EXPERIMENTAL

1. Preparation of α-oximino-acetoacetamides.

Preparation of α-oximinoacetoacetanilide was carried out by two methods:(a) nitrosyl chloride method (174); and (b) nitrous acid method(173),with modifications.

1(a). Nitrosyl chloride method.

(i) Preparation of nitrosyl chloride:

Dry sodium chloride powder was taken in a distilling flask to which a dropping (separatory) funnel was attached at the top and a calcium chloride tube on the side.Nitrosyl sulphuric acid (SO_5NH) was taken in the dropping funnel and was allowed to drop very slowly on the mass of sodium chloride.As a result of the interaction between sodium chloride and the acid,nitrosyl chloride gas was liberated:

$$NaCl + SO_5NH = NaHSO_4 + NOCl .$$

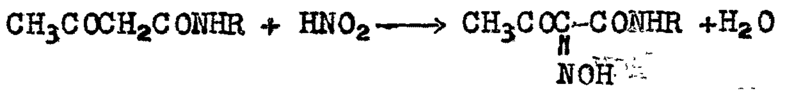
The gas was led through calcium chloride tube to the reaction flask.

(ii) Preparation of α-oximino-acetoacetanilide:

Acetoacetanilide (10 gms.) was dissolved in dry benzene (100 ml.) in a flask and was kept cool,by ice.Dry nitrosyl chloride gas was passed slowly through the solution, with occasional shaking of the solution,till it was saturated with nitrosyl chloride. During the reaction hydrochloric acid gas evolved. The solution gradually attained yellow colour and at the point of saturation assumed a deep reddish yellow colour. It was then refluxed on a water bath to remove excess of nitrosyl chloride and hydrochloric acid. The solution was then transferred to an evaporating dish and the solvent was allowed to evaporate when a yellow solid mass was obtained. The product was crystallised from chloroform + light petroleum (1:5) as needles melting at 99-100°C. The m.p. recorded by Naik, Trivedi and Mankad (174) is 99-100°C. It is easily soluble in chloroform, benzene, alcohol and acetone and sparingly soluble in water, ether and light petroleum.

1(b). <u>Nitrous acid method</u>.

Acetoacetanilide (10 gms.) and sodium nitrite (5 gms.) were dissolved in 60 ml. dilute sodium hydroxide solution and the solution was added, drop by drop, to 600 ml. dilute sulphuric acid solution which was kept cool by ice and well stirred during the reaction. Acetoacetanilide reacted with nitrous acid as follows:



$$CH_3COCH_2CONHR + HNO_2 \longrightarrow CH_3CO\underset{\underset{NOH}{\|}}{C}-CONHR + H_2O$$

α-Oximinoacetoacetanilide was obtained as yellow precipitates. stirring was continued for half an hour after the addition of the mixture was over. The solution was filtered, the precipitates were washed with water and dried. The product was recrystallised from aqueous alcohol,m.p.99-100°C.(Yield 75%).The m.p. recorded by Knorr(173) is 99-100°C.

It was observed that the products obtained in both processes were similar in chemical reactions and lowering of the mixed melting point was not observed. In the nitrosyl chloride method,maintenance of the precise conditions was found necessary;otherwise,tarry products were obtained which were difficult to work with. On the other hand,no tarry products were obtained in the nitrous acid method. Hence for the preparation of other α-oximino-acetoacetanilides,nitrous acid method was employed.(Yield 75-80%). The products obtained together with their colour, m.p., analysis (micro),etc.are recorded in table-1. It is worth noting that all these oximes possess yellow or pale yellow colour except α-oximino-acetoacet-p-chloranilide which is white.

2. Preparation of α-β-dioximinoacetoacetamides.

For the preparation of the dioximes,the method employed by Knorr and Reuter (181) was adopted.

α-Oximinoacetoacet(aryl)amide (4 gms.) was dissolved in a little alochol and was treated with hydroxylamine hydrochloride (2 gms.) in a little water. On gentle warming, abundant crystals appeared gradually. The product was filtered, washed with water and recrystallised from aqueous alcohol. (Yield 70-80%).

