An Automatic Recording Analyzer for the Determination of Dissolved Oxygen in Boiler Feed Water[*1]

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In thermal power plants, the dissolved-oxygen content of feed water for boilers is rigidly controlled in order to prevent the corrosion of the boiler and other equipment. The allowable dissolved-oxygen content is less than a few parts per billion.

The dissolved-oxygen content of the feed water in these plants is usually determined by means of an analyzer with thermal conductivity cells.[1,2),*2] However, when hydrazin is used for reducing the dissolved-oxygen content, the results of oxygen determination by the above type of analyzer are erroneous. This is because nitrogen is formed during the treatment of the feed water with hydrazin, and the thermal conductivity of nitrogen is nearly the same as that of oxygen. Therefore, a new type of oxygen analyzer is required for the determination of dissolved oxygen in hydrazin-treated feed water. The design of such an analyzer was undertaken at this laboratory; it is described in this paper. The underlying principle is to determine the dissolved oxygen automatically by Winkler's method.[3,4)]

Although, while the present work was being conducted, Ridley et al.[5)] published a paper describing the design of an instrument for dissolved-oxygen determination by the same method, their instrument appears to be useful only when the dissolved-oxygen content is of the order of some parts per million. On the other hand, the instrument described in this paper is designed for determination in the range of oxygen concentration up to 50 parts per billion.

Outline of the Method and the Reagents Used

Method.—Briefly, the method involves two main steps: (1) the fixation of dissolved oxygen, and (2) amperometric titration. The dissolved oxygen is fixed by adding the following reagents to the sample water in the order named: an alkaline iodide solution (made alkaline with potassium hydroxide), a manganous sulfate solution, and a sulfuric acid solution. The reactions taking place in this step are the formation of manganous hydroxide (Eq. 1), the oxidation of manganous hydroxide to manganic hydroxide by dissolved oxygen (Eq. 2), and the liberation of iodine (Eq. 3).

$$MnSO_4 + 2KOH = Mn(OH)_2 + K_2SO_4 \quad (1)$$

$$2Mn(OH)_2 + 1/2O_2 + H_2O = 2Mn(OH)_3 \quad (2)$$

$$2Mn(OH)_3 + 2KI + 3H_2SO_4 = 2MnSO_4 + I_2 + K_2SO_4 + 6H_2O \quad (3)$$

*1 Presented at the Autumn Meeting of the Chemical Society of Japan, Tokyo, November, 1962.

1) D. M. Considine, "Process Instruments and Controls Handbook," McGraw Hill, New York (1957), pp. 6–184.

2) H. W. Holy, *Trans. Soc. Instr. Tech.*, **12**, 145 (1960).

3) ASTM Standards, Designation D888-49T (1949).

4) Japanese Industrial Standard, B8224 (1961).

*2 Although a variety of dissolved-oxygen analyzers have been developed in these several years, this type of analyzer has been most widely used.

5) J. E. Ridley, D. B. L. Elliott and A. B. Oaten, *Analyst*, **85**, 508 (1960).

As may be seen from Eq. 3, the iodine liberated is equivalent to the dissolved oxygen. The iodine is, therefore, amperometrically back-titrated with a standard solution of potassium iodate after the addition of an excessive thiosulfate solution.

A blank determination is also carried out in order to make a correction for the effect of the interfering substances both in the sample water and in the reagents. In this case, the reagents for oxygen fixation are added to the sample water in the following order: an alkaline iodide solution, a sulfuric acid solution, and a manganous sulfate solution. The titration is then performed in the same way as has been described above.

The dissolved-oxygen content is calculated from the difference between the quantities of titrant used in the sample and blank titrations by the following equation:

$$X=\frac{8\times10^6}{V}\{m(K'-K)-D\} \quad (4)$$

Where X=the dissolved-oxygen concentration in parts per billion (p. p. b.)
V=the volume of sample water taken for analysis, ml.
m=the concentration of the potassium iodate solution, N
K=the volume of the potassium iodate solution used in the sample titration, ml.
K'=the volume of the potassium iodate solution used in the blank titration, ml., and
D=the correction for the dissolved oxygen in the reagents.

