Determination of Cations in Biodiesel

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ABSTRACT

Economic analysis predicts that biofuels have the potential to replace over 10 billion gallons of petroleum currently used in the United States by 2030. As petroleum fuels become more costly, biofuel use will increase as customers seek to lower fuel costs. ASTM International has adopted ASTM D6751, predominantly equivalent to the EU standard, EN 14214, to ensure reliable quality of biodiesel as it gains widespread acceptance.[1] This standard limits combined sodium and potassium concentrations to less than 5 ppm and combined magnesium and calcium to less than 5 ppm to prevent engine damage from deposits.

A method using the IonPac® CS12A-5µm column and suppressed conductivity detection has been developed for the determination of these cations in biodiesel. Biodiesel samples composed of 20% biodiesel (B20) and 99% biodiesel (B99) were analyzed using this method. The combined cation concentrations determined in B20 and B99 samples were well below the ASTM limits.

The interday precision for B99 sample extractions ranged from 3.2–5.7%. Recoveries range from 98.0–108% and show the method is accurate. These results show that ion chromatography is well suited for routine accurate cation analysis of biodiesel and biodiesel blends to ensure their quality.

EXPERIMENTAL

Equipment

A Dionex ICS-3000 RFIC™ system equipped with:

- EluGen® EGC II MSA cartridge
- IonPac CS12A-5µm (3 × 150 mm) and CG12A (3 × 30 mm)
- CSRS® 300 (2 mm) suppressor operating at 30 mA in the recycle mode

All separations used 20 mM MSA at a flow rate of 0.5 mL/min and a 25 µL sample injection volume.

Chromeleon® Chromatography Management Software was used for system control and data processing.

Sample Preparation[2]

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 and filter through a 25 mm, 0.2 µm IC Acrodisc® syringe filter into a vial for analysis.

RESULTS AND DISCUSSION

The IonPac CS12A-5µm 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.

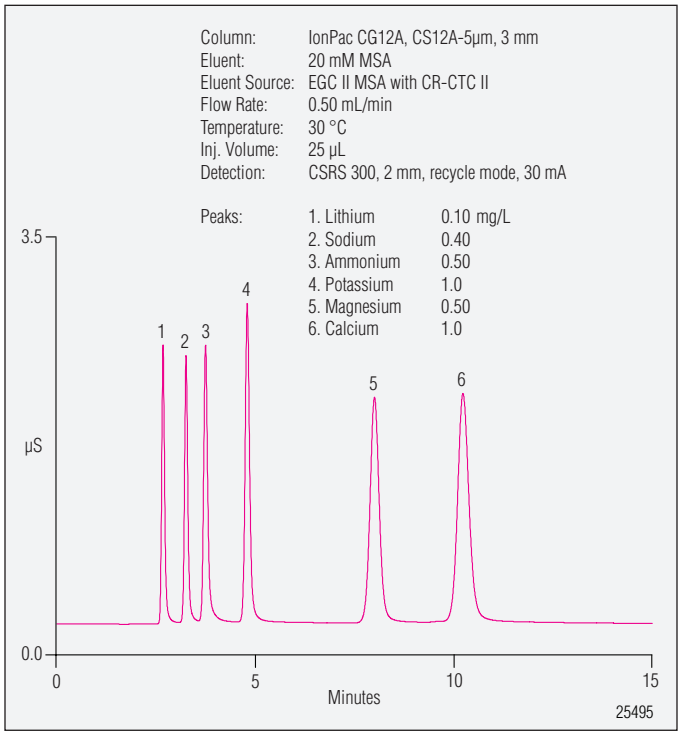

Figure 1. Separation of six cations on the IonPac CS12A-5µm.

Calibration standards were injected in triplicate covering the expected concentration range of cations in the samples. Calibration plots used least squares regression fitting with weighting to accurately represent the lower values of the calibration curve. Table 1 summarizes the linearity, LOD, and LOQ for each of the target cations. With the exception of magnesium as noted below, LODs were determined by the concentration of a cation that provided a signal to noise ratio of three.

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	0.002–2.500	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) × (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.

SAMPLE ANALYSIS

Extraction Efficiency

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. DI water extractions resulted in lithium recoveries in the range of 95–105%, indicating an efficient removal of the target cations from the biodiesel.

Sample Results

The method was used to determine the concentrations of sodium, potassium, magnesium, and calcium in biodiesel samples. Figure 2B shows a representative chromatogram of B99 after a liquid extraction with DI water in comparison to the chromatogram of a standard (Figure 2A).

