A New Spectrophotometric Method for the Determination of Some Reducible Compounds by the Reduction with Chromium(II) Ion

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A number of reducible compounds, such as nitrates, nitrites, nitro, nitroso, azoxy compounds, aldehydes, carbon tetrachloride, oximes, and chloramine T, can be determined by reducing them with chromium(II) ion prepared in an aqueous solution in a special vessel and measuring the absorbance of the resulting chromium(III) in the solution. In this reducing process, nitrate and nitrite are reduced to hydroxylamine quantitatively in hydrochloric acid at room temperature; carbon tetrachloride, nitrobenzene, and chloramine T each consume definite amounts of chromium(II) in an acidic medium at room temperature; propionaldehyde and azoxybenzene react with the reagent only in a basic solution; dimethylglyoxime and 1-nitroso-2-naphthol react only under heating at 80 °C in an basic medium. The absorbance of the resulting chromium(III) ion in the presence of the excess chromium(II) is found to obey Beer's law at the wavelengths of 410—425 nm over the range of 4×10^{-3}—8×10^{-2} mol/l of chromium(III). This concentration range corresponds to about 10^{-5}—10^{-4} mol of the reducible compounds mentioned above. A rapid and precise method has been established with few disadvantages.

Although the spectrophorometric method for nitrite with Griess-Romijin reagent[1] is strikingly simple and accurate, for nitrate we have few methods of accurate determination. Most of the spectrophotometric methods for nitrate are based on the nitration of some organic reagents; these are often difficult to perform, since some methods are only applicable to a solid nitrate sample (*e.g.*, the phenoldisulfonic acid method[2-6]) and others give hardly linear calibration curves at the wavelengths of maximal absorption of the colored compound (*e.g.*, the brucine method[7-8]). This may be caused by the fact that nitration is apt to be affected by the presence of chloride, bromide, or nitrite, and also by other experimental conditions.

On the other hand, both nitrate and nitrite were also found to be readily reduced to hydroxylamine by low valence ions such as Cr(II).[9] It has also been known that some organic compounds containing nitro,[10-12] nitroso,[11] and diazo groups[11] react with some low valence ions such as Cr(II), Ti(III), and V(II); furthermore, chloroform, carbon tetrachloride,[13] and oximes[14] are also reducible with these ions. In the titrimetric process a sample is put into a solution containing an excess of these ions and allowed to react perfectly under an optimum condition of acidity or temperature; then the unconsumed reducing agent is back-titrated with iron(III) standard solution using thiocyanate as an indicator. In this case, however, the color change at the end point was not precisely detectable. Chromium(II) ions are preferred as a reducing agent because the blue color changes to green by the oxidation, so if we can measure the absorbance of the green color of chromium(III) resulting after the reduction of the sample, even minute amounts of the above inorganic and organic compounds could be determined spectrophotometrically.

This paper describes a rapid and simple method based on the above principle with some devices to prevent the oxidation of the remaining chromium(II) by air: we use a new air-shielded vessel that resembles the ordinary reductor vessel with liquid amalgam. The vessel is also useful for pipetting an aliquot of the solution for measuring the absorbance of chromium(III). The absorbance at the wavelength of 420 nm gives the concentration of chromium(III) and is not affected by the excess chromium(II). Beer's law is obeyed over the range of 4×10^{-3}—8×10^{-2} mol/l of chromium(III).

Experimental

Reagents. Potassium dichromate standard solution (0.1 M): Potassium dichromate of the guaranteed reagent grade (29.422 g) was dissolved in 1000 ml of 1.5 M hydrochloric acid. This solution was diluted again with 1.5 M hydrochloric acid to prepare 0.01 M solution.

Standard Nitrate Stock Solution (0.03 M): Potassium nitrate of the guaranteed reagent grade was dried, weighed (3.033 g), and dissolved in 1000 ml of distilled water. A standard nitrate solution in desired concentration was prepared by diluting the stock solution appropriately.

