SHIMADZU

Energy Dispersive X-ray Fluorescence Spectroscopy for Analysis of Sulfur in Petroleum Products

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1. Shimadzu XRF Instrumentation and XRF Analysis of Petroleum Products

In 2017, the Environmental Protection Agency (EPA) enacted Tier 3 regulations on sulfur content in fuels which changed the maximum allowable sulfur content from 30 parts per million on an average annual basis to 10 parts per million. In addition to the Tier 3 regulations, the International Marine Organization (IMO) will implement on January 2020 a directive to reduce sulfur in marine/bunker fuels to less than 0.5 percent. With these two pieces of legislation, quantifying sulfur in petroleum products is now becoming ever more important. There are many methods of doing sulfur and elemental analysis in aqueous solutions and petroleum matrices including; ICP-MS, ICP-AES, and XRF. Each method has its own pro's and con's including detection limits, sample preparation, and analysis time. As of right now, for the EPA Tier 3 and IMO sulfur regulations X-ray fluorescence spectroscopy is the preferred method of elemental analysis due to its lack of sample preparation and overall simplicity compared to the other elemental analysis methods. In this poster, we demonstrate how a Shimadzu Energy Dispersive X-ray (EDX) spectrometer can be used for not only sulfur determination in petroleum products, but also for quantification of other elements in addition to sulfur.

There are two general types of X-ray fluorescence spectroscopy; energy dispersive (EDXRF) and wavelength dispersive (WDXRF). ASTM has established many methods for elemental analysis of petroleum products using these two instruments (section 7). Shimadzu manufactures many different kinds of elemental analyzers including both a sequential WDXRF system (XRF-1800) and an energy dispersive system (EDX 7000) (figure 1-1). Today, most analytical laboratories use the energy dispersive systems due to their smaller lab foot print, price, simplicity, and speed of analysis. In this poster we concentrate on the energy dispersive analysis. Future plans include a more thorough comparison between WDXRF and EDX. We also discuss the versatility of X-ray fluorescence spectroscopy in quantifying other elements besides sulfur. For example, Pb, which plays a role in the antiknock capabilities of the fuel, can also be quantified with this technique. Overall, this poster acts as a facilitator in discussing EDXRF elemental analysis of petroleum products.

