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Determination of the Protonation Constants of Some Substituted Salicylideneanilines by the Spectrophotometric Method in Ethanol-Water Mixtures

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Protonation constants of salicylideneaniline and methyl-, ethyl-, methoxy- fluoro-, chloro-, bromo- and iodo- substituted salicylideneanilines were determined by spectrophotomeric titrimetry in 10, 30, 50 and 70% ethanol-water mixtures at constant ionic strength and at 25°C. The results obtained from this work were compared with those obtained using the potentimetric method. The difference between the results found with these two methods was approximately ± 0.20 log$K$ units. The spectrophotometric method was judged to be more suitable than the potentiometric method for halogen substituted salicylideneanilines with the low log$K$values and in the solvent mixture containing 10% ethanol, due to the low solubility of Schiff's bases.

Key Words: Protonation constant, titrimetry, Schiff's base, ethanol-water mixture, potentiometric method, spectrophotometric method.

Introduction

Protonation constants of various compounds can only be determined in mixed solvents because of their insolubility or lower solubility in water[1−3]. Some compounds have even lower solubility so that their protonation constants cannot be determined by the potentiometric method even in mixed solvents. Furthermore, protonation constants of some compounds might be too large or too small to be determined by the potentiometric method. In such cases, the spectrophotometric method should be the preferred technique[4].

Schiff's bases are becoming increasingly important in biological, pharmaceutical and other industrial applications. In addition, they have received much attention due to their liquid crystal and complex formation tendencies[5−9]. The purpose of this study is to determine the stoichiometric protonation constants of the

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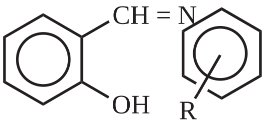
salicylideneanilines listed in Table 1 using the spectrophotometric titration method in ethanol-water mixtures of 10, 30, 50 and 70% ethanol (v/v) and to compare these protonation constants with the results obtained by the potentiometric method.

Table 1. Schiff's bases determined the protonation constants

	
R	**Schiff's base**
H	Salicylideneaniline(Reference)
2-CH_3	Salicylidene-2-methylaniline
3-CH_3	Salicylidene-3-methylaniline
4-CH_3	Salicylidene-4-methylaniline
2-C_2H_5	Salicylidene-2-ethylaniline
3-C_2H_5	Salicylidene-3-ethylaniline
4-C_2H_5	Salicylidene-4-ethylaniline
2-OCH_3	Salicylidene-2-methoxyaniline
3-OCH_3	Salicylidene-3-methoxyaniline
4-OCH_3	Salicylidene-4-methoxyaniline
2-F	Salicylidene-2-fluoroaniline
3-F	Salicylidene-3-fluoroaniline
4-F	Salicylidene-4-fluoroaniline
2-Cl	Salicylidene-2-chloroaniline
3-Cl	Salicylidene-3-chloroaniline
4-Cl	Salicylidene-4-chloroaniline
2-Br	Salicylidene-2-bromoaniline
3-Br	Salicylidene-3-bromoaniline
4-Br	Salicylidene-4-bromoaniline
2-I	Salicylidene-2-iodoaniline
3-I	Salicylidene-3-iodoaniline
4-I	Salicylidene-4-iodoaniline

Experimental

Materials and Standard Solutions

The Schiff's bases studied were synthesized by condensation of salicylaldehyde with aniline and substituted anilines in the 2-, 3- and 4- positions by methyl, ethyl, methoxy, fluoro, chloro, bromo and iodo groups in ethanol. The Schiff's bases were purified by recrystallization from ethanol. Salicylaldehyde, aniline, substituted anilines and all chemicals used in this work were purchased from Merck and were used as received.

Stock solutions of Schiff's bases were prepared in ethanol purified as described in Ref. 10. Stock solutions of perchloric acid prepared using perchloric acid with 70% (w/w) were standardized by titration against primary standard sodium carbonate. The concentrations of stock solutions of sodium hydroxide in 10, 30, 50 and 70% aqueous ethanol were 0.5 M, 0.02 M and 0.01 M in constant ionic strength with 0.1 M $NaClO_4$. These solutions were standardized potentiometrically against $HClO_4$ by the use of a linear least-squares fit of Gran's plot techniques, allowing determination of dissolved carbonate impurity[11,12]. The water used in all titrations was freshly boiled and twice distilled.

