

## RESEARCH ARTICLE

### Analytical Chemistry

# Fluoride analysis in aqueous solutions - a comparison of two colorimetric methods

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**Abstract:** Fluoride is beneficial for human health only in a narrow concentration range. Over the years, many analytical techniques have been developed to quantify fluoride in a variety of sample matrices. In this research, fluoride concentrations of twenty (20) natural water samples determined by SPADNS (SPA) and Eriochrome Cyanine R (ECR) colorimetric methods were evaluated to ascertain whether these methods can produce comparable fluoride concentrations. According to the paired t test for comparing individual differences, the two datasets are different at 95% confidence level suggesting that the two analytical methods produce statistically different fluoride concentrations for the analysed water samples. The potential interferences of  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  on the fluoride analysis was evaluated using  $0.85 \text{ mg L}^{-1}$  fluoride standard solutions spiked with various amount of the above-mentioned metal ions. The highest interference was observed with  $\text{Al}^{3+}$  ions, which underestimated the fluoride concentration by 26% and 23% for ECR and SPA methods respectively at  $20.0 \text{ mg L}^{-1}$   $\text{Al}^{3+}$  concentrations. The minimum interference was observed for  $\text{Ca}^{2+}$  ions which underestimated the fluoride concentration by 8% and 7% for ECR and SPA methods respectively at  $100.0 \text{ mg L}^{-1}$   $\text{Ca}^{2+}$  concentrations. Acid distillation resulted in the samples spiked with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions in the range of  $0.50$  to  $100.0 \text{ mg L}^{-1}$  reaching the theoretical concentration of  $0.85 \text{ mg L}^{-1}$ . Acid distillation also worked well for the  $\text{Al}^{3+}$ -fortified samples, except for  $\text{Al}^{3+}$  concentration at  $20 \text{ mg L}^{-1}$ . The efficiency of the acid distillation method was also tested with three (03) natural water samples. The fluoride concentration increased significantly after the acid distillation; however, even after the acid distillation, statistically comparable fluoride concentrations were not observed.

**Keywords:** Acid distillation, Eriochrome Cyanin R, fluoride, SPADNS, t test.

## INTRODUCTION

Fluoride is a ubiquitous anion in natural waters and fluorine is the 13<sup>th</sup> most abundant element in the Earth's crust that contain approximately  $0.6 \text{ g/kg}$  (García & Borgnino, 2015) of fluorine. Fluoride rich minerals gradually weathers and releases fluoride ions into ground and surface water (Rafique *et al.*, 2015). Fluoride is beneficial for human health as it promotes the growth of healthy bones and teeth (Edmunds & Smedley, 2013; Prasad *et al.*, 2018). Various dietary components help absorption of fluorides from the gastrointestinal tract and the absorbed fluoride is distributed throughout the body. According to World Health Organization (WHO), fluoride is beneficial only in the narrow concentration range of  $0.5$  to  $1.5 \text{ mg L}^{-1}$  in drinking water (Amini *et al.*, 2008; Edmunds & Smedley, 2013; García & Borgnino, 2015). Higher concentrations of fluoride cause serious health effects such as dental and skeletal fluorosis, brain damage and chronic kidney diseases (Edmunds & Smedley, 2013; Kanduti *et al.*, 2016). The hypo-mineralization of teeth commonly known as dental fluorosis develops at fluoride concentrations above  $1.5 \text{ mg L}^{-1}$  (O Mullane *et al.*, 2016; Akuno *et al.*, 2019). The excessive accumulation of fluoride in bones leads to development of skeletal fluorosis at fluoride concentrations above  $10 \text{ mg L}^{-1}$  (Mohammadi *et al.*, 2017). Skeletal fluorosis causes painful damages to bones and joints leading to abnormalities in bone structure. Brain damage due to hypocalcemia is caused by binding of calcium with fluoride (Mohammadi *et al.*, 2017). A fluoride concentration of approximately  $1.0 \text{ mg L}^{-1}$  in drinking water effectively promotes the growth of healthy teeth and bones without harmful effects on health (Edmunds & Smedley, 2013; García & Borgnino, 2015).

