Accuracy Problems Analyzing Additive and Wear Metals in Synthetic Lubricating and Fuel Oils Using ASTM Procedures for Rotating Disk Electrode Emission Spectroscopy

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Summary: The ASTM procedures for wear metal and additive analysis in oils are investigated with a view to improving the accuracy of the technique.

History

Wear metal analysis in Oil as a predictive technique for diesel engine problems was first used in 1946 by the Denver and Rio Grand Railroad. In 1955 the Naval Weapons Laboratory initiated a study in the use of wear metal analysis as a technique to predict aircraft component failures which ultimately lead to JOAP. In 1958 Pacific Intermountain Express became the first trucking fleet to use wear metal analysis as an engine failure predictive technique. Initially the technique was a trend analysis where increases in elemental levels triggered an action.

The first ASTM procedures were proposed in 1968 with a limited number of elements (Ag, Al, B, Cr, Fe, Pb, Si and Sn) in low concentrations (below 200 ppm) using photographic detection.

Principle of the Technique

An oil sample is picked up from a sample boat or cup by a rotating carbon disk electrode and transported to a pulsed AC Arc maintained between this electrode and a graphite rod counter electrode. The sample is vaporized, atomized and excited by the arc so that the emission spectra characteristic of the elements within the oil are generated and analyzed by a spectrometer.

Instrumentation

The basic instrument consists of a source, sample stand, spectrometer and supporting electronics.

Source & Operation
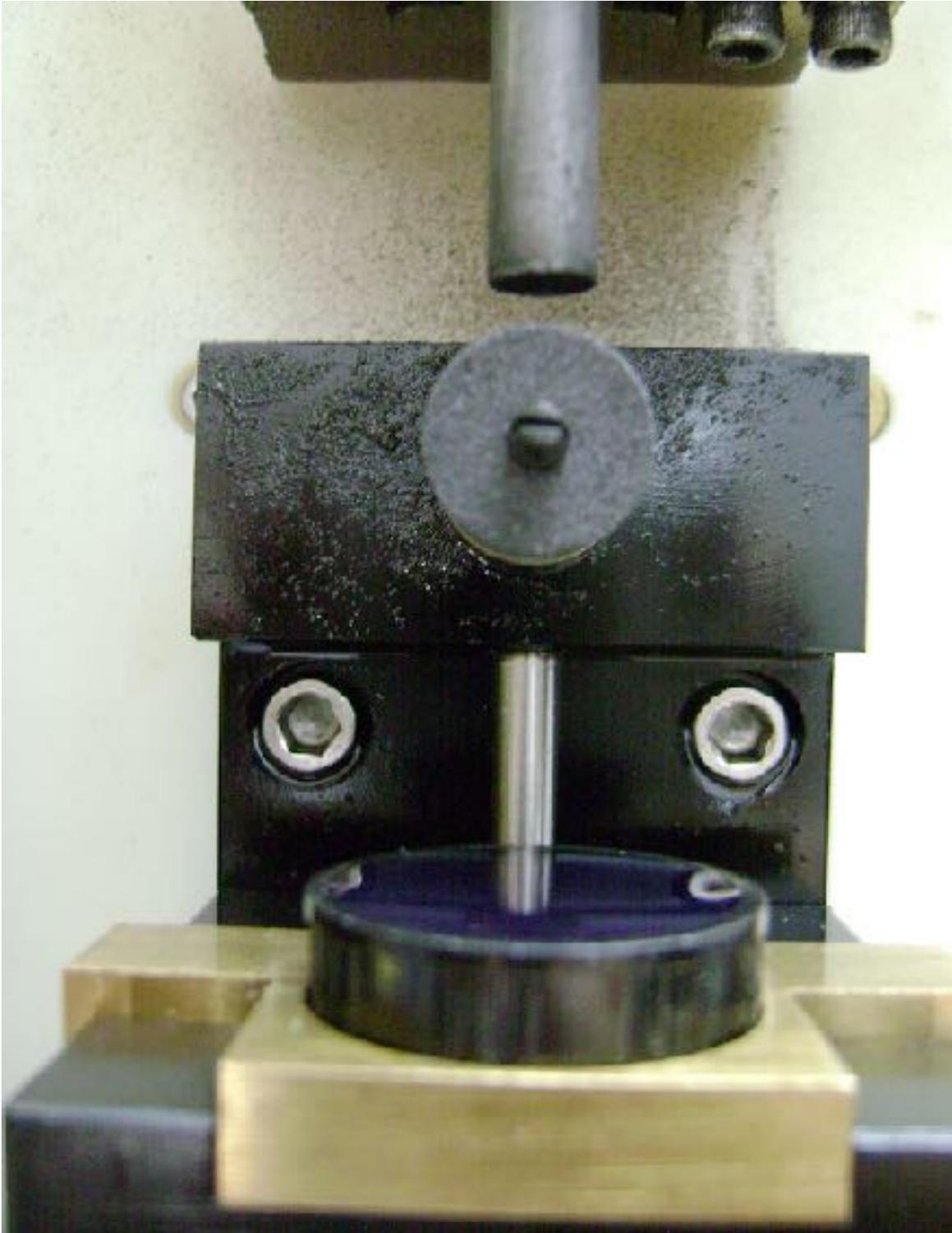
The pulsed AC arc operates at a frequency of 60 ± 0.1 hertz with a maximum peak voltage of 175 V. The frequency is generated from a pure sine wave generator and is independent of the actual line frequency in the facility. An ignition transformer charges a capacitor such that 5-6 pulses are generated per half cycle. In this study, the samples were contained inside aluminum boats fitted with a cover. The

cover is only required for fuel oil analysis but it was used in this study to ensure identical parameters. The analytical sequence was determined using a time distillation study on the most viscous oil, D19.
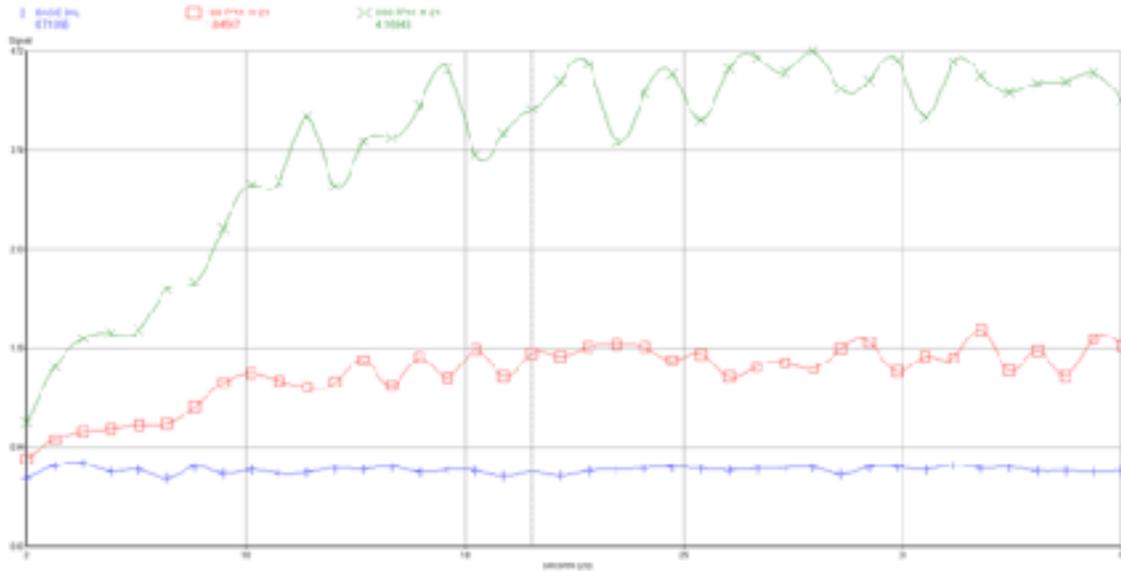
A typical time distillation is shown above and indicates that a pre-exposure of 20 seconds is more than sufficient for the element signals to stabilize. A 20 second exposure time was used for all samples.

Spectrometer

The basic components of a spectrometer are transfer optics to collect light from the source and focus it on the entrance slit of the spectrometer and a diffraction grating which splits the white light into its component wavelengths which impinge on the surface of a CCD detector where the light is transformed to a digital signal which is processed by a computer into concentrations.
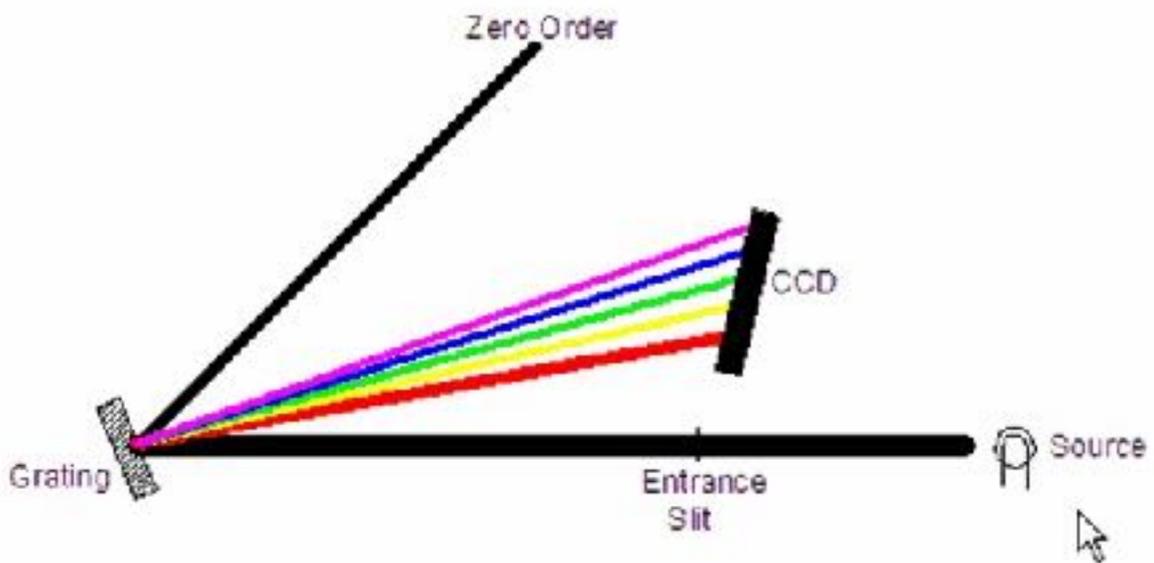
In the instrument used for this study, dual holographic gratings on a quartz substrate are used to diffract the light. The gratings were custom designed to produce multiple flat fields of the same approximate length as the active area of the CCD in a modified Littrow mount. The low wavelength spectrometer covers the wavelength range from 170 nm to 439 nm on four flat fields and the high wavelength spectrometer covers the range 430 to 790 nm also on four flat fields. The typical resolution of the spectrometer is 16 pm per pixel.