Apparatus

Potential measurements were carried out in a thermostated 80 mL glass vessel at 25.0±0.1°C under a nitrogen atmosphere. The vessel was equipped with a combined pH electrode (Ingold), nitrogen inlet and outlet tubes, a magnetic stirrer and a titrant inlet. The electrode was modified by replacing its aqueous KCl solution with 0.01 M NaCl + 0.09 M $NaClO_4$ saturated with AgCl. The cell e.m.f. was measured using an Orion 720A model pH-ionmeter equipped with a combined pH electrode.

The spectra and absorbance measurements were recorded on a Shimadzu UV-160A spectrophotometer over the wavelength ranges 200-500 nm. A Shimadzu UV-160 model spectrophotometer equipped with a 160C type sipper, capable of circulating constant temperature water both around its quartz cell of 2.5 mL in volume with an optical length of 10 mm and around the glass titration vessel was utilized for spectrophotometric titrations.

Procedure

The potentiometric cell was calibrated before each experiment to obtain pH (= $-\log[H^+]$) values for each medium studied[13−15]. Potentiometric and spectrophotometric measurements were made in aqueous ethanol media containing 10, 30, 50 and 70% ethanol (v/v). Titrations were performed at constant temperature and in a nitrogen atmosphere with CO_2-free standard sodium hydroxide, in concentrations of 0.5 M, 0.02 M and 0.01 M respectively, in 50.0 mL solutions containing 0.1 M $NaClO_4$ with: *i*−0.02 M, $2x20^{-4}$ M or $4x10^{-4}$ M $HClO_4$ (for cell calibration) *ii*-$2.5x10^{-2}$ M $HClO_4$ + $2.2x10^{-4}$ M Schiff's base (for spectrophotometric measurements between 275 and 395 nm wavelengths) *iii*-$1.5x10^{-2}$ M $HClO_4$ + $6x10^{-5}$ M Schiff's base (for spectrophotometric measurements between 230 and 260 nm wavelengths). During titrations, the ionic strength was maintained at 0.1 M $NaClO_4$ and potential and absorbance (A) reading were taken after a suitable time (normally 1-2 min) for establishing the equilibrium after each addition of titrant.

Titration spectra (absorbance (A) vs wavelength) resulting from spectrophotometric titration of Schiff's base were recorded with different pH values and are shown in Figure 1 as an example. The spectra of all Schiff's bases studied show three isosbestic points. The values of $A_{\lambda H2L}$ calculated with the protonation constants of Schiff's bases were recorded with the absorbance values at the start of the titration (at acidic region), and the values of $A_{\lambda L}$ were recorded with the absorbance values at the end of the titration where the titration solution was sufficiently basic.

The first and second protonation constants of Schiff's bases from potentiometric and spectrophotometric data were calculated using the linear regression method based on the following equations[16]:

$$(A_\lambda - A_{\lambda L}) \cdot 10^{pH} = -\frac{1}{K_1} \cdot A_\lambda + \frac{1}{K_1} \cdot A_{\lambda HL}$$

$$(A_\lambda - A_{\lambda H_2 L}) \cdot 10^{-pH} = -K_2 \cdot A_\lambda + K_2 \cdot A_{\lambda HL}$$

where $\mathbf{A}_{\lambda H2L}$= Absorbance of the H_2L species at λ wavelength; $\mathbf{A}_{\lambda L}$ = Absorbance of the L^{-2} species at λ wavelength; $\mathbf{A}_{\lambda HL}$ = Absorbance of the HL^- species at λ wavelength; $\mathbf{A}_\lambda$ = Absorbance at each titration point at λ wavelength)

Results and Discussion

First it was verified by graphic matrix rank analysis (the number of linearly independent variables required for unambiguous specification of a titration system is referred to as the rank of the system, s) of spectrophotometric titration data that there was indeed no overlap among the various subequilibria[16]. The corresponding A-diagrams showed the presence of two strictly linear segments for various wavelength combinations in the region 230-395 nm. Fig 2 is obtained by plotting the absorbance at 295 nm against the absorbance at 275 nm and 280 nm. Thus, the overall titration system has the rank s=2. This conclusion was supported by the ADQ-diagrams shown in Figure 3. Since all data points fell on one of the two linear segments within the limits of error and A-pH curves (Figure 4) displayed flat maxima and plateaus at pH 6-8, it was concluded that the titration curves could clearly be divided into two single-step subsystems.

