NaOH, KOH, LiOH, (NaOH)	MW : 40.00 (NaOH);	CAS: 1310-73-2	RTECS: WB490000
and basic salts	56.11 (KOH)	1310-58-3	TT2100000 (KOH)
	23.95 (LiOH)	1310-65-2	OJ6307070 (LiOH)

METHOD: 7401, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 2 mg/m^3 (NaOH)
NIOSH: C 2 mg/m^3/15 min (NaOH); Group I Pesticide
ACGIH: C 2 mg/m^3 (NaOH)

PROPERTIES: basic, hygroscopic, caustic solids and aerosols; VP not significant

SYNONYMS: alkali; caustic soda; lye; sodium hydroxide; potassium hydroxide

SAMPLING

SAMPLER: FILTER
(1-µm PTFE membrane)

FLOW RATE: 1 to 4 L/min

VOL-MIN: 70 L @ 2 mg/m^3
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: at least 7 days @ 25 °C [1,2]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.76 to 3.9 mg/m^3 [1]
(360-L samples)

BIAS: 5.6%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.062 [1]

ACCURACY: ± 16.2%

MEASUREMENT

TECHNIQUE: ACID-BASE TITRATION

ANALYTE: OH^- (alkalinity)

EXTRACTION: 5.00 mL 0.01 N HCl, 15 min under nitrogen with stirring

TITRATION: 0.01 N NaOH under nitrogen, endpoint by pH electrode

CALIBRATION: 0.01 N NaOH standardized with 0.01 N HCl

RANGE: 0.14 to 1.9 mg (as NaOH) per sample [1]

ESTIMATED LOD: 0.03 mg per sample (as NaOH) [1]
(7 x 10^{-4} moles of alkalinity)

PRECISION ($\bar{S}_r$): 0.033 @ 0.38 to 1.5 mg NaOH per sample [1]

APPLICABILITY: The working range is 0.4 to 5.4 mg/m^3 for a 360-L air sample. The method measures total alkalinity of alkali hydroxides, carbonates, borates, silicates, phosphates, and other basic salts, expressed as equivalents of NaOH.

INTERFERENCES: Carbon dioxide in the air may react with alkali on the filter to produce carbonates but does not interfere when titrated. The carbonates will produce the equivalent amount of strong alkali that was consumed on the filter [1]. Acid a erosols may neutralize the sample, if present, producing a negative interference.

OTHER METHODS: This revises Methods S381 [2] and P&CAM 241 [3].

REAGENTS:

1. Sodium carbonate, primary standard grade.
2. Hydrochloric acid stock solution, 0.1 N. Standardize with sodium carbonate primary standard.
3. Dilute hydrochloric acid, 0.01 N. Dilute 10.0 mL 0.1 N stock HCl to 100 mL in a volumetric flask with distilled water.
4. Water, distilled, CO_2-free. Boil and cool under N_2 or bubble nitrogen through distilled water for 30 min. Store with an Ascarite trap.
5. Nitrogen, compressed.
6. Sodium hydroxide, 50% w/v.* Dissolve 50 g NaOH in CO_2-free distilled water and dilute to 100 mL.
7. Stock sodium hydroxide, 0.1 N. Dilute 8 mL 50% NaOH to 1.0 L with CO_2-free distilled water. Store under Ascarite or other CO_2-absorbing trap.
8. Working sodium hydroxide solution, 0.01 N. Dilute 10 mL stock (0.1 N NaOH) to 100 mL with CO_2-free distilled water.
9. Standard buffer solutions, pH 4 and 7.

* See Special Precautions

EQUIPMENT:

1. Sampler: 37-mm diameter PTFE membrane filter (Millipore, Fluoropore or equivalent), 1.0-µm pore size, supported by a cellulose backup pad in a cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. pH meter with pH electrode and recorder.
4. Titration vessel, 150 to 200 mL beaker, flask or jar with cover containing openings for the pH electrode and N_2 inlet and outlet.
5. Stirrer, magnetic, and stir bar.
6. Glass rod, ca. 5-mm diameter and 10 cm long to hold filter under liquid surface in titration vessel.
7. Pipets, 5- and 10-mL.
8. Volumetric flasks, 100-mL and 1-L.
9. Burets, 50-mL, readable to 0.1 mL.
10. Tweezers.

