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Synthesis and characterization of lanthanum chloranilate complex: Application to spectrophotometric determination of anions

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Abstract

Lanthanum chloranilate complex has been synthesized and characterized using different techniques like Infrared spectroscopy and CHN analysis. It has been used for the development of spectrophotometric method of determination of anions like fluoride, EDTA and iodate. The determination is based on the reaction of these anions with the lanthanum ion in the chloranilate complex resulting in the liberation of an equivalent amount of chloranilate anion, the colour of which was measured. The experimental conditions, which affect the optical density, are studied to get maximum sensitivity. Interference studies were carried out with various ions. The method has been applied to the determination of these ions in actual samples viz. EDTA in detergents and iodate in salt.

Keywords: Lanthanum chloranilate; Synthesis; Characterization; Spectrophotometric determination of iodate; EDTA; Fluoride

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1. Introduction

Many ions like fluoride and iodate [1,2] are very important micronutrients at low concentration levels but the very same anions at high concentrations are toxic in nature. Excess amounts of fluoride are known to cause fluorosis and renal gastro intestinal immulogical toxicity. Optimum level of fluoride in drinking water should be 0.6–1.1 ppm. Samples from hot water spring contain 10–13 ppm of fluoride. Iodine is an important nutrient, the deficiency of which results in brain damage and mental retardation. Edible salt, which is a broad-spectrum seasoning, is compulsorily iodized by coating potassium iodate on salt crystals and recommended concentration of iodate is about 40 ppm [3]. Excess of iodine causes thyrotoxicosis. There is large number of techniques for the determination of these anions. The fluoride ion is determined using spectrophotometric methods based on Zr SPADNS and other dyes [4,5], ion chromatography [6] and various other methods [7–10]. In most of these methods, the limit of detection was reduced by using solvent extraction coupled with fluorimetry [8] or derivatization followed by determination using gas chromatography [9]. There are reports, which deals with the determination of iodate in table salt by electrochemical [11,12] and spectrophotometric methods [13–15]. The determination of iodate and iodide in various matrices has also been reported [16,17].

EDTA is an important constituent present in most detergents. It is added to function as a foam stabilizer as an alternate to phosphate in detergent formulation [18]. There are a large number of reports, which deal with different methods for the determination of EDTA [19–22]. Spectrofluorimetric determination using Zr-Alizarin Red S and FIA are used for ppb and ppm levels of EDTA respectively. The method of solid phase extraction based on Ni chelate developed by Shippard [20] uses capillary electrophoresis and tandem MS and the determination limit was reduced to as low as 0.15 ppb.

Studies on chloranilic acid or its metal complexes have been reported [23–32]. Some of these reports deal with the structural studies of the complex [23–26] and the others deal with determination of different species [27–32]. The very first reports deal with use of silver [30] and barium [31] chlorani-

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late complexes for the determination of chloride and sulphate respectively.

In this paper, the lanthanum chloranilate complex has been used for the determination of iodate, fluoride and EDTA. The lanthanum complex has been synthesized and characterized prior to its use for the determinations. The method developed has been applied to actual samples.

2. Experimental

2.1. Reagents

i. Lanthanum solution: was prepared from the spectra pure oxide obtained from E. Merck and dissolved in nitric acid. The solution was standardized by EDTA titration using xylenol orange as indicator.
ii. Chloranilic acid solution: weighed 0.1 g of chloranilic acid (E. Merck, GR) and made up to 100 ml to obtain a 0.1 wt.% solution.
iii. Anion solutions: weighed appropriate amounts of the sodium or potassium salts of the three anions to make stock solutions of 0.1 M. The stock solutions were further diluted to get the required concentrations.

