Feasibility Study to Determine Soap Concentration in Biodiesel from Alkali Metal Content

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1   Executive Summary

This report examines the feasibility of determining soap in biodiesel from the alkali metal content. Soap may be present in biodiesel and has been linked to precipitates above the cloud point. To calculate soap, the measurement of the alkali metals by ion chromatography (IC) and Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) were investigated. The IC and ICP-OES soap calculations were compared to the American Oil Chemists' Society (AOCS) Cc 17-95 titration method. For the ICP-OES, three procedures to isolate the alkali metals from the biodiesel before measurement were studied: a water extraction procedure, a sulfated ash procedure, and a solid phase extraction (SPE) procedure.

Sodium soap in the range of 4 to 65 ppm in biodiesel was successfully determined using IC. While using IC to determine calcium soaps, the soaps were not efficiently extracted into the water phase leading to underestimation of the soap concentration.

The use of ICP-OES to measure sodium soaps in aqueous extracts of biodiesel gave suppressed values compared to IC and titration. Modification to the ICP-OES procedures may be required if the technique is to be used to quantify soaps in water extracts of biodiesel. The measurement of alkali metals by ICP-OES concentrated in the sulfated ash from biodiesel was unsuccessful. The use of SPE to concentrate alkali metals for measurement by ICP-OES was also ineffective.

During this study, it was observed that the presence of calcium soap may affect the determination of total soap by AOCS Cc 17-95. Hence, when calcium soap is present in biodiesel, the total soap content may be underestimated due to the incomplete neutralization of the calcium soap by the acidic titrant.

2 <u>Acknowledgements</u>

3 <u>Disclaimer</u>

This report contains guidelines, procedure and protocols for performing reactions and testing that includes biodiesel, petro diesel, specialty chemicals and solvents. The authors in no way imply that these procedures are described in complete details or are safe to reproduce. When performing chemical testing or analyzing products, there is no substitute for good judgment and thorough background research on hazards and toxicities.

A list of possible hazards and hazardous environments when synthesizing and testing products described in the report include, but are not limited to: mechanical failure; high pressures; high temperature; high voltage, chemical toxicity, chemical reactivity, chemical explosion, acid burns and toxic vapors.

The authors assume no responsibility for any incident that occurs when reproducing procedures similar to or the same as described in this report.

4   <u>Introduction</u>

Biodiesel is made by transesterification of fats and oils, using a sodium methoxide or potassium methoxide catalyst. Residues from the catalyst used in transesterification may be responsible for elevated levels of sodium or potassium in the biodiesel. Also, calcium and magnesium from hard water may be introduced into the biodiesel during the water washing steps.[1] These metals, when present during the production of biodiesel, can cause the formation of soap molecules.[1] In addition, free fatty acid and water in the feedstock can also form soap in biodiesel.[1,2,3] Soap in biodiesel can contribute to filter plugging and engine deposits when used as a fuel.[4]

The American Society for Testing and Materials (ASTM) D6751 specification requires that the concentrations of alkali metals be limited to less than 5 ppm for sodium and potassium combined and less than 5 ppm for magnesium and calcium combined.[4] The sodium detected using ASTM specifications can be related to the amount of soap expressed as sodium oleate. The ASTM D6751 limit for sodium of 5 ppm would correspond to 66 ppm of sodium oleate soap (see Table 1 for conversion). However, soap levels below 66 ppm can contribute to higher cold soak times and precipitates above the cloud point, leading to a need for quantification of soap at levels below 66 ppm.[5] Methods for quantification of soap below 66 ppm are presented.

To determine metals in biodiesel, ASTM D6751 specifies the use of Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) according to method EN 14538.[4,6] ICP-OES methods can have disadvantages including spectral interferences from other elements in the sample, effects of the matrix, and difficulty in simultaneously determining each of the metals. Because of these reasons, ion chromatography (IC) was chosen for investigation to determine metals in biodiesel. IC is beneficial because it is capable of simultaneously determining sodium, potassium, calcium, and magnesium after a simple aqueous extraction of a biodiesel sample.[1]

The determination of soap from IC and ICP-OES assume the metals are predominantly present as soap in biodiesel. To calculate a soap concentration from a metal concentration, the molecular weight of the soap is needed. This study adopts the AOCS Cc 17-95 convention and expresses the soap concentration as oleate soap. The conversion factors to convert alkali metal concentrations to oleate soap concentrations are shown in Table 1 below.

