



A Honeywell Company

Sodium in Liquefied Petroleum Gas by ICP-OES or AAS

UOP Method 699-09

Scope

This method is for determining the concentration of sodium (Na) as dissolved and suspended sodium compounds in liquefied petroleum gas (LPG) in the range of 0.1 to 10 mg/kg (mass-ppm) sodium. After sample preparation, either Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES, or ICP) or Atomic Adsorption Spectroscopy (AAS) can be utilized to determine the sodium concentration.

References

ASTM Specification D1193, Reagent Water, www.astm.org

UOP Method 516, “Sampling of Gasolines, Distillate Fuels and C₃-C₄ Fractions”

UOP Method 999, “Precision Statements in UOP Methods,” www.astm.org

Outline of Method

A clean, dry pressure vessel is utilized to obtain a stream sample of liquefied petroleum gas (LPG). The entire contents of the pressure vessel are discharged into an uncovered, one-liter, wide-mouth, plastic bottle containing a deionized water-methanol solution and allowed to evaporate. The empty pressure vessel is washed with a small quantity of the water-methanol solution and the washings are added to the sample in the one-liter open bottle. After the LPG has completely evaporated, the sodium in the water-methanol solution is diluted to 100 mL with deionized water. The concentration of sodium is determined by ICP or AAS and the total concentration in the sample LPG is calculated.

Apparatus

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

All plasticware is to be of low sodium content. In addition, all plasticware is to be thoroughly cleaned with deionized water, followed by washings with sodium-free acetone, and dried.

Balance, readability 0.1-mg

Balance, 5000-g capacity, readability 0.5-g

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

© COPYRIGHT 1969, 1991, 2009 UOP LLC. All rights reserved.

Nonconfidential UOP Methods are available from ASTM International, 100 Barr Harbor Drive, P.O. Box C700, West Conshohocken, PA 19428-2959, USA. The UOP Methods may be obtained through the ASTM website, www.astm.org, or by contacting Customer Service at service@astm.org, 610.832.9555 FAX, or 610.832.9585 PHONE.

Bottle, wash, polypropylene, 500-mL, VWR, Cat. No. 16651-904

Bottle, wide-mouth, Teflon FEP, 1000-mL, VWR, Cat. No. 16128-535. The bottle specified is resistant to temperature extremes and the solvents used in this method. It is also low in metals content and easy to clean. If alternative containers are used, they must possess equivalent properties.

Bottles, polypropylene, 1000- and 4000-mL, VWR, Cat. Nos. 16067-124 and 16067-168, respectively

Bucket, polypropylene, 10.4-L capacity, VWR, Cat. No. 17306-005

Clamp, 3-prong, VWR, Cat. No. 21573-265, to hold the chromatographic column (2 required)

Clamp, chain, VWR, Cat. No. 21573-275, and clamp holder, VWR, Cat. No. 12621-250, to hold the cylinder (2 required)

Column, chromatographic, 19-mm ID, 300-mm length, with integral reservoir, VWR, Cat. No. 17810-19300

Cylinders, graduated, polypropylene, 10-, 50- and 100-mL, VWR, Cat. Nos. 65000-000, -004, and -006, respectively

Flasks, volumetric, polypropylene, 100- and 1000-mL, VWR, Cat. Nos. 29615-007 and -062, respectively (several of each required)

Funnel, polypropylene, 55-mm diameter, VWR, Cat. No. 30253-049

Hood, laboratory

Hose connector, Swagelok, Cat. No. SS-4-HC-7-4

Pipets, volumetric, Class A, 5-, 10-, and 50-mL, VWR, Cat. Nos. 89003-348, -350, and -366, respectively

Pipet filler, VWR, Cat. No. 54397-053

Pressure vessel, cylinder, type 304 stainless steel, high pressure, 12,400 kPa gauge (1800 psig) maximum working pressure, 1000-mL capacity, Swagelok, Cat. No. 304L-HDF4-1000. Equip the cylinder with 2 stainless steel valves, Swagelok, Cat. No. SS-16DKM4, and caps, B-4-CP. Assemble and pressure test the vessel before use.

