



A Honeywell Company

Sodium in Petroleum Distillates by ICP-OES or AAS

UOP Method 549-09

Scope

This method is for determining sodium in petroleum distillate fractions, No. 2 fuel oil and lower boiling hydrocarbons, over a concentration range of approximately 0.05 ppm to 1 wt-%. Sodium in samples is present due to entrainment of aqueous droplets from a caustic washing operation or may be present as an oil-soluble salt. Total sodium, which includes suspended alkali plus oil-soluble salts, or oil-soluble sodium salts alone (organic sodium) are determined.

The total sodium content of the heavier distillates, whole crude, or residual oils should be determined by means of a wet-ashing technique, such as described in UOP Method 391, "Trace Metals in Petroleum Products or Organics by AAS."

References

UOP Method 391, "Trace Metals in Petroleum Products or Organics by AAS," www.astm.org

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

Outline of Method

Samples for the determination of total sodium (suspended aqueous alkali plus oil-soluble organosodium salts) are collected in cleaned plastic bottles. The entire sample, including the suspended material, are extracted with dilute hydrochloric acid. Sodium is determined in the acid extract by Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES, or simply, ICP) or by Atomic Absorption Spectroscopy (AAS).

Samples for the determination of oil-soluble organic sodium are filtered at the sampling point through glass wool which serves to coalesce the suspended aqueous alkali. The oil-soluble sodium in the filtered sample is determined by acid extraction and subsequent analysis of the extract for sodium.

Apparatus

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used. Wherever possible use plasticware in place of glassware as glass may contribute to sodium contamination over time, see *Note 1*.

Balance, capable of weighing to 0.1 mg

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).

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Balance, top loading, 1000-g capacity, capable of weighing to 0.1 g

Beakers, disposable, polypropylene, 30-mL, VWR, Cat. No. 47751-692

Bottle, Teflon™ FEP, 1000-mL, with screw cap, VWR, Cat. No. 16071-675

Cylinder, graduated, polypropylene, Class B, 50-mL, VWR, Cat. No. 83008-880

Flask, volumetric, polypropylene, Class B, 50-, 100-, 500-, and 1000-mL, VWR, Cat. Nos. 83008-970, -980, 83009-001, and -006, respectively

Funnel, polypropylene, 12-cm diameter, 1-cm diameter stem, VWR, Cat. No. 30252-913

Funnels, separatory, Teflon FEP, 1000- and 2000-mL, VWR, Cat. Nos. 30356-551 and -553, respectively

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.

Oven, laboratory, capable of operation at 105°C

Pipet, volumetric transfer, Class B, 5-, 10-, 20-, 25-, 50-, and 100-mL, VWR, Cat. Nos. 89003-482, -476, -444, -446, -448, and -462, respectively

Pipet filler, VWR, Cat. No. 53497-055

Ring, cork, VWR, Cat. No. 56250-068

Stand, support, VWR, Cat. No. 60100-105, with support ring, VWR, Cat. No. 60120-124, and swivel clamp, VWR, Cat. No. 21573-708

Stirrer, magnetic, with PTFE-coated stir bar, VWR, Cat. No. 11301-010

Timer, VWR, Cat. No. 62344-585

Reagents and Materials

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

Glass wool, VWR, Cat. No. EM-GX0090-2

Gloves, disposable, nitrile, VWR, Cat. No. 40101-356

Hydrochloric acid, concentrated, Certified ACS Plus, Fisher, Cat. No. A144S-212

Hydrochloric acid, 2-M. Dilute the concentrated acid with 5 volumes of deionized water.

Scandium standards, if needed for ICP internal standard use, SPEX. See Note 2.

Sodium standards, stock solutions

(A) 1000 µg Na/mL, SPEX, Cat. No. PLNA1-2X

(B) 100 $\mu\text{g Na/mL}$. Dilute 50 mL of A with deionized water to 500 mL in a volumetric flask.

(C) 20 $\mu\text{g Na/mL}$. Dilute 20 mL of A with deionized water to 1000-mL in a volumetric flask.

(D) 2 $\mu\text{g Na/mL}$. Dilute 100 mL of C with deionized water to 1000-mL in a volumetric flask.

Sodium standards, working standards for the range 0 to 10 $\mu\text{g Na/mL}$. To each of five 100-mL volumetric flasks add with a graduated cylinder 40 mL of 2-*M* hydrochloric acid. Pipet the prescribed sodium stock solution (see *Table 1*) and dilute to the mark with water. See *Notes 1 and 2*. These are suggested concentrations, and may be adjusted to match the composition of the samples to be analyzed.

