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WHITE PAPER

SpectrOil — The Accurate and Dependable Choice for In-Service Oil And Fuel Analysis

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Introduction

The basis of modern oil analysis programs is the use of optical emission spectroscopy (OES) to measure the ppm (parts per million) levels of wear metals, contaminants, and additives in oil samples. Whatever an oil lab may need to measure, multi-elemental analysis is the core of an in-service oil analysis program. This paper gives an overview of Rotating Disc Electrode Optical Emission Spectroscopy (RDE-OES), its applications, and the SpectrOil Series family of products, which combine the latest innovations for increased performance and reliability with 30+ years of experience in military and laboratory applications.

Early Background

Sometime after World War II, the Denver and Rio Grande Railroad, now defunct, began analyzing diesel locomotive engine oil by looking at the spectral lines emitted by an in service oil sample when excited by a strong electric arc using carbon electrodes. Early tests proved that monitoring the elements attributed to wear and contamination provided early warnings of chronic equipment failure.

Elemental spectroscopy is the backbone of an oil analysis program as it is widely applicable to a closed loop lubricating system such as those found in gas turbines, diesel and gasoline engines, transmissions, gearboxes, compressors and hydraulic systems. In practice, an oil sample is periodically taken from a system and analyzed. The resulting data, when compared to previous analyses and allowable limits, may indicate a sound mechanical system showing only normal wear, or it may point out a potentially serious problem in its early stages. With this advanced warning, steps may be taken to correct the situation before serious damage or injury occurs.

Spectroscopic oil analysis works by detecting the fine particles generated by relative motion of metallic parts in an oil-wetted system. Contaminants are also detected and lubricant mix-ups, or badly degraded lubricants, are identified by the concentration of additive elements. Multi-element analysis, coupled with knowledge of the materials used to build the engine, often allows identification of a specific component in distress. Table 1 shows that typical metal elements can be analyzed by spectroscopy and their typical sources.

METAL	ENGINE, TRANSMISSION, GEARS	HYDRAULIC FLUID	COOLANTS
Aluminum Al	Pistons or Crankcases on Reciprocating Engines, Housings, Bearing Surfaces, Pumps, Thrust Washers	Pumps, Thrust Washers, Radiator Tanks,	Coolant Elbows, Piping, Thermostat, Spacer Plates
Barium Ba	Synthetic Oil Additive Synthetic Fluid	Additive	Not Applicable
Boron B	Coolant leak, Additive	Coolant Leak, Additive	pH Buffer, Anticorrosion Inhibitor
Calcium Ca	Detergent Dispersant Additive, Water Contaminant, Airborne Contamination	Detergent Dispersant additive, Water Contaminant, Airborne Contamination	Hard Water Scaling Problem
Chromium Cr	Pistons, Cylinder Liners, Exhaust Valves, Coolant Leak from Cr Corrosion Inhibitor	Shaft, Stainless Steel Alloys	Corrosion Inhibitor
Copper Cu	Either brass or bronze alloy detected in conjunction with Zinc for brass alloys and Tin for bronze alloys. Bearings, Bushings, Thrust Plates, Oil Coolers, Oil Additive	Bushings, Thrust Plates, Oil Coolers	Radiator, Oil Cooler, Heater Core
Iron Fe	Most common of wear metals. Cylinder Liners, Valve Guides, Rocker Arms, Bearings, Crankshaft, Camshaft, Wrist Pins, Housing	Cylinders, Gears, Rods	Liners, Water Pump, Cylinder Block, Cylinder Head
Lead Pb	Bearing Metal, Bushings, Seals, Solder, Grease, Leaded Gasoline	Bushings	Solder, Oil Cooler, Heater Core
Magnesium Mg	Housings on Aircraft and Marine Systems, Oil Additive	Additive, Housings	Cast Alloys
Molybdenum Mo	Piston Rings, Additive, Coolant Contamination	Additive, Coolant Contamination	Anti-cavitation Inhibitor
Nickel Ni	Alloy from Bearing Metal, Valve Trains, Turbine Blades	Not Applicable	Not Applicable
Phosphorous P	Anti-wear Additive	Anti-wear Additive	pH Buffer
Potassium K	Coolant Leak, Airborne Contaminant	Coolant Leak, Airborne Contaminant	pH Buffer
Silicon Si	Airborne Dusts, Seals, Coolant Leak, Additive	Airborne Dusts, Seals, Coolant Leak, Additive	Anti-foaming and Anticorrosion Inhibitor
Silver Ag	Bearing Cages (silver plating), Wrist Pin Bushings on EMD Diesel Engines, Piping with Silver Solder Joints from Oil Coolers	Silver Solder Joints from Lube Coolers	Not Applicable
Sodium Na	Coolant Leak, Salt Water and Grease in Marine Equipment, Additive	Coolant Leak, Salt Water and Grease in Marine Equipment, Additive	Inhibitor
Tin Sn	Bearing Metal, Piston Rings, Seals, Solder	Bearing Metal	Not Applicable
Titanium Ti	Gas Turbine Bearing Hub Wear, Turbine Blades, Compressor Discs	Not Applicable	Not Applicable
Zinc Zn	Anti-wear Additive	Anti-wear Additive	Wear Metal from Brass Components

