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WATER CHEMISTRY STUDIES : CHEMICAL ANALYSIS MANUAL FOR MODERATOR  
AND COOLANT WATER SYSTEMS

by

P. K. Mathur, A. S. Gokhale and K. S. Venkateswaria  
Chemistry Division

BHABHA ATOMIC RESEARCH CENTRE  
BOMBAY, INDIA

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### ABSTRACT

The specifications of high purity water employed in the water moderated and cooled power reactors are very stringent. A strict control and regular monitoring of some of the specific dissolved impurities is extremely essential. Procedures for the quantitative determination of sub microgram amounts of dissolved oxygen (< 10 ppb),  $F^-$ ,  $Cl^-$ ,  $NO_3^-$ , boric acid,  $Al^{+3}$ ,  $Cr^{+3}$ ,  $Fe^{+3}$ ,  $Ni^{+2}$ ,  $Cu^{+2}$  and  $Zr^{+4}$  in high purity water have been developed and standardized, and are presented in this report.

# WATER CHEMISTRY STUDIES: CHEMICAL ANALYSIS MANUAL FOR MODERATOR AND COOLANT WATER SYSTEMS

by

P.K. Mathur, A.S. Golhale and K.S. Venkateswarlu

## INTRODUCTION

The use of high purity water, including heavy water, is an essential ingredient of the developing nuclear technology in India, consequent upon the gradual installation of water-moderated and water-cooled power reactors. According to the present plans, all the power reactors which might be built in the next five years are also going to be based on water as moderator and coolant. In view of this, water chemistry acquires considerable interest and importance.

Maintaining the chemical integrity of the various water systems of out of pile and in-pile loops and in the water moderated and cooled power reactors is of great importance to ensure smooth reactor operation, prevent hazardous conditions resulting from the build-up of radioactivity in the water, and minimise corrosion. Special mention has to be made regarding specific impurities like dissolved oxygen,  $F^-$ ,  $Cl^-$ ,  $NO_3^-$ , and some cations, where a strict control and regular monitoring is essential. Chloride, in combination with dissolved oxygen, can lead to stress corrosion cracking in stainless steel. Fluoride attacks the zirconium of the zircaloy tubes. Presence of dissolved  $Cl^-$  and  $NO_3^-$  in high pressure-high temperature water in presence of reactor radiation may give rise to the possibility of formation of  $HCl$  and  $HNO_3$  which are detrimental to the reactor piping, valves and auxiliary units. The determination of other cationic impurities such as  $Al^{+3}$ ,  $Cr^{+3}$ ,  $Fe^{+3}$ ,  $Ni^{+2}$ ,  $Cu^{+2}$ ,  $Zr^{+4}$ , etc., is essential to ensure that there is no appreciable build-up of these ions occurring in the system. Boric acid is often used to control initial excess reactivity and it is gradually removed and its monitoring is also essential.

At the suggestion of Reactor Engineering Division, B.A.R.C., the Chemistry Division has initiated a programme of work on water chemistry with a view to help in the running of out-of-pile water loops that are being set up

by Reactor Engineering Division. Developing and standardizing various analytical methods to meet their requirements is a necessary part of this programme. Keeping this objective in view, chemical procedures for determination of the above-mentioned impurities at the required levels of sensitivity were standardised and are presented in this report. In a subsequent report, other physical measurements such as electrical and thermal conductivities, pH, etc., will be described.

## 1. DISSOLVED OXYGEN

Stringent specifications have been prescribed for the dissolved oxygen content in the water of the PWR type loop being set up. The oxygen content should be less than 10 ppb. There is a possibility that such a low level of dissolved oxygen might be obtained by the addition of hydrazine as oxygen scavenger. It is also desirable that the dissolved oxygen content may be much lower, say, 5 ppb only.

1.1 Summary: The determination of dissolved oxygen in the sample is carried out by the Winkler method with some special modification. Freshly precipitated manganese hydroxide is oxidized by the dissolved oxygen, presumably to  $MnO(OH)_2$ . Upon acidification in the presence of iodide ion, the Mn (III) is reduced to Mn (II), and free iodine equivalent to the oxygen consumed is formed. Free iodine is then determined spectrophotometrically as its triiodide ion at 287.5 nm. Potassium iodate solution is used to prepare a standard curve, eliminating the need for standard oxygen samples. This is an important advantage over the titration procedure. It is possible to measure less than 10 ppb of dissolved oxygen by this method, if one uses 5 cm cells.

### 1.2 Preparation of Deoxygenated Water

Water is first demineralised using a mixed bed resin column. This column is prepared by mixing X E-77 cation exchanger ( $H^+$  form) and X E-78 anion exchanger ( $OH^-$  form) in 1:1 proportion. Water flow rate through the bed is maintained at about 500 ml/min (for a resin bed volume of 7 litres) so as to get the demineralised water with specific conductivity  $< 0.5 \mu mhos\ cm^{-1}$  and pH in the range of 6.5 to 7.0. Demineralised water so obtained is then passed through a deoxygenating IRA-402 anion exchange bed in the sulfite form. A flow

rate of about 400 ml/min (for a resin bed volume of 7 litres) is maintained through this column so as to get sufficiently good deoxygenated water ( $O_2$  concentration  $< 10$  ppb). Before sampling, deoxygenated water is once again passed through a second mixed bed demineraliser so as to get rid of any traces of sulfite ions present, as they seriously interfere in subsequent chemical analysis of residual dissolved oxygen.

### 1.3 Reagents

#### (i) Alkaline potassium iodide solution

22.5 g KOH (AnalaR) + 45 g KI (AnalaR) are dissolved in 100 ml of distilled water.

#### (ii) 0.0001 N potassium iodate solution

1.0 ml of standardized  $KIO_3$  (0.1 N) solution is diluted to 1000 ml by distilled water.

#### (iii) 9 M $H_2SO_4$

62 ml of pure conc  $H_2SO_4$  (AnalaR) is diluted to 250 ml by distilled water observing usual precautions.

#### (iv) Mangnous sulphate solution

50 g of  $MnSO_4 \cdot 4H_2O$  is dissolved in 100 ml of distilled water.

#### (v) Potassium triiodide solution

A little amount of resublimed iodine is dissolved in 10% KI and diluted to 200 ml by distilled water.

### 1.4 Calibration procedure

2 ml each of the three reagents are mixed with stirring with 354 ml of water in the order: alkaline KI,  $H_2SO_4$ ,  $MnSO_4$ . (These volumes are for a calibration to be used with 180 ml sample bulbs).

25 ml of this solution is added to each of six 50 ml glass stoppered volumetric flasks. One of these is filled to 50 ml mark with distilled water and is used as a reagent blank. Appropriate amounts of 0.0001 N  $KIO_3$  solution are pipetted into other flasks to give the equivalents of 4, 8, 16, 32, and

64 ppb oxygen (0.25, 0.50, 1.0, 2.0, and 4.0 ml). Each flask is then filled to the mark, and the solutions made homogenous by shaking. Optical density of each of the solutions is measured in a spectrophotometer using a 5 cm cell against the reagent blank at 475 nm. A curve of O.D. versus ppb oxygen is plotted as shown in Fig. 1.

#### 1.5 Procedure for the test samples

(i) Sampling:- A sample bulb made of pyrex glass (Fig. 2) is mounted vertically on a suitable support with both stop-cocks open. Nitrogen gas, free from oxygen, is passed through the bulb for about 15 minutes. The bottom tip is now connected to the sample line with the shortest possible length of the tygon tubing. The flow of the test water sample is adjusted to about 150 ml/min. All air bubbles must be removed from the tubing and the bulb. Test water is allowed to flow continuously for at least 15 minutes, and preferably 30 minutes. Both the stop-cocks are now closed.

(ii) Analysis of samples:- At the time of experiment with test samples all the three reagents, viz., alkaline KI,  $MnSO_4$ , and  $H_2SO_4$  are kept oxygen free by bubbling oxygen-free nitrogen through them continuously. The sample bulb containing test sample is mounted vertically with end "A" at the top. 0.5 ml of alkaline KI is transferred to the tip of the bulb by a measuring 1 ml pipette, and is quickly admitted to the bulb by carefully opening the lower stop-cock. Both the stop-cocks are closed, the tips rinsed with water, and contents mixed by turning over the bulb end several times.

In the same manner 0.5 ml of  $MnSO_4$  solution is added through end "B". Mixing must be thorough to ensure complete contact of the oxygen with the precipitated manganous hydroxide.

Following the same procedure, 0.5 ml of  $H_2CO_4$  is added through end 'B' and the contents are again mixed. All precipitate should dissolve.

During the draining of the treated sample, the first 10 to 15 ml of the solution are discarded and the next 50 ml are collected in a volumetric flask. This is taken in a 5 cm path length spectrophotometer cell after proper rinsing. Another 40 to 50 ml of the sample are taken into another flask, and one

Drop of 0.1 N sodium thiosulphate solution is added and mixed thoroughly. This serves as a blank. Optical density of the sample solution is measured at 267.5 nm with the same slit width as was used in the calibration procedure and the  $\mu$  of oxygen interpolated from the curve (Fig. 1). Use of 10 cm cells will increase the sensitivity of measurement.

## C. FLUORIDE

The limit for fluoride is less than 0.05 ppm.

2.1 Summary: Decolorization of the zirconium xylenol orange chelate in 1.2 N HCl medium by fluoride permits its rapid determination even in the presence of relatively large amounts of phosphate, sulfate, aluminium, iron (III) and many other ions. It is possible to accurately determine as low as 0.01 ppm of fluoride in the sample if 5 cm cells are used for O.D. measurement.

### 2.2 Reagents

#### (i) Zirconium standard solution

50.0 mg  $ZrOCl_2 \cdot 8H_2O$  is taken in 40 ml distilled water and added to cold dilute HCl (500 ml conc. HCl+400 ml water). The volume is made up to 1000 ml.

#### (ii) Xylenol Orange Solution

0.2 g, xylenol orange is dissolved in 100 ml distilled water, and stored in an amber coloured bottle.

