

4, 5-Dinitrochryszazin Complexes: Slovatochromism and Fluoride Determination in Jenin Groundwater Wells

Zaher Barghouthi¹ and Sameer Amereih²

¹ National Agricultural Research Center (NARC), Jenin, Palestine

^a Environmental and Community Health Department, AAUJ, Jenin, Palestine

² Palestine Technical University–Kadoori, Tullkarm – Palestine

Abstract:

A simple spectrophotometric determination of fluoride in groundwater has been developed using aluminium - 4, 5-dinitrochryszazin complex. The method is based on the reaction of fluoride with the colored complex to produce colorless aluminum fluoride complex and release the free ligand. The effect of methanol and ethanol solvent on the complex absorption spectra has been examined. The molar absorptivity for the complex in ethanol at 422 and 525 nm was 5630 ± 32 and $680 \pm 26 \text{ l mol}^{-1} \text{ cm}^{-1}$ respectively. Beer's law is obeyed in the range of 0.0–5.0 mg l⁻¹ at 370 and 427 nm. Sensitivity, detection limit, quantitation limit, and the percentage recovery of 1.0 mg l⁻¹ fluoride at 427 nm were found to be 0.072 µg ml⁻¹, 0.2mg l⁻¹, 0.5 mg l⁻¹, and 105.2, respectively. Sulphate was the only interfering anion. Still, its effect can be neutralized by adding barium chloride.

Keywords: 4, 5-Dinitrochryszazin complexes; Slovatochromism; Fluoride; Spectrophotometric method; Groundwater

Introduction

Fluoride (F⁻) occurs in almost all waters from trace to high concentration (Dar et al., 2011). It has been shown to cause significant effects in people through drinking water (WHO, 2006). Low concentration of fluoride in drinking water can prevent dental caries (Maliyekkal et al., 2008; Qin et al., 2009). Excessive exposure to fluoride, on the other hand, can lead to adverse effects such as fluorosis (Sunitha et al., 2004; WHO, 2006; Armienta and Segovia, 2008; Aldrees and Al-Manea, 2010; Arveti et al., 2011; and Dunne and Verrel, 2011). Around 62 million people, including 6 million children, suffer from fluorosis (UNICEF, 1999; Meenakshi et al., 2004; and Singh, 2007). There is a narrow margin between the desired and harmful doses of fluoride (Czarnowski et al., 1996). World Health Organization (WHO) has set a limit value of 1.5 mg L⁻¹ of fluoride in drinking water (WHO, 2004; and Rafique et al., 2008). Therefore, an accurate, simple, rapid and cost-effective analytical method is of high importance (Barghouthi and Amereih 2012a; Barghouthi and Amereih 2012b; and Barghouthi and Amereih 2012c).

Given their particular advantages (such as simplicity, facility, accuracy and reproducibility), spectrophotometric methods are widely used in the determination of fluoride (Zolgharnein et al., 2009). They are based on the reaction of fluoride with coloured metal chelate complexes, either producing a mixed-ligand ternary complex or replacing the ligand with fluoride to give a colourless metal-fluoride complex and a free ligand with a colour different from the metal-ligand complex (Einaga and Iwasaki, 1981).

Antraquinone (AQ) dyes are those in which the chromophore is the carbonyl group conjugated with two aromatic rings on which amino and hydroxyl groups and their substituted forms are frequently present and act as auxochromes (Hatch and Magee, 1998). Commercially useful AQ dyes are those with powerful electron donating groups such as amino or hydroxy at one or more of the four alpha positions (1, 4, 5, 8). Only AQ with donor contains substituents having filled 2p_z orbitals such as -NH₂ or -OH having intense absorption bands in the visible region of the spectrum, necessary for colour changes measurements (Arpe and Ullmann, 1985). AQ dyes with groups capable of holding metals in stable combination such as alizarin have been used successfully as spectrophotometric reagent for fluoride determination (Jacobson & Weinstein, 1977; Cholak, 1959).

This paper seeks to develop a spectrophotometric method for determination of fluoride in range of 0.0-2.0 mg l⁻¹, compatible with WHO limit value of 1.5 mg l⁻¹, using aluminium complexes of 4, 5-dinitrochryszazin as fluoride spectrophotometric reagent in the presence and absence of anion interferences. The paper examines the effect of ethanol and methanol solvents on the spectrophotometric properties of the reagent under investigation.

Experimental Apparatus

Beckman DU-7500 single beam spectrophotometer with 1.0 cm quartz cells was used for wavelength scanning and spectral studies. Hitachi U- 1500 UV/Vis single beam spectrophotometer with 1.0 cm quartz cells was used for the absorbance measurements at fixed wavelength.

Reagents

4, 5-dinitrochryszazin provided by Aldrich-Chemie (99%, D7924), and aluminium chloride hexahydrate (Purum p. a, 06232) provided by Fluka were used without any further purification. All the chemicals were of analytical reagent grade except where stated otherwise. Solutions were prepared using double distilled water. 4, 5-dinitrochryszazin ligand solutions and aluminium complexes solutions were prepared using ethanol or methanol from Merck (96%, 159010; or for synthesis, 822283, respectively). Standard fluoride stock solution was prepared by dissolving 0.1382 g of sodium fluoride provided by Merck (ACS reagent, 106449) in 250 ml water. The stock solution was further diluted as needed.

Preparation of the Metal Complexes Solutions

Job's method of continuous variation was adopted for the determination of the composition of the coloured complexes (Werner and Boltz, 1971a; Werner and Boltz, 1971b). Aluminium to ligand (4, 5-dinitrochryszazin) ratio was also considered in both ethanol and methanol solvents by preparing complexes with the most common molar ratios (1:1, 1:2, 1:3, 2:1, 3:1, 2:3, and 3:2) to enable comparison between the spectra of these different complexes. The blank was prepared by the same procedure using the solvent instead of the aluminium ionic solution.

