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SILVER FUEL LEVEL SENSOR CORROSION PROGRAM

May 2009

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Silver Fuel Level Sensor Corrosion Program

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Prepared by the

CRC Silver Fuel Level Sensor Corrosion Panel

of the

Deposit Group

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CRC Performance Committee
of the
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Abstract

During the spring of 2004, vehicles in the southeast region of the United States experienced fuel sender unit failures. It was later shown the sender unit failures were associated with sulfur components found in the fuel, which were found to be corrosive to the silver alloys used in fuel sender units. CRC during the fall of 2005 created a Silver Corrosion Panel to better understand the relationship between the fuel sulfur components and the sender unit failures. The Panel developed a two phase program, the first of which was designed to focus on understanding the corrosive relationship between elemental sulfur (S_8), hydrogen sulfide (H_2S) and mercaptans (ethyl and propyl) and the silver alloys used in fuel sender units. The first phase was conducted with a matrix of two fuels (one commercial and one blended from two hydrocarbon streams) with each fuel containing various concentrations of the above mentioned sulfur compounds. The Modified ASTMD 130 (Annex A1 of ASTM D4814-04b) test method and Petro-Canada's PCM 1005-33-111-test methods were used to evaluate silver corrosion.

Phase II was to focus on testing various types of fuel sender units with various fuels containing varying amounts of elemental sulfur, hydrogen sulfide and mercaptans (ethyl and propyl). The concentrations of each sulfur component would be determined from the results of Phase I. Unfortunately, during the completion of Phase I, the OEM that was to conduct Phase II was not in a position to support the program nor supply the necessary fuel sender units. It was therefore decided by the CRC Performance Committee to cancel Phase II of the program.

1. Introduction

There have been global field problems over the years concerning malfunctioning of vehicles fuel tank sender units. In early May 2004, consumers in Kentucky, Florida, Mississippi, Louisiana and Alabama[1] reported fuel sender unit failures from many locations after filling their vehicle fuel tanks.

The fuel sender unit would inaccurately measure the amount of fuel in the tank. In some cases, the fuel sender unit might register a full volume in the tank but the tank was actually empty or in other cases the tank might be full but the fuel sender unit would register empty. Most of the sender unit malfunctions that took place were with gasoline vehicles. However, during conversations with various CRC members, it was mentioned the problem had also occurred with some diesel sender units, though at a much smaller level.

The fuel sending unit failures were directly related to the sulfur compounds found in gasoline. It was determined the sulfur species found in the fuel were corroding the silver alloys used in the sending unit and preventing proper registration of the level of fuel in the vehicle tank.

The impact of the sulfur contained in the fuel on corrosion of fuel sender units was raised as an important issue during the April 2005 CRC Performance Committee meeting. Therefore, the CRC Deposit Group formed a Silver Corrosion Panel to investigate the relationship between sulfur species found in the fuel and the corroding silver contact on the sending unit.

2. Conclusions

The objectives for the program were met with the following conclusions:

1. The analysis of commercial field samples did confirm the corrosivity of the fuel toward silver.

2. Results showed that elemental sulfur (S_8) alone did not cause silver corrosion in laboratory tests. Interactions between elemental sulfur, hydrogen sulfide (H_2S), and mercaptans (ethyl and propyl) were necessary to cause silver corrosion.

3. Predictive equations with excellent R-square values were developed and can be used to predict the corrosive nature of a fuel or hydrocarbon to silver, and by inference silver alloys.

4. The Petro-Canada PCM 1005-33-111 Method was more sensitive than the Modified ASTM D130 (Annex A1of ASTM D4814-04b) Method and able to evaluate small interactive reactions.

5. The 3-D response Curve Charts generated using the CRC data set would have shown a much better response curve if more multipliable sulfur specie concentrations were used especially toward the lower concentrations. This became very clean when the CRC silver corrosion results were combined with the ASTM silver corrosion data set.

6. Olefins appear to have a positive effect in reducing the corrosivity of the sulfur species toward silver and, by inference, silver alloys. More testing would be needed to confirm this observation.

3. Test Program

The CRC Silver Corrosion Panel during the period May through September 2005 held a number of teleconferences to outline the program objectives and the approach to achieve the objectives.

3.1. Objectives

1. To understand the concentrations and interaction effects of elemental sulfur, mercaptan (ethyl and propyl) and hydrogen sulfide on the silver corrosion fuel level sensor malfunctions. (Ethyl and propyl mercaptan are also known as ethyl and propyl thiols.)

2. To ascertain the level of elemental sulfur, mercaptan (ethyl and propyl) and hydrogen sulfide found in commercial gasoline associated with failures of consumer fuel level sensor units.

3. To establish a pass/fail criteria while using the Modified ASTM D130 (Annex A1 of ASTM D4814-04b) Test Method and PetroCanada PCM 1005-03-111 test method in the evaluation of the corrosive nature of the elemental sulfur, hydrogen sulfide, and mercaptans (ethyl and propyl) toward silver.

3.2. Approach

Phase Ia: Fundamental role of reactive sulfur species toward silver metal.

- Select sulfur species concentration ranges to be tested.
- Design a test matrix by varying the levels of elemental sulfur, hydrogen sulfide and ethyl/propyl mercaptans blended into test fuels.
- Evaluate the corrosivity of the fuel / sulfur blends by two recognized industry test methods.

Phase Ib: Analysis of Problematic Commercial Gasolines.

- Acquire data concerning the levels of sulfur, hydrogen sulfide and mercaptans found in the commercial fuels during the spring of 2004.

4. Commercial Fuel Component Analysis

Phase Ib was initiated first to determine the amounts of elemental sulfur, hydrogen sulfide and mercaptans (ethyl and propyl), present in the commercial fuel during the spring of 2004. The commercial fuel findings from this analysis can be found in Table 1. The individual fuels were rated by using the IP 227 silver corrosion method, which was replaced by the Modified ASTM D130 (Annex A1 of ASTM D4814-

04b). A graphical representation of the Table 1 analysis can be seen in Figure 1, which clearly shows that combinations of elemental sulfur, hydrogen sulfide, ethyl mercaptan and propyl mercaptan can generate a silver strip result of 4. A silver strip rating of 0 is tarnish free and a silver strip rating of 4 is completely corroded / black. It can also be seen that 12 ppmw of elemental sulfur with hydrogen sulfide, ethyl mercaptan and propyl mercaptan at 0.1 ppmw generate a color rating of 2 while lower levels of elemental sulfur and higher levels of hydrogen sulfide or ethyl mercaptan or propyl mercaptan generate a color rating of 4. Individual correlations between the single sulfur species and silver corrosivity are shown in Figures 2 - 3. They clearly show that an increasing concentration of either elemental sulfur, or hydrogen sulfide or propyl mercaptan alone will cause silver to corrode. However, ethyl mercaptan had less of an effect on the corrosivity toward silver. The data contained in Figures 2 - 3 clearly indicates the higher the concentration of elemental sulfur, hydrogen sulfide, and propyl mercaptan in the fuel, the worse the silver corrosion rating. However, the opposite is seen for ethyl mercaptan (Figure 3) in which the higher the level of ethyl mercaptan in the fuel, the lower the silver corrosion rating. It is understandable that high levels of elemental sulfur and hydrogen sulfide can and do increase the corrosive nature of the base fuel toward silver. It is very difficult to understand how propyl mercaptan could be more corrosive toward silver than ethyl mercaptan. The molecular structure of ethyl mercaptan is less sterically hindered and more able to interact with the silver surface than propyl mercaptan, which contains a larger alkyl group. More testing will be necessary to fully understand this issue. It is very clear that single components as well as interactions from the various sulfur species have an important role in tarnishing the silver metal contact from the fuel pump sender unit.

A regression analysis concerning the data in Table 1 was conducted to better understand the sulfur component relationship, and selection of sulfur species for Phase Ia as well to develop a predictive equation. The regression analysis can be seen in Table 2.

The regression analysis of the data from Table 1 resulted in the development of a predictive equation which helped elucidate the relationship between elemental sulfur, hydrogen sulfide and the ethyl/propyl mercaptans found in the fuel and how this relationship influences the corrosive nature of the fuel containing these sulfur species toward silver. The predictive equation had an R-square value of 0.75.

The regression analysis clearly shows via the significance level that elemental sulfur, hydrogen sulfide, and propyl mercaptan strongly influence the corrosive action toward silver metal, though ethyl mercaptan corrosivity toward silver metal is much less influential to the silver corrosion rating value.

In addition, interactions between elemental sulfur and hydrogen sulfide as well as elemental sulfur and propyl mercaptan are just as corrosive toward the silver as the single component sulfur species. Therefore interaction between the various sulfur species must also be considered and studied to fully understand their influence.

However, the commercial fuel analysis clearly indicates the corrosive nature of the sulfur components toward silver and how interactions between the sulfur components can increase the severity of the corrosive nature toward silver.

5. Select Sulfur Species Ranges for Phase Ia

The overall analysis conducted concerning the commercial fuels from Table I and the resulting regression analysis from Table 2 were reviewed by the CRC Silver Corrosion Panel to select the range for the elemental sulfur (S_8), hydrogen sulfide (H_2S), ethyl mercaptan (EtSH) and propyl mercaptan (PrSH) to be used during Phase Ia of the program. In addition, the Panel conducted several teleconferences during April - May, 2005 time frame to assure the selected ranges for each sulfur species were broad enough to encompass any interactions which might take place between the individual sulfur species and silver metal. In addition, it was decided instead of individually looking at ethyl and propyl mercaptans, a 50/50 blend would be prepared and evaluated. The combination of ethyl and propyl mercaptans would reduce the number of components tested and reduce the test cost. The predictive equation developed for the commercial fuels found in Table 2 were used to confirm the sulfur species ranges found in Table 3. The selected sulfur ranges did, in fact, fall within the color corrosive scale used in the Modified ASTM D130 (Annex A1 of ASTM D4814-04b) test method. The Modified ASTM D130 (Annex A1 of ASTM D4814-04b) color scale rating can be seen in Table 4.

6. Base Fuel Selection for Phase Ia

The CRC Silver Corrosion Panel conducted several teleconferences concerning the test fuel or fuels, which would be used during the Phase Ia work. The CRC Silver Corrosion Panel selected two fuels for the evaluation. One fuel was a commercially available fuel while the second fuel blend, called Academic Fuel or Experimental Fuel", was a blend of two refinery fuel streams, which would contain zero sulfur components.

Chevron found a commercial California Air Resources Board (CARB) fuel that contained 0.4 ppmw of mercaptans and 0.1 ppmw of elemental sulfur. The CARB fuel had the lowest amount of sulfur found in the commercial fuel market and was selected.

The Academic Fuel was prepared by blending 70% by wt of Sweet Naphtha from Petro-Canada and 30% by wt of a High Octane Platformate from Shell. Neither the Sweet Naphtha nor the High Octane Platformate contained any sulfur species.

To confirm the CARB and Academic fuels were not corrosive toward silver, Petro-Canada evaluated each fuel (CARB and Academic) using Silver Corrosion Test (PCM 1005-03-111). Several petroleum companies reported using this test method in the Canadian market place. The Silver Corrosion Test (PCM 1005-03-111) confirmed that each fuel rating was zero. The Silver Corrosion color rating scale can be seen in Table 5. Therefore, the CARB and Academic fuel were used in the CRC Phase Ia program.

7. Silver Corrosion Statistical Experimental Design for Phase Ia

In designing the CARB and Academic fuel statistical experiments for Phase Ia, it was clear the design for each fuel would be slightly different. The initial CARB fuel analysis indicated a small amount of mercaptan (0.4 ppmw) and elemental sulfur (0.10 ppmw) present while no sulfur species were present in the Academic Fuel. Incorporating the treat rate ranges previously discussed and found in Table 3, an experimental design was developed for the CARB fuel while taking into consideration the initial CARB fuel sulfur level. The CARB fuel design can be found in Table 6 and the Academic fuel design can be found in Table 7.

8. Program Proposal

During this time CRC submitted the Silver Corrosion Panel Program Proposal to several outside laboratories. The silver corrosion committee selected Southwest Research Institute to conduct the Silver Corrosion Fuel Sender Unit Program. The Silver Corrosion Panel Program Proposal can be seen in Appendix A.

8.1 Test Protocol Overview

A complete summary of the test protocol can be found in Appendix A. The following is a brief overview of the test proposal.

1. Prepare a 50/50 blend of ethyl and propyl mercaptan mercaptans to be used for the work.

2. Preparation of an academic gasoline consisting of 70 /30 wt % of Sweet Naphtha and High Octane Platformate.

3. Stock solutions of the following were prepared as described in the protocol found in Appendix A.
   a. 5000 ppm by weight of a 50/50 blend of ethyl and propyl mercaptan mercaptans.
   b. 1000 ppm by weight of elemental sulfur.
   c. 40 ppm by weight of hydrogen sulfide.

4. Working solutions of the following must be prepared from the Stock solutions as described in the protocol found in Appendix A:
   a. Preparation of 110 ppm by weight of a 50/50 ethyl and propyl mercaptan blend.
   b. The preparation of 175 ppm by weight of elemental sulfur.
   c. The stock solution of hydrogen sulfide can be used.

5. The composition of sixteen CARB fuels with various concentrations of elemental sulfur, 50/50 ethyl and propyl mercaptan mercaptans and hydrogen sulfide as previously described can be found in Table 6. Each sample will be tested in triplicate to assure repeatability and reproducibility in each test method. An as-poured analysis for each sulfur species will be conducted for each corrosion test.

6. The composition of eleven Academic gasolines with various concentrations of elemental sulfur, 50/50 ethyl/propyl mercaptan mercaptans and hydrogen sulfide as previously described can be found in Table 7. The molecular weight, and densities for the individual sulfur species, which were used to prepare the blends can be found in Table 8. Each sample will be tested in triplicate to assure repeatability and reproducibility of each test method. An as-poured analysis for each sulfur species will be conducted for each corrosion test.

7. The procedures for both Modified ASTM D130 (Annex A1 of ASTM Method D4814-04b) and PCM1005-33-111 must be followed.

The density for both fuels was determined in triplicate following the ASTM D1217 method. The average density for each fuel can be found in Table 9. The average density was used in the preparation for all standards and test samples.

8.2 Blending and Analytical Overview

As a consequence of the reactivity of the sulfur species, the stock standards, calibration standards and the fuel blends were prepared in air free fuels. All fuels used in the preparation for standards and samples were cooled with ice for one hour prior to de-gassing. The chilled fuel was sparged with nitrogen for approximately ten minutes prior to doping with the reactive sulfur species. This was done to remove the oxygen or any free H_2S that might have already been present.

The blended concentrations of the sulfur species in each fuel sample were determined analytically in duplicate prior to beginning the corrosion test. After the blend was prepared, an aliquot was removed via the septum, placed into the test vial without any headspace and submitted for verification of the blend concentration. The fuels were kept at $4^{o}C$ until ready to be poured for testing. The hydrogen sulfide (H_2S), ethyl mercaptan (C_2H_5SH), and propyl mercaptan (C_3H_7SH) were determined using ASTM D5623 Standard test method for Sulfur Compounds in Light Petroleum Liquids by Gas Chromatography and Sulfur Selective Detection (GC-SCD). The concentration of hydrogen sulfide (H_2S), ethyl mercaptan (C_2H_5SH) and propyl mercaptan (C_3H_7SH) in each fuel blend was determined against a calibration curve. The elemental sulfur (S_8) was determined using EPA Method 8270 Semi-volatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS) in the selected ion monitoring (SIM) mode. The concentration of sulfur in each fuel was determined from a standard calibration curve. Since the doping amount was injected by volume, the concentrations were calculated in parts per million by volume (mg/L). The actual fuel blends for the Academic Fuel and the CARB fuel can be found in Tables 10 and 11, respectively.

