EXPERIMENT 1

DETERMINATION OF DISSOLVED OXYGEN IN WATER

INTRODUCTION

The dissolved oxygen content is an important index when considering its suitability for town supply. A good clean potable water will give dissolved oxygen value close to the theoretical value for the saturated solution of oxygen in water. When there is pollution from organic matter and other trade effluents, the dissolved oxygen is up in various biochemical oxidation processes and its is only slowly replaced through surface absorption. Such water will give a low dissolved oxygen content until oxidation is completed. Adequate dissolved oxygen is necessary for the life of fish and other aquatic organisms.

The methods described below for the determination of oxygen in water is based on that devised by Winkler. When manganese hydroxide is precipitated in the water sample it is quickly oxidized to higher hydrated oxides (probably in the four valent state) by the dissolve oxygen. Iodine, equivalent to the dissolved oxygen content, is then liberated on acidification in the presence of iodine, and it may be titrated with standard thio-sulphate.

INTERFERENCES AND PRE – TREATMENT

Most oxidising and reducing substances e.g dissolved organic substances, nitrite ions, higher-valency manganese compounds, active chlorine, sulphide and sulphite ions, iron (II) and irons interfere.

The influence of the dissolved organic substances can be excluded by conversion of the manganese hydroxides into oxygen-sensitive carbonates by subsequent addition of 4 cm$^3$ ammonium hydrogen carbonate solution.

Nitrite in acidic solutions catalyses the liberation of iodide and can be decomposed by addition of alkaline-iodide-azide solution.

Iron (III) ions are rendered inactive during the determination by the addition of 4 cm$^3$ phosphoric acid or 2 cm$^3$ potassium fluoride solution.

EXPERIMENTAL

Collection of sample

Collect the sample in a narrow necked 200-300 cm$^3$ glass bottle having an accurately fitting ground glass stopper. If the water from a tap, pass the water down a glass tube to the bottom of the bottle and allow water to overflow for 2-3 minutes before insertion of the stopper. When sampling stream water, displace the water in the bottle several times, before collecting the sample. The
PROCEDURE for the Determination of Dissolved Oxygen in Water

Carefully remove the stopper from the sample bottle and add in turn 1 cm$^3$ manganous sulphate solution followed by 1 cm$^3$ alkaline-iodide-azide solution. When introducing various reagents into the full bottle of sample, the tips of the pipettes should be well below the surface of the liquid. Replace the stopper carefully after each addition so as to avoid inclusion of air bubbles. Thoroughly mix the contents by inversion and rotation until a clear supernatant water is obtained. Add 1 cm$^3$ concentrated sulphuric acid with the tip of the pipette below the level of solution and again replace the stopper. Mix well by rotation until the precipitate has completely dissolved.

Pipette into a 250 cm$^3$ conical flask 100 cm$^3$ of the solution and immediately titrate it against standard sodium thiosulphate (0.0125 mol dm$^{-3}$) using freshly prepared starch solution as the indicator (add when solution becomes pale yellow). Carry out the titration in duplicate.

Standardisation of Sodium Thiosulphate

Mix 5 cm$^3$ of potassium iodide solution (10% w/v) and 10 cm$^3$ of the dilute sulphuric acid (1:3 v/v) and add 2 cm$^3$ of 0.025 mol dm$^{-3}$ potassium iodate solution in that order in a glass-stoppered flask. Add about 100 cm$^3$ of distilled water. Titrate immediately with sodium thiosulphate solution until the colour is pale yellow. Add 2 or 3 drops of starch solution (freshly prepared) and continue the titration until the blue colour just disappears.

REPORT

Explain the reaction involved in the determination of dissolved oxygen in water using Winkler methods.

Establish the relationship: 10 cm$^3$ of 0.0125 mol dm$^{-3}$ sodium thiosulphate = 1 mg O$_2$.

Report the result in mg dm$^{-3}$ and as percentage saturation (refer to the table attached)

REAGENTS

Managanous sulphate solution
Dissolve 100 g managanous sulphate (MnSO$_4$. 4H$_2$O) in 200 cm$^3$ distilled water.

Alkaline-iodide-azide solution
Dissolve 100 g sodium hydroxide in 100 cm$^3$ distilled water. Allow to stand for some days, during which any carbonate present sinks to the bottom. Siphon off all of the clear liquid, add 30 g potassium iodide and 2 g sodium azide and make up to 200 cm$^3$ with distilled water. Store in plastic container.

Sodium Thiosulphate (0.0125 mol dm$^{-3}$)
Dilute 125 cm$^3$ 0.1 mol dm$^{-3}$ sodium thiosulphate to 1 liter with distilled water.