Regulators, as required for gases for spectrophotometer used

Spectrophotometer, ICP or AAS:

Spectrophotometer, ICP, computer controlled, having sufficient resolving power and dispersion to separate the analytical lines in the 160-800 nm region. The computer must be capable of performing background corrections, blank corrections, and weight/volume and dilution corrections. A commercial grating spectrometer with a band pass of 0.018 nm or less in the first order is satisfactory. PerkinElmer Optima 5300 V

Spectrophotometer, AAS, computer controlled, with hollow cathode lamp for sodium. The computer must be capable of performing background corrections, blank corrections, and weight/volume and dilution corrections. PerkinElmer Analyst 800.

Support stand, VWR, Cat. No. 60100-105

Vacuum pump, or house vacuum

Wire, copper, for grounding, 16-gauge, VWR, Cat. No. 66248-029

Reagents and Materials

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Acetone (2-propanone), reagent grade, VWR, Cat. No. BJ010-1

Acetone, sodium-free. Prepare one liter by percolating reagent grade acetone down-flow through a bed of Amberlyst No. 15 cation exchange resin loosely packed in a chromatographic column. Maintain a flow rate of approximately 10 mL/min. Collect the percolated effluent and store it in a clean, one-liter, polypropylene bottle. Replace the resin for each additional batch.

Air, dry, for cylinder cleaning

Gases, instrument, as required for the specific spectrophotometer used

Ferric chloride, anhydrous, VWR, Cat. No. EM-FX0215-1

Gloves, disposable, nitrile, low ionic extractible, VWR, Cat. No. 40101-356 (size large)

Hydrochloric acid, concentrated, VWR, Cat. No. AA87617-K4

Hydrochloric acid, inhibited. Dissolve 1% by mass of ferric chloride in a mixture of equal volumes of deionized water and concentrated hydrochloric acid.

Ion exchange resin, Amberlyst No. 15, VWR, Cat. No. AAA44079-A1

Methanol, for spectroscopy, VWR, Cat. No. BJ230-4

Methanol, sodium-free. Prepare one liter by percolating spectroscopy grade methanol down-flow through a bed of Amberlyst No. 15 cation exchange resin loosely packed in a chromatographic column. Maintain a flow rate of approximately 10 mL/min. Collect the percolated effluent and store it in a clean, one-liter, polypropylene bottle. Replace the resin for each additional batch.

Potassium stock solution, 10,000- $\mu\text{g/mL}$, SPEX, Cat. No. PLK2-3X, used only for AAS analysis

Scandium stock solution, 1000- $\mu\text{g/mL}$, SPEX, Cat. No. PLSC2-2X, used only for ICP analysis as an internal standard

Scandium stock solution, 10- $\mu\text{g/mL}$. Pipet 10 mL of 1000- $\mu\text{g/mL}$ scandium stock solution into a clean 1000-mL polypropylene volumetric flask, fill to volume with deionized water, cap and invert several times to thoroughly mix the contents.

Sodium stock solution, 1000- $\mu\text{g/mL}$, SPEX, Cat. No. PLNA1-2X

Sodium stock solution, 10- $\mu\text{g/mL}$. Pipet 10 mL of 1000- $\mu\text{g/mL}$ sodium stock solution into a clean 1000-mL polypropylene volumetric flask, fill to volume with deionized water, cap and invert several times to thoroughly mix the contents.

Water, deionized to produce Type I Reagent Grade water (see ASTM Specification D1193, Reagent Water). Store in a 4-L polypropylene bottle.

Water, tap, hot

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of spectrophotometry, and the equipment being used. Use disposable gloves throughout the preparation and analysis procedures to minimize sodium contamination from the analyst's hands.

