

two lines are obtained as a result of measuring absorbance values of the formed complex at its characteristic wavelength as a function of the concentration of variable component (metal ion or ligand) using reference sample containing the same concentrations of ligand at the same pH.

The following work suggests an accurate choice of reference samples. This modified selection of reference samples can modify the obtained results to get only straight line instead of two in case of 1:1 complexes.

EXPERIMENTAL

All chemicals were of analytical grade. Studies proved that 1, 2 bis (beta-aminoethoxy) ethane N, N, N', N' sodium sulfonate triacetic acid, (which can be denoted by ASTA) formed stable 1:1 chelates Ce (III) and Fe (III) [2]. Solutions at different concentrations of ASTA, Ce (III) and Fe (III) were prepared and standardized [2, 4, 5].

ASTA formed with Ce (III) stable chelate at pH 5.5 with characteristic wavelength 278 nm. The values of absorbance were taken at this wavelength as a function of Ce (III) concentration, when ASTA concentration was kept at 28×10^{-4} M, and ASTA concentration, when Ce (III) concentration was kept at 10^{-4} M [2]. The reference samples in all measurements were solutions of ASTA of concentrations equal to the excess concentration of each in the measured sample at the same pH 5.5. The concentration of the reference for each sample can be expressed mathematically as the modulus value of the difference between [M III] and [ASTA] in the measured sample as follows:

Concentration of reference sample = $| [M III] - [ASTA] |$ Where M III represents the metal ion of Ce III or Fe III.

Slope ratio method was performed also for Fe III / ASTA chelate at wavelength 250 nm [2]. The absorbance values were measured and taken as a function of variable concentration of Fe III or ASTA in the presence of excess of the other at concentration 5×10^{-4} M. The measurements were done using reference samples of ASTA solutions that had the same concentration of ASTA as in the measured sample at the same pH 5.5. The absorbance measurements were repeated using reference samples that contained the excess Fe III or ASTA concentration as in the measured sample at pH 5.5 like what is shown by the mathematical expression.

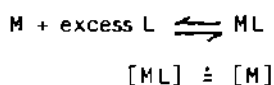
RESULTS AND DISCUSSION

Figure (1) shows the absorbance spectra of ASTA, $CeCl_3$ and Ce (III): ASTA complex. The composition of complex was studied by slope ratio method taking the usual reference samples as chelating agent at the same concentrations and pH like in measured samples. Figure (2) demonstrates that 1:1 complex was formed. The same result was obtained by molar ratio and continuous variation methods [2]. The absorbance measurements were repeated several times using reference samples having concentrations of ASTA or $CeCl_3$ equal to that still existing in excess without complexation in each measured sample. After this modification of choice of reference samples, Figure (3) was obtained demonstrating that the second straight line is superposed the first one. The disappearance of differences between the two straight lines after the modification in the reference samples, ensures that the difference between the two lines was due to the reference samples.

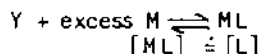
The same procedure was followed for Fe (III) : ASTA chelate. Figure (4)

shows the absorbance spectra of ASTA, FeCl_3 and Fe (III) : ASTA complex. When the slope ratio method was applied using usual reference samples, Figure (5) was obtained. After modification of reference samples to have concentrations of ASTA or Fe (III) equal to that excess in measured samples, Figure (6) was obtained. Therefore, it can be concluded that the good choice of reference samples modifies the result of the slope ratio method to obtain two superposed straight lines (or one straight line) instead of two parallel straight lines.

Let M represents Ce (III) or Fe (III) and Y represents ASTA. In 1:1 Complexes, like in our case, for excess concentration of ligand, the concentration of the formed chelate equals the concentration of M approximately as shown from the following:



For excess concentration of M , the concentration of formed ML equals approximately that of Y as shown :



Therefore at each point of x-axis where $[M_{\text{in excess } L}]$ equals $[L_{\text{in excess } M}]$, we must get approximately the same value of ML at that point. For the same values of concentration of ML we must get only unique value of absorbance $[6 \pm 10]$, not two. Since in 1 : 1 complex the concentration of free metal ion without complexation equals to that of free ligand, therefore for each point of x - axis, the formed complex is exactly the same and as a result the corresponding absorbance value must be the same. Consequently, from logical and theoretical point of view, if the reference sample are chosen correctly, we can obtain only one straight line instead of two as the results showed.

