Section : 1

INTRODUCTION

Most of the method s employed in the analysis of water are those Approved by the American public health Association, the Institution of water Engineers and British specification.

At the outset, it is important to note that care has to be Tekken in Analyzing water samples as usually these amount to only 500 ml, And it is not always convenient to take a further sample should there Be excessive wastage of the sample in carrying out determination.

Additionally, conditions frequently change between times of sampling and if a survey at a plant has been carried out, then it is normal that the raw, feed, boiler water and possibly condensate will be examined. These may vary from any given hour.

For cooling systems, raw, treated and tow3er or plant water should be examined, reference should be made to section 4 & 5 of the Current servicing standers when deciding on a sample program.

An example of the current sample detail form is appended and should Accompany every sample. It should be noted that some determinants e.g.: pH, alkalinity, nitrite sulphite, chlorine and suspended solids change in an unpredictable way after sampling and either preservation Or site testes are to be preferred For these parameters.

Also sampling refer to servicing standards and sample detail form it is generally recommended that results of chemical analysis are reported wherever possible in terms of milligrams per litre (mg /1) .

Examine the sample detail form in conjunction with table 1 and determine which test are necessary ; pH, alkalinity, nitrite, sulphite,chlorine etc may change once the sample has been opened. Therefore do these tests first.

Treatment reserves can often be determined on more than one component of the treatment . Reserves determined on different components will not necessarily agree , due, e.g. To preferential absorption or precipitation.

METHODS OF TESTING

1: Appearance

1:1 Colour and Turbidity

It is general to describe the appearance of the sample in such terms as clear, colour less , turbid,

Together with the colour of the water . the turbidity of the sample may be described by one of The following terms : clear , hazy, turbid, opaque

Additionally, on occasions the colour may be determined by use of the haze Disc , in conjunct With the lovibond nessleriser. This value is reported as colour – haze units- see the Nester hand Book for further details.

1:2 Odor

The other physical observation that may be made is odor. For this test it is essential that the sample Should have been collected and contained in a clean, odorless, bottle. Upon removing the cap from The sample odor of the air immediately above should be noted . In order to describe the odour its Intensity , it is preferable to refer to some of the following well-known characteristic odorous:

Earthy , musty , tarry , fishy , greasy, moldy, hydrogen subside decaying vegetation, foul Sewerage , peaty or oily.

If the sample container is non standard and probably contaminated the odor should be noted Suggest possible causes of contamination the odor should be noted to suggest possible of Contamination or anomalous results.

01:3 Suspended Matter

An estimation of suspended matter is the normal procedure and it should be as follows :

No Of PARTICLES	DESCRIPTION	ABBREVITION
0	No visible suspended matter	NV
Up to 3	Trace	T
Covers up to half Bottom of bottle	A little	
Covers bottom of Bottle	A lot	
Greater than a Quarter inch depth	Estimated % volume Suspended solids	% V

DETERMINATION OF SUSPENDED SOLIDS

Introduction

The amount of suspended solids in solution may be determined either:-

A: determining total solids by evaporation and the total dissolved solids also by evaporation and subtracting to obtain solids in suspension.

Or

B: Filtering off the suspended solids and weighing the amount of material obtained. The latter is the more normal approach. . the solids can be filtered off on glass micro fibber filter papers or a membrane filter. (weight losses on ordinary filter papers are too large for sensible results to be obtained, as the blank can often be greater than the suspended solids being determined) .

METHOD : Filtration With Glass Papers Or Membrane Filters

Take 2 glasses filters or membrane filters and weigh. Take the blank paper added water to wet and put aside to dry and use as blank.

Through the other paper filter a suitable aliquot under vacuum of sample taking care to wash out from the measuring receptacle any remnants of suspended solids.

Dry at 60^{o} c to constant weight.

Unless the suspended solids are low e.g.: less than 5 mg/1, a single membrane filter can be used as experience has shown that losses are less than 2mg on a membrane filter .

CALCULATION

Mg/1suspended solids = increase in weight mg X 1000 / Volume taken ml

ANALYTICAL NOTE :

1: If the suspended solids are low visible take the whole sample available .

2: If the suspended solids are high 50 – 200ml is an adequate aliquot .