Table 1 Factors to convert alkali metal ppm to oleate soap ppm

Element	Factor
Sodium	13.2
Potassium	8.2
Magnesium	24.1
Calcium	15.0

In this report, IC and ICP-OES were used to determine the soap content of biodiesel by measuring the alkali metal concentration and these values were compared with the amount of soap as determined by titration. In addition, water extraction, sulfated

ash, and solid phase extraction techniques for ICP-OES were investigated to isolate the alkali metals from the biodiesel.

5 <u>Titration</u>

The primary method currently used to measure the concentration of soap in biodiesel is based on American Oil Chemists' Society (AOCS) Cc 17-95, Soap in Oil Titrimetric Method.[7] In this method, soap (a weak base) is reacted with acid to form free fatty acid. This method assumes all the weak base is in the form of sodium oleate. AOCS recommends a sample size of 40 g, which generates a detection limit of 4 ppm sodium oleate.[7] Variations in sample size, volume of titrant added, and the concentration of base used in the titration can improve the detection limit to 2-4 ppm soap.

A limiting factor in achieving low detection limits in the titration may be human error. The endpoint, a change in color from green/blue to yellow, is determined visually, which can introduce an error in judging the end point.

<u>Materials and Methods</u>

The acetone was reagent grade purchased from Iowa State University Chemistry Stores. The 0.0100 N hydrochloric acid was purchased from Ricca Chemical Company. The bromophenol blue was purchased from TCI America. The titrations were performed based on AOCS Cc 17-95 with a biodiesel sample size of 50 to 100 g with a 1:1 dilution by weight with neutralized acetone.

<u>Results and Discussion</u>

Titration was used as a baseline test to determine the amount of soap in biodiesel. Titration results are found in sections 6 and 7 as related to IC and ICP-OES.

6 <u>Ion Chromatography</u>

The IC technique is a high pressure liquid chromatography procedure that measures ions in aqueous solutions using a conductivity detector. The method requires an aqueous sample that is obtained by a simple water extraction of the biodiesel. Application of this method to the analysis of soap in biodiesel requires an efficient water extraction of the alkali metals from the biodiesel.

<u>Materials and Methods</u>

Sodium oleate was from TCI, America. The sodium stearate (CAS 822-16-2) was purchased from Alfa Aesar. The distilled soy biodiesel was prepared in the laboratory. The distillation was done with an 18 inch Vigreux column under a vacuum of < 1 torr, to a pot temperature of 210 °C. Distillate was collected from 86 to 187 °C.

The IC analysis for biodiesel samples were performed at Inspectorate in Galena Park, Texas.

Preparation of Sodium Stearate Standard in Methanol

To a tared receiver was added 0.1025 g of sodium stearate, a portion of methanol was added, the sodium stearate was dissolved, and more methanol was added for a total mixture weight of 46.7129 g. The concentration of sodium stearate was calculated at 2194 ppm.

Preparation of Sodium Oleate Standard in Methanol

To a tared receiver was added 0.1084 g of sodium oleate, a portion of methanol was added, the sodium oleate was dissolved and more methanol was added for a total mixture weight of 48.1171 g. The concentration of sodium oleate was calculated at 2253 ppm.

Preparation of Calcium Stearate Standard in Methanol

To a tared receiver was added 0.1202 g calcium stearate, 44.2160 g of methanol and mixed to a fine milky dispersion. The calculated calcium stearate concentration was 2718 ppm.

