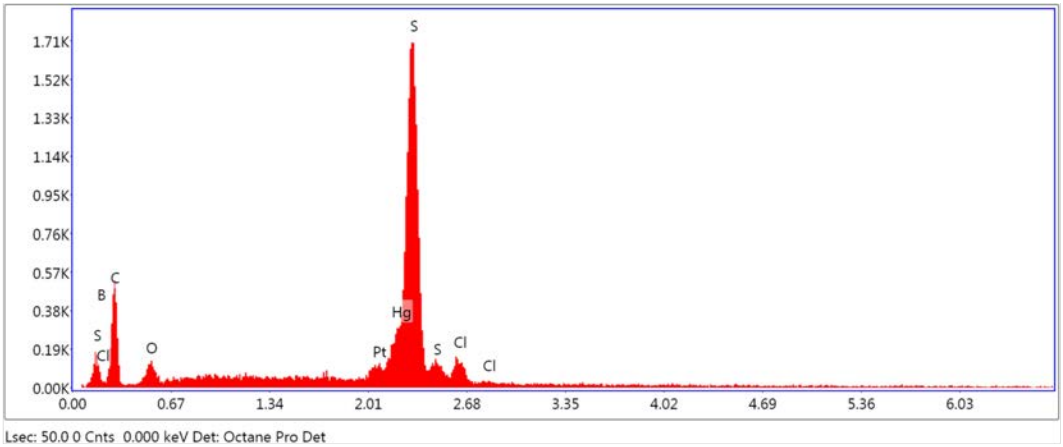


EDX Analysis II (EDS Spot 1) – This area was part of the region exposed to $HgCl_2$ and appears smooth. A relatively low percentage of Hg (7 wt%) was observed by EDX in comparison to the particulate regions (see next).



kV: 10 Mag: 3625 Takeoff: 33.8 Live Time(s): 50 Amp Time(μs): 1.92 Resolution:(eV) 122.7