#### (iii) Fluoride standard

0.5525 g NaF (BDH AnalaR) is dissolved in distilled water, and the volume made up to 250 ml in a volumetric flask.

One ml of the above solution when diluted to 100 ml gives a solution  $10 \mu g F^-/ml$ .

### 2.3 Operation

(i) A suitable aliquot of test water (containing 1 to  $10 \mu g$  of  $F^-$ ) is taken in a 50 ml volumetric flask into which 10 ml of the zirconium solution is already pipetted.



- (ii) The contents of the flask are then heated continuously at 60°C for 20 minutes.
- (iii) The flask is then cooled for 40 minutes.
- (iv) 2 ml of xylenol orange solution is then added, and the volume of the solution is made up to 50 ml.
- (v) After about 1 hour, this solution is taken in 5 cm path length cell and O.D. at 545 nm is measured against an equally treated reagent blank.
- (vi) Microgram amounts of fluoride are then determined with the help of a bleaching calibration curve (Fig.5) obtained similarly and simultaneously.

### 3. CHLORIDE

The limit for chloride is less than 0.3 ppm.

3.1 Summary: Test water having free chloride ion is made to react with a saturated solution of mercuric thiocyanate. Mercuric chloride is formed, liberating a corresponding amount of thiocyanate ions. The free thiocyanate could be determined spectrophotometrically after complexing with ferric iron. It is possible to estimate free  $\text{Cl}^-$  at concentration as low as 0.1 ppm if 5 c.m. cells are used for measurement of optical density at 460 nm.

#### 3.2 Reagents

(i) Standard sodium chloride solution

0.1649 g NaCl E. Merck G.R. quality is dissolved in 100 ml of double distilled water to give a solution 100  $\mu\text{g}$  of  $\text{Cl}^-$ /ml. 25 ml of this solution is further diluted to 100 ml to give 25  $\mu\text{g}$   $\text{Cl}^-$ /ml.

(ii) Ferric ammonium sulphate solution

12.05 g of ferric ammonium sulphate are dissolved in hot 9M  $\text{HNO}_3$ , and then diluted to 100 ml by double distilled water. 10 ml of this stock solution further diluted to 100 ml gives 0.025M ferric ammonium sulphate.

(iii) Saturated mercuric thiocyanate solution

Mercuric thiocyanate is added to redistilled ethyl alcohol. The solution is shaken for 30 minutes, and is filtered through Whatman No. 542 filter paper.

### 3.3 Operation:

- (i) A suitable aliquot of test water (containing 5 to 50  $\mu\text{g}$  of free  $\text{Cl}^-$  ion) is taken in a 25 ml volumetric flask.
- (ii) 2 ml of ferric ammonium sulphate solution are added.
- (iii) 2 ml of mercuric thiocyanate solution are then added.
- (iv) After thorough mixing and waiting for about 10 minutes, optical density is measured against a reagent blank at 460 nm using a 5 cm cell. It is essential to finish the entire operation within 30 minutes as the colour starts fading.
- (v) Microgram amounts of chloride in test samples are then determined with the help of a calibration curve (Fig.4) obtained similarly and simultaneously.

## 4. NITRATE

4.1 Summary: Nitrate ions present in the test sample are reduced to ammonia by Devarda alloy in strong alkaline medium. Ammonia so obtained is steam distilled, and condensed in cold water. It is then complexed with Nessler's reagent, and is determined spectrophotometrically by measuring the absorbance at 370 nm.  $\text{NO}_3^-$  concentration as low as 1.0 ppm can be determined.

### 4.2 Reagents

#### (i) Nitrate standard solution

1.5178 g of sodium nitrate (AnalaR) is dissolved in distilled water, and the volume made up to 250 ml.

5 ml of this solution when diluted to 500 ml gives a solution 10  $\mu\text{g}/\text{ml}$  of nitrogen (N) and hence 44  $\mu\text{g}/\text{ml}$  of Nitrate.

#### (ii) Nessler's reagent

6.25 g KI are dissolved in 25 ml distilled water. To this, a saturated solution of  $\text{HgCl}_2$  is added till a reddish precipitate persists after brisk shaking. The precipitate is dissolved by adding 30% KOH, and the volume made up to 200 ml with 30% KOH. This solution is taken in a beaker, and a few drops of saturated  $\text{HgCl}_2$  are added again till the precipitate reappears. It is allowed to stay overnight, and is then filtered. Filtrate is stored in a glass stoppered flask.

#### 4.3 Operation

- (i) A suitable aliquot of the sample water containing 25 to 150  $\mu$ g of nitrogen as nitrate is taken in a round bottomed distillation flask.
- (ii) About 2 grams of Devarda alloy are then added to the aliquot.
- (iii) Steam distillation assembly is then set up as shown in Fig. 5.
- (iv) 5 ml of 60% NaOH are now added to the reaction mixture.
- (v) Brisk reaction starts in the flask, which is allowed to subside.
- (vi) Hot steam is now passed through the reaction mixture, the ammonia so driven out is condensed, and absorbed in a flask containing very cold water.
- (vii) This solution is now quantitatively transferred to a 100 ml volumetric flask, and 1 ml of Nessler's reagent is added. The volume is made up to 100 ml and the solution thoroughly mixed.
- (viii) Absorbance of this solution is measured at 400 nm against a similarly treated reagent blank.
- (ix) Microgram amounts of nitrate are then determined with the help of a calibration curve. (Fig. 6).

#### 5. Boric acid

5.1 Summary: Test water having boric acid or borate is made to react with a polyvalent alcohol like d-mannitol, to produce an acid complex behaving like a monovalent acid of medium strength, which can be titrated potentiometrically against sodium hydroxide solution. The lowest concentration which can be estimated is 2.5 ppm of boron.

#### 5.2 Reagents

- (i)  $\frac{N}{10}$  to  $\frac{N}{400}$  NaOH solution (according to boron content in the sample).
- (ii) Saturated d-mannitol solution (app 200 g d-mannitol dissolved in 200 ml distilled water).

#### 5.3 Operation

- (i) An accurately known volume of sample solution is allowed to react

with 10 ml saturated mannitol solution in a beaker.

(ii) It is stirred thoroughly.

(iii) The solution is then titrated against  $\frac{N}{10}$  to  $\frac{N}{400}$  NaOH solution

(according to the boron content in the sample) and the end point is determined from the pH metric titration curve (Fig.7).

#### 5.4 Calculation

$$\text{mg } \beta / \frac{10}{\text{litre}} = \frac{V \times \frac{N}{10} \times 1.011 \times 1000}{E}$$

where with  $\frac{N}{10}$  NaOH solution

V = volume of  $\frac{N}{10}$  NaOH in ml

E = volume of  $\frac{10}{\text{sample}}$  pipetted out

### 6. ALUMINIUM ( $\text{Al}^{3+}$ )

6.1 Summary:- Aluminium is complexed with hematoxylin at pH 7.0, and is determined spectrophotometrically by measuring the difference in absorbance at 610 and 730 nm. The method is useful upto 0.05 ppm.

#### 6.2 Reagents

##### (i) Standard aluminium solution

0.1000 g of E. Merck G.R. metal aluminium is weighed and dissolved in 10 ml of 1:1 HCl. The solution is then diluted to 100 ml in a standard volumetric flask, with distilled water.

5 ml of this solution, when diluted to 500 ml, gives a solution containing 10  $\mu\text{g}$  Al/ml.

##### (ii) 0.8 N ammonium borate solution

93 g of boric acid are dissolved in 1000 ml of 1 N standardised ammonia. It is then titrated with standard HCl using methyl orange as indicator. Proper dilution to 0.8N is then made.

##### (iii) 10% Ammonium carbonate

50 g of  $(\text{NH}_4)_2\text{CO}_3$  are dissolved in 500 ml of distilled water.

(iv) 40% Ammonium acetate

200 g of ammonium acetate are dissolved in 500 ml of distilled water.

(v) Starch solution (fresh)

1 g boric acid and 1 g starch are made into a paste with a little water and then added to about 50 ml boiling distilled water. It is cooled, and made up to 100 ml.

(vi) 0.1% hematoxylin solution

0.1 g hematoxylin is dissolved in 100 ml of distilled water. It is filtered through Whatman No. 40 filter paper, and stored in an amber coloured bottle.

(vii) 1:1  $\text{HNO}_3$

(viii) 0.8 N  $\text{NH}_4\text{OH}$

6.5 Operation:-

(i) A suitable aliquot of the test water (containing 1 to 10  $\mu\text{g}$  of Al) is taken in a 50 ml volumetric flask.

(ii) 10 ml of freshly prepared starch solution are added.

(iii) 5 ml of 0.1% hematoxylin solution are added.

(iv) After waiting for 15 minutes, 10 ml of 40% ammonium acetate are added.

(v) After about 10 minutes, pH of the solution is adjusted to  $7.0 \pm 0.1$  by using 1:1  $\text{HNO}_3$  and/or 0.8 N ammonia.

(vi) Time of pH adjustment is noted and after about 40 minutes 2 ml of 0.8 N ammonium borate solution are added.

(vii) The solution is made up to 50 ml and the optical density is measured after a lapse of 30 minutes on Beckman Du spectrophotometer both at 610 nm and 730 nm against a reagent blank. Difference in O.D. at these two wave lengths corresponds to the amount of Al present.

(viii) Micrograms of aluminium are then determined with the help of a calibration curve (Fig.8) obtained similarly and simultaneously.

## 7. CHROMIUM ( $\text{Cr}^{3+}$ )

7.1 Summary: Chromium in water samples is determined spectrophotometrically by complexing it with diphenyl carbazide after oxidation with potassium permanganate in acid solution ( $\text{pH} = 1.0$ ). Absorption measurements are carried out at 540 nm, and it is possible to determine  $\text{Cr}^{3+}$  as low as 0.05 ppm.