In the present instrument, 550 ml. of sample water is analyzed by the use of the reagents described below; the quantities of reagents used for oxygen fixation are: 3 ml. of the alkaline iodide solution, 2 ml. of the manganous sulfate solution, and 3 ml. of the sulfuric acid solution. Therefore, Eq. 4 reduces to:

$$X=72.7\{(K'-K)-0.13\} \quad (5)^{*3}$$

This is a working formula for use with the present instrument. Although the concentrations and quantities of the reagents employed for oxygen fixation in the present method are different from those specified in the standard method, the present method gives the same results as the standard method.[*4]

Reagents.—The reagents used in the present instrument are as follows: Alkaline iodide solution (solution A): The concentrations of potassium hydroxide, potassium iodide, and iodine in the solution are: potassium hydroxide 8.3 N, potassium iodide 10%, and iodine 0.003 N.

Manganous sulfate solution (solution B): 32.5% solution.

Sulfuric acid solution (solution C): 18 N solution.

Standard potassium iodate solution: 0.005 N solution.

Thiosulfate solution: Approximately 0.005 N solution.

Automatic Recording Analyzer

A diagram of the automatic recording analyzer is shown in Fig. 1. This instrument was so designed as to perform automatically most of the operations involved in manual analysis, such as sampling, the addition of reagents, titration, recording, and cleansing. In order that such operations might be carried out in a systematic way, a time-cycle-control system was employed. The operations described below are automatically performed in the order of description.

Sequence of Operations.[*5]—*Cleansing and Sampling.*—The valves,[*6] V14, V12, V10, V13, and V11, are opened, and the water to be analyzed is passed through the two fixation vessels, K and L, for a fixed period of time in order to cleanse them. Thereafter, the valves are closed. Thus, the fixation vessels are filled with the sample water.

Fixation.—The fixation of dissolved oxygen in the fixation vessel, K, is carried out first. Solutions A, B, and C in the reservoirs are simultaneously fed to the respective reagent pipets, F, G, and H; then, after the pipets are filled with the reagents, the stirrer[*7] in the fixation vessel, K, is started. The reagents in the pipets are then injected into the fixation vessel in the following order: solution A, solution B, and solution C. When these solutions are forced into the fixation vessel, the surplus liquid in the vessel is drained from the top of vessel. After the injection of solution C is completed, the stirrer is stopped.

The blank operation in the fixation vessel, L, is carried out in the same way except that

*3 The value of D has been determined on the following ground. The concentrations of alkaline iodide and sulfuric acid solutions employed in the present method are, respectively, 2/3 the concentrations specified in the standard method; however, the quantities of these solutions used for dissolved-oxygen fixation are 1.5 times as large as the quantities specified in the standard method. The correction term, D, in Eq. 4 was calculated according to the equation of Adams et al.[6] and White et al.[7]

*4 For purposes of comparison, the results of analysis by the two methods are summarized in Appendix Table I.

*5 Wherever necessary, the literal symbols used to designate the parts of instrument in Fig. 1 are used in the description under this head.

*6 All the valves used in this instrument are of the electromagnetic type and systematically operated.

*7 This and two others (in vessels, L and M) are magnetic stirrers.

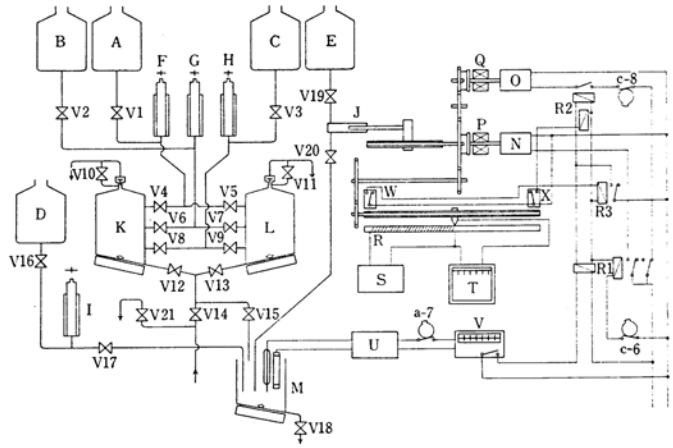

Fig. 1. Diagramatic representation of automatic recording analyzer.

