The use of a colorimeter in analyzing the fluoride content of public well water

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Abstract

Water samples from 110 public wells in Ohio were analyzed for fluoride content using both an ion-specific electrode and a colorimeter. In addition to the fluoride testing, analyses were performed on selected known interfering substances in the water. Sixty per cent of the samples differed by > 0.1 ppm fluoride with a mean difference of + 0.14 ppm. Prescriptions for dietary fluoride supplementation based on the colorimetric results would have been incorrect 44.6% of the time. Sulfate levels had a significant (P < 0.05) effect on the accuracy of the colorimetric results. Without prior distillation, the colorimetric method is unsatisfactory for determining fluoride concentration of well water.


Fluorides are the most effective agents in the prevention of dental caries (Wei 1976; Ericsson 1978). Fluoridation of water supplies is the most efficient and cost-effective method of supplying fluoride to communities (Backer Dirks et al. 1978; Driscoll 1985).

Individuals who live in nonfluoridated communities and those using private wells with inadequate fluoride levels rely on appropriate use of dietary fluoride supplementation for protection against dental caries. When taken from infancy, systemic fluoride supplements approach water fluoridation in effectiveness in preventing dental caries (Aasenden and Peebles 1974).

The Committee on Nutrition of the American Academy of Pediatrics (AAP) in 1986 made recommendations for the dietary supplementation of fluoride. This dosage schedule is nearly identical to the schedule recommended by the Committee on Dental Therapeutics of the ADA (1982) and the Committee on Nutrition of the AAP in 1979. This schedule resulted from several re-evaluations of previous fluoride supplementation schedules and included dietary and other sources of fluoride ingestion. These recommendations are based on the child’s age and the concentration of fluoride in his/her drinking water.

Various methods of fluoride analysis of water samples have been used. The colorimetric and fluoride ion-specific electrode methods are currently the most common methods employed (American Public Health Assn. [APHA], American Water Works Assn. [AWWA], and Water Pollution Control Federation [WPCF] 1985). A colorimetric method, the SPADNS (sodium 2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate) method, is based on the reaction between fluoride and a dark red zirconium dye lake, forming a colorless complex anion (APHA, AWWA, WPCF 1985). This method results in a bleaching of the red color in an amount proportional to the fluoride concentration. As the amount of fluoride increases, the resulting color becomes lighter. Color then is determined photometrically using a filter photometer or spectrophotometer (Bellack 1972).

Colorimetric methods are susceptible to interfering substances. High concentrations of alkalinity (CaCO₃), aluminum (Al³⁺), chloride (Cl⁻), turbidity, color, iron (Fe²⁺), hexamethaphosphate [(NaPO₄)₆], phosphate (PO₄³⁻), and sulfate (SO₄²⁻) in the sample will result in error in the determination of fluoride content (Hach 1983; APHA, AWWA, WPCF 1985).

The fluoride ion-specific electrode is designed to sense fluoride ions selectively. A standard reference electrode is attached to a pH meter which reads the potential established by the fluoride ions across a crystal between a standard solution and the sample solution (Bellack 1972). The fluoride ion-specific electrode method may be affected by the same substances to which the colorimetric methods are susceptible. With the exception of alkalinity, the concentrations of the interfering substances must be substantially higher to result in error in the electrode reading. Also, color and turbidity do not interfere with the results of the fluoride ion-specific electrode method (Bellack 1972; APHA, AWWA, WPCF 1985). This method also allows a wider range of fluoride concentrations (0.1-10.0 ppm) to be examined. The fluo-
ride ion-specific electrode has been found to be accurate to within 0.5% (Durst 1971).

Appropriate fluoride supplementation requires accurate determination of the fluoride content of drinking water. Because of lower cost and convenience the colorimeter is being advocated for use by health professionals to perform this function (Love 1984; Crall 1985), although there is evidence that this method may not be accurate. The purpose of this study was to assess the degree of accuracy of the colorimetric method in determining fluoride concentrations of water samples for the purpose of prescribing fluoride supplementation.

Methods and Materials

Samples of drinking water obtained from public wells in Ohio were analyzed for fluoride content using a colorimeter and fluoride ion-specific electrode. A list of 182 new public wells with initial water analyses completed between January 1, 1984, and November 30, 1985, was compiled from records at the Ohio Environmental Protection Agency, Division of Public Water Supply. The well site location, date of analysis, and test results of alkalinity, sulfate, chloride, fluoride, and iron levels were recorded for each well site included in the study. Of the original wells, samples were obtained from 110 sites. Most of the remainder were inactive (i.e., wells were closed off) by the initiation of this study.

Collection of water samples was performed by dental hygienists employed by the Ohio Department of Health, Division of Dental Health. In addition to verbal instructions from the primary investigator, the hygienists were given specific written instructions for water sample collection.

