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Determination of Cations in Biodiesel Using a Reagent-Free™ Ion Chromatography System with Suppressed Conductivity Detection

INTRODUCTION

By 2030, biofuels have the potential to replace more than 10 billion gallons of petroleum currently used in the United States, according to economic analysis.¹ As the supply of petroleum fuel tightens and its price increases, use of biofuels will increase to meet consumer demand. One example is biodiesel, which has become more prevalent in the consumer market and is financially supported by the U.S. Department of Energy and European Union Directive 2003/30/EC. This fuel is sold as unmodified biodiesel (B100) and for blending with petroleum diesel. One common biodiesel blend that is marketed for passenger vehicles is B20, which is a mixture of 20% biodiesel and 80% petroleum diesel.

Biodiesel is produced by reacting plant or animal oils with an alcohol, such as methanol, in the presence of a catalyst to produce the desired methyl esters and the byproduct glycerol. For most biodiesel currently being produced, a basic catalyst of either sodium or potassium hydroxide or alkoxides is used during this transesterification process.² Residues from these catalysts persist in the biodiesel and are responsible for elevated sodium or potassium levels in the fuel that must be washed out. In addition to the residual catalyst, glycerol is removed before the biodiesel can be used. Water is often

added during these steps to separate the glycerol from biodiesel and to remove the residual catalyst. The water purity has an impact on the quality of the biodiesel. If the water used is hard, magnesium and calcium can transfer into the fuel during the removal of glycerol and the washing steps.

To ensure reliable quality of biodiesel as it gains widespread acceptance, the ASTM International has adopted ASTM D6751.³ The requirements stated in the ASTM document are predominantly equivalent to the EU standard, EN 14214, and a significant effort is underway to globally harmonize biofuel quality standards.⁴ Currently D6751 applies to B100 biodiesel that is used for blending, ensuring that the source material, and therefore blends using B100 and petroleum diesel, will be of high quality.⁵ Among the many parameters controlled by this standard are the concentrations of sodium, potassium, magnesium and calcium in the biodiesel. Alkali and alkaline earth metals in the fuel can form ash and soaps, which may cause detrimental deposits in engines and damage emissions control systems.⁶ To prevent engine damage from the blended fuels, these cations are limited to concentrations less than 5 ppm for sodium and potassium combined and less than 5 ppm for magnesium and calcium combined.

ASTM D6751 specifies the use of ICP-OES by reference to EN 14538 for the determination of alkali and alkaline earth metals in biodiesel. In Europe, methods EN 14108 and EN 14109 are also specified and use atomic absorption (AA) for measuring sodium and potassium in biodiesel. These methods suffer several drawbacks, including potential spectral interferences from other elements in the sample, effects of the complex matrix, difficulty in simultaneously determining each of the cations of interest, and complicated sample pretreatment procedures to avoid interferences.⁷ Ion chromatography is capable of simultaneously determining, within a reasonable time, the target cations sodium, potassium, magnesium, and calcium after a simple liquid extraction of a biodiesel sample.

This Application Note describes a Reagent-Free ion chromatography method using the IonPac[®] CS12A-5 μm column and suppressed conductivity detection for the determination of cations in biodiesel. The IonPac CS12A-5 μm (3 x 150 mm) column is a high-efficiency, moderate capacity column specifically designed for fast separations of common inorganic cations. The substrate is functionalized with a mixed hydrophilic carboxylic acid/phosphonic acid allowing for convenient separation of cations. The proposed method is simplified by using an electrolytically generated methanesulfonic acid (MSA) eluent, requiring only a deionized water source for operation. The linearity, detection limits, precision, and recovery of sodium, potassium, magnesium, and calcium in biodiesel are demonstrated.

EQUIPMENT

Dionex ICS-3000 Reagent-Free Ion Chromatography (RFIC-EG[™]) system consisting of:

SP Single Pump or DP Dual Pump module

EG Eluent Generator module

DC Detector/Chromatography module (single or dual temperature zone configuration)

AS Autosampler

EluGen[®] EGC II MSA cartridge (P/N 058902)

Continuously-Regenerated Cation Trap Column, CR-CTC II (P/N 066262)

Chromeleon[®] 6.8 Chromatography Workstation

Polystyrene Autoselect vials with caps and septa, 10 mL (Dionex P/N 055058)

Norm-ject[™] syringes, 10 mL (VWR P/N 53548-006)

Nalgene[®] 125 mL polypropylene separatory funnel (VWR P/N 30356-744)

