Credibility and Limitations of Fluoride Analysis Using the Pack Test® Kit

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SUMMARY: There has been an increasing need for an 1) easy, 2) rapid, 3) cheap and 4) reliable method for spot testing of fluoride concentration in drinking water and potential drinking water sources. The Pack Test® kit seems to fulfil the first three criteria. Its limitations and credibility are tested compared to the potentiometric selectrode method.
It is found that even the selectrode method has to be used with care. The calibration curve, being systematically deviating from a straight semi-logarithmic line, inquires interpolation and the detection limit in normal laboratory procedures should be stated while indicating lower concentrations as ≤ 0.2 mg/L. Furthermore, double electrode testing is recommended in order to keep deviations from average values below 5 % of average.
On a large concentration interval, the Pack Test kit does not coordinate with potentiometric testing. Further it is found that the Pack Test slightly overestimates concentrations lower than 0.5 mg/L, but underestimates concentrations above 1 mg/L. It is discussed that Pack Test could be improved by adjustment of the colour scale and standardisation of the illumination and visualisation. At the time being the relationship is found to be acceptable in the range 0.2 - 3 mg/L. Especially within the most interesting concentration interval between 0.5 and 1, the relationship seems to be quite convincing. It is thus concluded that the Pack Test kit, the mentioned serious limitations taken into consideration, provides a very handy, rapid and quite reliable tool for decision on whether a given water is fit for drinking or not or whether a defluoridator in operation should be discontinued or not.

Key words: Fluoride analysis, pack test, spot test, potentiometric method, electrode analysis, ion selective electrode, selectrode analysis, colorimetric method, qualitative method.

INTRODUCTION

One of the factors that engrave the problems facing any research and any attempts of mitigation of fluorosis is related to the properties of fluoride and the difficulties in measuring it in aquatic media. Fluoride in water is tasteless, odourless and colourless. Furthermore, being an ion, fluoride does not cause any turbidity in the water. That leaves any detection of fluoride in the water dependent on regular analysis, so far only available in the laboratory at relatively high costs.

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During the recent yours, an urgent need for simple spot testing of fluoride has been experienced. This is because water resources increasingly are suspected to be fluorotic and need to be tested at domestic level and in remote rural areas, i.e. far from laboratories and at affordable costs. Furthermore, as a consequence of such testing, a small-scale defluoridation of drinking water is increasingly introduced at domestic or institutional level. Such a defluoridation is mostly carried out in column filters that need to be monitored by the users themselves in order to be in control of the process and the filter period, before the breakthrough. In such situations the spot testing of fluoride is a must.

For the same reasons different testing kits have been developed and made commercially available for more or less unofficial use and as a first check. To the authors knowledge all of these kits are based on colorimetric comparators, making them subject to high individual variation and much error of interference. Furthermore, even these simple kits may still be too complicated and too costly for domestic use by lay people.

One of these kits is the Pack Test® launched by the Kyoritsu Chemical-Check Lab. Corporation. This kit represents a further simplification of the comparator methods, because the sample is compared, while in the disposable pillows, using a disposable colour scale-pamphlet.

The objective of this paper is to investigate the credibility and limitations of the Pack Test kit, as for analysing the fluoride concentration in drinking water when using the standard electrode potentiometric method as a reference.

BACKGROUND

Few methods of analysis of fluoride are available, the most promising of which are supposed to be included in the "Standard Methods", i.e. The Standard Methods for Examination of Water and Wastewater [1, 2]. These are the potentiometric electrode method and the colorimetric SPADNS method. Another colorimetric method is the Alizarin Visual Method, which has been included in the Standard Methods until 1989.

The potentiometric method utilises a fluoride selective electrode, selectrode, based on a crystal of Lanthanum Fluoride, LaF_6 , across which a potential is established by the presence of fluoride ions. The crystal contacts the sample solution at one face and a reference solution at the other, either internally as in the combined electrode or externally through a connected reference electrode. The potential can be measured by any modern pH-meter having an expanded millivolt scale. The electro-potential is directly related to the logarithm of the fluoride activity in the solution.