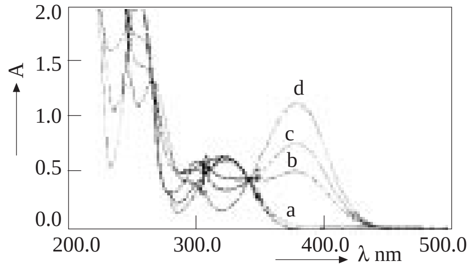


Figure 1. Titration spectra resulting from spectrometric titration with sodium hydroxide (0.02 M) for salicylidene-4-methoxyaniline under nitrogen atmosphere at 25°C in 10% ethanol-90% water (a) pH<4.2 (b) pH=6.8 (c) pH=7.1 (d) pH=10

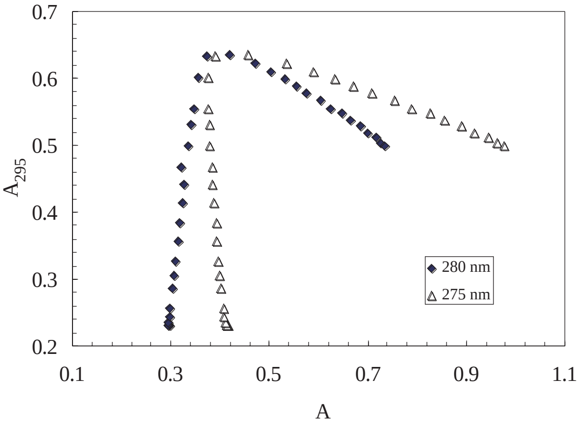


Figure 2. A-diagrams from spectrophotometric titration of salicylidene-4-methoxyaniline in 10% ethanol-90% water mixture. (A: absorbance at 275 and 280 nm; A_{295}:absorbance at 295 nm).

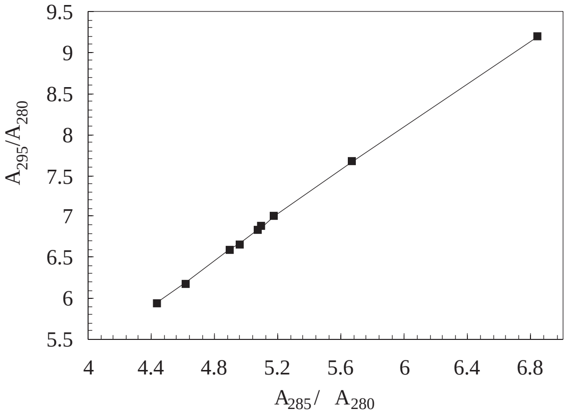


Figure 3. ADQ-diagrams from spectrophotometric titration for salicylidene-4-methoxyaniline in 10% ethanol-90% water mixture.

The stoichiometric protonation constants of Schiff's bases obtained using the spectrophotometric titration method are listed in Table 2 together with relative standard deviations. The protonation constants in Table 2 are the mean values of at least seven results. These constants are defined by Equations 1 and 2 where HL represents the Schiff's base:

Table 2. The stoichiometric protonation constants of substituted salicylideneanilines at 25.0±0.1°C for different ethanol-water mixtures (μ=0.1 M $NaClO_4$)