SPECIAL PRECAUTIONS: NaOH solutions are corrosive to tissue [4]. Handle with care.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a sample size of 70 to 1000 L. Do not exceed a filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

3. Transfer the sample filter to a titration vessel with tweezers. Place the filter face down in the titration vessel.
4. Place the end of a glass rod in the center of the filter to maintain the filter below the liquid surface during the analysis.
5. Cover the titration vessel, add 5.00 mL 0.01 N HCl, start the magnetic stirrer and N_2 purge (ca. 0.1 L/min).
6. Allow to stand 15 min (with stirring).

CALIBRATION AND QUALITY CONTROL:

7. Calibrate the pH meter with pH 4 and pH 7 buffer solutions.
8. Standardize aliquots of the 0.1 N HCl stock solution with sodium carbonate in triplicate [3].
   a. Dry 3 to 5 g primary standard grade Na_2CO_3 at 250 °C for 4 h. Cool in a desiccator.
   b. Weigh ca. 2.5 g Na_2CO_3 to the nearest mg. Dissolve and dilute to exactly 1 L with CO_2-free distilled water. The concentration is ca. 0.05 N Na_2CO_3.
   c. Place 5.00 mL 0.05 N Na_2CO_3 solution into a titration vessel and titrate potentiometrically to a pH of 5.

d. Remove electrodes, rinse them into the titration vessel, and bubble N_2 gas through contents of the titration vessel for 3 to 5 min to remove dissolved CO_2.
e. Proceed with the titration to the inflection point.
f. Calculate the normality of the stock HCl solution:

$$N_{HCl} = \frac{(\text{g } Na_2CO_3 \text{ weighed})(\text{mL } Na_2CO_3 \text{ solution used in titration})}{(52.99)(\text{mL HCl used})}$$

9. Standardize the working (ca. 0.01 N) NaOH solution against the standardized HCl solution by following steps 8.c. and 8.e, substituting the standardized HCl stock solution for the Na_2CO_3 solution and the 0.01 N NaOH solution for the 0.1 N HCl solution. Calculate the normality of the NaOH titrating solution.

$$\underline{N}_{NaOH} = (N_{HCl})(\text{mL HCl used})/(\text{mL NaOH used})$$

10. Prepare at least three spiked media blank samples to check analytical recoveries at levels expected on the field samples.

MEASUREMENT:

11. Back-titrate the excess HCl in the samples, blanks and spiked blank solutions with the standardized NaOH solution while maintaining the N_2 purge.
12. Observe the pH meter. Calculate the endpoint (mL of 0.01 N NaOH used).

CALCULATIONS:

13. Using the normality (N) and volumes of NaOH in the titration of the sample (V_{NaOH-s}) and average blank filter (V_{NaOH-b}), and the volume of air sampled, V(L), calculate the concentration, C (mg/m^3), of alkalinity (as NaOH with equivalent weight = 40.0):

$$C = \frac{(V_{NaOH-b} - V_{NaOH-s}) \cdot N \cdot 4 \times 10^4}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Method S381 [1] was issued on July 8, 1977, and was validated using generated atmospheres of NaOH over the range 0.76 to 3.9 mg/m^3 using a 360-L sample [1,6]. Overall precision, $\hat{S}_{rT}$, was 0.062 with an average recovery of 105%, representing an insignificant bias. The NaOH concentration was independently verified by analyzing additional samples for sodium by atomic absorption spectrophotometry. An overall average collection efficiency of greater than 99% was found by sampling 1 to 360 L in an atmosphere of 7.50 mg/m^3 (NaOH) using backup Fluoropore filters and also by collecting two 615-L samples using backup impingers filled with water.

REFERENCES:

[1] Backup Data Report No. S381, Sodium Hydroxide, prepared under NIOSH Contract No. 210-76-0123, available as Order No. PB 275-838 from NTIS, Springfield, VA 22161 (July 8, 1977).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 4, S381, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[3] Ibid, V. 1, P&CAM 241, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).

[4] Criteria for a Recommended Standard...Occupational Exposure to Sodium Hydroxide, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-105 (1975).
[5] Standard Methods for the Examination of Water and Wastewater, 15th Edition, American Public Health Association, American Water Works Association and Water Pollution Control Federation (1981).
[6] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

Mary Ellen Cassinelli, NIOSH/DPSE; S381 originally validated under NIOSH Contract No. 210-76-0123.