Both colorimetric methods are based on reagents of dye lake, the SPADNS and respectively the Alizarin, made translucent by means of Zirconyl ions ZrO^{2+}. Mixing

the coloured reagent with fluoride sample results in dissociation of a portion of the dye lake into a colourless complex anion of ZrF_6^{2-} and the dye. The degree of discolouration or colour modification is proportional to the concentration of fluoride in the sample. Similarly, other colorimetric methods are described in the literature [3, 4].

It is characteristic for the above mentioned analysis methods that they need a high degree of standardisation and instrumentation in order to obtain a satisfactory quantitative response free of interference. Thus conducting these analyses involves relatively high cost of instrumentation and chemicals and high skills of laboratory work.

MATERIALS AND METHODS

Samples and testing: Fifty-seven authentic water samples, all collected in the Arusha Region in Tanzania, were double tested for their contents of fluoride using the potentiometric F-electrode method according to the Standard Method [2]. The samples were then stored in plastic bottles for a period of 3-7 months and then analysed again according to the same method. The analyses were carried out in the Ngurdoto Defluoridation Research Station, the most experienced laboratory in Tanzania with respect to testing fluoride. Simultaneously with the renewed potentiometric testing the same samples were tested in field using the Pack Test® kit.

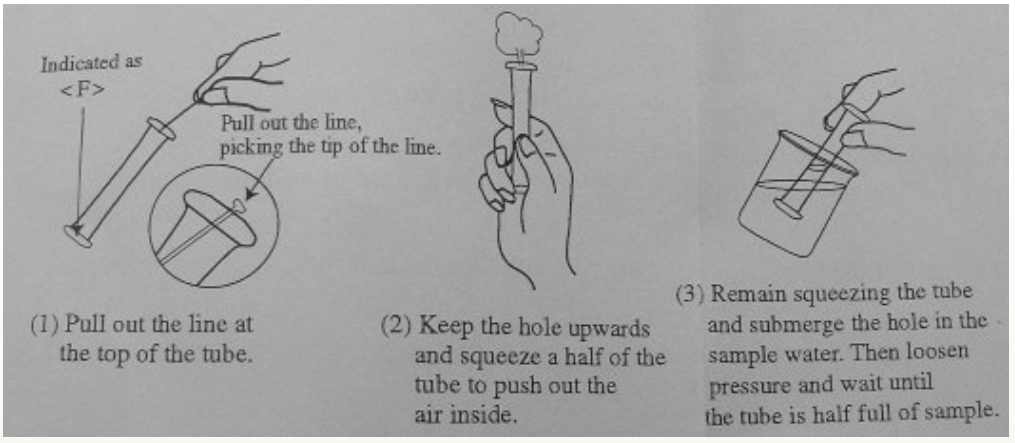
Pack Test measurements: The Pack Test kit is launched by the Kyoritsu Chemical-Check Laboratory Corporation [5]. The kit is a simple cartoon box containing a colour pamphlet and an instruction, beside 50 polythene pillows distributed in 10 smaller packages, cf. Figure 1. The pillows contain the reagent mix in powder form. They are sealed to contain about 4 mL of air or maybe an inert gas. On one side of each pillow a small plastic needle is pricking through in a tight manner. As the polythene pillows are opal-transparent to light and maybe not perfectly airtight, they are packed in batches of 5 pieces. The batches are sealed in aluminium foil bags that protect them from humidity, atmospheric oxygen and light.

Taking out the in-built plastic needle punctures the pillow. Then, pressing the pillow with the fingers, about half of the air content is blown out and the pillow is directly lowered in the water sample to allow for sucking up about 2 ml of it.

The sample aliquot is then mixed with the reagent chemicals and allowed to stand for 10 minutes for standardised complete colour development. The developed colour is compared with colour spots on the pamphlet. The pamphlet shows 6 colour spots corresponding to the concentrations 0, 0.4, 0.8, 1.5, 3 and equal or above 8 mg/L. The colour changes from clear reddish in the low or no fluoride level to dark blue at the higher concentration levels.