Preparation of 65.7 ppm Oleate Soap in Distilled Soy Biodiesel (Table 2, Replicate #1)

To a tared vacuum filter flask was added 1.9526 g of sodium oleate standard in methanol (prepared above), 0.9913 g of sodium stearate standard in methanol (prepared above), 100.0 g of distilled biodiesel, and the mixture was heated to 88 °C for 10 minutes under a vacuum of 23 inches of Hg to remove methanol. The sodium oleate concentration was calculated at 44.0 ppm, the sodium stearate concentration was calculated at 21.7 ppm and the total sodium soap concentration was calculated at 65.7 ppm.

Preparation of 65.5 ppm Oleate Soap in Distilled Soy Biodiesel (Table 2, Replicate #2)

To a tared vacuum filter flask was added 1.9057 g of sodium oleate standard in methanol (prepared above), 1.0226 g of sodium stearate standard in methanol (prepared above), and 99.9236 g of biodiesel. The mixture was heated to 88 °C for 10 minutes under a vacuum of 23 inches of Hg to remove methanol. The sodium oleate concentration was calculated at 43.0 ppm, the sodium stearate concentration was calculated at 22.5 ppm and the total sodium soap concentration was calculated at 65.5 ppm.

Preparation of 63.8 ppm Sodium Oleate in an Undistilled Blend of Corn-soy Biodiesel

To a tared vacuum filter flask was added 22.3650 g of sodium oleate standard in methanol (prepared above), 789.2 g of corn/soy methyl ester and the mixture was heated to 88 °C for 10 minutes under a vacuum of 23 inches of Hg to remove methanol. The sodium oleate concentration was calculated at 63.8 ppm.

Preparation of 30.9 ppm Calcium Stearate in an Undistilled Blend of Corn-soy Biodiesel

To tared vacuum filter flask was added 2.2530 g of calcium stearate standard in methanol (prepared above), 200.6 g of an undistilled blend of corn-soy biodiesel and the mixture was heated to 75 °C for 10 minutes under a vacuum of 25 inches of Hg to remove methanol. The calcium stearate concentration was calculated at 30.9 ppm.

6

Results and Discussion

Hurum et al. have reported that IC can measure alkali metals with a standard deviation ranging from 0.009 ppm to 0.032 ppm in B20 and B99 samples.[1] One concern with this IC application is that the alkali metal calibration standards were prepared using water soluble salts.[8] The alkali metals present in biodiesel are assumed to be associated with soap. These soaps are only partially water soluble and may not partition into the water phase as readily as the water soluble salts. To test the feasibility of the Hurum procedure with soap, a two variable, two level experimental design was used. The variables were biodiesel type and soap concentration. The types of biodiesel examined were distilled soy biodiesel and undistilled corn biodiesel. The soap concentration varied from 4-10 ppm on the lower end to 42-65 ppm on the higher end. The results are summarized in Table 2. The concentration of soap was calculated from the concentration of sodium, with a conversion factor of 13.2.

Table 2   Ion chromatography for sodium and calculated soap on selected biodiesel samples

Sample	Soap Level	Replicate #	Soap Prepared ppm	Soap by Titration ppm	Sodium by IC ppm	Soap by IC ppm (calculated)
Distilled Soy Biodiesel	Low	1	--	4.5	0.45	5.9
Distilled Soy Biodiesel	Low	2	--	4.5	0.32	4.2
Distilled Soy Biodiesel	High	1	65.7	--	5.02	66.3
Distilled Soy Biodiesel	High	2	65.5	--	4.86	64.2
Undistilled Corn Biodiesel	Low	--	--	10.3	0.50	6.6
Undistilled Corn Biodiesel	High	--	--	42.5	1.49	19.7

For distilled soy biodiesel, the soap determined by IC agreed with the soap determined by sample preparation and titration. The pooled standard deviation based on two degrees of freedom for the replicates was ± 1.38 ppm.

In the undistilled corn biodiesel, soap by IC was less than the amount of soap by titration at both low and high soap levels. In Table 2, the high undistilled corn biodiesel measured 42.5 ppm soap by titration but the concentration of soap calculated by IC was only 19.7 ppm soap. This was less than 50% of the total amount of soap given by the titration method. Possible reasons for the difference may be that IC did not detect the total amount of sodium in the aqueous phase, water extraction did not separate all the sodium from the organic phase, or some of the soap came from other alkali metals.