Potassium iodide solution (0.025 mol dm$^{-3}$)
Dry analytical grade potassium iodate at 120°C. Dissolve 5.35 g in distilled water and dilute to exactly 1 litre. This solution is stable for long periods if stored in a glass stopper bottle.

**Potassium iodide solution (10% W/ v)**
Dissolve 10g KI in 100 cm3 distilled water.

**Potassium fluoride solution (10% W/V)**
Dissolve 10g potassium fluoride in distilled water and make up to 100 cm3

**Ammonium hydrogen carbonate solution**
Dissolve 70g ammonium hydrogen carbonate in 185 cm3 distilled water.

**Phosphoric acid (85% V/V )**

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
<th>30</th>
<th>35</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂ content mg Kg⁻¹</td>
<td>11.2</td>
<td>10.2</td>
<td>9.1</td>
<td>8.3</td>
<td>7.6</td>
<td>7.1</td>
</tr>
</tbody>
</table>

**OXYGEN CONTENT IN AIR-SATURATED WATER**
EXPERIMENT 2
DETERMINATION OF CHEMICAL OXYGEN DEMAND OF WATER

INTRODUCTION

The chemical oxygen demand gives information on the oxygen required by a water of oxidation of almost all water-soluble organic substance, the exceptions being a number of compounds containing nitrogen and only very slightly soluble hydrocarbons.

The following method is used to determine the quantity of organic material in a sample which may be oxidised chemically. The sample is refluxed with an accurately known amount of a potassium dichromate in a large excess of sulphuric acid for definite time. Most organic substances are completely oxidised and the remaining dichromate is determined by titration with ferrous ammonium sulphate. Silver sulphate is added as a catalyst for the oxidation and mercuric sulphate is added to overcome chloride interference.

The methods has a theoretical range of 0-500 mg dm$^{-3}$ chemical oxygen demand (COD) when using a 5 cm$^3$ sample and is suitable for highly polluted water. It should be noted that if a larger sample is used organic matter may not be oxidised to the same extent by the more dilute reagents.

EXPERIMENTAL

(All apparatus should be washed in chromic acid before used and should be free of dust. The ground-glass joints should free grease).

Collection of Sample

Collect the sample in a narrow necked 200-300 cm$^3$ glass bottle having an accurately fitting ground glass stopper. When sampling stream water, displace the water in the bottle several times before collecting the sample. Avoid contamination.

Procedure for Determination of Chemical Oxygen Demand

Introduce 10.0 cm$^3$ of the water sample into 100 cm$^3$ round-bottomed flask, and add 2 cm$^3$ potassium dichromate, 2.5 cm$^3$ mercuric sulphate solution, 10-15 ml concentrated sulphuric acid containing silver sulphate, and an anti-bumping rod. Heat to gentle, but steady boiling over an electric hot plate or heating mantle and under a reflux condenser. After exactly 45 minutes boiling, allow to cool briefly, wash 20 cm$^3$ distilled water through the condenser into the flask and the cool completely in cold water. Add 2 drops of ferroin solution and titrate the excess potassium dichromate with ammonium iron (II) sulphate until the colour changes from bluish-green to reddish-brown.

Determine a blank with 10.0 cm$^3$ distilled water under exactly the same conditions.

Standardization of Ammonium Iron (II) Sulphate
Add 10 cm$^3$ concentrated sulphuric acid carefully to 20 cm$^3$ water and cool. Add 2 cm$^3$ potassium dichromate and titrate with ammonium iron(II) sulphate using drops of ferroin as indicator. The colour changes from bluish-green to reddish-brown.

**REAGENTS**

**Standard Potassium Dichromate** (K$_2$Cr$_2$O$_7$) (0.025 mol dm$^{-3}$)
Dissolve 7.3548g AR potassium dichromate in distilled water, and make up to 1 litre. Dry the potassium dichromate for two hours in a drying chamber at 105$^0$C before weighing out.

**Ammonium Iron (II) Sulphate** (NH$_4$)$_2$SO$_4$. FeSO$_4$. 6H$_2$O (0.0125 mol dm$^{-3}$)
Carefully add 20 cm$^3$ concentrated sulphuric acid to 200 cm$^3$ water, mix, and cool. Dissolve 4.902g ammonium iron(II) sulphate in the cooled acid and make up to 1 litre.

**Mercuric sulphate**
Dissolve 5 gm mercuric sulphate in a mixture of 25 cm$^3$ concentrated sulphuric acid and 225 cm$^3$ water.