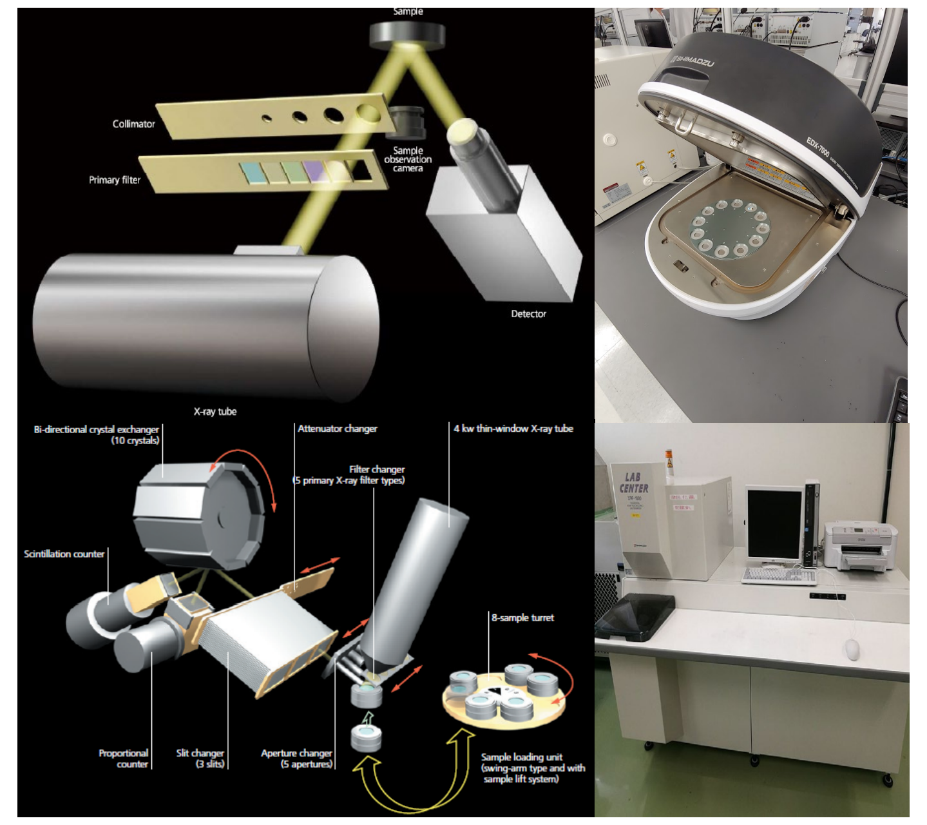


Figure 1-1: Schematics and pictures of Shimadzu's EDX 7000 (top) and XRF-1800 (bottom).

Shimadzu's Elemental Analyzers!

ASTM has specified a number of different standards for the elemental analysis of petroleum products. Each of these standards is a unique method with its own corresponding instrument. Shimadzu manufactures a variety of elemental analyzers that can comply with these ASTM standards. Pictured below is a "snapshot" of some of the elemental analyzers Shimadzu manufactures. Each analyzer has its own advantages and disadvantages such as measurement speed, sample preparation time, and detection limits. In this poster, we explore just one, out of the many, of these elemental analyzers, the EDX 7000.

Figure 1-2: Shimadzu's range of elemental analysis products.

2. Qualitative-Quantitative Scans: Getting the Big Elemental Picture

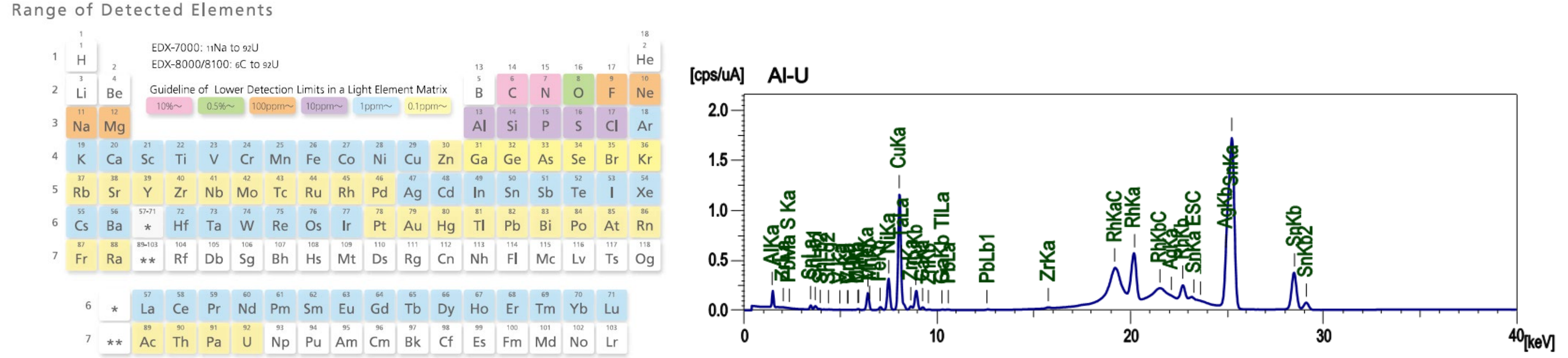


Figure 2-1: Above is a periodic table with detection limits for all the standards. Below is a spectrum of a metal puck that contains multiple elements.

Although this poster concentrates on sulfur analysis in petroleum, the EDX 7000 is capable of detecting a wide range of elements. Depending on the element, detection limits range from sub ppm to percent levels. Above is a spectrum of an aluminum puck with a variety of elements (figure 2-1). Multiple elements are easily observed with the spectrometer. Some ASTM methods have been established for multielement analysis by EDXRF. For example, ASTM D7751 is a test method for additive elements in lubricating oils as quantified by EDXRF, and ASTM 6481 is also a test method for lighter elements in lubricating oils by EDXRF.