Standard Nitrite Stock Solution (0.18M): In distilled water 12.42 g of sodium nitrite of the guaranteed reagent grade was dissolved and the solution was diluted to 1000 ml. A 100 ml portion of the solution was diluted again to 1000 ml with distilled water and standardized as follows:[15] 50 ml of the 0.05 M potassium permanganate solution, 1 ml of concentrated sulfuric acid, and 50.00 ml of the sodium nitrite solution were taken in a glass-stoppered bottle. The reaction was made to proceed completely under occasional shaking for 15 min, then 2 g of potassium iodide were put into the solution. The liberated iodine was titrated with 0.025 M sodium thiosulfate standard solution using starch as an indicator. From the amount of potassium permanganate consumed by the sodium nitrite the concentration of the standard solution of nitrite was determined. A standard solution of a suitable concentration was prepared by diluting the stock standard solution.

Zinc Amalgam: 3—4 g of mossy zinc metal were washed with 1 M sulfuric acid and the metal pieces were put into 100 g of mercury placed in a porcelain casserole; then they were covered with 20 ml of 1 M sulfuric acid. The casserole was placed on a boiling water-bath to amalgamate the zinc with the mercury under occasional stirring; the liquid zinc amalgam thus prepared was separated from the solid by means of a separating funnel. The liquid zinc amalgam was stored in a glass stoppered bottle which contained 1 M sulfuric acid, enough to cover the amalgam.

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Organic Compounds: Carbon tetrachloride, chloroform, nitrobenzene, and propionaldehyde, all of the guaranteed reagent grade, were submitted to analysis without any purification.

Chloramine T: 0.845 g of chloramine T (guaranteed reagent grade) was dissolved in 10 ml of distilled water.

Dimethylglyoxime: 0.363 g of dimethylglyoxime was dissolved in 20 ml of 3 M sodium hydroxide.

1-Nitroso-2-naphthol: 0.733 g of 1-nitroso-2-naphthol (guaranteed reagent grade) was dissolved in 20 ml of benzene.

Other Chemicals: Sulfuric acid, sodium hydrogensulfide, and amidosulfuric acid were of the guaranteed reagent grade.

Apparatus. A Hitachi 239 type digital spectrophotometer and Hitachi 323 type recording spectrophotometer with 1 cm glass cells were used.

The devised reductor is shown in Fig. 1, where (A) is a 300-ml glass vessel similar to a separating funnel, with the glass stopcock (E), fitted with a 10-ml glass reservior (C) through a rubber tube (B). (F) is the sample inlet.

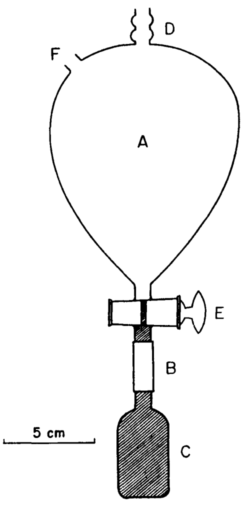

Fig. 1. Amalgam reductor.
A: Amalgam reductor, B: rubber tube, C: glass reservior, D: N_2-gas inlet, E: stopcock, F: sample inlet and outlet.

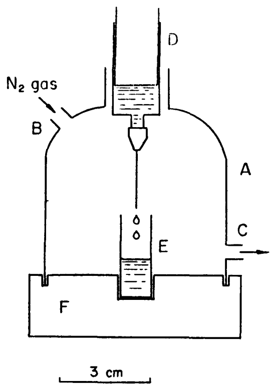

Fig. 2. New designed air-shielded vessel.
A: Air-shielded vessel made of 500 ml polyethylene bottle, B: N_2-gas inlet, C: N_2-gas outlet, D: 10 ml glass injector, E: absorption cell, F: base, made of wood.

