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Spectrophotometric methods for the determination of fluoride ion using indole-3-acetic acid interaction with iron(III)

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Abstract: This study is related to the determination of fluoride ion by the conversion of pink-colored Fe(III) and indole-3-acetic acid (IAA) into a colorless hexafluoride ferrite complex with the addition of fluoride. The optimum conditions of the complex formation were found to be pH 1.7 and a temperature of 60 °C. The maximum absorption wavelength of the complex and the detection limit of the method were 525 nm and 0.26 mg/L, respectively. The interfering effects of the different cations (Ag^+, Al^{3+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, K^+, Mg^{2+}, Na^+, Ni^{2+}, Pb^{2+}) and anions (SO_4^{2-}, SO_3^{2-}, NO_2^-, I^-, Br^-, Cl^-, SCN^-, CH_3COO^-, $H_2PO_4^-$, ClO_4^-) were also investigated. The method was applied to standard and real samples and the resulting data were statistically compared at a confidence level of 95% with those obtained with the use of a fluoride-selective electrode.

Key words: Fe(III) indole-3-acetic acid complex, fluoride, spectrophotometric method

1. Introduction

Fluoride ions are present in almost all media at low concentrations. That is why the analysis of fluoride at low concentrations is of great importance. There are two main methods related to the determination of fluoride ions proposed in literature, namely the use of fluoride-selective electrodes[1,2] and the use of spectroscopic methods.[3,4] Among other methods that could be employed in fluoride determination are fluorometry,[5] ion chromatography, gas chromatography, capillary zone electrophoresis, radio analysis,[6] and inductively coupled plasma atomic emission spectrometry.[7]

The areas in which ion-selective electrodes are commonly used are fluoride determination in tea,[8] food,[9,10] protective dentistry materials,[11–13] waters,[14–16] atmosphere,[17] serum, blood, urine,[18,19] and coal.[20,21] Spectroscopic methods are equally applicable in fluoride determinations in various water samples,[22–26] plants,[27] protective dentistry materials,[28] silicone grease,[29] and samples prepared in the laboratory.[30]

Ion-selective electrodes have certain advantages such as the ease of applicability and shorter analysis time.[12,17–19]

However, since the electrodes have certain lifetimes, their use in routine analysis may be quite costly. On the other hand, although the analysis time is longer, the spectroscopic methods have the advantage of constant applicability. There are many studies based on the use of different complexing agents in spectroscopic fluoride detection. Studies including aluminium-resorcin[4] and thorium phenyl fluorone[22] are common examples.

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Fluoride ions occupy an important place in regard to human health. They are particularly popular in protective dentistry. Fluoride ions are present in certain amounts in mouthwash solutions, toothpastes, and some chewing gums. The human body needs a certain amount of fluoride. Drinking water must also contain a certain amount of fluoride ions. If the water lacks fluoride ions it must be supplemented with them.[6,14–16,25] However, excessive intake of fluoride ions has an adverse effect on human health.[6,15,17,20,27] To control all these parameters is only possible with a detailed fluoride analysis. That is why there is an urgent need for developing easily applicable and cost-effective fluoride analysis methods.

The indole-3-acetic acid (IAA) used in the method is an easily available, cheap, and popular plant hormone, which plays an important role in the development of the roots of plants.[31,32] IAA is known to form a complex with Fe(III) ions.[33] The complex formed is highly stable and the absorbance value remains constant during measurements.

This study deals with the applicability of the newly developed method to fluoride-containing matrices.

2. Results and discussion

2.1. The determination of optimum conditions of Fe(III)-indole-3-acetic acid complex

2.1.1. The determination of maximum adsorption wave length

Two milliliters of 2×10^{-3} M indole-3-acetic acid solution and 1 mL of 1×10^{-3} M $FeCl_3$ solution were mixed in a glass tube. The resulting mixture was kept in a water bath at 50–60 °C for 10 min and its UV spectra were taken against the experimental solution between 700 and 200 nm (Figure 1). The maximum absorption wavelength was found to be 525 nm.

2.1.2. Determination of pH effect

The pH range in which the complex that formed between Fe^{3+} ions and indole-3-acetic acid gave the highest absorption value at the working wavelength was determined. The complex was formed between pH 1.0 and 2.5 with the use of 0.14 M HCl and 0.5 M NaOH. It was found that the complex gave the maximum adsorption in the pH range of 1.5–2.0 and dissociated at higher pH values. The complex had a pink color at pH 1.5–2.0 and turned yellow at higher pH values. The adsorption values of the complex are plotted against pH values in Figure 2. The working wavelength of the complex was chosen as 525 nm, where neither Fe^{3+} ions nor indole-3-acetic acid caused any absorption.