IC Acrodisc[®], 22 mm, 0.2 μm Supor (PES) membrane syringe filters (PALL P/N 4583T)

Nalgene 125 mL HDPE narrow mouth bottles (Nalgene P/N 2002-0004)

REAGENTS AND STANDARDS

Deionized water, Type I reagent grade, 18 M Ω -cm resistivity or better

1000 ppm Lithium Standard (Ultra Scientific P/N ICC-104)

1000 ppm Sodium Standard (Ultra Scientific P/N ICC-107)

1000 ppm Potassium Standard (Ultra Scientific P/N ICC-106)

1000 ppm Magnesium Standard (Ultra Scientific P/N ICC-105)

1000 ppm Calcium Standard (Ultra Scientific P/N ICC-103)

Nitric Acid, ULTREX[®] Ultrapure Reagent (JT Baker P/N 6901)

Hydrochloric Acid, OmniTrace[®] Ultra (EMD P/N HX0608/7)

Combined Six Cation II Standard (Dionex P/N 046070)

Samples

B99 and B20 samples were collected from local retail outlets in HDPE gasoline containers. Due to the potential for oxidation of biodiesel, samples should be analyzed on the day of collection.⁸

CONDITIONS

Columns: IonPac CG12A-5 μm , 3 \times 30 mm (P/N 057184)
IonPac CS12A-5 μm Analytical, 3 \times 150 mm (P/N 057185)

Eluent: 20 mM MSA

Eluent Source: EGC II MSA with CR-CTC II

Flow Rate: 0.50 mL/min

Temperature: 30 °C (column compartment)
30 °C (detector compartment)

Inj. Volume: 25 μL

Detection: Suppressed conductivity, CSRS 300 (2 mm), Autosuppression recycle mode, power setting – 30 mA

Background

Conductance: <0.250 μS

Noise: ~0.1–0.2 nS

System

Backpressure: ~2500 psi

PREPARATION OF SOLUTIONS AND REAGENTS

Eluent Solution

Generate the methanesulfonic acid (MSA) eluent online by pumping high quality deionized and degassed water through the EGC II MSA cartridge. Chromeleon software will track the amount of MSA used and calculate the remaining lifetime.

Alternatively, prepare 20 mM MSA by carefully adding 1.92 g of concentrated MSA to a 1-L volumetric flask containing about 500 mL of deionized water. Dilute to the mark and mix thoroughly. Degas the eluents and store in plastic labware.

Standard Solutions

Stock solutions of 1 mg/L were prepared gravimetrically by pipetting 0.100 mL of a commercial 1000 mg/L standard into a 125 mL HDPE bottle and diluting to a total volume of 100 mL (100 g). The stock solutions were stored at 4 °C when not in use. Combined working standards with each of the four cations were prepared from the 1 mg/L stock solutions or the 1000 mg/L standards by making the appropriate dilutions with DI water.

Sample Preparation

Accurately dispense 25.0 mL of biodiesel into a 125 mL polypropylene separatory funnel. Add 25.0 mL of deionized water and vigorously shake the funnel for 1 min. Allow the emulsion to separate for 15 min. Collect the aqueous layer (bottom layer) in a 10 mL plastic syringe fitted with a PALL 25 mm, 0.2 μm IC Acrodisc syringe filter. Filter 3 mL of the solution to waste and the remaining solution directly into a Dionex 10 mL polystyrene Autoselect vial for analysis.

Comparative biodiesel extractions were performed to evaluate the suitability of using DI water as the extractant. Hydrochloric acid and nitric acid were each tested at concentrations of 1–10 mM. No improvement in extraction efficiency was observed when using the acidified extractants. Weakly acidic solutions (< 5 mM) had a disadvantage of significantly stabilizing the water-fuel emulsion leading to very poor extractions. Acidic extraction solutions are not recommended due to the lack of improvement in the extraction efficiency and the stabilization of the water-biodiesel emulsion.

RESULTS AND DISCUSSION

In preliminary experiments, the IonPac CS12A was investigated for the determination of cations in biodiesels; however, the IonPac CS12A-5 μm was superior for this application due to its smaller particle size and column format that is specifically designed for the fast analysis of cations. The IonPac CS12A-5 μm column can simultaneously separate six common cations in less than 15 min using an optimized 20 mM MSA eluent (Figure 1). This column is also well suited for the separation of extractable amines, which may be present in the biodiesel, reducing the potential for interfering peaks. The IonPac CS12A-5 μm provides advantages over ICP-OES, as described in the current ASTM method, by separating the cations with limited interferences from other elements and matrix components that may be present in the biodiesel, and by delivering equal or better sensitivity than the ASTM ICP-OES method.

