



Determination of formic and acetic acids in petroleum products by ion chromatography

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Keywords

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Goal

To develop and evaluate a novel automated analytical IC method for the direct determination of acetic acid and formic acid in diesel and oil-containing diesel mixtures.

Introduction

Organic acids in crude oil, refined products, fuel, etc., are one of the biggest concerns of the oil, oil refining, and car manufacturing industries. As a result of their corrosive properties and the associated costs of corrosion, organic acids have become a topic of great industrial interest¹. Crude oil may contain more than a thousand different organic acids with a mass range up to 1500 Da and a carbon number of about C₈₀². To assess the acidity of petroleum products the 'total acid number' (TAN), defined by the ASTM as milligrams of KOH required to neutralize one gram of oil or petroleum product³, is commonly used. Recently, it was determined that TAN is no longer a reliable indicator as a surrogate parameter. The corrosivity of organic acids is related to their molecular mass, size, and structure,¹ so more information about the chemical identity and concentration of organic acids is needed. In particular, low molecular weight organic acids are reported as the most aggressively corrosive in the refining process^{4,5}.

Different chromatographic approaches are used to identify and quantify organic acids in petroleum products with gas chromatography (GC) being the traditional choice. The organic acids—typically with a chain length above C₆—are extracted by solid phase extraction (SPE), then methylated and analyzed by GC-MS^{6,7}. Yang et al. followed a different approach by injecting the aqueous extracts from oil cracking fractions directly onto a polyethylene glycol coated capillary GC column, detecting a small number of low molecular weight acids, except for formic acid⁸. Wang and Kasperski used HPLC-MS/MS for the determination of organic acids (C₆ and above) in aqueous oil sand extracts⁹. None of these methods allowed an easy to setup and reliable determination of smaller organic acids in petroleum products.

Ion chromatography (IC) can be used for the selective and sensitive determination of low molecular weight organic acids in aqueous or water-miscible matrices^{10,11}.

At first glance, water-immiscible samples, like diesel and diesel mixed with oil, appear to be challenging for the application of IC, as they cannot be directly injected. In modern IC applications, however, in-line matrix elimination techniques are available to remove the hydrophobic matrix and specifically retain ionic analytes prior to the injection. A comparable approach was applied to determination of sodium in diesel by IC analysis¹², while the application of IC to the determination of short-chained organic acids in petroleum products has not been described.

This application note summarizes the use and evaluation of an automated analytical IC method for the direct determination of acetic acid and formic acid in diesel, oil, and diesel/oil mixtures, to support research on corrosion processes of industrial production installations and car engines.

Equipment

- Thermo Scientific™ Dionex™ ICS-2100* with Degasser (P/N 069576) with additional auxiliary-valve (P/N 069472)
- Thermo Scientific™ Dionex™ UltiMate™ LPG-3400 SD (P/N 5040.0031)
- Thermo Scientific Dionex UltiMate WPS-3000 RS (P/N 5840.0010)
- Thermo Scientific™ Chromeleon™ Chromatography Data System Software, Version 7.2 (or higher)

*Thermo Scientific Note: Methods performed using a Dionex ICS-2100 system are now run on the Thermo Scientific™ Dionex™ Integration™ HPIC™ system.

Reagents and standards

- Deionized (DI) water, Type I reagent grade, Barnstead GenPure UV, Thermo Fisher Scientific, (P/N 50132156)
- 2-Propanol, Optima™ LC/MS, Thermo Fisher Scientific, (P/N A-461-1)
- 1-Butanol p.a., Chem-Lab NV, Zedelgem, Belgium, (P/N CL00.0220)
- Acetic acid, 99.6%, Across Organics, Geel, Belgium, (P/N 29532)
- Formic acid, 99%, Across Organics, Geel, Belgium, (P/N 27048)

Samples

Diesel and synthetic motor oil (5W-40) were bought at a local gas (petrol) station.