3: PH

This is normally determined by use of the pH meter. The meter should be standardized normally once per day against standard buffer solution at a pH of 7 and 9. Care should be taken in ensuring that the electrodes are well washed between each determination, and particularly after buffering of the meter, or measurement of a solution with a high or low pH value.

When measuring the pH value of low conductivity waters e.g. : condensate or demineralised water several successive aliquots should be measured until the measured values differ by no more than ± 0.1 pH units.

Report pH value to nearest 0.1 unit unless there are special circumstances .

4: ELECTRICAL CONDUCTIVITY /TDS

For conductivity direct reading is obtained on the conductivity meter in micro siemens/cm at 20^{0-c} but boiler water TDS, due to the high conductance of hydroxyl 1 ion, the water must be neutralized with acetic acid to the phenolphthalein and point.

$$\text{TDS} = \text{conductivity } (\mu s/cm) \times 0.7$$

After each determination IT IS ESSWENTIAL that the electrode is flushed completely clear with distilled water and check conductivity for distilled water of approximately 2 micromhos should be obtained.

5: FREE CARBON DIOXIDE

In natural waters part of the total carbon dioxide content is combined in the form of salts such as calcium, magnesium, sodium carbonates or bicarbonates, and this is normally determined in the total alkalinity of the water. The presence of carbon dioxide in excess of this, though not directly concerned with the formation of the carbonates and bicarbonates, is termed the free carbon dioxide. Water may consequently lose or gain free carbon dioxide when in contact with the air for this reason these determination should be carried on site, or as soon as the sample bottle is opened, upon receipt. Results bottles with a marked ullag have no significant value.

METHOD

Take 25 mls of sample in a white porcelain evaporating basin and titrate with 0.01M sodium carbonate solution , using phenolphthalein as the indicator. The titration should take place dropwise and gentle agitation of the sample should take place to assist mixing. A distinct pink colour which persists for one minute marks the end point .

CALCULATION OF RESULTS

$$\text{Free carbon dioxide} = \text{ml } \frac{Na_2CO_3 \times 1000}{\text{Ml of sample}} \qquad \text{mg/1 as } CaCO_3$$

$$\text{PPM } CaCO_3 \times 0.44 = \text{PPM as } CO_2$$

ANALYTICAL NOTE

If a very high titre is observed it is essential that 50mls of t5he sample should be blown through with a gentle stream of air in order to remove free carbon dioxide and the determination repeated . if a high value still persists, then it indicates the probability of free acid or an acid salt being present .

The value is then subtracted from the first determination to give CO_2 value and the second determination is reported as organic acidity to phenolphthalein as mg/1 $CaCO_3$.

6 : ALKALINITY

The alkalinity of water is determined by titration with standard 0.01m sulphuric acid to end points which correspond with the pH of a dilute bicarbonate solution, that is, 8.3, and a dilute carbonic acid solution withpH 4.5. In order to determine these and points ,phenolphthalein is used as the indicator for 8.3 and methyl orange or BDH 4.5 may be used for the second end point .

The alkalinity of a raw water is due to bicarbonate of calcium and magnesium, and in certain waters , e.g. well waters , or base exchange softened waters , sodium bicarbonate may also be present in solution. Certain moorland waters and those contaminated with mine drainage may have a pH less than 4.5, and the acidity to the pH of 4.5 is determined . In the case of feed waters and boiler waters it is possible to encounter sodium carbonate and hydroxide as alkali additions which are used in the treatment of the water . In order to determine the concentration of these , the alkalinity to phenolphthalein and methyl orange should be continued on the same sample after the phenolphthalein alkalinity P_1 has been determined.

Additionally , a fresh sample should be taken and the alkalinity to phenolphthalein determined after barium chloride has been added. This is referred to as the P_2 reading . this is equivalent to the free hydroxide concentration.

ALKALINITY TO PHENOLPHTHALEIN (P_1)

METHOD

Take 25m Is or a suitable aliquot of the sample in a porcelain basin and add approximately 2-4 drops of phenolphthalein. If the sample turns pink on the addition of the indicator titrate with 0.0 IM sulphuric acid at the same time gently agitating the sample with a glass rod until the colour just disappears.

CALCULATION OF RESULT

$$\text{Alkalinity to phenolphthalein } (P_1) = \frac{\text{ml 0.0IM acid x 1000}}{\text{Ml of sample}} \quad \text{mg/1 as } CaCO_3$$

This determination will have half the total carbonate plus all the caustic alkalinity present .

