

A Guide to Spectroscopy for Used Oil Analysis

Overview

Evaluating the wear condition of equipment is a primary requirement of condition monitoring programs. Oil wetted equipment will generate wear particles throughout its lifetime, the nature and rate of the wear varies from initial break in through to end of life seizure. The technique employed to detect wear and its severity is 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. Typically these techniques get their names from the method used to excite the elements.



Techniques most commonly employed for oil analysis



The Spectro Scientific SpectrOil 100 Series spectrometer

■ ARC/SPARK/ROTATING DISK ELECTRODE SPECTROSCOPY (RDE)

A typical method used for 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 two electrodes. Two types are commonly used: fixed tungsten or silver electrodes; or disk and rod graphite electrodes. Both operate with an 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 that vaporizes a portion of the sample forming a plasma. The light given off as a result of this

process contains emissions from all the elements present in the sample.

These emissions can be separated into individual wavelengths and measured using a properly designed optical system. The graphite electrode (Rotating disk RDE) technique is widely used for oil analysis throughout the world, and is the standard for the United States Department of Defense Joint Oil Analysis Program (JOAP). JOAP has also been adopted by many different organizations who want to balance ease of use and ruggedness with multi-elemental analysis with lab quality results.

RDE Spectrometers can analyze up to 31 elements simultaneously in less than a minute without the use of solvents or gases. This ease of use, combined with repeatability of 3 to 6% RSD make it the practical choice for condition monitoring teams. Typically systems are placed in field workshops or less than ideal lab environments where they perform reliably for years.

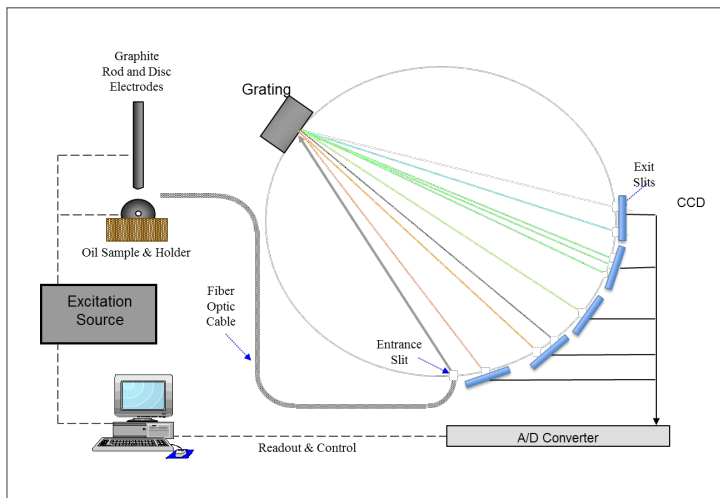
Another variation of this technique uses fixed tungsten or silver electrodes. This method is often used for flow-through systems where a number of different oil analysis tests are performed sequentially on an oil sample. The intent of these systems is to incorporate many different types of oil analysis tests with the goal of creating a complete picture of the oil condition including wear particles, chemistry, viscosity and contamination. These systems will typically sacrifice some repeatability and accuracy in order to prioritize ease of use in running a full suite of oil tests.

ADVANTAGES

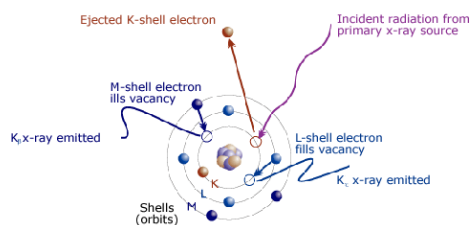
- Simple to operate
- Robust; operates in non-laboratory environment
- No sample preparation
- Readily available consumables
- Good sensitivity of wear metals up to 10 μm

DISADVANTAGES

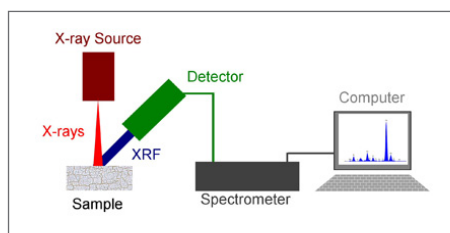
- Detection limit good for oils and fuels, not as low as ICP or AAS
- Matrix effect on some lubricants
- Repeatability poorer than ICP
- Requires separate calibration curve for blending quality control
- Inefficient on particles above 10 μm



Spectro Scientific MicroLab Series



Oxford Instrument
X-ray fluorescence
(XRF) spectrometer



■ X RAY FLORESCENCE SPECTROSCOPY (XRF)

Another approach for elemental analysis uses X-rays to energize the sample. X-ray radiation of a high enough energy will knock electrons out of the inner shells of elements. These vacancies are filled by electrons with a higher energy level. In order to move down to a lower energy level, these electrons lose energy in the form of emitted X-rays. These emitted X-rays have a specific energy typical of the element being analyzed. The intensity of X-rays produced is proportional to the concentration of elements present.

For routine detection of elements in oil analysis, energy dispersive XRF instruments are used. One common use of XRF is for maintaining quality control of new oils by checking the additives concentration. To prepare a liquid sample, a sample accessory is first made using mylar film stretched across both ends of a polyethylene cylinder, with care to place the oil sample in the cylinder before the top film cover is clamped on. It is then placed in the sample chamber and irradiated- the time is dependent on the settings and accuracy desired, however 3 to 5 minutes is routine. XRF compares very well with Atomic spectroscopy for additives in high concentrations, but spectroscopy remains the dominant choice when trace wear metals are employed and remain suspended in the oil.

