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Spectrophotometric method vs ion selective electrode for field determination of fluoride in water and complex samples

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Abstract

Spectrophotometric method based on the bleaching effect of fluoride ions on the dark red zirconium dye lake was used for determination of fluoride in water samples in field conditions and results obtained were compared with the results of potentiometric ion selective electrode method. It was found that results of spectrophotometric method were very close to those of potentiometric method. Therefore spectrophotometric method can be used for field determination of fluoride with an error limit of ±0.1 mg/l. Spectrophotometric method was also used to determine fluoride concentration in complex samples such as toothpastes and mouthwashes and the result obtained was in good agreement with that obtained from potentiometric method. Study also confirmed that higher concentration of chloride ion in water samples does not affect fluoride determination by this method. Spectrophotometric method is easy to operate and less expensive than potentiometric ion selective method, hence more suitable for field determination of fluoride in samples.

Keywords: Spectrophotometric, Bleaching effect, Potentiometric, Fluoride, Field determination.

Introduction

Fluoride is a natural constituent of some ground water as it is present in many minerals such as topaz, fluorite, apatite, fluorapatite, cryolite, phosphorite and mica[1-9]. Large population in India is still dependent on ground water for their daily requirements. So ground water is one of the important sources of fluoride for people in our country. Small concentration of fluoride in drinking water is required for good dental health. But higher concentration of fluoride causes dental and skeletal fluorosis. In India permissible limit of fluoride in drinking water is 0.6 – 1.5 mg/l (BIS). When concentration of fluoride becomes more than 1.5 mg/l in water, it shows adverse effect on human health in terms of fluorosis.

Many states of India are suffering from dreadful fate of fluorosis. Some of them are Andhra Pradesh[10], Punjab[11], Haryana[12], Rajasthan[13], Gujrat[7], Orissa[6] and Uttar Pradesh[14]. Recently some highly fluoridated areas in Chhattisgarh have also been located and dental and skeletal fluorosis was reported there. Many parts of Rajnandgaon, Raigarh and Surajpur district of Chhattisgarh are badly affected by fluorosis[15-17]. Therefore to avoid the dreadful health effects of fluoride, regular monitoring of fluoride concentration in water and removal of higher concentration of fluoride from water is essential.

One of the constraints in fluorosis mitigation work is the testing of fluoride in the water. Fluoride concentration in water is determined by various methods which includes potentiometry with fluoride ion selective electrodes (ISE)[18], spectrometry[19], chromatography[20] and electrochemical methods[21]. In the present study spectrophotometric SPADNS method and potentiometric ion selective electrode methods were used to determine fluoride concentration in water samples. In addition to this, efficacy of spectrophotometric method in fluoride determination was also studied in complex samples. For this purpose samples of toothpaste and mouthwash which contains fluoride in them were considered because they are one of the most important sources of fluoride ingestion in human beings other than water.

As fluoride is beneficial for dental health in small concentration, many toothpaste and mouthwash have fluoride in them. These dental products generally contain fluoride in the form of sodium fluoride and sodium monoflourophosphate. In toothpaste bioavailability of fluoride depends on the compatibility of fluoride compound present and abrasive used in it. It is evident from literature review that toothpaste containing 1000 mg/l fluoride is helpful in reducing dental cavities[22,23].

Mouthwash is used to control bad breath and to maintain oral hygiene. The composition of mouthwash has mainly antibacterial agents, flavours, humectants and colorants in them[24]. Fluoride is used as antibacterial agent in mouthwash. The most common fluoride compound used in mouth wash is sodium fluoride. Generally solutions of 0.05% sodium fluoride (225 ppm fluoride) for daily rinsing are available in mouthwash as declared by the manufacturer. Therefore it is important to measure the available concentration of fluoride in toothpaste and mouthwash to ensure their function in reducing dental carries.

Along with fluorine, chlorine another member of halogen family, is also a natural constituent of water and exist in the form of chloride in water samples. Presence of chloride with fluoride in samples may affect the process of decolourization of dye in spectrophotometric SPADNS method. This may affect the efficiency of fluoride determination by this method. This fact had also been taken into consideration in this study.