The spectrometers are maintained at a temperature of 20.0 ± 0.1 C using a thermoelectric chiller. As the temperature of a CCD increases, so does the dark current with a resulting loss in dynamic range. If the CCD surface is below the dew point, any moisture in the spectrometer can condense on the surface and reduce the light impinging on the CCD. The basic spectrometer which has a lower wavelength limit of 190 nm is filled with air which is circulated through a desiccant. For the extended wavelength spectrometer, nitrogen is used as the fill gas and an optional oxygen scrubber may be added to the recirculation system.

Why did we initiate this study?

Several years ago when participating in the JOAP correlation program we questioned why the D19 samples obviously contained less than four spiking levels, yet the synthetic oil samples had multiple spike levels. A typical result from one correlation test is shown below:

Element	Target	D19	Turbo
Ag	9	8.4	10.3
Al	9	8.1	9.1
B	9	8.0	*10.0*
Cr	9	9.5	8.6
Cu	9	8.5	9.6
Fe	9	9.7	***12.7***
Mg	9	10.4	***12.0***
Mo	9	8.7	*11.5*
Na	27	26.0	*40.7*
Ni	9	8.1	9.2
Pb	9	8.5	9.6
Si	9	8.7	9.4
Sn	9	8.5	*11.0*
Ti	9	9.0	***11.2***
V	9	8.2	***12.1***
Zn	9	8.7	***12.4***

When we simulated this sample, we obtained similar results, except for Na in Turbo where we read 35.7 ppm. Presumably the difference is due to a slight contamination in the Turbo oil used in the study. In the table, values in *italics* or ***bold italics*** indicate that the accuracy of the Turbo result is outside the acceptable range from the D19 or target values respectively.

Clearly all elements read higher in the Turbo Oil compared to the D19 and ionic lines generally read higher than atomic lines. At the higher concentration, Na is clearly inaccurate.

Evolution of ASTM Procedures

In 1968, ASTM proposed three methods (D2) for oil analysis using rotating disk electrode spectroscopy for a limited number of elements at low concentrations. D2-P1 used a simple dilution of four parts of sample to one of a cobalt internal standard. The technique used a high voltage spark with detection performed using a photographic spectrometer. The procedure recommend making calibration standards using the same oil brand as the samples or a non additive oil of the same viscosity and that these oils be free of the elements to be analyzed. D2-P2 used an ashing technique to destroy the oil matrix, D2-P3 addressed fuel oils and gave a suggested method of making calibration standards.

Element	#1	#2	#3	#$	#5
Cu	178	27	9	2.3	90
Fe	178	27	9	2.3	90
Pb	178	27	9	2.3	90
Sn	2.3	27	9	2.3	90
Al	2.3	9	27	178	90
B	2.3	9	27	178	90
Cr	2.3	9	27	178	90
Ag	0.34	1.35	4.05	26.7	12.5
Si	44	6.75	2.25	0.56	22.5
Total Metals	587.54	143.1	123.3	570.40	665.0

 While the concentrations of some elements are the same in all standards, it is generally possible in most cases to calculate interference corrections as part of the calibration process. Additionally the total metal content is kept reasonably constant especially for the higher concentrations. A distinct disadvantage is that the calibration standards were required to be prepared on site. In 1977 this procedure was deemed no longer valid.

The current ASTM procedure for lubricating oils by rotating disk electrode spectroscopy is D6595 which has now expanded to 23 elements (Ag, Al, B, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sn, Ti, V, W and Zn) with a concentration range of 0-100 ppm for wear metals and 0-900 ppm for additives. Hydrogen at 486.13 nm has replaced cobalt as an internal standard presumably as it is present in oil and thus requires no sample preparation; the actual wavelength is incorrectly stated at 486.10 nm

in the document . Photomultiplier based spectrometers were used for this method when adopted, as evidenced by the fact that recommended wavelengths are not always the optimal lines for the analysis but rather those than can be accommodated in a spectrometer because of the problem of packing large photomultipliers into a small area. With the use of the CCD in contemporary spectrometers, there should no longer be a conflict problem in selecting the optimal wavelength.

The selection of elements is also an interesting one based upon the commercially available standards. The commercially available D19 standard contains Ag, Al, B, Ba, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, Pb, Si, Sn, Ti, V, W and Zn. S21 adds Ca and P to the D19 standard. S21+K+Li (aka S23) adds K and Li to S21. Cd is the standard but apparently not required while W is required but not in the commercially available mixed standards. This omission is understandable as tungsten compounds are inherently not stable and fall out of solution and in a mixed standard will drag other elements out of the standard as well.

As virtually all laboratories use these commercially available standards there is a major change in viscosity of the different standards used for calibration. The following table shows the total metal content of the calibration standards.

Concentration	D19	S21	S21+K+Li
0	0	0	0
5	85	95	105
10	190	210	230
30	570	630	690
50	950	1050	1150
100	1900	2100	2300
300	5700	6300	6900
500	9500	10500	11500
700	13300	14700	16100
900	17100	18900	18745

As all elements are present at the same concentration, it is impossible to calculate interference correction factors as part of the regression analysis used to generate calibration curves.

The current ASTM procedure for fuel oils by rotating disk electrode spectroscopy is D6728 which has been expanded to 15 elements (Al, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Si, V and Zn) with a concentration range of 0-10 ppm for light oils and 0-100 ppm for heavy oils with Mg at three times these levels. As with D6595, photomultiplier based spectrometers were used when this method was first adopted. Hydrogen 486.13 is recommended as the internal standard for light oils and the cyanogen band head at 387.14 nm for heavy oils. Originally this band was identified as a carbon line which, if true, would have been remarkable as it is a line of the doubly ionized carbon atom which is not found in the source. After we informed ASTM of this error, the cyanogen band head is now stated but as with

hydrogen, the wavelength is incorrectly stated as 378.10 nm. Aside from the fact that nitrogen is not part of the sample and can only come from the air within the discharge, a second problem is that this wavelength is also the 1,1 band head of the R branch of one of the CH band systems.

The current ASTM procedures for lubricating and fuel oil analysis by ICP (D5185 and D7151) cover the same concentration ranges and suggest a dilution and use of Y as an internal standard. The use of an internal standard is somewhat surprising as internal standards are rarely used in ICP analysis. As late as 1981, xylene was recommended as the solvent even though it had been previously classified as a carcinogen and we had stopped using it in 1978 after switching from MIBK which was classified in 1976 . The latest version recommends kerosene and leaves the dilution up to the user. Initially the principle ICP sample introduction used a pneumatic nebulizer to aspirate the oil sample but by 1981 all ICP manufacturers offered a high solids nebulizer where the sample is pumped at a fixed rate into the system to obviate the effects of viscosity and lower sample dilutions could be successfully used.

Why use an internal standard?

An internal standard is supposed to behave lust like the analyte. And yet the measurement technique can distinguish between the two. Ideally, any of the sources of error will affect **both** the internal standard and analyte signals and presumably any change in analytical signal would be reflected in a similar change in the internal standard signal.

Using rotating disk emission spectroscopy for oil analysis, the most common of these errors are fluctuations in the sample uptake caused by different viscosities and a change in temperature of both the samples and discharge.

The correlation between the signals of the internal standard and analyte are the key to this method. If there is no correlation, then the internal standard does nothing and can, in fact, adversely affect the analytical technique.

What are the requirements for an internal standard

1. The signal is generated ONLY from the sample and standards.

2. The internal standard should be the same concentration in all samples and standards.

3. The internal standard line should have similar properties to the analytical line.

4. The internal standard line should be free of spectral and physical interferences.

5. The internal standard analytical line should have a linear response over the range found in samples and standards

Gerlach and Scweitzer first used the internal standard principle in 1926 using the concept of homologous pairs where each analytical line was ratioed to an internal standard line with similar spectroscopic properties. Their work was first published in German but an English translation was published by Hilger in London and titled *Foundations and Methods of Chemical Analysis by the Emission Spectrum* in 1929. With the photographic detection available at the time, it became common practice to

use multiple internal standard lines for analysis. By the early 1970's, direct reading photomultiplier based spectrometers became the norm. As photoelectric detection provided a significant decrease in the analysis time and improvement in precision of the measurements compared to photographic detection. It became common practice to drop back to a single internal standard line for each different matrix. The rational being that the added cost of additional detectors plus the problem of physically building an instrument with extra hardware offered no significant improvement in accuracy. Today with CCD detection most of the spectrum is captured, as it was with photographic detection, it makes sense to return to the use of homologous pairs where appropriate. Indeed today some metal scrap sorters using CCDs utilize this procedure.