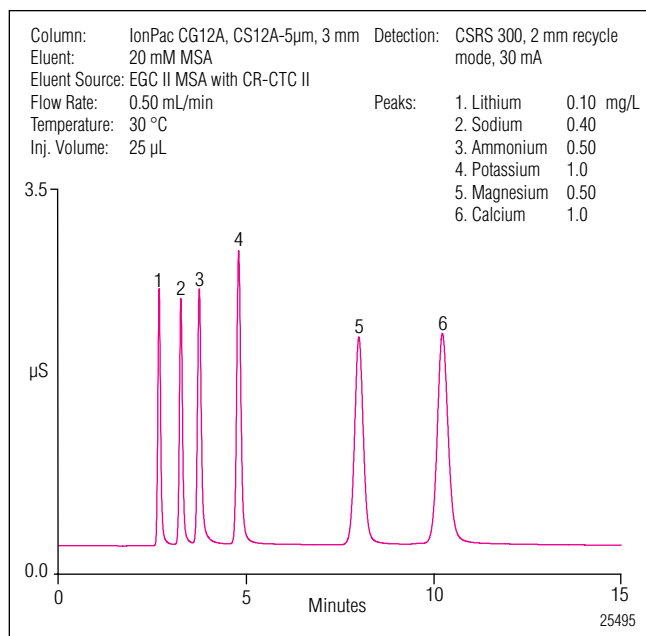


Figure 1. Separation of six cation standard on the IonPac CS12A-5 μm

Linear Range, Limit of Quantitation, Limit of Detection

To determine the linearity of the method, calibration standards were injected in triplicate covering the expected concentration range of cations in the samples. Calibration plots produced correlation coefficient (r^2) values between 0.9956 and 0.9984 using least squares regression fits with weighting to accurately represent the lower values of the calibration curve. The CS12A-5 μm column is a medium capacity column and over-loading can occur when analyzing high ionic strength samples. This is most evident in the chromatography of magnesium and calcium. For samples that contain 2.5 mg/L or more of these cations it is recommended that the injection volume be reduced to 10 μL .

The limit of detection (LOD) was determined by measuring the peak-to-peak noise in a representative one-minute segment of baseline where no peaks elute followed by analyzing a standard at a concentration expected to provide a chromatogram with a signal-to-noise (S/N) ratio of 3. Typical baseline noise for this method using the CSRS 300 suppressor in the recycle mode is ~0.1–0.2 nS/min. Similarly, the limit of quantification (LOQ) was determined by injecting a standard at a concentration that resulted in a S/N ratio of 10. The LODs ranged from 0.1 to 0.4 $\mu\text{g/L}$ and LOQs ranged from 0.3 to 1.1 $\mu\text{g/L}$. As an alternative to measuring the concentration at the S/N ratio of 3, the LOD for magnesium was determined by performing seven replicate injections of a 0.2 $\mu\text{g/L}$ magnesium standard and applying the student's t-test at a 99% confidence level. Table 1 summarizes the linearity, LOD, and LOQ for each of the target cations.

Table 1. Linear Range, LOD, LOQ, and Precision Data for Cations

Analyte	Range (mg/L)	Corr. Coeff. (r ²)	LOD (µg/L)	LOQ (µg/L)	Concentration Used for Precision Injections (mg/L)	Retention Time Precision (RSD) ^a	Peak Area Precision (RSD) ^a
Sodium	0.002–2.50	0.9958	0.1	0.3	0.0523	0.04	0.37
Potassium	0.002–0.150	0.9956	0.2	0.6	0.0098	0.02	1.83
Magnesium	0.010–0.250	0.9977	0.2 ^b	0.6	0.0479	0.03	1.83
Calcium	0.020–0.465	0.9984	0.4	1.1	0.0730	0.03	0.81

^a Relative Standard Deviation, n=20

^b LOD for magnesium = (t) x (S) Where t = Student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom (t = 3.14 for seven replicates of the LOD Standard), and S = standard deviation of the replicate analysis.

Accuracy and Precision

The method performance was initially evaluated with replicate injections of a standard. Relative standard deviations (RSDs) of the retention times and measured peak areas were calculated from 20 injections of a mixed cation standard solution prepared at concentrations ranging between 0.0098–0.0730 mg/L for the target cations. The retention time and peak area RSDs were ≤0.04% and ≤1.83%, respectively. The individual values for each cation are summarized in Table 1.

