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Investigation of Sulfate Salt Solubilities in Ethanol and Gasoline-Ethanol Blends

Final Report

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5755 NORTH POINT PARKWAY • SUITE 265 • ALPHARETTA, GA 30022

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Prepared by:
S. Kent Hoekman

Desert Research Institute
Reno, NV 89512

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1. Executive Summary

During a period of rapid fuel ethanol expansion in the early 2000s, a number of field problems were observed related to fuel filter plugging and fuel injector deposit formation. Based on limited evidence available at the time, it was concluded that these problems were related to fuel contamination by insoluble sulfate salts, particularly sodium sulfate (Na_2SO_4). Further evidence suggested that these contamination issues originated with the ethanol blending component of the E10 fuels being used at the time. (E10 consists of 10 volume percent ethanol in gasoline.) Based on this and other stakeholder information, in 2005 ASTM established a maximum limit of 4 ppm inorganic sulfate (by mass) as part of the Standard Specifications for Denatured Fuel Ethanol (ASTM D4806). Following incorporation of this specification, field problems related to sulfate deposits disappeared.

More recently, increasing use of ethanol prompted renewed interest in this problem of sulfate contamination. Thus, in 2016-2017, CRC Project CM-136-15-1 was conducted to investigate the ethanol solubility of several sulfate salts: ammonium, calcium, potassium, and sodium. Sodium bisulfite was introduced later in the project, once it became known that this substance is (or was) utilized within corn ethanol production plants. Additionally, the presence of sodium bisulfite – and its oxidation to sulfate – could help explain discrepancies between existent and potential sulfate measurements. Solubility experiments were conducted in this earlier CRC project by stirring a large excess of each salt in ethanol, followed by filtration and ion chromatography (IC) analysis of the clear filtrates. Results indicated extremely low solubility (<1 ppm) of calcium, potassium, and sodium sulfate; slightly higher solubility (~10 ppm) of ammonium sulfate; and even higher solubility (~100 ppm) of sodium bisulfite. After aging in clear glass bottles for several months, the filtrates from sodium bisulfite experiments (but none of the other salts) became noticeably cloudy, suggesting that oxidation of soluble bisulfite to insoluble sulfate had occurred.

The current project focused on solubilities of sodium sulfate and sodium bisulfite ($NaHSO_3$) in ethanol and gasoline-ethanol blends – specifically E10, E30, E50, and E60. The originally-proposed experimental matrix called for a very large number of IC analyses, as a wide range of spiked salt concentrations were used in these ethanol and gasoline-ethanol solutions, and measurements were made after several periods of aging. Consequently, a simpler IC analysis method was employed (ASTM D7319), which utilizes direct injection of the samples, as opposed to the previously used ASTM Method D7328, which requires sample blowdown and reconstitution in water.

Sodium sulfate containing ethanol solutions were prepared by adding small amounts of a concentrated aqueous Na_2SO_4 solution to 200 proof ethanol. The final concentrations of spiked Na_2SO_4 were 0, 1, 2, 4, 8, 16, 32, and 64 ppm. All ethanol solutions contained 0.50 vol.% water. Direct-injection IC results from these ethanol solutions showed much lower measured concentrations than the spiked levels, especially as the samples aged – i.e., values measured after 1-week and 4-weeks of settling were generally lower than those measured when the solutions were first prepared. This suggests that upon sample preparation, some amount of finely-dispersed salt particles remain suspended in ethanol for an extended period of time. Although the true solubility of Na_2SO_4 in ethanol is probably <1 ppm, sulfate concentrations as high as 10-20 ppm were measured in freshly prepared ethanol solutions that had been spiked with 64 ppm of the salt. Such elevated sulfate levels were not observed in any of the gasoline-ethanol blends, suggesting that the suspended salts present in high-polarity ethanol rapidly precipitate when mixed with low-polarity gasoline.

Similar results were obtained from direct injection of the $NaHSO_3$-spiked ethanol solutions that were prepared like the Na_2SO_4 ethanol solutions described above. Although spiked with sodium bisulfite, only the sulfate ion was observed by IC – suggesting that oxidation of bisulfite to sulfate readily occurred during the processes of sample preparation, storage, handling, and analysis. As with the Na_2SO_4 samples, much lower sulfate concentrations were measured from the $NaHSO_3$ samples than had been spiked into the solutions. A significant difference seen with the $NaHSO_3$ samples is that the measured sulfate concentrations did not vary much with sample age. This suggests that some amount of the spiked $NaHSO_3$ (perhaps 10-15 ppm) may actually have been dissolved, and not merely present as suspended solids that eventually settle out. Once gasoline was added to these ethanol solutions containing $NaHSO_3$, near-zero sulfate levels were measured, suggesting that $NaHSO_3$ (like Na_2SO_4) is virtually insoluble in gasoline-ethanol blends.

Although originally planning to analyze these $NaHSO_3$-spiked solutions for potential sulfate, this was not done due to chromatographic problems resulting from direct injection of solutions containing hydrogen peroxide. Additionally, it was discovered that $NaHSO_3$ is not available in highly pure form, but is contaminated with a significant amount of sodium metabisulfite ($Na_2S_2O_5$), as well as a smaller amount of Na_2SO_4. Because of these problems, additional experiments were conducted to examine the behaviors of $NaHSO_3$ and $Na_2S_2O_5$ in ethanol, using only the ASTM D7328 method (involving sample blowdown and re-constitution in water) to analyze for existent and potential sulfate.

Two sets of ethanol solutions were prepared containing varying amounts of $NaHSO_3$ and $Na_2S_2O_5$, ranging from 1 to 64 ppm. The initial sample sets were prepared by adding the appropriate amounts of solid, anhydrous salts to ethanol. After vigorously shaking, these solutions were left undisturbed for 48 hours, before removing two 10-mL aliquots for existent and potential sulfate determinations. The solutions were then re-shaken to mix all soluble and insoluble materials, and two additional 10-mL aliquots were removed for existent and potential sulfate determination. Thus, four IC analyses were conducted on each spiked ethanol solution: shaken and unshaken (to distinguish dissolved and total salts) and existent and potential (to distinguish oxidized and reduced forms of the salts).

In all IC analyses, only sulfate ion was observed, not bisulfite or metabisulfite. Sulfate results from these experiments were very similar between the sodium bisulfite and sodium metabisulfite sample sets. The most significant difference was in existent sulfate measured from unshaken samples, which may be considered a measure of salt solubility in ethanol. These sulfate concentrations were approximately twice as high with the metabisulfite samples, as compared to bisulfite samples. However, the main observations from these experiments were that the sulfate concentrations measured in all samples increased linearly with spiked amount, and these levels were similar to the spiked levels. This suggests that these salts undergo some type of complexation with ethanol, thus keeping substantial amounts of the salts in suspension, although not fully solubilized. Centrifugation of representative samples was conducted, but was not very effective in removing insoluble material. However, addition of gasoline to produce E50 blends significantly reduced the amount of salts in solution, suggesting that whatever complexation existed between ethanol and the salts was readily disrupted upon addition of a non-polar solvent, like gasoline.

These sodium bisulfite and sodium metabisulfite experiments in ethanol were repeated using concentrated aqueous solutions of the salts, rather than their solid, anhydrous forms. In these experiments, the concentration of water in all samples was 0.50 vol.% Precautions were taken during sample preparation and handling to minimize exposures to air. Consequently, existent sulfate analyses of these samples showed two chromatographic peaks: one for sulfate; the other for bisulfite/ metabisulfite. (No chromatographic distinction could be made between bisulfite and metabisulfite ions.) In quantification of these peaks, it is important to apply separate response factors, as the IR detector was approximately twice as sensitive to sulfate as to bisulfite/metabisulfite.

As with the earlier experiments, four IC analyses were conducted on each salt-spiked ethanol solution. Results from the sample sets spiked with sodium bisulfite and sodium metabisulfite were virtually identical. In both cases, the unshaken samples (presumably containing only dissolved salts) had slightly lower concentrations than the corresponding shaken samples. Potential sulfate measurements were higher than existent sulfate measurements, whether shaken or not. These results suggest that both sodium bisulfite and sodium metabisulfite have slight solubility in ethanol – on the order of 10 ppm – whereas considerably higher concentrations may be present in the form of suspensions/agglomerations. Addition of gasoline to produce E50 blends apparently disrupted these suspensions/agglomerations, resulting in significantly reduced soluble concentrations.

In this project, a large number of experiments were conducted to examine the solubility of three sulfate salts (Na_2SO_4, $NaHSO_3$, and $Na_2S_2O_5$) in ethanol and gasoline-ethanol blends. Despite careful efforts in sample preparation and analysis, accurate determination of salt solubility remains elusive. A major factor contributing to the difficulty in quantifying solubility is that the salts (particularly $NaHSO_3$ and $Na_2S_2O_5$) appear to undergo some form of complexation with ethanol, thereby keeping relatively high concentrations in suspension (perhaps up to 50 ppm), though not fully solubilized. Addition of gasoline to produce gasoline-ethanol blends readily disrupts these suspensions, resulting in greatly reduced levels of the salts in solution.

Additional factors complicating this work include the oxidative instability of bisulfite, which readily transformed to sulfate during sample preparation and analysis; the presence of significant impurities in reagent-grade sodium bisulfite; and the different behaviors of anhydrous and hydrated forms of these salts. Measurement of sulfate salts by a direct injection IC method (ASTM D7319) was shown to be unreliable in some cases. Given all these complexities and uncertainties, specific conclusions from this project are as follows:

- Accurately determining the solubility of sodium sulfate in neat ethanol is very difficult. Based on literature reports[2] and observations from the present study, this solubility is probably less than 1 ppm.
- The solubility of sodium sulfate in gasoline-ethanol blends is extremely low – certainly less than 1 ppm.
- The solubility behaviors of sodium bisulfite and sodium metabisulfite in ethanol are very similar to each other, though different from the behavior of sodium sulfate.

- Sodium bisulfite and sodium metabisulfite are significantly more soluble in ethanol than is sodium sulfate – perhaps by an order of magnitude – but not by 2-orders of magnitude, as was previously thought.
- Due to complexation or other factors that keep finely dispersed sodium bisulfite (and metabisulfite) suspended, the salt "carrying capacity" of ethanol may be an order of magnitude higher than the actual solubility of these salts.
- Addition of gasoline to salt-containing ethanol solutions appears to disrupt these suspensions, causing the salts to drop out of solution, thereby greatly reducing the salt "carrying capacity" of gasoline-ethanol blends as compared to neat ethanol.
- Investigation of these issues regarding solubility and suspensions of salt solutions requires analysis of both existent and potential sulfate, using ASTM Method D7328.
- Quantification of insoluble salts in ethanol and gasoline-ethanol blends by direct visual observation is very difficult. Levels below 10 ppm are imperceptible to most observers, while levels above 20 ppm are readily seen as slightly cloudy solutions.

Applying these findings to real-world fuel situations suggests a possible route by which sulfate salt contamination could occur in gasoline-ethanol blends. Ethanol's relatively high carrying capacity for salts – whether they are dissolved or not, and whether they are in an oxidized or reduced form – provides an effective way for the salts to be transported throughout the ethanol distribution system. Once blended with gasoline, the salts readily drop out of solution as small, insoluble particles, which conceivably could contribute to filter plugging and deposit problems in the field.

2. Introduction and Background

2.1. Historical concerns

Concerns about sulfate contamination in fuel ethanol and gasoline-ethanol blends have existed since the early 2000s, when a large number of corn ethanol plants were built and/or expanded, and a substantial amount of ethanol (billions of gallons/year) began to be used in U.S. gasoline. A series of well-documented field problems with ethanol-containing gasoline occurred at that time, involving filter plugging, injector fouling, and vehicle operational problems.[1-3] Evidence suggested that these problems were related to sulfate contamination in the denatured ethanol that was blended into finished gasoline. The composition of deposit materials isolated from filters and fuel injector hardware included sulfate anions along with various associated cations, generally including sodium, potassium, calcium, and ammonium. Several more recent laboratory studies have also investigated the potential role of sulfate in gasoline-ethanol blends with respect to engine deposit formation.[4-6]

In 2005, ASTM modified the Standard Specification for Denatured Fuel Ethanol (ASTM D4806[7]) to include a maximum specification of 4 ppm (by mass) for "existent sulfate." The term "existent sulfate" refers to sulfate anions already present in a sample, prior to any oxidative treatment. The term "potential sulfate" refers to sulfate ions present in a sample after oxidative treatment with hydrogen peroxide. This oxidative treatment has the effect of transforming various reduced forms of sulfur oxides – such as SO_2, HSO_3, and SO_3 – into fully oxidized sulfate, SO_4. Following adoption of this sulfate specification, field problems related to sulfate contamination in the fuel disappeared. This development supported the hypothesis that high levels of sulfate in denatured ethanol were responsible for the earlier field problems.

Although there is considerable evidence that sulfates were involved in these earlier field problems, the root cause of the sulfate salts was never unequivocally established. One problem was that although detectable levels of sulfate were frequently measured in ethanol, the corresponding cation (such as sodium or potassium) was usually not detectable. It has been hypothesized that the cations present in the observed sulfate salt deposits on filters and fuel injectors originated from fuel storage and distribution systems, or from hardware within fuel injection equipment, although none of these pathways has been clearly demonstrated. A conclusion from a recent NREL report on sulfate salts in fuels is that the counter cation in fuel ethanol is most likely the hydrogen ion, H^+.[2] A possible source of H^+ is the reaction between water and sulfur dioxide, to produce sulfurous acid:

$$SO_2 + H_2O \rightarrow H_2SO_3 \qquad \text{(Eq. 1)}$$

Corn ethanol production plants utilize SO_2 in various ways, creating at least a possibility of the final ethanol product being contaminated with SO_2, which is not removed by the normal distillation or dehydration processes. Another possible source of sulfur oxides in ethanol is the use of bisulfite within the plant's fermentation scrubber to control aldehyde emissions. Equation 2 illustrates the reaction of sodium bisulfite with acetaldehyde to produce a water-soluble sulfonic acid salt of acetaldehyde, which is then removed from the ethanol product.

$$NaHSO_3 + CH_3CHO \rightarrow CH_3CH(OH)SO_3^-Na^+ \qquad \text{(Eq. 2)}$$

There is at least anecdotal evidence that during the early days of bisulfite usage, improper operation of bisulfite scrubber systems led to sporadic sulfate contamination problems.[1] This could happen with overdosing of bisulfite, coupled with improper pH control, such that sulfurous acid was produced, which then distilled with the ethanol and was retained in the finished product. However, as bisulfite scrubbers were not commonly used until 2006, this could not have been a major cause of the field problems observed in the early 2000s.

Problems associated with sulfate contamination in fuel ethanol and gasoline-ethanol blends may have diverse origins. It is possible that certain sulfur-containing contaminants originally introduced into the fuel may chemically transform (likely through oxidation) to other substances during transport and storage. Through these processes, contaminants that are slightly soluble in ethanol may convert to less soluble materials. Additionally, materials that are slightly soluble in ethanol may be completely insoluble once the ethanol is added to gasoline. The sulfur-containing species possibly involved in these processes are sulfur oxides and their anions. The oxidation transformations involved likely result in conversion of sulfur-IV to sulfur-VI ions. Appendix I provides a listing and brief summary of properties of the sulfur oxides and their anions that could be involved in these processes.

2.2. Prior CRC work

Because adoption of the 2005 sulfate specification in ASTM D4806 appeared to solve the problem, further investigation into the sources of sulfates (and their associated cations) was not conducted at that time, nor was any formal research program undertaken to define acceptable levels of sulfate salts in denatured ethanol. However, current interests in using higher ethanol blend gasolines has also stimulated a desire to develop a more complete mechanistic understanding of how these sulfate deposits form, and to obtain information upon which to base a fully protective ASTM standard. Thus, in 2016-2017, CRC sponsored Project CM-136-15-1, entitled "Investigation into filter plugging due to sulfate salt contamination of ethanol, gasoline, and gasoline-ethanol blends."

CRC Project CM-136-15-1 investigated solubility behaviors of five sulfate salts in anhydrous, 200-proof ethanol: ammonium sulfate [$(NH_4)_2SO_4$], calcium sulfate ($CaSO_4$), potassium sulfate (K_2SO_4), sodium sulfate (Na_2SO_4), and sodium bisulfite ($NaHSO_3$). Solubility was assessed using ion chromatography (IC) to measure sulfate ions within filtrate solutions obtained by filtering a concentrated slurry/solution of each salt in ethanol. The IC method utilized was that described in ASTM D7328.[8] Results showed that calcium sulfate, potassium sulfate, and sodium sulfate all had extremely low solubilities (<1 ppm), whereas ammonium sulfate and sodium bisulfite appeared to have somewhat higher solubilities, estimated to be approximately 10 ppm and 100 ppm, respectively. These results were not greatly affected by inclusion of 2 wt.% water in the ethanol, or by temperature changes (5 °C vs. 25 °C). All filtrate solutions analyzed by IC were clear and bright.

After sitting at room temperature for several months, a white sediment was seen on the bottom of the bottles containing filtrates from the sodium bisulfite experiments, but not in filtrates from the other salt experiments. Upon shaking the bottles, these sediments were readily dispersed, creating cloudy solutions, as seen in Figure 1. Note that in this figure, the 2nd group of bottles from the left (which appear the most cloudy) contained filtrates from anhydrous ethanol solutions containing sodium bisulfite, whereas the far right group of bottles (which also appear somewhat cloudy) contained filtrates from sodium bisulfite solutions in ethanol that included 2 wt.% water. Based on these observations, we hypothesized that gradual oxidation of dissolved sodium bisulfite occurred within the stored sample bottles, leading to formation of insoluble sodium sulfate. However, results obtained from the present study raise some questions about this.

Figure 1. Photo of collected filtrates from earlier project experiments (CRC CM-136-15-1) in which sulfate salts were added to ethanol.
Samples were stored on a laboratory benchtop in the glass bottles shown for 1-3 months, then were shaken prior to photographing. Note cloudiness of filtrates from experiments using sodium bisulfite.

Additional experimentation was conducted to investigate the solubility of sodium sulfate and sodium bisulfite in non-oxygenated gasoline. Two different gasoline samples were used: one with high aromatics content (40 vol.%) and one with low aromatics (1 vol.%). In addition, the effects of adding low and high concentrations of two different detergent additives were examined: (1) a polyether amine (PEA) additive and (2) a polyisobutyl amine (PIBA) additive. Results showed that the solubility of both sodium sulfate and sodium bisulfite in all the gasolines (as determined by IC analysis of filtrate solutions) was very low (<1 ppm), regardless of aromatic content or additive type. One possible exception was the slightly increased solubility of sodium bisulfite (2-3 ppm) when a high amount of PIBA was present in the high aromatics gasoline.

