# GNR RotrOil - Monitoring wear metals, additives and contaminants in diesel engine oils

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## Introduction

The analysis of wear metals contaminants and additives in used lubricating oils is a valuable diagnostic tool enabling a preventive maintenance program of engines and machinery to avoid sudden failures, high costs due to production downtime and maintenance.

The identification of different elements and the determination of their concentration provides valuable and timely indications of the possible criticalities of the different components of an engine

Modern lubricating oils are a complex mixture of organometallic compounds added to the base oil to improve anti-wear and anti-oxidative characteristics, the progressive decrease in their concentration can lead to the loss of lubricant characteristics to the point of catastrophic consequences.

On the other hand, during the exercise of the engine, the concentration of metal particulate matter produced by wear, increases as a function of the time (Annex 1).

GNR RotrOil provides precise, accurate and fast information about all these needs by direct simultaneous analysis of wear metals, contaminant elements and additives in lubricant oils.
Principle of operations of RotrOil Analyzer is based on Rotating Disc Electrode Atomic Emission Spectroscopy (RDE-AES) and it is compliant with ASTM D6595 norm.

## Summary of test method

Exhaust oil specimens are analysed directly without any sample treatment or dilution.
The sample, contained in a 2 ml plastic container it is placed under a dual electrode system made of a graphite rod electrode and a rotating disc electrode.
The latter, in contact with the oil sample, when rotating, brings the metal particles into such a position that they can be excited by the arc generated between the two electrodes.
The solid particles dispersed in used oils are then excited and the intensities of characteristic emission lines from excited elements are collected and compared with a calibration curve to return simultaneously the concentration of each element

## Equipment

GNR RotrOil spectrometer is compliant with the requirements of ASTM D6595 “Standard Test Method for determination of Wear Metals and Contaminants in used lubricating oils or used hydraulic fluids by Rotating Disc Electrode Atomic Emission Spectrometry.”
The unique large focal length of RotrOil provides highest resolution, assuring better selectivity and specificity.
The direct light path between the sample and the optical system (no fibre optic), its large dynamic range, allows the element detection from sub-ppm to %, with high precision and accuracy.


## Method

### Reagents and Materials

To avoid any possible contamination, disc and rod Electrode are made of high-purity graphite (spectroscopic grade).

Calibration of the spectrometer has been performed with:

- Base Oil, a 75 cSt Hydrocarbon base oil (VHG LGC) free of analytes to be used as a calibration blank or for blending calibration standards;
- oil-based multi-element standards with certified values of metals VHG V-21+K up to 900 mg/kg (containing Ag, Al, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sn, Ti, V and Zn).
- Metal Additives Standard VHG MA4 with certified values of Ca (5000 mg/kg), Mg, P, Zn (1600 mg/kg) combined in hydrocarbon oil

Table 1. Samples of tested oils

| Sample | Time (h) |
|---|---|
| Fresh oil 5W-40 Diesel oils | 0 |
| 1_USED 5W-40 Diesel oils | 2 |
| 2_USED 5W-40 Diesel oils | 22 |
| 3_USED 5W-40 Diesel oils | 57 |
| 4_USED 5W-40 Diesel oils | 76 |
| 5_USED 5W-40 Diesel oils | 99 |
| V21+K_10 (10 mg/kg) | - |
| V21+K_100 (100 mg/kg) | - |

Engine oils SAE 15W40 from a diesel engine test trial were taken at different operating times. (Table 1)
V21+K Wear Metal Standards at 10 mg/kg and 100 mg/kg were analysed as check standard samples (Table 1).

### Sample and standard preparation

The used oil sample was placed in a heated ultrasonic bath (60°C) to break down the clusters of the largest particles and bring them back into suspension. Then, it was vigorously shaken prior to pouring a test specimen for analysis.
To verify the instrument calibration, the check standards have been tested.

