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Method development for the determination of fluorine in toothpaste via molecular absorption of aluminum mono fluoride using a high-resolution continuum source nitrous oxide/acetylene flame atomic absorption spectrophotometer

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ABSTRACT

Fluorine was determined via the rotational molecular absorption line of aluminum mono fluoride (AlF) generated in C_2H_2/N_2O flame at 227.4613 nm using a high-resolution continuum source flame atomic absorption spectrophotometer (HR-CS-FAAS). The effects of AlF wavelength, burner height, fuel rate (C_2H_2/N_2O) and amount of Al on the accuracy, precision and sensitivity were investigated and optimized. The Al–F absorption band at 227.4613 nm was found to be the most suitable analytical line with respect to sensitivity and spectral interferences. Maximum sensitivity and a good linearity were obtained in acetylene-nitrous oxide flame at a flow rate of 210 L h^{-1} and a burner height of 8 mm using 3000 mg L^{-1} of Al for 10–1000 mg L^{-1} of F. The accuracy and precision of the method were tested by analyzing spiked samples and waste water certified reference material. The results were in good agreement with the certified and spiked amounts as well as the precision of several days during this study was satisfactory (RSD < 10%). The limit of detection and characteristic concentration of the method were 5.5 mg L^{-1} and 72.8 mg L^{-1}, respectively. Finally, the fluorine concentrations in several toothpaste samples were determined. The results found and given by the producers were not significantly different. The method was simple, fast, accurate and sensitive.

1. Introduction

Fluorine is a natural element which is found abundantly in world crust. Like various elements, fluorine is also required in the body but in small amounts. It is essential for human body in a very small critical concentration range and many harmful effects occur in case of its excess or deficiency. Fluorine is helpful for dental health in low dosage and added to many dental products like toothpastes, mouth rinses, gels and varnish as active ingredient. However, chronic exposure to fluoride in large amounts interferes with bone formation and can cause skeletal fluorosis, hence the amount of fluoride intake is very important [1].

There are numerous methods for determining fluorine and fluorine forms in toothpastes such as analytical methods [2], ion-selective electrodes [3,4], potentiometric determination [5], ion chromatography [6], spectrophotometric methods [7] and capillary electrophoresis [8] while each of them have their own disadvantages. There are some extraordinary studies about determining fluorine in toothpastes with atomic absorption spectrometry [9,10]. Gomez et al. formed gaseous AlF molecule in nitrous oxide–acetylene flame and measured its absorption by Pt hallow cathode lamp's absorption line. Method's sensitivity is very low (around 60 mg L^{-1}) because of line source spectrometer, hence it enables the determination of low concentrated fluorine samples [9].

Atomic absorption spectrometry (AAS) has been a routine analytical method for quantitative determination of trace metals and metalloids for years but with recent developments in high-resolution continuum source atomic absorption spectrometry, halogens and sulphur can be determined as well. It is impossible to determine fluorine directly by traditional line source spectral lamp since its main resonance line is located at 95 nm. With traditional AAS, some studies have been performed for the determination of fluorine which are well reviewed in literature [11]. In order to achieve these kinds of studies, diatomic molecules of fluorine in gas phase were generated by adding some metals. The absorption of a suitable hyperfine rotational line selected from the molecular absorption spectrum (MAS) of diatomic molecule was evaluated using corresponding emission line of any hollow cathode lamp (HCL). However, this method has some drawbacks: (i) a suitable HCL may not always be found, (ii) selected HCL's emission line may not exactly overlap with MAS line of diatomic molecule

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causing low sensitivity as well as spectral interference. On the other hand, high resolution continuum source atomic absorption spectrometer (HR-CS-AAS) with high intensity xenon short-arc lamp, high resolution double monochromator, CCD detector [12], it is possible to get whole wavelength range from vacuum-UV to near IR with a line width of 2 pm which is narrower than that of HCL as well as any line of rotational hyperfine structure of the diatomic molecule. In this case, the above mentioned drawbacks of HCL do not occur. Many studies have been performed for the determination of fluorine by HR-CS-AAS using any rotational molecular absorption line of GaF, AlF, MgF and CaF [13–19].

The aim of this study is to develop a novel method for the determination of F in toothpaste samples by HR-CS-AAS using molecular absorption line of AlF formed in acetylene–nitrous oxide flame. The experimental parameters were optimized and the method was validated. To the best of our knowledge, this is the first time that aluminum is used as a molecule forming element for the determination of F in flame by high-resolution continuum source atomic absorption spectrometry.