Chemical Analysis of Different Oils

As a first step in investigating the use of hydrogen, we had the most common types of oil analyzed and the results are summarized below:

| Oil Type	% C	% H
Aviation (D19)	86.5	13.5
Synthetic (Turbo)	68.0	10.0
Fuel (Kerosene)	85.0	15.0

Clearly, the hydrogen concentration is vastly different in the aviation and synthetic oils and the second rule of an internal standard is violated. The following shows wavelength scans for different oils around the H 4861 nm line.
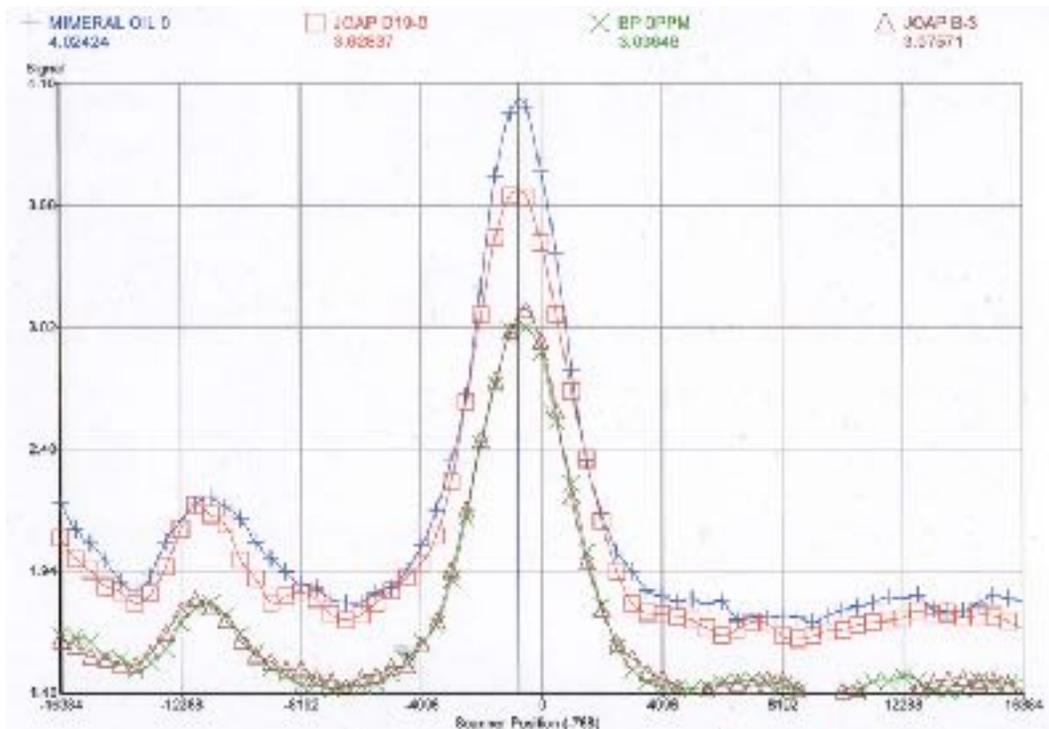
From the above scan it is apparent that the synthetic oil (BP and JOAP) have a lower background and, even after correction for the shift in background, a lower signal than either the JOAP D19 or MINERAL OIL. The mineral oil has a much bigger signal than the D19 even though they are both are reported as 75 cSt oils and have a similar chemical composition, both being primarily aliphatic hydrocarbons but it is obvious when pouring these two oils that mineral oil has a much lower viscosity than D19. Although both oils are stated to have the same viscosity, the temperatures at which these viscosities are measured is different.

 Synthetic oil is a mixture of aliphatic hydrocarbons and olefins and has also a lower viscosity than D19.

The following shows a wavelength scan in the region 170-190 nm for sulfur free base oil and a profile solution which is essentially a 200 ppm solution of S23.
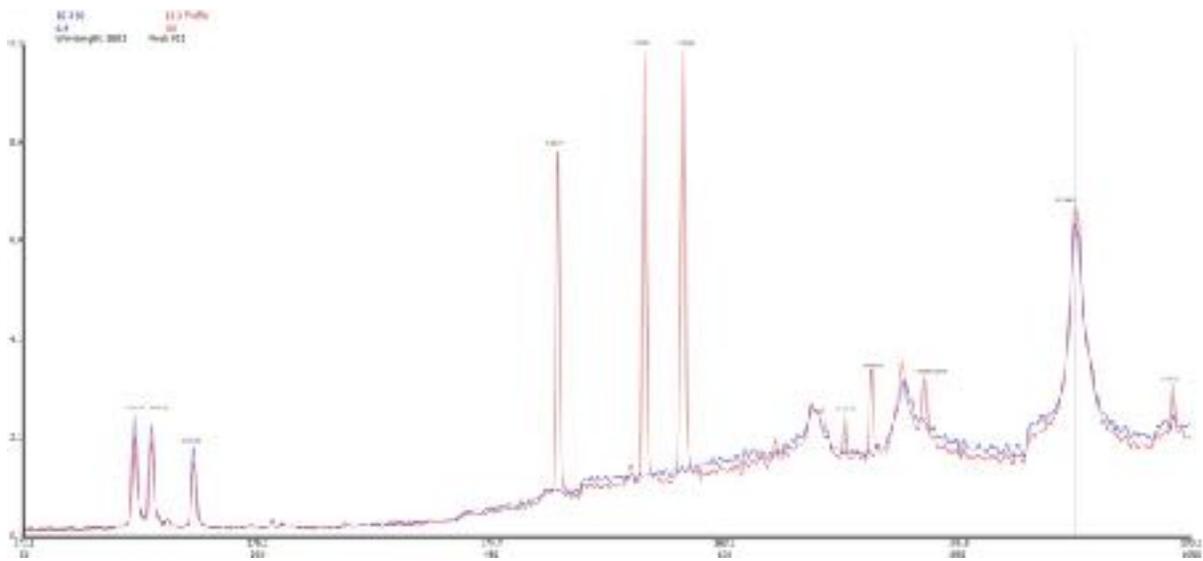

