

SPECTRO REPORT

APPLICATION REPORT 69

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ANALYSIS OF OILS WITH THE SPECTROFLAME MODULA



ABSTRACT

This paper describes use of the SPECTROFLAME MODULA for the elemental analysis of oils. Very different fractions are obtained from the raw material oil during the refining process. All of these must be analyzed as to the elemental contents. Gasoline and motor oil are bulk products that must be constantly monitored. The analysis of motor oils for the contents of added elements and for trace impurities is one of the main application areas for ICP-OES. It is a matter of true mass analysis that must meet the requirements of: „high sample throughput“, „strong detection capabilities“ and „precision“.

The precision of the analysis of additive elements can be improved using simultaneously measured internal standards. The handling of samples and the analytical method decide whether or not the above mentioned requirements can be fulfilled. Good short- and long-term stability of the analytical instrument is an advantage as the number of repeat measurements and the frequency of standardizations can be reduced to a minimum.

Special usages are described in addition to the main application, „Analysis of Element Contents in Motor Oils“.

1. INTRODUCTION

The ICP-OES analytical technique is mainly used for environmental analysis. Most users also recognize that the ICP is utilized in the steel industry, for geology and in general for production control. Very few take the analysis of oils and products derived from oils into consideration. Strictly speaking, there is no material that is so frequently analyzed as oil and products derived from oil.

This appears, at first, to be improbable. However, consider the object of daily use, the „car“; it consists of approximately a ton of steel which is typically - and quite well - analyzed using spark emission spectrometry or ICP-OES. During the lifetime of a car, it consumes many tones of gasoline, oil, grease and hydraulic cooling liquid. In addition, it contains a given portion of plastic materials. All of these different products - derived from crude oil - are continually analyzed to ensure high quality. The analysis of these products is divided into approximately 2/3 organic analysis and 1/3 elemental analysis. The „classic“ analytical procedures for the elemental analysis of oils are: Flame AAS (FAAS), RFA, combustion analysis for the determination of the sulfur content and the rotrode technique ⁽¹⁾. ICP-OES is, however, the most flexible analytical method, because it is capable of analyzing multiple elements. Trace and main components can also be analyzed in a prepared sample at a high sample throughput rate.

In the last five to ten years the tendency towards higher quality requirements has lead to a clear increase in the number of analyses together with the range of elements to be analyzed. Thus, the highly efficient analytical method of ICP has almost completely replaced the „classic“ methods for the analysis of traces, secondary and main components. Only the analysis of wear metals in engine oils for the monitoring of the onset of abnormal wear has remained the domain of spark emission spectrometry with the rotrode technique (SPECTROIL).

2. THE OIL CYCLE

If one considers the state of oil from its origin as crude oil through the individual refining stages to the waste product of oil/oil sludge, then there are four stations to be described; each with different demands for elemental analysis.

Crude Oil

In its raw form (crude oil), the parameter „sulfur“ is particularly important. It is used to decide whether an oil is „sour“ or „sweet“. High sulfur contents in oil lead to corrosion on metallic surfaces and to the destruction of the catalysts used during refining. In addition to sulfur, the alkali elements and the elements vanadium, copper, nickel and iron, arsenic and phosphorous are of importance and determine the later use or processing.

High contents of these elements also lead to destruction of the precious metal catalysts used in the refining process. When analyzing these elements, there is no special demand on the precision of the measurement results; it is simply necessary to monitor the tolerance values.

The concentration distribution of various elements in crude oil represents a fingerprint of the oil and can be used to determine the origin of the oil. The following table shows examples of the element distribution for various oil sources. Again, the precision of the analytical result is not of special importance.

Table 1: Typical element contents in crude oil from different sources (in mg/kg) ⁽¹⁾

	Vanadium	Nickel	Iron
Alaska	55	1.4	0.5
Egypt	135	4.5	50
Indonesia	8	3.6	3.6
Iran	265	6.5	0.5
Venezuela	650	8.6	1.5

When researching new oil sources, the fingerprint of the oil found is an important indication as to whether a new oil field has been bored or an existing, nearby oil field has been tapped. Other elements, such as Cu, Mo and Na, are also used to fingerprint oil, in addition to V, Ni and Fe displayed in table 1.

The Refining Process

Crude oil is a complex mixture of hydrocarbons with different concentrations of metal ions and organometallic compounds that are decomposed during the refining procedure. The refining process is divided into four steps ⁽¹⁾:

- 1 Removal of undesired components (such as sulfur)
 - 2 Conversion of the various hydrocarbons into the desired molecular structure
 - 3 Separation of the various fractions during the refining procedure (e.g., paraffin, kerosene, diesel, gasoline, oil, etc.)
 - 4 Addition of additives (such as tetraethyl lead for leaded gasoline, or MoS₂)
- Note:* „Unleaded“ gasoline also contains lead in concentrations less than 5 mg/kg.

The following elements are important during the refining process and must be monitored during the steps listed above:

Potassium This element occurs naturally in crude oils, but can also be introduced through sea water. It is undesirable in automotive, heating, and jet fuels.

Selenium Mainly found in fossil fuels, esp. coal

Sodium Is contained in all crude oils. Like potassium, sodium is either naturally occurring or due to the addition of sea water. Sodium is a less desirable element that can contribute to the corrosion of metal surfaces and negatively influence the activity of catalysts.

Sulfur This element is also found in differing concentrations in practically all crude oils. Its occurrence is marked by unpleasant odors and corrosion, contamination of air and water and it interferes with the function of antiknock effectiveness in gasoline..

Tin Tin is frequently found in crude oils from Mexico. In general, higher contents are found in inferior crude oils.

Vanadium Is present in high concentrations in many crude oils. The vanadium content determines flow and viscosity of the oil. At high temperatures, all organic vanadium compounds are converted to vanadium pentoxide (V_2O_5). Vanadium pentoxide is very corrosive and damages turbine blades and other surfaces in combustion ovens during the combustion process. More detailed information about the analysis of vanadium, within the framework of „Online Analysis of Heavy Oils“ (see chapter 7.2), is presented in the final section of this application report. During the refining process, vanadium „poisons“ the catalysts used, leading to increased coke and gas formation with a lower yield of the desired distillates in the high melting point range. In addition, vanadium is the key component in the aqueous solution - known as „Stretford water“ - that is used to remove sulfur from crude oil.

Zinc The element zinc occurs naturally in crude oils; is, however, also added to all types of lubricating oils. As an additive, it has antioxidizing properties, thus preventing corrosion. Zinc also prevents mass fractions in oil and gives high load carrying properties.

The elements mention here and their characteristics in the refining procedure make the constant monitoring of these elements absolutely necessary. Special precision of the analytical results is only required for the additives, as an oil is characterized by the fraction of additives.

