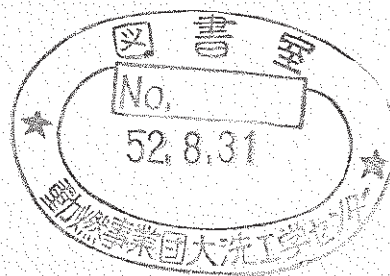# Sodium Impurities Measurement and Control Experiments (No. 5)

Determination of the Solubility of Oxygen in Liquid Sodium by Vacuum Distillation

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POWER REACTOR AND NUCLEAR FUEL DEVELOPMENT CORPORATION

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Determination of the Solubility of Oxygen in Liquid Sodium by Vacuum Distillation

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Abstract

The solubility of oxygen in liquid sodium was determined by vacuum distillation. Oxygen concentration was controlled by a cold trap in a dynamic sodium loop, and sodium was sampled from an expansion tank by dipping cup method and analysed by on line vacuum distillation method.

A least-squares fit of the 37 experimental data over the range from 150 to 250 °C of cold trap temperature yielded a correlating equation of

$$\log_{10}S = 6.118 - (2383/T)$$

where S = wt ppm of oxygen in sodium assumed to be Na_2O.

T = absolute temperature (°K)

The heat of solution ΔH of Na_2O in liquid sodium was calculated from this equation to be 10902 cal/mole. The reproducibility of results was obtained at equillibrium temperature of 150, 200, and 250 °C with a standard deviation of 1.2, 1.8, and 4.1 ppm, respectively.

The oxygen analysis results with cold trapping sodium from various sodium test loops in Oarai Engineering Center almost correspond with the solubility curve of this work.

CONTENTS

FIGURES

I. Introduction

Oxygen in sodium has a large effect on the compatibility of the materials to sodium in the primary and secondary heat transport system in sodium cooled reactors. Accordingly, concentration of oxygen in liquid sodium must always be monitored and controlled within the permissible level. Concentration of oxygen in sodium in the loop is usually controlled by cold trap and can be determined in relation to the saturated oxygen concentration or solubility.

Many solubility equations have so far been published. Claxton[6], Eichelberger[3] and Noden[5] statistically treated the published experimental data and recommended solubility equations respectively. Rutkauskas[7] and other investigators derived solubility equations from the data of their own experiments respectively. However, various solubility equations are not in good agreement. This may be attributable to the difference in the method of sodium sampling and oxygen analytical method or difference in elimination of causes of error arising from the development of analytical method.

The present work was performed on a sodium loop made of stainless steel. The oxygen concentration in sodium was controlled by cold trapping. After equilibrium state was attained, sodium was sampled by dipping cup method and distilled in the on-line sampling device. To eliminate systematic errors arising from the use of a single method, sodium was sampled out from the various kinds of loops and analyzed and the data obtained therefrom were discussed comparatively with the solubility equation obtained in the present work and its propriety was ascertained.

II. Equipment

1. Test loop

In the present work, the daughter loop of General Purpose Sodium Test Loop installed in the Sodium Engineering Division was used. The flow sheet for the loop is shown in Fig. 1. The loop consists of an pot which served as an expansion tank, a plugging meter, two oxygen meters, an on-line vacuum distillation sampler, a by-pass flow through sampler and cold trap for controlling concentration of impurities.

Sodium was charged from the storage tank of the mother loop through V8-1, then separated from the mother loop by closing V8-1 to make possible the operation under independent conditions. The piping material was type 304 stainless steel, diameter of the main pipe was 3/4B and that of the oxygen meter line and the flow-through sampler line was 3/8B. The volume of sodium in the loop while in operation was 192 ℓ.

The sodium flow from the electromagnetic pump on the main line was directed into the cold trap line, the plugging meter line and the flow rate adjusting line (V8 - 8 line), and other lines respectively. Temperature of sodium was controlled by heaters, H8-1, H9-1, H-0 and cooler C-0. Then sodium flowed into the expansion tank and mixed there and came into the electromagnetic pump again. Flow rate fluctuation in the system during plugging meter operation was absorbed by V8-8 which prevents almost all the effects of flow-rate fluctuation on other lines. Table 1 shows the operating conditions of this loop.

2. Vacuum Distillation Sampler

Outline of this device is shown in Fig. 2.

This device consists of vacuum distillation section, the vacuum argon gas line and heating and cooling system.

This is mounted on the upper part of the expansion tank. Sodium was sampled from the expansion tank into a nickel crucible and impurities were separated from sodium by vacuum distillation. Namely, this is an on-line dipping cup vacuum distillation sampler.

2.1 Vacuum Distillation Section

Fig. 3 shows the vacuum distillation section. This section was connected by flange to the nozzle of the expansion tank and separated from the cover gas of the expansion tank by closing the bellows seal gate valve. The upper and lower ends of the pyrex glass tube (outer diameter 60 m/m, length 250 m/m and thickness 5 m/m) used for the distillation chamber was pressed by the upper and lower keep plates respectively. The upper keep plate was fixed with a stop bolt to prevent it from coming off caused by a rise in internal pressure in the distillation chamber. The glass tube permitted to be taken out by removing the stop bolt and the upper flange. For the vacuum seal between the glass tube and the upper and lower keep plates, a modified type of Wilson seal was used. Biton O-ring and a doughnut-shaped metal keep plate were piled alternately up to 3 stages so as to obtain a high vacuum and the glass tube permitted to be fixed vertically.

In order to prevent air in-leakage caused by vertical movement of the crucible holder at the time of sodium sampling and to maintain the vacuum seal during distillation, Wilson seal was adopted as a shaft seal between the upper keep plate and the crucible holder. The shaft seal consists of 2 silicon rubber packings, teflon packing gland and a shaft guide, which ensured smooth vertical movement of

the crucible holder.   The crucible holder and the crucible are pre-pared to sample sodium as shown in Fig. 4-1 and 4-2.   Type-(1) in the Fig. is the prototype and Type-(2) is an improved type.   In the present test, both types were used.   In both types, the holder by it-self made an earthing type sheath thermocouple.   In Type-(1), the crucible was put on the saucer and fixed by inserting the projection on its side into the hole on the side of the saucer.   The crucible was in horizontal contact with the saucer.   In Type-(2), the bottom of the crucible was fixed by setting the external threads around the periphery of the crucible into the internal threads on the saucer.   To insure exact measuring of temperatures until the end of distillation, the bottom of the crucible was made convex-shaped and was in contact with the saucer between curved surfaces.   The material for the crucible was nickel and its capacity was 6mℓ.*

2.2   Vacuum and Argon line

Fig. 5 shows the gas line flow-sheet of the vacuum distillation sampler.   High purity argon gas was supplied directly from the bomb. For a rough evacuation, an oil rotary pump, and for the final evacua-tion, an oil diffusion pump were used in series.   For cooling the oil diffusion pump, turbine oil was circulated by a gear pump and air cooling was given by a radiator.   Liquid nitrogen was used for the cold trap of the oil diffusion pump.   Pressure in vacuum distillation was $10^{-3} - 10^{-4}$ Torr which was continuously measured by an ionization

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* When liquid sodium was sampled, its meniscus was convex caused by the surface tension.   Accordingly, the capacity of the sample sodium was determined by gravimetric method, sampling cold water by dipping cup method. The sodium sample weight was corrected for the sodium density and the expansion of the crucible at sampling temperature. Sampling volume at room temperature was 6mℓ and sodium sampling weight at 375 °C ~ 400 °C was 5.2 g.

gauge near the distillation section.

2.3   Heating & Cooling System

Medium-frequency induction heater was used as the heat source for distillation,   The frequency produced by this device is 5 - 10 KHz and the output power was continuously variable maximum 900W. The work coil (copper, cross section being 13m/m x 6.5m/m□), 62$^\phi$m/m in internal diameter, 88$^\phi$m/m in external diameter and 70 in height, were used.   The work coil was set outside the distillation chamber and the crucible in which sodium was sampled was placed in the center of the work coil and then heating and distillation were performed.   Crucible temperature is automatically controlled while heating.   Near the distillation chamber, air cooling duct was fitted and the chamber was cooled by air to condense the evaporated sodium.

3.   Expansion Tank

This tank served also as a loop expansion tank and a sampling pot. (Fig. 6)   Sodium flowed into the pot from its side at a rate of 10ℓ/min. and went out downward.   The sodium level was measured by an inductive level gauge.   Usually, the over-flow line was not used.

The sodium level in operation is about 350m/m from the tank bottom and the volume of sodium in the tank is about 16ℓ for sodium.   Sodium temperature in the tank was controlled at 375 $^\circ$C - 400 $^\circ$C.   For sodium sampling, the crucible was brought down about 100 m/m below the sodium surface and washed by sodium for 10 minutes.   Then the crucible was brought up and sodium was sampled.

4. Cold Trap

Cold trap was used as a means of controlling concentration in sodium. The construction of the cold trap is shown in Fig. 7. Five buffer plates were fitted in its body and wire mesh are filled between the plates. About 200 pieces of 30-mesh wire mesh, wire diameter being 0.3 m/m, made of SUS-304 were arranged one over the other. Mesh packing density was 0.43 g/cm^3 and the capacity of mesh zone (apparent effective capacity) was 19.2ℓ. Sodium flowed in from the upper part and went down the mesh zone during which it was cooled. When it reached the settling zone at the bottom, temperature fell to the lowest, and then went up in the return tube and heated, then it flowed out. Thermocouples were inserted, 3 from the upper side and 2 from the lower side, and the temperature distribution in the cold trap could be measured. Two thermocouples in the settling zone indicated the same temperature. The sodium temperature distribution in the cold trap showed nearly uniform falling of temperature from the upper side to the lower side. In case the flow rate is 3ℓ/min. and cold trap operation temperatures (lowest) were 250, 200 and 150 °C, the temperature gradient for each was about 0.78, 0.70 and 0.63 °C/cm. The residence time in the trapping zone (mesh zone) was approximately 6 minutes and that in the settling zone (cold zone) is about 1.5 minutes. The cold trap was cooled by forced convection air. Adjusting air flow rate by a P.I.D. controller, the cold trap temperature was controlled continuously and automatically. The lowest temperature in the cold trap was maintained at 120 °C - 250 °C ± 3 °C.

5. Plugging Meter

An orifice type plugging meter was used to ascertain whether the oxygen concentration in sodium reached the equilibrium state, and also

used to monitor the oxygen level in the transient state.

The principle of the plugging meter is shown in Fig. 8. The orifice plate had 24 holes, each 0.5 $^\phi$ m/m x 2.5 $^\ell$ m/m, on the 31 $^\phi$ m/m concentric circle. In the plugging meter, 6 thermocouples were inserted making it possible to measure sodium temperature distribution. The rate of temperature drop along the sodium flow direction was nearly constant, about 8 $^\circ$C/cm, and 5 $^\circ$C/cm when the cold trap temperature was 120 $^\circ$C and 200 $^\circ$C and the lowest temperature is found in the orifice section. Impurities were precipitated and dissolved at the orifice section alone.

6. Oxygen Meter

The UNC oxygen meter (TP-1) made in USA was used to observe the activity of oxygen in sodium. A schematic diagram of the oxygen meter is shown in Fig. 9. The oxygen meter is shown in Fig. 9. The oxygen meter is an instrument to measure the electromotive force generated between the reference electrode, Cu, Cu_2O and sodium monoxide dissolved in sodium through solid electrolyte by a potentiometer. Temperature of sodium was maintained at 315 $^\circ$C $\pm$ 1 $^\circ$C.

III. Experimental Procedure

In the present work, sodium was sampled from the sodium loop by the dipping cup and on-line vacuum distillation method was adopted to measure the oxygen concentration in sodium. Ascertaining the results of the following 3 tests, solubility of oxygen was determined.

(1) Test to ascertain that the oxygen concentration in sodium reached the equilibrium state at the cold trap temperature.

(2) Test to determine the conditions of vacuum distillation in terms of temperature and time required to separate sodium oxide quantitatively from sampling sodium.

(3) Test to obtain the data of oxygen solubility, using the conditions determined in the above (1) and (2) tests.

1. Control of oxygen concentration by cold trap

1.1 Control under transient state

The cold trap temperature was changed stepwise 120 → 199 °C, 199 → 254 °C (process of impurities dissolution) and 254 → 199 °C, 197 → 120 °C (process of impurities precipitation) and the process thereof was monitored by the plugging meter. Relations between cold trap temperature and the indicating temperature of the plugging meter are shown in Fig. 10-1 to 10-4.

Equilibrium automatic measurements were made by the plugging meter under conditions where the orifice section of the meter was partially plugged (about 10% decrease in flow rate) with impurities and yet a constant flow rate was maintained. Accordingly, at the orifice section, dissolution and precipitation of impurities processed at the same speed, suggesting a state very close to an equilibrium at

this temperature.   The plugging temperature of the equilibrium meas-
urement was considered to be a saturated temperature of oxygen in
sodium.   Judging from Fig. 10-1 to 10-4, a steady state seemed to
have attained in 5 - 10 hours.

Under assumption that sodium in the loop is completely mixed
and no impurities come in from other system and the cold trap temper-
ature is changed by stepwise, equation (1) is obtained.

$$\frac{C_t - C_\infty}{C_o - C_\infty} = \exp\left(-\frac{W}{M}t\eta\right) \quad \dots \dots \dots \dots \dots \dots \dots \quad (1)$$

where t :   Time from cold trap temperature change (min).

$\quad$ Co: System oxygen concentration at t = 0 (W ppm)

$\quad C_\infty$:   Final oxygen concentration at t = ∞ (W ppm)

$\quad$ M :   Total quantity of sodium (ℓ)

$\quad$ W :   Flow rate of sodium in the cold trap (ℓ/min), and

$\quad \eta$:   Efficiency of the cold trap

In this test, M = 192ℓ and W = 3ℓ/min.

The relation between the indicating temperature of the plugging
meter and the saturated oxygen concentration was calculated from the
following Eichelberger's (3) equation for oxygen solubility.   The
efficiency of the cold trap, η , was shown in Fig. 11.

$$\log_{10} C = 6.239 - \frac{2447}{T} \quad \dots \dots \dots \dots \dots \dots \dots \dots \dots \quad (2)$$

where T :   Absolute temperature ($^\circ$K)

$\quad$ C :   Satulated oxygen concentration (wppm O)

As shown in Fig. 11, the efficiency of the cold trap, η , in this work
was $0.5 \leq \eta \leq 1$ and this relation was presumed to exist all the time
while the cold trap temperature was 120°C to 250°C.   Therefore, the

time required to shift equilibrium state from one to another could be obtained from equation (1) as follows.

$$t = 9.8 \ (hr)$$

where $\eta = 0.5$, Equilibrium ratio $(C_t - C_\infty) / (C_o - C_\infty) = 0.99$

For the measurement of oxygen solubility, equilibrium state was made from transient state for the cold trap temperature, $120 \rightleftarrows 150 \rightleftarrows 200 \rightleftarrows 250$. Sodium sampling from the loop was made about 12 hours (approx. 1.2 times the shortest necessary hours) after the start of transient state and upon confirmation by the plugging meter of the equilibrium state attained.

1.2 Control under steady state

Relations between the cold trap temperature and the indicating temperature of the plugging temperature in the steady state are shown in Fig. 12. Measurements were made manually and automatically under a special condition to ascertain the steady state during the present test. The results suggest the following.

(1) The varying range of the indicating temperatures of the plugging meter for respective cold trap temperatures was $5^{\circ}C - 7^{\circ}C$ both at the plugging and unplugging temperatures.
Taking into consideration the varying range of the cold trap temperatures, $\pm 3 ^{\circ}C$, the steady state was well maintained.