CRC Project CM-136-15-1 was successful in demonstrating extremely low solubility of anhydrous sodium sulfate in both 200-proof ethanol and in gasoline. This agrees with the recent NREL report that states: "… there is experimental evidence that sodium sulfate solubility in ethanol is particularly low, i.e., no more than 0.3 ppm, and likely much lower."[2] Thus, fuel ethanol at the ASTM D4806 limit of 4 ppm sulfate would contain significant levels of insoluble salt (assuming this originated from sodium sulfate). Use of this ethanol to produce E10 would dilute the sulfate to 0.4 ppm, but even this level probably exceeds the solubility limit of sodium sulfate. Based on results of the present study, we now know that ethanol containing up to 4 ppm of insoluble sodium sulfate would appear clear and bright, as this level of contamination is nearly imperceptible to the human eye. However, concentrations that are much higher (e.g., >20 ppm) would have a noticeably cloudy appearance.

In these earlier experiments to determine the solubility of various sulfate salts in ethanol and gasoline, sulfate concentrations in the filtrates were determined according to both the existent sulfate method and the potential sulfate method described in ASTM D7328. For the sulfate salts of calcium, potassium, sodium, and ammonium, no large differences would be expected between the existent and potential sulfate results, because the starting salts contain no oxidizable sulfur species, as they are already in the fully oxidized sulfate form; i.e., sulfur-VI oxidation state. For sodium bisulfite, however, a large difference between existent and potential sulfate would be expected – and was seen. Surprisingly, even without addition of hydrogen peroxide, the sodium bisulfite samples that were analyzed showed significant levels of sulfate ions to be present. The explanation for this was not clear at the time, though we suspected that some oxidation of bisulfite (sulfur-IV) to sulfate (sulfur-VI) occurred during the normal procedures of sample preparation, handling, storage, and analysis. During the present study, we confirmed that this oxidative conversion of bisulfite to sulfate occurs readily, making it very difficult to quantify bisulfite itself in any sample.

It should also be noted that sodium bisulfite cannot be purchased in highly pure form, as it always contains some amount of sodium sulfate and sodium metabisulfite. However, contamination of the sodium bisulfite reagent with sodium sulfate does not by itself explain the significant existent sulfate concentrations seen in these bisulfite experiments, as any sulfate initially present would be insoluble in ethanol, and would be filtered out.

Another complication discovered in the earlier CRC project stems from differences in solubility between the anhydrous and hydrated forms of sodium sulfate. In nature, sodium sulfate exists most commonly in the form of a decahydrate ($Na_2SO_4 \cdot 10\ H_2O$), also known as Glauber's salt. Based upon simple, preliminary experiments involving addition of small increments of solid sodium sulfate (both anhydrous and hydrated forms) to ethanol and observing their dissolution, it appeared that the hydrated form had considerably higher solubility compared to the anhydrous form. This issue may be important in field situations where water is likely to be present, and in laboratory experiments where aqueous solutions of sodium sulfate are used to prepare known concentrations of sulfate solutions in ethanol.

2.3. Project objectives

While the previous CRC project did provide useful information about the solubilities of various sulfate salts in ethanol and gasoline, data regarding solubility in gasoline-ethanol blends was quite limited. In the present work, the initial objective was to investigate the solubility of sulfate salts in realistic fuels containing 10, 30, and 60 vol.% ethanol in gasoline: E10, E30, and E60, respectively. However, only two sulfur species were initially considered here – sodium sulfate and sodium bisulfite – as compared to five sulfur species in the earlier work. Also, in the present work, a single non-oxygenated gasoline sample (provided by CRC) was used, and no variations in detergent additive, water content, or temperature were included. A further objective of this work was to carefully observe the appearance of the fuel blends, and document any precipitation and/or cloudiness that appeared in these blends.

As this project proceeded, it became apparent that sodium metabisulfite ($Na_2S_2O_5$) was present as a significant contaminant of sodium bisulfite ($NaHSO_3$). (In both compounds, sulfur is in oxidation state IV.) According to the supplier-provided information, high purity $NaHSO_3$ is not available. The sample used in this project (purchased from Fischer Scientific) had an assay value of 63% $NaHSO_3$, which implies that it could contain over 30% $Na_2S_2O_5$. Thus, an additional objective was included to investigate the solubility behavior of sodium metabisulfite in ethanol and gasoline-ethanol blends. $Na_2S_2O_5$ can be purchased in relatively pure form – the sample used here was 97% pure.

3. Methods and Materials

3.1. Materials

The non-oxygenated gasoline used in this project was obtained by one of the CRC member companies and shipped to DRI in 1-gallon metal cans. This material was a typical RBOB (refinery blendstock for oxygenate blending), and was not intended to have a specific aromatics content or meet other compositional specifications. Qorpak™ Square glass bottles with Teflon-lined caps (4 oz. 120-mL; Fisher Scientific) were used to contain the various ethanol and gasoline-ethanol blends that were prepared (see Figure 2).

Figure 2. Qorpak™ square glass bottles used for observing and photographing gasoline/ethanol blends containing varying levels of Na_2SO_4 and $NaHSO_3$

It was originally thought that square bottles would be better than round ones for observing and photographing the cloudiness of salt-containing solutions, but this did not prove to be true. Results from this work showed that effectively photographing cloudiness was extremely difficult, regardless of the type of container used. Ultimately, efforts to obtain photographic documentation of cloudiness were abandoned.

Anhydrous, 200-proof ethanol was obtained from Acros Organics. The sulfate salts were purchased from several commercial vendors, and were used “as is.” The sources and purity levels of these materials are shown below:

- Ethanol (C_2H_6O) – 99.5%, ACS Reagent, absolute, 200-proof (Acros Organics)
- Sodium sulfate (Na_2SO_4) – 99+%, ACS Reagent, granular, anhydrous (Acros Organics)
- Sodium sulfate decahydrate ($Na_2SO_4.10H_2O$) – 99% (Alfa Aesar)
- Sodium bisulfite ($NaHSO_3$) – Certified ACS, powder, assay 63.4% (Fischer Scientific)
- Sodium metabisulfite ($Na_2S_2O_5$) – 97%, granular (Alfa Aesar)

3.2. Preparation of stock solutions of Na_2SO_4, $NaHSO_3$, and $Na_2S_2O_5$ in ethanol

In the first phase of this experimental project, sets of ethanol and gasoline-ethanol blends were prepared containing specific amounts of Na_2SO_4 and $NaHSO_3$. These sample sets were prepared from a series of ethanol stock solutions containing 0, 1, 2, 4, 8, 16, 32, and 64 ppm of the appropriate salt. The E10, E30, and E60 fuel blends were then prepared by mixing appropriate amounts of the ethanol stock solutions with gasoline. In the second phase of the project, a similar set of ethanol stock solutions was prepared using sodium metabisulfite, although these were not mixed with gasoline to make E10, E30, and E60 blends.

To prepare the ethanol stock solutions, 1.00 wt.% aqueous solutions of the appropriate salt were first created. Using gravimetric means, specific amounts of these 1.00 wt.% aqueous concentrates were added to 1.00 L volumetric flasks, along with the necessary amount of water to provide a final water concentration of 0.50 vol.% in each stock solution. Detailed procedures for preparing the stock solutions are provided in Appendix II. Note that the concentrations of these stock solutions are expressed as wt.% of the total salt in ethanol, including the sodium cation. Thus, the concentrations of sulfate, bisulfite, and metabisulfite ions are lower than the nominal concentrations of the salts. (Sodium sulfate is 67% sulfate by mass, sodium bisulfite is 78% bisulfite by mass, and sodium metabisulfite is 76% metabisulfite by mass.)

After preparation, the ethanol stock solutions were observed and photographed to document the degree of cloudiness that was apparent. The cloudiness behaviors of the Na_2SO_4 and $NaHSO_3$ solutions were indistinguishable. At concentrations of 4 ppm and below, no cloudiness was visible. At 8 ppm, a very faint degree of cloudiness was perceptible to some observers, though not to all. The intensity of this cloudiness increased in the 16, 32, and 64 ppm samples. A photo of the 4, 8, 16, 32, and 64 ppm Na_2SO_4 solutions in ethanol is provided in Figure 3. Also shown in this figure is the numerical scale that was used to semi-quantitatively rate the degree of cloudiness in these (and other) salt-containing solutions.

Note: photographing these salt-containing solutions proved to be ineffective in distinguishing differing levels of cloudiness. Variations from one sample to another were subtle and difficult to quantify. A range of cloudiness levels as defined by the semi-quantitative scale shown in Figure 3 could be detected by the laboratory technician making these assessments, but this too proved to be somewhat subjective. During later phases of the project, when a different laboratory technician was employed, application of this cloudiness rating scale was abandoned. It is noteworthy that salt concentrations in excess of 16 ppm were necessary to be clearly visible to most observers. Thus, visual observation is not a reliable way to judge whether a particular sample of ethanol meets the ASTM D4806 standard of 4 ppm maximum sulfate.

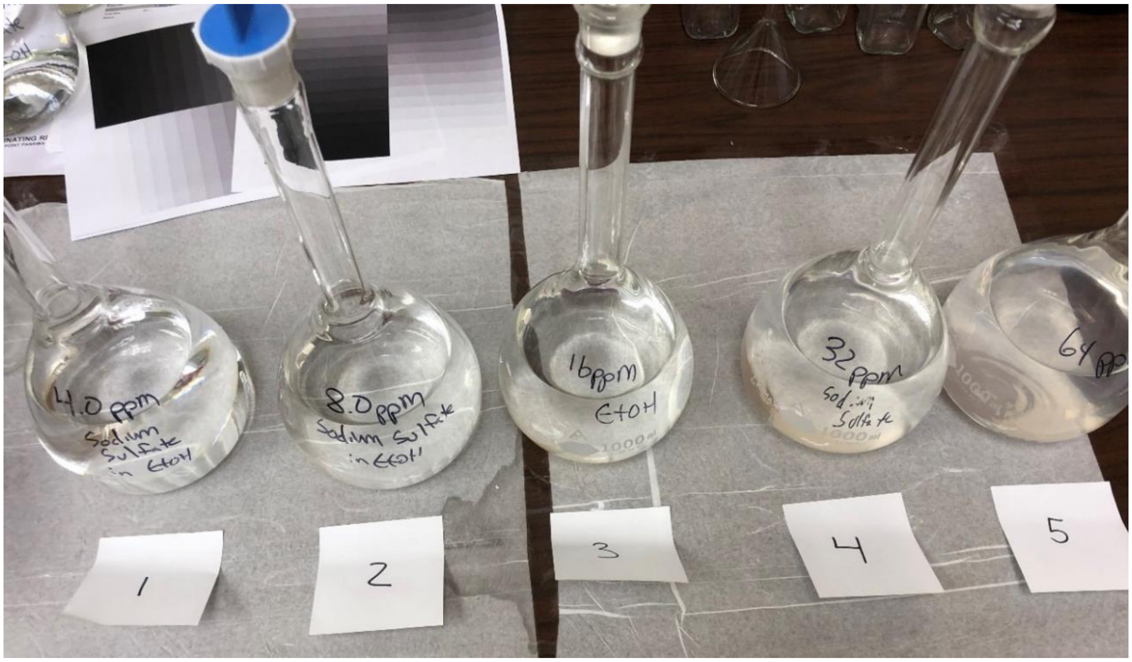

Figure 3. Ethanol solutions containing 4, 8, 16, 32, and 64 ppm of sodium sulfate
The numbers beneath each flask indicate the semi-quantitative scale used to define the degree of cloudiness

3.3. Laboratory Methods

Following preparation of the salt-containing solutions in ethanol and gasoline-ethanol blends, samples of each solution were placed in the square sample bottles shown in Figure 2. A naming convention was developed to clearly identify each sample – and indicate the time of sample inspection/analysis. This convention has the form "SS-XX-YY-ZZ," where the terms have the following meaning:

- "SS" refers to the type of salt used: "SS" indicates sodium sulfate, "SBS" indicates sodium bisulfite, and "SMB" indicates sodium metabisulfite
- "XX" refers to the percentage of ethanol in the fuel blend: 10, 30, 60, or 100
- "YY" refers to the concentration of the sodium salt (sulfate, bisulfite or metabisulfite) in the ethanol component of the fuel blend (0, 1, 2, 4, 8, 16, 32, or 64 ppm)
- "ZZ" refers to the aging time prior to inspection/analysis ("0" for time 0, "D" for 1-day (24 hours), "W" for 1-week, and "4W" for 4-weeks"

The solubilities of Na_2SO_4, $NaHSO_3$, and $Na_2S_2O_5$ in the various ethanol and gasoline-ethanol blends were assessed using IC analyses of small aliquots removed by pipette from the top of each sample bottle. Thus, unlike the previous CRC Project CM-136-15-1, where insoluble salts were removed by filtration, in this project insoluble salts were simply allowed to settle by gravity. Following removal of each aliquot for analysis, the sample bottles were closed and shaken vigorously for 15 sec. before photographing and assigning a cloudiness rating based on the numerical scale shown in Figure 3. After sitting for the prescribed period of time, the sample bottles were re-opened and additional aliquots were removed for IC analysis. Following each sample aliquot removal, the bottles were again closed, shaken, photographed, and rated for cloudiness.

In the previous CRC study, IC analysis of sulfate ions was conducted according to ASTM D7328. In this method, the samples to be analyzed (ethanol and gasoline-ethanol blends) are first evaporated to dryness under a stream of nitrogen, then are re-constituted in water before injection into the IC instrument. For potential sulfate determination, a small amount of aqueous hydrogen peroxide is included during the evaporation and re-constitution process, thereby causing oxidation of reduced forms of sulfur oxides to produce sulfate. Typically, 0.5 mL of 30% aqueous hydrogen peroxide is added to 10.0 mL of sample before blowing down to dryness.

This sample evaporation and aqueous reconstitution process is quite labor intensive, and hence, is expensive. Because of the large number of sulfate analyses required in the current project, a simpler (and less costly) IC method was chosen – namely, ASTM D7319.[9] In this method, the samples to be analyzed are injected directly onto the IC column, without first evaporating and re-constituting in water. By adding a small amount of aqueous hydrogen peroxide to the sample, potential sulfate can be measured. This direct injection ASTM method was developed for use with ethanol samples, not for gasoline-ethanol blends. Therefore, before employing ASTM D7319, experiments were conducted to demonstrate that direct injection of gasoline samples could be tolerated by the IC column, and that the baseline disruptions caused by gasoline injection did not interfere with detection and quantification of the sulfate and bisulfite peaks in the chromatograms.

All IC analyses were conducted using a Dionex ICS-5000+ instrument system, utilizing a liquid chromatographic separation of ions based on an ion exchange mechanism. The analytical column used was an IonPac AS19 (4 x 250 mm), preceded by an IonPac AG19 guard column. (In later phases of the project, these columns were updated to AS20 and AG20.) The isocratic eluent used during the analysis was 15 mM aqueous KOH, with a flow rate of 1.0 mL/min. After exiting the analytical column, the eluent ions were neutralized by passing through an anion electrolytically-regenerated suppressor (AERS). The AERS used was a Dionex model ADRS. This system converts the sample ions to their corresponding strong acids, which are then detected and quantified with a conductivity detector.

Initial chromatographic experiments were conducted to demonstrate that sulfate and bisulfite anions could be satisfactorily separated by this IC method, and to define the detection limits for these ions. To do this, a series of standard aqueous solutions was prepared containing 1.00, 0.100, and 0.010 ppm of both ions, starting from anhydrous Na_2SO_4 and $NaHSO_3$. (Due to their extremely low solubilities, it was not possible to prepare a valid set of similar samples in ethanol or gasoline.) Chromatograms from IC analysis of these aqueous standards are shown in Figure 4. In these example chromatograms, the sulfate peak (retention time of 10.7 min.) is colored, while the bisulfite peak (retention time of 10.2 min.) is not. The earlier peak at 9.6 min. is attributed to carbonate that originates from atmospheric CO_2, which is present in all solvents used in these analyses.

Although the sulfate and bisulfite anions elute close together, it is still quite easy to distinguish the two peaks, even at concentrations as low as 0.01 ppm. When analyzing real samples in ethanol, and especially gasoline-ethanol blends, the IC baseline is not as flat as shown in Figure 4, and peak definition/quantification becomes more difficult. Given this situation, we estimate a minimum quantification limit of 0.05 ppm for both sulfate and bisulfite ions in realistic samples when analyzed using an aqueous injection technique. Thus, instrumental detection limit was not an issue in analyzing any of the samples prepared in this experimental program. Our estimated detection limit is an order of magnitude lower than the pooled limit of quantification (PLOQ) value for sulfate of 0.55 ppm given in ASTM D7328. The stated PLOQ for sulfate in ASTM D7319 (direct injection of ethanol) is 0.01 ppm. Additional information about the precision of both ASTM methods is provided in Appendix III.