Additives

Additives that increase the lifetime as a lubricating material or that, like zinc, keep contamination in suspension or prevent corrosion, are mixed into many oils. The correct addition of the material must, of course, be monitored; i.e., the analytical results must be as precise as possible. Thus, the respective standard (ASTM D 4951) requires analysis with an internal standard.

Mineral Oils

The elements described below are important and are typically analyzed for the mineral oils:

Arsenic Arsenic is found in crude oils at $\mu\text{g}/\text{kg}$ concentration levels, but can be added as bactericides or anticorrosion agents. Arsenic poisons the catalysts in the refining process. In practice, determination of arsenic traces can only be conducted after previous extraction and preconcentration. Only concentrations in upper $\mu\text{g}/\text{kg}$ ranges can be determined with ICP-OES during determination in crude oil or in a heavy fraction.

Barium Barium is added to fuels and lubricating oils as detergent-dispersive additives. Other Barium components help to inhibit oxidation.

Boron Organic boron compounds are added together with organic lead compounds as anti-knock agents in combustion fuels.

Calcium Calcium functions as an indicator that sea water has been added to gasoline and other combustion materials. In lubricating oils, it is added to improve the lubricating properties and to disperse oil contamination.

Chromium .. Naturally occurring chromium is found with a concentration below 1 mg/kg. It is used as an antioxidant in combustion fuels.

Cobalt Cobalt can also be naturally occurring in oils, it is, however, often added in the form of cobalt chelates to lubricating oils and heating fuels in low concentrations to destroy mercaptan and to prevent its formation.

Copper is almost always found in crude oils. Its occurrence is often due to contact between the oil and copper alloys or to the addition of copper chloride for the removal of mercaptan. Copper also poisons the catalysts used in the refining process and has a destabilizing effect on some mineral oil products. It is also an important analytical parameter when examining wear metals in oils.

Iron Iron occurs naturally in oils. It can also appear due to corrosion of oil pipes and tanks. The concentration of iron should be as low as possible, because this element is also a catalyst poison. The element iron is also an important parameter for the analysis of wear metals in oil.

Magnesium .. When found in lubricating oils and heating fuels, then magnesium indicates contamination by sea water. In some oils, however, magnesium compounds are added as detergent-dispersives and to improve lubricating properties.

Manganese .. Manganese also occurs naturally in crude oils and can, like iron, occur due to the corrosion of metal surfaces.

Molybdenum This element occurs naturally as organic compound in crude oil. Its concentration depends on the geological conditions of the area where it was found. Molybdenum is used in sulfur removing catalysts and serves as an additive (e.g., MoS₂) for the improvement of lubricating properties in oils and greases.

Nickel Nickel appears at high concentrations together with the element vanadium in petroleum crude. Its appearance correlates with the depth and the age of the underground reservoirs. Nickel harms the catalysts.

Phosphorous Phosphorous occurs naturally or due to contamination in oils. It poisons platinum catalysts and is added to gasoline.

The analysis of the elements discussed here is important during production monitoring of lubricating oils. There are often a large number of samples to be analyzed, making the simultaneous analysis of trace, secondary and additive elements necessary. The only way to do this cost-effective, is to use ICP-OES. A high precision in the analytical results is required in addition to detection sensitivity. The analysis of these elements is discussed in this application report (section 4).

Wear Metals

Oils that have been used are examined for wear metals. This is less to characterize the quality of the oil than as a preventative monitoring for abnormal wear (motors, gears). In this case, the alloying components used in the drive units are of interest. In determinations of wear metals, the magnitude of the analytical value is of importance, because mainly tolerance values are controlled.

Waste Oil

Generally, all of the heavy metals must be analyzed together with the element chlorine in waste oils in order to determine, if combustion of the oil is permissible or if special waste treatment is required. Chlorine has an influence on the dioxin fraction in the waste gas. A limit of 1000 mg/kg is set for waste oils and 4000 mg/kg for combustion materials in the TOX 8010/8260 (SWA46, 9054) US EPA method⁽¹⁾. The element chlorine is normally determined using x-ray fluorescence analysis. The extended spectral range of the SPECTROFLAME MODULA enables simultaneous analysis of the element chlorine and other elements to be analyzed. The analysis of waste oil is described in detail in section 4.

3. INSTRUMENT DESCRIPTION

All measurements were conducted with an instrument of the type SPECTROFLAME MODULA, equipped as described in the following section. All optical systems that function in the UV/VUV range are enclosed in a vacuum tank that is filled with high purity nitrogen. This nitrogen filling is continuously circulated through a gas purifying unit by a pump. This ensures the best possible light transparency in the UV and VUV regions at all times. At the same time, the optical components in the tank are protected from contamination.

3.1 Spectrometer

The following system was used for this application: SPECTROFLAME MODULA (radial plasma observation), equipped with:

- 1 UV polychromator, wavelength range 120-336 nm, grating with 3600 grooves/mm
- 1 monochromator, wavelength range 210-460 nm, grating with 2400 grooves/mm
- 2 polychromator, wavelength range 210-420 nm, grating with 3600 grooves/mm
- 1 polychromator, wavelength range 270-790 nm, grating with 1800 grooves/mm

Up to 5 optical systems can be built into the standard SPECTROFLAME ICP. The instrument can be equipped with one UV spectrometer (either a UV polychromator or a UV monochromator) and a maximum of 2 monochromators. Every other combination of optical systems (simultaneous and sequentiell) is possible. Selection of the optical systems is conducted according to the customer-specific requirements. The distribution of the spectral range from 120 - 850 nm over multiple spectrometers enables the careful selection of optical components - particularly the grating. This is also true for the wavelength range and the light intensities for the detectors (electron multipliers, PM).

3.2 Instrument Parameters

Generator	free-running at 27.12 MHz
Gas flows	only argon
Power	1300 W
Coolant gas	12 l/min
Plasma/	
Auxiliary gas	2 l/min
Nebulizer gas	0.8 l/min

For special applications the instrument can be equipped with a gas mixing box to modify the plasma conditions with additional oxygen and argon (see also section 4 and 7: „Online Analysis of Heavy Metals).

Sample introduction:

peristaltic pump	2 ml/min
12 rollers	
	Viton tubing for sample introduction
nebulizer	crossflow (SPECTRO)
spray chamber	acc. Scott (SPECTRO)

The sample introduction system consists of the nebulizer, spray chamber and torch. The liquid sample is transported to the nebulizer by a software controlled peristaltic pump that can be operated at 5 different speeds.

When analyzing oil, it is important to make sure that all tubing connections are resistant to the solvents used (kerosene, xylene, toluol, n-hexane, etc.). The material has proven itself as the pump tubing material; PE or Teflon can be used for the connections.