According to the result of this publication, modifications of reference samples can be suggested similarly for studying complex formation either by continuous variation or molar ratio method. This modification enables us to get more accurate spectra for the formed complex and also more precise values of its stability constant.

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Ligands Figure

Figure (1) : Absorbance spectra of $ASTA$, $CeCl_3$ and $Ce(III)$: $ASTA$ chelate each of concentration 2.8×10^{-3} M at pH 5.5 .

Figure (2) : Variation of absorbance at $\lambda = 278$ nm for $Ce(III)$: $ASTA$ chelate using reference samples of chelating agent as a function of concentration of $Ce(III)$ or $ASTA$ in the excess of the other (excess concentration = 28×10^{-4} M) .

Figure (3) : Variation of absorbance at $\lambda = 278$ nm for $Ce(III)$: $ASTA$ chelate using the modified reference samples as a function of $[Ce]$ or $[ASTA]$ in the presence of excess concentration of the other (28×10^{-4} M) .

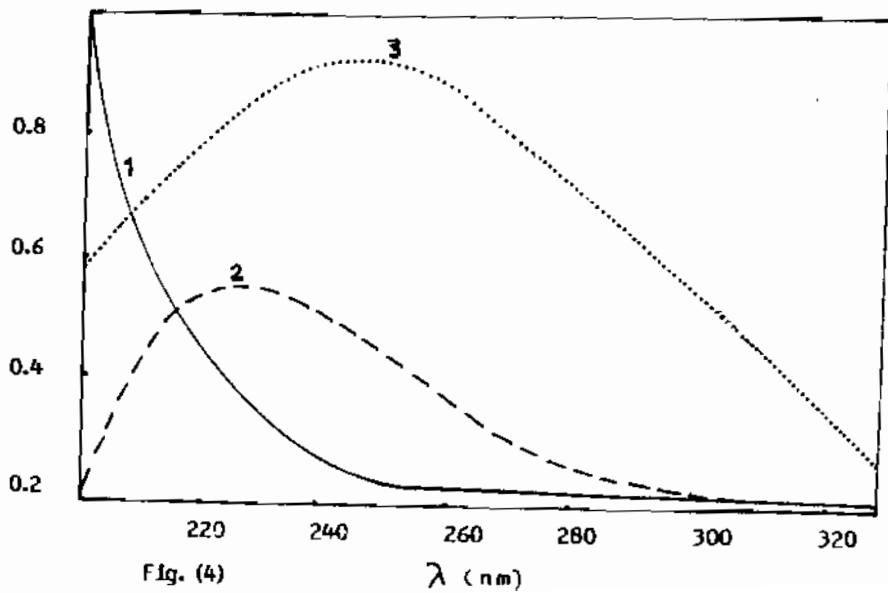
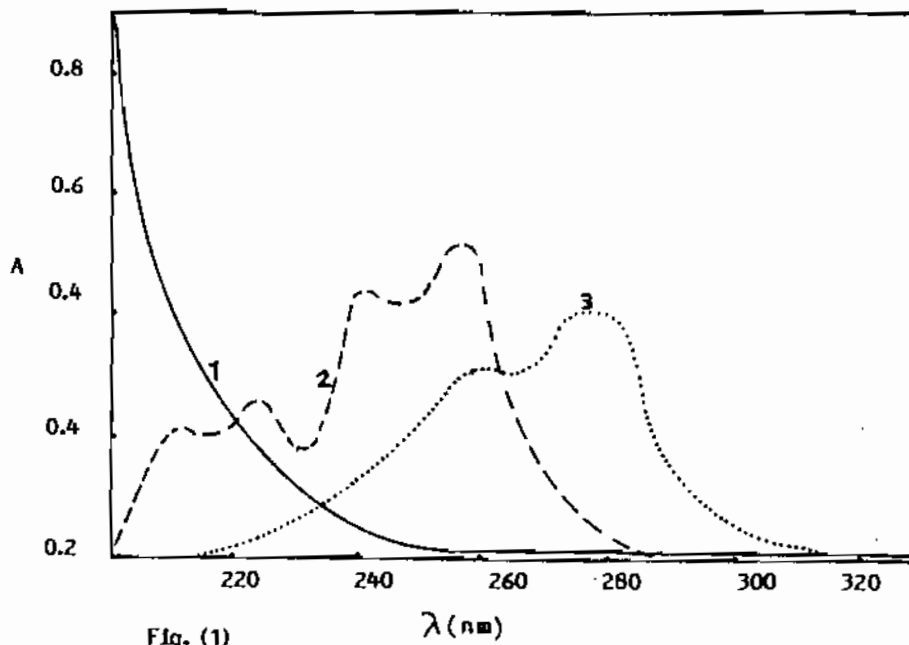
Figure (4) : Absorbance spectra of $ASTA$, $FeCl_3$ and $Fe(III)$: $ASTA$ chelate each of concentration 1×10^{-4} M at pH 5.5 .