Procedure. The liquid zinc amalgam was introduced into the vessel (A) through the inlet (D) and dropped into the reservoir to fill out (C) up to the upper level of the stopcock (E). After the stopcock (E) was closed, and excess of the amalgam was rejected through (D) by turning the vessel upside down. The vessel was then returned to the normal position. For the determination of nitrate and nitrite, 10 ml of 0.02 M potassium dichromate solution (in 1.5 M hydrochloric acid) was pipetted into the reductor. Nitrogen gas was introduced through an alkaline pyrogallol washing solution into the reductor for 2—3 min to displace the air in the vessel completely; the gas flowed through the vessel from (D) to (F); (F) and (D) were then closed respectively with small silicon rubber stoppers. The zinc amalgam in the reservoir (C) was transferred back to the reductor by turning the vessel upside down, the stopcock (E) was closed, and the reductor was shaken for about 5 min till the orange color of the solution completely changed to sky blue. After the vessel was returned to normal, the zinc amalgam was completely restored to the reservoir through the cock (E) by pushing on the side of the rubber tube (B) with one's fingers; then the stopcock (E) was sclosed. Ten milliliters of a sample solution were introduced through the inlet (F), under the passage of nitrogen gas from (D) through the vessel. The reductor was shaken for about 5 min. About 5 ml of the solution were carefully sucked up into a 10-ml injector through the silicone rubber stopper and transferred into a 1-cm glass cell placed in a newly designed enclosed vessel, in Fig. 2, which was filled with nitrogen gas from the continuous passage of the gas. The cell was closed with a glass cover plate to protect it from the air. The absorbance of chromium(III) in the solution was measured at 420 nm with distilled water as the reference.

Carbon tetrachloride, nitrobenzene, and chloramine T were found to react with chromium(II) ion in 1.5 M hydrochloric acid solution at room temperature. A suitable amount of the sample was introduced to the chromium(II) solution by means of a microsyringe through the inlet rubber stopper (F). After the reductor was shaken for 30 min, the absorbance of the resulting chromium(III) was measured.

Propionaldehyde and azoxybenzene were reduced very slowly in acidic solution at room temperature, whereas they react smoothly in a weak alkaline solution. Five milliliters of 3 M sodium hydroxide solution were slowly introduced with a pipette through (F) into the reductor containing 10 ml of 0.02 M chromium(II) under nitrogen gas flow, and at that time a greyish blue precipitate appeared in the solution. A suitable amount of the sample solution was injected into the reductor with a microsyringe through the rubber stopper (F). After the reductor was shaken for about 30 min, the solution was made acidic by adding 5 ml of 6 M hydrochloric acid with a pipette through (F) under nitrogen gas flow. The absorbance of the resulting chromium(III) was measured in the same way as described above.

Dimethylglyoxime and 1-nitroso-2-naphthol react with chromium(II) ions in a weak alkaline solution at 80 °C. After 5 ml of 3 M sodium hydroxide was introduced into the reductor which contained chromium(II) solution, a suitable amount of the sample was injected with a microsyringe in the same way as above. Then, the reductor was warmed at 80 °C in a thermostat for about 30 min. After the reductor was cooled to room temperature, the solution was made acidic with 5 ml of 6 M hydrochloric acid, and the absorbance of the resulting chromium(III) was measured.

Results and Discussion

Absorption Curves of Chromium(II) and Chromium(III). Twenty milliliters of 0.01 M potassium dichromate solution were reduced to chromium(II) with zinc amalgam

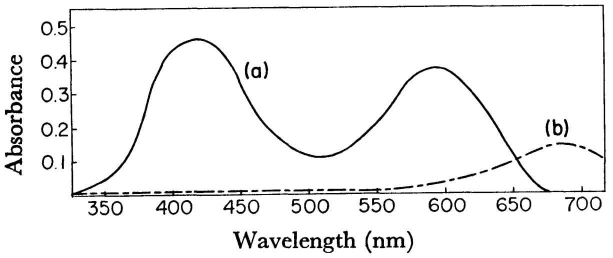

Fig. 3. Absorption spectra of chromium(II) and chromium(III) (0.02 M of metals in 1.5 M hydrochloric acid).
(a): Chromium(III), (b): chromium(II).