Water, deionized

Table 1

<u>Working Standard Solution</u>	<u>Stock Solution Used</u>
0.0 $\mu\text{g/mL}$	0 mL (Calibration Blank)
0.1 $\mu\text{g/mL}$	5 mL of D
0.5 $\mu\text{g/mL}$	25 mL of D
2.0 $\mu\text{g/mL}$	10 mL of C
10.0 $\mu\text{g/mL}$	10 mL of B

Preparation of Sample Bottles

Prepare the 1000-mL Teflon bottles for sampling as follows:

1. Rinse the Teflon bottles with about 40 mL of 2-*M* hydrochloric acid and then deionized water.
2. Dry the bottles in an oven at 105°C.
3. Obtain and record the tare weight of the bottle with closure to the nearest 0.1 g.

Sampling

Total Sodium

Obtain the sample directly from a flowing line into the cleaned and tared 1000-mL Teflon bottle as follows:

1. Thoroughly purge the sample connection and line with 300 to 400 mL of sample.
2. Flush the bottle with sample several times and then fill the bottle to approximately 900 mL.
 - Dispose of the waste according to local practices and in an environmentally safe manner.

Organic Sodium

Take the sample directly from a flowing line into the cleaned and tared 1000-mL Teflon bottle through a filtering funnel fitted with a 2.5-cm plug of glass wool.

1. Thoroughly purge the sample connection and line with 300 to 400 mL of sample.
2. Pass sample through the filtering funnel fitted with a 2.5-cm plug of glass wool and fill the bottle to approximately 900 mL.
 - Take care not to touch the glass wool or the filter funnel with bare hands (use gloves) as this could be a source of sodium contamination.
 - The glass wool serves as a coalescing medium for suspended aqueous solutions, e.g., aqueous sodium hydroxide.

- Samples that contain little or no suspended aqueous solutions will be clear upon passing through the glass wool and the receiving bottle will not contain any separated aqueous solution. Samples containing a considerable amount of suspended water, when coalesced, will have distinct droplets or a separate phase on the bottom of the bottle. In either case, the glass wool will have coalesced the haze without removing oil-soluble organosodium compounds.

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of ICP or AAS, and the equipment being used.

Total Sodium

Prepare the sample for instrumental analysis for total sodium as follows:

1. Weigh the bottle, closure and contents to the nearest 0.1 g and obtain the weight of the sample.
2. Transfer the sample to a 2000-mL separatory funnel.
3. Using a graduated cylinder, add 40 mL of 2-M hydrochloric acid to the bottle.
4. Recap the bottle and shake it for 2 minutes.
5. Transfer the contents of the bottle to the separatory funnel.
6. Place a stirring bar in the separatory funnel and set the funnel in an inclined position on the magnetic stirrer (see Figure).
 - If necessary use a clamp, tape, or a cork ring to hold the separatory funnel in place.

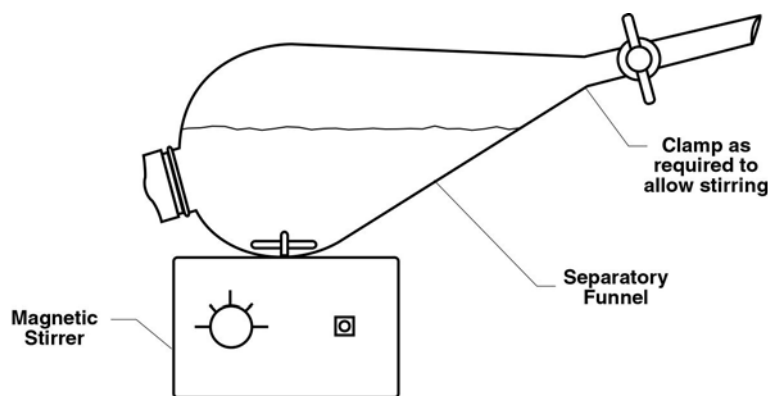


Figure
Stirring Apparatus

7. Turn on the stirrer, adjust to a rapid stirring rate, and stir for one hour.
8. Remove the separatory funnel, place it on a ring stand and allow the layers to separate.
9. Draw off the lower layer directly into a 100-mL volumetric flask.
10. Using a graduated cylinder, add 40 mL of deionized water to the sample bottle and rinse it by shaking for 2 minutes.
11. Transfer this washing to the separatory funnel.

12. Stir for 30 minutes as described in Steps 6 and 7.
13. Return the separatory funnel to the ring stand and allow the layers to separate.
14. Draw off the lower (water) layer into the 100-mL volumetric flask.
15. Add deionized water to bring the volume to the mark. This is the solution for subsequent analysis by the ICP or AAS. See *Note 2*.

