

X. APPENDIX II
ANALYTICAL METHODS FOR FLUORIDE

Principle of the Method

(a) A known volume of air is drawn through a treated filter to collect fluoride particulate and gases.

(b) The filters are returned to the laboratory where the sample is isolated and/or analyzed. Hydrated aluminum fluoride should be treated as a special case, requiring an alkaline fusion for conversion to a soluble form.

(c) If water-insoluble material is present in the sample an isolation procedure is required.

(d) After isolation and initial sample preparation with TISAB, the fluoride concentration in the sample is measured by ion-selective electrode.

Range and Sensitivity

(a) The limit of detection of the method is 0.02 ppm of fluoride in the liquid sample.

(b) The upper limit of the method may be varied, according to the sample requirements, by appropriate selection of the size aliquot taken for analysis.

Interferences

In the isolation process, interfering materials that volatilize from an acid medium must be eliminated. Relatively large amounts of chloride may be fixed in the diffusion vessel by the cautious addition of 0.2 g

silver perchlorate. Samples high in carbonates require caution upon acidification to control effervescence. The ion-selective electrode is relatively free from interferences. Certain cations (notably those of hydrogen, aluminum, silicon, and ferric iron) will bind fluoride and reduce the fluoride activity in acid solution. By pH adjustment and addition of a complexing agent such as CDTA (1,2-diamino cyclohexane N,N,N',N'-tetraacetic acid) these interferences are minimized.

Precision

The precision of electrode methods is 1.5-3.5%; an electrode method tested by 111 laboratories was found to have a precision of 0.030 at a concentration of 0.85 mg/liter (ppm) of fluoride. [208]

Advantages of the Method

- (a) No evaporation losses.
- (b) Rapid, simple analyses are usually possible.
- (c) Potential interferences are easily minimized.
- (d) Minimal clean-up time (no elaborate glassware); electrode easily rinsed clean with distilled water.

Apparatus

(a) General

(1) Filters, cellulose acetate, membrane, 0.8- μ m. Two- or 3-piece plastic filter holders (field monitors) are convenient for taking the sample and transporting the filters.

(2) Glassware should be borosilicate; plastic ware should be used for preparation and storage of fluoride standards and samples. Apparatus is cleaned in a hot detergent solution, followed by a rinse in

warm, dilute nitric or hydrochloric acid solution and a rinse with distilled water. All sampling devices, volumetric glassware, and reagent solutions must be stored under suitable conditions to protect from airborne dust and fumes, and should be reserved for exclusive use in low-fluoride analyses.

(3) An ion-selective meter having a direct reading concentration scale or a pH meter with an expanded mV scale and a precision of $\pm 1\%$ should be used. A fluoride ion-selective electrode and single-junction or glass sleeve type saturated potassium chloride reference electrode are used in conjunction with the meter.

(4) A magnetic stirrer having fluorocarbon-coated stirring bars equipped with a heat shield between the stirring motor and sample should be used.

(b) Isolation by Diffusion

(1) Microdiffusion dish--disposable plastic Petri dish. The Conway Microdiffusion dish with Obrink modification, made of methyl methacrylate resin or similar plastic capable of withstanding 60 C may be used. [116]

(2) A thermostatically controlled oven capable of maintaining ± 1 C in the 50-60 C range.

(3) A Mohr pipet with a capacity of 0.1 ml, having 0.01 ml subdivisions.

Reagents

All reagents are ACS reagent grade except where noted.

(a) Filter

Alcoholic Sodium Formate--dissolve 10 g sodium formate in 50 ml distilled water; dilute to 100 ml with ethyl alcohol.

(b) Diffusion

(1) Perchloric acid, 70-72%

(2) Silver perchlorate, anhydrous, C.P.

(3) Alcoholic sodium hydroxide, 1.0 N solution--dissolve 4 grams sodium hydroxide in 5 ml of water and dilute to 100 ml ethyl or methyl alcohol.

(c) Analysis

TISAB is commercially available or can be prepared as follows: Place approximately 500 ml of distilled water in a 1-liter beaker. Add 57 ml of glacial acetic acid, 58 g of sodium chloride, and 4 g of disodium CDTA. (CDTA is available commercially as cyclohexylene dinitrilotetraacetic acid, or 1,2-diaminocyclohexane N,N,N',N'-tetraacetic acid.) Stir to dissolve. Place beaker in a water bath for cooling, insert a calibrated pH electrode into the solution, and slowly add approximately 5 N sodium hydroxide until the pH is between 5.0 and 5.5. Cool to room temperature. Pour into a 1-liter flask and add distilled water to the mark.