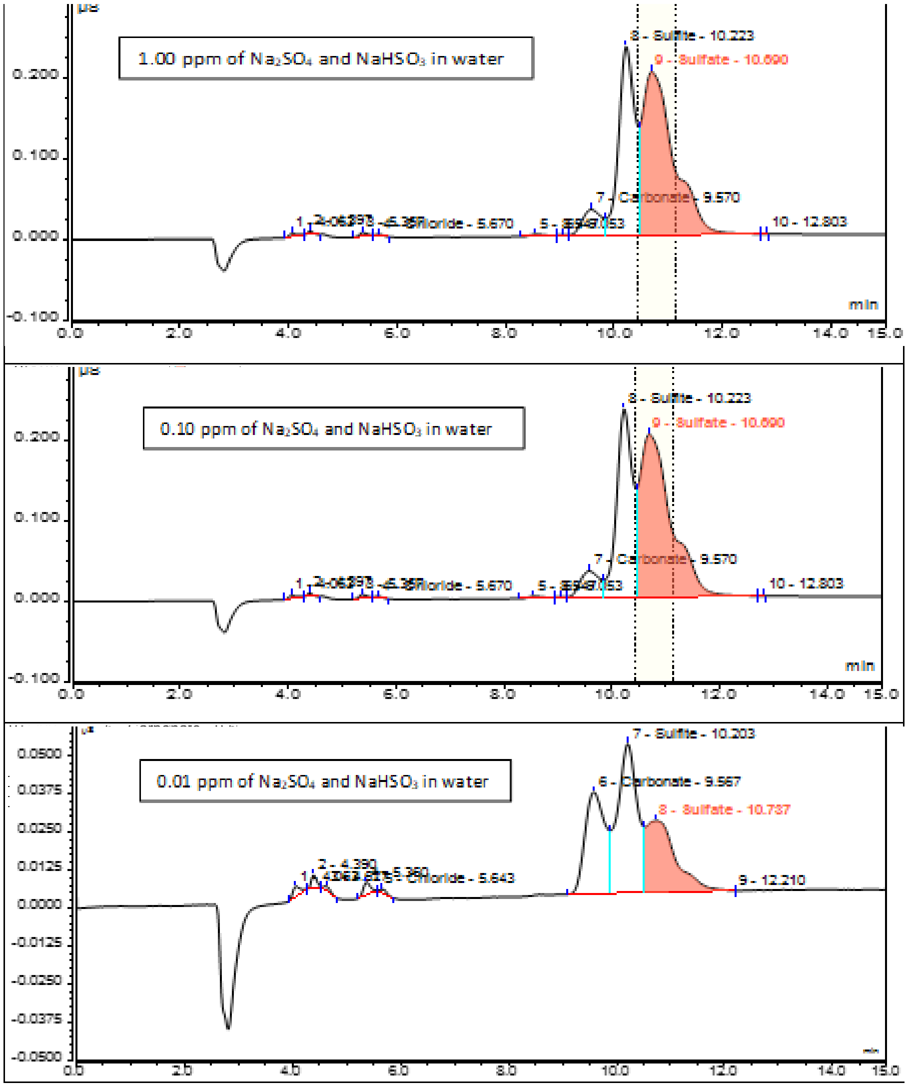

Figure 4. IC analysis of aqueous standards containing both sodium sulfate and sodium bisulfite at 1.00 ppm (top), 0.100 ppm (middle) and 0.010 ppm (bottom)

Due to its ease of oxidation, bisulfite is somewhat difficult to work with, as it readily converts to sulfate under certain conditions. To explore this issue of oxidative instability, the three standard solutions represented by the chromatograms in Figure 4 were re-analyzed 2-days later (taken from the same autosampler vials). This reanalysis showed a slight decrease in size of all the bisulfite peaks, and a slight increase in all the sulfate peaks, suggesting that a small degree of conversion of bisulfite to sulfate occurred within the autosampler vials. Although bisulfite appeared relatively stable within these aqueous samples, later evidence showed nearly complete conversion to sulfate occurred during normal handling and analysis of other experimental samples.

4. Experimental Results and Discussion

4.1. Solubility of sodium sulfate (aqueous) in ethanol and gasoline-ethanol blends

Following the methodology defined in Appendix II, a set of 32 samples was prepared to examine the solubility of Na_2SO_4 in ethanol, and in gasoline-ethanol fuel blends. The experimental matrix is shown in Table 1, which also identifies the time at which aliquots of each sample were removed for IC analysis of existent sulfate by ASTM D7319. In total, this experimental matrix involved 128 IC analyses for sulfate.

The sulfate concentrations determined in each sample at each measurement time are depicted graphically in Figure 5, and are presented in tabular form in Appendix IV. All measurements were made using the direct injection method of ASTM D7319. The green bars in Figure 5 represent the amount of sulfate ion (not Na_2SO_4) that was spiked into each sample. The other colored bars represent the amount of sulfate measured by IC after the samples had aged for 0-hour, 24-hours, 1-week, and 4-weeks. The samples identified as "0-Hour" represent aliquots removed from the sample bottles and placed within autosampler vials for IC analysis within 1 hour of sample preparation, although the exact IC analysis time varied from 2-8 hours after preparation. The samples identified as "1-Day" represent aliquots removed 24-hours after sample preparation, with IC analysis being conducted within the following 2-8 hours.

Figure 5 illustrates that in every case, considerably less sulfate was measured by IC than was spiked into the sample. This suggests that most of the sodium sulfate simply dropped out of solution, and that the true solubility of sodium sulfate in ethanol (and especially in gasoline-ethanol blends) is extremely low. In pure ethanol (E100), sodium sulfate appeared to have slight solubility initially, with the measured concentrations decreasing over time. However, we do not believe these IC measurements represent changes in sodium sulfate solubility alone, but also reflect changes occurring with respect to agglomeration and sedimentation of insoluble materials.

When preparing the sodium sulfate-spiked ethanol stock solutions, it was apparent that all samples containing sulfate levels over 16 ppm were visibly cloudy, due to the presence of small, insoluble particles. Upon standing, this cloudiness gradually diminished, as the particles agglomerated and settled to the bottom. However, with very slight agitation, these particles were easily re-suspended. In the solutions containing gasoline (E10, E30, and E60), this sedimentation of particles and reduction of cloudiness appeared to occur more rapidly. We speculate that the polarity of the solvent may influence the agglomeration and sedimentation processes, and hence the cloudiness of the sodium sulfate solutions. In a highly polar solvent such as ethanol, sodium sulfate particles remain suspended more readily, while addition of non-polar gasoline to the ethanol results in more rapid sedimentation. This may explain why virtually no sulfate was measured by IC in any of the gasoline-ethanol blends, while minimal concentrations were measured in the E100 samples.

Figure 6 shows the cloudiness rating results determined from all samples (and times) within the experimental matrix of Table 1. The top panel of this figure shows the cloudiness results of sodium sulfate solutions in E100. These are the solutions that were used to define the numeric cloudiness scale from 1 (for 4 ppm Na_2SO_4) to 5 (for 64 ppm Na_2SO_4). This panel also shows that the degree of cloudiness remained constant with time for all samples. (At each time period, the degree of cloudiness was rated after shaking the bottles.)

Table 1. Experimental Matrix for Investigating Solubility of Na_2SO_4 in Ethanol and Gasoline-Ethanol Blends

	Na_2SO_4 Conc., ppm		0-Hour	24-Hours	1-Week	4-Weeks	Total Number of Analyses
	In Ethanol	In E100					
1	0.0	0.0	O, E	O, E	O, E	O, E	32 existent sulfate
2	1.0	1.0	O, E	O, E	O, E	O, E	
3	2.0	2.0	O, E	O, E	O, E	O, E	
4	4.0	4.0	O, E	O, E	O, E	O, E	
5	8.0	8.0	O, E	O, E	O, E	O, E	
6	16	16	O, E	O, E	O, E	O, E	
7	32	32	O, E	O, E	O, E	O, E	
8	64	64	O, E	O, E	O, E	O, E	
	In Ethanol	In E10					
1	0.0	0.0	O, E	O, E	O, E	O, E	32 existent sulfate
2	1.0	0.1	O, E	O, E	O, E	O, E	
3	2.0	0.2	O, E	O, E	O, E	O, E	
4	4.0	0.4	O, E	O, E	O, E	O, E	
5	8.0	0.8	O, E	O, E	O, E	O, E	
6	16	1.6	O, E	O, E	O, E	O, E	
7	32	3.2	O, E	O, E	O, E	O, E	
8	64	6.4	O, E	O, E	O, E	O, E	
	In Ethanol	In E30					
1	0.0	0.0	O, E	O, E	O, E	O, E	32 existent sulfate
2	1.0	0.3	O, E	O, E	O, E	O, E	
3	2.0	0.6	O, E	O, E	O, E	O, E	
4	4.0	1.2	O, E	O, E	O, E	O, E	
5	8.0	2.4	O, E	O, E	O, E	O, E	
6	16	4.8	O, E	O, E	O, E	O, E	
7	32	14.4	O, E	O, E	O, E	O, E	
8	64	19.2	O, E	O, E	O, E	O, E	
	In Ethanol	In E60					
1	0.0	0.0	O, E	O, E	O, E	O, E	32 existent sulfate
2	1.0	0.6	O, E	O, E	O, E	O, E	
3	2.0	1.2	O, E	O, E	O, E	O, E	
4	4.0	2.4	O, E	O, E	O, E	O, E	
5	8.0	4.8	O, E	O, E	O, E	O, E	
6	16	9.6	O, E	O, E	O, E	O, E	
7	32	19.2	O, E	O, E	O, E	O, E	
8	64	38.4	O, E	O, E	O, E	O, E	

Notes: O = Observe before and after shaking; photograph after shaking
E = Existent sulfate measurements of samples withdrawn before shaking (by ASTM D7319)

The cloudiness results for the E10, E30, and E60 solutions containing varying levels of Na_2SO_4 are shown in the lower panels of Figure 6. In these panels, the green bars represent expected cloudiness values based on the known concentrations of Na_2SO_4 that were spiked into each ethanol sample, and the dilution of these concentrations by addition of gasoline. It is apparent that the observed cloudiness values are lower than the expected values for these gasoline-ethanol blends. This is attributed to difficulties in discerning such slight degrees of cloudiness in colored solutions. Due to the yellow color of the gasoline, the E60, E30, and E10 solutions had increasingly intense colored backgrounds, making it more difficult to detect and rate cloudiness. As with the E100 samples, no change in cloudiness with time was observable in any of these gasoline-ethanol blend samples.

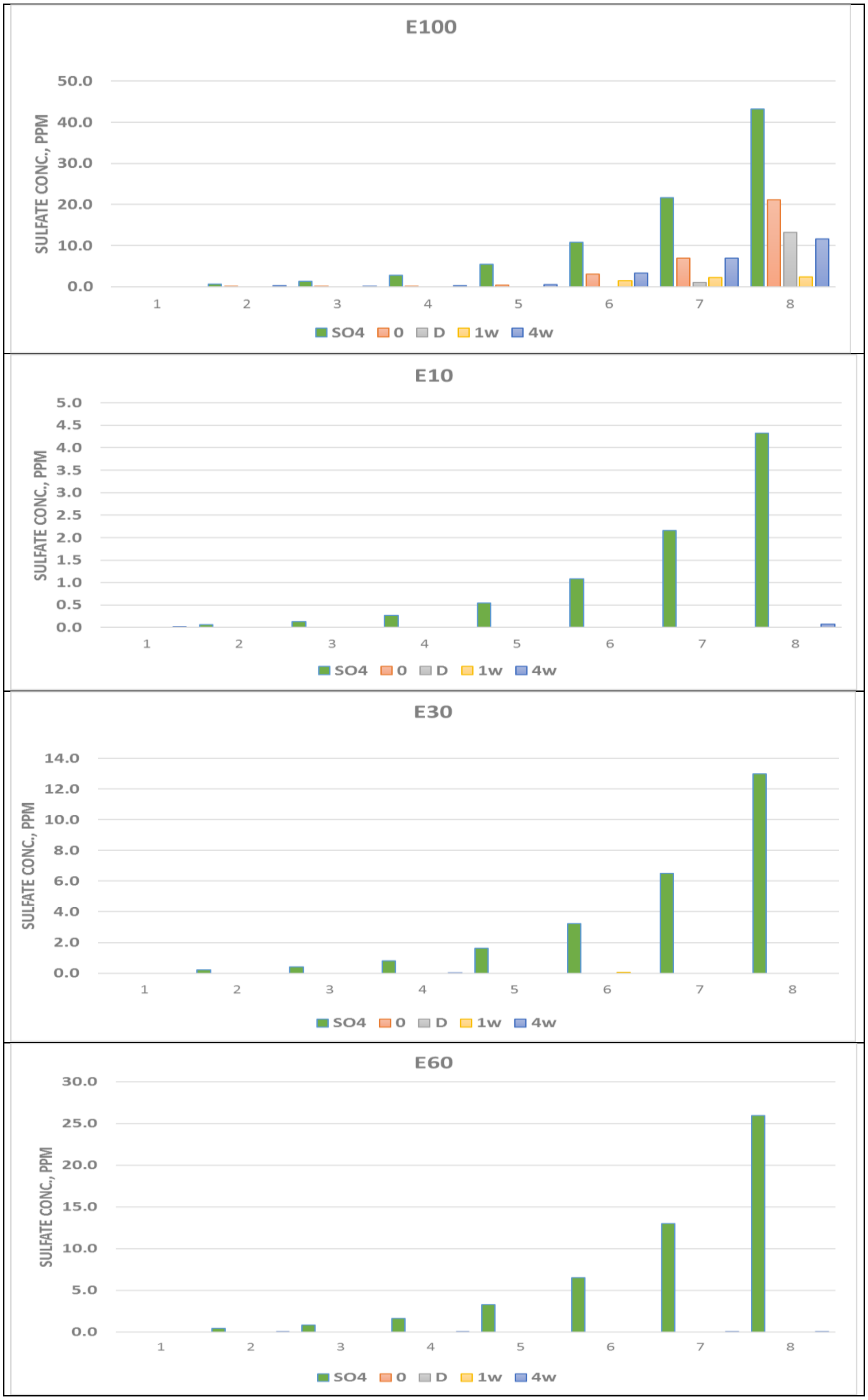

Figure 5. IC measurements of sulfate in ethanol and gasoline-ethanol blends spiked with sodium sulfate. Green bars represent the spiked sulfate levels in each sample. Other colored bars represent IC-measured sulfate levels after 0 days, 1 day, 1 week, and 4 weeks. Numbers on x-axis refer to samples in Table 1 matrix.

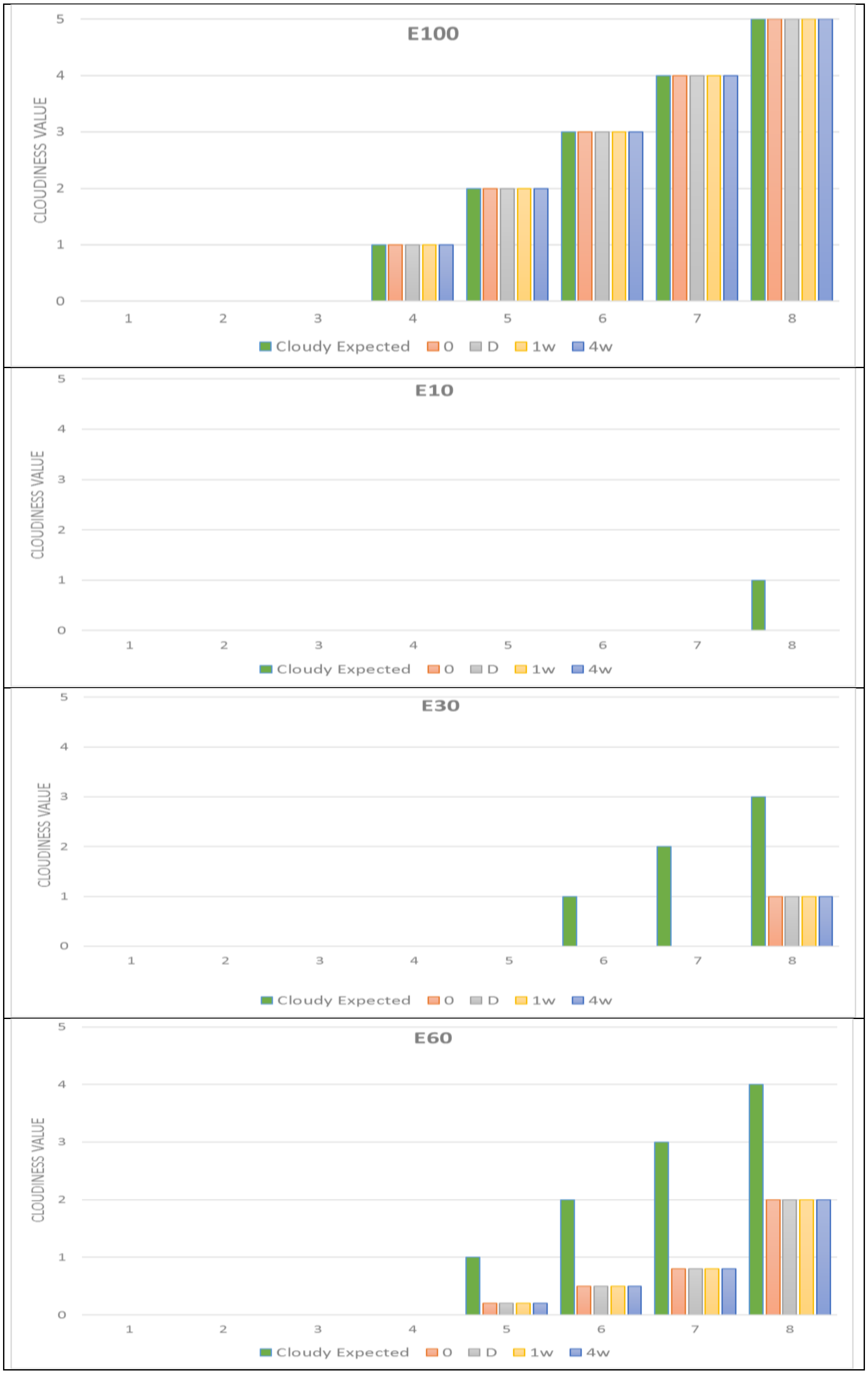

Figure 6. Cloudiness rating values of sodium sulfate solutions in ethanol and gasoline-ethanol blends. Green bars represent expected values based on E100 solutions. Other colored bars represent observed values after 0 days, 1 day, 1 week, and 4 weeks. Numbers on x-axis refer to samples in the Table 1 matrix.

4.2. Solubility of sodium bisulfite (aqueous) in ethanol and gasoline-ethanol blends

To investigate the solubility of $NaHSO_3$ in ethanol and gasoline-ethanol blends, the experimental matrix shown in Table 2 was prepared. This matrix of 32 samples mirrors the Table 1 matrix used to investigate sodium sulfate solubilities. In both cases, 128 IC analyses were conducted using the direct injection method of ASTM D7319 to measure solubilized ions (sulfate and bisulfite) present in the samples at various times.