Aluminium to ligand ratio was found to be 1:2. Thus, the complex solutions for the spectrophotometric measurements were prepared as 1:2 ratios from aluminium and a ligand of 1 ×

10^{-4} M or 2.5×10^{-4} M in methanol or ethanol solutions, respectively. This concentration is particularly suitable for spectrophotometric measurements.

Reaction of Fluoride with the Prepared Complex Solutions

Various amounts of fluoride were added in the range 0 – 2 mg l⁻¹ to 25 ml volumetric flask containing aluminium complex solutions of 4, 5-dinitrochryszin in ethanol (2.5×10^{-4} M, 24.5 ml). Water was added to the solution to give it its ultimate volume. The absorbance was measured at the wavelengths of the maximum difference (370 and 427 nm) in the electronic spectra between the ligand and the complex. The spectrums of the reaction of different amounts of fluoride with the complex were compared.

Determination of Fluoride in Real Drinking Water Samples

The method under investigation was tested using two real groundwater samples collected and analyzed by the Ministry of Health's Central Public Health Laboratory responsible for protecting and restoring water quality. Samples were collected in October 2012 from two groundwater wells in Jenin District (Yamoun Well and Sa'adah Well). Fluoride was analyzed calorimetrically using SPADNS as fluoride reagent and Hack – DR/2010 as spectrophotometer. Nitrate, chloride, and other characteristic data of the two samples are given in table 1. According to the Ministry of the Health, fluoride ranges between 0.2 and 0.8 mg l⁻¹ in the West Bank groundwater resources. Accordingly, fluoride was measured after the water samples had been spiked by 0.5 mg l⁻¹ fluoride. The results were compared with that reported by the Central Public Health Laboratory using SPADNS method (table 1 and table 2).

Table 1. Analytical data of the two water samples analyzed by Ministry of Health laboratories

	Well	pH	Conductivity Micro.S cm ⁻¹	Fluoride mg L ⁻¹	Nitrate mg L ⁻¹	Chloride mg L ⁻¹	Sulfate mg L ⁻¹	TDS Mg L ⁻¹
Sample 1	Yamoon	7.28	841.00	0.46	4.50	186.00	54.00	420.00
Sample 2	Saadeh	7.52	636.00	0.38	10.68	101.77	37.30	318.00

Table 2 Sensitivity, detection limit, quantification limit, and recovery of the proposed methods at 370 and 427 nm

	Wavelength	
	370 nm	427 nm
Sensitivity [$\mu\text{g}^{-1} \text{ ml}$]	0.061 ± 0.004	0.72 ± 0.006
Detection limit [mg l^{-1}]	0.2	0.2
Quantification limit [mg l^{-1}]	0.5	0.5
Recovery of 1.0 mg l^{-1} [%]	108.3 ± 6.4	105.2 ± 7.6
Recovery of 1.5 mg l^{-1} [%]	109.4 ± 5.8	109.9 ± 5.4
Recovery of sample 1 %	111.1 ± 6.5	109.6 ± 6.8
Recovery of sample 2 %	105.9 ± 7.7	104.9 ± 7.1

Results and discussion

4, 5-Dinitrochrysazin

Alizarin is an AQ dye commonly used as spectrophotometric reagent for determination of fluoride (Jacobson & Weinstein, 1977; and Cholak, 1959). Thus, this group of ligands; i.e. AQ dyes, was the initial step to obtain a new fluoride reagent.

In commercial terms, AQ dyes are second only to azo dyes, largely due to the former's less tinctorial strength and complexity of preparation in comparison with the latter (Lubs, 1955; Arpe and Ullmann, 1985). The commercial importance of AQ dyes is that they are all derivatives of the pale yellow 9,10-AQ. Coloured AQ dyes due to absorption bands in the visible region of the spectrum are those with donor substituents such as $-\text{NH}_2$ or $-\text{OH}$ having filled $2p_z$. Other types of electron donating groups, such as alkyls or phenyl, exert only a small bathochromic effect (an increase in the wavelength) on the long wavelength $\pi \rightarrow \pi$ band. Electron-accepting groups have little effect on the absorption spectrum. However, they do weaken the $n \rightarrow \pi^*$ transition of the carbonyl group (Arpe and Ullmann, 1985).

4, 5-Dinitrochrysazin is a member of the AQ group of dyes commonly known as 1, 8-dinitro-4, 5-dihydroxyanthraquinone. Technically speaking, this dye is a very useful chemical in the synthesis of disperse blue anthraquinone dyes possessing good light and sublimation fastness

(Brown and Colclough, 1983; Ukponmwan and Freeman, 1990; and Chao and Yu, 1992). The structure of 4, 5-dinitrochryszazin is given in figure 1 below.