Two 120-ml, clear, flint glass bottles were used to collect water from each site. One sample from each well site was submitted to the Ohio Department of Health laboratory where analysis of fluoride content was performed on all samples by the same certified laboratory technician using a fluoride ion-specific electrode. The results from the ion-specific electrode served as the standard for fluoride content. The results of the logistic regression analyses of the individual potential interfering factors are presented in Table 2 (next page). Sulfate was the only factor found to be significant (P < 0.05) by logistic regression analysis. The linear regression analysis was performed to quantify the influence of the individual interferences on the error of the colorimeter.

Results

The fluoride concentrations from both the colorimetric and ion-specific electrode were compared. The sample range for the colorimeter was 0.00-3.00 ppm and for the ion-specific electrode was 0.07-2.29 ppm. Sixty-six of the samples differed by > 0.1 ppm. Forty-four of the same 110 samples (40%) differed by 0.2 ppm or more. The mean difference was + 0.142 ppm with a 95% confidence interval (0.091, 0.193). Of the 110 samples, 52 of the colorimetric discrepancies were > 0.1 ppm high and 14 samples had colorimetric readings that were inaccurately low by more than 0.1 ppm.

A summary of the reported interference levels is presented in Table 1 (next page). Of the 110 samples, 25 had no known potential interfering factors; 53 had 1 factor; 27 had 2; 4 had 3; and 1 had 5 factors. The results of the logistic regression analyses of the individual potential interfering factors are presented in Table 2 (next page). Sulfate was the only factor found to be significant (P < 0.05) in influencing the colorimetric error. The colorimeter consistently overestimated the fluoride concentration of the samples when there were more than small levels of sulfate present. This trend became more pronounced when the concentration exceeded 200 mg/L. Twenty-seven samples were in excess of this figure.

Discussion

This study was designed to simulate use of a colorimeter for fluoride determination, fluoridation control proficiency testing. Each sample was examined by both investigators independently and results were recorded. Total agreement was achieved in the trial examination. Initial interexaminer reliability for the entire group was very good (rho > 0.9). For the few samples where there was disagreement for a given property, the sample was re-examined by the investigators together until agreement was reached.

Each of this second group of samples then was analyzed for fluoride using a colorimeter. The results of the logistic regression analyses of the individual potential interfering factors are presented in Table 2 (next page). Sulfate was the only factor found to be significant (P < 0.05) in influencing the colorimetric error. The colorimeter consistently overestimated the fluoride concentration of the samples when there were more than small levels of sulfate present. This trend became more pronounced when the concentration exceeded 200 mg/L. Twenty-seven samples were in excess of this figure.

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Each of this second group of samples then was analyzed for fluoride using a colorimeter. The procedure described in the colorimeter manual was followed, except that there was no distillation of the samples performed. One reading was performed on each sample. Readings were recorded to 2 decimal places. The first decimal place was read directly from the meter scale on the colorimeter and the second decimal place was rounded to the nearest 0.05 mg/L.

A logistic regression analysis was performed for each potential interfering factor (i.e., alkalinity, chloride, iron, sulfate, color, turbidity, sediment) to determine if the interference resulted in errors > 0.1 ppm. A linear regression analysis was performed for any interfering factors determined significant (P < 0.05) by logistic regression. The linear regression analysis was performed to quantify the influence of the individual interferences on the error of the colorimeter.
TABLE 1. Summary of Selected Reported Interference Levels for Colorimetric Testing of Fluoride

<table>
<thead>
<tr>
<th>Variable</th>
<th>Minimum Concentration for Potential Colorimetric Error*</th>
<th>Mean</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkalinity (mg/L)</td>
<td>5000</td>
<td>240.34</td>
<td>10</td>
<td>474</td>
<td>464</td>
</tr>
<tr>
<td>Sulfate (mg/L)</td>
<td>200</td>
<td>219.72</td>
<td>5</td>
<td>1810</td>
<td>1805</td>
</tr>
<tr>
<td>Chloride (mg/L)</td>
<td>7000</td>
<td>50.80</td>
<td>2</td>
<td>1160</td>
<td>1158</td>
</tr>
<tr>
<td>Iron (µg/L)</td>
<td>10,000</td>
<td>1557.68</td>
<td>5</td>
<td>24,200</td>
<td>24,195</td>
</tr>
<tr>
<td>Sediment (+/-)†</td>
<td>0.71</td>
<td>0.12</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Color (+/-)</td>
<td>0.05</td>
<td>0.05</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

* APHA, AWWA, WPCF, p. 354.
† For sediment, color, and turbidity: + = 1, - = 0.