### 7.2 Reagents:

#### (i) Chromium ( $\text{Cr}^{3+}$ ) standard solution

0.5148 g of pure chromium metal is dissolved in dilute  $\text{H}_2\text{SO}_4$  by gentle boiling. It is left overnight for complete dissolution. This solution is then transferred to a 500 ml flask and the volume is made up with distilled water.

4.9 ml of the above solution when diluted to 500 ml with distilled water give a solution containing  $10 \mu\text{g Cr}^{3+}/\text{ml}$ .

#### (ii) Diphenyl carbazide solution

0.25 g of diphenylcarbazide is dissolved in A.R. acetone, and made up to 250 ml with A. R. acetone only.

#### (iii) Potassium permanganate (0.1N)

0.316 g of potassium permanganate is dissolved in 100 ml distilled water.

#### (iv) Sodium azide solution (1%)

1.0 g of sodium azide is dissolved in 100 ml of water, and is filtered if necessary.

#### (v) 50% Sulfuric acid

500 ml of conc sulfuric acid are added slowly to 400 ml of water with stirring and cooling. It is diluted to 1 litre with water.

### 7.3 Operation:-

(i) A suitable aliquot of the test water (containing 5  $\mu\text{g}$  to 30  $\mu\text{g}$  of  $\text{Cr}^{3+}$ ) is taken in a 100 ml beaker.

(ii) pH of this solution is adjusted to  $1.0 \pm 0.1$  with dilute  $\text{H}_2\text{SO}_4$ .

(iii) A few drops (2-3) of 0.1 N  $\text{KMnO}_4$  are added to get a deep pink colouration. The contents are then boiled on a hot plate taking care that no spurting occurs. Continuous boiling is maintained for 20 minutes. Pink colouration should persist even after boiling, which ensures the complete oxidation of  $\text{Cr}^{3+}$  to  $\text{Cr}^{6+}$ .

(iv) Excess  $\text{KMnO}_4$  colouration is destroyed by the addition of a few drops of sodium azide solution (only one or two drops are required). Boiling is continued for 10 more minutes for the complete decomposition of any residual azide present.

(v) The contents of the beaker are then cooled in an ice water bath. They are transferred to a 50 ml volumetric flask containing 1 ml of 0.1% diphenyl carbazide. Violet colour develops in about 2 minutes. The volume is made up to the mark and homogenised.

(vi) Optical density is measured in 1 cm cells against a reagent blank similarly treated, at 540 nm within 5 minutes of mixing.

(vii) Micrograms of  $\text{Cr}^{3+}$  are then determined with the help of a calibration curve (Fig.9) similarly and simultaneously prepared.

## 8. IRON ( $\text{Fe}^{3+}$ )

8.1 Summary: Iron is complexed with butanolic thiocyanate, and is determined spectrophotometrically by measuring the absorbance at 480 nm at concentrations upto 0.05 ppm.

### 8.2 Reagents

#### (i) Standard solution of iron (III)

0.1000 g of E. Merck G.R. metal iron or electrolytic iron is weighed and dissolved in 10 ml of conc HCl. The solution is then diluted to 100 ml in a standard volumetric flask.

10 ml of this solution when diluted to 1000 ml gives a solution containing 10  $\mu\text{g}$  of  $\text{Fe}^{3+}$ /ml.

#### (ii) Butanolic thiocyanate

10 g of KCNS is dissolved in 10 ml of water, diluted to 100 ml with n-Butanol and shaken thoroughly.

### 8.3 Operation

- (i) A suitable aliquot of the test water (containing 1 to 10  $\mu\text{g}$  of iron) is taken in a 50 ml volumetric flask.
- (ii) 0.5 ml of conc AR HCl is added.
- (iii) 1 ml of saturated ammonium persulphate solution is added.
- (iv) 10 ml of butanolic thiocyanate are added and the mixture made up to 50 ml. The contents of the flask are then shaken well.
- (v) The alcoholic aliquot is taken in a dry cell, and its optical density measured at 480 nm against a similarly treated reagent blank.
- (vi) The amount of iron ( $\text{Fe}^{3+}$ ) is then determined with the help of a calibration curve (Fig. 10) similarly and simultaneously taken.

### 9. NICKEL ( $\text{Ni}^{2+}$ )

9.1 Summary: Nickel is extracted in the form of dimethylglyoxime complex into chloroform, and the absorbance is measured at 375 nm. It is possible to estimate nickel at concentrations upto 0.2 ppm, if 5 cm path length cells are used for measurement of optical density.

#### 9.2 Reagents

##### (i) Standard solution of nickel

0.1273 g of G.R. NiO is dissolved in 1:1 HCl. The solution is then poured into a flask, and diluted to 100 ml with distilled water. This solution contains 1.0 mg  $\text{Ni}^{2+}$ /ml.

10 ml of the above solution are further diluted to 100 ml so as to give a solution containing 100  $\mu\text{g}$  of  $\text{Ni}^{2+}$ /ml.

##### (ii) 1% dimethylglyoxime solution

1 g pure dimethylglyoxime is taken along with 50 ml distilled ethanol in a beaker. It is dissolved by heating and allowed to cool. The solution is made 100 ml with ethanol.

- (iii) Anhydrous sodium sulphate
- (iv) A.R. Chloroform
- (v) 1:1 HCl
- (vi) 1 M ammonia solution



### 9.3 Operation:

- (i) A suitable aliquot of the test water (containing 20 to 120  $\mu\text{g}$  of  $\text{Ni}^{2+}$ ) is taken in a beaker.
- (ii) pH of the solution is adjusted to 9.5 with 1 M ammonia solution.
- (iii) 10 ml dimethylglyoxime solution is added
- (iv) The solution is poured into a separating funnel, 20 ml A.R. chloroform are added, and equilibrated with the aqueous solution for 2 minutes.
- (v) After the chloroform clearly separates out from the aqueous phase, it is transferred to a 30 ml conical flask having about 1 g of anhydrous sodium sulfate. By gentle stirring, the moisture present is eliminated, and the absorbance of the solution is measured at 375 nm against a reagent blank.
- (vi) Micrograms of  $\text{Ni}^{2+}$  are then determined with the help of a calibration curve (Fig.11) similarly and simultaneously taken.

### 10 COPPER ( $\text{Cu}^{2+}$ )

10.1 Summary: Copper is extracted into chloroform as 8-hydroxyquinoline complex, and by measuring absorbances at 410 nm and 580 nm the error due to possible presence of iron is corrected. It is possible to estimate copper at concentrations as low as 0.05 ppm, if 5 cm path length cells are used for measurement of optical density.

#### 10.2 Reagents:

##### (i) Standard solution of copper

0.1251 g of G.R.  $\text{CuO}$  is dissolved in 10 ml of 1:1  $\text{HCl}$ , and is diluted to 100 ml with distilled water. This solution contains 1.0  $\text{mg Cu}^{2+}/\text{ml}$ .

10 ml of this solution is diluted to 100 ml with distilled water so as to give a solution containing 100  $\mu\text{g Cu}^{2+}/\text{ml}$ .

##### (ii) 2% 8-hydroxy quinoline solution

2.000 g 8-hydroxyquinoline are taken along with 10 ml glacial acetic acid in a 100 ml beaker. It is dissolved by heating, and the resulting solution is diluted to 100 ml with distilled water.

(iii) 1 M sodium hydroxide solution

40 g NaOH are dissolved in about 50 ml of distilled water, cooled, and finally made up to 100 ml in a volumetric flask.

(iv) 4 M ammonium acetate solution

30.335 g of ammonium acetate are dissolved in about 50 ml of distilled water, and diluted to 100 ml in a volumetric flask.

(v) A.R. chloroform

(vi) Anhydrous sodium sulphate

(vii) 1:1 HCl

10.3 Operation:

(i) A suitable aliquot of test water (containing 0. to 20  $\mu\text{g}$  of  $\text{Cu}^{2+}$ ) is taken in a beaker.

(ii) 2.5 ml of 8-hydroxyquinoline solution are added and the pH adjusted to 5.0 with ammonium acetate.

(iii) The solution is poured into a separating funnel, 20 ml of A.R. chloroform is added, and it is equilibrated well for 2 minutes.

(iv) After the chloroform layer separates out from the aqueous phase, it is transferred to a conical flask having about 1 g of anhydrous sodium sulphate. By gentle stirring the moisture present is eliminated. Absorbance is then measured at 410 and 580 nm against a reagent blank. Difference in O.D. at these two wavelengths corresponds to the amount of copper present in the sample.

(v) Micrograms of  $\text{Cu}^{2+}$  are then determined with the help of a calibration curve (Fig. 12) similarly and simultaneously taken.

11. ZIRCONIUM ( $\text{Zr}^{4+}$ )

11.1 Summary: Zirconium is complexed with xylenol orange and determined spectrophotometrically by measuring the absorbance at 535 nm against a reagent blank. It is possible to determine as low as 0.05 ppm of  $\text{Zr}^{4+}$  by this method.

11.2 Reagents:

(i) Zirconium standard solution

1.7660 g  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  are dissolved in 500 ml of distilled water. It gives 1 mg  $\text{Zr}^{4+}$ /ml solution.

5 ml of this solution on dilution to 500 ml with distilled water give  $10 \mu\text{g Zr}^{4+}/\text{ml}$  solution.

(ii) Xylenol orange solution

0.200 g Xylenol orange is dissolved in 100 ml distilled water.

(iii) 2.5 M  $\text{H}_2\text{SO}_4$

(iv) 5 M  $\text{HClO}_4$ .

11.3 Operation:

(i) A suitable aliquot of the sample containing 5 to  $40 \mu\text{g}$  of  $\text{Zr}^{4+}$  is taken in a 25 ml volumetric flask.

(ii) 2 ml of 2.5M  $\text{H}_2\text{SO}_4$  is added.

(iii) 4 ml of 5M  $\text{HClO}_4$  is added.

(iv) 2 ml of 0.2% xylenol orange solution are now added.

(v) The contents of the flask are then diluted to the mark and mixed well.

(vi) Optical density of the solution is then measured against a similarly treated reagent blank at 535 nm.

