

METHODS FOR THE ANALYSIS OF BOILER WATER

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INTRODUCTION

At Tongaat we have become aware of the necessity of treating and conditioning our boiler waters, and during the coming 1955 season we are going to carry out a regular procedure for analysing them. This subject is of interest to the Sugar Industry and for that reason the Secretary has asked me to introduce this paper detailing the commonly accepted methods of analysis.

The detrimental effect of untreated boiler waters is only too well known to engineers. Dissolved gases, soluble and insoluble solids, extraneous liquids all have to be controlled to maintain peak boiler efficiency. Boiler control is designed to decrease to a minimum (1) scale formation in boilers and auxiliaries; (2) the possible formation of caustic embrittlement (intercrystalline cracking); (iii) corrosion throughout the water and steam side of the plant.

It is not my intention to discuss the various processes whereby this control is affected, but merely to give in detail methods of analysis which would be suitable for determining the more important chemical quantities. For a better understanding of the need

for control I refer you to an excellent paper by Hillier.¹ These quantities must be maintained within strict limits which will vary depending on boiler design and local conditions. As a guide to boiler control, I give the recommendations of four major concerns interested in boiler treatment for boilers up to 250 psig (Table I).

The modern practice is to express a number of quantities (including chlorides) in ppm CaCO₃. This may confuse those more accustomed to expressing quantities in different terms, in which case the conversion table may help (Table II).

TABLE II

Conversion Factors

If it is desired to express readings in terms other than CaCO₃, multiply by the factors in Column A. If the results are expressed in terms shown in the first column, they may be converted into terms of CaCO₃ by multiplying by the factors in Column B.

Terms of	A	B	Terms of	A	B
Ca	0.40	2.50	Na	0.46	2.17
CaO	0.56	1.79	NaOH	0.80	1.25
Ca(HCO ₃) ₂	1.62	0.617	Na ₂ CO ₃	1.06	0.943
CaSO ₄	1.36	0.735	NaHCO ₃	1.68	0.60
CaCl ₂	1.11	0.901	Na ₂ SO ₄	1.42	0.704
Mg	0.24	4.17	NaCl	1.17	0.855
MgO	0.40	2.48	CO ₂	0.44	2.27
MgCO ₃	0.84	1.19	CO ₃	0.60	1.67
Mg(HCO ₃) ₂	1.46	0.685	HCO ₃	1.22	0.82
MgSO ₄	1.20	0.833	SO ₄	0.96	1.04
MgCl ₂	0.95	1.053	Cl	0.71	1.41

TABLE I

Recommendations for Boilers up to 250 psig

	Boiler Water	Feed Water
pH	> 10.5 (D) 10-11 (R)	> 8.5 with unde-aerated feed water (B)
Total hardness ppm CaCO ₃	None (ALL)	< 10 (B)
Total alkalinity ppm CaCO ₃	20% of TDS (R) Less than twice P reading (D) 15-20% of TDS (B)	—
Caustic alkalinity ppm CaCO ₃	15% of TDS (R)	—
Phenolphthalein alkalinity ppm CaCO ₃	15% of TDS (R)	—
Chlorides ppm CaCO ₃	450 max (D)	—
Na ₂ SO ₄	> 2.5 (B)	> 2.5 (B)
NaOH	2.0 (R)	—
Na ₂ SO ₄	2.0 (D)	—
Total alkalinity as Na ₂ CO ₃	50-100 (B) 100-150 (D)	—
Phosphate as ppm Na ₃ PO ₄	4000 max (R) 7000 max (B)	—
TDS ppm	—	< 0.05 (B)
Dissolved oxygen ccs/litre	—	—
Oil	None (ALL)	—
Suspended matter	—	None (ALL)
Sucrose ppm	< 10 (A)	—
Silica ppm	< 25 (B)	—
Sulphite ppm Na ₂ SO ₃	50-100 (B) Excess 30-50 (D)	—

(D), (B), (R), (A) are large concerns interested in boiler treatment.

METHODS OF ANALYSIS

In the Appendix appear details of some nineteen methods for analysing boiler and feed waters. Most of them are so well known that I will confine my remarks principally to three determinations, i.e. oil, hardness and phosphates.

1. The Determination of Oil

The elimination of oil in the boiler feed is of supreme importance. Oil separators, separating tanks and coke filter beds are used for this purpose. Major concerns recommend that the oil content of feed water should be zero, but where flocculating agents such as starch are used in the conditioning, up to 5 ppm can be tolerated. Where the oil is in the form of an emulsion the method using ammonia alum as a flocculating agent will give good results. For instance an oil emulsion containing 60 ppm oil, yielded 51 ppm on analysis. Where the oil is in the form of droplets floating on the sample, a straight

extraction with carbon tetrachloride is sufficiently accurate. The method using a flocculating agent is unsuitable here.

2. The Determination of Hardness

Two methods are generally accepted: (a) the Wanklyn Soap method, and (b) the modified Schwarzenbach method.²

The Wanklyn soap method is inaccurate for TDS above 6000 ppm. It is difficult to determine the "ghost point" for reporting Ca^{++} and Mg^{++} hardness, and a lather correction amounting in some cases to more than the actual titration value has to be applied. Dissolved CO_2 gives high results and has to be removed. Hydroxides and carbonates also upset the reading.