2-1 Sample Description

Two sets of Conostan sulfur standards were used, diesel and crude oil. All standards were diluted from the nearest higher concentration standard with kerosene. An aliquot of standard was poured into a polyethylene sample cup (figure 2-1). A precut polypropylene film was used to hold the standard in the sample cup. A total of 12 standards could be run without breaking atmosphere due to the EDX 7000 sample turret (figure 1-1).

Figure 2-1: A picture of the Conostan standards used. Both a crude oil and diesel standard were used.

3. Testing Reproducibility

An approximately 225 ppm crude oil standard was measured in replicate 10 times with four different measurement times. The sample was never removed from the spectrometer. The general trend is that longer measurement times result in lower standard deviations and therefore lower detection limits.

5 s measurement time		
Replicate Number	Intensity (cps/µA)	Concentration (ppm)
1	0.0679	228.6
2	0.0753	254.2
3	0.0703	236.9
4	0.0672	226.3
5	0.0675	227.3
6	0.0859	290.6
7	0.0679	228.6
8	0.0588	197.4
9	0.0698	235
10	0.0694	233.6
Average	0.0700	235.85
Standard Deviation	$6.91x10^{-3}$	23.78
Relative Standard Deviation	9.87	10.08

30 s measurement time		
Replicate Number	Intensity (cps/µA)	Concentration (ppm)
1	0.0684	230.3
2	0.0687	231.3
3	0.0627	210.6
4	0.0747	252.1
5	0.0739	249.4
6	0.0664	223.4
7	0.0650	218.6
8	0.0702	236.7
9	0.0560	187.6
10	0.0707	238.4
Average	0.0677	227.84
Standard Deviation	$5.53Ex10^{-3}$	19.10
Relative Standard Deviation	8.17	8.38

100 s measurement time		
Replicate Number	Intensity (cps/µA)	Concentration (ppm)
1	0.0690	232.3
2	0.0650	218.5
3	0.0693	233.3
4	0.0668	224.9
5	0.0707	238.1
6	0.0644	216.5
7	0.0652	219.3
8	0.0655	220.5
9	0.0720	242.8
10	0.0657	221.1
Average	0.0674	226.73
Standard Deviation	$2.68x10^{-3}$	9.21
Relative Standard Deviation	3.98	4.06

200 s measurement time		
Replicate Number	Intensity (cps/µA)	Concentration (ppm)
1	0.0666	224.1
2	0.0668	224.7
3	0.0677	227.9
4	0.0674	226.7
5	0.0660	222.2
6	0.0676	227.6
7	0.0651	219
8	0.0672	226.3
9	0.0673	226.5
10	0.0647	217.5
Average	0.0666	224.25
Standard Deviation	$1.05x10^{-3}$	3.61
Relative Standard Deviation	1.58	1.61

Table 3-1: Replicate measurements of the same ~225 ppm S Conostan standard. The difference between each set is measurement time. The shortest measurement time was 5 s and the longest measurement time was 200 s.

4. Increasing Sensitivity

With stricter limits on sulfur soon being implemented, it will soon be necessary to design methods that optimize sensitivity and decrease detection limits. From the perspective of the instrument itself, the Shimadzu EDX 7000 has three ways to improve detection limits; increasing measurement time, using a helium atmosphere, and using an X-ray filter. In section 4 we describe the effects of these three parameters on the signal to noise ratio.

4-1 Measurement Time

Often detection limits will decrease with an increase in total measurement time. The spectra below were collected by measuring a 200 ppm Conostan diesel standard with an aluminum filter, and in helium atmosphere. The difference between the four spectra was measurement time. Four measurement times were ran with a shortest time of 5 seconds to the longest time of 300 seconds. It is clear that the signal to noise does improve with longer measurement times, therefore a decrease in detection limit would be expected with increasing measurement times. However, after 300 seconds of measurement time there is little improvement in signal to noise ratio. The signal to noise ratio follows the theoretical function of square root of n which states that the signal to noise will increase with the square root of analysis time.