A Reservoir for solution A
B Reservoir for solution B
C Reservoir for solution C
D Reservoir for sodium thiosulfate solution
E Reservoir for potassium iodate solution
F Reagent pipet for solution A
G Reagent pipet for solution B
H Reagent pipet for solution C
I Reagent pipet for sodium thiosulfate solution
J Titration pipet
K Sample fixation vessel
L Blank fixation vessel
M Titration vessel
N Titration motor
O Back-drive motor
P Titration clutch
Q Back-drive clutch
R Potentiometer
S Constant voltage source
T Recorder
U Amplifier
V Indicating controller
W Safety switch
X Slide-range=setting switch
R1, R2, R3 Relays
V1, V2,··· V21 Valves
a-7 Cam switch in controller a
c-6, c-8 Cam switches in controller c

the reagents in the pipets are injected into the fixation vessel in the order: solution A, solution C, and solution B.

Titration and Recording.—As soon as the fixation in the fixation vessel, K (sample), is completed, all the solution in this vessel is transferred to the titration vessel, M. (Here, the V10 valve, besides V12 and V15, is opened.) At the same time, the reagent pipet, I, is filled with the thiosulfate solution from the reservoir, D. The thiosulfate solution is then delivered to the titration vessel, and the stirrer in this vessel started. Next, the titration motor, N is started in order to deliver the standard potassium iodate solution (in pipet, J) to the titration vessel. (The titration pipet is filled with the titrant as soon as the previous titration is completed.)

In the course of titration, a small residual current flows between the platinum and calomel electrodes in the titration vessel until the end point is reached. After this point is reached, the diffusion current, the magnitude of which is proportional to the quantity of iodine liberated from the excess iodate added, flows between the electrodes. The diffusion current is amplified by the amplifier, U. As soon as the diffusion current attains the predetermined value, the switch in the indicating controller, V, closes, stopping the titration motor. During the titration, on the other hand, the contactor of the potentiometer, R, is driven by the screw connected by gears and a clutch to the titration motor.

After the titration is completed, the titration pipet, J, is refilled with the titrant, and the potentiometer contactor is brought back to the original position. The titrated solution in the vessel is drained, and the vessel washed with the fresh sample water delivered via the V14 and V15 valves. The vessel is then emptied and made ready for the next titration.

After the sample titration, the blank titration is carried out in the same way.

As has been indicated, all the above operations are systematically carried out as a result of the adoption of a time-cycle-control system. This system consists of four controllers, designated as a, b, c, and d. Controller b operates those parts of the instrument which are concerned with the fixation operation. Controller c operates the parts concerned with the titration operation. Controller d operates the indicating lamps. These controllers are, in turn, operated by controller a, which also carries out the operations not performed by the other controllers.

The series of operations described above (the operations in sample analysis together with the operations in blank analysis) is

