

Determination of Used Crankcase Oil Condition by Capillary Electrophoresis Analysis of Extracted Organic Acids

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ABSTRACT

Organic acid degradation products and other anions in engine oil were speciated by capillary electrophoresis (CE) and liquid chromatography-mass spectrometry (LCMS) with electrospray ionization. The sample preparation procedure involved selectively extracting the acids and other water soluble salts into 0.05M aqueous potassium hydroxide. Samples of engine-aged mineral oil and synthetic engine oil contained formic acid, acetic acid, and complex mixtures of fatty acid degradation products. CE analysis of formic acid, acetic acid and selected fatty acids is proposed as a new chemical analysis method for evaluating the condition of engine oil and for studying the effects of high temperature-high load (HTHL) oxidation. Because the overall pattern of CE peaks in the electropherogram changes with oil age or condition, CE-fingerprint (i.e., pattern recognition) techniques may also be useful for evaluating an aged oil's condition or remaining service life.

INTRODUCTION

There is little doubt that eliminating the need for frequent engine oil changes would increase customer satisfaction, conserve petroleum resources, and reduce environmental pollution from discarded oil. Consequently, a team at General Motors is looking for improvements that will minimize oil changes. The research involves the identification of durable, long-life oils for automotive applications, hardware modifications to minimize oil degradation, modeling of oil degradation, and the development of better methods for detecting and accurately predicting the end of an oil's lifetime. Recent efforts by members of the team have included the creation of dynamometer tests to measure oil durability

under harsh conditions [1]. The subject of this report is the development of new chemical analysis methods to accurately and reliably determine the condition of used crankcase oil. To achieve that goal the methods were designed to measure specific, distinctive oil decomposition products, such as organic acids.

The need to measure specific carboxylic acids and other distinctive decomposition products is due to the increasing chemical complexity and enhanced performance characteristics of modern engine oils. Currently, a few well established techniques, including Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), kinematic viscosity (KV), total base number (TBN) and total acid number (TAN) titrations, are the standard methods for quantitating oil oxidation and nitration [2-5]. These rapid, routine methods continue to provide general, mostly phenomenological, information about oil quality and age. However, because of the sophistication of modern oil chemistry, the traditional test methods that rely on bulk properties are rapidly reaching the limits of their applicability and reliability.

Modern engine oils contain multi-component additive packages [6-8] that frequently affect non-specific, bulk-property indicators such as TAN and TBN. Usually the exact additive formulations are proprietary and are known only to the additive suppliers. Typical packages include detergents, dispersants, antioxidants, viscosity index improvers, corrosion inhibitors, anti-wear compounds, and friction modifiers. Several of the additives function by undergoing transformations that produce new or different salts, which can alter the way that an oil responds to laboratory tests.

Carboxylic acids are particularly attractive as oil-condition indicators: They are minor components in fresh oils, their chemical properties (e.g., acidity) distinguish them from oil hydrocarbons, and they are expected to be ubiquitous degradation products in oxidized oil. The prevailing mechanistic view of high temperature oil oxidation invokes the formation of hydroperoxide radicals that readily attack the aliphatic hydrocarbons in most mineral or synthetic oils [6, 9-11]. Hydroperoxide chemistry apparently leads to polymers that increase oil viscosity and to oxidized species such as alcohols, aldehydes, and carboxylic acids. Presumably, damage from hydroperoxides is limited by antioxidants and acid-neutralizing additives until those additives are consumed. Subsequently, polymerization and acidification of the oil occur at an accelerated pace.

Unfortunately, the measurement of individual carboxylic acids and other specific degradation products in crankcase oil is not a simple task. Conventional speciation methods, such as gas chromatography and mass spectrometry, are hampered by the formidable complexity of the hydrocarbon matrix in mineral oils [12-14]. Engine oils contain literally tens of thousands of C_{20} to $>C_{40}$ hydrocarbon isomers of relatively low volatility. Consequently, pre-separation of target analytes from the sample matrix by extraction or other means [15, 16] continues to be an important part of the speciation strategy for engine oils. One useful extraction procedure is described in the experimental section of this report.

A limited number of literature articles document efforts to characterize polymerized hydrocarbons in oxidized oil and sludge by size exclusion chromatography, NMR spectroscopy, and other laboratory techniques [17-20]. Few, if any, reports demonstrate the existence of specific short-chain carboxylic acids or larger fatty acids in oxidized motor oil. More often, the presence of carboxylic acid degradation products is inferred from TAN measurements and from the relative intensity of characteristic bands in FTIR spectra. The dearth of published speciation methods and results attests to the need for additional types of measurements that can overcome the limitations of traditional chemical analysis tools.

