Project 105 Quantification of Trace Levels of Sulfur Using ICP-MS

University of Dayton Research Institute

Project Lead Investigator

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- P.I.: Zachary West, PhD
- FAA award number: 13-C-AJFE-UD-059
- Period of Performance: January 21, 2025, through January 20, 2026
- Tasks:
  1. Background Information Collection and Method Development
  2. Formalization and Documentation of Final Method
  3. Conduct Robustness Study

Project Funding Level

Amendent	Funding
Amendment No. 59	$150,014.00

Investigation Team

Dr. Zachary West (P.I.)
Dr. Joe Gord (Staff Scientist)
Dr. Amanda Mae Arts (Staff Scientist)

Project Overview

Existing sulfur quantitation methods (Table 1) have a lower quantitation limit of approximately 1 parts per million by weight (ppm wt) of sulfur. As more synthetic aviation turbine fuel (SATF) producers enter the market and the industry considers lower sulfur specification limits, a method for accurately measuring low-level sulfur is needed. Lower sulfur is desirable in fuels because it affords decreased soot production which supports improved equipment robustness, reduced aircraft signature, and improved air quality. This effort aims to develop a relatively accessible method using inductively coupled plasma – mass spectrometry (ICP-MS) for the quantitation of sulfur at the tens to hundreds of parts per billion by weight (ppb wt) level in middle distillate fuels to include SATF, synthetic blend components (SBC), and traditional jet fuel (e.g., Jet A/A-1).

Table 1. List of existing Sulfur test methods and inductively coupled plasma (ICP) methods for testing jet fuels. UV: ultraviolet; N/A: not applicable.

Method	Lower Limit (Sulfur)	Measurement Technique	Use Case (Sulfur)
ASTM D5453	1 mg/kg	UV Fluorescence	D1655, D7566
ASTM D2622	3 mg/kg	Wavelength Dispersive X-Ray Fluorescence (XRF)	D1655, D7566
ASTM D4294	16 mg/kg	Energy Dispersive XRF	D1655, D7566
ASTM D1266	100 (5*) mg/kg	Lamp	Withdrawn 2025
IP 336	300 mg/kg	Energy Dispersive XRF	D1655, D7566
ASTM D7111	N/A	ICP-Atomic Emission Spectroscopy	N/A – Metals
ASTM D8110	N/A	ICP-Mass Spec	N/A – Metals

Task 1. - Background Information Collection and Method Development

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Objective

Develop an ICP-MS method capable of quantitating low levels of sulfur in the middle distillate fuels.

Research Approach

Existing methods for both sulfur detection and application of inductively coupled plasma (ICP) were considered (Table 1) as models/benchmarks to guide this project. Additionally, a literature search was conducted, focused on applications of ICP for measuring sulfur in a variety of sample matrices by several different experimental methods. Measuring low-level sulfur in jet fuel samples by ICP is difficult for several reasons. Sulfur has a low ionization efficiency at the energy of an argon plasma, which is the plasma most often used with ICP techniques. There is a high coking potential for fuel samples because of the high-carbon character of the matrix. To prevent coking, oxygen gas is added to the plasma. Oxygen gas is a source of barometric interference for sulfur. Several approaches were tested to overcome these challenges. Such methods included monitoring of ^{34}S, SO^+ ion formation using collision cell technology, and application of xenon gas for kinetic energy discrimination to filter $^{16}O_2$ signal from the m/z = 32 mass channel.

After testing these different approaches in the laboratory, it was determined that formation and detection of SO^+ provided the best performance given the target concentrations and the sample matrices involved. Efforts then revolved around establishing a consistent test method, determining performance metrics of the calibration, applying the method across a wide range of fuels, and evaluating the limits of detection achievable given under the test conditions.

Method development has been completed with testing results in the low hundreds of ppb sulfur. Figure 1 shows a typical calibration curve covering a concentration range from 100 ppb wt to 3000 ppb wt of sulfur. This range was selected to overlap with the low end of existing test methods.