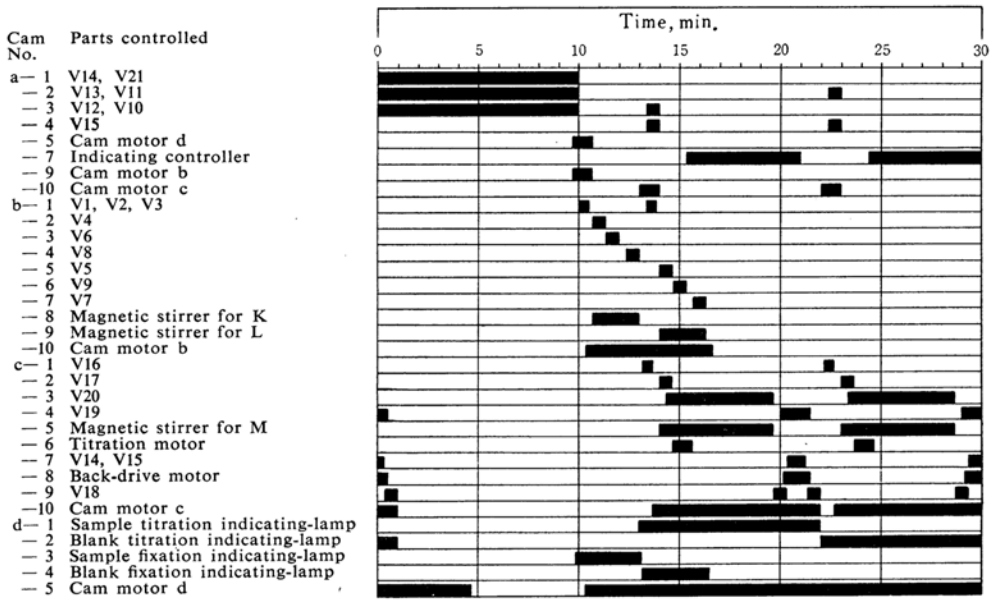

Fig. 2. Time table.
V1, V2, ····· , V21 : Valves indicated in Fig. 1. K : Fixation vessel K.
L : Fixation vessel L. M : Titration vessel M.

completed in 30 min. The time table for this series of operations is given in Fig. 2.

Apparatus and Some Particular Parts.—*Reagent Pipet.*—As is shown in Fig. 3, the pipet is a modified hypodermic syringe fitted with a branched capillary tube. One of the branches is an entry tube, and the other, an exit tube. When the entry valve is opened, the piston is raised by the hydrostatic head up to the movable stop, which is placed in position by a fine adjustment. When the entry valve is closed and the exit valve opened, the reagent in the pipet is discharged by the hydrostatic head and the weight of the piston. Table I shows that the precision in operation of the pipet is very high and is not affected by the movement of the plugs in the entry and exit valves.

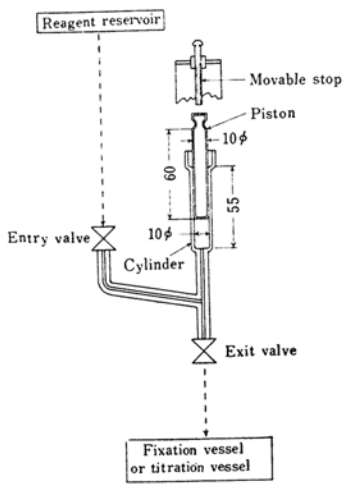

Fig. 3. Reagent pipet.

TABLE I. PRECISION IN OPERATION OF REAGENT PIPET

Pipet	Quantity of reagent transferred, g.*	
	Mean of 10 determinations	Standard deviation
With electromagnetic valves	2.1541	0.0024
With ordinary glass cocks†	1.9857	0.0030

* The reagent is the sodium thiosulfate solution.
† The valves attached to the pipet in the analyzer were replaced by ordinary glass cocks, and the cocks were manually operated.

Fixation Vessel.—In the fixation operation it is necessary that the sample water should not come in contact with air and that the reagents should be mixed thoroughly with the sample in order that complete reactions may be effected. It is also necessary that the quantity of solution remaining in the vessel after the transfer to the titration vessel should be as small as possible. These requirements were met by employing a vessel of the type shown in Fig. 4. The full capacity of the vessel used is 550 ml. The mercury-sealed

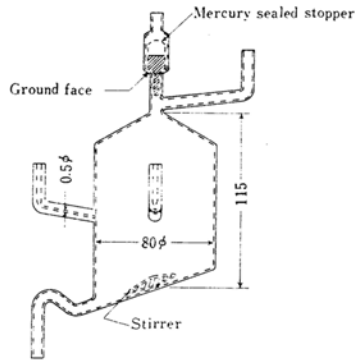

Fig. 4. Fixation vessel.

stopper can readily be raised by the liquid in the vessel when an excess of liquid is introduced. Through the capillary tube (0.5 mm. in inside diameter) attached to the side of vessel, the reagents are introduced into the vessel. The U-bent part of the tube attached to the bottom corner prevents manganese precipitate from entering the valve at the end of the tube.

Electromagnetic Valve.—The construction of the valve and the circuit diagram are shown in Fig. 5. The upper coil is used to open the valve, while the lower coil used to close the valve. The current for the coils is transmitted through a cam-switch-operated relay.