Figure (5) : Variation of absorbance at $\lambda = 250$ nm for $Fe(III)$: $ASTA$ chelate using reference samples of chelating agent as a function of concentration of $Fe(III)$ or $ASTA$ in the excess of the other (excess concentration = 5×10^{-4} M) .

Figure (6) : Variation of absorbance at $\lambda = 250$ nm for $Fe(III)$: $ASTA$ chelate using the modified reference samples as a function of $[Fe]$ or $[ASTA]$ in the presence of excess concentration of the other (5×10^{-4} M) .

In Figures(1)and(4): 1 for $ASTA$, 2 for $M(III)$, 3 for $M(III)$: $ASTA$

In Figures(2)and(3): 1 for excess chelate , 2 for excess $M(III)$.



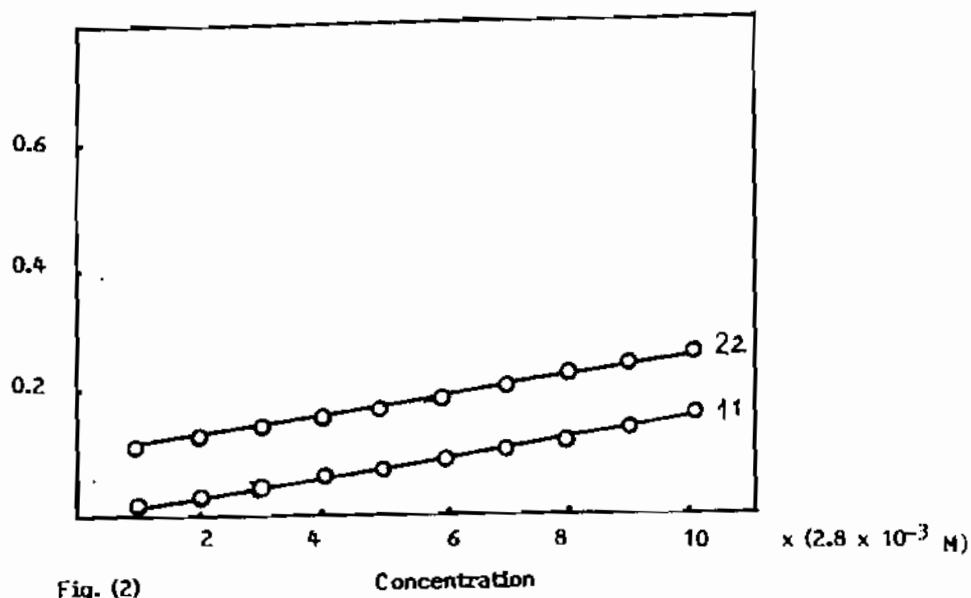


Fig. (2)