The presence of the sulfur triplet centered on 182 nm indicates that the calibration standards contain the various elements as sulfonates which further increase the non-oil content of these series of standards by about 150-200%. Most commercial automotive oils also contain high concentrations of sulfur as shown below.
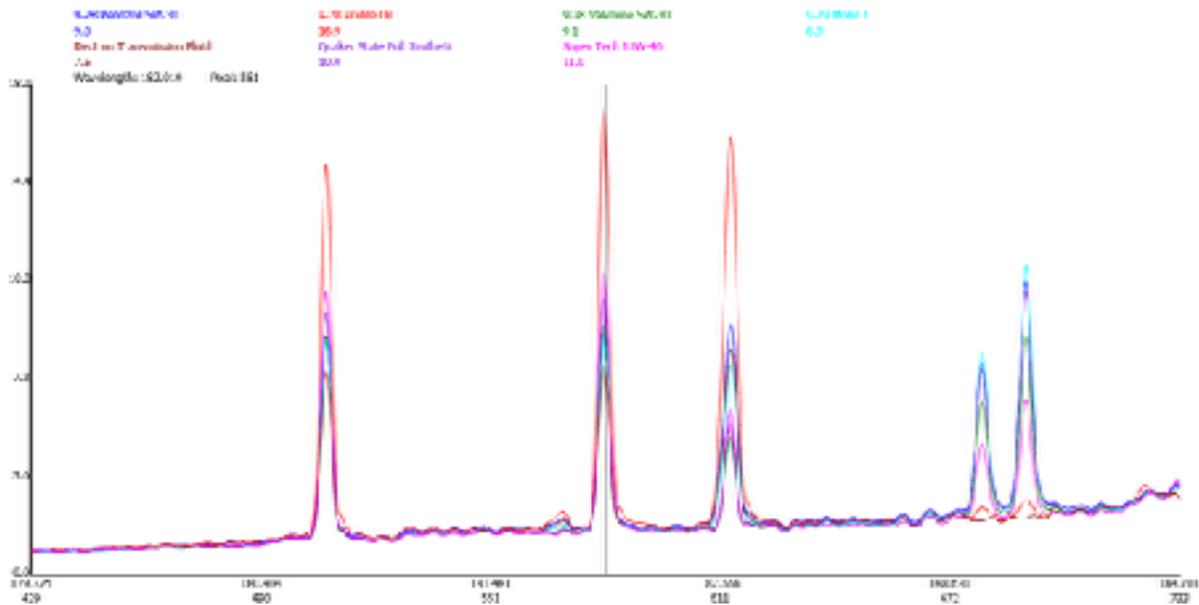
The nitrogen lines around 174 nm and the carbon 175 nm line have similar signals in most commercial automotive oils as shown below.
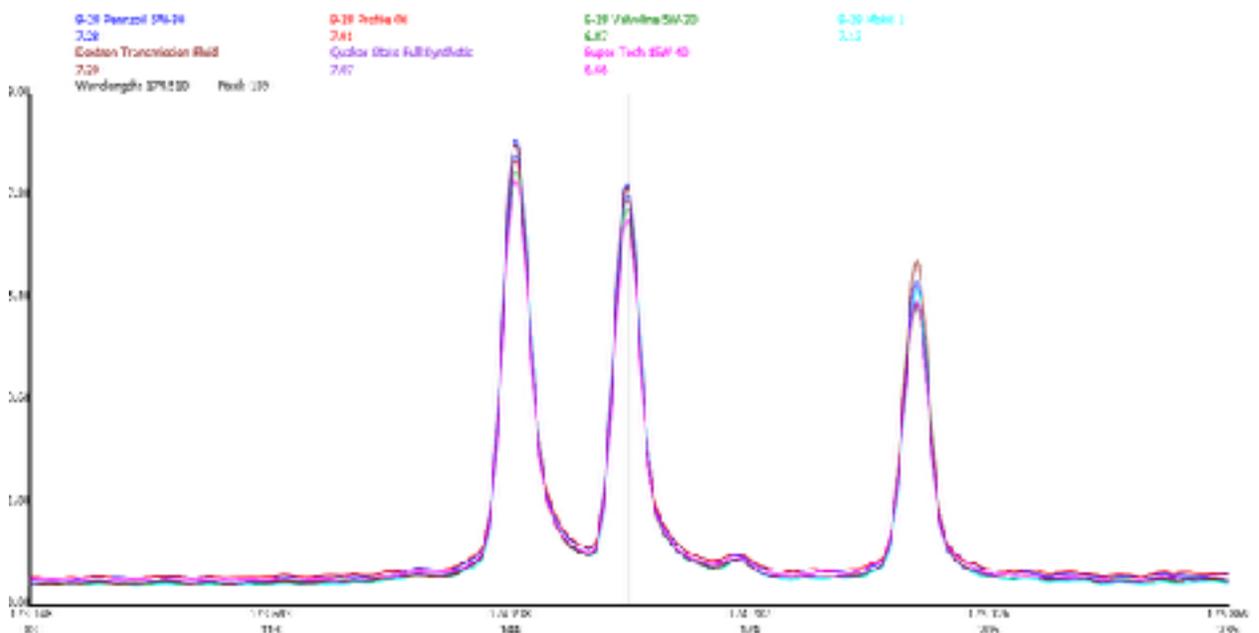
As these three lines are ground state lines of these elements used in normal spark emission for low level analysis in steel samples, these lines are obviously non linear as are the normal carbon lines at 193.0 nm and 247.8 nm. The much weaker carbon line at 199.33 nm should be linear over the carbon concentrations in oil. The following shows a wavelength scan of different oils around this wavelength.
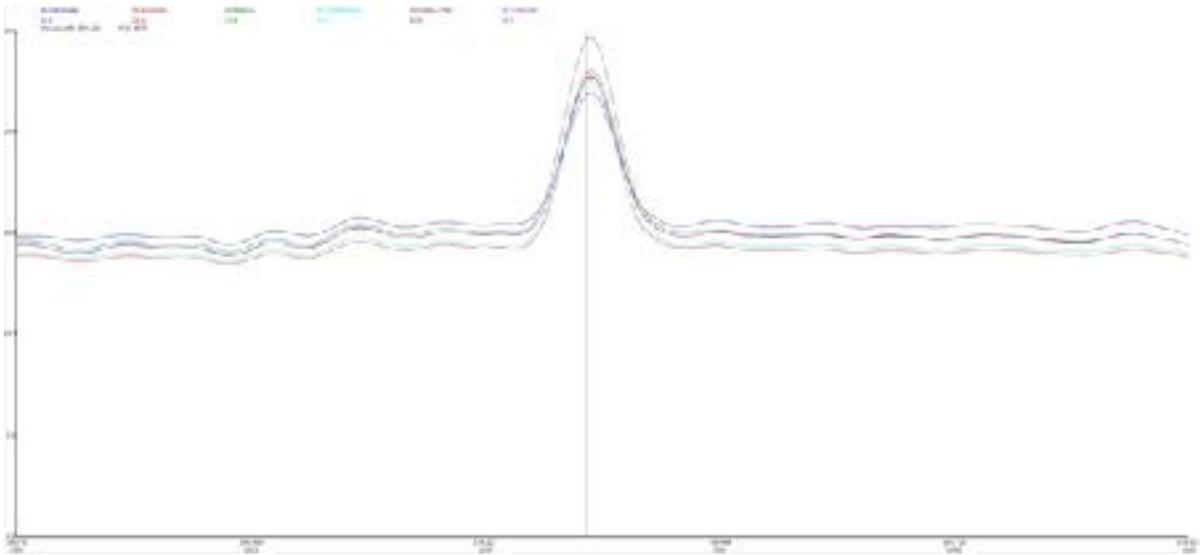
After correction for the change in background emission, there is no great change in signal. This is not surprising as the bare electrodes contributes the majority of the carbon signal and this violates the first rule of an internal standard.

What else is in synthetic oil

| Oil Type	% C	% H	% Other
Aviation (D19)	86.5	13.5	0.0
Synthetic (Turbo)	68.0	10.0	22.0
Fuel (Kerosene)	85.0	15.0	0.0

The certification for both Eastman and BP Turbo oil indicates that a phosphate is added to the oil. It is also likely that nitrogen compounds are present. However since the discharge burns in air, it is impossible to ascertain if either nitrogen or oxygen is present because air contains about 80% and 20% of these elements respectively. A scan of the phosphorous lines does, however, indicate that phosphorus is present.

These scans indicate that phosphorus is present in the synthetic oil but not the other oils. The recommended analytical line at 255.33 nm is shown by the cursor while the line at 263.56 nm is clearly more sensitive but will not fit in photomultiplier based spectrometers because of the need to use the B 249.6, Si 251.6 and Fe 259.9 nm lines.

The alternate phosphorous wavelength recommended at 214.9 nm sits on top of a band head and is not a good choice and along with the 213.6 nm have a major interference from copper. It should also be noted that the recommended phosphorous line at 255.33 nm has a major interference from a vanadium doublet centered on 255.3 and located in the normal background correction positions.

A better choice for phosphorus analysis would be the 178.28 nm line but this requires a nitrogen filled spectrometer and purged optical path.
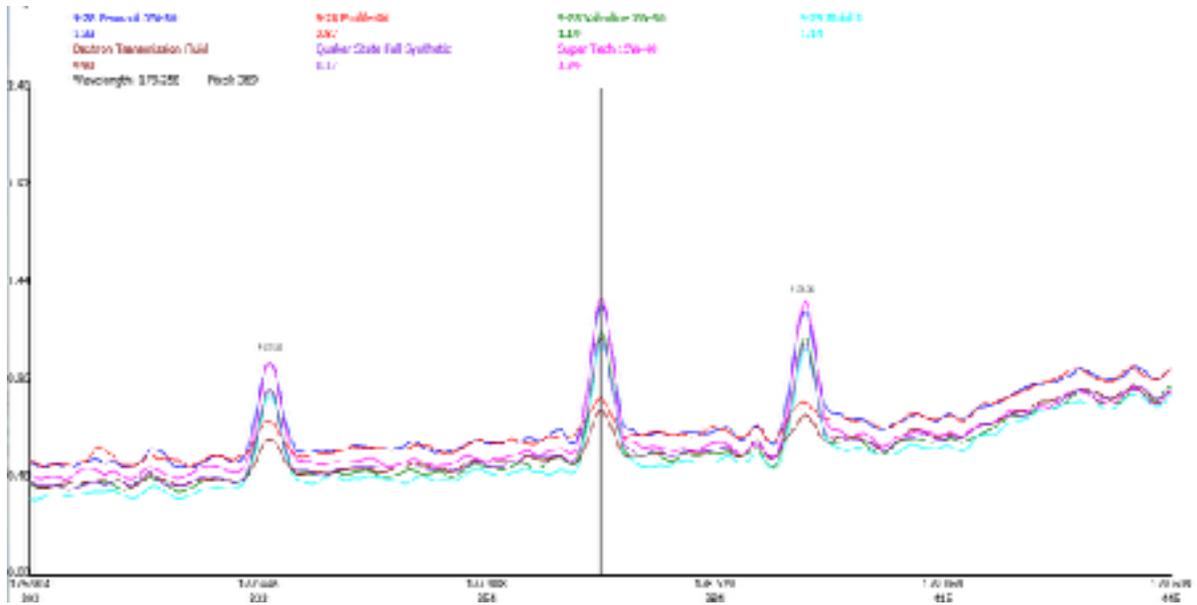
Hydrogen as an internal standard

The most obvious limitation of using hydrogen as an internal standard is the fact that is not linear at these concentrations even in an ICP which has a dynamic range at least two to three orders of magnitude above a rotating disk electrode system and this violates the fifth rule of an internal standard.

