

SPECTROPHOTOMETRIC DETERMINATION OF CITRACONIC ACID IN THE PRESENCE OF MESACONIC ACID

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A new spectrophotometric method for the determination of citraconic acid in the presence of mesaconic acid is proposed. It has been found that citraconic acid (or more exactly, the hydrogencitraconate anion) forms a stable red-colored association compound with the *tris*(1,10-phenanthroline)iron(II) cation ($\lambda_{\text{max}} = 516 \text{ nm}$) which can be selectively extracted with nitrobenzene. The optimal parameters of the determination are estimated (pH = 4, the molar ratio of the citraconic acid and indicator 1 : 36, measuring after 15 min after the formation of the complex). Under these conditions a large amount of mesaconic acid is not extracted making possible the determination of citraconic acid in the presence of mesaconic acid. In the concentration range from $8 \cdot 10^{-5} \text{ mol/l}$ to $2.4 \cdot 10^{-4} \text{ mol/l}$ a linear relationship between the absorbance value (at 516 nm) and the concentration of the citraconic acid has been found. The relative standard deviation is 4.03 % and the recovery is from 96.9 % to 102.5 %.

Key words: citraconic acid; mesaconic acid; spectrophotometric determination; *tris*(1,10-phenanthroline)iron(II)

INTRODUCTION

Citraconic acid (which, as it is well known, very often appears together with its geometric *trans* isomer mesaconic acid) is widely used as a starting material in the production of polymers, ion-exchange resins etc. [1]. This is why it is important to have an efficient and reliable method for the determination of the concentration of citraconic acid in the presence of its geometric isomer.

Several approaches are known in the literature. Thus, Ravindranath *et al.* [2] have proposed a spectrophotometric method with the use of curcumin and boric acid in the presence of which the citraconic acid forms a stable colored complex, while mesaconic acid does not react under these conditions. More recently, chromatographic methods for a quantitative determination of citraconic acid in the presence of its geometric isomer have been developed [3, 4].

In the course of our earlier studies [5] on the behavior and properties of the *cis-trans* isomeric

dicarboxylic acid, we developed a polarographic method for the determination of the two acids in a mixture. In the present study we attempted to develop a spectrophotometric method for determination of citraconic acid in the presence of mesaconic acid which would be both simpler and more precise than the few already known. Thus, we used the findings [6, 7] that some organic acids with a symmetric structure (e.g., phthalic acid, picric acid, maleic acid and some others) could be selectively extracted with a suitable organic solvent in the presence of cationic metal chelates such as *tris*(1,10-phenanthroline)iron(II), *tris*(2,2'-bipyridyl)iron(II), bis(cuproine)copper(AND) or bis(neocuproine)-copper(AND) with a subsequent use of the extract for a spectrophotometric determination of the organic acids. Since citraconic acid has a structure similar to that of the above-named acids, we believed that our previous experience would be beneficial in our present efforts.

EXPERIMENTAL

Reagents and solutions

All reagents for the preparation of the solutions were analytical-grade chemicals. Redistilled water was used as a solvent.

Standard solutions of dicarboxylic acids were prepared from recrystallized citraconic and mesaconic acid. The concentration of the two acids was $5 \cdot 10^{-3}$ mol/l. Before use, the stock solutions of carboxylic acids were diluted as required. The concentration of the two acids in the diluted solutions varied from $0.2 \cdot 10^{-4}$ mol/l to $2.4 \cdot 10^{-4}$ mol/l. The solution of *tris*(1,10-phenantroline) iron(II) sulfate ($c = 1.6 \cdot 10^{-2}$ mol/l) was prepared by dissolving 1.485 g of this compound and 0.695 g of ammonium iron(II) sulfate hexahydrate in diluted sulfuric acid (0.1 mol/l).

The phosphate buffer solutions with various pH were prepared by mixing the solution of potas-

sium dihydrogenphosphate (0.3 mol/l) and sulfuric acid (0.5 mol/l).

Procedure

5 ml of carboxylic acid solution, 5 ml of the phosphate buffer solution, 5 mL of standard solution of *tris*(1,10-phenantroline)iron(II) sulfate and 10 ml of water were transferred by pipette into a separating funnel. 10 ml of nitrobenzene was added and the funnel was shaken for 1 min (some other extractants were also used but the results were unsatisfactory). After 15 min the nitrobenzene extract was transferred to a 25 ml glass tube and anhydrous sodium sulphate was added to dry the benzene extract.