I suggest that wherever possible the Schwarzenbach method is used. It is far quicker and simpler than the Wanklyn method. The titration is affected, however, by certain metallic ions. Heald, Coates and Edwards² studied the effect of the more common ions and reported as follows: Cu^{++} ions greater than 0.2 ppm gave no end-point in the total hardness titration and titrated as hardness in the calcium hardness determination. Fe^{+++} and Al^{+++} ions were studied up to 20 and 50 ppm respectively and did not affect the total hardness titration. However, Fe^{+++} greater than 5 ppm tended to give low Ca^{++} hardness figures. Mn^{++} and MnO_4^- (hydroxylamine present in the indicator reduces this to Mn^{++}) titrate as total hardness. Small quantities greater than 2 ppm are able to mask the colour in the calcium hardness titration. Zinc, calcium and mercury also give colour changes to murexide.

It is usual to eliminate traces of hardness in the boiler feed by the addition of orthophosphates or polyphosphates. These remove calcium hardness as a precipitate of $\text{Ca}_3(\text{PO}_4)_2$. Sodium hexametaphosphate is used at Tongaat in a powder form containing 10 per cent. starch and 90 per cent. hexametaphosphate. In solution this compound contains poly-metaphosphate ions thought to be in groups of 6, with their equivalent of Na^+ ions. Up to two-thirds of the Na^+ ions can be replaced by Ca^{++} before precipitating and at high temperatures hydrolysis to insoluble $\text{Ca}_3(\text{PO}_4)_2$ takes place. The effect of this polyphosphate on known total hardnesses of 200 and 10 ppm respectively was studied (Table III). It was found that in the former case precipitation commenced after 40 ppm, giving lower readings for the soap method than the EDTA. On standing the titrating solution regained its red colour, probably due to an unbalanced state of dissociation. In the case of 10 ppm total hardness, up to 200 ppm polyphosphate powder did not affect the result and 60 and 200 ppm orthophosphate gave readings which were only slightly low.

The Schwarzenbach method is based on the great affinity of disodium ethylene di-amine tetra-acetate for Ca^{++} and Mg^{++} ions. Experiments have shown it to be a very useful descaling reagent in evaporators³ where the hard calcium scales are partially taken back into solution. It is possible that some of the hardness present in an unharmed form may be titrated as direct hardness when analysing boiler waters with this reagent.

The determination of hardness is divided into (a) methods applicable to hardness greater than 10 ppm, and (b) hardness less than 10 ppm. The methods in (a) can be used throughout if great accuracy is not required. Boiler waters are sometimes so discoloured that the end point of the titration is masked. For these cases a decolorisation method using activated charcoal is included.

TABLE III

Effect of Polyphosphates and Orthophosphates on Total Hardness

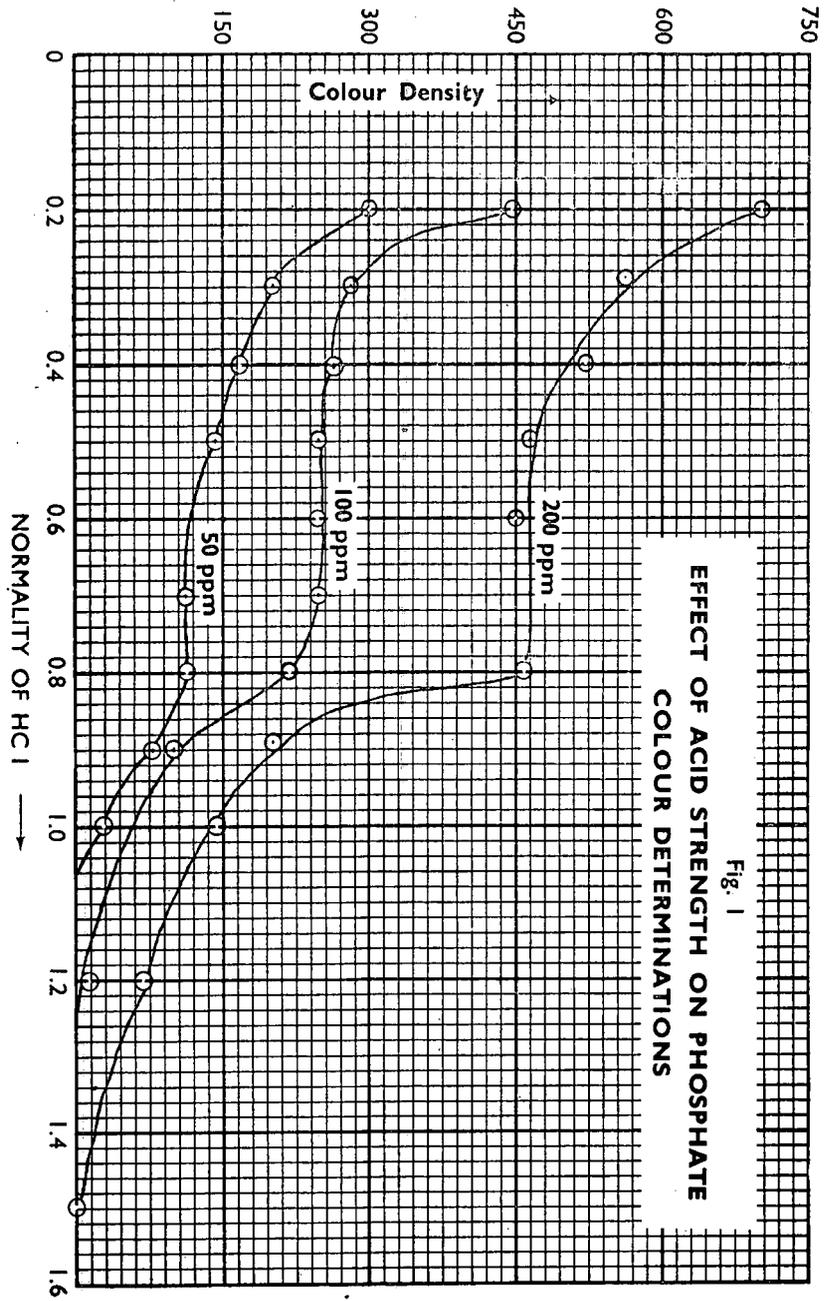
ppm as polyphosphate powder or ($\text{Na}_4\text{P}_6\text{O}_{18}$)	200 ppm CaCO_3 + polyphosphate powder		10 ppm CaCO_3 + polyphosphate powder		10 ppm CaCO_3 + orthophosphate	
	Wanklyn	EDTA	Wanklyn	EDTA	Wanklyn	EDTA
0	199	201	11.0	9.8	—	—
10	—	—	11.0	9.8	—	—
20	—	—	—	—	—	—
40	192	200	—	—	—	—
50	184	196	10.5	9.8	—	—
60	169	181	10.5	9.8	9.5	8.5
200	68	66	10.0	9.8	9.0	8.0