(2) The plugging and unplugging temperatures well followed the cold trap temperatures, and the quantity of oxygen and other impurities in the loop was sufficient enough to obtain saturated concentration at $120 ^{\circ}C - 250 ^{\circ}C$.

(3) The cold trap temperature was between the plugging and unplugging temperatures when manually measured (started in a condition

where impurities were not precipitated at the orifice section) as shown in Fig. 12.

When measured by oscillating method (precipitation and dissolution were repeated in a state where orifice section was partially plugged with impurities), the plugging temperature became close to the un-plugging temperature (almost constant) which became very close to the cold trap temperature (Fig. 13).

When measured continuously by the equilibrium method, the plugging meter temperature was close to the unplugging temperature that measured by manual and oscillating method, namely, close to the cold trap temperature (Fig. 10-1 ~ 10-4 and Fig. 12).

Thus, oxygen concentration in the loop was maintained by the cold trap at a saturated concentration corresponding to the cold trap temperature in a steady state. Therefore, saturated oxygen concentration could be obtained by measuring the oxygen concentration in the steady state. Then, oxygen solubility could be obtained from the relations between the concentration thus obtained and the cold trap temperature.

2. Determination of distillation conditions

In vacuum distillation, analytical results were remarkably affected by the crucible temperature, the overheating temperature and time. These distilling conditions were determined by the following tests.

2.1 Crucible temperature measurement

Using Type 1 and Type 2 crucible holders and crucibles, corre-lation between the temperature of the thermocouple of the holder and that of the inside bottom of the crucible was obtained in a condition

with no sodium in the crucible. The power of the induction heater was changed stepwise, keeping the pressure in the distillation chamber lower than 10^{-3} Torr. and temperature was measured when the crucible temperature reached constant. The results are shown in Fig. 14. Using these results, degassing temperature of the crucible and the over heating temperature were obtained.

Temperature of sodium in the crucible is determined by the relation between pressure and the heating capacity. The heating capacity was kept constant during distillation, but the pressure changed between $1 \times 10^{-3} \sim 1 \times 10^{-4}$ Torr. and accordingly the temperature didn't become constant. The distilling temperatures measured by the thermocouple of the holder in steady state was about 300 $^{\circ}$C with Type 1 and 370 $^{\circ}$C with Type 2.

2.2 Detection of the End of Distillation

Generally, the end of distillation is detected by a sharp rise in crucible temperature. However, in the present work, temperature fluctuated often according to the manner of contact between the crucible and its holder and the change in matching with the induction coil. This resulted a profile of rising temperature that resembles the end of distillation, and therefore, it was difficult to detect exactly the end of distillation only by the temperature profile. A typical example of the pressure and temperature in such case is shown in Fig. 15-1, Pattern (1). In this case, heating was shutoff at point C when distillation temperature started rising at point A, and no change was observed in the pressure. When the temperature rise in such case was mistaken for the end of distillation and heating was shutoff, distillation ended imperfect with metallic sodium remaining in the crucible. Accordingly,

in the case of Pattern (1), needed for continuing further heating.

Fig. 15-2 Pattern (2) shows a typical example of the end of distillation. In this case, temperature rise was observed at point A but no change was observed in the pressure and therefore heating was continued. Thereafter, a sharp peak of pressure appeared at point B together with a temperature rise and heating was shutoff at point C. In such case distillation was nearly perfect but in some case small quantity of sodium was found with distillation residue as mentioned later.

2.3　Correlation between overheating time and analytical values

A very small quantity of metallic sodium was found with the residue and a tendency was observed for the occurrence of positive errors in the analytical value when heating was shutoff immediately after appearance of pressure peak. Therefore, overheating was performed to the crucible at a constant temperature after the end of distillation to distil metallic sodium perfectly.

The effect of overheating time on the oxygen analytical value is shown in Fig. 16. In case the overheating time was shorter than 3 minutes, the analytical value showed a higher level. When it exceeded 4 minutes, a tendency was observed for very slight reduction in analytical value with overheating time. (the reduction rate was 0.15 ppm/min. when calculated by the least square method, but for the duration of 4 - 30 minutes, such rate could be regarded constant within the limits of analytical errors.) For the measurement oxygen solubility, overheating was applied for 10 minutes.

2.4　Correlation between overheating temperature and analytical value

As a result of off-line vacuum distillation test[4], it was

clarified that oxygen analytical value was affected by the overheating temperature and that temperatures higher than 500 $^{\circ}$C caused a large loss of oxide. The effects of overheating temperature on analytical value in this work are shown in Fig. 17. In case of overheating time is 10 minutes, the analytical values are nearly constant until 500 $^{\circ}$C within the limits of analytical errors. When overheating temperature was higher than 500 $^{\circ}$C, loss of oxide was observed. In case of overheating time was within 3 - 3.5 minutes, maximum allowable temperature was about 550 $^{\circ}$C. But, as mentioned before, there was a possibility of leaving metallic sodium in case of the overheating time was less than 3 minutes.

Fig.-18 shows the allowable condition of overheating temperature and time obtained from the data of 2.3 and 2.4 above. The Fig. suggests that the overheating temperature lower than 500 $^{\circ}$C and heating time longer than 4 minutes are the adequate condition. Measurement of oxygen solubility was conducted under this condition.

3. Measurement of oxygen solubility

Loop sodium, while in steady operation at cold trap temperature 120, 150, 200, 250 $^{\circ}$C, was sampled by dipping cup method from the expansion tank (impurities pot). By on-line vacuum distillation, metallic sodium was separated from distillation residues, then the residue was dissolved in dilute nitric acid, and sodium in the solution was determined by frame spectrophotometry. The quantity of oxygen in the sodium sample was calculated on the basis that the distillation residue in a form of Na_2O.

Fig. 19 shows the typical profiles of temperature and the pressure in the vacuum distillation process. The distillation conditions were used on

the basis of the following values obtained from the preceding tests.

Sodium sampling temperature:	375 °C - 400 °C
Crucible cleaning time (in Na):	10 min.
Distillation temperature: (thermocouple of the holder)	249 °C - 386 °C
Distillation pressure:	Order of 10^{-4} Torr.
Overheating temperature (in crucible):	430 °C - 500 °C
Overheating time:	10 min.

(Distilling temperature indicate the lowest in the case of Type-(1)

holder and the highest in the case of Type-(2) holder.)

The distillation procedure was taken as follows. The crucible were fitted to the crucible holder in the distillation chamber and degassing was applied about for 5 minutes at about 400 °C in the pressure of 10^{-4} Torr. The argon gas was supplied in the distillation column and after making the pressure in the column about the same as that of the expansion tank, the gate valve was opened and the crucible was brought down into the expansion tank. The reaching of the crucible to the surface of liquid sodium was detected by the thermocouple in the holder with a sharp increase in temperature. The crucible was brought down about 100 mm below the liquid surface and subjected to cleaning for 10 minutes in liquid sodium circulation. Then the crucible containing sodium sample was brought up quietly into the distillation chamber. Next, the gate valve was closed and evaluation and induction heating was begun. The pressure dropped rapidly and distillation began immediately. The distillation temperature became nearly constant when the pressure came to constant. About 30 minutes after the start of distillation, a sharp change appeared in the pressure which was immediately followed by a sharp rise in temperature, indicating the end of distillation. Thereafter, heating power

was increased a little and overheating was continued for 10 minutes at a specified temperature, then heating was terminated. Keeping the vacuum in the distillation chamber, the crucible was cooled down to the room temperature. Then, the crucible was taken out from the distillation chamber and the distillation residue in the crucible was dissolved in 0.1 N nitric acid solution. Sodium concentration in the solution was determined by the flame spectrophotometry and the oxygen equivalent of the sample was calculated.

The cold trap temperature and the analytical value of oxygen in sodium are shown in Table-2 and their correlation in Fig. 20. Generally, solubility, S, can be expressed by $\log_{10} S = A + B\ T^n$ (A, B = constant). This equation fits the practical use when $n = -1$ is used therein, and in many cases solubility has so far been obtained in this way. Using $n = -1$, a straight line (1) was obtained in the present test as shown in Fig.20. The straight line (1) was derived from all the data at 43 points using the least squares method but the analytical values for each temperature didn't agree well with that from the equation. The reason was that no change was observed in the analytical values corresponding to the change of temperature as seen in the values which were nearly the same for 150 °C and 120 °C. If the solubility at 150 °C didn't differ from that at 120 °C, the solubility curve must break in the neighborhood of 150 °C and a curve (2) which was deviated to upper direction from lineality is conceivable. However, such solubility curve (2) was not reasonable in view of the indicating values of the oxygen meter (Fig.21) in the present work (refer to the paragraph of discussion). It might be reasonable to consider that actually the oxygen concentration at 120 °C was lower than that at 150 °C, and analytical value at 120 °C was greatly affected by analytical blank error, and

accordingly, the analytic value became higher than the actual value.
Therefore, the data at 120 $^\circ$C were excluded. From the data at remaining 37 points, a best fit straight line was derived using the least squares method and the following equation (3) was obtained.

$$\log_{10} S = 6.118 - \frac{2383}{T} \quad \dots\dots\dots\dots\dots\dots\dots\dots \quad (3)$$

where S : Oxygen solubility in sodium (W ppm O)

T : Absolute temperature (K$^\circ$)

The equation (3) is explained in the Fig.22. This was the solubility of oxygen in sodium obtained in the present work based on the experimental values at 150 $^\circ$C - 250 $^\circ$C. Viewed from the behaviors of the plugging meter and oxygen meter, it was presumed that the above equation was in applicable upto 120 $^\circ$C by extraporation. The resultant relations are plotted linear coordinates in Fig. 23. The temperature dependence of the saturation concentration S would be described by:

$$\log_{10} S = \left(\frac{-\triangle H}{2,303R}\right) \cdot \frac{1}{T} + \text{const.} \quad \dots\dots\dots\dots\dots \quad (4)$$

where R : Gas constant. 1.987 cal/deg-mole

H : Differential heat of solution of Na_2O in liquid sodium

at infinite dilution

From (3) and (4) above, $\triangle H = 10902$ cal/mole is obtained by calculation.
Reproducibility of the analytical results at equilibrium temperature of 150 $^\circ$C, 200 $^\circ$C and 250 $^\circ$C were obtained with a standard deviation of 1.2 ppm (35%), 1.8 ppm (18%), 4.1 ppm (10%). The figure in each parenthesis mean the relative standard deviation.

IV. Discussion

1. Comparison of the test results by different authors

The results of the present test and different solubility curves are compared in Fig. 24. Values obtained in the present test was well agreement with equations recommended by Noden[5] and Eichelberger[3] but fairly lower than those from Claxton[6] and higher than those from Rutkauskas[7]. These recommended equations and experimental equation of oxygen solubility are shown in Table-3.

The characteristics of these solubility equations were as follows: Claxton[6] derived a least-squares best fit equation using all the data (88 results) presented by earlier investigators. Eichelberger[3] derived a generalized equation based on the following criteria for the selection of data.

(1) Experimental data obtained by using glass apparatus were excluded as they involved high errors caused by sodium-glass reaction.

(2) Experimental data obtained by mercury amalgamation analysis obtained at a saturated temperature below 250 °C were excluded. Noden[5] applied criteria (1) and (2) in case of the temperature above 250 °C for the selection of data. As regards the data for temperatures lower than 250 °C, Eichelberger[3] and Noder[5] selected the data obtained from the vacuum distillation using metallic apparatus. Such criterion of selection was in accord with the temperature range and test method of this work and that was a supporting factor that the present test results agreed with those from the recommended equations. Rutkauskas, using an overflow type on-line vacuum distillation, obtained a lower solubility than that of the present test, especially in a range of low temperature.

2. Analytical blank

Generally, in the on-line distillation, blank corrections are not required because the equipment design eliminates the probability of sample contamination by atmospheric impurities. In the present work, it was impossible to obtain oxygen-free sodium and accordingly blank correction was not attempted.

Under assumption that blank value is constant regardless of the quantity of sodium sampled, the blank value in the present test can be estimated as follows. Changing the capacity of the crucible, sampling was made. Relations between the quantity of sodium sampled and the analytical values (total oxygen) are shown in Fig.-25. Though the data varied widely, linear relation was sought by the method of least squares method, and blank value was obtained by intercept method. Quantity of oxygen was about 10 μg in case the sampled sodium quantity was zero. This was the theoretical blank value throughout all processes of measurement which corresponded to 2 ppm when 5 g of sodium was sampled. This might indicate a possibility that the blank value in this work might be around 10 μg. However, no correction was made in the present test as the blank value was not determined.

3. Relation between the indicating values of the plugging meter and those of oxygen meter

The analytical value for 120 $^{\circ}$C was excluded in the calculation of the solubility curve. The actual oxygen concentration was lower than the analytical value and yet the analytical value for 120 $^{\circ}$C was nearly the same with that for 150 $^{\circ}$C under a remarkable effect of analytical error. The reason that the analytical value for 120 $^{\circ}$C should be excluded in the calculation of solubility was as follows:

(1) Under a equilibrium state, the indicating temperature of the plugging meter and cold trap temperature were nearly in a linear relation in a range of 120 °C - 150 °C (Fig.-12). The indicating temperature of the plugging meter for 120 °C of the cold trap was clearly lower than that for 150 °C. The oxygen concentration in sodium for 120 °C in this work was controlled at the saturation temperature by the cold trap. Such behavior of the plugging meter was clearly noted in manual and automatic measuring.

(2) Relation between the output of the oxygen meter and the cold trap temperatures in equilibrium state, 120, 150, 200 and 250 °C respectively are shown in Fig. 21. The oxygen meter used here was that of UNC Corp. in USA. A schematic diagram is given in Fig. 9. From Fig. 21, the following relation was clarified between the output of this oxygen meter and the oxygen concentration in sodium.

$$E = A + \frac{B}{T} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

where   A, B: Constant from experimental value

E :   Output of oxygen meter (V)

T :   Cold trap temperature (saturation temperature) (°K)

On the other hand, the theoretical voltage generated by the oxygen meter, Cu, Cu_2 O || ThO_2 - Y_2O_3 || Na, Na_2O (dissolved) can be represented as follows:

$$E = Eo - \frac{2,303Rt}{nF} \cdot \log_{10}\frac{C}{Co} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

where   E :   Cell EMF

Eo :   Standard cell EMF

n   :   Number of electron involved in the cell reaction

R : gas constant

F : Faraday constant

C : Oxygen concentration in sodium

Co : saturated oxygen concentration at temperature
(sodium temperature) of the oxygen meter
$t({}^{\circ}K)$ ..... constantly 315 ${}^{\circ}C$ in the present
test

From the equation (6) the following is obtained:

$$E = K_1 - K_2 \log_{10} C \qquad \cdots\cdots\cdots\cdots\cdots\cdots\cdots \qquad (7)$$

where K_1, K_2 : constant.

Then $\log_{10} C = a + \dfrac{b}{T}$ (where a, b: const.) is introduced from
(5) and (7).

The experimental results in the present work with the oxygen meter
revealed that the logarithm of saturated oxygen concentration and 1/T
were in a linear relation. To this the phenomenon that the analytical
value for 150 ${}^{\circ}C$ was on the same level with that for 120 ${}^{\circ}C$ was con-
tradictory.

(3) In light of the tendency in analytical values and the blank value
mentioned above, 150 ${}^{\circ}C$ was considered to be a detectable limit
for the oxygen analysis in the present test and the analytical value
for 120 ${}^{\circ}C$ was under greater effects of blank value as compared
with others. Therefore, it might be appropriate to exclude it in
the calculation.

