METHODS AND MATERIALS FOR FLUORIDE ANALYSIS

A useful article for all interested in proper surveillance of fluoridation programs appears on pages 62-66 of the January 1972 issue of the Journal of the American Water Works Association. The article, "Methods and Materials for Fluoride Analysis," was written by Ervin Bellack, Chemist, Water Supply Programs Division, Environmental Protection Agency. It describes various analytical methods, the materials necessary, and the costs of such materials. As the article was originally written for publication in 1970, the cost figures may be below current costs and should be used only as rough estimates. Current costs should be checked with appropriate manufacturers.

We wish to clarify items specified as needed in Table 3 for the SPADNS method. This method requires a photometer as listed in paragraph 1 or a spectrophotometer as listed in paragraph 2.

Mr. Bellack has informed us that, since his article was written, Corning and Orion have marketed specific fluoride testing kits containing all necessary equipment for use in fluoride analysis by the electrode method. The cost of these kits runs from $585 to $685. They are limited to fluoride testing only and do not provide for testing of other chemicals where necessary. Flexibility to provide for additional tests can be obtained by assembling individually advertised parts.

Reprints of the above-mentioned article are being provided to state dental directors and regional dental program directors as an enclosure to this memorandum. Other interested persons may obtain reprints from Mr. Bellack, Water Supply Programs Division, Environmental Protection Agency, Washington, D.C. 20460.

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Preventive Practices Branch
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Bethesda, Maryland 20014

Enclosure
Methods and Materials for Fluoride Analysis

Ervin Bellack

Making fluoride additions to drinking water, according to the author, is less difficult than ascertaining how much is present after it has been added. Several methods are available for making such determinations. The one chosen will depend, among other things, on the abilities of the technician. The author offers a rundown of what is available and offers guidance for suitable choices.

The inception of municipal water fluoridation occurred more than 25 yr ago. Today over 80 million people in the US receive water containing controlled amounts of fluoride ion. Moreover, the current trend is toward state legislation requiring water fluoridation in all but the smallest communities served by municipal water-supply systems.

The addition of fluoride to water does not impose a particularly new or more difficult duty on the water-plant operator, except that, perhaps, more attention is required for the precise feed rates recommended. In contrast, the analytical methods required for precision in feeding fluorides are both foreign and onerous.

Three analytical methods for fluoride determinations are described in the latest (13th) edition of Standard Methods, but the choice of method and equipment is left to the individual. The following descriptions and attendant lists of equipment for each of the three analytical methods are presented to acquaint the uninitiated with the options available and to assist the undecided.

The three analytical methods are Alizarin visual (Scott–Sanchis), photometric (SPADNS), and electrode.

Alizarin Visual (Scott–Sanchis) Method

Nessler-tube technique. The basis for the alizarin visual method is the zirconium–alizarin reaction in which a red lake (a deep color) is produced by the combination of alizarin and zirconium. Any fluoride present in the water sample or standard solution removes zirconium from the reaction, thus decreasing the intensity of color present. In water samples that are high in fluoride, the only color apparent is the yellow color of the unreacted dye. (Alizarin is sensitive to pH and its color will vary from purple in alkaline solutions to yellow in acid). Conversely, in low-fluoride samples, the color approaches the deep red of the zirconium–alizarin lake. Intermediate fluoride concentrations give colors that are intermediate between these two.

The reaction is not an immediate one, but progresses with time. After 1 hr, the reaction rate is extremely slow, and for this reason the time interval between adding reagent and making the measurement has been selected as 60 min.

The reaction rate is affected by a number of factors, among them are the acidity and temperature of the reaction mixture. The acidity is controlled by the fixed ratio of reagent volume to sample volume, but the temperature control becomes a necessary function of the analyst.