Standards

Serially dilute commercial standards or prepare standards as follows:

(a) Standard solution #1: Dissolve 2.2105 g of pure sodium fluoride in distilled water and dilute to 1 liter in a volumetric flask, mix, and transfer to a plastic storage bottle (1 ml = 1.00 mg F).

(b) Standard solution #2: Dilute 10 ml of standard #1 to 1 liter with distilled water in a volumetric flask, mix, and transfer to a plastic

storage bottle (1 ml = 0.01 mg F).

Filter Preparation

Cellulose acetate filter paper (0.8 μ pore, 37-mm diam.) is dipped in a solution of 50% ethanol-10% sodium formate and allowed to air dry.

Filter Treatment

If in the judgment of the analyst water-insoluble fluorides are present in the air sample, remove the filter from the holder and place it in the bottom section of the microdiffusion vessel; follow diffusion procedure. If it is known that only water-soluble fluorides are present, remove the filter from the holder and place in a 50-ml plastic beaker. Add 10 ml TISAB solution and stir the sample for 30 minutes. Follow analysis procedure.

Diffusion Procedure

With a 0.1-ml Mohr pipet, place 0.05 ml of the alcoholic sodium hydroxide solution on the center of the inside top of the plastic Petri dish. Use the tip of the pipet to spread the droplet into a circular spot at least 3-4 cm in diameter. Dry for about 1 hour under slightly reduced pressure in a desiccator containing activated alumina. To the bottom portion of the Petri dish containing the filter, cautiously add 1 ml distilled water, 0.2 g silver perchlorate, and 2.0 ml perchloric acid. Immediately close the dish with a prepared lid. Place the unit in an oven maintained at 50-60 C and allow to remain 16-20 hours. Carefully remove the unit from the oven and take off the lid. Follow analysis procedure.

Analysis Procedure

(a) Air Samples

If the diffusion step was included, wash the Petri dish lid with successive portions of distilled water (10 ml total) and collect the washings in a 50-ml plastic beaker. To the beaker containing the diffusion washings, add 10 ml distilled water and 20 ml TISAB solution. If the diffusion step was not included, add 20 ml distilled water and 10 ml TISAB solution. The final solution should be a 1:1 dilution of 20 ml distilled water and 20 ml TISAB. Using an expanded scale pH meter or a ion-selective meter, place the electrodes in appropriate standard solutions and record the mV readings as the solution is stirred. Rinse and blot electrode surfaces between solutions. After the meter has been calibrated using manufacturer's recommendations and a standard curve has been established, place the electrodes in the sample solution and record the mV reading. The meter will require several minutes to come to equilibrium. It should be read at equivalent elapsed times for each sample. Determine F concentration by referring to the standard curve.

Note: Since the rate of stirring speed affects the electrode response time, a constant and consistent speed should be used for air and urine samples and standards.

(b) Urine Samples

Urine samples should be collected in plastic or wax-impregnated cardboard specimen bottles. Care must be taken when collecting and handling urine specimens to avoid F contamination. Upon receipt of the sample, either analyze immediately or refrigerate to retard bacterial action on urea which increases the sample pH through release of ammonia. Determine

the specific gravity before analysis. Dilute the sample 1:1 with TISAB and proceed directly with electrode analysis. Determine F concentration in mg fluoride per liter of urine by referring to a previously prepared standard curve. Adjust the measured concentration to a specific gravity of 1.024 as follows [40,41]:

$$\text{Adjusted mg F/liter at specific gravity 1.024} = \frac{0.024 (A)}{B-1.000}$$

where A = measured F concentration mg/liter
 B = measured specific gravity

If a urinometer is used which has been calibrated against water at 4 C, a temperature correction must be made. [41]

Note: Urine samples with specific gravities of less than 1.010 are not indicative of the normal range and should be discarded. Failure to do so will result in an erroneously high F concentration when an adjustment to a specific gravity of 1.024 is accomplished.