Conditions	
Columns	Thermo Scientific™ Dionex™ IonPac™ AG11-HC, 2 × 50 mm (P/N 052963) Dionex IonPac AS11-HC, 2 × 250 mm (P/N 052961) Dionex IonPac UTAC-LP1 Trace Anion Concentrator Column (P/N 063079)
Eluent	KOH-Gradient (Table 1)
Eluent Source	Thermo Scientific™ Dionex™ EGC KOH Eluent Generator Cartridge (P/N 074532) with Dionex IonPac CR ATC II (P/N 060477)
Flow Rate	0.38 mL/min
Inj. Volume	10 µL
Temperature	30 °C
Detection	Suppressed Conductivity, Thermo Scientific™ Dionex™ AERS™ 500 Anion Self-Regenerating Suppressor (2 mm), (P/N 082541)
Regenerant Flow Rate	0.4 mL/min (external water mode)
System Backpressure	1700 psi
Background Conductance	<0.8 µS/cm
Typical Noise	<2 nS/cm

Table 1. Experimental conditions for matrix elimination and chromatography.

Time (min)	Sample transfer flow rate (mL/min)	Sample transfer and matrix elimination solvent*	KOH (mM)	Suppressor current (mA)	Comment
-5.0	0.1	H ₂ O	100	95	Begin conditioning of concentrator and analytical column
-4.5	1.0		1		
-3.0					
-2.5					
0.0		2-Propanol	2	Begin matrix elimination	
5.0	H ₂ O	Matrix elimination finished			
9.0		Injection and begin analysis			
20.0			0.1	100	95
22.5					
37.0		20		34	End sample run

* To remove possible contaminants, the solvents used for sample transfer and matrix elimination were pumped over a Dionex ATC-500 polymeric anion exchange column (P/N 075976).

Preparation of solutions and reagents

Calibration solutions

An aqueous stock solution with a final concentration of 1000 mg/L was prepared for acetic acid and formic acid. External standard calibration solutions were obtained by diluting the stock solution with water. Solutions used to evaluate the potential influence of organic diluents on the analytical results were made by mixing the stock solution with 2-propanol.

Sample preparation

Samples were diluted with the same volume of 1-butanol and stored in glass HPLC autosampler vials until injection. Mixtures of diesel and the synthetic motor oil were prepared at different volume ratios to investigate the potential influence of oil on the method. For standard addition experiments a small volume of the analyte stock solution was added to the selected diesel/oil mixture, e.g., 1 mL of the analyte stock solution to 100 mL of the diesel/oil mixture. The acids were quantitatively extracted into the organic layer by vortexing for 10 min. The non-aqueous layer was then diluted with the same volume of 1-butanol. Aliquot volumes were stored in glass HPLC autosampler vials until injection.

In-line matrix elimination

The sample was delivered to the Dionex IonPac UTAC-LP1 concentrator column using 2-propanol. The analytes were extracted and the organic sample matrix was removed with an excess of 2-propanol. The Dionex IonPac UTAC-LP1 column was then rinsed with water, removing the 2-propanol. The sample was injected by switching the valve holding the concentrator column into the eluent. Analytes were then eluted and separated on the analytical column (for analytical conditions see Table 1). Figure 1 shows a schematic of the setup.

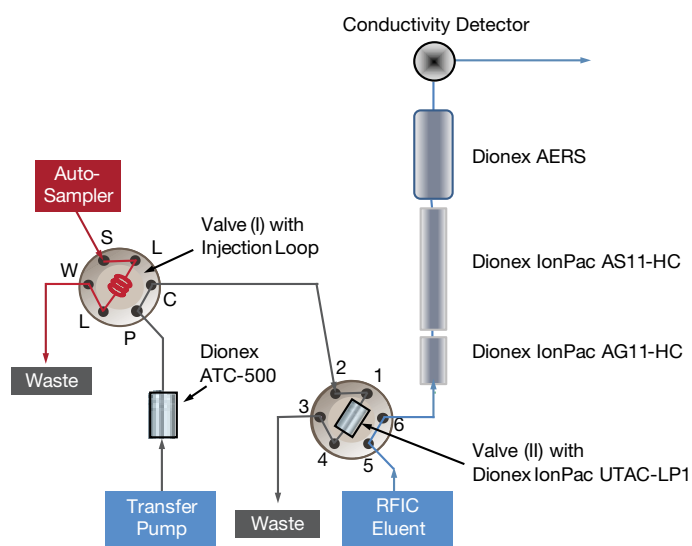


Figure 1. Schematic configuration of the analytical system.

