FLUORIDE in urine 8308

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

METHOD: 8308, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
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BIOLOGICAL INDICATOR OF: exposure to inorganic fluorides [1,2].

SYNONYMS: none.

SAMPLING		MEASUREMENT	
SPECIMEN:	urine, pre- and post-shift	**TECHNIQUE:**	ION SELECTIVE ELECTRODE (ISE)
VOLUME:	50 mL in chemically clean polyethylene bottles	**ANALYTE:**	fluoride ion (F^-)
PRESERVATIVE:	0.2 g EDTA added to bottles before collection	**DILUTION:**	mix equal volumes of urine with TISAB
SHIPMENT:	in insulated containers using bagged refrigerant	**CALIBRATION:**	solutions of sodium fluoride in water
SAMPLE STABILITY:	2 weeks @ 4 °C, longer if frozen	**QUALITY CONTROL:**	spiked urine pools; correct for creatinine content
CONTROLS:	collect 3 sets of specimens from unexposed workers (pre- and post-shift)	**RANGE:**	1 to 100 mg/L urine
		ESTIMATED LOD:	0.1 mg/L urine
		RECOVERY:	0.95 [3]
		PRECISION ($\bar{S}_r$):	0.04
		ACCURACY:	± 23.6%

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 ($Na_3C_6H_3O_7 \cdot 2H_2O$).
3. Ethylene dinitrilotetracetic acid (EDTA), disodium salt.
4. Acetic acid, glacial.
5. Sodium chloride.
6. Sodium hydroxide, 5 M. Dissolve 20 g NaOH in distilled water; dilute to 100 mL.
7. Sodium fluoride.
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 waterbath 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.

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. Waterbath.

SPECIAL PRECAUTIONS: Samples of urine collected from humans pose a real health risk to laboratory workers who collect and handle these samples. These risks are primarily due to personal contact with infective biological samples and can have serious health consequences, such as infectious hepatitis, and other diseases. There is also some risk from the chemical content of these samples, but this is much less. Those who handle urine specimens should wear protective gloves, and avoid aerosolization of the samples. Mouth pipetting, of course, must be avoided.

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., [5]).

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 calibration graph on three-cycle semi-log paper plotting millivolts on the linear scale and fluoride concentration, µg/mL, on the log scale.
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 graph.
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 [6]. Preshift 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 [7]. 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 (1.024) [1,2].

The Biological Exposure Indices for fluoride are 3 mg/g creatinine prior to shift and 10 mg/g creatinine at end of shift [8].

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 $\bar{S}_r = 0.04$.

REFERENCES:

[1] Criteria for a Recommended Standard...Occupational Exposure to Inorganic Fluorides, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-103 (1976).
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[3] Tusl, J. Direct determination of fluoride in human urine using fluoride electrode, Clin. Chim. Acta, 27, 216-218 (1970).
[4] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 114, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[5] Tietz, N. W. Fundamentals of Clinical Chemistry, 2nd ed., W. B. Saunders Co., Philadelphia, PA, 994-999 (1976).
[6] Baselt, R. C. Biological Monitoring Methods for Industrial Chemicals, Biomedical Publications, Davis, CA, 140-143 (1980).
[7] Lauwreys, R. R. Industrial Chemical Exposure: Guidelines for Biological Monitoring, Biomedical

Publications, Davis, CA, 26-27, 134 (1983).
[8] 1993-1994 Threshold Limit Values and Biological Exposure Indices, American Conference of Governmental Industrial Hygienists, Cincinnati, OH (1993).

METHOD WRITTEN BY:

William P. Tolos, NIOSH/DBBS.