Determination of Low Molecular Weight Organic Acids in Petroleum Products by Ion Chromatography

By Paul Voelker[1], Richard F. Jack[1], Ph.D., and Barbara van Cann[2],
[1]Thermo Fisher Scientific, 490 Lakeside Dr, Sunnyvale, CA 94085, USA
[2]Thermo Fisher Scientific, Takkebijsters 1, 4817 BL Breda, The Netherlands

The presence of organic acids in crude oil is a significant challenge for the oil and automotive industries due to their corrosive properties. While ion chromatography (IC) can be used for the selective and sensitive determination of low molecular weight organic acids in aqueous or water-miscible matrices, water-immiscible samples such as diesel and oil prove to be more challenging. Here, we describe an automated IC method for the direct determination of small molecular weight organic acids in diesel/oil mixtures using in-line matrix elimination, and highlight how this robust technique can be incorporated into routine testing workflows using integrated informatics.

Introduction

The presence of organic acids in crude oil is a significant concern for the oil and automotive industries, as their corrosive properties can result in extensive and costly damage to automotive engines [1]. Crude oil may contain over a thousand different organic acids with molecular weights of up to 1500 Daltons and carbon numbers of up to C80 [2]. The corrosivity of organic acids is closely related to their molecular mass and structure, with low molecular weight organic acids typically amongst the most corrosive [3,4]. As a result, there has been much interest in the development of methods for the robust, reliable and accurate analysis of organic acids in petroleum products [1].

An analytical technique that is often used for the identification and quantification of long chain organic acids in petroleum products is gas chromatography coupled with mass spectrometry (GC-MS). Using this approach, organic acids are typically isolated by solid phase extraction, methylated and subsequently analyzed by GC-MS [5,6]. However, this technique requires lengthy experimental set-up and is not well suited for the accurate analysis of short chain organic acids, as the lower hydrophobicities limit binding to the solid phase extraction columns.

An alternative approach, developed by Yang and colleagues, involves the direct injection of aqueous extracts of oil cracking fractions onto a polyethylene glycol coated capillary GC column [7]. This method enabled the detection of several low molecular weight acids, with the notable exception of formic acid. A high performance liquid chromatography (HPLC) method for the determination of organic acids with carbon numbers greater than C6 in aqueous oil sand extracts has also been developed by Wang and Kasperski, however small chain organic acids such as acetic acid and formic acid were not studied [8].

One technique that has been used for the selective and sensitive determination of low molecular weight organic acids in aqueous or water-miscible matrices is ion chromatography (IC) [9,10]. However, for samples such as diesel or diesel mixed with oil, this approach is challenging, as these samples cannot be injected directly into the instrument due to their water immiscibility.

Herein, we demonstrate an IC method for the direct determination of small molecular weight organic acids in diesel, oil and diesel/oil mixtures. This approach is made possible thanks to in-line matrix elimination techniques capable of

Table 1. Chromatographic columns and conditions.

Conditions	
Columns	Thermo Scientific™ Dionex™ IonPac™ AG11-HC, 2 x 50 mm (P/N 052963)
	Dionex IonPac AS11-HC, 2 x 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	10µL
Temperature	30ºC
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 2. Experimental conditions for matrix elimination and chromatographic analysis.

Time (min)	Sample transfer flow rate (mL/min)	Sample transfer and matrix elimination solvent*	KOH (mM)	Suppressor current (mA)	Comment
-5.0	0.1	H₂O	100	95	Begin conditioning of concentrator and analytical column
-4.5					
-3.0					
-2.5	1.0	2-Propanol	1		
0.0					Begin matrix elimination
5.0		H₂O		2	Matrix elimination finished
9.0					Injection and begin analysis
20.0			100		
22.5	0.1			95	
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).

removing the hydrophobic matrix prior to chromatographic analysis. This automated technique can be adopted into routine testing workflows through the use of integrated informatics solutions.

Experimental

Calibration solutions: Aqueous stock solutions of acetic acid and formic acid at a concentration of 100 mg/L were prepared. External standard calibration solutions were obtained by diluting the stock solution with water. Solutions used to evaluate the potential impact of organic diluents on the analytical results were prepared by mixing the stock solution with 2-propanol.

