New Spectrophotometric Determination of Chromium and Cobalt with Disodium Ethylenediaminetetraacetate

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Synopsis

The light absorptions of complexes between EDTA and various metallic ions were measured by using Beckmann model DU spectrophotometer and it was found that a new double complex consisting of EDTA, $Cr_2O_7^{2-}$ and Co^{2+} had strong absorbancy. Utilizing the nature of this complex spectrophotometric determinations of chromium and cobalt were investigated and 5~30 γ/ml of chromium and 10~80 γ/ml of cobalt could be determined under certain conditions. The composition of this complex was suggested to be $(Co-EDTA)_7Cr_2O_7$.

I. Introduction

In consequence of many investigations[1] on the so-called "Komplexone" by Schwarzenbach and the co-workers, the ethylenediaminetetraacetate, EDTA for short, has, since 1947, come out as a new analytical reagent and widely been studied for various applications, not only in analytical chemistry but also in many other fields because of its special complexibility for various metallic ions[2]. The present authors investigated the application of EDTA as photometric reagent; in other words the absorbancies of the complexes between EDTA and various metals, and the photometric determinations of $Cr_2O_7^{2-}$ and Co^{2+}, utilizing strong absorbancy of a new double complex, and the composition of the double complex were studied.

II. Experimental results and considerations

1. Absorptions of complexes between EDTA and metallic ions

Some workers[1],[3] have studied the absorption of complexes between EDTA and various mtallic ions. In the present experiments the same absorption curve as the former was obtained, that is, the complexes of Ca^{2+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, Al^{3+}, Ba^{2+}, Pb^{2+} and Mn^{2+} were colorless but had a strong absorption in ultraviolet range below about 250 mμ. Curve 1 in Fig. 1 shows the absorbancy of complex of Mg^{2+} representing these colorless complexes whose absorption curves were almost of the same shape. The complexes of Fe^{3+}, Cr^{3+}, Ni^{2+}, Cu^{2+}, Co^{2+} and Mn^{3+} had absorptions in visible range, but their absorbancies were generally weak as shown in curves 2~6 in Fig. 1. The complex of Mn^{3+} had the absorption maximum at 500 mμ, but was

(1) G, Schwarzenbach and co-workers, Helv. Chim. Acta., **30** (1947), 1798 ; **31** (1948), 459 ; 679 ; **32** (1949), 1314 ; 1543.

(2) Ueno and Yamaguchi, Kagaku no Ryôiki, **6** (1952), 670 communicated summarily.

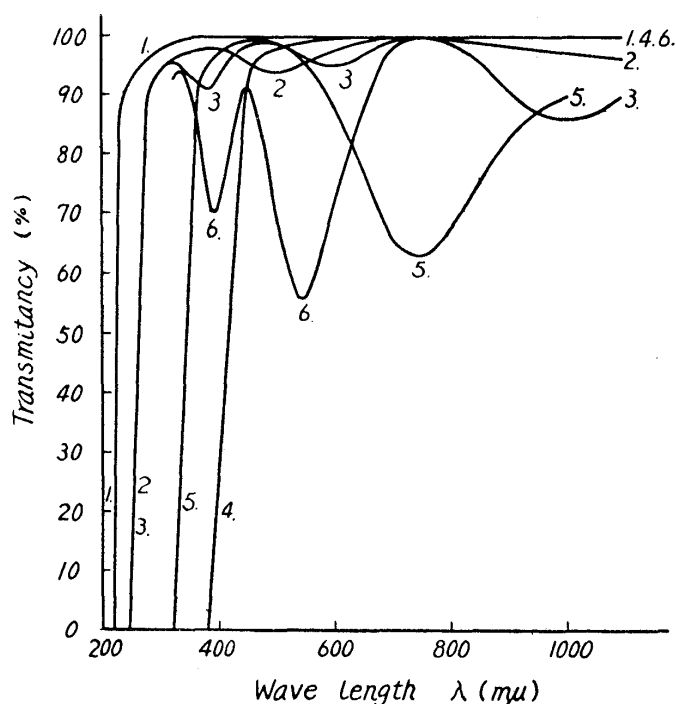(3) R.C. Plumb, A.E. Martell and F.C. Bersworth, J. Phys. and Colloid. Chem., **54** (1950), 1208.