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Because of the very narrow concentration range of fluoride that differentiate between its adverse and beneficial effects on human health, quantification of fluoride in drinking water is important to ensure good quality water (Dissanayake, 2005; De Silva *et al.*, 2020). Fluoride in different sample matrices has been quantified by a variety of analytical methods including gravimetric (Shell & Craig, 1954), volumetric (Banerjee, 1955; Abramović *et al.*, 1992), polarographic (Bond & O'Donnell, 1968), potentiometric (Frant & Ross, 1968; Harwood, 1969; De Silva *et al.*, 2020; Stonebridge *et al.*, 2020), colorimetric (Mesdaghinia *et al.*, 2010; Karimi *et al.*, 2018; Prasad *et al.*, 2018) and chromatographic (Szmagara & Krzyszcak, 2019) methods. The analytical methods based on flow injection analysis have also been reported in literature (Shimada *et al.*, 2005; van Staden & Stefan-van Staden, 2010). A good review of the recent developments in fluoride analytical techniques has been done by Yahyavi and coworkers (Yahyavi *et al.*, 2016). The popular SPADNS colorimetric method recommended for the analysis of fluoride in water and wastewater by the American Public Health Association (APHA) is based on the reaction between fluoride and zirconium - SPADNS dye lake (Eaton *et al.*, 2005). The bright-red SPADNS solution is mixed with colourless zirconyl solution in an acid medium to produce dark-red zirconyl - SPADNS complex. In the presence of fluoride ions, zirconyl-SPADNS complex breaks down to form stable  $ZrF_6^{2-}$ . The working fluoride concentration range of the SPADNS method is up to  $1.6 \text{ mgL}^{-1}$  (Eaton *et al.*, 2005). The SPADNS method has been used to determine the fluoride concentration in aqueous samples (Patel *et al.*, 1999; Rafati *et al.*, 2013; Somasundaram *et al.*, 2015; Karimi *et al.*, 2018), and in food and beverages (Marier & Rose, 1966). The SPADNS method is usually carried out in 0.7 M HCl because at this pH, the reaction between Zr(IV) and SPADNS dye is very rapid and also eliminate interferences from alkalinity, Fe(III) and chloride ions (Bellack & Schouboe, 1958). The Eriochrome Cyanine R (ECR) based colorimetric method was once a popular colorimetric method for fluoride analysis (Megregian, 1954; Dixon, 1970; Lenarczyk & Marczenko, 1986). Currently it is used in certain types of field portable photometers that uses powder-pillow reagents for fluoride analysis (Gül *et al.*, 2014). The ECR method has been used to determine the fluoride concentration in aqueous samples (Sarma, 1964; Dixon, 1970; Lenarczyk & Marczenko, 1986) and in urine (Megregian, 1954; Rowley & Farrah, 1962). According to the literature, Zr: ECR ratio of 1:4 is favourable in the analysis and maintaining an acidity higher 0.1 M HCl is important to prevent other metal ions such as Fe(III), Al(III) and Pb(II) reacting with Eriochrome Cyanine R to produce coloured complexes (Megregian, 1954).

The quantification of fluoride in different sample matrices can be analytically challenging because fluoride is present as free and complex bound fluoride in samples. The quantification of total fluoride requires the breakdown of complex bound fluoride to free fluoride. It has been reported that  $Ca^{2+}$ ,  $Fe^{3+}$ ,  $Al^{3+}$ , and  $Mg^{2+}$  can significantly interfere with fluoride analysis by forming strong metal-fluoro complexes (Devine & Partington, 1975; Nicholson & Duff, 1981; Frenzel & Brätter, 1986; Patel *et al.*, 1999). The potentiometric method uses strong metal chelating ligands such as (cyclohexylenedinitrilo)tetraacetic acid (CDTA) to breakdown metal-fluoro complexes in total fluoride measurements (De Silva *et al.*, 2020). In addition, higher concentrations of  $OH^-$ ,  $Cl^-$  and  $PO_4^{3-}$  also interfere due to the poor selectivity (Devine & Partington, 1975; Frenzel & Brätter, 1986; Patel *et al.*, 1999). It is generally recommended to perform acid distillations of the sample prior to the analysis to eliminate or at least to reduce matrix interferences. The classical Willard and Winter distillation method to separate fluoride from the sample matrix involves acid distillation with a strong non-volatile acid such as  $H_2SO_4$ . It is a slow and lengthy process which takes about 80 minutes per sample (Patnaik, 2010). Moreover, this method requires extreme care and a strict temperature control to prevent liberation of hazardous HF gas to the environment. As a result, almost all the fluoride analyses in natural waters reported in the literature have been carried without the distillation step (Chandrajith *et al.*, 2012; Jayawardana *et al.*, 2012; Karimi *et al.*, 2018). Every analytical method has its own advantages, limitations, and interferences. Therefore, depending on the sample matrix, different analytical methods will produce fluoride concentrations that may be statistically comparable or incomparable to each other. Often, a single analytical method has been used in fluoride analyses (Msonda *et al.*, 2007; Jayawardana *et al.*, 2012; Yeşilnacar *et al.*, 2016; Yadav *et al.*, 2019); however, it is not uncommon to use two or more techniques to analyse fluoride and to use pooled data as a single data set for interpretation (Chandrajith *et al.*, 2012). The combination of fluoride concentration data obtained from two or more analytical techniques as a single data set for interpretation may be problematic if the methods produce statistically incomparable data.

