

Diesel Engine Coolant Analysis, New Application for Established Instrumentation

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Abstract: Rotating disk electrode (RDE) arc emission spectrometers are used in many commercial, industrial and military laboratories throughout the world to analyze millions of oil and fuel samples each year. In fact, RDE spectrometers have been used exclusively for oil and fuel analysis for so long, that most practitioners have probably forgotten that when RDE spectrometers were first introduced more than 40 years ago, they were also routinely used for aqueous samples.

This paper describes recent work to calibrate and modify Rotating Disk Electrode (RDE) arc emission spectrometers for the analysis of engine coolant samples; a mixture of approximately 50% water and 50% glycol. The technique has been shown to be effective for the analysis of wear metals, contamination and supplemental coolant additives in ethylene and propylene glycol. A comparison of results for coolant samples measured by both Inductively Coupled Plasma (ICP) and RDE spectrometers will be presented. The data correlates extremely well on new and relatively clean coolants. However, not surprisingly, RDE results are sometimes higher for samples containing particles larger than a few micrometers.

This paper suggests that RDE spectrometers are appropriate, and sometimes preferred, for most types of coolants and certain types of aqueous samples. Actual field data is presented to support the arguments.

Key Words: Engine coolants, coolant analysis, rotating disk electrode (RDE) spectrometers, inductively coupled plasma (ICP) spectrometers, debris monitoring, physical property monitoring.

Introduction: When an internal combustion engine burns fuel, heat is created at temperatures as high as 4000°F (2200°C). This heat must be removed by some form of cooling. The two most common ways to dissipate heat are by air cooling or liquid cooling. This paper discusses only the liquid cooling systems used in most modern engines.

A liquid cooling system contains the following components; radiator, fan, thermostat, water pump, engine water jacket and the cooling liquid. This paper will concentrate on the liquid contained inside the cooling system.

The analysis of used coolant samples has been a successful technique for scientific preventive maintenance. It is applicable to any closed loop cooling system, but is applied primarily to diesel and gasoline engines because they are the most likely component to suffer from a poorly operating cooling system. Overheating causes oil deterioration, oxidation, reduced lubricity and damage to all oil wetted components. The longevity of liquid cooled transmission and hydraulic system components are also dependent on a properly operating cooling system. A properly maintained cooling system not only

prevents overheating but also maintains a constant engine temperature. Improperly maintained engine temperatures can result in the type of problems shown in Table 1.

Table 1 - Problems due to Improper Engine Temperatures

High Temperature Problems	Low Temperature Problems
<ul style="list-style-type: none">• Pre-ignition• Detonation/Knock• Lubrication Failure• Burnt Pistons & Valves	<ul style="list-style-type: none">• Unnecessary Wear• Poor Fuel Economy• Accumulation of Water & Sludge

Why Coolant Analysis: Most people don't give much thought to the condition of their engine coolant system until it is too late. More than 40% of all diesel engine maintenance problems can be attributed to poor cooling system maintenance [1]. Poorly operating cooling systems cause the engine to run hotter which in turn causes the lubricant to oxidize and lose its lubricity thus causing abnormal wear in all oil wetted areas. The following is a list of reason why to do coolant analysis.

- Protect against gel formation
- Protect against corrosion and rust
- Protect against over/under concentration of SCA's
- Extend drain intervals
- Protect your engine
- Environmental/disposal concerns

Another factor that recently gained world-wide attention is the impact of used coolant disposal on the environment. Ethylene glycol is extremely hazardous if ingested by humans or animals. Because of this, most large users of coolants operate the coolants longer in order to reduce the need for disposal. Others have started recycling and reconditioning the used coolants. Because of this, the need for coolant analysis has increased dramatically over the past few years. Disposal of used coolants can be difficult and expensive and must be done in accordance with local, state or federal laws.

The following is the Cummins Engine Company recommended cooling system maintenance intervals: [2]

- Replace coolant filter at every oil change.
- Top off the cooling system at filter changes.
- Test/replenish SCA package at filter change.
- Test the coolant twice a year.
- Replace coolant every two years or 240,000 miles (6,000 hours).