The Determination of Phosphates

It is usual to determine phosphates colorimetrically. Molybdates are reduced by suitable reducing agents in the presence of orthophosphate ions as catalyst to a blue complex having molybdenum in 5 and 6 valence forms.⁴ The depth of blue colour depends on the PO_4^- ion concentration.

A number of reducing agents have been found suitable including Sn , SnCl_2 , hydroquinone and 1-2-4 aminonaphthol sulphonic acid. The Sugar Millers Research Institute adapted the use of SnCl_2 for the determination of phosphate in mixed juices and their procedure has been found suitable for boiler waters. The Hilger 810 Brochem Absorptiometer is used at Tongaat.

For leaf analysis Cotton⁴ prefers the use of 1-2-4 aminonaphthol sulphonic acid as reducing agent. He maintains that compared with SnCl_2 interfering effects are reduced (of these only arsenites are specifically named). The reagent is stable for two weeks compared with the six to eight hours for dilute SnCl_2 . Using SnCl_2 the blue molybdenum colour deepens rapidly and is stable from 4 to twenty



minutes. The colour deepens slowly with sulphonic acid and is stable after twenty-five minutes.

The hydrogen ion concentration of the solution under observation is most important. Cotton⁴ made up his molybdate reagent with H_2SO_4 and showed that using 1-2-4 aminosulphonic acid as reducing agent steady colorimetric readings could be obtained within the fairly broad limits of 0.8 to 1.65N. Outside these limits the blue colour decreased progressively and gave very low readings. Lindner,⁵ using $SnCl_2$, made his solution 0.6N wrt H_2SO_4 . In the SMRI method it will be seen that the molybdate is made up with HCl, giving a test solution of 0.7N. Fig. 1 gives colorimetric readings vs. acid concentrations for different phosphate compositions. It will be seen that steady readings are obtained from 0.5 to 0.8N.

Lindner⁵ found that Beers law was followed for P_2O_5 contents lying between 0.004 to 0.4 per cent. on a 100 mgm sample. Obviously this can only be true for solutions having the same hydrogen ion concentrations. It is best to plot a standard curve of known P_2O_5 contents for comparison with the unknown solutions.

By means of the method outlined, no difficulty was experienced in determining orthophosphate ions. Polyphosphates would be hydrolyzed to orthophosphates in the boiler and determined as such. Polyphosphates in boiler feed are a somewhat different problem. Samples containing sodium hexameta-phosphate did not appear to be hydrolyzed even after fifty minutes boiling. When excess Ca^{++} ions were added to the solution hydrolysis appeared to be rapid on heating and a precipitate of $Ca_3(PO_4)_2$ appeared. There were then sufficient $PO_4^{=}$ ions present to produce a blue colour.

The hexameta-phosphate hydrolyses rapidly in acid solutions and this forms the basis of an indirect determination of this substance in boiler feed water. The difference in P_2O_5 content before and after reversion of the metaphosphate to orthophosphate,⁶ indirectly determines the metaphosphate present. The acid strength used for the hydrolysis is 0.4N H_2SO_4 and two hours boiling is required before completion.

Turbid boiler water samples containing precipitates, e.g. $Ca_3(PO_4)_2$, must be filtered before analysing.

GENERAL

Difficulty may be experienced determining the end point of the methyl orange indicator in the total alkalinity test. This may be overcome by preparing a standard colour for comparison by titrating N/50 H_2SO_4 against N/50 NaOH to pH4 as determined by a pH meter. M.O., however, is unsatisfactory in the presence of organic substances.