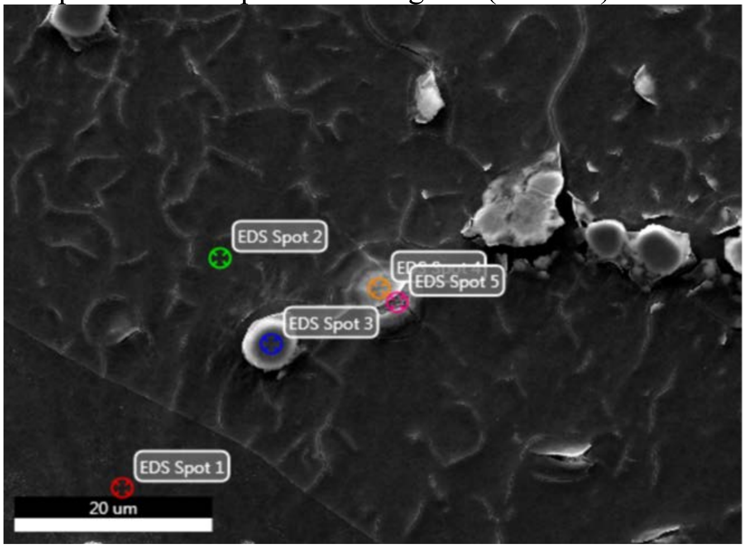
EDS Spot 1



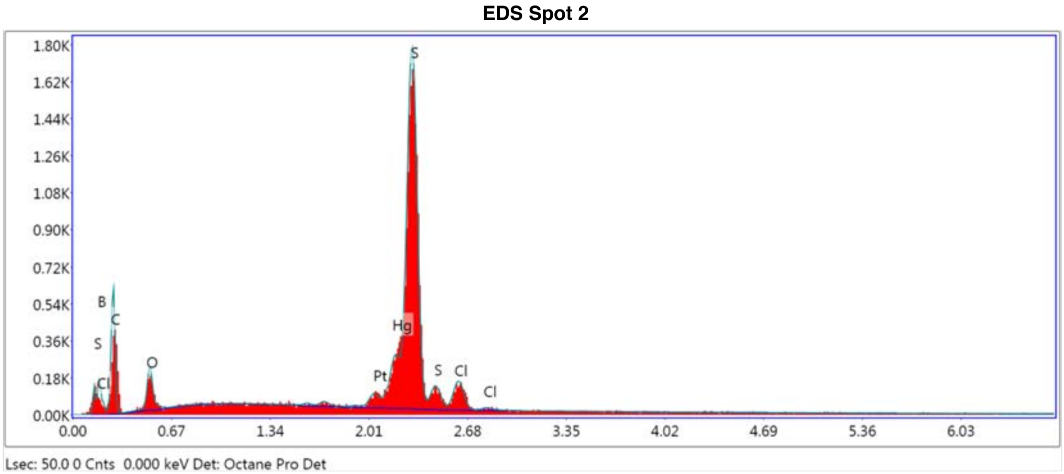
eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	R	A	F
B K	27.47	41.38	10.04	15.64	0.05	1.08	0.94	0.17	1
C K	29.78	40.39	44.01	12.99	0.04	1.13	0.95	0.13	1
O K	1.65	1.68	8.57	19.88	0.01	1.07	0.97	0.31	1
PtM	2.29	0.19	10.11	18.88	0.02	0.56	1.33	1.21	1.03
HgM	7.54	0.61	31.04	11.63	0.05	0.56	1.33	1.19	1.02
S K	28.46	14.46	285.36	3.27	0.26	0.93	1.02	0.99	1
ClK	2.81	1.29	21.17	11.24	0.02	0.88	1.03	0.92	1

EDX Analysis II (EDS Spot 2) – This area was part of the region exposed to $HgCl_2$ and appears as a rippled sheet. A relatively low percentage of Hg (10 wt%) was observed by EDX in comparison to the particulate regions (see next).



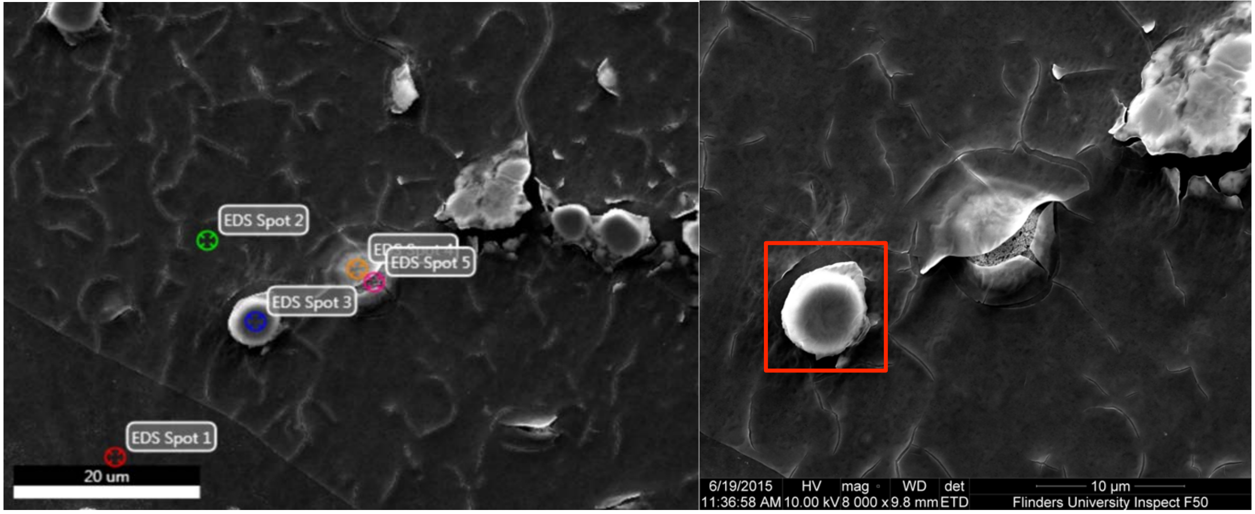
kV: 10 Mag: 3625 Takeoff: 33.8 Live Time(s): 50 Amp Time(μs): 1.92 Resolution:(eV) 122.7