Table 2. Experimental Matrix to Investigate Solubility of $NaHSO_3$ in Ethanol and Gasoline-Ethanol Blends

	$NaHSO_3$ Conc., ppm		0-Hour	24-Hours	1-Week	4-Weeks	Total Number of Analyses
	In Ethanol	In E100					
1	0.0	0.0	O, E	O, E	O, E	O, E	32 existent sulfate
2	1.0	1.0	O, E	O, E	O, E	O, E	
3	2.0	2.0	O, E	O, E	O, E	O, E	
4	4.0	4.0	O, E	O, E	O, E	O, E	
5	8.0	8.0	O, E	O, E	O, E	O, E	
6	16	16	O, E	O, E	O, E	O, E	
7	32	32	O, E	O, E	O, E	O, E	
8	64	64	O, E	O, E	O, E	O, E	
	In Ethanol	In E10					
1	0.0	0.0	O, E	O, E	O, E	O, E	32 existent sulfate
2	1.0	0.1	O, E	O, E	O, E	O, E	
3	2.0	0.2	O, E	O, E	O, E	O, E	
4	4.0	0.4	O, E	O, E	O, E	O, E	
5	8.0	0.8	O, E	O, E	O, E	O, E	
6	16	1.6	O, E	O, E	O, E	O, E	
7	32	3.2	O, E	O, E	O, E	O, E	
8	64	6.4	O, E	O, E	O, E	O, E	
	In Ethanol	In E30					
1	0.0	0.0	O, E	O, E	O, E	O, E	32 existent sulfate
2	1.0	0.3	O, E	O, E	O, E	O, E	
3	2.0	0.6	O, E	O, E	O, E	O, E	
4	4.0	1.2	O, E	O, E	O, E	O, E	
5	8.0	2.4	O, E	O, E	O, E	O, E	
6	16	4.8	O, E	O, E	O, E	O, E	
7	32	14.4	O, E	O, E	O, E	O, E	
8	64	19.2	O, E	O, E	O, E	O, E	
	In Ethanol	In E60					
1	0.0	0.0	O, E	O, E	O, E	O, E	32 existent sulfate
2	1.0	0.6	O, E	O, E	O, E	O, E	
3	2.0	1.2	O, E	O, E	O, E	O, E	
4	4.0	2.4	O, E	O, E	O, E	O, E	
5	8.0	4.8	O, E	O, E	O, E	O, E	
6	16	9.6	O, E	O, E	O, E	O, E	
7	32	19.2	O, E	O, E	O, E	O, E	
8	64	38.4	O, E	O, E	O, E	O, E	

Notes: O = Observe before and after shaking; photograph after shaking
E = Existent sulfate measurements of samples withdrawn before shaking (by ASTM D7319)

As before, samples identified as “0-Hour” indicate aliquots removed from the sample bottles and placed in autosampler vials within 1-hour of sample preparation. Actual IC analyses were conducted over the following 2-8 hours. Similarly, the samples identified as “24-Hours,” “1-Week,” and “4-Weeks” represent aliquots placed in autosampler vials at the indicated times, followed by subsequent IC analyses. Due to IC instrument problems, the “1-Week” and “4-Week” samples could not be analyzed promptly; thus, these samples were stored in refrigerated autosampler vials for 2-4 weeks before analysis.

Originally, we had planned to analyze these sodium bisulfite-spiked samples for both existent and potential sulfate. However, upon seeing the initial existent results (which showed no bisulfite, but only sulfate, as described below) and observing that repeated IC injection of peroxide-containing samples adversely affected the chromatography, it was decided to not conduct potential sulfate measurements on these samples. Instead, the effects of adding hydrogen peroxide to sodium bisulfite-spiked samples were examined with different sets of experiments, as described later.

Existent sulfate results from IC analyses of all sodium bisulfite-spiked samples are shown graphically in Figure 7, and are presented in tabular form in Appendix V. The green bars in Figure 7 represent the actual amount of bisulfite ion (not $NaHSO_3$) that was spiked into each sample. The other colored bars represent the amounts of sulfate measured by IC after the samples had aged for 0-hour, 24-hours, 1-week, and 4-weeks. Surprisingly, no detectable levels of bisulfite ions were measured – only sulfate ions. This suggests that oxidation of bisulfite to sulfate occurs quite readily under the conditions of sample preparation, storage, and analysis.

The low measured concentrations of sulfate (originating from sodium bisulfite) shown in Figure 7 are very similar to the concentrations shown in Figure 5 (originating from sodium sulfate). In both cases, there appeared to be slight solubility in pure ethanol, but virtually no solubility once gasoline was blended with the ethanol. It is not clear whether the sulfate concentrations measured in the E100 samples represent true solubility of the salts, or simply reflect the agglomeration of invisible particles. Likely, both soluble and suspended insoluble materials were present. In this situation, it may be more appropriate to refer to the total “carrying capacity” of ethanol with respect to sodium bisulfite, rather than solubility.

One slight, but noticeable difference between the Na_2SO_4 (Figure 5) and $NaHSO_3$ (Figure 7) results is the more consistent sulfate values measured over time in the E100 samples with $NaHSO_3$. With the Na_2SO_4 samples, the highest sulfate concentrations were generally seen at the time-zero point, with lower concentrations being measured at later times. This might be expected if some time was required for insoluble, agglomerated particles to settle out. With the $NaHSO_3$ samples, however, the measured sulfate concentrations were nearly the same at all times, suggesting that more of the salt may actually have been dissolved, or that the suspended insolubles were very stable.

In E100 samples containing either Na_2SO_4 or $NaHSO_3$, adding gasoline apparently caused deposition of nearly all suspended particles, resulting in virtually no measured sulfate concentration in any of the gasoline/ethanol blends. This supports the notion that complexes or agglomerations between salts and polar ethanol are disrupted upon addition of nonpolar gasoline.

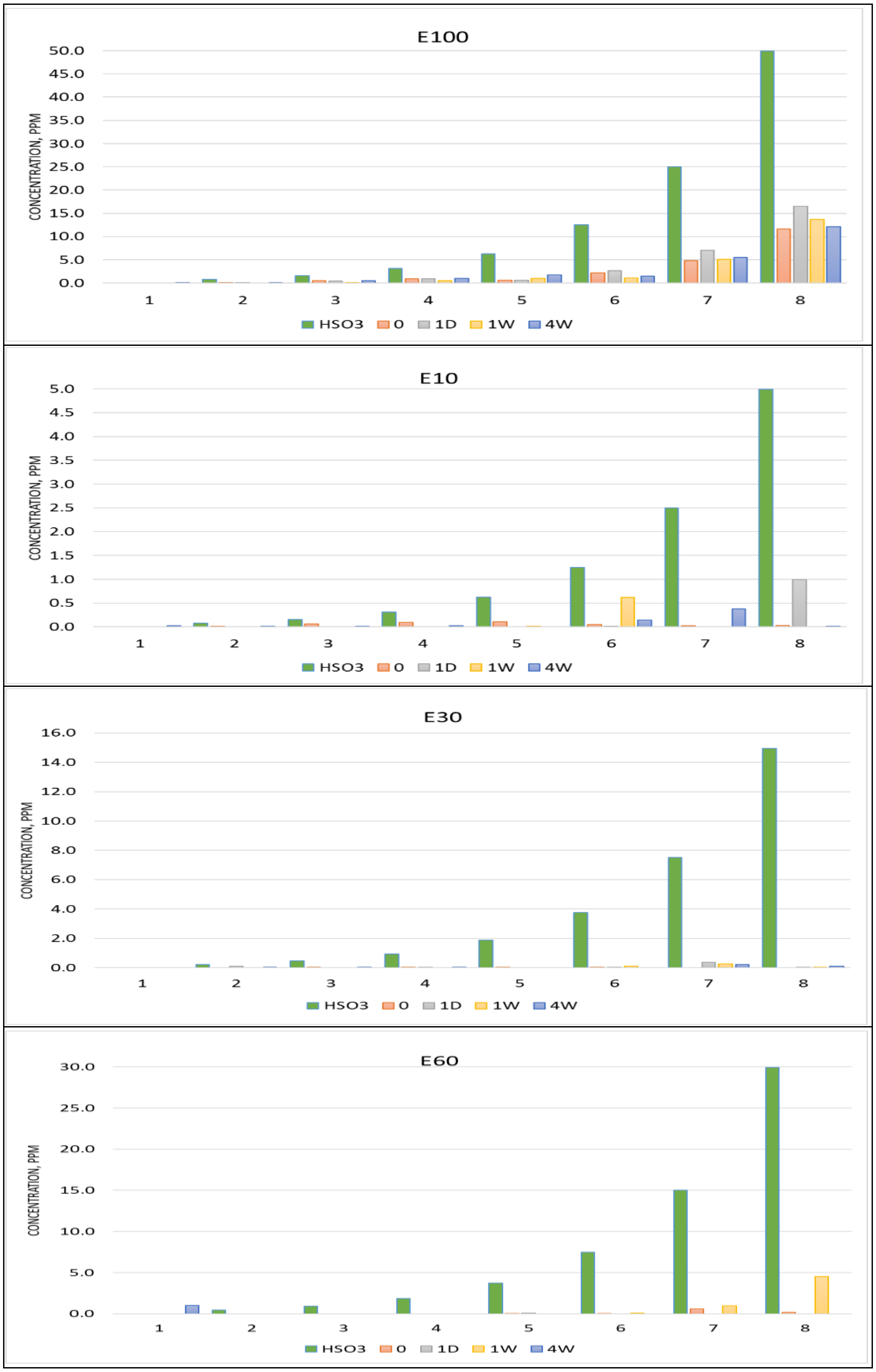

Figure 7. IC measurements of existent sulfate in ethanol and gasoline-ethanol blends spiked with $NaHSO_3$. Note: no measurable levels of bisulfite anions were observed in any sample. Green bars represent the spiked bisulfite levels in each sample. Other colored bars represent IC-measured sulfate levels after 0 days, 1 day, 1 week, and 4 weeks. Numbers on x-axis refer to samples in Table 2 matrix.

Based on results from the previous CRC Project CM-136-15-1, we had expected the solubility of sodium bisulfite in ethanol to be much higher (perhaps by two orders of magnitude) than that of sodium sulfate. However, this was not seen in the present project. We now believe much of this discrepancy resulted from differences in the way solubilities were measured in the two studies. In the previous project, solubility was assessed by analyzing solutions obtained by filtering slurries of the salts through 0.4 µm Nuclepore filters. It is possible that small, non-visible amounts of $NaHSO_3$ passed through these filters, although this problem was not apparent with any of the other sulfate salts used in the earlier project. Perhaps notable is the fact that the $NaHSO_3$ reagent we used was in the form of a fine powder, while the Na_2SO_4 reagent was in granular form. This difference may have had an influence on the amount of material that passed through the Nuclepore filter. However, two other sulfate salts used in the earlier project ($CaSO_4$ and K_2SO_4) were also in powdered form, yet did not exhibit this problem.

Another significant methodological difference between the current and previous CRC projects is the IC method used to quantify sulfate and bisulfite ions. The previous study utilized ASTM D7328, in which the salt-containing ethanol solutions were evaporated to dryness and then re-constituted in water, thereby capturing both soluble and insoluble salts. In the present study, the direct injection method of ASTM D7319 was employed, which would capture only dissolved salts (and perhaps finely-dispersed microscopic particles).

Finally, as clearly seen in Figure 1, filtrates obtained from the $NaHSO_3$-spiked ethanol solutions from the previous project became visibly cloudy upon standing for extended periods of time. While we originally attributed this to chemical oxidation of soluble bisulfite to form insoluble sulfate, it is also possible that physical agglomeration processes may have occurred, resulting in growth of small, non-visible particles into larger, visible particles; thereby causing the cloudy appearance. While there remain some uncertainties about the different solubility results measured in the previous and current projects, we now believe the behaviors of Na_2SO_4 and $NaHSO_3$ are not so dissimilar as suggested in the previous project. Based on all the data accumulated in this and the previous CRC project, we still believe that $NaHSO_3$ has higher solubility in ethanol than does Na_2SO_4, but the difference may be only 1-order of magnitude, rather than 2-orders of magnitude. It also appears that with both salts, the solubility drops to near zero upon addition of gasoline.

The cloudiness values from the $NaHSO_3$-spiked experimental matrix depicted in Figure 8 are indistinguishable from those shown in Figure 6 for the Na_2SO_4-spiked samples. This is consistent with the observation that both $NaHSO_3$ and Na_2SO_4 have very low solubility in ethanol, and nearly zero solubility in gasoline-ethanol blends. It is also consistent with the possibility that the bisulfite had oxidized to sulfate, so that we are really observing sulfate in both cases.

It should also be remembered that $NaHSO_3$ is not available in highly pure form, but contains Na_2SO_4 and $Na_2S_2O_5$, and possibly other impurities. In our IC analysis of the $NaHSO_3$ reagent used in these experiments, the material was found to contain approximately 10% sulfate - see chromatogram in Figure 9. Thus, when spiking with $NaHSO_3$, some amount of Na_2SO_4 is also included. (Note that in Figure 9, the elution order of the sulfate and bisulfite peaks is reversed from what is shown in Figure 4. This is a consequence of different IC columns being used in these two cases.)

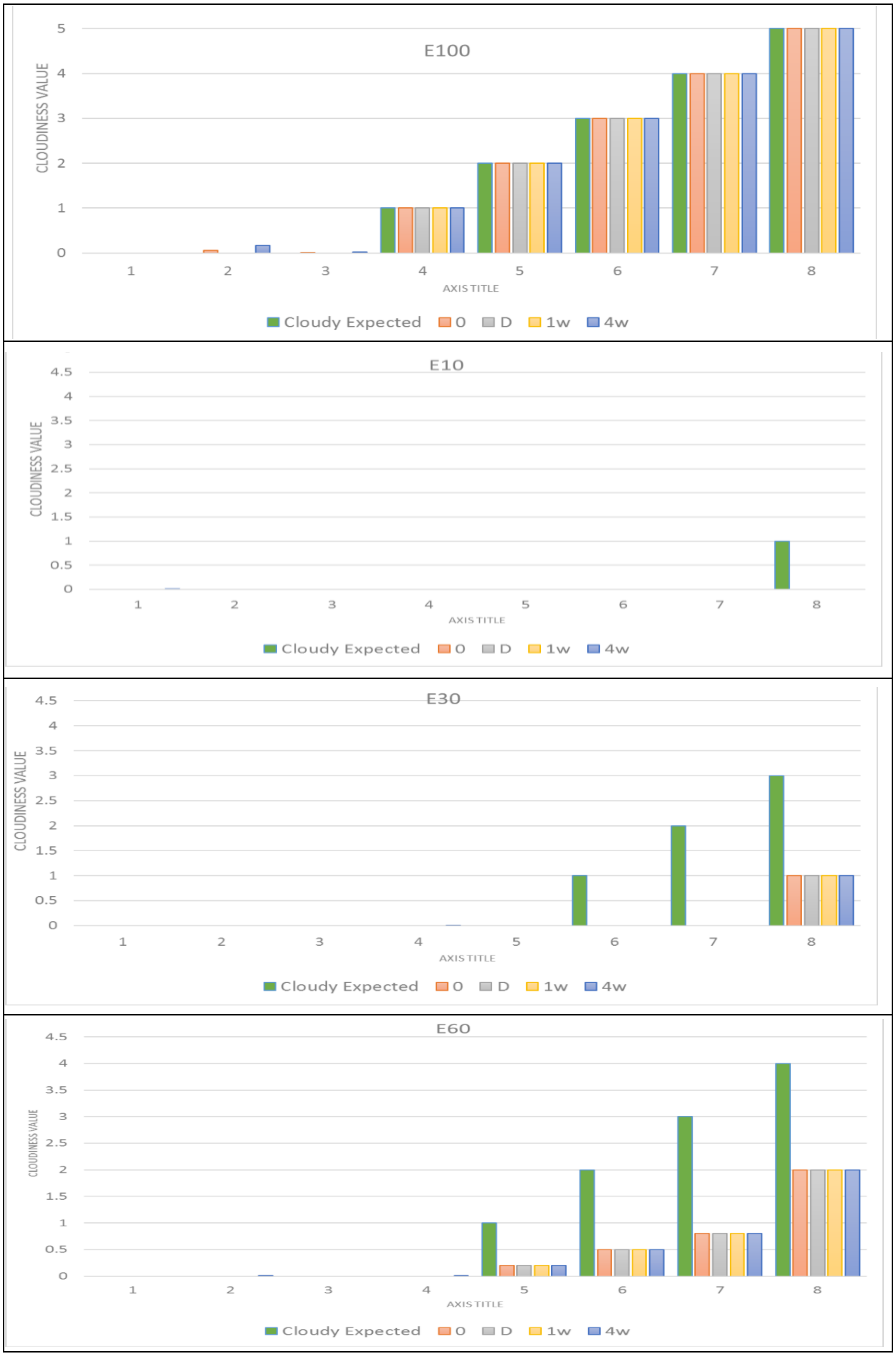

Figure 8. Cloudiness values of sodium bisulfite solutions in ethanol and gasoline-ethanol blends. Green bars represent expected values based on E100 solutions. Other colored bars represent cloudiness values after 0 days, 1 day, 1 week, and 4 weeks. Numbers on x-axis refer to samples in the Table 2 matrix

Based on information from the chemical supplier, we know that the sodium bisulfite reagent contained a significant amount of sodium metabisulfite (perhaps up to 30%). Yet, no separate peak for metabisulfite is visible in Figure 9. However, this chromatogram does show the presence of trace levels of chloride, nitrite, and nitrate in the sodium bisulfite reagent. Further examination of the chromatographic behavior of Na_2SO_4, $NaHSO_3$, and $Na_2S_2O_5$ is described in the next section.

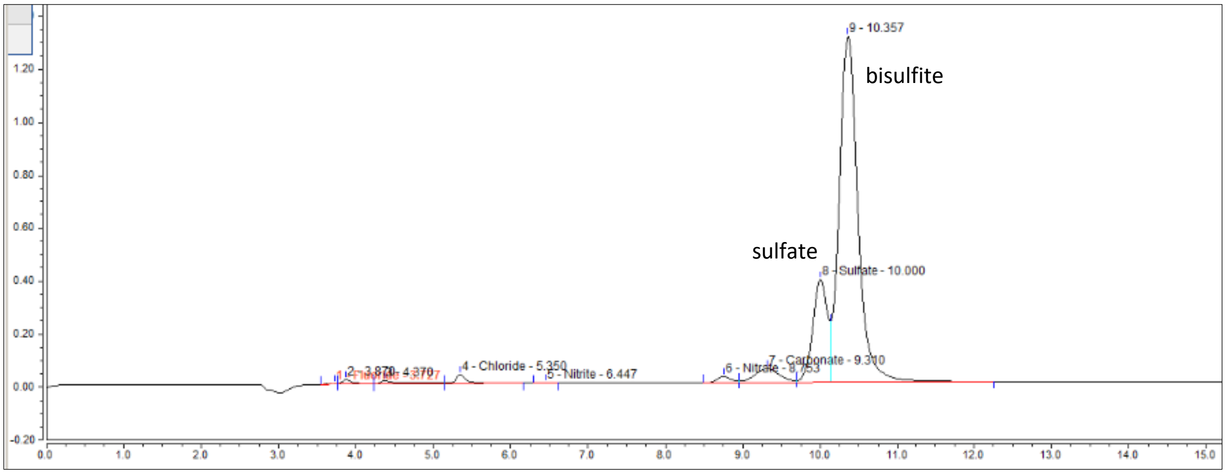

Figure 9. IC Chromatogram of 5 ppm aqueous solution of $NaHSO_3$ reagent

4.3. Chromatographic behavior of sulfate salts

Throughout the course of this project, we noticed several instances of strange and erratic chromatographic behavior. This was especially the case when using the direct injection method of ASTM D7319. One notable oddity was the reversal of elution order of sulfate and bisulfite ion peaks, depending upon column conditions. This can be seen by comparing the chromatograms of Figure 4 (where bisulfite elutes before sulfate) and Figure 9 (where bisulfite elutes after sulfate). The same column types [IonPac AS20 (4 x 250 mm) preceded by an IonPac AS20 guard column] were used in both cases, although newer columns were used in the later experiments of Figure 9, due to column deterioration from earlier injections of peroxide-containing samples.