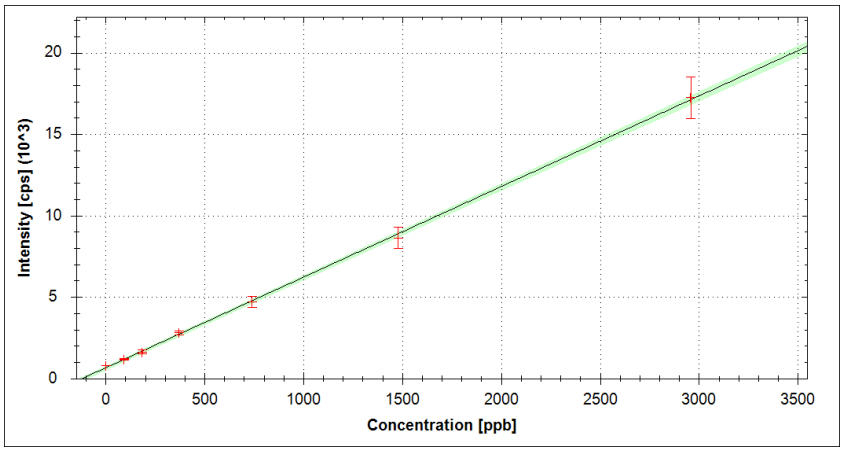

Figure 1. Inductively coupled plasma – mass spectrometry (ICP-MS) sulfur calibration curve from 100 to 3000 ppb wt sulfur in kerosene.

Initial assessments of the accuracy and precision of the method were determined using spiked kerosene samples. Figure 2 (left panel) shows the measured sulfur concentration values vs known (prepared) concentrations for a set of test samples. Samples were prepared and tested over the course of two separate days. The measured data correspond reasonably well with the known concentration values over much of the test range. The inset on the left panel reports the percent error as a function of sulfur concentration. It can be seen from the inset that the percent error increases significantly as the total concentration decreases. The percent error improves to ≤10% at concentrations at or above about two times the background equivalent concentration (BEC). There also appears to be a positive bias to the measured values compared to the prepared concentrations, however, it is yet unclear what might be causing this bias. The right-hand panel of Figure 2 shows that for all test concentrations precision is very good with relative standard deviation (%RSD) below 7% at the lowest concentrations and otherwise below 5%.