Table 1: Typical source of elements analyzed by spectroscopy

Principles of Spectroscopy

Spectroscopy is a technique for detecting and quantifying the presence of elements in a material. Spectroscopy utilizes the fact that each element has a unique atomic structure, and when subjected to the addition of energy, each element emits light of specific wavelengths or colors. If this light is dispersed by using a dispersing element, such as a prism, a line spectrum will result. Since no two elements have the same pattern of spectral lines, the collected light can be analyzed and each element contained in the sample identified. Additionally, the intensity of the emitted light is proportional to the quantity of the element present in the sample, allowing the concentration of that element to be determined.

Figure 1: Emission Spectrum of Hydrogen

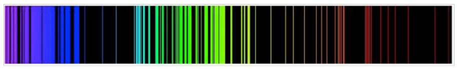

Figure 2: Emission Spectrum of Iron

These spectral lines are unique to the atomic structure of only one element. For the hydrogen atom, with an atomic number of 1, the spectrum is fairly simple (Figure 1). On the other hand, the spectrum of iron with an atomic number of 26 is much more complicated with many emission lines in the visible spectrum corresponding to the many possible electronic transitions that may occur (Figure 2). If more than one element is present in the sample, spectral lines of distinctively different wavelengths will appear for each element. These lines must be separated in order to identify and quantify the elements present in the sample. Usually only one spectral line among many is chosen to determine the concentration of a certain element. This line is chosen for its intensity and freedom from spectral line interference of other elements. To accomplish this, an optical system is required.

Rotating Disc Electrode Optical Emission Spectroscopy (RDE-OES)

Spectrometers that look at the multitude of spectral lines from a heated, or "excited," sample are called optical emission spectrometers. All optical emission spectrometers consist of three main components.

1. **Excitation Source** – introduces energy to the sample.
2. **Optical System** – separates and resolves the resulting emission from that excitation into its component wavelengths.
3. **Readout System** – detects and measures the light that has been separated into its component wavelengths by the optical system and presents this information to the operator in a usable fashion.

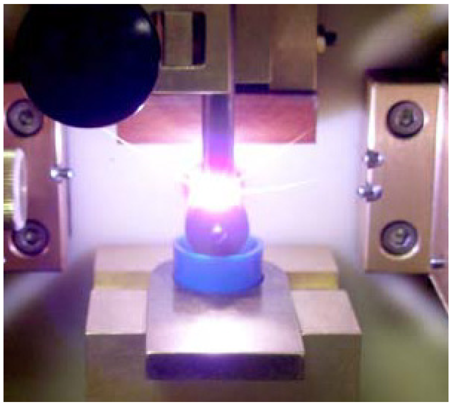

Figure 3: RDE spectrometer sample stand showing oil sample being "burned"