The spectra were recorded from 400 nm to 650 nm. The absorbance was measured at 516 nm, 15 min after the preparation of the benzene extract, using a reagent blank extract or nitrobenzene as a reference.

RESULTS AND DISCUSSION

The spectrum of the nitrobenzene extract of citraconic acid ($c = 1.2 \cdot 10^{-4}$ mol/l) of the aqueous solution which contains *tris*(1,10-phenantroline)-iron(II) sulfate with a concentration of $32 \cdot 10^{-4}$ mol/l in phosphate buffer (0.3 mol/l) with a pH value of 3.5 is shown in Fig. 1. As it can be seen from Fig. 1, an absorption band appears at around 516 nm.

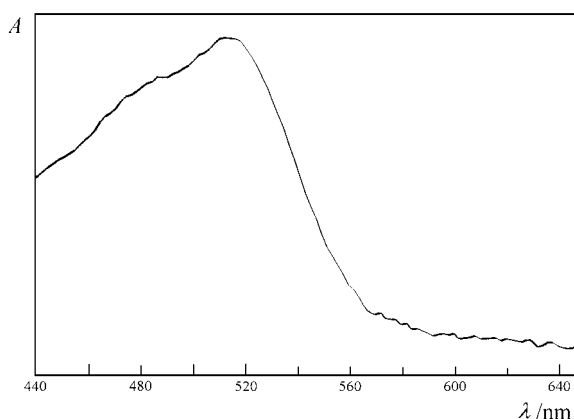


Fig. 1. UV-VIS spectrum of citraconic acid extracted with nitrobenzene in presence of *tris*(1,10-phenantroline)iron(II) sulfate and a phosphate buffer with pH = 3.5

The band is most probably due to the complex formed between the citraconic acid and

tris(1,10-phenantroline)iron(II) sulfate, a reaction which is expected for acids with a similar structure [7]. To confirm such an origin of the band in the spectrum, first of all the influence of pH values of the solution on the position and values of the absorbance of this band was studied. Several solutions were prepared with an identical concentration of the citraconic acid ($c = 1.2 \cdot 10^{-4}$ mol/l) and of the indicator *tris*(1,10-phenantroline)iron(II) sulfate ($c = 32 \cdot 10^{-4}$ mol/l) with different acidity. The acidity of the solutions was regulated with phosphate buffers with pH values from 3 to 5. The results of these measurements are shown in Table 1.

Table 1

*Absorbance values of the nitrobenzene extract of citraconic acid ($c = 1.2 \cdot 10^{-4}$ mol/l) in presence of *tris*(1,10-phenantroline)iron(II) sulfate and phosphate buffers with pH from 3 to 5*

pH	3.0	3.5	4.0	4.5	5.0
A_{516}	0.1707	0.3775	0.3990	0.3475	0.2173

It turned out that the *position* of the band does not change whereas the value of the absorbance of

the citraconic acid extract has a maximal value at a pH value of 4, although satisfactory absorbance values were obtained in the whole region of pH values between 3.5 and 4.5. Distribution curves for the individual forms of citraconic acid present at different acidity were obtained from the pK values of the acid: $pK_{a1} = 2.95$ and $pK_{a2} = 5.98$ [8] and are shown in Fig. 2. On the basis of these curves it is deduced that at the pH range from 3.5 to 5.5 the predominate form is the monodissociated citraconate ion which under the given conditions forms an ion-association complex with *tris*(1,10-phenantroline)iron(II) sulfate. It is this form to which the spectral band is assigned. In the course of the subsequent measurements the pH value of 4 is used as the optimal one.

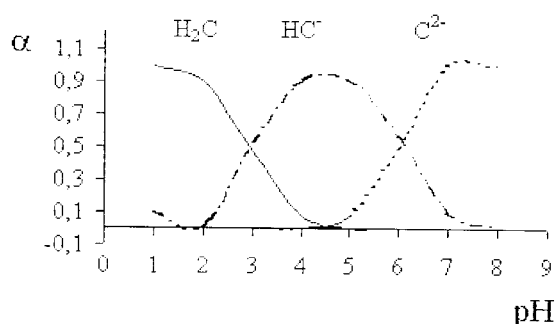


Fig. 2. Distribution of citraconate species (H_2C , HC^- and C_2^-) as a function of pH value

To determine the metal : ligand ratio in the formed complex, a series of solutions in which the concentration of citraconic acid was held constant ($1.2 \cdot 10^{-4}$ mol/l) and that of the indicator was varied from $0.12 \cdot 10^{-4}$ mol/l to $48 \cdot 10^{-4}$ mol/l. The pH value was 4 (a phosphate buffer). The results of these measurements are given in Table 2 in which $[cit] / \{[cit] + [ind]\}$ denotes the ratio of the equilibrium concentrations of citraconic acid (in the nominator) and the sum of the equilibrium concentrations of the acid and the indicator (in the denominator).