Knorr and Reuter(181) have recorded that the α-βdioximinoacetoacetanilide had yellow colour, but it was observed in the present investigations that the product was white and assumed slight yellowish brown colouration on long standing.

The products obtained together with their colour, m.p., analysis(micro), etc., are tabulated in the table-2.

3. Preparation of the nickel chelates of the dioximes.

10 ml. M/2 nickel chloride solution were gradually added to 20 ml. alcoholic solution of the dioxime (0.011 mole) with shaking. The solution was diluted to about 100 ml. with distilled water and digested on the water bath for about an hour; the precipitates obtained were filtered, washed with water and alcohol and dried. The products obtained together with their colour, m.p., analysis(micro), etc., are given in the table-3.

4. Preparation of the copper chelates of the dioximes.

10 ml. M/2 copper chloride solution in water were gradually added to 20 ml. alcoholic solution of the dioxime (0.011 mole) which was slightly acidified with a little hydrochloric acid. The solution was diluted to about 100 ml. with distilled water and digested on the water bath for about an hour; the precipitates obtained were filtered, washed with water and alcohol and dried. The products obtained together with their colour, m.p., analysis(micro), etc., are given in the table-4.

5. Preparation of the cobalt chelates of the dioximes.

10 ml.M/2 cobalt chloride solution in water were added to 20 ml. alcoholic solution of the dioxime(0.011 mole) rendered acidic with hydrochloric acid. To the mixture was then added, with shaking, ammonium acetate solution when precipitates were obtained. The solution was diluted to about 100 ml. with distilled water and allowed to stand for about an hour. The precipitates were then filtered, washed with water and alcohol and dried. The products obtained together with their colour, m.p., analysis (micro), etc., are recorded in the table-5.

It may be noted here that slight variations in the reaction process varied the nature of the products obtained and that the addition of alkali appeared to precipitate basic products.

6. Preparation of the palladium chelates of the dioximes.

10 ml.M/4 palladium chloride solution in water (acidified with hydrochloric acid) were gradually added to 20ml. alcoholic solution of the dioxime(0.0055 mole), acidified with hydrochloric acid. The solution was diluted to about 100 ml. with distilled water and digested on the water bath for about an hour; the precipitates obtained were filtered, washed with water and alcohol and dried. The products obtained together with their colour, m.p., analysis(micro), etc., are given in the table -6.

7. Absorption spectra.

All measurements of O.D.(optical density)of the oxime solutions in the ultraviolet and visible region were carried out on Beckmann spectrophotometer-model DU at room temperature.

7(a). Theory

When light is passed through a solution or a substance, light radiation of certain wave-lengths is absorbed by it; this absorption is characteristic of the substance, and is obtained from the curve-the absorption spectrum-obtained by plotting absorbance against wave-length.

The total energy of the molecule is made up of electronic binding energy and kinetic(rotational and vibrational) energy. Changes in the electronic energy are usually associated with the absorption bands in the visible and ultraviolet region. If the energy changes in the molecule were electronic only, the absorption spectra would be simple, consisting of lines only as is observed in the case of atoms; for every electronic change, however, there occur simultaneous vibrational and rotational energy changes so that the absorption bands result.

The great complexity of the electronic(band)spectra of polyatomic molecules, in general, makes the complete mathematical interpretation of these spectra so difficult as to be almost impossible at the present time. Nevertheless, attempts have been made to account for the observed positions and intensities of the absorption bands of some polyatomic molecules(187-190).

The study of the absorption spectra has grown from the early attempts to correlate colour with constitution. These attempts had led to the recognition that unsaturation (as exemplified by multiple bonds or free radicals) and polarisability are essential features of any molecular structure (chromophore) exhibiting colour (light absorption) and that this colour is affected by the introduction of other polarisable groups (auxochromes) into the coloured system.

It is rather unfortunate that although attempts have been made to attain standard terms for the presentation of absorption spectroscopic data, different workers have used different terms for expressing their data. The terms used in the present investigation (with their definitions) are:

I_o : intensity of incident light ;
I : intensity of transmitted light after passage through the cell of length b ;
b : length of the cell (cm.);
c : concentration(gm-mol. per litre) ;
T : transmittance = I/I_o ;
A : absorbance (optical density: O.D.) = $-\log_{10} T$;
E_m : molar extinction coefficient = $A/(b \times c)$; .