For this work we investigated two relatively new methods of chemical analysis for speciating organic acids and anions: {1} capillary electrophoresis (CE) and {2} liquid chromatography / mass spectrometry (LCMS) with electrospray ionization [21-27]. Other researchers have successfully used CE, electrospray mass spectrometry, and various sophisticated methods to study the composition and chemistry of zinc dithiodiphosphate (ZDDP) additives [15, 26-32]. In the future, powerful new methods of chemical analysis, including comprehensive two-dimensional gas chromatography combined with mass spectrometry (GCxGC-MS) may further simplify the speciation process [33-35].

EXPERIMENTAL

ENGINE DYNAMOMETER TESTS AND OIL SAMPLES

Several sets of aged oil samples were analyzed for this work. Results from three representative sets are presented in this paper. The samples were generated using a dynamometer test for evaluating oil durability under severe high-temperature high-load (HTHL) driving conditions [1].

The first oil (Oil A) was an ILSAC GF-4 quality SAE 5W-30 mineral-based oil meeting the GM 6094M specification. The dynamometer test used to age the oil was run under the same conditions as the "failure point" double-length tests described in Ref. [1]. The engine used was a 3.4L V6 engine, operated at 3000 r/min, 103 Nm load at an oil sump temperature of 140 °C. Drains from two identical runs of 125 hours were combined, and the test was continued for a total time on the oil of 333 h. This two-step process is necessary because a significant volume of fresh oil is consumed during the first portion of the test, and oil aeration due to a low oil level will begin before a typical GF-4 quality oil reaches its oxidation "breakpoint".

Oils B and C were also run under HTHL-type conditions. However, the engine used was a 6.2L V8 engine operated under similar conditions to the prior test (3000 r/min, 90 Nm load, and an oil sump temperature of 140 °C). Drains from two identical runs of 100 hours were combined, and the tests were continued for a total time on Oils B and C of 265 and 283 h, respectively. Oil B was also an ILSAC GF-4 quality SAE 5W-30 mineral-based oil meeting the GM 6094M specification. Oil C was a fully formulated SAE 0W-20 synthetic prototype oil provided by Infineum International Ltd. No fresh make-up oil was added during any of the tests.

The aged oil samples were analyzed for viscosity, TAN, and pentane-insoluble material by standard ASTM methods (www.astm.org). In particular, viscosity at 100 °C, KV100, was determined by ASTM method D 445. The total acid number was determined by ASTM method D 664, and pentane-insoluble content was measured according to ASTM method D 893. Resistance to oxidation was evaluated by an FTIR method and involved measuring the relative intensity of a specific peak in the oil's infrared spectrum.

EXTRACTION PROCEDURE

A novel extraction scheme was devised to separate organic acids and water-soluble salts from the engine oil. As outlined in Figure 1, 1 mL of oil and 3 mL of toluene were weighed into a 50-mL disposable plastic centrifuge tube. The 1-ml aliquot of oil was conveniently transferred from the sample bottle to the centrifuge tube with a 3-ml disposable plastic syringe or with a disposable glass pipette. In general, labware and consumable supplies were purchased from VWR Scientific (www.vwr.com).

Eight milliliters of 0.05 M potassium hydroxide were then weighed into the centrifuge tube. In the early experiments the tube was capped and shaken vigorously for 5 minutes by hand to extract acids into the aqueous phase as their potassium salts. For later experiments a motorized sample rotation device was used to automate and standardize the extraction process (Figure 2). Samples were rotated at 20 revolutions per minute (rpm) for four hours with a Glas-Col tissue culture rotator (www.vwr.com).

The toluene diluent was added to decrease the viscosity of the oil sample and to create a more reproducible organic phase for extraction. Essentially, acids are extracted from the toluene-diluted oil into 0.05 M potassium hydroxide.

As might be expected, the extraction procedure produced most often a stubborn, stable emulsion of oil and water. A distinct aqueous phase was re-established by centrifuging for about 20 minutes at 7,500 rpm. Centrifugation generally provided a clear aqueous phase for subsequent testing. Fresh oil, with unaltered dispersant additives, typically produced emulsions that were the most difficult to separate. In general, freezing the centrifuged liquids and allowing the solid mass to gradually melt at ambient room temperature improved the separation between organic and aqueous phases.