## Results

The results of the sample analysis are resumed in Table 2.
The goal is to show a timely dependant trend of wear metal and additive concentrations in the set of engine oils used for testing a new diesel motor. Each sample was measured in triplicate and average values with their standard deviation are reported. The median of Relative Standard Deviation ($RSD_m$) for the wear metals in the used oils was calculated.
The $RSD_m$ is 8% for concentrations lower than 5 mg/kg, 6% for concentrations between 5 and 10 mg/kg and 3% for concentrations larger than 10 mg/kg. The recovery of expected values was better than (100±5) % and (100±10) % for 100 and 10 mg/kg check standards, respectively.

Although ASTM D6595-17 expects detectability in low mg/kg range for most elements, the RotrOil is capable to measure, with suitable sensitivity, even lower concentrations and their variation with the time, as shown in Table 2 and Figure 1.

Table 2. Concentration (mg/kg) of elements in oils with increasing usage time.

| Sample | Fresh Oil | 1_USED 5W-40 | 2_USED 5W-40 | 3_USED 5W-40 | 4_USED 5W-40 |
|---|---|---|---|---|---|
| Time (h) | 0 | 2 | 57 | 76 | 99 |
| Ag | 0.0 ± 0.0 | 0.2 ± 0.2 | 0.5 ± 0.1 | 1.1 ± 0.1 | 2.6 ± 0.1 |
| Al | 1.5 ± 0.9 | 1.9 ± 1.6 | 3.1 ± 0.1 | 5.0 ± 0.5 | 6.5 ± 0.7 |
| B | 71.9 ± 2.6 | 68.9 ± 3.6 | 55.0 ± 1.0 | 53.5 ± 1.3 | 56.8 ± 3.1 |
| Ba | 0.9 ± 0.2 | 0.9 ± 0.2 | 0.7 ± 0.2 | 0.8 ± 0.2 | 1.4 ± 0.1 |
| Ca | 3303 ± 86 | 3318 ± 49 | 3224 ± 41 | 3281 ± 106 | 3392 ± 27 |
| Cd | 0.2 ± 0.0 | 0.0 ± 0.0 | 0.1 ± 0.0 | 0.1 ± 0.0 | 0.1 ± 0.0 |
| Cr | 0.9 ± 0.4 | 2.1 ± 0.4 | 3.4 ± 0.2 | 7.9 ± 0.6 | 7.1 ± 0.4 |
| Cu | 0.0 ± 0.1 | 1.2 ± 0.1 | 2.2 ± 0.1 | 6.9 ± 0.3 | 12.0 ± 0.2 |
| Fe | 0.9 ± 0.2 | 22.9 ± 0.7 | 43 ± 1 | 115 ± 3 | 128 ± 3 |
| K | 2.8 ± 0.6 | 3.8 ± 1.8 | 2.8 ± 0.5 | 4.2 ± 0.7 | 6.7 ± 0.2 |
| Mg | 20.0 ± 0.7 | 31.4 ± 0.7 | 22.9 ± 0.4 | 30.9 ± 1.6 | 28.2 ± 0.1 |
| Mn | 0.0 ± 0.0 | 0.9 ± 0.1 | 0.6 ± 0.1 | 3.7 ± 0.2 | 5.2 ± 0.3 |
| Mo | 46.8 ± 1.8 | 45.6 ± 1.1 | 40.6 ± 0.6 | 39.8 ± 0.8 | 39.8 ± 0.9 |
| Na | 5.8 ± 0.5 | 7.0 ± 0.5 | 7.0 ± 0.6 | 8.6 ± 0.7 | 10.2 ± 0.3 |
| Ni | 0.9 ± 0.1 | 1.2 ± 0.1 | 2.6 ± 0.1 | 3.1 ± 0.1 | 6.2 ± 0.3 |
| P | 1197 ± 18 | 1199 ± 20 | 1101 ± 32 | 1050 ± 14 | 1080 ± 9 |
| Pb | 0.5 ± 0.4 | 1.2 ± 0.5 | 1.7 ± 0.3 | 3.1 ± 0.1 | 2.4 ± 0.3 |
| Si | 6.3 ± 0.4 | 8.6 ± 0.6 | 15.5 ± 0.4 | 18.5 ± 0.9 | 44.2 ± 2.4 |
| Sn | 0.3 ± 0.4 | 1.5 ± 0.9 | 3.1 ± 0.3 | 8.3 ± 0.4 | 7.5 ± 0.8 |
| Ti | 0.3 ± 0.0 | 0.3 ± 0.0 | 0.3 ± 0.0 | 0.3 ± 0.0 | 0.3 ± 0.0 |
| V | 3.0 ± 0.1 | 3.0 ± 0.2 | 2.7 ± 0.4 | 2.3 ± 0.1 | 2.7 ± 0.2 |
| Zn | 973 ± 55 | 1033 ± 52 | 914 ± 18 | 875 ± 14 | 875 ± 57 |