Fig. 1. Absorption curves of complexes between EDTA and metals in acetate buffered solution, (0.0025M in concentration of complex).
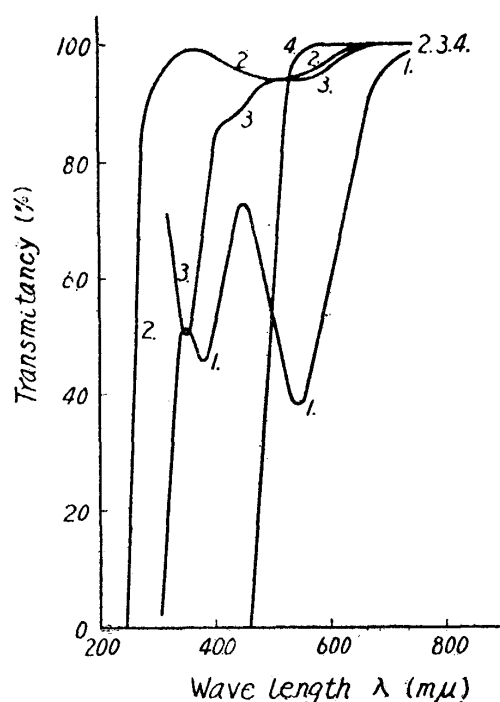1. Mg^{2+}, 2. Co^{2+}, 3. Ni^{2+}, 4. Fe^{3+}, 5. Cu^{2+}, 6. Cr^{3+}.

Fig. 2. Absorption curves of complexes.
1. [Co–EDTA–Cr$_2$O$_7$], measured after 24 hours
2. Co–EDTA
3. [EDTA–Cr$_2$O$_7$], measured after 24 hours
4. $K_2Cr_2O_7$ alone

so unstable that it was difficult to measure it constantly; hence, it was not shown in the figure. Pribil and the co-wokers[4], [5] tried colorimetries on Cr^{3+} and Mn^{3+} because those complexes had relatively strong colors, but no instance except them has been known where EDTA was used as a photometric and colorimetric reagent of metal.

The double complex consisted of EDTA, $Cr_2O_7^{2-}$ and Co^{2+} showed a strong reddish violet color. Curve 1 in Fig. 2 shows the absorption of this complex measured about 24 hours after mixing an equal volume of each of 0.01 M EDTA, 0.01 M cobaltous sulphate, 0.01/12 M potassium · bichromate and 0.1 N hydrochloric acid. Curves 2, 3 and 4 show respectively the absorptions of Co-EDTA complex, EDTA-Cr_2O_7 compound and bichromate ion alone, for a comparison with that of the double complex. This reddish violet complex had a first absorption maximum at 550 mμ and a second at 380 mμ, but the latter could not be defined to be constant, because its maximum point moved or its absorbancy piled up with that of reagent when the different kind of buffer solution or the excess of reagent existed under different conditions.

2. Investigations on conditions for complex formation

(i) Temperature

The formation velocity of complex decreased slowly with temperature rise, that is, it scarcely changed with a change in room temperature, but decreased slightly at

(4) R. Pribil and E. Hornychova, Chem. Listy., **44** (1950), 101 ; Chem. Abst., **45** (1951), 5564.
(5) R. Pribil and J. Klubalova, Colection Czechoslova. Chem. Communs., **15** (1950), 42 ; Chem. Abst., **44** (1950), 10597.

about 60°C and greatly at boiling point.

(ii) Hydrogen ion concentration

Citrate, phosphate and acetate were used as a buffer solution. Considering the absorbancy and stability of the complex, the acetate buffer was the most suitable for the present purpose. Furthermore, this reaction was greatly affected by pH, that is, the rate was largest at 1.2~2.0 of pH and suddenly decreased at pH outside this range. It seemed also that the complex could not be formed in a strong acidic or alkaline solution. The complex was somewhat unstable even in good liquid condition, being decolorized slowly, and its absorption maximum moved from 560 mμ to 550 mμ by keeping it standing.

