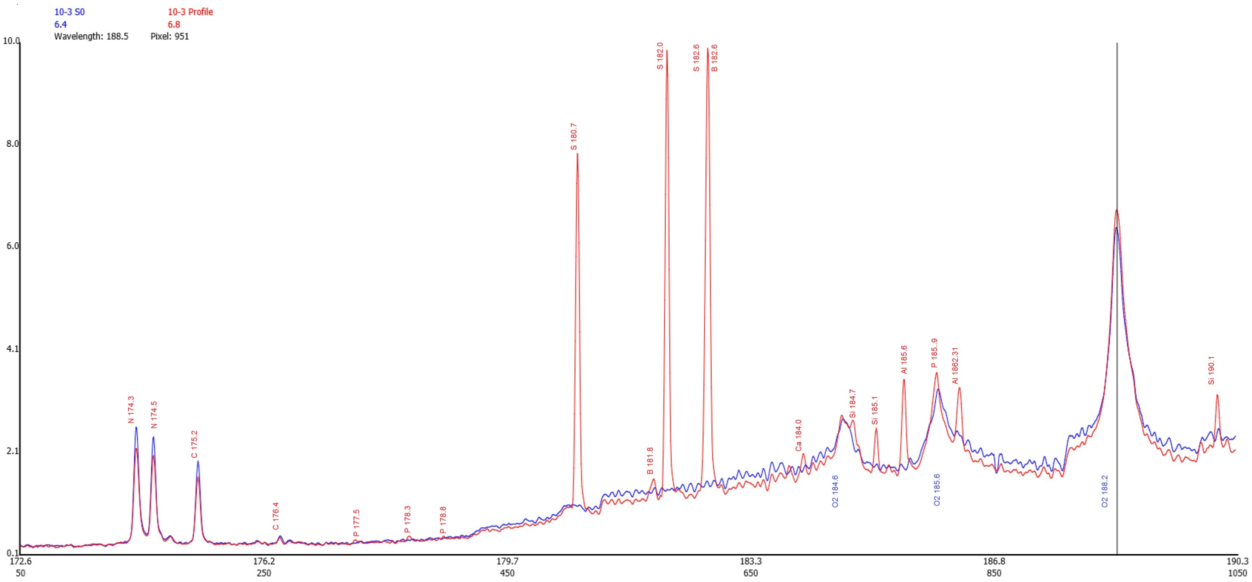
Analysis of Sulfur in Lubricating Oils by Rotating Disk Electrode Emission Spectroscopy

INTRODUCTION

Sulfur is often added to oils to improve its lubricating properties at elevated temperatures by forming a sulfide layer on meshing surfaces. This analysis is not normally performed using rotating disk electrode spectroscopy as the primary analytical lines for sulfur lie below the threshold of the normal spectrometers at around 190 nm caused by the absorption of light by oxygen and water vapor in the air.

With the advent of the MOA III direct reading spectrometer, it is now possible to access wavelengths down to 170 nm with the extended ultraviolet option. The standard MOA III optic features a direct view of the source and thus eliminates absorption of low wavelengths by the fiber normally used to transfer light from the source to the spectrometer. In addition to filling the spectrometer with nitrogen, the optical path between the spectrometer and source is purged with a trickle flow of nitrogen as a standard feature of the extended ultraviolet option.

The figure below shows a typical wavelength scan for a sulfur free base oil (10-3 S0) and a profile solution (10-3 Profile) containing approximately 200 ppm of the elements diluted from a Conostan 900 ppm S21 standard. The S21 standard contains the elements of interest as sulfonate which accounts for the strong emission from the sulfur triplet at 180.7.182.0 and 182.6 nm; sulfur is present at approximately 12500 PPM. Several other observed spectral lines and molecular bands of interest are noted on the scan in red and blue respectively. Most of the molecular bands arise from the excitation of entrained air in the discharge often combined with the carbon in the sample and electrode.



Oxygen has several emission bands in the region 176 to 200 nm. Carbon has a strong emission from the CO molecular bands at 185.94 nm and is close to the oxygen band at 186.3. As these bands overlap, only a single broad band degraded to the red is observed in the scan.

