

## Rapid Methods of Boiler-water Analysis

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Methods are described for the rapid analysis of boiler-water samples, particularly those from high-pressure boilers. The total acidity of a sample that has been treated with a cation-exchange resin is found, after which the phosphate is determined by a simple titrimetric procedure. The chloride concentration is found by the oxycyanide method and the sulphate by difference. Possible interference is examined, and a method for the determination of sulphite is suggested.

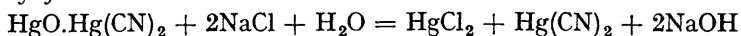
WATER samples from high-pressure boilers (above 400 lb per sq. inch) and, in particular, power-plant boilers, usually contain only hydroxide, orthophosphate, sulphate, chloride and silicate, normally as their sodium salts. Sometimes, in plant working below 600 lb per sq. inch, sodium sulphite can be used as an oxygen scavenger and, in a few very isolated instances, tannins, often combined with hexametaphosphate, can be added. Tannins are, however, generally little used in high-pressure plant, and sulphite may even be deleterious.

Boiler-water analysis, therefore, consists in determining orthophosphate, sulphate, chloride and silica, hydroxide often being found by computation. This is a lengthy task when carried out by conventional analytical methods and some of the results may be of doubtful value. It appeared that a cation-exchange process could be usefully applied in the determination of at least some of the constituents of a normal boiler-water sample. Although apparently not widely applied in this country to boiler water, ion-exchange methods have been reported in another country.<sup>1</sup> It was also intended to examine and apply, if satisfactory, methods for phosphate and chloride determination not generally used in boiler-water analysis.

### EXPERIMENTAL

#### CHLORIDE—

It has been customary in boiler-water analysis to determine chloride by the classical Mohr titration, after first suitably adjusting the pH value, but this method has been much criticised and its unsuitability is well known. It was considered that a more reliable method was required. Of the titrimetric methods available, that due to Vieböck<sup>2</sup> appeared most attractive. In this procedure, the neutralised sample is allowed to react with a solution of mercuric oxycyanide. The reaction involved is—



and the liberated sodium hydroxide is titrated with standard acid.

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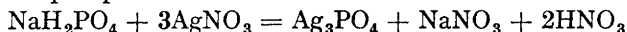
In the routine analysis of boiler water, it is essential to determine the total alkalinity in order to determine later the sodium hydroxide concentration. In our laboratory, alkalinity is determined by titration with 0.1 *N* sulphuric acid, B.D.H. "4.5" indicator being used. This appeared to be a convenient point at which to apply the Vieböck reaction, the liberated alkali being titrated to the end-point of B.D.H. "4.5" indicator. Experimental work confirmed that chloride could be determined in this way.

Belcher, Macdonald and Nutten<sup>3</sup> have studied the Vieböck reaction and have found that it is not always stoicheiometric. They have suggested applying a comparison titration procedure with a standard solution of sodium chloride. This method was examined, but, despite its excellence, it was decided that the small errors involved in the present work did not justify the extra expenditure of time, and the direct titration was adopted.

#### PHOSPHATE—

It is usual in boiler-water analysis to determine phosphate by one of the conventional methods depending on the formation of the molybdenum-blue colour. Results are excellent when a photometric finish can be applied, but when visual comparison is necessary an alternative method would be valuable.

Töller<sup>4</sup> has suggested that for phosphate contents greater than 5 p.p.m. as  $P_2O_5$  (approximately 10 p.p.m. as  $Na_3PO_4$ ) the absorptiometric method is not sufficiently accurate and has suggested the use of a simple volumetric procedure. In this, the phosphate is brought to the dihydrogen stage and sufficient silver nitrate is added to precipitate all the chloride and phosphate. The phosphate reacts as follows—



and the liberated nitric acid is titrated with standard alkali.

Previous work<sup>5</sup> had proved the accuracy and convenience of this procedure and originally the method was designed around this reaction. More recently, however, a similar procedure has been described,<sup>6</sup> in which silver nitrate is replaced by cerous nitrate. The mechanism is similar, but, since cerous chloride is soluble, the bulk of the precipitate formed is considerably less and end-points are much more distinct.