For reasons mentioned in (1), (2) and (3) above, the analytical
values at 120 ${}^{\circ}C$ was excluded. It might be appropriate to use 250 ${}^{\circ}C$ -
150 ${}^{\circ}C$ lineality as exterpolation for the oxygen solubility at 120 ${}^{\circ}C$.

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4. Comparison of results of test using other sodium loops

Table-4 shows the relation between the oxygen concentration in sodium and the cold trap temperature in various kinds of loops operating at Oarai Engineering Center. Fig. 26 shows a comparison between the values obtained and solubility curves for the present test. Sodium in loops were sampled by the vacuum thief or bypass flow-through method, then conveyed to the laboratory for analysis and subjected to the secondary sampling in the globe box and analyzed by amalgamation method or vacuum distillation method. Thus, analytical method was different from the on-line vacuum distillation method for the measurement of solubility.

As shown in Fig. 26, the data obtained from various loops agreed well with the solubility curves obtained in the present test. The loops included large-size ones such as a test loop for 50MW steam generator and a small one for material test. The cold traps were of forced convection and gas cooling type, including large and small sizes. It was clarified that while the loop was in a steady state, the oxygen concentration was controlled by the cold trap quite close to the saturated oxygen concentration at the trapping temperature within a range of 120 °C to 250 °C.

V. Summary

1. The experimental results for the solubility of oxygen in liquid sodium within the temperature range, 250 $^{\circ}$C - 150 $^{\circ}$C, was expressed by the following equation.

$$\log_{10} S = 6.118 - \frac{2383}{T}$$

where   S :   Weight (ppm) of oxygen in sodium assumed to be Na_2O

T :   Absolute temperature ($^{\circ}$K)

2. Reproducibility of the results obtained at each temperature was 1.2 ppm at 150 $^{\circ}$C, 1.8 ppm at 200 $^{\circ}$C and 4.1 ppm at 250 $^{\circ}$C as shown by the standard deviation.

3. From the solubility equation obtained in the present test, the heat of solution of Na_2O in liquid sodium was:

$\triangle H = 10902$ cal/mole

4. In the case of various sodium loops, the oxygen concentration in sodium and cold trap temperature relations were in good agreement with the oxygen solubility curve obtained in this experiment.

5. A possibility was noted that the analytical blank in this method was about 10 μgO throughout all processes.

6. 1) The end of distillation was detectable by a sharp change in pressure.

2) The allowable temperature for overheating was below 500 $^{\circ}$C.

VI. Acknowledgement

The authors express their thanks to Mr. Saito, Director of the Sodium Technology Dept., Mr. Mochizuki, leader of the Sodium Group of FBR of this Corporation, Mr. Yamamoto, Mr. Yoshida, for their guidance to the authors.

The authors also express their thanks to Mr. Owada, and Mr. Nakasugi, for their help in the operation of the sodium technology development loops and in preparation of this report.

VII.   References

1)   Chemical Society of Japan;

      "Handbook of Chemistry,", p.686, Maruzen Co., Ltd. (1975)

2)   O.J. Foust, Edit;

      "Sodium-Nak Engineering Handbook", Vol. 1, p.13 Gordon and

      Breach, Science Publishers, Inc. (1972)

3)   R.L. Eichelbelger;

      "The Solubility of Oxygen in Liquid Sodium:

      A Recommended Expression", AI-AEC-12685 (1968)

4)   Takeda, Ito, et al;

      "Sodium Impurities Measurements and Control Experiments (No.3)

      under preparation (1975)

5)   J.D. Noden;

      "A General Equation for the Solubility of Oxygen in Liquid Sodium",

      J. Brit. Nucl. Energy. Soc. vol. 12, No. 1 (1973)

6)   K.T. Claxton;

      "Review of Solubility Date for the Liquid Sodium-Oxygen System",

      AERE-R.   4879

7)   V.J. Rutkauskas;

      "Determination of the Solubility of Oxygen in Sodium by Vacuum
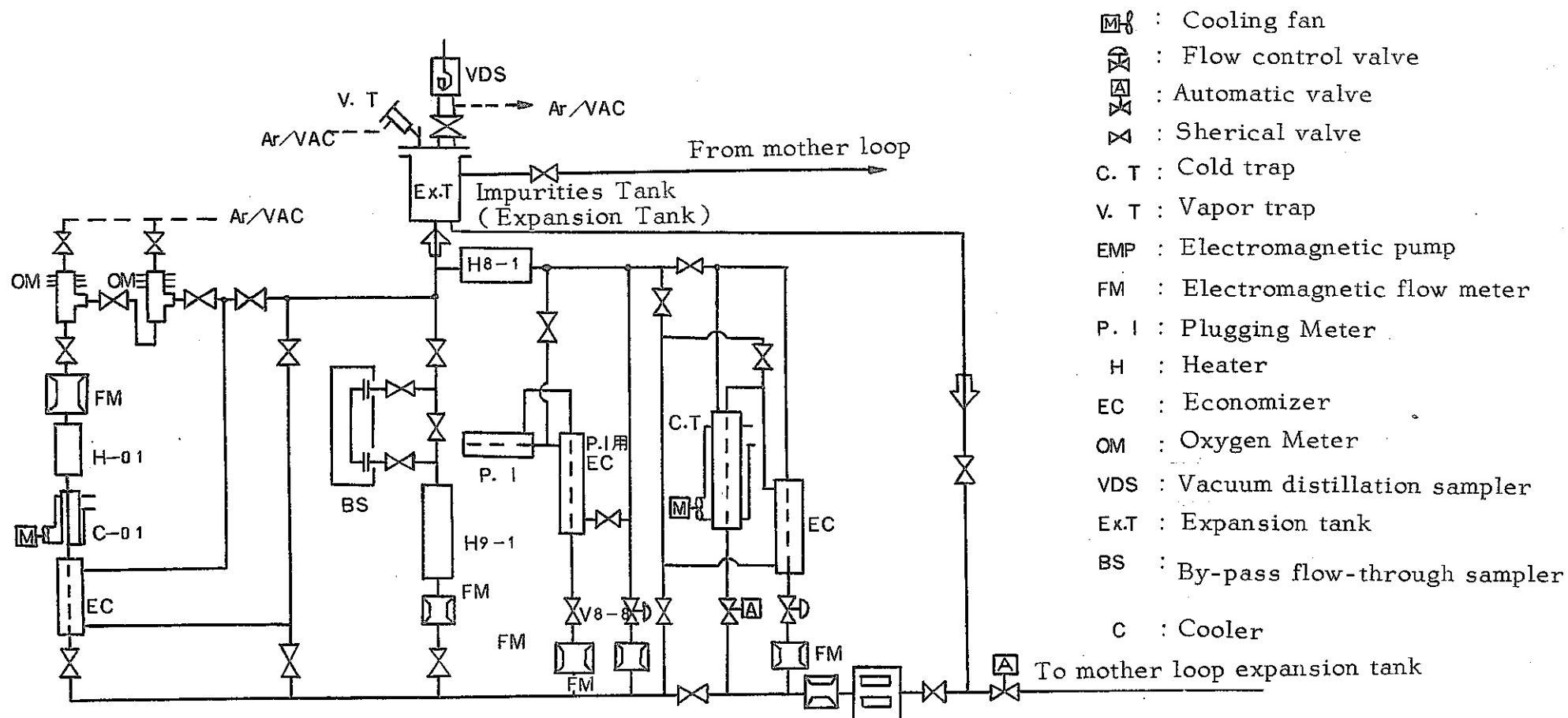
      Distillation", LA-3879 (1968)

VDS

V. T

Ar/VAC

Ar/VAC ---→ Ar/VAC

From mother loop

Ex.T   Impurities Tank
       (Expansion Tank)

OM   OM

H8-1

FM

H-01

C-01

M

EC

BS

P. I

P.I用
EC

H9-1

FM

FM

C.T

M

EC

V8-8

FM

FM

FM

To mother loop expansion tank

☒⧗ : Cooling fan
☒ : Flow control valve
Ⓐ☒ : Automatic valve
☒ : Sherical valve
C. T : Cold trap
V. T : Vapor trap
EMP : Electromagnetic pump
FM : Electromagnetic flow meter
P. I : Plugging Meter
H : Heater
EC : Economizer
OM : Oxygen Meter
VDS : Vacuum distillation sampler
Ex.T : Expansion tank
BS : By-pass flow-through sampler
C : Cooler

Fig.-1   Flow sheet of General Purpose Sodium Test Loop.
       (Sodium Impurity Test Loop)
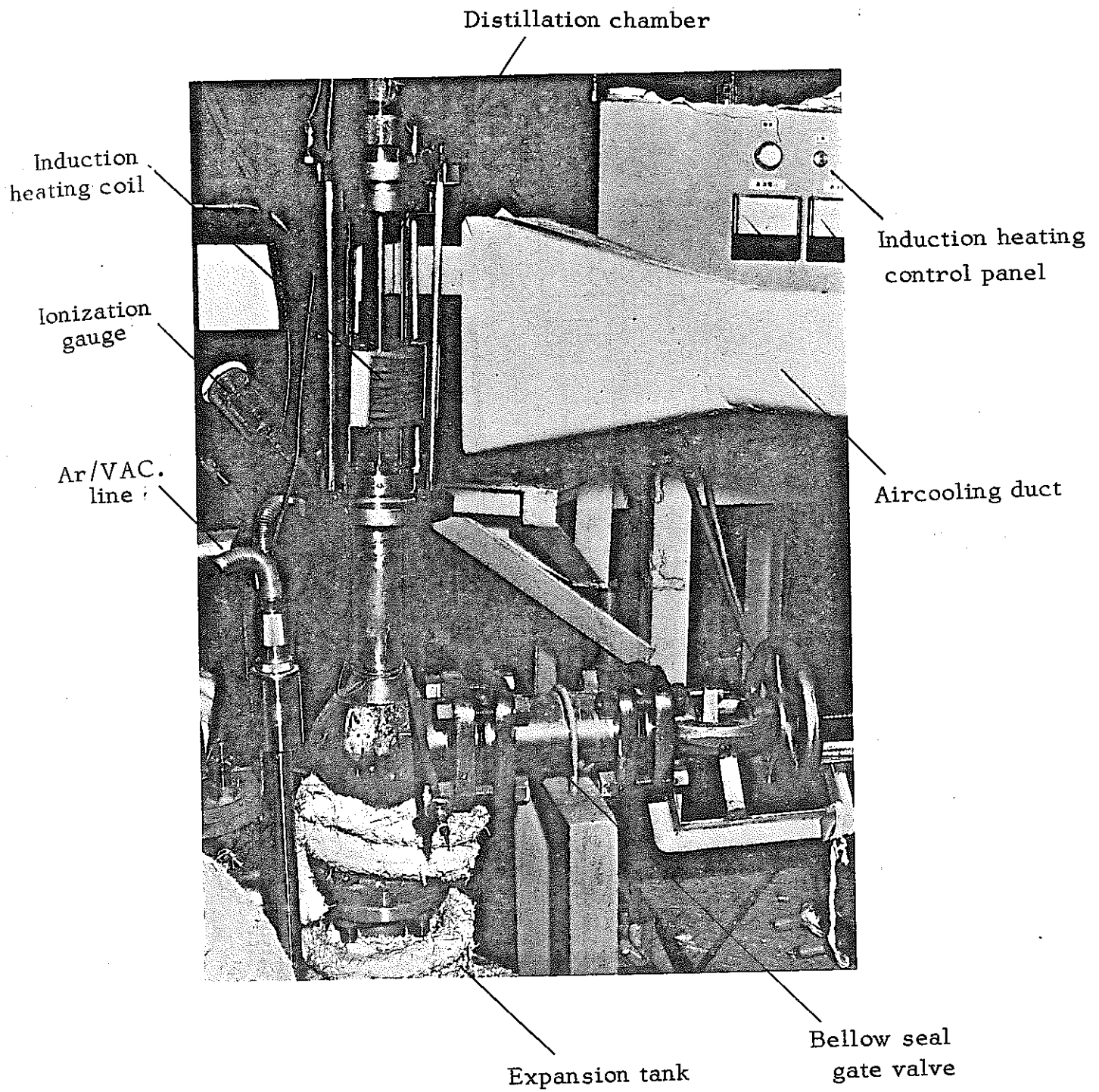
Fig. 2　General View of Vacuum distillation Sampler

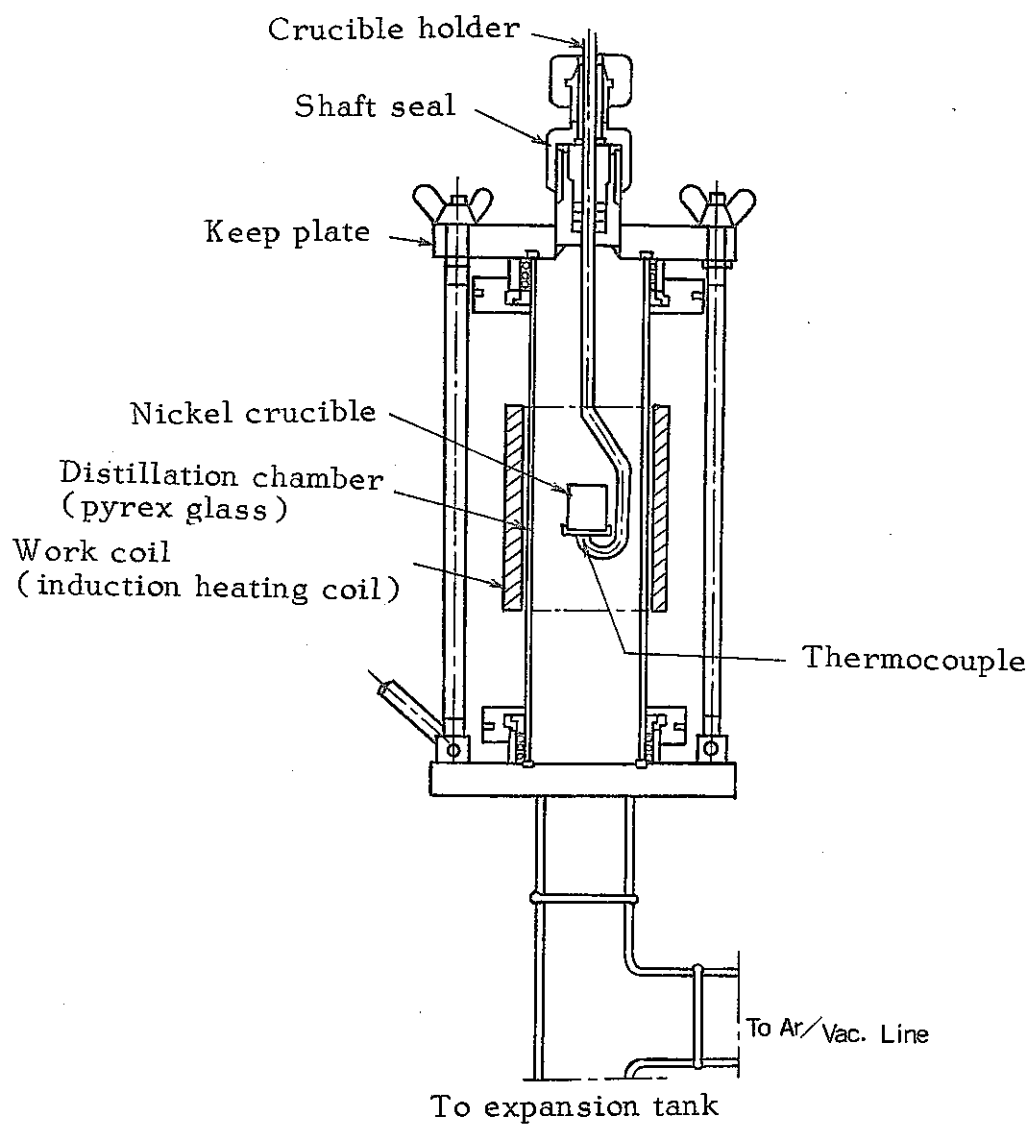Crucible holder

Shaft seal

Keep plate

Nickel crucible

Distillation chamber
(pyrex glass)