in the reductor according to the above procedure, and the absorption spectrum of a portion of the resulting chromium(II) solution was measured using a recording spectrophotometer. The solution which remained in the reductor was allowed to come in contact with air in order to change chromium(II) to chromium(III) completely; then the absorption spectrum of this solution was measured. As shown in Fig. 3, the absorption spectra exhibit the absorption maxima at 420 nm and 590 nm for chromium(III) and at 690 nm for chromium (II). From this figure it can be seen that the absorption maxima of the chromium(III) are isolated from that of chromium(II) and the spectrophotometric determination of the former is unaffected by the latter. These absorption curves almost coincide with those determined by Kranz and Duczmal[16] in 0.5 M sulfuric acid. Although it has been pointed out that chromium(III) forms a wide variety of complex ions, depending on the concentration of chromium, pH, and other ionic species present, the complication due to polynuclear compounds of chromium(III) is minimized in an acidic solution such as 1.0—1.5 M and the chromium(III) ion species seem rather invariable.

Calibration Curve for Chromium(III). The chromium(III) solutions in various concentrations were prepared in a similar way to that described above: chromium(VI) of varying concentrations was reduced to chromium(II) with zinc amalgam and oxidized to chromium(III) by exposing the solution to air. The absorbances of the resulting solutions were measured at 420 nm with a spectrophotometer. Beer's law was obeyed over the range of 4×10^{-3}—8×10^{-2} mol/l of chromium(III), with notably higher precision in the range of 4×10^{-3}—2×10^{-2} mol/l.

Table 1. Relationship between absorbance of Cr(III) at 420 nm and concentration of nitrate and nitrite

Nitrate taken[a] 10^{-5} mol	Absorbance	Cr(III) produced 10^{-5} mol	Nitrite taken[a] 10^{-5} mol	Absorbance	Cr(III) produced 10^{-5} mol
2.4	0.159	14.1	3.6	0.158	14.0
3.6	0.238	21.2	5.4	0.243	21.7
4.8	0.318	28.2	7.2	0.318	28.4
6.0	0.399	35.7	9.0	0.403	36.0
6.5	0.435	38.9			

a) Both nitrate and nitrite ions are present in 30 ml of the solution, respectively.

Nitrate and Nitrite. In Table 1 are shown the relations between the concentration of nitrate and nitrite ions and the absorbances measured. From this data it is found that 1 mol of nitrate oxidized exactly 6 mol of chromium(II) to chromium(III), and nitrite exactly 4 mol. Therefore, the reactions can be written as follows:

$$NO_3^- + 6Cr^{2+} + 7H^+ \longrightarrow NH_2OH + 6Cr^{3+} + 2H_2O$$

$$NO_2^- + 4Cr^{2+} + 5H^+ \longrightarrow NH_2OH + 4Cr^{3+} + H_2O$$

Hydroxylamine may be the final product, because no further reduction was found when an aqueous solution of hydroxylamine was put in the chromium(II) solution.

Determination of nitrate and nitrite in their mixture: From the above equations, under the present conditions 6.67×10^{-4}—3.3×10^{-3} mol/l of nitrate and 1.00×10^{-3}—5.00×10^{-3} mol/l of nitrite will be determined by measuring the absorbance of the resulting chromium(III). Therefore, if both nitrate and nitrite are present in a sample solution, their sum can be determined by the method. Then, if the nitrite can be removed from the sample by an appropriate reagent, the nitrate alone may be determined by this method. Thus the nitrite could be calculated as the difference between the total and the nitrate. Brasted[17] reported that nitrite was decomposed by amidosulfuric acid in the following process:

$$NaNO_2 + HSO_3NH_2 \longrightarrow N_2 + NaHSO_4 + H_2O$$

In the present study this reaction was employed. A definite volume of a sample solution containing both nitrate and nitrite was put into an Erlenmeyer flask and a suitable amount of amidosulfuric acid(solid) was added to decompose the nitrite. When the violent evolution of gas bubbles ceased, an aliquot of the solution was submitted to the reduction with chromium(II) ions, followed by the spectrophotometric measurement of the resulting chromium(III) ions. When the reaction between nitrite and amidosulfuric acid was performed in the air, the value of the resulting nitrate was often higher than the theoretical one, and was subject to wide fluctuations in every case. This fact is assumed to be caused by the following side reactions:

$$2NO_2^- + 2H^+ \longrightarrow N_2O_3 + H_2O$$

$$2N_2O_3 + O_2 \longrightarrow 4NO_2$$

$$2NO_2 + H_2O \longrightarrow NHO_3 + HNO_2$$

Thus, an appreciable amount of nitrate may be produced and consumes chromium(II) ions, yielding a higher value in the determination of the nitrate. The decomposable percentage of sodium nitrite varies with the concentration of the salt taken initially: about 2% of nitrite for 0.1—0.3 mol/l and about 10% for above 0.5 mol/l are decomposed in the way described above. In order to overcome this difficulty, the nitrite was decomposed under a nitrogen atmosphere in a glass-stoppered Erlenmeyer flask. The results indicated that satisfactory analyses were possible with solutions containing as much as 0.4 g sodium nitrite, but the concentration should not exceed 0.25 mol/l NO_2^-. Moreover, it was found that the amidosulfuric acid treatment did not affect nitrate ions in the range of concentration between 6.67×10^{-4} and 3.33×10^{-3} mol/l, and the chromium(II) reduction process could also be carried out without any trouble.

Table 2. Determination of nitrate and nitrite in their mixture

No.	NO_3^- taken 10^{-5} mol	NO_2^- taken 10^{-5} mol	Absorbance for (NO_3^-+NO_2^-)	Absorbance for (NO_3^-)	NO_3^- found 10^{-5} mol	NO_2^- found 10^{-5} mol
1	1.80	1.80	0.203	0.122	1.82	1.78
2	1.80	2.70	0.242	0.125	1.85	2.61
3	2.40	3.60	0.320	0.165	2.44	3.49
4	1.80	2.01	0.105	0.126	1.85	2.05
5	1.80	1.96	0.102	0.123	1.83	2.22

Therefore, one part of nitrate can be determined in the presence of about 350 parts of nitrite. The results for samples containing various amounts of nitrate and nitrite are shown in Table 2. Samples 4 and 5 in the table were diluted 10 and 100 times, respectively, prior to the determination of nitrite. A small amount of nitrite ions can be removed by the amidosulfuric acid method even in the air.

Determination of Nitrate Ions Present as Impurities in a Commercial Sodium Nitrite Reagent: It is well known that bulk nitrite reagents being used in the laboratory are not so stable and always contain some nitrate after the exposure to the air. By the method proposed so far, it is impossible to determine a small amount of nitrate contained in such a large amount of nitrite, since nitrite interferes with the determination of nitrate in many cases. Hence there have not been any reports on this subject. As described above, it seems possible to determine the nitrate impurity in a commercial sodium nitrite by the present method.

0.345 g of dried, ground sodium nitrite was weighed accuralately and dissolved in 20 ml of distilled water in a 200-ml glass-stoppered Erlenmeyer flask. After nitrogen gas was introduced into the flask sufficiently to replace the air, about 2 g of amidosulfuric acid were put in the flask. After 2—3 min the flask was warmed on a water bath (about 60 °C) for 5—10 min to make the reaction complete. The solution was diluted to 25 ml with distilled water in a measuring flask. Ten milliliters of an aliquot was taken in the reductor containing 10 ml of 0.04 M chromium(II) solution and the procedure was carried out as described in the Procedure section.