2. Experimental

2.1. Instrumental

An Analytik Jena ContrAA 700 High Resolution Continuum Source Atomic Absorption Spectrophotometer (Analytik Jena, Jena, Germany) equipped with a 300 W xenon short-arc lamp as a continuum radiation source was used throughout the work. AlF was formed in acetylene-nitrous oxide flame with a flow rate of $210\,\mathrm{L\,h^{-1}}$. The molecular absorption measurements of AlF were carried out at 227.4613 nm and at a burner height of 8 mm. The number of pixels of the array detector used for detection of AlF line was 1 (central pixel). All measurements were carried out in triplicates. In order to prepare samples, ultrasonic bath (Bandelin Sonorex, Waldorf, Germany) has been used.

2.2. Reagents and solutions

High-purity water was obtained from a TKA reverse osmosis connected with a deionizer (TKA Wasseraufbereitungsysteme GmbH, Niederelbert Germany). All chemicals were of Merck, Darmstad, Germany). The stock solutions of $5000\,\mathrm{mg\,L^{-1}}$ of fluorine and $10{,}000\,\mathrm{mg\,L^{-1}}$ aluminum standards were prepared by dissolving high purity sodium fluoride and aluminum nitrate (Merck, Darmstad, Germany) in water and further diluted daily appropriately. The waste water standard reference material SPS-NUTR-WW2, which includes $10.0 \pm 0.1\,\mathrm{mg\,L^{-1}}$ of F^-, $50.0 \pm 0.5\,\mathrm{mg\,L^{-1}}$ of Cl^-, $7.5 \pm 0.08\,\mathrm{mg\,L^{-1}}$ of $PO_4{}^{3-}$, $5.0 \pm 0.05\,\mathrm{mg\,L^{-1}}$ of $NO_3{}^-$and $100 \pm 1\,\mathrm{mg\,L^{-1}}$ of $SO_4{}^{2-}$, was provided from LGC Standards (Midlesex, England). Six different brands of toothpaste samples containing sodium fluoride and sodium monofluorophosphate were purchased from market in Istanbul, Turkey.

2.3. Procedure

Matrix-free standard solutions of fluorine, waste water reference standard and blanks were mixed with aluminum $3000\,\mathrm{mg\,L^{-1}}$ as the molecule forming element and aspirated to the flame at optimized conditions. Blank solution was $3000\,\mu\mathrm{g\,mL^{-1}}$ Al as the nitrate. In order to prepare the toothpaste solution (or suspension), 1 g of sample was precisely weighed, dispersed in ultra pure water and completed to 50 mL again with ultra pure water. The mixture was homogenized in ultrasonic bath at $50\,^\circ\mathrm{C}$ for 30 min and an aliquot of 5 mL was then immediately made up to 10 mL with $6000\,\mu\mathrm{g\,mL^{-1}}$ of Al as the nitrate. In spite of an effective ultrasonic homogenization, the samples slowly precipitated upon waiting. Therefore, the mixture was vortexed for about 1 min prior to aspiration in to the flame. The samples were introduced as their suspensions (or dilute slurries). The slurry was diluted to a certain level that it was aspirated like a solution without any problem (e.g. without clogging or deposition in the burner head and aspiration capillar tube). The results were given as the mean of 3 repetitive aspiration of each sample.

3. Results and discussion

3.1. Choice of molecule forming element

In this method a diatomic molecule is formed in the flame among the analyte and an element (molecule forming element) and MAS of the molecule is measured. The element is chosen so that the diatomic molecule containing the analyte should be stable enough to stay in the flame during the measurement while its sensitivity is sufficient for the detection of the analyte concentrations (strictly speaking the concentration of diatomic molecule formed from the analyte) in the samples studied. It is assumed that diatomic species with bond dissociation energies higher than $500\,\mathrm{kJ\,mol^{-1}}$ are suitable for this purpose [16]. The dissociation bond energy of AlF is $653\,\mathrm{kJ\,mol^{-1}}$ [18]. Therefore, Al is an appropriate element for the determination of F. In addition, it is easily available and cheap. AlF may be formed by decomposition of AlF_3 ($AlF_3(g) \rightarrow AlF(g) + F(g)$) and/or recombination of Al and F atoms in the gas phase ($Al(g) + F(g) \rightarrow AlF(g)$). However, we do not make overestimations on the formation mechanisms of AlF(g).