Calculations

(a) Calculate the fluoride concentration in the atmosphere at 25 C and 760 Torr, in terms of mg of fluoride/cu m as follows:

$$\text{Total fluoride (mg/cu m)} = \frac{(2550)(F)(273 + t)}{pv}$$

where F = mg of fluoride in total sample
 p = sampling pressure in torr (mm of mercury)
 t = sampling temperature in degrees Celsius
 v = sample volume in liters
 2550 = STP correction factor

(b) Conversion factors for fluoride in solution:

To convert from moles per liter (molarity) fluoride to:

parts per million (ppm)	multiply by 19,056
milligrams per liter	" " "

(c) Standard Curve Preparation

Using semilogarithmic graph paper, plot millivolts on the linear axis and fluoride concentration on the logarithmic axis.

XI. APPENDIX III
MATERIAL SAFETY DATA SHEET

The following items of information which are applicable to a specific product or material shall be provided in the appropriate block of the Material Safety Data Sheet (MSDS).

The product designation is inserted in the block in the upper left corner of the first page to facilitate filing and retrieval. Print in upper case letters as large as possible. It should be printed to read upright with the sheet turned sideways. The product designation is that name or code designation which appears on the label, or by which the product is sold or known by employees. The relative numerical hazard ratings and key statements are those determined by the rules in Chapter V, Part B, of the NIOSH publication, An Identification System for Occupationally Hazard Materials. The company identification may be printed in the upper right corner if desired.

(a) Section I. Product Identification

The manufacturer's name, address, and regular and emergency telephone numbers (including area code) are inserted in the appropriate blocks of Section I. The company listed should be a source of detailed backup information on the hazards of the material(s) covered by the MSDS. The listing of suppliers or wholesale distributors is discouraged. The trade name should be the product designation or common name associated with the material. The synonyms are those commonly used for the product, especially formal chemical nomenclature. Every known chemical designation or

competitor's trade name need not be listed.

(b) Section II. Hazardous Ingredients

The "materials" listed in Section II shall be those substances which are part of the hazardous product covered by the MSDS and individually meet any of the criteria defining a hazardous material. Thus, one component of a multicomponent product might be listed because of its toxicity, another component because of its flammability, while a third component could be included both for its toxicity and its reactivity. Note that a MSDS for a single component product must have the name of the material repeated in this section to avoid giving the impression that there are no hazardous ingredients.

Chemical substances should be listed according to their complete name derived from a recognized system of nomenclature. Where possible, avoid using common names and general class names such as "aromatic amine," "safety solvent," or "aliphatic hydrocarbon" when the specific name is known.

The "%" may be the approximate percentage by weight or volume (indicate basis) which each hazardous ingredient of the mixture bears to the whole mixture. This may be indicated as a range or maximum amount, ie, "10-40% vol" or "10% max wt" to avoid disclosure of trade secrets.

Toxic hazard data shall be stated in terms of concentration, mode of exposure or test, and animal used, ie, "100 ppm LC50-rat," "25 mg/kg LD50-skin-rabbit," "75 ppm LC man," or "permissible exposure from 29 CFR 1910.1000," or if not available, from other sources of publications such as the American Conference of Governmental Industrial Hygienists of the American National Standards Institute, Inc. Flammable or reactive data

could be flash point, shock sensitivity, or other brief data indicating nature of the hazard.

(c) Section III. Physical Data

The data in Section III should be for the total mixture and should include the boiling point and melting point in degrees Fahrenheit (Celsius in parentheses); vapor pressure, in conventional millimeters of mercury (mmHg); vapor density of gas or vapor (air = 1); solubility in water, in parts/hundred parts of water by weight; specific gravity (water = 1); percent volatiles (indicated if by weight or volume) at 70 degrees Fahrenheit (21.1 degrees Celsius); evaporation rate for liquids or sublimable solids, relative to butyl acetate; and appearance and odor. These data are useful for the control of toxic substances. Boiling point, vapor density, percent volatiles, vapor pressure, and evaporation are useful for designing proper ventilation equipment. This information is also useful for design and deployment of adequate fire and spill containment equipment. The appearance and odor may facilitate identification of substances stored in improperly marked containers, or when spilled.

(d) Section IV. Fire and Explosion Data

Section IV should contain complete fire and explosion data for the product, including flash point and autoignition temperature in degrees Fahrenheit (Celsius in parentheses); flammable limits, in percent by volume in air; suitable extinguishing media or materials; special firefighting procedures; and unusual fire and explosion hazard information. If the product presents no fire hazard, insert "NO FIRE HAZARD" on the line labeled "Extinguishing Media."