One typical method used in the excitation source in modern spectrometers is an electric discharge. The source is designed to impart the energy generated in an arc, or spark, to the sample. For oil analysis spectrometers, a large electric potential is set up between a disc and rod electrode with the oil sample in the gap between them. An electric charge stored by a capacitor is discharged across this gap creating a high temperature electric arc, which vaporizes a portion of the sample, forming a plasma. A plasma is a hot, highly ionized gas which emits intense light. The light given off as a result of this process contains emissions from all the elements present in the sample. These emissions can now be separated into individual wavelengths and measured using a properly designed optical system. Temperatures in the 5000 to 6000°C range are achieved and even difficult to excite elements emit enough light to be readily detected.

Since the early days of spectroscopic oil analysis, oil has been sparked, or "burned," between a rotating carbon disc electrode and a carbon rod electrode. The sample is placed in a sample cap, the disc is partially immersed in the oil sample and the disc rotates as the burn proceeds (Figure 3). This requires about 2 or 3 ml of sample, depending on the exact cap being used.

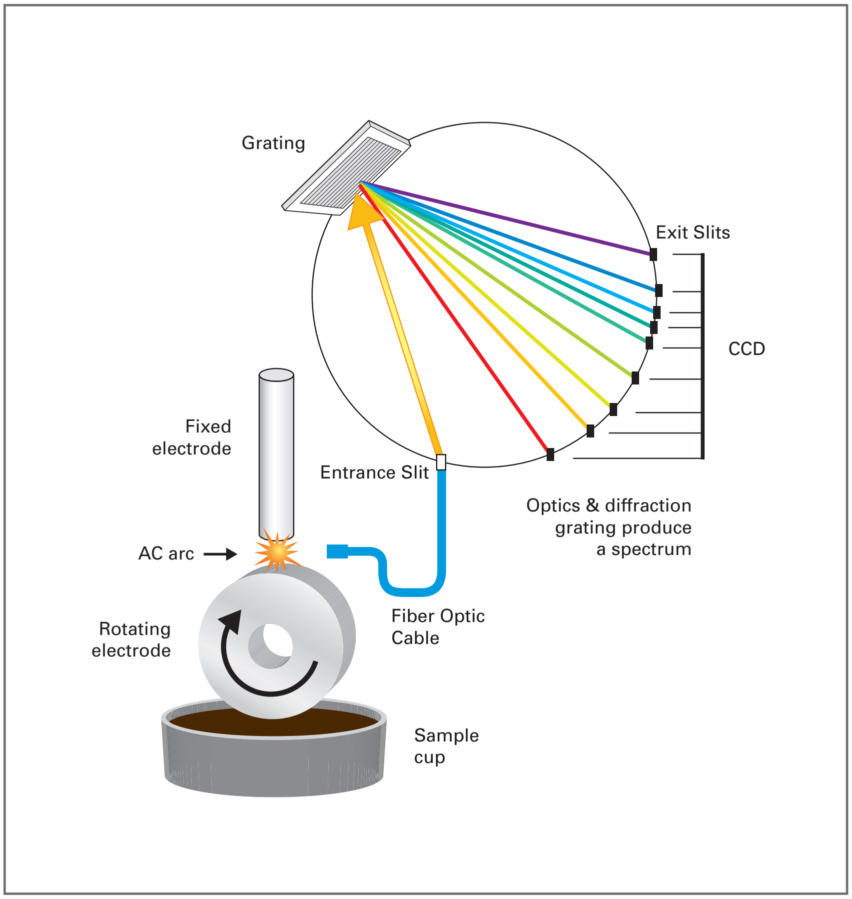

Figure 4: Schematic of a Rotating Disc Electrode Optical Emission Spectrometer for Oil Analysis

A fresh disc and a newly sharpened rod are required for each sample to eliminate sample carryover. This method is called rotating disc electrode (RDE) optical emission spectroscopy (OES), or combining the two, RDE-OES. Alternatively, it is referred to as RDE-AES, which stands for rotating disc electrode atomic emission spectroscopy.