After the blended verifications were completed, the blended fuels were warmed to 15°C prior to the corrosion test. Confirmation of the sulfur species during the pouring of the test samples were discussed several times during teleconferences between May and September 2005. It was decided that only the hydrogen sulfide concentration needed to be confirmed since it was the most volatile. Therefore, after the CARB and Academic Fuel samples were poured, the poured samples, which contain hydrogen sulfide, were tested and compared to the blended results. The results can be seen in Tables 12 and 13, respectively. There were differences observed between the blended and poured samples concerning the concentration of hydrogen sulfide, but it was the poured concentrations, which were used in the analysis, discussed in section 10.

9. Color Scale Correlation between the Modified ASTM D130 (Annex A1 of ASTM D4814-04b) and PCM 1005-33-111 Test Methods.

In order to be able to compare results between each silver corrosion test methods, a rating scale correlation between the Modified ASTM D130 (Annex A1 of ASTM D4814-04b) and PCM 1005-33-111 rating scale was necessary to understand results between each method. Petro-Canada had already established the rating scale ranking relationship between each method. The rating scale comparison between the Modified ASTM D130 (Annex A1 of ASTM D4814-04b) Method and the PCM 1005-33-111 Method can be reviewed in Table 14. A relation was necessary because the Petro-Canada PCM 1005-33-111 separates the rating scale into sixteen slightly different color maps while the Modified ASTM D130 (Annex A1 of ASTM D4814-04b) only separates the rating scale into four color maps. As previously discussed, the variation in the rating scheme for both methods can be seen in Table 4 and Table 5.

It was realized that no statistical analysis could be conducted using an alphanumeric rating from the Petro-Canada PCM 1005-33-111 Method. The PCM 1005-33-111 uses a letter ranking system instead of the number ranking system of the Modified ASTM D130 (Annex A1 of ASTM D4814-04b) method. Therefore, a statistician developed a numeric rating system for the PCM 1005-33-111 methods to allow statistical analysis of the data. The PCM 1005-33-111 numeric values that were used can be seen in Table 14.

10. CARB and Academic Experimental Design Results Discussion

The Academic and CARB fuel silver corrosion test results can be found in Tables 15 and 16 respectively. The CARB and Academic data were statistically reviewed; Pareto Charts and 3-D response curves were generated to clearly review the effect the sulfur species, as well as their interactions, had toward the corrosivity of the silver surface. A Pareto chart is used to graphically summarize and display the relative importance of the contribution of the "predictor variables" to the response. A Pareto chart is constructed by segmenting the range of the data into variables and calculating the average response when each variable (or interaction) is at its "high" level versus the average response for the "low" level. This difference (high – low) is deemed the effect. The variables seen in Figures 4 - 9 are elemental sulfur, hydrogen sulfide (H_2S), ethyl mercaptan and propyl mercaptan as well as the interaction between them. The data from the Pareto chart is used to investigate which variables and their combinations are essential to the goodness-of-fit of our model. Therefore the Pareto chart shows the extent of these variables and their interactions in a bar chart for ease of interpretation. The length of the bars shows the magnitude (standardized effect) of the explanatory contribution; a longer bar is better, implying more contribution of that variable to the overall prediction of the response.

The fuel analysis was conducted in the following order:

- CARB Fuel via the PCM 1005 -33-111
- Academic Fuel via the PCM 1005 -33-111
- Combined CARB and Academic Fuels via the PCM 1005-33-111
- CARB Fuel via the Modified ASTM D130 (Annex A1 of ASTM D4814-04b)
- Academic Fuel via the Modified ASTM D130 (Annex A1 of ASTM D4814-04b)
- Combined CARB and Academic Fuels via the Modified ASTM D130 (Annex A1 of ASTM D4814-04b)

The Pareto Charts and 3-D response curves can be found in Figures 4 - 9.

In addition, regression analyses as well as predictive equations were also generated to determine how well the data agreed and could it be used to predict the corrosivity of the sulfur components or their interaction with the silver metal surface in the future. The fuel regression analyses were conducted in the following order:

- CARB Fuel via the PCM 1005 -33-111
- Academic Fuel via the PCM 1005 -33-111
- Combined CARB and Academic Fuels via the PCM 1005-33-111
- CARB Fuel via the Modified ASTM D130 (Annex A1 of ASTM D4814-04b)
- Academic Fuel via the Modified ASTM D130 (Annex A1 of ASTM D4814-04b)
- Combined CARB and Academic Fuels via the Modified ASTM D130 (Annex A1 of ASTM D4814-04b)

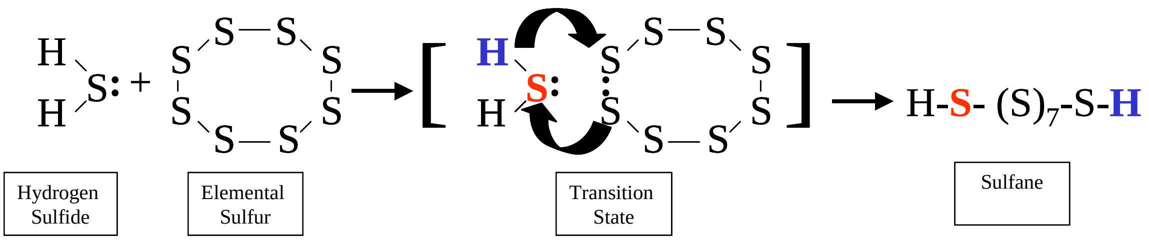
The regression analyses and prediction equations can be found in Tables 17 - 22.

The statistical analysis generated Pareto and the response curve charts contained in Figures 4 - 9 give a good insight into the corrosive significance of the individual sulfur species; the significance of the sulfur specie interactions and their aggressive corrosive nature toward silver. The Pareto Chart contains a dashed line on the left side, which represents the 95% significance level . If the bar passes the 95% point line, that sulfur species or combination has a significant impact on causing significant corrosion issues with the silver.

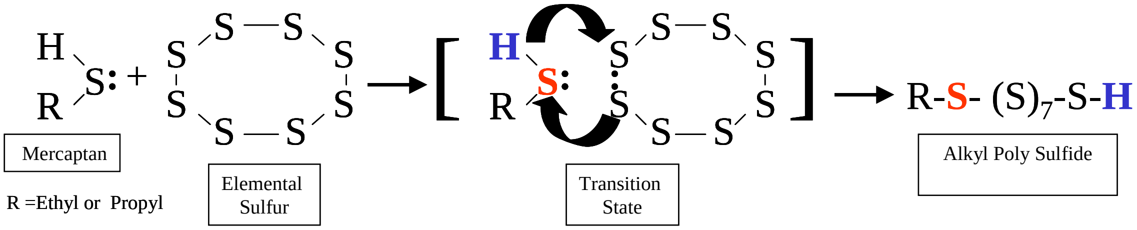
The statistical analysis of the data confirms that elemental sulfur (S_8) and hydrogen sulfide (H_2S) are very corrosive to silver at specific concentrations. Combinations of elemental sulfur (S_8) and hydrogen sulfide (H_2S) become more corrosive at lower concentrations toward silver. Reviewing the Pareto Charts and the 3-D response graphs contained in Figures 4 - 9, shows these observations visually. Ethyl and propyl mercaptans are less corrosive toward silver; however, addition of the ethyl and propyl mercaptans with elemental sulfur (S_8) in the presence of hydrogen sulfide (H_2S) increases the corrosivity of the mixture toward silver. An example of this observation is Figure 5 and 5a in which three different concentrations of the 50/50 mixture of ethyl/propyl mercaptans where evaluated. The response graphs seen in Figure 5 and 5a show a progressive change to the curvature of the 3-D graphs as the concentration of the ethyl/propyl mercaptan mixture is increased. The starting point of the curvature increases and does indicate an interaction is taking place among the various sulfur species, which does increase the PC rating value of the silver wool used in the evaluation.

Equations 1 and 2 are believed to be the interactive reactions, which are taking place between the elemental sulfur and hydrogen sulfide as well as elemental sulfur and mercaptans. The reactions in both equations represent a nucleophilic substitution (SN_2) type reaction in which the hydrogen sulfide or the mercaptan species is the nucleophile, which opens the sulfur ring to create the more corrosive component toward silver.

Equation 1 provides a sulfane, which is an acidic polysulfide, and very corrosive toward silver, while Equation 2 provides an alkyl polysulfide, which is also reactive toward silver and silver cations.



Equation 1



Equation 2

The interactions between the elemental sulfur, hydrogen sulfide and ethyl/propyl mercaptans seem to be less obvious with the CARB fuel than with the Academic fuel. A perfect example of this observation can be seen by comparing Figure 4 (CARB Fuel via the PCM 1005-33-111) with Figure 5 (Academic Fuel via the PCM 1005-33-111). The difference in reactivity between the CARB and Academic fuel had been discussed within the CRC Silver Corrosion Panel discussions. The CARB fuel contains olefins while the Academic fuel does not. Olefins are known to react with nucleophiles such as hydrogen sulfide, mercaptans, alkyl polysulfides and sulfanes. It is this reaction, which would remove some of the components from reacting with each other to produce the sulfanes or alky polysulfides or from removing the more corrosive components from reacting with the silver metal. Therefore, it should not be a surprise to observe a reduction in interactions for the CARB fuel and see more from the olefin free Academic fuel. The incorporation of an olefin component into the Academic fuel could be the basis for some future silver corrosion fuel programs.

Predictive equations and R-squares were developed for each fuel and associated method. The predictive equations and R-squared values can be reviewed in Tables 17 - 22.

The R-squared values for the CARB and Academic fuels using the PCM 1005-33-111 method were 0.96 for the CARB fuel and 0.92 for the Academic fuel. When both fuels were combined, the R-squared value decreased to 0.86.

Additional R-squared values for the CARB and Academic fuels using the Modified ASTM D130 (Annex A1 of ASTM D4814-04b) method was 0.98 for the CARB Fuel and 0.98 for the Academic Fuel. When both fuels were combined, the R-squared value decreased to 0.80.

The data from each fuel and method generated good predictive equations and outstanding R-squared values. The individual fuels were defined with very specific sulfur sets and designs. When data are combined from two very different sets, we introduce more variability into the mix by combining the variabilities, though small for each set. In addition, the interaction within the CARB fuel between the sulfur species and olefins add to the variability in the combination analysis. Therefore, when you combine all of the variabilities together, the result is a reduced R-square value.

Differences in rating sensitivity between the PCM 1005-33-111 method and the Modified ASTM D130 (Annex A1 of ASTM D4814-04b) method can be seen between the 3-D response curves of Figure 5 vs. Figure 8. Figure 5 and Figure 8 both are using the Academic fuel but Figure 5 is rating the data via the PCM 1005-33-111 method while Figure 8 is rating the data via the Modified ASTM D130 (Annex A1 of

ASTM D4814-04b) method. The PCM 1005-33-111 3-D response curve has more of a curvature than the Modified ASTM D130 (Annex A1 of ASTM D4814-04b) 3-D response curve, which is somewhat flatter. It is important to remember the PCM 1005-33-111 method has 16 separate rating levels while the Modified ASTM D130 (Annex A1 of ASTM D4814-04b) method has a color rating scale between 0 - 4. Small interactive differences between the sulfur species may be misread or mis-interpreted when using the Modified ASTM 130 method. In other words, when using the Modified ASTM D130 (Annex A1 of ASTM D4814-04b) method, a 2 rating could be misinterpreted as a 3 or a 2 rating could be misinterpreted as a 1. In addition if the results fall between ratings, then one must choose one rating.

However, the PCM 1005-33-111 method has an alphanumeric color rating containing approximately 16 levels, which allows a more thorough analysis. These 16 levels of color variation spread the analysis, which helps to pick up the small sulfur interactions. This is seen in having more of a curvature in the response graphs using the PCM 1005-3 111 method than with the Modified ASTM D130 (Annex A1 of ASTM D4814-04b) method.

11. ASTM Data Discussion

During this time ASTM conducted a silver corrosion program, which was similar to the CRC program, except the ASTM design focused on the lower concentration sulfur treat rates with only a few at the higher level.

If some of the results from the ASTM program were incorporated into the statistical analysis, a better surface response curve could be developed and thus better refine the model. Kevin Bly from ASTM conducted their silver corrosion program and shared the results with CRC. However, only the PCM 1005-33-111 method results from combining the CRC and ASTM data for both the CARB and Academic Fuel are reported here. The Pareto Chart and 3-D response curve for these combined fuels can be found in Figure 10. When Figure 6, which is the CRC combined results from the CARB and Academic fuel is compared with Figure 10, which includes the ASTM and CRC data combined for the Academic fuels, a sharper 3-D response curve is shown in Figure 10 than is seen in Figure 6. The 3-D response curve represented in Figure 10 starts closer to zero than the response curve in Figure 6. This is the result of the much finer and smaller concentrations of the sulfur species used within the ASTM study. Figure 6 and Figure 10 were all evaluated using the Petro-Canada method; however, a similar response was seen using the Modified ASTM D130 (Annex A1 of ASTM D4814-04a) Method. The addition of the lower concentrated sulfur values did help to improve the response surface curvature with an R-square of 0.78. As has previously been discussed for the individual program designs, differences in each set added to the overall combined variability of the data and hence the lower R-square value. In addition, the Pareto Chart in Figure 10 did show more of an interaction between the elemental sulfur and the mercaptan at lower concentrations.