Precipitation of sulphates by benzidine mono- or di-hydrochloride is much quicker than the longer gravimetric procedure of precipitating as $BaSO_4$. This method gives satisfactory results in the laboratory.

Winkler's method is given for dissolved oxygen. It is based on the oxidation of the manganous ion to a manganic form and subsequent reduction of the iodide to liberate free iodine. The chief difficulty in this determination lies in the precautions taken during sampling and testing (see Appendix) thereby preventing entrainment of atmospheric oxygen. For the determination of large quantities of oxygen (greater than 0.5 ccs/litre) a method using $FeSO_4$ has been advocated.⁷

The method for determining silica and soluble silicates is a colorimetric one adapting the Hilger Absorptiometer. Calibrated colour standards of picric acid or potassium chromate are used. No precautions are taken for interfering substances except phosphates (see Appendix). Nevertheless fair results are obtained for quantities up to 50 ppm SiO_2 . A study has been made by Alexander and Parrish⁸ of the existence of silica in soluble and insoluble forms in raw juices. Much of their paper is applicable to boiler water analysis, particularly their colorimetric determination of soluble silica adapted from the method of Cerny. They affect a reduction of ammonium molybdate to the blue complex using 1-2-4 aminonaphthol sulphonic acid in the presence of silicate ions.

REFERENCES

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A P P E N D I X

DETERMINE TDS (TOTAL DISSOLVED SOLIDS) BY HYDROMETER OR DIONIC TESTER AND pH BY METER

OIL IN FEED AND BOILER WATER

- Reagents (i) Saturated lime water.
 (ii) Ammonia alum (5 per cent. w/v).
 (iii) CCl_4 .
 (iv) HCl (A.R.) N/2.

Method—Measure out 1000 mls of well shaken sample into a glass cylinder. Add 100 mls of clear saturated lime water solution and 10 mls of 5 per cent. ammonia alum solution. Shake and allow to stand for 10 minutes for floc to appear.

Filter sample through No. 4 Whatman paper (15 cms). Place filter paper and precipitate in a clean beaker, dilute with 100 mls of distilled water and add 5 mls of N/2 HCl. Add 50 mls CCl_4 and agitate well with a rubber policeman. Pour off the supernatant liquid. Add further portions of distilled water 50 mls at a time until most of the filter paper has been removed. Finally pour into a 250 ml separating funnel and collect the lower tetrachloride layer in an open tared dish. Evaporate to dryness over a water bath and determine increase in weight.

Weight of oil in milligrams = ppm oil present in sample.

TOTAL HARDNESS

(a) Wanklyn Soap Method

- Reagents** (i) Standard soap solution (1 ml = 10 ppm CaCO_3).
(ii) Standard CaCl_2 solution (1 ml = 1 mgm CaCO_3) used for standardising soap solution.

Method—Measure out 100 mls of sample. Add a few drops of phenolphthalein (1 per cent. solution) to boiler feed samples, making alkaline with NaOH if necessary. Add the soap solution 0.2 mls at a time until a lather begins to form. Then add more carefully 0.1 mls at a time, shaking vigorously after each addition. A persistent lather which disappears on further addition of soap is known as the false end point or ghost point. Its value is determined by subtracting the lather correction from the total mls soap added and it represents very approximately the magnesium hardness present in the solution. The lather correction is the number of mls soap required to produce a permanent lather on 100 mls of distilled water and is usually 0.5 mls.

Continue adding soap solution until a stable lather, persisting for five minutes, is produced. If the TDS is above 6000 it will be necessary to dilute the sample down. Smaller samples may be used depending on the total hardness value.
Total Hardness =

$$1000 \times \frac{(\text{No. of mls soap solution} - \text{lather correction})}{\text{Volume of sample in mls}} \text{ ppm } \text{CaCO}_3$$

(b) Modified Schwarzenbach Method for Hardness Greater than 10 ppm CaCO_3

- Reagents** (i) N/50 disodium ethylene diamine tetra-acetate. Dissolve 3.72 gms per litre. Check against the standard CaCl_2 solution.
(ii) Ammonia buffer solution. Weigh out 67.5 gms NH_4Cl . Dissolve in 570 mls NH_4OH (25 per cent. solution). Dilute to 950 mls with distilled water. In 50 mls distilled water dissolve 0.300 gms MgSO_4 anhydrous and 0.93 gms EDTA reagent. Add this solution to the former.
(iii) Total hardness indicator. Weigh out 0.5 gms solochrome black W DFA and 4.5 gms hydroxylamine hydrochloride. Dissolve in 100 mls commercial alcohol or 90 mls absolute alcohol diluted with 10 mls distilled water.