The color comparisons are made in 100-ml Nessler tubes—tall glass cylindrical tubes with flat bottoms. Usually, these are held in a rack with a reflector below the tubes so that light is reflected up through the longitudinal axis of the tubes to the eye of the observer. In practice, a number of tubes containing standard fluoride solutions at fixed concentration intervals are prepared in addition to the tubes containing the unknown samples. Fluoride reagent is added to both standards and samples, and after the 1-hr color-development time, the unknown samples are compared visually with the standards and a determination is made by matching the colors. Sometimes, this process involves interpolation. For example, if the color of the unknown sample appears to be midway between that of an 0.8-ppm standard and a 1.0-ppm standard, the unknown sample is determined to have a fluoride concentration of 0.9 ppm. Obviously, the smaller the interval between standards, the greater the likelihood of attaining a close match between the color of the sample and that of one of the standards.

The visual method has both advantages and disadvantages. It is simple, requires relatively inexpensive equipment, and, because of the long light path, offers potentially good sensitivity. In most cases, the color development reaction can be carried out directly in the tube, thus eliminating the need for much additional glassware.

One of the disadvantages stems from the necessity for visual comparison of the colors. First, since laboratory workers vary greatly in their ability to distinguish small differences in color intensity, the determination may vary in accuracy between several workers. The quality of light will have an effect; therefore, changes in room illumination may significantly change the interpretation of the color comparisons. Further, the human eye is not equally responsive to all wavelengths of light in the visible range. Thus, the ability to distinguish small changes in color is restricted to blue-green–yellow solutions, whereas color comparisons in purple and deep-red solutions are not nearly as good. Unfortunately, many fluoride determinations involve colors that are shades of red.

An additional disadvantage is that the eye has poor “memory sense.” Color comparisons must be made simultaneously in order to judge the.

A contribution submitted to the JOURNAL on Nov. 17, 1970, by Ervin Bellack, chemist, Div. of Water Hygiene, Office of Water Programs, Environmental Protection Agency, Washington, D.C.
color match. This requirement necessitates use of a series of color standards each time a determination is made, and since the colors change with time, the series of standards must be freshly prepared. The reagent itself has limited stability, necessitating the preparation of fresh batches at relatively frequent intervals.

**Color comparators.** The principle of visual comparison by matching standards and sample, as used in the Nessler tube technique, has led to the development of allied methods. Modification of the tubes to reduce their size and bulk, the use of permanently colored standards, standardization of the light source, and control of the positioning of the components have all been used to make the comparisons easier and faster.

Preparation of a series of standards for each determination, as used by the Nessler tube technique described previously, is laborious and time-consuming. To eliminate the necessity for preparing fresh standards each time, permanent standards have been developed for fluoride analysis by the visual methods. These standards are in the form of colored glasses or colored liquids sealed in glass tubes.

Devices, or “kits,” utilizing these permanent standards are widely used in the water-utility industry for determinations involving the comparisons of colors. Two of the best-known color-comparator kits have been thoroughly investigated to determine their suitability for routine fluoride determinations. The conclusions reached in these studies are that acceptable results can be obtained with them if the manufacturer’s directions are closely followed and the reagents are correctly and precisely prepared by the user from the concentrates furnished by the manufacturer. The standards furnished by the manufacturer also should be checked against standard fluoride solutions prepared by an analyst, and they should be corrected, if necessary.

**Photometric (SPADNS) Method**

The basis for the SPADNS photometric method for fluoride determinations in water is a reaction similar to the one used for the alizarin visual determination—a dye is formed by the SPADNS dye, and any fluoride present has the effect of decreasing the intensity of color. However, the colors produced by different concentrations of fluoride are all shades of red, making it almost impossible to detect these differences by eye: The use of a photometer is imperative.

Because of the deficiencies of room light, as a source of illumination, and the human eye, as a detector, instruments have been developed that incorporate a constant light source (tungsten lamp) and a photoelectric color-measuring intensity detector.

These instruments, called photometers, have several definite advantages over visual methods. The built-in lamp stabilizes the intensity and color of the light source, and the phototube provides an impersonal evaluation of the light intensity transmitted by the solution. When used with an indicating meter, the phototube provides numerical values for color intensity that can be used for the construction of standard curves. Such curves eliminate the need for preparing fresh color standards for each comparison, as required in the Nessler tube technique.