All components in the sample introduction system are mounted on a user friendly mounting plate. Installation and removal of the mounting plate or individual components can be accomplished in less than three minutes.

3.3 Measurement Parameters

Because analyses using ICP-OES generally include multiple elements, it was not necessary to optimize the power and observation height for specific elements. The use of fiber optics to connect the optical systems makes optimization of the observation height for individual elements unnecessary, as a large section of the plasma is observed. The following measurement parameters for the spectrometer were used to obtain the analytical results:

Spectrometer	<ul style="list-style-type: none"> • simultaneous measurement at the positions of the wavelengths for the element being analyzed • integration time 10 seconds • 3 or 5 repeat measurements for calculation of the average
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3.4 Duration of the Analysis

The simultaneous analysis of 12 elements with the parameters listed above and a sample pre-rinse time of 45 seconds for stabilization of the measurement signal, requires ca. 75 seconds. With an additional background correction, the duration of the analysis may increase to 140 seconds, because of the time required to drive the entrance refractor to the position of the spectral background and measurement at the background position. The integration time given here refer to the simultaneous analysis of trace elements and additive elements. During routine analysis, an integration time of 5 seconds is often sufficient. The SPECTRO monochromator works with integration times of 3 or 5 seconds due to specially selected detectors.

A special analytical program, with which 21 elements (trace elements and additive elements) can be simultaneously determined, was developed for the routine analysis of lubricating oils. This method is described in section 4.

4. ANALYSIS OF OILS WITH SPECTROFLAME MODULA

The analysis of trace and main components in lubricating oils and the analysis of wear elements is described in the following section. Specialized applications, such as the analysis of chlorine in oil and the analysis of heavy oil, are also summarized.

In general, the following must be taken into consideration when analyzing oil:

1. The viscosity of the oil can vary greatly; it is important to select high dilution with typical solvents (e.g., kerosene, xylene, toluol) when possible. Highly pure „base oil“ can be used to adjust the viscosity of samples and standards.
2. The elements to be analyzed must be homogeneously distributed; it is important to stir/homogenize during sample taking and sample preparation. Even when taking samples, it is important to be sure of homogeneity.
3. The concentration range of the element contents to be determined in a sample may vary from ppm to percent; i.e., it is possible that not all of the elements are within the calibrated range - it is sometimes necessary to dilute twice. However, when the SPECTROFLAME ICP is used, it is possible to work with automatic line switch (sensitive/less sensitive analytical line). This often makes it unnecessary to conduct multiple dilutions.
4. Because of the many different oil products, it is not always possible to have comparable matrices; standard addition may be required in few cases.

Table 2: Analytical elements in oil samples

Wear metals	Contaminants	Additive elem.
Al, Cu, Cr Fe, Mo, Ni, Pb, Sn, Ti, V, Zn	B, Ca, Co, Cr, Cu Fe, K, Mg, Mn, Na, Ni, P, Si, S, Sn V, Zn	B, Ba, Ca, Mg Co, Mo P, Zn

There are, altogether, 21 elements that are important for the analysis of oil.

4.1 Typical Sample Preparation

All samples are weighed and diluted by weight. For the analysis of wear metals in oil, the dilution ratio 1:10 (sample:kerosene) is selected. Because precision is not of particular importance, the dilution is often conducted using an automatic dilution instrument (SPECTRO OIL Autodilutor). The precision of these autodilutors is not sufficient for the analysis of additives! In this case, automatic precision burettes can be used.

For the determination of additives in oil, a dilution ratio of 1:100 is typically used. Standards and samples are prepared and handled in the same way. Single or multiple element standards in oil are utilized for the calibration; e.g., CONOSTAN S 21.

A base oil is applied to adjust for differences in the viscosity. Base oil is a pure hydrocarbon mixture that can be obtained with varying viscosity. It is also used to prepare the blank sample, because it is not contaminated (should not be) by the elements listed in table 2.

Table 3: Preparation of standard samples and samples (here, the element boron, in accordance with E-DIN 51443-2)

Preparation of standards:
Parent Solution (S) = 1000 mg B/kg
Std 0 10 g base oil,
filled to 100 ml with e.g. kerosene
Std 1 0.100 g S + 9.9 g base oil,
filled to 100 ml with e.g. kerosene
Std 2 0.500 g S + 9.5 g base oil,
filled to 100 ml with e.g. kerosene
Std 3 1.000 g S + 9.0 g base oil,
filled to 100 ml with e.g. kerosene
Std 4 2.000 g S + 8.0 g base oil,
filled to 100 ml with e.g. kerosene
10.000 g sample (weigh exactly) filled to
100 ml with e.g. kerosene

The sum of the diluted oil is 10 g in every standard and in every prepared sample. This ensures that the viscosity is identical in every sample. The concentration range from 0 - 200 mg B/kg oil can be calibrated with these standards.

As seen in this example, it is important that the sample and standards (= parent solution + base oil) are diluted with the same ratio in order to obtain identical viscosities. When parent solutions with different concentrations are used, one step in the procedure becomes unnecessary: addition of the base oil.

Table 4: Preparation of calibration standards from parent solutions with different concentrations

Std 0	10.00 g base oil, filled to 100 g with kerosene
Std 1	10.00 g parent solution (c=100 mg/kg), filled to 100 g with kerosene
Std 2	10.00 g parent solution (c=500 mg/kg), filled to 100 g with kerosene
Std 3	10.00 g parent solution (c=1000 mg/kg), filled to 100 g with kerosene

If standards with different concentrations are available, it is not necessary to weigh the base oil and sample preparation time can be saved.

The following standards are often used:

- ASTM D - 4951-89 the analysis of additives in oils
- ASTM D - 5185 the analysis of wear metals in oil
- DIN 51391-3 the analysis of additives in oils

The DIN 51443-2 standard differs from the ASTM standards - for which all sample preparation steps are performed gravimetrically - in that the dilution to the end concentration is performed volumetrically.

Application reports for this can be obtained from SPECTRO (application sheet 89 „The Analysis of Wear Metals“). The analytical lines, the calibration ranges, the repeatability and the reproducibility for the respective measurements are given for ICP-OES in the ASTM's.

