

Determination of Trace Sodium in Diesel and Biodiesel Fuel

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Key Words

Fuel, Ion Chromatography (IC), RFIC System, In-Line Sample Preparation, Dionex IonPac CS12A Column

Goal

To develop an automated in-line matrix removal technique to enable direct trace determination of sodium in nonwater miscible liquids such as diesel, biodiesel, and other fuels

Introduction

Diesel engines used in today's cars are almost exclusively equipped with common rail direct fuel injectors that can achieve compression of 2500 bar or greater for the diesel fuel. Because of the high pressure and multiple injections of diesel into the engine's cylinders prior to ignition, production of the injector parts requires high precision. The tight tolerances for the mechanical parts of such injectors create susceptibility to fuel contamination. Since 2008, producers of common rail diesel engines have reported precipitation in injectors that sometimes results in mechanical blockages. In addition to organic deposits, scanning electron microscope images reveals that sodium salts are present and contribute to these blockages.¹⁻³ Known possible sources for sodium contamination include the remaining catalyst from biodiesel fuel production, drying agents, corrosion inhibitors, sea water from tanks (i.e., ballast water), and sodium components from pipelines.

Sodium determination in diesel fuel using inductively coupled plasma-optical emission spectrometry (ICP-OES) is possible, although realistic limits of detection are ~0.1 ppm under routine conditions. Adding oxygen to the ICP gas and a background correction improves results.⁴ Although ICP-mass spectrometry (ICP-MS) has better limits of detection, it is a technique that is neither widely found nor routinely used in the laboratories tasked with fuel analysis.



Most of the currently published IC methods use liquid-liquid extractions to isolate sodium. The fuel is extracted using an aqueous phase, which is subsequently analyzed by IC. Even though the concept seems simple, the choice of the best aqueous extraction agent is not routine. Some work has been done using diluted nitric acid,^{5,6} but other authors have rejected acidic extraction solvents because they neither improve the extraction yield nor stabilize the extracts. Hurum et al.⁷ reported that acidic extraction solvents support the formation of emulsions, thus hampering or even preventing the phase separation. Liquid extractions are also laborious and slow.

Consequently, the goal of this study was to develop and test an alternate approach using IC for the determination of cations in diesel fuel. The approach focused on the use of commercially available modules and existing standard chromatographic conditions when possible. The challenge was to design an automated, cost-effective, fast, and sensitive method that can provide 10–100 times greater sensitivity than the ICP-OES method and does not require manual extraction steps.

Equipment

- Thermo Scientific™ Dionex™ ICS-2100 Regent-Free™ IC (RFIC™) system (P/N 069576), including:
 - Degasser
 - Additional Auxiliary 6-Port Valve Kit (P/N 069472)
 - CD Conductivity Detector
- Thermo Scientific™ Dionex™ CSRS™ 300 Cation Self-Regenerating Suppressor
- Thermo Scientific™ Dionex™ UltiMate™ 3000 LPG-3400SD Quaternary Analytical Pump (P/N 5040.0031)
- Thermo Scientific Dionex EGC III Methanesulfonic Acid (MSA) Eluent Generator Cartridge (P/N 074535)
- Thermo Scientific Dionex CR-CTC II Continuously Regenerated Cation Trap Column (P/N 066262)
- Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System software, version 6.8 (or higher)

Reagents and Standards

- Deionized (DI) water, Type I reagent grade, 18 MΩ-cm resistance or better
- IC Multi-Element Standard VII, 100 mg/L (Merck KGaA P/N 110322)
- 2-Propanol for Analysis, EMSURE® ACS, ISO, Reag. Ph Eur, 2.5 L bottle, plastic bottle (Merck KGaA P/N 1096342511)

Samples

All samples were standard fuels purchased at gas (petrol) stations.

Conditions

Columns: Thermo Scientific™ Dionex™ IonPac™ CG12A Guard, 2 × 50 mm (P/N 046076)
 Dionex IonPac CS12A Analytical, 2 × 250 mm (P/N 046075)
 Dionex IonPac TCC-ULP1 Ultralow Pressure Trace Cation Concentrator Column (P/N 063783)

Eluent: 20 mM MSA

Eluent Source: Dionex EGC MSA Eluent Generator Cartridge with Dionex CR-CTC II Continuously Regenerated Cation Trap Column

Flow Rate: 0.5 mL/min

Injection Volume: 1000 µL

Temperature: 30 °C

Detection: Suppressed Conductivity, Dionex CSRS 300 Cation Self-Regenerating Suppressor (2 mm), recycle mode, 30 mA current

System

Backpressure: 2100 psi

Background Conductance: <0.5 µS

Typical Noise: <5 nS

Preparation of Solutions and Reagents

Prepare standard solutions by diluting commercially available stock standards in two steps. Use DI water as the diluent in Step 1; use 2-propanol and DI water in Step 2.

For Step 2, place the aqueous standard in a 100 mL plastic volumetric flask, mix with 50 mL 2-propanol, then fill to the mark with DI water. For best results, use 2-propanol from the same bottle for the preparation of all standards, check standards, and samples.