The method was used to determine the concentrations of sodium, potassium, magnesium, and calcium in B20 and B99 biodiesel from triplicate sample extractions over three days. The combined sodium and potassium concentration determined in B20 samples was 0.0463 ± 0.0009 mg/L and the combined magnesium and calcium was 0.0306 ± 0.0012 mg/L, both well below the ASTM limits. Figure 2A shows an example chromatogram of a B20 extraction. The four cations are well resolved from one another and easily quantified in less than 15 min. This figure also demonstrates the advantage of separating potential interferences from the target cations. The unidentified peak shown in Figure 2A (Peak #2) is likely a primary amine that was extracted from the B20 biodiesel sample. However, this peak is well resolved from sodium and potassium and does not interfere with the determination of these cations. B20 contains only 20% biodiesel and would likely have low concentrations of cations after processing and blending with petroleum diesel. B99 is expected to be representative of B100, the biodiesel formulation the ASTM standards apply to, due to the higher percentage of biodiesel. The combined

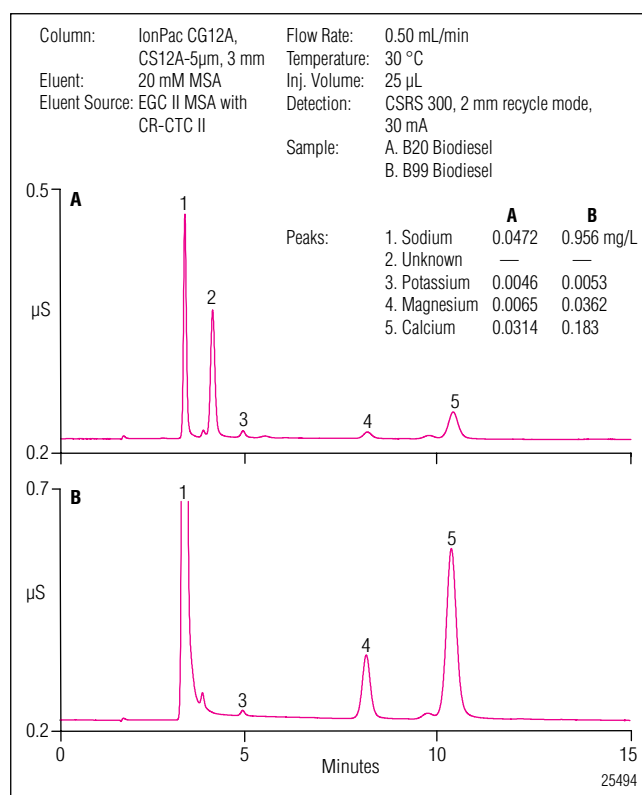


Figure 2. Comparison of the separation of B20 and B99 Biodiesel.

sodium and potassium concentration determined in B99 was 0.991 ± 0.032 mg/L with a combined magnesium and calcium concentration of 0.207 ± 0.010 mg/L, both of which are also well below the ASTM limits, but significantly higher than the concentrations found in B20. Figure 2B shows a representative chromatogram of B99 after a liquid extraction with DI water. Similar to the B20 sample, the cations were easily identified and quantified.

Prior to testing the precision of the method with biodiesel sample extracts, the extraction efficiency was evaluated by spiking biodiesel with lithium, which was not detected in the samples. Lithium (0.050 mg/L) was spiked into a biodiesel sample and the mixture was thoroughly mixed to ensure transfer of the lithium prior to extraction. DI water extractions resulted in lithium recoveries in the range of 95–105% for B20 and B99 samples, which indicates an efficient removal of the target cations from the biodiesel.

Intraday and interday precision for B99 biodiesel extractions were evaluated over three consecutive days (Table 2). Intraday peak area precisions of a single biodiesel extraction ranged from 0.07% to 2.27%. The peak area and retention time precision results for the other target cations in the extract were equivalent to or better than those determined for standards (Table 1). The interday precision, determined by performing three separate extractions of B99 over three days, was between 3.2% and 5.7%. This interday variability is primarily a measure of the reproducibility of the sample preparation.

The accuracy of the method was verified by determining recoveries of spiked B99 extractions over three days. Recoveries were calculated based on the difference in response between the spiked and unspiked samples, with average recoveries of the four target cations

ranging from 98.0% to 108% (Table 3). Interday RSDs of the determined concentrations ranged from 0.05% to 2.4%. The recoveries for these samples are excellent and show that an analysis of B99 is accurate. Similar results are expected for analysis of B100 samples.