To assess the capability of the IC method to detect all the sodium present, a sample of undistilled corn biodiesel (at 1.49 ppm sodium by IC) was spiked with 1.98 ppm of sodium as sodium nitrate. This made the total sodium concentration in the sample 3.47 ppm. The undistilled corn biodiesel was washed with water and IC detected

in the aqueous phase 3.37 ppm sodium or 95% of the spike ((3.37-1.49)/1.98) confirming that IC was accurately measuring all the sodium.

To test if sodium was being satisfactorily extracted, an undistilled blend of corn-soy biodiesel (7.6 ppm soap by titration) was spiked with 63.8 ppm of sodium oleate. These samples were extracted using water to remove the soap from the biodiesel blend. After extraction, the soap concentration in the biodiesel blend was measured at < 2.3 ppm soap by titration, indicating that at least 96.7% of the soap was removed from the biodiesel phase. The water extraction was effective in removing the sodium soap from the biodiesel blend.

An alkali metal other than sodium may affect the total soap content in the biodiesel. To test if this was the reason for the difference in soap content between titration and IC for the undistilled corn biodiesel, a sample of undistilled corn biodiesel containing 42.5 ppm soap (determined by titration) was washed with water and the aqueous phase was analyzed for potassium, calcium, and magnesium by IC. In this sample, potassium was not detected, the calcium concentration was 0.28 ppm, and a concentration of less than 0.1 ppm was found for magnesium. These metal levels plus the sodium level (1.49 ppm) calculated to 26.3 ppm oleate soap, which was significantly lower than the 42.5 ppm measured by titration. Therefore, the presence of other common alkali metal soap in the water phase did not explain the difference between the IC and titration methods.

To further investigate the origin of the different concentrations between titration and IC methods, the extraction of calcium soap from biodiesel was examined. An undistilled blend of corn-soy biodiesel spiked with calcium stearate was titrated and was found to contain 16.0 ppm of soap as sodium oleate. After the water extraction of this sample, the concentration of soap in the extracted biodiesel blend was found to be at least 9.5 ppm. This indicated that the calcium soap was not completely removed by the water extraction. The incomplete removal of calcium soap by the water extraction could be a possible reason for the differences between the soap values measured using the titration and IC methods.

During the course of this investigation, an undistilled blend of corn-soy biodiesel that contained 7.6 ppm sodium oleate was spiked with 30.9 ppm calcium stearate (which would be equivalent to 31.0 ppm sodium oleate). It was expected that the titration of this sample would yield around 38.6 ppm sodium oleate but this was not the case. The titration method detected only 16.0 ppm of sodium oleate, which is far less than the expected 38.6 ppm. The titration technique may not be efficiently neutralizing the calcium stearate spike. Therefore, the presence of calcium soap may cause the titration method to underestimate the total soap concentration. Further work to address this observation was not pursued.

7   Water Extraction of Soap for ICP-OES

Method EN 14538 is approved by ASTM D6751 to determine alkali metals in biodiesel. Method EN 14538 using ICP-OES is recommended for the measurement of sodium down to 1 ppm which translates to 13 ppm sodium oleate.[6] Attempts were made to determine the feasibility of ICP-OES to measure soap in aqueous extracts of distilled

soy and undistilled corn biodiesel. The following section describes a method to remove soap from the biodiesel using water extraction and calculation of soap via ICP-OES.

Materials and Methods

Sodium oleate, calcium stearate and potassium oleate were from TCI, America. The water was LC-MS Chromasolv® obtained from Fluka Analytical. The sodium stearate (CAS 822-16-2) was purchased from Alfa Aesar. The magnesium stearate was obtained from Sigma-Aldrich Co. The sodium, potassium, calcium, magnesium and yttrium ICP-OES standards were purchased from PerkinElmer Inc. The biodiesel samples were obtained from a commercially available source. All reagents were used as received unless otherwise stated.

ICP-OES analysis for biodiesel samples were performed at Inspectorate in Galena Park, Texas.