The main objective of this research is to statistically evaluate comparability of the fluoride concentrations determined by two colorimetric methods: SPADNS and ECR methods. In addition, the effect of  $Ca^{2+}$ ,  $Mg^{2+}$  and  $Al^{3+}$  on the accuracy of the methods was evaluated with the use of  $0.85 \text{ mg L}^{-1}$  standard fluoride solutions

fortified with the above-mentioned metal ions. Finally, the acid distillation method was evaluated as an intervention to overcome the interferences from the above-mentioned metal ions.

## MATERIALS AND METHODS

All calibration standards and other reagents were prepared using analytical grade chemicals and 18.2 M $\Omega$  deionized water. Twenty (20) natural water samples were collected from different geographical areas of Sri Lanka in pre-cleaned polyethylene bottles and stored at 4 °C in a refrigerator. The conductivity and pH of the samples were measured using a DDSJ-308A conductivity meter and a MP103 pH meter, respectively. The concentrations of Ca, Mg, and Al were determined using a Thermo Scientific iCE 3000 series Atomic Absorption Spectrometer in flame and graphite modes. The concentration of anions: Cl<sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, and SO<sub>4</sub><sup>2-</sup> were determined using a Metrohm 930 Compact IC Flex instrument. The instrument uses a Metrosep Supp 5–250/4.0, 250 × 4.0 mm separation column in the suppressed conductivity mode. The eluent was a mixture of 3.2 mmol L<sup>-1</sup> Na<sub>2</sub>CO<sub>3</sub>, and 1.0 mmol L<sup>-1</sup> NaHCO<sub>3</sub> and the eluent flow rate was 0.70 mL min<sup>-1</sup> at 35 °C. The sample injection loop was 20  $\mu$ L.

The fluoride concentration in water samples were determined by two analytical methods: Eriochrome Cyanine R- based photometric (ECR), and SPADNS (SPA) colorimetric methods. In the ECR method, a field portable photometer and power-pillow reagents were used as in the case fluoride is determined in the field. The method uses 10.0 mL of the sample, Palintest YAP179 reagent and a YSI 9500 photometer. The YSI 9500 photometer gives a direct concentration readout and it is with an internal calibration in a linear range up to 1.5 mg L<sup>-1</sup> of fluoride. It operates at wavelengths of 445  $\pm$  5 nm, 495  $\pm$  5 nm, 555  $\pm$  5 nm, 570  $\pm$  5 nm, 605  $\pm$  5 nm and 655  $\pm$  5 nm. According to Megregian (1954), Zirconium–Eriochrome Cyanine R Lake dye has a maximum absorbance between 525 to 530 nm; however, due to the limited availability of wavelengths in photometers, the fluoride analysis by ECR was carried out at 555  $\pm$  5 nm. Most of the direct read field portable photometers are capable of analysing more than dozens of water quality parameters and the wavelength selection for a particular analysis is automated based on the selection of the water quality parameter. The YSI 9500 photometer use cylindrical 20 mm outer diameter optical glass cells with 10.0 mL internal volume as the sample holder. The photometer was used with manufacturer's default calibration which was corrected using standard fluoride solutions of 0.20, 0.60, and 1.00 mg L<sup>-1</sup> concentrations. The experiment was triplicated. The zirconyl-acid reagent for the SPADNS method was prepared using zirconyl chloride octahydrate and concentrated hydrochloric acid. The SPADNS reagent was prepared using sulphanilic acid azochromotrop and distilled water. Then equal volumes of zirconyl-acid reagent and SPADNS reagent were mixed to prepare the zirconyl-SPADNS reagent. The calibration curve was prepared in the range from 0.0 to 1.40 mg L<sup>-1</sup>. The method is explained in detail in APHA (2005) (Eaton *et al.*, 2005). The absorbance was recorded at 570 nm with a Thermo Fisher Scientific GENESYS 10S UV-Vis Spectrophotometer. Samples were diluted with deionized water when necessary. All the analyses were carried out in triplicate. The performance of the calibration was evaluated with a different set of standard fluoride solutions of 0.20, 0.60, and 1.00 mg L<sup>-1</sup> concentrations that was used to evaluate the performance of the YSI 9500 photometer. The experiment was triplicated.

