

Determination of Total and Potential Sulfate and Total Chloride in Fuel-Grade Butanol Per ASTM D7319-09

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Key Words

- Renewable Energy
- ASTM D4806-11A
- Ion Chromatography (IC)
- Biofuels
- Suppressed Conductivity Detection
- High Octane Rating

Introduction

Butanol is increasingly regarded as a source of clean energy and an alternative to ethanol as a fuel additive by the global energy market. Compared to ethanol, butanol has lower vapor pressure, higher energy density, and an octane rating similar to gasoline. These attributes allow it to be blended into gasoline at much higher proportions relative to ethanol with no compromise to performance, mileage, and organic pollution standards.¹ Butanol can be produced from annual cereal crops (e.g., corn, rice, and barley) and from cellulosic biomass. The flexibility to use lignocellulosic biomass for the production of butanol makes it a more economically viable source of renewable energy compared to fossil fuels.

Growing consumer acceptance for butanol, incentives to agriculture and industry, falling production costs, increasing prices and taxes for fossil fuels, and the desire for cleaner-burning sources of energy are leading to an increase in butanol production. Despite having several cleaning steps, the butanol production process can result in a final product containing several impurities, i.e., dissolved salts that can damage engines. Therefore, the determination of sulfate and chloride in butanol to be used in a fuel is an important quality assay.²⁻⁴

Sulfate and chloride concentration limits have not yet been defined for butanol by ASTM International. However, specifications for ethanol are a good benchmark for the quality of butanol. According to ASTM D4806-11A, a maximum concentration limit that is permissible in ethanol is 4 mg/L sulfate and 40 mg/L chloride.⁵

Thermo Scientific Application Note 296 describes one approach to determine total and potential sulfate and total chloride in butanol by ion chromatography (IC) per ASTM D7328-07, by evaporating a sample to dryness and reconstituting in deionized (DI) water or 0.90% hydrogen peroxide solution.⁶ Here we present a direct injection IC approach to determine total and potential sulfate and total chloride in butanol intended as a gasoline additive. This IC method is consistent with the procedure described in ASTM D7319-09, a standard intended for the analysis of ethanol samples containing 1.0–20 mg/kg of total or potential inorganic sulfate and 1.0–50 mg/kg of inorganic chloride. Total sulfate and chloride were determined in 20 min by directly injecting 5 µL of sample onto a Thermo

Scientific Dionex IonPac AS22 Carbonate Eluent Anion-Exchange Column and detecting the analytes using suppressed conductivity detection. Potential sulfate was determined by adding 0.5 mL of 30% hydrogen peroxide solution to 9.5 mL of butanol, mixing thoroughly, and directly injecting onto the column. Linearity, limits of detection and quantification, and precision of potential and total sulfate and total chloride are demonstrated. This IC method allows for the analysis of butanol samples according to ASTM D7319-09,⁸ and has the sensitivity to meet the specifications described in ASTM D4806-11A.

Equipment

- Thermo Scientific Dionex ICS-2100* Ion Chromatography System including:
 - Single isocratic pump
 - Vacuum degasser
 - High pressure, 6-port injector
 - Column heater enclosure
 - Conductivity cell and detector
 - EO Eluent Organizer, including pressure regulator and 2 L plastic bottle
- Thermo Scientific Dionex AS-DV Autosampler* with 5.0 mL PolyVials (plain caps)
- Thermo Scientific Dionex Chromeleon Chromatography Data System (CDS) Version 6.8 or greater
- Helium or nitrogen, 4.5 grade (99.995%) or better, <5 ppm oxygen (Praxair)
- Filter unit, 0.2 µm nylon (Nalgene Nunc International, P/N 164-00200 or equivalent nylon filter)
- Vacuum pump for degassing eluents (Gast Manufacturing Corp. P/N DOA-P104-AA or equivalent)
- Thermo Scientific Dionex PolyVials and Plain Caps, 250 each, for 5.0 mL vials (P/N 038008)
- Vial Holder for 5.0 mL vials (Dionex P/N 038141)
- Cap Removal Tool (Dionex P/N 068925)
- Three 4-L plastic bottle assemblies for chemical regeneration mode of operation

**The AS-DV is the recommended autosampler for this application. Optimizations, i.e., using an organic wash solution, may be needed if using other autosamplers.*