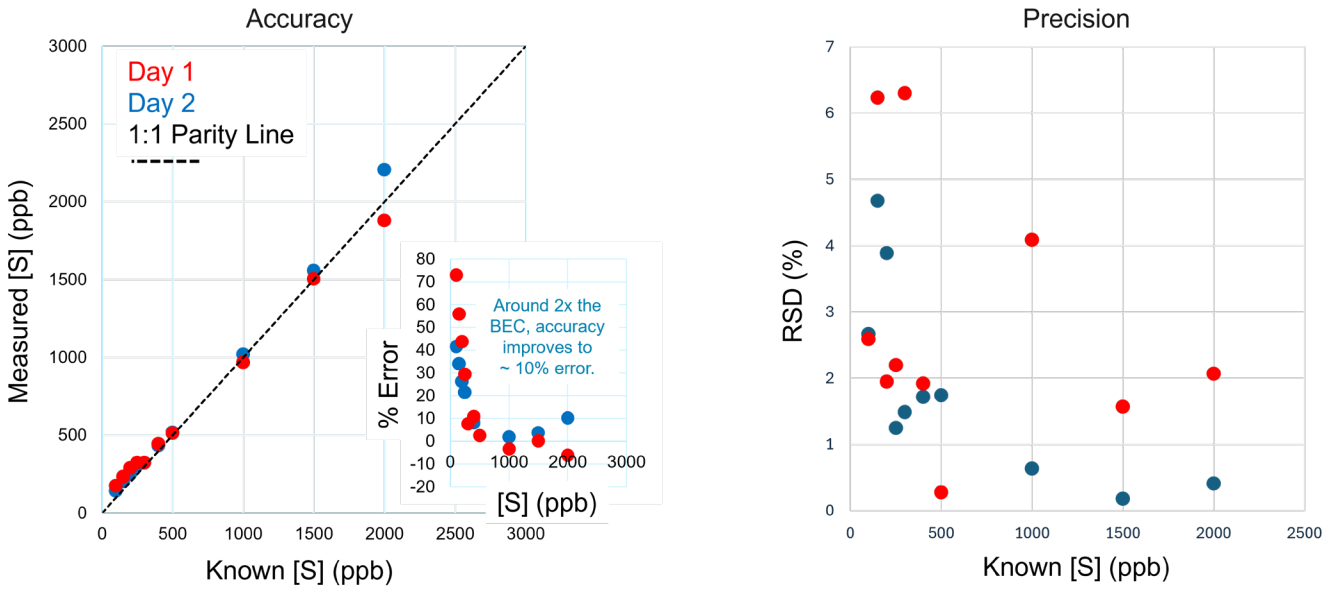

Figure 2. (Left) Measured vs known sulfur concentrations with parity line, showing accuracy of the test method. (Inset) % Error vs Sulfur concentration. (Right) %RSD vs known sulfur concentration reporting on precision of the method.

A selection of samples—three SBCs (including one hydroprocessed esters and fatty acids synthetic paraffinic kerosine [HEFA-SPK]), a low sulfur Jet A, a nominal Jet A (POSF 10325), and a kerosene spiked at 1000 ppb wt—were evaluated using this test method to demonstrate method robustness. Due to the low levels of sulfur, e.g., ≤5 ppm wt, in some of the samples a high confidence reference value for sulfur concentration was not always available. Regardless, Figure 3 shows the measured values, number of replicates (n), volumetric dilution factors (DF), and +/- 2σ error bars for each sample tested. Similar to the results seen in Figure 2, analysis of these six samples showed good precision across a large range of absolute concentrations. Even sample POSF-10325, which has a nominal sulfur content well outside of the intended target range for this method (ca. 500 ppm wt) exhibited reasonable precision (i.e., %RSD = 3%) after significant dilution to get the sample within the target range of linearity for the method (i.e., 100 – 300 ppb wt). In the next performance period, additional fuels will be procured for expanded testing.

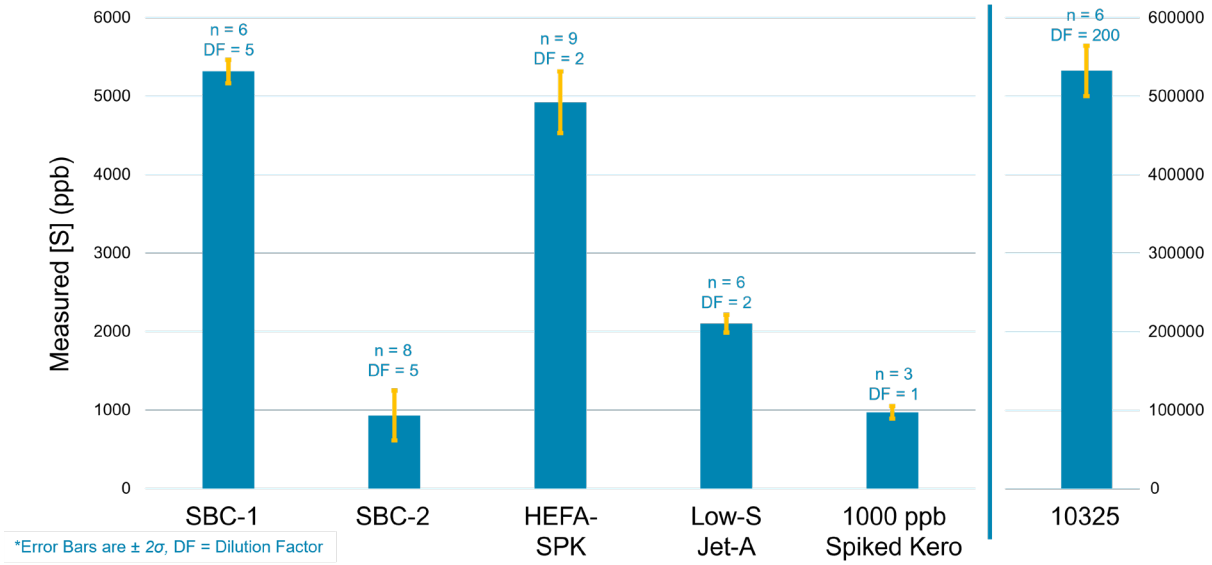

Figure 3. Measured sulfur values for real fuel samples. n: number of replicates; DF: dilution factor.