Sample preparation: Diesel and synthetic motor oil (5W-40) were purchased from a local petrol station. Mixtures of diesel and synthetic motor oil were prepared at different volume ratios to investigate the potential influence of different oils on the method. For the standard addition experiments, a small volume of the analyte stock solution (e.g. 1 mL) was added to each diesel/oil mixture (e.g. 100 mL). The acids were quantitatively extracted into the organic layer by vortexing for 10 minutes and the non-aqueous layer was then diluted with the same volume of 1-butanol. Aliquots were stored in glass HPLC autosampler vials prior to injection.

Chromatographic analyses: A Thermo Scientific Dionex ICS-2100 system possessing a degasser with an additional auxiliary valve, UltiMate LPG-3400 SD standard quaternary pump, and UltiMate WPS-3000 RS autosampler was used in this study. A Dionex IonPac AG11-HC (2 × 50 mm) column, Dionex IonPac AS11-HC (2 × 250 mm) column, and Dionex IonPac UTAC-LP1 trace anion concentrator column were used in the set-up shown schematically in Figure 1.

Samples were delivered to the Dionex IonPac UTAC-LP1 concentrator column using 2-propanol. Following extraction of the analytes, the organic sample matrix was removed with an excess of 2-propanol. The Dionex IonPac UTAC-LP1 column was subsequently rinsed with water, removing the 2-propanol. The sample was then injected by switching the valve holding the concentrator column into the eluent.

Analytes were then eluted and separated on the analytical column.

Chromatographic conditions and details of the gradient method employed are reported in Table 1 and Table 2. Thermo Scientific Chromeleon Chromatography Data System (CDS) software was used to initiate and control all analytical sequences, which were stored centrally using SampleManager Laboratory Information Management System (LIMS) software.

Results and Discussion
Method Calibration

External calibrations were performed using five concentrations of acetic acid and formic acid ranging from 1 mg/L to 20 mg/L. For each concentration, two separate preparations were analyzed, with duplicate injections of each solution. Optimal correlations were obtained using a linear calibration for formic acid and a quadratic calibration for acetic acid. The quadratic calibration for acetic acid results from the concentration-dependent dissociation of a weakly dissociated acid impacting on the area of peaks in measured by the conductivity detector [11].

The coefficients of determination, corresponding to the deviation of the measured data from the calibration curve, were found to be $r^2=0.999$ for acetic acid and $r^2=0.996$ for formic acid. Calibrations were checked each working day and remained stable for several weeks. The limit of determination, as calculated according to
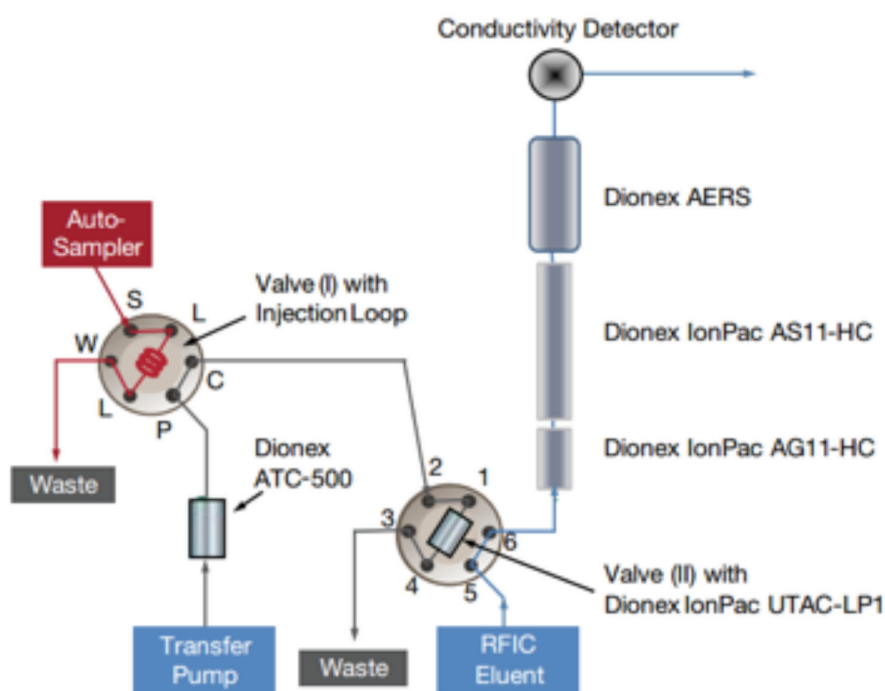