Method—Transfer 100 mls of sample to a clean 250 ml porcelain casserole. Add 2 mls of the buffer solution and 6 drops of indicator solution. This will impart a purplish-pink colour to the solution. Titrate directly against the standardised EDTA solution until a sharp colour change varying from blue to grey is observed.

$$\text{Total hardness} = \frac{\text{Titration in mls}}{\text{Volume of sample in mls}} \times 1000 \text{ ppm } \text{CaCO}_3$$

(c) Modified Schwarzenbach Method for Hardness Less than 10 ppm CaCO_3

Method—Five mls of standard hard water (or about 50 mls of natural water) is added to 50 mls distilled water contained in a large porcelain dish. 10 mls ammonia buffer solution and 6 drops indicator are added and solution titrated to end point. 500 mls of the low hardness water are then added and a further 1 ml of indicator added and titration continued until the end point. The difference in titration is a measure of the hardness of the water.

$$\text{Total hardness} = \frac{\text{Titration difference in mls}}{\text{Volume of sample in mls}} \times 1000 \text{ ppm } \text{CaCO}_3$$

CALCIUM HARDNESS

(a) Modified Schwarzenbach Method for Calcium Hardness Greater than 10 ppm CaCO_3

- Reagents** (i) EDTA standard as above.
(ii) 4N NaOH. Dissolve 16 gms of sodium pellets in 100 mls distilled water.
(iii) Calcium hardness indicator. Weigh out 0.20 gms murexide (ammonium purpurate) and grind to a fine powder with 100 gms of NaCl.

Method—Transfer 100 mls sample to a clean 250 mls porcelain casserole. Add 1 ml of 4N NaOH and 0.2 gms of calcium indicator. The latter is weighed out roughly on a tared scoop. The indicator imparts a red colour to the solution. Titration against EDTA is carried out until no further deepening of the violet colour is observed. The end point is approximately 0.1 ml after the first initial pale violet colour.

$$\text{Calcium hardness} = \frac{\text{Titration in mls}}{\text{Volume of sample in mls}} \times 100 \text{ ppm } \text{CaCO}_3$$

(b) Modified Schwarzenbach Method for Calcium Hardness Less than 10 ppm CaCO_3

Method—To 500 mls of the low hardness water contained in a large porcelain dish add 5 mls of 4N NaOH and 0.6 gms indicator. The titration is carried out as above.

$$\text{Calcium hardness} = \frac{\text{Titration in mls}}{\text{Volume of sample in mls}} \times 1000 \text{ ppm } \text{CaCO}_3$$

(c) Decolorisation of Boiler Samples using Activated Carbon

- Reagents** (i) Activated carbon. Activated charcoal powder for decolorising purposes (BDH).
(ii) Brom phenol blue indicator.
(iii) HCl 25 per cent. w/w.

Method—To 1 gm of activated carbon add 100 mls distilled water containing 1 ml 25 per cent. w/w HCl. Mix thoroughly and filter on a pad of paper pulp and wash with 100 mls distilled water.

500 mls of coloured boiler water is first filtered and acidified using 25 per cent. HCl to adjust the pH to 2.5 using brom phenol blue indicator. The treated water is then filtered through the bed of activated carbon, refiltering if necessary. Total and calcium hardness are then determined as above.

MAGNESIUM HARDNESS

This is determined indirectly from the relationship

$$\text{Magnesium hardness} + \text{Calcium hardness} = \text{Total hardness.}$$

FREE CARBON DIOXIDE

- Reagents** (i) N/50 Na_2CO_3 . Dissolve 1.06 gms in 1000 mls. Standardise this solution against HCl using M.O. indicator.
(ii) Phenolphthalein indicator (1 per cent. w/v). Weigh out 1 gm phenolphthalein in a mixture of 55 mls commercial alcohol and 45 mls distilled water.

Method—Measure out 100 mls of sample and pour into a casserole. Add 10 drops of phenolphthalein indicator and titrate against standardised N/50 sodium carbonate solution until a faint pink colour forms and persists for thirty seconds.

$$\text{Free Carbon Dioxide} = \frac{\text{Titration in mls}}{\text{Vol. of sample in mls}} \times 1000 \text{ ppm } \text{CaCO}_3$$

ALKALINITY

Determination of the P, M and $\text{P}(\text{BaCl}_2)$ readings where—

P = Alkalinity up to the end point of phenolphthalein indicator and represents in ppm CaCO_3 the hydroxides and half the carbonates present.

M = Total alkalinity as determined by the end point of methyl orange indicator. It represents in ppm CaCO_3 the carbonates and hydroxides or bicarbonates.

$P_{(BaCl_2)}$ = Phenolphthalein alkalinity found by titrating a standard acid after precipitation of carbonates by $BaCl_2$.

For treated water containing organic matter and for all boiler waters—the P and $P_{(BaCl_2)}$ readings should be used to give the M reading where $M = 2P - P_{(BaCl_2)}$.

Reagents (i) N/50 H_2SO_4 . 0.98 gms conc. H_2SO_4 in 1000 mls distilled water. Standardise against NaOH using phenolphthalein as indicator.

(ii) Phenolphthalein indicator as for free carbon dioxide.

(iii) Methyl orange indicator. Weigh out 0.04 gms and dissolve in 100 mls distilled water.

(iv) 10 per cent. w/v $BaCl_2$ solution.