METHOD

The ASTM method for lubricating oil analysis (D 6595) recommends the use of hydrogen as an internal standard. In traditional optical emission spectroscopy in the deep ultra violet, however, it is common practice to use an internal standard in the same spectral region as the line to be analyzed and try to

Excitation Energies of Spectral Lines

Spectral Line	Lower Level	Upper Level
S 180.7	0.00	6.86
S 182.0	0.00	6.86
S 182.6	0.00	6.86
N 174.3	3.58	10.69
C 175.2	2.68	9.76
C 199.2	1.26	7.49
H 486.1	10.20	12.75
H 653.6	10.20	12.09

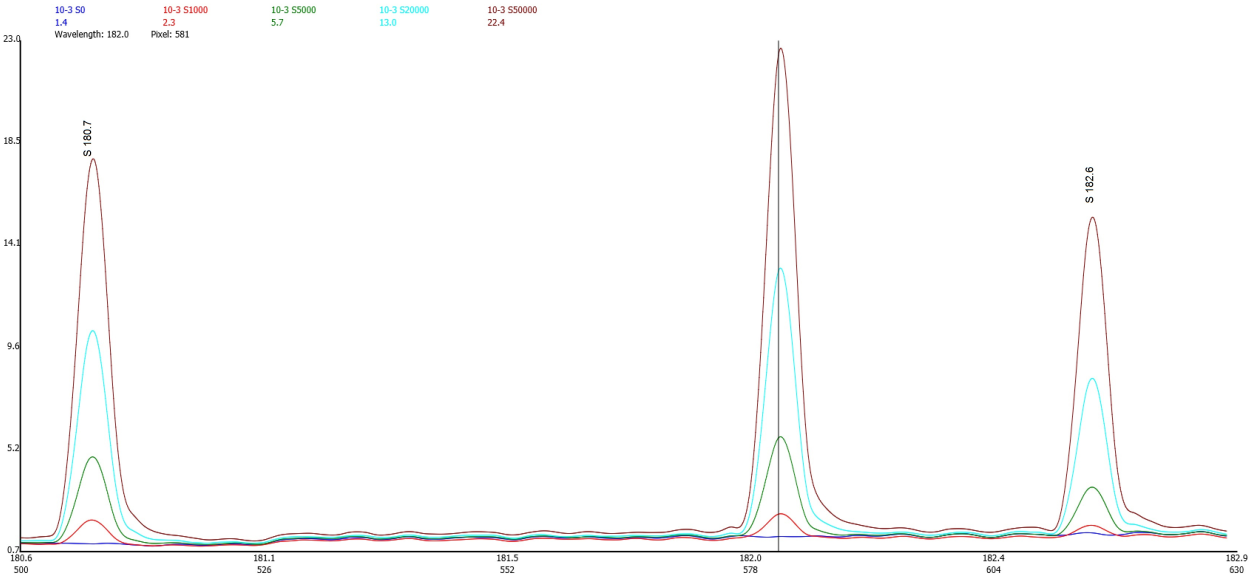
match the excitation energy of both lines. Additionally using a similar wavelength should also account for variations of oxygen levels in the optical path.

From the table to the left where the energies of the upper and lower electronic states involved in the transition are shown in electron volts, it is apparent that both hydrogen lines are a bad match based upon their spectroscopic properties. As the 486.1 nm line of hydrogen is in a region of strong emission from the C_2 radical, it was decided to test only the H 653.6 nm line.

Additionally using the carbon and nitrogen internal standard lines was investigated along with the possibility of not using an internal standard.

Detection Limits and Linearity

The linearity of the three sulfur lines was checked by scanning a series of standards up to 50,000 ppm.



Estimated Detection Limits for Sulfur in Oil (PPM)

Internal Standard	S 180.7	S 182.0	S 182.6
H 656.3	27	19	120
N 174.3	22	18	63
C 175.2	22	17	60
C 199.3	22	21	75
None	20	22	72

Estimated detection limits were determined by assuming a linear calibration between 0 and 1000 ppm sulfur and measuring the standard deviation of a sulfur free base oil standard in concentration units.

From this table it is apparent that the detection limit for the 182.6 nm line is significantly poorer than the other two lines. Additionally there is a severe interference from two boron lines located on either side of the sulfur line.

Although spectroscopic theory predicts that the 180.7 nm line should have better sensitivity than the 182.0 nm line, the data obtained does not reflect this and the 182.0 nm line appears to have a marginally lower detection limit.

The instrument was then calibrated up to a concentration of 50,000 ppm using each of the internal standards. As the best estimated detection limit is around 20 ppm, the lowest concentration, apart from the blank, included in the calibration curve was 100 ppm.

The following table lists the accuracy and precision measured at each of these levels.