The data in the Table 2 show that the absorbance has a maximal value at the $[cit] / \{[cit] + [ind]\}$ ratio of 0.7, which suggests that in the formed ionic associate the mole ratio of the *tris*(1,10-phenantroline)iron(II) cation and the citraconate anion is 1 : 2.

The subsequent studies were carried out towards the goal of finding the optimal conditions for developing an analytical method for determination of citraconic acid in the presence of mesaconic

acid. As it turned out, the optimal ratio of the concentrations of citraconic acid and the indicator is 1 : 36, that is the one for which the maximal absorbance value was observed.

Table 2

Absorbance values of the nitrobenzene extract of citraconic acid at 516 nm in presence of tris(1,10-phenantroline)iron(II) sulfate with varying concentrations and a phosphate buffer with pH = 4.

$c_{ind} / \text{mol l}^{-1} \cdot 10^{-4}$	$[cit] / \{[cit] + [ind]\}$	A_{516}
0.12	0.90	0.2151
0.30	0.80	0.3605
0.54	0.70	0.5659
0.78	0.60	0.5203
1.20	0.50	0.4657
1.80	0.40	0.3965
2.70	0.30	0.3527
4.80	0.20	0.1998
10.80	0.10	0.0898
24.00	0.05	0.0712

In order to establish the influence of the isomeric form of the citraconic acid (mesaconic acid) on the formed ionic associate we tried to form, under identical experimental conditions as those for citraconic acid, an ionic associate between the mesaconate anion and *tris*(1,10-phenantroline)iron(II) sulfate at pH value of 4 (phosphate buffer). The extract from the reaction mixture in nitrobenzene is spectroscopically inactive (the band characteristic for the complex formed by the indicator with dicarboxylic acids is absent in the spectrum). Thus, it is very likely that the mesaconic acid does not form an ionic associate with *tris*(1,10-phenantroline)iron(II) sulfate. Then it follows that citraconic acid may be quantitatively determined in the presence of the mesaconic acid.

To determine the optimal period during which the absorbance of the formed complex could be measured, the stability of this associate was measured at subsequent periods after mixing the reagents. It was found that the absorbance values did not change during a period of 24 hours. The measurements were started 15 min after the preparation of the investigated sample because of practical reasons (the necessity of extraction etc.).

The concentration range in which the formed ionic associate obeys the Beer's law was determined too. The series of solutions with a varying content of the citraconic acid were prepared, in which the concentration of the *tris*(1,10-phenantroline)iron(II) sulfate (used as an indicator) was $32 \cdot 10^{-4}$ mol/l. The acidity of the solutions was, as previously described, regulated with a phosphate buffer (pH = 4). After the extraction in nitrobenzene, measured values of the absorbance at 516 nm, for one of the series of solutions, are shown in Table 3. On the basis of the obtained results the calibration diagram was constructed.

Table 3

The absorbance values at 516 nm of the nitrobenzene extract of citraconic acid in presence of tris(1,10 phenantroline)iron(II) sulfate with $c = 32 \cdot 10^{-4}$ mol/l and a phosphate buffer with pH=4

$c / \text{mol} \cdot \text{l}^{-1} \cdot 10^{-4}$	0.8	1.2	1.6	2.0	2.4
A_{516}	0.2516	0.4024	0.4389	0.5647	0.5988

The equation describing the linear relationship between the absorbance and the concentration of the citraconic acid is:

$$A_{516} = 0.1086 + 2.142 \cdot 10^3 c / \text{mol} \cdot \text{l}^{-1} \quad (R^2 = 0.988)$$

Consequently, it is clear that there are favorable conditions for development of an analytical method for the determination of the citraconic acid in the presence of the mesaconic acid.

The measurements done to evaluate the precision of the determination showed that the relative standard deviation (RST) is 4.03 %.

In addition to the study of the influence of the presence of the mesaconic acid on the results obtained from the determination of the concentration of the citraconic acid, the influence of several other acids: oxalic, tartaric and fumaric was studied too.