Work coil
(induction heating coil)

Thermocouple

To Ar/Vac. Line

To expansion tank

Fig.-3   Vacuum Distillation Section

Enlarged saucer
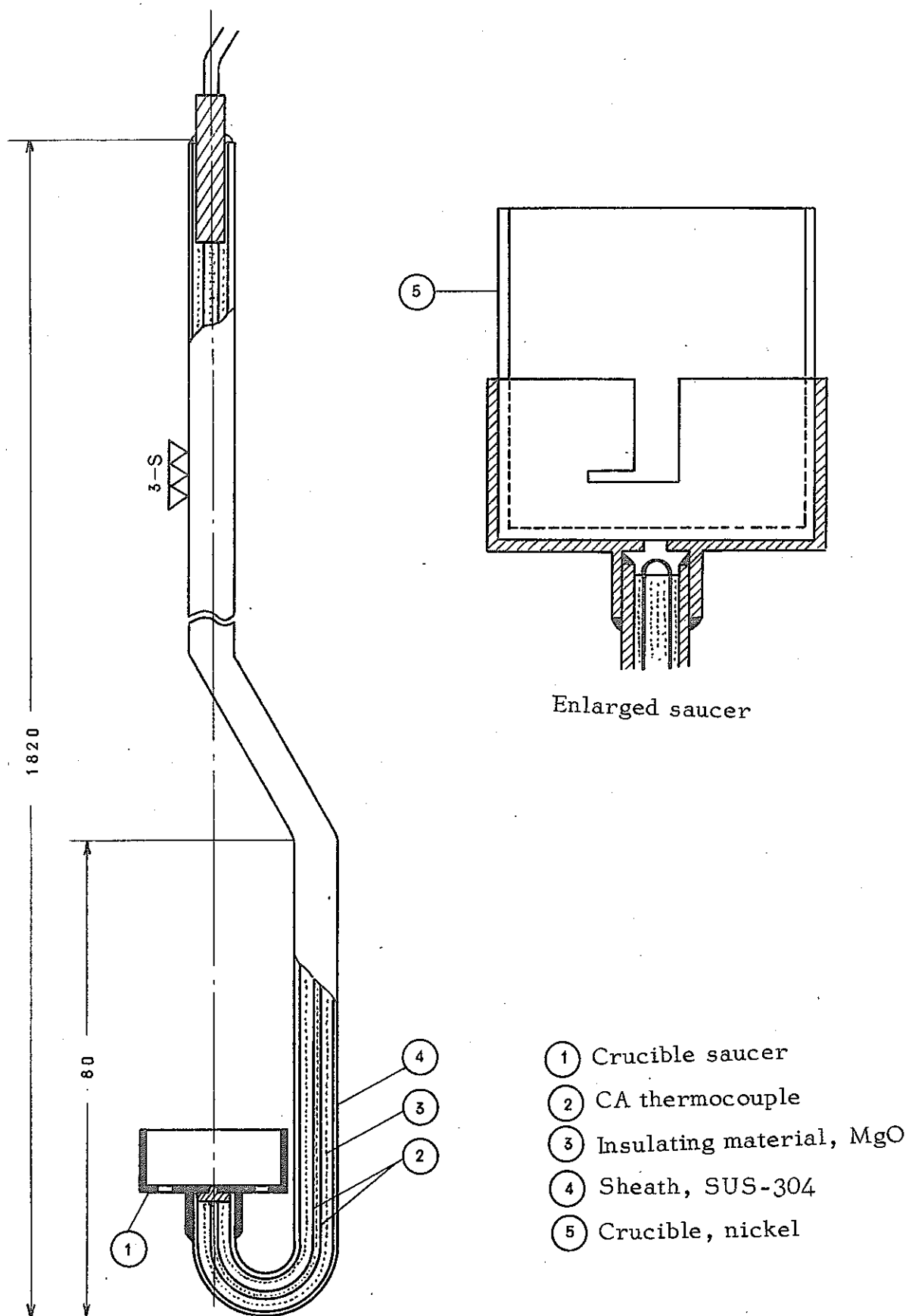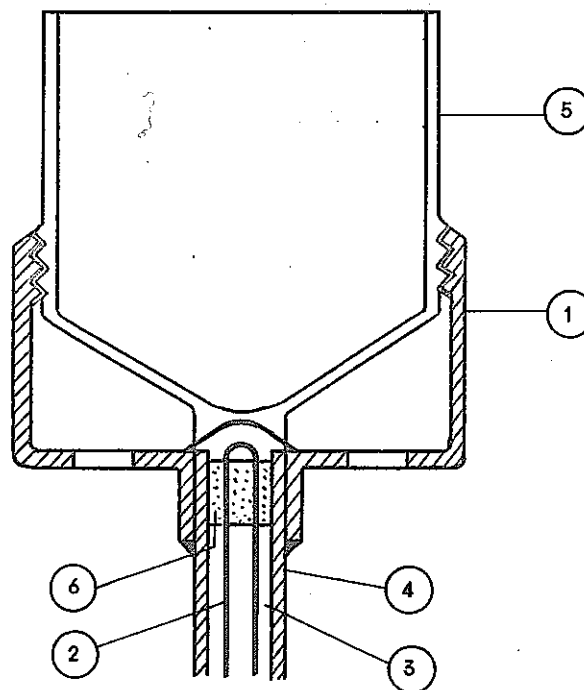
Fig.-4-1.　Crucible Holder and Crucible (Type-1)

1　Crucible saucer

2　CA thermocouple

3　Insulating material, MgO

4　Sheath, SUS-304

5　Crucible, nickel

① Crucible saucer

② C, A thermocouple

③ Insulating material (MgO)

④ Sheath, SUS-304

⑤ Crucible, nickel

⑥ Aluminium oxide

Shaft is same as that of Type-1
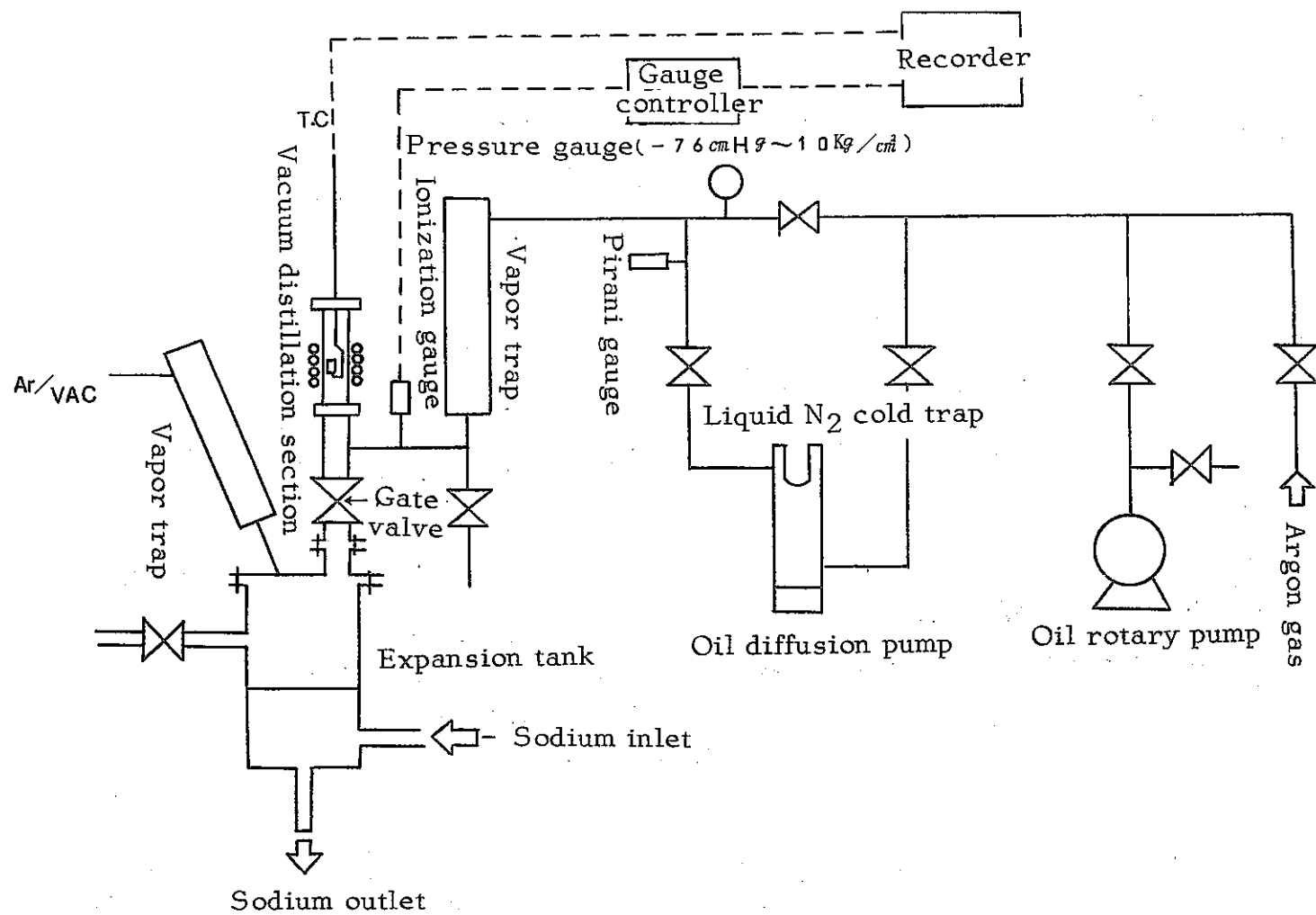
Fig.-4-2.   Crucible Holder and Crucible (Type-2)

Fig.-5.   Schematic diagram of vac-inert gas system for vacuum distillation
equipment

Crucible holder

Vacuum distillation chamber
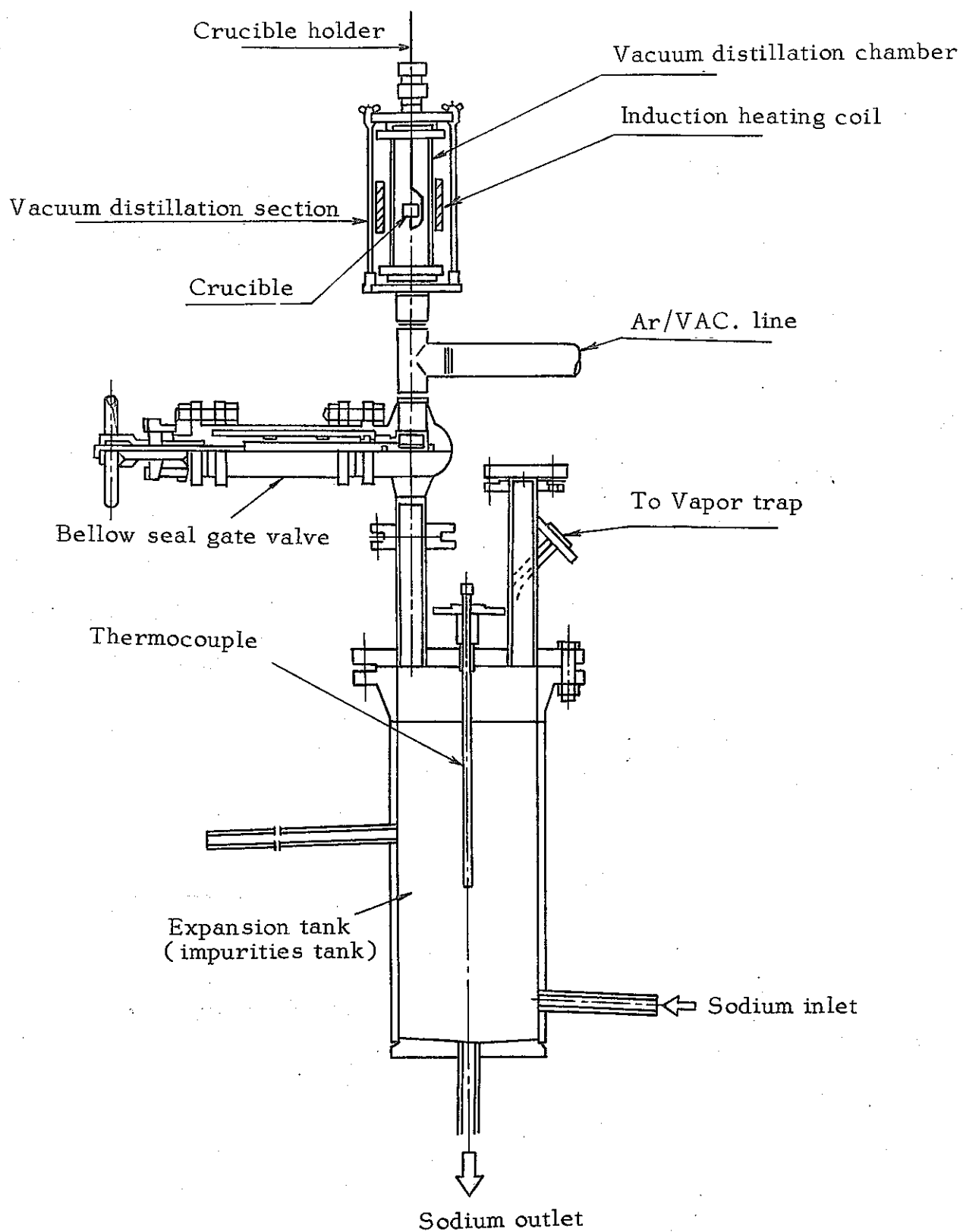
Induction heating coil

Vacuum distillation section

Crucible

Ar/VAC. line

Bellow seal gate valve

To Vapor trap

Thermocouple

Expansion tank
(impurities tank)

Sodium inlet

Sodium outlet

Fig.-6. Vacuum Distillation Sampling System

Na outlet   Na inlet

27.2φ   27.2φ

30

34φ   6.5

216.3

Duct
(air outlet)

Thermocouple well

300

530

Return tube

740

Cooling fin

980

Mesh

Baffle

35

165 170

Specification
  Type-Forced convection air cooled cold
  trap

Na flow rate	$3\,\ell/\text{min}$
Design pressure	$5\,kg/cm^2$
Quantity of air required	$25m^3/\text{min}$
Full capacity	29.8ℓ
Effective apparent capacity	19.2ℓ
Mesh(SUS 304)	0.3ϕ, 30 mesh,
	$0.43\,g/cm^3$

6.3φ   10.3φ   Duct
(air inlet)