2.1.3. Determination of the complex formation temperature

In order to determine the optimum formation temperature of the complex formed between Fe^{3+} and indole-3-acetic acid, eight 25-mL tubes were taken. One of the tubes was filled with 2 mL 1×10^{-3} M Fe^{3+} and 2 mL 2×10^{-3} M indole-3-acetic acid solutions and its pH value was adjusted to 1.7. The tube was kept in a water bath at 40 °C for 10 min and its absorbance value at the working wavelength was measured. Using other tubes, the same procedure was repeated at 45 °C, 50 °C, 55 °C, 60 °C, and 65 °C. The complex was observed to give the maximum absorbance at 60 °C. The absorbance values showed a decrease above this temperature. Figure 3 illustrates the relation between the absorbance values and temperature.

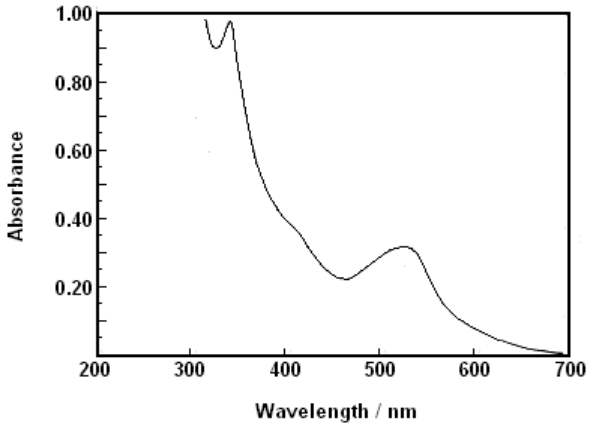

Figure 1. The UV spectrum of the complex structure formed between Fe^{+3} and indole-3-acetic acid (Fe^{+3}: 2×10^{-3} M, indole-3-acetic acid: 1×10^{-3} M).

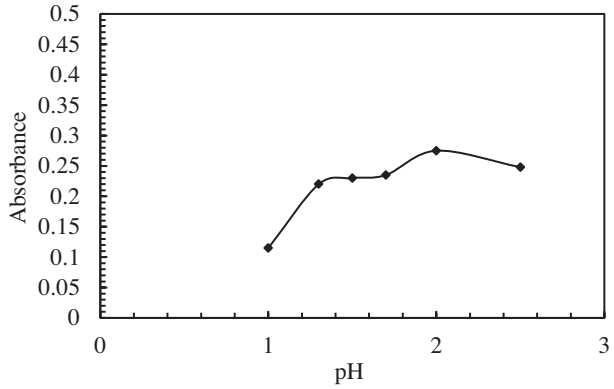

Figure 2. The absorption of complex solution against pH at 525 nm.

2.1.4. Determination of the stoichiometry of the complex

The stoichiometry of the complex was determined by Job's method. The solutions were prepared by taking different volumes of Fe^{3+} and indole-3-acetic acid at equal concentrations (6.6×10^{-3} M), keeping the total volume constant. The absorbance values of the solutions at the working wavelength were measured at optimum pH and temperature values. The stoichiometry of the complex formed between Fe^{3+} and indole-3-acetic acid was found as 1:2 (Table 1). This value was found as 3.3:6.7 from the graph of ligand volume against absorption (Figure 4).

Table 1. The determination of the stoichiometry of the complex formed between Fe^{3+} and indole-3-acetic acid by use of Job's method ($\lambda =$ 525 nm; pH 1.7; t = 60 °C).

Fe^{3+} (6.6×10^{-4} M) volume (mL)	Indole-3-acetic acid (6.6×10^{-4} M) volume (mL)	Absorbance
1	9	0.073
2	8	0.147
3	7	0.187
4	6	0.174
5	5	0.147
6	4	0.084
7	3	0.038
8	2	0.013
9	1	0.005

2.1.5. Plotting the calibration curve

A calibration plot was drawn based on the dissociation of Fe^{3+} and indole-3-acetic acid with fluoride. Let us assume that the fluoride concentration we want to determine lies between 2 and 20 ppm. There were six glass tubes containing 1 mL 1.76×10^{-3} M indole-3-acetic acid, 1 mL 0.88×10^{-3} M Fe^{3+}, and 2 mL of deionized