Preparation of Calibration Standards

1. Using pipets, add 5 and 50-mL aliquots of 10- $\mu\text{g/mL}$ sodium stock solution into each of two 100-mL volumetric flasks. A third flask is used as a blank.
2. Using a graduated cylinder, add 50 mL of sodium-free methanol to each of the three flasks.
3. For AAS analysis only, using a pipet, add 10 mL of 10,000- $\mu\text{g/mL}$ potassium stock solution to each of the three flasks.
 - The presence of potassium increases the sensitivity of the AAS to sodium.
4. For ICP analysis only, using a pipet, add 10 mL of 1000- $\mu\text{g/mL}$ scandium stock solution to each of the three flasks.
 - Scandium is used as an internal standard in ICP analyses.
5. Dilute each of the three flasks to volume with deionized water, cap and invert several times to mix thoroughly.
 - These solutions contain 0.5, 5.0 and zero $\mu\text{g/mL}$ of sodium, respectively.

Pressure Vessel Preparation

Clean the pressure vessel thoroughly before use, using the following procedure:

1. Rinse the pressure vessel with hot (approximately 50°C) tap water for approximately 5 minutes.
2. Half fill the vessel with inhibited hydrochloric acid and close the valves.
 - CAUTION: All steps involving acids must be performed in a properly operating fume hood, and appropriate personal protective equipment must be worn. See the MSDS for the acid for additional safety information.
3. Place the pressure vessel containing the inhibited acid in a bucket of hot tap water for 30 minutes. Invert and shake the vessel several times during the 30 minutes.
4. Open both valves and drain the acid from the pressure vessel.
 - Dispose of this and other solutions in an environmentally safe manner according to local practices.
5. Flush the vessel, up-flow, with hot tap water until the rinse water is colorless.
6. Half fill the vessel with deionized water, then shake and drain. Repeat this step five times, alternating the valve through which the water enters and is drained. Use deionized water on the last rinse.
7. Close one of the valves and evacuate the vessel. Draw in approximately 200 mL of sodium-free acetone, shake and allow to drain. Repeat the acetone wash and drain a second time through the other valve.
8. Dry the vessel by purging with air.
9. Cap the vessel with plugs that have been washed with deionized water, rinsed with sodium-free acetone and dried.
10. Tag the vessel: "clean, dry and air purged".

Pressure Vessel Sampling

Sampling from a refinery unit is performed in accordance with UOP Method 516.

Sample Analysis

1. Weigh the pressure vessel containing the sample, with caps, to the nearest 0.5 g.
2. Add 45 mL of sodium-free methanol and 20 mL of deionized water to a wide mouth, Teflon, 1000-mL bottle, using a graduated cylinder.
3. For AAS analysis only, pipet 10 mL of 10,000- μ g/mL potassium stock solution into the bottle.
4. Remove the cap from the lower valve of the cylinder and screw on the hose connector that has been previously washed and dried with deionized water and acetone.
5. Clamp the cylinder in a vertical position to a support stand.
 - All of the following operations associated with sampling of the pressure vessel must be conducted in a hood.
6. Position the bottle beneath the bottom valve of the pressure vessel.
7. Lower the vessel until the outlet of the hose connector is approximately 50 mm below the lip of the bottle.
8. Attach a copper ground wire from the bottom valve to a water line or other grounding point in the hood or nearby.
 - This will ground any static charge that may develop when the sample is being discharged from the pressure vessel.
9. Open the bottom valve, slowly, and allow the LPG sample to discharge completely into the bottle without splashing. Allow the discharge to continue until no further trace of liquid or gas evolves.
10. Open both valves completely and add approximately 10 mL of a solution composed of 5 mL of sodium-free methanol and 5 mL of deionized water through the top valve with a wash bottle.
 - The cylinder is rinsed with this solution.
11. Allow this washing to drain into the bottle.
12. Move the bottle from beneath the cylinder.
13. Rinse the cylinder with acetone, which is discarded, and dry it by purging with air.
14. Reweigh the pressure vessel, with caps, to the nearest 0.5 g.
15. Place the bottle containing the sample and washing solution on a paper towel toward the rear of the hood.
 - The paper towel will absorb moisture that condenses on the bottle during evaporation of the LPG.
 - To avoid sodium contamination, it is recommended that no other operations be performed in the hood while the sample is evaporated.
 - Take precautions to keep sources of ignition such as open flames or hot electric coils away from the hood used for the sample evaporation.
16. Allow the LPG to evaporate completely at room temperature.
17. Cap the bottle *loosely* as soon as the sample evaporation is complete and remove it from the hood.
18. Transfer the methanol-water solution remaining in the bottle to a 100-mL volumetric flask, quantitatively with deionized water, using a funnel.