The sensitivity of photocell detectors is increased by the use of monochromatic light. For this reason photometers are equipped with some means of modifying the light source to project a narrow band of pure color. This objective may be accomplished by placing a filter—a piece of colored glass—in the light beam, or by mechanical means—providing light of almost any wavelength in the visible range. Devices of the latter type are called spectrophotometers. The colors of the spectrum are produced in them by movable prisms or diffraction gratings. Although a selection of color filters will provide the light colors for various determinations with an ordinary photometer, the spectrophotometer provides more versatility, better selectivity, and higher sensitivity to changes in light intensity.

The operating procedure for the use of the photometer or spectrophotometer in the photometric (SPADNS) method for fluoride analysis depends on the particular instrument used. In general, however, the determination consists of adding a measured volume of reagent to a measured volume of sample, placing a portion of the mixture in a photometer cell or cuvette, placing the cell in the instrument, and taking the absorbance reading. The absorbance reading is then converted to fluoride concentration by referencing a curve prepared by plotting the absorbance of known standard solutions against their concentrations. Some spectrophotometers, particularly the small, portable models, have precalibrated meters that give concentration readings directly.

The advantages of the photometric method for fluoride determination include greater sensitivity and accuracy, elimination of some facets of the human element, and much greater speed and convenience. The SPADNS method is virtually instantaneous because of the higher acidity of the reagent. The reaction mixture is extremely stable, so that the determination can be made any time after the reagent is added (as long as the mixture is adequately protected from evaporation). The reagent itself also is extremely stable, so large quantities can be prepared at one time, taking only the precaution of storage in a tightly closed container away from direct sunlight and excessive heat.

Since there is a straight-line relationship between fluoride concentration and absorbance (the spectrophotometer reading) from 0 to 14 ppm F, only two standards are needed

<table>
<thead>
<tr>
<th>TABLE 1</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Concentration of Substances Required to Cause an Error of ±0.1 mg/l at 1.0 mg/l F- mg/l</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Method</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Scott-Sanchis</td>
<td>SPADNS</td>
<td>Electrode</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>400 (—)</td>
<td>5,000 (—)</td>
<td>7,000 (—)</td>
</tr>
<tr>
<td>Aluminum</td>
<td>0.25 (—)</td>
<td>0.1 (—)*</td>
<td>2.0 (—)</td>
</tr>
<tr>
<td>Chloride</td>
<td>2,000 (—)</td>
<td>1,000 (+)</td>
<td>20,000 (—)</td>
</tr>
<tr>
<td>Iron</td>
<td>2 (+)</td>
<td>10 (+)</td>
<td>300 (—)</td>
</tr>
<tr>
<td>Uranium</td>
<td>1.0 (+)</td>
<td>1.0 (+)</td>
<td>&gt;50,000</td>
</tr>
<tr>
<td>Phosphate</td>
<td>3 (+)</td>
<td>16 (+)</td>
<td>&gt;50,000</td>
</tr>
<tr>
<td>Sulfate</td>
<td>300 (+)</td>
<td>200 (+)</td>
<td>&gt;5,000</td>
</tr>
<tr>
<td>Chloride</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Color and turbidity</td>
<td>Must be completely removed with arsenite</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Must be removed or compensated for</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*For immediate reading. If allowed to stand 2 hr tolerance is 3.0 mg/l. The 4-hr tolerance is 30 mg/l.|

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to provide a curve that can be used for any sample with a concentration between these limits. Such a curve will remain valid throughout the life of the batch of reagent used for the preparation of the two standards employed to develop the curve. The only real "disadvantage" of the photometric method is the high cost of equipment. Even this factor is often offset by the multiple uses to which a photometer may be put, however.

**Electrode Method**

One of the principal faults of most analytical methods is their lack of specificity—the fact that other substances present in the sample can affect the desired determination. Although the methods previously described were designed to be as specific for fluoride as possible, other constituents of water—such as, iron, sulfate, and phosphate—can interfere if their concentrations are sufficiently high (Table 1). These interfering substances can be eliminated by a distillation procedure, but the introduction of such a step means work, more time, and more chance for error. What every analyst has always wanted was a method that was specific for the ion to be determined and that was so simple as to be virtually foolproof. This wish most nearly has been attained with the development of the specific-ion electrodes.