In-Line Sample Preparation

The determination of samples that are immiscible with water presents a special IC challenge. Upon injection of such samples, drastic unwanted pressure changes can occur. In addition, interactions of hydrophobic nonpolar matrix components—in particular, those from diesel samples—can lead to a rapid loss of column capacity. To prevent such effects, inject a 1 mL aliquot of the diluted sample (1 mL sample + 1 mL 2-propanol) into the solvent-compatible and high-pressure-tolerant Dionex IonPac TCC-ULP1 concentrator column. The cationic analytes are retained, while the hydrophobic matrix components are eluted with 2-propanol to waste. After rinsing the concentrator column with DI water, the injection occurs and the analytes are eluted. The sample preparation and elution steps are summarized in Table 1.

Table 1. Conditions for in-line sample preparation (time protocol for Pump 2 in Figure 1).

Time (min)	Flow (mL/min)	Eluent	Comment
0.0	0.1	H ₂ O	Conditioning of the Dionex IonPac TCC-ULP1 column
0.1	0.1		
0.5	1.0		
2.5	1.0	2-Propanol	Change to 2-propanol
3.0	1.0		Conditioning of the Dionex IonPac TCC-ULP1 column
5.1	1.0		Sample to Dionex IonPac TCC-ULP1 column
9.5	1.0		Matrix elimination completed
10.0	1.0	H ₂ O	Conditioning of the Dionex IonPac TCC-ULP1 column to aqueous conditions
14.0	1.0		Injection
14.6	0.1		Lower flow rate for the pump

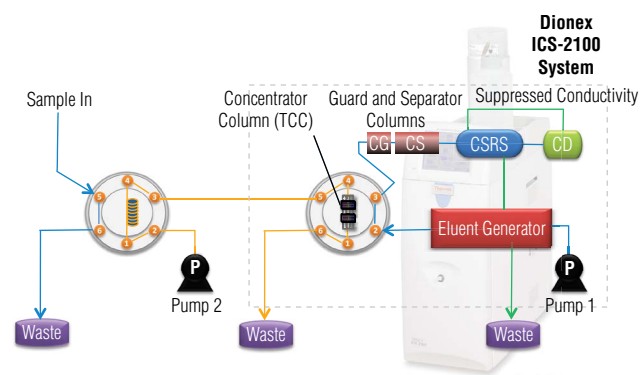


Figure 1. Schematic configuration of the analytical system.

Comparison with Atomic Absorption Spectrometry (AAS) and ICP-OES

The analytical results obtained with the new IC approach were cross-checked with results obtained by AAS and ICP-OES. The instrument conditions are summarized in Tables 2 and 3.

Table 2. Experimental conditions for the AAS spectrometer measurements.

Parameter	Value
Instrument	Thermo Scientific™ iCE™ 3400 AAS Atomic Absorption Spectrometer
Wavelength	589.0 nm
Band Pass	0.2 nm
Flame	Air Acetylene
Software	Thermo Scientific™ SOLAAR™ V11

Table 3. Experimental conditions for the ICP-OES measurements.

Parameter	Value
Instrument	Thermo Scientific™ iCAP™ 7400 ICP-OES Analyzer
RF Power	1150 W
Coolant Gas Flow	12 L/min
Auxiliary Gas Flow	1.5 L/min
Nebulizer Gas Flow	0.53 L/min
Wavelength	589.592 nm
Pump Rate	50 rpm
Pump Tubing	Viton® Seal
Nebulizer	V Groove for ICP-OES
Spray Chamber	Organic (Baffled)
Software	Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ V2.1

Results

Figure 2 shows a representative chromatogram of a diesel sample after in-line matrix elimination. Chromatograms obtained from biodiesel fuel analyzed with this method show similar chromatographic results. This approach enabled interference-free sodium determination, and the column capacity of both guard and separator columns remained stable during investigations that involved approximately 400 injections. Suppressed conductivity facilitates the application of more concentrated eluents at a higher flow rate, which enabled the separation of alkaline and alkaline earth metals in <12 min with satisfactory chromatographic resolution. Typical chromatograms for diesel and biodiesel samples show traces of ammonium, potassium, magnesium, and calcium. Though not within the scope of this work, the evaluation of the concentrations of such compounds may provide additional fuel-quality information. The large sodium peak in Figure 2 represents a mass concentration of approximately 0.2 ppm (mg/kg). The high sensitivity obtained is the result of both the injection volume (1 mL) and the use of 2 mm columns and 2 mm suppressors.