As a rigorous test of the method, recoveries from spiked B20 extraction samples were determined. These samples were previously analyzed and contain target cation concentrations >100 times less than the ASTM limits. Fractions of a single B20 sample extraction were spiked with known concentrations of approximately one, two, and three times those previously determined. Average recoveries ranged between 71.1% and 106% (Table 4). The recoveries of the individual cations improve as the spiking concentration increases. This is particularly true for calcium and magnesium, which are present in concentrations near the lowest calibration standard. The cation concentrations found in B20 are minor in comparison to the ASTM standard, and while they are not representative of an analysis of B100, the recovery values do show that the method is suitable for analysis of a sample containing low concentrations of cations. The precision of recovery experiments when the amounts of endogenous cations are low will be dependent on the reproducibility of the blank. During these studies we observed variable calcium amounts in the blanks.

Table 2. B99 Extraction Precision

Day	Analyte	n	Average Amount (mg/L)	Average Retention Time (min)	Retention Time Precision (RSD)	Peak Area Precision (RSD)
1	Sodium	3	1.02	3.3	0.00	0.07
	Potassium		0.0048	4.8	0.04	1.61
	Magnesium		0.0346	8.1	0.02	0.31
	Calcium		0.170	10.3	0.02	0.32
2	Sodium	3	0.985	3.3	0.06	0.16
	Potassium		0.0049	4.8	0.04	2.27
	Magnesium		0.0324	8.1	0.05	1.26
	Calcium		0.165	10.3	0.05	0.65
3	Sodium	3	0.956	3.3	0.06	0.15
	Potassium		0.0054	4.8	0.00	1.49
	Magnesium		0.0362	8.1	0.02	0.28
	Calcium		0.182	10.3	0.02	0.42

Table 3. Cation Recoveries from B99 Biodiesel Extracts

Day	Analyte	n	Amount Found (mg/L)	Amount Added (mg/L)	Average Recovery (%)
1	Sodium	3	1.02	0.859	103 ± 0.3
	Potassium		0.0053	0.0075	104 ± 1.2
	Magnesium		0.0360	0.0419	98.1 ± 2.1
	Calcium		0.174	0.164	102 ± 0.3
2	Sodium	3	0.985	0.963	103 ± 0.3
	Potassium		0.0054	0.0084	108 ± 1.3
	Magnesium		0.0345	0.0470	98.0 ± 0.6
	Calcium		0.169	0.183	102 ± 0.3
3	Sodium	3	0.910	1.03	103 ± 0.2
	Potassium		0.0051	0.0091	104 ± 4.1
	Magnesium		0.0337	0.0505	98.0 ± 1.4
	Calcium		0.164	0.197	101 ± 0.3

Table 4. Recoveries of Spiked B20 Samples

v/v% Spiked	Analyte	n	Amount Found (mg/L)	Amount Added (mg/L)	Average Recovery (%)
1%	Sodium	3	0.0414	0.0527	103 ± 0.3
	Potassium		0.0043	0.0051	93.5 ± 3.5
	Magnesium		0.0055	0.0102	71.1 ± 6.6
	Calcium		0.0221	0.0205	74.6 ± 2.8
2%	Sodium	3	0.0416	0.0991	102 ± 0.2
	Potassium		0.0046	0.0097	95.2 ± 1.2
	Magnesium		0.0055	0.0191	76.7 ± 0.6
	Calcium		0.0206	0.0386	77.4 ± 0.4
3%	Sodium	3	0.0424	0.145	106 ± 0.1
	Potassium		0.0050	0.0141	106 ± 1.6
	Magnesium		0.0055	0.0279	82.7 ± 2.4
	Calcium		0.0191	0.0564	82.4 ± 2.5

CONCLUSION

This Application Note describes the use of the IonPac CS12A-5 μm with 20 mM MSA eluent and suppressed conductivity detection to determine cations in biodiesel samples at concentrations ranging from 0.002 to 2.50 mg/L. The high resolution and column design of the CS12A-5 μm allows for rapid separation of the target cations with a wide response range. This method simplifies determination of the four cations of interest compared to AA and ICP by requiring a simple sample preparation, simultaneous determination of the target cations, and limited interferences from other elements in the sample. Commercially available biodiesel samples were evaluated and samples with low concentrations of cations (B20) and nearly 1 ppm combined sodium and potassium (B99) were successfully analyzed using this method.

LIST OF SUPPLIERS

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