The changes in the transmitancy at 558 mμ of the complex in the solutions of various pH with time are shown in Fig. 3. As acetic acid concentration became high, the formation velocity of complex increased, whereas the decolorizing velocity increased. As seen in Fig. 3, the transmitancy measured in 0.5 N acetic acid solution was constant 15~30 minutes after the addition of reagents.
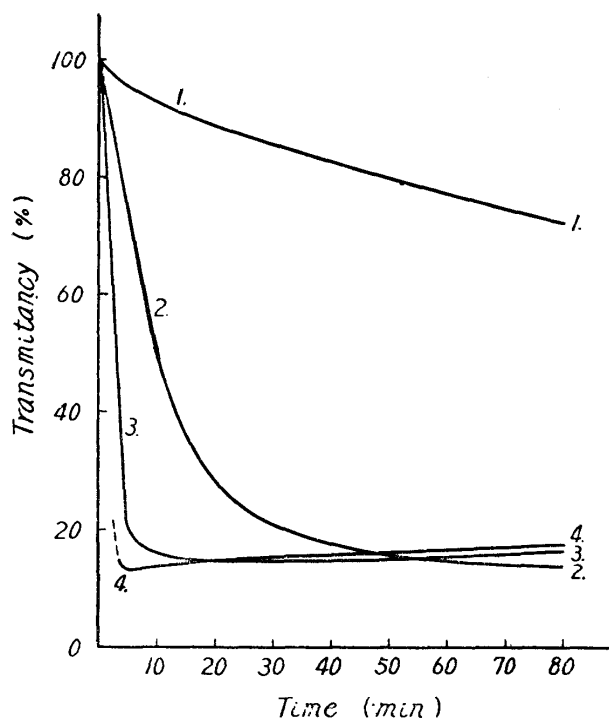
From those experimental results, the most suitable condition for the estimation of absorbancy was found, that is, the absorbancy of the complex should be measured at room temperature of about 20°C, in 0.5 N acetic acid solution, 20 minutes after adding reagents and at the wavelength of 558 mμ.

Fig. 3. Formation velocities of complex in various pH solutions.

1.	Acetate buffer solution	pH 4.6
2.	Acetate buffer solution	3.7
3.	Acetic acid 0.5 N solution	2.0
4.	Acetic acid 4N solution	1.2

3. Preparation of calibration curve

In the case of preparing the calibration curve for the determination of chromium, 5 ml of 0.01 M EDTA was added to the mixed solution containing 5 ml of 0.01 M cobaltous sulphate, 5 ml of various concentration of potassium bichromate and 5 ml of 2 N acetic acid, while in the case of cobalt, it was added to the solution containing 5 ml of various concentration of cobaltous sulphate, 5 ml of 0.001 M potassium bichromate and 5 ml of 2 N acetic acid. In each case, the total volume of complex solution was brought to 20 ml. A few ml of it was taken into 1 cm cell and the absorbancy of the solution was measured with Beckmann Model DU spectrophotometer after about 20 minutes.