Potentiometric measurements: The fluoride concentrations were measured using a Metrohm potentiometer, 704 pH/Ion Meter, in connection with a Metrohm fluoride electrode, 6.0502.150, and a Metrohm Ag/AgCl reference electrode, 6.0726.100. An

aliquot of 5.0 ml of the sample solutions was mixed with 5.0 ml CDTA-tisab and the fluoride concentration was measured using the calibration method as described in the Standard Methods [2], in agreement with the manufacturer's instructions [6].



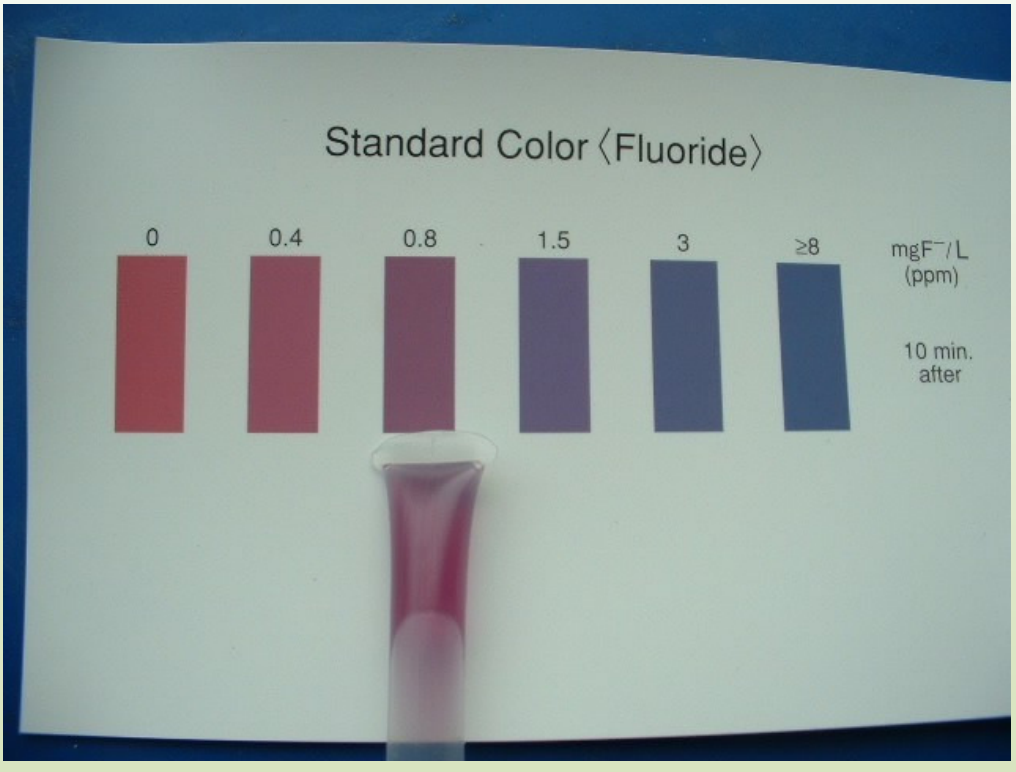


FIGURE 1. The four steps in the Pack Test measurements. Upper: 1) puncturing the pillow. 2) Blowing some of the inert gas content out. 3) Sucking a sample aliquot into the pillow. Lower: Comparison of the developed colour after 10 minutes.

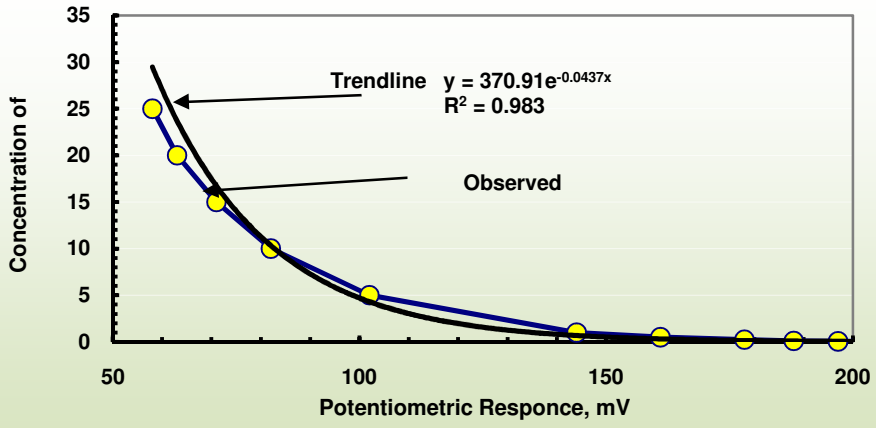


FIGURE 2. The relationship between the fluoride concentrations in prepared standards and the observed potentiometric response in the electrode method.