(vii) Micrograms of  $\text{Zr}^{4+}$  are then determined with the help of a calibration curve (Fig. 13) similarly and simultaneously taken.

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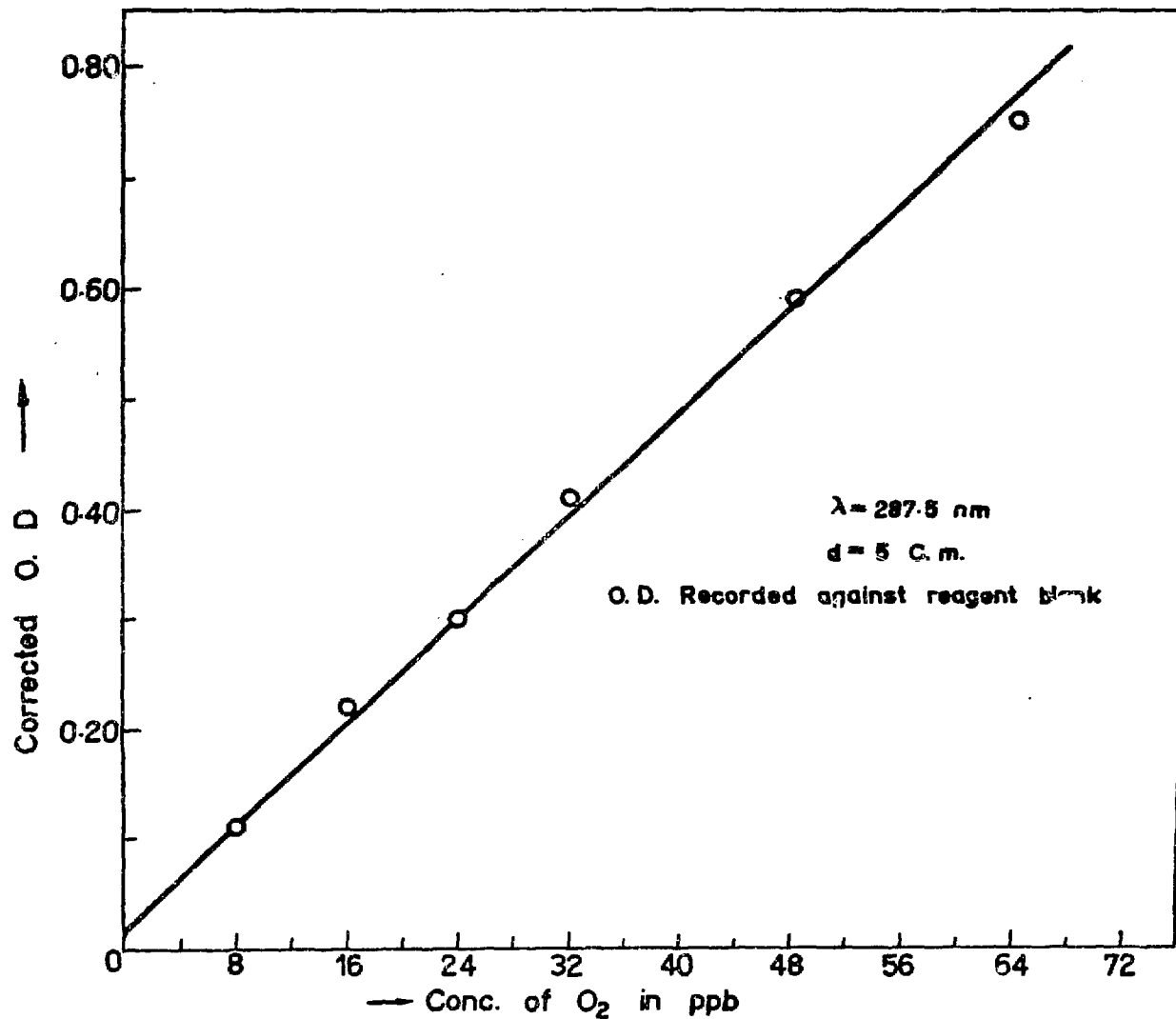
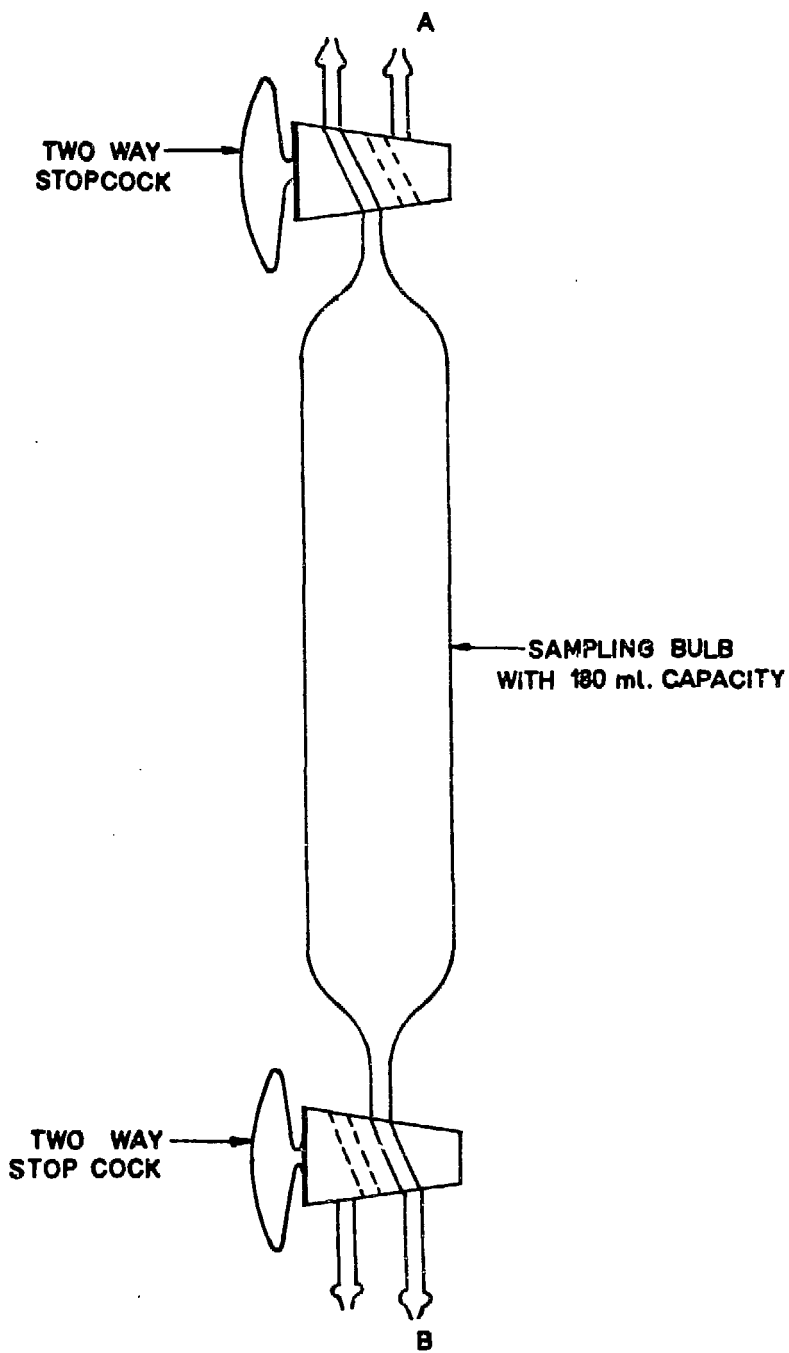


Fig. 1 Calibration curve for determination of ppb levels of dissolved oxygen.