Consumables

Dionex IonPac™ AS22 Analytical Column, 2 × 250 mm (P/N 064137)

Dionex IonPac AG22 Guard Column, 2 × 50 mm (P/N 064135)

Thermo Scientific Dionex AMMS 300 Anion MicroMembrane Suppressor, 2 mm (P/N 064559)

Reagents and Standards

DI water, Type I Reagent grade water, 18 MΩ-cm resistance or better

Chloride Standard, 1000 mg/L (P/N 037159)

Sulfate Standard, 1000 mg/L (P/N 037160)

Dionex IonPac AS22 Eluent Concentrate (100x), 250 mL (P/N 063965)

Anion Suppressor Regenerant Concentrate 0.50 N Sulfuric Acid, 4 Pack (P/N 37164)

Sulfuric Acid, A.C.S Reagent Grade (J.T Baker, P/N 11-9681-05)

Tetrabutylammonium Bisulfate, ≥ 99.0% (AT) (Sigma-Aldrich, P/N 86868)

Tetrabutylammonium Chloride, ≥ 97.0% (AT) (Sigma-Aldrich, P/N 86870)

Isobutanol, ACS, 99% (Cat # AA36643K7 Fisher Chemical)

Hydrogen Peroxide, 30% ACS Grade (Mallinckrodt, P/N V340-04)

Samples were obtained from a leading renewable fuels manufacturer.

Conditions

Column: Dionex IonPac AS22 Analytical, 2 × 250 mm
Dionex IonPac AG22 Guard, 2 × 50 mm

Eluent: 4.5 mM sodium carbonate, 1.4 mM sodium bicarbonate

Flow Rate: 0.3 mL/min

Inj. Volume: 5.0 µL

Temperature: 30 °C

Detection: Suppressed Conductivity, Dionex AMMS 300 2 mm in the chemical regeneration mode with 50 mN sulfuric acid

Background: ~20 µS

Backpressure: 1200 psi

Run Time: 20 min

ASDV Conditions*:

Sampler Flush Factor: 10

Sampler Delay Volume: 125 µL

*The delay volumes need to be increased proportionally if using a 4 × 250 mm column.

Caution: Flush the autosampler with large amounts of butanol sample to remove any remnant water in the system. Failing to do so will lead to low sulfate recoveries.

Preparation of Solutions and Reagents

0.5 N Sulfuric Acid

Carefully transfer 13.7 mL of reagent-grade sulfuric acid to approximately 500 mL of filtered and degassed DI water in a 1 L volumetric flask. Allow the solution to cool before bringing volume to 1000 mL using DI water. Invert the solution several times to mix.

50 mN Sulfuric Acid

Dilute 200 mL of the prepared 0.5 N sulfuric acid concentrate by adding approximately 1700 mL of filtered and degassed DI water or use Thermo Scientific Dionex Anion Regenerant Concentrate (PN 37164). Invert the flask several times to mix the contents and bring volume to 2000 mL using DI water. Repeat this several times to fill three 4 L regenerant bottles.

Eluent Solution (4.5 mM Sodium Carbonate/1.4 mM Sodium Bicarbonate)

Transfer 10 mL of the Dionex IonPac AS22 Eluent Concentrate to a 1 L volumetric flask and add approximately 700 mL of filtered and degassed DI water. Invert several times to mix and bring to 1000 mL volume using DI water.

Inorganic Stock Standard Solutions

Thermo Scientific Dionex chloride and sulfate standards at concentrations of 1000 mg/L were used in this study, although standards can also be purchased from another reliable supplier. Alternatively, 1000 mg/L chloride standard can be prepared by dissolving 0.1648 g of sodium chloride in 100 mL of filtered and degassed DI water, or by dissolving 0.1814 g of potassium sulfate in 100 mL of filtered and degassed DI water.

Table 1. Preparation of calibration standards.

Anion Concentration (mg/L)	Volume of 1000 mg/L Chloride Stock (mL)	Volume of 1000 mg/L Sulfate Stock (mL)	Total Volume with DI Water (mL)
0.3	0.03	0.03	100
0.5	0.05	0.05	100
1.0	0.10	0.10	100
5.0	0.50	0.50	100
10.0	1.00	1.00	100
20.0	2.00	2.00	100
50.0	5.00	—	100

Preparing Calibration Standards (Inorganic)

To prepare chloride and sulfate calibration standards, deliver appropriate volumes of the 1000 mg/L stock standards using calibrated pipettes (Table 1).