**Silver Sulphate/ Sulphuric acid**
Dissolve 5g silver sulphate in 500 cm$^3$ AR concentrated sulphuric acid by mixing.

**Ferroin Indicator**
Dissolve 0.695g FeSO$_4$. 7H$_2$O in distilled water (100 cm$^3$), add 1, 10-phenanthroline monohydrate (1.485g) and shake until dissolved.
EXPERIMENT 3
COMPLEXOMETRIC TITRATION OF METALION

INTRODUCTION

The titration of metals by chelating agents (complexometric titrations) developed rapidly after the initial work by schwarzenbach about 30 years ago. The most important molecule in this field is the disodium salt of ethylenediamine-triacetic acid (EDTA). EDTA forms stable complexes with almost all metals (in a 1:1 molecular ratio) the reaction quickly proceeding near enough to completion for all practical purpose if a suitable pH is maintained.

Because of its wide applicability EDTA lacks selectivity. Control of pH by buffer solutions may sometimes be used to enable metals in mixture to be titrated individually and successfully in the same solution. Masking agents are also frequently used, for example potassium cyanide stabilises silver, cadmium, mercury, iron(II), zinc, cobalt and nickel against EDTA complex formation permitting the titration of lead, manganese and the alkaline earths in the presence. Potassium iodide likewise used in the masking of mercury in the determination of cadmium.

Bismuth forms a strong complex with EDTA which persists even in quite strong mineral acid (ph 1-3). Consequently the selectivity of determination of bismuth is quite good. The bismuth/EDTA complex is also colourless so that quite large amounts may be determined without the difficulties associated with intensity of colour.

Cadmium may be determined by EDTA titration in weakly acidic, near neutral or alkaline media.

Mercury (I) disproportionate upon reaction with EDTA Hgo and the Hg (II) EDTA complex; consequently no use has been made of Hg(I) in complexometric titration with EDTA. The mercury (II) complex is, however, very complex and can be utilized over a very great pH range. The masking action of iodide ion for Hg (II) is virtually specific in EDTA titrimetry.

Lead may be titrated with EDTA over several pH ranges using a variety of indicators. In acidic media (pH 4-6), xylene orange is suitable indicator.

Bismuth and lead may be determined together in one solution using the same indicator. The bismuth is first determined at pH 1-2, then lead at pH 5-6 using xylene orange as indicator each time.

Cadmium and mercury are determined together with EDTA solution and eriochrome black T as indicator. Potassium iodide is added to the titrated solution. In this, the mercury chelate is converted into potassium mercury iodide, liberating EDTA. The liberating EDTA may be titrated with standard zinc solution.
EXPERIMENTAL

Standardisation of EDTA

Weight out accurately about 0.15 g of zinc metal (“granulated zinc”), and dissolve in a few drops of 1:1 nitric acid. Rinse the watch glass and the resulting solution quantitatively into 250 cm\(^3\) standard flask, make up to the mark with distilled water and mix well.

Measure out 25 cm\(^3\) of the about zinc solution and dilute to about 100 cm\(^3\) flask, add 1 or 2 drops of xylenol orange indicator solution and dilute to about 100 cm\(^3\) with distilled water. Add hexamine solution (10% w/v) until the colour become red-purple, and add 1 – 2 cm\(^3\) more. Titrate the solution with EDTA. At the end point colour changes to a yellow-orange

Carry out the standardisation in triplicate and calculate the molarity of the EDTA solution.

PROCEDURE for Determination of Bismuth and Lead

Pipette 10 cm\(^3\) of sample solution into a 250 cm\(^3\) conical flask. Add 1 or 2 drops xylenol orange indicator solution and dilute to about 100 cm\(^3\) with distilled water. Titrate with standard EDTA solution until the colour changes from red-purple to clear orange-yellow.

Add hexamine solution (10% w/v) until the colour becomes red-purple, add 1-2 cm\(^3\) more. Continue the titration with standard EDTA solution until a clear orange yellow colour is obtain again.

Carry out the determination in triplicate and the calculation of concentrations of the metal ions in g dm\(^{-3}\).

PROCEDURE for Determination of Cadmium and Mercury

Pipette 10 cm\(^3\) of sample solution into 250 cm\(^3\) conical flask. Add the accurately measured excess of standard EDTA solution (35 cm\(^3\) will be sufficient in this case). After about 5 minutes, add 5 cm\(^3\) of ammonia-ammonia chloride buffer (pH 10) and some solochrome black T/KCl indicator mixture. Back titrate the excess EDTA solution with standard zinc solution (from the EDTA standardization) until the colour changes via blue to purple.

Add 1-2 g of potassium iodide to the titrated sample. Titrate the liberated EDTA with the standard zinc solution into the pink-red colour is obtained again.

Carry out the determination in triplicate and calculate the concentrations of the mental ions in g dm\(^{-3}\).