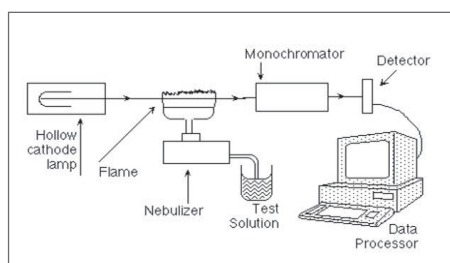
ADVANTAGES

- Minimum sample preparation
- Nondestructive
- Analysis of large wear particles
- Wide dynamic range for high concentration elements like additives
- Ease of use

DISADVANTAGES

- Poor detection limits for some key elements such as silicon and boron
- Penetration depth must be considered
- Several minutes test time
- Licensing requirements and additional safety training
- Matrix effects from oil and local environment need constant correction

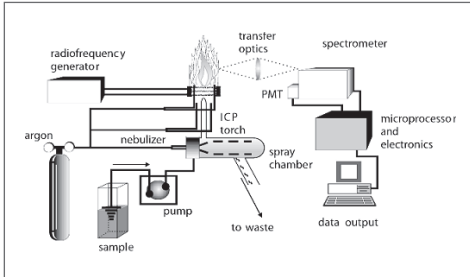
■ FLAME ATOMIC ABSORPTION SPECTROMETER (AAS)



PerkinElmer atomic absorption
spectrometer

An atomic absorption (AA) spectrometer is a low cost spectrometer with excellent sensitivity, often employed when only a few elements are monitored. This technique relies on atomic absorption- where a unique atom will absorb light at exactly those wavelengths at which they would emit light when they are excited. An oil sample is prepared by dilution with a solvent, or acid digestion, and this sample is atomized by a nebulizer and introduced into an oxygen-acetylene and nitrous oxide-acetylene flame. A radiation source, such as a hollow cathode ray tube, provides the light, usually for the element(s) of interest, and the light is directed through the flame to the detector. If none of the element is present in the sample, the amount of light going through the flame and being measured at the detector is maximum. As the concentration of the element of interest increases (from the oil sample) absorption occurs, and the detector signal decreases. If none of the element is present in the sample, the light passing through the flame is not absorbed and all the incident light is measured at the detector. AA spectrometers are capable of doing a good job analyzing typical elements of interest in oil samples, but they are rarely used for condition monitoring because they measure only one element at a time. Measuring the next element requires a change to the lamp being used and the process is repeated. They are designed to be operated by a trained lab technician who can rotate out the reference lamps, and prepare the solutions.

■ INDUCTIVELY COUPLED PLASMA SPECTROSCOPY (ICP)



Spectro Analytical Instruments
ICP optical emission spectrometer

Another type of spectrometer that is used extensively for aqueous solutions and also applied to oil samples, is the inductively coupled plasma (ICP) spectrometer. In this approach, argon gas flowing through a quartz tube (or “torch” in industry jargon) is excited to a very high temperature by a rapidly alternating electric current carried by a copper coil wound around the quartz tube. A plasma is a hot, highly ionized gas that emits intense light. The plasma is initiated by an electric spark that partially ionizes some of the argon gas.

The most common approach used by oil labs for routine oil analysis, is the “dilute and shoot” approach. An oil sample is diluted with kerosene (usually 9:1 kerosene to oil) and nebulized with a spray chamber to produce an aerosol spray. Only 1% of the sample is pumped to the torch and energized in the plasma. This technique provides for high accuracy and excellent repeatability (less than 3% RSD). However this technique can’t analyze particles larger than 5 microns. This requires additional preparation with microwave acid digestion. The time required to process samples (typically 2 minutes per sample) makes this technique unsuitable for manual loading, therefore Autosamplers are typically used. The technique is used most often in high volume analytical labs where clean argon gas and dedicated technicians, are readily available. Argon gas usage can cost in excess of \$1000 per month and can be supplied in either large Dewar tanks or bulk storage. The argon is in use (for optics) even when instrument is not in use. ICP spectrometers are workhorses but require a lot of maintenance. Sample volumes greater than 250 samples/day are essential to justify the high overhead costs required to maintain the system to a level of analytical readiness.

ADVANTAGES

- Lower detection limits
- Limited matrix effect
- Good accuracy & precision
- High throughput with automation
- Flexibility to test other materials

DISADVANTAGES

- Requires special gases
- Requires sample preparation for most lubricants
- Requires laboratory environment
- More complex to operate
- Inefficient on particles larger than 5 μm

Summary

There are many approaches to measuring wear metals in oil and each has its advantages and limitations. Always determine the range of interest, the wear metals desired, volume of samples and resources available before considering what solution to investigate.

Spectrometric oil analysis is applicable to any closed loop lubricating system, such as those found in diesel and gasoline engines, gas turbines, transmissions, gear boxes, compressors and hydraulic systems. In good practice, periodic oil samples are taken from the equipment being monitored. The spectrometer chosen needs to be able to analyze the sample for trace levels of metal worn from moving parts, as well as for extraneous 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. When considering a spectrometer to measure wear metals consider the following:

- The variety of elements, contaminants and additives sourced from the variety of equipment and oils you are trying to measure.
- The ranges and performance of those elements you need to measure
- The number of samples you will need to test on a given day, month or year.
- The human resources you have available to maintain and operate the instrument
- The running costs and reliability over time