The following is the Caterpillar Inc. (CAT SOS coolant analysis) recommended cooling system maintenance intervals: [3]

- Every 250 hours check glycol level, freeze and boil protection, SCA concentration, pH, and conductivity.
- Every 1000 hours or a minimum of twice a year check the same as above, plus identify metal corrosion, contaminant levels and built-up impurities.


Coolant Analysis: To be effective, a used coolant analysis program should determine 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 not only heat away from the engine parts but also carries 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. However, the condition of the coolant itself is important to know. Does the coolant meet specification? Is the SCA package correct? Is the coolant contaminated with solids, metal particulate or chemical degradation products?

In a modern condition monitoring program based on coolant analysis, a coolant sample is taken from a piece of equipment at periodic sampling intervals. Good and consistent sampling practice is extremely important. Samples should be taken from the radiator or block drain, never from the surge tank or coolant recovery bottle. The sample is sent to the laboratory for analysis. Based on the analysis, a diagnostic report is made and a recommendation is sent to the personnel responsible for the equipment. The report may show that everything is normal, warn of a possible problem or make a specific maintenance recommendation. The entire process, from sample taking to the diagnostic report, should take less than 24 hours. A sample report is shown in Fig. 1.

In a modern coolant analysis program, the data generated and collected by the laboratory is also used to provide periodic maintenance summaries. These reports can be statistical in nature and provide an insight to management personnel on the effectiveness of the program, efficiency of the maintenance department, repair status of equipment, recurring problems, and even information on the performance of coolants.

Condition monitoring by coolant analysis can be broken down into two main categories: Debris Monitoring and Coolant Condition Monitoring. Debris Monitoring spectrochemically measures the trace elements carried away from the cooling system by the coolant. Coolant Condition Monitoring determines if the coolant itself is fit for service based on physical and chemical tests. These two techniques, when combined with statistical trending and data-based management, provide a complete program of condition monitoring by coolant analysis.



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Coolant Analysis

Condition: Abnormal

COOLANT PERSON
 JOHN DOE COOLANT
 123 YOUR STREET
 ANYTOWN, US 12345-0000

Unit No. : 2
 Customer No. : 12804
 Sample Date : 04/08/96
 Received Date: 04/08/96
 Serial No. : 15589
 Lab No : 43544

Unit Description : COOLANT
 Fluid Brand/Type :

**** Recommendation

RESERVE ALKALINITY APPEARS LOW.
 FREEZE POINT APPEARS HIGH.
 CORROSION METAL(S) ARE HIGH - RECOMMEND DRAIN AND FLUSH COOLANT.
 SUGGEST YOU ADJUST THE ANTIFREEZE/WATER MIXTURE TO A 50:50 MIXTURE.

Tests	Method	Result	Condition
COOLANT ELEMENTS			
PB		9.9	HIGH
CU		11	HIGH
FE		15	HIGH
AL		0.9	ACCEPTABLE
NA		2314	ACCEPTABLE
K		2237	ACCEPTABLE
BORON		1232	ACCEPTABLE
P		967	LOW
SI		32	ACCEPTABLE
MO		132	ACCEPTABLE
RESERVE ALKALINITY	D-1121	1.9	LOW
pH	D-1287	6.8	LOW
FREEZING POINT	D-1177	+5 F	HIGH
NITRITES		484 ppm	LOW
% ANTIFREEZE		25	LOW
VISUAL APPEARANCE		GREEN	ACCEPTABLE

Figure 1, Sample Coolant Analysis Report

Debris Monitoring for Coolants: Debris monitoring pertains primarily to the detection of metallic wear particles, corrosion products, degradation products and contaminants. Spectroscopy is the most widely applied technique for debris monitoring. Commercial labs in the USA have been using either ICP or AA spectrometers for coolant analysis. Table 2 lists elements routinely detected and quantified for coolant analysis.

Table 2 - Elements Routinely Detected and Quantified Coolant Analysis

<u>Wear Metals</u>	<u>Contaminants</u>	<u>Additives</u>
Iron	Silicon	Potassium
Zinc	Magnesium	Silicon
Lead	Calcium	Boron
Copper		Sodium
Aluminum		Molybdenum
Magnesium		Phosphorus

Table 3 lists the typical elements which are routinely analyzed and provides examples to their origin in a diesel engine cooling system.

Table 3 - Sources of Various Elements in Used Coolants

WEAR METALS

Iron (Fe) - Liners, water pump, cylinder block, cylinder head.