**Fig. 2. OXYGEN SAMPLING ASSEMBLY .**

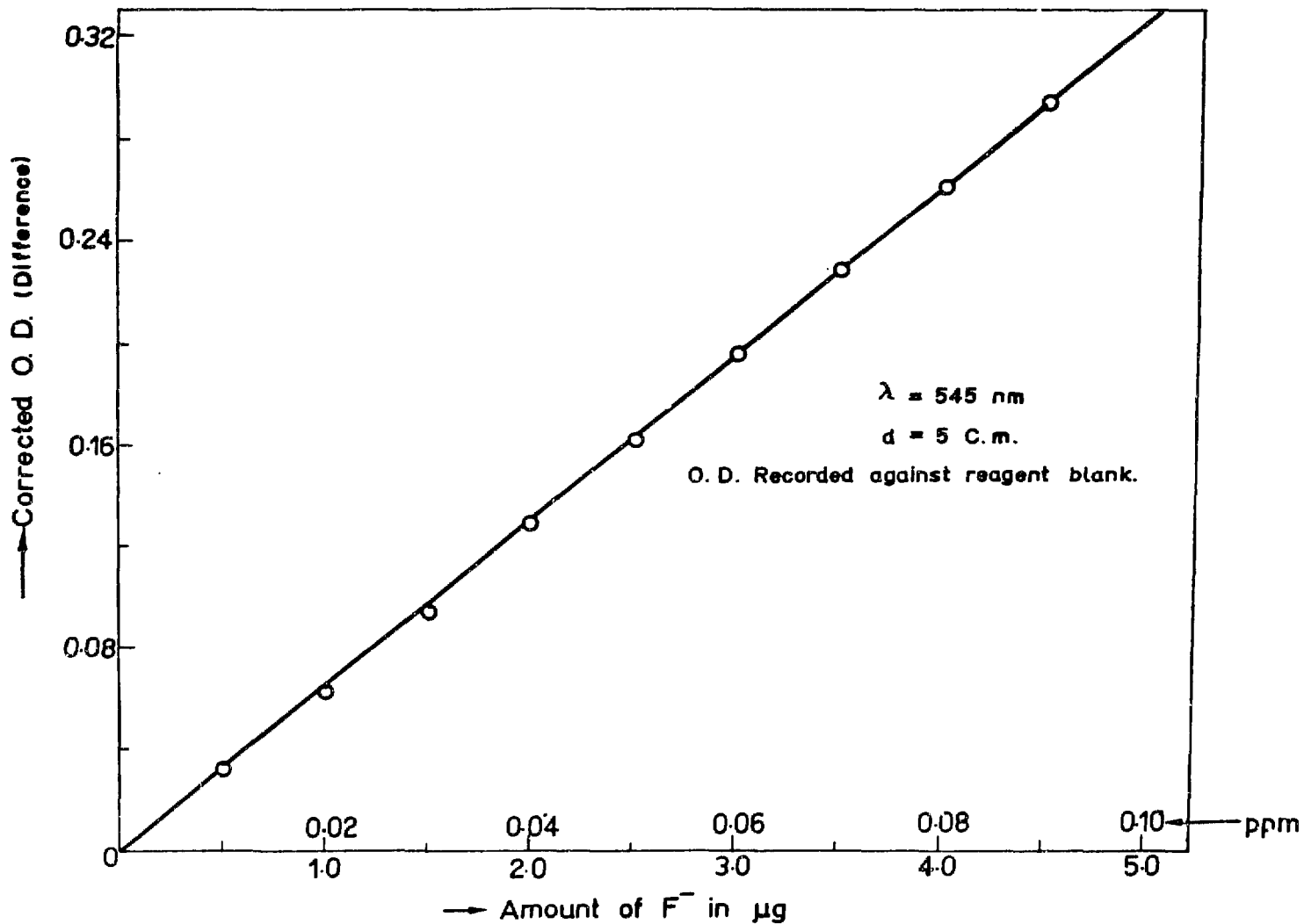


Fig. 3. Bleaching calibration curve for determination of  $\mu\text{g}$  amounts of  $F^-$ .

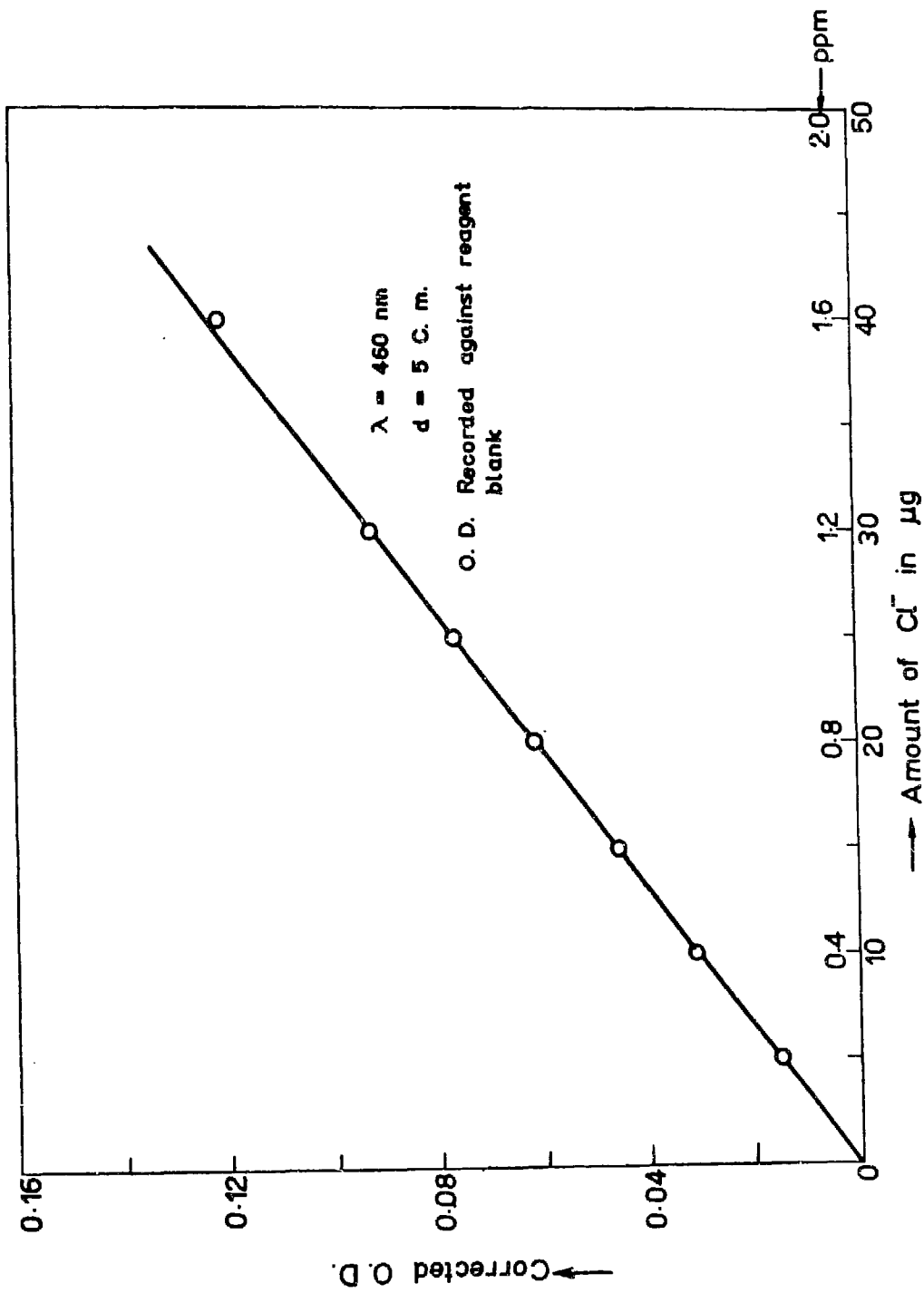


Fig. 4. Calibration curve for determination of  $\mu\text{g}$  amounts of  $\text{Cl}^-$  ion.

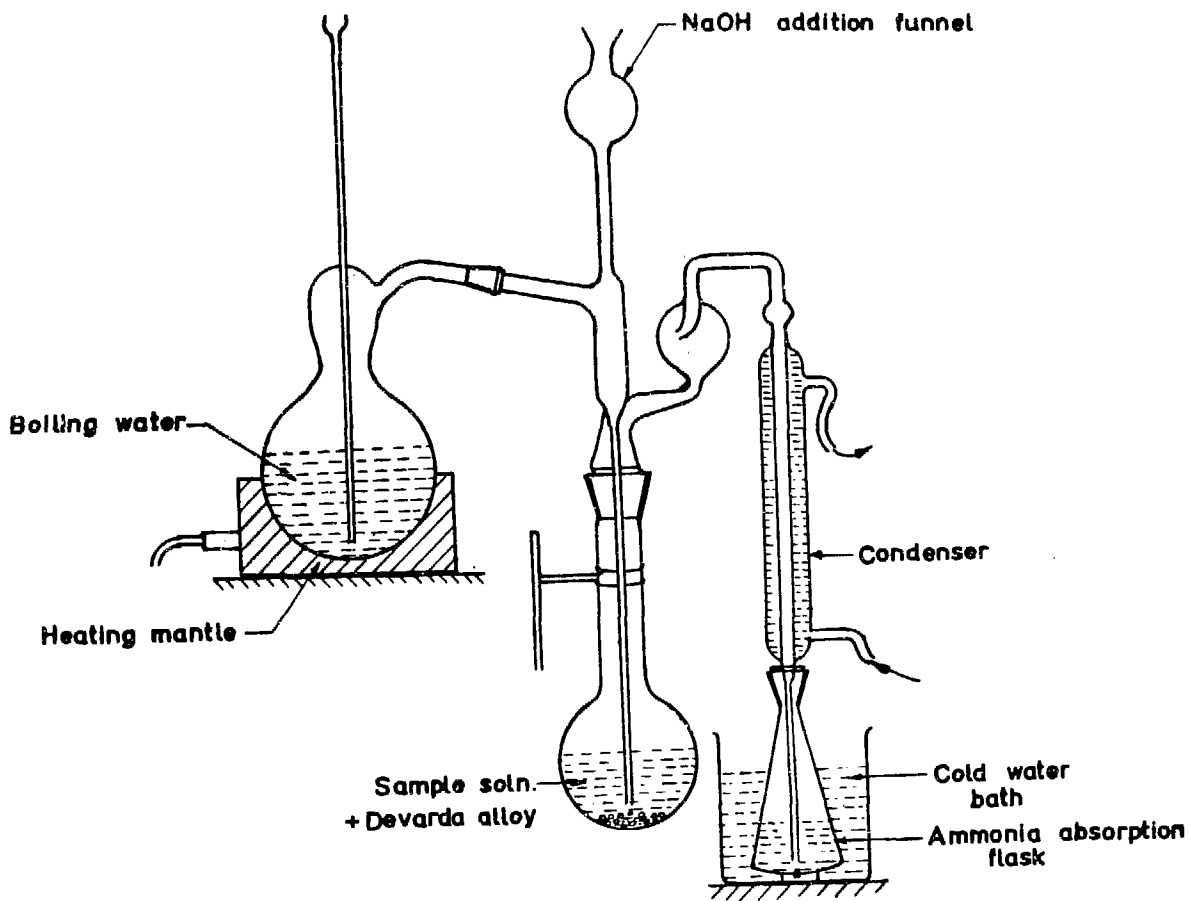


Fig. 5. Steam distillation assembly for determination of  $\text{NO}_3^-$  ion.