Wavelength scans for and water and isopropyl alcohol around the H 486.13 nm line shows that the signals from these compound is vastly lower than that obtained for mineral oil.
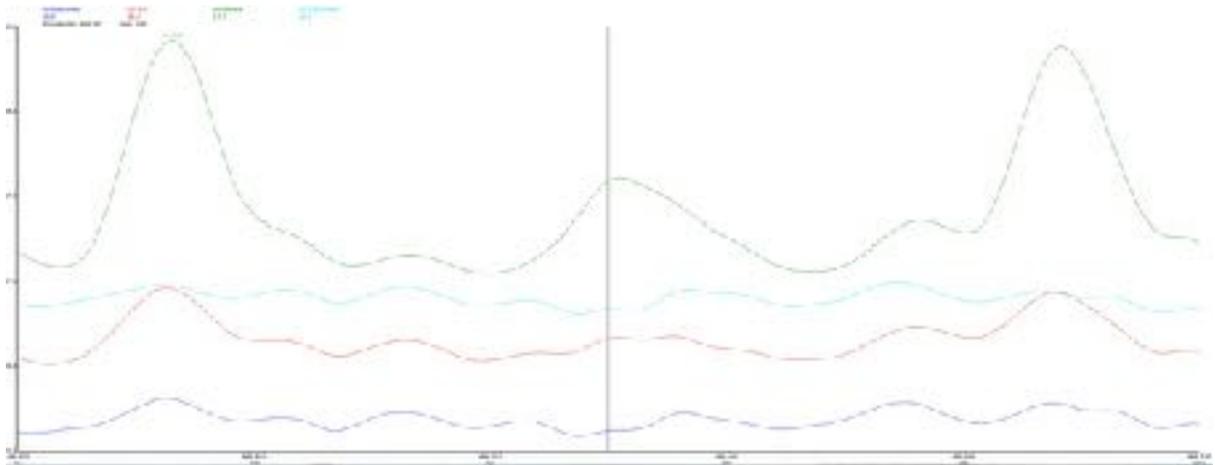
This line is located between two stronger CH band heads and also in the region of the weaker end of the green C2 Swan bands. For different oils, there is a distinct change in background but after correction, the intensities at the H line and any of the CH bands in the area correlate well but are clearly different depending upon the type of oil.
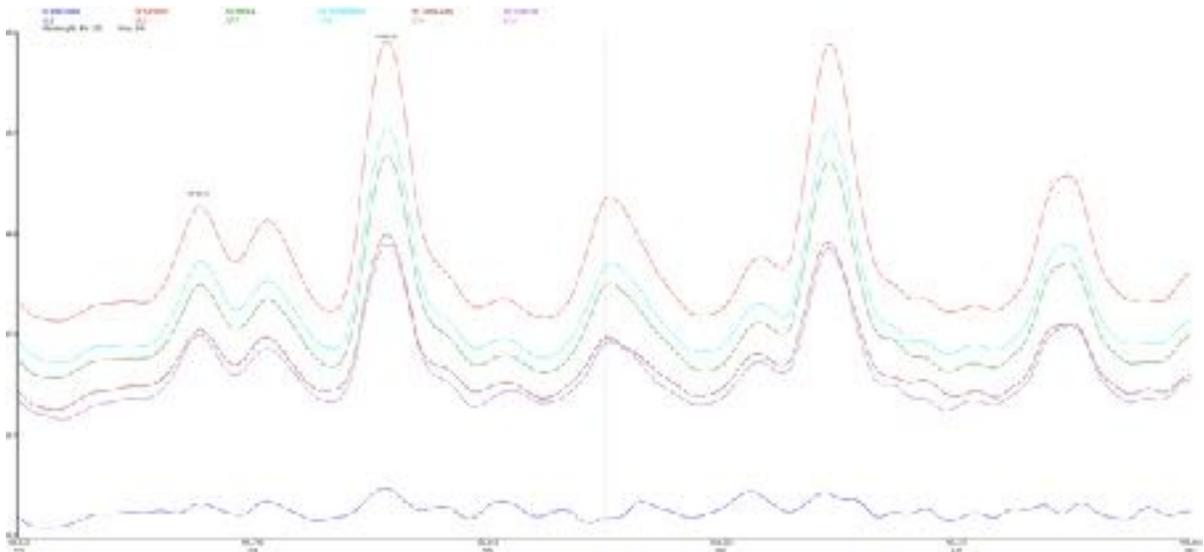

With the CCD instrument used in this study, a better hydrogen doublet centered at 625.27 nm was also investigated. The same two scans as shown above for the H 486.31 nm line are shown below.
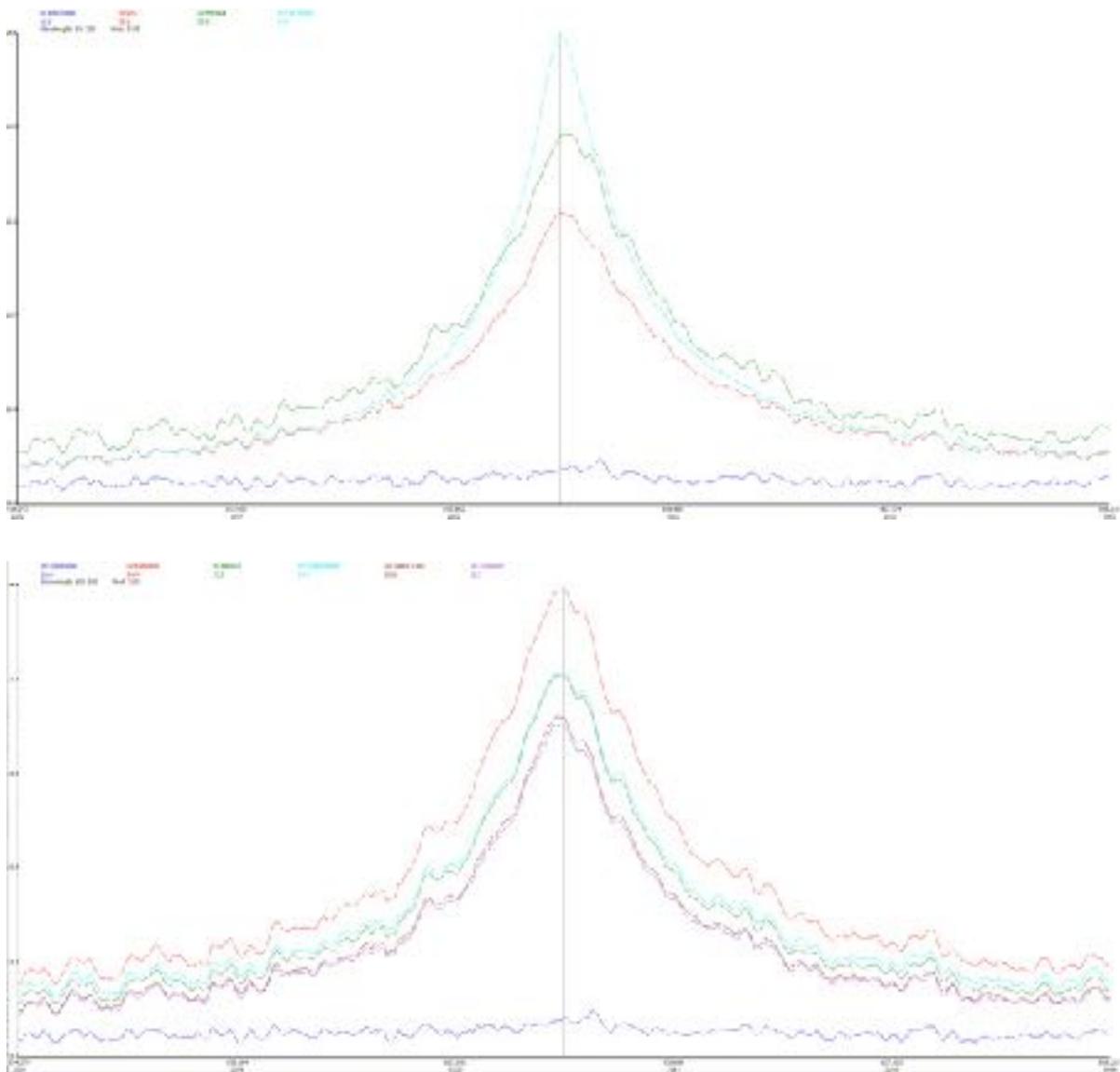
As with the H 486.13 nm line, this unresolved doublet also has different signals based upon the type of oil but with both water and isopropyl alcohol the signals are vastly enhanced.

## Cyanogen band heads as internal standards

As with hydrogen, the suggested band head at 387.14 nm is one of the strongest bands of the cyanogen system and extremely unlikely to be linear. The following shows wavelength scans over this area for water, isopropyl alcohol and mineral oil
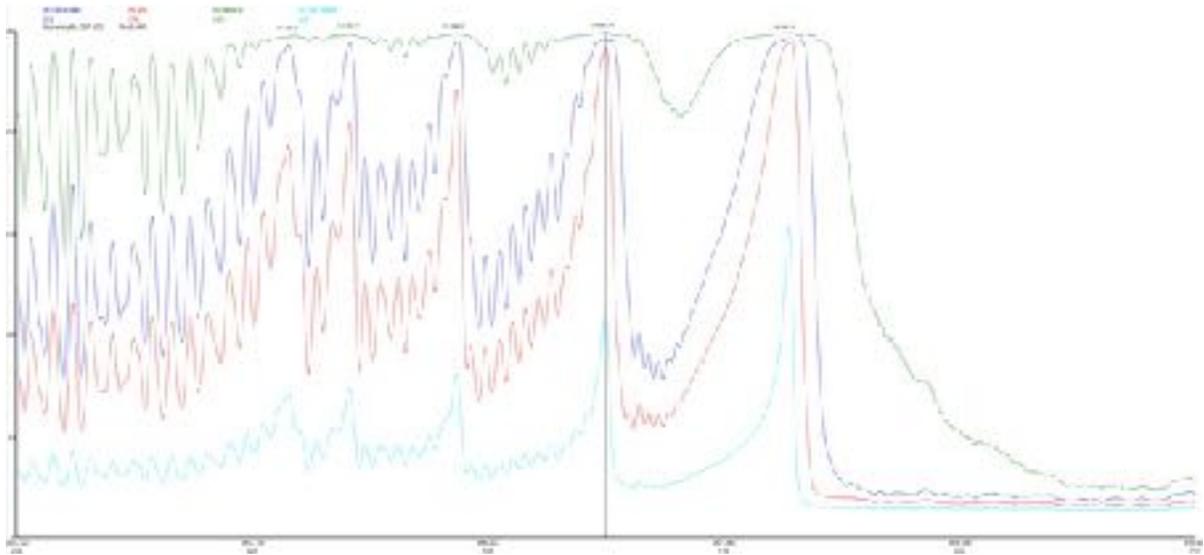
As can be readily seen, the blank electrode generates a very high signal for these bands which decrease when water and isopropyl alcohol are analyzed. Mineral oil does increase the signal but the fact that a large signal is obtained from the blank electrode violates the first rule of an internal standard. A second problem with these bands is that there is no really good region to background correct because of the structure of the band head system. This is particularly true of a photomultiplier based system where the background positions are fixed but is less of a problem with the CCD where any wavelength may be chosen for background correction but this does beg the question of how far away from the analytical wavelength does the background remain valid.

