



ALKALI METAL CATIONS Na⁺, K⁺, Li⁺

7405

NaOH, KOH, LiOH

MW: 40.00 (NaOH);
56.11 (KOH);
23.95 (LiOH)

CAS: 1310-73-2 (NaOH)
1310-58-3 (KOH);
1310-65-2 (LiOH)

RTECS: WB4900000 (NaOH)
TT2100000 (KOH);
OJ6307070 (LiOH)

METHOD: 7405, Issue 1

EVALUATION: FULL

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OSHA: 2 mg/m³ (NaOH)

NIOSH: C 2 mg/m³ (NaOH, KOH); IDLH 10 mg/m³ (NaOH)

OTHER OELs: Refs. [1,2]

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

SYNONYMS: sodium hydroxide; potassium hydroxide; lithium hydroxide; alkali (LiOH, NaOH, KOH); caustic soda (NaOH); caustic potash (KOH); lye (NaOH, KOH)

SAMPLING		MEASUREMENT	
SAMPLER:	FILTER, 37-mm quartz fiber, in 2- or 3-piece filter holder	TECHNIQUE:	Ion Chromatography
FLOW RATE:	2-4 L/min	ANALYTE:	Na ⁺ , K ⁺ , Li ⁺
VOL-MIN:	30 L	DISSOLUTION:	10 mL 0.005 M H ₂ SO ₄ , 15 minutes in ultrasonic bath
-MAX:	1000 L	ELUENT:	0.005 M H ₂ SO ₄
SHIPMENT:	routine	DETECTOR:	Conductivity detector
SAMPLE STABILITY:	≥7 days at 25 °C & ≥27 days at 4 °C [3].	CALIBRATION:	≈0.5 to ≈10 mg/L Na ⁺ , K ⁺ , Li ⁺ in 0.005 M H ₂ SO ₄
BLANKS:	3 field blanks minimum per sample set	RANGE:	<0.01 to >5 mg Na ⁺ , K ⁺ per sample; <0.05 to >2.5 mg Li ⁺ per sample [3,4]
ACCURACY		ESTIMATED LOD:	0.003 mg Na ⁺ , K ⁺ per sample; 0.002 mg Li ⁺ per sample [3]
RANGE STUDIED:	NaOH: 0.08 to 3.7 mg/m ³ KOH: 0.07 to 7.4 mg/m ³ ; LiOH: 0.16 to 7.2 mg/m ³ [3]	PRECISION (\bar{S}_r):	NaOH: 0.009 to 0.030; KOH: 0.008 to 0.019; LiOH: 0.007 to 0.010 [3,4]
BIAS:	negligible		
OVERALL PRECISION ($\hat{S}_{r,T}$):	NaOH: 0.023 to 0.066; KOH: 0.018 to 0.043; LiOH: 0.016 to 0.023 [3]		
EXPANDED UNCERTAINTY*:	<22% for all three cations [6]		

*Accuracy calculations were carried out in accordance with ISO guidelines [5] rather than NIOSH accuracy criteria.

APPLICABILITY: The method is meant for the measurement of alkaline dusts. It is specific for Na⁺, K⁺, and Li⁺ but does not differentiate between the hydroxides and their corresponding salts if both are present in the air. If the cations are present only in the form of hydroxides, the method is specific for these basic compounds. In other circumstances, the results obtained represent the highest air concentration of the hydroxides that could be extant. The method can also be used to measure alkaline earth hydroxides such as calcium hydroxide [3,4].

INTERFERENCES: Sodium and potassium are ubiquitous in the environment and, if present in the sampled air at high concentrations, other soluble salts of Na and K can positively interfere. High concentrations of ammonium can interfere with the sodium peak in the chromatographic signal.

OTHER METHODS: NIOSH Method 7401 for alkaline dusts is an acid-base titrimetric procedure that measures hydroxide concentration (alkalinity), $[\text{OH}^-]$ [7]. A harmonized international standard, ISO 17091 [4], has been published.