2.2. Procedure

i. Synthesis of the complex:

   Fifty millilitres of 0.1 M La $(NO_3)_3$ and 50 ml of 0.1 wt.% chloranilic acid solutions were mixed together with constant stirring. Initially a green precipitate was formed which was allowed to stand in the mother liquor overnight at room temperature. A black precipitate was formed which was easily filtered and then washed well with distilled water until washings are free of lanthanum ion (tested using xylenol orange indicator). Washed well with 50% ethanol and then with pure ethanol. The washed precipitate was first air-dried and then vacuum dried for half an hour and stored in a cool and dried place. The precipitate was now ready for use for different analysis.

ii. Characterization of the complex.
   - *Determination of the lanthanum content*: weighed about 0.1 g of lanthanum chloranilate complex and ignited. The weight after ignition was taken. The ignition results in the formation of lanthanum oxide and knowing the weight of lanthanum oxide formed, it was possible to calculate the amount of lanthanum present in the complex originally taken. The oxide formed was then dissolved in nitric acid and amount of lanthanum was determined by EDTA titration using xylenol orange as indicator.
   - *Determination of the elemental composition*: the complex analyzed using LECO WR 12 Carbon Determinator CHN analyser.
   - *Structural analysis*: IR spectra were recorded using Bomem Hartmaun and Braun MB series IR spectrophotometer.

iii. Determination of anions.
   - *Method of determination*: the method for determination of all the anions was the same. To an aliquot of the anions, say F^-, of known concentration, adjusted to a particular pH, added about 0.02 g of lanthanum chloranilate and 5 ml of 50% ethanol and made up to 10 ml using distilled water. Shake well and wait for about 10 min. A deep red colour was formed. Filtered and measured the absorbance of the filtrate at 530 nm using a Shimadzu UV-Vis 210A double beam spectrophotometer.
   - *Optimization of experimental parameters*: the different factors like pH of the solution, amount of complex used that can affect the sensitivity of the above determination are studied to arrive at optimum experimental conditions. Interference studies were carried out with various ions.
   - *Sample analysis*: the above method was applied to the analysis of fluoride in water, EDTA in detergents and iodate in salt. The water samples did not require any pre-treatment except for filtration in case of suspended particles. The salt samples were weighed and dissolved in deionized water. In the case of detergents, weighed amount of the detergents were treated with acid and then made up to the required volume. Once the samples were in solution form, the determinations were carried out as above.

2.3. Validation methods

The above method of determination for various anions was validated using different analytical techniques.

The fluoride ion determination was carried out using Fluoride ion selective electrode. For this, different aliquots containing varying concentrations of fluoride ion were taken and adjusted their pH to 5.5. Then an equal volume of TISAB buffer is added and stirred and measured the potential using the electrode. The values of potentials are plotted as a function of concentration and calibration plot is used to determine the fluoride content of the unknown samples.

The determination of iodate was carried out spectrophotometrically using starch iodide mixture. Different aliquots of containing various concentrations of iodate in presence of 4% NaCl were treated with 0.75 ml starch-iodide mixture (1 g of starch + 1.5 g KI in 100 ml of distilled water) and the pH was adjusted to 3 using NaOH or HCl and made upto fixed volume. The solutions were allowed to stand in the dark for half an hour and their absorbance were measured at 570 nm using the corresponding blank. The sample solutions were also treated in a similar manner.

EDTA determination was carried out by titrating against standard zinc solution at pH of 5.5 using xylenol orange as indicator.

3. Results and discussion

Chloranilic acid, a red solid with a molecular weight of 208.9 is a dibasic acid with low solubility in water. It is known as 2,5 dichloro 3,6 dihydroxy p benzoquinone. The lanthanum chloranilate complex, a black solid was characterized using different techniques to get an idea of the nature of the complex.

In the present studies, the results of both CHN analysis and lanthanum content determination are used to deduce the metal to ligand ratio of the lanthanum chloranilate complex. The determination of elemental composition of both the chloranilic acid and lanthanum chloranilate complex have been carried out using CHN analyzer. It was observed that the red chloranilic acid was found to contain 34% C and 2% H whereas the black chloranilate complex contained 28% C and about 0.03% H. The determination of lanthanum content gave a value of about 24% lanthanum. These results correspond to a 1:3 complex and this in accordance with the structure proposed by Miyanga and Sudoh [33]. The structure is given in Fig. 1. The IR spectra of the pure chloranilic acid (red solid) and chloranilate complex (black solid) are shown in Fig. 2. It was observed that the complexation resulted in a change in the spectra of the pure chloranilic acid. The spectrum of the complex has a peak at 437 cm^{-1} corresponding to the La-O vibration. This is in accordance with the report of Verdaguer et al. [34].