12. References

(1) Ralph Vertabedian," Los Angeles Times Newspaper", May 3, 2006

13. Acknowledgment

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Tables

Table 1
Commercial Fuel Analysis of Field Samples vs IP 227* Analysis

		Elemental Sulfur	Hydrogen Sulfide	Ethyl Mercaptan	Propyl Mercaptan
Sample	IP 227	ppmw	ppmw S	ppmw S	ppmw S
1	4	33.3	10.7	0.1	0.1
2	4	21.3	0.1	0.2	0.1
3	4	20.0	0.1	0.1	0.1
4	4	18.7	0.1	0.3	0.2
5	4	18.7	0.1	0.2	0.1
6	4	16.0	0.1	0	0
7	4	13.3	0.1	0.6	0.2
8	4	12.0	2	0.1	0.1
9	4	12.0	0.1	0.1	0.1
10	4	11.3	0.1	0.1	0
11	4	10.7	0.3	0.3	0.2
12	4	10.7	0.2	0.1	0.1
13	4	10.0	0.1	0.3	0.1
14	4	9.3	0.2	0.2	0.1
15	4	9.3	0.1	0.2	0.1
16	4	8.7	9.1	0.2	0.2
17	4	8.0	2.5	0.4	0.4
18	4	8.0	0.1	0.4	0.2
19	4	6.7	8.7	0.1	0.1
20	4	6.7	0.8	0.2	0.2
21	4	6.7	0.1	0.3	0.2
22	4	5.3	10.2	0.1	0.1
23	4	5.3	0.1	0.1	0.1
24	4	2.0	7.5	0.1	0.1
25	3	9.3	0.1	0	0
26	3	5.3	0.1	0.2	0.2
27	3	4.0	0.2	0.3	0.1
28	2	12.0	0.1	0.1	0.1
29	2	4.0	0.1	0.8	0.3
30	2	2.7	0.1	0.7	0.3
31	2	1.3	0.1	1	0.3
32	2	0.0	1.5	0.2	0.2
33	2	0.0	0.3	0.1	0.1
34	1	2.7	0	0	0
35	1	1.3	0.1	3	0.6
36	1	0	0.1	0.7	0.3
37	1	0	0	0.7	0.3
38	1	0.0	0	0.7	0.2
39	1	0.0	0	0.2	0.1
40	1	0.0	0	0.1	0.1
41	0	4.0	0.1	0	0
42	0	1.7	0.1	3.2	0.5
43	0	1.3	0	1.3	0.3
44	0	0.4	0.1	3.2	0.7
45	0	0.4	0.1	3.1	0.5
46	0	0.4	0.1	2.2	0.4
47	0	0.4	0	0.3	0.2
48	0	0.4	0	0.2	0.1
49	0	0.0	0	0.7	0.1
50	0	0.0	0	0.6	0.2
51	0	0	0	0.4	0.4
52	0	0.0	0	0.4	0.2
53	0	0.0	0	0.4	0.1
54	0	0.0	0	0.2	0.1
55	0	0.0	0	0.1	0.1
56	0	0	0	0	0

* IP 227 was replaced by the Modified ASTM D130 (Annex A1 of ASTM D4814-04b) method.

Table 2
Commerical Sample Data Variables:
All data Coefficients Fit to Original Units

Model fitting results for: Rating

Independent variable	Coefficient	Std. error	T-value	Sig. level
Constant	0.56768	0.247719	2.2916	0.0259
Elemental Sulfur (S_8)	0.20447	0.029921	6.8337	0.0000
Hydrogen Sulfide (H_2S)	0.35445	0.065723	5.3932	0.0000
Ethyl Mercaptan (EtSH	-0.89368	0.302199	-2.9573	0.0046
Propyl Mercaptan (PrSH)	3.226743	1.60396	2.0117	0.0493
(S_8)* (H_2S)	-0.02205	0.004124	-5.43463	0.0000
(S_8) * (EtSH)	0.10904	0.105654	1.0320	0.3068

R-SQ. (ADJ.) = 0.7523 SE = 0.883102 MAE = 0.687878 DurbWat = 1.420
Previously: 0.0000 0.00000 0 .00000 0.000
60 observations fitted, forecast (s) computed for 0 missing val. of dep. var.

Reasonably good model with R-Square of 0.75 given the discrete corrosion rating scale.

Y = Fuel corrosion rating toward silver coupons. The fuel corrosion rating scale can be seen in Table 14.

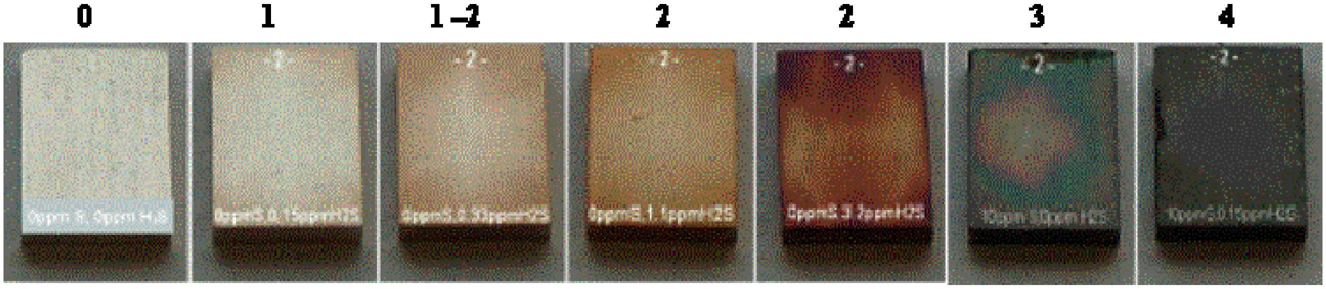
Rating is equal to the following predictive equation:

Y = 0.56768
+ 0.20447 * (Elemental Sulfur)
+ 0.35445 * (Hydrogen Sulfide)
- 0.89368 * (Ethyl Mercaptan)
+ 3.22674 * (Propyl Mercaptan)
- 0.02205 * (Elemental Sulfur)*(Hydrogen Sulfide)
+ 0.10904 * (Elemental Sulfur)*(Ethyl Mercaptan)

Table 3
Sulfur Species Range Selection for Phase Ia

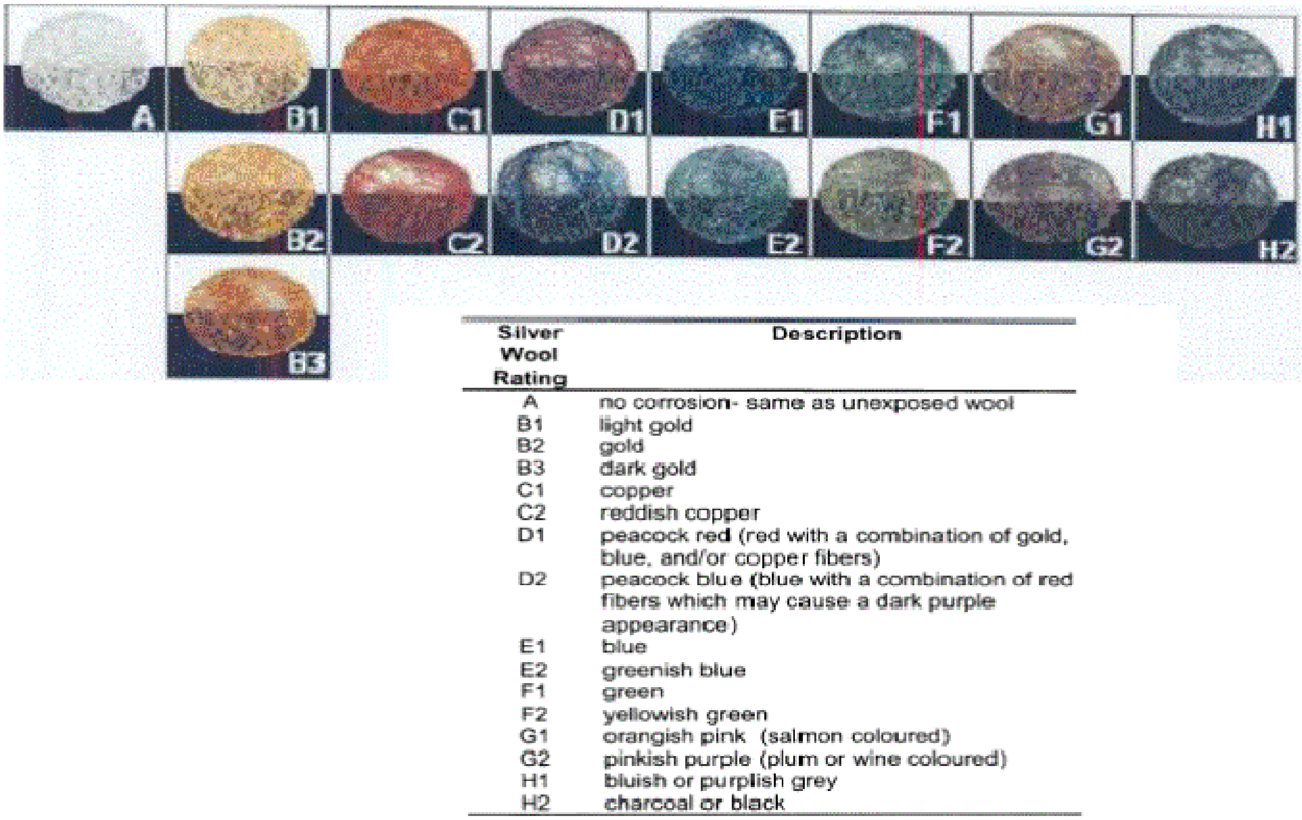
		Medium		
	Low (ppmw)	**Low (ppmw)**	**High (ppmw)**	**High (ppmw)**
Elemental Sulfur (S_8)	0	2	4	8
Hydrogen Sulfide (H_2S)	0	0.070	0.15	0.33
Ethyl Mercaptan (EtSH) / Propyl Mercaptan (PrSH)	0	0.750	1.5	3.0
Predicted Rating	0 - 1	2	3	4

Table 4
Modified ASTM D130 (Annex A1 of ASTM D4814-04b) Color Scale



Classification	Designation	Description
0	No Tarnish	Identical to a freshly colored strip but may have a slight loss of luster.
1	Slightly Tarnish	a. Light orange, almost the same as freshly polished strip. b. Dark orange
2	Moderate Tarnish	a. Claret red b. Lavender c. Multicolored with lavender blue or silver, or both, overlaid on claret red. d. Silvery e. Brassy or gold
3	Dark Tarnish	a. Magenta overcast on brassy strip b. Multicolored with red and green showing (peacock), but no gray.
4	Corrosion	a. Transparent black, dark gray or brown with peacock green barely showing. b. Graphite or lusterless black. c. Glossy or jet black.

Table 5
Petro-Canada (PCM 1005 - 03-III) Color Scale



Silver Wool Rating	Description
A	no corrosion- same as unexposed wool
B1	light gold
B2	gold
B3	dark gold
C1	copper
C2	reddish copper
D1	peacock red (red with a combination of gold, blue, and/or copper fibers)
D2	peacock blue (blue with a combination of red fibers which may cause a dark purple appearance)
E1	blue
E2	greenish blue
F1	green
F2	yellowish green
G1	orangish pink (salmon coloured)
G2	pinkish purple (plum or wine coloured)
H1	bluish or purplish grey
H2	charcoal or black

Table 6
CARB Fuel Sulfur Experimental Design

Run Number	**Elemental Sulfur (S_8)**	**Hydrogen Sulfide (H_2S)**	**RSH [1]**
	PPM by weight		
1	0.10	0.00	0.40
2	8.0	0.0	0.40
3	8	0.30	0.40
4	0.10	0.30	0.40
5	0.10	0.00	3.00
6	8.00	0.00	3.00
7	8.00	0.30	3.00
8	0.10	0.30	3.00
9	4.00	0.00	1.50
10	8.00	0.15	1.50
11	4.00	0.30	1.50
12	0.10	0.15	1.50
13	4.00	0.15	0.40
14	4.00	0.15	3.00
15	4.00	0.15	1.50
16	4.00	0.15	1.50

RSH[1] is a 50/50 blend of ethyl mercaptan and propyl mercaptan.

Table 7
Academic Fuel Sulfur Experimental Design

Run Number	**Elemental Sulfur (S_8)**	**Hydrogen Sulfide (H_2S)**	**RSH [1]**
	PPM by weight		
1	0.00	0.00	0.00
2	0.00	0.00	3.00
3	0.00	0.30	0.00
4	0.00	0.30	3.00
5	8.00	0.00	0.00
6	8.00	0.30	0.00
7	0.00	0.15	1.50
8	4.00	0.15	0.00
9	4.00	0.15	0.00
10	8.00	0.30	3.00
11	8.00	0.00	3.00

RSH[1] is a 50/50 blend of ethyl mercaptan and propyl mercaptan.

Table 8
Molecular Weight / Formula / Density of Sulfur Species

Name	Molecular Weight	Formula	Density (g / ml)
Elemental Sulfur	31.97	S	
Hydrogen Sulfide	34.08	H_2S	0.0015
Ethyl Mercaptan	62.13	C_2H_5SH	0.839
propyl mercaptan Mercaptan	76.16	C_3H_7SH	0.841

Table 9
CARB and Academic Average Fuel Density

Fuel	**Number of Tests**	**Density, g/mL**
Academic	1	0.757
	2	0.757
	3	0.758
	Average	**0.757**
CARB	1	0.723
	2	0.723
	3	0.723
	Average	**0.723**

Table 10

Academic Fuel Blend

Sample	Final Volume (mL)	Spike Concentration (mg/Kg)			
		Sulfur	Hydrogen Sulfide	Ethanethiol	Propane thiol
Acad 1	1008	0.00	0.00	0.00	0.00
Acad 2	1004	0.00	0.00	1.49	1.49
Acad 3	1004	0.00	0.30	0.00	0.00
Acad 4	1005	0.00	0.30	1.49	1.49
Acad 5	1007	7.94	0.00	0.00	0.00
Acad 6	1002	7.98	0.30	0.00	0.00
Acad 7	1013	0.00	0.15	0.74	0.74
Acad 8	1005	3.98	0.15	0.00	0.00
Acad 9	1009	3.96	0.15	0.00	0.00
Acad 10	1005	7.96	0.30	1.49	1.49
Acad 11	1009	7.93	0.00	1.49	1.49

Acad: Academic

Table 11
CARB Fuel Blend

Sample	Final Volume (mL)	Spike Concentration (mg/Kg)			
		Sulfur	Hydrogen Sulfide	Ethane thiol	Propane thiol
CA 1	998	0.10	0.00	0.20	0.20
CA 2	1009	7.93	0.00	0.20	0.20
CA 3	1005	7.96	0.31	0.20	0.20
CA 4	1003	0.10	0.31	0.20	0.20
CA 5	1002	0.10	0.00	1.50	1.50
CA 6	1001	7.99	0.00	1.50	1.50
CA 7	1007	7.94	0.31	1.49	1.49
CA 8	1004	0.10	0.31	1.49	1.49
CA 9	1007	3.97	0.00	0.74	0.74
CA 10	1010	7.92	0.15	0.74	0.74
CA 11	1012	3.95	0.31	0.74	0.74
CA 12	1010	0.10	0.15	0.74	0.74
CA 13	1007	3.97	0.15	0.20	0.20
CA 14	1002	3.99	0.15	1.50	1.50
CA 15	1000	4.00	0.15	0.75	0.75
CA 16	1010	3.96	0.15	0.74	0.74

CA: CARB

Table 12
CARB Hydrogen Sulfide (H_2S) Fuel Verification between Target and as Blended Samples

Sample	H_2S Concentration Verification (mg/kg)		% Difference
	Target	As Blended	
CA0	<0.05	<0.05	---
CA3	0.314	0.281	-10.4 %
CA4	0.294	0.249	-15.3 %
CA7	0.281	0.302	7.4 %
CA8	0.262	0.258	-1.6 %
CA10	0.156	0.174	12.0 %
CA11	0.254	0.234	-8.2 %
CA12	0.135	0.153	13.4%
CA 13	*	0.184	*
CA14	*	0.162	*
CA15	*	0.164	*
CA16	*	0.176	*

*** Major instrument (SCD) failure, unable to verify concentrations**

Table 13
Academic Hydrogen Sulfide (H_2S) Fuel Verification between Target and as Blended Samples