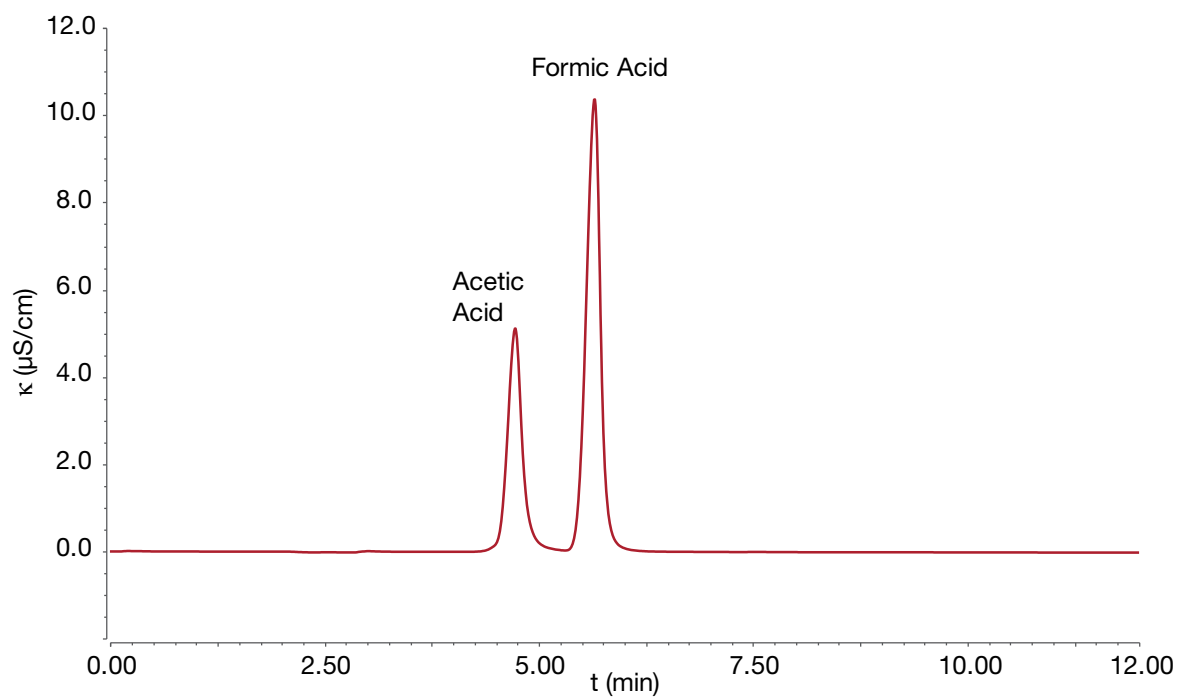


Figure 2. Chromatogram of a standard solution containing acetic acid and formic acid at 5 mg/L each.