It is reported in literature that chloranilic acid complexes, which have low solubility in water, have been used for various determinations [30–32]. The various factors that affect the sensitivity of the method are method of preparation of chloranilate complex, solvent composition, pH and interfering ions.

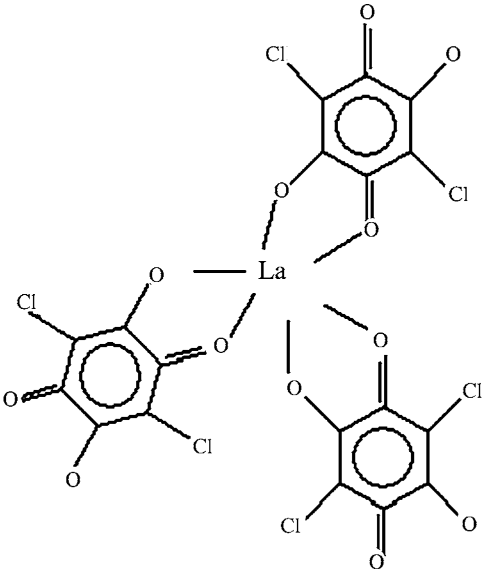

Fig. 1. Structure of lanthanum chloranilate complex.

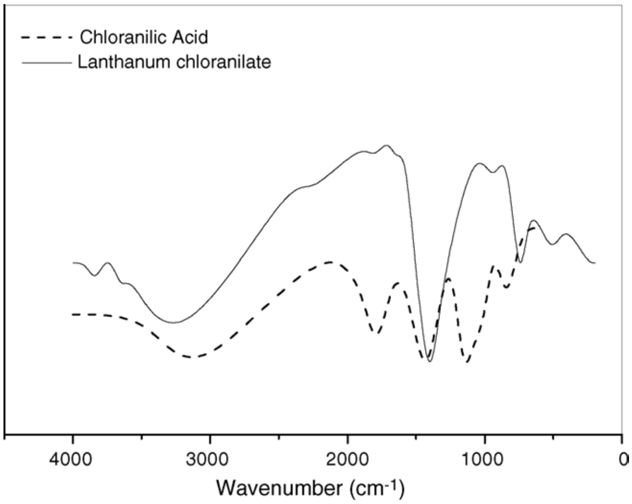

Fig. 2. IR spectra of chloranilic acid and lanthanum chloranilate.

3.1. Nature of the chloranilate complex

When the two aqueous solutions of lanthanum nitrate and chloranilic acid were mixed, initially a light green precipitate was formed. Upon aging it forms a blackish purple precipitate. The green precipitate when treated with the anion solution results in a colloidal suspension, which cannot be easily separated from the solution, whereas the black precipitate after use can be easily filtered.

3.2. Effect of solvent composition

It is reported [31] that the solvent composition has an effect on the sensitivity of the measurement. This has been attributed to the lower solubility of the chloranilate complex or the salt in the mixed solvent. Hence in the present study, all the experiments were carried out in 50% ethanolic medium.

3.3. Effect of pH on the sensitivity

It is reported that the absorbance of chloranilic acid is affected by pH of the solution and therefore there must be strict adherence to the pH conditions. It is because the different structures of chloranilic acid have different colours: the chloranilic acid is yellow whereas the chloranilic acid anion is dark purple and the chloranilate anion is light purple in colour [30]. It is reported that all these three species exist in equilibrium and the formation of either of them is dependent on their proton affinity and therefore the external pH. In order to obtain maximum sensitivity, the pH of the solution was varied. The results of the pH variation are shown in Fig. 3. It was seen that at lower pH, the absorbance values decrease. This could be due to the increased solubility of the chloranilate complex. It was seen that optimum pH for measurement was 2.6. It is observed that the formation of acid chloranilate anion is complete in the pH of about 2.2 and therefore maximum sensitivity is achieved at pH of 2.6.