Linearity & Accuracy for Sulfur in Oil (PPM)

Concentration	Internal Standard	S 180.7	S 182.0	S 182.6
0	H 656.3	-6 ± 13	8 ± 10	-70 ± 61
	N 174.3	13 ± 11	12 ± 9	14 ± 31
	C 175.2	5 ± 11	9 ± 8	20 ± 30
	C 199.3	12 ± 11	8 ± 10	-65 ± 38
	None	3 ± 10	-9 ± 11	-11 ± 36
100	H 656.3	57 ± 18	111 ± 17	51 ± 6
	N 174.3	74 ± 9	89 ± 10	81 ± 13
	C 175.2	69 ± 11	89 ± 10	90 ± 13
	C 199.3	98 ± 10	111 ± 17	47 ± 15
	None	94 ± 11	99 ± 19	96 ± 7
500	H 656.3	522 ± 54	489 ± 40	525 ± 63
	N 174.3	482 ± 42	485 ± 33	513 ± 33
	C 175.2	478 ± 40	487 ± 36	518 ± 31
	C 199.3	479 ± 50	489 ± 40	521 ± 63
	None	481 ± 44	480 ± 27	536 ± 53
700	H 656.3	744 ± 54	684 ± 29	436 ± 69
	N 174.3	598 ± 6	604 + 19	559 ± 96
	C 175.2	588 ± 16	600 ± 8	604 ± 16
	C 199.3	698 ± 66	684 ± 29	733 ± 69
	None	724 ± 49	697 ± 20	755 ± 44
1000	H 656.3	1065 ± 12	990 ± 16	1053 ± 32
	N 174.3	994 ± 35	1002 ± 38	998 ± 63
	C 175.2	982 ± 51	996 ± 50	991 ± 73
	C 199.3	968 ± 19	990 ± 16	1051 ± 32
	None	999 ± 7	1009 ± 9	1060 ± 38
5000	H 656.3	4982 ± 221	5033 ± 221	5131 ± 213
	N 174.3	5319 ± 404	5176 ± 376	4955 ± 333
	C 175.2	5298 ± 370	5165 ± 353	4937 ± 316
	C 199.3	5154 ± 212	5033 ± 221	5132 ± 213
	None	5112 ± 196	4984 ± 199	4999 ± 185
10000	H 656.3	9894 ± 616	10008 ± 45	9958 ± 127
	N 174.3	10360 ± 601	10241 ± 512	9917 ± 502
	C 175.2	10346 ± 522	10247 ± 491	9931 ± 461
	C 199.3	10145 ± 269	10008 ± 45	9960 ± 127
	None	10026 ± 365	9863 ± 165	9812 ± 182.6

Concentration	Internal Standard	S 180.7	S 182.0	S 182.6
20000	H 656.3	19455 ± 1422	19639 ± 564	19879 ± 557
	N 174.3	19578 ± 881	19685 ± 884	20161 ± 1093
	C 175.2	19474 ± 889	19652 ± 888	20189 ± 1116
	C 199.3	19630 ± 621	19639 ± 564	19880 ± 557
	None	19502 ± 1304	19510 ± 1228	199378 ± 1141
50000	H 656.3	50325 ± 2625	50472 ± 3038	50689 ± 2646
	N 174.3	50369 ± 3376	50292 ± 3632	49936 ± 2812
	C 175.2	50618 ± 4176	50451 ± 4458	44902 ± 3512
	C 199.3	50435 ± 2798	50472 ± 3038	50657 ± 2643
	None	50051 ± 1598	50427 ± 1598	50216 ± 1245

Values show in red are considered to be inaccurate as they deviate from the stated concentration by more than the greater of the detection limit or twice the measured standard deviation.

From this table, it is apparent that an accuracy problem exists at low concentrations when any one of the H 653.6, N 174.2 or C 175.2 lines are used as an internal standard. At higher concentrations, use of any of these three internal standards provides acceptable accuracy but generally with poorer precision than either the C 199.3 line or no internal standard. Both the C 199.3 line or no internal standard provide acceptable accuracy and precision over the entire range of concentrations tested.

Aside from the occasional anomaly in the above table, use of no internal standard in conjunction with the 182.0 nm sulfur line gives the best precision and accuracy and this the recommended procedure.

RESULTS

Sulfur was added to the standard analytical program used in our laboratory for routine analysis of wear metals in lubricating oils. The complete analytical channel assignment and working calibration ranges are shown in the table below:

Analytical Program

	Wavelength	Internal Standard	Detection Limit (ppm)	Upper Range
Ag	338.2	H 653.6	0.4	900
Al	396.1	H 653.6	0.2	900
B	249.7	H 653.6	0.3	900
Ba	455.4	H 653.6	0.2	750
	230.4	H 653.6		5000
Ca	422.6	H 653.6	0.1	200
	445.5	H 653.6		5000
Cd	226.5	H 653.6	0.2	900
Cr	425.4	H 653.6	0.3	900
Cu	327.4	H 653.6	0.1	200
	223.0	H 653.6		900
Fe	259.9	H 653.6	0.6	900
K	766.4	H 653.6	12	900

	Wavelength	Internal Standard	Detection Limit (ppm)	Upper Range
Li	670.7	H 653.6	0.1	900
Mg	280.2 279.0	H 653.6 H 653.6	0.1	200 5000
Mn	257.6	H 653.6	0.1	900
Mo	281.6	H 653.6	0.6	900
Na	589.6	H 653.6	0.1	900
Ni	341.5	H 653.6	0.5	900
P	255.3	H 653.6	12	5000
Pb	283.3	H 653.6	1.1	900
Si	251.6	H 653.6	0.5	900
Sn	317.5	H 653.6	1.2	900
Ti	334.9	H 653.6	0.2	900
V	292.4	H 653.6	0.5	900
Zn	213.9 481.0	H 653.6 H 653.6	0.2	200 5000
S	182.0	None	22	50000

Where multiple analytical lines are used for the same element (Ba, Cd, Mg and Zn), the software automatically reports the result using the analytical line appropriate for the measured concentration.

