Field Use of the SPADNS Qualitative Technique by Beneficiaries

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SUMMARY: One of the constraints in fluorosis mitigation work is the testing of fluoride in the water that needs to be carried out by trained professionals using costly and complicated chemicals and instruments. This study elaborates on the usability of the SPADNS qualitative method for screening of water samples and the possibility of it being conducted by health volunteers in field. A simple procedure is developed based on addition of two drops of a ready made zirconyl-SPADNS reagent to 2 mL of the water sample and comparing the resulting colour with a 1.0 mg/L standard fluoride solution. The test would indicate whether the sample contains more or less than 1 mg/L. Twenty volunteers were instructed in using the test for half an hour. Then they exercised the test on 20 water samples containing 0.2 – 8.0 mgF/L.

The volunteers could smoothly use the test and, on an average, they delivered correct indications in 80 % of the cases. Of the 20 % erroneous the underestimation, i.e. statement that the fluoride concentration was < 1 while it was > 1, was 6.2 times the overestimation, the probabilities being 0.17 and 0.03 respectively.

There was a major variation between the volunteers, 10 % of them made error in 45 % of their testing, i.e. close to arbitrary. It is concluded that volunteers should, apart from training, be sorted and selected.

The probability of error, whether under or over estimating, as a function of the concentration of fluoride in the water is subject to larger variation, from 0.05 and up to 0.8. Within 1.0 ± 0.5 mg/L, the probability of error is estimated to be 0.08 and 0.38, respectively. Only at concentrations above 3 mg/L and lower than 0.5 mg/L, the probability of error seems to be of an acceptable level < 0.08.

It is concluded that the test is useful only in cases where concentrations of fluoride higher then 3 mg/L are needed to be identified, whereas the other samples can be taken in to a further laboratory testing for a more reliable measurement of the fluoride concentration.

Key words: Fluoride, intensity, test kit, sensitivity, specificity, accuracy

INTRODUCTION

Like many other countries Thailand has endemic fluorosis [1], and the Intercountry Center for Oral Health, being situated close to the fluorotic area, has been committed to deal with fluorosis problem for decades. One of the constraints in the mitigation

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work is the testing of the water for fluoride content that needs to be carried out so far only by trained professionals using costly and complicated chemicals and instruments as in the Ion Selectrode method [2].

The idea of this study is to investigate whether the standard SPDNS qualitative method could be developed for use by the beneficiaries themselves in the routine screening of water sources with respect to the fluoride concentration.

MATERIALS AND METHODS

Chemical background: The traditional method for qualitative measurement of fluoride in water utilises SPADNS, a chemical compound whose generic name is Sodium-2-(parasulfophenylazo)-dihydroxy-3,6-napthalene disulfonate, in combination with Zirconyl acid in spectrophotometric technique [3].

When the bright red solution of SPADNS is mixed with colourless zirconyl acid solution, a dark red complex of Zirconyl acid – SPADNS is formed. When zrirconyl acid–SPADNS solution is added to water containing fluoride, the fluoride ions reacts with the complex and bonds with zirconium. The concentration of the complex decreases in approximate proportion to the concentration of fluoride in the water and the colour of the reagent-mixture becomes brighter.

Zr-SPADNS	+	$6F^-$	$\Rightarrow$	ZrF_6^{2-}	+	SPADNS
Dark Red		Colourless		Colourless		**Bright Red**

In the developed technique, a standard solution of 1.0 mgF/L is prepared along with the colour reagent in dissolved form, ready for use. The sample and the standard solution are mixed with the reagent and two brighter colours are obtained. Comparing the two colours indicates whether the fluoride concentration in the sample is more or less than the standard.

Reagent solution: The SPADNS solution, $3.72 \cdot 10^{-3}$ M, is prepared by dissolving 0.4750 g of SPADNS in 250 ml of deionised water [4]. The zirconyl acid solution, $3.75 \cdot 10^{-2}$ M, is prepared by dissolving 0.0665 g of $ZrOCl_2.8H_2O$ in 25 ml of deionised water. Then 25 ml of hydrochloric acid is added and deionised water is added until the total volume of solution is 250 ml. The concentration of zirconyl acid-SPADNS reagent is prepared by mixing the two solutions at 1:1 volume ratio. The reagent is then distributed in to plastic tubes, 20.0 mL in each. The tubes are sealed in the laboratory ready for use in the field.

TABLE 1. Numbers of errors made by the 20 volunteers concerning the different sample numbers and fluoride concentrations.

	Conc.	Error numbers		Sample error	
Sample No	mgF/L	Underestimate	Overestimate	Number Tot	Percentage
8	0.16	0	0	0	0
16	0.28	0	1	1	5
14	0.45	0	2	2	10
19	0.66	0	2	2	10
3	0.90	0	2	2	10
13	0.97	0	4	4	20
11	1.22	-16	0	16	80
12	1.54	-11	0	11	55
7	1.67	-13	0	13	65
5	1.90	-9	0	9	45
20	2.10	-4	0	4	20
18	2.20	-4	0	4	20
1	2.49	-3	0	3	15
2	2.80	-2	0	2	10
9	3.00	-1	0	1	5
4	3.69	-1	0	1	5
15	4.78	0	0	0	0
17	4.90	-2	0	2	10
6	5.74	0	0	0	0
10	8.00	-2	0	2	10
All, No		**-68**	**11**	**79**	
All, %		**-17**	**2.8**	**19.8**	**19.8**

Screening test: The screening test is carried out by sucking an aliquot of 2.0 mL water sample in a syringe and pouring it into a 3 cm diameter Petri dish. 7 drops of the zirconyl acid-SPADNS reagent are added. The solutions are mixed by rotating 10 times to right and 10 times to the left. In parallel 7 drops of the reagent are mixed with 2.0 mL of the standard solution, and the resulting colours are compared at a white background. Fainter colour is recorded as > 1 mg/L and darker colour is recorded as < 1 mg/L.