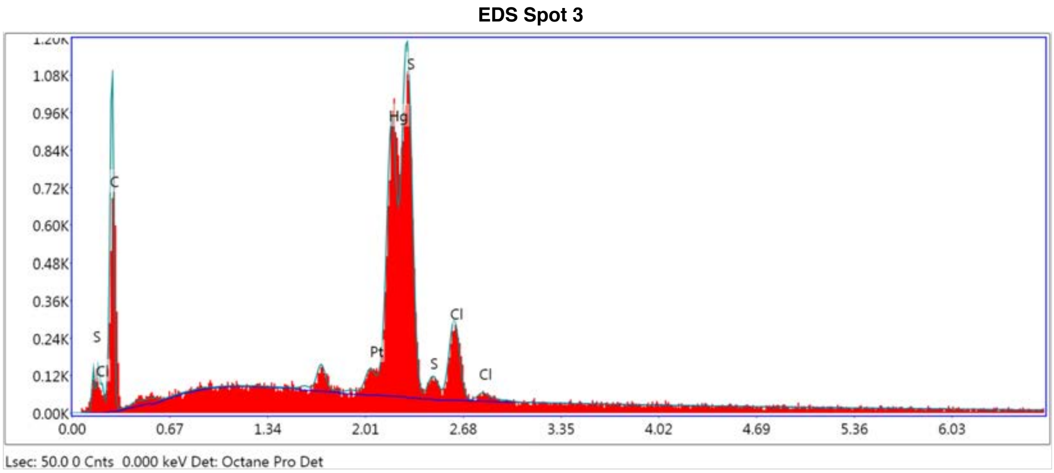
eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	R	A	F
B K	25.36	40.60	8.29	16.57	0.05	1.1	0.92	0.16	1
C K	25.92	37.36	35.04	13.28	0.04	1.15	0.94	0.13	1
O K	2.95	3.20	14.40	17.21	0.01	1.09	0.96	0.32	1
PtM	2.35	0.21	9.55	19.95	0.02	0.58	1.32	1.21	1.03
HgM	10.21	0.88	38.50	10.75	0.07	0.57	1.32	1.18	1.02
S K	29.66	16.02	273.28	3.40	0.28	0.95	1.02	0.98	1
ClK	3.54	1.73	24.41	11.36	0.03	0.9	1.02	0.91	1

EDX Analysis II (EDS Spot 3) – This area was part of the region exposed to $HgCl_2$. A microparticle (EDS Spot 3, left and red box, right) was formed that appeared to be bound to the surface of the polysulfide. EDX analysis revealed this particle to contain a high proportion of mercury (46 wt%).



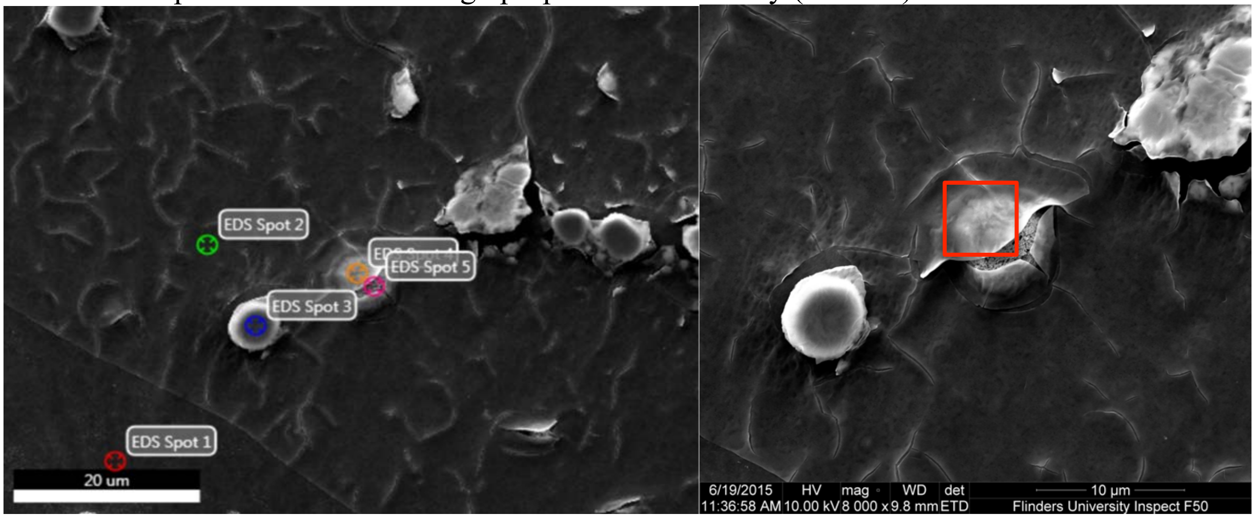
kV: 10 Mag: 3625 Takeoff: 33.8 Live Time(s): 50 Amp Time(µs): 1.92 Resolution:(eV) 122.7