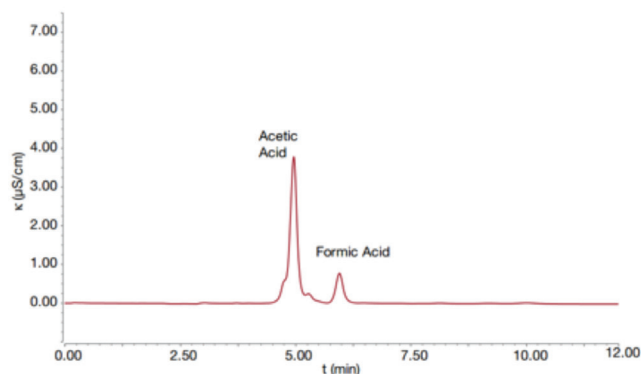Figure 1. Configuration of the chromatographic system.

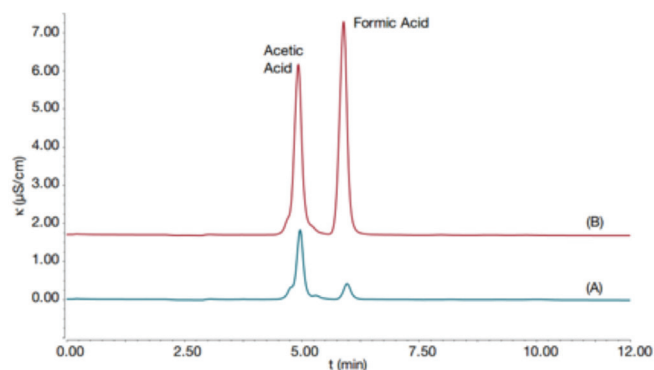*Figure 2. Representative chromatogram showing acetic acid and formic acid in diesel.*

Figure 3. 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).
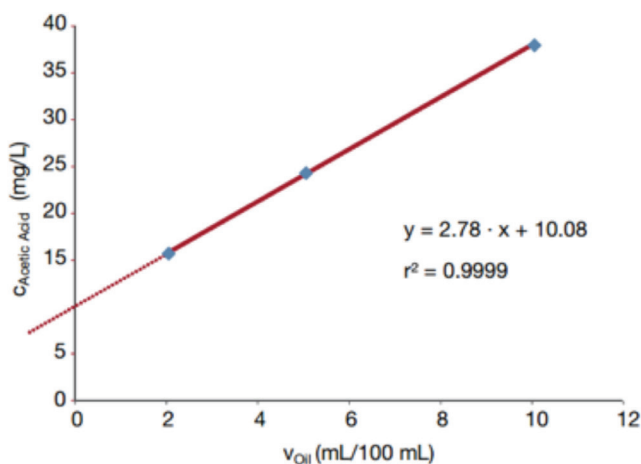

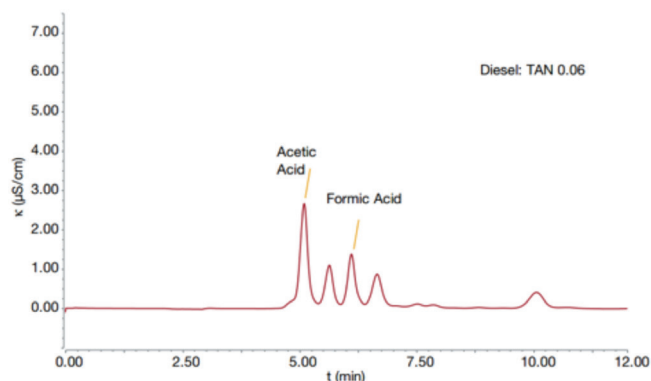*Figure 4. The addition, to diesel, of oil spiked with 10 mg/L of each acid.*

Figure 5. Representative chromatogram of diesel sample taken from a stressed diesel engine.