19. For ICP analysis only, pipet 10 mL of 1000-µg/mL scandium stock solution into the flask.
20. Bring the flask to volume with deionized water. Cap and invert several times to thoroughly mix the contents.

Instrumental Analysis

1. Set up the ICP or AAS for trace sodium analysis using conditions recommended by the manufacturer.
2. Analyze the standards and samples in the following order: blank, standards, samples and then analyze one of the standards again.
 - The final standard reading should be within 2% relative of its first reading. If it is not, check for problems and reanalyze the entire series.
3. If the sample sodium concentration in the initial dilution exceeds the 5.0-µg/mL standard, the sample requires a second dilution. Maintain the water-methanol ratio and the potassium or scandium concentration of the initial dilution in the subsequent dilution to matrix match the standards.

Calculations

When AAS is used for quantitation, samples are compared to an external standard with known sodium concentration. When ICP is used for quantitation, the relative response of scandium and sodium is determined from calibration standards, and scandium is added to each sample as an internal standard. In both cases, calculations are performed by the instrument data system to obtain the sodium concentration in the sample dilution analyzed.

Calculate the sodium in the LPG sample to the nearest 0.1 mg/kg by using the following equation:

$$\text{Sodium, mg/kg} = \frac{100 C}{M} \left(\frac{A}{B} \right) \quad (1)$$

where:

- A** = total volume of second dilution, mL
- B** = aliquot taken from initial dilution flask, mL
- If no second dilution is required, **A/B** = **1**.
- C** = sodium concentration in sample dilution, from instrument readout, µg/mL
- M** = sample mass, g
- 100** = initial dilution volume, mL

Precision

Precision will vary somewhat, depending upon whether an ICP or an AAS is used, and will also vary with the specific instrumentation and installation. Determine the precision for the specific installation according to the procedures listed in UOP Method 999, "Precision Statements in UOP Methods," or other valid statistical procedure. If the precision found is significantly worse than that listed in the Table, check the equipment and procedures used for problems.

Repeatability

The testing protocols of UOP Method 999, concerning the number of analysts and days were not used. The calculation protocols for UOP Method 999 were used. Four tests were performed by each of two analysts on the same day (8 tests). The instrumental analysis was done by AAS. The

precision data are summarized in the Table. Two tests performed by the same analyst on the same day should not differ by more than the repeatability allowable difference with 95% confidence.

Table			
<u>Repeatability, mg/kg</u>			
<u>Sample</u>	<u>Sodium Concentration</u>	<u>Within-Day esd</u>	<u>Allowable Difference</u>
LPG	1.3	0.06	0.2

The data in the Table are a short-term estimate of repeatability. When the test is run routinely, a control standard and chart should be used to develop a better estimate of the long-term repeatability.

Reproducibility

There is insufficient data to calculate the reproducibility of the test at this time.

Time for Analysis

The elapsed time for one analysis is 2 hours. The labor requirement is one hour.

Suggested Suppliers

PerkinElmer Analytical Instruments, 710 Bridgeport Avenue, Shelton, CT 06484-4794 (203-925-4600) www.perkinelmer.com

SPEX CertiPrep, Inc., 203 Norcross Ave., Metuchen, NJ 08840 (732-549-7144) www.spexcsp.com

Swagelok, 1540 N. Old Rand Road, Wauconda, IL 60084-0847 (847-526-6900)
www.swagelok.com

VWR International, 1310 Goshen Parkway, West Chester, PA 19380 (610-431-1700) www.vwr.com