(e) Section V. Health Hazard Information

The "Health Hazard Data" should be a combined estimate of the hazard of the total product. This can be expressed as a TWA concentration, as a permissible exposure, or by some other indication of an acceptable standard. Other data are acceptable, such as lowest LD50 if multiple components are involved.

Under "Routes of Exposure," comments in each category should reflect the potential hazard from absorption by the route in question. Comments should indicate the severity of the effect and the basis for the statement if possible. The basis might be animal studies, analogy with similar products, or human experiences. Comments such as "yes" or "possible" are not helpful. Typical comments might be:

Skin Contact--single short contact, no adverse effects likely; prolonged or repeated contact, irritation and possibly some blistering.

Eye Contact--some pain and transient irritation; possible corneal scarring.

"Emergency and First Aid Procedures" should be written in lay language and should primarily represent first aid treatment that could be provided by paramedical personnel or individuals trained in first aid.

Information in the "Notes to Physician" section should include any special medical information which would be of assistance to an attending physician including required or recommended preplacement and periodic medical examinations, diagnostic procedures, and medical management of overexposed workers.

(f) Section VI. Reactivity Data

The comments in Section VI relate to safe storage and handling of hazardous, unstable substances. It is particularly important to highlight instability or incompatibility to common substances or circumstances such as water, direct sunlight, steel or copper piping, acids, alkalies, etc. "Hazardous Decomposition Products" shall include those products released under fire conditions. It must also include dangerous products produced by aging, such as peroxides in the case of some ethers. Where applicable, shelf life should also be indicated.

(g) Section VII. Spill or Leak Procedures

Detailed procedures for cleanup and disposal should be listed with emphasis on precautions to be taken to protect workers assigned to cleanup detail. Specific neutralizing chemicals or procedures should be described in detail. Disposal methods should be explicit including proper labeling of containers holding residues and ultimate disposal methods such as "sanitary landfill," or "incineration." Warnings such as "comply with local, state, and federal anti-pollution ordinances" are proper but not sufficient. Specific procedures shall be identified.

(h) Section VIII. Special Protection Information

Section VIII requires specific information. Statements such as "Yes," "No," or "If Necessary" are not informative. Ventilation requirements should be specific as to type and preferred methods. Respirators shall be specified as to type and NIOSH or US Bureau of Mines approval class, ie, "Supplied air," "Organic vapor canister," "Suitable for dusts not more toxic than lead," etc. Protective equipment must be specified as to type and materials of construction.

(i) Section IX. Special Precautions

"Precautionary Statements" shall consist of the label statements selected for use on the container or placard. Additional information on any aspect of safety or health not covered in other sections should be inserted in Section IX. The lower block can contain references to published guides or in-house procedures for handling and storage. Department of Transportation markings and classifications and other freight, handling, or storage requirements and environmental controls can be noted.

(j) Signature and Filing

Finally, the name and address of the responsible person who completed the MSDS and the date of completion are entered. This will facilitate correction of errors and identify a source of additional information.

The MSDS shall be filed in a location readily accessible to workers potentially exposed to the hazardous material. The MSDS can be used as a training aid and basis for discussion during safety meetings and training of new employees. It should assist management by directing attention to the need for specific control engineering, work practices, and protective measures to ensure safe handling and use of the material. It will aid the safety and health staff in planning a safe and healthful work environment and in suggesting appropriate emergency procedures and sources of help in the event of harmful exposure of employees.

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MATERIAL SAFETY DATA SHEET

I PRODUCT IDENTIFICATION

MANUFACTURER'S NAME	REGULAR TELEPHONE NO. EMERGENCY TELEPHONE NO.
ADDRESS	
TRADE NAME	
SYNONYMS	

II HAZARDOUS INGREDIENTS

MATERIAL OR COMPONENT	%	HAZARD DATA

III PHYSICAL DATA

BOILING POINT, 760 MM HG		MELTING POINT
SPECIFIC GRAVITY (H ₂ O=1)		VAPOR PRESSURE
VAPOR DENSITY (AIR=1)		SOLUBILITY IN H ₂ O, % BY WT.
% VOLATILES BY VOL.		EVAPORATION RATE (BUTYL ACETATE=1)
APPEARANCE AND ODOR		