3.2. Choice of calibration standard

The stock solution of fluorine was prepared from high purity sodium fluoride and HF. Optimization was done with two different fluorine reagents, and no significant difference was found between the sensitivities of the two standards. Since HF is risky for health and corrosive to flame parts of instrument, NaF was used as a calibrant.

3.3. Choice of wavelength

The wavelength of the analyte containing diatomic molecule is chosen such that its sensitivity is high enough to detect the analyte in the sample while the analyte absorption line does not spectrally interfere with neighboring wavelengths of other species. The spectral interferences in HR-CS-AAS are less likely compared to line source AAS as a result of extraordinary high resolution power of the former at pm level. Spectral interferences occured due to the overlapping of the two wavelengths (analyte and the species formed in the flame) can be corrected if and only if the source of the interference is known.

In the literature, F has been determined by molecular absorption of AlF at lines 227.5 [14], 277.45 [9], 227.438 and 227.485 [20] by hollow cathode lamps. Some other lines are listed for AlF by Pearse and Gaydon [21] as 227.4613, 227.4659, 227.5790, 227.6631 nm. All of these lines were investigated with respect to their sensitivities and spectral interferences and the highest absorbances were obtained at 227.4613 nm. The absorption spectra obtained for toothpaste in the vicinity of molecular absorption peak of AlF at 227.4613 nm is depicted in Fig. 1. In the toothpaste samples used in this work, the background is low and there is no spectral interference from close environment of molecular absorption peak of AlF at 227.4613 nm.

3.4. The effect of the amount of Al on the sensitivity

The linearity of the calibration curve for the determination of halogens via MAS of their diatomic molecules needs extra

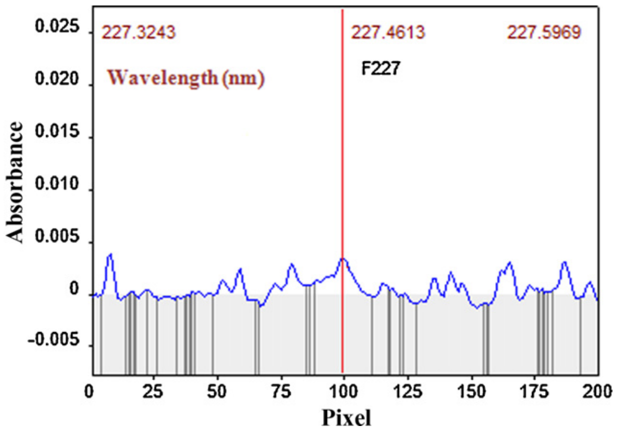

Fig. 1. The absorption spectrum of a toothpaste sample in the vicinity of molecular lines for AlF at 227.4613 nm (Al:3000 mg L^{-1}).

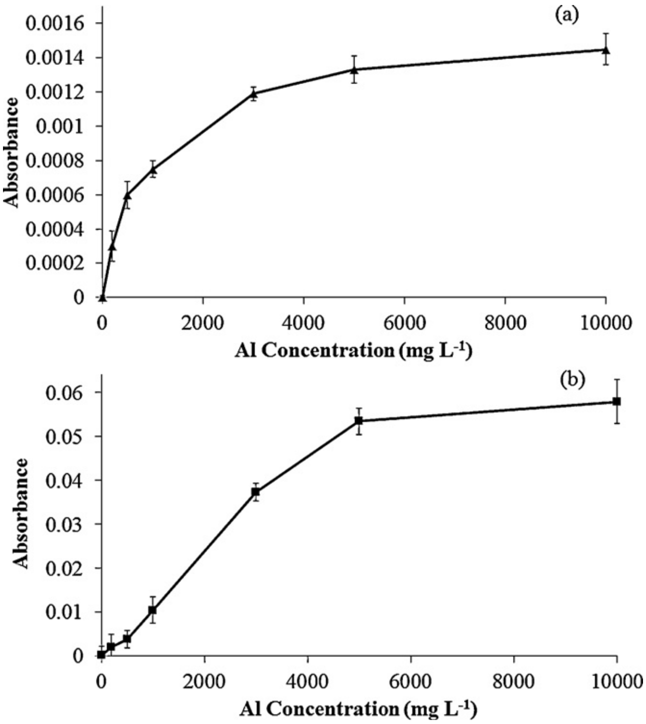

Fig. 2. The change of the AlF molecular absorption with the Al concentration at constant F concentration (a) 100 mg L^{-1} and (b) 500 mg L^{-1}. Error bars represent the standard deviation (N:3).