Organic Sodium

Prepare the sample for instrumental analysis for organic sodium as follows:

1. Weigh the bottle, closure and contents to the nearest 0.1 g.
 - Sample was taken into the bottle by filtering through glass wool, see *Sampling, Organic Sodium*.
2. Decant about 450 mL of sample into a 1000-mL separatory funnel. If a separate, coalesced aqueous phase is present, transfer the sample by pipet instead of decanting. Carefully immerse a 100-mL pipet into the clear hydrocarbon phase, fill, and transfer the contents to the extraction funnel. Take care not to include any of the water phase. Repeat 3 or 4 times to obtain a 400- to 500-mL sample.
 - Predetermine the level by adding this measured amount of water to the separatory funnel and mark the funnel accordingly.
3. Reweigh the bottle after decanting or pipeting the sample to obtain the exact weight of sample used.
4. Using a graduated cylinder, add 40 mL of 2-*M* hydrochloric acid to the separatory funnel.
5. Place a stirring bar in the separatory funnel and set the funnel in an inclined position on the magnetic stirrer (see Figure).
 - If necessary use a clamp, tape, or a cork ring to hold the separatory funnel in place.
6. Turn on the stirrer, adjust to a rapid stirring rate, and stir for one hour.
7. Remove the separatory funnel, place it on a ring stand and allow the layers to separate.
8. Draw off the lower layer directly into a 100-mL volumetric flask.
9. Using a graduated cylinder, add 40 mL of deionized water to the separatory funnel.
10. Stir on the magnetic stirrer for 30 minutes.
11. Return the separatory funnel to the ring stand and allow the layers to separate.
12. Draw off the lower (water) layer into the 100-mL volumetric flask.
13. Add deionized water to bring the volume to the mark. This is the solution for subsequent analysis by the ICP or AAS. See *Note 2*.

Preparation of Blanks

Preparation of the blank for total sodium is described in *Reagents and Materials, Sodium standards* Table 1.

A second blank solution is prepared when analyzing for organic sodium. Prepare a blank for organic sodium as follows:

1. Pipet 40 mL of 2-*M* hydrochloric acid through a 2.5-cm plug of glass wool and collect the filtrate in a 100-mL volumetric flask.

2. Rinse the plug with several 10-mL portions of water and finally dilute to the mark with water. See *Note 2*.
3. Label as Blank B for organic sodium. This Blank B (see *Calculations*) is read with the samples after the standards are run.

Instrumental Analysis for Sodium Content

Set up the ICP or AAS for sodium content using conditions recommended by the manufacturer. Prepare a calibration curve by aspirating the prepared working standard solutions, including the Calibration Blank, and analyze the samples. See *Note 2*.

Samples that read higher than 10 µg/mL are diluted so that they fall within the calibration range of the instrument, see *Note 3*. Dilute with the Calibration Blank (Blank B for organic sodium analysis). An appropriate dilution factor, *C*, must be applied in calculating results in such cases, see *Calculations*.

Water may be aspirated between the analysis of standards and between the analysis of samples to reduce the use of the calibration blank; however, the instrument must be zeroed while aspirating the calibration blank.

Calculations

Calculate the sodium in the distillate from Equations 1 or 2:

$$\text{Total sodium, mass-ppm} = \frac{100 AC}{W} \quad (1)$$

$$\text{Organic sodium, mass-ppm} = \frac{100 (A - B) C}{W} \quad (2)$$

where:

A = the sodium concentration in the diluted extract as read from the instrument or appropriate calibration curve, µg/mL

B = sodium concentration for the Blank B, µg/mL

C = dilution factor = (final dilution volume) / (aliquot volume)
If no aliquot is taken *C* = 1

W = sample weight, g

100 = volume of sample solution, mL

Notes

1. Glassware may be used for short-term operations such as pipetting, where equivalent plasticware is not available, but plasticware must be used for all sampling and storage, as sodium can leach out of glassware over time.
2. For analysis by ICP, a scandium internal standard is often used. If using the internal standard technique, prepare the internal standard solutions and analyze the samples according to standard ICP practices.
3. As an alternative to dilution of samples that read higher than 10 µg/mL, calibration standards may be prepared at higher levels, up to 100 µg/mL or more, to bracket the concentration in the sample.

4. For greatest accuracy it is best to obtain duplicate samples. Slight contamination at low sodium levels can cause significant differences.

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 Table 2, 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. One sample of kerosene was analyzed by AAS six times.

Table 2			
<u>Repeatability, mass-ppm</u>			
<u>Sample</u>	<u>Sodium Concentration</u>	<u>Within-Day esd</u>	<u>Allowable Difference</u>
Kerosene	0.16	0.013	0.05

The data in Table 2 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 reproducibility of the test at this time.

Time for Analysis

The elapsed time for one analysis is approximately 3 hours. The labor requirement is approximately 2 hours. Samples which tend to emulsify can take longer, waiting for the layers to separate in the separatory funnel. Analysis of multiple samples after the instrument is calibrated will reduce the time required for each sample.

Suggested Suppliers

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

Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785 (412-490-8300) www.fishersci.com

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

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