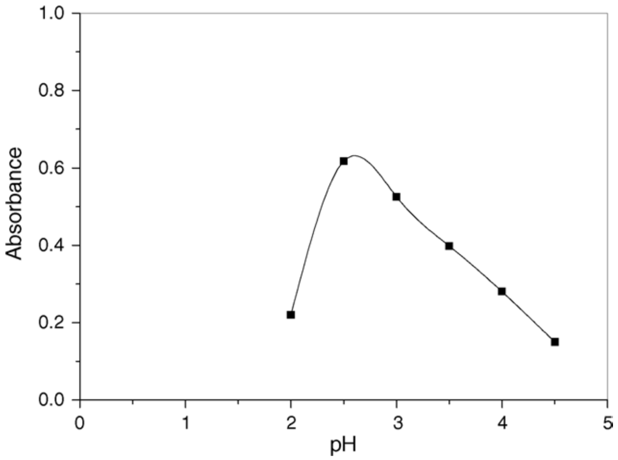

Fig. 3. Variation of absorbance as a function of pH of the solution.

It is possible to use dilute acid for pH adjustment because the chloranilate complex has low solubility in commonly used dilute acids. So all the further experiments were carried out at the pH of 2.6.

3.4. *Effect of amount of chloranilate complex*

The amount of chloranilate precipitate was varied to find out if this affects the sensitivity of the method. It was observed that there was practically no effect of the amount of complex used and therefore by using very low amount of the complex (0.02 g), the determinations could be carried out with good sensitivity. Hence all experiments were carried out using 0.02 g of lanthanum chloranilate.

3.5. *Determination of anions and sensitivity of determination*

The determination of anions were carried out under optimized experimental conditions using 0.02 g of chloranilate complex in 50% ethanolic medium at a pH of 2.6 and it is seen that a good linear calibration is obtained for the three different anions; the sensitivity depends on the nature of anion. The results of this study are shown in Fig. 4.

The spectrophotometric determination of the inorganic anions is based on a simple principle given by the following equation:

$$X^{n-} + \mathrm{LaCA}_{(\mathrm{solid})} + H^{+} \rightarrow [\mathrm{La(X)}m]^{3-n} + \mathrm{HCA}^{-}$$

It is seen that when lanthanum chloranilate reacts with the analyte anion X, it combines with lanthanum to form a complex LaX and an equivalent amount of chloranilate anion HCA^- is released into solution. The absorbance of the released chloranilate anion is measured. It is seen from the above equation that the nature of the analyte anion affects the molar composition of LaX. Since lanthanum forms a 1:3 complex with fluoride or iodate, it is seen that 3 equivalents of these anions react with one equivalent of lanthanum and therefore liberate three equivalents of chloranilate anion. In the case of EDTA, it is known that one equivalent of EDTA will react completely with one equivalent of lanthanum as it forms a 1:1 complex. Hence one equivalent of EDTA will liberate three equivalents of chloranilate anion. Hence for the same concentration, the amount of chloranilate anion liberated by EDTA is three times more than that by fluoride or iodate. Also the stability constant of the La EDTA complex ($\log K = 15.91$) is much higher than that of fluoride ($\log K = 3.19$) [35]. Hence all these factors combine to make the determination of EDTA more sensitive compared to other anions (Fig. 4).

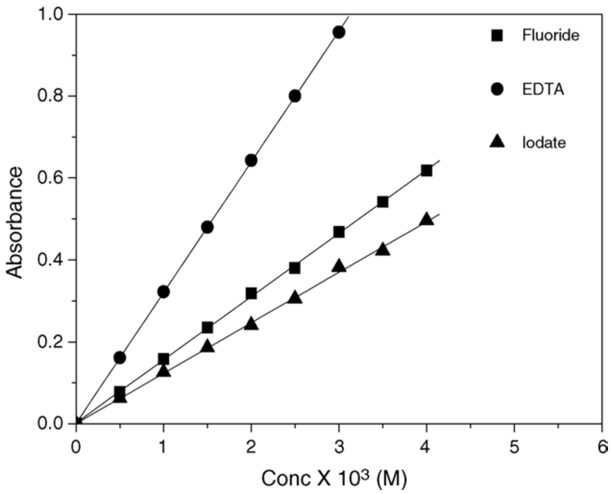

Fig. 4. Calibration plots for different anions.