The light coming from the plasma is separated by the optical system, in a spectrometer, into the discrete wavelengths that comprise it. An optical device called a diffraction grating, is used to separate the discreet wavelengths. The diffraction grating is a concave mirror with very fine lines on its surface that causes incident polychromatic light to be separated into component wavelengths and focused on an array of light detectors.

Figure 4 shows the major components of an oil analysis spectrometer using a polychromator optic, based on the Rowland Circle concept. Light from the excitation process, or the “burn,” exits the fiber optic cable and passes through the entrance slit, where it is concentrated on the diffraction grating by a lens. The entrance slit introduces light made up of all the elements present in the oil sample and defines the shape of the spectral lines at the focal curve after it is diffracted by the grating. The purpose of the grating is to separate, or “diffract,” this light into its component wavelengths. The spectral lines can be photographed or electronically quantified by photomultiplier tubes (PMTs) or charge coupled devices (CCDs).

The readout system of a spectrometer is typically controlled by an industrial grade processor and software. A clocking circuit and amplifier periodically read the charge on a Photo Multiplier Tube, or CCD chip, and convert it from an analog to a digital (ADC) signal to measure the light that has fallen on a pixel. The charge accumulated on a pixel is converted to an arbitrary number defined as “intensity” units. At the end of the analysis, the total intensities for each element are compared to calibration curves stored in memory, and are converted to the concentration of the element present in the sample (Figure 5). Concentration is usually expressed in parts per million (ppm). This information can either be displayed on a video screen, or printed. Once the analysis is completed and the results are recorded, the system is ready for the next analysis. The analysis results may be left on the screen, stored on the hard disk, or sent to an external computer.

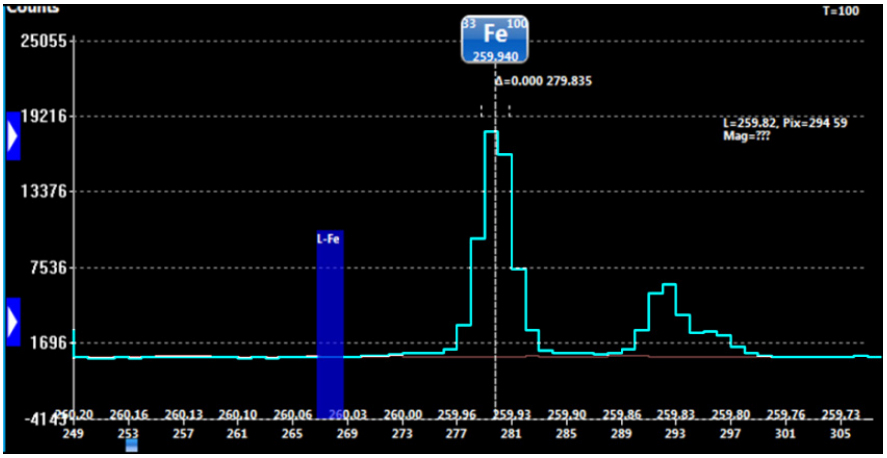

Figure 5: Readout system of an RDE-OES

SpectrOil Family of Spectrometers: The Market Leading RDE Spectrometers

RDE-OES spectrometers for used oil analysis continue to be the choice for elemental measurement. It has been more than 50 years since the technology was first used by railways and the military because of the instrument's ruggedness, reliability, and stability. Research and development continues with the technique, with major improvements in limits of detection, and long term stability, a result of new electronic hardware, software and optics. The latest innovations in these areas are incorporated into the SpectrOil 100 Series spectrometer, shown in Figure 6. This system has a very small footprint, and is easier to use than ever before, making it the solution of choice for lubricant, coolant, and on-site fuel labs within mining, power generation, and commercial laboratories. The SpectrOil is available in a variety of application specific configurations shown in the following table.