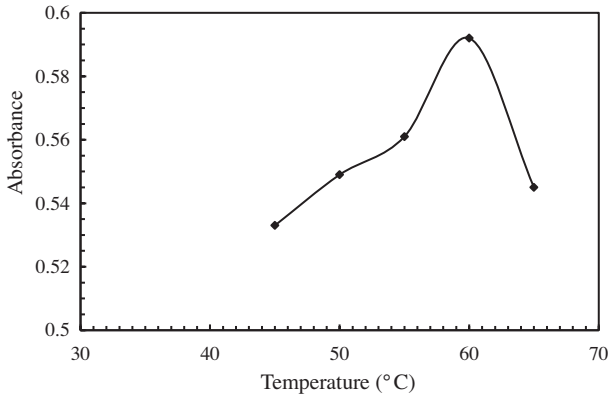

Figure 3. The change of absorbance values at 525 nm with temperature.

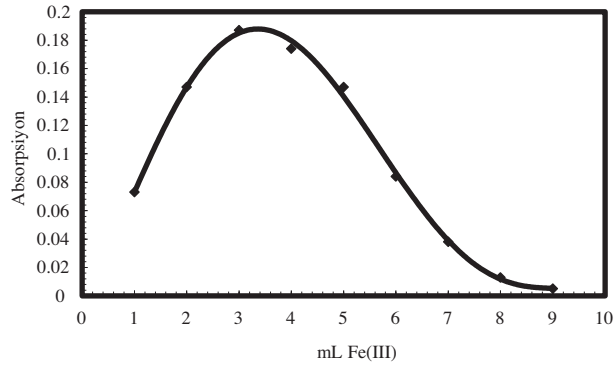

Figure 4. The determination of the stoichiometry of the complex formed between Fe^{3+} and indole-3-acetic acid by use of Job's method (λ = 525 nm; pH 1.7; [Fe^{3+}]: 6.6 × 10^{-4} M; [indole-3-acetic acid]: 6.6 × 10^{-4} M).

water. Fluoride solutions (100 ppm) of 0 mL, 0.1 mL, 0.3 mL, 0.6 mL, 0.8 mL, and 1.0 mL were added to these tubes (corresponding to 2 ppm, 6 ppm, 12 ppm, 16 ppm, and 20 ppm fluoride concentration in 5 mL). The pH of the solutions was adjusted to 1.7 and the total volume was made up to 5 mL with deionized water. The solutions were kept in a water bath at 60 °C for 10 min in order to facilitate the complex formation. The solutions were then cooled to room temperature before recording their UV spectra. The UV spectra of the solutions containing different concentrations of fluoride ion and their calibration curves are given in Figures 5 and 6.

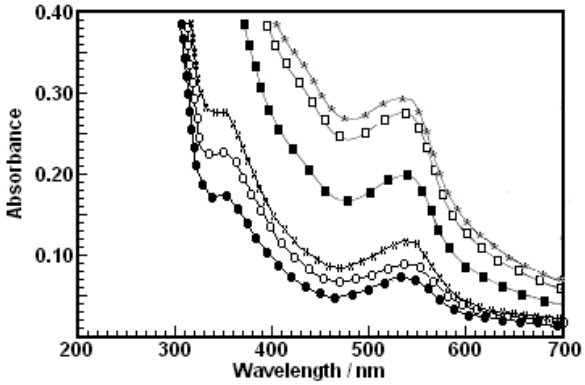

Figure 5. The UV spectra obtained by the addition of different amounts of fluoride ions to the complex structure formed between Fe^{3+} and indole-3-acetic acid (*), 0 mL F^- (□), 0.1 mL F^-(■), 0.3 mL F^- (x), 0.6 mL F^- (○), 0.8 mL F^- (×), and 1.0 mL F^- (λ = 525 nm; pH 1.7; [Fe^{3+}] = 0.88 × 10^{-3} M; $[IAA] = 1.76 \times 10^{-3}$ M).