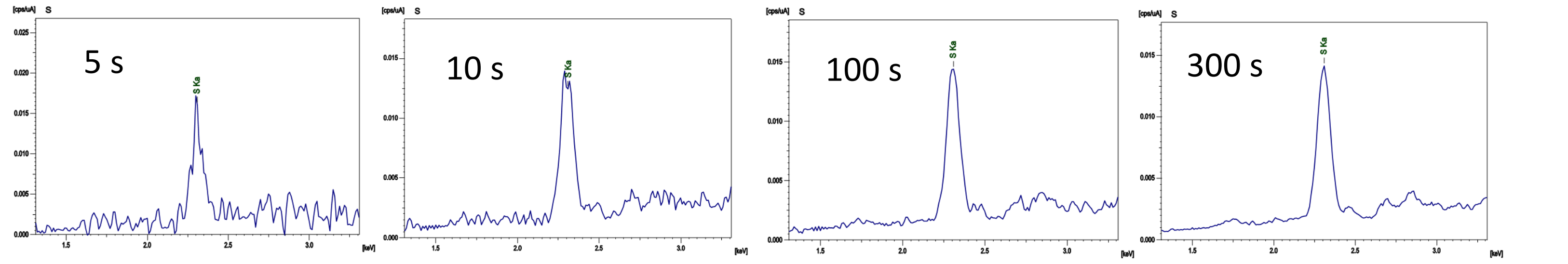


Figure 4-1: Sulfur Kα spectra and their dependence on measurement time. A 200 ppm Conostan diesel standard was used.

4-2 X-ray Filter

Suppose you have a hypothetical sample that does not contain any material that fluoresces X-rays. There still would be peaks in the EDX spectra due to both Compton scattering and elastic Rayleigh scattering. Both Compton and Rayleigh scattering contribute to an increase in the EDX background and therefore a decrease in detection limits. It if often necessary to use a filter between the X-ray source and sample to decrease the background coming from X-ray scattering. Below is a 200 second scan in helium atmosphere of a 200 ppm Conostan diesel standard. There are two spectra total with the difference between the two being that one has no X-ray filter applied while the other uses an X-ray filter. In the no filter spectrum there are two large Compton scattering peaks with an energy of 2.5 and 3 KeV. The sulfur peak is approximately 2.3 KeV. The high energy side of the sulfur peak never returns to absolute baseline due to the neighboring Compton scattering peak at 2.5 KeV. The overlapping Compton scattering makes it difficult to quantify sulfur content by either peak fitting or numerical integration. The left spectrum uses a X-ray filter, and although the absolute intensity has decreased, a negligible amount of scattering is apparent and the high energy side of the S Ka has returned to baseline.

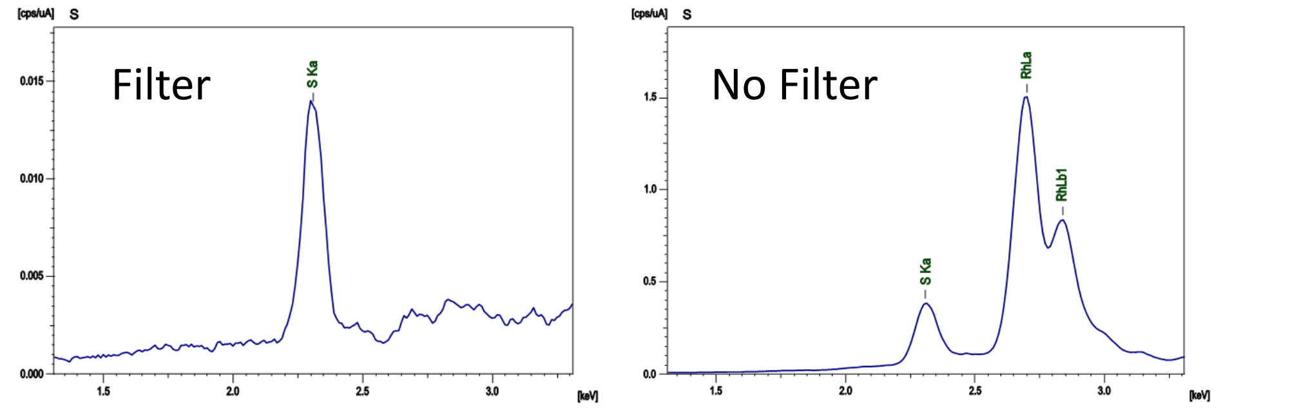


Figure 4-2: Two sulfur Kα spectra. The left spectrum is with a X-ray filter, and the right spectrum uses no X-ray filter.