IV FIRE AND EXPLOSION DATA

FLASH POINT (TEST METHOD)		AUTOIGNITION TEMPERATURE	
FLAMMABLE LIMITS IN AIR, % BY VOL.	LOWER		UPPER
EXTINGUISHING MEDIA			
SPECIAL FIRE FIGHTING PROCEDURES			
UNUSUAL FIRE AND EXPLOSION HAZARD			

V HEALTH HAZARD INFORMATION

HEALTH HAZARD DATA
ROUTES OF EXPOSURE
INHALATION
SKIN CONTACT
SKIN ABSORPTION
EYE CONTACT
INGESTION
EFFECTS OF OVEREXPOSURE
ACUTE OVEREXPOSURE
CHRONIC OVEREXPOSURE
EMERGENCY AND FIRST AID PROCEDURES
EYES:
SKIN:
INHALATION:
INGESTION:
NOTES TO PHYSICIAN

VI REACTIVITY DATA

CONDITIONS CONTRIBUTING TO INSTABILITY

INCOMPATIBILITY

HAZARDOUS DECOMPOSITION PRODUCTS

CONDITIONS CONTRIBUTING TO HAZARDOUS POLYMERIZATION

VII SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED

NEUTRALIZING CHEMICALS

WASTE DISPOSAL METHOD

VIII SPECIAL PROTECTION INFORMATION

VENTILATION REQUIREMENTS

SPECIFIC PERSONAL PROTECTIVE EQUIPMENT

RESPIRATORY (SPECIFY IN DETAIL)

EYE

GLOVES

OTHER CLOTHING AND EQUIPMENT

IX SPECIAL PRECAUTIONS

PRECAUTIONARY
STATEMENTS

OTHER HANDLING AND
STORAGE REQUIREMENTS

PREPARED BY: _____

ADDRESS: _____

DATE: _____

XII. TABLES AND FIGURE

TABLE XII-1

CONSUMPTION OF FLUORSPAR IN THE UNITED STATES IN 1971

End use or product	Short Tons of Fluorspar Consumed	Percentage of Total Fluorspar Consumed
Hydrofluoric acid	701,844	52.0
Glass	12,875	1.0
Enamel	2,258	0.2
Welding rod coatings	1,043	0.1
Primary aluminum	938	0.1
Primary magnesium	22,260	1.7
Other nonferrous metals	10,715	0.8
Iron and steel castings	31,565	2.4
Open hearth furnaces	82,133	6.1
Basic oxygen furnaces	377,266	28.0
Electric furnaces	81,511	6.1
Other uses or products	20,334	1.5
TOTAL	1344,742	100.0

From Wood [12]

TABLE XII-2

OCCUPATIONS WITH POTENTIAL EXPOSURE TO FLUORIDES

Abrasive wheel makers	Lead electroplaters
Adhesive makers	Lead smelters
Aluminum anodizers	Lenscoaters
Aluminum makers	Light metal casters
Aluminum refiners	Magnesium foundry workers
Aluminum solderers	Marble hardeners
Aluminum welders	Masonry preservers
Apatite workers	Metal cleaners
Bactericide workers	Metal coating workers
Beryllium refiners	Metal refiners
Brewers	Mica makers
Building workers	Miners (fluorspar, phosphate rock)
Carbon electrode workers	Mothproofers
Cement workers	Opal glass makers
Ceramic workers	Open hearth steel workers
Chemical manufacturers	Optical equipment makers
Chemical polisher workers	Ore flotation workers
Chlorofluorocarbon makers	Paint workers
Concreters	Petroleum refinery workers
Construction workers	Phosphorescent tube makers
Copper refiners	Phosphoric acid makers
Cryolite makers	Phosphorus makers
Dentifrice makers	Photoengravers
Diazosalt makers	Porcelain enamel workers
Disinfectors	Radiation dosimeter makers
Electric arc welders	Rock phosphate acidulators
Electric arc workers	Rodent exterminators
Electroplaters	Rubber coagulators
Embalming fluid workers	Sandy soil treaters
Fertilizer makers	Silver refiners
Fluoride workers	Silver solder flux workers
Fluorocarbon makers	Sinterers
Fluorspar workers	Soil improvers
Flux makers	Stainless steel welding rod users
Foundry workers	Submerged arc welders
Fruit workers	Superphosphate makers
Fungicide workers	Synthetic stone makers
Glass etchers	Tantalum refiners
Gold refiners	Textile mordanters
Grinding wheel makers	Vegetable growers
Hide and skin preservers	Vitreous enamel workers
Hydrofluoric acid makers	Water treaters
Insect exterminators	Welding rod makers
Insecticide makers	Wood preservative workers
Latex foam rubber workers	Wood preservers and stainers
Laundry workers	Zinc miners