Figure 6: The SpectrOil 100 Series RDE Spectrometer

APPLICATION	110E	120C			120F
	BASIC ENGINE	STANDARD LUBRICANTS	EXTENDED OPTION	COOLANT OPTION	FUELS
Ag	0 - 900	0 - 900			
Al	0 - 900	0 - 900		0 - 50	0 - 500
As			0 - 100		
B	0 - 900	0 - 900		0 - 1,000	
Ba		0 - 5,000			
Bi			0 - 100		
Ca	0 - 3,000	0 - 5,000		0 - 50	0 - 500
Cd		0 - 900			
Ce			0 - 100		
Co			0 - 100		
Cr	0 - 900	0 - 900			0 - 500
Cu	0 - 900	0 - 900		0 - 50	0 - 500
Fe	0 - 900	0 - 900		0 - 50	0 - 500
In			0 - 100		
K		0 - 900		0 - 10,000	0 - 500
Li		0 - 900			0 - 500
Mg		0 - 5,000		0 - 50	0 - 1,500
Mn		0 - 900			0 - 500
Mo	0 - 900	0 - 900		0 - 500	
Na	0 - 3,000	0 - 5,000		0 - 10,000	0 - 100
Ni	0 - 900	0 - 900			0 - 500
P	0 - 3,000	0 - 5,000		0 - 2,500	
Pb	0 - 900	0 - 900		0 - 50	0 - 500
S					
Sb		0 - 100			
Si	0 - 900	0 - 900		0 - 500	0 - 300
Sn	0 - 900	0 - 900			
Ti		0 - 900			
V		0 - 900			0 - 500
W			0 - 100		
Zn	0 - 3,000	0 - 5,000		0 - 50	0 - 500
Zr			0 - 100		

Table 2: The SpectrOil 100 Series models and calibration ranges in ppm

Figure 7: SpectrOil M Series elemental analyzer

The SpectrOil M is a rugged and transportable system primarily used for military applications as specified by the DoD JOAP program (Figure 7). SpectrOil 110E is tailored to the specific requirements of engine monitoring, while the SpectrOil 120C fulfills the requirements of ASTM D6595, and is the default option for commercial customers.[1] The SpectrOil 120F for fuel analysis meets the requirements for ASTM D6728, and an additional L/D program is available to meet the specific low vanadium and alkali element limits required by GE Power systems gas turbines, per the GE- MTD-TD-002 specification. These systems are also used for coolant analysis and washdown water analysis.[2]

Advanced Software for Stability and Accuracy

SpectrOil Version 8 software includes recent innovations such as advanced signal processing and background correction capabilities for significant performance improvements. The system provides an intelligent method of measuring peak signals, resulting in a lower LOD by 2x for most elements (Table 3). Active alerts allow a user to know when results could be affected due to instrument drift. New Integrated Standardization is a more efficient workflow that saves time when measuring real samples. Finally, improved instrument self monitoring means better long term stability, so standardization is needed less often and results are consistent over time (Figure 8).

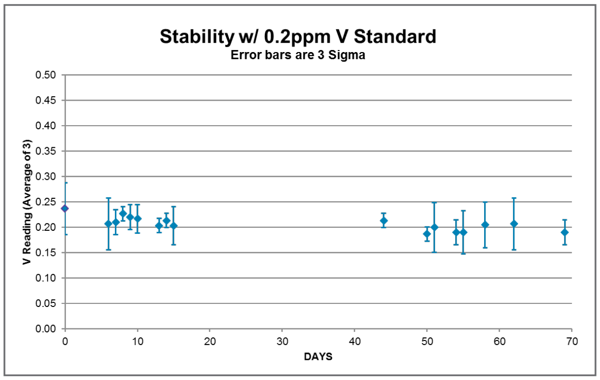

Figure 8: Measurement of a 0.2 ppm Vanadium base oil standard over 70 days at a power generation field laboratory

SpectrOil spectrometers provide exceptionally accurate and stable elemental analysis measurements for oils and fuels, making the technique the number one choice for laboratory managers and reliability professionals who require rapid results without sample preparation, gases, glassware or advanced training. SpectrOil analyzers are a natural fit for sites where time sensitive samples are generated and unpredictable sample volumes (frequently five samples, occasionally 100) are common. Consider that Formula 1 Race teams rely on this technology to support their cars, where time sensitivity, reliability, and sub-ppm changes in wear mean the differences between winning and going home (Figure 9).