eZAF Smart Quant Results

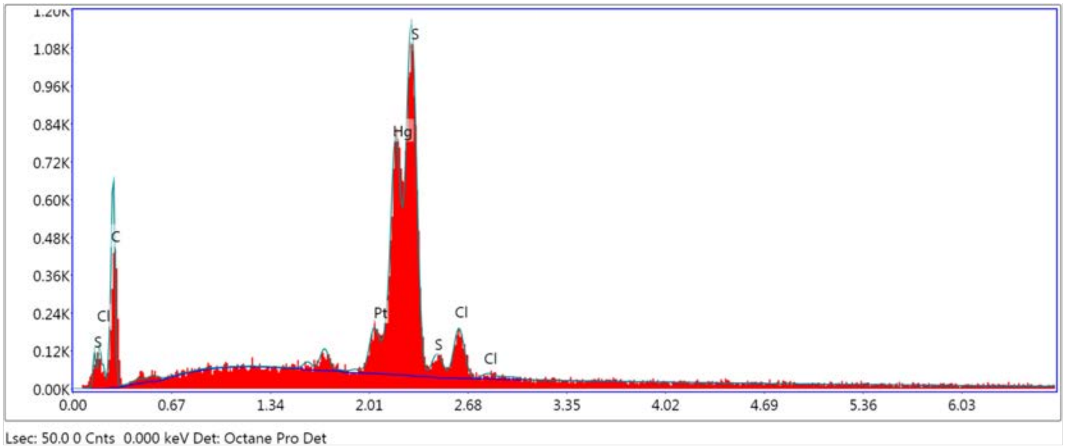
Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	R	A	F
C K	28.25	71.50	58.54	11.59	0.09	1.4	0.83	0.23	1
PtM	2.98	0.46	9.77	19.95	0.02	0.71	1.21	1.14	1.01
HgM	45.76	6.94	140.71	6.03	0.36	0.7	1.22	1.11	1.01
S K	14.99	14.21	113.33	5.60	0.16	1.17	0.93	0.92	1.01
ClK	8.02	6.88	44.56	10.16	0.07	1.11	0.94	0.83	1

EDX Analysis II (EDS Spot 4) – This area was part of the region exposed to $HgCl_2$. A microparticle was formed that appeared to be enveloped by the polysulfide. EDX analysis revealed this particle to contain a high proportion of mercury (46 wt%).



kV: 10 Mag: 3625 Takeoff: 33.8 Live Time(s): 50 Amp Time(μs): 1.92 Resolution:(eV) 122.7