To examine these chromatographic issues, and to define peak response factors, 10 ppm aqueous anion standards were prepared using each of three sulfate salts: sodium sulfate, sodium bisulfite, and sodium metabisulfite. In these experiments, we assumed that each starting salt was 100% pure. Sufficient salt was used to provide 10 ppm of the corresponding anion (sulfate, bisulfite, and metabisulfite) thus, the concentrations of the total salts (including sodium) were somewhat higher.

IC chromatograms of these three standards are shown in Figure 10, along with a chromatogram of our instrument calibration standard, which contains 1 ppm of six anions: fluoride, chloride, nitrite, bromide, nitrate, and sulfate. In these chromatograms, the sulfate peak, which elutes at approximately 11.4 - 12.0 min., is shaded. The bisulfite peak elutes later, at approximately 11.9 - 12.5 min. The bisulfite and metabisulfite samples gave virtually identical chromatograms, as shown in Figure 10C and Figure 10D. These observations are consistent with the possibility that in aqueous solution, the anion structures of bisulfite and metabisulfite are similar, as suggested by the equilibrium relationship shown in Eq. 3.

$$S_2O_5^{2-} + H_2O \leftrightarrow 2\ HSO_3^{-} \qquad \text{(Eq. 3)}$$

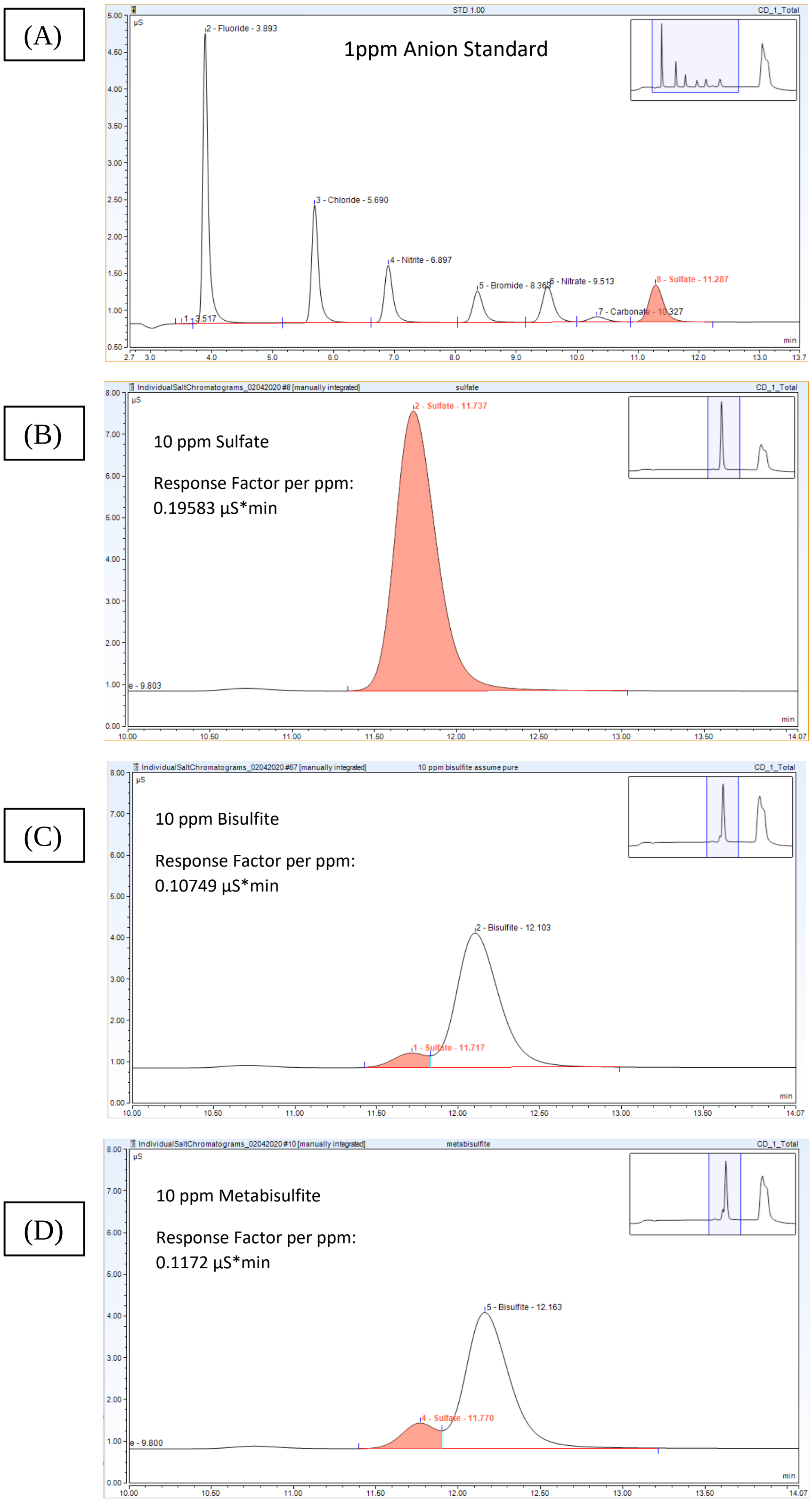

Figure 10. IC chromatograms of aqueous standard solutions. (A) Calibration standard containing 1 ppm of 6 anions, with sulfate peak shaded; (B) 10 ppm of sulfate from sodium sulfate salt; (C) 10 ppm of bisulfite from sodium bisulfite; (D) 10 ppm of bisulfite from sodium metabisulfite.

The measured IC detector responses to these three aqueous ion standards are shown on the chromatograms of Figure 10. The raw area counts for each sample, expressed in units of µS·min/ppm, were determined over the entire time period of 11.4 - 13.0 min., thereby combining the two peaks that existed in the bisulfite and metabisulfite chromatograms. These response factors are summarized in Table 3. Of the three materials, the sulfate ion gave the highest response. Response factors for bisulfite and metabisulfite are approximately 55-60% as large as that of sulfate. The nearly identical response factors for bisulfite and metabisulfite are consistent with the possibility that the same anion structures are present in both aqueous samples.

Table 3. IC detector response factors for aqueous anions

Anion	Absolute Response Factor, area counts/ppm	Relative Response Factor
Sulfate	0.196	1.00
Bisulfite	0.107	0.55
Metabisulfite	0.117	0.60

The chromatograms in Figure 10 show a small amount of sulfate impurity was present in both the bisulfite and metabisulfite samples. It is unknown how much of this impurity was present in the starting reagent chemicals compared to that produced by oxidation during sample preparation and handling. However, the amount of sulfate contaminant in the metabisulfite sample was approximately twice as large as that in the bisulfite sample. This discrepancy likely accounts for the small difference in relative response factors for bisulfite and metabisulfite shown in Table 3. By separately integrating the two chromatographic peaks, we defined an adjusted relative response factor of 0.50 for both bisulfite and metabisulfite, compared to a factor of 1.00 for sulfate. This adjusted response factor was used in the analysis of other samples produced later in the project.

Another example of odd chromatographic behavior observed in this project was the apparent change of measured concentrations of bisulfite as the samples age. This is illustrated in Figure 11. The top panel shows chromatograms of the 10-ppm aqueous sodium bisulfite sample within 1 hour of preparation and after aging (in an autosampler vial) for 24 hours. It appears that some oxidation of bisulfite to sulfate occurred during this aging, as the bisulfite peak decreased in size while the sulfate peak increased. This oxidative conversion process was even more pronounced in the 10 ppm metabisulfite sample, shown in the bottom panel of Figure 11.

Figure 12 shows chromatograms of the same 10 ppm bisulfite and metabisulfite aqueous standards after aging in the same autosampler vials for approximately 1 month. (These chromatograms are shown in a separate figure, rather than overlaying them on the chromatograms in Figure 11, because the retention times on the IC column shortened by about 0.5 minute over this month of use.) Figure 12 indicates that about one-half of the bisulfite sample converted to sulfate, while all the metabisulfite converted to sulfate. We believe that this observed oxidative instability explains why previous IC analyses of bisulfite- and metabisulfite-spiked ethanol solutions showed only sulfate peaks in the chromatograms. It is likely that more highly oxidizing conditions are experienced during the process of preparing and handling these spiked ethanol solutions than during simple aging of standards in sealed autosampler vials.

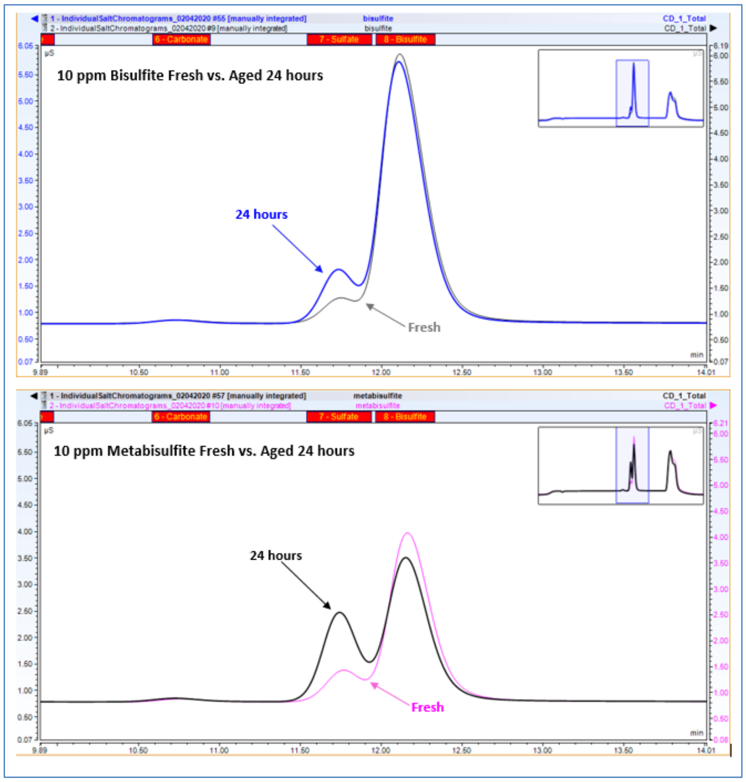

Figure 11. IC chromatograms of aqueous solutions of 10 ppm sodium bisulfite (top) and 10 ppm sodium metabisulfite (bottom) when prepared fresh and after aging for 24 hours.

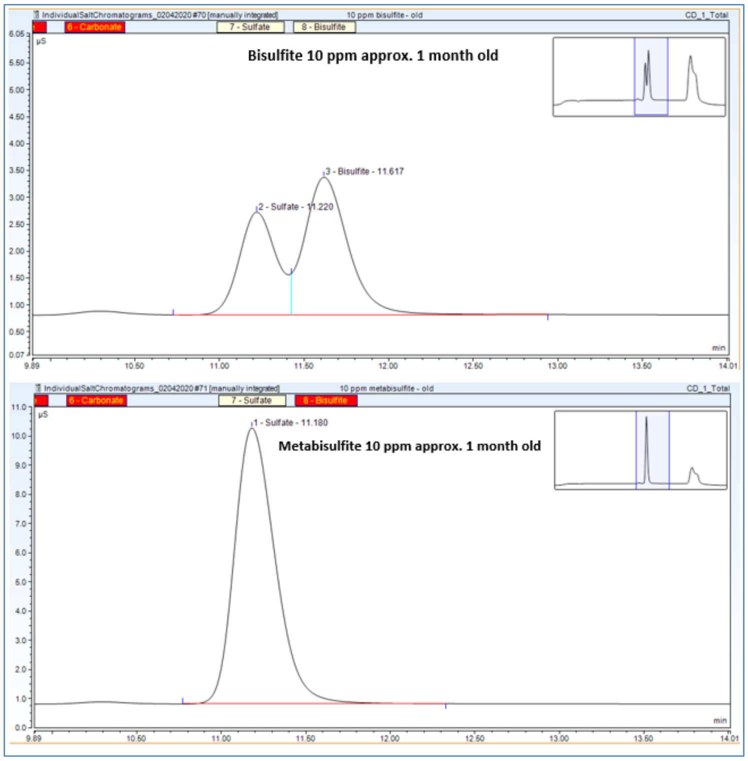

Figure 12. IC chromatograms of aqueous solutions of 10 ppm sodium bisulfite (top) and 10 ppm sodium metabisulfite (bottom) after aging for approximately 1 month.

4.4 Solubility of sodium bisulfite and sodium metabisulfite (solids) in ethanol

Due to unexpected results observed during early stages of this project, DRI and the CRC Project Team agreed to make several changes to the originally planned experimental methods and matrices. Most significant was the discovery that the solubility of sodium bisulfite in ethanol appears to be lower than we had previously believed. We now believe the seemingly high solubility observed in the earlier CRC Project, CM-136-15-1 resulted in part from methodological differences whereby high concentration slurries of sodium bisulfite in ethanol were vacuum filtered to obtain clear filtrates, which still contained relatively high levels of microscopic salt particles. It is also likely that sodium bisulfite is at least somewhat soluble in ethanol, though perhaps at levels of 20-40 ppm, which upon oxidation to sulfate would still contribute to the cloudy appearance of the filtrate solutions. In the current study, no filtration of $NaHSO_3$-spiked samples was done.

Another problem was the choice of IC method used to analyze sulfate and bisulfite anions in the sets of laboratory samples being studied. In the earlier project (CRC CM-136-15-1) we used ASTM Method D7328 to analyze for both existent and potential sulfate. This method involves evaporation of the ethanol (or gasoline/ethanol blend) and reconstitution in water, so that an aqueous solution is injected into the IC instrument. Because this is a rather time-intensive (and expensive) method, it was decided to use a simpler, direct injection method (ASTM D7319) to analyze sulfate and bisulfite in the current project. However, upon extensive use, it was found that direct sample injection – particularly samples for potential sulfate determination, which contained hydrogen peroxide – led to chromatographic problems, including column deterioration. Additionally, ASTM D7319 is meant for analysis of neat ethanol solutions, not blends of ethanol in gasoline. Injection of gasoline onto the IC column adversely affected the chromatograms baselines, making detection of the anions more difficult. It is also likely that the repeated injection of gasoline contributed to column deterioration. Also, determination of potential sulfate requires addition of aqueous hydrogen peroxide, which can cause phase separation problems with some gasoline-ethanol blends.

A further complication results from the fact that some of the salts used in this project are not available in high purity. In particular, sodium bisulfite ($NaHSO_3$) is only available as a mixture with sodium metabisulfite ($Na_2S_2O_5$). Given all these issues, it was agreed to complete the experimental portion of this project by conducting a final, smaller set of solubility experiments using only sodium bisulfite and sodium metabisulfite in ethanol, but with no gasoline-ethanol blends. The planned matrix is shown in Table 4.

The objective of these experiments was to determine the soluble and insoluble concentrations of sodium bisulfite and sodium metabisulfite in ethanol, when spiked at concentrations ranging from 0 to 64 ppm. It was thought that the soluble salt concentration could be determined by analyzing an aliquot drawn from the top of a sample bottle after it had sat undisturbed for 48 hours, whereas total salt concentration (sum of soluble and insoluble) could be determined by analyzing an aliquot drawn from a sample bottle that had just been vigorously shaken.

Both existent and potential sulfate measurements were made on shaken and unshaken samples. In all cases, the anion concentrations were measured using ion chromatography (IC), according to ASTM Method D7328, which involves evaporation of the ethanol solvent and reconstitution of the sample in water prior to IC injection. When determining potential sulfate, 0.5 mL of 30% aqueous H_2O_2 was added to a 10 mL sample aliquot prior to evaporation.

The original intent was to prepare these spiked ethanol solutions beginning with concentrated aqueous solutions of the appropriate salt, in the same way that the earlier sample matrices shown in Table 1 and Table 2 were prepared. However, due to miscommunication during personnel changes, the sample matrix shown in Table 4 was initially prepared by adding varying amounts of solid, anhydrous salts to ethanol. These solutions were analyzed for existent and potential sulfate, using shaken and unshaken samples as described above. Subsequently, the entire experimental matrix shown in Table 4 was repeated, using samples prepared from aqueous stock solutions, as originally intended. Results from this second set of samples are presented in Section 4.5 of this report.

Table 4. Experimental Matrix to Investigate Solubility Behavior of Sodium Bisulfite and Sodium Metabisulfite in Ethanol

	$NaHSO_3$ Conc. in Ethanol, ppm	0-Hour (after shaking)	48 hours (before shaking)	48 hours (after shaking)	Total Number of Analyses
1	0.0	O	E, P	O, E, P	16 existent sulfate 16 potential sulfate
2	1.0	O	E, P	O, E, P	
3	2.0	O	E, P	O, E, P	
4	4.0	O	E, P	O, E, P	
5	8.0	O	E, P	O, E, P	
6	16	O	E, P	O, E, P	
7	32	O	E, P	O, E, P	
8	64	O	E, P	O, E, P	
	$Na_2S_2O_5$ Conc. In Ethanol, ppm				
1	0.0	O	E, P	O, E, P	16 existent sulfate 16 potential sulfate
2	1.0	O	E, P	O, E, P	
3	2.0	O	E, P	O, E, P	
4	4.0	O	E, P	O, E, P	
5	8.0	O	E, P	O, E, P	
6	16	O	E, P	O, E, P	
7	32	O	E, P	O, E, P	
8	64	O	E, P	O, E, P	

Notes: O = Observe after shaking
E = Existent sulfate (and bisulfite) measurements of samples by ASTM D7328
P = Potential sulfate measurements of samples by ASTM D7328

4.4.1 Addition of solid sodium bisulfite to 200 proof ethanol

An initial set of $NaHSO_3$-spiked ethanol solutions was prepared by adding weighed amounts of solid sodium bisulfite into 1-L volumetric flasks. Because of the spiking method used, the final $NaHSO_3$ concentrations were slightly different from the desired, nominal concentrations. After vigorously shaking these volumetric flasks for about 1 minute, they were allowed to sit undisturbed for 48 hours. After this time, two 10-mL aliquots were removed by pipette from the top of the flasks, representing samples containing dissolved $NaHSO_3$. A small amount of aqueous hydrogen peroxide was added to one of these aliquots, for the purpose of determining potential sulfate. After shaking the volumetric flasks to mix soluble and insoluble materials, two additional 10-mL aliquots were removed, with hydrogen peroxide being added to one of the two. All four aliquots were then blown down to dryness and reconstituted in water. (Note that because of IC instrument problems, these aqueous samples were not analyzed immediately after being prepared. They were stored in sealed autosampler vials under refrigeration for 2-4 weeks before being analyzed.)

