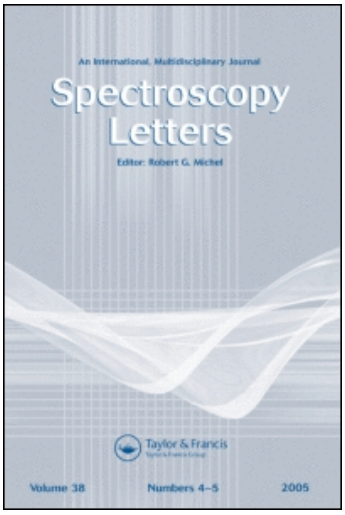

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Some Observations on the Spectrophotometry Determination of Di-And Trihydric Phenols by Edta Titration

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To cite this Article El-Dien, F. A. Nour(2000) 'Some Observations on the Spectrophotometry Determination of Di-And Trihydric Phenols by Edta Titration', Spectroscopy Letters, 33: 3, 347 — 357
To link to this Article: DOI: 10.1080/00387010009350081
URL: http://dx.doi.org/10.1080/00387010009350081

SPECTROSCOPY LETTERS, 33(3), 347–357 (2000)

SOME OBSERVATIONS ON THE SPECTROPHOTOMETRIC DETERMINATION OF DI- AND TRIHYDRIC PHENOLS BY EDTA TITRATION

Key words: Trioxalatoferrate(III), phenols, dopamine, adrenaline, sulbutamol, EDTA titration, urine analysis of tumor patients.

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ABSTRACT

Novel reaction between trioxalatoferrate (III) complex (A) and some di- and trihydric phenols were studied and found to form interesting mixed ligand chelates of iron (III) in the ratio 1:2:1 (Fe : oxalate : phenol) forming blue to violet colors at pH 4.0 to 6.5 and λ_{max} = 580 to 590 nm. These reactions were used for indirect volumetric and spectrophotometric microdetermination of catechol (PC), pyrogallol (PG), dopamine hydrochloride (DHCl), adrenaline hydrogen tartrate (AHT) and sulbutamol sulfate (SS) via EDTA titration using complex (A) as an indicator. PC, DHCl and PG were determined by EDTA titration within the concentration

ranges of 0.55-2.2, 0.95-3.79 and 0.65-2.52 μg ml^{-1}, respectively. AHT was determined in the concentration range of 96 to 204 μg ml^{-1} and SS was also determined in the range 5.75 to 57.7 μg ml^{-1}. Adrenaline in ampoules coming from two Egyptian companies: sulbutamol in sulbovent liquids, and dopamine in five urine samples of Egyptian tumor patients, was also determined using the suggested procedure with high accuracy.

INTRODUCTION

Phenolic compounds represent widely used raw materials in the chemical industry, where they are employed, in the production of pharmaceuticals and pesticides. The color reactions of phenolic compounds with heavy metal cations and their complexes [1-4] were used for spectrophotometric determination of hydroxybenzenes in pure states and after separation from their natural sources by different chromatographic techniques [5-7] . Owing to technical difficulty, until recently very few reports on the analysis of catechol and catecholamine in biological fluids have been published . A recent HPLC method described by Inoue et al.[8] using UV detection has been found to be non- specific and insensitive for low level detection. An improved method has been developed by Lee et al.[9] to assay the urine using HPLC with variable-wavelength fluorimetric detection.

In the present work there are many interesting color reactions between trioxalatoferrate (III) complex (A) and some di- and tri- hydric phenols[10]. This class of compounds has an important role in biological chemistry, including PC, PG , dopamine, adrenaline, and their derivatives; both in pure forms and in complicated natural materials. The proposed procedure requires no separation of these phenolic compounds from their sources to

determine them accurately, via an EDTA titration using complex (A) indicator.

EXPERIMENTAL

Effect of pH on behavior of the formed mixed ligand chelates

The absorption spectra of 0.1 to 3 x 10^{-3} M solutions in a 25 ml measuring flask of the obtained mixed ligand chelates were studied at pH range 3.8 to 12.3 in the visible region. The selected optimum pH that gave the best stable distinct colored chelates of λ_{max}= 580 to 590 nm was found to be in the range 4.0 to 6.5. The required pH was attained by the use of 0.2M NaOH, HNO_3, or acetate buffer in some instances, and followed by the measurement of pH with a pH-meter (Orion Research Model 701 A).