Element	Typical LOD
Li	≤0.01
Ag	
Cu	
K	
Na	0.05
Cr	
B	
Ti	
Ba	0.1
Zn	
Ca	
Mn	
Ni	
Si	
Al	
Fe	
Cd	
Mg	
V	0.2
Mo	
Sn	
Pb	0.3
Sb	1
P	

Table 3: Typical 2-Sigma LOD (ppm) for SpectrOil calibrated with the CS-24 commercial oil analysis program. The Version 8 software and latest optics technology provide exceptional signal to noise and system performance.

Figure 9: McLaren and Mobil 1 use the SpectrOil 100 Series on the global F1 circuit (Ref: Mclaren)

Laboratories with consistent volumes can avail of the lower cost of sample processing with high accuracy and stability; also automatic sample processing can be justified. RDE spectrometers have always been difficult to automate due to the need to replenish the graphite electrodes after each analysis. The practical solution to RDE spectrometer automation is the SpectrOil M/R D2R2, which employs an integrated autosampler and two graphite disc electrodes (Figure 10).

A robotic arm in the sample changer automatically introduces each of the 48 oil samples in succession, at a rate of 80 samples per hour, without the need for sample dilution.

Figure 10: Robotics in SpectrOil M/R spectrometer

The entire automation system mounts to the spectrometer sample stand and fulfills all the functions of sequentially introducing and removing oil samples and exchanging graphite electrodes. It is self-contained and works independent of the spectrometer's operating software. Although operation is automatic, it also has the capability to manually sequence through each of the robotics' functions. The newer signal processing and optics hardware make this solution very appealing to commercial laboratories and dedicated support laboratories with consistent volumes.

CASE STUDY: Railroad Field Laboratory

Railroad and power generation companies with older EMD high horsepower diesel electric engines rely on spectrometric oil analysis to detect abnormal bearing wear in its early stages. These fleets standardize on a low zinc “locomotive oil” to avoid premature wear of bearings and bushings. A commerical oil laboratory placed a SpectrOil in a field lab at a railroad switching yard to support daily maintenance operations. In a summary report of the last three SpectrOil oil analyses Ag (silver) was detected at 2 ppm. This level is a warning alarm, prompting an investigation. In this type of engine, incorrect oil containing a zinc-based additive package can result in severe wear problems. Several components, such as wrist pin bearings, have silver coatings that corrode and wear in the presence of zinc. The early stages of the corrosive action cause by the zinc additive are indicated by the increase in the iron, copper, and silver wear metals. The SpectrOil analysis of other elements – magnesium, phosphorus and zinc helped provide a clue to the root cause of the wear, that the locomotive was topped off with incorrect engine oil. A recommendation was made, based on the analysis, to drain and flush the system, as well as observe correct top-off oil requirements. This particular fault would not have manifested itself this early by any other condition monitoring technique such as vibration analysis, thermography, ultrasound, or performance monitoring. Without oil analysis, the wear problem could have resulted in a bearing failure and a major overhaul, costing over $150,000. Nuclear power generation facilities that employ large diesel engines for emergency backup power look for the low detection levels of wear that the SpectrOil can proide also.

	Fe	Cu	Ag	Mg	P	Zn
30-Sep	19	10	0	0	0	3
23-Dec	21	10	0	0	9	3
23-Mar	27	13	2	107	75	90

Table 4: Spectroscopic results in ppm for an EMD medium speed diesel locomotive. A SpectrOil 110 E system is ideal for railroad field labs.

In summary, the latest innovations in Optical Emission Spectroscopy, shown in the SpectrOil product line, provide the best elemental analytical performance available today. The new optics and analytical features, combined with the known reliability and stability of the SpectrOil technology make it the ideal solution for elemental analysis in used oil and fuel analysis.

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