27.2φ
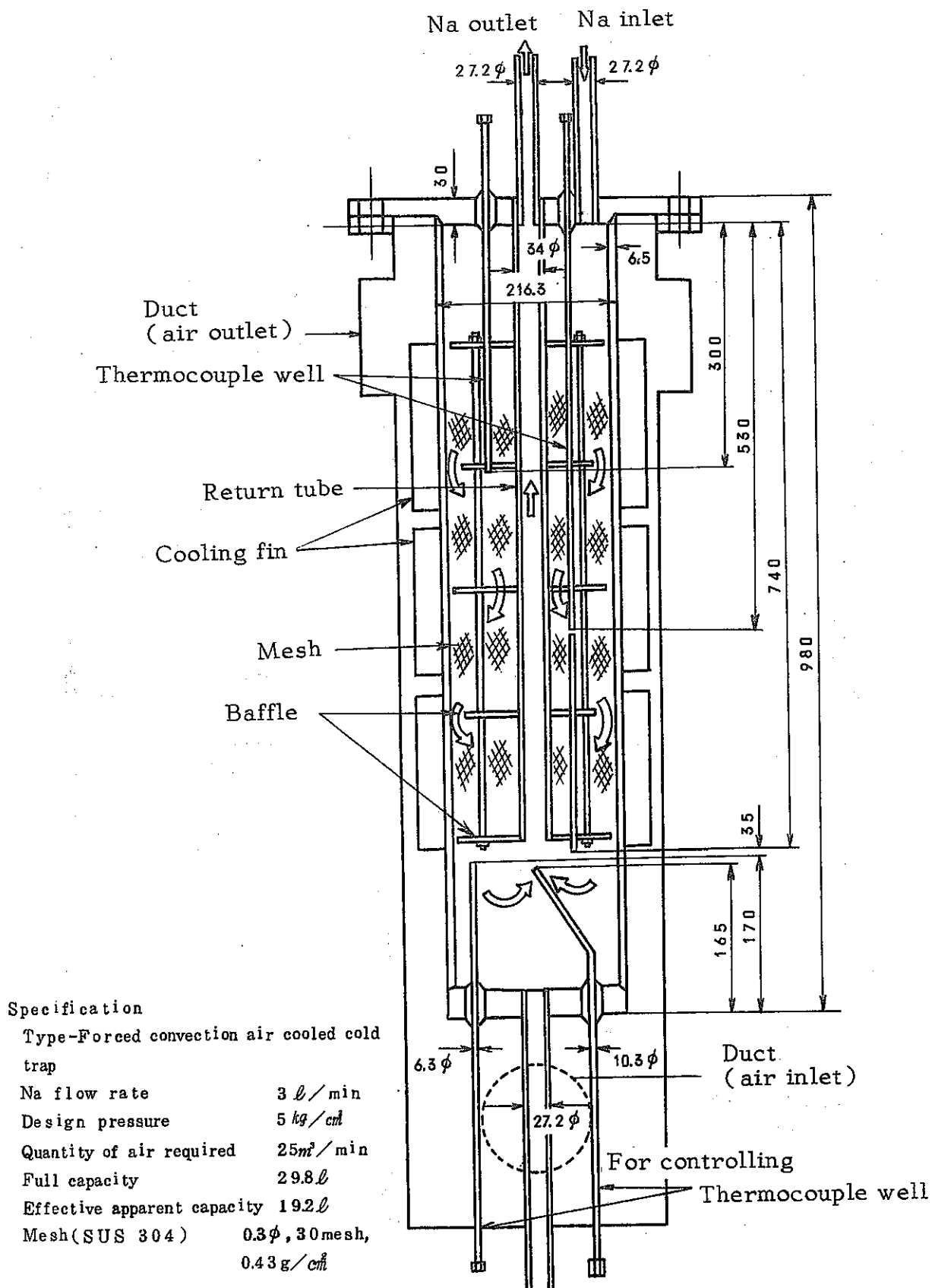
For controlling
Thermocouple well
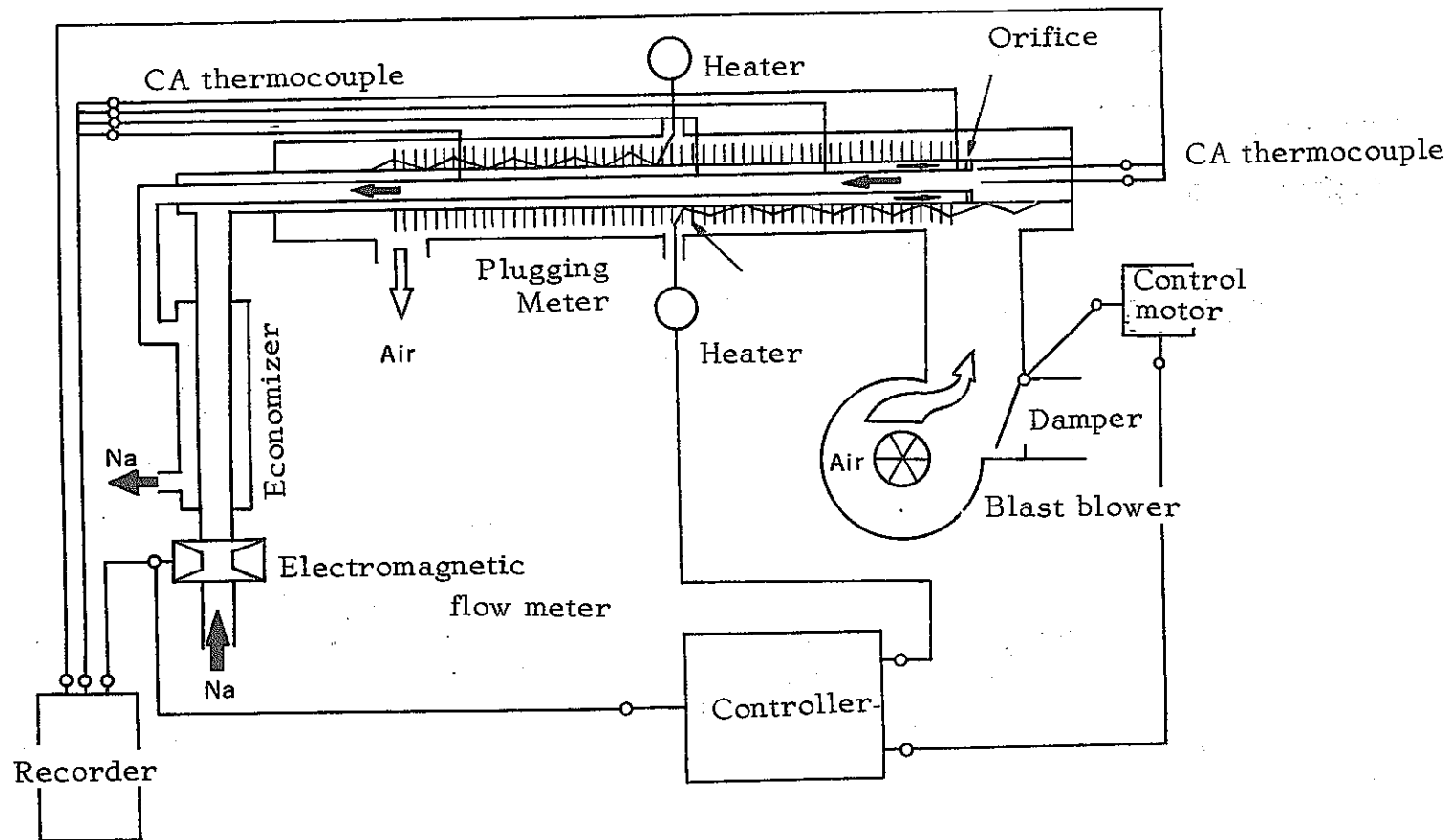
Fig.-7. Cold trap

- 34 -

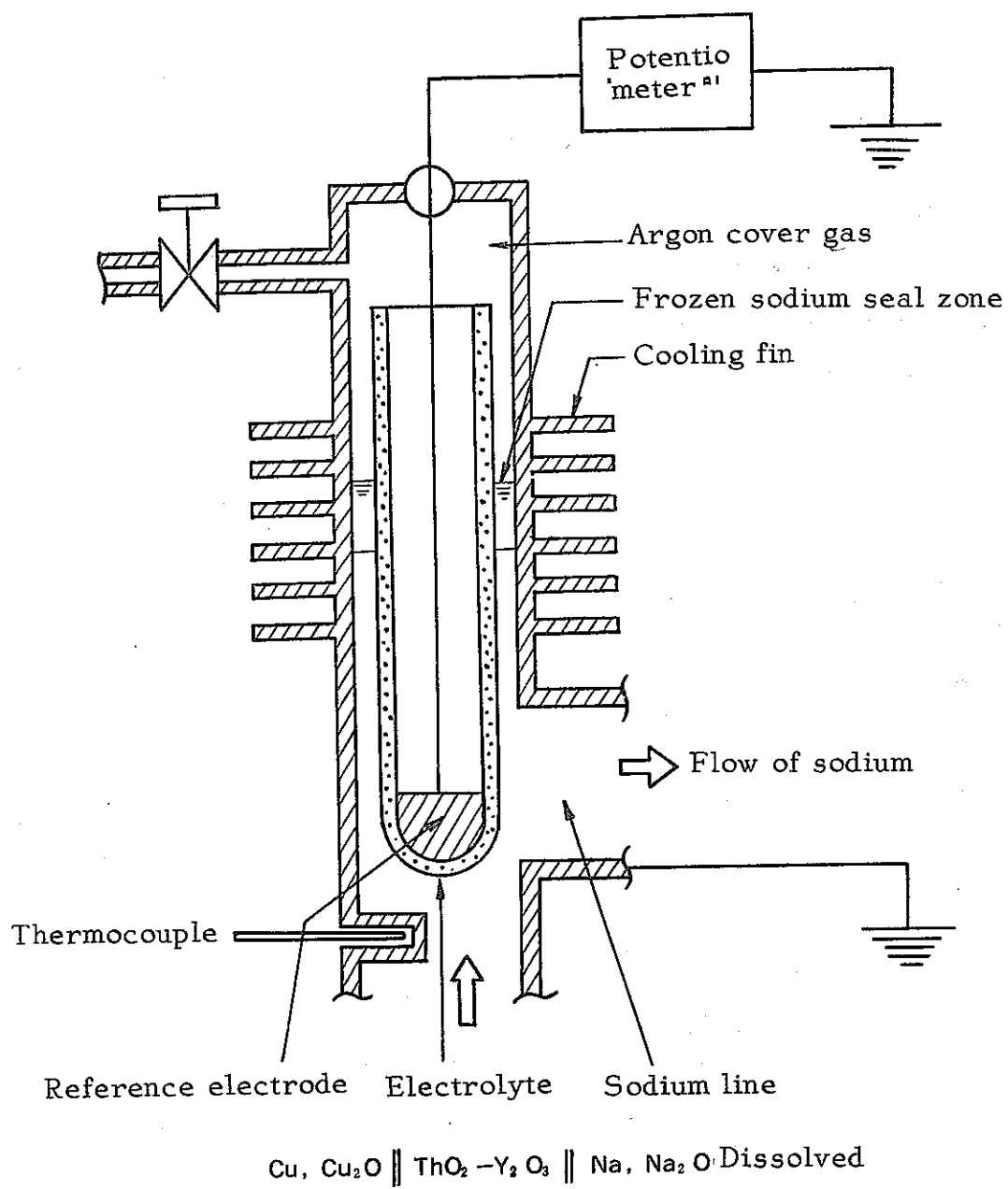Fig.-8.   Plugging Meter and Temperature Control System

Fig.-9. Schematic Diagram of Oxygen Meter for Liquid Sodium
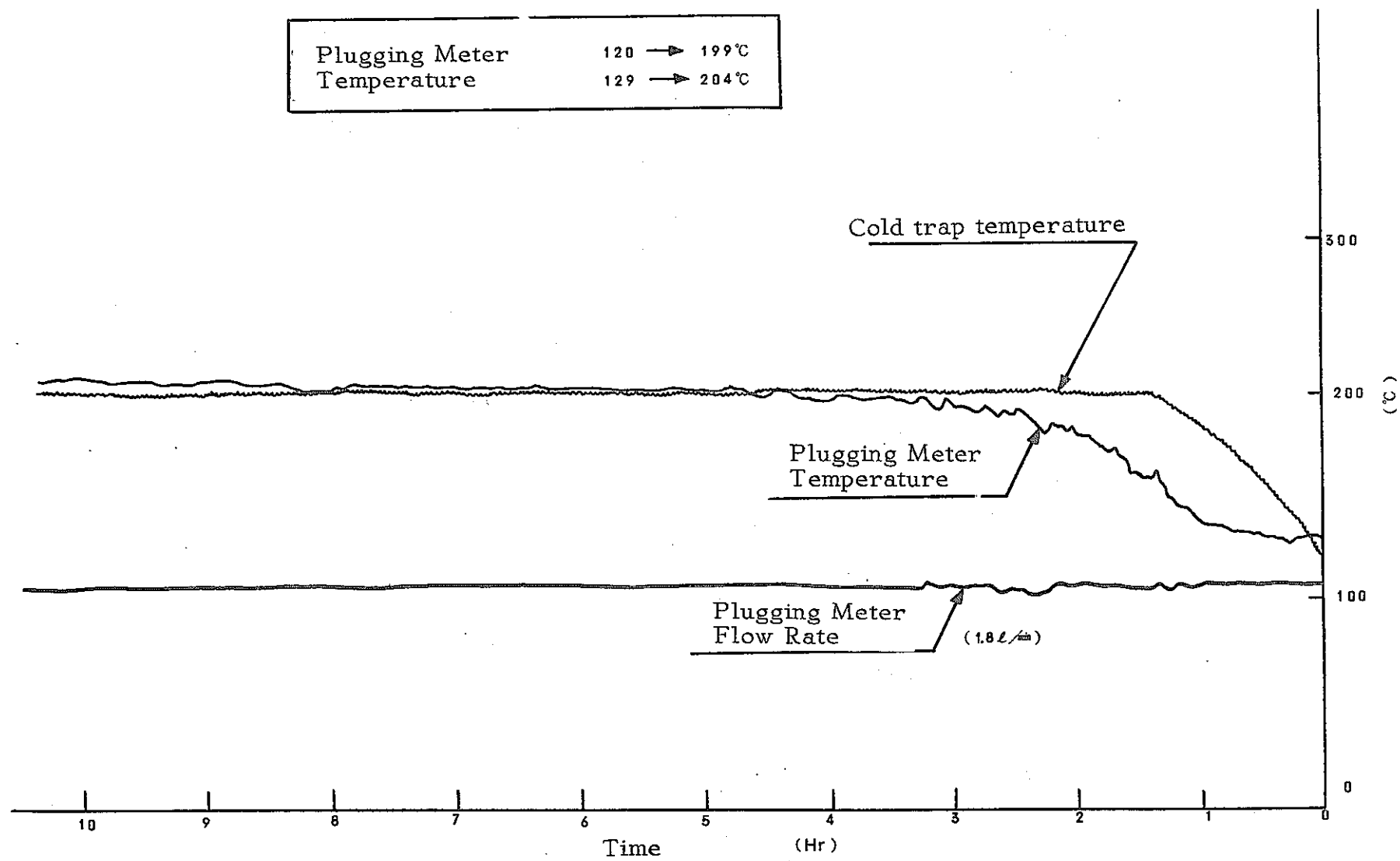
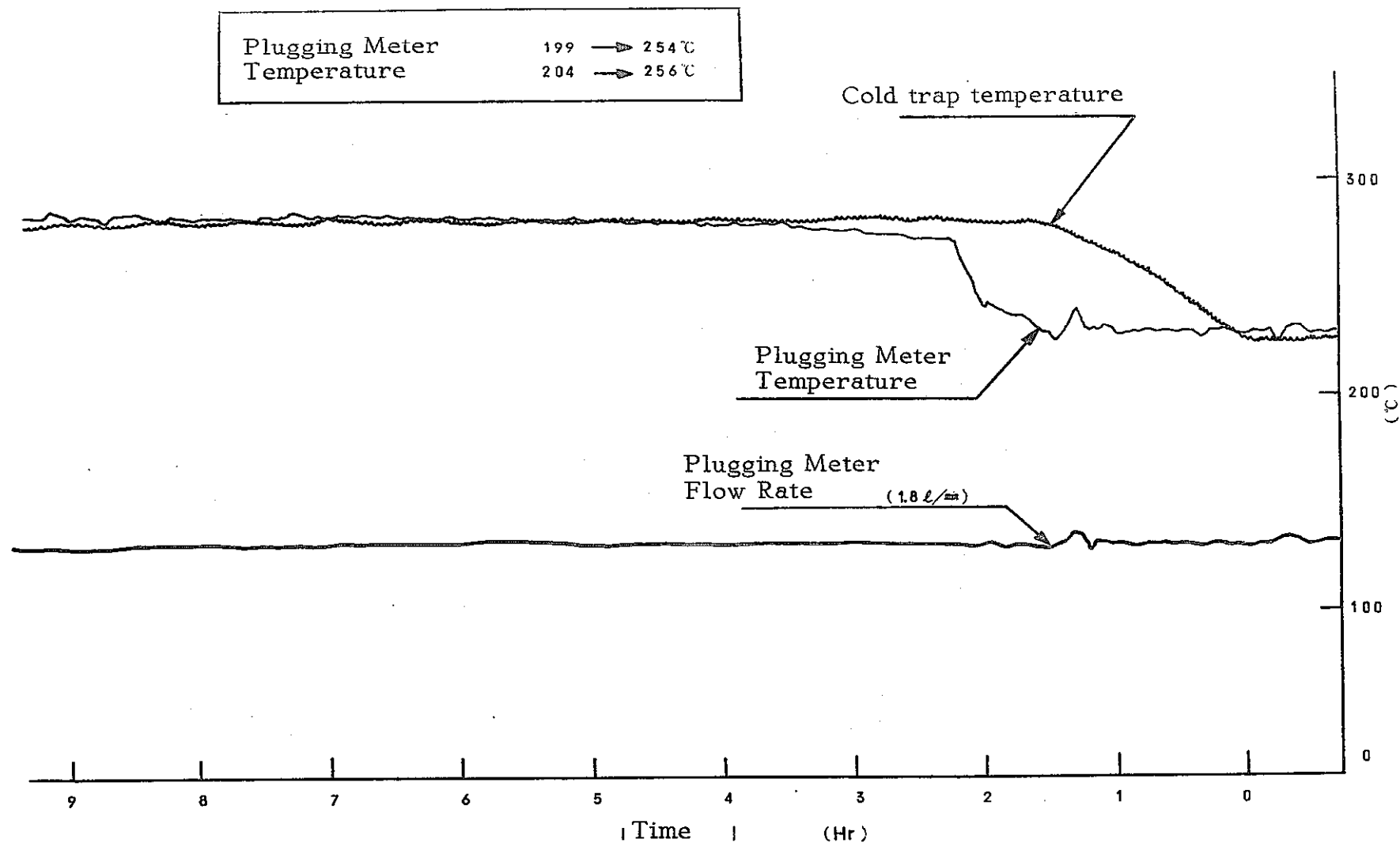Fig.-10-1. Behavior of Cold Trap in Transient State (leaching)