Adapted from Gafafer and Greenwood [258,259]

TABLE XII-3

PROPERTIES OF REPRESENTATIVE FLUORIDES

Name and Formula	Formula Weight	Density g/cc	Melting Point Degrees C	Boiling Point Degrees C	Solubility, g/100 cc F2O	
					cold	hot
Aluminum fluoride, AlF ₃	83.98	2.882	sublimes		0.559	soluble
Aluminum fluosilicate (topaz) 2AlFO.SiO ₂	184.04	3.58			insoluble	insoluble
Ammonium fluoborate, NH ₄ BF ₄	104.84	1.871	sublimes		25	97
Ammonium fluoride, NH ₄ F	37.04	1.009	sublimes		100	decomposes
Ammonium fluosilicate (alpha cryptohalite), (NH ₄) ₂ SiF ₆	178.14	2.011	decomposes		18.6	55.5
Ammonium hydrogen fluoride, NH ₄ HF ₂	57.04	1.50	125.6		v.s.*	v.s.*
Calcium fluoride (fluorspar), CaF ₂	78.08	3.180	1360	c 2500	0.0016	0.0017
Calcium fluosilicate, CaSiF ₆	182.16	2.66			sl.s.**	
Cesium fluoride, CsF	151.90	4.115	682	1251	367	
Fluorapatite (phosphate rock), Ca ₁₀ (PO ₄) ₆ F ₂					sl.s.**	
Hydrogen fluoride, HF	20.01	0.991(Sp.G.)	-83.1	19.54	sol. in all proportions	v.s.*
Lithium fluoride, LiF	25.94	2.635	842	1676	0.27	
Magnesium fluoride, MgF ₂	62.31		1266	2239	0.0076	insoluble
Magnesium fluosilicate, MgSiF ₆	166.39				65	
Potassium fluoborate, KBF ₄	125.91	2.498	decomposes 350	decomposes	0.44	6.27
Potassium fluoride, KF	58.10	2.48	846	1505	92.3	v.s.*

TABLE XII-3 (continued)

PROPERTIES OF REPRESENTATIVE FLUORIDES

Name and Formula	Formula Weight	Density g/cc	Melting Point Degrees C	Boiling Point Degrees C	Solubility, g/100 cc H ₂ O	
					cold	hot
Potassium fluosilicate, K ₂ SiF ₆	220.25	2.665	decomposes		6.9	
Potassium fluotantalate, K ₂ TaF ₇	392.14	4.56			sl.s.**	decomposes
Potassium fluotitanate, K ₂ TiF ₆ .H ₂ O	258.11		780	decomposes	0.556	1.27
Potassium fluozirconate, K ₂ ZrF ₆	283.41	3.48			0.781	25
Potassium hydrogen fluoride, KHF ₂	78.11	2.37	decomposes ca 225	decomposes	41	v.s.*
Rubidium fluoride, RbF	104.47	3.557	775	1410	130.6	
Sodium aluminum fluoride (cryolite), 3NaF.AlF ₃	209.94	2.90	1000		sl.s.**	
Sodium fluoborate, NaBF ₄	109.79	2.47	slowly decomposes 384	decomposes	108	210
Sodium fluoride, NaF	41.99	2.558	988	1695	4.22	
Sodium fluosilicate, Na ₂ SiF ₆	188.06	2.679	decomposes		0.652	2.46
Sodium hydrogen fluoride, NaHF ₂	61.99	2.08			soluble	soluble
Strontium fluoride, SrF ₂	125.62	4.24	1450+	2489	0.011	0.012
Zinc fluoride, ZnF ₂	103.37	4.95	872	1500	1.62	soluble

* v.s. = very soluble

** sl.s. = slightly soluble

From Weast [260]