Standard calibration curve: An extended standard curve was prepared to cover the normal fluoride concentrations prevailing in the water of the Arusha Region. This included 0.025, 0.05, 0.10, 0.25, 0.50,1.00, 5.00, 10.00, 15.00, 20.00 and 25.00 mgF/L. The obtained calibration curve is shown in Figure 2.

Double electrode measurements: The obtained analyses data are shown in Table 1. It is indicated that the average concentration of the tested water is measured to be 4.43 and 4.55 in initial double electrode analysis, giving a grand average 4.49 mg/L for all tested water samples. The lowest concentration measured is 0.04 mg/L and the highest is 23 mg/L, cf. table 2. It is seen that even in a double measurement the absolute deviation between the two obtained figures shows a high variation, between 0 and 81 %, 11 % on an average. This individual variation among double electrode measurements is demonstrated in Figure 3.

TABLE 1. Fluoride concentrations, all in mg/L, in the tested water samples as given through one double electrode analysis, one renewed electrode analysis and the Pack Test kit indication.

Sample No	Water Source/Sample	Double electrode analysis		Renewed electrode analysis	Pack Test indication
		I	II		
1	Arusha water supply	4.83	4.95	5.03	3.0
2	Maji ya chai at the bridge	13.27	13.14	14.38	4.5
3	Themi river at the bridge	2.34	2.55	2.75	2.3
4	Canal water near Kwamangusha	3.5	3.77	4.28	2.3
5	Ngarasero river at the bridge	2.15	2.27	2.53	2.3
6	Makumira river	1.62	1.80	1.91	2.3
7	Canal near Danish bridge	1.69	1.73	1.83	1.5
8	Mbembe river at Kilala	1.76	1.80	1.99	1.5
9	Bassotughang pond	1.22	1.31	1.38	1.2
10	Nyamuri spring	11.29	11.24	12.24	1.5
11	Gigamugho S/W	9.22	9.62	10.00	2.3
12	Mara bore hole	2.98	3.22	3.23	1.5
13	Swai Dug well near NAPOCO	6.41	6.51	6.68	1.5
14	Sahila Dug well near NAPOCO	7.24	7.32	6.95	2.3
15	Lisa Peterson sample	0.05	0.03	0.10	0.1
16	Ngurdoto gate	5.46	5.79	6.41	2.3
17	Charles Shams	2.34	2.45	2.43	1.5
18	Himiti spring	2.07	2.27	2.34	1.5
19	Qutesh S/ W	5.24	5.79	5.91	2.3
20	Nyamur S/ W at Mara	7.24	7.61	8.17	2.3
21	Kangaroo S/ W at Qutesh	3.64	3.92	3.95	1.5
22	Nyamur Dug well at Hidet	6.95	7.32	7.85	1.5
23	Kiliflowers	0.97	0.82	0.87	0.8
24	Shawasa tube well	3.79	4.08	4.28	1.5
25	Olbil tube well	5.03	5.15	5.68	2.3
26	Makisoro spring	23.36	22.70	23.36	1.5
27	KIA airport	0.06	0.03	0.03	0.1
28	A to Z B/H	3.23	2.15	2.15	1.5
29	Lanadanai B/H	0.28	0.22	0.29	0.4
30	Olasiti B/H	3.23	3.50	3.64	2.3
31	Prof.Dahi Domestic Filter	0.05	0.04	0.06	0.4
32	Prof. Dahi demonstration plant	0.14	0.12	0.17	0.6
33	Prof. Dahi tower tank	2.75	3.10	3.10	1.5
34	Ngurdoto pipeline	2.86	3.10	3.23	1.0
35	Saitabick Neeri tube well	4.64	4.76	5.03	2.3
36	Olbil primary school Tube well	6.68	7.04	7.54	2.3
37	Manyara ranch B/H	3.95	4.08	3.95	2.3
38	Haries Pipe water	3.95	4.08	4.11	2.0