Fe, Ni, Cr concentration increased over time indicating possible wear of a number of components such as piston rings, ball/roller bearings or gears. Iron and nickel show a different trend from Cr, which could be related to a different origin. Aluminium could realistically come from piston or push rods.

The concentration of Si and Al shows a common trend: this would suggest that both silicon and aluminium are wear metals coming from piston Si-Al alloy.
Copper, tin and lead could come from bushings or bearings, thus showing that the increasing amount of each wear metal can have different causes or origins.
Additive elements in oil such as P, Zn, B and Mo shows a slow but constant concentration reduction that can be addressed to the oil degradation.
Calcium instead remains constant in the oil samples. A small amount of Na and K was detected, probably due to a contamination from the cooling system.

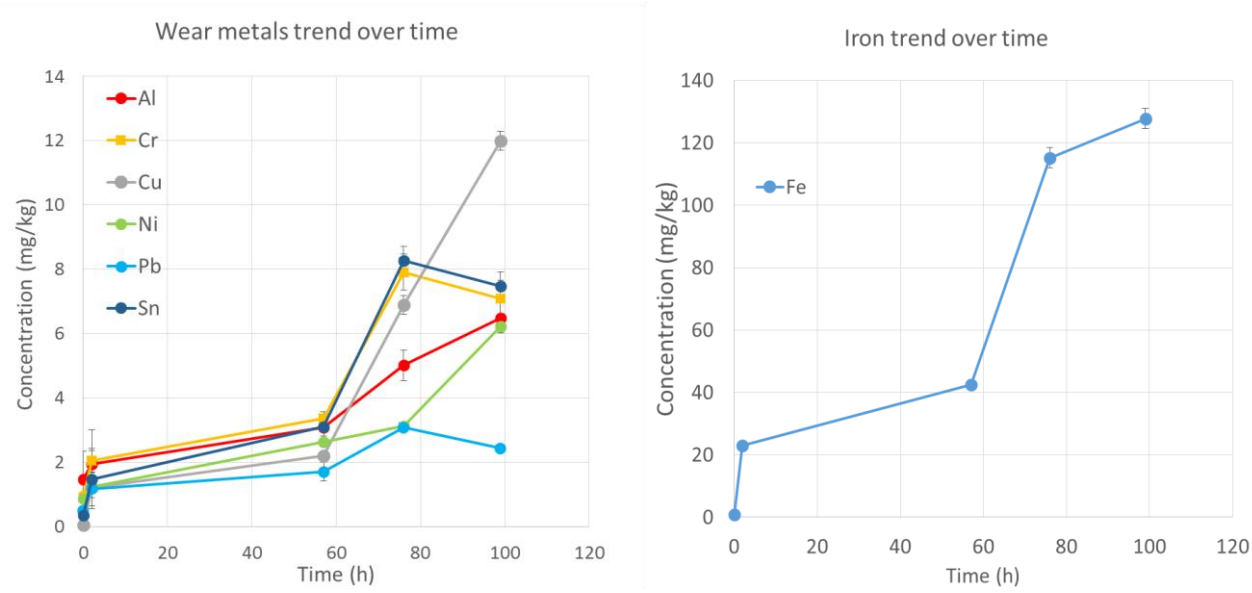


Figure 1. Concentration of iron and other wear metals coming from engine components with time

## Conclusions

GNR RotrOil meets the requirements of ASTM D6595-17, which regulates the direct analysis of wear metals and contaminants in used lubricating oils.
In addition, it is possible to determine elements from additive metallic-organic phases.