The objective of the study is to determine the efficacy of spectrophotometric method for field determination of fluoride in water samples as well as in complex samples (toothpaste and mouthwash) and effect of variation of concentration of chloride ion on determination of concentration of fluoride by this method.

Methodology

Water samples: Balod district is newly formed district in the state of Chhattisgarh, India. Balod is located at 20.73°N 81.2°E. It has an average elevation of 324 metres (1063 feet). Balod is 58 km from Durg and 44 km from Dhamtari. Beloda is a sub area, located in Balod district. This area was chosen for sampling because fluorosis in this area was reported by Dr. Gitte in his survey report[25].

Samples were collected from hand pumps of Aashram, Kunjampara, Aambahara, Kunjeli, Binghola, Snkdiguhaan and Mangaltarai of Belodi. All the samples were collected in plastic bottles of capacity one liter. The sampling bottles were pre cleaned with detergent, chromic acid, tap water and finally with double distilled water. Duplicate samples were collected from each sampling site.

Toothpaste and mouthwash samples: Samples of toothpaste and mouthwash of different companies were purchased from local market. 1 g of toothpaste of each sample was weighted and dissolved in 100 ml of distilled water. Then this solution is filtered and filtrate is used for test of free available fluoride. Similarly in case of samples of mouthwash 2 ml of mouthwash is pipette out in a volumetric flask of 100 ml and then it is makeup with distilled water up to the mark which is then used for fluoride analysis.

Equipments and chemicals: Fluoride concentrations in samples were determined by SPADNS method as well as by fluoride ion selective electrode. In SPADNS method fluoride concentration in samples were determined spectrophotometrically. The procedure described in the sprctrophotometer manual was followed[26], except that there was no distillation of the samples performed. SPADNS is sodium 2-(parasulfophenylazo)-l,8-dihydroxy-3,6-naphthalenedisulfonate. In this method fluoride of sample reacts with a dark red zirconium dye lake and form a colourless complex anion[27]. This bleaching action of red colour dye is directly proportional to the concentration of fluoride in sample. As the concentration of fluoride increases in sample, colour of dye becomes lighter and lighter[28].

Ion selective electrode with a fluoride selective membrane is used to determine fluoride concentration in samples. Measurement of fluoride ions by ion selective electrode is based on the selective passage of fluoride ions from one side of ion selective membrane to other. This creates a potential difference across the membrane. 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[29]. Analytical grade chemicals were used for all tests.

Results and discussion

Water samples from the study area were analyzed in laboratory for different water quality parameters such as pH measured using a single electrode pH meter, conductivity using a conductivity meter, alkalinity, hardness and chloride were analyzed titrimetrically, nitrate by the brucine method, phosphate by stanous chloride method, sodium and potassium by flame photometer and iron by spectrophotometer[28]. Results of analysis are shown in Table-1.

Water samples were analyzed for fluoride content using both ion selective electrode and spectrophotometer. The fluoride concentration from both methods was compared and the results are shown in Figure-1. The sample range for spectrophotometer was 0.0 ppm to 2.7 ppm and for ion selective electrode was 0.01 ppm to 2.6 ppm.

From the Figure-1 it is clear that for 80% samples, fluoride concentration determined by SPADNS method is slightly more than it is determined by ion selective method. Correlation coefficient obtained from regression statistics was 0.99 (Table-4), which showed good agreement between the results obtained for determination of fluoride concentration in water samples by both the methods mentioned above. So it was found that spectrophotometric determination of fluoride does not differ much from ion selective electrode, if interfering ions such as alkalinity, chloride, iron etc. are not present in large quantity. Similar result is also reported by Brossok et al.[30]. Interference level of ions on spectrophotometric determination of fluoride is shown in Table-2.

Then complex samples of toothpaste and mouthwash were analyzed for fluoride content by both ion selective electrode and spectrophotometric method and the comparison of results are shown in Table-3 and 4 and Figure-2 and 3. The range of fluoride concentration for toothpaste samples were 956 to 1008 ppm for spectrophotometer SPADNS method and 972 to 989 ppm for ion selective electrode whereas the range varies from 195 to 233 ppm for SPADNS method and 215 to 228 ppm for ion selective electrode in case of mouthwash samples (Table-3 and 4).