A better choice of cyanogen band head would be the 419.72 nm band head and these scans are shown below.
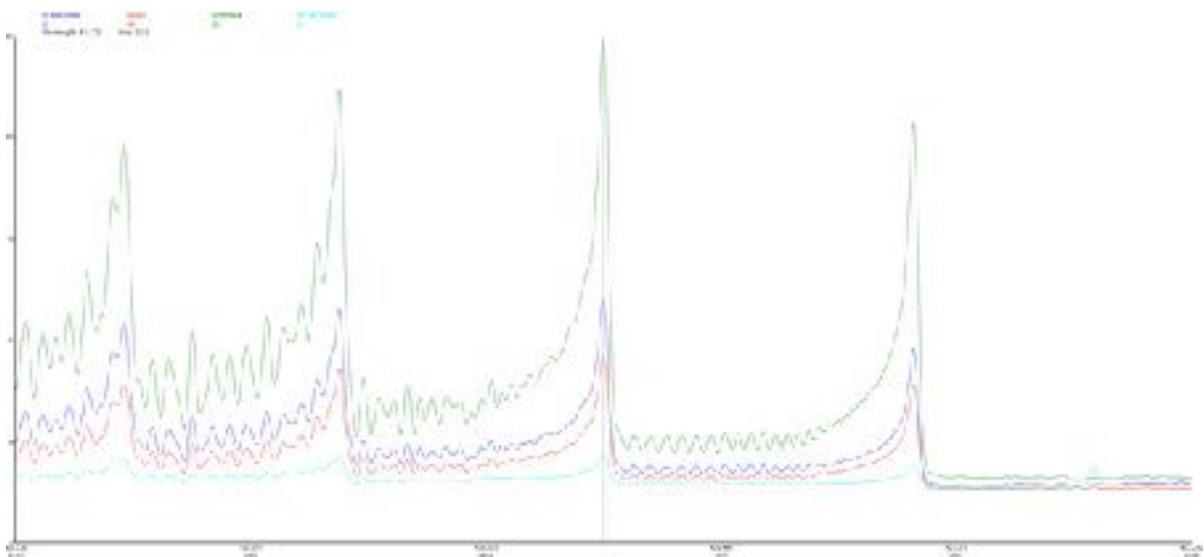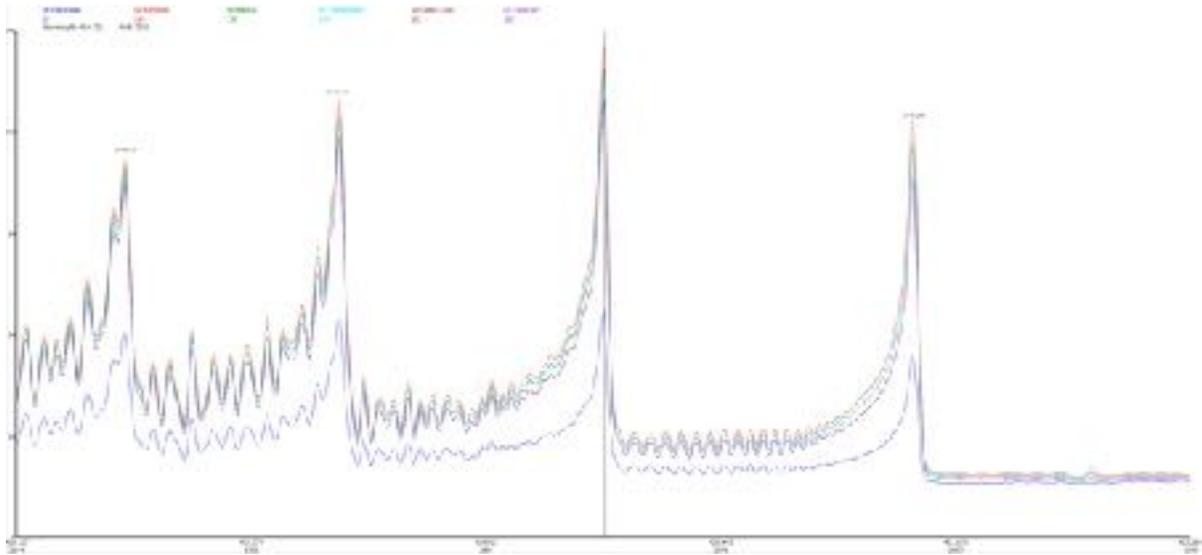
As with the CN 387.14 band head, the signal from the blank electrode is higher than the signal from either water or isopropyl alcohol but less than mineral oil. Each of the different oil types have different signals but again the electrode contributes a significant amount of the signal. The band head at 421.60 nm would offer a better choice for background correction but unfortunately, the strontium line at 415.55 nm produces a spectral interference on this band and violates rule 4 of an internal standard. Strontium is normally present in the additive standards as an impurity in the other alkali metals (Ba, Ca and Mg)

Oxygen Spectra in Oils

The oxygen triplet centered on 777.54 nm is distinctly visible in the rotating disk electrode system.
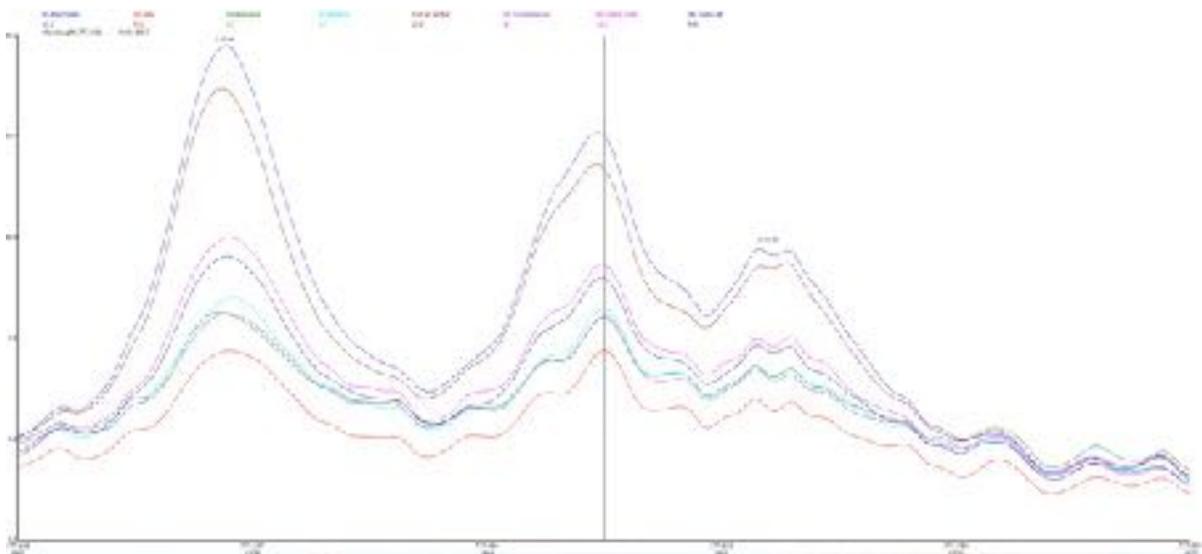
With blank electrodes, a strong oxygen spectrum is detected and this only decreases slightly when water is analyzed. With oils and isopropyl alcohol, this spectrum is suppressed but distinctive of each oil type.

Why match spectroscopic properties of internal standard and analytical lines

The Einstein-Boltzman equation defines the relationship between the particle density (N) of a species and the intensity (I) at the analytical wavelength:

$$I = N * h * c * g_k * A_{ki} * exp(-E_k / k_B /T) / \lambda / U$$

where g_k is the statistical weighting factor or the upper state of the transition, A_{ki} is the transition probability of the line at wavelength λ, E_k is the energy of the upper state, T is the temperature, U is the partition function. H is Planck's constant, c is the speed of light and k_B is Boltzmann's constant. For any given line this reduces to:

$$I = N * constant * exp(-E_k / k_B /T) / U$$

The following table shows the energy in electron volts of some common analytical lines:

Wavelength & Line	Lower Level	Upper Level
486.312 H I	10.20	12.75
656.280 H I	10.20	12.09
182.034 S I	0.00	6.86
213.857 Zn II	0.00	5.80
280.070 Mg II	0.00	4.42
327.395 Cu I	0.00	3.79
425.433 Cr I	0.00	2.91
589.589 Na I	0.00	2.10
766.491 K I	0.00	1.62

All of the analytical lines are transitions from the ground state while both hydrogen lines are transitions between higher energy levels. The Mg line at 280.270 is an ionic line which does require an additional 7.65 to ionize from the atomic ground state. From the energy levels of these transitions it is apparent that hydrogen is not an optimal choice for internal standard as changes in the temperature would affect the exponential component of the equation to a greater extent than the analytical wavelengths.

The partition function is also a function of temperature and is computed by summing the product of the exponential function for each energy level in the species and the statistical weighting factor of each level. This is an extremely laborious process but fortunately empirical equations are available in *The observation and analysis of stellar photospheres* written by David F, Gray and published in 1992 by Cambridge University Press in New York. A summary of these partition functions over the temperature ranges of normal DC and AC arcs is shown below.

Element	4000 K	4500 K	5000 K	5500 K
H I	2.00	2.00	2.00	2.00
S I	8.66	8.81	8.95	9.09
Zn I	1.00	1.00	1.00	1.00
Mg II	2.01	2.01	2.01	2.01
Cu I	2.15	2.23	2.33	2.44
Cr I	8.70	9.50	10.47	11.62
Na I	2.01	2.01	2.04	2.08
K I	2.06	2.11	2.20	2.32

As the temperature increases, the partition function generally increases but as the partition function is the divisor in the Einstein-Boltzmann equation, it counteracts the direct temperature effect that predicts higher temperatures should give higher signals. Hydrogen is a unique element in that it has only one electron so does not have an ion and its partition function cannot change with temperature. In practice, as the partition function generally negates the effect of temperature change, there is only about a 1% error from the combination of these two factors.