Zinc (Zn) - Brass from components.

Lead (Pb) - Solder in radiator, oil cooler, after cooler, heater core.

Copper (Cu) - Radiator, oil cooler, after collar, heater core.

Aluminum (Al) - Radiator tanks, coolant elbows, piping, spacer plates, thermostat housing.

Magnesium (Mg) - Cast alloys.

CONTAMINANTS

Silicon (Spectro Incorporated) - Dirt.

Magnesium (Mg) - Hard water scaling problem.

Calcium (Ca) - Hard water scaling problem.

ADDITIVES

Potassium (K) - Buffer.

Silicon (Si) - Anti-foaming agent, anti-corrosion for aluminum.

Boron (B) - pH buffer, anti corrosion for ferrous metals.

Molybdenum (Mo) - Anti-cavitation, silicate.

Phosphorus (P) - pH buffer, anti corrosion for ferrous metals.

The RDE/AES technique has been in use for over 50 years for the analysis of a variety of samples. Water samples were routinely analyzed by RDE spectrometers [4]. Low limits of detection were achieved by first concentrating the sample by evaporating most of the water by putting the water sample in an oven.

With the introduction of the ICP/AES technique in the late 1970's, water samples were no longer run on RDE spectrometers because of the significantly lower limits of detection as well as superior precision offered by ICP spectrometers. Concentration of water samples by evaporation was no longer necessary, at least not for routine samples, because the limits of detection were so very much lower.

For lubricating oil and fuel analysis, the RDE technique continued to be a preferred method due to its simplicity of operation and reliability. Sample introduction is simple. Both AA and ICP spectrometers require that the oil sample first be diluted, usually with kerosene, so that the sample can be nebulized to form an aerosol. The RDE technique also has the ability to more efficiently analyze the larger particulate in the used sample. RDE spectrometers lend themselves to on-site analysis in less than optimum working environments whereas AA or ICP spectrometers required a laboratory environment as well as more highly skilled personnel for their successful operation.

Recently, several RDE spectrometers for commercial customers were calibrated with coolant standards so that these spectrometers could be used not only for oil analysis but also for coolant analysis.

The limits of detection (LOD) that can be achieved on a RDE instrument are not as low as can be achieved using an inductively coupled plasma (ICP) spectrometer, but for coolant analysis low limits of detection are not very important since the results are rounded off to the nearest ppm for reporting purposes and sub-ppm levels are of no practical

consequence.. Table 4 compares the LOD's for ICP and RDE spectrometers and shows that the RDE spectrometers are appropriate for coolant samples.

Table 4 - Limits of Detection

	<u>RDE, Oil</u>	<u>ICP, Oil</u>	<u>ICP, Water</u>	<u>RDE, Water</u>
Na	0.04	0.20	0.015	0.03
Mo	0.46	0.08	0.005	0.37
Mg	0.01	0.20	0.0002	0.01
P	3.00	0.50	0.008	3.20
B	0.07	0.01	0.002	0.13
Ca	0.03	0.03	0.0001	0.03
Cu	0.04	0.02	0.002	0.06
Al	0.35	0.02	0.001	0.43
Pb	0.80	0.10	0.02	0.75
Fe	0.23	0.02	0.002	0.21
Si	0.20	0.10	0.006	0.33
Zn	0.10	0.02	0.002	0.18

It may be of interest to note that the LOD's for oil are not substantially different than those obtained for water (or for water/glycol mixtures).

LOD's are not by any means the only measure of spectrometric performance. In the case of coolant analysis the purpose is to detect abnormal circumstances. LOD's have little to do with the quality of coolant analysis furthermore, real measurements are many times LOD so that LOD's much less than 1 ppm are not important.

The ICP technique measures only the most finely divided material, i.e., the material cannot be in the form of large particles. This is because the sample introduction system of an ICP spectrometer includes a spray chamber, the purpose of which is to remove the largest aerosol droplets generated by the nebulizer. The size of the aerosol droplets which reach the plasma torch where emission takes place are on the order of 1 or 2 μm . The RDE spectrometer, on the other hand, is able to detect somewhat larger particles, up to and beyond 10 μm in size.