The interference of Ca<sup>2+</sup>, Mg<sup>2+</sup> and Al<sup>3+</sup> on the determination of fluoride by the above-mentioned analytical methods was assessed as follows. Three series of 0.85 mg L<sup>-1</sup> fluoride solutions were prepared with variable amounts of Ca<sup>2+</sup>, Mg<sup>2+</sup> and Al<sup>3+</sup> ions in the solution. The Mg<sup>2+</sup>, Ca<sup>2+</sup> and Al<sup>3+</sup> solutions were prepared using analytical grade MgSO<sub>4</sub>, CaCl<sub>2</sub> and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. The first and second series of fluoride solutions contained Mg<sup>2+</sup>, and Ca<sup>2+</sup> in the concentration range from 0.50 to 100.0 mg L<sup>-1</sup>. The third series contained Al<sup>3+</sup> in the concentration range from 0.10 to 20.0 mg L<sup>-1</sup>. The solutions were kept for 24 h to attain equilibrium and then analysed for fluoride. All the analyses were triplicated.

The fluoride was separated from the matrix using the acid distillation method as described in detail in APHA (2005) with minor modifications (Eaton *et al.*, 2005). Three (03) natural water samples and several 0.85 mg L<sup>-1</sup> fluoride solutions containing Ca<sup>2+</sup>, Mg<sup>2+</sup> and Al<sup>3+</sup> were analysed by the ECR and SPA methods before and after acid distillation. All the analysis was triplicated. The triplicate measurements obtained using the two methods were statistically compared to determine whether they are the same or different. The standard deviation of the triplicate measurements was very small or zero for most of the results because triplicate measures produced the

same or very close values. Therefore, paired t test for comparing individual differences were used even though all the experiments were triplicated. The t calculated ( $t_{cal}$ ) values were compared with the t tabulated ( $t_{tab}$ ) values at 95% confidence level.

## RESULTS AND DISCUSSION

The default internal calibration of the YSI 9500 photometer (ECR method) and the calibration of the SPANDS (SPA) method were re-evaluated with a different set of standard fluoride solutions and the experimental data is illustrated in Table 1. The SPA method produced experimental fluoride concentrations identical to the theoretical values (expected values); however, the ECR method overestimated the fluoride concentration. The ECR method used the default calibration accompanied with the YSI 9500 photometer.

**Table 1:** The evaluation of calibration using the standard fluoride solutions

Theoretical fluoride concentration (mg/L)	Fluoride concentration reported by the methods mg L <sup>-1</sup>	
	ECR	SPA
0.20	0.21	0.20
0.60	0.63	0.60
1.00	1.06	1.00

The fluoride concentration and other physico-chemical characteristics of the natural water samples are shown in Table 2. The percentage standard deviation of the triplicate measurements was always within  $\pm 5\%$  and therefore, standard deviations of triplicate measurements (errors) were not included in fluoride concentrations. According to the SPADNS (SPA) method, the fluoride concentration varied between 0.13 to 3.36 mg L<sup>-1</sup>. In addition, the Ca, Mg and Al concentrations were in the range of 0.19 to 120.8 mg L<sup>-1</sup>, 3.51 to 59.06 mg L<sup>-1</sup> and 0.05 to 6.55 mg L<sup>-1</sup>, respectively. The chloride and sulphate concentrations were in the range of 8.8 to 601.5 mg L<sup>-1</sup> and 1.46 to 298.3 mg L<sup>-1</sup>, respectively. The phosphate concentration of the samples was very low except in samples #9, #11 and #12 with concentrations of 0.44, 0.27 and 1.12 mg L<sup>-1</sup>, respectively.