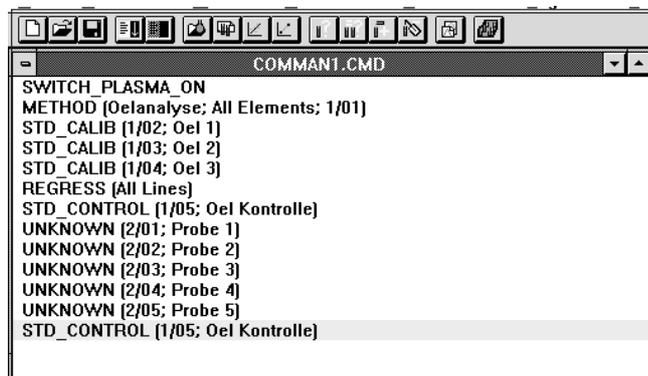
4.2 Analytical Procedure

Analytical sequences should include control samples that are analyzed after a defined number of samples or after a given time interval. During the measurement of control samples, an analytical value must be found again within given tolerances. If this is not the case, then the SPECTROFLAME ICP prompts for/conducts a standardization.

The SPECTROFLAME software makes it very easy to create automatic analytical sequences (measuring programs) using the „Command Editor“. It is also simple to create routines for quality checking (accuracy).



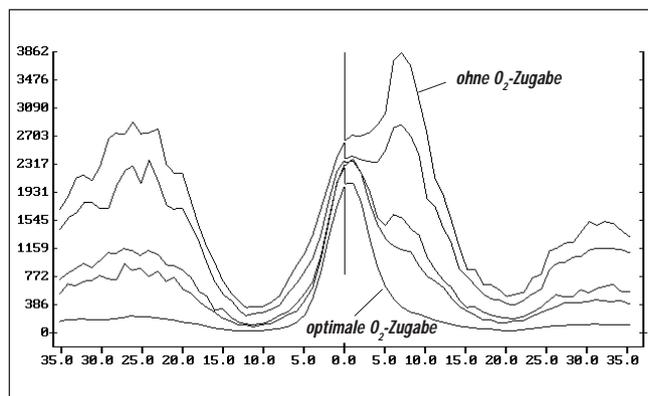
Pic. 1: Command Editor in the „Smart Analyzer“ SPECTROFLAME software - analytical sequence for the analysis of wear metals in oil



The solvent, kerosene, behaves similarly to aqueous solutions in the plasma. However, it is absolutely necessary to use a separate sample introduction system (SPECTRO mounting plate) for this application. Cleaning the nebulizer, nebulizer chamber and torch when the application is changed would require too much time. The detection limits that can be obtained for pure kerosene are comparable with the detection limits for water. They may, however, be considerably higher for some elements depending on the oil being examined. The reason for this is that the oils have different structures (heavy oil/light oil - different chain lengths for the carbon bonds).

Carbon causes many spectral interferences: C, C₂, CO and CO₂ lines appear in the short wavelength spectral region (<230 nm); CN, CH and C radical emission lines appear in the long wavelength spectral region (>300 nm). The main detection line for sodium (Na 589.592), for example, is disturbed by a carbon emission line, which negatively influences the detection limit. Pic. 2 (The addition of oxygen to the auxiliary gas) shows a spectral disturbance by carbon which can be almost completely „burned away“ by the addition of oxygen.

Pic. 2: Spectral disturbance of the Na 589 nm analytical line by carbon emission lines



4.3 Analysis of Trace Elements and Wear Metals

Wear metals in oils (gear oils) are periodically analyzed. Abrasion is caused by friction between working machine parts. The analytical results can be used to obtain information as to the condition of the mechanical components (gears, cogs, bearings). The analysis is a precaution measure that can be used to prevent great damage to the machine. For mobile use, the „SPECTROIL“ rotrode instrument can be used; for stationary use, the SPECTROFLAME MODULA.

4.3.1 Sample Preparation and Production of Calibration Standards

Sample preparation for the analysis of wear metals is, like other trace elements in oil, conducted as described in section 4.1. The dilution ratio is typically 1+9 (w/w). The alloying components of the mechanical parts and the chassis - on which corrosion may occur - are of particular interest for this type of analysis (Al, Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Si, Sn, Ti, and V). It may also be important to analyze some of the additives in the oil, in order to determine the quality of the oil used (B, Ba, Ca Mg, Zn, P). The incorrect oil can also be a cause of increased friction. The element sodium is also of importance, as it can be an indicator that water from the cooling system is leaking.

In order to ensure complete detection, the particle size of the metal should not be greater than 1 µm. This requirement is normally met by particles suspended in the oils used (see also the draft for DIN 51396-1 from September 1996).

Samples and standards are diluted with kerosene in a ratio of 1+9 (w/w). Because only the magnitude of the individual elements is to be determined, a simple 2-point calibration is sufficient.

Table 5: Production of calibration standards for the analysis of wear metals in oil (in g)

- parent solutions used:
CONOSTAN S 21 (90 mg/kg per element)
- base oil to adjust the viscosity of the blank solution
- dilution with kerosene: 1+9 (w/w)

	Base oil	S 21 CONOSTAN	Sum of oil
standard 1	10	0	10
standard 2	0	10	10

A base oil with a viscosity that corresponds to that of the lubricating oil should be selected. Both of the standards can be periodically analyzed as control samples during long measurement series (>30 minutes). The dilution factor does not need to be taken into consideration for the

calculation, because it is constant for samples and standards. Concentration information for production of the standard sample list is always based on the original oil. The repeatability of the analytical results for the control sample should lie within a tolerance of 10% relative. A long-term test using a control sample is displayed in section 5.

4.3.2 Calibration, Line Selection and Detection Limits

Detection limits found for a calibration for some of the elements analyzed in lubricating oils are displayed in table 6. The lines were selected in accordance with the ASTM standards or DIN standards respectively.

Table 6: Detection limits in lubricating oils

- detection limits are calculated from three times the standard deviation of the blank
- integration time: 10 seconds
- average from $n = 3$
- dilution from sample preparation: 1+9 (w/w)

Element	Line nm	Detec. limit (3s) mg/kg
Al*	308.215	0.15
Cd	228.802	0.06
Cr*	267.716	0.14
Cu*	324.754	0.15
Fe*	259.940	0.10
Mg	279.553	0.0045
Mn	257.610	0.015
Mo	281.615	0.3
Na	588.990	3.3
Ni	231.604	0.0
Pb*	220.353	0.6
Si*	251.610	0.45
Sn*	189.980	0.6
Ti	337.280	0.08
V	311.071	0.14
* Element selection according to DIN 51396-1 (draft)		

4.4 Analysis of Additive Elements in Oil Samples

When analyzing additive elements, it is important to know that there are two types of analysis: The analysis of samples that are used as additives in oils with high element contents of the individual elements (Ca, Mg, Zn, S, P at % levels) and the analysis of additives in oil samples (usually lubricating oils). The analysis of both types of samples can be conducted in the same way, they must simply be prepared with different dilution ratios. The addition of an internal standard is required for the precise determination of additive elements. The internal

standard is utilized to compensate for sample influences on the measurement results from the sample introduction system to the plasma.