Detection sensitivity increased significantly compared to standard conditions, which resulted in a low limit of detection (LOD) of <50 ppt, calculated from a signal-to-noise ratio (S/N) = 3 and a low limit of quantification (LOQ) of <0.5 ppb for S/N = 10. Because sodium is a ubiquitous element and detectable sodium was likely present in the blank, the usual analytical caution must be applied to these LOD and LOQ values. Additionally, although both values emphasize the high sensitivity of this chromatographic approach, the analytical possibilities to improve sensitivity (such as using a larger injection volume) have not yet been fully explored. Lower LODs and LOQs seem likely, though the laboratory environment here (i.e., the requirement to produce a low-sodium blank) must reflect the needs of a trace sodium determination. Calibrations were conducted regularly for the range between 0.02 ppm and 0.5 ppm, with a linear correlation coefficient of $R > 0.999$. The results presented in this work were obtained under standard laboratory conditions (i.e., not a clean room or similar environment).

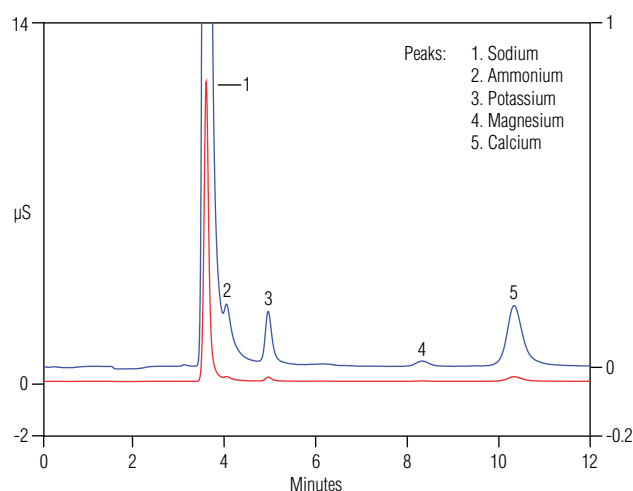


Figure 2. Determination of sodium in diesel and biodiesel fuels at a concentration of 0.2 ppm. The red trace is the original chromatogram (left y-axis), whereas the blue trace is an enlarged chromatogram (right y-axis).

Table 4. Comparison of analytical results for sodium present in different diesel samples (n = 3 – 10).

Sample	IC (ppm)	RSD	AAS (ppm)	Comparability* (%)	ICP-OES (ppm)	Comparability* (%)
1	0.218	2	0.22	103	0.24	108
2	0.120	2	0.11	92	0.13	109
3	0.125	2	0.10	77	0.13	102
4	0.184	1	0.24	132	0.18	100
Average Comparability				101	—	104

*In comparison to the IC data

Table 4 compares the determination of sodium in different diesel samples using IC, AAS, and ICP-OES and shows good comparability for the data obtained with the three methods. The RSD values for the IC data always were in the low, single-digit percentage range, indicating a highly reproducible method. The recovery for sodium was 99% by different standard addition experiments (e.g., using sodium oleate at different concentration levels), additionally confirming the low RSD data obtained from the sample measurements.

It was important to check the applicability of this new method to regular fuels. Figure 3 shows four chromatograms obtained after the analysis of different nondiesel fuels using the described in-line matrix elimination. Significantly lower sodium content was found for all the examined samples, ranging from ~0.003 to 0.05 ppm (confirmed by AAS), compared to diesel fuels. When comparing these chromatograms with the ones obtained for diesel samples, a notable difference regarding the cationic compounds became apparent. Based on the retention times of the unknown peaks, one must assume the presence of short-chained mono- and dialkylamines or -alkanolamines in addition to the inorganic components. The concentration of these amines in relation to the sodium concentration appears to be higher in regular fuel than in diesel.

Conclusion

An automated in-line matrix elimination technique facilitates the determination of trace sodium in diesel, biodiesel, and regular fuels with both the LOD and LOQ in the sub- $\mu\text{g/L}$ range. In comparison to existing IC methods, no manual extraction steps are needed. Eluent generation and a continuously regenerated suppressor for conductivity detection further simplify the method and increase ease of use. Analysts need only to provide DI water. The eluent is generated in situ and the regeneration of the suppressor is performed automatically without the use of an external base solution.

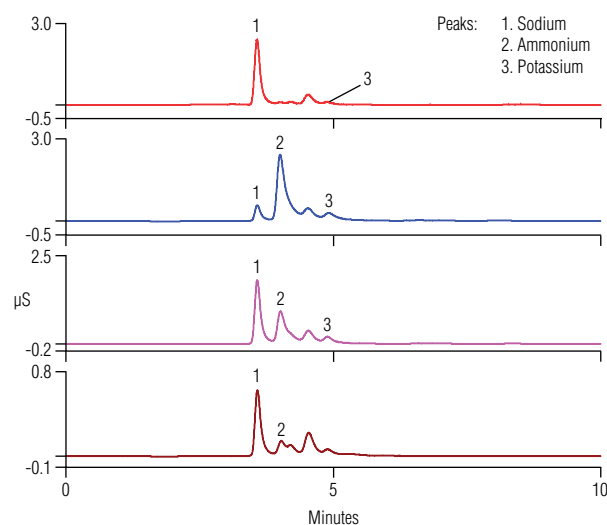


Figure 3. Examples of four different commercially available regular (nondiesel) fuels.

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