**Table 2:** The fluoride concentration and other physico-chemical characteristics of natural water samples

Sample no.	pH	EC $\mu\text{S cm}^{-1}$	Fluoride mg L <sup>-1</sup>		Concentration mg L <sup>-1</sup>					
			SPA	ECR	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Al <sup>3+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	PO <sub>4</sub> <sup>3-</sup>
1	8.16	634.3	0.66	0.56	5.39	59.06	0.26	63.5	24.3	N/D
2	8.27	471.6	0.93	0.76	5.32	14.64	0.41	18.5	28.4	N/D
3	7.65	743.5	0.62	0.57	1.41	30.05	0.23	81.1	23.3	N/D
4	8.02	793.8	0.13	0.10	3.23	5.50	4.19	23.5	31.2	N/D
5	7.04	363.2	0.26	0.22	42.29	15.27	1.04	96.5	29.6	N/D
6	8.02	793.8	2.63	2.43	4.77	3.83	0.05	23.2	31.2	N/D
7	8.14	856.3	1.08	0.92	0.19	4.75	0.09	111.7	52.2	N/D
8	7.02	126.0	0.21	0.21	22.21	31.44	6.55	18.3	1.5	N/D
9	7.55	363.2	0.55	0.48	15.12	20.97	0.16	107.6	18.4	0.44
10	7.29	237.6	0.21	0.22	30.91	26.28	4.74	15.1	5.5	N/D
11	7.36	254.0	0.57	0.47	39.18	31.57	0.66	27.9	8.4	0.27
12	7.07	1,500.0	1.24	1.09	0.09	7.21	0.06	365.8	42.4	1.12
13	7.80	353.0	0.36	0.35	43.21	28.86	1.55	27.4	10.7	N/D
14	8.22	401.0	0.60	0.60	9.85	30.34	0.53	31.2	22.2	N/D
15	7.89	891.0	0.60	0.50	8.10	32.62	0.55	328.3	58.5	N/D
16	7.56	1,810.0	1.11	1.16	93.93	34.13	0.08	601.5	298.3	N/D
17	7.33	630.0	0.69	0.57	120.8	50.77	1.89	12.8	5.5	N/D
18	7.26	570.1	3.36	2.87	7.91	3.51	0.10	8.8	4.0	N/D
19	8.00	1,087.0	0.92	0.77	15.63	15.43	1.20	382.2	58.0	N/D
20	7.15	58.4	0.86	0.71	23.26	31.00	2.18	12.1	5.1	N/D

N/D: not detected

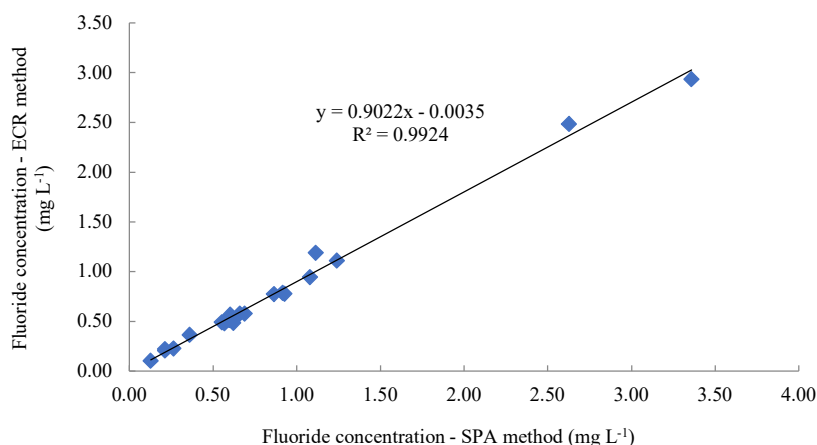
A brief description of the natural water samples analysed in this study is given in Table 3.

**Table 3:** Details of the natural water samples analysed in the study.

Sample no.	Sample location	Source of water
1	Kurunegala	Bore well
2	Eheliyagoda	Bore well
3	Dambulla	Bore well
4	Raththota	Spring
5	Horton Plains	Waterfall
6	Trincomalee	Bore well
7	Puttalam	Bore well
8	Nuwara Eliya	Spring
9	Badulla	Bore well
10	Rathnapura	Waterfall
11	Matara	Bore well
12	Embilipitiya	Bore well
13	Kalupahana	Waterfall
14	Kohuwala	Bore well
15	Matale	Spring
16	Galle	Bore well
17	Negambo	Bore well
18	Polonnaruwa	Reservoir
19	Daagonna	Bore well
20	Vavuniya	Bore well

The ion chromatographic (IC) method was also used to obtain the concentration of fluoride ions; however, the fluoride data produced by the IC method was not used in this study due to the appearance of the negative dead volume peak close to the fluoride peak in some of the chromatograms. This issue is documented in literature. The overlap of the dead volume peak with fluoride peak distorts the original shape of the fluoride peak, making it difficult to integrate. This may lead to inaccurate fluoride concentrations reported by the IC method (Roden & Tallman, 1982; Saari-Nordhaus *et al.*, 1994).

According to the experimental data, higher fluoride concentrations were mostly (85 %) produced by the SPA method except for the samples #10, and #16. Samples #8 and #14 produced identical values from the two methods. There is a strong correlation ( $r^2 = 0.99$ ) between fluoride concentrations determined by the SPA and ECR methods as shown in Figure 1. These two analytical methods are based on the same working principle, where a metal-dye complex breakdown in the presence of fluoride ions due to the formation of much stable metal-fluoro complexes. As a result, it can be expected that SPA and ECR methods are subjected to similar matrix interferences.