Parent solutions (CONOSTAN, etc.) with internal standards (Y, Sc) that must be measured simultaneously with the analytes can be purchased. Typical standard deviations for $n=10$ repeat measurements lie between 0.1 and 0.3% depending on the concentration of the element being considered. A control sample must be analyzed after n sample measurement or after a given amount of time in order to control the applicability of the calibration. The main components (Ba, Ca, Mg, P, S, Zn) must be found again within a given tolerance interval of 5%, for example (see also repeatability in DIN 51391-3 and ASTM D4951-89). If these values are not found, then the instrument must be standardized. The stability of the analytical instrument is decisive for the frequency of the control sample measurements. A long-term test for several additive elements with the SPECTROFLAME MODULA is given in section 5.

4.4.1 Sample Preparation and Production of Calibration Standards

The samples and standards are diluted with kerosene in the same mass/mass ratio, as already discussed. Five point calibrations for the elements Ba, Ca, Mg, P and Zn and a three point calibration for S are used. A five point calibration is suggested in the DIN 51391-3 standard which considers only the elements Ba, Ca, Mg and Zn. The ASTM D4951-89 standard allows for individual calibrations. Thus, simply a proposal for a possible calibration is given in table 7. The contents of the elements to be analyzed generally lie in concentration ranges to 0.5% and are covered by the proposed calibration. The middle concentration standards can be used as control samples.

Table 7: Preparation of the oil standards for analysis of the additive elements (in g)

- standards used: - base oil
- CONOSTAN AM special
(5000 mg/kg of each: Ba, Ca, Mg, P, Zn)
- MERCK sulfur standard, dissolved in oil (10 g/kg)
- dilution with kerosene: 1:100 (w/w)

	White oil		Ba, Ca, Mg, P, Zn (AM special)	S	Sum
Stand. 1	10.000	+	0	0	10
Stand. 2	7.500	+	2.500	0	10
Stand. 3	5.000	+	5.000	0	10
Stand. 4	2.500	+	7.500	0	10
Stand. 5	0	+	10.000	0	10
Stand. 6	9	+	0	1.000	10
Stand. 7	5	+	0	5.000	10
Sample		10.000 g	0		10

The samples are diluted with a ratio of 1:100 (w/w) with kerosene. A supply of solvent (kerosene) to which the internal standard has been added should be made before beginning with the dilution, in order to ensure that there is a constant concentration of the internal standard (yttrium) in all samples. To do this, fill a solution of 2 g of the Y parent solution (1000 mg/kg) to 1000 g with kerosene. The Y concentration in the kerosene is then 2 mg/kg. Standards and samples are diluted with this.

Precision for weighing in of the sample should be 0.1 mg (see also DIN 51391-3).

4.4.2 Calibration

The analytical lines listed in table 8 are selected for the calibration. The analysis is conducted using background correction; the internal standard (yttrium) is measured simultaneously with the analytes. The integration time is 10 seconds.

Table 8: Analytical lines for determination of additive elements (in nm)

Element	Line
Ba	233.53
Ca	317.93
Mg	279.08
P	178.29
Zn	213.86
Y (internal standard)	371.03

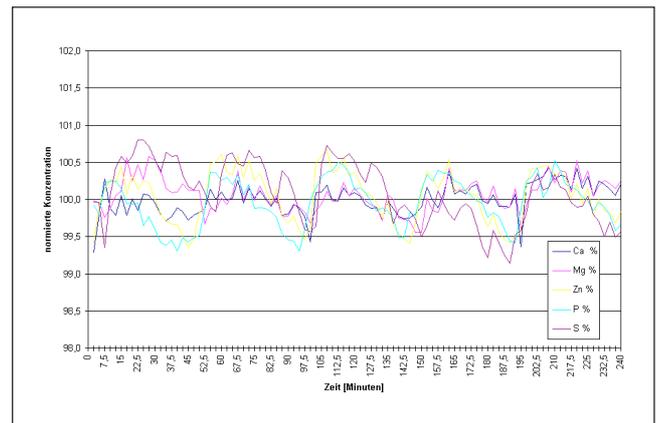
Calibration is conducted with the above mentioned standards after creating the method.

5. REPEATABILITY AND PRECISION

The results for a long-term test using two control samples are displayed in the following graphs: Pic. 3 additive elements and pic. 4 wear metals. The error bars for the individual measurement points give the pre-cision as relative standard deviation of the measurement. A very good precision - with an average of <0.3% for the additive elements concerned - is shown by the standard deviations of the analytical results.

Pic. 3: Long-term test (4 hours) for the additive elements: Ba, Ca, Mg, Zn, P and S

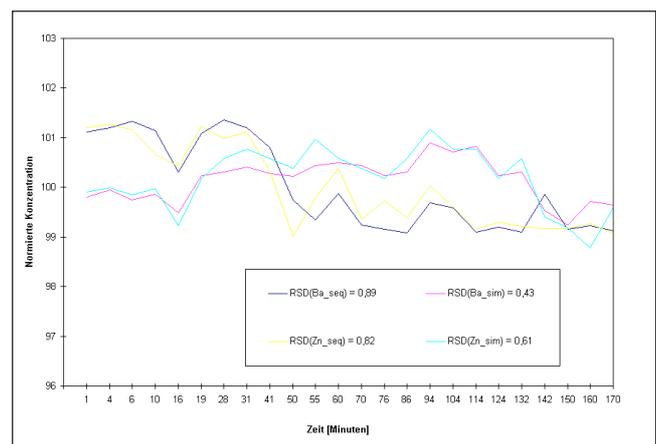
- sample preparation as described in section 4.4
- concentration of the analytes: 300 mg/kg
- dilution: 1:100 (w/w)
- integration time: 10 seconds
- average of n=5
- measurement with background and internal standard (Y)



An average relative standard deviation (RSD) of 0.3% was found for the elements concerned over a time period of 4 hours. The maximum relative deviation from the expected value of the control sample was 0.9%; i.e., it was not necessary to standardize during this measurement sequence, because, according to DIN 51391-3, a maximum relative deviation of 10% and, according to ASTM 4951 a relative deviation of 2-4% depending on the element, is permissible.