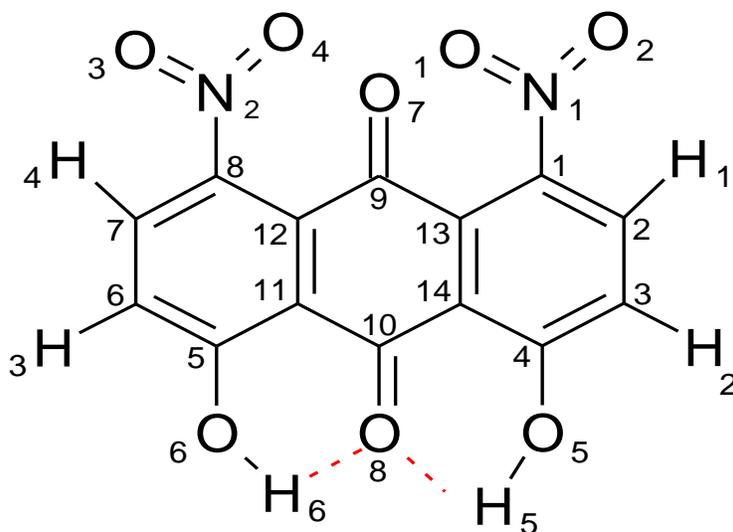


Figure 1. Structure of 4, 5-dinitrochryszazin ligand

The solubility of 4, 5-dinitrochryszazin is very low in water. However, it is soluble in alcohol solvents such as ethanol and methanol. In fact, 4, 5-dinitrochryszazin gives a light orange color in methanol. It has bands at 223, 258 and 424 nm. The molar absorptivity at 424 nm is $8510 \pm 68 \text{ l mol}^{-1} \text{ cm}^{-1}$. On the other hand, it exhibits an orange colour in ethanol with one band in the UV region at 256 nm, and another broad band with several maximums at 321, 379, 426, and 515 in the visible region. The molar absorptivity values at these maximums are 2810 ± 45 , 4670 ± 79 , 8170 ± 85 , and $7100 \pm 51 \text{ l mol}^{-1} \text{ cm}^{-1}$, respectively. The absorption spectra of 4, 5-dinitrochryszazin in ethanol and in methanol is given in figure 2a and figure 2b. 4, 5-Dinitrochryszazin may be regarded as a donor – acceptor chromogen. The –OH group acts as electron donor systems and the rest of the ring system accepts the electrons (Banerjee and Dey, 1981).

The transition $\sigma \rightarrow \sigma^*$ due to C–C and C–H bonds requires very high energy and appears in the vacuum UV i.e., below 200 nm. The bands in the UV region (223 nm, 256 nm, 258 nm, and 321 nm) are attributed to $n \rightarrow \pi^*$ transition involving one electron of the lone on the oxygen atom of OH groups (Banerjee and Dey, 1979; and Banerjee and Dey, 1981).

The visible band in the spectra of 4, 5-dinitrochryszazin is attributed to $n \rightarrow \pi^*$ transition due to the lone pair of electrons peculiar to a heteroatom. The lone pair electrons of a heteroatom is usually highest in energy, as the electrons receive no stabilization from conjugation, thus $n \rightarrow \pi^*$ transition requires less energy and occurs at higher wavelengths. Although isolated $-C=C-$ gives $\pi \rightarrow \pi^*$ transition at shorter wavelengths, pronounced changes occur only when multiple bonds exist in conjugation, and the band position $\pi \rightarrow \pi^*$ transition increases considerably in anthracene as compared to benzene. Anthracene is a colourless compound showing only $\pi \rightarrow \pi^*$ band in UV region. 9, 10-anthraquinone is a yellow compound with the color resulting from $n \rightarrow \pi^*$ transition of $-C=O$ group and the $\pi \rightarrow \pi^*$ transition band showing a red shift (bathochromic) as a result of the conjugation of $-C=O$ with the rest of the molecule. The high intensity of the broad peak in the visible region for the ligand (dye) under investigation produces a $\pi \rightarrow \pi^*$ band, while the $n \rightarrow \pi^*$ weak transition band is obscured by the former band (Banerjee and Dey, 1981; and Banerjee and Dey, 1979).

Figure 2. Absorption spectra of 4, 5-dinitrochryszazin ligand and its aluminium 1:2 complexes in ethanol (a) at 2.5×10^{-4} M, and in methanol (b) at 1×10^{-4} M.

Aluminium Complexes of 4, 5-Dinitrochryszazin

The molar ratio of aluminium to 4, 5-dinitrochryszazin ligand in the complex was determined by both Job's method of continuous variations and spectrophotometrical comparison between the most common metal and ligand ratios (1:1, 1:2, 1:3, 2:1, 3:1, 2:3, and 3:2). The results indicate that the molar ratio is 1:2. The presence of quinoid oxygen atoms, together with two nitro- groups and two hydroxyl groups in the 1-, 8-, and 4, 5- respectively, yields alternative positions where the chelation might occur. Therefore, it is possible for the complex to be 1:1, 1:2, 1:3, 2:1. However, the maximum difference in the absorption spectra between the ligand and the complex occurs with 1:2 complex.