**Figure 1:** A graphical comparison of the fluoride concentrations determined by the SPA and ECR methods. The solid line represents the linear regression curve

The paired t test for comparing individual differences was applied to the two datasets to determine whether they are the same or different at 95 % confidence level. The calculated t value is 4.16 and the tabulated t value is 2.086, making  $t_{\text{cal}} > t_{\text{tab}}$ . Therefore, it can be concluded that the two datasets are different, and the two analytical methods have generated two statistically different fluoride concentrations for the twenty natural water samples. Correlation analysis showed that the fluoride concentration determined by the SPA method negatively correlated with the concentration of  $\text{Al}^{3+}$  (-0.465),  $\text{Mg}^{2+}$  (-0.449), and  $\text{Ca}^{2+}$  (-0.172) and the fluoride concentration determined by the ECR method negatively correlated with that of  $\text{Al}^{3+}$  (-0.465),  $\text{Mg}^{2+}$  (-0.440) and  $\text{Ca}^{2+}$  (-0.147). The negative correlation with metal ions is most likely due to the formation of metal-fluoro complexes. The correlation also strongly agrees with the studies done with the standard fluoride solutions spiked with metal ions and a summary of data is given in Table 4.

It was assumed that the observed differences in fluoride concentration measured by the SPA and ECR methods are most likely due to the presence of various amounts of  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$  in water samples. In order to investigate the validity of this hypothesis, 0.85 mg L<sup>-1</sup> standard fluoride solutions were spiked with different amounts of  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$  and then analysed for the fluoride concentration using the above-mentioned colorimetric methods. The experimental data are summarized in Table 4.

A careful look at the experimental data reveals that both ECR and SPA methods produce fluoride concentrations statistically comparable to the true value only at very low  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$  concentrations. The highest interference was observed with  $\text{Al}^{3+}$  ions, which underestimated the fluoride concentration obtained using ECR, and SPA methods by 26%, and 23% respectively at 20.0 mg L<sup>-1</sup>  $\text{Al}^{3+}$  concentration when compared to the theoretical value. In contrast, the interference was minimum with  $\text{Ca}^{2+}$  ions. It underestimated the fluoride concentration by a maximum of 8% at 100.0 mg L<sup>-1</sup>  $\text{Ca}^{2+}$  concentration for the ECR method. The percentage underestimation was 7% for the SPA method at 100.0 mg L<sup>-1</sup>  $\text{Ca}^{2+}$  concentration. There is a pronounced underestimation of the fluoride concentration even at low concentrations of  $\text{Mg}^{2+}$ . The interferences caused by metal ions on the determination of fluoride is mainly due to the formation of stable metal-fluoride complexes that are not easily decomplexed to release free fluoride ions that need to be determined by the analytical methods. The metal-fluoride complexes such as  $\text{AlF}_4^-$  ( $K_f = 1.26 \times 10^{19}$ ),  $\text{CaF}_2(\text{s})$  ( $K_f = 2.50 \times 10^{10}$ ) and  $\text{MgF}_2(\text{s})$  ( $K_f = 1.58 \times 10^8$ ) are stable (Stumm *et al.*, 1996) and the method using ion selective electrode for fluoride analysis use strong metal chelating agents such as CDTA to decomplex metal-fluoro complexes (De Silva *et al.*, 2020). However, in colorimetric methods such as SPADNS and Eriochrome Cyanine R methods, decomplexation of metal-fluoro complexes is determined by the relative stabilities of these complexes and  $\text{ZrF}_6^{2-}$ . Therefore, interferences caused by metal ions at higher concentrations are non-negligible for the determination of fluoride by colorimetric methods. In addition to making complexes with fluoride ions, certain metal ions such as Fe(III) make stable complexes with the Eriochrome cyanine R and SPADNS dyes and the metal-dye complexes absorb light at different wavelengths making the colorimetric method more complicated (Langmyhr & Stumpe, 1965, Hulanicki *et al.*, 1983). Moreover, dissolved organic compounds such as fulvic and humic acids can interfere with colorimetric method by either complexing with the Zr(IV) or producing a colour that overlaps with the analytical wavelengths.

The observed interferences from  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$  cannot be used as it is to explain the experimental data given for natural water samples in Table 1. The matrix of natural water samples is more complicated than fluoride standard solutions due to the presence of organic matter, and a variety of cations and anions that could interfere with fluoride analysis. In general, natural water samples containing high concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$  resulted in significantly different fluoride concentrations reported by SPA and ECR methods. Some of the examples to support this observation include samples #1, #11, #15, and #19. It should be noted that, this statement cannot be generalized for all the samples because there are deviations from this observation such as in samples #6 and #20 where significantly different fluoride concentrations were reported by the ECR and SPA methods even though the  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Al}^{3+}$  concentrations are comparatively lower.