Table-1: Physico chemical analysis of water samples.

	pH	Cond	TDS	TH	Alk	Cl^-	Na	K	NO_3^{3-}	PO_4^{3-}	Fe	F^- (spadns)	F^- (ISE)
Mean	6.80	0.50	251.05	184.8	553.32	24.39	43.78	0.89	3.9	0.08	0.2	1.21	1.18
Standard Error	0.10	0.08	39.64	32.73	56.96	5.52	10.85	0.14	0.95	0.01	0.10	0.27	0.27
Median	6.68	0.43	213	158	568.4	19.86	32	0.9	3	0.08	0	1.20	1.12
Mode	0	0.29	0	96	313.2	17.02	0	0.6	7.8	0.06	0	0.00	0
Standard Deviation	0.33	0.25	125.36	103.50	180.13	17.44	34.31	0.43	3.01	0.03	0.33	0.86	0.84
Sample Variance	0.11	0.06	15715.53	10712.18	32445.41	304.18	1177.32	0.18	9.03	0.00	0.11	0.73	0.71
Kurtosis	1.82	1.27	1.25	3.62	-1.20	4.65	2.77	-1.16	-1.44	6.20	1.41	-0.84	-1.08
Skewness	1.29	1.25	1.25	1.79	-0.18	1.92	1.73	0.17	0.44	2.32	1.62	0.27	0.24
Range	1.11	0.76	381	340	510.4	62.39	109.1	1.3	8	0.1	0.9	2.70	2.59
Minimum	6.43	0.29	144	96	313.2	5.67	15.3	0.3	0	0.06	0	0.00	0.01
Maximum	7.54	1.05	525	436	823.6	68.06	124.4	1.6	8	0.16	0.9	2.70	2.6
Sum	68.0	5.03	2510.5	1848	5533.2	243.9	437.8	8.9	39	0.82	2	12.10	11.83
Confidence Level (95.0%)	0.23	0.18	89.68	74.04	128.85	12.48	24.55	0.31	2.15	0.02	0.24	0.61	0.60

Table-2: Interference level of ions on spectrophotometric determination of Fluoride.

Interfering ion	Minimum Concentration for interference (mg/l)	Error
Alkanility	5000	-0.1 mg/L F^-
Chloride	7000	+0.1 mg/L F^-
Iron	10000	-0.1 mg/L F^-
Sulphate	200	-0.1 mg/L F^-

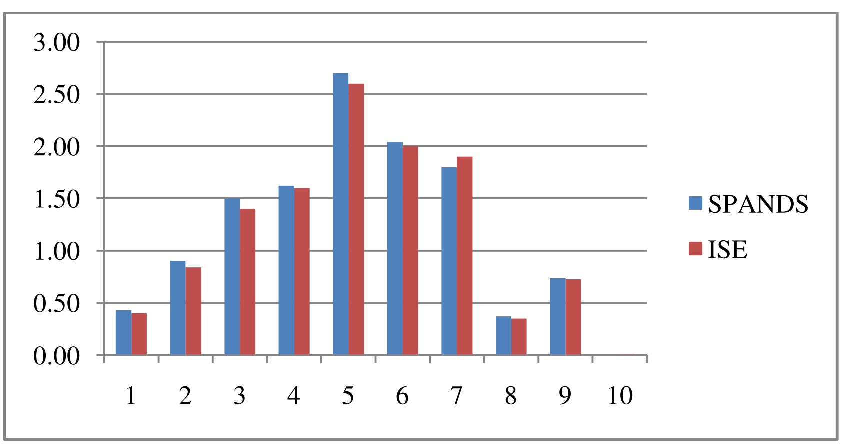

Figure-1: Comparison of results obtained by spectrophotometer and ion selective electrode.

Table-3: Fluoride content in toothpaste samples.