Table 3. Determination of nitrate ions in a commercial sodium nitrite reagent

$NaNO_2$ taken g	NO_3^- found g	NO_3^- content %
0.34503	0.00333	0.97
0.34493	0.00341	0.99
0.34514	0.00336	0.97
0.34544	0.00324	0.94

The results obtained are shown in Table 3. It was found that the nitrite reagent contained about 0.97% of nitrate. These results agree with that obtained by the gravimetric method with nitron carried out as follows: 1.380 g of sodium nitrite was dissolved in 100 ml of distilled water. 1.80×10^{-4} mol of nitrate was also added in order to obtain the precipitate of nitron which was filterable in the conventional manner. The solution was divided into four nearly equal portions (*ca.* 25 ml), which were put in four separate Erlenmeyer flasks. Two grams of amidosulfuric acid were added in each flask.

After the nitrite was removed, each solution was collected together in a beaker, 10% nitron solution (in 5% acetic acid) was added in the solution, and the beaker was cooled in an ice bath to precipitate the nitron nitrate completely. The precipitate was filtered off onto a previously weighed glass-fiber filter paper (Toyo Roshi, GB-100), washed, dried at 110 °C for about 3 h, and weighed. This value coincided with that obtained by the recommended reduction method; the latter method is accurate and more simple and rapid than the former gravimetric one.

Interferences: Some oxidizing salts, such as chlorate, bromate, periodate, iodate, selenate, and selenite, oxidize chromium(II) to chromium(III) and thus interfere with this method; perchlorate, chloride, bromide, iodide, sulfate, and arsenate ions do not (Table 4). Some metal ions, such as copper(II) and iron(III), also interfere. Chlorate, bromate, and periodate and iodate ions are reduced to chloride, bromide, and iodide with chromium(II) ion, while selenate and selenite and copper(II) ions are reduced to their metals and iron(III) ion to iron(II) ion. However, periodate and iodate can be reduced by the addition of a small amount of hydrogensulfite to their 0.01 M hydrochloric acid solution; excess hydrogensulfite can be removed by gently boiling the solution. In this case, however, if the sample solution is

Table 4. Effect of diverse substances

Substance	Concentration, ppm	Effect
Cu^{2+}	100	positive
Fe^{3+}	40	positive
K^+, Na^+	large amount	none
AsO_4^{3-}	2000	none
Cl^-, Br^-, I^-	large amount	none
Cl_2	small amount	positive
ClO_3^-, BrO_3^-, IO_3^-	400	positive
ClO_4^-	large amount	none
CO_3^{2-}	large amount	none
IO_4^-	70	positive
SeO_3^{2-}, SeO_4^{2-}	10	positive
SO_3^{2-}	small amount	positive
SO_4^{2-}	large amount	none
PO_4^{3-}	large amount	none
Carbon tetrachloride	small amount	positive
Nitrobenzene	small amount	positive
Chloramine T	small amount	positive
Alcohol	large amount	none
Ester	large amount	none
Ketone	large amount	none
Aldehyde	large amount	none
Sufamic acid	large amount	none
Urea	large amount	none

more acidic than 0.1 M, a loss of nitrite occurs along with the evolution of gaseous nitric oxide. Nitrite and nitrate are not affected at all by the hydrogensulfite treatment under the present conditions. Some interfering metal ions, such as copper(II) and iron(III), can be removed by passing the sample solution through a column of cation exchange resin, Dowex 50 W×8 in hydrogen form, 100—200 mesh. Chlorate, selenate, and selenite ions can not be removed by any treatment, but as these ions seem to exist in commerical nitrites in only trace concentrations, and therefore except for some special cases, they may not give a serious error to the determination on a semi-micro scale.

