

OVERVIEW OF ROTATING DISC ELECTRODE (RDE) OPTICAL EMISSION SPECTROSCOPY FOR IN-SERVICE OIL ANALYSIS

Spectro Scientific

Introduction

The basis of modern oil analysis 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 else an oil lab may measure, a multi-elemental analysis is the core of in-service oil analysis. This paper gives an overview of Rotating Disc Electrode Elemental Spectroscopy and its use for in-service oil analysis applications.

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. Today, spectrometric oil analysis is widely applicable to any 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. The spectrometer analyzes the sample for trace levels of metals worn from moving parts as well as contamination and additive element levels. The resulting data, when compared to previous analyses and allowable limits, may indicate a sound mechanism 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.

Spectrometric oil analysis works because fine particles are generated by relative motion of metallic parts in an oil-wetted system. The lubricating oil may be thought of as a diagnostic medium because the oil carries with it the particles generated by the wear contact. Abnormal wear modes such as corrosion, abrasion, severe wear, spalling, etc., cause an increase in the concentration of wear metals in the oil. Contaminants are 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 of construction, often allows identification of a specific component in distress. Table 1 shows typical metal elements can be analyzed by spectroscopy and their sources.

So how does a spectrometer work?



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 in oil of the fluid. This data is taken using a Spectro FluidScan

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. When subjected to the addition of energy, each element emits light of specific wavelengths or colors. Since no two elements have the same pattern of spectral lines, the elements can be differentiated. 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. The light has a specific frequency or wavelength determined by the energy of the electron in transition. Since many transitions of different energy are possible for complicated atoms which have many electrons, light of many different wavelengths is emitted. If this light is dispersed by using a dispersing element such as a prism, a line spectrum will result.

These spectral lines are unique to the atomic structure of only one element. For the hydrogen atom with atomic number 1, the spectrum is fairly simple (Figure 1). On the other hand, the spectrum of iron with atomic number 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 possible choices is chosen to determine the concentration of a certain element. This line will be chosen for its intensity and freedom from spectral line interference of other elements. To accomplish this, an optical system is required.



Figure 1: Emission Spectrum of Hydrogen

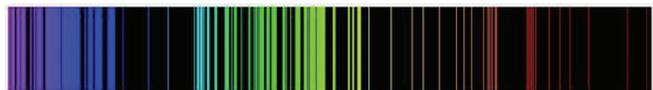


Figure 2: Emission Spectrum of Iron

Rotating Disc Electrode Optical Emission Spectroscopy (RDEOES)

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, these components are:

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.

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 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 hard 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. 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, RDEOES. Alternatively, one often sees it referred to as RDE-AES, 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 of which it is comprised. An optical device called a diffraction grating is used to separate the discrete 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.

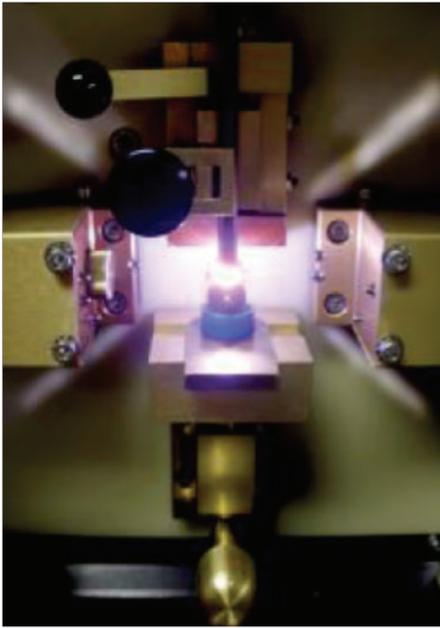


Figure 3: RDE Spectrometer Sample Stand Showing Oil Sample Being "Burned"

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 (burn) exits the fiber optic cable and passes through the entrance slit and 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 (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).