7(b). Procedure.

Absorption in the visible region was determined in the following way:

(1) Beckmann model DU and W-lamp leads were connected to a 6-volt storage battery. Shutter switch was turned off, W-lamp switch was turned on and the selector switch was set to check. Sensitivity control was kept at mid-point and the instrument was allowed to warm up for about 10 minutes. The standard and the sample cells(corex) in the cell holder were placed in the cell compartment and the cover was replaced on the compartment.

(2) Wave length was set to a desired value and the proper phototube and filter were selected. The standard was kept in the light path, and the dark current control was rotated to zero the needle. Then the shutter switch was turned on, the slit adjustment control was rotated to approximately zero the needle, the sensitivity control was rotated to accurately zero the needle and the shutter switch was turned off.

(3) The unknown sample was brought in the light path, the selector switch was set to 1 (or 0.1) and the shutter switch was turned on. The transmittance control was rotated to zero the needle, the shutter switch was turned off and the transmittance or the absorbance reading was recorded.

(3) was repeated when readings were to be taken with other samples by bringing them in the light path, at the same wave length and with the same slit-width. (2) and (3) were repeated when another wave length was to be used.

For measuring absorption in the ultraviolet, the W-lamp back-plate was replaced by hydrogen lamp back-plate connected to the hydrogen lamp power supply. Model DU was connected to the storage battery and the selector switch was set to check. Hydrogen lamp power supply switch was turned on, the filament control was turned to its clockwise limit and allowed to stand for 5 minutes to warm up. Then the press button switch was pressed to start the arc in the hydrogen lamp and the filament control was turned counterclockwise. The sensitivity control was set 3 turns from its clockwise limit. The standard and the sample cells(silica) in the cell holder were placed in the cell compartment and the cover was replaced on the compartment. The steps (2) and (3) were then carried out as described above.

The solvents used in the present investigation were distilled water, 0.1 N aqueous solution of sodium hydroxide, rectified spirit, methanol and chloroform. Alcohols were dried with calcium oxide before distillation. Chloroform was well shaken with water and then dried with calcium chloride before distillation. All distillations were carried out with the use of quickfit distillation assembly.

The results obtained are recorded in tables 7 to 10 for monoximes and tables 11 to 13 for dioximes.

8. Magnetic measurements.

A number of methods are in use for the measurement of the magnetic susceptibility of substances in the solid and the liquid states(191-197).Amongst these,the Gouy's method is widely used as it offers several advantages;e.g.the apparatus can be easily set up and is very convenient to handle;and the susceptibilities of small quantities of substances can be measured very accurately in a relatively short time.

For the present investigations,a Gouy's magnetic balance was set up from the Government of India grant,as shown in the fig.1.

8(a). Theory.

If a cylindrical specimen of matter is suspended between the poles of a magnet so that one end of the specimen is in a region of large field intensity and the other end in a region of smaller field,the specimen will experience a force along its length.The magnitude of this force, f, is given by the expression

$$f = \frac{1}{2}(k_1 - k_2)(H_1^2 - H_2^2)A$$

where k_1 and k_2 are the volume susceptibilities of the specimen and the surrounding atmosphere respectively;H_1 and H_2 are the maximum and minimum magnetic fields to which the specimen is

