The Spectrophotometric Determination of Small Amounts of Oxygen in Waters

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This paper describes the development of a method for the determination of dissolved oxygen in boiler feed waters applicable to concentrations in the range 0·001 to 0·1 ml of oxygen per litre, with a precision better than 0·001 ml at the lower concentrations. The method is based on that of Bairstow, Francis and Wyatt, but the precision is improved by avoiding the use of starch and by determining the liberated iodine by means of the ultra-violet absorption of the tri-iodide ion. The procedure has been simplified by the elimination of the step involving volumetric dilution before photometric measurement.

The increasing use of high pressures in boiler plant has shown the need for a reliable method for the determination of concentrations of dissolved oxygen in feed waters at least as low as 0·002 ml per litre. An excellent review of the analytical methods available for the determination of oxygen has been given by Bairstow, Francis and Wyatt.[1] The most promising method now available appears to be that devised by these workers; this uses the same reaction as the well-known Winkler method, but the liberated iodine is determined absorptiometrically after the addition of starch. The effect of interfering substances is automatically compensated for by performing duplicate tests on each sample, in one of which the order of addition of the reagents is altered so that only the interfering substances react.

Bairstow *et al.* have paid close attention to the drawbacks associated with the use of the starch - iodine - iodide system for quantitative absorptiometric analysis, and they have included appropriate precautions in their procedure, such as the control of temperature, the recalibration with fresh starch stocks and the addition of a small amount of iodine to the system immediately before the addition of starch, to correct for the non-linear relation between the formation of the blue complex and the iodine concentration in the very low concentration ranges.[2] This method has been further studied by Pieters and Hanssen,[3] who showed that greater stability of the blue complex could be achieved by the addition of potassium sulphate. Nevertheless, they do not claim to determine oxygen contents below 0·0035 ml per litre.

Method

In another application, Ovenston and Rees[4] have drawn attention to the advantages to be gained over the starch method for determining small amounts of iodine, by making use of the strong absorption shown by the tri-iodide ion at 353 mμ. It was decided to apply this principle to the method of Bairstow *et al.* in an attempt to extend the range to cover lower concentrations.

The procedure finally adopted, given in detail below, is substantially the same as that recommended by these authors to the point at which the iodine is liberated, except that a higher concentration of potassium iodide is used to ensure satisfactory tri-iodide formation. Further manipulations have been simplified by arranging that a part of the solution is placed directly into the spectrophotometer cuvette without the necessity for any volumetric dilution; this enables maximum photometric sensitivity to be attained.

The samples of water of low oxygen content required for the development of this method were provided at first by passing a stream of pure nitrogen through a large aspirator containing distilled water. Subsequently, water from the outflow of a de-aerating condenser was used.

Apparatus—

Sample tubes—These are similar to the Romijn pipettes described by Pieters and Hanssen, and they have a capacity of 50 ± 2 ml between the taps. Both stems carry zero graduation marks close to the taps and one stem is graduated at 0·2 ml beyond the zero mark while the other stem is graduated at 0·4 ml beyond the zero mark. The volume between the taps

and the zero marks is unimportant. A pair of these sample tubes is required for each determination.

The internal surfaces of the tubes must be free from adsorbed impurities capable of reacting with potassium iodide. It has been found satisfactory to cleanse the tubes with warm water containing Teepol, followed by copious rinsing with pure water then with warm dilute sulphuric acid, and further rinsing with water. On no account should chromic acid mixture be used.

REAGENTS—

All reagents should be of recognised analytical grade.

Alkaline potassium iodide solution—Dissolve 300 g of sodium hydroxide and 430 g of potassium iodide in water and make up to 1 litre.

Manganous sulphate solution—Dissolve 450 g of manganous sulphate tetrahydrate in water and make up to 1 litre.

Sulphuric acid, approximately 18 N.