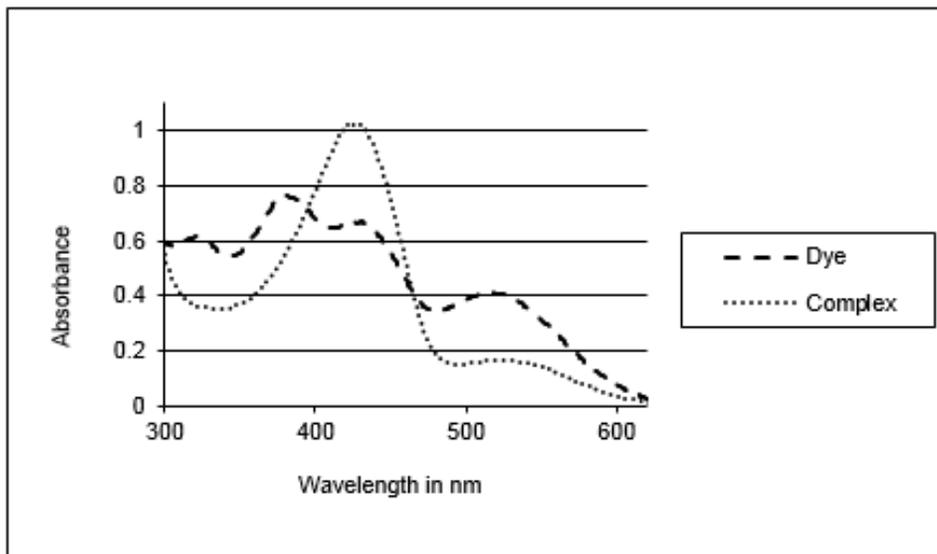


Figure 2a

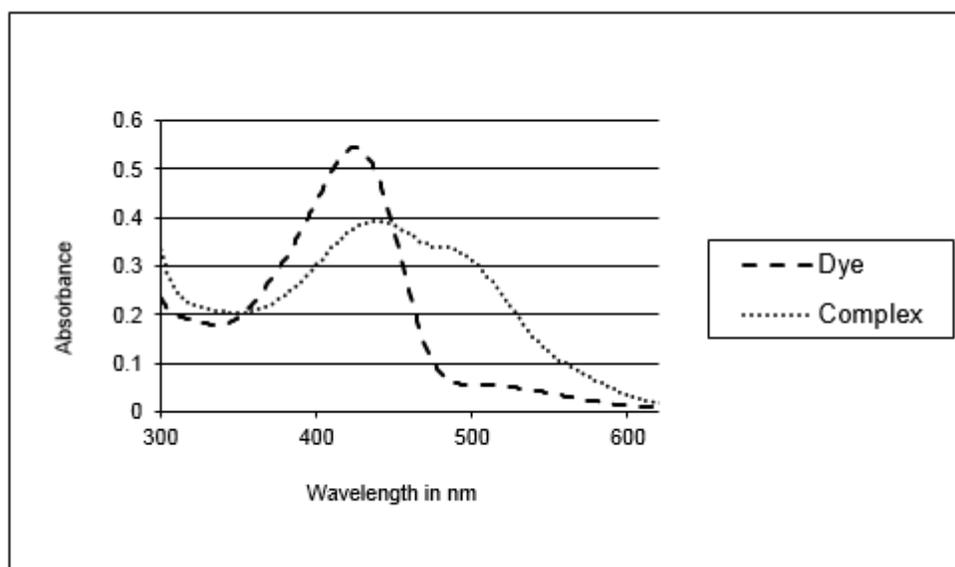


Figure 2b

The absorption spectra of aluminium 1:2 complex in ethanol and in methanol are given in figure 2a and figure 2b, respectively. The complex exhibits yellow colour in ethanol and displays one band in the UV region at 256 nm with a molar absorptivity of $8960 \pm 54 \text{ l mol}^{-1} \text{ cm}^{-1}$, and one band in the visible region with two heads at 422 nm and 525 nm (figure 2a). The molar absorptivity at these two heads is 5630 ± 32 and $680 \pm 26 \text{ l mol}^{-1} \text{ cm}^{-1}$ respectively. On the other

hand, aluminium 1:2 complex in methanol exhibits two bands in the UV region at 223 nm and 258 nm with a molar absorptivity of 1930 ± 72 and $1700 \pm 48 \text{ l mol}^{-1} \text{ cm}^{-1}$, and one band in the visible region with two heads at 445 with a shoulder at 486 nm. The molar absorptivity at 445 nm is $5420 \pm 47 \text{ l mol}^{-1} \text{ cm}^{-1}$. The stability of aluminium 4, 5-dinitrochryszin ligand 1:2 complex in both of the two solvents, methanol and in ethanol, was examined by measuring the absorbance of each complex solution at different time intervals during one week. The absorbance remained stable, suggesting stability of the complexes.

Aluminium 4, 5-dinitrochryszin ligand 1:2 complex in methanol is yellow. The yellow colour is a product of the bathochromic shift (red shift) as well as both the hyperchromic effect (increasing in the absorbance) in the ranges (270 – 360 nm and 451- 600 nm) and the hypochromic shift (decreasing in the absorbance) in the range (360 – 451 nm) that occurs after the complexation with aluminium (figure 2b). On the other hand, the yellow colour of the 1:2 complex in ethanol results from the bathochromic shift as well as both the hyperchromic effect in the range (401 – 466 nm), and the hypochromic shift in the ranges 297 – 401 nm and 466 – 600 nm (figure 2a). These shifts - in the wavelength and in the absorbance - are responsible for the changes in the colour between the ligand and its aluminium complex. Obviously, there is an increase in the wavelength of the maximum absorption of the complex in methanol and in ethanol by 62 nm and 10 nm, respectively, over that of the ligand. Different factors (including the magnitude, direction and distance of the electronic charge transfer, effect of the substituents on the charge transfer through the molecule, effect of the complexation on the plan geometry of the ligand, and ligand to metal charge transfer) determine whether a bathochromic or hypsochromic shift will take place after complexation.

Effect of the Solvent and Solvatochromism

The effect of methanol and ethanol solvents on the absorption spectra of the aluminium 1:2 complex and the free ligand was examined (figure 2). Solvent can influence the electronic transitions by different mechanisms. In the ground state, solvent molecules orient around polar solute groups, which creates an average solvent electrostatic field influencing the geometry, vibrational frequencies and intensities. However, charge transfer and interaction with solvent orbitals are still fundamental to understanding the excited electronic states (Sebek et al, 2006).

Such a charge transfer is originated mainly from the hydroxyl group of ethanol or methanol to the antibonding orbitals of the nitro group, which is known by its high accepting propriety, which, in turn, functions through weakening the O—H bond as a result of the decrease in the electron density in the oxygen atom.