precaution and effort since it depends not only on the concentration of the analyte but also that of the molecule forming reagent as well. As shown in Figs. 2 and 3, molecular absorbance for AlF changed linearly with both Al and F concentrations. Therefore, the change of absorbance with F concentration was investigated at different Al amounts simultaneously. In the presence of a fix amount of Al selected for the quantification of F in samples studied, absorbances should linearly change with F concentration in a wide range. Otherwise, depending on the F concentration in the sample, recalibration with different amounts of Al should have been required. As shown in Fig. 2, the maximum sensitivity for AlF was obtained with different Al concentrations depending on the F concentration. When F concentration was fixed to 100 mg L^{-1}, optimum Al concentration was 3000 mg L^{-1}, whereas for 500 mg L^{-1} F, the most suitable Al concentration was found as 5000 mg L^{-1}. Since the slurries of toothpaste samples were expected to contain around 20–30 mg L^{-1} of F, which corresponds to around 1000–1500 μg g^{-1} F in toothpaste, 3000 mg L^{-1} Al could be safely used as the optimum amount in all quantifications. After finding optimum Al concentration, in the presence of 3000 mg L^{-1} of Al, a linear calibration curve was obtained up to 1000 mg L^{-1} of F which was much higher than F concentrations in the sample solutions prepared for analysis (Fig. 3). In other words, 3000 mg L^{-1} of Al can be used for the determination of F in toothpaste samples without any problem. The precisions of measurements in Fig. 3 were quite satisfactory. However, since the data points are very close to each other in a very narrow range below 100 mg L^{-1}, they are appeared more than once and their error bars could not be distinguished clearly.

In real samples, many concomitants are likely to react competitively with Al and F, e.g. ametals with Al; metals with F causing the concentration of AlF(g) (i.e. the sensitivity of F) to decrease compared to matrix-free solutions. This interference depends on the matrix concomitants and their concentrations which are mostly unknown. In this case, since the use of linear calibration technique with aqueous standards may be risky, standard addition technique is more appropriate to eliminate any potential interference for quantifications of F in all real samples. Therefore, if the results found by the two techniques are not in agreement, those found by standard addition technique is more reliable.

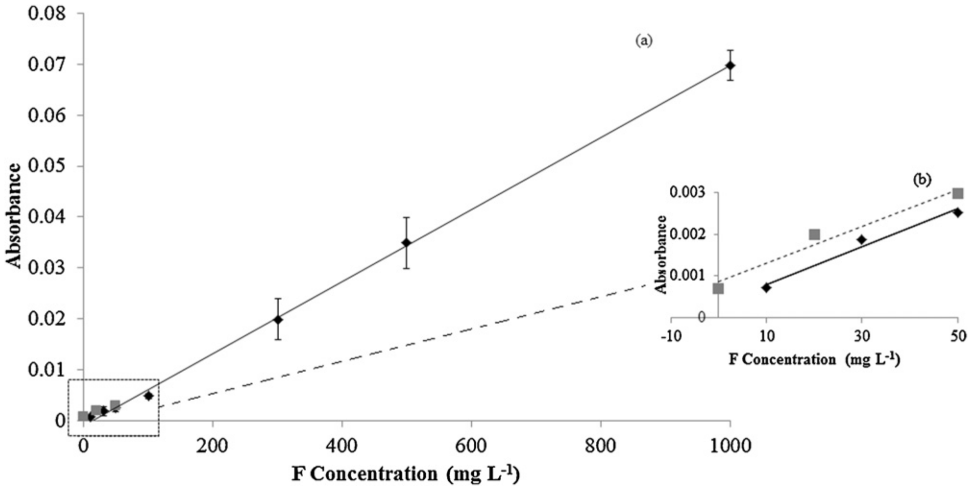

Fig. 3. Linear calibration curve (◆) and standard addition curve (■) for F as AlF. Sample: waste water SPS-NUTR WW2; Al:3000 μg mL^{-1}. Error bars represent the standard deviation (N:3).