The fluoride ion-activity electrode resembles the electrodes used for pH determinations, but its construction is somewhat different. The key element is a doped single crystal through which only fluoride ions can move. When the electrode is immersed in a solution containing fluoride ions, an electric potential is set up between the external solution and an internal one. This potential, expressed in millivolts, can be either positive or negative depending on whether the fluoride concentration of the sample is lower or higher than that of the internal solution. Since only fluoride ions can move through the crystal, the electrode essentially is specific for fluoride. However, conditions that affect the activity of fluoride ions will affect the response of the electrode, so some provision must be made to ensure the uniform activity of the fluoride ions in the sample. This action is accomplished by adding to each sample an equal volume of total ionic strength activity buffer (TISAB).

In addition to the fluoride electrode itself, the equipment needed for fluoride determinations includes a reference electrode and a meter for reading millivolt potential. The meter can be either a conventional pH meter with an expanded scale that can be read to 0.1 mv, a digital pH meter, or an instrument specifically designed for use with specific-ion electrodes. Accessory equipment consists of a magnetic stirrer and a stirring bar for agitating the sample while the potential is being measured.

As with the photometric method, fluoride electrode method requires that a standard curve be prepared using solutions of known fluoride concentration. Such a curve, with concentration plotted against millivolts on semilog graph paper, can be used for any fluoride concentration normally found in drinking water. As with the portable photometers, portable specific-ion meters are available that give readings directly in fluoride concentrations. If there is, indeed, any "disadvantage" of the electrode method, it is in the cost of equipment, particularly if a digital or expanded-scale pH meter is not available and a meter must be purchased specifically for the fluoride analysis. However, with the advent of specific-ion electrodes for many other common ions, the burden of cost can be ameliorated by using the same meter for multiple analyses.

**Choosing a Method for Fluoride Analysis**

A number of factors will govern the ultimate choice of analytical method: facilities available, skill required, accuracy desired, cost, personal preference, and legal requirements. Another determining factor may be the type of equipment already on hand, for most of the equipment used for fluoride analysis can be used for other analyses, and often the converse is true.

In their order of increasing amount of laboratory facilities required, the methods for fluoride analysis are listed as follows*:

1. Colorimetric with permanent standards comparator
2. Colorimetric with portable photometer or electrode with portable meter
3. Electrode with laboratory meter
4. Colorimetric with laboratory photometer or spectrophotometer
5. Visual colorimetric (Nessler tubes)

In their order of increasing degree of accuracy attainable, the methods are as follows:

1. Colorimetric with permanent standards comparator
2. Colorimetric with portable photometer
3. Visual colorimetric (Nessler tubes)
4. Electrode with portable meter
5. Colorimetric with laboratory photometer or spectrophotometer
6. Electrode with laboratory meter

The above lists are generalizations, of course. Undoubtedly, there will be exceptions to the opinions expressed. The assessment of skill required is based on that skill necessary to achieve a certain degree of proficiency, which will vary with the individual. For example, an individual who has never used laboratory instruments may have difficulty mastering a method that requires the use of laboratory instruments, but may easily master the visual colorimetric method.

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* The comparative ratings of the fluoride analytical methods are merely the opinion of the author, and each analyst is left to draw his own conclusions.
On the other hand, an individual whose color perception is poor would never be able to use a permanent standards comparator but might have little difficulty using a laboratory instrument.

Equipment costs are based on minimum figures and on the assumption that no equipment exists beforehand. Again, there can be exceptions—a spectrophotometer might cost several times as much as a digital electrode meter.

Substances present in the water supply, or added during treatment, in some cases, may require preliminary distillation before analysis can be performed (Table 1). This requirement could change the whole picture when choosing a method for fluoride analysis, because distillation requires more laboratory facilities and more skill than any of the analytical methods. Since the electrode method will seldom, if ever, require that the water sample be distilled, the need to distill will have the effect of reducing the relative cost of equipment for the electrode analysis with respect to that of the photometric and visual colorimetric methods. The distillation-step requirement for laboratory facilities and concomitant skill also pretty much would eliminate from consideration the permanent standards comparator and the portable photometer, since they are essentially field kits to be used where facilities and skills are lacking.