Standard iodine solution, for the preparation of the calibration graph—Prepare a preliminary solution by dissolving 1·2 g of iodine and 10 g of potassium iodide in 1 litre of water, and standardise the solution with 0·01 *N* thiosulphate. Dilute accurately a suitable aliquot 500 times with distilled water to give the standard solution (containing about 2·4 μg of iodine per ml).

Potassium iodide solution, for the preparation of the calibration graph—Prepare a 21·5 per cent. w/v aqueous solution of potassium iodide by dissolving the solid in distilled water.

Before use, the first three reagents must be de-oxygenated. This is done by passing a stream of oxygen-free nitrogen through each reagent for about half an hour, preferably when the reagent is in its storage bottle. The latter should be fitted permanently with an alkaline pyrogallol solution trap at the inlet, through which a slight pressure of nitrogen can be applied subsequently in order to facilitate delivery of the reagent by way of an outlet tube fitted with a tap. The end of the delivery jet should be narrow enough to allow it to reach the base of the stem of the sample pipette.

PROCEDURE—

Feed the water to be tested through a Y-tube connected, by means of rubber tubing fitted with screw clips, to the lower stems of two sample pipettes. Allow the water to flow up and out at the top stems and lead it to waste through rubber tubing. Take care that no air bubbles are trapped in the pipettes. Pass at least 300 ml of the sample through each pipette, then stop the flow, close the top taps of the pipettes and tighten the screw clips. Remove the rubber tubing from the top stems and also the Y-tube from the tubing attached to the lower stems.

The lower taps on the pipettes should not be closed until the actual determination can be carried out, which should be delayed as little as possible after taking the samples. As the sample is usually warmer than room temperature, a gradual contraction takes place inside the pipette, but the elasticity of the piece of rubber tubing attached to one end of each pipette offsets the risk of air being drawn into them.

Clamp the pipettes vertically, side by side, with the stems bearing the 0·4-ml graduation uppermost. Allow them to stand for 5 minutes, then close the second pair of taps and remove the tubing. Remove the bulk of the water left in the stems. (A narrow tube connected to a filter-pump is useful for this purpose.) Remove the last traces of water from the stems by means of filter-paper and fill them to the 0·4-ml graduation with alkaline potassium iodide reagent, taking care to prevent needless contact with air. Introduce 0·4 ml of the reagent into each pipette by opening first the upper taps and then controlling the flow by means of the lower taps until the level of the reagent has fallen to the zero graduation; then close all taps again, the lower taps first. Mix the contents of the pipettes by a rocking motion, replace the pipettes in the clamps in the same position and wash out the stems with distilled water. Invert the pipettes and dry the stems with filter-paper, the 0·2-ml graduation now being uppermost.

Fill the stem of one of the two pipettes (the oxygen-determination pipette) to the 0·2-ml graduation with manganese sulphate reagent, and introduce 0·2 ml of the reagent into the pipette as already described. Mix the contents and allow the pipette to stand for about 3 minutes, rocking it once or twice during this period, to ensure complete reaction between

the precipitated manganous hydroxide and the dissolved oxygen. Wash the pipette, dry the same stem again and then introduce 0·2 ml of 18 *N* sulphuric acid. Rock the pipette occasionally during 3 minutes to ensure complete dissolution of the precipitate.

At the same time introduce 0·2 ml of 18 *N* sulphuric acid followed by 0·2 ml of manganous sulphate reagent into the other pipette (the blank-determination pipette). No precipitate is formed in this pipette, and the time intervals between the introductions of reagents are not important.

Wash out the uppermost stem (with 0·2-ml graduation) of each pipette and dry it. Open the upper taps and by means of the lower taps allow sufficient of the solutions to pass through the lower stems to ensure that the liquid trapped in the bores of the lower taps is washed away. (The entry into the pipettes at this stage of the small amount of acid left in the bores of the upper taps does not matter.)

Fill 4-cm cuvettes with the remaining solutions and measure their optical densities at 353 mμ by means of a spectrophotometer. (Measurements must be made within 20 minutes of the introduction of the acid into the pipettes.) Deduct the optical density of the blank from that of the oxygen sample and determine the oxygen content of the water from the calibration graph.