3.6. *Interference studies*

The interference of different ions in the determinations of fluoride, iodate and EDTA has been studied in detail. The results are presented in Tables 1–3. These studies were carried out using interfering ions in the same concentration range as that of the analyte anion.

In the determination of fluoride, it was seen that the presence of anions like chloride, nitrate and sulphate did not cause any serious interferences but EDTA and iodate caused positive interferences. In order to reduce the interferences from these ions, barium was used as masking agent. The determination of iodate was not affected by the presence of chloride, nitrate and sulphate but the serious interferences

Table 1
Interference studies in the determination of Fluoride

Interfering anion		Conc. of fluoride ($\times 10^3$ M)		Interference
	Conc. $\times 10^3$ (M)	Taken	Measured	
Cl^-	4.0	4.02	4.15	No
NO_3^-	4.0		4.11	No
IO_3^-	4.0		5.12	Yes
SO_4^{2-}	4.0		4.54	No
EDTA	4.0		5.89	Yes

Table 2
Interference studies in the determination of iodate

Interfering anion		Conc. of iodate ($\times 10^3$ M)		Interference
	Conc. $\times 10^3$ (M)	Taken	Measured	
F^-	4.0	4.12	5.23	Yes
Cl^-	4.0		4.21	No
NO_3^-	4.0		4.19	No
SO_4^{2-}	4.0		4.43	No
EDTA	4.0		6.04	Yes

Table 3
Interference studies in the determination of EDTA

Interfering anion		Conc. of EDTA ($\times 10^3$ M)		Interference
	Conc. $\times 10^3$ (M)	Taken	Measured	
F^-	3.0	3.11	4.01	Yes
Cl^-	3.0		3.21	No
NO_3^-	3.0		3.33	No
IO_3^-	3.0		3.79	Yes
SO_4^{2-}	3.0		3.32	No

due to EDTA and fluoride could be reduced by masking with Al^{3+}.

Though it is reported that both barium and aluminium [24,25] do form chloranilate complexes, in the present study the use of these ions did not show serious interferences and they could be used as masking agents. This could be possibly due to the fact that presence of other anions, which react with these cations. Further these cations would have to react with the solid lanthanum chloranilate to form the chloranilate complex and this would be kinetically slower in presence of other reacting anions.

3.7. Sample analysis

The above method was used for the analysis of fluoride, EDTA and iodate in water, detergent and salt samples respectively. The data of this analysis is given in Table 4. It is seen that the values of fluoride in water and iodate in salt samples, obtained by this method was in close agreement with those obtained by other methods. For the detergent samples, the values obtained were in close agreement with those given in the specifications and also with those obtained by other method.

Table 4
Analysis of samples

Sample	Anion of interest	Value expected	Value obtd by LaCA method	Value obtained by other method
Water	Fluoride		2.5 ppm	2.12 ppm
			3.4 ppm	3.09 ppm
Salt	Iodate	30–50 ppm	39 ppm	42 ppm
			35 ppm	40 ppm
			47 ppm	50 ppm
Detergent	EDTA	1%	0.96%	1.01%
		0.92%	0.86%	0.91%
		0.94%	0.89%	0.92%

4. Conclusion

The chloranilate complex was synthesized, characterized by different techniques and could be successfully applied to the analysis of anions in actual samples. This method is very simple and easy. The main advantage of this above method is seen in the case of analysis of iodate in salt and EDTA in detergent samples as this method eliminates the need for the pre-treatment of the samples to remove the matrix species. The analysis of iodate can be carried out in salt samples with great ease, as there is no interference from matrix chloride ion present at high concentration levels.

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