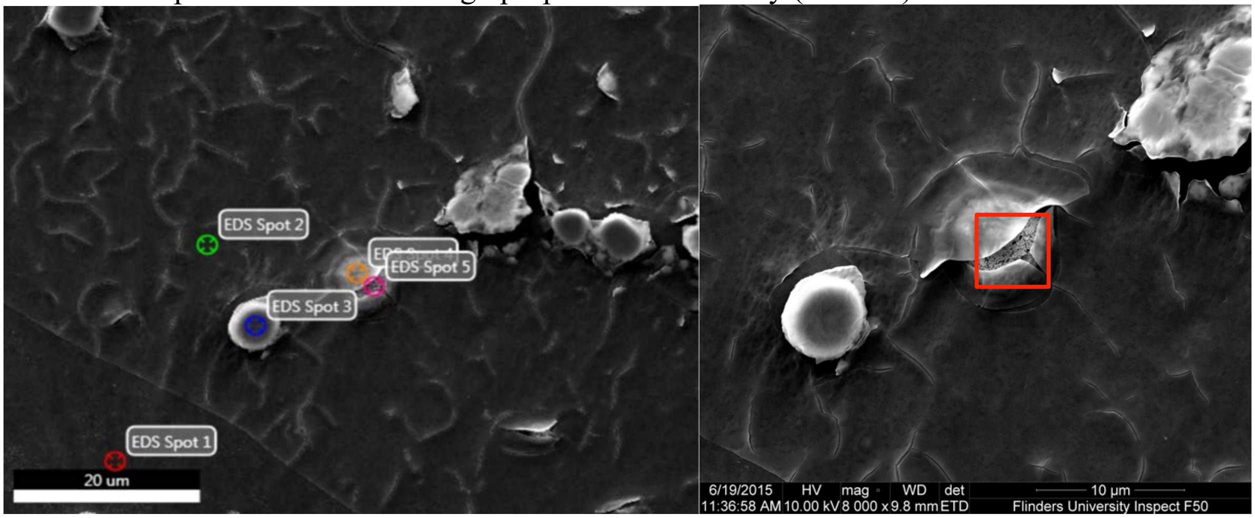
EDS Spot 4



eZAF Smart Quant Results

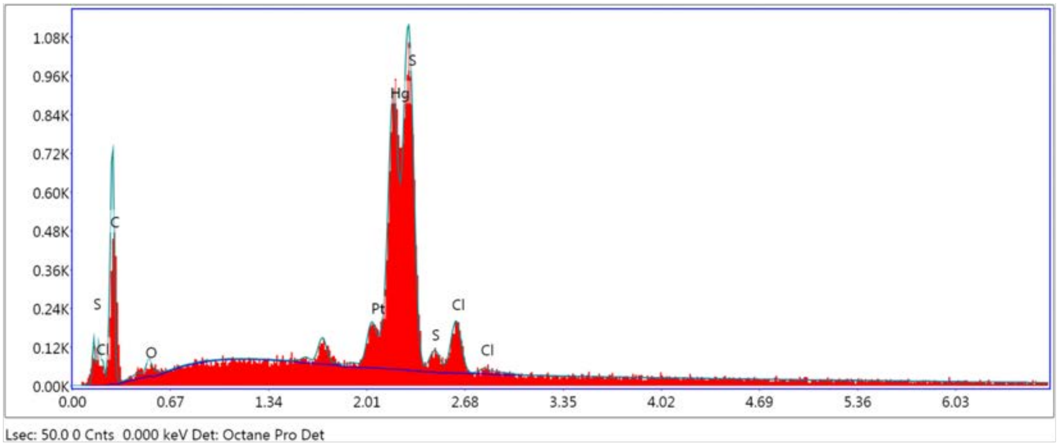
Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	R	A	F
C K	21.09	62.80	33.89	12.44	0.06	1.45	0.81	0.21	1
PtM	7.22	1.32	19.86	14.74	0.06	0.74	1.19	1.12	1.01
HgM	46.38	8.27	119.05	6.21	0.37	0.73	1.19	1.09	1.01
S K	19.37	21.61	122.04	5.22	0.21	1.22	0.92	0.9	1
ClK	5.94	6.00	27.23	12.14	0.06	1.16	0.92	0.81	1

EDX Analysis II (EDS Spot 5) – This area was part of the region exposed to $HgCl_2$. A microparticle was formed that appeared to be enveloped by the polysulfide. EDX analysis revealed this particle to contain a high proportion of mercury (50 wt%).



kV: 10 Mag: 3625 Takeoff: 33.8 Live Time(s): 50 Amp Time(µs): 1.92 Resolution:(eV) 122.7