Sample	H_2S Concentration Verification (mg/kg)		% Difference
	Target	As Blended	
Acad 1	<0.03	<0.03	---
Acad 3	0.332	0.275	-17.1 %
Acad 4	0.325	0.279	-14.2 %
Acad 6	0.297	0.262	-11.8 %
Acad 7	0.159	0.153	-3.8 %
Acad 8	0.147	0.168	13.9 %
Acad 9	0.168	0.153	-9.4 %
Acad 10	0.317	0.265	-16.5 %

Table 14
Petro-Canada PCM 1005-33-111 method and Modified ASTM D130 method Alphanumeric vs Numeric Correlation

PCM 1005-33-111 Rating			Numeric Rating Equivalent			Modified ASTM D 130 Rating
A	A1		10	11		0
B1	B2		21	22		1
B3	C1	C2	31	32	33	2
D1	D2		35	36		
E1	E2		38	39		
F1	F2		41	42		3
G1	G2		44	45		
H1	H2		51	52		4

Table 15
Academic Fuel Corrosion Rating Results

Sample	Replicate	PCM 1005-33-111	Modified D130*	Petro-Canada Numeric Value	Modified D130 Comments
Acad 1	1	A	0	10	No Change
	2	A	0	10	
	3	A	0	10	
Acad 2	1	A	0	10	No Change
	2	A	0	10	
	3	A	0	10	
Acad 3	1	B1	1	21	Slightly tarnished. JFTOT tube rating: 1-2
	2	B1	1	21	
	3	B1	1	21	
Acad 4	1	B1	1	21	Slightly tarnished. JFTOT tube rating: 1-2
	2	B1	1	21	
	3	B1	1	21	
Acad 5	1	A1	0	11	Loss of luster
	2	A1	0	11	
	3	A1	0	11	
Acad 6	1	H2	3	52	Dark peacock coloring
	2	H2	3	52	
	3	H2	3	52	
Acad 7	1	H1	1	51	Slightly tarnished. JFTOT tube rating: 1
	2	H1	1	51	
	3	H1	1	51	
Acad 8	1	H2	2	52	Light peacock coloring
	2	H2	2	52	
	3	H2	2	52	
Acad 9	1	G2	2	45	Light peacock coloring
	2	G1	2	44	
	3	G2	2	45	
Acad 10	1	H2	3	52	Dark peacock coloring
	2	H2	3	52	
	3	H2	3	52	
Acad 11	1	H2	3	52	Dark peacock coloring
	2	H2	3	52	
	3	H2	3	52	
Acad 8 repeat	1	H2	2	52	Light peacock coloring.
	2	H2	2	52	
	3	H2	2	52	

***: Modified ASTM D130 (Annex A1 of ASTM D4814-04b) method**

Table 16
CARB Fuel Corrosion Rating Results

Sample	Replicate	PCM 1005-33-111	Modified D130*	Petro-Canada Numeric Value	Modified D130 Comments
CA 0	1	A	0	10	
	2	A	0	10	
	3	A	0	10	
CA 1	1	A	0	10	No Change
	2	A	0	10	
	3	A	0	10	
CA 2	1	H2	3	52	No Change
	2	H2	3	52	
	3	H2	3	52	
CA 3	1	H2	3	52	
	2	H2	3	52	
	3	H2	3	52	
CA 4	1	B3	1	31	
	2	B3	1	31	
	3	B3	1	31	
CA 5	1	A	0	10	
	2	A	0	10	
	3	A	0	10	
CA 6	1	H2	3	52	
	2	H2	3	52	
	3	H2	3	52	
CA 7	1	H1	3	51	
	2	H2	3	52	
	3	H2	3	52	
CA 8	1	B2	1	22	
	2	B2	1	22	
	3	B2	1	22	
CA 9	1	G1	2	44	
	2	G2	2	45	
	3	G2	2	45	
CA 10	1	H1	3	51	
	2	H1	3	51	
	3	H1	3	51	
CA 11	1	D2	2	36	
	2	E2	2	39	
	3	F1	2	41	
CA12	1	B2	1	22	
	2	B2	1	22	
	3	B2	1	22	
CA 13	1	G2	2	45	
	2	G2	2	45	
	3	G2	2	45	
CA 14	1	--	2		
	2	G2	2	45	
	3	G2	2	45	
CA 15	1	G2	2	45	
	2	G1	2	44	
	3	G1	2	44	
CA 16	1	G2	2	45	
	2	G2	2	45	
	3	G1	2	45	

***: Modified ASTM D130 (Annex A1 of ASTM D4814-04b) method**

Table 17
CARB Fuel Regression Data Predictive Equation
(PCM 1005-33-111 Method)

Independent variable	Coefficient	Std. error	Sig. level
Constant	11.35969		
Sulfur (S_8)	8.98669	1.057628	0.0000
Hydrogen Sulfide (H_2S)	88.95063	1.043417	0.0000
Ethyl/Propyl Mercaptan (RSH)	-1.36947	1.352604	0.1205
(S_8) * (H_2S)	-7.29448	1.173632	0.0000
(S_8) * (RSH)	0.18037	1.325904	0.1104
(H_2S) * (RSH)	-5.94143	1.31227	0.0483
$(S_8)^2$	-0.49545	2.178438	0.0000
$(H_2S)^2$	-103.11304	2.121751	0.0347
$(RSH)^2$	0.27463	2.760639	0.6666

Reasonably good model with R-squared of 0.96.

Y = Fuel corrosion rating toward silver coupons. The fuel corrosion rating scale can be seen in Table 14

Rating is equal to the following predictive equation:

Y = 11.35969
\+ 8.98669 * (Elemental Sulfur)
\+ 88.95063 * (Hydrogen Sulfide)
\- 1.36947 * (Ethyl / Propyl Mercaptan)
\- 7.29448 * (Elemental Sulfur) *(Hydrogen Sulfide)
\+ 0.18037 * (Elemental Sulfur) *(Ethyl / Propyl Mercaptan)
\- 5.94143 * (Hydrogen Sulfide) * (Ethyl / Propyl Mercaptan)
\- 0.49545 * (Elemental Sulfur)^2
\- 103.11304 * (Hydrogen Sulfide)^2
\+ 0.274635 * (Ethyl / Propyl Mercaptan)^2

Table 18

Academic Fuel Regression Data Predictive Equation (PCM 1005-33-111 Method)

Independent variable	Coefficient	Std. error	Sig. level
Constant	**4.875**		
Sulfur (S_8)	**11.68402**	**2.135238**	**0.0000**
Hydrogen Sulfide (H_2S)	**144.16666**	**2.135238**	**0.0000**
Ethyl/Propyl Mercaptan (RSH)	**3.46667**	**2.135238**	**0.0001**
(S_8) * (H_2S)	**3.95833**	**2.135238**	**0.0347**
(S_8) * (RSH)	**0.85416**	**2.135238**	**0.0001**
(H_2S) * (RSH)	**-22.77777**	**2.135238**	**0.0001**
$(S_8)^2$	**-1.28472**	**7.599368**	**0.0000**
$(H_2S)^2$	**-244.44444**	**6.752216**	**0.1149**

Reasonably good model with R-squared of 0.92.

Y = Fuel corrosion rating toward silver coupons. The fuel corrosion rating scale can be seen in Table 14

Rating is equal to the following predictive equation:

Y = 4.875
+ 11.68402 * (Elemental Sulfur)
+ 144.16666 * (Hydrogen Sulfide)
+ 3.46667 * (Ethyl / Propyl Mercaptan)
+ 3.95833 * (Elemental Sulfur) * (Hydrogen Sulfide)
+ 0.854167 * (Elemental Sulfur) * (Ethyl / Propyl Mercaptan)
- 22.77777 * (Hydrogen Sulfide) * (Ethyl / Propyl Mercaptan)
- 1.28472 * $(\text{Elemental Sulfur})^2$
-244.44444 * $(\text{Hydrogen Sulfide})^2$

Table 19

Combined CARB and Academic Fuel Regression Data Predictive Equation (PCM 1005-33-111)

Independent variable	Coefficient	Std. error	Sig. level
Constant	**9.12775**		
Sulfur (S_8)	**8.49712**	**1.763236**	**0.0000**
Hydrogen Sulfide (H_2S)	**128.6965**	**1.790673**	**0.0000**
Ethyl/Propyl Mercaptan (RSH)	**1.19610**	**1.832013**	**0.0897**
$(S_8) * (H_2S)$	**-1.38206**	**1.907782**	**0.3967**
(S_8) * (RSH)	**0.61400**	**2.019209**	**0.0005**
(H_2S) * (RSH)	**-15.49535**	**2.009285**	**0.0009**
$(S_8)^2$	**-0.68401**	**4.04913**	**0.0000**
$(H_2S)^2$	**-218.76802**	**4.040952**	**0.0172**
$(RSH)^2$	**-0.09272**	**3.800365**	**0.9140**

Reasonably good model with R-squared of 0.86.

Y = Fuel corrosion rating toward silver coupons. The fuel corrosion rating scale can be seen in Table 14

Rating is equal to the following predictive equation:

Y = 9.12775
+ 8.49712 * (Elemental Sulfur)
+ 128.6965 * (Hydrogen Sulfide)
+ 1.19610 * (Ethyl / Propyl Mercaptan)
- 1.38206 * (Elemental Sulfur) * (Hydrogen Sulfide)
+ 0.61400 * (Elemental Sulfur) * (Ethyl / Propyl Mercaptan)
- 15.49535 * (Hydrogen Sulfide) * (Ethyl / Propyl Mercaptan)
- 0.68401 * (Elemental Sulfur)^2
-218.76802 * (Hydrogen Sulfide)^2
- 0.09272 * (Ethyl / Propyl Mercaptan)^2

Table 20

CARB Regression Data Predictive Equation
Modified ASTM D130 (Annex A1 of ASTM D4814-04b)

Independent variable	Coefficient	Std. error	Sig. level
Constant	**-0.10780**		
Sulfur (S_8)	**0.52270**	**0.145884**	**0.0000**
Hydrogen Sulfide (H_2S)	**0.99393**	**0.143946**	**0.0050**
Ethyl/Propyl Mercaptan (RSH)	**0.52431**	**0.186472**	**0.4204**
(S_8) * (H_2S)	**-0.39974**	**0.16191**	**0.0210**
(S_8) * (RSH)	**0.00489**	**0.182908**	**0.7608**
(H_2S) * (RSH)	**0.04903**	**0.181033**	**0.9077**
$(S_8)^2$	**-0.02097**	**0.293932**	**0.0564**
$(H_2S)^2$	**8.22583**	**0.286325**	**0.2371**
$(RSH)^2$	**-0.16565**	**0.365341**	**0.0807**

Reasonably good model with R-squared of 0.98.

Y = Fuel corrosion rating toward silver coupons. The fuel corrosion rating scale can be seen in Table 14.

Rating is equal to the following predictive equation:

Y = - 0.10780
+ 0.52270 * (Elemental Sulfur)
+ 0.99393 * (Hydrogen Sulfide)
+ 0.52431 * (Ethyl / Propyl Mercaptan)
- 0.39974 * (Elemental Sulfur) * (Hydrogen Sulfide)
+ 0.00489 * (Elemental Sulfur) * (Ethyl / Propyl Mercaptan)
+ 0.04903 * (Hydrogen Sulfide) * (Ethyl / Propyl Mercaptan)
- 0.02097 * $(\text{Elemental Sulfur})^2$
+ 8.22583 * $(\text{Elemental Sulfur})^2$
- 0.16565 * $(\text{Ethyl / Propyl Mercaptan})^2$

Table 21

Academic Regression Data Predictive Equation
Modified ASTM D 130 (Annex A1 of ASTM D4814-04b)

Independent variable	Coefficient	Std. error	Sig. level
Constant	-0.27500		
Sulfur (S_8)	0.55625	0.389645	0.0129
Hydrogen Sulfide (H_2S)	5.83333	0.406971	0.0372
Ethyl/Propyl Mercaptan (RSH)	0.25000	0.406971	0.1391
(S_8) * (H_2S)	0.20833	0.406971	0.5784
(S_8) * (RSH)	0.06250	0.406971	0.1391
(H_2S) * (RSH)	-1.66666	0.406971	0.1391
$(S_8)^2$	-0.05937	0.869686	0.0942

Reasonably good model with R-squared of 0.98.

Y = Fuel corrosion rating toward silver coupons. The fuel corrosion rating scale can be seen in Table 14.

Rating is equal to the following predictive equation:

Y = - 0.27500
+ 0.55625 * (Elemental Sulfur)
+ 5.8333 * (Hydrogen Sulfide)
+ 0.25000 * (Ethyl / Propyl Mercaptan)
+ 0.208333 * (Elemental Sulfur) * (Hydrogen Sulfide)
+ 0.06250 * (Elemental Sulfur) * (Ethyl / Propyl Mercaptan)
- 1.66666 * (Hydrogen Sulfide) * (Ethyl / Propyl Mercaptan)
- 0.05937 * (Elemental Sulfur)^2

Table 22

Both Academic and CARB Regression Data Predictive Equation Modified ASTM D130 (Annex A1 of ASTM D4814-04b)

Independent variable	Coefficient	Std. error	Sig. level
Constant	**-0.18298**		
Sulfur (S_8)	**0.43665**	**0.227831**	**0.0000**
Hydrogen Sulfide (H_2S)	**4.66670**	**0.231373**	**0.0010**
Ethyl/Propyl Mercaptan (RSH)	**0.66105**	**0.232779**	**0.1127**
(S_8) * (H_2S)	**-0.08531**	**0.246505**	**0.6870**
(S_8)* (RSH)	**0.04080**	**0.260903**	**0.0760**
(H_2S) * (RSH)	**-0.95060**	**0.259618**	**0.1159**
$(S_8)^2$	**-0.02820**	**0.519496**	**0.0985**
$(H_2S)^2$	**0.27341**	**0.518273**	**0.9816**
$(RSH)^2$	**-0.18420**	**0.484732**	**0.1035**

Reasonably good model with R-squared of 0.80.

Y = Fuel corrosion rating toward silver coupons. The fuel corrosion rating scale can be seen in Table 14

Rating is equal to the following predictive equation:

Y =
- 0.18298
+ 0.43665 * (Elemental Sulfur)
+ 4.66670 * (Hydrogen Sulfide)
+ 0.66105 * (Ethyl / Propyl Mercaptan)
- 0.08531 * (Elemental Sulfur) * (Hydrogen Sulfide)
+ 0.04080 * (Elemental Sulfur) * (Ethyl / Propyl Mercaptan)
- 0.95060 * (Hydrogen Sulfide) * (Ethyl / Propyl Mercaptan)
- 0.28200 * $(\text{Elemental Sulfur})^2$
+ 0.27341 * $(\text{Hydrogen Sulfide})^2$
- 0.18420 * $(\text{Ethyl / Propyl Mercaptan})^2$

Table 23

Both CRC and ASTM Regression Data Predictive Equation PCM 1005-33-111 Method

Independent variable	Coefficient	Std. error	Sig. level
Constant	0.02228		
Sulfur (S_8)	0.83682	0.279865	0.0000
Hydrogen Sulfide (H_2S)	6.85936	0.297763	0.0131
Ethyl/Propyl Mercaptan (RSH)	0.27352	0.304859	0.3457
(S_8) * (H_2S)	-0.22548	0.324987	0.4207
(S_8) * (RSH)	0.06856	0.344588	0.0237
(H_2S) * (RSH)	-1.24094	0.354004	0.1255
$(S_8)^2$	-0.06886	0.666868	0.0025
$(H_2S)^2$	-4.69910	0.624623	0.7410
$(RSH)^2$	-0.08649	0.589681	0.5214

Reasonably good model with R-squared of 0.78.