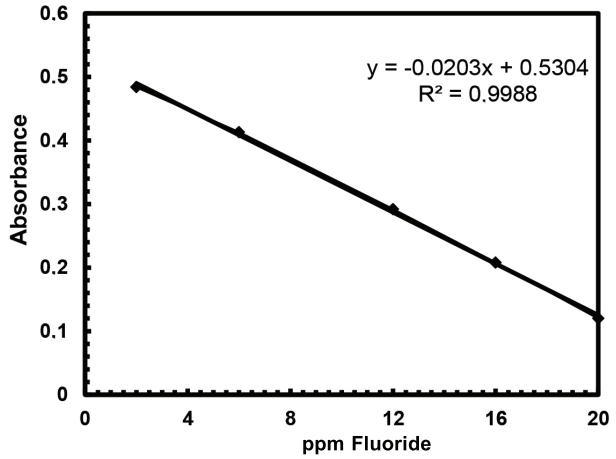

Figure 6. The calibration curve obtained for fluoride concentrations between 2.0 and 20.0 ppm (λ: 525 nm; pH 1.7; [Fe^{3+}] = 0.88 × 10^{-3} M; [IAA] = 1.76 × 10^{-3} M).

Figure 7 shows the calibration curve obtained with the addition of fluoride between 0.3 and 1.0 ppm to the complex structure formed between Fe^{3+} and indole-3-acetic acid.

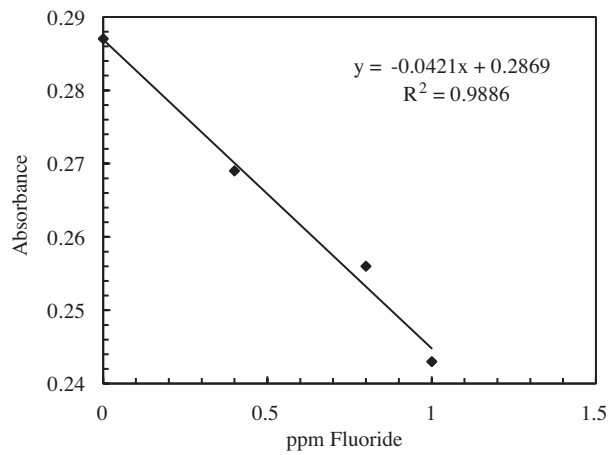

Figure 7. The calibration curve for fluoride concentrations between 0.3 and 1.0 ppm (λ: 525 nm; pH 1.7; $[Fe^{3+}] = 0.88 \times 10^{-3}$ M; $[IAA] = 1.76 \times 10^{-3}$ M).

2.1.6. Determination of the detection limit

The detection limit of the method (ΔX_{min}) was determined at 95% confidence level with the use of the data obtained from five blank experiments and five experiments with actual samples using the following formula:

$$\Delta X_{\min} = X_1 - X_b > tS_b.$$

Here S_b is the standard deviation of the blank experiments, N_1 is the number of analyses, and N_2 is the number of blank experiments.[34] The detection limit of the fluoride determination method, based upon the reaction of the Fe^{3+}-IAA complex with F^- ions, was found to be $\Delta X_{\min} = 0.26$ ppm.

2.1.7. Determination of the interfering species

Both the interfering effects of the anions and the cations upon the fluoride determination method with the use of Fe-IAA were investigated. The solutions of the interfering cations (Al^{3+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, K^+, Mg^{2+}, Na^+) and anions (NO_3^-, SO_4^{2-}, NO_2^-, I, Br^-, Cl^-, SO_3^{2-}, SCN^-, CH_3COO^-, ClO_4^-, and $H_2PO_4^-$) were prepared at concentrations of 1/10, equal, and 10 times the concentration of the Fe^{3+} present in the medium. The calibration curves were plotted as outlined in Section 2.3.5 and fluoride concentrations were determined with the analysis of standard fluoride solutions. It was determined that among the cations Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, K^+, Mg^{2+}, and Na^+ had no interfering effect while Ag^+ and Al^{3+} had an adverse effect upon the fluoride analysis. Among cations, NO_3^- SO_4^{2-}, I^-, Br^-, Cl^-, CH_3COO^-, and ClO_4^- were found to have no interfering effects, while NO_2^-, SO_3^{2-}, $H_2PO_4^-$, and SCN^- had a negative effect upon analysis.

2.1.8. Repeatability and reproducibility

Three sample sets with five replications prepared with commercial mouthwash solution were analyzed by the newly developed method for fluoride. The repeatability and the reproducibility of the method were calculated from the obtained data.[35] Hence, 0.32 and 0.42 were obtained for the 95% confidence level, respectively.

Thus, a maximum difference between the results obtained from the fluoride determinations performed by the method developed in the same laboratory can be greater than 0.32 among 20 results.

For reproducibility, a maximum difference between the results obtained in different laboratories can be greater than 0.42.