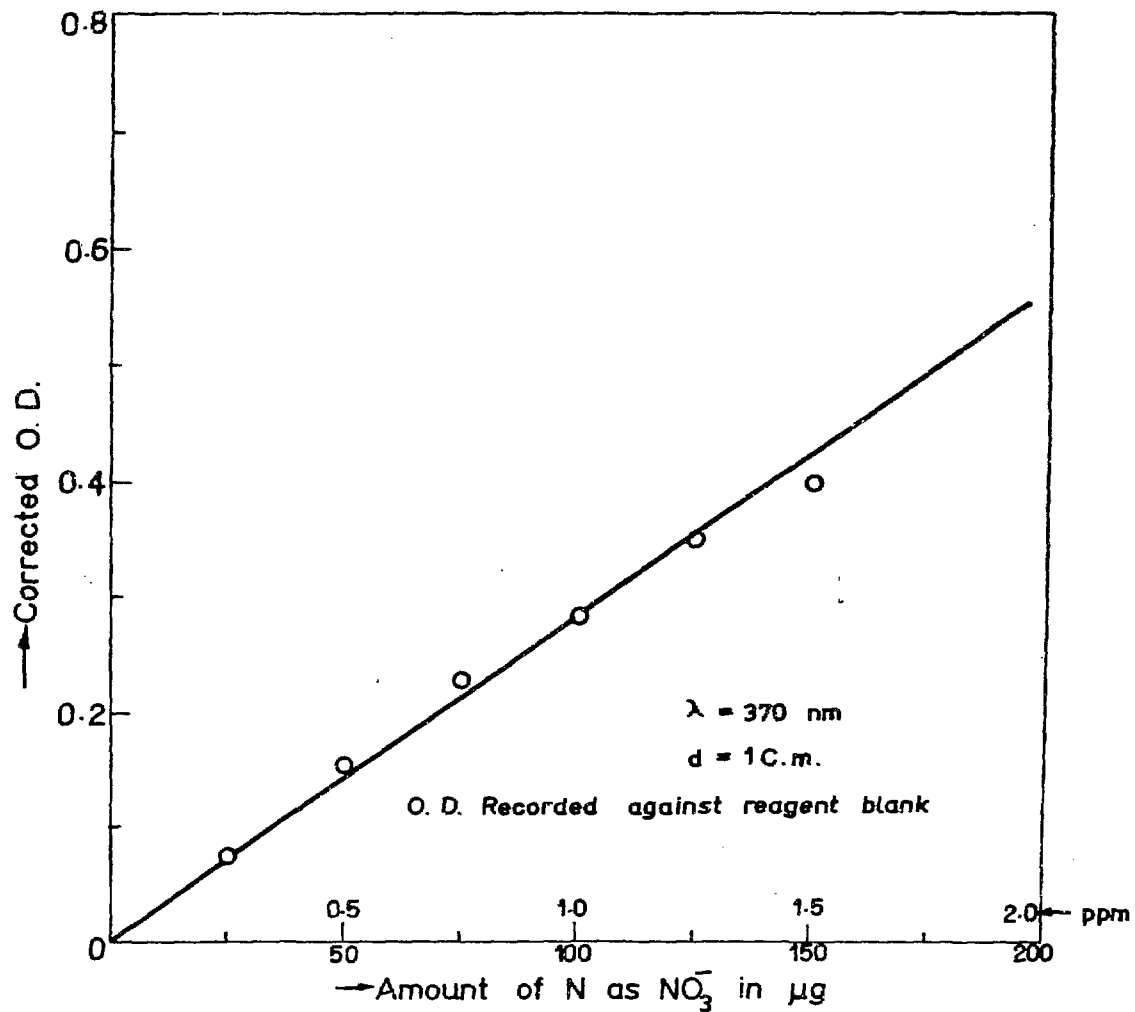


Fig. 6 Calibration curve for determination of  $\mu\text{g}$  amounts of  $\text{NO}_3^-$ .

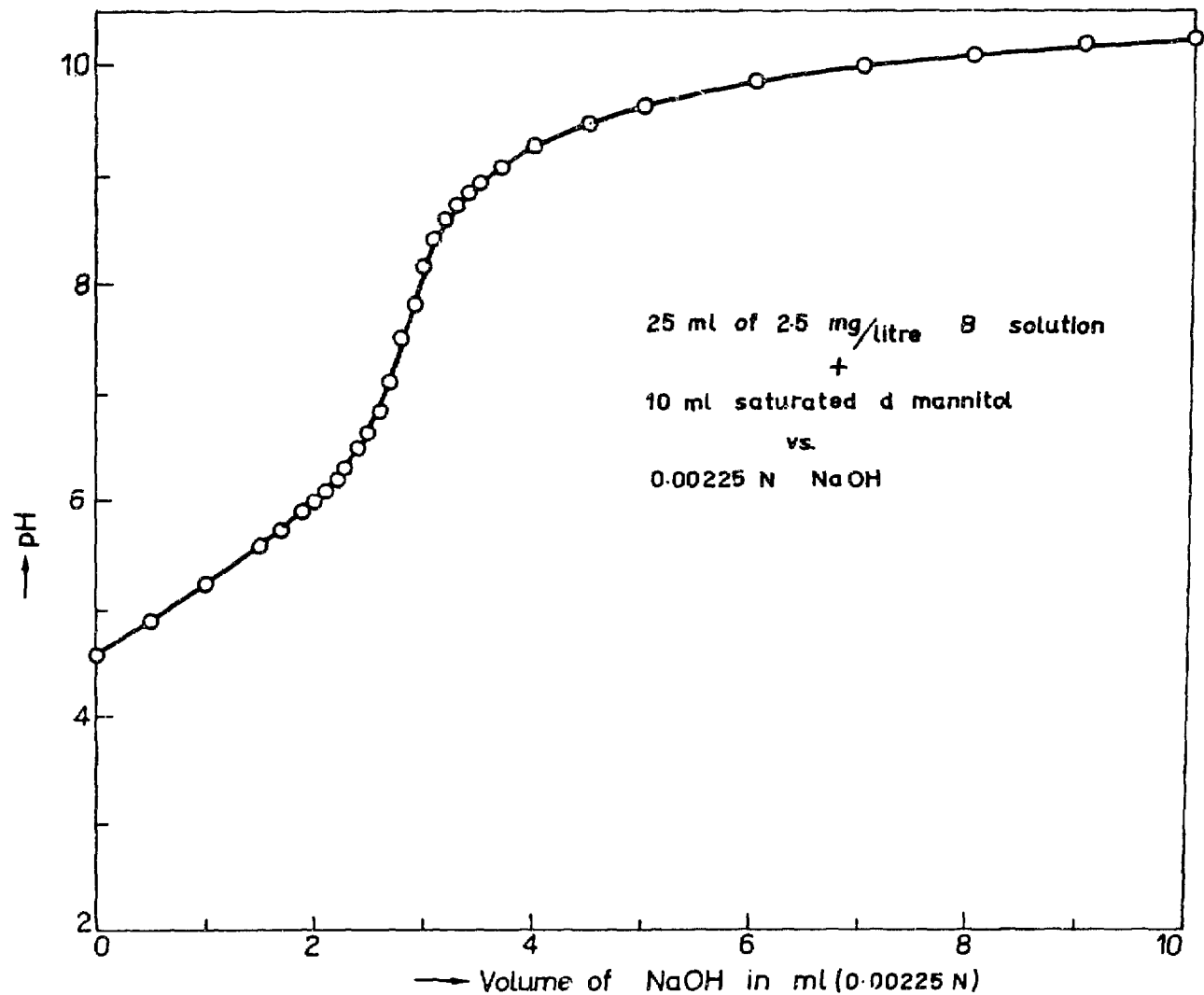


Fig 7. pH metric titration curve for determination of traces of Boric Acid.