A more important factor at work with temperature change in a plasma system was derived by Saha in 1925 which relates the particle densities of the atom (0), ions (+) and electrons (e) in a system to the temperature and Boltzmann distribution.

$$N_+ * N_e * N_0 = 2 * g_+ * \exp(-E_+ / k_B / T) / g_o / \Lambda^3$$

$$\Lambda = (h^2 / 2 / \prod / m_e / k_B / T)^{1/2}$$

where m_e is the mass of the electron and E_+ is the ionization potential of the atom. This equation predicts that as the temperature increases, the ratio of ions to atoms increases so that ionic lines become more intense and atomic lines less intense. This is why homologous pairs were originally used for spectroscopic analysis. As the hydrogen internal standard line is an atom and not easily ionized, the Saha equation predicts that an increase in temperature would enhance the ratio of the intensity and hence concentration of ionic lines such as Fe, Mg, Mo, Ti and V. In the pulsed arc source, the majority of the electron density is provided by the oil matrix as well any entrained air within the discharge so the main driving force in changing the ion to atom ratio is the temperature.

Cobalt as an internal standard

Theoretically using cobalt as an added internal standard should allow the use of homologous pairs. The original Co line at 304.40 nm used in the 1968 method has severe spectral interferences when used with the current concentration range requirements as shown below.
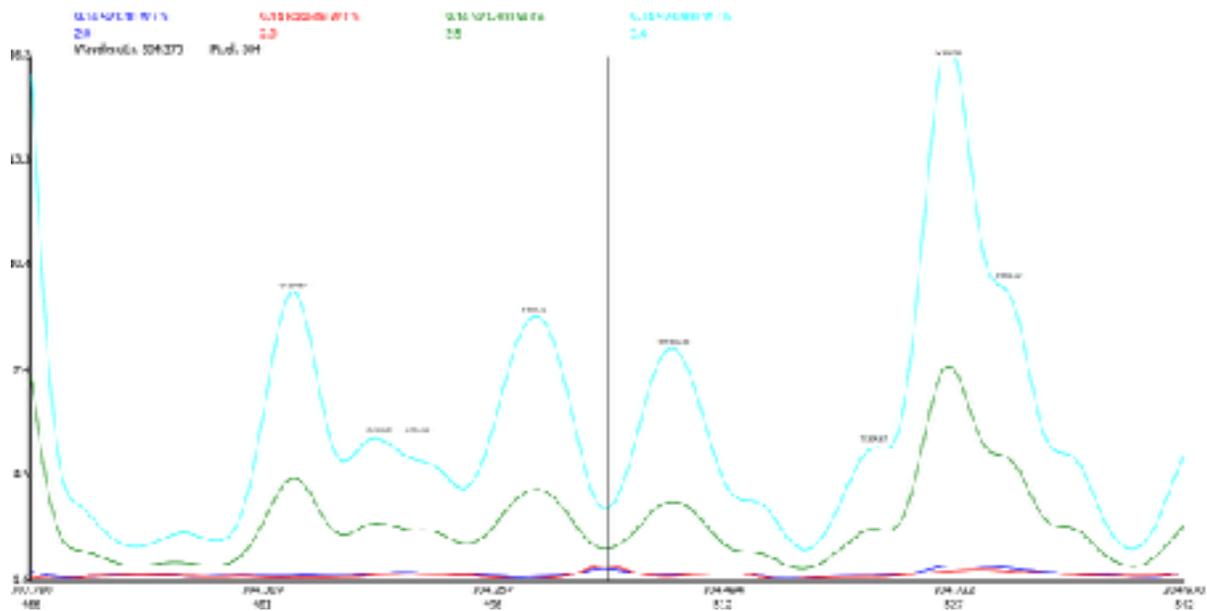
The internal standard line is surrounded by lines of V and Mo which make the wavelength unusable. The normal analytical cobalt line at 345.35 nm is cleaner but still has an interference from Al 345.27 which makes it unusable.
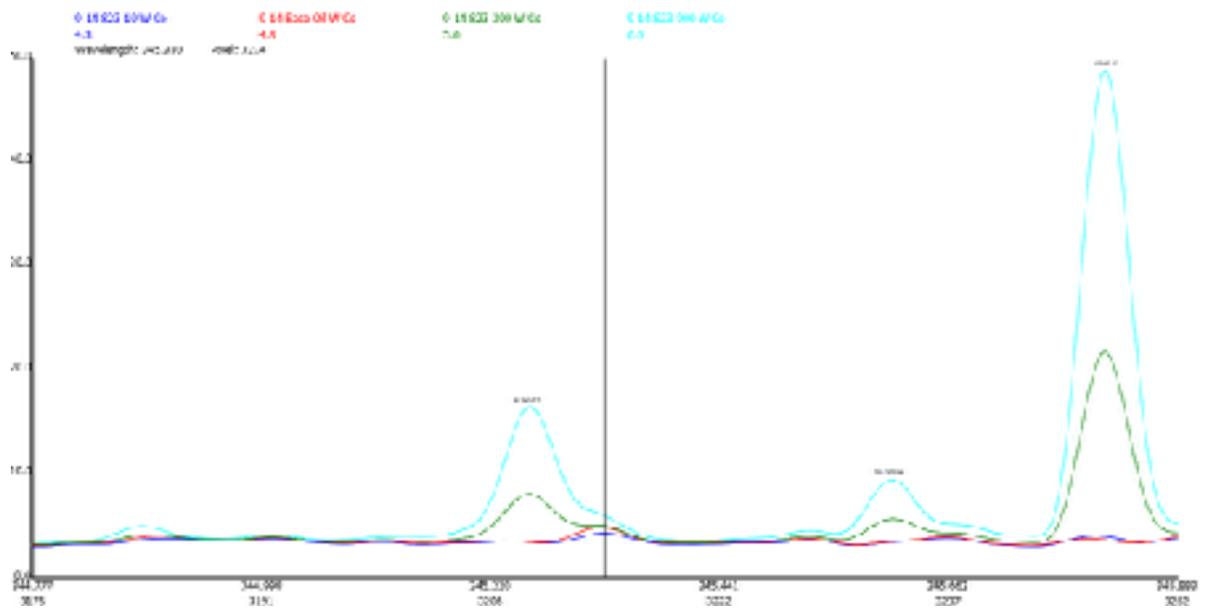

Finally the Co 228.61 nm line may be useable if a higher spiking level than the 50 ppm shown in the scan below
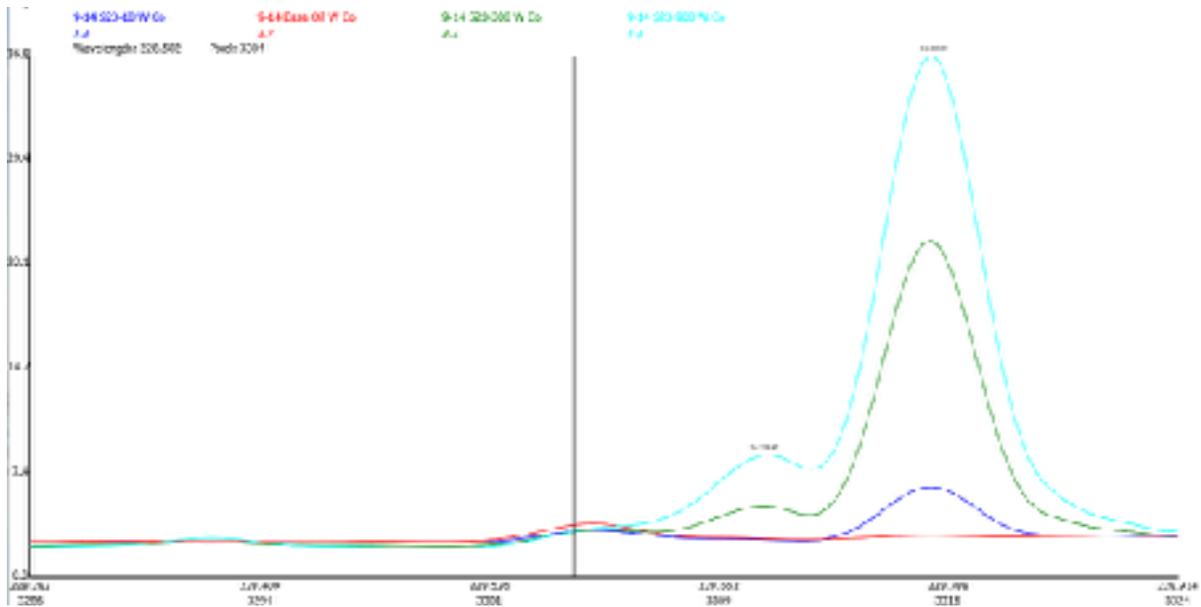
Although the Sn 228.67 nm line blocks the high wavelength side of the line for background correction, the lower wavelength side of the line is clean.