2.1.9. Analyses with ion-selective electrode sensitive to fluoride ions

The concentrations of standard fluoride solutions in the analysis were 1.0, 1.5, 2.0, 2.5, and 3 ppm, respectively. NaCl as an ionic intensity modifier and TISAB solubilizer consisting of acetic acid sodium acetate buffer were used in the measurements of cell potentials of standard solutions and sample solutions. The pH of the solutions was adjusted to 5.60. The calibration graph used in the measurement is shown in Figure 8.

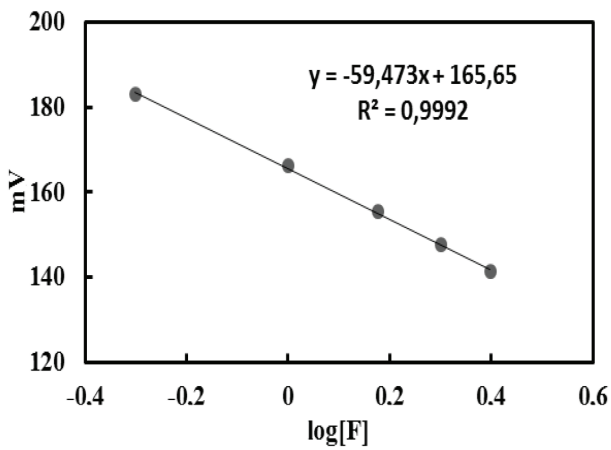

Figure 8. The calibration curve for ion-selective electrode (fluoride concentrations between 0.5 and 2.5 ppm).

2.1.10. Limit of quantification

The lower and upper limit determinations of the method were 0.26 ppm and 7.00 ppm, respectively.

2.2. Analytical application

2.2.1. Application of the method to the standard samples

The method was applied to a Flusspat III standard sample in order to determine its applicability to real samples. Using the absorption value obtained from the fluoride, the concentration was determined from the calibration. The data obtained were evaluated at 95% reliability level and are tabulated in Table 2.

Table 2. The statistical data of the results obtained from standard fluoride solutions at 95% confidence level.

μ, F^-%	$\overline{X} \pm \frac{ts}{\sqrt{N}}$	S	N	$\left\|\overline{X} - \mu\right\| < \frac{ts}{\sqrt{N}}$
44.81 Flusspat III	44.88 ± 0.19	0.27	10	0.07 <0.19
53.94 Kriyolith (IX)	54.13 ± 0.43	0.60	10	0.19 <0.43

When we look at the data given in Table 2 there is no difference between the data obtained with the method developed and the actual concentrations of the standard solutions at statistical significance at 95% confidence level.

2.2.2. Application of the method to the real samples

The method was used for the determination of the fluoride concentration of the commercially sold mouthwash solution in order to test its applicability to real samples. The fluoride concentration of the same amount of mouthwash solution was also determined with the use of fluoride-selective electrodes. The data obtained and their statistical comparison at 95% confidence level are given in Table 3.

Table 3. The statistical comparison of the data obtained for the commercial mouthwash solution and kriyolith (IX) standard sample with the spectrophotometric method developed and the fluoride-selective electrode (95% confidence level) under normality conditions.

The spectroscopic method developed				Ion-selective electrode			Comparison of both methods
	$\overline{X}_1 \pm \frac{ts}{\sqrt{N}}$	s	N	$\overline{X}_2 \pm \frac{ts}{\sqrt{N}}$	s	N	$\left\|\overline{X}_1 - \overline{X}_2\right\| < ts_b\sqrt{\frac{N_1+N_2}{N_1*N_2}}$
Mouth wash	1.11 ± 0.09	0.13	10	1.06 ± 0.02	0.03	10	0.055 <0.095
Kriyolith (IX)	54.13 ± 0.43	0.60	10	54.44 ± 0.60	0.84	10	0.31 <3.43

The Kolmogorov–Smirnov normality test was applied to determine whether the test results were obtained from normal distribution. Thus, according to normality test results, the t-test was used to determine whether there was a significant difference between the results obtained from the two different methods at the 95% confidence level. The results are given in Table 3. As an alternative to the t-test, the difference between two methods was also analyzed by Mann–Whitney U test as a nonparametric test. According to the Mann–Whitney U test, P-values were found to be 0.393 and 0.143 for mouthwash and kriyolith (IX), respectively. There was no significant difference between the results obtained with both methods since both P-values were greater than $\alpha = 0.05$.