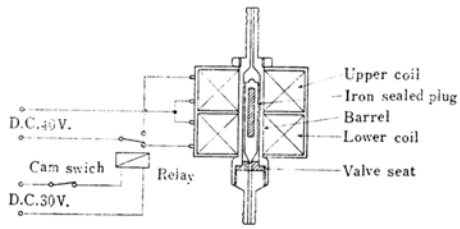

Fig. 5. Electromagnetic valve.

Titration Unit.—The titration pipet is made up of a cylinder and a narrow rod serving as a piston. The piston is 6 mm. in diameter. The pipet delivers the reagent at a rate of 0.42 ml./min., and it can discharge 2 ml. of reagent in the one-stroke operation of piston. The piston is connected by a gear mechanism and clutch either to the titration motor or to the back-drive motor. The clutches (P and Q in Fig. 1) are of the electromagnetic type; when the magnets are energized, the clutches are disengaged. During titration, the back-drive clutch, Q, is disengaged, and the connection between the piston and the back-drive motor (O in Fig. 1) is cut off. In the back drive of piston, the titration clutch, P, is disengaged to cut off the connection between the piston and the titration motor (N in Fig. 1).

The potentiometer has a slide wire 15 cm. long, and the range of movement of the contactor is adjusted by the position of the slide-range-setting switch (X in Fig. 1).

Titration Vessel and Electrodes.—The titration vessel has a capacity of 600 ml.; capillary tubes for delivering sodium thiosulfate and potassium iodate solutions are inserted in the vessel. The platinum electrode is a spiral made by winding a platinum wire 0.5 mm. in diameter and 50 mm. long.*8 The calomel electrode is one commonly used in pH measurement. These electrodes are connected by a 15 kΩ resistor*9 in the amplifier.

Indicating Controller.—The controller is a Hitachi indicating controller. The internal resistance is 100 Ω, and the reading range is 0~1000 μ.

Recorder.—A Hitachi TVK-B recorder is used. The full scale reading is 30 mV.

Performance Tests and Discussion

The instrument was tested by analyzing the water deaerated with or without the addition of hydrazin.

The deaeration was carried out in the following way by employing the apparatus shown diagrammatically in Fig. 6. Pure water was charged to both the boiler and the deaerator, and the boiler was heated. The steam from the boiler was blown into the water in the deaerator, and the water in the deaerator was, in turn, pumped into the boiler. The dissolved air was expelled with steam through

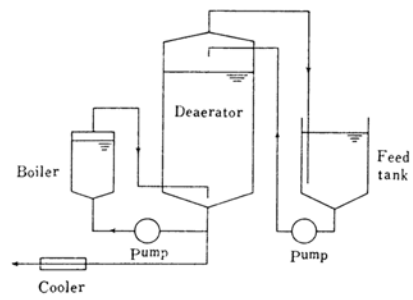

Fig. 6. Deaeration apparatus.

*8 The platinum electrode, after its preparation, is immersed in Mohr's salt solution. If this treatment has been made, the residual current, which flows before the end point is reached, can be not only minimized but also stabilized.

*9 The value of the resistor was determined experimentally. In the experiment, seven resistors (1, 5, 15, 50, 200 and 500 kΩ and 100 MΩ) were tried, and the reproducibility and the slope of titration curve were examined. From the results, a 15 kΩ resistor is considered appropriate for use in the present instrument. The data obtained in the experiment are given in Appendix Table II.

the submerged pipe in the feed tank. This procedure is based on the fact that, above 100°C., the concentration of oxygen in the vapor phase is far greater than the concentration in the liquid phase.[8] In two of the trials made, acidic hydrazin was added to pure water before deaeration by the above procedure.

After the dissolved-oxygen content of water in the deaerator had been reduced, the water was delivered to the analyzer through the cooler, and the analyzer was set in operation. The test was continued for several hours with no interruption in the operation of the deaerator.

A typical chart from the instrument, showing the results of analysis, is presented in Fig. 7. The full scale of the chart corresponds to 0.934 ml. of the titrant used. The oxygen contents calculated from such recorded data are summarized in Tables II and III, together with the results of determination by manual analysis. The data in Table III were obtained in the tests carried out by using the water deaerated with the addition of hydrazin. The hydrazin concentration decreased gradually during the run of test. However, according to Harshman and Woodmard,[9] the reaction between hydrazin and oxygen proceeds very slowly at low pH and low hydrazin concentrations, and it appeared that the conditions prevailing in the deaerator during the test were not such as to favor the reaction. It is, therefore, considered that the oxygen concentration actually remained constant, or nealry so, during the run of test. Hydrazin may have undergone thermal degradation.