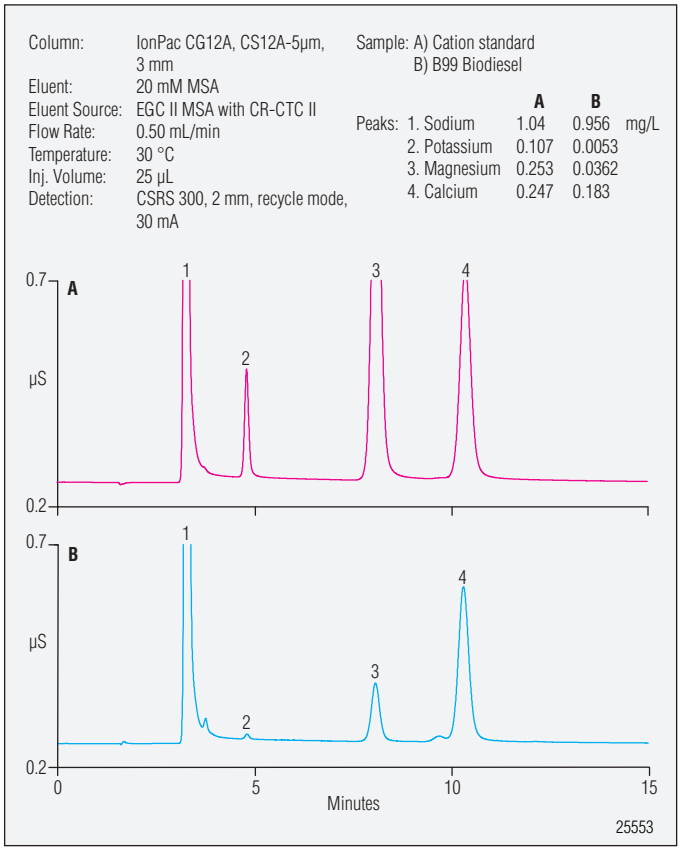

Figure 2. Comparison of the separation of a standard and B99 biodiesel.

Precision

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 0.07–2.27 %. 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).

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

Accuracy

The accuracy of the method was verified by determining recoveries of spiked B99 extractions over three days. Average recoveries of the four target cations ranged from 98.0% to 108% (Table 3). Interday RSDs of the determined concentrations ranged from 0.05–2.4%. The recoveries for these samples suggest the method is accurate.

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

Biodiesel Blends

Biodiesel blends with lower amounts of biodiesel are also successfully analyzed by this method. B20, commonly sold for automotive use, contains cation concentrations that are more than 100 times below the ASTM limits (Figure 3A).

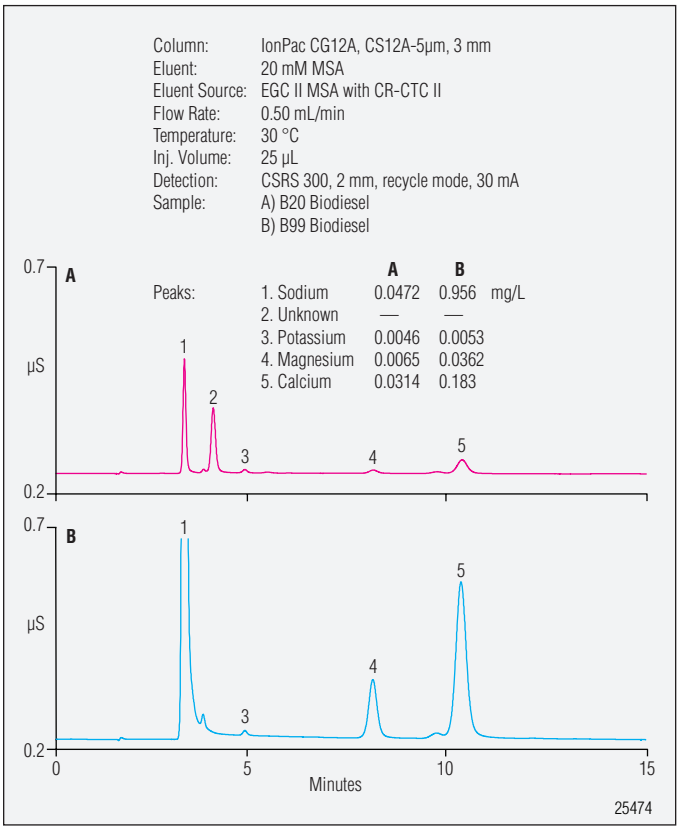

Figure 3. Comparison of the separation of B20 and B99 Biodiesel.

CONCLUSION

- The high resolution and column design of the IonPac CS12A-5µm allows for rapid separation of the target cations with a wide response range.
- This method simplifies the determination of the four cations of interest compared to AA and ICP by requiring only a simple sample preparation, allowing simultaneous determination of the target cations, and showing only limited interferences from other compounds 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.

REFERENCES

1. McCormick, R.L. and Westbrook, S.R.; Biodiesel and Biodiesel Blends, *ASTM Standardization News* **2007**, *35* (4). (available at: http://www.astm.org/SNEWS/APRIL_2007/mccwes_apr07.html, accessed August 14, 2008)
2. Dionex Corporation. *Determination of Cations in Biodiesel.* Application Note 203, LPN 2046. Sunnyvale, CA (submitted for publication).

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