B :ALKALINITY TO METHYL ORANGE (T. A)

Continuing on the same sample , the alkalinity to methyl orange is determined (T. A) .

METHOD

Add to the sample from the previous determination three drops of methyl orange indicator and the titration continued with stirring slowly adding 0 .01M sulphuric acid until the colour shows the first signs of change from yellow to orange .This marks the end point .In order to calculate the total alkalinity , the total titre of 0.01M acid used for the sample including that of the titration to phenolphthalein is required .

CALCULATION OF ESULTR

Alkalinity to methyl orange (M.O) = ml 0.01M acid X 1000 / ML of sample ml/l as $caco_3$

This result gives all the alkalinity due to the presence of bicarbonate, carbonate or hydroxide.

It is accepted that sodium bicarbonate and hydroxide do not co-exist to any significant extent.

C: ALKALINITY TO PHENOLPHTHALEIN AFTER ADDITION OF BARIUM CHLORIDE (P_2)

Frequently with waters which are treated with tannins the total alkalinity end point cannot be determined . additionally , it is found that an inaccurate result is obtained due to the fact that below pH of 8.3 there is a tendency to titrate the sodium ternate which may be present . in order to overcome this, and to accurately determine the amount of caustic alkalinity present, the titration to phenolphthalein is carried out after adding barium chloride solution.

METHOD

To 25mls of the sample or VA suitable aliquot add phenolphthalein indicator and about 5mls of 10% barium chloride solution. stir the sample and if a pink color persists this indicates the presence of sodium hydroxide in the sample . Slowly titrate with 0.0lm sulfuric acid until the pink colour just disappears. Any re-appearance of the pink colour should be disregarded.

CALCULATION OF RESULT

Alkalinity to phenolphthalein (P_2) = ml 0.0l M acid x 1000 / ML of sample (mg/1 as-$CaCO_3$)

Hence total alkalinity can be calculated by P_1 and P_2 determination

Total alkalinity = $2 P_1 – P_2$

ANALYTICAL

NOTE :

Waters containing trisodium phosphate will give a p reading equivalent to $1/3^{r}$rd of the orthophosphate. sodium silicate present in boiler waters will affect all three reading, sodium sulfite present in the sample does not affect either the p_1 or p_2 reading , but does affect the total alkalinity reading .

Results of these tests may be summarized in the following table, and the individual components giving the alkalinity so determined.

IF RESULT OF

TITRATION IS	HYDROXIDE	CARBONATE	BICARBONATE
P_1 = nil	Nil	Nil	M.A. = Bicarbonates
$2P_1 <$ M.A.	Nil	2P	M.A. = Bicarbonates
$2P_1 =$ M.A.	Nil	2P	
$P_1 =$ M.A.	M.A. = P2	Nil	
$2P_1 >$ M.A.	2P – M.A. = (= P_2)	2(M.A. – P)	

NB: Alkalinity are always reported as mg /L $CaCO_3$

7: HARDNESS

This is usually associated with the dissolved salts of calcium and magnesium in water , and is usually classified into two types, temporary or (carbonate hardness) and permanent or (non carbonate hardness

1. The temporary hardness usually consists of calcium and of the sulfate, chloride, or nitrate salts of these metals .The total hardness determined by titration using 0.0IM E.D.T.A. in the form of DI-sodium salt. The pH of the sample is adjusted by addition of an ammonia / ammonium chloride buffer , and the total hardness indicator of solochrome black or erichrome black T or calagmite or other suitable indicator added .

METHOD

Take 25mls of the sample or suitable aliquot in a porcelain dish and add 2mls of ammonium buffer together with 6 drops of total hardness indicator . Titrate immediately with 0.01M E.D.T.A. until the solution in the dish has lost all traces of red colour . it is normal for the colour at the end point to become pure blue, but with some waters a gray or green end point color may be obtained . If difficulty is encountered in obtaining an end point , then a decomplexing agent may be necessary.

HARDNESS CONTTINUED

NOTE : It is preferable to start with a small amount of hard water and reach the equivalence before starting determination Then adding the sample on to the neutralized buffer plus indicator.