It was at this stage that an ion-exchange technique was applied. In the phosphate determination it is immaterial whether the original solution is acid or alkaline, since it is brought to the dihydrogen phosphate stage, *i.e.*, pH 4.5, before the reaction with cerous or silver nitrate. By passing the boiler water through a small column of cation-exchange resin in the hydrogen form, the total acidity owing to the conversion of all the salts present to the corresponding acids could be found and used in the subsequent determination of sulphate.

The sample, after being treated with a cation-exchange resin, was boiled to remove carbon dioxide and then titrated with standard alkali to the end-point of methyl red - methylene blue indicator. Excess of a neutralised cerous nitrate solution was added and the liberated nitric acid was titrated with 0.02 *N* alkali to the same end-point. The original total-acidity titration was normally carried out with 0.1 *N* alkali, but, with samples of low dissolved-solids content, it was found preferable to use 0.02 *N* alkali. When 0.1 *N* alkali was used, it was found advisable to add a drop of 0.1 *N* acid, and to adjust the end-point with 0.02 *N* alkali to guard against over-titration. In all the titrimetric work described micro-burettes were used.

The results have been excellent with both silver and cerous nitrates. Some slight difficulty was experienced in dealing with very low phosphate contents, particularly when silver nitrate was used, but this was readily overcome by first adding a known amount of a standard phosphate solution previously neutralised to methyl red - methylene blue indicator. The necessity for the addition of standard phosphate may readily be judged from the amount of colour change of the indicator after adding the silver or cerous nitrate solution. With cerous nitrate solution the lower limit of phosphate determinable was considerably less than with silver nitrate and the results were good even with only 1 or 2 p.p.m. (as  $Na_3PO_4$ ) present.

Because of its many advantages, the use of cerous nitrate has been adopted as routine practice.

#### SULPHATE—

The conventional methods of determining sulphate in boiler water are the gravimetric barium sulphate method or the benzidine procedure with a volumetric finish. The distinct

solubility of the precipitate renders the benzidine method of doubtful value. In the presence of phosphate, the classical barium sulphate precipitation is open to considerable criticism. Previous work<sup>5</sup> had shown that the results are erratic and, in the present investigation, a barium sulphate precipitate was found to contain a considerable amount of phosphate.

In the proposed method, when the total acidity after cation exchange and the acidity equivalent to the chloride and phosphate by the Vieböck and cerous nitrate titrations, respectively, have been determined, the acidity equivalent to the sulphate, normally the only other anion present after ion exchange, may be found by difference. (In this connection it must be remembered that, although two equivalents of nitric acid are liberated in the phosphate method, only one equivalent of the phosphoric acid formed by cation exchange is titrated.)

In order to assess the accuracy of the proposed methods, artificial boiler-water samples were prepared and analysed. A sufficient range of composition was chosen to simulate conditions likely to arise in modern steam-raising practice. Pure sodium chloride, disodium hydrogen phosphate and sodium sulphate were used in the preparation of the samples. The results are shown in Table I. These results indicate that the methods are satisfactory over a wide range of boiler-water composition. The figures for phosphate determination show that cerous nitrate yields somewhat better results than silver nitrate and it is considerably easier to find the correct end-point when cerous nitrate is used.

TABLE I  
ANALYSIS OF SYNTHETIC BOILER-WATER SAMPLES

Sample No.	Chloride, p.p.m. as NaCl—		Phosphate, p.p.m. as Na <sub>3</sub> PO <sub>4</sub> —			Sulphate, p.p.m. as Na <sub>2</sub> SO <sub>4</sub> —		
	present	found	present	found by—		present	found by—	
				silver nitrate method	cerous nitrate method		silver nitrate method	cerous nitrate method
1	150	150 150	80	79 78	79 80	130	130 133	130 133
2	100	100 101	5	4 4	5 5	100	104 99	100 99
3	20	20 19	50	49 50	50 50	50	52 50	49 51
4	20	20 20	20	19 21	19 19	20	22 20	22 20
5	6	7 7	10	10 8	10 9	5	5 4	5 4
6	20	19 20	80	79 78	80 79	20	19 19	20 19
7	80	80 81	1	0 0	2 2	80	80 82	80 81
8	50	50 49	5	4 6	5 5	100	103 104	102 103
95 per cent. confidence limits		+1.5		+2.0	+1.4		+4.0	+3.0