The direct detection of element emission lines and the high resolution allow to get the maximum sensitivity in the detection of wear metals from sub-ppm to percent with high precision, accuracy and short sample preparation and analysis times.

Moreover, RotrOil is perfectly suited for laboratories with a high volume of samples and the constraint of fast turnaround analysis times, which is undeniably a key factor in preventative maintenance and reducing downtime costs. A Model with 48 sample carousel it is now available.

**About GNR SRL**

With 35 years of technological experience, GNR is a worldwide market manufacturer of advanced analytical instruments in Optical Emission Spectrometer and XRD / XRF domain, developing procedures of analysis for various applications, supplying the corresponding laboratory equipment and providing consulting and customer support worldwide.

GNR can rely on a well-established team of highly qualified researchers and technicians, supported by the cooperation with leading University departments, which ensures a constantly updated technological growth.

GNR is present on the main international markets through an efficient and motivated technical and commercial network, able to provide outstanding support for any customer requirements

Annex 1. Main sources of elements in lubricant oils

| | Wear metals | Contaminants | Additive |
|---|---|---|---|
| **Ag** | Helicopter parts as silver-coated mast bearings and coaxial main rotor. | | |
| **Al** | Pistons (Al-Si), push rods, bearings (Al-Sn), air coolers, gear casings. | | |
| **B** | | Coolants | Extreme pressure additive |
| **Ba** | | | Barium petroleum sulfonate is a detergent in oil formulation as well as corrosion inhibitor. |
| **Ca** | | Dust | Calcium sulfonate is a detergent. It cleans carbon deposits from engines and acts as a corrosion inhibitor and dispersant. |
| **Cr** | Cylinder liners, piston rings, bearings made of Cr-Steels, alloy steel valves. | | |
| **Cu** | Bearing, bushes (Cu-Pb-Sn), coolant core tubes. | | |
| **Fe** | Piston rings, ball/roller bearings, gears, valves guides. | | |
| **K** | | Coolants | |
| **Mg** | | Coolants | Magnesium sulfonate is a detergent. It reacts with sludge and varnish to neutralize them and keep them soluble. |
| **Mn** | Stainless steel engine components | | |
| **Mo** | Piston rings | Grease | It may be present in oil formulations as lubricant additive (molybdenum disulphide). |
| **Na** | | Coolants or sea water contamination in marine oils | In some instances, as a detergent |
| **Ni** | Bearing made of stainless steel, valve train, turbine blades | | |
| **P** | | | Organic Phosphorus or Dithiophosphate is used at extreme pressure as anti-wear/anti-oxidant and friction modifier in engine oils, hydraulic fluids and gear oils |
| **Pb** | Bearings (Pb-Sn), fuel contamination from brass parts | | |
| **S** | | | Neutral Metal Sulfonate and sulphide oxidation inhibitor |
| **Si** | Pistons (Al-Si), seal materials | Dust, seal materials, silicone lubricant (jet engines) | |
| **Sn** | Bearings (Pb-Sn), piston rings, solder Seals | | |
| **Ti** | Connecting rods, valves of some automobile engines, especially sports car, or components of aircraft engines | | |
| **V** | Stainless steel engine parts | | |
| **Zn** | Brass components | | ZDDP (Zinc Dialkyl Dithiophosphate) additive that acts as an anti-wear, anti-corrosive and anti-oxidant. |