Pic. 4: Long-term test (2.5 hours) without internal standard for the elements: Ba and Zn

- selected analytical line: Ba 455.40 nm simultaneous and sequential; Zn 213.86 nm simultaneous and sequential
- element concentration: 50 mg/kg
- dilution: 1+9 (w/w) with kerosene
- integration time: 10 seconds
- analysis with background correction

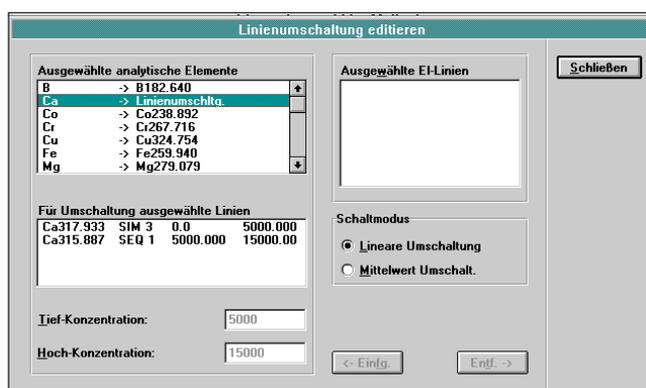


As shown in pic. 4, the relative long-term stability is <1% over a time period of more than 2.5 hours even without an internal standard. This is practically independent from whether the measurement is simultaneous or sequential. With its method of measuring on the positions of the analytical lines and the position set for correction of the spectral background (the same type of measurement as the polychromator), the „on-peak“ monochromator from SPECTRO also achieves a good long-term stability. The maximum occurring relative standard deviation of the analytical value from the expected value is 1.4%, i.e., even without an internal standard, it would not be necessary to standardize for the duration of an analytical time period of more than 2.5 hours according to DIN 51391-3 and ASTM 4951-89.

6. SIMULTANEOUS ANALYSIS OF TRACE ELEMENTS AND ADDITIVE ELEMENTS IN LUBRICATING OILS

Due to the modular construction and the free selection of analytical lines, it is possible to conduct the analysis of trace elements and additive elements (a total of 21 elements) in a sample. This enables the SPECTROFLAME MODULA to comply with the difficult requirements of high sample throughput, precise analysis of main components and good detection of trace elements. The additive elements are analyzed from a more highly diluted solution (1:100) than trace elements (1:10), as described in previous sections. If analyses are to be conducted with one-step dilutions, then it is necessary to have a separate line selection for the additive elements. If it is also taken into consideration that lubricating oils often display large differences in the concentrations of their contents (particularly true for calcium) for different applications, then it is necessary to work with an automatic line switch. A line switch within the analytical method is defined by the user and is dependent on the concentration. It ensures that the concentration being analyzed always lies within the linear region of the calibration function for the selected analytical line.

Pic. 5: Line switch in the „Smart Analyzer“ software for the SPECTROFLAME



A dilution factor of 1+14 was used for this analytical rule. The SPECTROFLAME MODULA's very good detection limits enables sufficient detection sensitivity for the trace elements even for this strong dilution. The frequently and often strongly changing concentrations of the additive elements can be precisely determined through correct selection of the analytical lines and the use of an internal standard.

6.1 Sample Preparation and Production of Calibration Standards

The samples and the manufactured parent solutions were diluted with kerosene in a ratio of 1+14 (w/w). The elements to be analyzed were separated into several groups for the calibration. This is necessary in order to avoid cross contamination due to impurities of the parent solution which is used in higher concentration. The calibration standards shown in Table 9 on page 11 were made-up

The internal standard is added directly to the solvent (kerosene) in order to simplify the sample preparation (5 g from a parent solution with a concentration of 1000 mg/kg yttrium in oil, diluted to 1 kg with kerosene).

Practically all normal lubricating oils can be analyzed from a single dilution using this calibration. The extensive calibration is necessary in order to enable interelement corrections for the element calcium. In high concentrations, calcium, has an influence on the other analytes. This „ionization influence“ is briefly described in the following section.

6.2 Interelement Correction

As explained above, calcium appears in the various lubricating oils (industrial oil, motor oil, marine oil) in very different concentrations. Thus, calcium becomes a component of the matrix and has an ionization influence that leads to results for the other analytes that appear to be lower than they really are. This is known as a line intensity suppression by the element calcium. This effect has been described for aqueous solutions in various papers^[I, III]. Examinations in oil matrices have led to comparable results^[III, IV]. The intensity suppression can be described by the following formula:

$$[\text{Formula 1}] \quad s = A \times [1 - e^{-Be}] \quad \text{Literature: I-IV}$$

where

s = the reduction in sensitivity of the analytical line (in relative %) (sensitivity is defined as the intensity/concentration unit)

A,B = constants to be determined for the analytical lines influenced by calcium

c = concentration of the element calcium in the sample

The functions shown in pic. 6 are obtained, for ex-ample, for the elements Cu, Fe, Mg, Mo, P, Pb. The spectral disturbance which occurs can be corrected using a multiplicative element correction based on the determined Ca concentration. Additive and multiplicative interelement corrections are components of the regression program in the „Smart Analyzer“ software for the SPECTROFLAME MODULA.

Explanation: *Multiplicative disturbances* are generated by matrix components that cause an increase in the spectral background and/or that influence the net signal intensity per concentration unit. *Additive disturbances* are caused by line overlaps between an analytical line and an emission line from a disturbing element.

In both cases, a correction function between the disturbing influence and the concentration of the disturbing element is calculated and used for the correction. The disturbing element(s) must be analyzed with the other elements.

The functions pictured above were determined for the individual analytical lines. A correction of the analytical result can be performed using the multiplicative disturbance calculation in the SPECTROFLAME software (ex-planation in the SPECTROFLAME ICP operation manual). For low calcium concentrations (e.g., 0-5000 mg/kg), a linear function for the correction can be a good approximation for correction of the analytical results or the calibration function. This is available in the regression program in the standard „Smart Analyzer“ SPECTROFLAME software. The calcium concentration and the analyte concentration must be varied with opposing concentrations within the standards for automatic calculation of the correction function (see description in the SPECTROFLAME ICP operation manual).

The screen printout on the following page shows the calculation of the size of the multiplicative disturbance of calcium on the analytical line for the element iron. The calculated factors are stored in the „Regression“ sub-program.