Inspection of the IC chromatograms indicated that in every sample, only sulfate ion was detected, not bisulfite ion. This is consistent with earlier observations, suggesting that during sample preparation, storage, and analysis, oxidation of bisulfite to sulfate occurred. Assuming complete conversion of bisulfite to sulfate, we examined the solubility/recovery of spiked sodium bisulfite on the basis of sulfate concentrations. Table 5 shows the amount of $NaHSO_3$ spiked into each sample, and the corresponding concentration of sulfate, based on 100% conversion of bisulfite to sulfate. [Note that because the final IC analyses were conducted on aqueous samples, with the results being expressed as ppm by mass (mg ion/kg water), an additional conversion was done to express the spiked amount in units of mg SO_4/kg water.]

Table 5. Solubility experiments involving addition of solid sodium bisulfite to 200-proof ethanol

	Spiked amounts				Sulfate concentrations measured by IC (ppm)*			
Nominal Conc., ppm	Mass of $NaHSO_3$ in ethanol, mg/L	Mass of HSO_3 in ethanol, mg/L	Corresponding Mass of SO_4 in ethanol, mg/L	Corresponding conc. of SO_4 in H_2O, mg/kg	Unshaken - existent	Unshaken - potential	Shaken - existent	Shaken - potential
0	0.000	0.000	0.000	0.000	0.003	0.015	0.012	0.066
1	1.115	0.869	1.029	1.303	0.924	1.611	1.308	1.658
2	1.883	1.467	1.738	2.200	1.449	2.414	2.868	2.788
4	4.010	3.124	3.702	4.686	3.397	6.158	6.447	6.324
8	7.315	5.699	6.753	8.548	6.793	10.474	10.035	10.943
16	15.862	12.358	14.643	18.535	9.561	23.399	19.245	22.808
32	30.369	23.660	28.034	35.486	21.195	42.875	32.476	42.625
64	66.405	51.734	61.300	77.595	36.958	84.740	83.224	92.526

* sulfate concentration expressed as mass of SO_4 ion per mass of water (mg/kg)

Table 5 also shows the IC-measured concentrations of sulfate in each sample, with these results being graphically displayed in Figure 13. Comparing the top panel of Figure 7 with Figure 13 shows somewhat different results for $NaHSO_3$ solubility in ethanol, depending upon whether the solutions were prepared from aqueous salt solutions (Figure 7) or solid addition of salt (Figure 13). The unshaken-existent samples in Figure 13 (gray bars) correspond most closely to the results in Figure 7. However, the measured sulfate concentration values shown in Figure 13 are 2-3 times higher than those shown in Figure 7 for the same level of spiked sodium bisulfite. When previously discussing the results shown in Figure 7, we speculated that the seeming maximum $NaHSO_3$ solubility of about 10 ppm in ethanol (top panel of Figure 7) may actually represent a suspension or insoluble complex of the salt, rather than true solubility. The same phenomena may be even more pronounced when dealing with solutions prepared by addition of solid salt to the ethanol.

Another significant factor to bear in mind when observing the different results shown in Figure 7 and Figure 13 is the analytical method used to measure sulfate. The existent sulfate results in Figure 7 were determined using ASTM D7319 (direct injection) while the results in Figure 13 were determined using ASTM D7328 (re-constituted in water).

An additional observation is that in most cases, the measured sulfate concentrations shown in Figure 13 were slightly higher than the spiked concentrations. (This was not true for the unshaken existent sulfate results.) One factor contributing to this counterintuitive result is the presence of impurities in the reagent grade $NaHSO_3$ used in making these ethanol solutions. It is not possible to purchase 100% pure $NaHSO_3$. The material we used, which is the highest grade available from Fisher Chemical (Catalog No. S654-500; Lot No. 180695), had an assayed purity of 63.4%. As stated by the manufacturer, this material is a mixture with $Na_2S_2O_5$. A given mass of sodium metabisulfite ($Na_2S_2O_5$; 33.7% S) contains more sulfur than the same mass of sodium bisulfite ($NaHSO_3$; 30.8% S). Consequently, samples prepared from a mixture of sodium bisulfite and sodium metabisulfite would contain slightly higher concentrations of sulfur (and potential sulfate) than indicated in Table 5. If we assume that the starting material was 63% sodium bisulfite and 37% sodium metabisulfite, this would increase the spiked potential sulfate by about 5% above the values shown in Table 5.

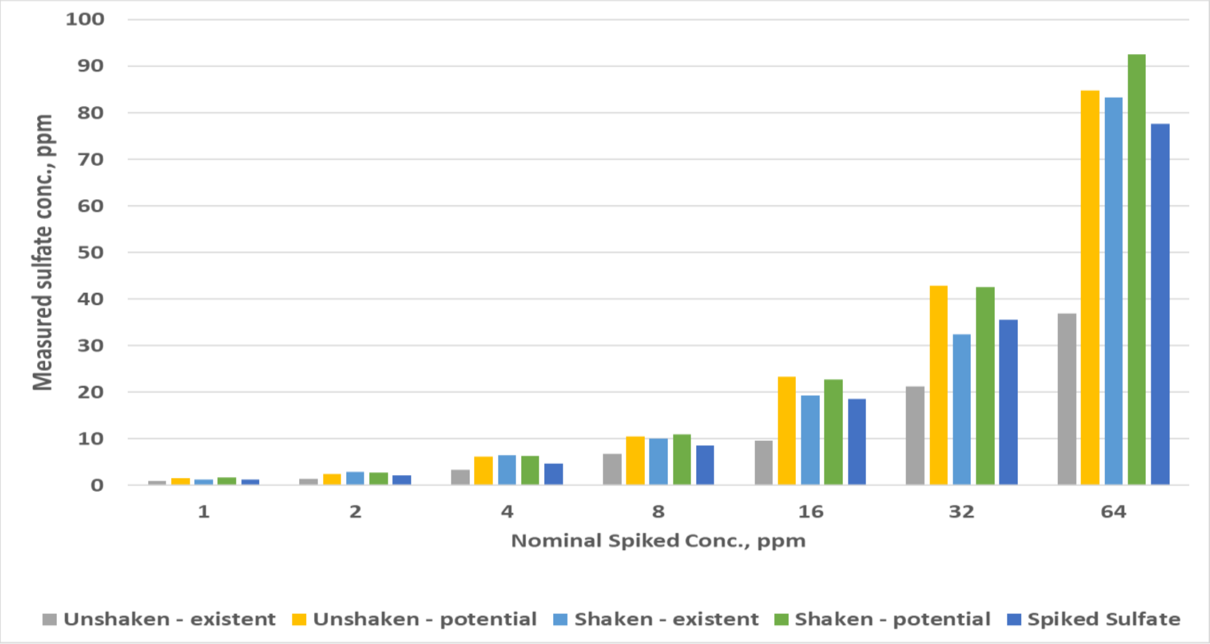

Figure 13. Sulfate concentrations spiked into ethanol (in the form of sodium bisulfite) and measured (using ASTM D7328) in shaken and unshaken aliquots drawn after 48 hours.

It is also seen from the results of Table 5 and Figure 13 that potential sulfate is significantly higher than existent sulfate in every one of the unshaken samples. This outcome would be expected if some bisulfite dissolved in the ethanol and was then oxidized to sulfate in the process used to determine potential sulfate. The difference in measured sulfate between the shaken existent and shaken potential samples was much smaller. This also is as expected, since all bisulfite/sulfate is captured during shaking, whether dissolved or not.

The existent sulfate measurements from unshaken samples may be considered to provide the best estimate of true solubility. Of course, this is complicated by the fact that bisulfite was spiked into the solutions, but sulfate was the measured ion. Also, the measured sulfate concentrations in these samples (gray bars in Figure 13) increased linearly with an increase in the spiked amount. This suggests that something more than solubility is occurring, and is consistent with the notion that some type of complex between ethanol and sodium bisulfite is involved in keeping the salt suspended.

4.4.2 Addition of solid sodium metabisulfite to 200 proof ethanol

A similar set of 8 samples was prepared by adding weighed amounts of solid sodium metabisulfite into 1-L volumetric flasks. After vigorously shaking, these solutions were allowed to sit for 48 hours before withdrawing aliquots for analysis as described above. Existent and potential sulfate concentrations were measured in shaken and unshaken aliquots. As with the sodium bisulfite-spiked samples, these sodium metabisulfite-spiked samples also showed only a single sulfate peak in the IC chromatograms. In fact, the chromatograms from the $NaHSO_3$ and $Na_2S_2O_5$ samples were nearly identical.

Table 6 shows the spiked amounts of $Na_2S_2O_5$ and the measured sulfate concentrations for each sample. Also shown are the spiked amounts of metabisulfite anion and the corresponding amounts of sulfate anion, assuming the metabisulfite was completely converted to sulfate. These results, which are graphically displayed in Figure 14, are very similar to the results from the sodium bisulfite experiments depicted in Figure 13, suggesting that the two salts behave very much alike in ethanol.

Table 6. Solubility experiments involving addition of solid sodium metabisulfite to 200-proof ethanol

	Spiked amounts				Sulfate concentrations measured by IC (ppm)*			
Nominal Conc., ppm	Mass of $Na_2S_2O_5$ in ethanol, mg/L	Mass of S_2O_5 in ethanol, mg/L	Corresponding Mass of SO_4 in ethanol, mg/L	Corresponding conc. of SO_4 in H_2O, mg/kg	Unshaken - existent	Unshaken - potential	Shaken - existent	Shaken - potential
0	0.000	0.000	0.000	0.000	0.012	0.012	0.013	0.019
1	1.315	0.997	1.329	1.682	0.606	1.809	1.809	1.841
2	2.015	1.528	2.036	2.577	2.569	2.836	3.033	2.952
4	4.685	3.552	4.735	5.994	7.162	7.492	7.447	7.435
8	7.995	6.061	8.080	10.228	9.306	11.718	10.114	12.961
16	16.775	12.718	16.953	21.459	21.555	25.663	22.969	28.038
32	36.043	27.326	36.425	46.108	45.322	53.906	51.721	61.453
64	71.191	53.972	71.946	91.071	79.009	95.690	99.928	119.007

* sulfate concentration expressed as mass of SO_4 ion per mass of water (mg/kg)

The most noticeable difference between the sodium bisulfite and sodium metabisulfite experimental results shown in Figure 13 and Figure 14 is in the existent sulfate concentrations from unshaken samples. With sodium bisulfite (Figure 13), these concentrations were only about one-half of the spiked concentration, whereas with sodium metabisulfite (Figure 14) they were almost the same as the spiked amount. This suggests a higher solubility of sodium metabisulfite compared to sodium bisulfite, or perhaps a higher degree of complexation keeping more of the metabisulfite suspended in ethanol.

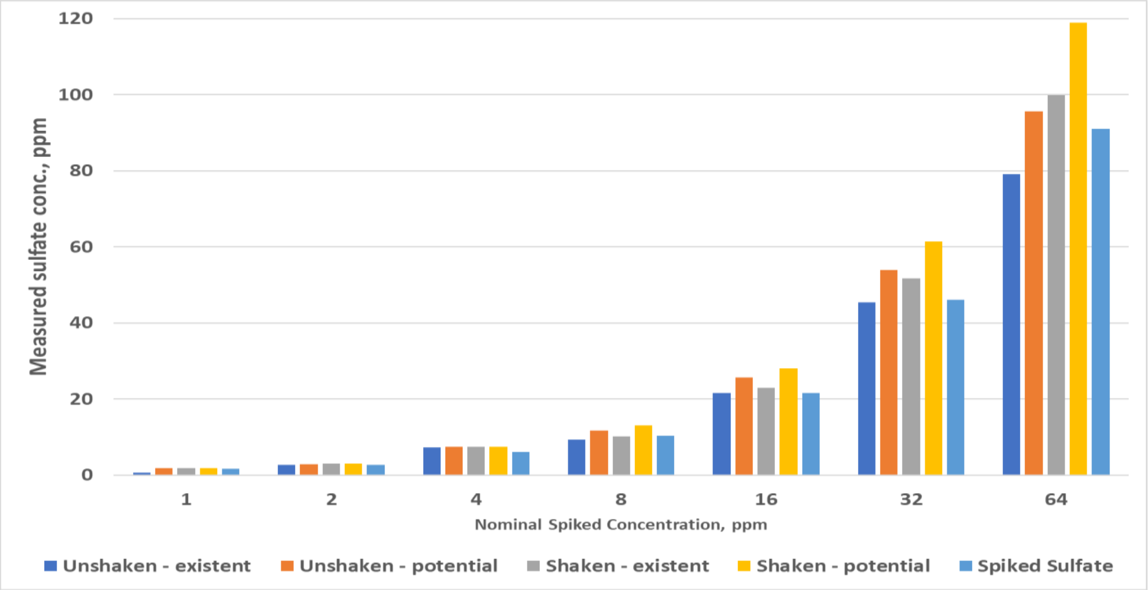

Figure 14. Sulfate concentrations spiked into ethanol (in the form of sodium metabisulfite) and measured (using ASTM D7328) in shaken and unshaken aliquots drawn after 48 hours.

4.4.3 Additional experiments to examine seemingly high salt solubilities

The high existent sulfate concentrations measured in the unshaken samples of sodium bisulfite and sodium metabisulfite imply relatively high solubilities of these salts in ethanol. An alternative explanation is that ethanol forms a type of complex with these salts, thereby keeping them suspended in solution. (It is likely that both solubility and complexation are involved.) To investigate this further, we utilized centrifugation in an effort to separate microscopic particles from truly dissolved salts. One sample of sodium bisulfite in ethanol (16 ppm nominal concentration from Table 5) and one sample of sodium metabisulfite in ethanol (32 ppm nominal from Table 6) were used in these experiments.

A Beckman Coulter Allegra X-22R centrifuge was used. Approximately 40-mL each of well-shaken samples were placed in 50-mL plastic centrifuge tubes and were spun for 30-min. at either 5,000 or 10,000 rpm. After centrifuging, two 10-mL aliquots were removed from the top of the tubes by pipette. One aliquot was analyzed for existent sulfate, while the other was analyzed for potential sulfate, using ASTM Method D7328 (with sample blowdown and re-constitution). Measured sulfate concentrations before and after centrifugation are shown in Table 7.

Table 7. Effect of centrifugation and gasoline blending on measured sulfate concentrations

Starting salt	Type of sulfate analysis	Measured sulfate concentration, ppm			
		In ethanol solution before centrifugation	In ethanol solution after 30-min. of centrifugation		In E50 after sitting 48 hours
			5000 rpm	10,000 rpm	
Sodium bisulfite	Existent	12.77	5.52		0.73
	Potential	15.24	18.82		4.06
Sodium metabisulfite	Existent	25.23	15.88	15.42	3.82
	Potential	25.26	35.20	38.61	7.68

Centrifugation appeared to reduce the amount of existent sulfate in both samples somewhat, but did not remove all sulfate. Centrifugation of the sodium metabisulfite sample at high speed was no more effective in removing sulfate than at lower speed. (The centrifuge tube containing the sodium bisulfite sample broke during high speed operation, so no results were obtained for this case.) On the other hand, centrifugation did not reduce potential sulfate concentrations; in fact, the concentrations appeared to increase in the case of sodium metabisulfite. We do not have a good explanation for this, but point out that these experiments were conducted several weeks after the ethanol salt solutions had been prepared, and that only single centrifugation experiments were done.

Earlier experiments using sulfate salts in ethanol suggested that once gasoline was added, the salts readily dropped out of solution, leading to very low measured concentrations in the ethanol-gasoline blends. To further examine this behavior, the same ethanol solutions of sodium bisulfite and sodium metabisulfite used in the centrifugation experiments described above were blended with gasoline to produce E50 blends. (The non-oxygenated gasoline provided to DRI for use in this project was used to prepare these blends.) After vigorously mixing the two E50 blends, they were allowed to sit for 48 hours. Two 10-mL aliquots were then removed from the top of each container and were analyzed for existent and potential sulfate using ASTM D7328. Results shown in the last column of Table 7 clearly indicate that addition of gasoline promoted removal of the sulfate salts. Existent sulfate concentrations were reduced substantially – though not to zero. Potential sulfate concentrations were also reduced, but not as dramatically.

4.5 Solubility of sodium bisulfite and sodium metabisulfite (aqueous) in ethanol

To investigate the ethanol solubility of $NaHSO_3$ and $Na_2S_2O_5$ in a manner consistent with the earlier experiments using Na_2SO_4, the experimental matrix in Table 4 was repeated, but starting with concentrated aqueous solutions of the salts rather than adding solid salts to ethanol. Each of the final salt-containing solutions contained 0.50 vol.% water, as explained in the procedures defined in Appendix II.

After preparing these solutions and vigorously shaking them for about 1 minute, they were allowed to sit undisturbed for 48 hours. After this time, two 10-mL aliquots were removed from the top of the solution by pipette, representing samples containing dissolved (and suspended) $NaHSO_3$ or $Na_2S_2O_5$. One aliquot was analyzed for existent sulfate, the other for potential sulfate, using ASTM Method D7328. The sample flasks were then vigorously shaken to mix the soluble and insoluble salts. Two additional 10-mL aliquots were immediately withdrawn from these mixed solutions, with one being analyzed for existent sulfate and the other for potential sulfate.

Inspection of the IC chromatograms revealed two peaks (sulfate and bisulfite) in each of the existent sulfate analyses, but only a single peak (sulfate) in the potential sulfate analyses. Example chromatograms are shown in Figure 15. The appearance of two peaks was surprising, as only a single sulfate peak had been observed in all earlier experiments involving ethanol solutions of $NaHSO_3$ and $Na_2S_2O_5$. We attribute this to the shortened time period between sample preparation and analysis, and greater effort to minimize exposure to air during these recent experiments, thereby reducing the inherent oxidation of bisulfite to sulfate. An important factor may have been retention of the salt solutions within the volumetric flasks used to prepare them for the 48-hr resting period. These flasks have very little air headspace. In earlier experiments, ethanol solutions prepared in volumetric flasks were transferred into square glass bottles (which have abundant air headspace) for aging and observation – as shown in Figure 2.

The chromatograms in Figure 15 all represent aliquots drawn from unshaken solutions that had been spiked with 16 ppm of $NaHSO_3$ or $Na_2S_2O_5$. The measured concentrations of bisulfite and sulfate ions in each sample are indicated within the textbox shown in each panel. In the existent sulfate samples (top panels), the sum of the two peaks is shown, using a detector response factor for bisulfite that is 50% that used for sulfate. The differences between the potential sulfate and existent sulfate concentrations are an indication of the amount of reduced-form sulfur that is present, which can be oxidized to sulfate by addition of hydrogen peroxide. For the samples shown in Figure 15, this difference is about 5 ppm, for both the $NaHSO_3$ and $Na_2S_2O_5$ samples – suggesting that about 5 ppm of sodium bisulfite and sodium metabisulfite were soluble in these unshaken ethanol solutions. However, this difference varied substantially over the range of spiked concentrations used (as described in the following section) being larger with higher spiked concentrations and smaller with lower spiked concentrations. Thus, quantification of the true solubility of these salts in ethanol remains uncertain.