The results of oxygen determination by the analyzer agree approximately with the results

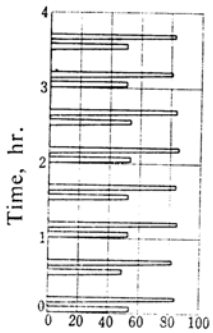

Fig. 7. Typical chart showing the results of analysis.

Table II. Analysis of the water deaerated without the addition of hydrazin

Run no.		Dissolved oxygen, p. p. b. Mean of n determinations	Standard deviation
1	Automatic analysis	12(n=5)	2.0
	Manual analysis	13(n=3)	1.2
2	Automatic analysis	11(n=8)	0.9
	Manual analysis	9(n=4)	1.2
3	Automatic analysis	11(n=8)	0.9
	Manual analysis	9(n=4)	1.5

Table III. Analysis of the water deaerated with the addition of hydrazin

Run no.		Dissolved oxygen, p.p.b. Mean of n determinations	Standard deviation
4*	Automatic analysis	1.6(n=9)	1.7
	Manual analysis	1.2(n=4)	2.4
5†	Automatic analysis	1.6(n=8)	1.3
	Manual analysis	1.0(n=2)	—

* pH: 4.0~4.1; hydrazin, p. p. b.: 7~12
† pH: 5.2~5.8; hydrazin, p. p. b.: 4~10

obtained by manual analysis. The precision of determination by the analyzer is not greater than 2 p. p. b., and the reproducibility is better than that of manual analysis.

Table IV shows the results of the test of the titration unit. In the test, a definite quantity

Table IV. Precision of automatic titration

	Titrant added, ml. Mean of 10 determinations	Standard deviation
Example 1	0.438	0.008
Example 2	0.637	0.006

of a sodium thiosulfate solution was automatically introduced into the titration vessel and titrated with the standard potassium iodate solution, the quantity of titrant added being recorded on the recorder chart. As may be seen from the table, the standard deviation is quite small. Since 0.006 ml. of the potassium iodate solution used corresponds to an oxygen concentration of 0.4 p. p. b., the difference between the error of the integral analytical operation performed by the analyzer and the error of the operation performed by the titration unit appears to be attributable mainly to the fixation operation. The titration unit may also be used for some other types of analysis.

As has been mentioned, the above tests were carried out in the laboratory by empolying a special apparatus for producing the deaerated water. Besides these tests, similar tests were also performed in a thermal power

6) R. C. Adams, R. E. Barnett and D. E. Keller, Jr., *Proceedings, Am. Soc. Testing Mats.*, **43**, 1252 (1943).
7) A. H. White, C. H. Leland and D. W. Button, *Proceedings, Am. Soc. Testing Mats.*, **36** part II, 707 (1936).
8) M. Abe, E. Okumura, K. Tanno and N. Kawashima, *Hitachi Hyoron*, **45**, 561 (1963).
9) R. C. Harshman and E. R. Woodmard, *Trans. Am. Soc. Mech. Eng.*, **77**, 869 (1955).

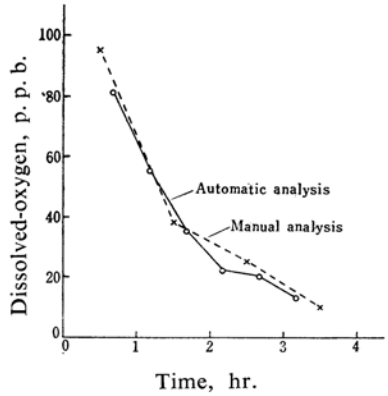

Fig. 8. Results of test in a power plant (During the start-up period)