Pic. 6: Decrease in sensitivity due to the ionization effect of calcium [11]

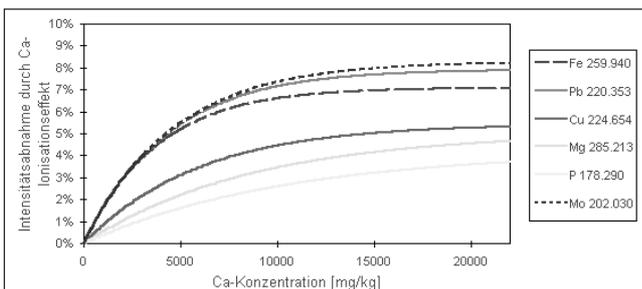


Table 9: Calibration standards for the simultaneous analysis of trace elements and additive elements in lubricating oils

El.	Std. 1 mg/kg	Std. 2 mg/kg	Std. 3 mg/kg	Std. 4 mg/kg	Std. 5 mg/kg	Std. 6 mg/kg	Std. 7 mg/kg	Std. 8 mg/kg	Std. 9 mg/kg	Std. 10 mg/kg	Std. 11 mg/kg	Std. 12 mg/kg	Std. 13 mg/kg
Ag	0											25	50
Al	0											50	100
B	0											100	200
Ca	0	500	2000	5000	10000	15000				250	0		
Cr	0											25	50
Cu	0											100	200
Fe	0											100	200
K	0									100	200		
Mg	0						250	600	1200				
Mn	0											50	100
Mo	0									100	200		
Na	0									100	200		
Ni	0											50	100
P	0						360	900	1800				
Pb	0											50	100
Sb	0											50	100
Si	0											50	100
Sn	0											50	100
V	0											100	200
Zn	0						400	1000	2000				

Pic. 7: Interference data for the multiplicative Ca disturbance on the Fe 259.940 nm analytical line

Here: for $c(\text{Ca}) = 1$, a concentration $c(\text{Fe})$ of 0.00116 is simulated for the Fe 259.940 nm analytical line

Interferenz Typ	Sperr.	Aktiv.	Lin. Fakt.	Lin. Fehl.	Quad. Fakt.	Quad. Fehl.
Ca	*	<input checked="" type="checkbox"/>	0.00116	0.0	0.0	0.0
Ca	*	<input checked="" type="checkbox"/>	0.0	0.0	0.0	0.0

In practice, the analytical method described here is used with calcium concentrations up to 15,000 mg/kg for the routine analysis of all normal lubricating oils. Using the SPECTROFLAME MODULA, 21 elements in a sample can be accurately and precisely determined within two minutes. Up to 250 unknown oil samples can be routinely analyzed during one work day (8 hours). In this case, the pre-rinse is 60 seconds, in order to wash out calcium with higher concentrations.

7. SPECIAL APPLICATIONS

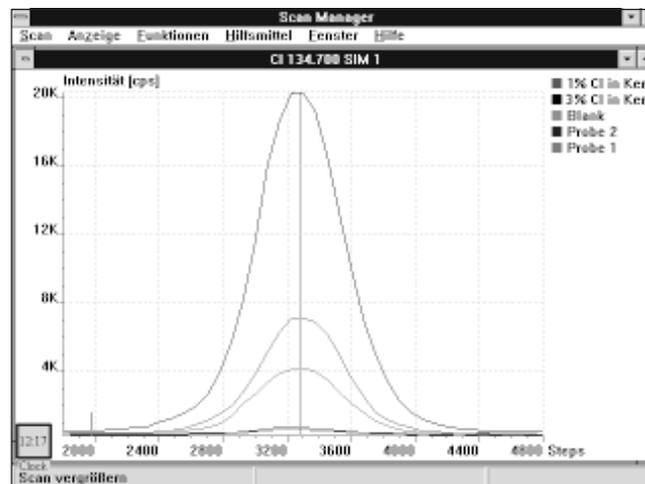
7.1 The Analysis of Waste Oils - The Analysis of Chlorine

The extended spectral range that can be achieved with the new VUV optics from SPECTRO make it possible to also analyze the halogens: Br, Cl and I. The element chlorine is of great importance when analyzing waste oils. Waste oils are often disposed in combustion facilities. The limiting value for chlorine lies at 1000 mg/kg. According to the TOX 8010/8260 (SWA46, 9054) US EPA3 method, a limiting value of 1000 mg/kg is set for waste oils and 4000 mg/kg in fuels.

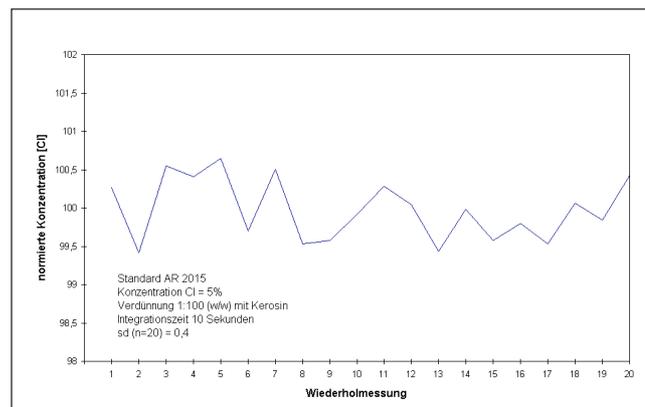
Traditionally, this analysis was conducted with XRFA. With the spectral range that has been extended to 130 nm in the VUV optic, it is now possible to monitor chlorine simultaneously with the heavy metals using the only sensitive analytical line for chlorine. In order to determine the limiting value of 1000 mg/kg Cl in waste oil, it is necessary to achieve a detection limit that is at least 5 times under the limiting value.

When the calculation of the dilution factor of 10 that occurs during sample pre-paration is taken into consideration, a detection limit of 20 ppm must be achieved for the sample solution. Detection limits <1 mg/kg can be achieved for the prepared sample with the SPECTROFLAME MODULA using the Cl 134.7 nm analytical line. Thus, it is very suitable for this application.

Pic. 8: Spectral environment for the Cl 134.7 nm analytical line in an oil matrix



Pic. 9: Repeatability of the analysis of chlorine in an oil sample

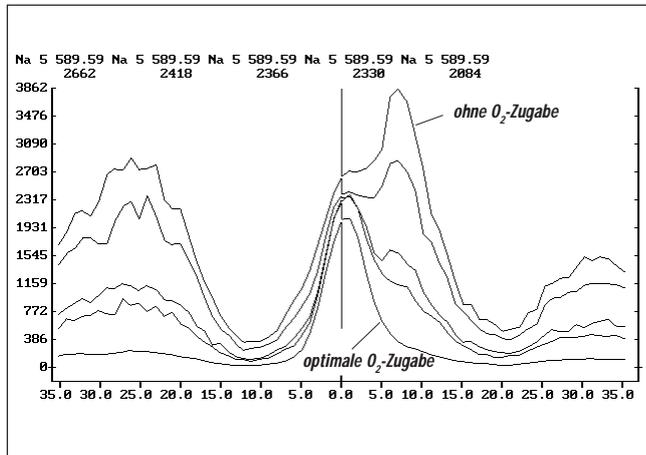


7.2 Online Analysis of Heavy Oils

There are applications for which the addition of oxygen is not sufficient for the achievement of the detection limits required for sodium (0.2 ppm). For the analysis of heavy oils that are used in combustion power plants, the contents to be analyzed lie in the range of 0.2 mg/kg Na. The detection limits should be a factor of 5 times lower. This is made possible by „cold blowing“ of the plasma. Like all of the alkali elements, sodium displays more intense emission at lower excitation conditions (see pic. 2: The addition of argon). The argon/oxygen must be correctly set for the respective application. Pic. 3 shows the optimization of this ratio, which leads to a detection limit of 0.02 mg/kg Na; a factor of 10 improvement in the detection limit.