Method—

(a) **P reading**—Measure out 100 mls of sample and pour into a 250 ml casserole. Titrate against the standardised N/50 H_2SO_4 until the solution just turns colourless.

$$P \text{ reading} = \frac{\text{mls N/50 } H_2SO_4}{\text{mls sample}} \times 1000 \text{ ppm } CaCO_3$$

(b) **M reading**—With the same sample continue to titrate using 2 drops of methyl orange. Titrate against the standardised H_2SO_4 until the orange colour changes to pink.

$$M \text{ reading} = \frac{\text{mls N/50 } H_2SO_4}{\text{mls sample}} \times 1000 \text{ ppm } CaCO_3$$

(c) **$P_{(BaCl_2)}$ reading**—Measure a fresh aliquot of 100 mls and precipitate the carbonates by the addition of 10 mls of 10 per cent. $BaCl_2$ solution. Add 10 drops of phenolphthalein indicator and rapidly titrate against the standardised H_2SO_4 solution.

$$P_{(BaCl_2)} \text{ reading} = \frac{\text{mls N/50 } H_2SO_4}{\text{mls sample}} \times 1000 \text{ ppm } CaCO_3$$

DETERMINATION OF SULPHATES

Reagents (i) Benzidine di-hydrochloride (1.6 w/v solution). Dissolve 16 gms in 1000 mls distilled water containing 10 mls N/1 HCl.

(ii) Methyl orange indicator.

(iii) N/7 NaOH solution. Weigh out 5.714 gms NaOH and dissolve in 1000 mls distilled water. Standardise against known acid solution using phenolphthalein as indicator.

Method—Measure out 100 mls of sample and to it add 10 mls of benzidine solution. Pour into a 250 ml flask. Add 3 drops of methyl orange to ensure that the solution is acid. The precipitate takes about 5 minutes to form. Filter through a No. 4 Whatman paper and test the filtrate for further precipitation by addition of 2 mls benzidine solution. Wash the filter paper and precipitate with distilled water until free of acid. This is ascertained by dropping methyl orange indicator on the filter paper.

Return the washed filter paper and precipitate to the Erlenmeyer flask and add about 50 mls distilled water. Add 3 to 4 drops of phenolphthalein and titrate against the N/7 NaOH with vigorous shaking between each addition from the burette.

$$\text{Sulphate Content} = \frac{\text{mls N/7 NaOH}}{\text{Vol. of sample used}} \times 10,000 \text{ ppm } Na_2SO_4$$

DETERMINATION OF CHLORIDES

Reagents (i) N/50 $AgNO_3$. Best to purchase the normal solution and dilute with distilled water to make up to N/50. Then standardise this against standard NaCl solution.

(ii) K_2CrO_4 indicator (5 per cent. w/v) neutral.

(iii) Methyl orange indicator.

(iv) N/50 H_2SO_4 .

(v) N/50 Na_2CO_3 .

Method—Measure out 100 mls (or less if the chlorides are high) and pour into a casserole. It is essential that the solution be neutral so add 2 drops of methyl orange and titrate against

N/50 H_2SO_4 until a pink colour appears. Now neutralise with N/50 Na_2CO_3 until the yellow colour reappears and then add 6 drops more.

To the neutral sample add 6 to 8 drops of dichromate indicator and titrate against N/50 $AgNO_3$ until a definite pale red colour appears.

$$\text{Chloride Content} = \frac{\text{mls N/50 } AgNO_3}{\text{mls sample}} \times 1000 \text{ ppm } CaCO_3$$

DETERMINATION OF PHOSPHATES

The method is a colorimetric one using the Hilger 810 Biochem Absorptiometer. A No. 7 filter with a peak wavelength of 610 μ was used.

Reagents (i) Ammonium molybdate. 15 gms ammonium molybdate dissolved in 300 mls distilled water at 50°C. Filter cool then add 350 mls 10N HCl slowly with shaking. Cool and dilute to 1000 mls with distilled water. Store in a dark place and replace every 2 months.

(ii) $SnCl_2 \cdot 2H_2O$ solution. 10 gms of dihydrate are dissolved in 25 mls conc. HCl. Replace every 2 months.

(iii) Dilute stannous chloride. Add 1 ml of above stock solution to 332 mls distilled water. Lasts for 8 hours.

(iv) Standard phosphate solution. Dissolve 0.7668 gms of pure mono potassium phosphate in distilled water and transfer to a litre flask. Add 10 mls of 10N H_2SO_4 and make up to the mark. 1 ml = 400 ppm P_2O_5 .

Method—Pipette 100 mls sample into a 200 ml flask and make up to the mark with distilled water. Pipette an aliquot (usually 10 mls) into a 100 ml flask, make up to approximately 70 mls. Pipette in 20 mls of the hydrochloric-molybdate reagent, mix and then pipette 5 mls of the dilute stannous chloride reagent. Make up to 100 mls and mix well. Measure the optical density reading on the absorptiometer.

Standards containing 0-200 ppm P_2O_5 are prepared and a graph of the optical density vs. P_2O_5 content drawn up. In this way the original sample can be calculated by multiplying by the appropriate factor.

DISSOLVED OXYGEN

Winkler's Method

Reagents (i) $MnCl_2$ anhydrous. 400 gms in 1 litre distilled water (or 480 gms $MnSO_4$ in 1 litre).

(ii) Alkaline iodide solution. 700 gms KOH and 150 gms KI in 1 litre of distilled water.