REPORT

Explain the reactions involved using equations and a consideration of the stability contents. Report the concentration of the metal ions in the mixtures in g dm\(^{-3}\).
REAGENTS

**Ethlyenediamintetraacetic Acid** (approx. 0.01 mol dm\(^{-3}\))
Dissolve 3.72 g of ethylene diamine tetra-acetic acid in a volumetric flaks in distilled water and make up to volume of 1 litre.

**Xylenol orange Indicator** (0.1% w/v)
Dissolve 0.1 xylenol orange in 100 cm\(^3\) distilled water.

**Solochrome Black T/KCl Indicator mixture**
Mix 1 part of solochrome black T with 99 part of potassium chloride (by weight) and store in bottle.

**Hexamine solution** (10% w/v)

**Ammonia-Ammonia Chloride solution** (pH 10 buffer solution)
Dissolve 54 g ammonium chloride in about 200 cm\(^3\) distilled water. Add 350 cm\(^3\) ammonia solution (0.89) and make up to 1 litre with distilled water.

QUESTIONS

1) Why should heating assist an EDTA reaction?
2) Would you expect positive or negative errors in the determination of Cd and Hg (or no error)? If so, why?
3) What would happen in a titration of metal M with EDTA with indicator H\(_{In}\) in the presence of a metal ion N that formed an indicator complex N\(_{In}\) that was more stable than the complex N\(_{Y}\) and the complex M\(_{In}\).
4) The formation contents for Bi-EDTA are \(1 \times 10^{23}\) and \(1.1 \times 10^{18}\) respectively. In a mixture of bismuth and lead ion (0.02 mol dm\(^{-3}\) for both ions) predict the pH at which each of the mental ion can be determined quantitatively using EDTA titrations. (Attempt this question before you start the experiment)

REFERENCE

3) T.S West, “Complexometry with EDTA and related Reagents”, 3\(^{rd}\) Ed., BDH Chemicals Ltd, Poole, 1969
EXPERIMENT 4

ABSORPTIOMETRIC (UV) ANALYSIS OF APC TABLETS

INTRODUCTIONS

The APC tablet is a common pharmaceutical preparation consisting of a mixture of aspirin, phenacetin, and caffeine. A common size APC tablet contains 3.5 grains aspirin, 2.5 grains phenacetin, and 0.5 grain caffeine, plus perhaps a small amount of starch or other inert material as binder. (1 grain is approximately 65 mg). Each of these substances has characteristic absorption in the ultraviolet, the principle maxima lying at 277 nm for aspirin, 275 nm for caffeine and 250 nm for phenacetin (all chloroform solution).

The method of analysis calls for the partition of the dissolved sample between chloroform and 4 per cent aqueous sodium bicarbonate, the aspirin alone passed into the aqueous layer. The phenacetin and caffeine are analyzed simultaneously in chloroform. The aspirin solution is acidified, extracted back into chloroform and determined spectrophotometrically.

EXPERIMENTAL

Grind one pre-weighed APC tablet into fine powder. Weigh accurately 0.10 g of the finely grinded tablet into a 100 cm³ beaker and add 20 cm³ of chloroform. Transfer the contents quantitatively into a 125 cm³ separatory funnel, rinsing the beaker with a little more chloroform if necessary.

Extract the chloroform solution with two 15-cm³ portions of chilled 4.0 per cent sodium bicarbonate solution and then with one 10-cm³ portion of chloroform. Wash the combined aqueous extracts with two 10-cm³ portions of chloroform extracts to the original chloroform solution. Filter the chloroform solution through a filter paper (to remove traces of water) previously wetted with chloroform into a 50-cm³ volumetric flask and dilute to the mark with chloroform. Further dilute 1-cm³ aliquot with chloroform.

Acidify the aqueous extract immediately (to prevent hydrolysis of the aspirin), still in the separatory funnel, with 10-cm³ of 1 mol dm⁻³ sulphuric acid. The acid must be added slowly in small portions. Allow complete evolution of carbon dioxide. Mix well by repeated inversion. The pH of the solution should be between 1 to 2 (pH test paper). Extract the acidified solution with four 10-cm³ portion of chloroform, and filter the chloroform extracts through a chloroform-wetted filter paper into 50-cm³ volumetric flask. Dilute to volume, and further dilute 1-cm³ aliquot to 25-cm³ with chloroform.

Standard solutions in chloroform, containing respectively about 75 mg aspirin, 10 mg of phenacetin, and 10 mg of caffeine per litre are provided.
Measure the absorbance of standard and unknown aspirin solution at 277 nm in 1cm silica cuverts. Correct for optical inequalities in the cuverts by interchanging the blank and solution in each case and averaging the results.

With similar precautions, measure the absorbance of standards and unknown containing phenacetin and caffeine at both 250 nm and 275 nm.