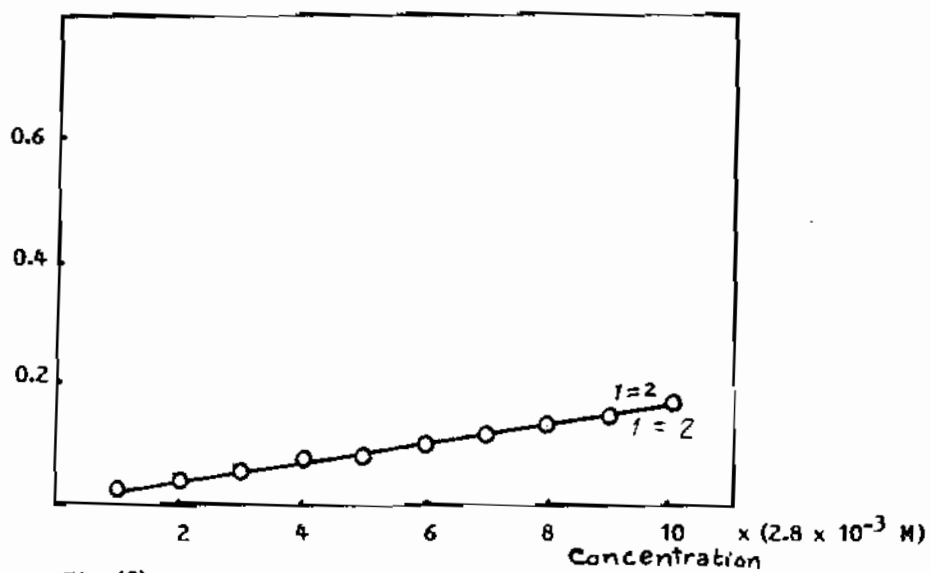


Fig. (3)

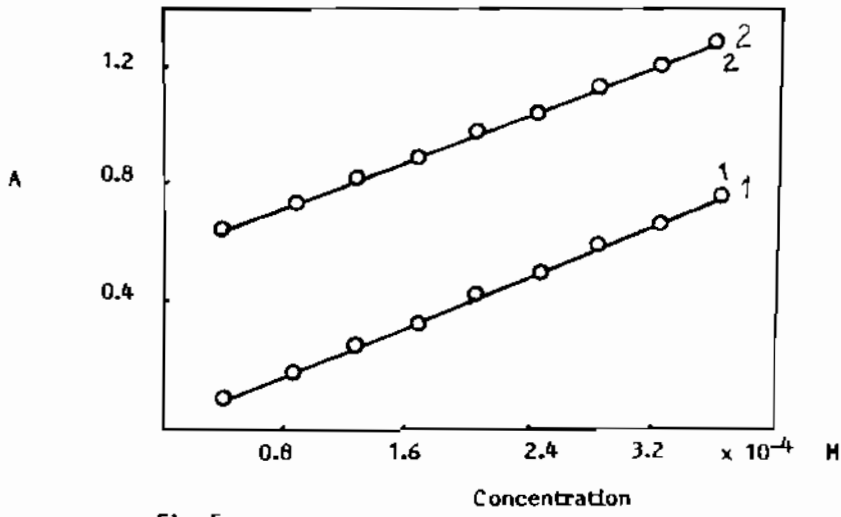


Fig. 5

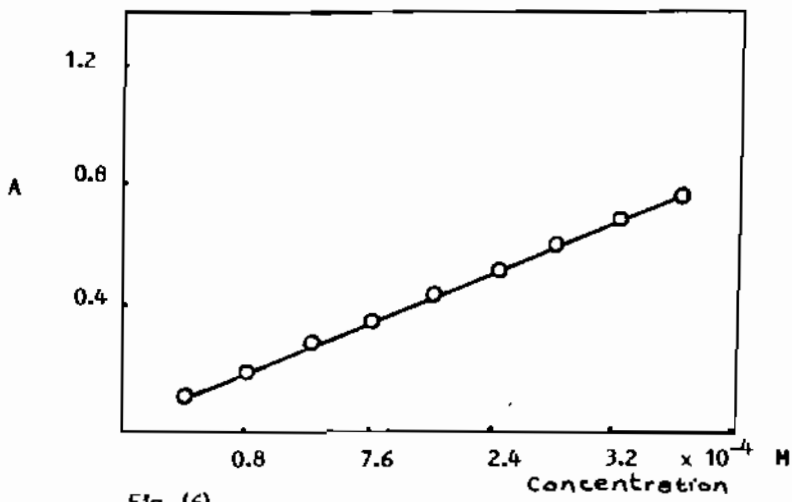


Fig. (6)