REAGENTS:

1. Sodium, potassium and lithium standard solutions, 1000 ± 10 mg/L; traceable to national standards.
2. Calibration stock solution: sodium and potassium, 50 mg/L; lithium, 25 mg/L. Pipet 625 μL Li standard solution and 1250 μL of each of the Na and K standard solutions into 25-mL volumetric flask. Dilute to volume with deionized water. This solution can be stored at 4°C for at least 2 months.
3. Sulfuric acid stock solution, 2.5 M H_2SO_4 .
4. Sulfuric acid extraction / eluent solution, 0.005 M H_2SO_4 . Pipet 2 mL 2.5 M sulfuric acid into a 1-L volumetric flask containing deionized water. Fill to volume using deionized water.
5. Water, deionized, ≥ 18.2 M Ω -cm $^{-1}$ resistivity.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Samplers: 37-mm diameter quartz fiber filters in cassette filter holders.
NOTE: Sodium and potassium are ubiquitous in the environment and their presence in filter materials can lead to high blanks. Thus it is essential to check blank levels of each batch of filters.
2. Personal sampling pump, 2 to 4 L/min, with flexible connecting tubing.
3. Flow meter, portable.
4. Ion chromatograph (IC) with autosampler, cation exchange column (e.g., 250 mm x 4 mm) with guard column (e.g., 50 mm x 4 mm), column oven capable of maintaining column temperature at 40°C, column thermostat, suppressor (e.g., cation self-regenerating suppressor) and conductivity detector.
5. Data analysis unit (e.g., computer).
6. Volumetric flasks, polypropylene, 25-mL, 50-mL, 1-L.
NOTE: For this method, it is preferable to use plastic labware rather than glassware.
7. Adjustable pipettors with plastic tips, 10-10000 μL .
8. Screw-cap polyethylene vessels, 15-20 mL.
9. Autosampler vials, polypropylene, with screw-caps and silicon-polytetrafluoroethylene (PTFE) septa.
10. Disposable syringes, 5-10 mL.
11. Disposable filters, 0.45 μm pore size PTFE, 25-mm diameter, suitable for IC.
12. Ultrasonic bath.
13. Ultrapure water system.
14. Tweezers, plastic or plastic-tipped.

SPECIAL PRECAUTIONS: Wear appropriate personal protection during sampling activities and analysis. It is essential that suitable gloves, eye protection, laboratory coat, etc., be used when working with the chemicals. Perform sample preparation and analysis in a clean, well-ventilated area that is well removed from any possible contamination. Any area of skin affected by the stock, dissolution or detection solutions must be immediately washed with plenty of water. Avoid exposure by contact with skin or eyes, or by inhalation of vapor.

SAMPLING, SAMPLE TRANSPORT AND STORAGE:

1. Calibrate each personal sampling pump with a representative sampler in line.

2. Sample at an accurately known flow rate between 2 and 4 L/min for a sample size of 30 to 1000 L. Do not overload the samplers.
3. When sampling is completed, remove the samplers and cap them.
4. Submit at least three blank filters as field blanks from the same lot as sample filters for each set of samples, and handle them in the same way as field samples.
5. Transport the samples to the laboratory in a manner that prevents contamination or damage to the filters, and in accordance with established chain-of-custody procedures [8].
6. The samples can be stored at room temperature for one week; for longer storage, refrigerate the samples at 4 °C.
NOTE: These storage times relate to the evaluated conditions. Longer storage at room temperature may be possible, but was not tested.
7. Samples should be analyzed no more than four weeks after sample collection.

SAMPLE PREPARATION:

8. Remove sample cassettes from storage and, if necessary, bring to room temperature.
9. Using tweezers, remove the sample filters from the filter holder (cassette) and place them in 15-20 mL plastic (polyethylene) screw-cap vessels.
10. Rinse the inside walls of the cassette with 2-3 mL of extraction / eluent solution (0.005 M H₂SO₄) and direct the rinsate(s) into the plastic vessels that contain the filters.
11. Bring the final volume of extraction / eluent solution inside the vessels to 10 mL, ensuring that the filters are completely immersed.
12. Seal the 15-20 mL plastic vessels and place them in an ultrasonic bath. Sonicate for 15 minutes and then allow to stand for at least 30 minutes.
13. For each prepared sample, using a disposable syringe, remove 5 mL of the extraction solution and filter into an autosampler vial through a disposable PTFE filter.

CALIBRATION AND QUALITY CONTROL:

14. Prepare at least five calibration working solution standards to cover the required concentration range, e.g., from 0.6 to 20 mg/L for Na⁺ and K⁺ and 0.3 to 10 mg/L for Li⁺. Accurately pipet appropriate volumes of calibration stock solution into individual, labeled volumetric flasks. Dilute to the mark with water, close, and mix.
NOTE: These calibration working solutions can be stored at room temperature for at least 2 weeks. Before use, their stability should be confirmed. If stability is inadequate, these solutions should be prepared fresh daily.
15. Calibrate the ion chromatograph with the above five calibration solutions by preparing a calibration graph of peak height (in e.g., μ S) vs. concentration (mg/L) for each cation.
16. Analyze calibration working standards together with samples, reagent blanks and field blanks at a frequency of at least 1 per 20 samples (3 minimum of each).
17. Check recoveries with at least two media blanks and 3 quality control spikes per 20 samples.