There is a bathochromic shift in the absorption spectra when the solvent was changed from ethanol to methanol. Therefore, it is expected that the excited state of the 4, 5-dinitrochryszazin is more polar than its ground state. To gain insight into this process, we must first know what is meant by 'solvatochromism dyes.' The term 'solvatochromic dyes' refers to a class of compounds that display solvent-dependent colours in solution. In physicochemical terms, solvatochromism can be described (in part) by changes in electronic charge distributions induced by solvents with different dielectric constants and solvation properties. Thus, knowledge of local charge densities for both the ground and the excited states of the dyes is instrumental to understanding these complicated phenomena. One can differentiate between positive and negative solvatochromism depending on whether bathochromic or hypsochromic shifts are induced with increasing solvent polarity. Since solvent / solute interactions mainly depend on charges and dipole moments, large changes in electron densities will cause strong positive solvatochromism. Bathochromic shifts are found with increasing solvent polarity if the excited state is more polar than the ground state. Hypsochromic shifts, in turn, are observed in more polar solvents due to a decreasing polarity of the excited state relative to that of the ground state. Generally speaking, the excited state of the solvatochromic dye is more polar than its ground state if increasing bathochromic shifts are measured in solvents of increasing polarity (Gordon and Gregory, 1983; and Zollinger, 2003).

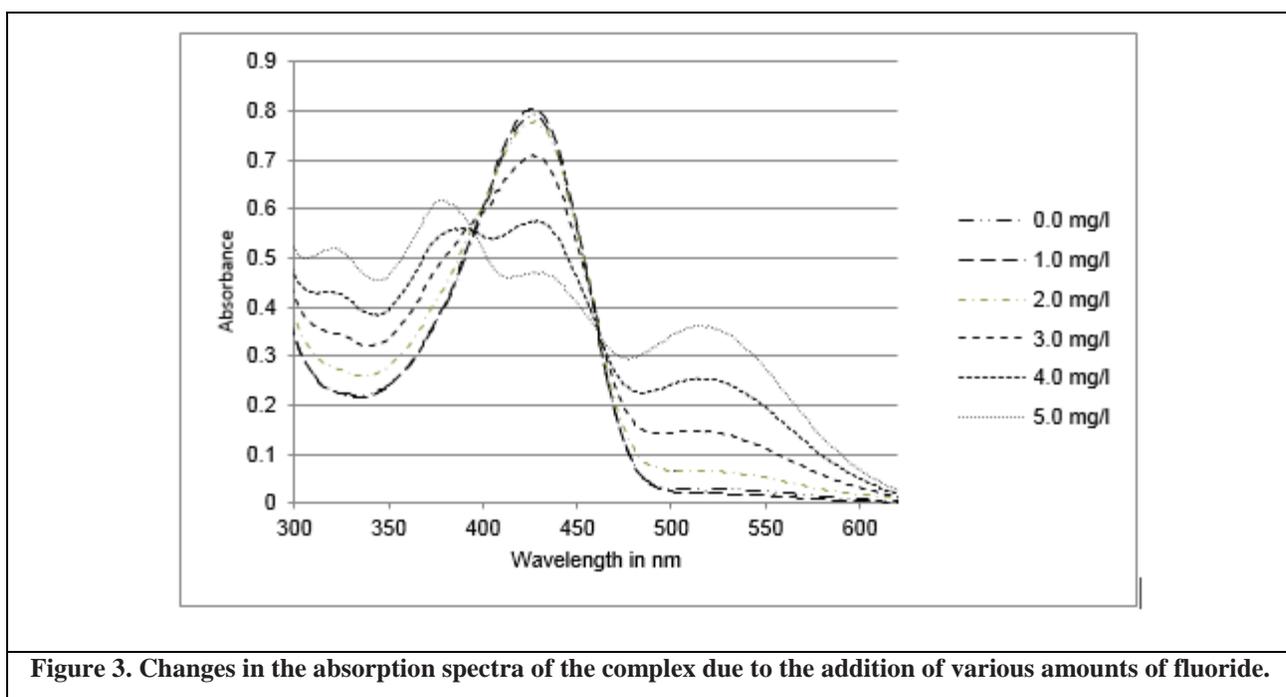
The formation of an intramolecular H-bond reduces the interactions with solvent molecules. Such a behaviour is typical for compounds in which the charges are more separated in the excited state than in the ground state. Thereby, the observed solvatochromism is smaller because solvent interactions are less crucial in this case due to the presence of intramolecular H-bond (Zollinger, 2003).

Reaction of Fluoride with 4, 5-Dinitrochryszazin Complex

The reaction of aluminium 4, 5-dinitrochryszazin 1:1, 1:2, 1:3, or 2:1 complexes in methanol and in ethanol with fluoride showed that the maximum difference in the absorption spectra occurred

with the complex of 1:2 ratio in ethanol. The remainder of this discussion will focus on this complex.

Fluoride reacts with the yellow aluminium 4, 5-dinitrochryszazin complex to produce a colourless aluminium fluoride complex through replacing the 4, 5-dinitrochryszazin with fluoride and liberating the free ligand. This changes the colour yellow (i.e., that of the complex) to orange (i.e., that of the free ligand), according to the equation below. Aluminium reacts with fluoride to give compounds of the nature of $(AlF_6)^{-3}$ or $(AlF_y(OH)_{6-y})^{-3}$ (Macnulty et al., 1956).