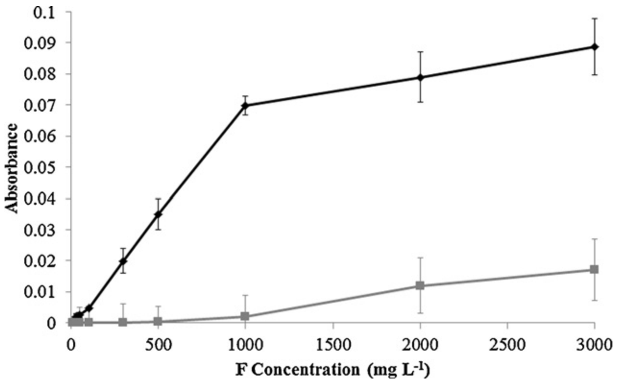

Fig. 4. Comparision of absorbances with flame type; ♦: nitrous oxide/acetylene flame, ■: air/acetylene flame (Al:3000 mg L^{-1}). Error bars represent the standard deviation (N:3).

Table 1
Comparison of figures of merit for the determination of F by flame AAS using different molecule forming elements.

	AlF[b] (this study)	AlF [9]	AlF [10]	GaF[b] [17]
Absorption wavelength, nm	227.461	227.5	227.5	211.248
Concentration of molecule forming agent, g L^{-1}	3	10.8	21.6	12
Characteristic concentration, mg L^{-1}	72.8	NG[a]	NG[a]	NG[a]
Linear range, mg L^{-1}	0–1000	0–6300	0–3800	0–4000
Limit of detection, mg L^{-1}	5.5	60	24	1
Coefficient of determination, *R*	0.9995	NG[a]	NG[a]	NG[a]

[a] NG: not given.

[b] Works accomplished by HR-CS-FAAS whereas the others were by LS-FAAS.

3.5. Optimization of flame conditions

One of the critical parameters optimized in the method is the type of the flame. As shown in Fig. 4, the usability of different flame types for the determination of MAS via AlF was investigated and it is found that the method is more stable and has lower RSD when nitrous oxide/acetylene flame is used.

For optimization, the fuel rate (nitrous oxide/acetylene ratio) and burner height in nitrous oxide/acetylene flame were simultaneously optimized. As shown in Fig. 5, the maximum molecular absorbance for AlF was gained at a fuel rate of 210 L h^{-1} and a height of 8 mm above the burner. The sensitivity in nitrous oxide/acetylene flame at 227.4613 nm was significantly better than that in air/acetylene flame and after optimization experimental/instrumental parameters, the former is effectively used.

3.6. Validation

The limit of detection for the determination of F was 5.5 mg L^{-1} based on 3 times of the standard deviations obtained from 10 repetitive measurements of the blank solution (3000 mg L^{-1} of Al) aspirated to the flame, i.e. 3σ/slope of linear calibration graph (N:10) whereas the characteristic concentration was 72.8 mg L^{-1} calculated as the concentration of F corresponding to 0.0044 A, i.e. 0.0044/slope of linear calibration graph. Blank signals were stable and around baseline level. The standard deviation of blank signals (N:10) were 1.8 mg L^{-1} with <10% RSD. Standard deviations of the slope and the intercept of the calibration curve given in Fig. 3 were calculated as 3.32 L mg^{-1} and 0.00374, respectively. The characteristic concentration and LOD of the method seem to be high for real samples analysis. Nevertheless, they are suitable for some samples containing quite high F concentrations such as toothpaste. The calibration curve was linear up to 1000 mg L^{-1} of F. The analytical performances of the method and the previous methods' were summarized in Table 1. The linear range for this method is less than the others. However, much less molecule forming element (Al) was used in this study. It should be stated that the F concentration of toothpaste samples were around 30–40 mg L^{-1} before aspiration and toothpaste is one of the most F rich samples. There is no use of extending the linear calibration curve to very high F concentrations. Therefore, the linear range with AlF is sufficient for almost all the samples for the determination of F. LOD was somewhat worse than that found by Gleisner et al. [17]. However, the LOD obtained is enough to detect the F concentrations in toothpaste samples. Also, the characteristics of calibration curves as well as the analytical parameters given in Table 1 are not strict because their values may vary for different set of experiments from day to day. After optimization of experimental parameters, the validity of the method was tested by analysis of a spiked certified reference material SPS-NUTR WW2 (Table 2). The certified concentration of F in CRM could be determined in the uncertainty limits as well as the added concentrations could be recovered satisfactorily (Table 2), which shows that the interference from the waste water matrix is not significant in the presence of 3000 mg L^{-1} of Al and F concentration. However, this does not mean that F can always be determined by using linear calibration technique in all samples.