Determination of Organic Compounds. The recommended procedures were carried out as described in the Procedure section. In the case of azoxybenzene, it is reduced with chromium(II) ions and gives azobenzene as a precipitate. Then, after acidifying the solution, the solution must be filtered through a dried absorbent cotton on the funnel to remove the precipitate, the filtrate is then received in a photometric cell. The results obtained are shown in Table 5 (1)—(7) together with the wavelength at which the measurement of the absorbance should be made.

Table 5. Determination of organic compounds

Sample taken 10^{-4} mol	Cr(III) produced 10^{-4} mol	Mol ratio of Cr(III)/Sample	Wavelength used for abs. meas., nm
(1) Carbon tetrachloride			
0.21	0.85	4.05	410
0.31	1.25	4.03	
0.52	2.05	3.94	
0.63	2.57	4.08	
0.94	3.74	3.98	
(2) Nitrobenzene			
0.20	0.90	4.50	420
0.29	1.33	4.51	
0.39	1.75	4.49	
0.49	2.23	4.55	
0.64	2.88	4.50	
(3) Chloramine T			
0.30	0.62	2.07	425
0.61	1.24	2.03	
0.91	1.83	2.01	
1.21	2.38	1.97	
1.51	2.90	1.92	
(4) Propionaldehyde			
0.55	1.01	1.84	420
0.96	1.93	2.01	
1.37	2.71	1.98	
1.78	3.58	2.00	
(5) Azoxybenzene			
0.39	0.77	1.97	410
0.79	1.65	2.09	
0.98	2.11	2.35	
1.38	3.82	2.04	
(6) Dimethylglyoxime			
0.16	1.33	8.31	410
0.31	2.48	8.00	
0.39	3.06	7.85	
0.47	3.55	7.77	
(7) 1-Nitroso-2-naphthol			
0.21	0.97	4.63	420
0.42	2.05	4.88	
0.63	3.13	4.97	
0.74	3.38	4.57	

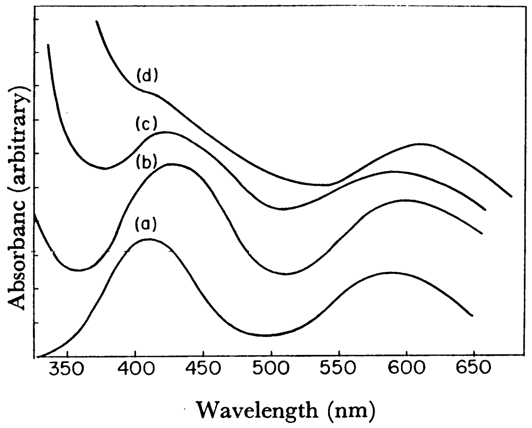

Fig. 4. Absorption spectra of chromium(III) complexes resulted by reaction between chromium(II) and some organic compounds.
(a): Carbon tetrachloride, nitrobenzene, and chloramine T, (b): propionaldehyde, azoxybenzene, and dimethylglyoxime, (c): 1-nitroso-2-naphthol, (d): *p*-benzoquinone and propiophenone oxime.

The absorption spectra of the resulting chromium(III) complex solutions are shown in Fig. 4. The spectra for carbon tetrachloride, nitrobenzene, and chloramine T (a) are very close to the standard one (Fig. 3), while those for propionaldehyde, azoxybenzene, and dimethylglyoxime (b) somewhat deviate from the standard one. On the other hand, the absorption spectra for 1-nitroso-2-naphthol (c) and *p*-benzoquinone and propiophenone oxime (d) exhibit another strong absorption peak at a wavelength shorter than 400 nm, which contributes to the absorption of chromium(III) at 420 nm. This absorption may be attributed to the reaction product in the solution. Consequently, the determined values are higher than the theoretical one, but in the case of 1-nitroso-2-naphthol an approximately linear relationship exists between the concentration of the sample and the absorbance of the resulting solution. Therefore, the determination of 1-nitroso-2-naphthol can be performed satisfactorily (Table 5(7)). However, in the case of *p*-benzoquinone and propiophenone oxime, the absorbance at about 420 nm is difficult to measure because the absorption peak is hindered by a strong absorption at a wavelength shorter than 400 nm. The absorption at 420 nm very quickly decreases, so the determination is impossible.