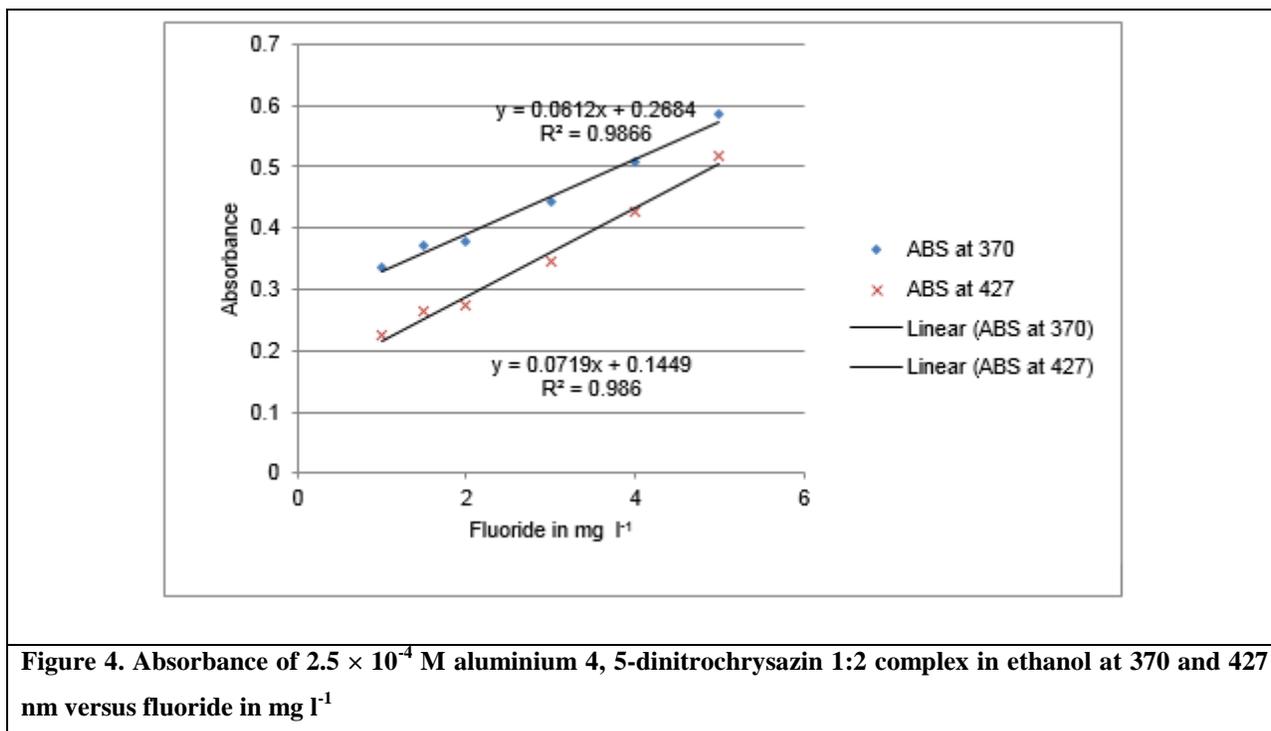


Figure 4. Absorbance of 2.5×10^{-4} M aluminium 4, 5-dinitrochryszin 1:2 complex in ethanol at 370 and 427 nm versus fluoride in mg l^{-1}

The conversion of the colour and the absorption spectra from that of the complex to that of the ligands is shown in Figure 3, which also illustrates the changes in the spectra of the complex in the course of the titration of fluoride. The absorption spectra of the reaction of fluoride with the aluminium 4, 5-dinitrochryszin complex reveal that fluoride interacts to cause an increase in the absorbance of the aluminium complex at 323, 370, and 518 nm, and a decrease in absorbance at 427 nm resulting from the formation of aluminium fluoride complex and the release of the free ligand. The absorbance of the aluminium complex is related linearly at 370 and 427 nm to the concentration of fluoride in the range 0.0 to 5.0 mg l^{-1} (figure 4). Meanwhile, the squared correlation coefficient R^2 values are 0.9866 and 0.9860, respectively, and the values for the equation of the linear calibration curve at 370 and 427 nm are ($y = 0.0612x + 0.2684$) and ($y = 0.0719x + 0.1449$), respectively.

The proposed method was tested by measuring fluoride contents in water samples which had been already analysed by the Central Public Health Laboratory. The recovery of fluoride by the proposed method (table 2) is harmonious with that reported by the Central Public Health Laboratory using SPADNS colourimetric method (table 1).

Sensitivity, detection limit, limit of quantification and the recovery of 1.0, and 1.5 mg l⁻¹ F of the Aluminium4, 5-dinitrochryszin ligand 1:2 complex for the spectrophotometric determination of fluoride at 370 and 427 nm are summarized in table 2. Sensitivity was taken as the average of the slope of the calibration curve for five replicates. The detection limit and the limit of quantification were calculated as (3.3σ/S) and (10σ/S), respectively, where σ is the standard deviation of response and S is the slope of the calibration curve. Recovery was measured as the average of 10 replicate.

Most of the dyes used for fluoride analysis exhibit a decrease in absorbance in the presence of fluoride (e.g., SPADNS, eriochrome cyanine R). Other indicators dyes, such as alizarin fluorine blue, increase the absorbance in the presence of fluoride. They are commonly used because their interferences bleaching the reagent can be readily distinguished (Jacobson & Weinstein, 1977; and Shah and Danishwar, 2003). The ligand under investigation is another example of the second type.

The interference studies were done by measuring the influence of the anions (such as chloride, nitrate, and sulphate in such concentration commonly found in the natural water) on the determination of 1.0 and 1.5 mg l⁻¹ fluoride. Chloride and nitrate- which were added in the range of 100 – 500 and 5 – 100 mg L⁻¹, respectively- do not interfere with the determination of fluoride. Sulphate interferes with the most visual and photometric methods for determining fluoride by its competition with fluoride to form a complex with the metal, and therefore it results in higher concentrations (Ruzicka et al, 1966; and Price and Walker, 1952). In the present work, sulphate up to 50 mg l⁻¹ does not interfere with the determination of fluoride. However, when the amount of sulphate is higher than 50 mg l⁻¹, it interferes with the determination of fluoride, causing a positive error, which can be overcome by precipitating sulphate using barium chloride (Dixon, 1970).