TABLE 2. Results of Individual Regression Analyses of Potential Interferences

<table>
<thead>
<tr>
<th>Variable</th>
<th>Chi-square</th>
<th>P Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkalinity</td>
<td>0.10</td>
<td>0.7500</td>
</tr>
<tr>
<td>Sulfate</td>
<td>5.34</td>
<td>0.0208*</td>
</tr>
<tr>
<td>Chloride</td>
<td>0.95</td>
<td>0.3295</td>
</tr>
<tr>
<td>Iron</td>
<td>0.01</td>
<td>0.9054</td>
</tr>
<tr>
<td>Sediment</td>
<td>3.18</td>
<td>0.0749</td>
</tr>
<tr>
<td>Color</td>
<td>1.15</td>
<td>0.2894</td>
</tr>
<tr>
<td>Turbidity</td>
<td>1.17</td>
<td>0.3908</td>
</tr>
</tbody>
</table>

* P < 0.05.

imeter in clinical practice. Although the manufacturer recommends distillation of water samples containing interfering substances, most health practitioners using this instrument do not distill water samples prior to analysis. Likewise, visual determination for turbidity, sediment, and color was used rather than actual laboratory testing. No attempt was made to determine the accuracy of the colorimeter under ideal laboratory conditions in which all interferences are known and removed by distillation.

Glass bottles are used routinely for collection of water samples for fluoride analysis by the Ohio Environmental Protection Agency. A review of the literature revealed references to possible etching of glass surfaces by fluoride (Jacobson and Weinstein 1977) and recommendations to use plastic bottles for collection of water samples (Crosby et al. 1968; Hach 1983). No controlled studies of this effect at fluoride concentrations found in the samples in this study were found.

Glass bottles have been accepted as satisfactory if they have not previously contained high concentration fluoride solutions or if they are rinsed prior to collection of the water sample (APHA, AWWA, WPCF 1985). The bottles in this study that contained the samples to be analyzed using the colorimeter were new bottles. The dental hygienists were instructed to rinse all bottles in this study prior to collection of the samples. The use of glass bottles in this study should not have influenced the results of the fluoride analyses.

Some of the potential interference factors tested have been shown to produce inaccurately low readings while others produce inaccurately high readings. These factors may cancel each other out or have a synergistic effect on the colorimetric error. A difference of 0.1 ppm can change the amount of dietary fluoride prescribed to an infant or child. For this reason, a difference of > 0.1 ppm fluoride was defined as a clinically significant error.

A comparison was made of potential fluoride supplement prescriptions based on both methods of fluoride analysis for all samples which the colorimetric results indicated a need for dietary supplementation (i.e., < 0.7 ppm). Of the 65 samples with < 0.7 ppm fluoride, a supplement (based on 1 prescription for 1 patient at each well site) would have been prescribed inappropriately in 29 (44.6%) of the cases. In 27 of these cases the fluoride supplement would have been inadequate and in 2 cases the fluoride supplement would have been excessive.

This study supports the results reported by Ringelberg and Allen (1986). In their study of surface and ground water samples, colorimetric readings averaged + 0.38 ppm greater than levels determined using the fluoride ion-specific electrode.

A colorimeter has been advocated for use by health practitioners to determine the fluoride concentrations of water samples prior to prescribing dietary fluoride supplementation (Love 1984; Crall 1985). While the colorimeter may be accurate when all interferences are known (e.g., a public water supply) and may be compensated for if present, it should not be used when these variables are unknown. Practitioners are advised to contact their state health departments or dental schools to receive the proper protocol for sample submission and testing.

The authors thank the dental hygienists of the Ohio Department of Health, Division of Dental Health, who collected the water samples for this study.

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American Dental Assn, Council on Dental Therapeutics: Accepted Dental Therapeutics, 39th ed. Chicago; ADA, 1982 pp 347-51.


Driscoll WS: What we know and don’t know about dietary supple-


What do dental patients fear most?

Patients say the "sound and feel of the drill" is their most feared aspect of dental treatment while dentists feel the injection of anesthesia is the dental treatment most feared by patients.

These disparate findings are the results of two separate surveys, one of consumers and one of dentists. These surveys point out differences of perception by dentists and patients. Besides dental anxiety, respondents were questioned about other aspects of dental treatment. For instance, the average time taken to prepare and restore a cavity seemed longer to dentists (more than 15 min) than to patients (less than 15 min).

Pain perception differed among the groups, too. When asked what percentage of their patients never complain about pain, nearly one-third of the dentists said 60%. Of patients surveyed, 26% said they rarely feel pain and 23% said they almost always do. Both groups agreed that hand movements by the patients are the favored way to signal discomfort during a procedure.

When questioned about anesthesia, 48% of dentists said they leave the question of whether or not to use anesthesia to the patient, and 39% said they use it automatically. Forty-nine per cent of patients said they always get anesthesia, while 19% said they never do.

More than half of the dentists felt the reason patients don’t visit them often is “fear of pain.” One-third of the patients said they go to the dentist every 6 months, another third said they go annually, and 8% said they would go only for an emergency.