Schiff	10% Ethanol-90% Water		30% Ethanol -70% Water		50% Ethanol-50% Water		70%-Ethanol -30% Water	
Bases	LogK_1	LogK_2	LogK_1	LogK_2	LogK_1	LogK_2	LogK_1	LogK_2
Reference	8.31 (±0.01)	4.78 (±0.01)	8.41 (±0.01)	4.53 (±0.01)	8.50 (±0.02)	4.08 (±0.01)	8.90 (±0.01)	4.18 (±0.01)
2-F	8.35 (±0.01)	3.04 (±0.01)	8.38 (±0.01)	2.99 (±0.01)	8.71 (±0.01)	2.55 (±0.01)	9.07 (±0.01)	2.50 (±0.01)
3-F	8.36 (±0.01)	3.57 (±0.01)	8.37 (±0.01)	3.26 (±0.01)	8.74 (±0.01)	2.83 (±0.01)	9.06 (±0.01)	2.79 (±0.01)
4-F	8.35 (±0.01)	4.67 (±0.01)	8.39 (±0.01)	4.32 (±0.01)	8.75 (±0.01)	4.01 (±0.01)	8.98 (±0.01)	3.65 (±0.01)
2-Cl	8.39 (±0.01)	2.88 (±0.01)	8.38 (±0.01)	2.46 (±0.01)	8.70 (±0.01)	2.22 (±0.01)	8.92 (±0.01)	2.03 (±0.03)
3-Cl	8.39 (±0.01)	3.51 (±0.01)	8.40 (±0.01)	3.20 (±0.01)	8.68 (±0.01)	2.66 (±0.01)	9.00 (±0.01)	2.61 (±0.02)
4-Cl	8.39 (±0.01)	3.99 (±0.01)	8.43 (±0.01)	3.63 (±0.01)	8.78 (±0.01)	3.30 (±0.01)	9.03 (±0.01)	3.07 (±0.01)
2-Br	8.39 (±0.01)	2.72 (±0.01)	8.43 (±0.01)	2.32 (±0.02)	8.69 (±0.01)	2.12 (±0.01)	8.87 (±0.01)	2.24 (±0.03)
3-Br	8.35 (±0.01)	3.37 (±0.01)	8.36 (±0.01)	3.15 (±0.01)	8.71 (±0.01)	2.66 (±0.01)	8.90 (±0.01)	2.79 (±0.01)
4-Br	8.35 (±0.01)	3.83 (±0.01)	8.44 (±0.01)	3.56 (±0.01)	8.73 (±0.01)	3.17 (±0.01)	8.95 (±0.01)	3.05 (±0.01)
2-I	8.37 (±0.01)	2.73 (±0.01)	8.38 (±0.01)	2.37 (±0.01)	8.72 (±0.01)	2.23 (±0.01)	8.90 (±0.01)	1.90 (±0.01)
3-I	8.37 (±0.01)	3.56 (±0.01)	8.41 (±0.01)	3.22 (±0.01)	8.76 (±0.01)	2.82 (±0.01)	8.89 (±0.01)	2.47 (±0.02)
4-I	8.39 (±0.01)	3.79 (±0.01)	8.39 (±0.01)	3.46 (±0.01)	8.78 (±0.01)	2.99 (±0.01)	8.87 (±0.01)	2.84 (±0.02)
2-CH_3	8.33 (±0.01)	4.70 (±0.01)	8.38 (±0.01)	4.52 (±0.01)	8.72 (±0.01)	4.07 (±0.02)	8.97 (±0.01)	4.19 (±0.01)
3-CH_3	8.33 (±0.01)	4.92 (±0.01)	8.39 (±0.01)	4.77 (±0.02)	8.59 (±0.01)	4.15 (±0.01)	9.03 (±0.01)	4.35 (±0.01)
4-CH_3	8.35 (±0.01)	5.18 (±0.01)	8.40 (±0.01)	4.99 (±0.01)	8.58 (±0.01)	4.41 (±0.02)	8.97 (±0.01)	4.52 (±0.01)
2-C_2H_5	8.36 (±0.01)	4.55 (±0.01)	8.41 (±0.01)	4.42 (±0.01)	8.56 (±0.01)	3.72 (±0.02)	8.97 (±0.01)	3.99 (±0.01)
3-C_2H_5	8.39 (±0.01)	4.98 (±0.01)	8.40 (±0.01)	4.70 (±0.01)	8.56 (±0.01)	4.08 (±0.01)	8.96 (±0.01)	4.35 (±0.01)
4-C_2H_5	8.36 (±0.01)	5.27 (±0.01)	8.42 (±0.01)	4.97 (±0.01)	8.63 (±0.01)	4.21 (±0.02)	8.91 (±0.01)	4.49 (±0.02)
2-OCH_3	8.32 (±0.01)	4.76 (±0.01)	8.37 (±0.01)	4.47 (±0.01)	8.53 (±0.01)	4.03 (±0.01)	8.94 (±0.01)	4.22 (±0.01)
3-OCH_3	8.37 (±0.01)	4.52 (±0.01)	8.42 (±0.01)	4.30 (±0.01)	8.40 (±0.01)	3.74 (±0.02)	8.93 (±0.01)	4.09 (±0.03)
4-OCH_3	8.33 (±0.01)	5.40 (±0.01)	8.43 (±0.01)	5.19 (±0.01)	8.66 (±0.01)	4.52 (±0.01)	8.99 (±0.01)	4.97 (±0.01)