Interference may also come from metal ions (that give a colour with the dye) or cations (e.g. iron, zirconium, magnesium) which form complexes with fluoride in competition with aluminium (Nishimoto et al., 2001; and Dixon, 1970). However, metal ions from scarce sources are not expected in drinking water. The stability constants of the metal fluoride complexes increase in this order: [CuF_n]²⁻ⁿ < [MgF_n]²⁻ⁿ < [FeF_n]³⁻ⁿ < [AlF_n]³⁻ⁿ < [ZrF_n]³⁻ⁿ (Aikens and Reilly, 1963). When the sample solution is expected to contain a large amount of these cations, and because of the high tendency of such type of ligands to form colour chelates with various metal ions (Snell,

1978; Srivastava and Banerji, 1967), it is better to mask the metal interferences by adding complexing agents such as DCTA (trans- 1,2- aminocyclohexane- N,N,N',N'- tetraacetic acid) (Nishimoto et al, 2001) or EDTA (ethylenediaminetetraacetic acid (Snell, 1978).

Conclusions

Aluminium 4, 5-dinitrochryszazin 1:2 complex was successfully used as new spectrophotometric reagent for determination of fluoride in groundwater. The proposed method is simple, rapid, and it allows a reliable determination of fluoride in the range of 0.0–5.0 mg l⁻¹, which is compatible with the WHO limit value of 1.5 mg l⁻¹. Due to its simplicity, it can be recommended as a reagent for controlling the amount of fluoride in countries suffering from fluoride health problems.

Acknowledgments

The author (ZB) thanks Professor Walter Kosmus from the Analytical Chemistry Institute in Karl-Franzens University of Graz, Austria, for his advice, suggestions, ideas, comments, helpful discussions, generous help with instruments and references, and for his supervision of the Ph.D. research. The authors thank the director (Mr Ibrahim Salem) and the staff of the Central Public Health Laboratory, Ramallah, for their cooperation and for sharing their data.

References:

- Aikens, D.A. and Reilly C.N., 1963. Formation Constants of Metal Complexes. In: Meites, L., Handbook of Analytical Chemistry. pp. 1-40. New York: McGraw-Hill Book Company.
- Aldrees, A. M., and Al-Manea, S. M. 2010. Fluoride Content of Bottled Drinking Waters Available in Riyadh, Saudi Arabia. Saudi Dental Journal. 22,189-193.
- Arminta, M. A., and Segovia, N. 2008. Arsenic and Fluoride in the Groundwater of Mexico. Environmental Geochemistry and Health. 30, 345-353.
- Arpe, H. J. 1985. 5th Edition. Ullmann's Encyclopedia of Industrial Chemistry. Vol. A2: Amines, Aliphatic to Antibiotics. VCH. Puplicher.
- Arveti, N., sarma, M. R. S., Atikenhead-Peterson, J. A., and Sunil, K. 2011. luoride Incidence in Groundwater: A Case Study from Talupula, Andhra Pradesh, India. Environmental Monitoring and Assessment. 172, 427-443.
- Banerjie, V., and Dey, A. 1979. Coordination Polymers of 1,2,5,8-tetrahydroxyanthraquinone. Makromolekulare Chemie, 180 (9), 2133-2137.

- Banerjee, V., and Dey, A. 1981. Visible Spectrum of 1,2,5,8-Tetrahydroxyanthraquinone. *Journal of Nepal Chemical Society*, 1 (1), 100-102
- Barghouthi, Z., and Amereih, S. 2012a. Field Determination of Fluoride in Drinking Water Using A Polymeric Aluminium Complex of 5-(2-Carboxyphenylazo)-8-hydroxyquinoline Impregnated Paper. *International Journal of Environmental Analytical Chemistry*. 93 (5), 565-577.
- Barghouthi, Z., and Amereih, S. 2012b. Spectrophotometric Determination of Fluoride in Drinking Water Using Aluminium Complexes of Triphenylmethane Dyes. *Water SA*. 38 (4), 543-548.
- Barghouthi, Z., and Amereih, S. 2012c. Spectrophotometric Determination of Fluoride in Groundwater Using Resorcin Blue Complexes. *American Journal of Analytical Chemistry*. 3 (9), 650-654.
- Brown, C. J., and Colclough, M. L. 1983. 1,8-Dinitro-4,5-Dihydroxyanthraquinone, C₁₄H₆N₂O₈. *Crystal Structure Communications*. C39 (2), 300-302.
- Chao, Y. C., and Yu, C. T 1992. Bis(arylamino) dihydroxyanthraquinones: bluish green dyes for synthetic polymer fibres. *Dyes and Pigments*. 19, 249-257.
- Cholak, J., 1959. Fluorides: A critical review. II. Analysis of fluorides. *Journal of Occupational Medicine*. 1, 648-654.
- Czarnowski, W., Wrzesniowska, K., and Krechniak, J. 1996. Fluoride in Drinking Water and Human Urine in Northern and Central Poland. *Science of the Total Environment*. 191 (1-2), 177-184.
- Dar, M. A., Sankar, K., and Dar, I. A. 2011. Fluorine Contamination in Groundwater: A Major Challenge. *Environmental Monitoring and Assessment*. 173, 955-968.
- Dixon, E.J., 1970. Determination of Micro Amounts of Fluoride with Zirconium and Solochrome Cyanine R. *Analyst*. 95, 272-277.
- Dunne, K., and Verrell, P. 2011. Acute Effect of Exposure to Sodium Fluoride on the Red Compost Earthworm *Eisenia Fetida*: Lethality and Avoidance Behavior. *Fluoride*. 44, 210-214.
- Einaga, H., and Iwasaki, I. 1981. Spectrophotometric Study of the Reaction of Zirconium with Chrome Azurol S and Fluoride. *Talanta*. 28, 889-900.
- Gordon, P. F., and Gregory, P. 1983. *Organic Chemistry in Colour*. Berlin: Springer-Verlag.
- Hatch, K. L., and Magee, P. S. 1998. A Discriminant Model for Allergic Contact Dermatitis in Anthraquinone Disperse Dyes. *Quantitative Structure-Activity Relationship*. 17(1), 20-26.
- Jacobson, J.S., Weinstein L.H., 1977. Sampling and Analysis of Fluoride: Method for Ambient Air, Plant, and Animal Tissues, Water, Soil and Foods. *Journal of Occupational Medicine*. 19, 79-87.
- Lubs, H. A. 1955. *The Chemistry of Synthetic Dyes and Pigments*. New York: American Chemical Society.