Table 5 and Table 6 compare results obtained with an ICP spectrometer to results obtained on an RDE spectrometer on used coolant samples. Table 5 is a comparison of used coolant samples that were relatively clean, (no particulate could be visibly detected). Table 6 is a comparison of used coolant samples where particulate could be visibly detected. The data clearly show that if particles are present the results for the wear metals and contaminants are substantially higher when the sample is run on the RDE spectrometer. It may be concluded from this data that neither instrument is entirely quantitative for these samples because there will typically be some fraction of larger particles that is not completely measured by either an ICP or RDE spectrometer. Nevertheless, the purpose of the analysis is served by indicating which coolant systems are in distress. It may be argued that since the RDE spectrometer is more responsive to large particles it is more capable of indicating abnormal coolant conditions than an ICP spectrometer.

Coolant Physical Property Monitoring: The second part of an effective coolant analysis program is coolant condition monitoring. Through periodic sampling of the coolant, the laboratory can determine the effectiveness and remaining life of the coolant based on additive degradation and contamination analysis.

ASTM (American Society for Testing and Materials) tests are mostly written for quality control and quality assurance requirements of new and sometimes used coolants. Therefore, ASTM procedures are often modified to reduce analysis times in the interest of economics. The number and type of tests that are performed on a used coolant sample vary. Table 7 summarizes the physical property tests performed by the typical used coolant analysis laboratory.

Table 5 - ICP/RDE Comparison of “Clean” Coolant Samples

<u>INST</u>	<u>Al</u>	<u>Cu</u>	<u>Fe</u>	<u>Pb</u>	<u>Zn</u>	<u>Mg</u>	<u>Ca</u>	<u>Si</u>	<u>Mo</u>	<u>P</u>	<u>B</u>	<u>Na</u>
RDE	1.1	0.4	0	0	0	0.5	0	47.6	18.6	590	389	2069
ICP	0	0	0	0	0	0	0	41	19	406	248	1078
RDE	14.8	6	7.8	8.7	2	0	0	37.6	0	122	263	1546
ICP	6.7	0	3.8	3.2	0	0	0	26	0	90.2	217	914
RDE	1.3	0.4	0	0	0	0.1	0	34.8	0.2	511	649	2541
ICP	0	0	0	0	0	0	0	28	0	315	421	1309
RDE	0.5	0	0	0	0	0	0	3.2	13.5	77.5	615	2409
ICP	0	0	0	0	0	0	0	3.7	18	60	480	1283
RDE	0.4	0.7	5.7	7.1	1.3	0.5	0.8	40	58.9	984	635	2835
ICP	0	0	2.7	2.8	0	0	0	26	44	585	345	1385
RDE	0.8	0.7	1	0	0	0	0	3.7	0	445	325	1364
ICP	0	0	0	0	0	0	0	3.6	0	335	213	852
RDE	0.3	0.9	0.6	6	1.9	0.4	12.1	61	1.2	122	840	5972
ICP	0	0	0	2.6	0	0	3.6	43	0	74	515	2650

Table 6 - ICP/RDE Comparison of Coolant Samples Where Particles Were Detected

<u>INST</u>	<u>AL</u>	<u>CU</u>	<u>FE</u>	<u>PB</u>	<u>ZN</u>	<u>MG</u>	<u>CA</u>	<u>SI</u>	<u>MO</u>	<u>P</u>	<u>B</u>	<u>NA</u>
RDE	0.2	39	0	39	8.7	0.9	0	53.6	0	1677	630	5440
ICP	0	12	0	17	2.5	0	0	34	0	1163	321	2733
RDE	11	23	60	2.8	4.3	1.3	0	34.2	2.5	61.8	806	3365
ICP	6	5.6	37	0	0	0	0	23	4	53.7	672	2134
RDE	0.5	47	0	0	0	0.2	0	59	23.3	583	1415	6471
ICP	0	8.7	0	0	0	0	0	30	15	271	748	2552
RDE	2	1	1	4.9	2.8	1.3	5.8	42.4	68.5	326	1088	5013
ICP	0	0	0	2.2	0	0	0	29	58	203	678	2668