Several types of lubricating oil were analyzed using the above analytical program. These sample types are detailed in the table below:

Identification of Oil Samples

#	Manufacturer	Oil Type	Use	Weight
1	SuperTech	Recycled	Car Engine	15W-40
2	Castrol Edge	Regular	Car Engine	
3	Pennzoil	Regular	Car Engine	5W-30
4	Valvoline	Regular	Car Engine	5W-30
5	Quaker State Fully Synthetic	Synthetic	Car Engine	
6	Eastman Turbo	Synthetic	Jet Engine	
7	Mobil One	Synthetic	Car Engine	5W-30

The results obtained from multiple replicates on the samples are shown below reported as the average bus or minus the standard deviation:

Analysis of Oil Samples

	# 1	# 2	# 3	# 4	# 5	# 6*	#7
Ag	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
Al	<0.2	<0.2	<0.2	<0.2	<0.2	9.8 ± 0.5	<0.2
B	0.6 ± 0.1	295 ± 9	97.8 ± 1.3	0.6 ± 0.1	0.4 ± 0.1	<0.1	73.5 ± 5.7
Ba	0.4 ± 0.3	<0.2	<0.2	<0.2	<0.2	<0.2	0.5 ± 0.4
Ca	931 ± 23	1513 ± 51	1524 ± 45	1456 ± 26	1545 ± 39	<0.1	2206 ± 151
Cd	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Cr	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Cu	0.2 ± 0.2	1.3 ± 0.4	0.9 ± 0.3	<0.1	1.1 ± 0.6	0.9 ± 0.3	1.1 ± 0.8
Fe	<0.6	1.6 ± 0.3	0.5 ± 0.4	1.0 ± 0.3	1.3 ± 0.4	<0.6	1.6 ± 0.2
K	<2	<2	<2	<2	<2	<2	3.9± 0.4
Li	<0.1	<0.1	<0.1	<0.1	0.2 ± 0.1	<0.1	7.7 ± 0.4
Mg	829 ± 34	10.5 ± 0.4	8.1 ± 0.2	11.8 ± 0.3	9.4 ± 0.3	<0.1	15.1 ± 0.9
Mn	0.2 ± 0.1	<0.1	<0.1	<0.1	0.1 ± 0.1	<0.1	<0.1
Mo	35.2 ± 0.8	47.5 ± 2.2	86.1 ± 4.9	1.0 ± 0.4	108 ± 5	<0.6	57.4 ± 6.0
Na	11.2 ± 0.2	4.2 ± 0.2	2.1 ± 0.1	223 ± 5	1.3 ± 0.1	0.7 ± 0.1	7.7 ± 0.4
Ni	<0.5	<0.5	0.6 ± 0.2	0.7 ± 0.2	0.5 ± 0.4	1.9 ± 0.3	<0.5
P	1025 ± 19	685 ± 38	662 ± 12	688 ± 28	611 ± 20	2751 ± 66	763 ± 62
Pb	30 ± 0.7	<1.1	<1.1	1.6± 1.4	<1.1	<1.1	<1.1
S	10323 ± 413	8949 ± 503	7485 ± 385	7633 ± 222	9887 ± 376	<20	6898 ± 315
Si	8.0 ± 0.2	6.8 ± 0.7	4.3 ± 0.4	7.6 ± 0.3	6.0 ± 0.2	1.3 ± 0.3	2.7 ± 0.5
Sn	<1.2	<1.2	<1.2	<1.2	<1.2	2.1 ± 0.6	<1.2
Ti	<0.2	20.6 ± 1.0	0.4 ± 0.1	0.2 ± 0.1	0.3 ± 0.2	<0.2	2.1 ± 0.5
V	2.0 ± 0.5	3.3 ± 0.5	6.2 ± 0.5	<0.5	9.3 ± 0.4	0.5 ± 0.4	5.4 ± 0.7
Zn	1089 ± 9	708 ± 18	787 ± 23	734 ± 8	658 ± 19	<0.1	716 ± 52

CONCLUSIONS

Sulfur can readily be analyzed using the extended vacuum ultraviolet attachment to the MOA III rotating disk electrode instrument simultaneously with the contaminant and additive elements at the levels found in normal lubricating oils.