According to Kiba and Terada,[13] carbon tetrachloride and chloroform were assumed to be reduced to methane by chromium(II) ions. However, in the present study, as the results of the gaschromatographic measurement of the resulting aqueous solution and of the gas phase remained after the reaction in the reductor, it was found that tetrachloroethylene could be detected in the solution and carbon monooxide in the gas phase, but not any methane at all. The mechanism for this reaction remains still obscure.

Carbon tetrabromide also can be determined in the same way, while chloroform reacts completely with chromium(II) under heating at 80 °C.

From the results in Table 5, which shows the mol number of chromium(III) produced by oxidation of chromium(II) with 1 mol of the sample, the reaction stoichiometry can be speculated about:

Nitrobenzene:

$$C_6H_5NO_2 + 6Cr^{2+} + 6H^+ \longrightarrow C_6H_5NH_2 + 6Cr^{3+} + 2H_2O$$

Although 1 mol of nitrobenzene oxidized only 4.5 mol of chromium(II), aniline was detected as a reaction product by gaschromatographic measurements. Consequently, it may be assumed that this reaction will proceed to the extent of 75% under these conditions. However, as an exact linear relationship was obtained between the concentration of the sample and the absorbance of the resulting chromium(III) solution, determination of nitrobenzene should be carried out satisfactorily in the range of 10^{-5}—2×10^{-4} mol.

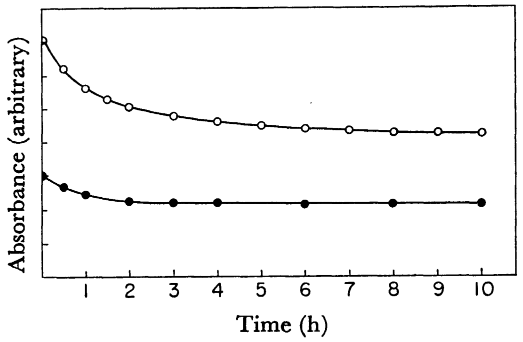

Fig. 5. Change of the absorbance of chromium(III) at 410 nm on the elapse of time.
—○—: 1-Nitroso-2-naphthol, —●—: azoxybenzene.

Chloramine T:

$$CH_3C_6H_4SO_2N\cdot ClNa + 2Cr^{2+} + 2H^+ \longrightarrow CH_3C_6H_4SO_2NH_2 + 2Cr^{3+} + Na^+ + Cl^-$$

Propionaldehyde:

$$CH_3CH_2CHO + 2Cr(OH)_2 + 2H_2O \longrightarrow CH_3CH_2CH_2OH + 2Cr(OH)_3$$

Azoxybenzene:

$$C_6H_5N(O){=}NC_6H_5 + Cr(OH)_2 + H_2O \longrightarrow C_6H_5N{=}NC_6H_5 + 2Cr(OH)_3$$

Dimethylglyoxime:

$$[(CH_3)C{=}NOH]_2 + 8Cr(OH)_2 + 6H_2O \longrightarrow [(CH_3)CHNH_2]_2 + 8Cr(OH)_3$$

1-Nitroso-2-naphthol:

$$C_{10}H_6(OH)NO + 4Cr(OH)_2 + 3H_2O \longrightarrow C_{10}H_6(OH)NH_2 + 4Cr(OH)_3$$

As shown in Fig. 5, the reaction of the last three compounds is not fast, so the contents must be kept standing for about 3, 1, and 6—7 h, to obtain invariable results for azoxybenzene, dimethylglyoxime, and 1-nitroso-2-naphthol, respectively.

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