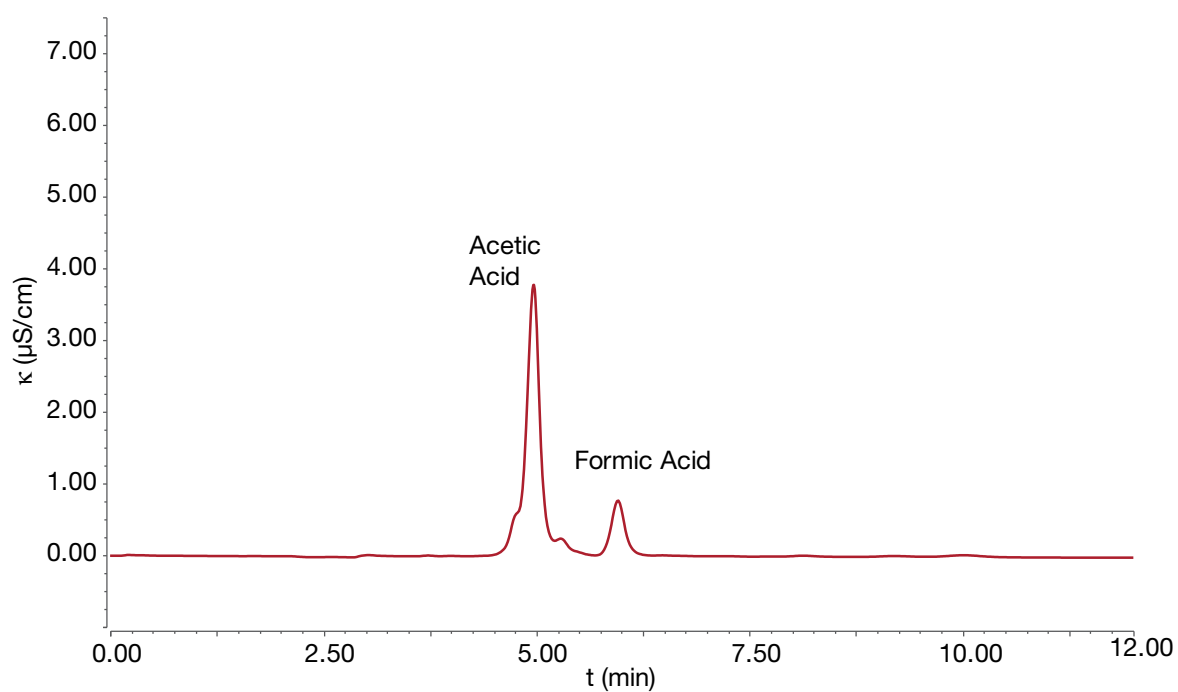


Figure 3. Acetic acid and formic acid in diesel.

Results and discussion

External calibrations were carried out using five concentration levels in the range of 1 mg/L to 20 mg/L, with two separate preparations and duplicate injections of each level. A typical chromatogram of a standard solution is shown in Figure 2. Best correlations were obtained using a linear calibration for formic acid and a quadratic calibration for acetic acid. The latter finding results from the concentration-dependent dissociation of a weakly dissociated acid impacting peak area in conductivity detection¹³. The coefficients of determination, reflecting the deviation of the measured data points from the calibration curve, resulted to r^2 (acetic acid)=0.9992 and r^2 (formic acid)=0.9996. The calibrations were checked every working day and they remained stable for several weeks. The analytical figures of merit were calculated as described in DIN 32645¹⁴. The detection limit for acetic acid was found to be 3.8 mg/L, and for formic acid 1.5 mg/L. The limit of determination for acetic acid was 6.3 mg/L and for formic acid 2.7 mg/L.

The potential impact of using organic diluents on the analytical recovery was tested comparing the response factors for standard solutions prepared in water and 2-propanol. The differences of response factors for both organic acids in both matrices were in the range of one percent, indicating the equivalency of the two approaches. Consequently, all external calibration

experiments were performed using aqueous standards, simplifying the daily routine. Figure 3 presents the analysis of acetic acid and formic acid in pure diesel, showing the elution of other components close to the acetic acid peak. This indicates the presence of additional, short-chained organic acids, though at a lower concentration than acetic acid.

Intra-day and inter-day repeatability and recovery were determined using diesel samples with 2% motor oil, being spiked with 10 mg/L of each acid. Intra-day repeatability was in the range of 2% for both analytes, with increasing variation towards lower analyte concentration. Intra-day recovery was determined to be 107% for acetic acid and 105% for formic acid. Corresponding chromatograms, with and without the addition of acetic and formic acid, are shown in Figure 4.