Water Extractions

To a clean 125 mL separatory funnel was added 25.0 g of biodiesel, 25.0 g of LC-MS Chromasolv® water, mixed, and allowed to separate until both layers were clear and the interface was clean. If separation did not occur overnight, the clear lower layer was removed, and the biodiesel and emulsion layers were centrifuged until a clear biodiesel layer and clean interface were obtained. The biodiesel layer was removed for analysis by titration.

Results and Discussion

The water extracts of the biodiesel samples were analyzed on an ICP-OES for elemental analysis. The same 2 x 2 design used in the IC analysis was run on the ICP-OES. The results are shown in Table 3.

Table 3 ICP of water extracts from selected biodiesel

Sample	Soap Level	Soap prepared ppm	Soap by Titration ppm	Soap by IC ppm	Sodium by ICP-OES ppm	Soap by ICP-OES ppm
Distilled Soy Biodiesel	Low	--	4.5	5.1	0.27	3.6
Distilled Soy Biodiesel	High	65.7	--	65.3	4.08	53.9
Undistilled Corn Biodiesel	Low	--	10.3	6.6	0.42	5.5
Undistilled Corn Biodiesel	High	--	42.5	19.7	1.28	16.9

In all cases, the soap calculation based on ICP-OES was lower than those measured by IC and titration. One of the possible reasons for lower ICP-OES values was the difference in pH between the calibration set which were prepared in 5% nitric acid and the actual samples. Further optimization of ICP-OES to calculate sodium soap in biodiesel is recommended.

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8   Soap Concentration Using Sulfated Ash for ICP-OES

Another technique used to concentrate alkali metals found in biodiesel is the mineralization of biodiesel in the presence of sulfuric acid according to ASTM D874-07. In this procedure, sulfuric acid and biodiesel are burned away leaving the alkali metals in the ash.   The sulfated ash residues resulting from the mineralization of the biodiesel samples were dissolved in an aqueous 1 % nitric acid solution and the sodium, potassium, magnesium, and calcium content were determined by ICP-OES.

To determine the feasibility of sulfated ash to concentrate soaps for ICP-OES, a 2 x 2 experimental design was used to screen effects of added soap concentration (2.5 ppm soap vs. 45 ppm soap) and type of matrix (distilled soy biodiesel versus undistilled corn biodiesel).   These four experiments were done in replicate to get an estimate of experimental error.   The samples were prepared by adding a known amount of soap dispersed in methanol to a known amount of biodiesel.

Additionally, an unspiked and undistilled corn biodiesel sample was chosen as a baseline.   The standards used in the ICP-OES calibration and the samples prepared from sulfated ash matched in pH in order to minimize this source of error.

Materials and Methods
The reagent grade tetrahydrofuran, trace metal grade nitric acid, and trace metal grade sulfuric acid were purchased from Fisher Scientific Inc.

The ICP-OES analyses on the sulfated ash samples were run at the Renewable Energy Group, Inc. Research Center in Ames, Iowa using a PerkinElmer Optima 7000 DV.   The samples were measured using the axial view.   The emission intensities were measured at 589.592 nm for sodium, 766.490 nm for potassium, 315.887 nm for calcium and 279.077 nm for magnesium.   Yttrium was used as an internal standard and measured at 371.029 nm.

Preparation of sulfated ash samples
A 10.0000 g sample of biodiesel was calcinated in accordance with ASTM D874, Standard Test Method for Sulfated Ash from Lubricating Oils and Additives.[9]   The crucible was rinsed with 20.0000 g of 1.00 % nitric acid to remove the ash from the crucible, and the rinses were collected and weighed to the nearest 0.0001 g for ICP-OES analysis.

Preparation of 2200 ppm soap standard
A combined standard solution of different metals was prepared by adding 0.1036 g of calcium stearate, 0.2082 g magnesium stearate, 0.3122 g of sodium oleate, and 0.4127 g of potassium oleate to a clean and dried 50 mL bottle with a magnetic stir bar. The solids were diluted with 46.7830 g of dry methanol and mixed until a stable milky dispersion was obtained.   This solution was added to undistilled corn biodiesel and distilled soy biodiesel samples to obtain the desired concentration of metals.

