FLUORIDE in URINE 8308

F MW: 19.00 CAS: 16984-48-8 RTECS: LM6290000

METHOD: 8308, Issue 3 **EVALUATION:** FULL **Issue 1:** 15 February 1984
Issue 3: 14 March 2016

BIOLOGICAL INDICATOR OF: exposure to inorganic fluorides [1,2]

SYNONYMS: None

SAMPLING

SPECIMEN: urine, pre- and post-shift

VOLUME: 50 mL in chemically clean polyethylene bottles

PRESERVATIVE: 0.2 g EDTA added to bottles before collection

SHIPMENT: in insulated containers using bagged refrigerant

SAMPLE STABILITY: 2 weeks @ 4 °C, longer if frozen

CONTROLS: collect 3 sets of specimens from unexposed workers (pre- and post-shift)

ACCURACY

RANGE STUDIED: not studied

BIAS: not determined

OVERALL PRECISION ($\hat{S}_{rT}$): not determined

ACCURACY: ± 23.6%

MEASUREMENT

TECHNIQUE: ION SELECTIVE ELECTRODE (ISE)

ANALYTE: fluoride ion (F^-)

DILUTION: mix equal volumes of urine with TISAB

CALIBRATION: solutions of sodium fluoride in water

QUALITY CONTROL: spiked urine pools; correct for creatinine content

RANGE: 1 to 100 mg/L urine

ESTIMATED LOD: 0.1 mg/L urine

RECOVERY: 0.95 [3]

PRECISION ($\bar{S}_r$): 0.04

APPLICABILITY: Any fluorine-containing substances that can be metabolized to fluoride (F-) can be monitored using this procedure. Inorganic compounds of fluoride can be absorbed by the body resulting in the excretion of fluoride ions as sodium fluoride. Dietary and domestic water sources of fluoride must be considered, as well as dental treatments.

INTERFERENCES: Hydroxide, the only positive interference, is eliminated by use of the buffer. Negative interferences from complexation of fluoride by cations, such as calcium, are minimized by EDTA preservative and the high ionic strength buffer.

OTHER METHODS: This method is P&CAM 114 [4] in a revised format. Other methods that have been used are those described in the NIOSH criteria documents on inorganic fluorides [1] and hydrogen fluoride [2].

REAGENTS:

1. Distilled or deionized water.
2. Sodium citrate tribasic dihydrate ($Na_3C_6H_3O_7 \cdot 2H_2O$), ACS reagent grade or better.
3. Ethylenediaminetetraacetic acid (EDTA) disodium salt, ACS reagent grade or better.
4. Acetic acid, glacial, ACS reagent grade or better.
5. Sodium chloride, ACS reagent grade or better.
6. Sodium hydroxide, 5 M. Dissolve 20 g NaOH in distilled water; dilute to 100 mL.
7. Sodium fluoride, ACS reagent grade or better.
8. Calibration stock solution, 100 µg F^- /mL. Dissolve 0.2211 g dry sodium fluoride in distilled water. Make 1000 mL solution.
9. Total ionic strength activity buffer (TISAB), pH 5. Add 57 mL glacial acetic acid, 58 g sodium chloride, and 0.30 g sodium citrate to a 1-L beaker containing 500 mL distilled water. Stir to dissolve. Place beaker in water bath for cooling. Slowly add 5 M sodium hydroxide until the pH is between 5.0 and 5.5. Cool to room temperature; dilute to 1 L with distilled water.
10. Fluoride in Urine Certified Reference Materials (CRMs).

EQUIPMENT:

1. Polyethylene bottles, 125-mL, wide-mouth.
2. Fluoride ion specific electrode (ISE), with reference electrode.
3. pH/millivolt meter, reading to ± 0.5 mV.
4. Stirrer, magnetic.
5. Stirring bars, PTFE-coated.
6. Beakers, plastic, 50-mL.
7. pH electrode.
8. Pipets, appropriate sizes for standards.
9. Volumetric flasks for standards.
10. Water bath.
11. Tissues, low-lint lab wipers.

SPECIAL PRECAUTIONS: Wear gloves, lab coat, and safety glasses while handling all chemicals and human urine products. Disposable plastic, glass, and paper (pipet tips, gloves, etc.) that contact urine should be placed in a biohazard container. Standard precautions should always be used when handling bodily fluids and/or extracts of bodily fluids [5]. Handle urine samples and urine extracts using proper gloves. Glacial acetic acid is flammable and corrosive and should be handled in a fume hood.

SAMPLING:

1. Collect pre- and post-shift spot urine samples in polyethylene bottles containing 0.2 g EDTA.
2. Ship samples in insulated container at about 4 °C using bagged refrigerant.

SAMPLE PREPARATION:

3. Perform a creatinine determination on an aliquot of the urine (e.g., [6]).

CALIBRATION AND QUALITY CONTROL:

4. Prepare at least five working standards in the range 0.1 to 100 µg F^- /mL by appropriate dilutions of the calibration stock solution with distilled water.

5. Analyze a set of working standards together with the samples and blanks (steps 9 through 12) starting with the lowest concentration.
   NOTE: Working standards, samples, and blanks must be analyzed under the same conditions, including temperature, for accurate results.
6. Prepare a semi-log calibration curve plotting millivolts on the linear scale (y-axis) and fluoride concentration, µg/mL, on the log scale (x-axis).
7. Maintain standardization by running a standard with every 10 specimens.
8. Run a spiked urine control specimen with every 10 specimens to maintain quality assurance.
   NOTE: Urine used for spiked controls must be analyzed before use to determine background fluoride concentration.

MEASUREMENT:

9. Add 10 mL well-mixed urine and 10 mL TISAB to a 50-mL plastic beaker.
10. Place a small stirring bar into beaker and mix continuously on a magnetic stirrer at room temperature.
11. Immerse electrodes. Allow sample to mix for 2 to 3 min and then record millivolt reading.
12. Rinse electrodes and stirring bar thoroughly with distilled water and wipe dry with tissue before next sample analysis.

CALCULATIONS:

13. Convert the millivolt readings to fluoride concentration using the calibration curve from step 6.
14. Express fluoride concentration as mg F^-/g urinary creatinine.

GUIDES TO INTERPRETATION:

Urine concentrations of fluorides in normal non-occupationally exposed workers have been reported to range from 0.2 to 3.2 mg/L depending on dietary intake [7]. Pre-shift levels of less than 4 mg/g creatinine and post-shift levels of less than 7 mg/g creatinine appears to protect workers against bony fluorosis [8]. NIOSH has recommended that post-shift urine specimens should not exceed 7 mg/L (corrected to a specific gravity of 1.024) and pre-shift specimens should not exceed 4 mg/L (corrected to a specific gravity of 1.024) [1,2].

The Biological Exposure Indices (BEI) for fluoride (as of the date of this method's publication) are 2 mg/L prior to shift and 3 mg/L at end of shift [9]. This BEI changed in 2011.

EVALUATION OF METHOD

No formal method evaluation has been reported; however, Tusl [3] reported recoveries of added fluoride from 94 to 100%. Precision based on analysis of 25 specimens in triplicate is estimated to be better than $\bar{S}_r = 0.04$. This method employs standard methodology that has been shown to provide adequate performance data for decades. Additional evaluation data may be found in, but is not limited to, the following references [10-13].

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