- Macnulty, B.J., Hunter, C.J., and Barrett D.G. 1956. The Determination of Microgram Quantities of Fluoride: The Use of Aluminium - Eriochrome cyanin Complex. *Analitica Chimica Acta*. 14, 368-380.
- Maliyekkal, S. M., Shukla, S, Philip, L., and Nambi, I. M. 2008. Enhanced Fluoride Removal from Drinking Water by Magnesia-Amended Activated Alumina Granules. *Chemical Engineering Journal*. 140, 183-192.
- Meenakshi, Garg, V. K., Kavita, Renuka, and Malik, A. 2004. Groundwater Quality in some Villages of Haryana, India: Focus on fluoride and Fluorosis. *Journal of Hazardous Materials*. 106B (1-2), 85-97.
- Nishimoto, J., Yamada, T., Tabata, M. 2001. Solvent Extraction and Fluorometric Determination of Fluoride Ion at ppb Level in the Presence of Large Excess of Aluminum(III) and Iron(III) by Using an Expanded Porphyrin, Sapphyrin. *Analitica Chimica Acta*. 428, 201-208.
- Price, M.J., Walker, O.J. 1952. Determination of Fluoride in Water. *Analytical Chemistry*. 24, 1593-1595.
- Qin, X., Wang, S., Yu, M., Zhang, L., Li, X., Zuo, Z., Zhang, X., and Wang, L. 2009. Child Skeletal Fluorosis from Indoor Burning of Coal in Southwestern China. *Journal of Environmental and Public Health*. 2009 1-7.
- Rafique, T., Naseem, S., Bhangar, M. I., and Usmani, T. H. 2008. Fluoride Ion Contamination in Groundwater of Mithi Sub-District, the Thar Desert, Pakistan. *Environmental Geology*. 56, 317-326.
- Ruzicka, J. A., Jakschova, H., Marklas, L. 1966. Determination of Fluoride in Bones and Teeth with Xylenol Orange. *Talanta*. 13, 1341-1344.
- Sebek, J., Kejik, Z., and Bour, P. 2006. Geometry and Solvent Dependence of the Electronic Spectra of the Amide Group and Consequences for Peptide Circular Dichroism. *Journal of Physical Chemistry A*, 110 (14), 4702-4711.
- Shah, M. T., and S. Danishwar, (2003). Potential Fluoride Contamination in the Drinking Water of Naranji area, N.W.F.P., Pakistan. *Environmental Geochemistry and health*, 25, 475-481.
- Singh K. 2007. National Scenario of Fluorosis: The Visible Villain. *Indian Journal of Environmental Protection*. 27 (8), 740-750.
- Snell, F.D. 1978. *Photometric and Fluorometric Methods of Analysis Metals*. New York: John Willy & Sons., pp. 41, 467, 659, 693, 1179, 1344, 1412, 1857, 1887, & 1916.
- Srivastava, K.C., and Banerji, S. K. 1967. Chelate Formation Between Lead (II) and 1,2,5,8-Tetrahydroxyanthraquinone (Quinalizarin): Spectrophotometric Studies of the Composition and Stability. *Australian Journal of Chemistry*. 20, 1385-1394.
- Sunitha, V., Reddy, R., and Srinivas, B. 2004. Fluoride in Groundwater of Anantapur Town, Anantapur District, Andhra Pradesh, India. *Journal of Applied Geochemistry*. 6, 368-372

-
- Ukponmwan, D. O., and Freeman, H. S. 1990. Characterization of the Products Derived from the Nitration of 1,5-Dihydroxyanthraquinone (Anthrarufin) and 1,8-Dihydroxyanthraquinone (Chrysazin). *Dyes and Pigments*, 12, 145-155
 - UNICEF, 1999. Fluoride in Water: An Overview. *WATERfront*. 13, 1-28.
 - Werner, L., and Boltz, D. F. 1971a. Theory of Continuous Variations Plots and A New Method for Spectrophotometric Determination of Extraction and Formation Constant. *Analytical Chemistry*. 43 (10), 1265-1272.
 - Werner, L., and Boltz, D. F. 1971b. Spectrophotometric Determination of Extraction Constants of Certain Metal 1-Pyrrolidinecarbodithioates. *Analytical Chemistry*. 43 (10), 1273-1277.
 - WHO, 2004. Guideline for Drinking-Water Quality. Recommendation, 2nd Edition. Vol. 1, Geneva: World Health Organization, pp. 375-377.
 - WHO, 2006. Fluoride in Drinking-Water. London: IWA Publishing, pp. 1-3, 83-95.
 - Zolgharnein, J., Shahrjerdi, A., Azmi, G., and Ghasemi, J. 2009. Spectrophotometric Determination of Trace Amounts of Fluoride Using An Al-Xylenol Orange Complex as A Colored Reagent. *Analytical Science*. 25, 1249-1253.
 - Zollinger, H. 2003. *Colour Chemistry: Syntheses, Properties, and Applications of Organic Dyes and Pigments*. Zurich: Verlag Helvetica Chimica Acta.