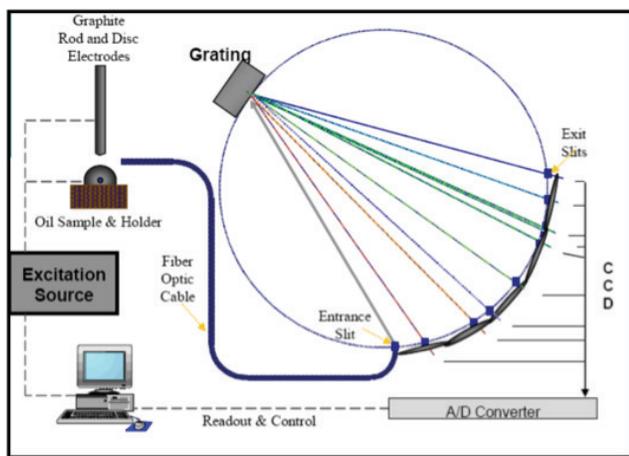


Figure 4: Schematic of a Rotating Disc Electrode Optical Emission Spectrometer for Oil Analysis

An important consideration when designing a spectrometer is the region of the spectrum where the wavelengths of interest occur. Many elements emit light in the visible region of the spectrum. However, there are elements that emit mainly in the Far Ultra Violet (FUV) region of the spectrum. This is significant because FUV radiation does not transmit well through air; rather, it is mostly absorbed. For the optic to see FUV spectral lines, it is necessary for the optical system to be mounted in a vacuum chamber or otherwise filled with gas transparent to FUV light, so the emitted light can reach the grating, be diffracted, and then be detected at the focal curve. Thus, a sealed chamber and a vacuum pump or gas supply system become part of the system.



Figure 5: A Direct Reading Oil Analysis Spectrometer from the 1970's

The readout system of a spectrometer is typically controlled by an industrial grade processor and software. A clocking circuit and amplifier periodically reads the charge on a Photo Multiplier Tube or CCD chip and converts it from an analog to 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. Concentration is usually expressed in parts per million (ppm). This information is displayed on a video screen or can be printed out on a printer. Once the analysis is completed and the results recorded, the system is ready for the next analysis. The analysis results may be left on the screen, stored on the hard disk, or can be sent to an external computer.

Older generations of spectrometers are heavy and bulky, such as the one in Figure 5, a Baird FAS-2C spectrometer from the 1970's, many

of which were deployed at various military bases throughout the world and were also installed on aircraft carriers. This was a rather large instrument with a one meter optic (the distance from the grating to the focal curve) and weighing about 800 lbs (364 kg). With original factory crating it weighed 1400 lbs (636 kg). It was hardly a field mobile instrument!

After decades of development and improvement, RDEOES today is much more compact and user friendly. Figure 6 shows the Spectroil Q100, which weighs only 163 lbs (74 kg) with a very small footprint while still maintaining the same analytical capability as the bigger systems in previous generations. Today, Spectro Inc.'s Spectroil M and Q100 are widely used in elemental analysis for lubricant, coolant and fuel for mining industry, power plants, as well commercial laboratories serving industrial plants for predictive maintenance and quality control. In addition, different performance enhancement options are available for special applications.



Figure 6: The Spectroil Q100 RDE Spectrometer

Automation: Automation for the RDE spectrometer has always been difficult due to the need to replenish the graphite electrodes after each analysis. The rod electrode, in particular, has been a challenge to handle by robotics, since it not only must be sharpened after each burn but also becomes shorter after each sharpening. The practical solution to RDE spectrometer automation is to use two graphite disc electrodes (Figure 7). This eliminates the need to sharpen electrodes and greatly simplifies operation. The automation system consists of two parts: a robot to exchange the consumable disk electrodes and an automatic sample changer. The robot dispenses new graphite electrodes for each analysis and removes the used ones. The need to set the analytical gap size has also been eliminated since the disk electrode shafts form a fixed gap. A robotics arm in the sample changer automatically introduces each of 48 oil samples in

succession, at a rate of 80 samples per hour and without the need for sample dilution.

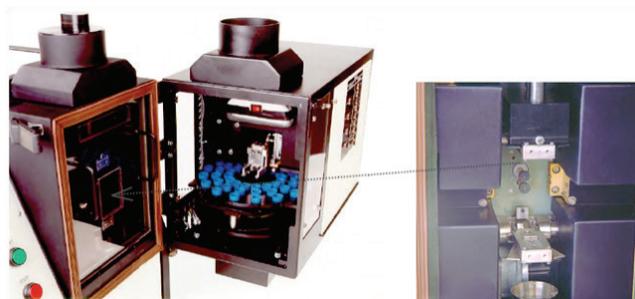


Figure 7: Robotics for RDE spectrometer

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 independently of the spectrometer operating software. Although operation is automatic, it also has the capability to manually sequence through each of the robotics functions. Automation also improves repeatability by eliminating operator variances and maintains cross unit correlation.