Continuous monitoring. Some brief mention also should be made with regard to continuous monitoring of fluoride concentration. A number of instruments are available, some operating on the photometric principle, some on the specific-ion-electrode principle, and still others on principles applicable to continuous flow, specifically. Although the merits of every instrument have not been evaluated, it is safe to say that, even with the best of them, the water-plant employee charged with control of fluoride level will still have to perform conventional analyses at regular intervals, if for no other purpose than to verify the results obtained by the continuous analyzer.

Equipment and Costs

Tables 2-6 list the equipment and chemicals necessary for each of the standard methods for fluoride analysis, as well as for the preliminary distillation step. Again, the presumption is made that no instruments (except for an analytical balance), glassware, or chemicals are on hand or available. The costs, particularly those of those instruments, are based on those listed by various laboratory supply houses in their most recent catalogs (as of Jul., 1970). Although only instruments costing less than $1,000 are listed, one could spend much more if so desired.

No attempt at completeness has been made—the instruments listed are representative and readily available. Listing of an instrument is not intended to imply an endorsement, and omission does not necessarily imply that any particular instrument is considered unsatisfactory for the intended analysis. The quantities of chemicals priced are the minimum practical amounts normally available.

The final table lists commercially prepared reagents and standards that can be used where convenience is more important than economy, or where laboratory facilities are not available.

Summary and Conclusions

From the foregoing discussion and lists, the prospective fluoride analyst should at least be able to make a preliminary judgment of the merits of each of the available analytical methods, insofar as they apply to his own particular situation. Although the highest degree of accuracy attainable should always be the goal when fluorides are fed, sometimes a small sac-

**TABLE 2**

<table>
<thead>
<tr>
<th>Material Needed</th>
<th>Cost $</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neisser Tube Technique</td>
<td></td>
</tr>
<tr>
<td>1. Neisser tubes—100 ml—tall form, set (2)</td>
<td>16.85</td>
</tr>
<tr>
<td>2. Tube support, for tall-form Neisser tubes</td>
<td></td>
</tr>
<tr>
<td>3. Pipet, volumetric—5 ml</td>
<td></td>
</tr>
<tr>
<td>4. Pipet, measuring—10 ml</td>
<td></td>
</tr>
<tr>
<td>5. Cylinder, graduated—100 ml</td>
<td></td>
</tr>
<tr>
<td>6. Flask, volumetric, 1,000 ml</td>
<td></td>
</tr>
<tr>
<td>7. Thermometer</td>
<td></td>
</tr>
<tr>
<td>8. Miscellaneous glassware for preparing dilutions</td>
<td></td>
</tr>
<tr>
<td>9. (Analytical balance)</td>
<td></td>
</tr>
</tbody>
</table>

**Chemicals**

<table>
<thead>
<tr>
<th>Neisser Tube Technique</th>
<th>Cost $</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Sodium fluoride—100 g</td>
<td></td>
</tr>
<tr>
<td>2. Sodium chloride—100 g</td>
<td></td>
</tr>
<tr>
<td>3. Zirconyl fluoride—100 g</td>
<td></td>
</tr>
<tr>
<td>4. Sulfuric acid, conc.—2.5 L</td>
<td></td>
</tr>
<tr>
<td>5. Hydrochloric acid, conc.—2.5 L</td>
<td></td>
</tr>
<tr>
<td>6. Sodium arsenite—0.5 mg</td>
<td></td>
</tr>
<tr>
<td>7. Distilled water</td>
<td></td>
</tr>
</tbody>
</table>
rifice in accuracy is unavoidable for the sake of economy, convenience, or simply personal aptitude.