CALCULATION OF RESULT

Total hardness (mg / L as $CaCO_3$) = V ml (0 .0 I M E.D.T.A.) x 1000 / ML of sample

INTERFERENCES

Certain substances are present in water samples, and cause interference in the hardness determination. The cupric ion present in quantities of greater than 0.2 PPM of copper result in no end point being determined Ferric iron may be tolerated up to 20 PPM , aluminum up to 50 PPM, and phosphate up to 200 PPM, Manganese and zinc whilst not interfering with the end point , does titrate as hardness . A decomplexing agent e.g.: 5ml of 10 % triethanolamine or 10 – 20 mg of potassium cyanide may Mg concentration can be determined by AAS and the total hardness calculated .

INTERPRETATION OF RESULTS OF HARDNESS TESTS

A: Carbonate Or Temporary Hardness (also know as alkaline hardness)

This is obtained from the total alkalinity to methyl orange , and the total hardness , and as already stated , consists of calcium and magnesium carbonate , bicarbonates . When the total hardness is less than the total alkalinity then it indicates that sodium bicarbonate is present and all the hardness is reported as temporary

B: NON CARBONATE OR PERMANENT HARDNESS (also know as non-alkaline hardness)

This has already been described as the calcium and magnesium chlorides , sulphates, or nitrate salts, and is equal to the difference between the temporary hardness and total hardness found . In a boiler water any hardness found is usually reported as permanent hardness , even though alkalinity may be present . This is on the basis that temporary hardness would be precipitated on heating the sample when in the boiler.

M.A. > T.H Temporary hardness = T.H and

M.A - T.H = sodium bicarbonate Expressed as $CaCO_3$

M.A. = T.H. Temporary hardness only

M.A. < T.H Temporary hardness = M.A. and

Permanent hardness = T.H. – M.A.

8: Calcium Hardness (see section 10)

9: SILICA

Measure 50mls of sample into a nester tube. Adjust the temperature to 25 – 30°c and add 2mls 10% ammonium molybedate. Mix then add 4mls to 0.5m sulphuric acid, mix and allow to stand for 10 minutes at 25 – 35 –° c. Then add 2mls 30% sodium citrate solution and mix. This sodium citrate prevents interference from phosphate up to 100PPM as po_4.

In another nester tube take 50mls distilled water and repeat the procedure. Compare the yellow colour in the nessleriser using the disc NN.

Silica as PPM = disc reading x 20

ANALYTICAL NOTE

If a blue colour is produced then a reducing agent, probably sodium sulphite, is present and should be oxidized with 1 – 2 drops of 20 vol. Hydrogen peroxide solution before performing the silica measurement.

10: CALCIUM HARDNESS

This is carried out on all raw waters , open evaporative cooling waters and when especially requested.

METHOD

Take 25mls or suitable aliquot in a porcelain dish . Add 5mls of 2m NaOH and knife end of indicator ./ (Patton 7 readers reagent in solid solution with NaC1) Titrate with 0.0IM E.D.T.A. to a pure blue end point .

CALCULATION

$$\text{Calcium Hardness} = \frac{\text{mls 0.0IM E.D.T.A.} \times 1000}{\text{Volume of sample (mls)}} \quad \text{mg /L as } CaCO_3$$

11: ANIONS

Fluoride , chloride , sulphate and nitrate are normally determined by ion chromatography . Alternative methods are attached for those occasions where this method is either not available or inappropriate .

12: CATIONS

Atomic absorption spectroscopy is the method of choice for most metals , and can be used for calcium and magnesium when titration is not possible . Alternative methods are attached for those occasions when this method is either not available inappropriate .

13: TREATMENT RESERVES

Various methods are appended for the determination of treatment reserves .

Section : 2

10: PERMANGANATE VALUE

Take 50mls of clear of filtered water and place in porcelain evaporating basin .Add 5 ml. of 1.287 S.G. sulfuric acid approximately 50% Add N / 50 $KMno_4$, 1 ml at a time , stirring on addition , until pink color which persists for 1 minute is obtained .

No. Of ml. N/50 $KMno_4$ used = permanganate value (NB: N/50 $KMno_4$ = 0.004M)

NOTES:

1. On raw waters, or where the nature of the treatment is unknown, record the permanganate value.

2. On waters treated with Tannins :-

Tannin (mg /L) = permanganate value x 10

3. On waters treatment with nitrite :-

Nitrite (mg / L as $N0_2$) = permanganate value x 9.2

An alternative method for Nitrite may be found in the Quality Control Manual, Appendix B, Test 38