#### METHOD

#### REAGENTS—

*Sulphuric acid, 0.1 and 0.02 N.*

*Sodium hydroxide, 0.1 and 0.02 N.*

*Mercuric oxycyanide solution*—Prepare a solution containing 20 g per litre. Remove 10 ml and add to 50 ml of distilled water neutralised to B.D.H. "4.5" indicator. Titrate this aliquot with 0.02 N sulphuric acid to the end-point of B.D.H. "4.5" indicator, using a micro-burette. Now add the calculated volume of 0.02 N sulphuric acid to the remainder of the oxycyanide solution and mix thoroughly. Test for neutrality by adding 10 ml to 50 ml of distilled water neutralised to B.D.H. "4.5" indicator. No colour change should occur. (This method of neutralisation is better than straightforward titration of the main solution, owing to the buffering action of mercuric oxycyanide.)

*Cerous nitrate solution*—Dissolve 25 g of cerous nitrate free from other rare-earth metals in distilled water. Neutralise to methyl red - methylene blue indicator and dilute to 1 litre.

*Methyl red - methylene blue indicator*—Dissolve 0.125 g of methyl red in 50 ml of ethanol; dissolve 0.083 g of methylene blue in 50 ml of ethanol. Mix equal volumes of these solutions.

#### PROCEDURE FOR DETERMINING CHLORIDE—

Titrate a 50-ml sample of boiler water with 0.1 *N* sulphuric acid (or 0.02 *N* if the alkalinity is low) to the end-point of B.D.H. "4.5" indicator.

Add 10 ml of neutralised mercuric oxycyanide solution and mix well. Titrate with 0.1 or 0.02 *N* sulphuric acid to the same end-point as before. The volume of 0.1 *N* sulphuric acid, in ml, multiplied by 117 (or 23.4 for the 0.02 *N* acid) gives the concentration of chloride, as p.p.m. of NaCl.

#### PROCEDURE FOR DETERMINING TOTAL ACIDITY AND PHOSPHATE—

Pass the boiler water through a column of Zeo-Karb 225 resin (hydrogen form), approximately 20 cm × 1.5 cm. Reject the first 20 to 30 ml of effluent and collect 50 ml over a period of 2 to 3 minutes. Boil the effluent to remove carbon dioxide (and sulphur dioxide if sulphite is present), cool and add methyl red - methylene blue indicator. By using a micro-burette, titrate with 0.1 *N* sodium hydroxide (or 0.02 *N* if a small titre is expected). This gives the total acidity. If 0.1 *N* sodium hydroxide is used, add a drop of 0.1 *N* sulphuric acid after the total acidity has been determined and adjust the end-point with 0.02 *N* sodium hydroxide before proceeding with the phosphate titration.

Add 5 ml of cerous nitrate solution, mix well and titrate to the same end-point with 0.02 *N* sodium hydroxide. The volume of 0.02 *N* sodium hydroxide, in ml, multiplied by 32.8 gives the concentration of phosphate, as p.p.m. of Na<sub>3</sub>PO<sub>4</sub>.

#### CALCULATION OF THE SULPHATE CONTENT—

Convert the total acidity and chloride titrations to the equivalent volumes of 0.02 *N* acid, then—

$$[A - (C + 0.5 P)] \times 28.4 \equiv \text{amount of sulphate, as p.p.m. of Na}_2\text{SO}_4,$$

where *A* = volume of 0.02 *N* sodium hydroxide, in ml, used for total acidity,

*C* = volume of 0.02 *N* sulphuric acid, in ml, used for chloride, and

*P* = volume of 0.02 *N* sodium hydroxide, in ml, used for phosphate.

#### POSSIBLE INTERFERENCES IN THE METHOD

Of the constituents found in boiler water apart from those already mentioned, only silicate, nitrate, sulphite and tannin will appear in amounts likely to affect the determination under consideration.

Silicate is present in boiler water in amounts ranging from 1 or 2 to between 20 and 30 p.p.m. (as SiO<sub>2</sub>), and, especially at pressures exceeding 600 lb per sq. inch, its ingress is closely controlled. In the present series of experiments, up to 20 p.p.m. of SiO<sub>2</sub> had no deleterious effect.