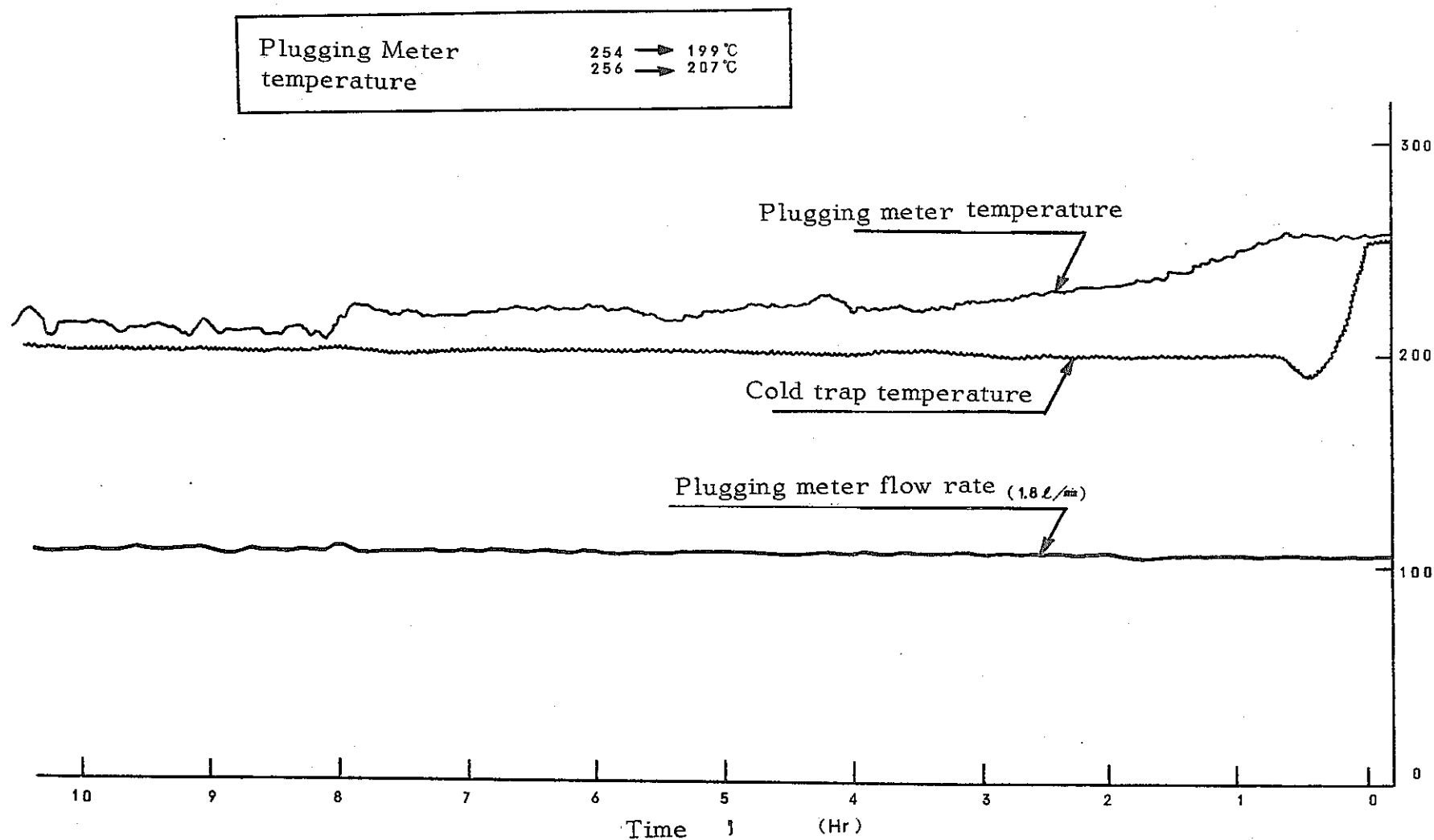Fig.-10-2.　Behavior of Cold Trap in Transient State (leaching)

Fig.-10-3. Behavior of Cold Trap in Transient State (trapping)
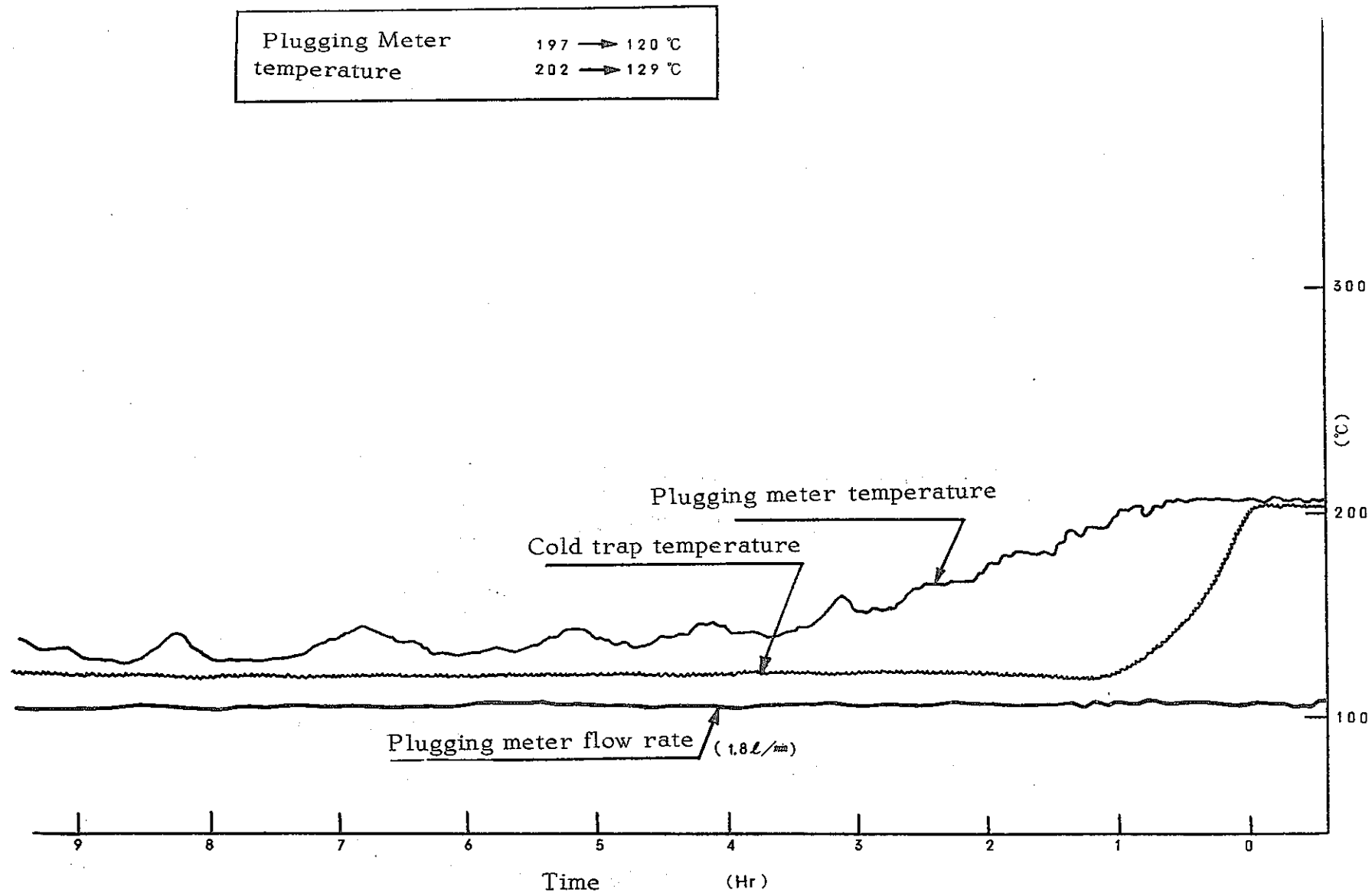
Fig.-10-4.   Behavior of Cold Trap in Transient State (trapping)

	Cold trap temperature ℃	Plugging Meter Temperature ℃
⊙	120 ⟶ 199	129 ⟶ 204
●	254 ⟶ 199	256 ⟶ 207
△	194 ⟶ 254	204 ⟶ 256
▲	197 ⟶ 120	202 ⟶ 129

$$\frac{C_t - C_\infty}{C_o - C_\infty} = \exp\left(-\frac{W}{M} t\eta\right)$$

$\eta = 0.5$

$\eta = 1$

$M = 192\,\ell$

$W = 3\,\ell/\text{min}$

y-axis: $\dfrac{C_t - C_\infty}{C_o - C_\infty}$
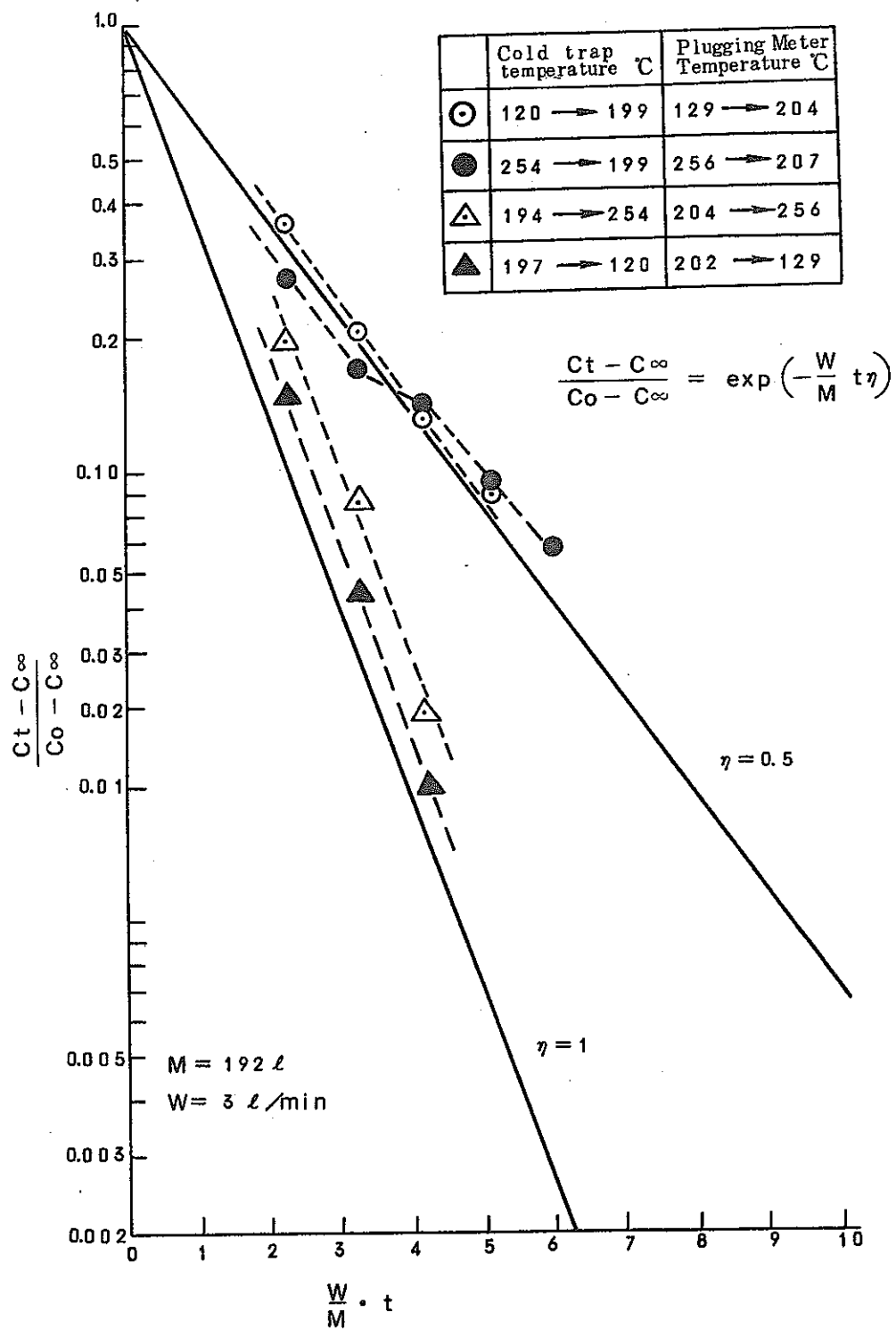
x-axis: $\dfrac{W}{M} \cdot t$

Fig.-11. Cold Trap Efficiency at Typical Runs

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Fig.-12. Relation between Cold Trap Temperature and Plugging Meter Temperature