(iii) 50 per cent. v/v H_2SO_4 (Sg. 1.83).

(iv) N/50 $Na_2S_2O_3 \cdot 5H_2O$. Weigh out 5 gms and make up to a litre. Standardise against KIO_3 using starch indicator.

(v) N/50 standard KIO_3 . Weigh out accurately 0.713 gms and dissolve in 1 litre. For standardisation against $Na_2S_2O_3$ taken an aliquot of 25 ccs add 0.2 gms iodate-free KI and 3 mls N. H_2SO_4 and titrate using starch indicator.

(vi) Starch indicator. Make a paste of 1 gm soluble starch with a little water. Pour the paste with stirring into 100 mls boiling water and boil for 1 minute. Allow to cool and add 3 gms of KI. Preserve under a layer of toluene.

Method—It is necessary to test for oxygen as soon as possible after sampling. This is done by adding 1 ml $MnCl_2$ to the 600 ml sample and shaking the stoppered bottle vigorously. 2 mls of alkaline iodide reagent are next added and the bottle again shaken, followed by 3 mls of 50 per cent. H_2SO_4 with shaking. The addition of the various reagents must be made quickly using pipettes with their lower stems immersed in the liquid.

One method recommends the addition of these chemicals by means of hypodermic syringes injected into the rubber tubing at the sample point. In this way the sample is immediately fixed.

500 mls of liquid are titrated against the standardised N/50 $\text{N}_2\text{S}_2\text{O}_3$ after adding 3 drops of starch solution. A blue colour on the addition of starch signifies the presence of dissolved oxygen in the original sample.

Oxygen Content: 1 ml N/50 $\text{Na}_2\text{S}_2\text{O}_3 = 0.225$ mls oxygen/litre.

Sampling—Care must be taken to avoid flashing and exposure to air. A $\frac{1}{8}$ " opening should be provided at the discharge piping of the deaerator heater. The sample should be cooled to 50-70°F. Braze all connections to eliminate air entrainment and do not use red lead for joints. Use brass fittings. Boil rubber tubing in caustic soda to remove sulphur. Flush the sample bottle through to expel all air before stoppering. The sample bottle should be about 600 mls capacity, have a narrow neck and tightly-fitting glass stoppers.

DETERMINATION OF SULPHITES

- Reagents** (i) N/50 iodine solution. Weigh out 2.54 gms of pure iodine and make up to 1 litre. Store in a dark place. Standardise against N/50 $\text{Na}_2\text{S}_2\text{O}_3$.
 (ii) N/50 $\text{Na}_2\text{S}_2\text{O}_3$.
 (iii) 2N HCl.
 (iv) Starch indicator.

Procedure—To 20 mls N/50 iodine solution add 500 mls sample and 5 mls 2N HCl. Titrate excess iodine against N/50 $\text{Na}_2\text{S}_2\text{O}_3$ using starch indicator.

It may be necessary to vary the quantity of iodine used depending on the sulphite content.

$$\text{Sulphite} = 2.52 \times \frac{(\text{mls } \text{I}_2 \text{ used} - \text{mls } \text{Na}_2\text{S}_2\text{O}_3)}{\text{mls sample}} \times 1000 \text{ ppm } \text{Na}_2\text{S}_2\text{O}_3$$

DETERMINATION OF SOLUBLE SILICATES

Discussion—The method is a colorimetric one using the Hilger 810 Biochem Absorptiometer. The yellow colour produced by the reaction between silicic acid and acid molybdate solution is compared with standard comparison solutions containing either potassium chromate or picric acid. The methods are applicable up to 50 ppm SiO_2 . Phosphates and arsenates interfere, as do reducing substances such as Fe^{++} ion and H_2S , which give a blue colour. Fe^{++} up to 20 ppm can be tolerated and $\text{PO}_4^{=}$ ions can be rendered inactive by addition of ammonium citrate.

(a) Potassium Chromate Standard

- Reagents** (i) A.R. ammonium molybdate. 30 gms dissolved in 200 mls of 1 : 1 HCl and 400 mls distilled water.
 (ii) Standard comparison solution. 0.630 gms A.R. potassium chromate in 100 mls distilled water. 1 ml diluted to 50 mls = 20 ppm SiO_2 .
 (iii) Ammonium citrate (20 per cent. w/v).

Method—To 50 mls of sample, filtered if not clear, add 5 mls of molybdate reagent. Stir and allow 15 minutes for colour, if any, to develop. Measure the colour density using a No. 3 filter with a peak wavelength of 490 mu.

All colorimetric methods assume Beers dilution law is valid for the limits studied. Prepare a calibration chart using the standard comparison solution for SiO_2 contents 0-50 ppm. Read the SiO_2 value of the sample direct from this chart.

If phosphates are present add 5 mls ammonium citrate solution.

(b) Picric Acid Standard

- Reagents** (i) A.R. ammonium molybdate (10 per cent. w/v).
 (ii) H_2SO_4 (6.25 per cent. v/v).
 (iii) Picric acid (0.04 per cent. w/v).
 1 ml diluted in 50 mls distilled water = 10 ppm SiO_2 .