EDS Spot 5

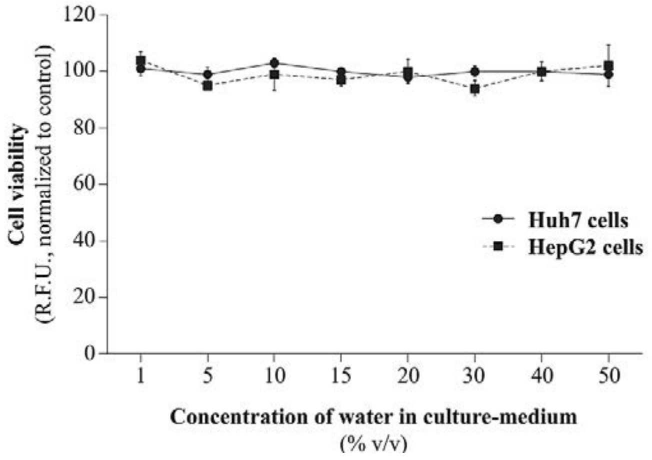


eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	R	A	F
C K	20.57	63.02	37.63	12.12	0.07	1.47	0.8	0.23	1
O K	0.95	2.18	3.45	34.56	0.00	1.4	0.83	0.31	1
PtM	6.57	1.24	18.97	15.26	0.06	0.75	1.18	1.12	1.01
HgM	50.14	9.20	135.41	5.88	0.41	0.74	1.19	1.09	1.01
S K	15.97	18.33	105.83	6.21	0.18	1.24	0.91	0.9	1
ClK	5.81	6.03	28.05	12.14	0.06	1.18	0.92	0.8	1

Toxicity assay for water exposed to the sulfur-limonene polysulfide

The sulfur-limonene polysulfide was added to the bottom of a 6 cm petri dish. Next, 17 mL of deionized water was added to the surface of the polysulfide. The petri dish was covered and incubated at room temperature for 24 hours at room temperature. After this time, the water was removed from the polysulfide by pipette. The toxicity of the water was tested to determine if any harmful substances are removed from the polysulfide after prolonged exposure to water. Accordingly, two hepatoma cell lines commonly used for cytotoxicity assays (HepG2 and Huh7) were seeded on 96 well-plates, at a concentration of 10^4 cells/well, and allowed to adhere for 24h. After this, the cells were incubated for another 24h with culture medium supplemented with either the deionized water exposed to the sulfur-limonene polysulfide, or with corresponding dilutions of sterile deionized water. At this time, cell viability was quantified using the Cell-titer Blue Cell Viability Assay (Promega), according to the manufacturer's instructions, which is based on the capacity of viable cells to convert resazurin to a fluorescent compound (resorufin). Results shown represent average of 3 independent experiments. Error bars indicate ± 1 standard error of the mean.



% of water	Huh7 cells		HepG2 cells	
	Control	**"Exposed water"**	**Control**	**"Exposed water"**
1	100 ± 2.3	101 ± 2.35	100 ± 0.93	104 ± 3.04
5	100 ± 2.66	99 ± 2.44	100 ± 0.67	95 ± 1.39
10	100 ± 2.45	103 ± 1.69	100 ± 1.41	99 ± 5.55
15	100 ± 0.93	100 ± 1.01	100 ± 1.12	97 ± 2.12
20	100 ± 0.99	98 ± 0.39	100 ± 1.78	100 ± 4.12
30	100 ± 1.97	100 ± 1.87	100 ± 1.72	94 ± 2.75
40	100 ± 1.34	100 ± 0.36	100 ± 0.91	100 ± 3.29
50	100 ± 2.23	99 ± 1.14	100 ± 1.23	102 ± 7.37

These experiments indicate that water that has been exposed to the polysulfide is not cytotoxic under the conditions examined (24 hour exposure). This result motivates further exploration of the polysulfide as a material useful in water remediation, where inorganic mercury is removed from water at the site of contamination. That is, the polysulfide could potentially be used directly in natural waterways contaminated with mercury, without immediate concern that the polysulfide would release harmful organic substances.

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