Sample Preparation

Proper sample preparation is crucial to the success of this method. Therefore this section begins with precautions related to sample preparation.

Precautions:

1. Butanol is immiscible in water, which can lead to low recoveries of sulfate due to its poor solubility in the organic phase. If using rinsed glassware for sample preparation, be sure that the glassware is dry. Rinsing all glassware twice with butanol containing chloride and sulfate concentrations below 0.1 mg/L and 0.3 mg/L, respectively, ensures that all the water from the rinsing is removed.* Failing to rinse washed glassware in butanol will lead to low recoveries.

**Isobutanol with the Cat # AA36643K7 purchased from Fisher Chemicals met this criterion.*

2. All samples must be sonicated for at least 15 min prior to placing into the autosampler vials to ensure that the sample is homogenous. Insufficient sonicating will lead to improperly mixed samples with varying amounts of chloride and sulfate in each aliquot.

Total Sulfate and Chloride

Butanol samples were injected directly without further preparation. All samples were sonicated for 15 min prior to injection.

Potential Sulfate

Add 9.5 mL of the butanol sample (sonicate the spiked sample for 15 min prior to aliquoting) to a 10 mL volumetric flask then add 0.5 mL of a 30% hydrogen peroxide solution. This is an aqueous solution of peroxide, so it will phase separate when first added to the butanol sample. A 5% dilution of the butanol sample in an aqueous solution of hydrogen peroxide is allowable by the method and does not cause problems, provided the sample is vortexed vigorously for at least 15 min to ensure good mixing. The final hydrogen peroxide concentration of this mixture is 1.5%. Analyze the sample immediately.

Sample Preparation for Spike Recovery

Precautions

1. Although ASTM D7319-09 does not require a bias determination, it is good scientific practice to qualify the method by calculating recoveries from spiked samples. Therefore, it is recommended that laboratories determine the recoveries of total chloride and sulfate and potential sulfates from the known amounts of the target analytes added directly to the butanol sample.
2. Organic salts of chloride and sulfate (i.e., tetrabutylammonium chloride and tetrabutylammonium bisulfate) must be used for spike recovery studies. These salts were chosen because they are readily soluble in butanol. Using inorganic salts and other organic salts of chloride and sulfate will lead to low recoveries.

5000 ppm Organic Chloride Stock in Butanol (100 mL)

Weigh 3.217 g of tetrabutylammonium chloride and add to approximately 70 mL of butanol. Sonicate the mixture for 15 min. When the entire solid is dissolved, allow the mixture to reach room temperature and bring to a volume of 100 mL using butanol.

2000 ppm Organic Sulfate Stock in Butanol (100 mL)

Weigh 0.708 g of tetrabutylammonium bisulfate and add to approximately 70 mL of butanol. Sonicate the mixture for 15 min. When the entire solid is dissolved, allow the mixture to reach room temperature and bring to a volume of 100 mL using butanol.

10 ppm Chloride and Sulfate Spikes in Butanol

Prepare by pipetting 1 mL of the 5000 ppm tetrabutylammonium chloride stock into a 500 mL volumetric flask. Add 2.5 mL of the 2000 ppm tetrabutylammonium bisulfate stock into same flask. Dilute to the mark with butanol. Sonicate for 5 min to mix the contents.

5 ppm Chloride and Sulfate Spikes in Butanol

Prepare by pipetting 0.5 mL of the 5000 ppm tetrabutylammonium chloride stock into a 500 mL volumetric flask. Add 1.25 mL of the 2000 ppm tetrabutylammonium bisulfate stock in same flask. Dilute to the mark with butanol. Sonicate for 5 min to mix the contents.