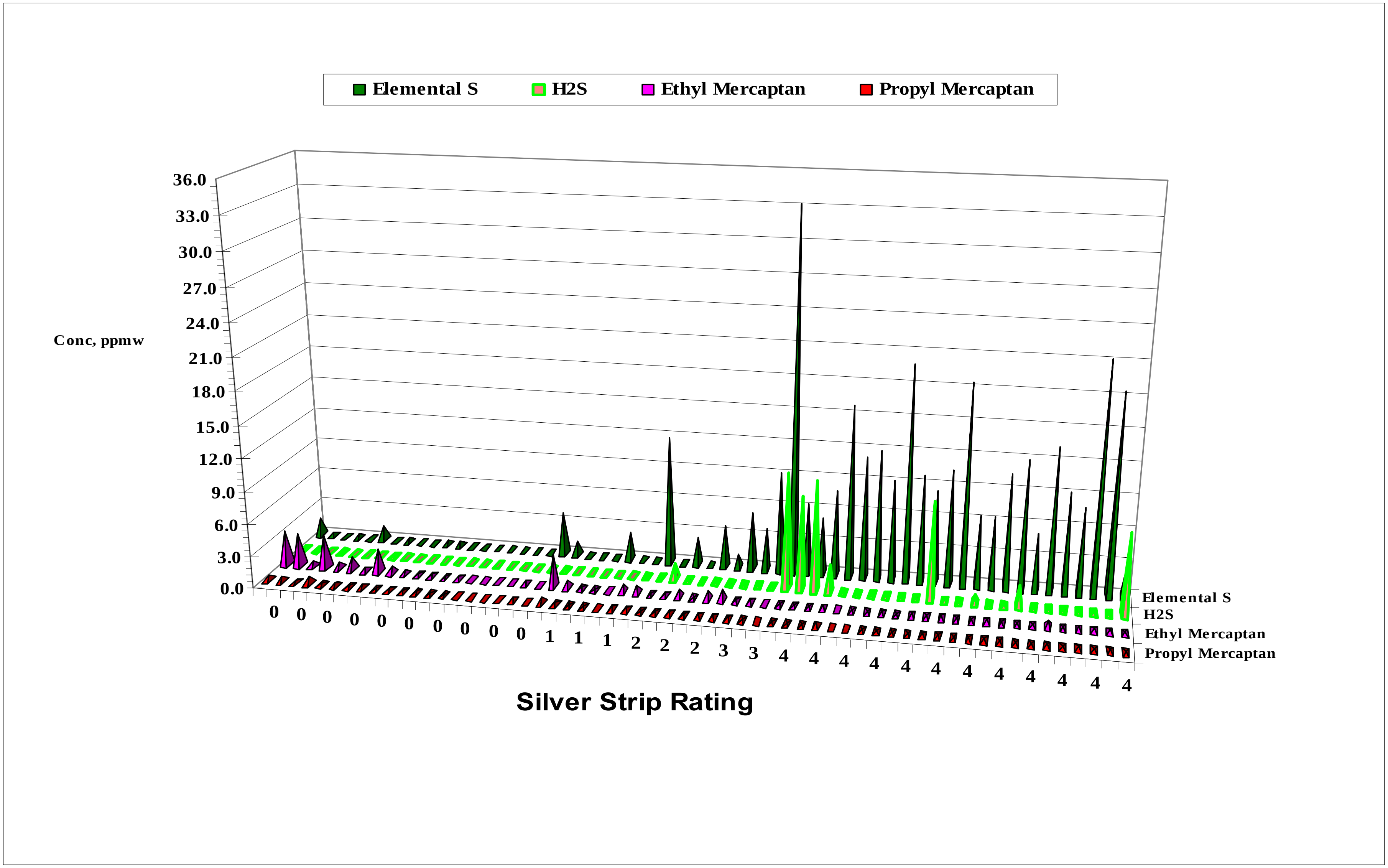
Y = Fuel corrosion rating toward silver coupons. The fuel corrosion rating scale can be seen in Table 14.

Rating is equal to the following equation:

Y = 0.02228
+ 0.83682 * (Elemental Sulfur)
+ 6.85936 * (Hydrogen Sulfide)
+ 0.27352 * (Ethyl / Propyl Mercaptan)
- 0.22548 * (Elemental Sulfur) * (Hydrogen Sulfide)
+ 0.06856 * (Elemental Sulfur) * (Ethyl / Propyl Mercaptan)
- 1.24094 * (Hydrogen Sulfide) * (Ethyl / Propyl Mercaptan)
- 0.06886 * (Elemental Sulfur)^2
- 4.69910 * (Hydrogen Sulfide)^2
- 0.08649 * (Ethyl / Propyl Mercaptan)^2

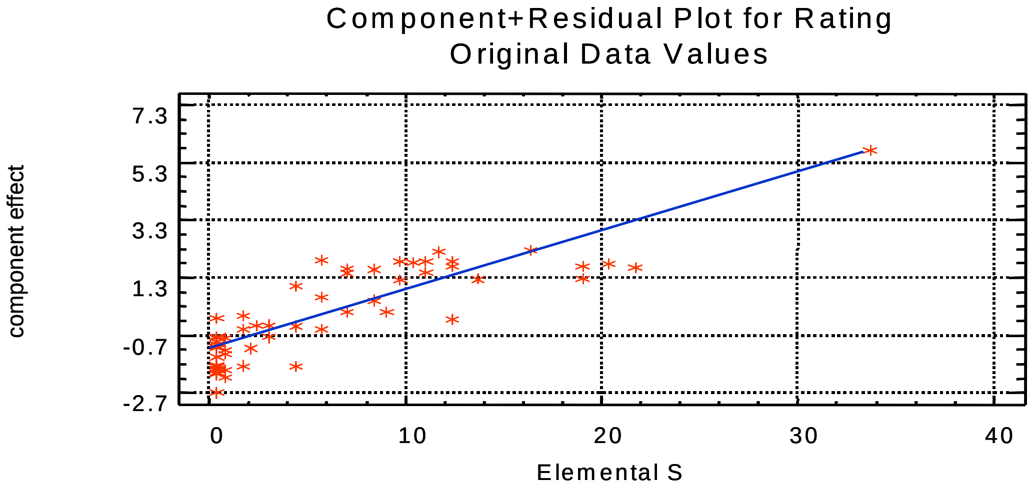
Figures

Figure 1: Commercial Fuel Sulfur Species Levels vs IP 227* Results



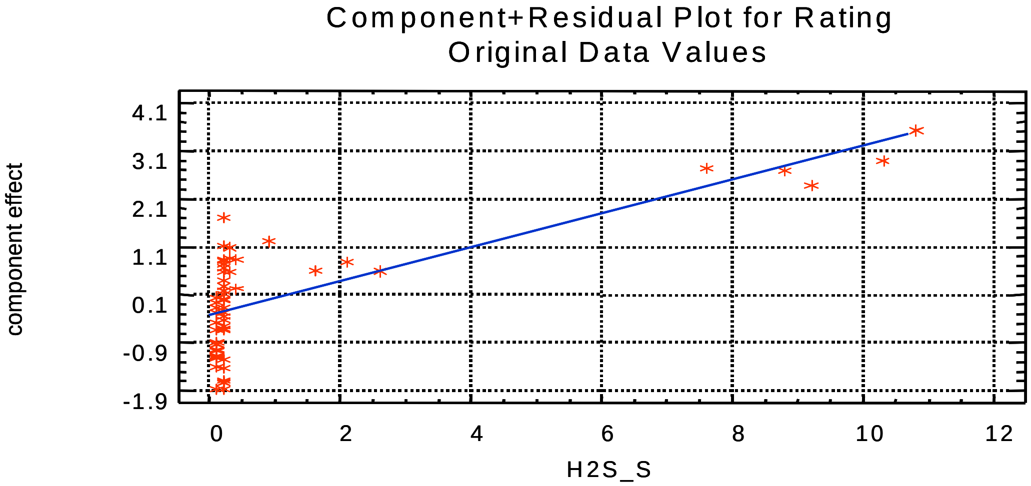
*** IP 227 has been replaced with Modified ASTM D130 (Annex A1 of D4814-4b)**

Figure 2: Silver Strip Field Samples
Regression Component Effect of S Source



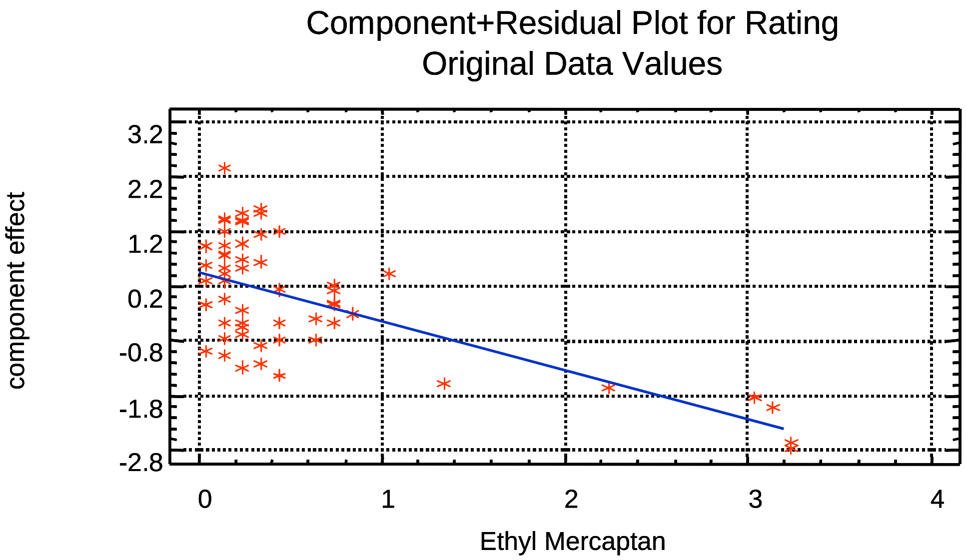
Field Samples Analysis

As both Elemental S and H2S increase, corrosion rating increases.



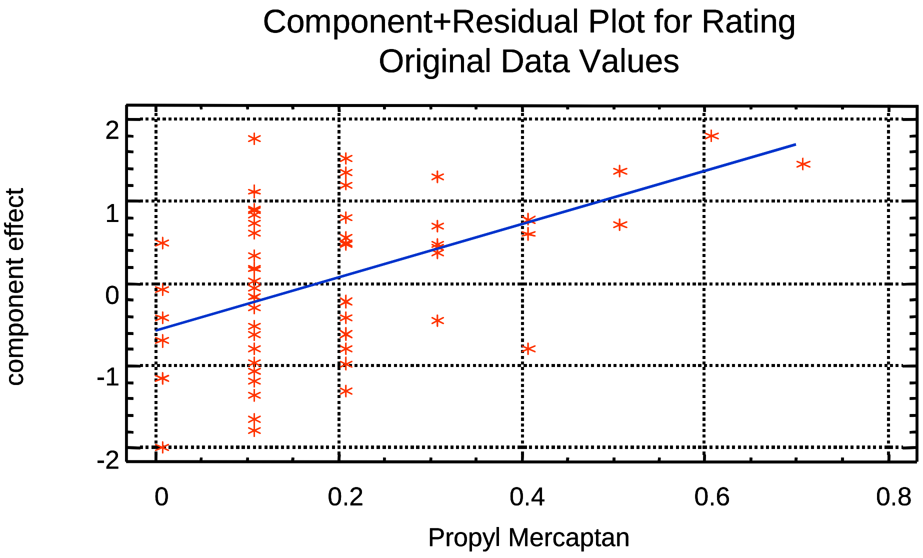
Field Samples Analysis

Figure 3: Silver Strip Field Samples
Regression Component Effect of S Source



Field Samples Analysis

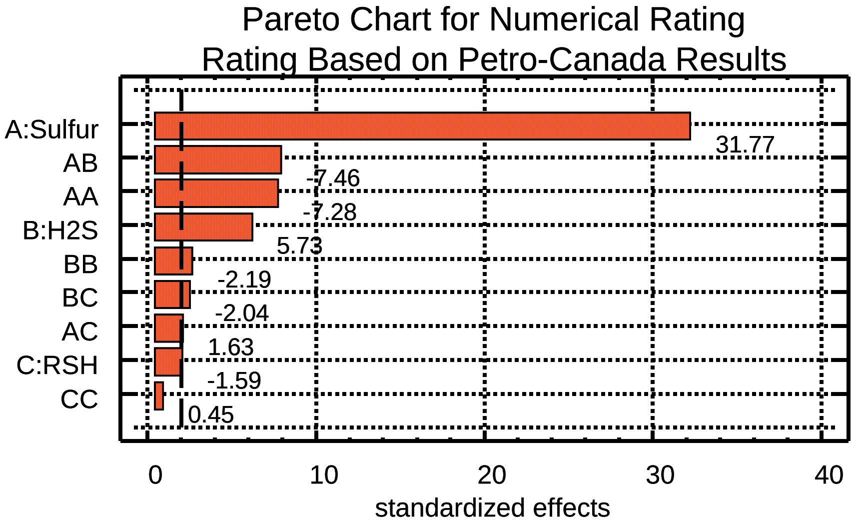
As Ethyl Mercaptan increases, corrosion rating decreases.



Field Samples Analysis

Slight positive relationship between Propyl Mercaptan and corrosion rating.