**REPORT**

Calculate the quantity of aspirin by direct application of Beer’s law, and of phenacetin and caffeine by mean of simultaneous equations. Report the results in terms of milligrams of each constituent per table and also as a percentage of the total weight.

**REAGENTS**

Spectro-grade chloroform
Used chloroform solutions should be returned a bottle, designated for the purpose (for the recovery of solvent).

Sodium bicarbonate solution (4% w/v)
Dissolve 4.0 g sodium bicarbonate in 100 cm³ distilled water. Add a few drops concentrated hydrochloric acid to each litre of solution.

Sulphuric acid (1.0 mol dm⁻³)
EXPERIMENTS 5
SPECTROPHOTOMETRIC DETERMINATION OF MANGANESE IN STEEL

INTRODUCTION

Plain carbon steel contains a certain amount of carbon, silicon, sulphur, phosphorus and manganese. For special purpose, varying amount of other elements such as chromium, vanadium, molybdenum, tungsten, titanium, nickel, cobalt, zirconium and copper are added. The physical properties of steel depend highly on the content of these elements. Thus, the quantitative analysis of these elements is of great practical importance.

In this experiments, manganese is determined spectrophotometrically as the purple coloured permanganate ion, MnO₄⁻. This is commonly used and accurate method of determining the low concentrations of manganese in steel. The steel is dissolved in nitric acid to give a solution of manganese (II) ions. The periodate ion, added as the potassium salt, KIO₄, readily oxidizes manganese (II) to permanganate according to the equation

\[ 2\text{Mn}^{2+} + 5\text{IO}_4^- + 3\text{H}_2\text{O} = 2\text{MnO}_4^- + 5\text{IO}_3^- + 6\text{H}^+ \]

The calibration curve is determined by measuring the absorbance of a series of standardised permanganate solution prepared. The permanganate can be accurately standardised using a primary standard, sodium oxalate. The Oxalate anion, C₂O₄²⁻, reduce permanganate to manganese (II) in acid solution at 60-70°C according to the equation

\[ 2\text{MnO}_4^- + 5\text{C}_2\text{O}_4^{2-} + 16\text{H}^+ = 2\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O} \]

EXPERIMENTAL

Standardisation of Permanganate with Oxalate

An approximately 1.000 g Mn dm⁻³ solution will be supplied. Standardise this solution with oxalate solution as follows; weigh out accurately about 1.6 g of sodium oxalate and make up to 250 cm³ in standard flaks. Acidify a 25 cm³ aliquot with 5 cm³ of 5mol dm⁻³ sulphuric acid, warm the mixture to 60-70 °C and titrate with potassium permanganate until a faint pink coloration which persists for at least 30 seconds. From the mean of three concordant titrations calculate the concentration of the potassium permanganate solution.

Determination of the Calibration curve
Accurately dilute the standard potassium permanganate solution and prepare a series of five standards so as to give an absorbance range between 0.1 to 0.9. Measure the absorbance of these five solutions using a spectrophotometer set at 525 nm. Use water as reference solution.

PROCEDURE for the Calibration curve

Accurately weigh out duplicate sample (approx. 0.2 g) of the steel sample provided into 150 cm$^3$ beakers.

Cover the beaker with watch glass; add 30 cm$^3$ of 1:1 nitric acid. Warm to dissolve the alloy (add further nitric acid if necessary) and then heat to gentle boiling for a few minutes to expel oxides of nitrogen. Cautiously add about 1 g of ammonium peroxysulphate and boil for 10 – 15 minutes. If the solution is pink or contains brown oxide of manganese, add about 10 0.1 g of sodium bisulphate and heat for further 5 minutes. Cool, rinse down the watch glass and transfer the solution quantitatively to a 100 cm$^3$ volumetric flask and dilute to the mark with distilled water. Make up to the mark and mix well.

Pipette two 25-cm$^3$ aliquots of the sample solution into small beakers, add 5 cm$^3$ of phosphoric acid. To one of the two aliquots add 0.5 g of KIO$_4$ and boil the solution for 5 minutes. The second aliquot is not treated with periodate and will serve as the blank. Cool to room temperature, transfer each aliquot quantitatively to a 50-cm$^3$ volumetric flask and dilute to the mark with distilled water.

Measure the absorbance of the solution and the blank using distilled water as the reference solution.

REPORTS

Prepare a calibration curve from the data obtained by plotting absorbance versus concentration.

From the measured absorbance values of the unknown sample duplicates, determine the concentration of MnO$_4^-$ from the calibration curve after making correction due to sample blank.

Express the final result as percentage of manganese in steel turnings.

REAGENTS

Potassium Permanganate Solution (1.00 g Mn dm$^3$)
Dissolve 2.877 g potassium permanganate in 1 liter of distilled water.