Sam. No.	Brand Name	Act. Ing.	Abrasive	F-Expected	ISE	SPADNS
A	Colgate Anti Cavity	NaMFP	$CaCO_3$	1000	978	976
B	Colgate Max Fresh	NaF	Silica	1000	989	1008
C	Pepsodent Germi Check	NaMFP	$CaCO_3$	1000	975	964
D	Sensodyne Fresh Gel	NaF	Silica	1000	980	992
E	Close Up Fresh Action	NaF	Silica	1000	972	956

Table-4: Fluoride content in mouthwash samples.

Sam. No.	Brand Name	Act. Ing.	F-Expected	ISE	SPADNS
F	Thermokind	NaF	226	224	222
G	Colgate Plax Freshmint Splash	NaF	225	228	233
H	Colgate Plax Fresh Tea	NaF	225	220	212
I	Listerine Cavity Fighter	NaF	220	215	195
J	Colgate Plax Pippermint	NaF	225	222	216

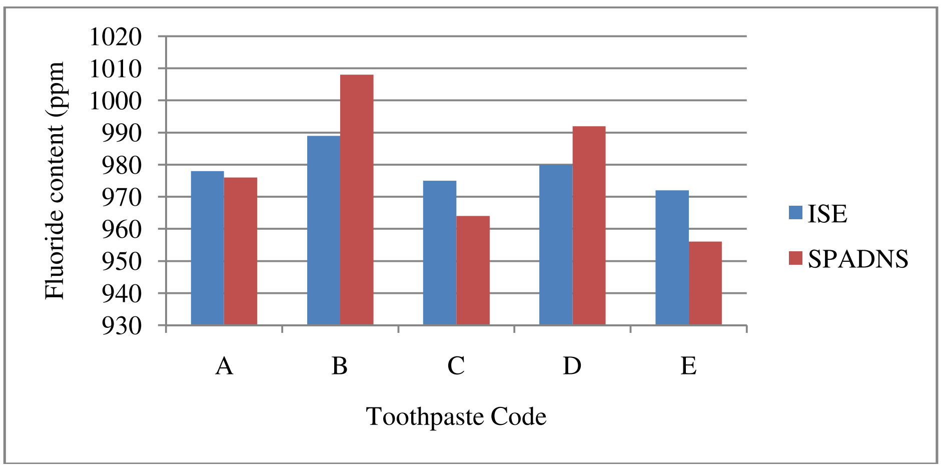

Figure-2: Comparison of results obtained by spectrophotometer and ion selective electrode for toothpaste samples.

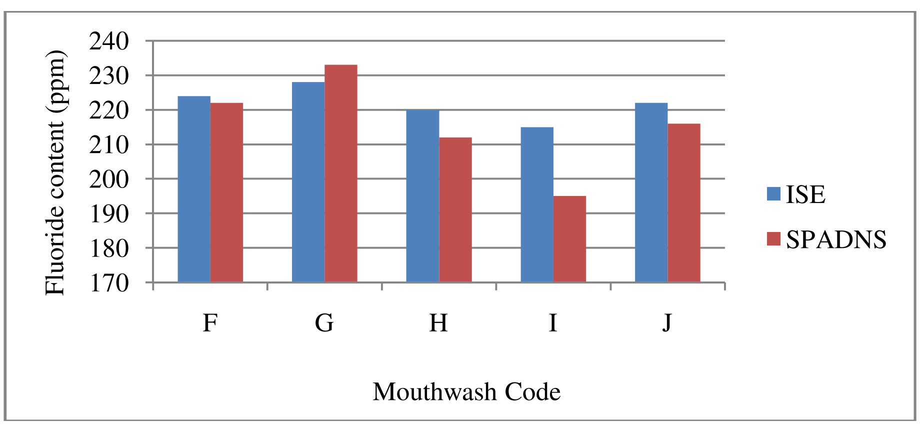

Figure-3: Comparison of results obtained by spectrophotometer and ion selective electrode for mouthwash samples.

From the Figure-2 it is clear that for 40% samples Fluoride concentration determined by SPADNS method is slightly more than it is determined by ion selective method in case of toothpaste samples whereas Figure-3 shows that only 20% mouthwash samples exhibit Fluoride concentration slightly more determined by SPADNS method than it is determined by ion selective method. Correlation coefficient obtained from regression statistics for both the methods was 0.96 in case of toothpaste samples and 0.99 for mouthwash samples (Table-4). Therefore the results obtained by both the methods do not differ much in measurement of fluoride concentration in toothpaste and mouthwash samples. So spectroscopic SPADNS method can be used for determination of fluoride in such samples without any significant deviation in results.