Figure 4: CARB Fuel Pareto Sulfur Species Sensitivity Chart
Petro-Canada PCM 1005-33-111 Method



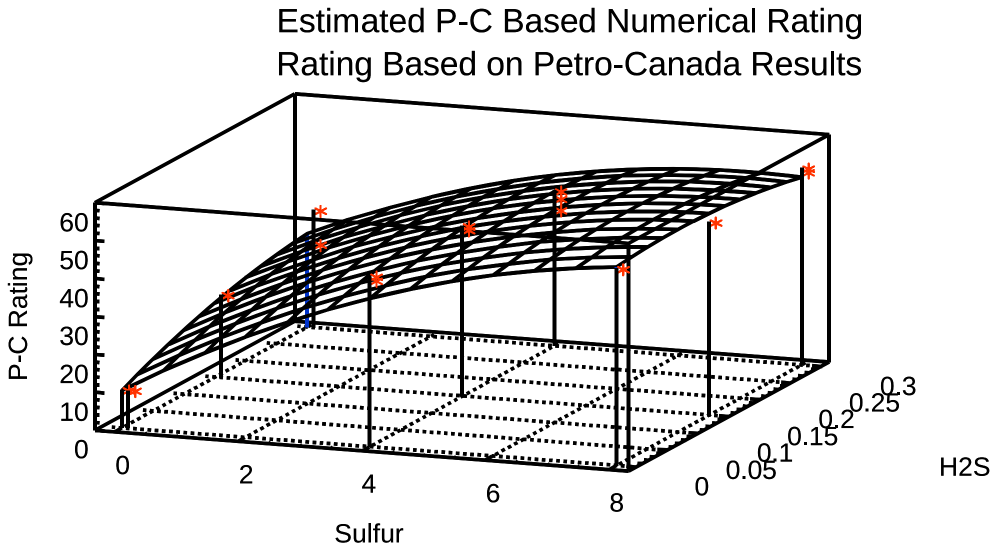
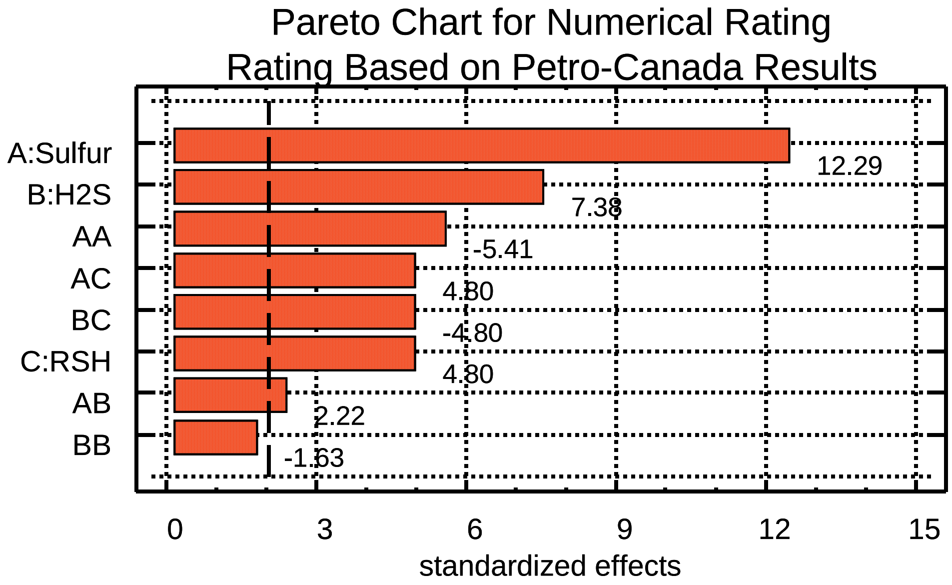


Figure 5: Academic Fuel Pareto Sulfur Species Sensitivity Chart
Petro-Canada PCM 1005-33-111 Method



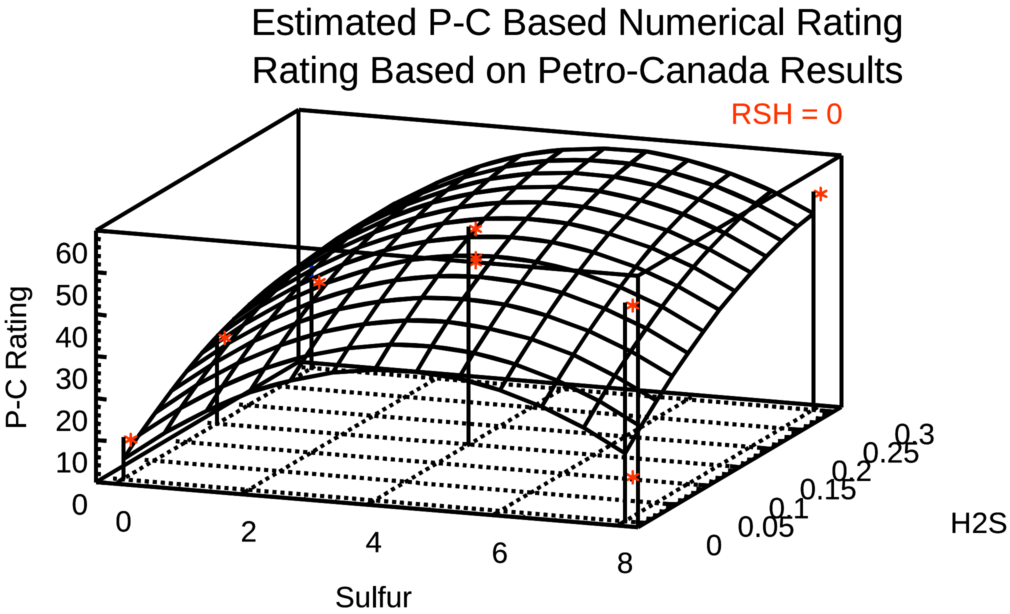
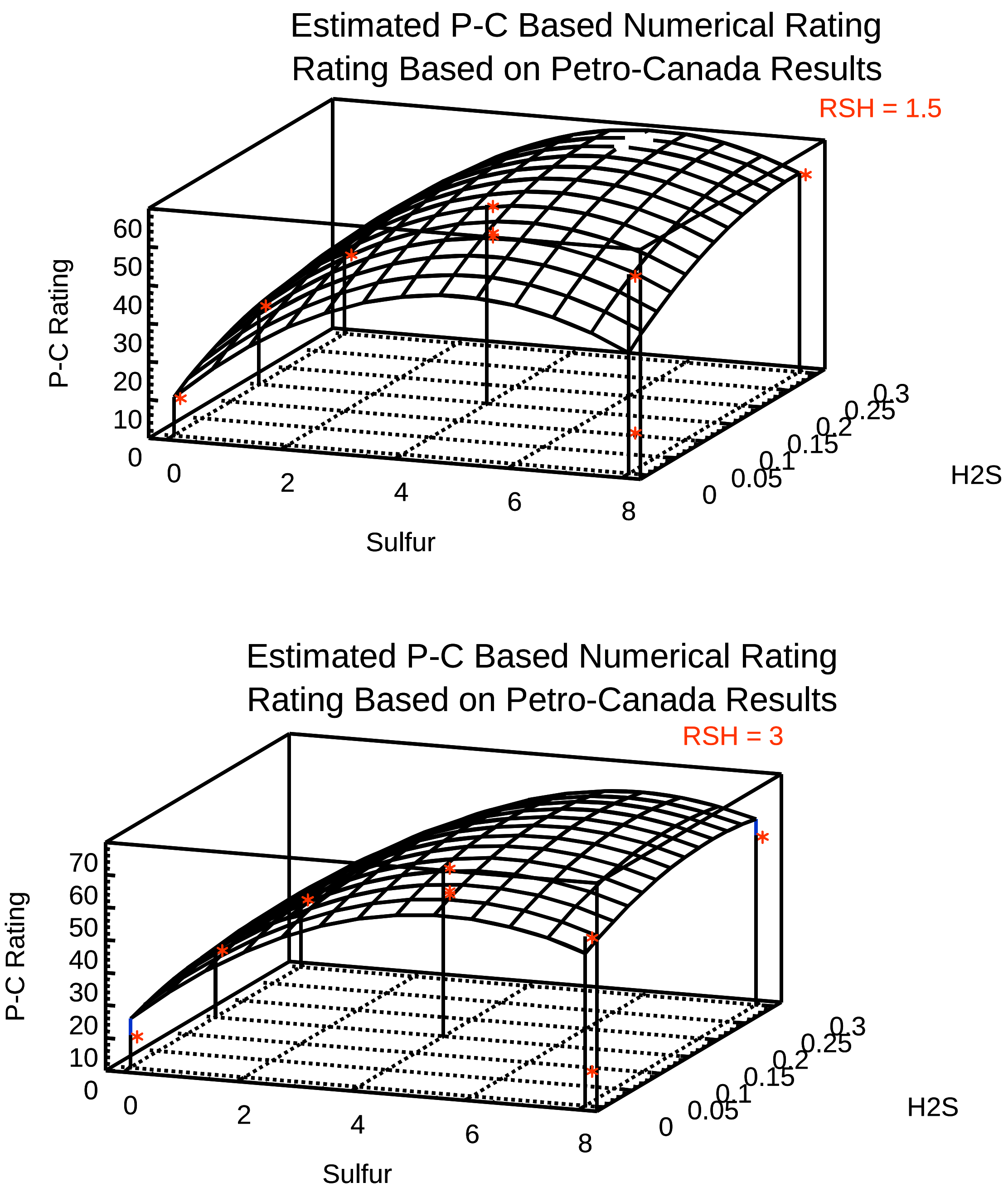


Figure 5a: Academic Fuel Pareto Sulfur Species Sensitivity Chart
Petro-Canada PCM 1005-33-111 Method

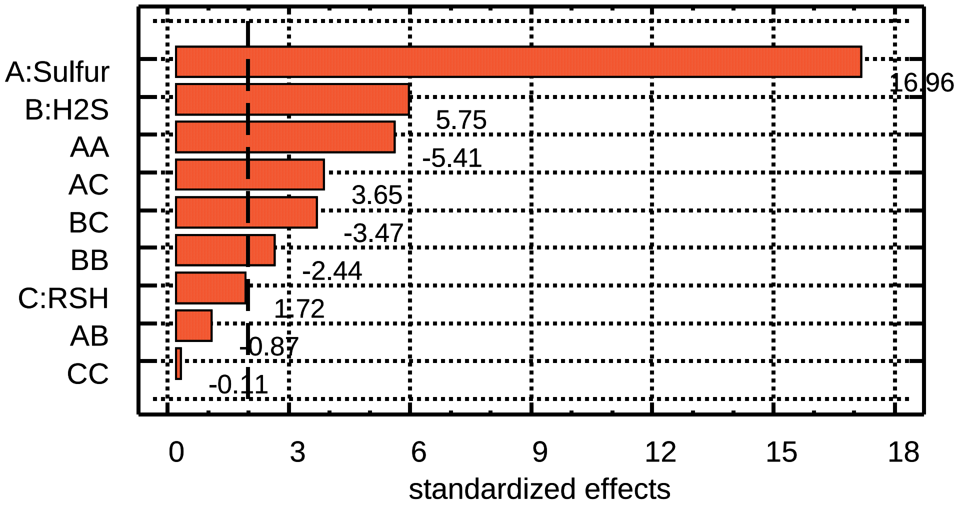
(Variation in mercaptan concentration)



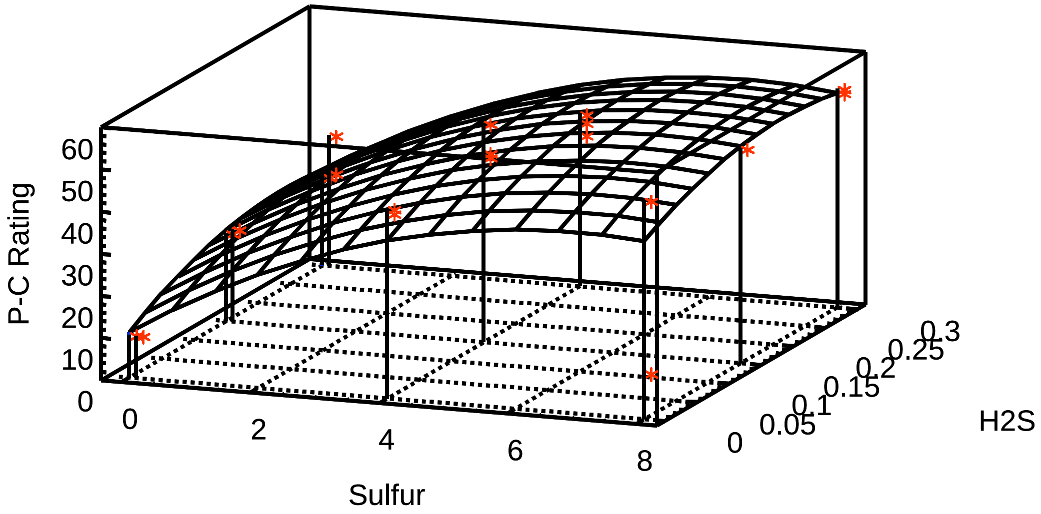
Estimated P-C Based Numerical Rating
Rating Based on Petro-Canada Results
RSH = 1.5

Estimated P-C Based Numerical Rating
Rating Based on Petro-Canada Results
RSH = 3

Figure 6: Combined CARB and Academic Fuel Pareto Sulfur Species Sensitivity Chart Petro-Canada PCM 1005-33-111 Method



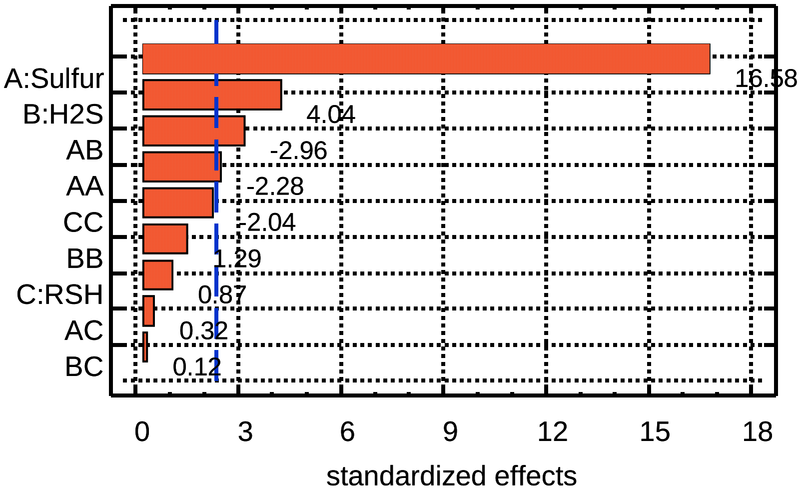
Pareto Chart for Numerical Rating
Rating Based on Petro-Canada Results



Estimated P-C Based Numerical Rating
Rating Based on Petro-Canada Results

Figure 7: CARB Fuel Pareto Sulfur Species Sensitivity Chart Modified ASTM D130 (Annex A1 of ASTM D4814-04b) Method

Pareto Chart for D4818 Rating
CRC Study Results



Estimated D4818 Rating
CRC Study Results

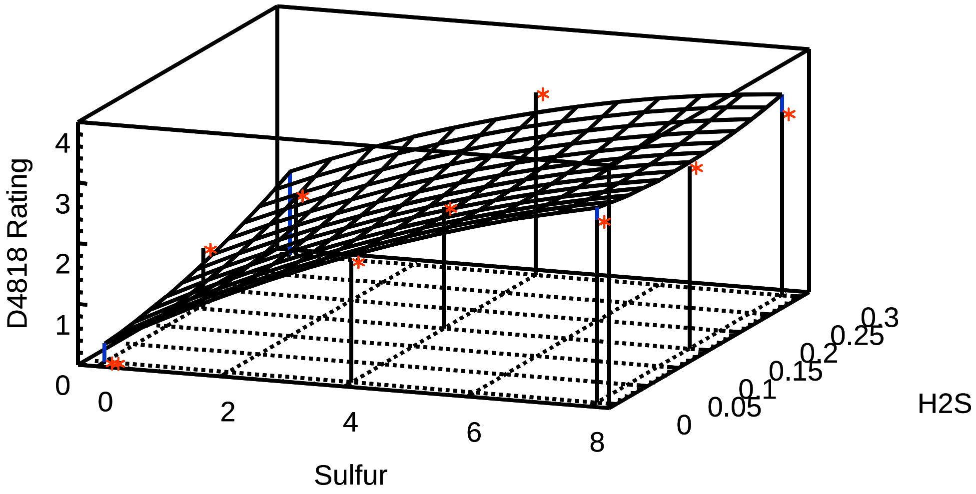
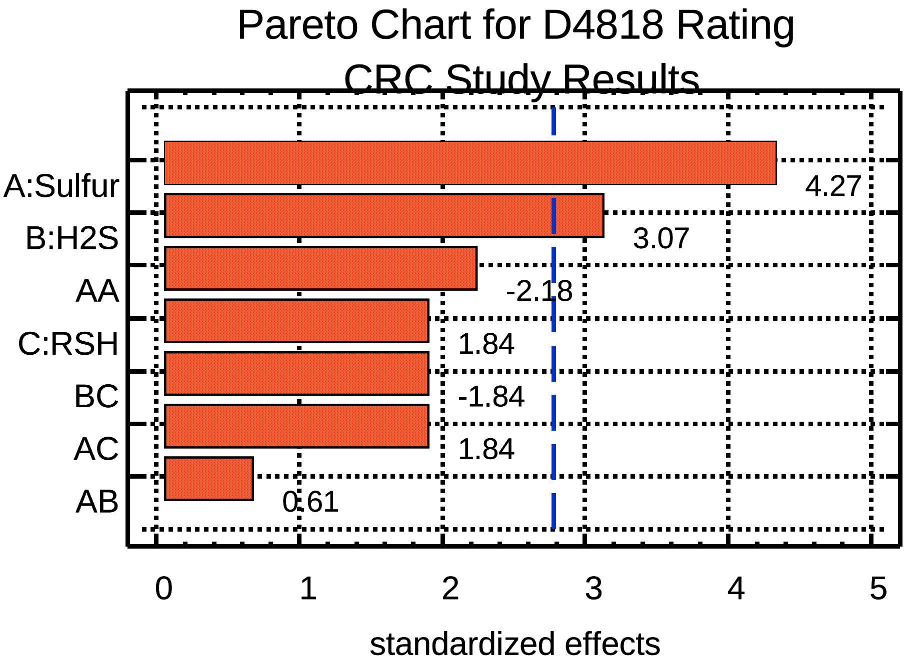