Method—Prepare a standard curve by diluting 0.5-3.0 mls standard picric acid solution in 50 mls distilled water. This gives a colour range corresponding to 5-30 ppm SiO_2 . Read the

colour densities on a suitable colorimeter and obtain a plot of colour density vs. SiO_2 content.

To 50 mls sample add 2 mls molybdate solution and 2 mls acid. Mix and allow 10 minutes for colour to develop. Observe colorimetric density and read off SiO_2 content from chart.

DETERMINATION OF IRON

The method is a colorimetric one using the Hilger Absorptiometer, depending on the colour produced by the action of thioglycollic acid on iron, both ferrous and ferric, in the presence of ammonia. The method is not appreciably disturbed by relatively large amounts of Al^{+++} , Ca^{++} , Mg^{++} ions or the alkali metals, while sulphates, phosphates and nitrates do not interfere. Zinc, however, depresses the intensity of the colour due to iron.

- Reagents** (i) Citric acid (20 per cent. w/v).
 (ii) Thioglycollic acid. Reagent quality.
 (iii) Ammonia solution (10 per cent. w/v).

Method—Take a suitable volume of sample (say 5 mls), make slightly acid, and add 0.5 mls of the 20 per cent. citric acid solution. Mix and add 1 drop of glycollic acid. Again mix and add 1 ml ammonia solution, or sufficient to render distinctly alkaline. Dilute with distilled water to 10 mls and read the colour density on the absorptiometer. The true density must be determined by subtracting the density produced by a blank solution using distilled water instead of sample.

The density thus produced is compared with a calibration chart employing known iron concentrations with their corresponding density values.

DETECTION OF TRACES OF SUGAR

- Reagents** (i) Alpha-naphthol (20 per cent. alcoholic solution).
 (ii) Concentrated H_2SO_4 (Sp. 1.83).

Method—To 2 mls of sample add 5 drops of alpha-naphthol solution. By means of a pipette slowly pour down the side of the test-tube 5 mls of concentrated H_2SO_4 . In the presence of sucrose a violet zone or ring appears at the junction of the two liquids. The depth of colour depends on the sucrose present and forms the basis of a colorimetric determination for traces of sucrose.

The reaction described above can be carried out by other phenols, e.g. thymol, menthol, resorcinol, lysol or cresol. Cresol can detect 1 ppm sucrose, produces stable colours varying from pale pink to reddish black depending on sucrose content, and unlike alpha-naphthol is unaffected by impurities such as iron and lime salts. Alpha-naphthol due to its great colour sensitivity is more popular.

Dr. Douwes Dekker recalled that the Sugar Milling Research Institute had been asked to undertake investigations in boiler feed difficulties, and said that Mr. Boyes had put forward a paper which would initiate considerable discussion.

Mr. Bouvet asked if the high pH over 10 recommended for boiler water would not be conducive to priming.

Mr. Boyes said that that figure was recommended by both the I.C.I. and Babcock & Wilcox. He did not think that this would be conducive to priming provided the total solids were kept to a low figure.

Dr. Douwes Dekker pointed out that priming would occur at such high pH if the organic matter

in the boiler water were high. He pointed out that it was necessary to keep a close watch on the organic matter in the boiler water. In this connection sugar was particularly important. He did not think it necessary to work at a higher pH with our present medium pressure boilers.

Mr. Phipson asked if the corrosion was due to the dissociation of magnesium chloride.

Mr. Boyes replied saying that he was not thinking of corrosion due to chlorides but rather to the dissociation of water itself.

Mr. Lindemann considered that caustic embrittlement could not be prevented by any chemical treatment because it was due merely to bad workmanship in the boiler construction. It was found only in seams below the water level of the cross-drum type of water tube boiler. He said in America it was shown that this so-called "caustic embrittlement" was not found in boilers up to 200 lbs. per square inch pressure. The Germans called this embrittlement "hydrogen disease." In the latest treatment of boiler plates, there was no trace of hydrogen present. In his experience a pH of 7.5 to 8.5 was best. He did not consider scaling of vertical boiler shells a serious matter. It helped in insulation. He thought that the methods of boiler water control suggested could not be universally applied to all boilers.

Mr. Boyes agreed with Mr. Lindemann's ideas on caustic embrittlement. He had inquired of the I.C.I. if it were worthwhile taking caustic embrittlement

into account, and they expressed the view that until the theory and effects of caustic embrittlement were clarified a definite sodium sulphite/sodium hydroxide ratio should be adhered to.

Mr. Phipson considered that if the scaling of boiler drums could be considered as insulation, what about scaling of tubes? Would that not interfere with the transference of heat?

Mr. Gunn related that as a consequence of a flood the pH of the boiler water dropped because of the extra organic matter present. This led to a large number of boiler tubes being seriously affected.

Mr. Phipson said that high pH was found to be useful but in recent years when the pH had been allowed to drop at Empangeni, corrosion was becoming a serious factor. Some of their trouble might of course be due to dissolved oxygen as well as to the presence of oil. They were now considering using sodium sulphite to reduce the oxygen.

Dr. Douwes Dekker pointed out that the high pH of itself would lower the activity of the oxygen present. We had now been given the methods of analysis of boiler feed water. He hoped that at some future date the results of boiler feed water treatment at Tongaat would be recorded.