Comparison of colorimeter and electrode analysis of water fluoride

Burton L. Edelstein, DDS, MPH David Cottrel, DDS David O'Sullivan, BS Norman Tinanoff, DDS, MS

Introduction

Fluoride supplement prescriptions must be based on the fluoride content of a child's drinking water.¹ Failure to analyze a child's water source for fluoride increases the possibility for either inducing fluorosis or providing inadequate cariostatic protection. Two methods of determining water fluoride content, the ion specific electrode (electrode or ISE) and the SPADNS reagent (colorimetric) methods, generally are used. The electrode method is known to be more accurate because it is less influenced by impurities in the sample², while the colorimetric method is popular among dentists because of its low cost and ease of implementation in the office. Presently, there is conflicting information regarding the usefulness of the colorimetric method. A study comparing the two methods for water fluoride analysis reported that prescriptions for dietary fluoride supplementation based on the colorimetric analysis would have been incorrect 45% of the time.³ Another report suggests that the colorimetric method "may be a valid, reliable, and affordable tool for fluoride analysis in the dental office."⁴ The purpose of the present study was to re-examine the difference between the electrode and colorimetric techniques to assess the clinical usefulness of colorimetric analysis in a dental practice setting.

Materials and Methods

Water samples were obtained from 222 consecutive new patients with private wells presenting to a private pediatric dental practice. All patients reside in New London County, Connecticut, an area of variable ambient fluoride. Each sample was tested for fluoride content one time each by the electrode and colorimetric methods. The samples analyzed by the electrode method were processed by a technician in a Connecticut-approved public health laboratory that is proficiency tested yearly, while samples analyzed by colorimetry were processed by assistants in the dental practice. The electrode method entailed diluting each sample 1:1 with 1,2- cyclohexylene dinitrilotetracetic acid (TISAB with CDTA; Orion Research, Cambridge, MA) to adjust pH and ionic strength. The fluoride concentrations of the samples then were determined using a fluoride electrode (Orion 94-09-00[®], Orion Research, Cambridge, MA) connected to a digital readout electrometer (Orion 601A[®], Orion Research, Cambridge, MA). The colori-

Short Communications

metric method entailed diluting each sample with SPADNS reagent and comparing transmitted light of the sample against transmitted light of a 1.0 ppm water fluoride standard using the Hach colorimeter that reads out fluoride level on an analog scale. The paired findings were examined for differences that would yield contradictory fluoride supplement prescriptions based on currently accepted supplementation schedules.

The range of fluoride content in the sample set based on the electrode method was < 0.01 to 2.6 ppm fluoride. Of the 222 samples, 21% exceeded 0.7 ppm, 12% showed fluoride content between 0.3 and 0.7 ppm, and 66% contained less than 0.3 ppm. The correlation coefficient for linear association between the two methods was very strong (r = .935). A scatter plot of paired findings for each sample was overlaid on a graph showing accepted threshold values for prescribing fluoride supplements of various doses (Fig 1). In 5% (N = 11) of the paired samples, differences between the two methods



Fig 1. Scatter plot of paired water sample fluoride content determinations by electrode and colorimetric methods. Shaded areas show pairs for which supplemental fluoride prescriptions based on both methods would be the same.

would yield contradictory fluoride supplement prescriptions. The plot shows that the colorimetric method tends to overstate fluoride content at low fluoride levels compared with the electrode method.

Decision analysis⁵ was used to calculate the relative accuracy of fluoride prescriptions that would result from each method as well as the relative risk of theoretical fluorosis from inaccurate prescriptions based on each method. Decision trees were constructed comparing electrode assay, colorimetric assay, and prescribing fluoride supplementation with no assay.

Results

Fig 2 shows a decision tree comparing accuracy of fluoride supplement prescription. The first branch,

"no assay," leads to full-strength prescriptions regardless of true sample fluoride content, since all water samples are assumed to be fluoride deficient. The true prevalence of fluoride at various levels, shown to the right of the probability nodes, will determine the chance of the prescription being accurate. In this sample, as measured by ISE, 66% of wells contained less than 0.3 ppm fluoride. Therefore, 66% of the prescriptions based on "no assay" were correct, leaving 34% incorrect. The colorimeter branch shows that the "colorimeter" measured 24% of the samples to contain > 0.7 ppm, 19% between 0.3–0.7 ppm, and 57% to be < 0.3 ppm. The next node shows the probability of the colorimeter being correct at each test level. In all cases in which the colorimeter was correct, the resultant prescriptions were accurate. Thus the weighted average for prescription accuracy using the colorimeter was 89.4% [(.94 x .24) + $(.52 \times .19) + (1.00 \times .57)$]. Since the electrode method is assumed to be 98% accurate⁶, the prescription accuracy for the electrode method is assumed to be 98%. Ratios between the alternative assay methods are used to determine relative accuracy of the three methods. The electrode was 33% more accurate than "no assay" (98 value for electrode vs. 66 for no assay), but only 10% more accurate than the colorimetric assay (98 value for electrode vs. 89.4 for the colorimeter).



Fig 2. Decision tree for comparing accuracy of fluoride supplement prescriptions based on no assay of water for fluoride content, assay by colorimeter, and assay by ion specific electrode (ISE). Decision nodes are represented by squares. Chance nodes are represented by circles. Probabilities on each branch are given by *P* values. The far right columns show 15 possible prescription outcomes and their associated accuracies.

Fig 3 (next page) shows the decision tree comparing the theoretical risk of induced fluorosis from fluoride supplementation. Risk of fluorosis was assigned for various fluoride supplementation levels in excess of the currently accepted dose schedule. Decision analysis shows that the risk of induced fluorosis is 14 times greater with no assay than with the electrode (28.2 vs. 2.0), and that the colorimetric assay results in slightly lower fluorosis risk than that of the electrode (1.8 vs. 2.0).

For any given set of samples, the relative prescription accuracy and induced fluorosis risk depend on the prevalence of the fluoride content in the ambient water supply. The greater the prevalence of ambient fluoride in area wells, the more likely that no assay will result in improper prescriptions.

Conclusions

The present study confirms previous findings that colorimetric assay of fluoride both produces generally higher findings than the electrode method³ and closely correlates to electrode findings.⁴ Fluoride prescription in clinical practice is intended to provide optimal systemic fluoride ingestion, but the actual fluoride intake of children is confounded by dietary fluoride, tooth-paste ingestion, exposure to multiple water sources and

variable compliance with prescribed supplements. When differences in prescriptions resulted from the two methods, the prescribed doses based on colorimetry in this study tended to be low, thereby minimizing the risk of fluorosis. These findings further suggest that the colorimeter should be accepted as a clinically useful alternative to the electrode method, particularly in areas of high ambient fluoride levels.

Dr. Edelstein is clinical instructor, Mr. O'Sullivan is research assistant, and Dr. Tinanoff is professor; all are in the Department of Pediatric Dentistry, University of Connecticut Health Center, Farmington, CT. Dr. Cottrel is former resident, Department of Dentistry, Yale New Haven Hospital. New Haven, CT. Reprint requests should be sent to Dr. Burton L. Edelstein, 190 Hempstead Street, New London, CT 06320.



Fig 3. Decision tree for comparing presumed fluorosis risk of fluoride supplement prescriptions based on no assay of water for fluoride content, assay by colorimeter, and assay by ion specific electrode (ISE). Decision nodes are represented by squares. Chance nodes are represented by circles. Probabilities on each branch are given by p values. The far right columns show 15 possible prescription outcomes and their associated risk for fluorosis.

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