Test volunteers: Twenty volunteers, being health workers from Ban-thi community hospital in Lamphoon, were trained for 30 minutes in how to conduct the screening test. Each volunteer was given:

TABLE 2. Numbers of errors made by the 20 volunteers concerning the different sample numbers and fluoride concentrations.

	Personal error			
Volunteer No	**Number Underestimate**	**Number Overestimate**	**Sum Number**	**Percentage**
12	0	0	0	0
10	-1	0	1	5
17	-1	0	1	5
1	-2	0	2	10
4	-2	0	2	10
3	-3	0	3	15
6	-2	1	3	15
8	-3	0	3	15
16	-3	0	3	15
7	-3	1	4	20
13	-4	0	4	20
18	-4	0	4	20
19	-3	1	4	20
20	-4	0	4	20
15	-5	0	5	25
2	-6	0	6	30
9	-4	2	6	30
11	-5	1	6	30
5	-6	3	9	45
14	-7	2	9	45
All, No	**-68**	**11**	**79**	
All, %	**-17**	**2.8**	**19.8**	**19.8**

1. One plastic bottle containing 50 ml zirconyl acid SPADNS-reagent.
2. One plastic bottle containing 10 mL standard fluoride solution of 1.0 mg/L.
3. Twenty samples of water.
4. Twenty pieces 3 cm diameter plastic Petri dishes.
5. One plastic dropper.
6. Two 5.0 mL syringes.
7. One chart of white paper.
8. A form for notifying the screening results.

Water samples: Each of the twenty volunteers attached to the study collected a water sample from a ground water source in Lamphoon Province.

Fluoride measurements: The fluoride concentration in the 20 water samples was measured by means of the fluoride selective electrode using an Orion Digital pH and fluoride meter model 720A, Orion Fluoride Electrode 94-90 and Orion Standard

Calomel Reference Electrode 900100, in agreement with the manufacturer's instruction [5].

RESULTS

The results of the screening are shown in Table 1 & 2.

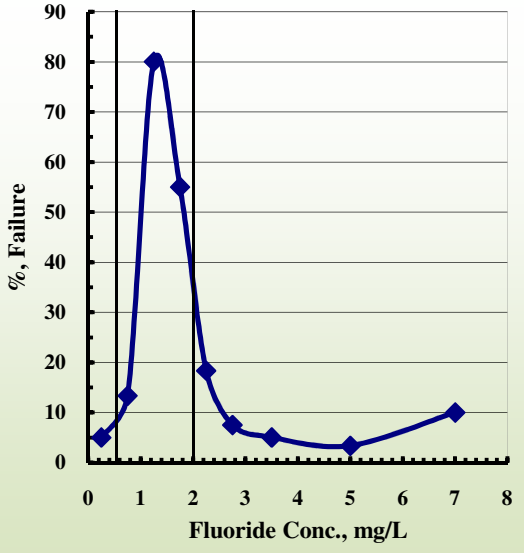

FIGURE 1. % error as a function of the concentration of fluoride.

DISCUSSIONS

Training need: Apparently the volunteers could smoothly use the test kit after the orientation and instruction of about 30 minutes and on an average finish the volunteers could do the testing of 20 samples within 1 1/2 hour. Furthermore, on an average, cf. table 1, as only 20 % of the answers were erroneous, the volunteers delivered correct answers in 80 % of the total of 400 testing.

α and β errors: Defining the errors as under or over estimates, Table 1 reveals that error α, the probability of marking a sample as < 1.0 mgF/L, while it is > 1.0 mg/L is 0.17 and error β the probability of defining a sample as < 1.0 mgF/L, while it is < 1.0 mg/L is 0.03. Thus on an average, the number of under-estimates is much, 6.2 times, larger than the number of over-estimates. ´

Personal error: Table 2 reveals that the error made by the volunteers is not of same magnitude for all the volunteers. Volunteers no 12, 10, 17, 1 & 4, i.e. 25 of the volunteers could make correct hit in 90 % of their testing, while the others, 75 %, made error in more than 10 % of their testing. 50 % of the volunteers could make correct hit in 50 % of their testing, while the other 50 % made 15 % of their testing. Volunteers no 5 and 14, i.e. 10 % of the volunteers made error in 45 % of their testing, i.e. very close to arbitrary guess that is expected to give 50 % error. Thus there is huge variation between the volunteers and this study shows that it is not enough to train volunteers for testing; they should also be sorted and selected.

Concentration range: Figure 1 is extracted from table 1 and it shows that the probability of error, whether under or over estimating, as a function of the concentration of fluoride in the water. The probability of error varies very much, from

0.05 and up to 0.8, depending on the concentration of fluoride in concern. Considering the concentrations of the standard solution ± 0.5 mg/L, i.e. 0.5 and 1.5 mg/L, the probability of error is estimated to be 8 % and 38 % respectively. Thus while the underestimation may be acceptable, the overestimation is too high. Only at concentrations above or equal to 3 mg/L, the probability of error seems to be of an acceptable level.

Screening usefulness: This study shows that normal health workers can be trained to carry out the simple testing of water sources in the field. It also indicates that the usefulness of the developed procedure can be increased by an appropriate selection of the field workers. I may be concluded that the qualitative SPADNS method, as in the developed procedure, should only be used with much care, e. g. in cases where concentrations of fluoride higher then 3 mg/L needed to be identified, whereas the other samples can be taken in to a further laboratory testing for a more reliable measurement of the fluoride concentration.

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