The lower aqueous phase was collected with the aid of a 5-mL Luer-Lok syringe fitted with a 3-inch, 22 gage, stainless steel needle (Figure 1). To reduce the high pH and potassium hydroxide content of the extract, a 2-mL aliquot of the extract was eluted through an Alltech Maxi-Clean IC-H ion exchange cartridge (www.alltechweb.com). The cartridge contained 0.5 cm³ of sulfonic acid cation exchange resin in the hydrogen (protonated) form. The IC-H cartridge was pre-washed with 2 mL of deionized water, and the first milliliter of the sample eluant was discarded.

Removal of excess potassium hydroxide from the extract simplifies the analysis by capillary electrophoresis and greatly improves the shape and resolution of the recorded CE peaks. However, larger carboxylic acids are more soluble as salts at a neutral or slightly basic pH than as free acids in an acidic solution. For that reason about 10 µL of 0.3 M potassium hydroxide was re-introduced into the acidified extract with a microsyringe to increase the pH from about 4 to 8. As noted below, the untreated potassium hydroxide extracts were suitable for analysis by LCMS with electrospray ionization.

ANALYSIS BY CAPILLARY ELECTROPHORESIS

The fundamental principles of ion analysis by capillary electrophoresis are well documented in numerous books and review articles [36-38]. A simple schematic diagram of a common CE instrument design with an ultraviolet (UV) absorbance detector is included in Figure 3. Separation of different anions and cations takes place in

a narrow fused silica capillary tube that is filled with a dilute solution of electrolyte. When a potential of several thousand volts is applied across the capillary tube, negatively charged anions move toward the positive electrode or anode, and positively charged cations move toward the negative electrode or cathode. Different types of anions or cations are separated from each other because large, bulky ions migrate more slowly through the capillary tube than small, compact ions. The apparatus in Figure 3 is configured for the detection of anions. The polarity of the electrodes would be reversed for the detection of cations.

Unfortunately, a single set of CE conditions cannot be optimized for the detection of all the different anions in a complex oil extract. One important distinction segregates the anions that absorb ultraviolet (UV) light from those that do not. The aromatic rings in many antioxidants and other additives absorb UV light at 254 nm. Those species can be detected directly in a non-absorbing electrolyte. Carboxylic acids and inorganic anions, such as sulfate and nitrate, do not absorb UV light at common detector wavelengths, and must be detected indirectly. The indirect method requires the use of a CE buffer / electrolyte that absorbs UV light at a convenient wavelength. Non-absorbing anions are detected indirectly as a momentary decrease in electrolyte absorbance when they displace UV-absorbing ions in the electrolyte.

Carboxylic acids and other non-absorbing anions were detected with a UV-absorbing electrolyte that others have used for measuring acid vapors in atmospheric samples and vehicle exhaust [22, 23]. The electrolyte consists of 4 mM 2,6-naphthalenedicarboxylic acid as a strong UV absorber, 14.4 mM BIS-TRIS as the pH buffer (pH 6.2), and 0.4-mM CTAOH as an osmotic flow modifier. BIS-TRIS, or 2,2-bis(hydroxymethyl)-2,2',2''-nitrilotriethanol, (CAS 6976-37-0), is a well-known biological buffer that effectively controls the pH of the electrolyte without having a major impact on electrolyte conductivity. Chemicals for the CE analysis, including BIS-TRIS and CTAOH (cetyl trimethylammonium hydroxide) were purchased from Sigma-Aldrich (www.sigma-aldrich.com).

The pattern of separated component peaks that results from the CE analysis of a sample is referred to as an electropherogram. Electropherograms for carboxylic acids were recorded at a detector wavelength of 284 nm for 15 minutes with an applied voltage of -16 kV relative to the grounded electrode at the detector end of the capillary. The response of the UV-absorbance detector was calibrated by analyzing standards that contained known concentrations of potassium formate, sodium acetate, and potassium propionate. A stock solution containing 1000 µg/mL acetate was prepared from reagent grade sodium acetate. Weighed amounts of formic acid and propionic acid liquids were neutralized with 0.3 M potassium hydroxide to prepare the standard stock solutions of formate and propionate.

A CE Resources instrument (Model CE-1, www.ce-resources.com) was used for this work (Figure 4). The autosampler was programmed to reproducibly inject each sample onto the capillary by pressurizing the selected sample vial to 0.3 psi for 15 seconds. A 65-cm length of 0.75-mm I.D. uncoated fused silica tubing from Polymicro Technologies (www.polymicro.com) was used for the CE separations. The effective capillary length from the injection point to the detector was 53 cm.