Inter-day recovery for acetic acid over four days was $101\% \pm 5\%$ and for formic acid it was $90\% \pm 9\%$. Inter-day repeatability for the analytes on the spiked levels was 4% for acetic acid and 9% for formic acid. Recovery for acetic acid remained stable over the time investigated, while the concentration of formic acid trended down, possibly due to evaporative losses as a consequence of higher vapor pressure compared to acetic acid. The determination of formic acid should therefore be done as fast as possible after the sample's arrival in the laboratory.

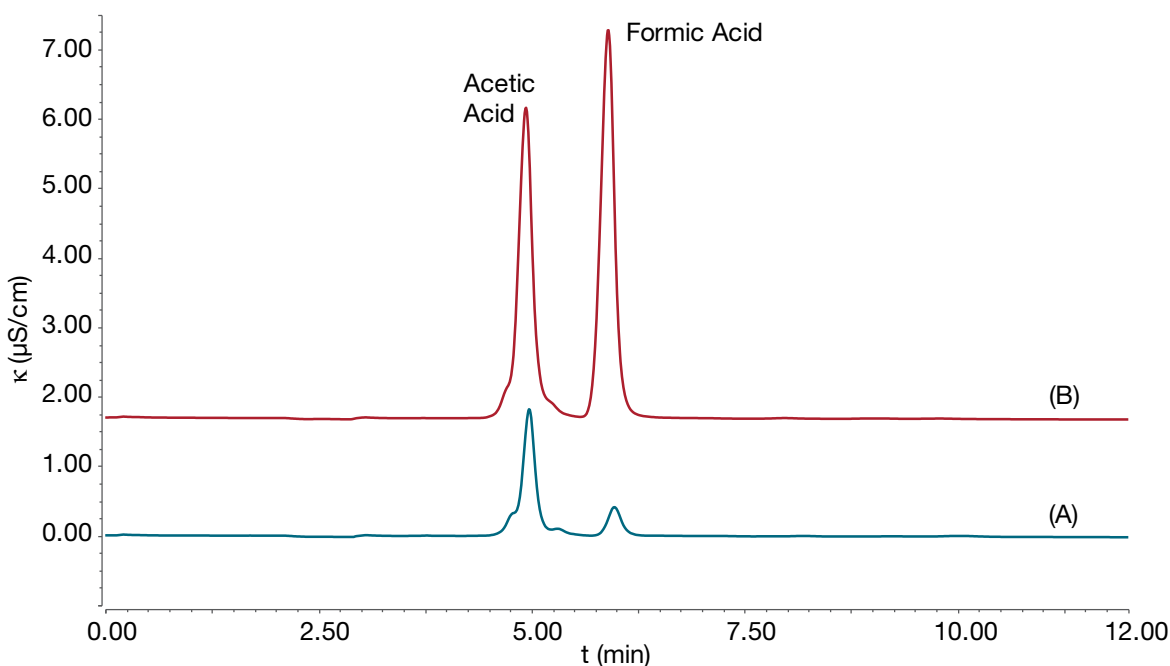


Figure 4. Determination of acetic acid and formic acid in diesel containing 2% motor oil.
(A) original sample (B) sample spiked with 10 mg/L of each organic acid (an offset of 20% was applied).

The possible impact of varying oil contents was evaluated by injecting diesel samples containing 2-, 5- and 10% motor oil, as well as being spiked with 10 mg/L of both organic acids. As an example, the chromatogram of the diesel sample containing 10% oil is presented in Figure 5. While the oil used to spike the diesel sample contained a negligible amount of formic acid, acetic acid was present at a significant level (278 mg/L). The values for acetic acid

were blank-corrected, resulting in an average recovery rate of $101\% \pm 4\%$ for both organic acids and for samples with varying oil content. Applying the standard addition approach of adding oil to diesel allows the determination of both organic acids even in pure oil samples—basically using diesel as additional diluent for the oil (Figure 6).