Under the above mentioned condition, the relation between the absorbancy and
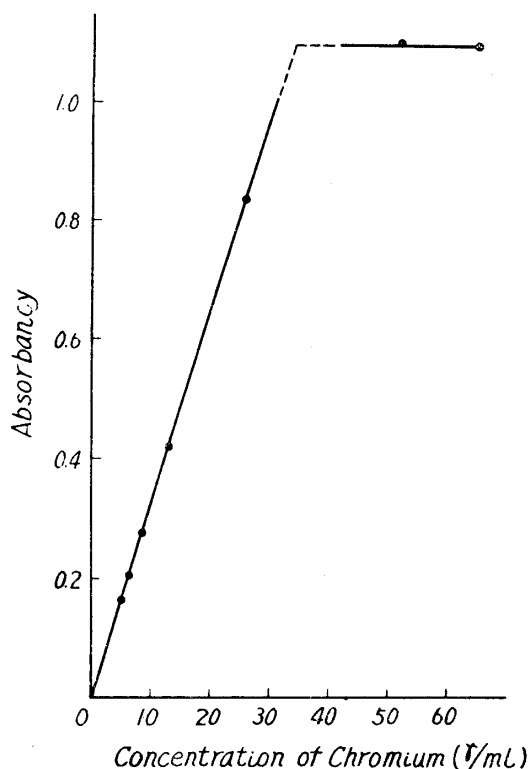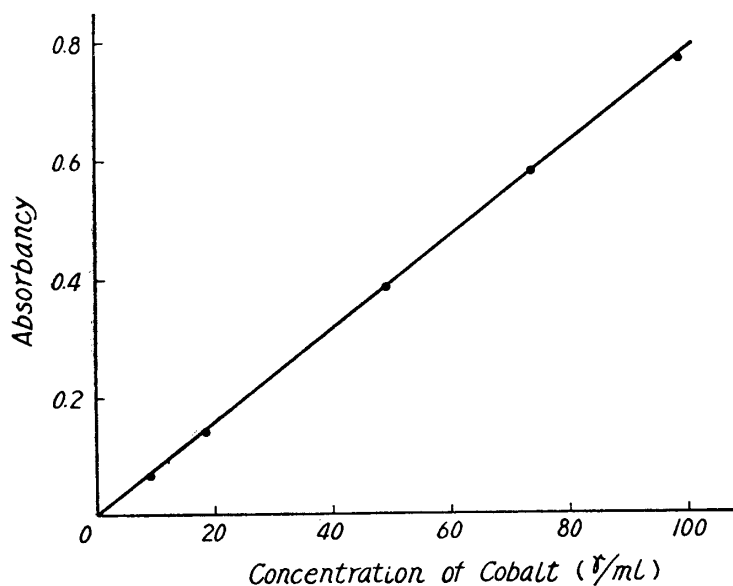
Fig. 4. Calibration curve of chromium.

Fig. 5. Calibration curve of cobalt.

concentration of chromium or cobalt was subjected to Beer's law and was suitable for the determinations of $5\sim30\,\gamma/ml$ of chromium, and $10\sim80\,\gamma/ml$ of cobalt as shown respectively in Figs. 4 and 5.

4. Composition of complex

The absorbancy first increased linearly with the concentration of chromium and then suddenly became constant, showing a sharp bend or a knee point in the curve as shown in Fig. 4. This must have been due to insufficient amounts of Co-EDTA to combine with bichromate ion existing, and suggested that Yoe's method[6] was appropriate for the determination of complex composition. The point of bend corresponded to about 7:1 as molecular ratio of Co-EDTA to Cr_2O_7.

As to the determination of complex composition, there are widely known Shibata and Inoue's method[7] or Job's method[8], etc. They are useful in the case of two components, but in the present case, the complex consisted of three components, so the following method was adopted.

By keeping the amounts of two components constant, the calibration curve for the third component was prepared. Thus, three straight lines were obtained, corresponding respectively to EDTA, $Cr_2O_7^{2-}$ and Co^{2+}. Then, three molecular extinction coefficients calculated from the range of a straight line in those calibration curves were compared with one another. The results are shown in Table 1.

(6) J. H. Yoe and A. Jones, Ind. Eng. Chem. Anal. Ed., 16 (1944), 111.
(7) Shibata and Inoue, J. Chem. Soc. Japan, 48 (1927), 1 ; 177 ; 559.
(8) P. Job, Ann. Chim., X9 (1928), 113.

Table 1.

Cr$_2$O$_7$			Co			EDTA		
Molal concent-ration	Ab-sorbancy	Molecular extinction coefficient	Molal concent-ration	Ab-sorbancy	Molecular extinction coefficient	Molal concnnt-ration	Ab-sorbancy	Molecular extinction coefficient
0.01/ 40	0.837	3348.0	0.01/ 6	0.771	462.6	0.01/16	0.332	531.2
0.01/ 80	0.421	3368.0	0.01/ 8	0.583	466.4	0.01/24	0.245	588.0
0.01/120	0.279	3348.0	0.01/12	0.387	464.4	0.01/48	0.095	456.0
0.01/160	0.208	3328.0	0.01/32	0.142	454.4			
0.01/200	0.172	3440.0						
	Mean	3364.8		Mean	461.9		Mean	525.1

In this range the component to be calibrated completely forms a complex compound; therefore, it seems that the ratio of reciprocals of three molecular extinction coefficients directly indicates the molecular ratio of the complex composition. The result of calculation was as follows:

$$Cr_2O_7 : Co : EDTA = \frac{1}{3364.8} : \frac{1}{461.9} : \frac{1}{525.1} \doteqdot 1 : 7 : 7$$

Therefore, considering this result together with that by the above-mentioned Yoe's method, the composition of the complex was supposed to be $(Co\text{-}EDTA)_7Cr_2O_7$.