To determine the efficiency of the acid distillation method to overcome the interferences by  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$  ions on the determination of fluoride by the ECR, and SPA methods, standard fluoride samples spiked with these metal ions were analysed for fluoride ions before and after the acid distillation step. The experimental data are given in Table 4.

**Table 4:** Fluoride concentration of the 0.85 mg L<sup>-1</sup> standard fluoride solutions spiked with the selected metal ions before and after the acid distillation (AD) step

Metal ion concentration (mg L <sup>-1</sup> )	Fluoride concentration mg L <sup>-1</sup>			
	ECR		SPA	
	Before AD	After AD	Before AD	After AD
Mg <sup>2+</sup>				
0.5	0.82	0.87	0.79	0.88
10.0	0.79	0.87	0.77	0.88
60.0	0.78	0.83	0.76	0.88
100.0	0.67	0.82	0.73	0.87
[Ca <sup>2+</sup> ]				
0.5	0.86	0.87	0.83	0.88
10.0	0.83	0.87	0.82	0.88
60.0	0.81	0.87	0.82	0.88
100.0	0.78	0.83	0.79	0.87
[Al <sup>3+</sup> ]				
0.5	0.82	0.86	0.81	0.88
8.0	0.71	0.82	0.73	0.86
20.0	0.63	0.76	0.65	0.83

AD: Acid distillation

The experimental data showed that the measured fluoride concentration of the standard solutions spiked with Ca<sup>2+</sup>, Mg<sup>2+</sup> and Al<sup>3+</sup> increased after the acid distillation. With acid distillation, the samples spiked with Ca<sup>2+</sup> and Mg<sup>2+</sup> in the range of 0.50 to 100.0 mg L<sup>-1</sup> reached their theoretical concentration of 0.85 mg L<sup>-1</sup>. Acid distillation also worked well for the Al<sup>3+</sup>-spiked standard solutions except at 20 mg L<sup>-1</sup>. The efficiency of the acid distillation method was also tested with three (03) natural water samples and the experimental data is shown in Table 5. The fluoride concentration of the natural water samples determined by the analytical methods also increased significantly after the acid distillation as observed for the fluoride standard solutions. It should be noted that even after the acid distillation, the fluoride concentration from the two methods were not statistically comparable.

**Table 5:** Effect of acid distillation on natural water samples

Sample ID	Metal concentration (mg L <sup>-1</sup> )			Fluoride concentration (mg L <sup>-1</sup> )			
	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Al <sup>3+</sup>	ECR		SPA	
				Before AD	After AD	Before AD	After AD
A	30.45	10.72	0.65	0.08	0.08	0.04	0.09
B	31.57	39.18	0.66	0.47	0.59	0.51	0.71
C	7.20	0.09	0.06	1.09	1.29	1.19	1.49

AD: Acid distillation

It has been well documented that, high concentrations of organic matter, Fe<sup>3+</sup>, Al<sup>3+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, OH<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> can either underestimate or overestimate the fluoride concentration (Eaton *et al.*, 2005). The ECR colorimetric method has higher interferences from Fe<sup>3+</sup>, PO<sub>4</sub><sup>3-</sup> and Al<sup>3+</sup> ions than the SPADNS method (Megregian, 1954). It can be assumed that a specific analytical method determines free fluoride and a fraction of complex bound fluoride. The extent of complex-bound fluoride analysed by a method will depend on the chemistry of the method. The SPANDS, ECR and IC colorimetric methods use the kinetics of ligand exchange to free complex-bound fluorides (Megregian, 1954; Banerjee, (1955); Devine & Partington, 1975; Lenarczyk & Marczenko, 1986; Hatsis & Lucy, 2001) and the potentiometric method depends on strong metal chelating ligands to free complex-bound fluorides (Nicholson & Duff, 1981; De Silva *et al.*, 2020). It is almost impossible to obtain statistically comparable fluoride concentrations using different analytical techniques if the sample matrix is complicated. This is mainly due to the unique set of interferences encountered by an analytical technique at a given sample matrix. As a result, careful attention must be paid when fluoride concentrations determined by different techniques are pooled together as a single dataset for interpretations.