TABLE XII-4

FLUORIDE CONTENT OF FRESH FOOD AND BEVERAGE, MILLIGRAMS PER KILOGRAM*

Reference and year	Fruit	Vegetable	Meat excl Bone	Breads & Grain	Fish	Black Tea
[18] 1937		0.01-5.9				
[21] 1939	0.21-0.70	0.08-1.34	0.20-1.67	0.82-1.33	1.58-1.63	
[24] 1949	0.00-1.32	0.08-6.4	<0.02-3.3	<0.1-0.7	<0.2-26.9	7.8-398.8
[19] 1959	0.02-1.32	0.1-3.0	0.01-7.7	<0.1-20.0	0.1-24.0	3.2-4.00
[20] 1970	0.03-0.84	0.02-0.9	0.14-2.0	0.18-2.8	0.05-19.0	0.1-2.0
[261] 1970	0.07-0.72 •	0.06-1.05 (polished peas, 14.06)	0.19-0.51	0.04-0.24 (polished rice, 10.67)	1.37-5.21	10.08-10.78

* The variability of the given values may be explained by the variability in F content among different plant and animal species and/or the differences in analytical techniques.

TABLE XII-5

F LEVELS IN BLOOD--MICROGRAMS PER 100 MILLILITERS

Author	Year	Values	Number of Tests	Method	Subjects' Exposure
Smith et al [52]	1950	0.33	34	Smith & Gardner	0.06 in water
		1.38	20		
		3.93	12		1.0-1.2
Singer & Armstrong [262]	1960	14	16	Singer & Armstrong	0.15 in water
		15	18		1.1 "
		19	36		1.1 "
		16	26		2.5 "
		26	22		5.4 "
Armstrong et al [263]	1964	79	5	Singer & Armstrong	50-100 mg F/day therapeutically
		85			
		65			
		177			
		45			
		48			
		23			
		34			
		30			
		25			
		27			
		32			
		28			
Taves [53]	1966	1.3	16	modified diffusion process of Singer & Armstrong	about 1 mg F/liter in water
Armstrong et al [57]	1970	11	12-16	Singer & Armstrong	
Hall et al [54]	1972	3.7	26	ion-selective electrode	about 1 mg F/liter in water

TABLE XII-6
FLUORIDE IN BONE

Subjects	Age	F in Water ppm	Years in Area	Bone Site	F in bone (mg/100 g) dry, fat-free ash	
New York City resident		0.0		rib		10
Washington, D.C., resident		0.0		humerus		100
Washington, D.C. resident		0.0		tibia		20
Washington, D.C. resident [64]		0.0		toe		160
Autopsy; most deaths sudden; 33 subjects [60]	55.5 (SE 2.8)	0.1-0.4	10-87	vertebra	54 (SE*5)	
				rib	50 (SE 4)	
				iliac crest	41 (SE 3)	
Longterm resident [62]	74	0.2	24	lumbar vertebra	77	177
				calvarium	92	135
				iliac crest	78	135
In counties with industrial; 90 subjects [61]	15+	<0.5	10+	vertebrae	61.5	
				iliac crest	51.0	
				rib	53.7	
Autopsy; most deaths sudden; 5 subjects [60]	75.6 (SE 1.5)	1.0	10+	vertebra	160 (SE 2)	
				rib	139 (SE 2)	
				iliac crest	138 (SE 1.6)	
11 subjects [18]	33-80			rib	93 average	48-210
Colorado resident		2.0		rib	300	
" "				rib	300	
" "				rib	350	
" "				rib	120	
[64]						