System Preparation and Setup

Install the analytical and guard columns. Install the Dionex AMMS 300 in the chemical regeneration mode by connecting the eluent line from the column outlet to the ELUENT IN port of the Dionex AMMS 300 and the ELUENT OUT port of the Dionex AMMS 300 to the Cell In of the conductivity detector. Connect a regenerant line to the REGEN IN port of the Dionex AMMS 300 from the regenerant reservoir and connect a line from the REGEN OUT port of the Dionex AMMS 300 to a waste container. Start the column eluent flow and adjust the head pressure on the chemical regenerant reservoir to deliver a flow rate of 2.5–5 mL/min. If necessary, add restriction tubing to the regenerant waste line to achieve the required flow rate. Allow approximately 5 mL of eluent to flow through the Dionex AMMS 300 ELUENT IN port and 5 mL of regenerant through the REGEN IN port. Stop the eluent and regenerant flow to the suppressor, allowing the suppressor to hydrate for approximately 15–20 min. After the suppressor is properly hydrated, restart the liquid flow to the Dionex AMMS 300 and equilibrate the column with eluent for at least 30 min prior to analyzing a system blank of butanol. The system background conductance and noise should be what is displayed in the Conditions section of this document. Inject a standard containing 5 mg/L of chloride and sulfate in water. The column is equilibrated when at least three consecutive chromatograms resemble the overlaid chromatograms in Figure 1.

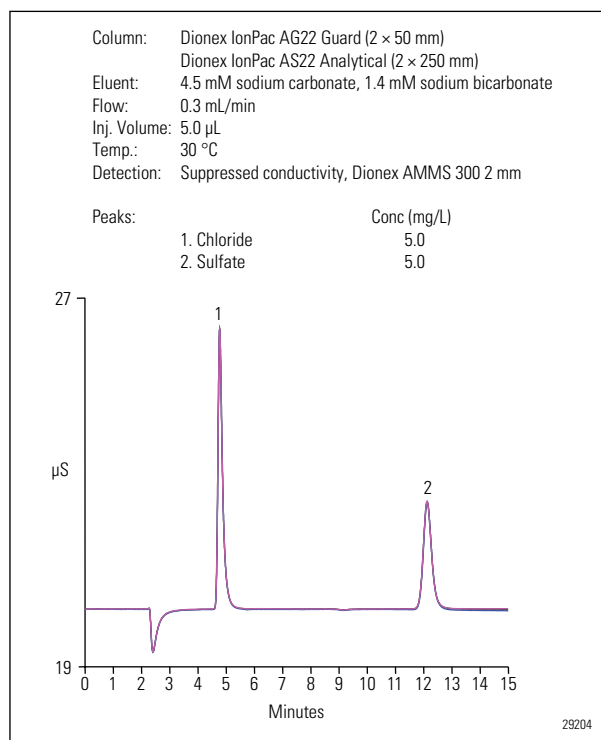


Figure 1. Overlay of three chromatograms of chloride and sulfate in water separated on the Dionex IonPac AS22 column.

Results and Discussion

Described here is a direct injection IC method to determine whether butanol used as a blending agent in gasoline meets the chloride and sulfate specifications described in ASTM D4806-11A.⁷ A procedure to determine potential sulfates in butanol is also described. Total inorganic sulfate and chloride can be determined by a direct injection onto a Dionex IonPac AS22 column. To determine potential sulfate, 0.5 mL of 30% hydrogen peroxide was added to 9.5 mL of the butanol sample, mixed thoroughly, and directly injected onto the Dionex IonPac AS22 column. The oxidizing agent (i.e., hydrogen peroxide) is used to convert all the sulfur species to sulfate.

The direct injection approach described here is a time- and cost-effective method of determining total and potential sulfate and total chloride in butanol samples. The linearity, limits of detection (LODs), and limits of quantification (LOQs) were evaluated to determine the suitability of the method for this analysis. ASTM D7328-07 was used to set the appropriate calibration ranges. Table 2 summarizes the linearity obtained by injecting calibration standards from 0.3–50 mg/L for chloride and 0.3–20 mg/L for sulfate. The calibration curves were linear, with coefficients of determination (r^2) greater than 0.999. The LODs for chloride and sulfate were 0.03 mg/L and 0.1 mg/L, respectively, and the LOQs were 0.1 mg/L for chloride and 0.3 mg/L for sulfate.

Table 2. Data for linearity, LOD, and LOQ of chloride and sulfate.