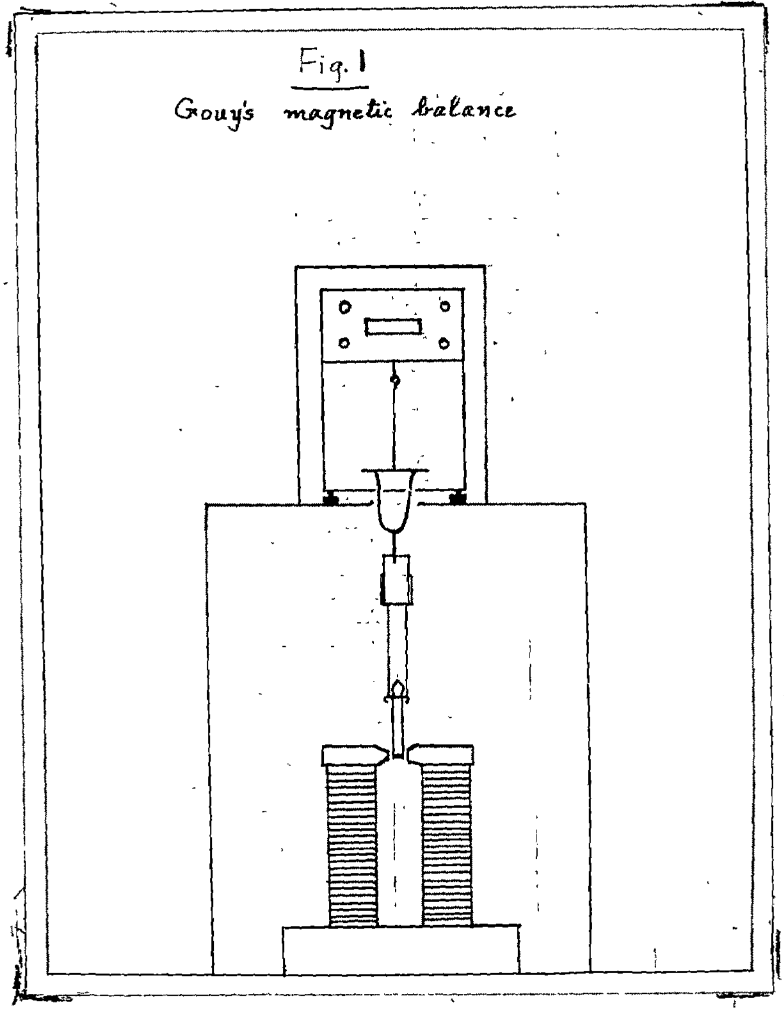


Fig.1 : Gouy's magnetic balance

subjected ; and A is the cross-sectional area of the specimen. In practice, H_2 is neglected; hence the expression reduces to

$$f = \frac{1}{2} \times (k_1 - k_2) \times H_1^2 \times A \quad .$$

Again, $(k_1 - k_2) = (\chi_1 \rho_1 - \chi_2 \rho_2)$,

where χ_1 and χ_2 are the mass susceptibilities and ρ_1 and ρ_2 the densities of the specimen and the medium respectively. Therefore,

$$f = \frac{1}{2} \times (\chi_1 \times \rho_1 - \chi_2 \times \rho_2) \times H_1^2 \times A \quad .$$

If the specimen is suspended from a balance, the force exerted on the specimen will cause an apparent change in the weight of the sample; hence

$$f = g \times dw$$

where g is the gravitational constant and dw the apparent change in weight of the specimen on application of the magnetic field.

$$g \times dw = \frac{1}{2} \times (\chi_1 \times \rho_1 - \chi_2 \rho_2) \times H_1^2 \times A \quad ,$$

$$\text{or} \quad \chi_1 = \frac{1}{\rho_1} \times \left(\frac{2 \times g \times dw}{H_1^2 \times A} + \chi_2 \rho_2 \right) \quad .$$

Since $\rho_1 = \dfrac{m_1}{v_1}$, where m_1 is the mass of the specimen of volume v_1 ,

$$\chi_1 = \frac{\left(\frac{2 \times g \times v_1}{H_1^2 \times A} \right) \times dw + \chi_2 \times \rho_2 \times v_1}{m_1} \quad .$$

Further, $\chi_m = \chi_1 \times M$

where M is the molecular weight of the specimen.

8(b). Apparatus: Gouy's magnetic balance.

The magnetic balance (fig.1), set up here, essentially consists of 3 parts

(1) sensitive balance,

(2) suspension arrangement and the specimen tube, and

(3) electromagnet with electrical accessories.

(1) Sensitive balance: An air-damped, single-pan, automatic, semi-micro 'Mettler' balance was used. It was housed in a glass case, provided with glass shutters to turn the balance knobs. The readings were taken when the glass case was closed. The case containing the balance was placed on a marble slab so as to minimise the vibration effects on the balance.

Two holes were drilled in the base of the balance and circular openings were made in the base of the glass case and in the marble slab for the purpose of passing the suspension wires (suspended from the balance pan) through the box and the marble slab.