Finally, a series of fuels with available reference data (by ASTM D5453 [ASTM, 2025]) was tested using this ICP-MS method. All fuels received a two-times dilution to ensure they were within the calibration range of the current test method under development. The samples included low-sulfur Jet-A fuel and HEFA-SPK samples (yellow and green, respectively). In all instances the ICP-MS determined values were found to be higher than the reported values by ASTM D5453. The lower limit for reference data is 1000 ppb, so samples with "<1000ppb" values reported are plotted *at* 1000 ppb in Figure 4. Data reported by ICP-MS have +/- 2σ values (vertical error bars) that are significantly lower than the reproducibility values (horizontal error bars) for the D5453-determined data.

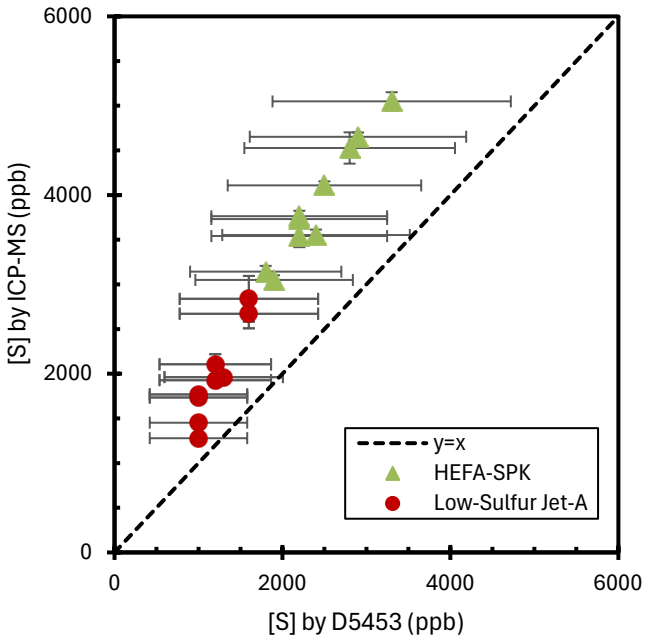

Figure 4. Inductively coupled plasma – mass spectrometry (ICP-MS) vs ASTM D5453 for a selection of low-sulfur Jet-A fuel (red markers) and hydroprocessed esters and fatty acids synthetic paraffinic kerosine (HEFA-SPK) (green markers) samples. Dashed line is a 1:1 parity line. Horizontal error bars are reproducibility values as determined by ASTM D5453. Vertical error bars are +/- 2σ.

Milestones

- Engage literature. **Complete.**
- Select Method Approach. **Complete.**
- Develop Calibration/Cal Curve. **Complete.**
- Test with "model" samples. **Complete.**
- Test with "real" samples. Ongoing.
- Solicit Partners for robustness study. Next period.
- Finalize Method. Next period.
- Complete report. Next period.

Major Accomplishments

- Completed method development phase.
- Established calibration range from 100 to 3000 ppb of sulfur.
- Achieved significant progress into method finalization and performance determination.

Publications

None.

Outreach Efforts

Presented at the Fall 2025 ASCENT Meeting.

Awards

None.

Student Involvement

None.

Plans for Next Period

- Finalize preliminary method for robustness study.
- Procure additional low-sulfur fuels for robustness testing.
- Identify robustness-testing partners.
- Conduct robustness study of preliminary method to confirm method applicability (with other labs).
- Compile report.

Reference

ASTM International. (2025). *ASTM D5453-24: Standard Test Method for Determination of Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence.* https://doi.org/10.1520/D5453-24