2.3. Conclusion

It was shown that the spectroscopic method developed can be conveniently applied to samples, especially to materials used in preventive dentistry, containing fluoride concentrations at the level of 1 mg/mL. The repeatability and reproducibility values of the developed method were calculated as 0.32 and 0.42, respectively. Considering it is always desirable to have a simple, cost-effective, and easily applied method in the selection of analysis methods, there is no doubt that the proposed method will make important contributions to the literature.

3. Experimental

3.1. Apparatus

All spectrophotometric determinations were carried out at 25 ± 1 °C using a Digilab Hitachi U-2800 UV-VIS spectrophotometer. The pH measurements and cell potentials related to the fluoride determinations were carried out with a Consort pH/mV ionmeter (model C863) and Ingold U402-S7/120 glass electrode and fluoride-sensitive electrode (Orion 96-09).

3.2. Reagents and materials

All the chemicals were of analytical grade and used without further purification. The metal ion stock solutions were 0.1 M. The working solutions were prepared with the dilution of the stock solution with deionized water obtained from Elgestat-prima 2 and Elgestat-maxima UF with conductivity of 2.5×10^{-6} S. NaF (99.0%), NaCl

(99%), $AgNO_3$ (99.8%), $Ba(NO_3)_2$ (99.0%), $Ni(NO_3)_2.6H_2O$ (99.0%), $Pb(NO_3)_2$ (99%), $Cd(NO_3)_2.4H_2O$ (99.0%), $Cu(NO_3)_2$ (97.0%), $Co(NO_3)_2.4H_2O$ (99.5%), NaOH (97.0%), HNO_3 (65%; d = 1.42 kg/L), KNO_3 (99.0%), $NaCH_3COO$ (99%), KNO_2 (99%), $Fe(NO_3)_3$ (99.0%), $NaNO_3$ (99.9%), $Mg(NO_3)_2$ (98.0%), K_2SO_4 (99%), and methanol (99.8%) were purchased from Merck; indole-3-acetic acid (98%) was from Aldrich; K_3PO_4 (99%), HCl (37%; d = 1.19 kg/L), $Al(NO_3)_3$ (99.8%), KI (99%), and KSCN (98.5%) were from Riedel-de Haen; $Ca(NO_3)_2.4H_2O$ (99%) was from Fisher; and ionic strength adjusting buffer solution (TISAB) and standard fluoride solution (100 ppm) were from Orion.

3.2.1. Standard solutions employed

The working solutions were prepared by the dilution of 100 mg/L standard fluoride solutions. Indole-3-acetic acid solution was prepared at a concentration of 2×10^{-3} M by dissolving an appropriate amount of Indole-3-acetic acid with 20 mL of methanol in a 100-mL flask and it was made up to 100 mL with deionized water. $FeCl_3$ was used from 1×10^{-3} M stock solution. The solutions of the interfering anions (SO_4^{2-}, SO_3^{2-}, NO_2^-, I^-, Br^-, Cl^-, SCN^-, CH_3COO^-, ClO_4^-, $H_2PO_4^-$) and cations (Ag^+, Al^{3+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, K^+, Mg^{2+}, Na^+, Ni^{2+}, Pb^{2+}) were prepared as 10 times, equal to, and 1/10 times the concentration of Fe^{3+} ion.

3.2.2. Standard reference material

Flusspat III was obtained from Dr Hoefner's Substanz Company: CaF_2 (92.07%), Al_2O_3 (0.21%), Fe_2O_3 (0.15%), K_2O+Na_2O (0.51%), $BaSO_4$ (3.3%), SiO_2 (3.45%), heating loss (0.31%), moisture (2.05%).

Kriyolith (IX) was also obtained from Dr Hoefner's Substanz Company: AlF_3 (40.2%), SiO_2 (0.19%), FeO (0.09%), water (0.37%), $Al_2(SO_4)_3$ (0.28%), NaF (58.09).

Appropriate amounts of standard materials were fused with Na_2CO_3 at 900 °C, the melt was dissolved in deionized water filtered from blue band filter paper, and the filtrate was taken into a 100-mL round-bottomed flask and made up to 100 mL with deionized water.

3.2.3. Commercial mouthwash solution (neutral sodium fluoride solution)

A volume of 100 mL of 100 ppm stock solution of a mouthwash solution (fluoride content of which was stated as 2%) was prepared. The experimental solutions were prepared with the appropriate dilution of the stock solution and adjusted to pH 1.7 with the use of HNO_3 and NaOH.

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