(2) Suspension arrangement and the specimen tube: A brass tube to the lower end of which was fitted a brass cylindrical rod was suspended by means of a stout nickel-coated brass wire from the balance pan. From the lower end of the cylindrical rod was extended a wire suspension with hooks at its extreme end. The specimen tube with hooks rested on the wire-hooks, such that the end of the specimen tube was in the centre of the pole gap of the

electro-magnet. A thermometer was also suspended separately in the pole gap.

The specimen tube was of pyrex glass tubing. It was about 14 cms. long with a uniform bore of about 0.4 cm. and was provided with a glass stopper and glass hooks. All substances were packed in the tube upto a fixed height of 7 cms. from the bottom end of the tube. This height was such that when the tube was placed in the magnetic field, the lower end of the sample was in the region of maximum field and the upper end in the region of negligible field. This was ascertained by filling the specimen tube with ferrous ammonium sulphate to different heights and measuring the force exerted on it. It was also established by plotting the field strength at different heights by means of a fluxmeter.

(3) Electromagnet with electrical accessories: The electromagnet was housed below the balance and was enclosed on all sides. It gave a field strength of about 5000 Gauss with the pole gap of about 1 cm. and a current of 4.5 amperes. The magnet was run on 110 volts D.C. It was run for short periods only and an electric fan was provided for cooling. The pole pieces used were of truncated conical shape. An ammeter and a rheostat were connected in series with the magnet.

8(c). Precautions.

(1) It is important that the magnetic field to be employed for the measurements should be kept constant. This was done by keeping the current passing through the electromagnet constant. Fluctuation in the current was indicated by the deflection of the ammeter needle and was immediately adjusted by means of the rheostat placed in series with the magnet.

(2) Uniform packing of the substance is important. This was mainly achieved by filling the specimen tube under uniform conditions. The effect due to packing was further minimised by taking measurements for the same substance with two tubes.

8(d). Experimental procedure.

The speciment tube was throughly cleaned with chromic acid and was then washed with distilled water and acetone. It was dried at 120°C in an electrically regulated oven. The tube with its stopper, cooled to room temperature, was suspended vertically in the pole gap and kept there for 10 minutes. The temperature was recorded and the weight of the tube was determined. A current of 4.5 amperes was passed through the electromagnet and the weight of the tube was again determined taking care to see that the current was maintained constant during the determination. After 2 minutes, the weights of the tube before and during the passage of the current were again determined. Three such readings were taken and a mean of the change in weight (dw) was calculated. Because glass is diamagnetic, an apparent loss in weight was observed.

According to the theory, the equation is

$$\chi_g = \frac{\left(\frac{2 \times g \times v}{A \times H^2}\right) dw + \chi_2 \varrho_2 \times v}{m}$$

Since g, χ_2 *and* ϱ_2 are constant, H is maintained constant and A and v are constant for a particular tube,

$$\chi_g = \frac{\alpha + \beta \times dw}{m}$$

where

$$\alpha = \chi_2 \times \varrho_2 \times v \quad = 0.029 \times v \times 10^{-6} \qquad \text{and}$$

$$\beta = \frac{2 \times g \times v}{A \times H^2}$$

both being constants.

For the determination of v, the tube was filled with distilled water upto the fixed height and the weight of water was determined. For the determination of the tube constant β, the tube was filled with ferrous ammonium sulphate (whose magnetic susceptibility is accurately known) upto the fixed height and the weights were determined before and during the passage of the current. Since the standard substance used was paramagnetic, an apparent gain in weight was observed. The effective gain in weight for the substance would be equal to the sum of the gain in weight for the substance with the tube and the diamagnetic correction of the tube.

For the purpose of determining the magnetic susceptibilities of the unknown samples,measurements were made with two tubes and usually with two fillings(for each tube).The magnetic susceptibilities together with the values of the magnetic moment(B.M.) obtained for some of the metal chelates under investigation are presented in table-14.