Finally, F contents of different toothpaste samples were determined applying standard addition and linear calibration techniques. Since the samples were introduced directly as their suspensions (or dilute slurries), the results reflect their total fluorine content. As shown in Table 3, the results found by the two techniques were generally not in agreement (at least in 95% confidence level). However, in case of any significant difference, the results found by standard addition technique should be more reliable due to the non-spectral interferences originating from cross reactions of Al and F with the matrix concomitants. It should be

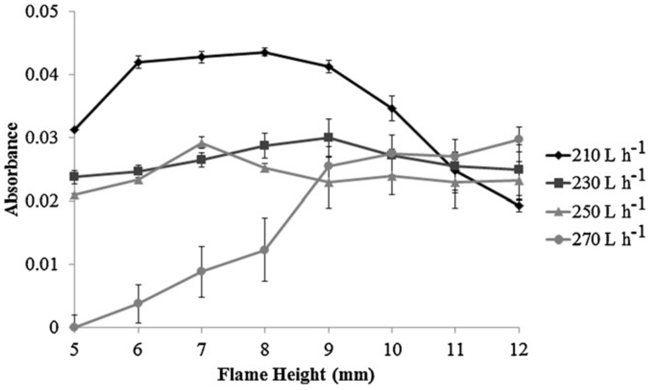

Fig. 5. Optimization of flame parameters with 3000 mg L^{-1} Al and 500 mg L^{-1} F.

Table 2
Determination of fluorine concentrations in waste water SPS-NUTR WW2 and recovery of added F concentrations found by using via molecular absorption of AlF at 227.4613 nm (Al:3000 mg L^{-1}; N:3).

Sample	Certified value (mg L^{-1})	Found value (mg L^{-1})	Recovery (%)
Waste water (SPS-NUTR WW2)	10.0 ± 0.10	10.1 ± 0.3	–
+20 mg L^{-1} of F		31.4 ± 0.2	104
+50 mg L^{-1} of F		59.5 ± 0.5	99

Table 3
Determination of fluorine in various toothpaste samples (N:3).

Sample	Expected (mg kg^{-1}) value[a]	Value found by lineer calibration[b] (mg kg^{-1})	Value found by standard addition[b] (mg kg^{-1})
Toothpaste 1[c]	1000	1110 ± 45	910 ± 30
Toothpaste 2[d]	1450	1495 ± 35	1395 ± 25
Toothpaste 3[d]	1450	1520 ± 20	1390 ± 25
Toothpaste 4[d]	1450	1455 ± 45	1510 ± 40
Toothpaste 5[d]	1450	1410 ± 35	1505 ± 55
Toothpaste 6[c]	1450	1565 ± 40	1510 ± 40

[a] The value given by the producer on the package of toothpaste.
[b] Mean ± SD.
[c] Toothpaste samples with sodium monofluorophosphate.
[d] Toothpaste samples with sodium fluoride.

stated that the values given by the producers on the packages of the toothpastes are only informative and cannot be used as a reference. Therefore, although not being the sole criteria for the accuracy of the our experiments, it is observed that the results were found quite close to the values given by the producers.

The ionic fluorine (fluoride) and covalent bounded fluorine originated from dissolution of toothpaste samples containing NaF and sodium monofluorophosphate, respectively could be determined around those given by the producers. It should be stressed that the fluorine in monofluorophosphate cannot be determined with IC or ICE because fluoride is slightly released. As a result, after optimization of experimental conditions, the fluorine concentrations in toothpaste samples can be easily and successfully determined via MAS of AlF by HR-CS FAAS.

4. Conclusion

The present work proves that the HR-CS FAAS can be employed for the determination of fluorine in toothpaste samples by measuring an appropriate molecular absorption line of AlF generated in a nitrous oxide–acetylene flame. It is reliable, fast and simple. Therefore, after the validation of the method, nitrous oxide/acetylene flame came into prominence for the determination of F via AlF by HR-CS-AAS. The most remarkable advantages of the method proposed in this study are as such; Al is a cheap and an easily available molecule forming element and flame used as an atomizer in this study is a cheaper atomizer than graphite furnace that is used extensively in the previous studies.

However, this is an indirect method and like other similar studies, there are extra parameters to be optimized such as appropriate concentration of molecule forming reagent. In addition, the interferences due to competitive reactions of complicated heavy matrix constituents with analyte and the molecule forming element are potential sources of error and cannot be prevented. Therefore, in case of any difference between the results found by linear calibration and standard addition techniques, the latter is more reliable due to the above-mentioned reasons.

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