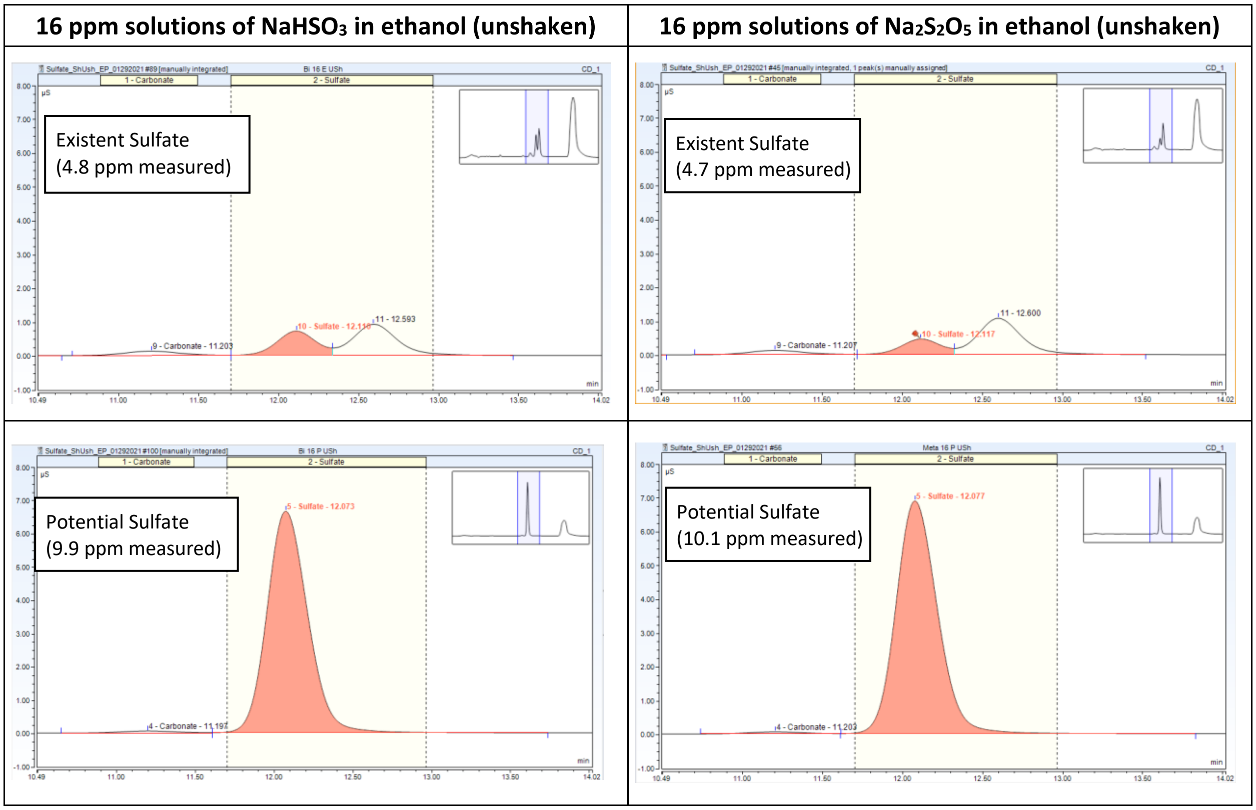

Figure 15. IC chromatograms (all at same scale) from existent and potential sulfate analyses of $NaHSO_3$ and $Na_2S_2O_5$ solutions in 200 proof ethanol. Colored peak is sulfate ion; following peak is bisulfite ion.

4.5.1 IC results from sodium bisulfite solutions in 200 proof ethanol

Results from the series of sodium bisulfite experiments in ethanol are summarized in Table 8 and Figure 16. The spiked concentrations are expressed on a mass basis, in terms of total $NaHSO_3$, HSO_3

ion, and corresponding SO_4 ion in ethanol. The IC results are also expressed on a mass basis, as ppm sulfate in the re-constituted aqueous solutions generated using ASTM Method D7328.

In the existent sulfate measurements, the two peaks were integrated separately and quantified using different response factors for sulfate and bisulfite. (The response factor for bisulfite was 0.50 times that for sulfate.) The "unshaken-existent" and "shaken-existent" sulfate results shown in Table 8 represent the sum of the measured sulfate and bisulfite ions. Interestingly, the ratio of the sulfate/bisulfite peaks varied in an inconsistent manner from sample-to-sample, suggesting that the extent of bisulfite oxidation during sample preparation and handling was quite variable.

Table 8. Solubility experiments involving addition of aqueous sodium bisulfite to 200-proof ethanol
(Spiked concentrations expressed as mg salt or ion per kg ethanol; IC-measured concentrations expressed as mg ion per kg water)

Spiked Conc. of $NaHSO_3$, ppm	Spiked Conc. of HSO_3, ppm	Corresponding Conc. of SO_4, ppm	Sulfate concentrations measured by IC (ppm)*			
			Unshaken - existent	Unshaken - potential	Shaken - existent	Shaken - potential
0.0	0.000	0.000	0.013	0.012	0.014	0.012
1.0	0.778	1.037	0.601	0.700	0.623	0.716
2.0	1.558	2.077	0.739	1.502	0.708	1.486
4.0	3.116	4.154	1.327	2.855	1.364	2.909
8.0	6.233	8.309	2.659	5.555	3.075	6.163
16	12.465	16.616	4.778	9.884	6.184	11.716
32	24.930	33.232	10.801	20.224	14.113	23.573
64	49.860	66.465	27.924	41.279	30.996	45.329

* existent sulfate values represent the sum of bisulfite and sulfate ions

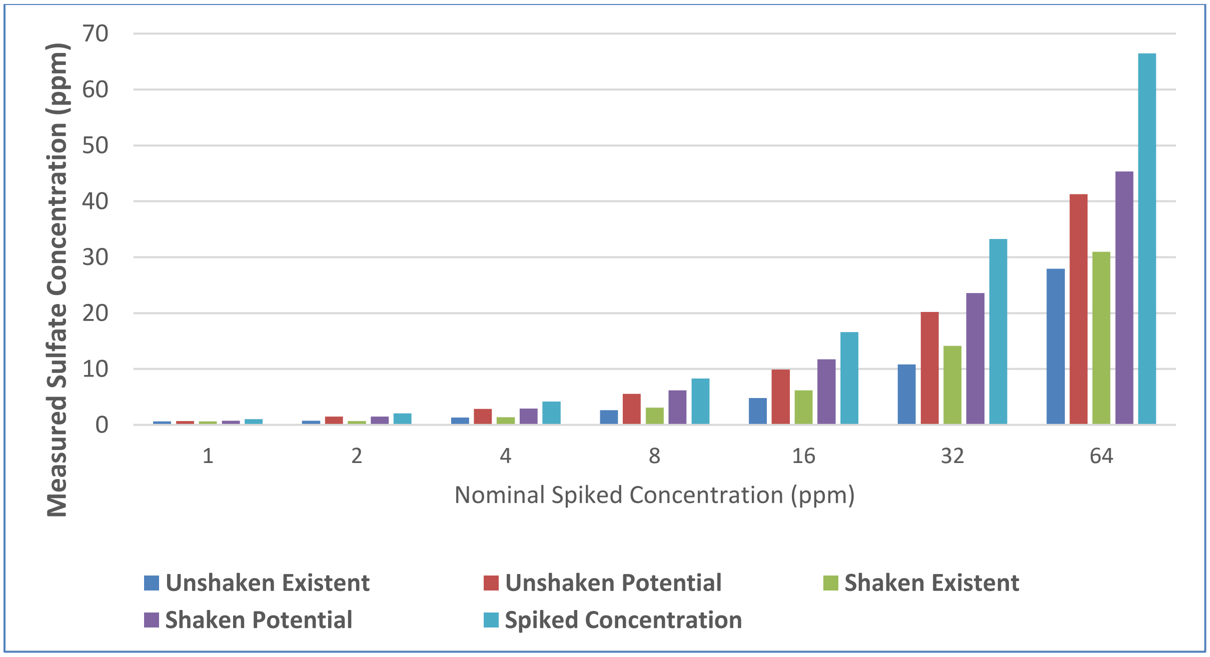

Figure 16. Sulfate concentrations spiked into ethanol (as aqueous sodium bisulfite) and measured in shaken and unshaken aliquots in re-constituted aqueous solutions.

These IC results are interesting, and a bit confusing. The unshaken samples (which presumably contained only dissolved salts) had slightly lower concentrations than the corresponding shaken samples (which presumably contained both dissolved and non-dissolved salts). This was true for both the existent and potential sulfate measurements. This is as expected, and is consistent with the notion that some (but not all) of the added $NaHSO_3$ was dissolved in the ethanol. However, the differences between shaken and unshaken sample measurements were quite small, ranging from almost zero in the 1-4 ppm spiked samples up to about 3 ppm in the 64 ppm spiked samples. The nearly linear increase in amount of insoluble material (defined as the difference between shaken and unshaken samples) with increasing spiked amount is consistent with the starting sodium bisulfite reagent being contaminated with a certain percentage of insoluble sodium sulfate.

Also observed in Figure 16 is that potential sulfate measurements were higher than existent sulfate measurements in all cases, whether shaken or not. The difference between potential and existent measurements is an indication of how much reduced-form bisulfite remains in the sample, with the potential to be oxidized to sulfate. This difference ranged from almost zero in the 1-2 ppm spiked samples to over 10 ppm in the 64 ppm spiked samples.

It might be expected that measurement of potential sulfate in the shaken samples would match the amount spiked into each sample. (Shaken samples should capture all salts, whether dissolved or not, and potential samples should have converted all ion forms to sulfate.) However, the results shown here indicate about a 30% deficit in measured values compared to spiked values. Most of this deficit is explained by a difference in units between spiked and measured concentrations. Spiked concentrations are expressed as mass ppm in ethanol, whereas measured concentrations are expressed as mass ppm in water. Due to differences in density between ethanol (0.79 g/mL) and water (1.00 g/mL), 1 ppm spiked into ethanol equates to 0.79 ppm in water once the ethanol solution is blown down and re-constituted in water.

It is difficult to ascertain the true solubility of $NaHSO_3$ in ethanol from these experiments. While it might be argued that the unshaken existent sulfate results provide some measure of solubility, this is complicated by the presence of contaminants in the starting sodium bisulfite reagent and the inherent oxidation of bisulfite to sulfate that occurs during sample handling. Also, it is not obvious why the existent and potential values are so different for these unshaken samples. Furthermore, the systematic increase in all measured values with increasing spiked amounts suggests that some process other than solubility (such as complexation between $NaHSO_3$ and ethanol) is involved.

4.5.2 IC results from sodium metabisulfite solutions in 200 proof ethanol

A similar set of ethanol salt solutions was prepared beginning with a concentrated aqueous solution of sodium metabisulfite. The spiked amounts and IC-measured results for this set of samples are summarized in Table 9 and Figure 17. These results are so similar to those from the sodium bisulfite experiments described above as to be nearly indistinguishable. The same IC-measured differences between shaken and unshaken samples, and between existent and potential sulfate results are seen in both sets of experiments. Also, the same general increase in all measurements with increasing spiked concentrations is observed. These results indicate that the bisulfite and metabisulfite species behave virtually identically in ethanol solutions.

Table 9. Solubility experiments involving addition of aqueous sodium metabisulfite to 200-proof ethanol
(Spiked concentrations expressed as mg salt or ion per kg ethanol; IC-measured concentrations expressed as mg ion per kg water)

Spiked Conc. of $Na_2S_2O_5$, ppm	Spiked Conc. of S_2O_5, ppm	Corresponding Conc. of SO_4, ppm	Sulfate concentrations measured by IC (ppm)*			
			Unshaken - existent	Unshaken - potential	Shaken - existent	Shaken - potential
0.0	0.000	0.000	0.016	0.013	0.004	0.013
1.0	0.758	0.898	0.362	0.604	0.402	0.455
2.0	1.516	1.796	0.680	1.386	0.771	1.495
4.0	3.033	3.594	1.318	2.695	1.460	2.902
8.0	6.065	7.186	2.317	4.856	2.980	5.840
16	12.130	14.373	4.741	10.146	6.119	10.909
32	24.260	28.746	9.044	19.478	15.335	22.657
64	48.520	57.492	25.613	40.338	29.681	43.525

* existent sulfate values represent the sum of bisulfite and sulfate ions

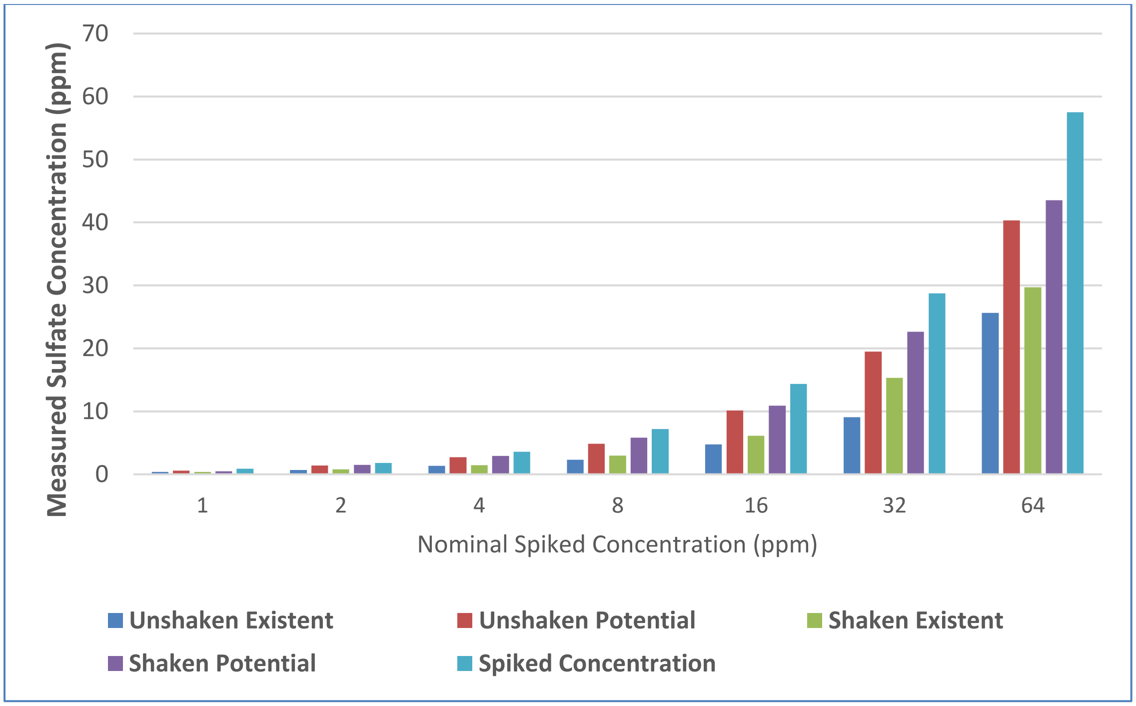

Figure 17. Sulfate concentrations spiked into ethanol (as aqueous sodium metabisulfite) and measured from shaken and unshaken aliquots in re-constituted aqueous solutions.

4.5.3 Blends of ethanol salt solutions with gasoline

A final set of experiments was conducted to examine how the behaviors of sodium bisulfite and sodium metabisulfite in the ethanol solutions described above change when these solutions are blended with gasoline. For these experiments, a single $NaHSO_3$-spiked ethanol solution and a single $Na_2S_2O_5$-spiked ethanol solution were used (nominal 16 ppm spiked amounts in both cases). An E50 blend of each solution was prepared using the same non-oxygenated gasoline that was supplied to DRI for this project.

After thoroughly mixing the E50 blends, they were allowed to sit undisturbed for 48 hours. Two aliquots were then removed from the top of the solutions using pipettes: one for existent sulfate analysis, the other for potential sulfate analysis. The E50 blends were then shaken to mix dissolved and undissolved salts, and two more aliquots were removed for existent and potential sulfate determination.

Results of these IC measurements are shown in Table 10 and Figure 18. In all the IC analyses, only a single peak was observed, that corresponding to sulfate. The absence of a separate bisulfite (or metabisulfite) peak indicates complete oxidation to sulfate occurred during sample preparation and handling. These samples had considerable exposure to oxygen, as they were prepared, shaken, and aged in relatively large containers, having approximately 60% air headspace.

Table 10. Existent and Potential Sulfate Measurements of E50 Gasoline Blends

Spiked Salt	Nominal Spiked Conc. in Ethanol, ppm	Corresponding Conc. of SO_4 in Ethanol, ppm	Corresponding Conc. of SO_4 in E50 (after H_2O reconstitution)	Sulfate concentrations measured by IC (ppm)*			
				Unshaken - existent	Unshaken - potential	Shaken - existent	Shaken - potential
$NaHSO_3$	16	16.616	6.56	1.71	1.21	1.97	6.12
$Na_2S_2O_5$	16	14.373	5.68	1.54	1.58	1.58	6.04

* only a single peak for sulfate ion was observed; no peak for bisulfite ion

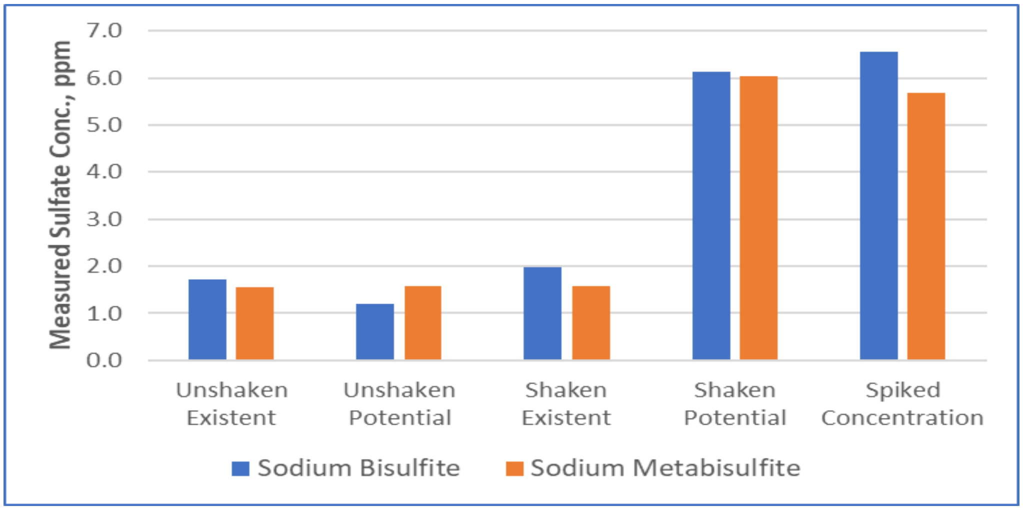

Figure 18. Existent and potential sulfate measurements of E50 blends

While not identical, results from these E50 blend experiments are similar to those from the earlier experiments shown in Table 7. They indicate that once gasoline is added, most of the sulfate salts spiked into ethanol drop out of solution (or suspension), resulting in very low (but not zero) remaining concentrations. Results from the unshaken samples suggest that the solubility of these sulfate salts in E50 is below 2 ppm. The good agreement between the shaken-potential results and the spiked amounts indicates that we are able to account for virtually all of the salts, whether in a reduced or oxidized form.