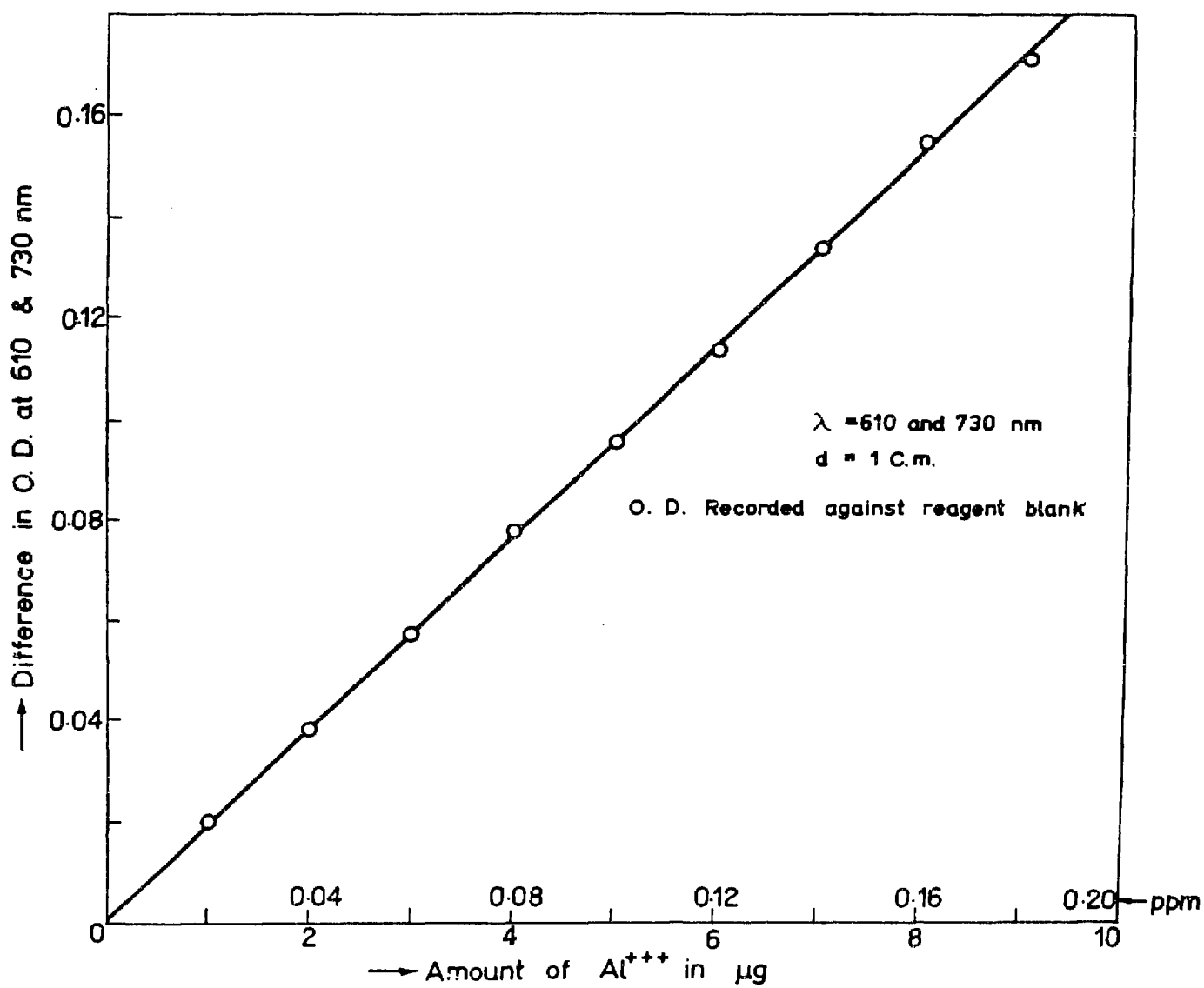


Fig. 8. Calibration curve for determination of µg amounts of Al<sup>+++</sup>

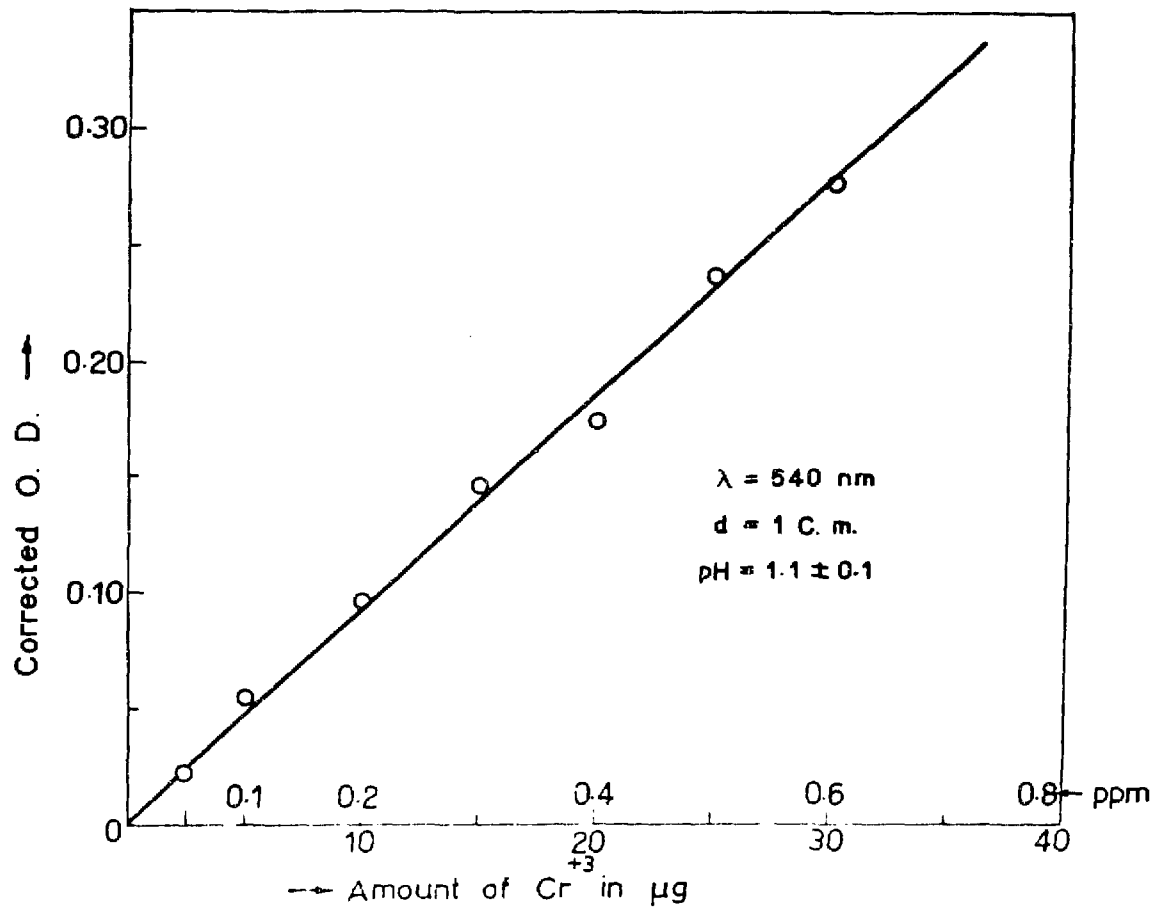


Fig. 9. Calibration curve for determination of  $\mu\text{g}$  amounts of  $\text{Cr}^{+3}$

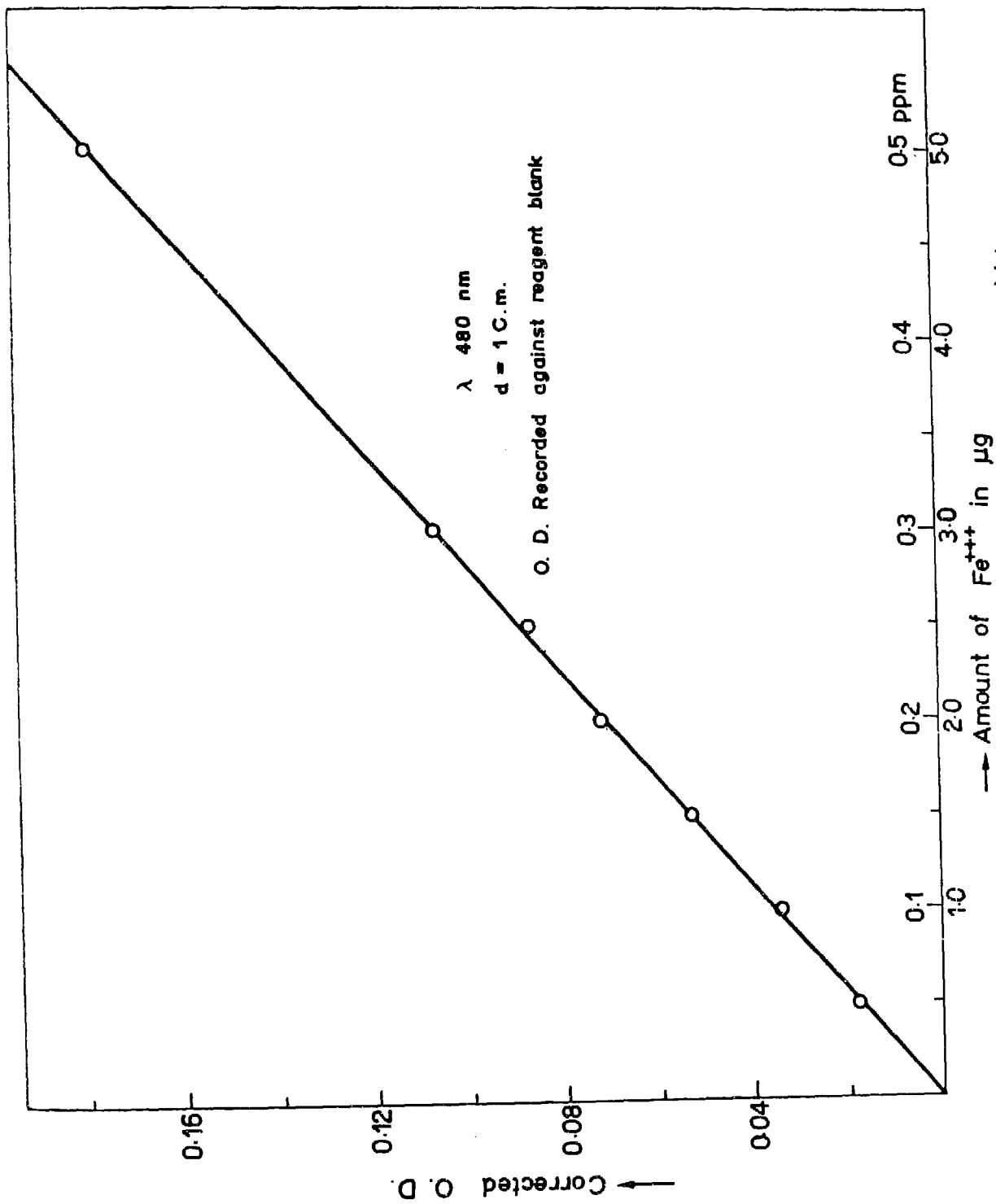


Fig. 10. Calibration curve for determination of  $\text{Fe}^{+++}$  in  $\mu\text{g}$