References


TABLE 3

<table>
<thead>
<tr>
<th>Needs for Photometric (SPADNS) Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material Needed</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td><strong>Apparatus</strong></td>
</tr>
<tr>
<td>1. Photometer (one of the following)</td>
</tr>
<tr>
<td>▪ Coleman Model 8</td>
</tr>
<tr>
<td>▪ Delta, ac model (portable)</td>
</tr>
<tr>
<td>▪ Delta, ac model (portable)</td>
</tr>
<tr>
<td>▪ Fisher Photometer II (Fig. 4)</td>
</tr>
<tr>
<td>▪ Haas DR, ac model (portable) (Fig. 6)</td>
</tr>
<tr>
<td>▪ Elett-Summermon Model 900-3 (Fig. 3)</td>
</tr>
<tr>
<td>▪ Lumenator-Photovolt. Model 401</td>
</tr>
<tr>
<td>2. Spectrophotometer (one of the following)</td>
</tr>
<tr>
<td>▪ B &amp; L Spectronic 20, regulated model (Fig. 4)</td>
</tr>
<tr>
<td>▪ Coleman Jr., Model 6A</td>
</tr>
<tr>
<td>▪ Coleman Universal, Model 14</td>
</tr>
<tr>
<td>▪ Coleman Jr., Model 11</td>
</tr>
<tr>
<td>▪ Coleman Jr., Model 11A</td>
</tr>
<tr>
<td>▪ Coleman Model 44</td>
</tr>
<tr>
<td>▪ B &amp; L Spectronic 70</td>
</tr>
<tr>
<td>3. Pipet, coulometric—50 ml (for nonportable instrument)</td>
</tr>
<tr>
<td>4. Pipet, volumetric—10 ml (for nonportable instrument)</td>
</tr>
<tr>
<td>5. Flask, Erlenmeyer—125 ml—12 at $0.51 each</td>
</tr>
<tr>
<td>6. Flask, volumetric—1,000 ml—1 at $7.29 each</td>
</tr>
<tr>
<td>7. Pipet, volumetric—5 ml (for portable instrument)</td>
</tr>
<tr>
<td>8. Cylinder, graduated—25 ml (for portable instrument)</td>
</tr>
<tr>
<td>9. Thermometer</td>
</tr>
<tr>
<td>10. Miscellaneous glassware for preparing dilutions</td>
</tr>
<tr>
<td>11. Analytical balance</td>
</tr>
</tbody>
</table>

Chemicals

1. Sodium fluoride—100 g | 1.60 |
2. SPADNS (4,5-dihydroxy-3-(p-milophenylazo)-2,7-naphthalanedicarboxylic acid, trisodium salt) | 35 g | 6.80 |
3. Zirconyl chloride—100 g | 4.55 |
4. Hydrochloric acid, conc.—2.5 | 3.85 |
5. Sodium arsenite, 0.5 kg | 2.00 |
6. Distilled water |      |