Cold trap temperature

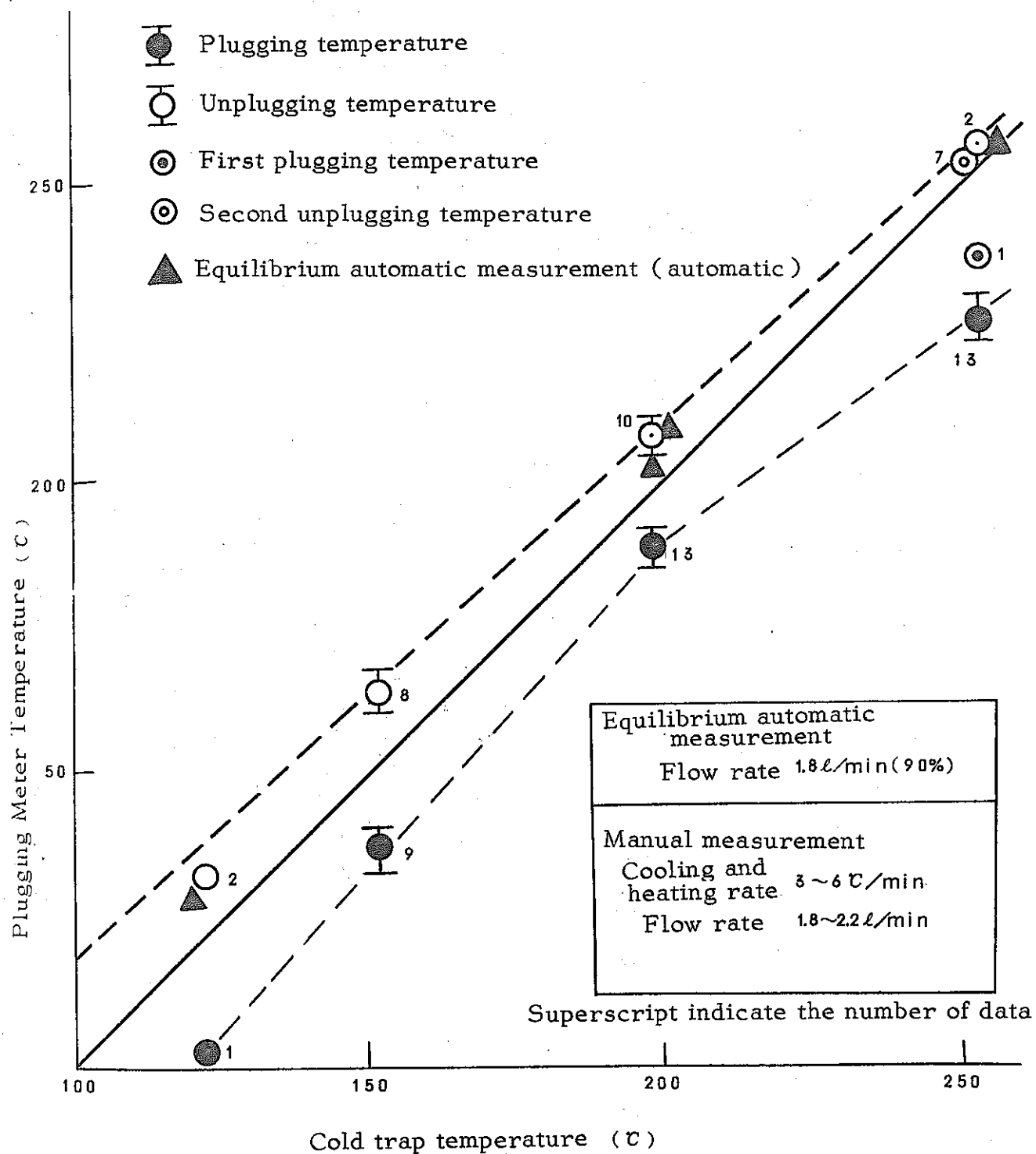Plugging meter temperature

Plugging Meter Temperature

Time   ↑ Hr

Plugging temperature
Cold trap temperature
Plugging meter flow rate
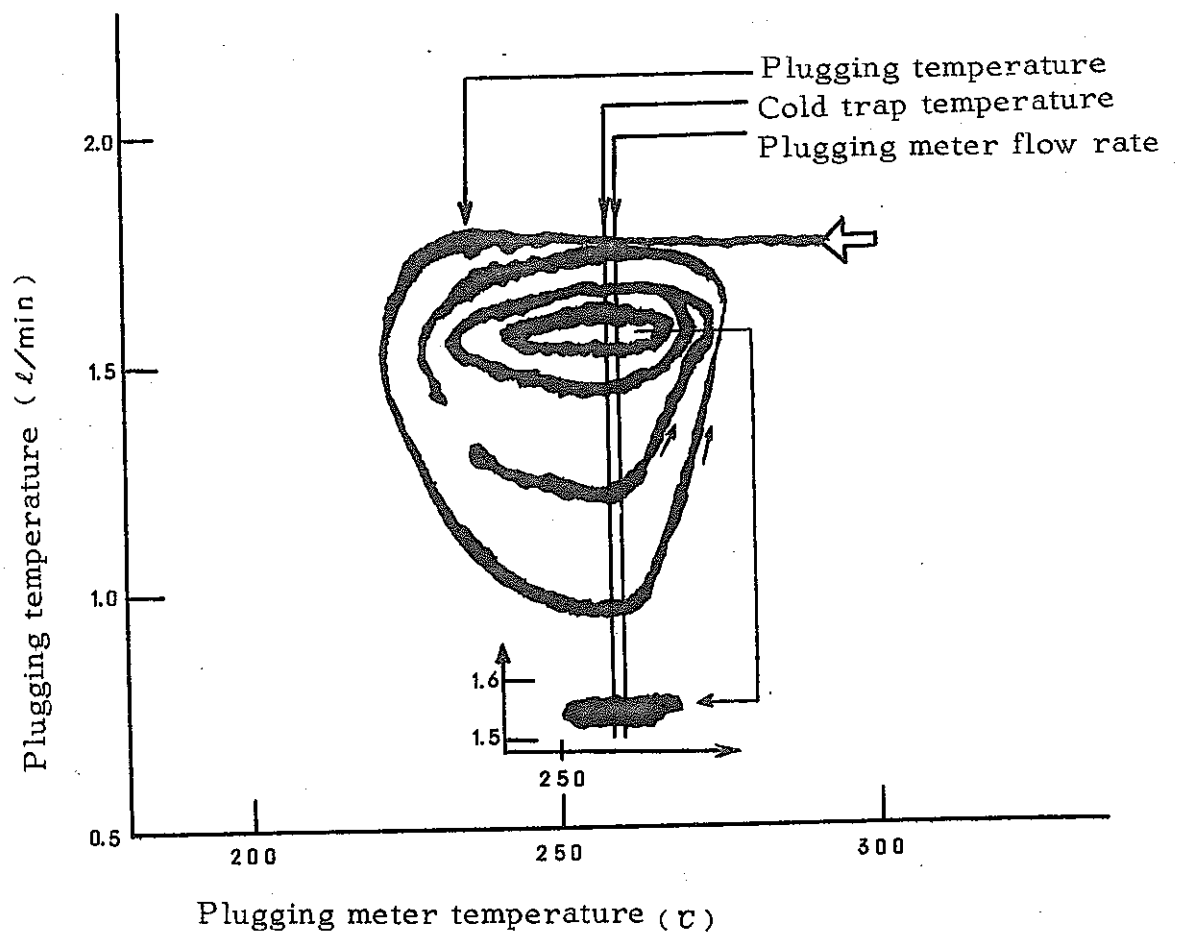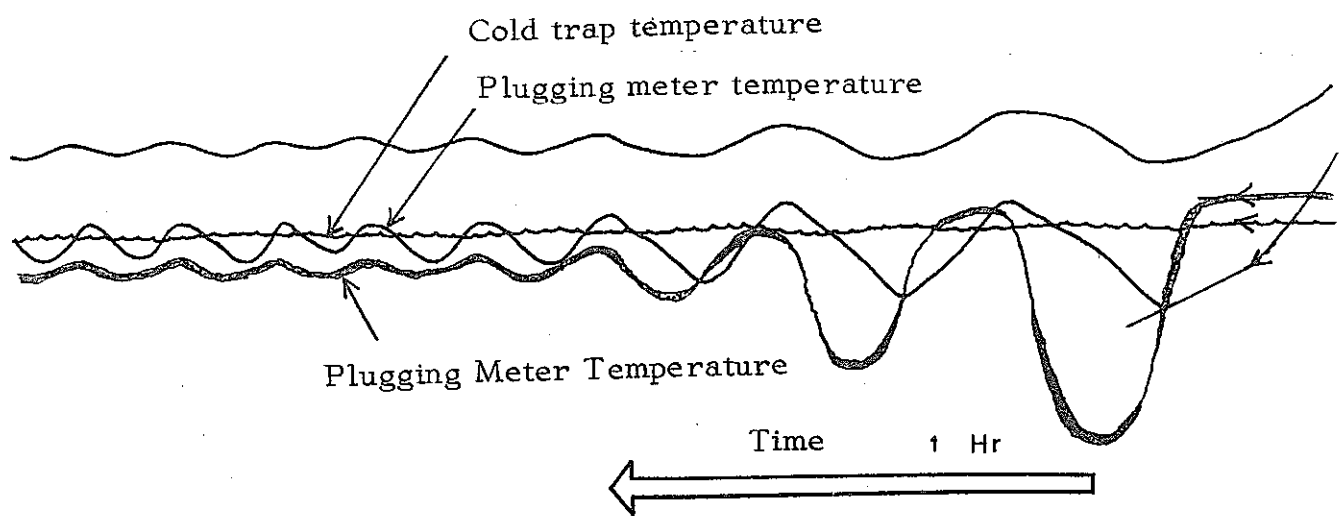
Fig.-13.   Relation between Cold Trap Temperature and Plugging Temperature
(automatic measurement by oscillating method)
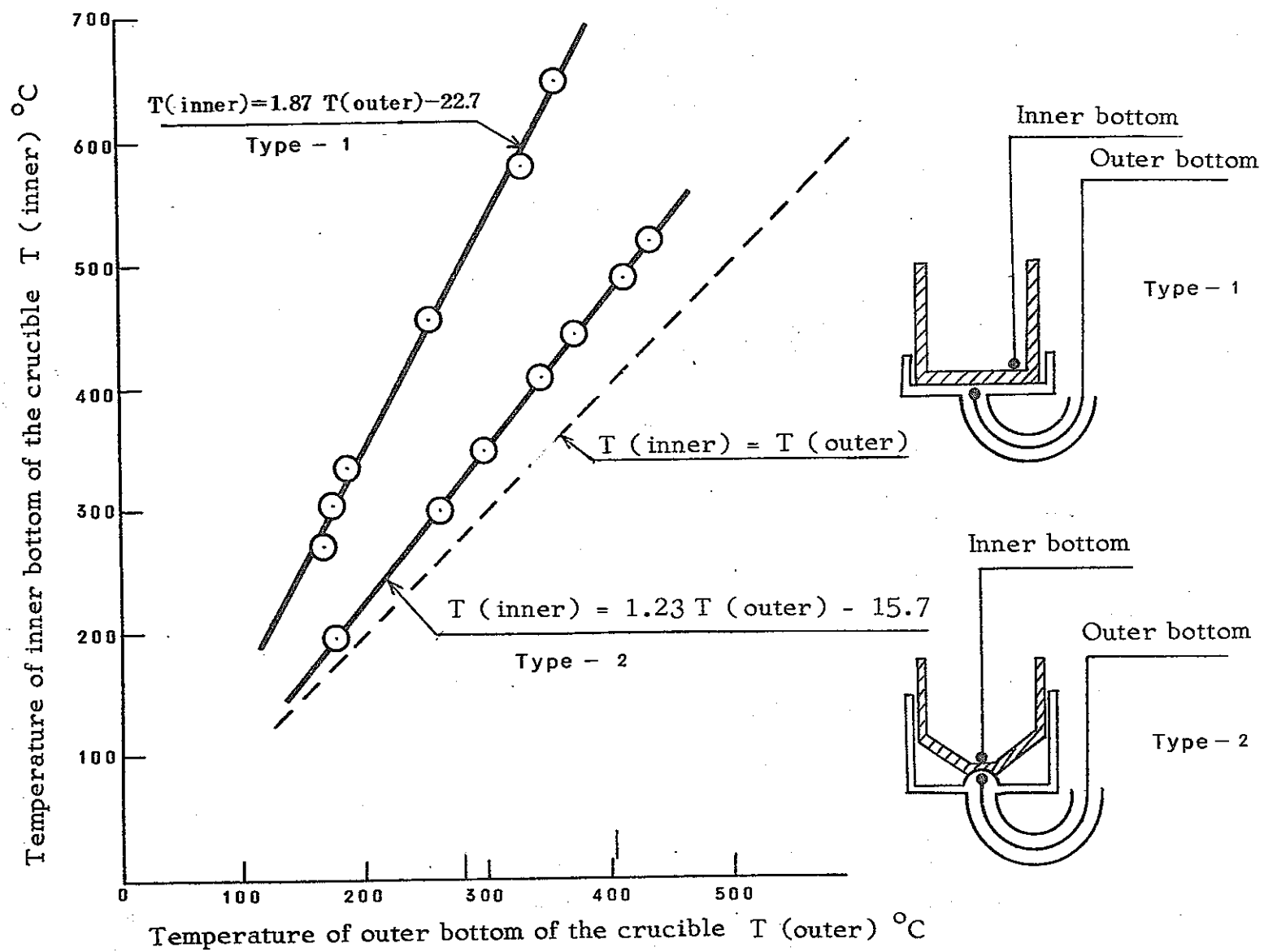
Fig.-14. Relation between the Temperature of Inner and Outer bottom of
the Crucible
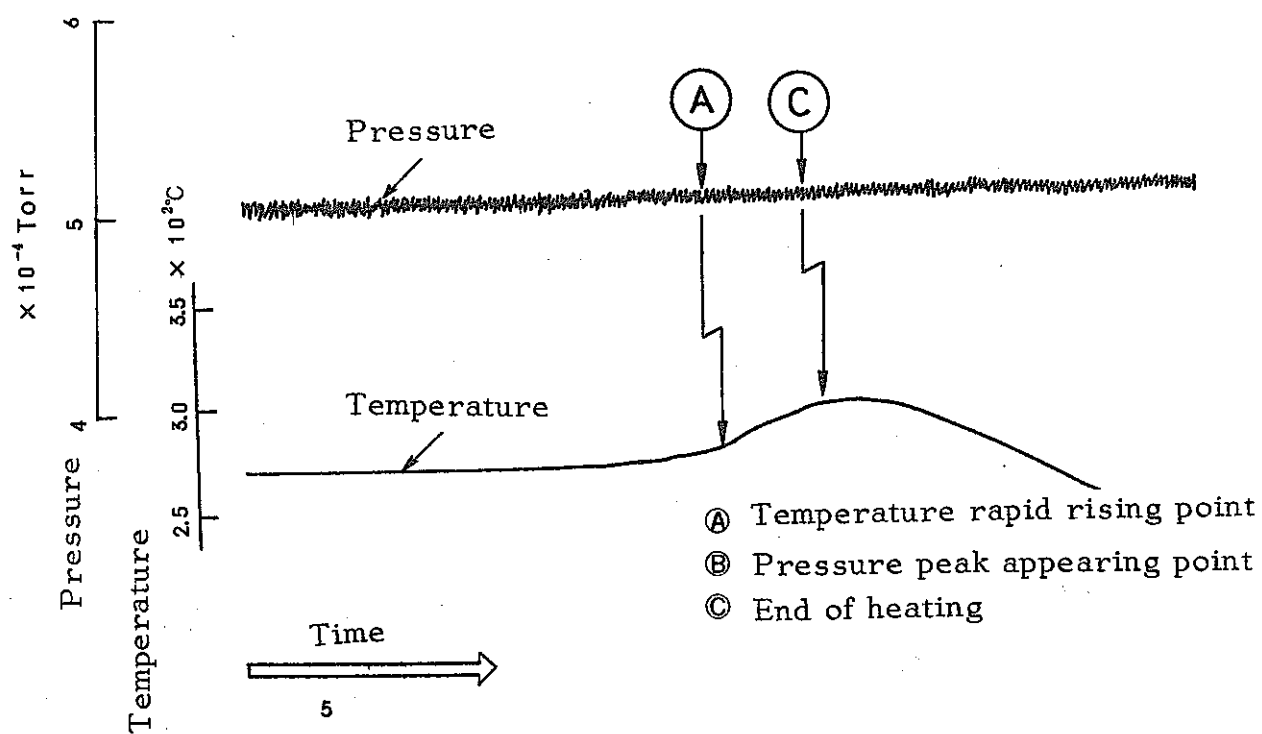
Fig.-15-1.   Profile of temperature and pressure during distillation (1)