The fluoride concentrations determined by the two methods produced slightly different concentrations for 0.85 mg/L fluoride standard solutions in the absence of metals ions: Ca<sup>2+</sup>, Mg<sup>2+</sup> and Al<sup>3+</sup>. The SPA method accurately determined the fluoride concentration as 0.85 mg/L; however, the ECR method determined it as 0.87 mg/L which differed from the theoretical value by 0.02 mg/L. This difference could have been negligible if the

random error of the repeated measurements were large for the SPA and ECR methods. However, the random error of the repeated measurements was very small for both methods and the percentage standard deviation of the triplicate measurements were always within  $\pm 5\%$ . As a result, whatever the differences in fluoride concentrations determined by the two techniques have to be caused by systematic and gross errors. The probability of having gross errors in the experimental data is small because all the analyses were done with utmost care. The best method to identify systematic errors in an analytical method is by the method validation using standard reference materials (SRMs). Due to the unavailability of a suitable SRM, method validation was not done for both SPA and ECR methods. However, the SPA method was performed as described by APHA (2005) (Eaton *et al.*, 2005) and the ECR method was performed as described in the User Manual of YSI 9500 photometer. The differences observed in the fluoride concentrations by the two analytical methods could have been caused by the instruments used in the experiment. The SPA method used a sophisticated spectrophotometer to measure the absorbance while the ECR method used a photometer for the same purpose. Spectrophotometers have high-end optics, light sources, and detectors to accurately measure the absorbance or emission at a given wavelength. Photometers, in contrast, use filters instead of monochromators to isolate wavelengths. Often, because of the availability of limited number of wavelengths for analysis by the light sources, the analysis is not carried out using the optimum wavelengths suitable for analysis. As a result, concentrations of analytes obtained by spectrophotometers are more accurate than photometers.

There are a few limitations to this study. A more accurate picture of the two analytical methods can be obtained by analysing more samples from a wide variety of natural sources. Unfortunately, the number of samples had to be limited to 20 due to the limited availability of YAP179 reagent. In addition, interferences from  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{PO}_4^{3-}$  need to be investigated. Most importantly interference from different combinations of cations and anions such as phosphate has to be investigated using standard fluoride solutions.

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## CONCLUSIONS

In this research, SPADNS (SPA) and Eriochrome Cyanin R (ECR) colorimetric methods were used to determine fluoride concentrations in twenty natural water samples. The fluoride concentration data were statistically evaluated by the paired t test for comparing individual differences to determine whether the two datasets are statistically the same or different at 95 % confidence level. According to the t test, the two datasets are different suggesting that the two analytical methods produce statistically different fluoride concentrations for the same water samples. However, there is a very strong correlation between the fluoride concentrations determined by the SPA and ECR methods with a correlation coefficient ( $r^2$ ) of 0.99. It was assumed that the different fluoride concentrations were produced due to the presence of interfering chemical species in the test samples. The potential interferences by  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  on the fluoride analysis were evaluated using  $0.85 \text{ mg L}^{-1}$  fluoride standard solutions spiked with various amount of these metal ions. The highest interference was observed with  $\text{Al}^{3+}$  ions, which underestimated the fluoride concentration obtained using ECR and SPA methods by 26 % and 23 % respectively at  $20.0 \text{ mg L}^{-1}$   $\text{Al}^{3+}$  concentrations. The interference was minimum for  $\text{Ca}^{2+}$  ions. The presence of  $\text{Ca}^{2+}$  underestimated the fluoride concentration by 8 % at  $100.0 \text{ mg L}^{-1}$  concentration. After acid distillation, the fluoride standard solution spiked with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the range of 0.50 to  $100.0 \text{ mg L}^{-1}$  reached its theoretical concentration of  $0.85 \text{ mg L}^{-1}$ . Acid distillation also worked well for the  $\text{Al}^{3+}$ -fortified samples, except for the  $\text{Al}^{3+}$  concentration of  $20 \text{ mg L}^{-1}$ . The efficiency of the acid distillation method was also tested with three (03) natural water samples. The fluoride concentration increased significantly after the acid distillation; however, even after the acid distillation, statistically comparable fluoride concentrations were not observed. Currently colorimetric methods are hardly used to determine fluoride concentrations in aqueous samples due to interferences from many common cations and anions present in natural systems. Furthermore, colorimetric methods are time consuming and also suffer from poor sensitivity if 1.0 cm cuvettes are used to measure the absorbance. It is always better if acid digestion is carried out before the sample analysis if the concentration of interfering ions such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$  are present at elevated concentrations. In addition, for large scale environmental studies, it would be better if fluoride concentrations determined using colorimetric methods are statistically compared with other standard methods for fluoride analysis that include ion chromatography and ion selective electrode methods.



## Supplementary data

All the necessary analytical data is included in the manuscript. Addition experimental data can be requested through the corresponding author.

## Conflict of interest

The authors declare that they have no known competing financial interest or personal relationship that could have appeared to influence the work reported in this paper.

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