Preparation of the calibration graph—

Measure into separate 50-ml calibrated flasks 0·5, 1, 2, 3, 4, 5, 10, 20, 30, 40 and 50-ml volumes of standard iodine solution and make each aliquot up to 50 ml with distilled water. To each flask add 0·8 ml of 21·5 per cent. w/v potassium iodide and mix the contents. The omission of the sodium hydroxide, sulphuric acid and manganous sulphate does not affect the slope of the calibration graph, but does improve the stability of the standards.

Prepare at the same time a blank consisting of 50 ml of water (free from standard iodine solution) to which 21·5 per cent. w/v of potassium iodide has been added, as described for the standards.

Measure the optical density at 353 mμ of each standard and of a blank in 4-cm cuvettes. Deduct the optical density of the blank from each of the standard optical densities, and plot the differences against concentration of dissolved oxygen in ml per litre, knowing the actual quantity of iodine added to each standard and noting that 1 mg of iodine (in 50 ml) is equivalent to 0·882 ml of oxygen per litre.

In practice it is convenient to construct a separate calibration graph for the lower part of the range, covering optical densities up to 0·1 as found from the first six standards.

Oxygen in reagents—

Owing to the fact that any oxygen in the reagents is active in the oxygen-determination sample and not in the blank-determination sample, because of the altered order of addition of reagents to the latter, it has been the custom of earlier workers[1,3] to correct the final result by deducting the amount of oxygen present in the small volumes of added reagents. This correction was usually about 0·005 ml of oxygen per litre.

For the present purpose it was considered that a correction of this magnitude, liable to slight variation, would materially reduce the accuracy of the method at the lower end of the range. By de-oxygenating the reagents as described, the oxygen content can be reduced to a negligible amount, which makes a correction unnecessary.

Concentration of potassium iodide—

The alkaline iodide reagent used by Bairstow *et al.* contained only sufficient iodide to bring the iodide molarity of the final solution to between 0·003 and 0·004. At this concentration significant dissociation of tri-iodide occurs and the proposed method of measurement would not be feasible.

By increasing the iodide concentration of the reagent to 430 g per litre and the volume taken to 0·4 ml, the final molarity was raised to 0·02. Although this is still lower than the value of 0·1, which is regarded as ideally desirable for this system,[4] only an insignificant loss in sensitivity occurs, and an error of 5 per cent. in the reagent addition results in one of but 0·5 per cent. in the determination.

LINEARITY OF CALIBRATION—

In the analytical range for which this method is designed, the calibration graph is a straight line passing through the origin. No deviation from Beer's law occurs at the lower concentrations in contrast to that observed when starch is used.

With a Unicam model SP500 spectrophotometer set at 353 mμ, it was found that 0·1 ml of oxygen per litre in the sample was equivalent to an optical density of 0·82 for a 4-cm optical depth.

STABILITY AND EFFECT OF TEMPERATURE—

The stability with time of the iodine - iodide - tri-iodide system depends on pH, being greatest for nearly neutral solutions. It is inevitable after the dissolution of the manganous hydroxide that the residual solution should be slightly acid and the residual acid normality is about 0·01. The conditions, therefore, correspond to those for experiment B described in the earlier paper by Ovenston and Rees,[4] from which it may be judged that sufficiently reliable results can be expected at this acidity provided that the taking of measurements is not long delayed.

In practice it has been found that the results are satisfactory when the spectrophotometric measurements are made within 20 minutes of the acidification of the solution. Any scheme for the batching of samples for routine analytical purposes should therefore take this into account.

Slight variations of temperature within a range of 10° C do not affect the extinction coefficient of the solution significantly, but it is preferable for the working temperature to be kept as low as is convenient because the stability of the tri-iodide decreases with rise in temperature. It is necessary for the solutions after acidification to be shielded from direct sunlight for a similar reason.