Effect of oil viscosity

The viscosity of an oil has a pronounced effect on the amount of sample consumed during the analysis as shown by the following pictures of the sample boat containing turbo oil (left) and kerosene (right).
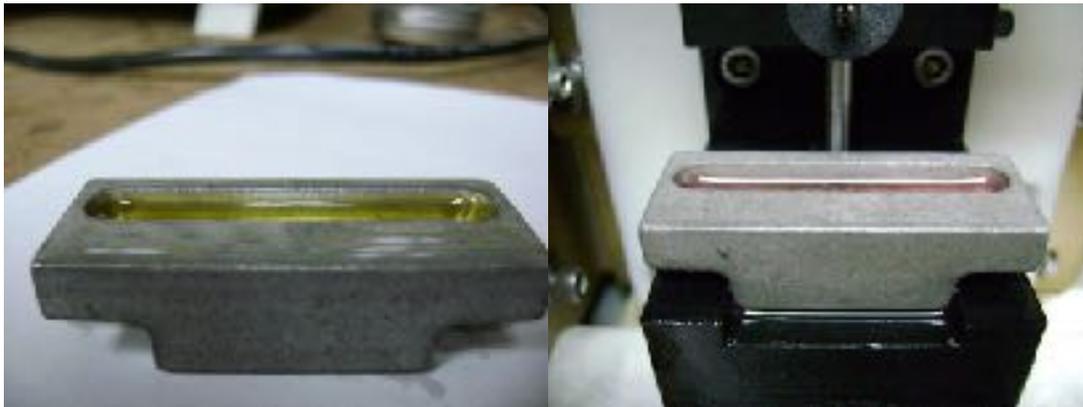
As the viscosity of the oil decreases, the amount of sample consumed increased which increases the particle densities of the elements in the discharge and directly resulting in higher analytical signals. As the amount of sample in the discharge has increased, however, more energy is taken from the discharge to atomize the matrix resulting in less energy available to excite the elements which reduces the signal based upon temperature but this is offset by the lower partition function which increases the signal. Also as the ratio of atoms to ions has changed, the effect is predicted to be different for every element.

Analytical signals with different oils

The following table shows the analytical signals obtained from different oil types where the signal from mineral oil has been normalized to 100%.

Sample	C 199.3 nm	CN 419.7 nm	H 486.1 nm	CH 485.8 nm	H 656.3 nm
Mineral Oil	100	100	100	100	100
Kerosene	88	104	110	123	104
Eastman Turbo	83	93	80	77	76
BP Turbo	86	92	80	77	76
Transmission	94	97	90	108	87
Electrode	69	42	0	8	2

Accuracy and precision for sulfur at 182.03 nm

The following table summarizes the results obtained for an accuracy and precision check for sulfur over the normal analytical working range.

S concentration in ppm	H internal standard	No internal standard
0	8 ± 10	-9 ± 11
100	111 ± 17	99 ± 19
500	489 ± 40	480 ± 27
700	684 ± 29	697 ± 20
1000	990 ± 16	1009 ± 9
5000	5033 ± 221	4984 ± 188
10000	10008 ± 45	9863 ± 165
20000	19879 ± 557	19378 ± 1141
50000	50689 ± 2646	50216 ± 1245

There is no significant difference between using hydrogen as an internal standard or not using an internal standard when

Using D19 calibration curves to analyze other oil samples

The following table summarizes the repeated analysis of turbo oil at the 30 ppm level over a period of one week.

Element	H internal standard	CH internal standard	No internal standard
Ag	38.7	42.5	33.1
Al	43.9	48.1	37.8

B	52.6	57.2	44.9
Cr	40.8	44.6	34.8
Cu	40.1	43.7	34.3
Fe	48.7	53.5	41.6
Mg	51.5	56.5	44.0
Mn	50.9	55.4	43.4
Na	40.3	42.5	33.4
Ni	43.4	46.5	37.6
Pb	48.8	52.5	42.1
Si	49.5	53.8	42.3
Sn	49.5	55.5	38.1
Ti	49.4	51.6	42.1
V	50.1	54.6	42.8
Zn	46.9	51.1	40.1

Form the above table, it is apparent that synthetic or turbo oil CANNOT be accurately analyzed using calibration curves generated using aviation or D19 oil. Indeed as the hydrogen content of these oils are different, the error is exacerbated if any hydrogen species are used as the internal standard. Although the ASTM procedure makes no mention of the validity of this approach, the requirement for the JOAP correlation program based upon the ASTM method does require this. The one saving grace of this is that as the procedure causes wear metal levels to read higher than they really are, it is ob1viously safer to react to a false positive and service the engine sooner than required by the engine manufacturer's specification.

If no internal standard is used, Turbo oil typically reads about 10-15% high. With hydrogen or CH as an internal standard, this error becomes 12-18% and 14-19% respectively. The signal increase is caused primarily because of the higher sample uptake rate and the shift between atom an ion lines is caused by an increase in

When no internal standard is used there appears to be cluster of results around 42 ppm and another around 34 ppm. The majority of the lines in the high concentration cluster are ionic analytical lines however some such as B, Pb and Si are related to changes in background structure between the two oil types. The lower cluster of lines is all atomic analytical lines. Al, Ni and Zn while being atomic analytical lies lie is areas of significant background structure which different between D19 and Turbo Oil. In addition to the phosphorus as phosphate detected in the Turbo oil, there is clearly oxygen in the sample and probably nitrogen. As most of the lines that fall outside of the normal atom and ion grouping are in areas where there are known bands of both oxygen and nitrogen species.

Although kerosene is normally analyzed using a different set of source operating parameters, kerosene was also tested using the same D19 calibration curves as used for the above analysis as it has become the practice to calibrate on mineral oil when analyzing fuel oils. The following table summarizes

the repeated analysis of kerosene at the 30 ppm level over a period of one week. The kerosene standards were prepared on a daily basis as it has been reported that these standards are not stable for more than few hours. However, at the end of the study, the sample prepared on day one and stored in a closed desk draw for the duration of the study showed no significant degradation.

Element	H internal standard	CH internal standard	No internal standard
Ag	25.2	25.9	27.1
Al	28.1	28.8	30.5
B	30.6	31.2	33.0
Cr	27.7	28.2	29.9
Cu	29.1	29.7	31.4
Fe	24.7	26.7	26.7
Mg	23.1	23.5	24.9
Mn	27.4	27.7	29.0
Na	27.7	27.4	29.0
Ni	26.0	26.4	27.7
Pb	27.8	28.3	29.6
Si	31.3	31.9	33.8
Sn	22.8	23.3	26.5
Ti	25.2	25.7	27.3
V	30.1	30.7	32.5
Zn	27.9	28.4	30.0

It is remarkable that the results of analyzing kerosene using D19 calibration oils are so close to the known concentration given that much more kerosene sample is consumed compared to D19 oils.

Generally the ionic analytical lines read lower than the ionic lines indicating that the ratio of atom to ion is higher in kerosene than D19 probably caused by an increase in electron density from the kerosene matrix as well as lower excitation temperature.

If a hydrogen based internal standard is used, the analytical results are only slightly lower than those obtained with no internal standard and the error is reasonably close to that expected from the difference in hydrogen concentration of kerosene compared to D19.

Analysis of Turbo oil using Turbo Oil calibration curves

If the data collected using the D19 curves is reprocessed using calibration curves established for Turbo oil, the correct answer is obtained for a 30 ppm standard regardless of the internal standard.

Element	H internal standard	CH internal standard	No internal standard
Ag	29.2 ± 0.4	29.6 ± 0.7	30.7 ± 0.5
Al	30.2 ± 0.8	29.4 ± 0.9	30.7 ± 0.6
B	30.2 ± 1.2	30.6 ± 1.5	30.5 ± 1.2
Cr	30.2 ± 0.8	29.7 ± 0.9	29.7 ± 0.7
Cu	29.5 ± 0.8	29.1 ± 0.8	29.8 ± 0.8
Fe	28.9 ± 1.1	28.7 ± 1.4	29.2 ± 0.8
Mg	30.0 ± 0.9	29.3 ± 1.0	30.5 ± 0.5
Mn	29.5 ± 0.9	29.2 ±0.3	30.0 ± 0.6
Na	28.7 ± 0.9	28.3 ± 0.5	29.0 ± 0.5
Ni	29.3 ± 1.1	29.1 ± 0.4	30.5 ± 0.5
Pb	29.2 ± 0.8	28.6 ± 1.9	29.3 ± 0.9
Si	30.9 ± 1.3	29.3 ± 0.8	30.2 ± 0.6
Sn	29.0 ± 1.3	29.2 ± 0.9	29.4 ± 0.7
Ti	29.7 ± 1.3	29.8 ± 0.7	30.4 ± 0.8
V	29.2 ± 0.9	29.8 ± 0.8	29.5 ± 0.8
Zn	29.1 ± 1.2	30.7 ± 0.8	30.5 ± 0.6

There is no significant difference in either accuracy or precision by the use of hydrogen or CH as internal standard or not using an internal standard.

Conclusions

.For accurate analysis of oil samples, the instrument MUST be calibrated using standards prepared in the same matrix as the oil type to be analyzed or falling that an oil of similar viscosity and chemical composition. This is not surprising as it the basis of all optical emission spectroscopy used for the analysis of metals using spark excitation such as steels, brass and alloys of magnesium and zinc using ASTM procedures. Optical emission spectroscopy using an ICP also uses a similar matrix usually dilute acid or organic solvent.

If the decision to service an engine is based purely upon the specification limit provided by a manufacturer, matrix matching is a requirement. It may be possible to determine correction factors for different oil types and such studies have been performed but at present no such table exists in the public domain.

If the purpose of the analysis is to provide a trend and engine service is triggered by a sharp rise in a wear metal, then a global calibration for all oils may be used for screening purposes provided that it is clearly recognized that the results are not accurate but are more of a semi-quantitative nature.

Suggestions for future revisions

In addition to fixing errors in the current procedures and clarifying the matrix requirements, the recommended wavelengths should be revised with the prevalent use of CCD detection in modern instrumentation.

As multiple wavelengths can now be used for analysis, the use of atom and ion pairs for elements such as zinc, calcium and magnesium would provide an immediate indication that the oil is of a different type to the calibration curves.

The use of multiple wavelengths for all elements allows for a statistical analysis to be performed on a single replicate which can only improve the accuracy.

A procedure for determining spectral interference corrections should be provided. Normal optical emission determines these factors as part of the regression analysis perform to calibrate the analytical line. However as the commercially available D19, S21 or S23 standards have all elements at the same concentration, this is not possible.