9. Solubility of the oximes.

About 200 ml. of distilled water was taken in a flask and the oxime was suspended in it.The suspension was allowed to stand for 15 days with occasional shaking.It was then filtered and the amount of the oxime present in 10 ml. of the filtrate was determined by evaporating 10 ml.of the filtrate in a crucible and weighing the residue.The results are recorded in table-15.

10. pH of incipient and complete precipitation.

N/1 solution of sodium hydroxide was added,with stirring,to 200 ml.of 0.001 M solution of the metal ion containing sufficient free acid and about 20% excess of the equivalent quantity of the reagent solution in alcohol till a turbidity just appeared.pH of the solution at this point was determined with the help of the L and N pH meter and this gave the pH of incipient precipitation of the metal ion by the reagent under prescribed condition. These values are recorded in table-16. From this point onward the addition of alkali was continued and the pH of the filtered solution was ascertained at intervals and the presence of the metal ion in the filtrate was tested for. pH just corresponding to the complete precipitation was thus obtained. These values are recorded in table-17.

11. Qualitative analysis.

Tests for the detection of cations were carried out as follows:

To 2 ml. of distilled water (neutral or made slightly acidic or alkaline) was added 10 drops of 1% reagent solution (alcoholic) and 1 drop of the salt solution (M/2). The reaction was observed in cold and in hot solution. While testing for bismuth with the dioxime solution, the solution was made ammoniacal and heated. Similarly to test for cobalt with dioximes, it was found that addition of ammonium acetate to the acidic reaction solution gave a better and uniform result. The results obtained are recorded in table-18.

12. Gravimetric estimation of palladium by the dioximes.

12 (a). Reagents.

1% alcoholic solution of α-β-dioximino acetoacet (aryl) amide, where aryl amide = anilide, o-toluidide or o-chloranilide were prepared. Palladouss chloride was dissolved in a little warm conc. hydrochloric acid and was then diluted with distilled water to a definite volume. Palladium content of the solution was determined by the dimethyl glyoxime method(198). M/2 solutions of calcium, strontium, barium, magnesium, zinc, manganese, cobalt, nickel, ferric iron, chromium, antimony, bismuth, mercury and cadmium were prepared from their salts. The following solid reagents were also used: sodium acetate, sodium nitrate, potassium iodide, potassium sulphate, tartaric acid and citric acid. All the reagents used were of C. P. grade.

12 (b). Preparation and composition of the complex.

Palladium chloride solution(10 ml.) was diluted to about 100 ml. with distilled water and acidified with 0.5 ml. conc. hydrochloric acid. The solution was warmed and to this solution was added, with stirring, sufficient amount of the dioxime reagent solution. Yellow precipitates were obtained and were digested on the water bath for about an hour. The precipitates were filtered, washed with water and alcohol and dried at 110-20°C.

In order to find the composition of the precipitate a weighed quantity of the complex was taken in a crucible and its palladium content was estimated after ignition(by the ignition method)(199). The results are recorded in table-19.

12 (c). Analytical procedure.

An aliquot quantity of the palladium chloride solution was diluted with about 200 ml. of distilled water and acidified with about 5 ml. of conc. hydrochloric acid. To the warm solution was added, with shaking, sufficient excess of 1 % alcoholic solution of the reagent (1 gm. reagent for 0.1 gm. palladium). The precipitates were digested on the waterbath for about an hour. They were then filtered through the sintered glass crucible or quantitative filter paper, washed with water and dried at 110-20°C, to constant weight. The results are given in table-20.

12 (d). Effect of pH.

In order to study the pH ranges over which palladium could be completely precipitated by these reagents, estimation of palladium was carried out in solutions having different pH values. pH values of the undiluted filtrates were determined by L and N pH meter. The results are recorded in the table-21.

12 (e). Effect of anions.

To study the effects of various anions, the estimation of palladium was carried out in presence of different anions at definite pH values. The results are recorded in the table-22.

12 (f). Effect of cations.

In order to study the effect of various cations, palladium was estimated in presence of various metal ions at pH 0.4 to 0.7 by following the procedure outlined above. (The precipitates were washed with dilute hydrochloric acid before washing with water.) The results are shown in <u>table-23</u>.

13. Gravimetric estimation of copper by the dioximes.

13 (a). Reagents.