Namely, in real samples these acids could be present together with the citraconic acid. The investigations show that these other acids do not react with *tris*(1,10-phenantroline)iron(II) and have no significant influence on the spectrum of the complex of this reagent with the citraconic acid.

The influence of the chloride and sulfate ions was also studied. Several solutions with an identical concentration of the citraconic acid ($c = 1.2 \cdot 10^{-4}$ mol/l) and of the indicator *tris*(1,10-phenantroline)iron(II) sulfate ($c = 32 \cdot 10^{-4}$ mol/l) and varying concentrations of chloride (from $1.5 \cdot 10^{-4}$ mol/l to $2.0 \cdot 10^{-2}$ mol/l) and of sulfate (from $3.0 \cdot 10^{-4}$ mol/l to $3.2 \cdot 10^{-2}$ mol/l) ions were prepared, respectively. It was shown that these ions influence the final results when their concentration is about 10 times higher than that of the acid.

The developed method for determination of the citraconic acid with *tris*(1,10-phenantroline)iron(II) ion in the presence of the mesaconic acid (method of standard addition) was tested on simulated samples in which the content of the citraconic and of the mesaconic acid was varied. In all studied cases the analytical recovery, R , was in the allowed range (see Table 4).

Table 4

Determined values of the concentration of citraconic acid in the presence of mesaconic acid

$c_{\text{mesac.acid}} / \text{mol} \cdot \text{l}^{-1} \cdot 10^{-4}$	$c_{\text{citraconic acid}} / \text{mol} \cdot \text{l}^{-1} \cdot 10^{-4}$		A_{516}	(R in %)
	Taken	Found		
0.5	1.00	1.02	0.3278	102.0
1.0	1.20	1.22	0.3830	101.7
1.5	1.50	1.45	0.4198	96.9
2.0	2.00	2.05	0.5479	102.5
3.0	2.50	2.48	0.6409	99.2

CONCLUSIONS

Our studies showed that the method for determination of the citraconic acid in the presence of the mesaconic acid developed by us, is not only characterized by satisfactory accuracy (RST = 4.03 % and R from 96.9 % to 102.5 %) and sensitivity, but is also suitable for the determination of the content of

the citraconic acid in samples which contain oxalic, tartaric and fumaric acid, as well as chloride and sulfate ions.

Acknowledgement. In the far-away year 1977, the University of Skopje was caught in the storm called

“the University reform”. The authors of the present paper, as a consequence of the reform moved from the Faculty of Technology and Metallurgy to the newly established Faculty of Chemistry. Because of many reasons, the group from the Faculty of Technology and Metallurgy was treated as “the newcomers”. Among those who treated us as colleagues of equal standing

thus helping us to overcome the anxiety we felt was Dr. Ivan Petrov whom we then simply called “the professor”. As a sign of recognition and appreciation for everything “the professor” did during his working life but especially the treatment of us, with a feeling of great respect for him we dedicate this paper to him.

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Резиме

СПЕКТРОФОТОМЕТРИСКО ОПРЕДЕЛУВАЊЕ НА ЦИТРАКОНСКА КИСЕЛИНА ВО ПРИСУСТВО НА МЕЗАКОНСКА КИСЕЛИНА

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Клучни зборови: цитраконска киселина; мезаконска киселина; спектрофотометриско определување; *tris*(1,10-фенантролин)железо(II).

Предложен е нов спектрофотометриски метод за определување на цитраконска киселина во присуство на мезаконска киселина. Најдено е дека цитраконската киселина (или, поточно, хидрогенцитраконатниот анион) формира стабилно, црвено обоено соединие со катјонот на *tris*(1,10-фенантролин)железо(II) ($\lambda_{\max} = 516 \text{ nm}$), кое може селективно да се екстрахира со нитробензен. Определени се оптималните експериментални параметри (pH = 4, моларниот однос цитраконска киселина : индикатор = 1 : 36, спектрофотоме-

трирање по 15 min од формирање на комплексот), при кои мезаконската киселина не гради комплекс, што го овозможува определувањето на цитраконска во присуство на мезаконската киселина. Во концентрациското подрачје од $8,0 \cdot 10^{-5} \text{ mol/l}$ до $2,4 \cdot 10^{-4} \text{ mol/l}$ постои линеарна зависност меѓу вредноста на измерената апсорбанца и концентрацијата на мезаконската киселина. Релативната стандардна девијација изнесува 4,03 %, а аналитичкиот принос се движи од 96,9 до 102,5 %.