Volumetric and spectrophotometric titration

(a)Volumetric procedure:

Add 0.5 to 2 ml of 10^{-2} M complex (A) to a specified volume of 10^{-2} M of the phenolic compound, followed by the addition of 0.2 M NaOH to obtain the selected pH 4.0 to 6.5. Dilute to a volume of 25 ml (calibrated flask) with doubly distilled water, making certain to determine the precise final pH. The colored solution was visually titrated against 10^{-2} M EDTA. The endpoint was achieved at blue-violet color change to slight yellow. The concentration of the titrated phenol or drug was directly estimated from its molarity.

(b)Spectrophotometric procedure:

Add 2 ml of 10^{-2} M complex (A) to a specified volume of 10^{-2} M of phenolic compound or drugs, followed by the addition of 0.2 to 2 ml of 10^{-2}

M EDTA. With thorough mixing, add 0.4 ml of 0.2 M NaOH to obtain the required pH between 4.0 to 6.5. The mixture was completed by diluting with distilled water in a calibration flask, and the final pH was rechecked. The absorbance of the solutions was measured against a distilled water blank and plotted against volume of EDTA. The sharp inflection of the curve indicates the endpoints from which the molarity of the unknown phenolic compound was determined, and consequently its concentration.

(c) Determination of catecholamine (in terms of Dopamine) in urine of Egyptian Tumor Patients:

i-Collection and preparation of urine samples: Five samples of some hypertensive and Tumor diagnosed Egyptian patients were collected and prepared as previously recommended [11].

ii- 2.0 ml of 10^{-2} M complex (A) was added to 0.45 ml of 0.010 M DHCl as a standard followed by 1 ml of acetate buffer, 0.1 to 2.0 ml of 10^{-2} M EDTA and 0.4 ml of 0.2 M NaOH to keep the pH of the solution at pH 5.0. The mixture was completed by diluting with doubly distilled water to 25 ml in a calibration flask, and the final pH was rechecked. The absorbance of the standard was measured at λ_{max}=580-590 nm and plotted against different volumes of standard EDTA added. From the inflection of the titration curves the molarity of DHCl standard was estimated.

iii-This procedure was repeated using mixtures of 2.0 ml of 10^{-2} M complex(A), 2.0 ml of urine sample, 0.45 ml of 0.010 M DHCl, 1 ml of acetate buffer, 0.2 to 2.0 ml of 10^{-2} M EDTA and the required volume of NaOH to keep the pH at 5.0. The volume of mixture was diluted to 25ml, and final pH was rechecked . The absorbance of unknown dopamine in urine and standard DHCl were measured and their concentrations were

estimated. The dopamine in urine samples were calculated using the difference in data from ii and iii.

RESULTS AND DISCUSSION

The interesting color reactions between trioxalatoferrate (III) complex (A) with PC, DHCl, PG, AHT, and SS were studied spectrophotometricaly at different pH values in the range 3.8 to 12.3, and wavelengths from 300 to 800 nm. The selected optimum pH was found to be 4.0 to 6.5, and the best color of the obtained mixed ligand chelates was achieved at λ_{max} =580 to 590 nm. This color was proved to be due to the formation of mixed ligand chelates Fe(III):oxalate:phenol (1:2:1) [10-12]. These color reactions are used as a basis for volumetric and spectrophotometric titration of the phenolic compounds in pure and complex matrices.

(a) volumetric titration results:

In the volumetric analysis, excess indicator (A) is added to phenolic compound, or drugs in solution. Under the optimum condition of pH, titration with standard EDTA is accomplished until the endpoint is achieved at a color change from blue-violet to yellow. The concentrations of phenolic compounds PC, DHCl and PG are recorded in Table (1). The concentrations are varied form 0.55 to 2.20, 0.95 to 3.79 and 0.61 to 2.52 $\mu g\ ml^{-1}$ for PC , DHCl and PG; with standard deviation (SD) = 1.48 , 1.32 and 1.63 (n = 3-5), and percent recovery of 95 to 100, 95.1 to 105.2 and 93.9 to 104.4 percent, respectively. These results refer to the accuracy and precision of the application of the proposed volumetric procedure.