5. Summary and Conclusions

In this project, numerous experiments were conducted to examine the solubility of three sulfate salts (Na_2SO_4, $NaHSO_3$, and $Na_2S_2O_5$) in ethanol and gasoline-ethanol blends. Despite careful efforts in sample preparation and analysis, accurate determination of salt solubility remains elusive. Considering data from both this study and the earlier CRC Project CM-136-15-1, certain findings are difficult to fully explain. For example, the seemingly high solubility of sodium bisulfite in ethanol observed in the earlier study (~100 ppm) was not confirmed in the present study.

One major factor contributing to the difficulty in quantifying solubility is that the salts (particularly $NaHSO_3$ and $Na_2S_2O_5$) appear to undergo some form of complexation with ethanol, thereby keeping relatively high concentrations in suspension (perhaps up to 50 ppm), though not fully solubilized. Addition of gasoline to produce gasoline-ethanol blends appears to disrupt these suspensions, resulting in greatly reduced levels of the salts in solution.

Additional factors complicating this work include the oxidative instability of bisulfite, which readily transformed to sulfate during sample preparation and analysis; the presence of significant impurities in reagent-grade sodium bisulfite; and the different behaviors of anhydrous and hydrated forms of these salts. It was also discovered that measurement of sulfate salts by a direct injection IC method (ASTM D7319), which was used for some analyses in this project, may not be highly reliable in this application. This direct injection method is meant for analysis of neat ethanol solutions, not blends of ethanol in gasoline. Additionally, it appears that repeated analysis of samples containing hydrogen peroxide (which is used for potential sulfate determinations) resulted in rapid degradation of the IC column. Given all these complexities and uncertainties, specific conclusions from this project are as follows:

- Accurately determining the solubility of sodium sulfate in neat ethanol is very difficult. Based on literature reports[2] and observations from the present study, this solubility is probably less than 1 ppm.
- The solubility of sodium sulfate in gasoline-ethanol blends is extremely low – certainly less than 1 ppm.
- The solubility behaviors of sodium bisulfite and sodium metabisulfite in ethanol are very similar to each other, though different from the behavior of sodium sulfate.
- Sodium bisulfite and sodium metabisulfite are significantly more soluble in ethanol than is sodium sulfate – perhaps by an order of magnitude – but not by 2-orders of magnitude, as was previously thought, based on results from the earlier CRC Project CM-136-15-1.
- Due to complexation or other factors that keep finely dispersed sodium bisulfite (and metabisulfite) suspended, the salt "carrying capacity" of ethanol may be an order of magnitude higher than the actual solubility of these salts.
- Addition of gasoline to salt-containing ethanol solutions appears to disrupt these suspensions, causing the salts to drop out of solution, thereby greatly reducing the salt "carrying capacity" of gasoline-ethanol blends as compared to neat ethanol.

- Investigation of these issues regarding solubility and suspensions of salt solutions requires analysis of both existent and potential sulfate, using ASTM Method D7328.
- Quantification of insoluble salts in ethanol and gasoline-ethanol blends by direct visual observation is very difficult. Levels below 10 ppm are imperceptible to most observers, while levels above 20 ppm are readily seen as slightly cloudy solutions.

Applying these findings to real-world fuel situations suggests a possible route by which sulfate salt contamination could occur in gasoline-ethanol blends. Ethanol's relatively high carrying capacity for salts – whether they are dissolved or not, and whether they are in an oxidized or reduced form – provides an effective way for the salts to be transported throughout the ethanol distribution system. Once blended with gasoline, the salts readily drop out of solution as small, insoluble particles, which conceivably could contribute to filter plugging and deposit problems in the field.

6. References

1. Hoekman, S. K.; Broch, A. *Investigation into Filter Plugging Due to Sulfate Salt Contamination of Ethanol, Gasoline, and Gasoline-Ethanol Blends*; Coordinating Research Council - CRC Report No. CM-136-15-1: January 2018; pp 1-47.

2. McCormick, R. L.; Alleman, T. L.; Yanowitz, J. *Sulfate Salts in Gasoline and Ethanol Fuels - Historical Perspective and Analysis of Available Data*; National Renewable Energy Laboratory - NREL Technical Report: NREL/TP-5400-69001: September 2017, pp 1-36.

3. Minutes of ASTM D02.A0 Gasoline and Oxygenated Fuel; Open Forum on Sulfates. 2005.

4. DuMont, R. J.; Cunningham, L. J.; Oliver, M. K.; Studzinski, W. M.; Galante-Fox, J. M., Controlling Induction System Deposits in Flexible Fuel Vehicles Operating on E85. *SAE Technical Paper Series* **2007,** *2007-01-4071*.

5. Schwahn, H.; Lutz, U.; Kramer, U., Deposit Formation of Flex Fuel Engines Operated on Ethanol and Gasoline Blends. *SAE Int. J. Fuels Lubr. 2010-01-1464* **2010,** *3* (2), 22-37.

6. Stepien, Z.; Krasodomski, W., Investigation into Engine Deposit-Forming Tendency Due To Sulfate Salt Contamination of Gasoline−Ethanol Blends. *Energy & Fuels* **2019,** *33* (5), 4244-4253.

7. ASTM D4806-15, A., Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel. *ASTM International* **2015**, 1-8.

8. ASTM D7328-13, A., Standard Test Method for Determination of Existent and Potential Inorganic Sulfate and Total Inorganic Chloride in Fuel Ethanol by Ion Chromatography using Aqueous Sample Injection. *ASTM International* **2013,** *Designation ASTM D7328-13*, 1-8.

9. ASTM-D7319-17, Standard Test Method for Determination of Existent and Potential Sulfate and Inorganic Chloride in Fuel Ethanol and Butanol by Direct Injection Suppressed Ion Chromatography. *ASTM International* **2018,** *Designation: D7319-17*, 1-10.

Appendix I

Basic Information about Sulfur Oxides and their Anions

Sulfur Oxides

1. **Sulfur dioxide** (SO_2)
    - Sulfur oxidation state IV
    - Gas at room temp. (bp -10 °C)
    - Soluble in water
    - Corresponding acid, sulfurous acid (H_2SO_3), does not occur to a large extent

2. **Sulfur trioxide** (SO_3)
    - Sulfur oxidation state VI
    - Liquid at room temp. (bp 45°C)
    - Reacts rapidly with water to form sulfuric acid (H_2SO_4)
    - SO_3 in H_2SO_4 is called oleum

Sulfur Oxide Anions

1. **Ions of Sulfur-III**
    a. Dithionate ($S_2O_4^{2-}$)
        - Sodium salt: sodium dithionate ($Na_2S_2O_4$)
        - Readily oxidizes to S-IV; used commercially as reducing agent

2. **Ions of Sulfur-IV** [Corresponding acid: sulfurous acid: (H_2SO_3)]
    a. Sulfite (SO_3^{2-})
        - Corresponding sodium salt: sodium sulfite (Na_2SO_3)

    b. Bisulfite (HSO_3^-)
        - Corresponding sodium salt: sodium bisulfite ($NaHSO_3$)
        - Sodium salt also called sodium hydrogen sulfite

    c. Metabisulfite ($S_2O_5^{2-}$)
        - Corresponding sodium salt: sodium metabisulfite ($Na_2S_2O_5$)

3. **Ions of Sulfur-V**
    a. Metabisulfate (also called dithionate) ($S_2O_6^{2-}$)
        - Corresponding sodium salt: sodium dithionate ($Na_2S_2O_6$)
        - Sodium dithionate is a very stable compound

4. **Ions of Sulfur-VI** [Corresponding acid: sulfuric acid (H_2SO_4)]
    a. Sulfate (SO_4^{2-})
        - Corresponding sodium salt: sodium sulfate (Na_2SO_4)

    b. Bisulfate (HSO_4^-)
        - Corresponding sodium salt: sodium bisulfate ($NaHSO_4$)

Appendix II

Procedure for Preparing Ethanol-Diluted Stock Solutions of Na_2SO_4, $NaHSO_3$, and $Na_2S_2O_5$ Containing 0.50 vol.% Water

1. Prepare 1.00 wt.% aqueous stock solution of Na_2SO_4
   - Add 1.00 g of anhydrous Na_2SO_4 into tared 100-mL volumetric flask
   - Add deionized water to the mark

   Repeat above process using $NaHSO_3$ and $Na_2S_2O_5$

   Note: 1.00 wt.% Na_2SO_4 represents 0.67 wt.% sulfate (SO_4)
   1.00 wt.% $NaHSO_3$ represents 0.78 wt.% bisulfite (HSO_3)
   1.00 wt.% $Na_2S_2O_5$ represents 0.76 wt.% metabisulfite (S_2O_5)
   The density of 200-proof ethanol is 0.790 g/mL

2. Dilute appropriate amount of stock solution with water to prepare 5.00 g aliquots for mixing with 1.00 L of 200-proof ethanol

   [Note: 5.00 g of aqueous solution, when added to 1.00 L of ethanol, provides 0.63 wt.% water in ethanol, which equals 0.50 vol.% water. 5.12 g of aqueous stock solution (required for the 64 ppm salt solutions) will provide 0.51 vol.% water.]

   - To prepare 1 ppm Na_2SO_4, $NaHSO_3$, or $Na_2S_2O_5$ solution: add 0.080 g of stock solution into a tared 10-mL sterile, disposable polystyrene cup. Add sufficient water to bring wt. to 5.00 g.
   - Using a glass funnel, transfer the contents of the disposable cup into a 1.00 L volumetric flask. Rinse the cup several times with 200-proof ethanol and add the rinsing solutions to the volumetric flask.
   - Using 200-proof ethanol, fill the 1.00 L volumetric flask to the mark

   Use the same procedure to prepare the 2, 4, 8, 16, 32, and 64 ppm salt solutions in ethanol. In each case, water is added to bring the total weight in the 10-mL sterile, disposable polystyrene cup to 5.00 g, and the entire mixture is then transferred to a 1.00 L volumetric flask. The amount of aqueous stock solution required to produce each desired concentration is shown in the table below.

Table 1. Amount of Aqueous Stock Solution Required to Produce Range of Salt Concentrations

(Concentrations are expressed as mass of ion (mg) per kg of ethanol)

Nominal Salt Conc.	Stock Solution Added	Sulfate Conc. (from Na_2SO_4)	Bisulfite Conc. (from $NaHSO_3$)	Metabisulfite Conc. (from $Na_2S_2O_5$)
1.0 ppm	0.080 g	0.67 ppm	0.78 ppm	0.76 ppm
2.0 ppm	0.160 g	1.34 ppm	1.56 ppm	1.52 ppm
4.0 ppm	0.320 g	2.68 ppm	3.12 ppm	3.03 ppm
8.0 ppm	0.640 g	5.36 ppm	6.24 ppm	6.06 ppm
16 ppm	1.280 g	10.7 ppm	12.5 ppm	12.1 ppm
32 ppm	2.560 g	21.4 ppm	25.0 ppm	24.3 ppm
64 ppm	5.120 g	42.9 ppm	49.9 ppm	48.5 ppm

Appendix III

Precision of ASTM Methods D7319 and D7328 for Sulfate Determination

ASTM D7319 - Direct injection of ethanol solution

Existent Sulfate	
Applicable Range	1.0 – 20 ppm
Pooled Limit of Quantitation (PLOQ)	0.01 ppm
Repeatability Equation*	$0.09030 \times (X + 0.0001)^{0.623}$
Reproducibility Equation*	$1.2291 \times (X + 0.0001)^{0.623}$
Potential Sulfate	
Applicable Range	1.0 – 20 ppm
Pooled Limit of Quantitation (PLOQ)	0.01 ppm
Repeatability Equation*	$0.09645 \times (X + 0.59494)^{0.8642}$
Reproducibility Equation*	$0.9408 \times (X + 0.59494)^{0.8642}$

* Parameter “X” is sulfate concentration, in ppm

Existent Sulfate	**Repeatability, ppm**	**Reproducibility, ppm**
1 ppm	0.09	1.23
5 ppm	0.25	3.35
10 ppm	0.38	5.16
20 ppm	0.58	7.95
Potential Sulfate		
1 ppm	0.14	1.41
5 ppm	0.46	4.17
10 ppm	0.78	7.23
20 ppm	1.32	12.85

ASTM D7328 – Injection of aqueous solution

Existent Sulfate	
Applicable Range	0.55 – 20 ppm
Pooled Limit of Quantitation (PLOQ)	0.55 ppm
Repeatability Equation*	$0.2319 \times (X + 0.0001)^{0.500}$
Reproducibility Equation*	$1.0963 \times (X + 0.0001)^{0.500}$
Potential Sulfate	
Applicable Range	4.0 – 20 ppm
Pooled Limit of Quantitation (PLOQ)	4.0 ppm
Repeatability Equation*	$0.1763 \times (X^{0.400})$
Reproducibility Equation*	$1.0505 \times (X^{0.400})$

* Parameter “X” is sulfate concentration, in ppm

Existent Sulfate	**Repeatability, ppm**	**Reproducibility, ppm**
1 ppm	0.23	1.10
5 ppm	0.52	2.45
10 ppm	0.73	3.47
20 ppm	1.04	4.90
Potential Sulfate		
1 ppm	0.18	1.05
5 ppm	0.33	2.00
10 ppm	0.44	2.64
20 ppm	0.58	3.48

Appendix IV

Spiked and Measured Concentrations of Na_2SO_4 in Ethanol and Gasoline-Ethanol Blends[(a)]

ID	Spiked Concentration, ppm		IC-Measured Concentration, ppm[(b)]			
	Na_2SO_4	SO_4	0-Day	1-Day	1-Week	4-Week
E100	0.0	0.0	0.00	0.00	0.00	0.00
	1.0	0.7	0.06	0.00	0.00	0.17
	2.0	1.4	0.01	0.00	0.00	0.02
	4.0	2.7	0.12	0.00	0.00	0.27
	8.0	5.4	0.33	0.00	0.00	0.43
	16	10.8	3.02	0.00	1.44	3.32
	32	21.6	6.89	0.95	2.24	6.91
	64	43.3	21.10	13.24	2.40	11.54
E10	0.0	0.0	0.00	0.00	0.00	0.01
	1.0	0.1	0.00	0.00	0.00	0.00
	2.0	0.1	0.00	0.00	0.00	0.00
	4.0	0.3	0.00	0.00	0.00	0.00
	8.0	0.5	0.00	0.00	0.00	0.00
	16	1.1	0.00	0.00	0.00	0.00
	32	2.2	0.00	0.00	0.00	0.00
	64	4.3	0.00	0.00	0.00	0.07
E30	0.0	0.0	0.00	0.00	0.00	0.00
	1.0	0.2	0.00	0.00	0.00	0.00
	2.0	0.4	0.00	0.00	0.00	0.00
	4.0	0.8	0.00	0.00	0.00	0.01
	8.0	1.6	0.00	0.00	0.00	0.00
	16	3.2	0.00	0.00	0.04	0.00
	32	6.5	0.00	0.00	0.00	0.00
	64	13.0	0.00	0.00	0.00	0.00
E60	0.0	0.0	0.00	0.00	0.00	0.00
	1.0	0.4	0.00	0.00	0.00	0.01
	2.0	0.8	0.00	0.00	0.00	0.00
	4.0	1.6	0.00	0.00	0.00	0.01
	8.0	3.2	0.00	0.00	0.00	0.00
	16	6.5	0.00	0.00	0.00	0.00
	32	13.0	0.00	0.00	0.00	0.00
	64	26.0	0.00	0.00	0.00	0.00

(a) Concentrations are expressed as mass (mg) per Liter of ethanol

(b) IC-measured concentrations were determined using the direct injection method of ASTM D7319

Appendix V

Spiked and Measured Concentrations of $NaHSO_3$ in Ethanol and Gasoline-Ethanol Blends[(a)]

ID	Spiked Concentrations, ppm		IC-Measured Concentrations, ppm (b)(c)			
	$NaHSO_3$	HSO_3	0-Day	1-Day	1-Week	4-Week
E100	0	0	0.00	0.00	0.00	0.00
	1	0.78	0.16	0.10	0.00	0.00
	2	1.56	0.51	0.41	0.12	0.50
	4	3.12	0.92	0.93	0.55	0.98
	8	6.24	0.64	0.63	0.99	1.81
	16	12.5	2.19	2.70	1.09	1.48
	32	25	4.85	7.08	5.09	5.53
	64	49.9	11.68	16.49	13.70	12.15
E10	0	0	0.00	0.00	0.00	0.03
	1	0.078	0.00	0.00	0.00	0.01
	2	0.156	0.06	0.00	0.00	0.01
	4	0.312	0.09	0.00	0.00	0.02
	8	0.624	0.10	0.00	0.00	0.00
	16	1.25	0.05	0.01	0.62	0.15
	32	2.5	0.02	0.00	0.00	0.38
	64	4.99	0.03	0.99	0.00	0.01
E30	0	0	0.00	0.00	0.00	0.00
	1	0.234	0.00	0.12	0.00	0.00
	2	0.468	0.00	0.00	0.00	0.00
	4	0.936	0.01	0.00	0.00	0.01
	8	1.872	0.01	0.00	0.00	0.00
	16	3.75	0.03	0.02	0.10	0.00
	32	7.5	0.00	0.36	0.26	0.23
	64	14.97	0.00	0.02	0.03	0.11
E60	0	0	0.00	0.00	0.00	0.00
	1	0.468	0.00	0.00	0.00	0.00
	2	0.936	0.00	0.00	0.00	0.00
	4	1.872	0.00	0.00	0.00	0.16
	8	3.744	0.01	0.07	0.00	0.00
	16	7.5	0.02	0.00	0.10	0.18
	32	15	0.58	0.00	0.97	0.60
	64	29.94	0.20	0.00	4.55	1.74

(a) Concentrations are expressed as mass (mg) per Liter of ethanol

(b) IC-measured concentrations were determined using the direct injection method of ASTM D7319

(c) Chromatographic peaks were observed only for sulfate ion, not bisulfite ion