39	Mark Farren Well Water	10	10.40	11.29	3.0
40	Makundus B/H " B "	1.69	1.94	1.83	1.2
41	Holili B/H	1.04	1.17	1.08	0.8
42	Olbil Kwa Michael Tube well	7.24	7.32	7.85	1.5
43	Mount Meru Hospital	3.23	3.49	3.64	1.5
44	Shambarai kwa Kisaria tube well	3.5	3.92	4.11	2.3
45	Shamabarai kwa Edward tube well	0.08	0.19		
46	Ngaramtoni kwa Iddi B/H	5.91	6.26	6.16	1.5
47	Cranes B/H	0.33	0.35	0.34	0.6
48	Olasiti kwa Paul B/H	3.64	3.77	3.50	2.3
49	TAC Water tap	14.4	14.40	14.38	2.3
50	Unknown sample	2.86	3.10	3.23	1.5
51	Worthholds			2.07	1.1
52	Worthholds			1.44	0.6
53	Worthholds			4.83	1.5
54	Joe Cook, treated			0.09	0.2
55	Joe Cook, Untreated			1.69	1.5
56	Prof. Dahi Well			2.34	1.5
57	Prof. Dahi Domestic filter			0.19	0.4
All	**Mean**	**4.43**	**4.55**	**4.46**	**1.63**

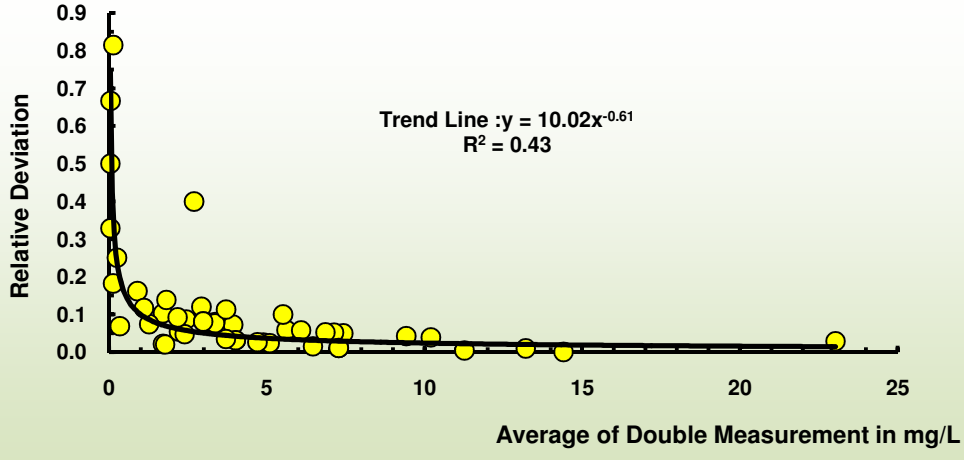


FIGURE 3. Observed deviations between double measurements of water samples, related to the average of the obtained values as a function of the average value.