RDE	0.9	16	75	25	40	0.9	4.2	12.4	0.2	12.1	1368	5118
ICP	0	2.3	28	7.5	19	0	0	5.2	0	12.5	870	2495
RDE	1.1	1.7	24	2.5	2.5	0.4	0.1	24.5	66.3	709	385	1652
ICP	0	0	7.5	0	0	0	0	19	61	522	232	959
RDE	9.4	12	114	49	6.9	10	66.4	29.4	0.6	948	1424	6567
ICP	0	0	25	8.9	0	2.2	12	12	0	561	746	2904
RDE	0	28	130	70	14	3.7	1.2	39	7	327	322	1671
ICP	0	0	47	18	6.7	0	0	32	8.7	222	211	939
RDE	5.7	44	1.5	3.4	28	27	269	150	260	2110	751	3585
ICP	0	12	0	0	7.6	7.4	44	83	193	1315	334	1564

Table 7 - Typical Physical Property Tests for Used Coolant Analysis

- pH, ASTM 1287
- Reserve Alkalinity, ASTM D1121
- Percent EG/PG
- Freeze/Boiling Point
- Nitrite, ppm NO₂
- SCA Levels
- Total Dissolved Solids (TDS)
- Appearance

pH: Measures the acidity or alkalinity of the used coolant sample. This can be measured by performing ASTM D1287, which is very precise. The use of an inexpensive pH meter can provide quick and accurate results in a non-laboratory environment. Most pH meters have the capability to measure the conductivity of the coolant which also can be used to determine the percentage of TDS. Most major engine manufacturers recommend coolant pH levels between 8.5 to 10.5. If pH levels fall below 8.0 rapid nitrite depletion will occur. Coolant pH levels above 11.5 will corrode aluminum and promote scaling[2].

Reserve Alkalinity: Measures the amount of alkaline inhibitors present in the used coolant. This gives an indication of the coolant's ability to provide corrosion protection. This test can be performed by ASTM D1121. If the buffering agents are not at correct levels, corrosion and rapid additive depletion will occur due to a reduction in pH values. The result will be cylinder liner pitting.

Percent Antifreeze EG/PG: This test uses a refractometer to quantify the amount of EG/PG in a coolant sample. Most major engine manufacturers recommend coolants composed of 50/50 water/glycol solution to provide satisfactory freeze and boil point protection. An operating range of 40 to 60 % antifreeze is acceptable, however, the use of antifreeze in concentrations over 65% may cause SCA drop-out, water pump seal damage and engine overheating.

Freeze/Boiling Point: Once the percent of EG or PG is determined, the freeze and boiling point can be calculated by using charts provided by the antifreeze manufacture. Freeze point can also be measured by performing ASTM D1177. If the percent antifreeze is not known, an inexpensive hydrometer can be used to measure the density of the coolant and then calculate the freeze point. The amount of freeze protection required should be based on the lowest expected temperature in your region.

Nitrites/SCA Package Analysis: The analysis of the primary corrosion inhibitor, nitrite, can be performed by various tests. The most accurate method is by ion chromatography. For the most accurate results this test must be performed in a laboratory. The second method is the colormetric analysis with nitrite test sticks. This is a very quick and easy way to measure the concentration of NO_2^- . Fleetguard offers a test stick that will measure nitrites (NO_2^-), molybdates (MoO_4^{2-}) and freeze point protection colormetricly on the same test stick. As with all elements contained in the SCA package, the concentrations must remain within 10% of the new coolant SCA additive level.

Total Dissolved Solids (TDS): This is a measurement of the dissolved solids in the coolant. The dissolved solids are composed of the basic inhibitor chemicals, silicates, active SCAs, spent SCAs, contaminants and water hardness compounds[2]. The higher the dissolved solids the higher the conductance. The percentage TDS can be quantified with a conductivity meter. This meter will also be capable of measuring the pH of the coolant. Cummins recommends a maximum of 5% TDS, higher levels may cause water pumps seal failure[2].

Appearance: This quick and easy test records the overall condition, color and visible contamination of the coolant. Color is important because most manufacturers identify coolants by color. It is important to notify maintenance personnel if oil or large particles are present in the coolant sample.

Conclusion: RDE spectrometers, when appropriately calibrated, may be used as part of a condition monitoring program based on coolant analysis. The same instrument as used for used oil analysis can be modified and calibrated to also effectively analyze coolants. The added capability provides the laboratory with an supplementary tool to increase its capabilities and effectiveness.

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