4-3 Helium Atmosphere versus Air

X-ray analysis in air for the lighter elements such as sulfur can be a challenge since air molecules (H_2O, N_2, O_2) absorb the same radiation that sulfur absorbs. In addition, there may be molecules in air that have a fluorescent energy near sulfur. Pictured below are two spectra of a 300 ppm Conostan diesel standard. The spectrum on the left is with a helium atmosphere and the spectrum on the right is in air. A filter was used, and the measurement time was 200 seconds. It is clear that replacing the atmosphere with helium increases the absolute intensity of the sulfur peak and therefore the detection limit. In addition, two argon peaks are observed in the air spectrum. It is possible that argon absorbs much of the same radiation that sulfur also absorbs. The similar absorption band between argon and sulfur would also decrease the detection limit of sulfur.

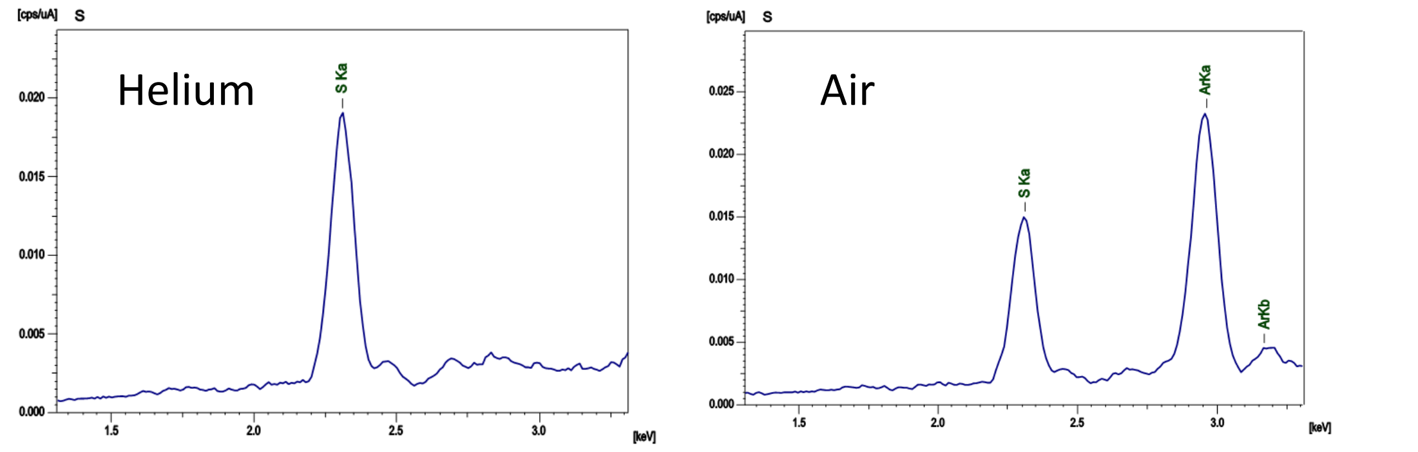


Figure 4-3: Two sulfur Kα spectra. The left spectrum was acquired with a helium atmosphere, the right spectrum was acquired in air.

5. Calibration Curves

5-1 Measurement Times

The four calibration curves below were acquired with a helium atmosphere and X-ray filter. The top two curves are made from Conostan diesel standard diluted with kerosene and the bottom two are made from Conostan crude oil standard diluted with kerosene. The insets are zoomed in regions of the low concentration area. The detector shows linearity on an order of at least three magnitudes. Also, it is apparent that longer measurement times yields a higher correlation coefficient in the low concentration regions. For quantifying sulfur concentrations below 100 ppm a 300 second measurement time is suggested.