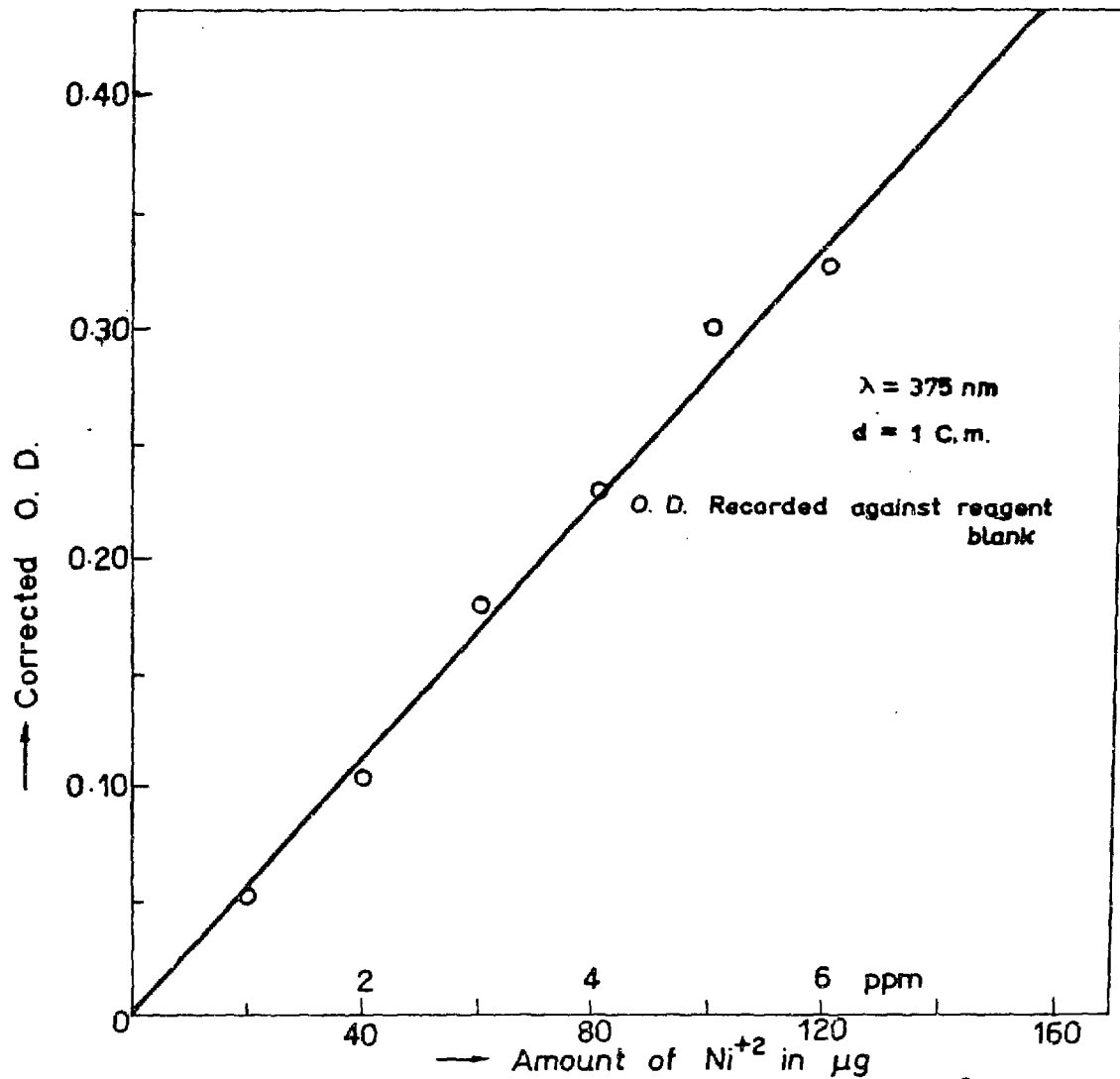


Fig. 11 Calibration curve for determination of  $\mu\text{g}$  amounts of  $\text{Ni}^{+2}$

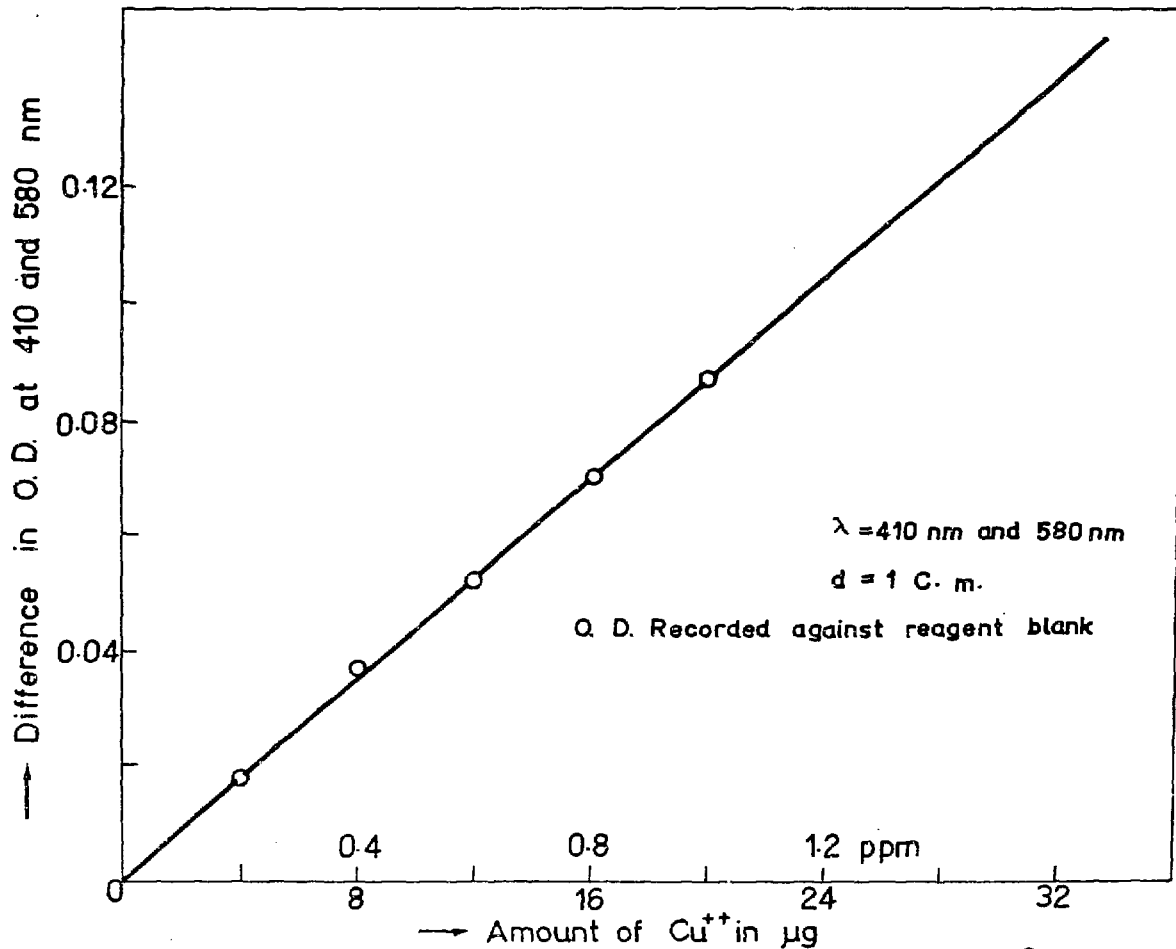


Fig. 12 Calibration curve for determination of  $\mu\text{g}$  amounts of  $\text{Cu}^{+2}$ .

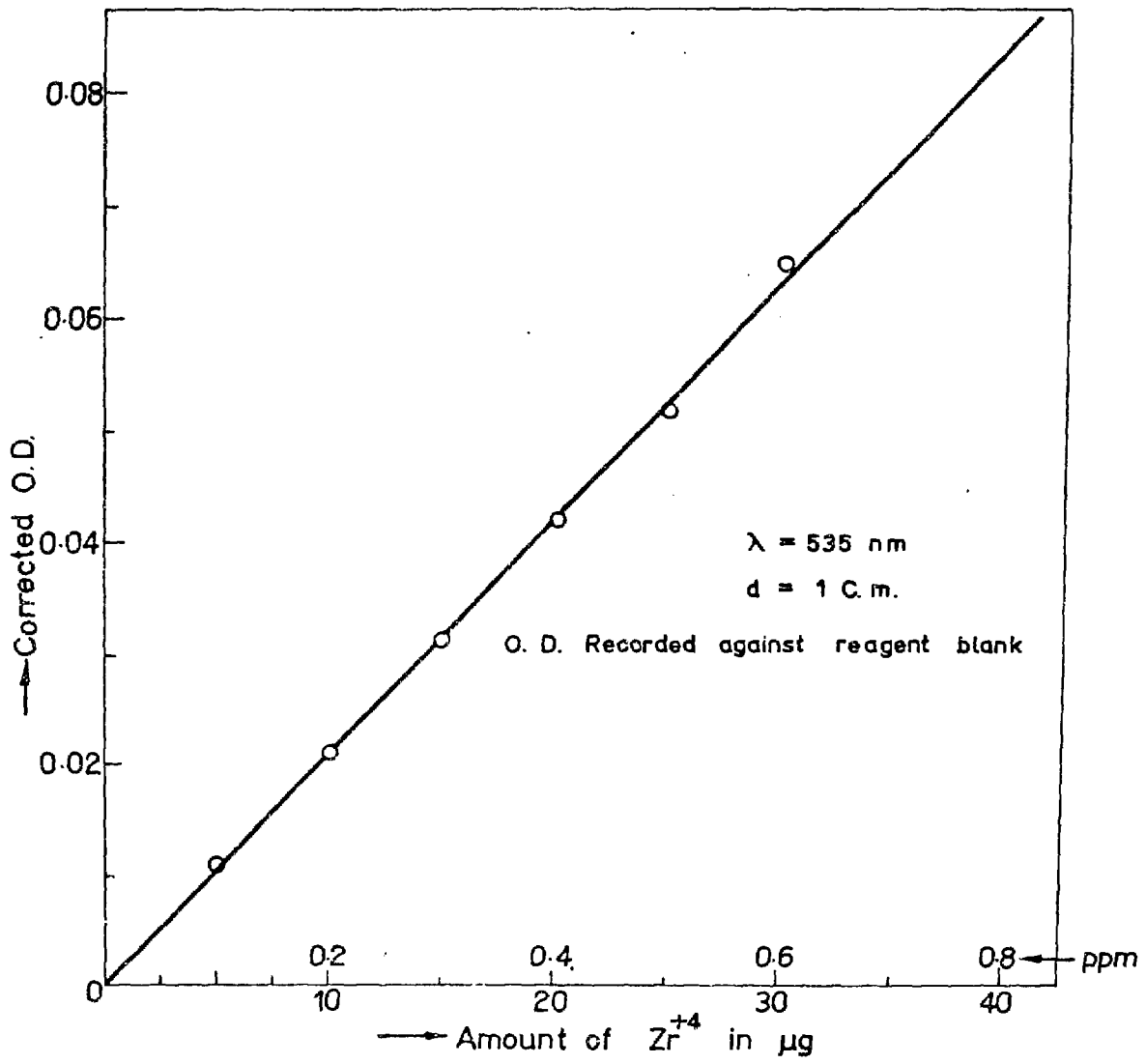


Fig. 13 Calibration curve for determination of  $\mu g$  amounts of  $Zr^{+4}$