Table-4: Results of regression statistics

Type of Sample	Correlation Coefficient	Coefficient of determination
Water Samples	0.99	0.99
Toothpaste Samples	0.96	0.94
Mouthwash Samples	0.99	0.99

However higher concentration of chloride or other halogen ions may negatively affect the colour development in spectrophotometric SPADNS method. Therefore this study conducts a field test in condition of higher chloride to find out the effect on fluoride determination. In order to study the effect of chloride on fluoride determination by spectroscopic SPADNS method, field sample having certain amount of fluoride is taken and different amount of chloride is added to it. Then absorbance is measured by spectrophotometer. Results obtained are shown in Table-5 and Figure-4.

Table-5: Effect of chloride on Fluoride in SPADNS method.

Concentration of Fluoride in sample (mg/l)	Concentration of chloride added to sample (mg/l)	Absorbance
2.7	6000	-0.54
	7000	-0.56
	8000	-0.57
	9000	-0.59
	10000	-0.62
2.04	6000	-0.41
	7000	-0.40
	8000	-0.44
	9000	-0.46
	10000	-0.48
1.8	6000	-0.36
	7000	-0.38
	8000	-0.40
	9000	-0.40
	10000	-0.44
1.62	6000	-0.33
	7000	-0.34
	8000	-0.36
	9000	-0.38
	10000	-0.39

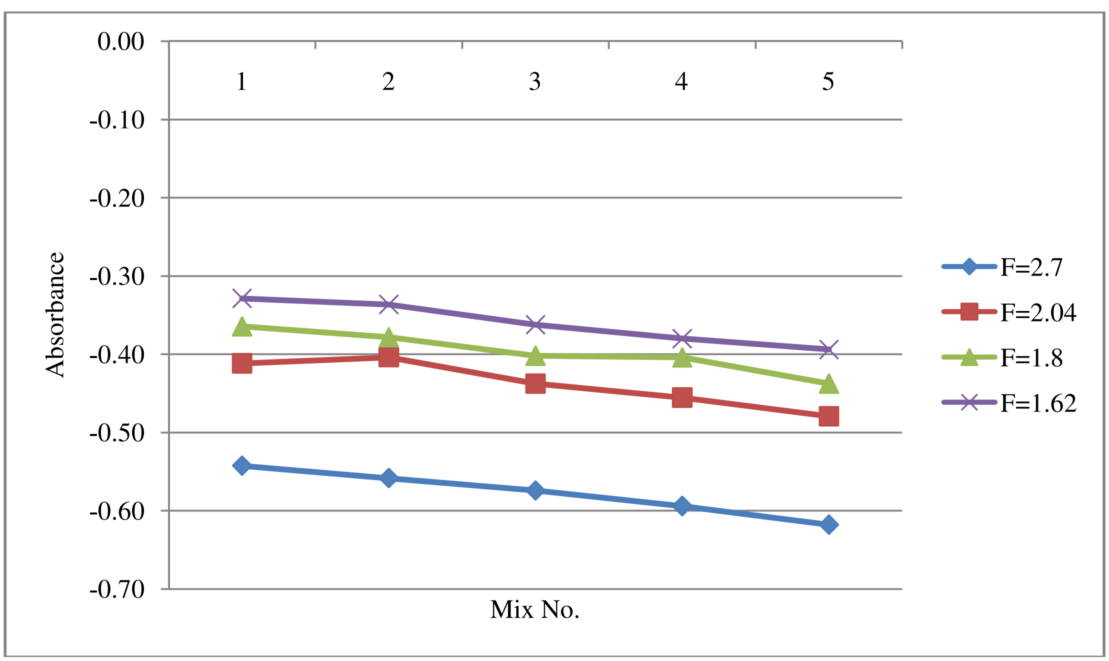

Figure-4: Effect of chloride on Fluoride in SPADNS method.