$$L^- + H^+ \rightleftharpoons HL \qquad K_1 = \frac{[HL]}{[L^-]\,[H^+]} \tag{1}$$

$$HL + H^+ \rightleftharpoons H_2L^+ \qquad K_2 = \frac{[H_2L]^+}{[HL]\,[H^+]} \tag{2}$$

where K_1 corresponds to the protonation equilibrium of the phenolic hydroxyl group and K_2 to the azomethine nitrogen. The values of logK_1 and logK_2 of all Schiff's bases suggest that the protonations of L^- and HL species take place in two distinct steps.

The results obtained in the present paper were compared with those obtained under the same conditions by the potentiometric method reported in our previous paper[17]. The values of protonation constants obtained by the spectrophotometric method for both logK_1 and $logK_2$ are in good agreement with those obtained by the potentiometric method. The differences between the protonation constants obtained by these two methods were found to be less than 0.20 log$K$ unit.

However, the potentiometric method is not suitable to determine the logK_2 values of the halogen substituted Schiff's bases because of their low value of protonation constants (log$K$ < 2.50)[17]. However, the logK_2 values of ortho and meta substituted halogen derivatives of Schiff's bases were readily determined by the spectrophotometric titration method. It can now be claimed that the spectrophotometric method is preferable to the potentiometric method for the determination of the protonation constants of these types of Schiff's base.

The protonation constants of the Schiff's bases studied could not be determined by potentiometric titration in the solvent mixture containing 10% ethanol-90% water, due to their low solubilities. Since the spectrophotometric method has the advantage of determining the logK_1 and logK_2 values of Schiff's bases in extremely low concentrations, such as 10^{-4}- 10^{-5} M, it was applied to all Schiff's bases synthesized in this study (Table 1).

The solvent effect itself upon the protonation constants of various compounds has been studied by several authors[1-3,16,18,19]. The effect of solvent mixture on the protonation constants of Schiff's bases was reported in reference 17 with values missing for the 10% ethanol - 90% water mixture. After determining protonation constants in this solvent mixture, it can now be stated that the trend of solvent effect on protonation constants remains the same. In addition, for a discussion of the effect of solvent composition on ortho and meta substituted halogen derivatives of Schiff's bases which can only be determined by the spectrophotometric method, the variation of logK_2 values with the mol fraction of ethanol is plotted in Figure 5. This figure shows that the variation of these values with solvent composition follows the same trend as those of the other Schiff's bases. When it comes to the variation of the logK_1 values of all halogen substitted Schiff's bases studied with the solvent composition, it has been observed that these constants increase with increasing ethanol content in the solvent mixture.

The effect of substituents on logK_2 values for the Schiff's bases whose protonation constants can be determined by potentiometric titration were reported in reference 17. Using the protonation constants obtained in this work, the effects of the halogen substituents on the basicity of the azomethine group of salicylideneaniline (reference compound) were discussed. The logK_2 values of the fluoro-, chloro-, bromo- and iodo- subtituted salicylideneanilines show that the substituents on phenyl ring of the amine component influence the electron density in azomethine nitrogen. An inspection of the logK_2 values (Table 1) for halogen derivatives of differing patterns of substitution reveals that the orders are

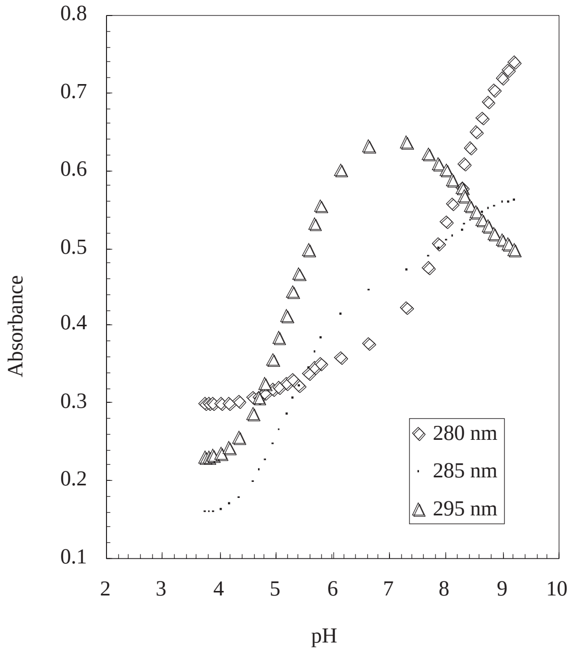


Figure 4. A-pH curves from spectrophotometric titration for salicylidene-4-methoxyaniline in 10% ethanol-90% water mixture.