EFFECT OF IMPURITIES—

With the twin pipette technique, in which the oxygen is allowed to contribute to the total iodine release in only one of the pipettes, the effect of other oxidising impurities in the water is automatically compensated for, provided that these impurities are in solution. Care must still be taken to avoid small pieces of oxide scale from finding their way into one of the pipettes.

The method similarly compensates for very small amounts of reducing impurities in solution, provided these are not sufficient to reduce the optical density of the blank to zero. A zero blank optical density would indicate the presence of a probable excess of reducing impurity, and the determination would accordingly be rendered useless. If excessive amounts of reducing impurities are present, these can be compensated for by dissolving a sufficient quantity of iodine in the alkaline potassium iodide reagent to ensure a positive blank optical density.

REPRODUCIBILITY OF RESULTS

For the purpose of checking the reproducibility of the method for low oxygen contents a series of determinations was carried out in duplicate, that is, one blank and two oxygen determinations per set. The results, shown in Table I and found by an analyst already familiar with the method, suggest that the method can provide useful analytical figures to 0·001 ml or less of oxygen per litre.

COMMENTS ON A POSSIBLE EXTRACTION MODIFICATION

The sensitivity of the method would be improved if the liberated iodine could be concentrated by extraction into a comparatively small volume of chloroform or carbon tetrachloride. For this purpose it would be necessary to reduce the iodide content of the alkaline potassium iodide reagent to the absolute minimum in order to encourage dissociation of the tri-iodide complex.

There would be no point in extracting into such a solvent in order to measure the optical density of the molecular iodine in that solvent, because the extinction coefficient of iodine in such solvents at 510 mμ is only about one-thirtieth of that of iodine, as the tri-iodide complex, at 353 mμ. However, it has been found[5] that, by adding an equal volume of alcoholic

potassium iodide to a solution of iodine in chloroform or carbon tetrachloride, the iodine is practically completely converted to tri-iodide, and in this composite medium there is an extinction maximum at 360 mμ having about the same molar value as is found at 353 mμ in aqueous solution. With this reaction it would be necessary, therefore, to reduce the total volume of the solvent extract only to one-half in order to equal the sensitivity attainable without extraction and any further reduction should result in a gain.

An extraction procedure based on these principles was tried, but was abandoned because of the difficulty found in attaining reproducible extraction.

TABLE I

RESULTS FOR THE DETERMINATION OF OXYGEN IN WATERS OF LOW OXYGEN CONTENT

E_{blank}	$E_{samples}$	$E_{diff.}$	Oxygen per litre, ml	Duplicate differences
0·013	0·143	0·130	0·0151	0·0004
	0·146	0·133	0·0155	
0·015	0·071	0·056	0·0065	0·0007
	0·077	0·062	0·0072	
0·014	0·056	0·042	0·0049	0·0006
	0·051	0·037	0·0043	
0·013	0·198	0·185	0·0215	0·0005
	0·194	0·181	0·0210	
0·004	0·056	0·052	0·0060	0·0004
	0·052	0·048	0·0056	
0·007	0·084	0·077	0·0090	0·0005
	0·089	0·082	0·0095	
0·004	0·041	0·037	0·0043	0·0002
	0·043	0·039	0·0045	
0·004	0·040	0·036	0·0042	0·0004
	0·037	0·033	0·0038	
0·003	0·046	0·043	0·0050	0·0002
	0·048	0·045	0·0052	

ADAPTATION FOR USE WITH THE SPEKKER ABSORPTIOMETER

For the best results a spectrophotometer having a high performance in the near ultra-violet region is required. However, with a slight sacrifice of precision, a Spekker absorptiometer (or similar filter instrument) with a mercury-arc source may be used with Wood's glass filters. In order to make use of all the available radiant energy, the Spekker absorptiometer should be calibrated by setting the drum at zero with the standard in the light beam, and the drum difference is measured after moving in the blank. Similarly, when making the determination, the drum should be set to zero with the sample in the beam.

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