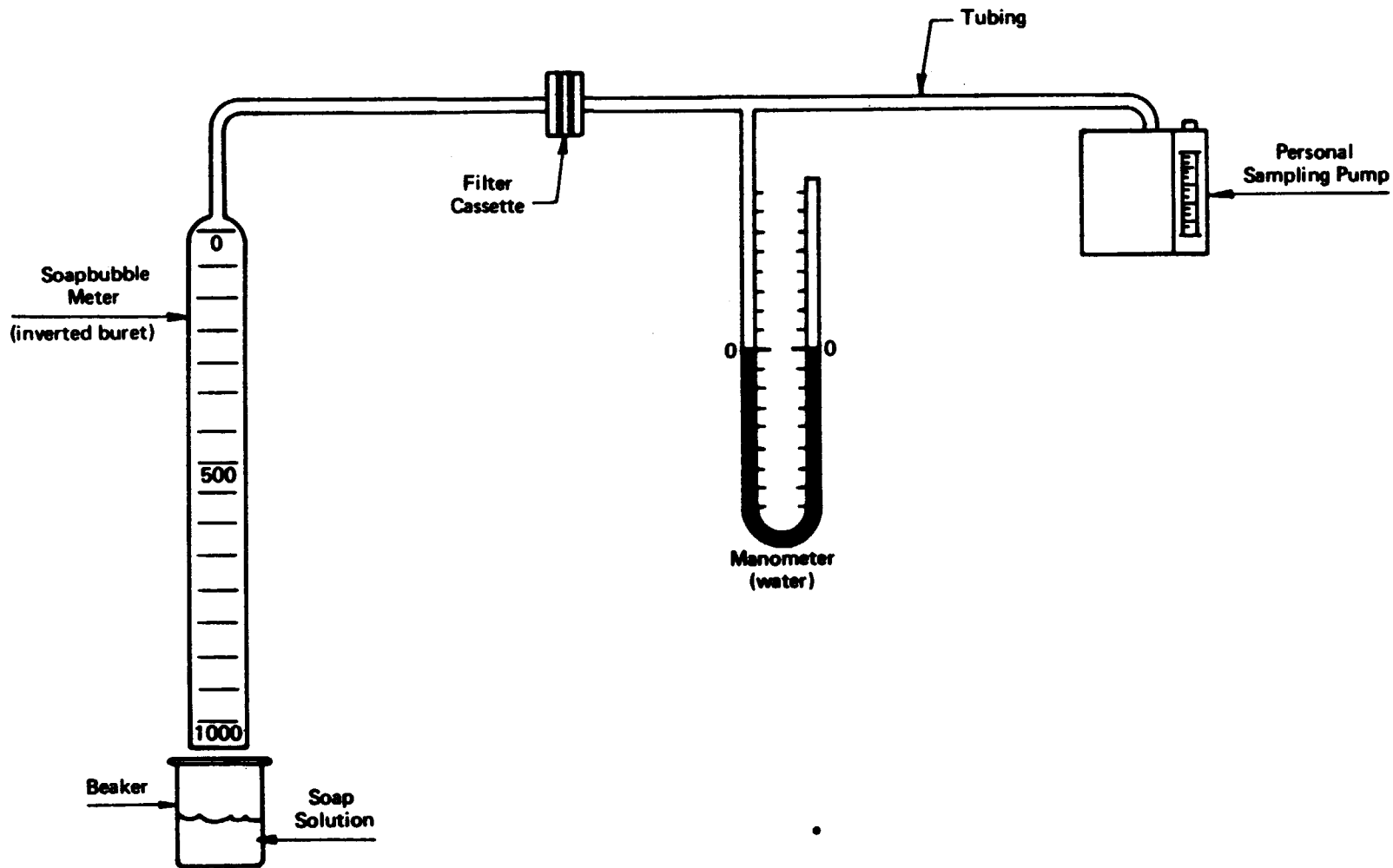
TABLE XII-6 (continued)

FLUORIDE IN BONE

Subjects	Age	F in Water (ppm)	Years in Area	Bone Site	F in bone (mg/100 g) dry, fat-free ash	
27 subjects [60]	65.9 (SE 3.0)	2.6	10-76	vertebra	286 (SE 2.3)	
				rib	257 (SE 2)	
				iliac crest	257 (SE 2.3)	
4 subjects [60]	56 (SE 11.0)	4.0	10-48	vertebra	411 (SE 6.8)	
				rib	398 (SE 4.0)	
				iliac crest	13 (SE 5.3)	
Long-term resident [62]	78	8	34	lumbar vertebra	550	913
				calvarium	653	914
China resident [65]	37	2.4& 13.1	life	lumbar vertebra	1175	1865
				skull	1502	2209
				rib	1355	2083
				ilium	1124	1756
				calcaneum	1322	2066
London residents [63]		under 0.5		rib	24	
	1			"	33	
	2			"	69	115
	15			"	88	174
	22			"	180	397
	25			"	61	
	27			"	280	591
	32			"	89	194
	37			"	310	687
	37			"	150	280
	54			"	230	
	59			"	90	186
	60			"	230	473

*Standard Error

FIGURE AII - 1. CALIBRATION SETUP FOR PERSONAL SAMPLING PUMP WITH FILTER CASSETTE



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