Figure 8: Academic Fuel Pareto Sulfur Species Sensitivity Chart Modified ASTM D130 (Annex A1 of ASTM D4814-04b) Method



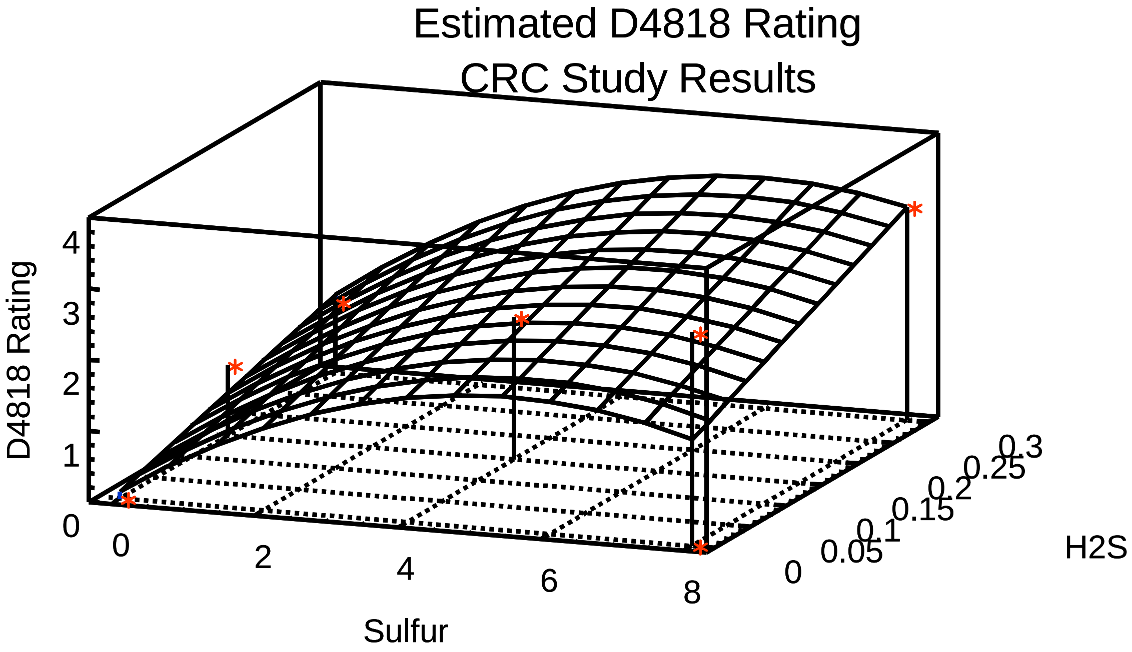
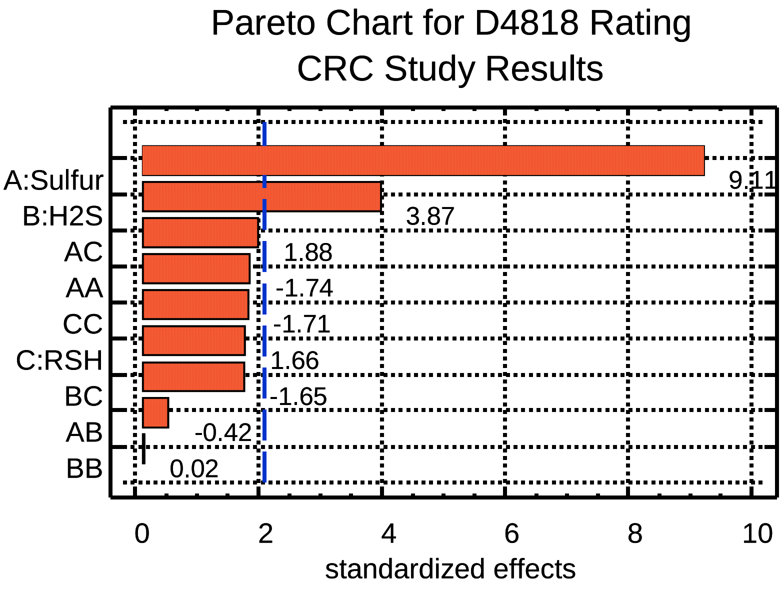


Figure 9: Combined of CARB and Academic Fuel
Pareto Sulfur Species Sensitivity Chart
Modified ASTM D130 (Annex A1 of ASTM D4814-04b) Method



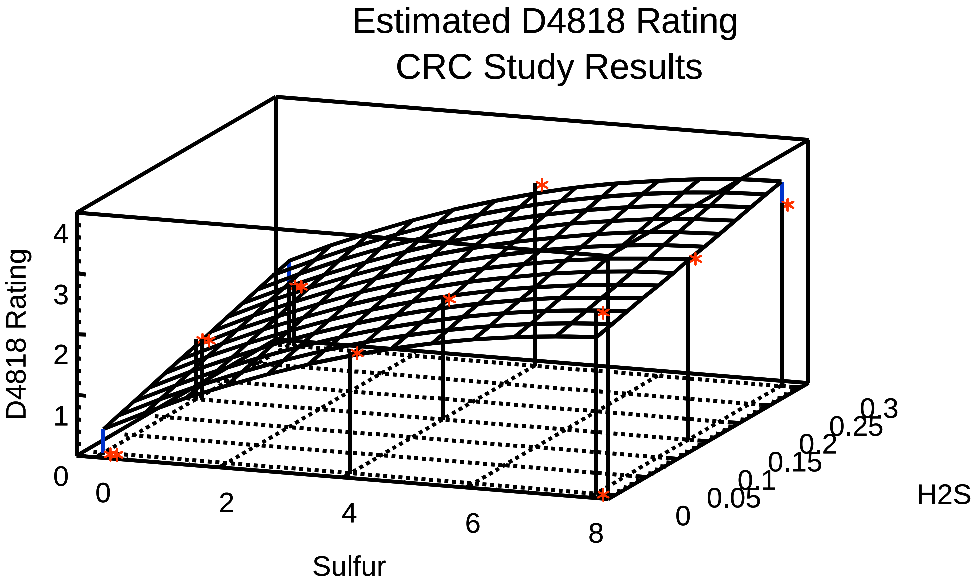
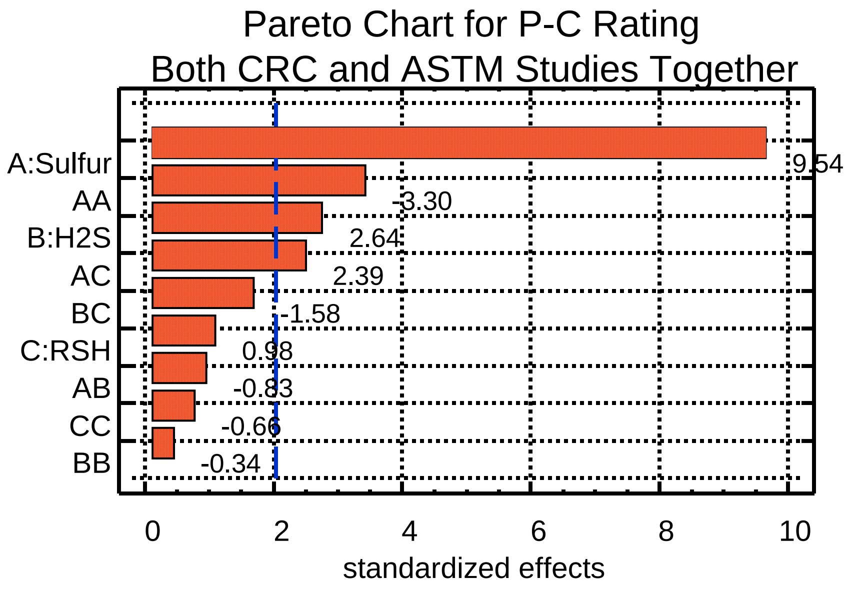
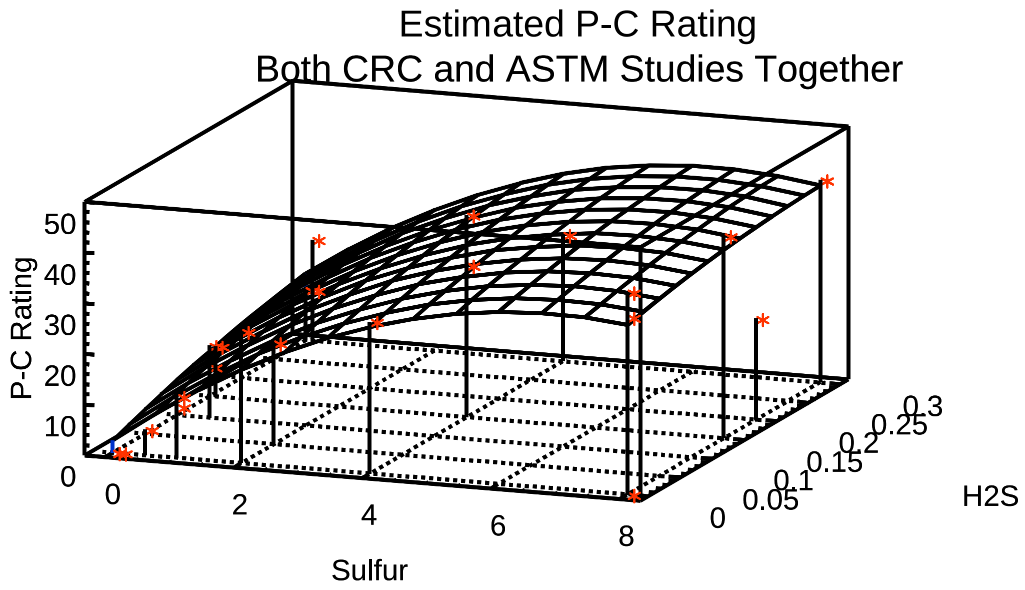


Figure 10: Combined CARB, Academic Fuel and ASTM Fuels Pareto Sulfur Species Sensitivity Chart Petro-Canada PCM 1005-33-111 Method





Appendix A
CRC Silver Fuel Level Sensor Corrosion Test Protocol
(CRC Project No. CM136-01/1)

Determining the Effect of Elemental Sulfur, Mercaptans, and Hydrogen Sulfide in Gasoline
on Silver Corrosion as Measured by Two Laboratory Test Procedures.
(CRC Project No. CM136-01/1)

1. Introduction

Incidents of fuel level sensor failures have been reported worldwide in recent years and are believed to result from corrosion of some silver electrical contacts by reactive sulfur species, such as elemental sulfur, mercaptans, and hydrogen sulfide.

Current ASTM D4814 Specification for Automotive Spark-Ignition Engine Fuel test methods, such as D130 Test Method for Corrosiveness to Copper from Petroleum Products by Copper Strip, were designed for other performance properties and are not adequate to detect low ppm levels of the reactive sulfur species. In response to recent events, ASTM Subcommittee D02.A successfully balloted a new requirement for inclusion in D4814 of a silver corrosion maximum limit and test method based on the D130 copper strip test method, but using the aviation apparatus and a silver coupon in place of a copper coupon.

It is the intent of this request is to receive bids from various laboratories to conduct the worked described. The bid request will cover preparing several fuels at various levels of hydrogen sulfide (H_2S), elemental sulfur and mercaptans and testing the prepared fuels in triplicate by both the Modified ASTM D130 test method (Annex A1 of D4814-04b) and the new silver wool test method (PCM I1005-33-111) from Petro-Canada. The fuels will be supplied to the contract laboratory to cover the work contained in this proposal.

2. Scope/Objective

The program will focus on understanding the corrosive action of elemental sulfur, H_2S and mercaptans as well as combinations thereof at various ppm levels in a matrix of two fuels (one commercial and one blended from two hydrocarbon streams) toward silver metal. The testing will establish a relationship between the reactive sulfur species (elemental, hydrogen sulfide and mercaptans) and the silver corrosion test ratings of fuels as determined by the modified ASTM D130 test method and a new Petro-Canada silver wool method PCM 1005-33-111.

3. Fuel Sulfur Test Design

Phase Ia: CARB Fuel

The sulfur species test matrix using varying levels of elemental sulfur, H_2S, and mercaptans in a CARBOB base fuel is attached in Table 6 .

Phase Ib: Synthetic gasoline prepared by blending HT Reformer Feed/Reformate.

The synthetic gasoline is a volume blend of 70 wt% Sweet Naphtha and 30 wt% High Octane Platformate. The sulfur species test matrix using varying levels of elemental sulfur, H_2S, mercaptans in a Synthetic gasoline blend can be found in Table 7.

4. Sulfur Species Blending Protocol

The intent of these protocols is to provide a basis for estimating the cost for blending test fuels to determine the effects of active sulfurs on Ag coupons in test methods described in Appendices A and B. These blending protocols call for the formulation of test fuels by inoculating a set of air free test gasolines with active sulfurs from a set of "working concentrates." Working concentrates are made from stock solutions tailored to yield the test matrix of Table 6 and 7. The prescribed blending strategy is to split active sulfurs into three classes and to make individual stock solutions for each of the active sulfur classes. Elemental sulfur, H_2S and light mercaptans are the three classes of active sulfurs of which respective stock solutions are to be produced. A 50/50 by weight sulfur mixture of ethyl and propyl mercaptan mercaptans will be used to represent light mercaptans. The concentration of active sulfur in each "working" concentrate is picked so that respectively 0.2 to 1.0 gram of "working" concentrate is used in the final blending of a single 30 mL batch of an Ag corrosion test fuel.