Large Particle Size Analysis Capability:

The ability to detect and quantify large wear and contaminant particles has been considered one of the shortcomings of spectrometers. Few will agree as to the actual detrimental impact on a condition monitoring program, but most will agree that the practical particle size limitation of spectrometers are at particles below 5 micrometers for ICP and AAS and at particles below 10 micrometers for RDE [1, 2]. Today, the particle size limitation of RDE spectrometers has been eliminated with simple ancillary systems such as the rotrode filter spectroscopy (RFS) method.

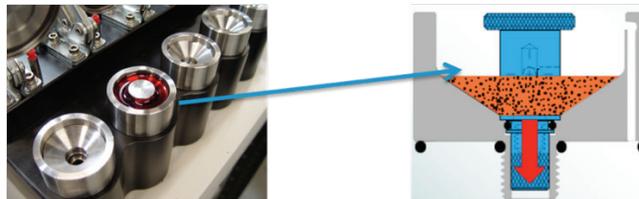


Figure 8: Automatic Rotrode Filter Spectroscopy (A-RFS) Fixture

Rotrode filter spectroscopy (RFS) makes use of the fact that the carbon disc electrodes used in rotating disc electrode (RDE) spectrometers are porous. A fixture is used to clamp the discs so oil can be drawn through the outer circumference of the discs when a vacuum is applied to the inside of the discs (Figure 8). The particles in the oil are captured by the disc. The oil is then washed away with

solvent, the disc is allowed to dry, and the particles are left on the disc electrode so they are vaporized and detected when run on the RDE spectrometer. It is a technique whereby the normal analysis of the oil sample serves to provide data on particles dissolved to 10 micrometer in size, and the RFS technique analysis provides data on large particles [3]. A multi-station fixture is used so a number of samples can be filtered at one time. Several commercial laboratories offer RFS to provide a more comprehensive analysis of used oil samples.

Extended Application Development: Although the RDE spectrometer is still designed primarily for used oil and fuel analysis, several methods and recent enhancements have increased productivity through expanded capabilities. They include the ability to analyze engine coolants, sulfur in oil and fuel, etc. A used coolant analysis program determines both the coolant condition and the presence of any contaminants or debris. The coolant fluid can be used as a diagnostic medium as the coolant carries heat away from the engine parts as well as fine debris from the interior surfaces of the cooling system. Analysis of the wear debris can provide important information about the condition of the internal parts of the cooling system.

Some machine condition monitoring programs have gone beyond used oil analysis and also provide data on the coolant system. The application of coolant analysis; however, has been limited due to additional cost and the time required to analyze the samples. Today, several major commercial oil analysis laboratories have switched to the RDE technique for coolant analysis. This was made possible with minor hardware and software modifications to the RDE spectrometer. It has been shown that the RDE technique correlates well with ICP and AAS techniques on new coolants and is more efficient on used coolants that contain particulates [4].

A case where the RDE spectrometer helped a big saving for a customer in one incident can easily demonstrate its value. A serious recurring problem in maintenance procedures is the use of an incorrect lubricant. A condition monitoring program can readily identify such problems through the analysis of the lubricant additive package and lubricant physical property analysis.

Lubricant mix-ups often occur when an oil system is "topped off" to replace the oil that has been lost due to use or leakage. Usually a small amount of incorrect oil in a large closed loop system presents few immediate problems. This is, however, not the case in certain diesel engines as illustrated by this example [5]. Table 2 is a summary of the last four spectrometric oil analyses for a medium speed diesel engine from a locomotive. Only the data for the most relevant elements are shown.

The data clearly show that after the first two samples, an incorrect

oil was used to top off the reservoir. The three additive metals, magnesium (Mg), phosphorus (P), and zinc (Zn), appear in the third analysis and increase in the fourth -- a clear indication that the oil formulation has changed. 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. A recommendation based on the analysis was made to drain and flush the system and to observe correct top-off oil requirements. This particular fault would not have manifested itself 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.

In summary, RDE Optical Emission Spectroscopy has come a long way and today has been widely used in many industries as a reliable tool to analyze fluid samples for condition monitoring and quality control applications.

	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
11-Jun	25	30	10	220	110	123

Table 2: Spectrometric Results in ppm for an EMD Medium Speed Diesel Locomotive

References

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