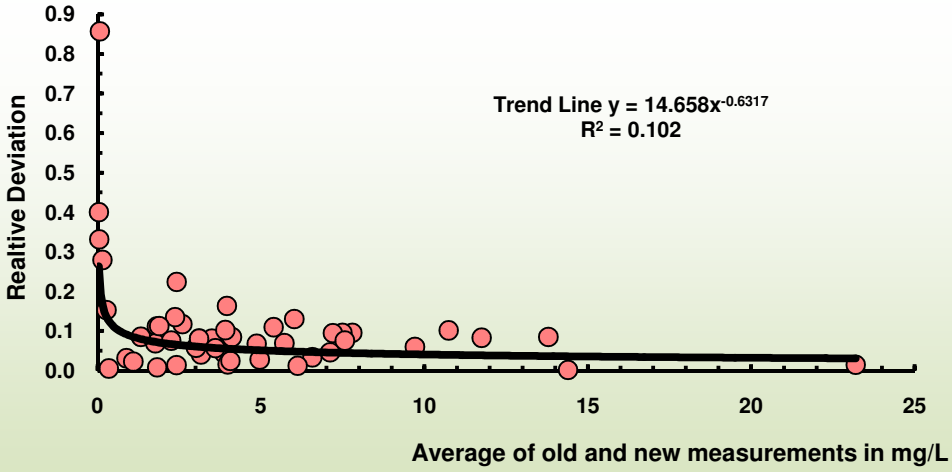


FIGURE 4. Observed deviations between previous and new electrode measurements of water samples, related to the average of the obtained values as a function of the average value.

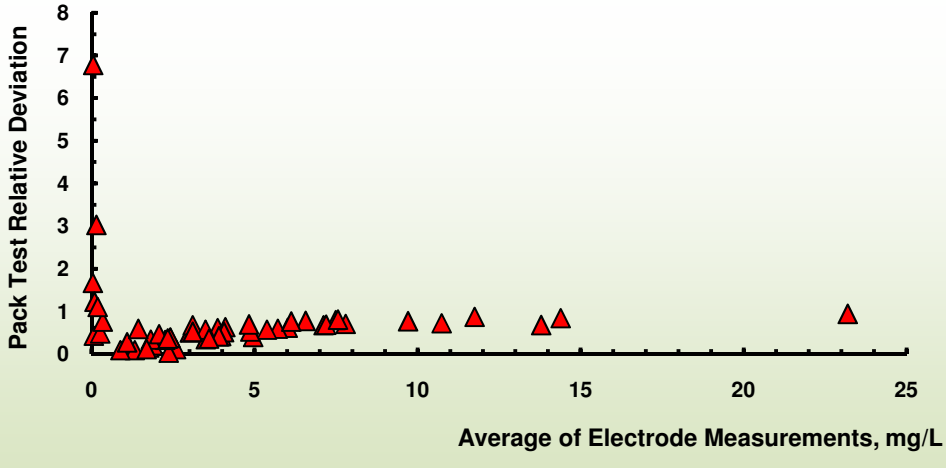


FIGURE 5. Observed deviations between previous and new electrode measurements of water samples, related to the average of the obtained values as a function of the average value.

TABLE 2. The relative variation from average within double potentiometric testing, between two different potentiometric testing and the variation of Pack Testing from the potentiometric testing.

	Parameter	Mean	Median	Range
1	Absolute deviation between double electrode measurement as related to the average	0.11	0.07	0.00 - 0.81
2	Absolute deviation between first double and second single electrode testing as related to the average	0.10	0.08	0.00 - 0.86
3	Absolute deviation between Pack Testing and two electrode measurements related to the average of the electrode measurements	0.87	0.55	0.03 – 6.77

Table 1 indicates the average values obtained by the renewed electrode testing, 4.84 mg/L for the samples 1-44 and 46-50. Compared to the first double testing, where the corresponding value is 4.58 mg/L, this is a deviation of 5.6 %. However, the individual values of the renewed electrode testing deviate up to 86 %, 10 % on an average, cf. Table 2. This individual deviation is shown in Figure 4.

Table 1 indicates that the average value obtained by the Pack Test is only 1.63 mg/L, compared to the renewed testing, where the corresponding value is 4.46 mg/L. This is a deviation of 63 %. The individual values of the pack testing deviate from the potentiometric testing up to 700 %, 87 % on an average. This individual deviation is shown in Figure 5. It was experienced that the visual impression of the developed colour was very much dependent on type of illumination, especially whether it is daylight or artificial light of white or reddish nature. Furthermore, whether the light is directed along or across the visualising line. Last but not least, whether the pillow during comparison is lifted from the pamphlet or it is directly laying on it.

DISCUSSION

Calibration curve: It is clear that the Pack Test kit has its serious limitations compared to the potentiometric electrode method. Probably there is no surprise in that. However, on the same line, this study demonstrates that even the potentiometric electrode method, which is supposed to be the most reliable fluoride testing method developed so far, does have obvious limitations, at least when used as done in the laboratory of this study.