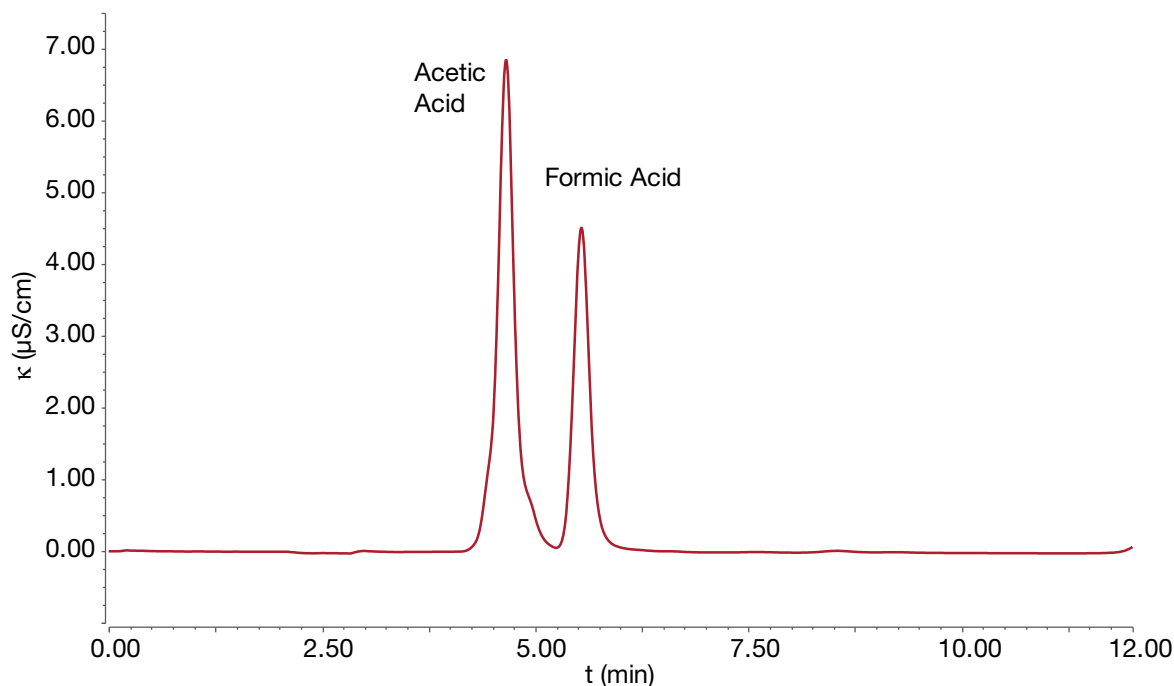


Figure 5. Acetic acid and formic acid in diesel plus 10% motor oil. Standard addition of 10 mg/L of each acid.

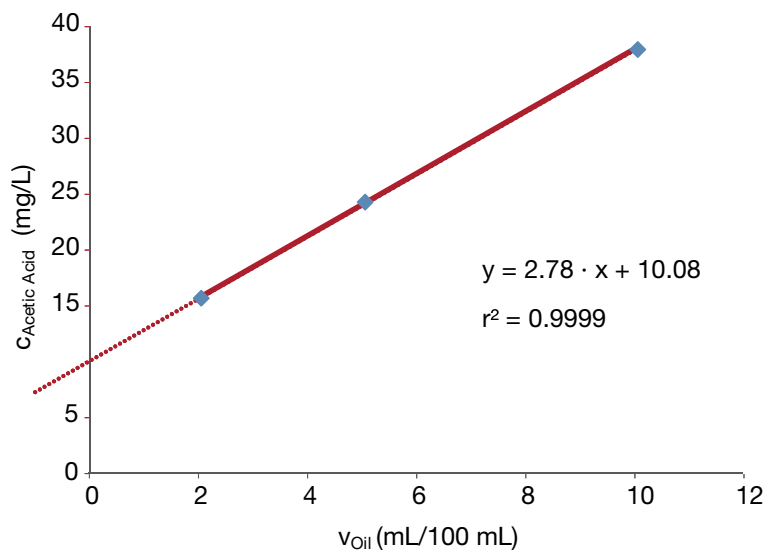


Figure 6. Addition of oil to diesel spiked with 10 mg/L of each acid.