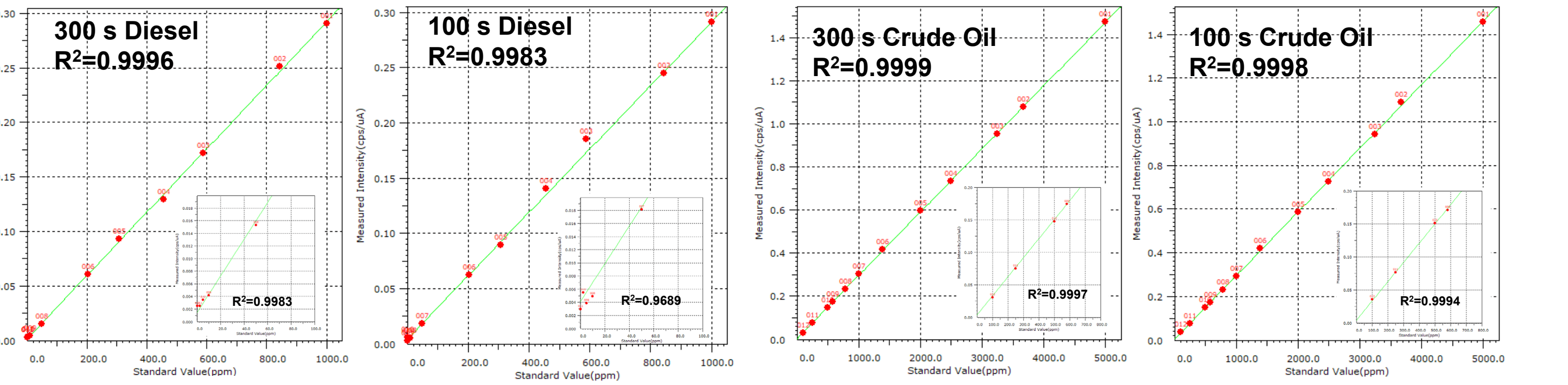


Figure 5-1: Four different calibration curves. Displayed on the curve is a zoomed in region at lower concentration.

5-2 Atmosphere and Matrix

Molecules in air absorb much of the same X-ray radiation that sulfur does. It is often necessary to use a helium atmosphere or vacuum to increase the fluorescence signal of lighter elements such as sulfur. If solid samples are being measured both a helium and vacuum atmosphere can be used, however, with liquid samples helium must be used. In the calibration curve below the x symbols are crude oil standards that have been acquired in air. The o symbols are crude oil standards that have been acquired in helium. An increase in slope, and therefore detection limit, is observed when using helium atmosphere. The right curve is comparing crude oil with diesel. Both matrices lie on the same curve indicating minimal matrix effect.