The first limitation is related to the calibration curve. It is in most brochures illustrated to be a straight line in agreement with the Nernst equation; maybe only

deviating from the straight line at concentrations lover than 2 mg/L. Looking at figure 2, this is not confirmed. The indicated trend line represents the best fitting logarithmic function and even this is seen to deviate systematically from the obtained calibration curve. Thus the calibration should remain subject to interpolation between two bordering points above and below the point of the sample.

Double electrode measurements: More serious is that deviations between two single testing supposed to make up one double testing seem to be unacceptably high. According to the "Standard Methods" the relative standard deviation between laboratories was 3.6 % with a relative error of 0.7 % in 111 laboratories testing an unknown synthetic sample of 0.85 mg/L. Thus there is a reason to conclude that the procedures used to determine the concentration of fluoride by double potentiometric testing were inadequate and in lake of quality check. For example if the laboratory in concern decided to discard results deviating more than 10 % of each others, i.e. each value is deviating more than 5 % of the average, 28 % of the measurements would have been discardable, cf. Figure 3.

Figure 3 also shows that the relative deviation in double testing increases sharply to extreme values as the fluoride concentration becomes low. A closer look at the data proves that all double measurements less than 0.2 mg/L are showing such variation. Thus 0.2 mg/L should have been used as the lower limit in the adopted procedures for double testing in the potentiometric method.

Single electrode testing: The single electrode testing and its deviation from previous double testing can not be taking as a deviation from a true value, especially when taking into consideration that the two measurements were not carried out in an inter-laboratory calibration. The average values show however that the concentration of fluoride in the containers does not change during months of storage in room temperature. Furthermore, a previous double testing of an unknown sample is after all the most likely figure of the true value. As the average deviation is of same magnitude as above, it is clear that single potentiometric measurements are loaded with unacceptable risk of error. If the laboratory in concern decided to discard results deviating more than 10 % from a previous double testing, 36 % of the measurements would have been discardable. Thus single potentiometric measurements, as carried out in the mentioned laboratory is of limited use.

Also here Figure 4 shows that the relative deviation increases sharply to extreme values as the fluoride concentration becomes low. A closer look at the data proves that all double measurements less than 0.3 mg/L are showing such variation. Thus 0.3 mg/L should have been used as the lower limit in the adopted single testing of the potentiometric method.