Sulphuric Acid (5 mol dm$^{-3}$)
QUESTIONS

1) What is the purpose of using the following chemicals in this experiment? Brief discuss them with the chemical reaction involved.
   a) Nitric acid
   b) Bisulphite
   c) Phosphoric acid
   d) Peroxydisulphate

2) Could water be used as a blank in the measurement of the absorbance of the standard solutions?

3) “The measurement of the absorbance due to the sample blank is essential”
   Comment on the above statement.
EXPERIMENT 6
DETERMINATION OF PHOSPHATE IN WATER

INTRODUCTION

Phosphates which are added to boiler feed to prevent scaling may be analysed by a variety of methods but normally these determine only the orthophosphate. Pyrophosphate is readily converted to orthophosphate by boiling in acidic solution but metaphosphate requires about 20 minutes boiling in 10% sulphuric acid to get satisfactory conversion to orthophosphate. Calgon or sodium hexametaphosphate which is frequently used is normally hydrolysed in the boiler but hydrolysis by boiling in acidic solution may be necessary particularly if the sample is removed soon after the addition of calgon.

The method described here consists of adding ammonium molybdate to an acid solution of the phosphate. The ammonium phosphomolybdate formed is then reduced to the blue colored lower oxidation state molybdenum compound by reaction with ascorbic acid at 100 °C. The resulting colors are compared with a series of standards prepared from phosphate solution of know concentration in a colorimeter or spectrometer.

EXPERIMENTAL

Preparation of Calibration Curves

Prepare a series of standard solution by measuring the appropriate volume of P2O5 stock solution (10 mg dm\(^{-3}\)) as listed in table 1 into each of a series of 100 cm\(^3\) beakers and dilute each sample to about 40 cm\(^3\). Add to each solution 4.0 cm\(^3\) ammonium molybdate-sulphuric acid reagent, mix, and then add 0.1 g ascorbic acid. Cover with a watch glass, heat to boiling, boil for 1 minute, cool quickly, and transfer the solution quantitatively into a 50 cm\(^3\) volumetric flasks using distilled water to complete the transfer. Dilute to the 50 cm\(^3\) mark and mix well.

Measure the optical densities (or absorbance) of the blank and standard solution at 810 nm.

TABLE 1
### Solution No. | Volume of P2O5 stock solution used, cm³ | Concentration mg dm⁻³ P2O5
---|---|---
1 | 1 | 0.2
2 | 2 | 0.4
3 | 3 | 0.6
4 | 4 | 0.8
5 | 5 | 1.0
6 | 10 | 2.0

**PROCEDURE – Analysis of Boiler Water Samples**

Filter the test sample through a fine filter paper. Sludge in the test solution may contain phosphate and give rise to incorrect phosphate values.

Measure 20 cm³ of the sample into a 100 cm³ beaker, neutralise the solution with 0.5 mol dm⁻³ sulphuric acid and dilute to about 40 cm³. Add ammonium molybdate-sulphuric acid reagent, ascorbic acid, and treat in the same manner samples used in the preparation of the calibration curve. Measure the optical density.

Where the sample is in the form of hexametaphosphate, neutralize the 20 cm³ sample with 0.5 mol dm⁻³ sulphuric acid 1 cm³ conc. Hydrochloric acid and evaporate just to dryness. Then dilute to 40 cm³ and proceed as before.

**Report**

Calculate the concentration of P2O5 in the test sample. Explain the reactions involved using chemical equations.

**REAGENTS**

**Ammonium Molybdate-sulphuric Acid**
Dissolve 10 g ammonium molybdate in distilled water and dilute to 100 cm³. Carefully add this solution to a cold mixture of concentrated sulphuric acid (150 cm³) and water (150 cm³). Protect the solution from light in a plastic bottle.

**Ascorbic Acids**
As required dissolve 1 g ascorbic acid in 10 cm³ distilled water. Add 1 cm³ of this solution for 0.1 ascorbic acid.

**Stock Phosphate Solution**
Dissolve 0.7669 g of potassium dihydrogen orthophosphate in distilled water and dilute to 1 liter.

**Standard Phosphate Solution (10 mg dm⁻³ P₂O₅)**
Dilute 25 cm³ of the above stock solution to 1 liter with distilled water.
EXPERIMENT 7
ANALYSIS OF TRACE METALS BY FLAME EMISSION AND ATOMIC ABSORPTION SPECTROPHOTOMETRY

INTRODUCTION

This experiment is designed to acquaint student with the techniques of atomic emission and absorption spectroscopy for the analysis of metals. The use of a multipurpose emission-absorption instrument is illustrated for the determination of the sodium by emission and magnesium by absorption. The effect of ionization interference on the determination of sodium and chemical interference on the estimation of magnesium are investigated.