DIN 32645 [12], was 6.3 mg/L for acetic acid and 2.7 mg/L for formic acid, and the limit of detection was 3.8 mg/L for acetic acid and 1.5 mg/L for formic acid.

The effect of organic diluents on analytical recovery was also investigated, by comparing the response factors for standard solutions prepared in water and 2-propanol. The two approaches were found to be essentially equivalent, as the response factors for the organic acids in water and 2-propanol were within 1% of each other. As a result, all calibration experiments were performed using aqueous standards in order to simplify the analysis protocol. A representative chromatogram of acetic acid and formic acid in pure diesel is shown in Figure 2. The presence of other components close to the acetic acid peak likely indicates the presence of additional, short-chained organic acids, at a lower concentration than acetic acid. Additional experiments based on coupling IC with mass spectrometry should be performed to investigate this further.

Assessments of intra-day and inter-day repeatability and recovery were made using diesel samples containing 2% motor oil spiked with 10 mg/L of each acid. The reproducibility of the intra-day experiments was found to be in the region of 2% for both organic acids, with greater variation at lower analyte concentrations. Intra-day recovery was found to be 107% for acetic acid and 105% for formic acid. Chromatograms for the samples with and without the addition of acetic and formic acid are shown in Figure 3.

Inter-day recovery over four days was found to be 101% ± 5% for acetic acid and 90% ± 9% for formic acid. Inter-day repeatability for the analytes in the spiked samples was 4% for acetic and 9% for formic acid. Our experiments showed that the recovery of acetic acid remained stable over the entire period studied, whereas the concentration of formic acid decreased, potentially due to evaporative losses as a consequence of the higher vapor pressure relative to acetic acid. We conclude that the determination of formic acid in samples should therefore be performed as soon as possible after receipt.

Effect of Varying Oil Content

The impact of varying the oil content was investigated by analyzing diesel samples containing 2, 5 and 10% motor oil, spiked with 10 mg/L of both organic acids. While a negligible amount of formic acid was present in the oil used to spike the sample, acetic acid was present at a significant concentration (278 mg/L). The values for acetic acid were therefore corrected using a blank, and an average recovery rate of 101% ± 4% was recorded for both organic acids and for samples with varying oil content. A determination of both organic acids could be made by adding oil to diesel, even in pure oil samples (Figure 4).

Analysis of Oil Samples from Stressed Car Engines

This analytical method was applied to real diesel samples taken from stressed car engines. Figure 5 shows a representative chromatogram taken from a stressed diesel engine. This sample was found to contain 8.4 mg/L acetic acid and 1.8 mg/L formic acid. In addition to formic acid and acetic acid, a number of additional peaks were detected in the chromatogram, indicating the presence of other short-chain organic acids. The identification of these unknown components could potentially be undertaken using IC coupled with mass spectrometry. 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 mass spectrometric analysis. The results of initial experiments based on this approach have already identified unexpected organic acids, suggesting that a number of different sources contribute to the presence of organic acids in real world diesel samples.

As the damage caused by corrosive compounds in petroleum products can result in substantial financial costs and operational hold-ups, it is essential that organic acid determinations are accurate and reliable. By storing the standard operating procedures for this method centrally within the LIMS, the chromatographic method parameters could be downloaded to the instrument and initiated using the CDS. This automated experimental set-up is well suited for large-scale testing, allowing testing laboratories to process potentially hundreds of samples quickly and efficiently. Having all results readily available for continuous monitoring of product quality allows for rapid intervention if required.

Conclusions

The IC method described here, employing in-line matrix elimination techniques, is a robust and reliable approach for the accurate determination of organic acids in petroleum products. This automated set-up, when incorporated within an integrated informatics solution, may help testing laboratories rapidly and efficiently analyze large numbers of samples quickly and cost effectively.

This article is based on research by Joachim Trick[1], Cornelia Wanner[1], Cees Bruggink[2], Detlef Jensen[3]. 1Daimler AG, Stuttgart, Germany [2]Thermo Fisher Scientific, The Netherlands, [3]Thermo Fisher Scientific GmbH, Dreieich, Germany.

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