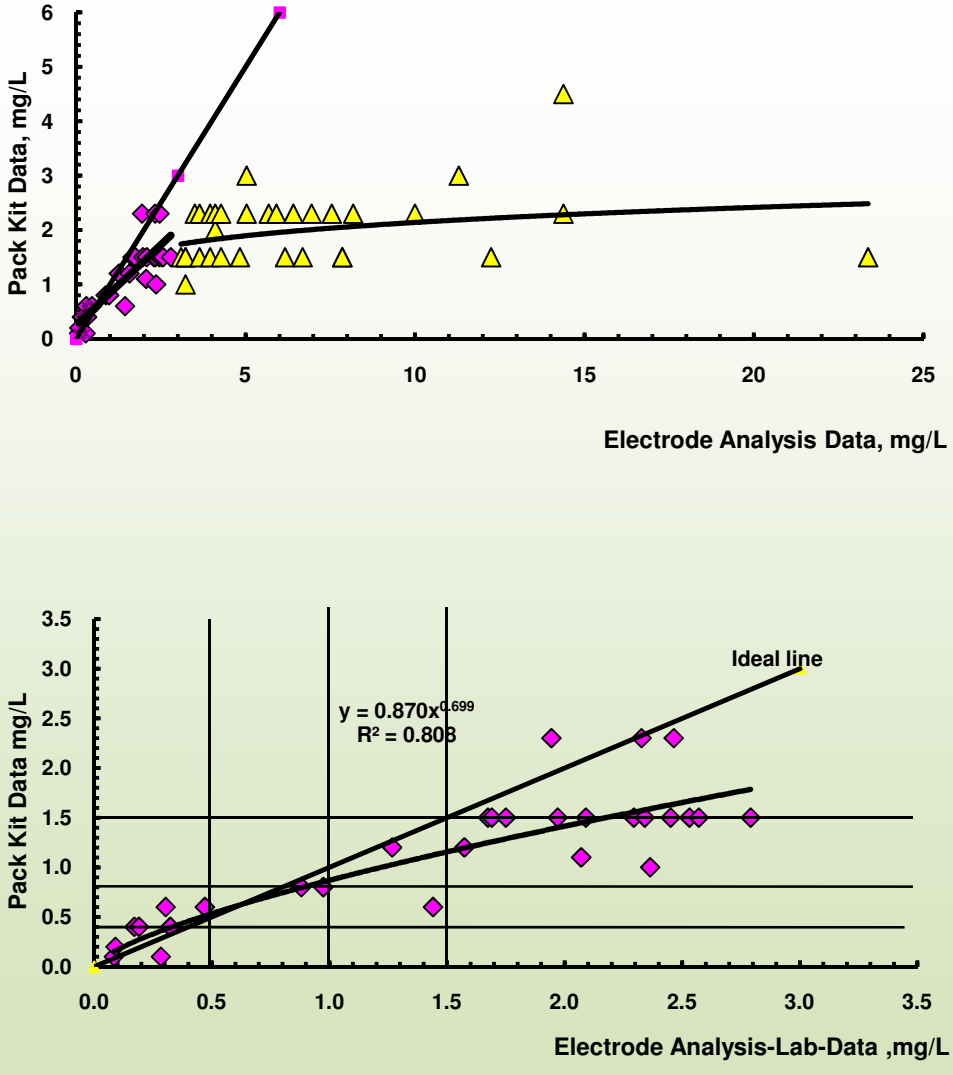


FIGURE 6. Obtained relationship between measurements of fluoride concentrations using the Pack Test kit and the potentiometric electrode method. Above: Total set of date. Below: Conc. Interval 0-3 mg/L.

Also here figure 4 shows that the relative deviation increases sharply to extreme values as the fluoride concentration becomes low. A closer look at the data proves that all double measurements less than 0.3 mg/L are showing such variation. Thus 0.3 mg/L should have been used as the lower limit in the adopted single testing of the potentiometric method.

Pack Test: Obviously the pack test could not make a reasonable estimate even on an average; 1.6 against 4.5. Also the deviation from what is most likely shows a huge deviation, up to 700 %. This could give a reason to reject the method at least as a direct quantitative tool.

Figure 5 shows that the deviation comes to such extreme values only at very low concentrations. As concluded above this could be avoided by adopting an appropriate detection limit for the method. The variation of these data suggests 0.2 mg/L, as the limit where the variation starts increasing very sharp with decreasing concentration.

Figure 6 illustrates the deviation in absolute terms. It demonstrates that Pack Kit data could in no concentration interval follow a straight relationship with the potentiometric data. Figure 6 lower shows the relationship for waters containing less than 3 mg/L. Even the relationship with this limited interval demonstrates systematic variation from the straight line, indication that the Pack Test slightly overestimates concentrations lower than 0.5 but underestimates concentrations above 1 mg/L. In this concern the Pack Test needs further development, especially concerning the adjustment of the colour scale and the standardisation of illumination conditions.

At the time being it is concluded that there is a convincing relationship between the Pack Test measurements and the potentiometric measurements between 0.2 and 3 mg/L. Actually at the concentration interval between 0.5 and 1 the relationship seems to be quite good.

It may be recalled that the most common objectives of spot testing are:

- To evaluate if a given source is safe with respect to fluoride for human consumption and
- If a filter in use should be rejuvenated or recharged.

In both situations one is interested to know if the fluoride concentration is more or less than a given optimum-maximum value. In a fluorotic area this critical value would be in the range 0.5 – 1 mg/L [5]. It is thus concluded that the Pack Test kit, in spite of serious limitations especially when testing relatively high fluoride concentrations, is a very handy, rapid and quite reliable for decision on whether the water is fit for drinking or not or whether a defluoridator in operation should be discontinued or not.

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