

## Chapter IV



### Conclusion and Recommendation

The complex formations between some food dyes with transition metal ions such as Ti (IV), Cr (III), Mn (II), Co (II), Fe (II), Fe (III), Ni (II), Cu (II) and Zn (II) were investigated in this study. The food dyes used are certified grade of Azorubine, Sunset Yellow FCF, Orange G, Orange RN, Tartrazine and Green S. They are food additives of red, orange, yellow and blue colors. The use of Orange RN was terminated whereas Azorubine, Sunset Yellow FCF and Tartrazine are still permitted to use (23).

By chromatographic and spectrophotometric techniques, no contaminant was found in the certified grade of Azorubine, Sunset Yellow FCF, Orange G, Tartrazine and Green S and their purities were found to be 85.23%, 88.73%, 95.43%, 89.20% and 94.94%, respectively. The certified grade of Orange RN was found to be contaminated, thus, it was purified by column chromatographic technique. The purified Orange RN was tested and found that its purity was 85.65%. These revealed that the purities of food dyes are sufficiently high to be used in the study of complex formations with metal ions.

By visible spectrophotometric study, linear relationships between absorbances and concentrations of the dyes in aqueous solutions were obtained in the range of concentrations of  $0.50 \times 10^{-5}$  M -  $5.00 \times 10^{-5}$  M for Azorubine,  $0.40 \times 10^{-5}$  M -  $3.20 \times 10^{-5}$  M for Tartrazine,  $0.40 \times 10^{-5}$  M -  $6.40 \times 10^{-5}$  M for Sunset Yellow FCF,  $0.40 \times 10^{-5}$  M -  $5.50 \times 10^{-5}$  M for Orange G,  $0.40 \times 10^{-5}$  M -  $5.00 \times 10^{-5}$  M for Orange RN or  $0.20 \times 10^{-5}$  M.

for Green S. The linear relationships between absorbances and concentrations of Azorubine in acetate buffer and phosphate buffer were found to be in the range of  $0.80 \times 10^{-5} \text{ M} - 5.60 \times 10^{-5} \text{ M}$ , of Sunset Yellow FCF, Orange G or Orange RN in acetate buffer were found in the range of  $0.80 \times 10^{-5} \text{ M} - 5.60 \times 10^{-5} \text{ M}$ .

By atomic absorption spectrophotometric study, linear relationships between absorbances and concentrations of Cu (II) ion in acetate buffer and phosphate buffer were found to be in the range of 2.00–8.00  $\text{g/cm}^3$ .

The  $\text{pK}_a$  of Azorubine, Sunset Yellow FCF, Orange G, Orange RN and Tartrazine were found to be 7.00, 6.00, 10.20, 10.30 and 9.80, respectively.

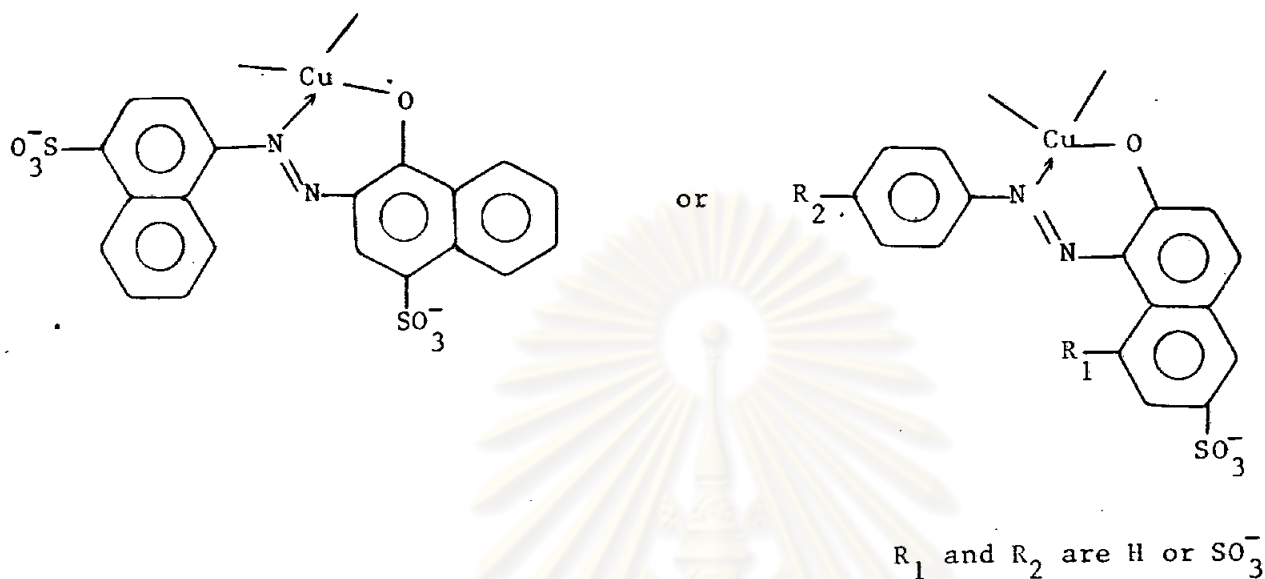
Complex formations of the dyes and the metal ions were studied in many buffer systems such as McIlvaine buffer, phosphate buffer, acetate buffer, diethylamine, phosphoric acid and acetic acid. No reaction was found when Sunset Yellow FCF, Orange G, Orange RN, Tartrazine or Green S was mixed with each metal ion in the buffer systems, such as McIlvaine buffer, phosphate buffer, phosphoric acid, acetic acid and diethylamine. Since the absorption spectra of the metal ion-dye mixtures were not different from their dye solutions and no physical change was observed.