Results showed that higher concentration of chloride up to 7000 mg/l had no effect on fluoride determination by SPADNS method. Concentration of chloride above 7000 mg/l showed a slight positive interferes in this determination. If proper measures are taken such as addition of sodium arsenite solution to the sample, then this interference can be removed.

Conclusion

Fluorosis is a wide spread disease in the world and a large part of India is also affected by it. Water is the major source of fluorosis. In order to treat this problem, the first step is to identify the fluoridated areas. For this purpose it is must to adopt proper method for determination of fluoride concentration in water sample. Method selected must be easy to operate in field and cost effective. Ion selective electrode determines fluoride concentration in samples accurately, but it is very sensitive, expensive and need special training to operate it. Therefore it is not so suitable for field determination of fluoride in samples. Spectroscopic method is quite suitable for field determination of fluoride in water samples as it is easy to operate without any particular kind of training and is less expensive. Results of this study showed that spectrophotometric SPADNS method can be used for field determination of fluoride with an error limit of ±0.1 mg/l in comparison of ion selective electrode. This method is not only suitable for water samples but also for complex samples of toothpastes and mouthwashes which contains fluoride in them for good dental health. Correlation coefficients obtained for determination of fluoride concentration by both the methods are 0.99, 0.96 and 0.99 for water, toothoaste and mouthwash samples respectively. This showed that SPADNS method can be used for fluoride determination in simple as well as complex samples with excellent efficiency. Moreover higher concentration of chloride ion in water samples has no interference on fluoride determination by this method. Study established the fact that the spectrophotometric method of fluoride determination not only gives accurate results but also it is economic for field conditions. Therefore spectroscopic SPADNS method can be used with ease for field investigation of fluoride in samples.

References

1. Singh R. and Maheshwari R.C. (2001). Defluoridation of drinking water–a review. *Ind. J. Environ. Protec.*, 21(11), 983-991.
2. Matthess G. (1982). The Properties of Groundwater. John Wiley & Sons, New York, ISBN 10: 0471085138 / 0-471-08513-8.
3. Pickering W.F. (1985). The Mobility of Soluble Fluoride in Soils. *Environ. Pollution*, 9(4), 281-308.
4. Haidouti C. (1991). Fluoride Distribution in Soils in the Vicinity of a Point Emission Source in Greece. *Geoderma*, 49(1-2),129-138.
5. Datta P.S., Deb D.L. and Tyagi S.K. (1996). Stable Isotope (180) Investigations on the Processes Controlling Fluoride Contamination of Groundwater. *Journal of Contminant Hydrology*, 24(1), 85-96.
6. Kundu N., Panigrahi M.K., Tripathy S., Munshi S., Powell M.A. and Hart B.R. (2001). Geochemical Appraisal of Fluoride Contamination of Groundwater in the Nayagarh District of Orissa, India. *Environmental Geology*, 41(3), 451-460.
7. Dhiman S.D. and Keshari A.K. (2006). Hydrogeochemical Evaluation of High-Fluoride Ground Waters: A Case Study from Mehsana District, Gujarat, India. *Hydrological Sciences Journal*, 51(6), 1149-1162.
8. Mohapatra M., Anand S., Mishra B.K., Giles D.E. and Singh P. (2009). Review of Fluoride Removal from Drinking Water. *Journal of Environmental Management*, 91(1), 67-77.
9. Mody Manan, Chaudhari Prashant L. and Attar S.J. (2010). Influence of other Contaminants on Removal of Fluoride from Ground Water by Adsorption. National Conference on Recent Advances in Chemical Engineering. Jalgaon. 10-16.
10. Sai Sathish R., Ranjit B., Ganesh K.M., Nageswara Rao G. and Janardhana C. (2008). A Quantitative Study on the Chemical Composition of Renal Stones and their Fluoride Content from Anantapur District, Andhra Pradesh, India. *Current Science*, 94(1), 104-109.
11. Jolly S.S., Singh B.M., Mathur O.C. and Malhotra K.C. (1968). An Epidemiological, Clinical and Biochemical Study of Endemic Dental and Skeletal Fluorosis in Punjab. *Br Med J*, 4(5628), 427-429.
12. Meenakshi Garg V.K., Kavita, Renuka and Malik A. (2004). Ground Water Quality in Some Villages in Haryana, India: Focus on Fluoride and Fluorosis. *Journal of Hazardous Material*, 106(1), 85-97.
13. Muralidharan D., Nair A.P. and Sathyanarayana U. (2002). Fluoride in Shallow Aquifers in Rajgarh Tehsil of Churu District Rajasthan—An Arid Environment. *Current Science,* 83(6), 699-702.
14. Sharma B.S., Agrawal Jyoti and Gupta Anil K. (2011). Emerging Challenge: Fluoride Contamination in Groundwater in Agra District, Uttar Pradesh. *Asian Journal of Experimental Biological Sciences*, 2(1), 131-134.
15. Beg M.K., Srivastav S.K., Carranza E.J.M. and de Smeth J.B. (2011). High Fluoride Incidence in Groundwater and Its Potential Health Effects in Parts of Raigarh District, Chhattisgarh, India. *Current Science*, 100(5), 750-754.
16. Ambade B. and Rao C.M. (2012). Assessment of Ground Water Quality with a Special Emphasis on Ground Water Contamination in Rajnandgaon District in Chhattisgarh State in Central India. *International Journal of Environmental Sciences*, 3(2), 851-858.