EXPERIMENTAL

PROCEDURE for Emission Analysis of Sodium Ion

Using either a burette or pipette, make up in 50 cm³ volumetric flask the solutions listed in table 1.

**TABLE 1**

<table>
<thead>
<tr>
<th>Solution No</th>
<th>Na⁺</th>
<th>K⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
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<tr>
<td>2</td>
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<td>7</td>
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</tr>
<tr>
<td>11</td>
<td>50</td>
<td>200</td>
</tr>
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</table>

Turn the instrument on, ignite the flame, and allow the instrument to warm up for about 10-15 minutes. Set the instrument accordingly to instructions given in the operation manual. Set the monochromator at 589.0 wavelength and set emission to 100% with the 50 mg dm⁻³ Na solution and 0% with distilled water. Measure the emission intensities of solution 1-11, rising the burner between measurements by aspirating distilled water.

Tab water and unknown Na samples were aspirated likewise. Also, tab water and unknown sodium samples with added potassium (2000 mg dm⁻³) were determined for
the sodium contents. The tap water and unknown Na sample solution should be diluted by 5 times.

REPORT

Plot the emission intensity versus concentration of sodium ion from the experimental data.

Calculate the sodium ion concentration in the tap water and unknown sodium samples in the mg dm$^{-3}$.

Compare the date obtained with and without the added potassium. Compare the results.

PROCEDURE for Absorption Analysis of Megnessium Ion

Using either a pipette or burette, make up in 50 cm$^3$ volumetric flask the solution listed in the table 2. Use MgSO$_4$, stock solution, and 0.5 mol dm$^{-3}$ hydrochloric acid for dilution.

TABLE 2

<table>
<thead>
<tr>
<th>Solution No</th>
<th>Mg$^{2+}$</th>
<th>La$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>0.5</td>
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</tr>
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<td>1.0</td>
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</tr>
<tr>
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</table>

Optimize the instrument conditions according to the operation manual. Set the monochromator at the 285.2 nm wavelength and set the zero absorption by aspirating 0.5 mol dm$^{-3}$ hydrochloric acid info flame. Using solution no 5 (2 mg dm$^{-3}$) adjust by
rotating the burner head so as to get an absorbance of about 0.8 only. Measure the absorbance of this solution 1-11, rinsing the burner between measurements by aspirating 0.5 mol dm$^{-3}$ hydrochloric acid.

Dissolve about 0.1 g (accurately weighted) of the cement sample in 10 cm$^3$ concentrated hydrochloric acid and dilute 250 cm$^3$ in a volumetric flask. Further dilution may be necessary in order that the absorbance is within the range of the calibration curve.

Water sample and cement sample solution with and without added lanthanum are aspirated in order to determine the magnesium concentrations. The Mg solution should only be diluted 5 times in both cases.

**REPORT**

Plot the absorbance versus concentration in the tap water and cement sample by comparison with calibration curve. Express magnesium as percentage MgO in the cement sample.

Compare the results obtained with and without added lanthanum ion.

**REAGENTS**

**Sodium Stock Solution** (1000 mg dm$^{-3}$)
Dissolve 2.543 g AR sodium chloride in 1 liter of distilled water.

**Potassium Stock Solution** (5000 mg dm$^{-3}$)
Dissolve 9.534 g potassium chloride in 1 liter distilled water.

**Magnesium stock Solution** (500 mg dm$^{-3}$)
Dissolve 5.069 g MgSO$_4$.7H$_2$O (or the equivalent for other hydrate) in 0.5 mol dm$^{-3}$ hydrochloric acid, and make up to 1 liter.

**Lanthanum Stock solution** (5000 mg dm$^{-3}$)
Dissolve 11.700 g La(NO$_3$)$_3$ in 0.5 mol dm$^{-3}$ hydrochloric acid and dilute to 1 liter.

**Hydrochloric Acid** (0.5 mol dm$^{-3}$)
QUESTIONS

1) Why is flame emission a more sensitive technique for some cations, mainly the alkaline and earth alkali cations, while atomic absorption has greater sensitivity for other cations, such as the transaction metal ions?

2) What difficulties would you anticipate in the analysis of the mixture of Na⁺ and K⁺?

3) Explain why ASS is so selective, i.e. why do other elements not usually interfere in the analysis?

4) Why does the deviation from linearity of absorption versus concentration increase with increasing concentration?
EXPERIMENT 8
SOLVENT EXTRACTION OF COPPER (II) COMPLEX

INTRODUCTION

A typical separation of metal ions by solvent extraction consists of extracting one of the metal ions from aqueous solution into an organic solvent. Conditions must be found which will permit quantitative transfer of the metal ion from an aqueous to the organic phase and which will avoid transfer of appreciable amounts of the other metal ions present. A useful way of characterizing the degree of transfer of a metal ion is to determine the distribution coefficient, $D_m$.