No reaction between Azorubine and Ti (IV), Cr (III), Mn (II), Co (II), Fe (II), Fe (III), Ni (II) or Zn (II) ion in McIlvaine buffer, phosphoric acid, acetic acid or diethylamine was found. However, Azorubine reacted with Cu (II) ion in phosphate buffer pH 5.85–7.00 and in acetate buffer pH 5.10–6.10 since the physical change and the shift of the maximum absorption spectra of the Cu (II) ion-Azorubine were observed. The method of continuous variation and the molar ratio method were used for determining the compositions of the complexes formed.

It was found that Cu (II) ion and Azorubine formed 1:1 complex in acetate buffer pH 5.10 and 1:2 complex in acetate buffer pH 6.10 and in phosphate buffer pH 5.85 or 7.00. The stability constants of the complexes were calculated, they were found to be in the order of ninth for 1:2 Cu (II)-Azorubine complex at pH 6.10, 5.85 and in the order of tenth at pH 7.00 as well as the stability constant for 1:1 Cu (II)-Azorubine complex at pH 5.10 was found to be in the order of seventh.

In addition, Sunset Yellow FCF, Orange G and Orange RN formed complexes with Cu (II) ion in the acetate buffer as evidenced by the physical change as well as the absorption spectra of the mixtures of Cu (II) ion and the dye shifted from their dye solutions. It was found that complex formations between Cu (II) ion and Sunset Yellow FCF were 1:1 and 2:1, Cu (II) ion and Orange G was 1:1, Cu (II) ion and Orange RN was 1:1. The stability constants were found in the order of seventh for 1:1 Cu (II)-Sunset Yellow FCF, Cu (II)-Orange G or Cu (II)-Orange RN complex and in the order of tenth for 2:1 Cu (II)-Sunset Yellow FCF complex at pH 6.10.

Since Azorubine, Sunset Yellow FCF, Orange G, Orange RN are hydroxyazo dyes. One of hydroxy group and the lone pair electrons of nitrogen atom of azo group are able to take part in bonding with the metal ion (38). Therefore, the possible structures of Cu (II)-Azorubine, Cu (II)-Sunset Yellow FCF, Cu (II)-Orange G and Cu (II)-Orange RN can be generalized by the following formular:



The unfilled valencies, either correspond to another dye molecule attached in the same way as the first, or other molecule that can act as ligand for the metal ion such as water.

The structure of 2:1 (Cu (II) ion:Sunset Yellow FCF) was proposed as a salt forming Cu (II) ion and a coordinated Cu (II) ion per dye molecule (21). Since the exact location of the salt forming Cu (II) ion at sulfonate group is not known. This should be interested in the further study.

Future study should be made for the confirmation of the ratio of the metal-dye complex and the structure of complex formed, such as polarography, nmr spectrophotometry and X-ray in solution. In addition, complex formations of other food dyes and the metal ion should be suggested for interest.