Results and Discussion

It was found that the sulfated ash method was inappropriate to prepare samples for ICP-OES because the alkali metal spikes were not recovered and variability between the replicates was uncontrolled. The mineralization of the biodiesel samples proved ineffective in accurately measuring soap content, and a different technique is required to get the alkali metal of the soaps into aqueous solutions.

9   Soap Concentration Using Solid Phase Extraction for ICP-OES

Another sample preparation that could be used for ICP-OES to concentrate soap other than sulfated ash or water extraction is solid phase extraction (SPE). SPE has been successfully used to concentrate minor components in distilled biodiesel.[10] In this study, SPE was used to concentrate the soap from biodiesel by accumulating soap on an absorbent. The soap was freed from the absorbent using an appropriate solvent. To test the feasibility of the SPE procedure, an undistilled blend of corn-soy biodiesel with a soap content of 7.6 ppm was chosen. Since the EN 14538 method uses a 10 g sample of biodiesel to detect sodium down to 0.5 ppm, a 5-fold sample size was chosen to allow the measurement of sodium down to 0.1 ppm. Therefore, a 50 g sample of biodiesel was used. The titration method was utilized to determine the concentration of soap in the evaluation of the SPE technique.

Materials and Methods

SPE cartridges from Alltech were used to determine the type and size of the absorbent bed necessary to separate soap from biodiesel. The cartridges were conditioned with 5 g of heptane. The heptane was added to the cartridge and allowed to drain by gravity. After conditioning, a sample of 50 g of biodiesel was added to the cartridge and allowed to drain at the rate of 1 drop every 1-3 seconds. The rate of drain was controlled by applying air pressure to the top of the barrel of the cartridge. The eluate was collected in a tared container and was titrated for soap content using AOCS Cc 17-95 as the guiding method. The cartridge was washed with 10.0 g of tetrahydrofuran. The washes were drained from the cartridge by gravity and collected in a tared scintillation vial. The solvent was removed on a hotplate at 130 °C.

Results and Discussion

Silica and alumina neutral were chosen for the absorbent phase. Ion exchange resins were avoided since removal of absorbed materials has been reported to be difficult.[11] The results of the solid phase extractions are shown in Table 4.

Table 4 SPE for soap removal in an undistilled blend of corn-soy biodiesel

Absorbent Bed	Weight of Bed mg	Soap in Biodiesel ppm	Soap in Eluate ppm
Silica	1000	7.6	6.8
Silica	2000	7.6	3.5
Alumina Neutral	500	7.6	6.4

From Table 4, it can be seen that the use of silica and neutral alumina as the absorbent beds was not successful in removing the soap present in the undistilled blend of corn-soy biodiesel, even when the quantity of soap is relatively low (7-8 ppm). The SPE technique did not remove soap from the biodiesel and does not appear feasible for ICP-OES methods and further investigations were discontinued.

10 Conclusions

The use of sodium concentration to estimate low levels of sodium soap was found to be feasible for biodiesel using IC. The water extraction used for IC did not adequately separate the calcium stearate from the biodiesel making IC incapable to accurately measure the calcium concentration in the aqueous samples. The water extraction technique used on the biodiesel needs further investigation to ensure the transfer of calcium ions to the water phase.

The aqueous ICP-OES technique used in this study did not measure sodium accurately in the form of sodium soap in water extracts. ICP-OES methods that measure alkali metals in water need to be modified to calculate sodium soap. One possible modification could be the acidulation of the aqueous extracts to match the pH of the calibration standards for ICP-OES.

The sulfated ash method, ASTM D874-07, and the SPE method were not found to be adequate to isolate alkali metals from biodiesel into the aqueous phase.

During the course of this study, it was also found that the titration described in AOCS Cc 17-95 appeared to have difficulty in the neutralization of calcium soap in biodiesel and may have underestimated the total soap when calcium soap was present.

11 <u>References</u>

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