In addition to 'clean' diesel and lab-made mixtures of diesel with oil, the method was applied to samples taken from stressed car engines. An example is shown in Figure 7. It contained 8.4 mg/L acetic acid and 1.8 mg/L formic acid. In addition to the two focus analytes of this study, additional peaks were detected, suggesting the presence of other short-chained organic acids. Identification of these unknowns could be done by applying MS-detection in conjunction with IC. The use of continuously regenerated suppressors permits the use of high-pH eluents, as well as gradients due to the neutralization of the column's effluent prior to the MS-interface. Results of initial experiments already identified unexpected organic acids, suggesting additional sources contributing to the potpourri of organic acids found in real world samples.

Conclusions

A new IC method was developed allowing the determination of acetic acid and formic acid in diesel and oil-containing diesel samples. Prior to the chromatographic analysis, the analytes were extracted and the matrix was eliminated based on a non-aqueous anion exchange step. With detection limits and quantification limits in the single-digit mg/L range and high repeatability and recovery—both intra-day and inter-day—the organic acids can be determined at low concentrations in diesel, diesel oil mixtures, and motor oil. Mixtures with up to 10% oil content were analyzed, showing no impact on the analytical performance, or method stability.

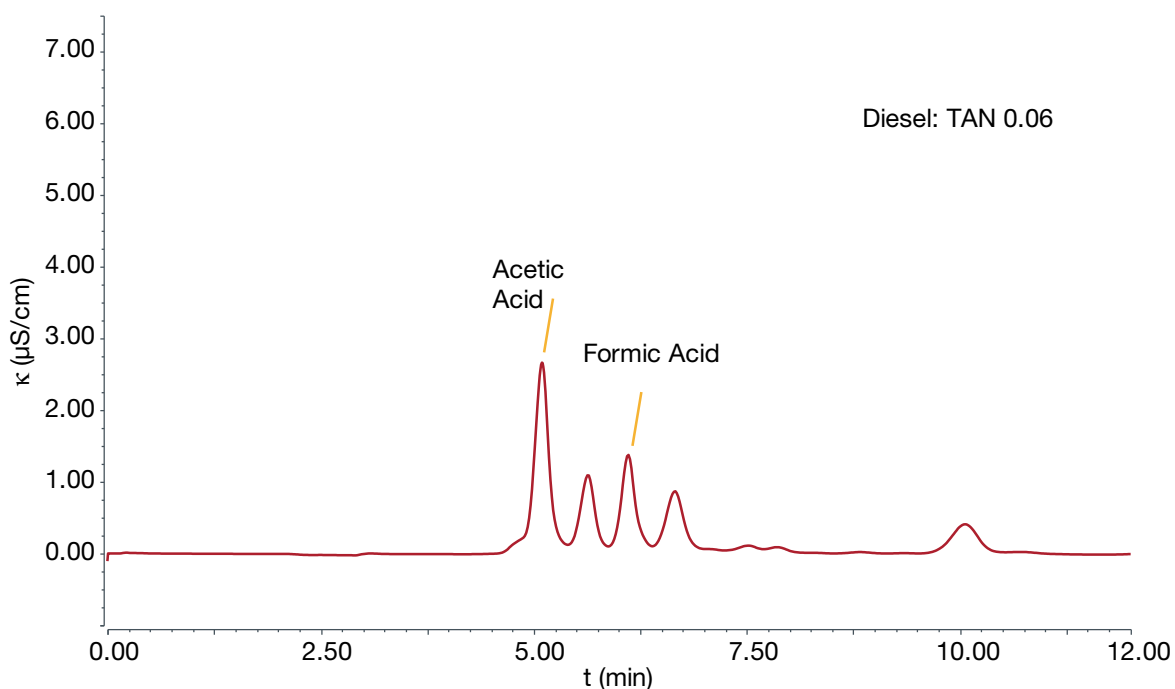


Figure 7. Diesel sample taken from a stressed diesel engine (TAN = 0.06).

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