Actual "working" concentrates of elemental sulfur and light mercaptans are produced by inoculating nitrogen purged 90-95 mL test matrix aliquots in a septum capped 100 mL serum bottle with appropriate amounts of stock solution. The stock H_2S solution contains some 40-ppm of H_2S as sulfur and also serves as a "working" concentrate. The ethyl/propyl mercaptan mercaptans and elemental sulfur stock solutions contain, respectively, some 5000 and 1000 ppm by weight sulfur.

Verification of "as poured" active sulfur concentrations can be done by the use of a GC equipped with a sulfur specific detector (GC-SCD) or comparable analytical tool; i.e., Hg polarography for elemental sulfur. In the case that GC-SCD protocols are used to verify active sulfur levels in a California test fuel, non-active internal standards can be doped into the test gasoline matrix to serve as a verification reference. For experimental fuel testing, diethyl sulfide (3-Thiapentane - boiling point of 197.8°F) or low levels of thiophene (boiling point of 183.5°F) can serve as an internal standard.

Correlating "as poured" concentrations can be difficult because of the stringent timing requirements designed into each testing protocols. In the event that the injection of a sample into a sulfur speciation GC cannot be carried out at exactly the time of pouring, "as poured" concentrations can be approximated from "as blended" concentrations by setting up two sets of test samples, one to be used in each test method and the other to be poured near the sulfur speciation GC so as to mimic an "as poured" sample. A minimum of 6 checks between "as poured" and "as blended" need to be carried out to verify the "as poured" – "as blended" correlation: (0.15 ppm H_2S, 3.0 ppm mercaptans and no elemental sulfur), (0.15 ppm H_2S, 1.50 ppm mercaptan and 2 ppm elemental sulfur), (0.15 ppm H_2S, 1.5 ppm mercaptan and 4 ppm elemental sulfur), (0.30 ppm H_2S, 3 ppm mercaptan and no elemental sulfur), (0.3 ppm H_2S, 1.5 ppm mercaptan and 2 ppm elemental sulfur) and (0.30 ppm H_2S, 3 ppm mercaptan and 4 ppm elemental sulfur). The molecular weight, formula and density of sulfur species can be found in table 8.

Part 1

4.1 Protocols for formulating a 5000 ppm ethyl/propyl mercaptan mercaptans stock solution

1. Trained lab technicians with good wet chemistry techniques should attempt this protocol. Care should be given to working with inspected beakers and glassware since they will be temperature cycled.
2. To prevent oxidation of the mercaptans with air after doping, fuels which are to be stored for long time periods should be nitrogen purged before doping.
3. At room temperature, the ratio of mercaptans concentration in the headspace to that in the liquid phase as a numerical ratio of ppm by volume in the gas phase to ppm by weight sulfur in the liquid phase per respective component is greater than 1.0 but less then 5.0. Though the ratio is not extraordinarily high, care should be given to minimize headspace.
4. Stock solution consists of 2500 ppm of ethyl and 2500 ppm of 1-propyl mercaptans by weight sulfur.

Items need:

1. Exact requirements and calculations for doping
2. Experimental Fuel – 329.3 g is weighed from a 70 vol % naphtha reformer feed, 30 vol % reformate mix – nominal density of 0.74 g/mL
3. Reagent mercaptans as +98% pure or as a known secondary standard
4. 20% caustic - 200 mL (a 20% caustic mixture density is 0.606 g/ml)
5. 2 decimal scale
6. Supply of dry ice and a dry ice bucket – 1 liter
7. Supply of 500 mL beakers
8. Three 2000 mL beakers
9. Supply of 2 mL Pasteur pipettes
10. Catch pan
11. Plastic wrap
12. Dump caustic-recycle caustic set up for disposal of caustic
13. 16-ounce stock solution bottle with a good cap

Site area requirements:

1. Fuels to be purged in a hood having 1 psig regulated nitrogen supply.
2. All areas to have grounding points if large quantities of fuels are being transferred.
3. Fuels to be doped in a process area lab in a maintained hood with minimal backflow out of the hood.
4. Make sure the lab where doping protocols are to be followed has good eyewash since caustic is being used.
5. Reagent mercaptan bottles to be either recycled or stored in a freezer after use.
6. Doped fuel to be stored in a refrigerator.

Personal protective equipment:

1. Protective eyeglasses with side shields.
2. Good lab coat, long-sleeve shirt, pants and good shoes.

3. Good fitting gloves when doping with mercaptans, good-fitting warm gloves when working with dry ice.

4. If procedures are followed and the hood is in good working condition, then a respirator should not be required. Things do happen, so a respirator equipped with acid gas cartridge is recommended.

Pre-doping set-up:

1. Obtain all needed mercaptans or secondary standards, small bottles – 100 mL or less.
2. Check all doping calculations.
3. Purge stock solvent with nitrogen prior to doping.
   a. Find a well-maintained hood with a 1-psig-nitrogen supply-sparging rig
   b. Cool down he stock solvent with dry ice–note the fuel may freeze– if so, cool with ice.
   c. Depending on viscosity, freeze temperature and volume, sparge with dry nitrogen.
      1) Add 342 g (about 462.1 mL) of experimental fuel to a nitrogen purged 16 oz. bottle which as been pre-weighted with cap, cool the experimental fuel containing bottle externally with dry ice and sparged for 5 min at 100 mL min nitrogen.
      2) Put a cap on the bottle just sparged with nitrogen; do not tighten the cap.

   Allow the bottle to equilibrate to room temperature. Blow the head space off with nitrogen and tighten the cap after equilibration. Determine weight after sparging by subtracting the weight of the empty bottle/cap from the experimental fuel containing bottle/cap.
4. Find a well-maintained – clean hood in a process area for doping protocols.

Mercaptan doping protocols:

1. Put the catch pan into a well-maintained hood; allow enough space for free hand movement. Sides of the catch pan need not be higher then 2 inches.
2. Put the scale into the catch pan. Secure the cord to prevent accidental movement, which could hit the mercaptan bottles.
3. Put the reagent mercaptan bottles or secondary standards into 500 mL beakers.
4. Add dry ice to each beaker containing the mercaptan bottles. Leave enough room at the top of the bottle so that the mercaptan bottles can be uncapped when needed.
5. Put each 500 mL beaker containing a reagent mercaptan bottle and dry ice inside the catch pan. Put two 2000 mL beakers alongside of the catch pan in the hood for clean up.
6. Add 200 mL of 20% caustic into a 500 mL beaker and place this inside the catch pan. This will be your dumpsite for pipettes inside the hood.
7. Put a layer of plastic wrap over the scale – just in case.
8. Take the cap off the stock solvent bottle and place the stock solvent bottle and cap on the scale.
9. Open and close one mercaptan bottle at a time starting with the highest boiling mercaptan; if an accident happens, stop the procedure and determine the scope of the accident. Call for

help if needed. If it is minor, put on a respirator and go to the clean up phase. Need to add 2.03 g of propane thiol followed with 1.66 g of ethane thiol.

a. Using a new 2 mL Pasteur pipette, suck up about 1.5 mL of mercaptan and discharge the pre-determined amount of mercaptan into the stock solvent bottle; repeat until the known amount of mercaptan has been added.
b. Put the used Pasteur pipette into the caustic dumpsite.
c. Close the opened bottle of mercaptan.
d. Close the stock solvent bottle being doped.
e. Draw some caustic from the 500 mL caustic dumpsite up into the used pipette and discharge back into the 500 mL beaker. Do this a couple of times.
f. Repeat above from step 8 until all mercaptans have been doped, capping and uncapping the stock solvent bottle between mercaptan additions.

4.2 Protocols for generating a 1000-ppm stock solution of elemental sulfur

1. Source of elemental sulfur is important. Use precipitated sulfur because of ease of solubility. Fumed sulfur is not recommended because of it is difficulty to dissolve (if it is to be used, heat the pure fumed sulfur for 1 hour at 105-110°C to convert amorphous sulfur).
2. Choose an appropriate C8 rich aromatic hydrocarbon solvent for the elemental sulfur stock solution (remaining calculations are based on using the 30/70 Experimental fuel). Typically add about 333 g (450 mL) of solvent into a 16-ounce bottle. An aromatic doped Experimental fuel is used as the stock solution matrix because of the relatively high solubility limit of elemental sulfur in aromatics.
   in Heptane, ~0.12 wt% at 0°C
   in Toluene, ~0.92 wt% at 0°C
   in test fuel FR42488 (~ 25 wt% aromatics) likely < 0.33 wt% at 0°C
   Note: This solvent should be sparged with dry nitrogen at dry ice temperatures to eliminate dissolved air/oxygen as a source for reacting with either H_2S or mercaptans in test fuels.
3. Elemental sulfur stock solution – add 0.334 g of precipitated sulfur to the chosen purged solvent. Typically allow 20 min to dissolve elemental sulfur.

4.3 Protocols for generating a 40-ppm H_2S stock solution

1. Obtain certified purity H_2S source. Scott Specialty Gases 99.5% H_2S or 1% H_2S in nitrogen has been used. The same vendor can supply sources at lower certified H_2S concentrations.
2. Check all doping calculations.
3. Use a 100 mL serum vial, septum capped to retain H_2S.
4. Add about 70.3 g experimental fuel (about 95 mL) to a 100 mL serum bottle leaving 10 to 15 mL of headspace. Cap the bottle.
5. Find a well-maintained – clean hood in a process area for doping protocols.
6. Purge stock solvent with nitrogen prior to doping.
   a. Find a maintained hood with a 1-psig supply dry nitrogen-sparging rig.

b. Puncture the cap with two luer-hooked needles.
c. Connect one end to a vent by the use of a tube – place the tip of the needle just under the septum.
d. Connect the other end to a supply of dry nitrogen – place tip of needle at the bottom of the serum bottle.
e. Cool down the fuel with dry ice – note the fuel may freeze – if so, cool with ice.
f. Depending on viscosity, freeze temperature and volume, sparge with dry nitrogen – make sure there is sufficient headspace to allow for sparge gas disengagement. Sparged for 5 min at 50 mL min nitrogen.

7. Take out only the nitrogen purge needle and check final weight of solvents. Adjust doping protocols to match final solvent weights.
8. (A) From a H_2S lecture cylinder equipped with appropriate purges and bleed sample manifold (consult safety office for an acceptable configuration), pull about 3 mL of H_2S into a gas tight syringe. Vent about 1.1 mL of H_2S out through the needle; then again puncture the septum trying to use the same puncture hole as the one used in the purging step. Push the remaining 1.9 mL of H_2S into the purged solvent.

8. (B) if a diluted source of H_2S is to be used, connect the cylinder to an appropriate purge and bleed sample manifold that has a 1-psig-relief valve. Connect the manifold to a sparging needle. With the flow directed to vent, set delivery flow to 10 mL a min and puncture the septum with the sparging needle. After establishing a controlled flow, switch the flow to the serum bottle. After allowing sufficient flow to produce a 40 ppm H_2S stock solution, switch the flow from the serum bottle, turn off the diluted H_2S cylinder, remove the sparging needle and purge the “purge and bleed” sample manifold.

9. Take out all needles and shake inoculated stock solution.

10. Repuncture with the vent needle equipped with a 1-psig pop valve and allow the serum bottle to thermally equilibrate. Take out all needles.

11. Concentration of H_2S to be checked through sulfur speciating techniques capable of detecting 50 ppb H_2S at a 10/1 signal to noise ratio. If the initial H_2S concentration is too high, dilute with sparged solvent or test fuel or sparge some of the H_2S off. If the stock solution is to low, add more H_2S.

Part 2

4.4 Protocols for generating “working concentrations” of ethyl/propyl mercaptan mercaptans along with elemental sulfur for experimental fuels, density of 0.74 g/ml. Calculation will need to be redone when the fuel density is known.

Nominal 111 ppm of mercaptan sulfur experimental fuel “working concentrate”

1. Add 68.7 g of experimental fuel to a 100 mL serum bottle.
2. Purge per instruction in H_2S doping section.
3. Add nominally 1.56 g of 5000-ppm mercaptan stock solution.

Nominal 178 ppm of elemental sulfur experimental fuel “working concentrate”

1. Add 57.8 g of experimental fuel to a 100 mL serum bottle.
2. Purge per instruction in H_2S doping section.
3. Add nominally 12.5 g of 1000-ppm elemental sulfur stock solution.

Nominal 40 ppm of H_2S “working concentrate” is the same as stock solution and will be used for both synthetic gasoline and California fuel doping.

Clean up:

1. Make sure all reagent bottles are capped and then remove each reagent mercaptan bottle from its respective dry ice beaker and place the bottles in one of the larger 2-liter beaker in the hood to warm up before eventually storing.
2. Take the 500 mL beakers, which contain dry ice and put them into the other 2-liter beaker. Allow the dry ice to sublime.
3. Take the plastic wrap off the scale and put it into the beaker containing the 500 mL dry ice beakers.
4. Unsecure the power cord from the scale and remove the scale
5. Take each of the pipettes from the dumpsite and wash with water collecting the discharge water in the third 2000 mL beaker – discard the washed pipettes into the oily trash.
6. Take the 500 mL caustic dumpsite out from the catch pan and leave it in the hood.
7. If there is any mercaptan drops in the catch pan, rinse the catch pan with caustic putting the rinsed caustic into the 500 mL dump caustic site. Rinse the catch pan again with two washings of water, putting each wash water into the third 2000 mL beaker.
8. Dump the 500mL beaker dump caustic into the caustic disposal-recycle container.
9. Wash the 500mL beaker dump caustic with water collecting the wash water in the third 2000 mL beaker. Dump wash water into the caustic disposal-recycle container.
10. Remove gloves and place gloves into the 2000 mL beaker that is in the hood, which now contains the 500 mL beakers that had the dry ice in them.
11. Over the next few hours check for odors.
12. Store reagent mercaptans in freezer and send beaker out to be cleaned.
13. Put plastic wrap and gloves into oily trash.

4.5. Protocols for generating California fuel “working concentrations” of ethyl/propyl mercaptan mercaptans along with elemental sulfur for California Fuels, density of 0.731 gm/ml. Calculation will need to be redone when the fuel density is known.

Nominal 110 ppm of mercaptan sulfur California fuel “working concentrate”

1. Add 67.9 g of California fuel to a 100 mL serum bottle.
2. Purge per instruction in H_2S doping section.
3. Add nominally 1.52 g of 5000-ppm mercaptan stock solution.

Nominal 175 ppm of elemental sulfur California fuel “working concentrate”

1. Add 57.2 g of California fuel to a 100 ml serum bottle.

2. Purge per instruction in H_2S doping section.
3. Add nominally 12.2 g of 1000-ppm elemental sulfur stock solution.

Nominal 40 ppm of H_2S “working concentrate” is the same as stock solution and will be used for both experimental fuel and California fuel doping.

Appendix B

Membership of the CRC Silver Corrosion Sender Unit Panel

Name	**Affiliation**
Robert Halsall	General Motors (retired)
Ben Bonazza	TI Group Automotive Systems (retired)
Andrew Buczynksy	General Motors
Julie Galante-Fox	Afton Chemical
Lew M. Gibbs	Chevron Products Company
Joe T. Joseph	BP Naperville Center (retired)
David Surette	Petro-Canada
Ken Mitchell	Shell
Joseph Russo	Shell Global Solutions
N.L. (Toby) Avery	ExxonMobil Company (retired)