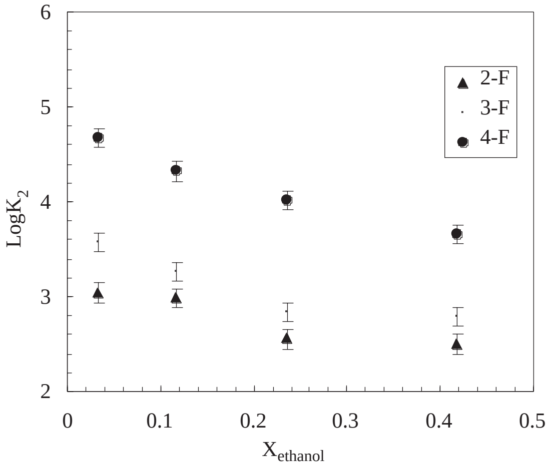


Figure 5. The variation of logK$_2$ values of 2-fluoro, 3-fluoro, 4-fluoro-salicylideneaniline against the mol fraction of ethanol (X$_{ethanol}$)

Reference > 4-X >3-X >2-X (X : F, Cl, Br, I)

This order of logK_2 values for all derivatives is also expected in the light of the steric, resonance and inductive effects of substituents.

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References

1. R.A. Delorenzo and A.D. Kowalok, **J. Inorg. Nucl. Chem.,** 36(1974) 2329.
2. H. Irving and H. Rossotti, **Acta Chem. Scand.**, 10(1956) 72.
3. L.G. Van Uitert and C.G. Haas, **J. Am. Chem. Soc.**, 75(1953) 451.
4. F.J.C. Rossotti and H. Rossotti, The Determination of Stability Constants, McGraw-Hill Book Company, Inc. 1961.
5. B.L.Kaul, Fr. Demande FR 2,586,421 (Cl. CO9K19/22), *C.A.*, 104(1986) 150788t.
6. M. Butez, L. Rabas and F. Vinet, Ger. Offen DE 3,314,603 (Cl. CO9B55/00), *C.A.*, 107(987) 124755x.
7. C. Monticelli, G. Brunora, A. Fignani and A. Marchi, **Korroz. Figy**, 28(1988) 118.
8. B. Dash, P.K. Mahapotra, D. Panda and J.M. Pattnaik, **J. Indian Chem. Soc.**, 61(1984)1061.
9. J. Casaszar, J. Morvay and O. Herczeg, **Acta Phys. Chem.**, 31(1985)717.

10. D.D. Perrin and W.L.F. Armarega, **Purification of Laboratory Chemicals**, Pergamon Press, Oxford, 1991.
11. G.Gran, **Acta Chem. Scand.**, 4(1950) 559.
12. G. Gran, **Analyst**, 77(1952) 661.
13. A. E. Martell and R.J. Motekaitis, **The Determination and Use of Stability Constants**, VHC Publishers, Wienheim, 1988.
14. M. Mekoun, J. Havel and E. Högfeldt, **Computation of Solution Equilibria**, Wiley, New York, 1988
15. T. Gündüz, E. Kılıç, E. Canel and F. Köseoğlu, **Anal. Chim. Acta**, 282(1993) 489.
16. J. Polster and H. Lachmann, **Spectrometric Titrations**, chap. 6-7, 1989.
17. F. Köseoğlu, E. Kılıç, E. Canel and N. Yılmaz, **Anal. Chim. Acta,** 293(1994) 87.
18. C.L. Norman, J.M. White and R.L. Yoest, **J. Am. Chem. Soc.,** 78(1956) 5218.
19. T. Gündüz, N. Gündüz, E. Kılıç and A. Kenar, **Analyst,** 111(1986) 1345.