Analyte	Range mg/L	Coefficient of Determination r^2	LOD ^a (mg/L)	LOQ ^b (mg/L)
Chloride	0.3–50	0.9999	0.03	0.1
Sulfate	0.3–20	0.9993	0.1	0.3

^a Estimated from $3 \times S/N$

^b Estimated from $10 \times S/N$

Figure 2 compares replicate injections of a butanol sample containing 7.9 mg/L of chloride and 4.7 mg/L of sulfate (Sample A) to a butanol sample containing 16.5 mg/L of chloride and 9.4 mg/L of sulfate (Sample B). As shown in Figures 2A and 2B, chloride and sulfate demonstrate stable retention times and peak area responses at different concentrations.

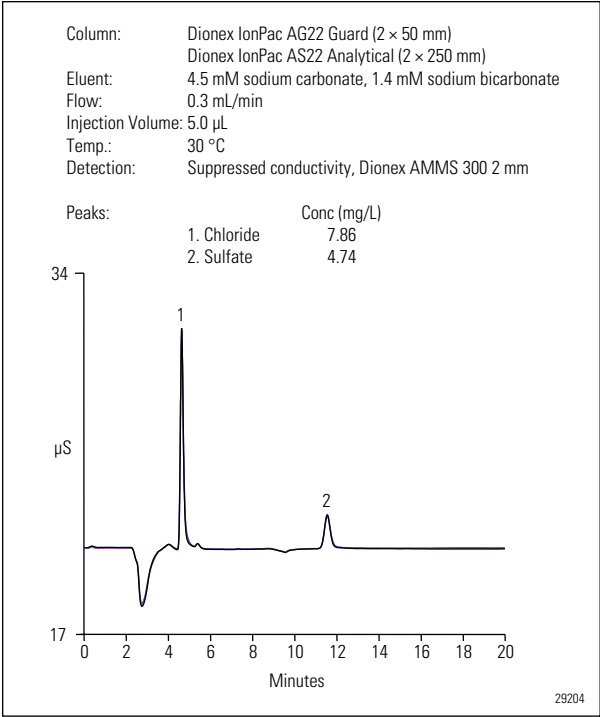


Figure 2A. Overlay of three chromatograms determining total chloride and sulfate in butanol Sample A using a Dionex IonPac AS22 column.

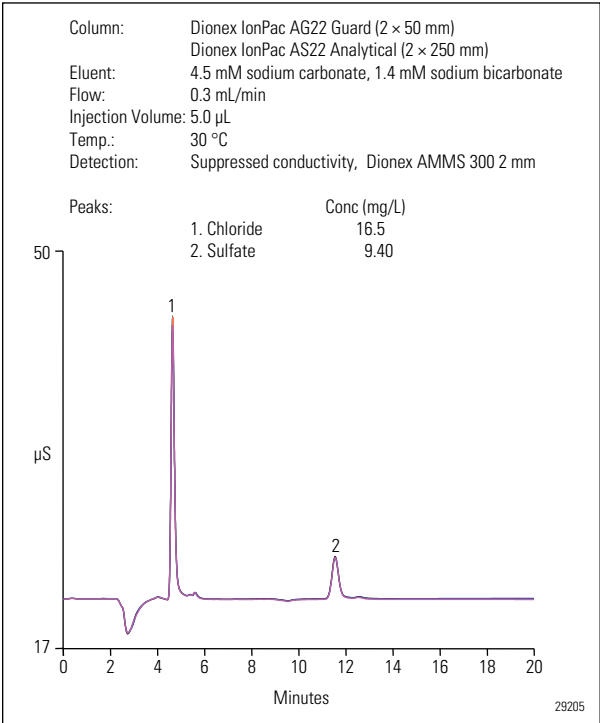


Figure 2B. Overlay of three chromatograms determining total chloride and sulfate in butanol Sample B using a Dionex IonPac AS22 column.

Figure 3 demonstrates the determination of potential sulfate in a butanol sample. The sample was prepared as described in the sample preparation section by adding 0.5 mL of a 30% hydrogen peroxide solution to 9.5 mL of the sample. The sample was then vortexed vigorously for 10 min to ensure good mixing, and analyzed immediately. The final hydrogen peroxide concentration in the sample is 1.5%. Figure 3 shows that the peak area responses and retention times remain stable over the replicate injections even in the presence of low concentrations of the oxidizing agent.