MEASUREMENT:

18. Set the ion chromatograph to the recommended eluent flow rate (e.g., 1.0 mL/min) and system pressure (ca. 10 MPa) and other conditions specified by the instrument manufacturer.
19. Using the autosampler, a 25- μ L sample aliquot of the contents of each autosampler vial is injected into the ion chromatograph.
20. Measure the peak heights of the lithium, sodium and potassium peaks (at retention times of approximately 4, 4.5 and 6 min, respectively) (Figure 1). If the peak height exceeds the linear calibration range, dilute with eluent, reanalyze, and apply the appropriate dilution factor in calculations.

CALCULATIONS:

21. Calculate the mass concentration of each cation, C (mg/m³), in the air volume sampled, V (m³):

$$C = \frac{(C_i \times V_i \times F) - (C_0 \times V_0)}{V},$$

where:

C_0 = mean concentration, in mg/L, of cation in field blank test solution;

C_i = concentration, in mg/L, of the i^{th} cation ($i = \text{Na}^+, \text{K}^+, \text{Li}^+$) in sample test solution;

V = volume of air sample (m³), where 1 L = 0.001 m³

V_0 = volume of field blank test solution (L)

V_i = volume of sample test solution (L) for i^{th} cation ($i = \text{Na}^+, \text{K}^+, \text{Li}^+$)

F = dilution factor for each sample test solution

EVALUATION OF METHOD:

The method was evaluated in accordance with an applicable international consensus standard, ISO 20581 [9]. The component of variation of the method arising from analytical variability, as determined from spiked and dried quartz fiber filters, was found to be in the range of 0.9% to 3.0% for NaOH, 0.8% to 1.9% for KOH, and 0.7% to 1.0% for LiOH [3,6]. Mean recoveries from these samples were $102 \pm 2\%$ for NaOH, $100 \pm 2\%$ for KOH and $101 \pm 2\%$ for LiOH [3]. The expanded uncertainty of the method, using a coverage factor (k) of 2 [10], was estimated as <22% for all three hydroxides [6]. Method quantitation limits were calculated based on the use of low-spike calibration standards [3, 11]. For a sampled air volume of 420 L, the quantitation limits were 0.041 mg/m³ for NaOH and LiOH and 0.034 mg/m³ for KOH. Storage stability of four weeks was demonstrated by recoveries >95% for quartz fiber filters spiked with NaOH, KOH and LiOH and stored at room temperature for 7 days and 4 °C thereafter [6]. Influence of humidity was investigated at a relative humidity (RH) of 70%, established by means of a dynamic test gas apparatus [3]. Amounts of 0.1 – 0.2 mg of NaOH, KOH and LiOH were spiked onto quartz fiber filters and then dried. Over two hours, air with RH=70% was drawn through these filters at 3.5 L/min; humidity was not found to influence the analytical recoveries of the three hydroxides.

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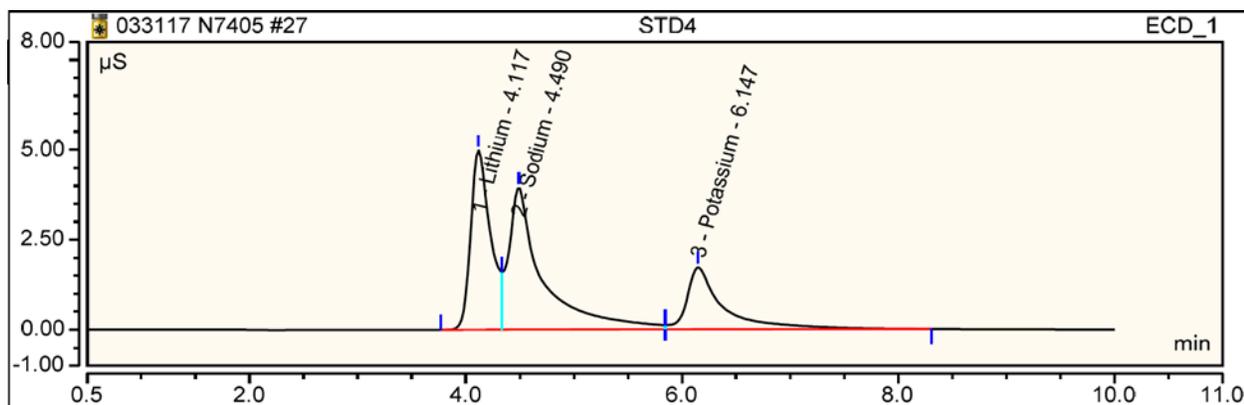


FIGURE 1. Chromatogram of standard solution containing Li, Na, and K.