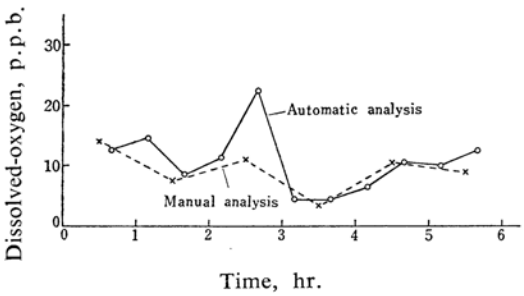

Fig. 9. Results of test in a power plant (During the start-up period)

plant. The analyzer was set in operation at the start-up of the power plant, and in each run, a manual analysis was made at intervals for purposes of comparison. The potassium iodate and thiosulfate solutions used for the analysis in the start-up stage of the boiler operation were 0.01 N solutions, because, during the start-up period, the dissolved-oxygen content was greater than that to be determined by the use of the reagents specified in this paper. The results obtained during the start-up period are shown in Fig. 8, while the results obtained after this period are shown in Fig. 9. In spite of the facts that it was impossible to take the samples simultaneously for both automatic and manual analyses and that the dissolved-oxygen content was apt to fluctuate, a relatively good agreement is again observed between the automatic and manual analyses.

Besides dissolved oxygen and hydrazin, traces of ammonia, iron, copper and silica are contained in feed water. The concentration of ammonia is controlled to around 0.1 part per million[8] as to keep the pH value of feed water within the limits shown in Appendix Table III, and the amounts of other components are usually kept below the limits in the table. Iron and copper exist in ionic state in part, but their possible disturbing influence on the determination of dissolved oxygen is removed by the blank operation as mentioned above.

Summary

An automatic recording analyzer for the determination of dissolved oxygen (in concentrations up to 50 p. p. b.) in boiler feed water by Winkler's method has been described. The instrument is so designed as to perform automatically most of the operations involved in manual analysis, such as sampling, the addition of reagents, titration, recording, and cleansing. The series of required operations (all of the operations in both sample and blank analyses) is completed in 30 min. and is automatically repeated. A more important feature of the instrument is that hydrazin-treated feed water, as well as feed water not treated with hydrazin, can be analyzed with accuracy. The oxygen content, however, cannot be read directly on the recorder chart and must be calculated from the recorded quantities of the titrant used. The precision of oxygen determination is within 2 p. p. b. The reproducibility is better than that of manual analysis.

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APPENDIX TABLE I. DISSOLVED-OXYGEN DETERMINATION WITH THE REAGENTS PREPARED ACCORDING TO DIFFERENT SPECIFICATIONS

Run no.	Dissolved-oxygen content*, p. p. b., determined with: Reagents prepared according to the standard specifications	Reagents prepared according to the present specifications
1	7	—
	—	6
	7	—
	—	9
2	5	—
	—	5
	6	—
	—	4
	4	—
	—	2
	1	—
	—	2
	2	—

* The data are arranged in the order of increasing time in the run.

Appendix Table II. Data for the selection of the resistor for coupling the platinum and calomel electrodes

Resistance Ω	Maximum difference in three determinations (Expressed in ml. of titrant)		Voltage increase per unit volume of titrant, E' (mV./0.1 ml.)	E'/E	Response†
	At equivalence point	At predetermined voltage, E (mV.)*			
1 k	0.03	0.06(0.9)	0.44	0.5	F
5 k	0.01	0.03(6)	2.4	0.4	F
15 k	0.01	0.01(15)	6.6	0.4	F
50 k	0.02	0.02(50)	22	0.4	F
200 k	0.01	0.03(160)	76	0.5	RS
500 k		0.02(200)	155	0.8	S
100M		0.02(300)	55	0.2	VS

* The voltage is such that the titrant volume reading at this voltage exceeds the reading at the equivalence point by a small fixed amount.

† F: fast, RS: rather slow, S: slow, VS: very slow

Appendix Table III. Examples of feed water limits

	Natural circulation boiler with operating pressure (kg./cm²)			Monotube boiler
	100	130	180	
pH	8.6~8.9	8.6~8.9	8.6~8.9	8.6~8.9
Dissolved oxygen, p. p. b.	7	7	7	7
Total iron, p. p. b.	20	20	10	10
Total copper, p. p. b.	20	10	5	5
Silica, p. p. b.	—	—	—	20