5. Effects of diverse ions

The effects of diverse ions in the present determination were examined and the results are shown in Table 2.

Table 2.

When amount of EDTA is only equivalent with Co^{2+}				When amount of EDTA is sufficient for each metallic ion co-existed			
ion	concentration		difference of absorbancy on calibration curve	ion	concentration		difference of absorbancy on calibration curve
	M/l	γ/ml			M/l	γ/ml	
NH$_4$$^+$	1/10		±0.000	Al^{3+}	0.01/8	33.7	±0.000
Ca^{2+}	0.01/8	50.1	±0.000	Zn^{2+}	0.01/8	81.7	±0.000
Mg^{2+}	0.01/8	30.4	±0.000	Cd^{2+}	0.01/8	140.5	±0.000
				Ba^{2+}	0.01/2	686.8	±0.000
Al^{3+}	0.01/8	33.7	−0.004	Pb^{2+}	0.01/8	259.0	±0.000
Zn^{2+}	0.01/8	81.7	−0.216		0.01/2	279.2	±0.000
Cd^{2+}	0.01/8	140.5	−0.076	Fe^{3+}	0.01	558.4	+0.001
Ba^{2+}	0.01/2	686.8	−0.036		0.015	837.6	+0.033
Pb^{2+}	0.01/8	259.0	−0.130		0.01/6	97.8	±0.000
				Cu^{2+}	0.01/4	146.7	+0.002
Mn^{2+}	0.01/4	137.0	−0.215		0 03/8	220.1	+0.017
Fe^{2+}	0.01/8	69.8	—		0.01/8	73.4	±0.000
				Ni^{2+}	0.01/6	97.9	+0.005
					0.01/4	146.8	+0.014

The results were obtained in the constant amounts of 0.01/8 M (73.7 γ/ml) of Co^{2+} and 0.01/80 M of Cr$_2$O$_7$$^{2-}$ (13γ/ml as Cr).

NH$_4$$^+$, Ca^{2+}, Mg^{2+} showed no interference. In pH 2.0, Ca^{2+} and Mg^{2+} could scarcely form complexions with EDTA, or even though it were formed, the dissociation constants of their complexes should be much larger than that of cobalt. Al^{3+}, Zn^{2+}, Cd^{2+}, Ba^{2+} and Pb^{2+} interfered with it only when the amount of EDTA was

insufficient to combine simultaneously with those metallic ions, and the results of the present determination were lower. This is the reason why they have the complexibilities of the same degree as that of Co^{2+}. Fe^{3+}, Ni^{2+} and Cu^{2+} interfered also for the same reason as above; furthermore, these three ions interfered for another reason that the absorbancy of the double complex was piled up with the absorbancies of the complexes between EDTA and their ions at 558 mμ as shown in Fig. 1. Even sufficient amounts of EDTA being used, the results, for the latter reason, were higher when these three ions existed beyond certain amounts, namely, 549.7 γ/ml of Fe^{3+}, 75.0 γ/ml of Ni^{2+} and 136.9 γ/ml of Cu^{2+}. They were computed from the results shown in Table 2, assuming that the deviation from the calibration curve due to this interference is proportional to the concentration. Fe^{2+}, Mn^{2+}, Sn^{2+}, NO_2^- interfered and the results were lower.

Summary

（1） Utilizing the strong absorbancy of the complex consisting of EDTA, $Cr_2O_7^{2-}$ and Co^{2+}, new spectrophotometric determinations of chromium and cobalt were investigated.

（2） The most suitable condition was to measure the absorbancy at room temperature, in 0.5 N acetic acid solution, about 20 minutes after adding reagents and at wave length of 558 mμ.

（3） By the present method the determinations of 5~30 γ/ml of chromium and 10~80 γ/ml of cobalt could effectively be carried out.

（4） The effects of diverse ions in this determination were examined and the chief interfered ions were Fe^{3+}, Ni^{2+} and Cu^{2+}.

（5） The composition of the complex seemed to be $(Co\text{-}EDTA)_7Cr_2O_7$.