All SPECTROFLAME ICP's can be equipped with an additional gas mixing unit that can be controlled with the standard software.

Pic. 10: Zusatz von Argon zur Abkühlung des Plasmas (Alkali-Bedingungen)

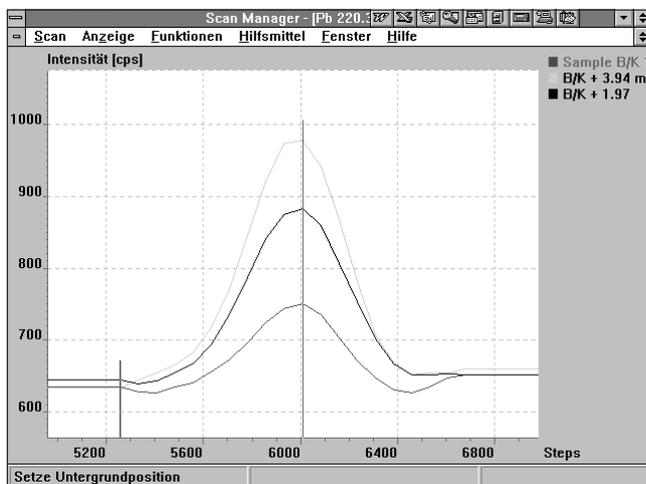


7.3 The Analysis of Lead in Gasoline

The analysis of the element lead belongs to the routine controls of gasoline for combustion motors. Unleaded gasoline has been mainly used for years in most European countries. However, unleaded does not mean that the gasoline contains no lead. The lead content must simply remain below the limiting value (5 mg/kg) and, therefore, it must be constantly monitored.

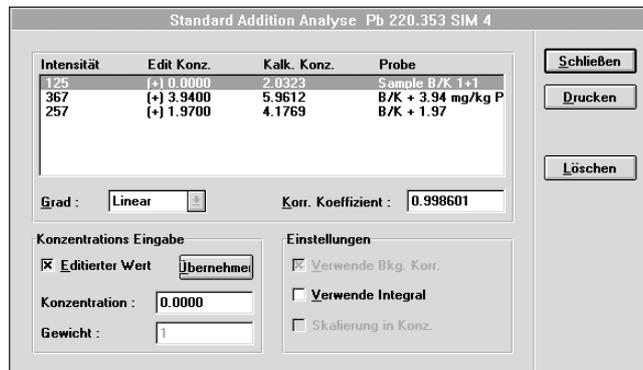
Pic. 11: Standard addition analysis of lead in super gasoline

- dilution: 1+1 (w/w) with kerosene
- modified measurement parameters for the SPECTROFLAME MODULA:
 - sample introduction rate: 0.5 ml/min
 - nebulizer gas: 0.5 l/min argon



Pic. 12: Standard addition analysis of lead (evaluation for pic. 9)

- sample: gasoline, diluted 1+1 (w/w) with kerosene



The added lead concentration is displayed under the heading „Edited Concentration“ - based on the original sample; the calculated concentration is displayed under the heading „Calculated Concentration“.

For the gasoline application, the SPECTROFLAME MODULA achieves detection limits (3s) of 0.3 mg/kg. Thus, a determination limit of 1 mg/kg is attained. This is entirely sufficient to monitor the limiting value of 5 mg/kg.

8. SUMMARY

From an analytical standpoint as well as an economic standpoint, the elemental analysis of oil and various oil products can only be effectively realized with an inductively coupled plasma (ICP). The abundance of oil products and the sometimes difficult sample handling require the flexible employment of the ICP. The sample introduction know-how and modification of the plasma gas are the deciding factors as to the application possibilities for ICP-OES.

The entire spectrum of known and described applications are available to the user of the SPECTROFLAME MODULA. From low boiling gasoline to heavy oils that lead to heavy decay under „normal“ plasma conditions for which practically all oil fractions can be analyzed with a low dilution ratio. The weak dilution of the sample enables high detection sensitivity for the analytes. The SPECTROFLAME generator’s high power reserves and the excellent plasma stability and the optical system enable usage of the SPECTROFLAME MODULA for online monitoring and high sample throughput during routine analysis.

9. APPENDIX: DETECTION LIMITS

9.1. Detection Limits in Kerosene (Aldrich)

Element	Line (nm)	DL (2s) $\mu\text{g}/\text{kg}$ Kerosene
Ag	328.068	2
Al	167.080	1.6
Al	308.215	14
Ba	455.403	0.2
Ca	317.933	2
Cd	228.802	2
Cr	267.716	2
Cu	324.754	2
Fe	259.940	2
Mg	285.213	0.6
Mn	257.610	0.3
Mo	202.030	2
Na	589.592	1.5 (#)
Ni	231.604	19
Pb	220.353	20
Sn	189.989	16
V	311.071	2
Zn	206.200	4

(#) using alkali conditions (SPECTRO)



9.2 Detection Limits in High Viscosity Oils

here in "Mobil Jet" oil (weight dilution 1+1 with Kerosene)

Elem.	Line (nm)	BEC	DL (2s) mg/kg Oil
<i>Dilution: 1+1 (W/W) with Kerosene</i>			
Ag	328.068	0.25	0.005
Al	167.080	0.21	0.004
Al	308.215	2.13	0.043
Ba	455.403	0.05	0.001
Ca	317.933	0.39	0.008
Cd	228.802	0.19	0.004
Cr	267.716	0.37	0.007
Cu	324.754	0.23	0.005
Fe	259.940	0.19	0.004
Mg	285.213	0.10	0.002
Mn	257.610	0.05	0.001
Mo	202.030	0.60	0.012
Mo	281.615	0.38	0.008
Na	589.592	4.42	0.088
Ni	231.604	0.84	0.017
Ni	341.476	5.12	0.102
Pb	220.353	3.35	0.067
Pb	168.220	30.2	0.604
Si	251.611	3.06	0.061
Sn	175.790	40.5	0.810
Sn	189.989	4.81	0.096
Ti	334.941	0.09	0.002
V	311.071	0.22	0.004
Zn	206.200	0.36	0.007
Zn	213.856	0.35	0.007

I Spark emission analysis using the rotrode technique, e.g., SPECTROIL.

II Literature:

M. Lukas, Spectro Inc. USA

Internal notes on the analysis of hydrocarbons.

III US EPA = United States Environmental Protection Agency.