(b) Spectrophotometric titration results:

The spectrophotometric detection of endpoint in EDTA titration using

TABLE 1.

Volumetric microdetermination of PC, DHCl, and PG by titration with EDTA using trioxalatoferrate (III) complex as indicator.

PC μg ml^{-1}			DHCl μg ml^{-1}			PG μg ml^{-1}		
W_T	W_F	Recovery (%)	W_T	W_F	Recovery (%)	W_T	W_F	Recovery (%)
2.20	2.09	95.0	3.79	3.75	98.9	2.52	2.63	104.4
1.65	1.60	97.0	2.84	2.70	95.1	1.89	1.89	100.0
1.10	1.09	99.1	1.89	1.86	98.4	1.26	1.24	98.4
0.55	0.55	100	0.95	1.00	105.2	0.65	0.61	93.9
* SD (n = 3-5)		± 1.48			± 1.32			± 1.63

W_T and W_F are weight taken and found respectively.

the complex (A) as an indicator is more efficient as than visual detection. The sharp inflection of the titration curve near the intermediate vicinity of the endpoint indicates its accurate detection. Therefore, this proposed procedure was applied for EDTA titration of phenolic compounds, PC, DHCl, and PG (Table 2); catecholamines (AHT and adrenaline in ampoules coming from two Egyptian companies) and noncatecholamines (SS and sulbutamole in sulbovent liquid) (Table 3); and Dopamine in five urine samples coming from Egyptian tumor patients of different ages (Table 4).

The results in Table (2) show that the applied spectrophotometric EDTA titration of di- and trihydric phenols, PC, DHCl and PG succeeded in microdetermination of these compounds in the same concentration ranges as in volumetric technique but with low SD = 0.38 ,0.36 and 0.37; and

TABLE 2.

Spectrophotometric microdetermination of PC, DHCl, and PG via EDTA titration using trioxalatoferrate (III) complex as indicator.

PC μg ml^{-1}			DHCl μg ml^{-1}			PG μg ml^{-1}		
W_T	W_F	Recovery (%)	W_T	W_F	Recovery (%)	W_T	W_F	Recovery (%)
0.55	0.55	100	0.95	0.95	100.0	0.63	0.62	98.4
1.10	1.06	97.3	1.90	1.88	99.0	1.26	1.27	100.8
1.65	1.65	100	2.84	2.88	101.4	1.90	1.96	103.2
2.20	2.16	98.2	3.79	3.70	97.6	2.52	2.46	97.6
* SD (n = 3-5)		±0.38			± 0.36			± 0.37

W_T and W_F are weight taken and found respectively.

percentage recovery of 97.3 to 100, 97.5 to 101.4, and 97.6 to 103.2 percent, respectively. This refers to the more reliable use of EDTA in spectrophotometric titration for determination of these phenolic compounds.

Table (3) shows the results of microdetermination of standard AHT in the concentration range from 96 to 204 μg ml^{-1} with SD = 0.38 (n=5) and percentage recovery of 96.6 to 102 percent. These results encourage the use of this procedure for the microdetermination of the effective adrenaline in adrenaline ampoules, supplied by MISR Pharmaceutical Company (0.25 mg ml^{-1}, 1.364 x 10^{-3} M), and from Memphis Egyptian Pharmaceutical Company (1 mg ml^{-1}, 5.4 x10^{-3}M). The results for these samples from concentration ranges 10 to 99 μg ml^{-1}, were SD= 0.40 (n=5) and percentage recovery of 95 to 105 percent. These results indicate a reliable and precise

TABLE 3.

Microdetermination of catecholamines (adrenaline) and non-catecholamines (sulbutamole) in Egyptian pharmaceutical preparations via EDTA titration using trioxalatoferrate (III) complex as indicator .