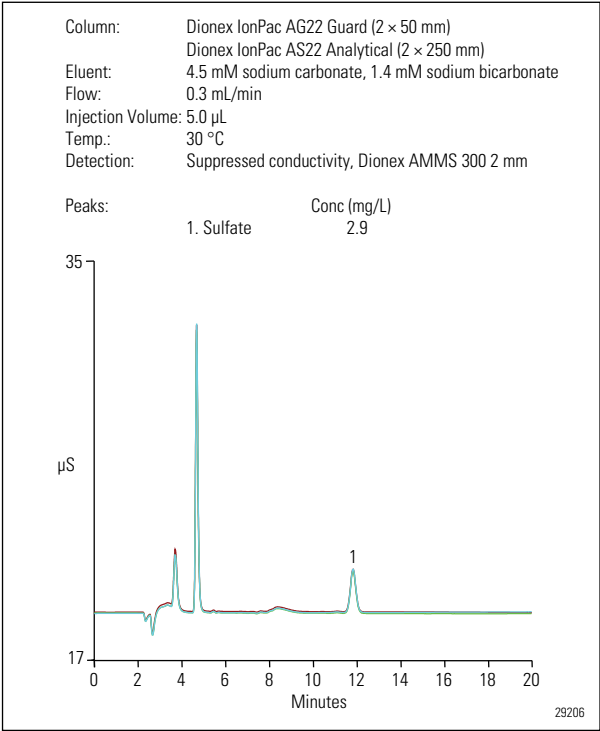


Figure 3. Overlay of three chromatograms determining potential sulfate in butanol using a Dionex IonPac AS22 column.

As seen in Figures 2A, 2B, and 3, the Dionex AMMS 300 suppressor in the chemical regeneration mode ensures a stable baseline for each injection. The overlays of the replicate injections in all three figures exhibit consistent peak responses with no baseline drift, thereby allowing the determination of low concentrations of chloride and sulfate in a sample. As shown in Table 3, method precision is good for total sulfate and chloride and potential sulfate for triplicate injections with retention time RSDs ranging from 0–0.08% and peak area response RSDs ranged from 0.06–0.73%.

Table 3. Peak area precision of total and potential sulfate and total chloride in butanol.

Sample	Analyte	Amount (mg/L)	Precision RSD	
			Ret. Time (n = 3)	Peak Area (n = 3)
A	Chloride	7.9	0.04	0.06
	Sulfate	4.7	0.02	0.51
	Potential Sulfate	4.9	0.02	0.73
B	Chloride	3.7	0.00	0.41
	Sulfate	3.3	0.00	0.58
	Potential Sulfate	3.5	0.08	0.56

Recovery studies were performed on butanol purchased from Fisher Scientific by spiking known amounts of chloride and sulfate to determine method accuracy. A butanol blank was run to determine the endogenous amounts of the analytes of interest, and both chloride and sulfate were present in amounts below 0.1 mg/L and 0.3 mg/L, respectively (below the system LOD). Table 4 summarizes the amounts spiked and the calculated recoveries. The reported recoveries are an average of five replicate injections at each of the concentrations. Recoveries ranged from 88–90% for chloride and 103–104% for sulfate, suggesting good method accuracy.

Table 4. Recovery of chloride and sulfate at different concentrations in butanol.

Analyte	Amount (mg/L)	% Recovery (n = 5)	RSD
Chloride	10.0	90	0.36
	5.0	88	0.42
Sulfate	10.0	104	0.91
	5.0	103	0.76

Conclusion

This method describes a fast, simple, and direct injection method to determine total and potential sulfate and total chloride in butanol according to ASTM D7319-09. The method described in this application note can reliably quantify sulfate and chloride in butanol at 0.1 and 0.3 ppm, respectively, which is well below the ASTM D4806-11A specification of 4 ppm for sulfate and 40 ppm for chloride.

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Suppliers

Sigma-Aldrich, 3050 Spruce Street, St. Louis, MO 63103, Tel: 800-521-8956, www.sigmaaldrich.com.

J.T.Baker, A Division of Mallinckrodt Baker, Inc., 222 Red School Lane, Phillipsburg, NJ, 08865, USA, Tel: 908-859-2151; 800-582-2537 www.mallbaker.lookchem.com.

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AN297_E 08/16S LPN3042