TABLE 4

<table>
<thead>
<tr>
<th>Needs for Electrode Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material Needed</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td><strong>Apparatus</strong></td>
</tr>
<tr>
<td>1. pH meter (one of the following)</td>
</tr>
<tr>
<td>▪ Beckman Century Model 76006</td>
</tr>
<tr>
<td>▪ Beckman Digital Model 76006</td>
</tr>
<tr>
<td>▪ Beckman Expandomatic Model 76007</td>
</tr>
<tr>
<td>▪ Coleman Model 37A</td>
</tr>
<tr>
<td>▪ Coleman Model 38</td>
</tr>
<tr>
<td>▪ Corning Model 10</td>
</tr>
<tr>
<td>▪ Corning Model 12</td>
</tr>
<tr>
<td>▪ Corning Model 111 (digital)</td>
</tr>
<tr>
<td>▪ Fisher Accumet, Model 320</td>
</tr>
<tr>
<td>▪ Leeds &amp; Northrup, Model 7405-A2</td>
</tr>
<tr>
<td>▪ Leeds &amp; Northrup, 7405-A3</td>
</tr>
<tr>
<td>▪ Orion Model 701 (digital)</td>
</tr>
<tr>
<td>▪ Orion Model 801 (digital)</td>
</tr>
<tr>
<td>▪ Orion Model 401 (portable)</td>
</tr>
<tr>
<td>▪ Photovolt. Digi 120 (digital)</td>
</tr>
<tr>
<td>▪ Photovolt Expander IV IL 112</td>
</tr>
<tr>
<td>2. Fluoride electrode (one of the following)</td>
</tr>
<tr>
<td>▪ Beckman 39600</td>
</tr>
<tr>
<td>▪ Coleman 3-803</td>
</tr>
<tr>
<td>▪ Corning 45100</td>
</tr>
<tr>
<td>▪ Orion 94-09</td>
</tr>
<tr>
<td>▪ Orion 94-09</td>
</tr>
<tr>
<td>3. Reference electrode (one of the following)</td>
</tr>
<tr>
<td>▪ Beckman 10663</td>
</tr>
<tr>
<td>▪ Coleman 3-723</td>
</tr>
<tr>
<td>▪ Coleman 3-741</td>
</tr>
<tr>
<td>▪ Corning 476812</td>
</tr>
<tr>
<td>▪ Corning 476829</td>
</tr>
<tr>
<td>▪ Fisher 13-60-02</td>
</tr>
<tr>
<td>▪ Orion 90-01</td>
</tr>
<tr>
<td>4. Magnetic stirrer</td>
</tr>
<tr>
<td>5. Stirring bar</td>
</tr>
<tr>
<td>6. Beakers—100 ml—12 each at $0.46 each</td>
</tr>
<tr>
<td>7. Flasks, volumetric—1,000 ml—2 each at $7.29 each</td>
</tr>
<tr>
<td>8. Pipets, volumetric—25 ml—2 each at $1.98 each</td>
</tr>
<tr>
<td>9. Cylinder, graduated—100 ml</td>
</tr>
<tr>
<td>10. Thermometer</td>
</tr>
<tr>
<td>11. Miscellaneous glassware for preparing dilutions</td>
</tr>
<tr>
<td>12. Analytical balance</td>
</tr>
</tbody>
</table>

Chemicals

1. Sodium fluoride, 1.00 ppm | 1.60 |
2. Sodium chloride, 0.5 kg | 3.80 |
3. Acetic acid—0.5 | 6.10 |
4. Sodium nitrate—0.5 kg | 1.85 |
5. Sodium hydroxide—0.5 kg | 1.65 |
6. Distilled water |      |

TABLE 5

<table>
<thead>
<tr>
<th>Needs for Distillation Step</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material Needed</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td><strong>Apparatus</strong></td>
</tr>
<tr>
<td>1. Fluoride disc, manually operated, as illustrated in Standard Methods, including support, burner, receiving flask, and double-jacketed condenser</td>
</tr>
<tr>
<td>2. Fluoride disc, manually operated, type used for ammonia and phenol, including support, burner, and receiving flask</td>
</tr>
<tr>
<td>3. Fluoride disc, manually operated, laboratory-assembled using minimum-cost materials, including support, burner, and receiving flask</td>
</tr>
<tr>
<td>4. Fluoride disc, automatic, complete with magnetic stirrer, quartz heating mantle, double-jacketed condenser, and receiving flask</td>
</tr>
</tbody>
</table>

Chemicals

1. Sulfuric acid, conc.—2.5 | 4.40 |
2. Silver sulfide—30 g | 5.15 |

TABLE 6

<p>| Prepared Standards and Reagents |
|--------------------------------|------|</p>
<table>
<thead>
<tr>
<th><strong>Reagent</strong></th>
<th><strong>Cost</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Standard fluoride solution, 1.00 ppm</td>
<td>3.00</td>
</tr>
<tr>
<td>2. SPADNS fluoride reagent (replaces SPADNS, stronoyal chloride, arsenite, hydrochloric acid, and 1 volumetric flask in photometric method)</td>
<td>2.50</td>
</tr>
<tr>
<td>3. TISAB (replaces sodium chloride, acetic acid, sodium hydroxide, sodium citrate, and 1 volumetric flask in electrode method)</td>
<td>4.1</td>
</tr>
<tr>
<td>4. Fluoride activity standard, 100 ppm</td>
<td>9.00</td>
</tr>
<tr>
<td>5. Fluoride reagent set (for Delta Portable Photometer) (replaces sodium fluoride, SPADNS, arsenite, stronoyal chloride, hydrochloric acid, and volumetric flasks)</td>
<td>13.50</td>
</tr>
</tbody>
</table>