AHT μ g ml^{-1}			Adrenaline (in ampoules)μg ml^{-1}			Sulbutamol sulfate (SS) μg ml^{-1}			Sulbutamol sulfate (in sulbovent liquid) μg ml^{-1}		
W_T	W_F	Recovery (%)	W_T	W_F	Recovery (%)	W_T	W_F	Recovery (%)	W_T	W_F	Recovery (%)
96	98	102.1	99	101	102	5.7	5.7	100	13.0	14.0	107.7
109	109	100	80	80	100	14.9	14.7	98.7	16.0	16.0	100
133	138	103.7	51	51	100	24.2	24.2	100	32.0	34.0	106.2
142	143	100.7	39	39	100	28.4	29.0	102	48.0	49.0	102.1
162	162	100	20	19	95	31.7	31.7	100			
177	170	96.6	10	10.5	105	42.7	42.7	100			
204	210	102.9				53.1	53.1	100			
						58.0	60.0	103			
		SD = ±0.38 (n = 5)			SD = ±0.4 (n = 5)			SD = ±0.37 (n = 3-5)			SD = ±1.30 (n = 5)

Original : 0.25 mg ml^{-1} (1.364 x 10^{-3} M) (Misr Co.).
1 mg ml^{-1} (5.4 x 10^{-3} M) (Memphis Chem. Co.).

TABLE 4.

Spectrophotometric determination of catecholamine in urine (in terms of Dopamine) by using trioxalatoferrate (III) complex as indicator via titration with standard EDTA.

Sample No.	**Kind**	**Age (Years)**	**Concentration (μg ml^{-1})**	
			Applied method*	Standard method
1	male	8	110	108
2	male	13	133	128
3	male	25	166	163
4	female	45	133	129
5	male	54	133	129

* SD = 0.37 (n = 3 - 5).

application of spectrophotometric titration of adrenaline to standard Egyptian drug preparations using EDTA. This procedure was also applied to the microdetermination of standard SS in the concentration range 5.7 to 58 $\mu g\ ml^{-1}$ to check the ability of the procedure in the microdetermination of the noncatecholamines. The results yielded a SD= 0.37 (n=3-5) with percentage recovery of 98.7 to 103 percent. These results encourage the application of this procedure for microdetermination of subutamole in sulbovent liquid coming from MISR Pharmaceutical Company in the concentration range of 13 to 48 $\mu g\ ml^{-1}$ with SD = 1.3 (n=5), and percent recovery of 100 to 107 percent.

Table (4) shows the results of application of the proposed spectrophotometric EDTA titration in microdetermination of the possible catecholamines (in terms of DHCl); which may be present in urine of some Egyptian tumor patients from the Institute of Cancer of Cairo University, using the method of standard addition. The concentrations of catecholamines, directly determined in urine without separation, in terms of DHCl are found to be in the range of 110 to 166 $\mu g\ ml^{-1}$. This range applies for different ages of 8 to 54 years old, for male and female. The five samples measurements were compared with the results (i.e., 108 to 163 $\mu g\ ml^{-1}$) obtained using the conventional method. The standard method, usually applied in the Institute, is generally considered tedious and expensive[13]. The comparative study of these results between the standard method and the applied procedure gives a confidence level of 95.6 percent applying the F and t statistical tests .

CONCLUSION

From the above obtained results, it is concluded that the trioxalatoferrate -(III) complex (A) provides an inexpensive alternative quantitative

technique for measuring several important phenolic compounds. Complex (A) can be commercially prepared and forms an intense blue -violet color with di- and trihydric phenols, catecholamines and noncatecholamines. The colored mixed ligand chelates formed are used as a basis for volumetric and spectrophotometric titration of phenolic compounds (PC, DHCl, PG, AHT and SS), adrenaline, and sulbovent drugs. The spectrophotometric titration has shown successful preliminary results when applied for the microanalysis of dopamine using five urine samples collected from Egyptian tumor patients from the Institute of Cancer, Cairo University. The method demonstrated accurate results as compared with the traditional and expensive current procedure.

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Date Received: May 5, 1999
Date Accepted: October 20, 1999