17. Upadhyay M. (2012). Depleting Ground Water Levels and Increasing Fluoride Concentration in Villages of Surajpur District, Chhattisgarh, India: Cost to Economy and Health. *IOSR Journal of Applied Chemistry*, 1(5), 15-22.

18. Kahama R.W., Damen J.J. and Cate J.M. (1997). Enzymatic release of sequestered cows' milk fluoride for analysis by the hexamethyldisiloxane microdiffusion method. *Analyst*., 122(8), 855-858.

19. Gutsche B., Kleinoeder H. and Herrmann R. (1975). Device for trace analysis for fluorine in reaction tubes by atomic-absorption spectroscopy. *Analyst*, 100(1188), 192-197.

20. Jones P. (1992). Development of a high-sensitivity ion chromatography method for the determination of trace fluoride in water utilizing the formation of the AlF2+ species. *Anal. Chim. Acta*, 258, 123-127.

21. Villa A.E. (1988). Rapid method for determining very low fluoride concentrations using an ion-selective electrode. *Analyst*, 113(8), 1299-1303.

22. Walsh T., Worthington H.V., Glenny A.M., Appelbe P., Marinho V.C. and Shi X. (2010). Fluoride toothpastes of different concentrations for preventing dental caries in children and adolescents. *Cochrane Database Syst Rev*., 1: CD007868.

23. Sebastian Shibu Thomas and Siddanna Sunitha (2015). Total and Free Fluoride Concentration in Various Brands of Toothpaste Marketed in India. *Journal of Clinical and Diagnostic Research*, 9(10), 09-12.

24. Teki Kesavarao and Bhat Ramachandra (2012). Composition Analysis of the Oral Care products available in Indian Market Part I: Mouthwashes. *International Journal of Advanced Research in Pharmaceutical & Biosciences*, 2(3), 338-347

25. Gitte S.V. (2013). Community based fluorosis survey of village Beloda, District Balod, Chhattisgarh State.

26. Hach Co: DR 100 Colorimeter Manual. Loveland, Colorado, 1983, 3-21.

27. American Public Health Assn (1973) American Water Works Assn, and Water Pollution Control Federation, 1985. *Standard Methodsf or the Evaluation of Water and Wastewater*, 16th ed. Washington, DC; American Public Health Assn, I985, 352-61.

28. Manivasakam N. (1996). Physico-chemical Examination of Water, Sewage and Industrial Effluents. 3rd Edn. Pragati Prakashan, Coimbatore.

29. Bellack E. (1972). Methods and materials for fluoride analysis. *J AmWater Works Assoc*, 64, 62-66.

30. Brossok Gall E., McTigue Dennis J. and Kuthy Raymond A. (1987). The use of a colorimeter in analyzing the fluoride content of public well water. *The American Academy of Pediatric Dentistry*, 9(3), 204-207.