LIQUID CHROMATOGRAPHY – MASS SPECTROMETRY WITH ELECTROSPRAY IONIZATION

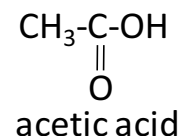
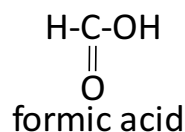
The electrospray LCMS experiments were conducted at Wayne State University, Detroit, Michigan, in the Chemistry Department's Central Instrumentation Facility. The main components of the LCMS system were a Waters model Alliance 2695 liquid chromatograph interfaced to a Micromass model Quattro-LC triple quadrupole mass spectrometer (www.micromass.com). Typically, 5 microliters of oil extract or IC-H neutralized extract were injected onto a Waters Symmetry C18 reverse-phase LC column. The dimensions of the column were 15 cm x 2.1 mm I.D., and the average particle diameter was 3.5 μm . Compounds were eluted with a linear solvent gradient that began with 1:1 methanol:water and ended with 100% methanol after 8 minutes. Elution was continued for an additional 12 minutes with 100% methanol at the same constant flow rate of 210 μL per minute.

The polarities of the voltages in the electrospray ion source were selected for the detection of negative ions. The potential difference between the repeller electrode and the entrance to the mass analyzer was switched between 30 volts and 60 volts for alternate scans. Mild collisions with argon nebulizer gas at 30 volts minimized the fragmentation of molecular ions. More energetic collisions at 60 volts produced fragment ions that provided structural information.

RESULTS AND DISCUSSION

CAPILLARY ELECTROPHEROGRAMS

Figure 5 contains a set of electropherograms that were obtained from samples of Oil A. The oil samples were collected at various times during the high-temperature, high-load engine dynamometer test, as noted on the figure. In each electropherogram fast-moving inorganic anions, such as sulfate and nitrate, appear first at about 4 minutes of migration time. The peaks for inorganic anions are followed by prominent peaks for formate and acetate anions, along with peaks for many other anion species at lower relative abundances. As indicated in the experimental section, the CE analysis conditions were optimized for the detection of fast-moving inorganic anions and low molecular weight anions from carboxylic acids such as formic acid and acetic acid.



Even a cursory examination of the electropherograms in Figure 5 suggests that the concentrations of formate and acetate anions increase significantly between 137 and 237 hours of engine run time. The broad peaks that appear after 9-minutes of migration time (eg., peaks labeled E, F and G in Figure 5) also appear to be informative because they change in relative abundance with engine run time. In particular, Peak E dominates the electropherograms representing short engine run times of less than 30 hours. Components F and G appear to increase in relative abundance during the first part of the oil durability test and then decrease or disappear. Although Peaks E, F and G have not been identified, we speculate that the anions may be related to ZDDP products or other oil additives, based on their changing concentrations with engine run time, their relatively long CE migration times, and their lack of UV absorbance at 284 nm.

The important point is that the changing pattern of increasing oil oxidation products and decreasing oil additives creates a set of electropherograms with patterns that are indicative of the oil's age or remaining service life. Therefore, the distinctive fingerprint or peak pattern of a CE electropherogram could be a valuable diagnostic tool. So far, our limited number of tests with different sets of oil samples suggest that the results in Figure 5 are commonplace, and not an isolated, fortuitous anomaly. For example, an analogous set of electropherograms from Oil C, a synthetic fluid, are shown in Figure 6. Small anions, including formate and acetate tend to grow in relative abundance with engine run time. Peaks labeled A and B reveal a pattern of decay for peak A or initial growth followed by decay for peak B.

The fact that the patterns in Figures 5 and 6 are different is also interesting. The differences between the two sets of oil extracts suggests that, on one hand, there is probably not a universal set of CE electropherograms that can be used to characterize the age or extent of oxidation for every available engine oil. On the other hand, because the sets of CE electropherograms differ from one oil to another, they may contain useful information about the specific additive package or chemistry of the oil.

ACID CONCENTRATION MEASUREMENTS

Our original goal was to relate the concentrations of individual carboxylic acid decomposition products to the condition and remaining service life of a used oil. To illustrate the feasibility of the approach, we have measured the concentrations of formate and acetate anions in the various oil samples. As shown in Figure 7,