This experiment involves the determination of $D_m$ for the extraction of Cu (II) with 8-hydrochloric acid into chloroform. The effect of pH on the extraction process is investigated and the value of $y$ (the number of ligands bonded to the mental ). pH1/2 (the pH at which 50% of metal is extracted ) and the completeness of the extraction process are evaluated.

EXPERIMENTAL

1) Pipette exactly 1.0 cm$^3$ of standard Cu (II) solution to 125 cm$^3$ separatory funnel. Add 49 cm$^3$ (use measuring cylinder) of distilled water and about 25 drops of 1 mol dm$^{-3}$ HCl. Then add 1.0 cm$^3$ of 0.10 mol dm$^{-3}$ 8-hydroxyquinoline solution and 19.0 cm$^3$ of pure chloroform. Stopper the funnel, grasp it by the stopper and stopcock, and shake (avoid vigorous shaking! ) for about 2 minutes by tilting the funnel. Allowed the funnel to stand for a few minutes and repeat the 2-minutes shaking for a further four times. Now allow the layers to separate and become clear. Carefully drain off the chloroform layer through a piece of cotton wool ( or filter paper ) barely moistened with chloroform directly into glass cells and measure the optical intensity of the extract at 450 nm using Unicam SP 600 spectrophotometer. As reagent blank use 1.0 cm$^3$ of (0.1 mol dm$^{-3}$ 8-hydroxyquinoline in chloroform) diluted to 20 cm$^3$.

Carefully pour the aqueous layer into a 50 cm$^3$ beaker and measure the pH of the solution accurately using a pH meter.

2) Repeat step 1 with 23, 20, 17, 14, 11, 8, 5 and 0 drop of 0.1 mol dm$^{-3}$ HCl

3) The optical density data obtained can be converted to amount of Cu (II) present in the chloroform phase by just reading it from a given calibration curve previously prepared.

REPORT

1) Calculate the amount of copper (II) in the organic and aqueous phases and then calculate the distribution coefficient, $D_m$, for each extraction. Plot $D_m$ against pH determine the number of ligands that react with each Cu (II) metal ion.

2) Calculate the percentage of extraction (%E) from the data obtained.

3) Determine pH1/2 value for Cu (II) 8-hydroquinolate complex.

REAGENTS

Hydrochloric Acid (1.0 mol dm$^{-3}$)
Standard Copper Sulphate Solution (0.5 mg cm-3 Cu (II))
Dissolved 3.932 g CuS04.5H20 in 2 litre of distilled water

8-hydroxyquinoline Solution (0.1 mol dm-3)
Dissolve 1.452 g of salt in chloroform and make 100 cm3

QUESTIONS

1) Why do you drain the extract through a piece of cotton wool (or filter paper)?
2) Suggest another methods of obtaining the value of Dm.
3) Using chemical equation, explain the reaction (s) involved in the extraction of Cu(II). Draw the structure of the copper-hydroxyquinolinate complex.
EXPERIMENT 9
DETERMINATION OF FLUORIDE USING SPECIFIC ION ELECTRODE

INTRODUCTION

A conventional glass electrode used in the measurement of pH develops electrical potential in response to the activity of the hydrogen ion in a solution. A specific ion electrode is designed to develop a potential in response to the activity of the ion for which it is selective. In dilute solution the activity of an ion approaches concentration and thus such electrodes are useful for determining the concentration of ion under these conditions. This is particularly so when electrode response is compared with a calibration graph using solution of known concentration. The specific ion electrode may also be used as indicator electrode to detect the end point of a titration. A wide range specific ion electrode is now available. These include electrodes specific for bromide, cadmium, chloride, cupric, cyanide, fluoride, iodide, lead, nitrate and sodium ions.

The sensing element in the electrode is a specially treated crystal of lanthanum fluoride, but the electrode must be used in conjunction with a reference electrode such as calomel electrode. The reference electrode may be separate but the fluoride electrode is available as a combination electrode with the reference built into the electrode. The relationship between ion activity and electrode potential is logarithmic.

\[
RT \quad E = EA - 2.3 \log \text{af} \quad (Ea \text{ is a constant})
\]

Where af- is the activity of the fluoride ion in the sample solution. When sensing an anion the electrode potential becomes more negative with increasing ionic activity. At 25°C the electrode potential changes by 59.1 mv for a tenfold change in ionic activity if the ion being measured is monovalent. The lower limit of detection is determination by the solubility of the electrode sensing element.