The presence of nitrate in a high-pressure boiler arises only from contamination by cooling water and the nitrate content is unlikely to rise above a few parts per million. Such amounts are of no operational consequence, and would be calculated as sulphate. Should nitrate be present in significant amounts, it would have to be determined separately and its equivalent acidity deducted from the acidity equivalent to the sulphate. A method for the titrimetric determination of nitrate has been proposed by Ungar.<sup>7</sup>

As indicated earlier, the use of sulphite has largely disappeared, but it is employed in some units that work below 600 lb per sq. inch. It is normal in these waters to add 10 p.p.m. of sulphite (as Na<sub>2</sub>SO<sub>3</sub>), but amounts up to 50 p.p.m. are not unknown. No sulphite is used in our boilers, but it was deemed advisable to investigate its effect.

There is no interference from sulphite in the determination of phosphate, since, after cation exchange and boiling, sulphur dioxide is expelled. In the Vieböck chloride method up to 50 p.p.m. of sodium sulphite had no ill effect.

During the period in which the methods above were being examined by other Divisions of the C.E.A., it was reported<sup>8</sup> that, for a boiler in which a proprietary compound consisting

of tannin and sodium hexametaphosphate (Alfloc "28" powder) was used, the results were very erratic when the original Töller method<sup>4</sup> was applied.

This was, in fact, found to be so. The tannin interference can, however, be removed by treating the sample with charcoal free from inorganic impurities. The boiler-water sample is then filtered and passed through the column of Zeo-Karb 225, and the total acidity and phosphate are determined by the proposed method. Tannins do not interfere in the Vieböck chloride method.

The sodium hexametaphosphate present in the Alfloc "28" powder is, under boiler operating conditions, rapidly hydrolysed to orthophosphate and is therefore included in the phosphate determination.

#### DISCUSSION

The method as outlined has been used successfully in the authors' laboratory for many months. It has yielded excellent results, which relate to operational practice more closely than when conventional methods were used.

It is found convenient to use a set of four columns. When a sample has been dealt with on a column, it is found that the rejection of the first 20 to 30 ml of the subsequent sample provides sufficiently thorough rinsing of the column. The frequency of regeneration of the columns with dilute acid is a matter of experience and depends on the salt concentration of the water samples.

The saving in time over the conventional methods is substantial. One ion-exchange process and four simple titrations enable all except the silica and sodium hydroxide concentrations to be determined, compared with the more laborious processes of dealing separately with each ion by titrimetric, colorimetric or gravimetric methods.

We have found a Kipp tilt-measure of appropriate capacity excellent for addition of the mercuric oxycyanide and cerous nitrate solutions, the volumes of which need not be exact.

Although the use of silver nitrate for phosphate has been abandoned, it still yields good results. It is used in the same concentration as cerous nitrate.

#### SUGGESTED METHOD FOR SULPHITE

Neutralise a 50-ml sample of boiler water to thymol blue - phenolphthalein indicator. Add a solution of formaldehyde (2 g per 100 ml) neutralised to the same indicator. Titrate the resulting alkaline solution with 0.02 N acid to the same end-point. The volume of 0.02 N acid, in ml, multiplied by 50.4 gives the concentration of sulphite, as p.p.m. of  $\text{Na}_2\text{SO}_3$ .

As previously stated, sulphite is not used in our boilers, but the results with synthetic solutions are encouraging.

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#### REFERENCES

1. Leick, J., *Mitt. Ver. Grosskesselbesitzer*, 1954, 67.
2. Vieböck, F., *Ber.*, 1932, 65B, 496.
3. Belcher, R., Macdonald, A. M. G., and Nutten, A. J., *Mikrochim. Acta*, 1954, 104.
4. Töller, W., *Mitt. Ver. Grosskesselbesitzer*, 1946, 88.
5. Banks, J., unpublished work.
6. Rancke-Madsen, E., and Kjaergard, T., *Acta Chem. Scand.*, 1953, 7, 735.
7. Ungar, J., *J. Appl. Chem.*, 1956, 6, 245.
8. Central Electricity Authority, South Wales Division, unpublished work.

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