Copper chloride solution was prepared by dissolving a weighed quantity of copper chloride in little water and diluting it to a definite volume. Copper content of the solution was determined iodometrically (200). Other reagents used were the same as described in 12(a).

13 (b). Preparation and composition of the complex.

Copper chloride solution(10 ml.) was diluted to about 100 ml. with distilled water and the solution was slightly acidified with dilute hydrochloric acid. The solution was warmed and to the warm solution was added, with stirring, sufficient amount of the dioxime reagent solution. Brown precipitates were obtained and were digested on the water bath for about an hour. The precipitates were filtered, washed with water and alcohol and dried at 110-20°C.

To determine the composition of the precipitate, a weighed quantity of the precipitate was digested with aqua regia so as to decompose the organic matter and the liquid was nearly evaporated to dryness. A little concentrated sulphuric acid was added to it and it was once again evaporated. The residue was extracted with dilute sulphuric acid and the copper content of the solution was determined iodometrically (200). The results are recorded in table-24.

13 (c). Analytical procedure.

An aliquot quantity of copper chloride solution was taken and diluted to about 200 ml. with distilled water. The solution was acidified with a little dilute hydrochloric acid and warmed. To the warm solution was added, with stirring, sufficient quantity of the dioxime reagent solution(1 gm. reagent for 0.09 gm. copper). pH of the solution was adjusted and the solution was then digested on the water bath for about an hour. The precipitates were, then, filtered through sintered glass crucible or quantitative filter paper, washed with water and dried at 110-20°C. to constant weight. The results are recorded in the table-25.

13 (d). Effect of pH.

In order to study the pH ranges over which copper can be completely precipitated by these reagents, estimation of copper was carried out in solutions having different pH values. pH values of the undiluted filtrates were determined by L and N pH meter. Results are recorded in the table-26.

13 (e). Effect of anions.

Estimation of copper was carried out in presence of different anions within the pH range of the reagents as determined in 13(d). The results are recorded in table-27.

13 (f). Effect of cations.

Copper was estimated in presence of various metal ions within the pH range of the reagents as determined in 13(d). The results are recorded in table-28.

14. Gravimetric estimation of nickel by the dioximes.

14 (a). Reagents.

Nickel chloride solution was prepared by dissolving a weighed quantity of nickel chloride in little water and diluting it to a definite volume. Nickel content of the solution was determined by the dimethyl glyoxime method (201). Other reagents used were the same as described in 12(a).

14 (b). Preparation and composition of the complex.

Nickel chloride solution (10 ml.) was diluted to about 100 ml. with distilled water and the solution was warmed; to the warm solution was added, with stirring, sufficient amount of the dioxime reagent solution. Yellow or orange precipitates were obtained which were digested on the water bath for about an hour. The precipitates were, then, filtered, washed with water and alcohol and dried at 110-20°C.

In order to find the composition of the precipitate, a weighed quantity of the precipitate was digested with aqua regia to decompose the complex and oxidise organic matter. The residue was treated with conc. hydrochloric acid to boil off nitric acid. It was then extracted with dilute hydrochloric acid and its nickel content was determined by the dimethyl glyoxime method(201). The results are recorded in <u>table-29</u>.

14 (c). <u>Analytical procedure</u>.

An aliquot quantity of nickel chloride solution was diluted to about 200 ml. with distilled water and the solution was warmed. To the warm solution was added, with stirring, sufficient amount of the reagent solution (1 gm. reagent for 0.09 gm. nickel). pH of the solution was adjusted and the precipitates were digested on the water bath for about an hour. The precipitates were filtered through a sintered glass crucible or quantitative filter paper, washed with water and dried at 110-20°C. to constant weight. The results are recorded in <u>table-30.</u>

14 (d). <u>Effect of pH.</u>

In order to study the pH ranges over which nickel could be completely precipitated by these reagents, estimation of nickel was carried out in solutions having different pH values. pH values of the undiluted filtrates were determined by L and N pH meter. The results are recorded in <u>table-31.</u>

14 (e) and (f). <u>Effect of anions and of cations.</u>

Estimation of nickel was carried out in presence of various anions and cations within the pH range of the reagents as determined in 14(d). The results are given in <u>tables-32 and 33.</u>