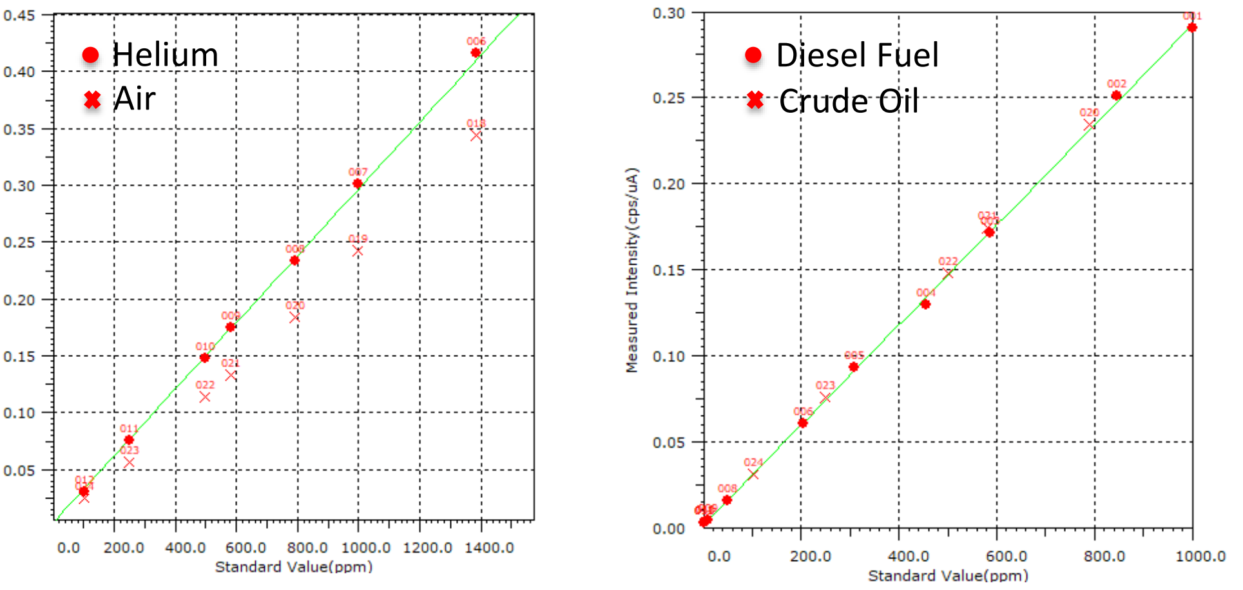
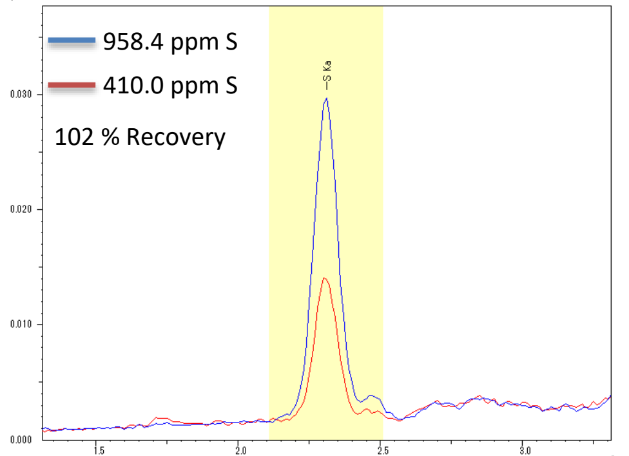


Figure 5-2: The left graph is a comparison of a curve acquired in air and helium. The right graph is a comparison of the crude oil and diesel calibration curve.

6. An Application: XRF Analysis of Jet Fuel and Matrix Correction Methods

A jet fuel sample obtained from our local airport was measured for sulfur content by EDX. The solution was also diluted by a factor of 2.33. Using the corresponding dilution factor and measured concentration by EDX a recovery of 102 percent was obtained.

Figure 6-1: Jet fuel sample that was diluted by a factor of 2.33.



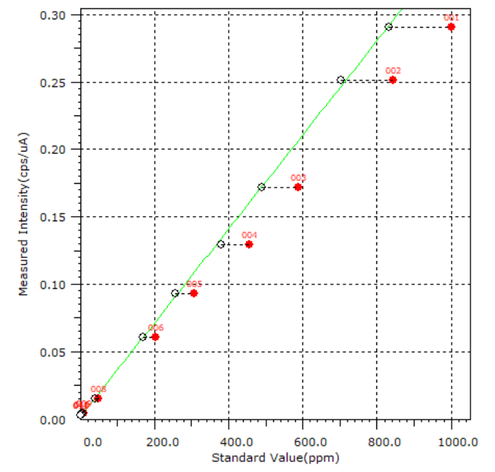


Figure 6-2: A theoretical effect that a 20 ppm concentration of phosphorous would have on the sulfur signal.

Pictured to the right is a graph that has taken into account a fictitious 20 ppm concentration of P in the sample that gives a P Kα intensity of 0.80 CPS/ma. Due to P having a similar X-ray absorption band as S, the P and S intensity are not mutually exclusive. There are a variety of methods to take into account this type of interference. In the graph to the right (figure 6-2) the red dots are the actual measured intensity. The empty circles are the S intensity if there was no 20 ppm of phosphorous in the sample. The method of correction is called multiple linear regression d_j method. Other methods of correction that Shimadzu can use are SFP and L-T.

7. Example ASTM Methods that Use EDXRF

ASTM D6481, ASTM D7220, ASTM D7212, ASTM D7343