Ⓐ Temperature rapid rising point
Ⓑ Pressure peak appearing point
Ⓒ End of heating
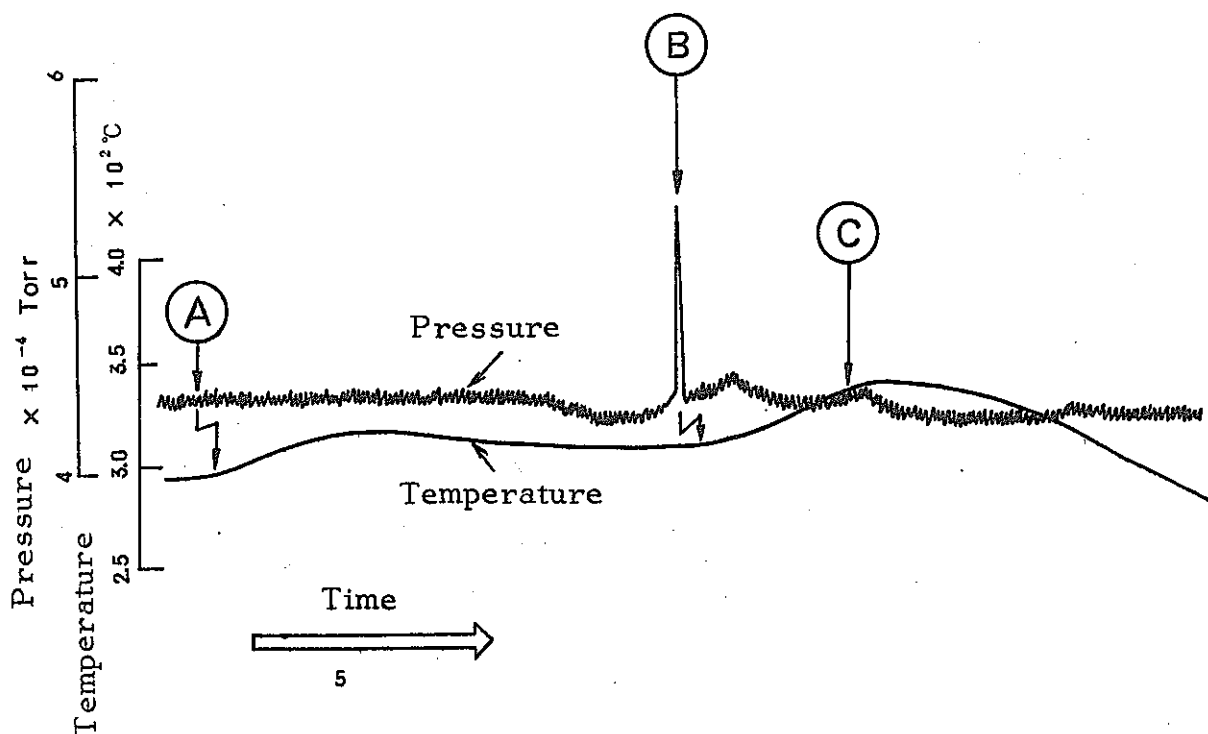
Fig.-15-2.   Profile of temperature and pressure at the end of distillation (2
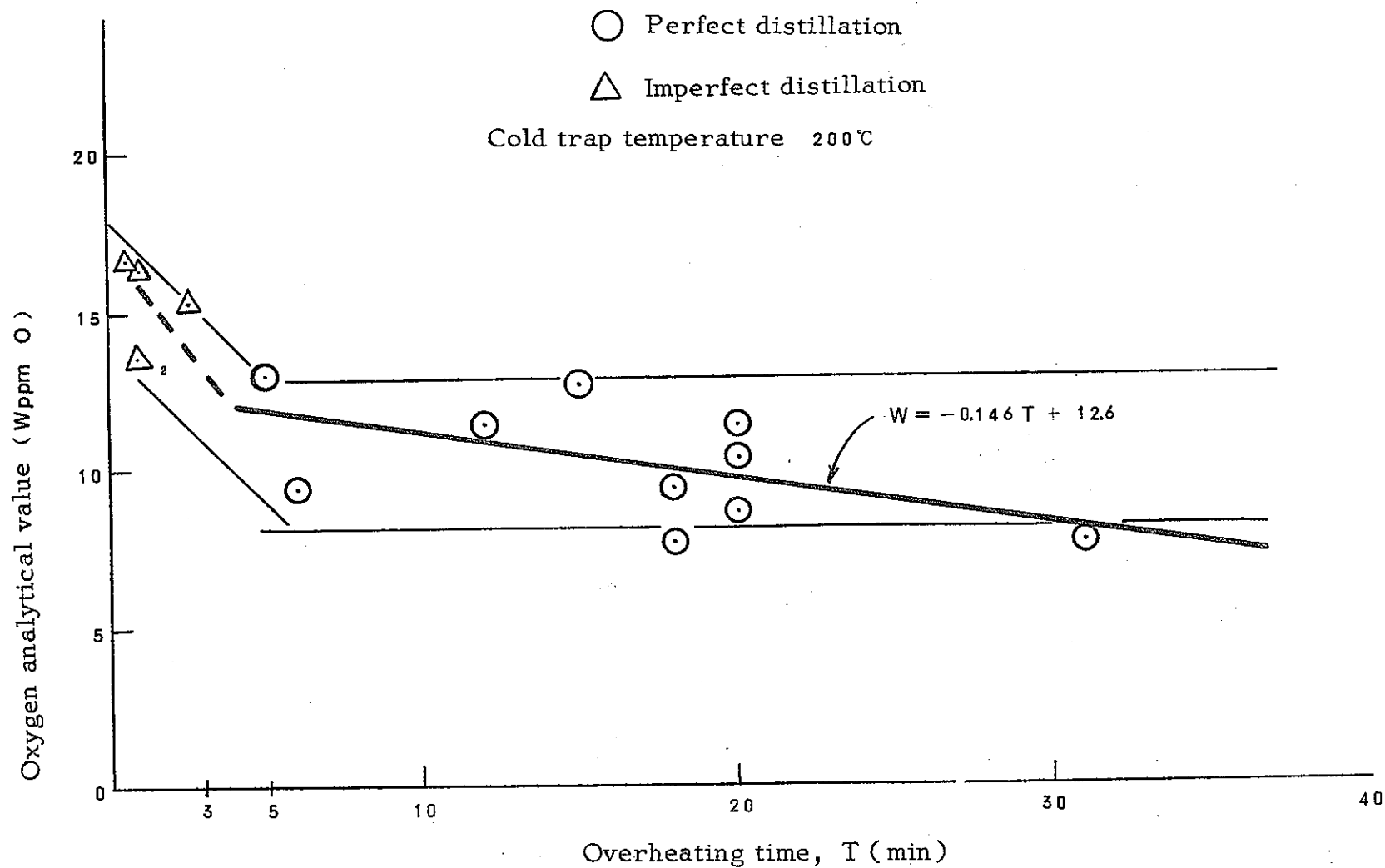
Fig.-16. Effects of Overheating Time on Oxygen Analytical Value
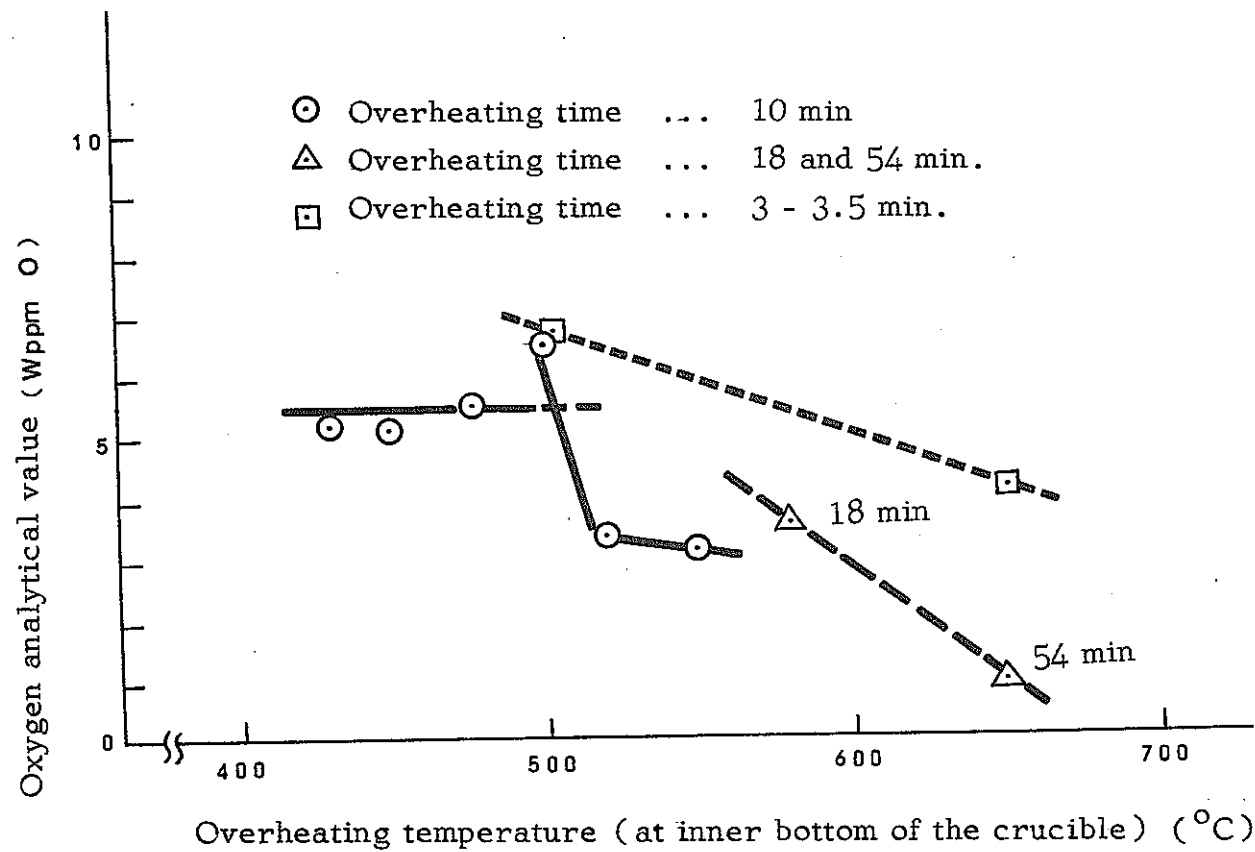
Fig.-17.   Effects of Overheating Temperature on Oxygen Analytical Value
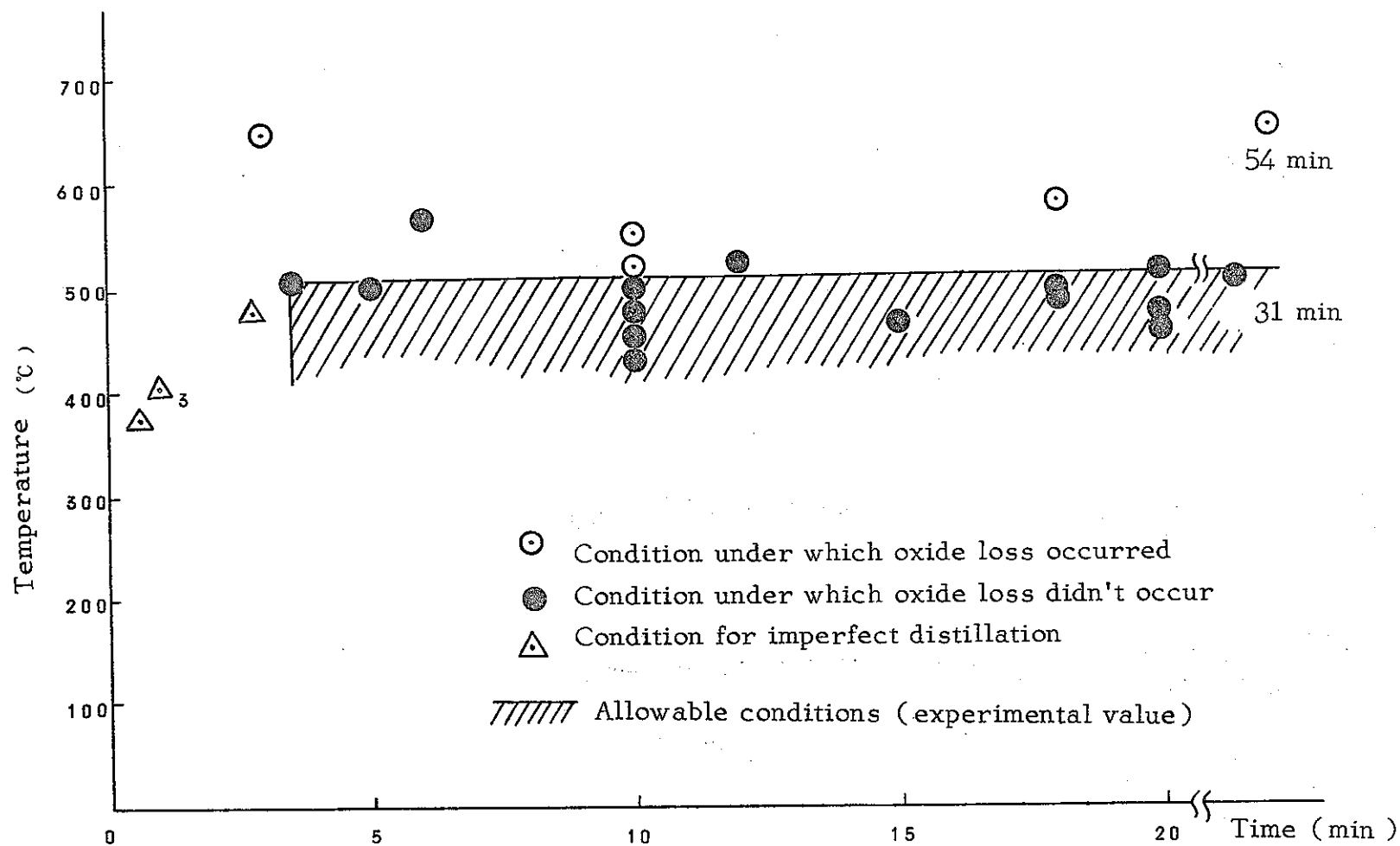
Fig.-18. Allowable Conditions for Overheating

- 47 -
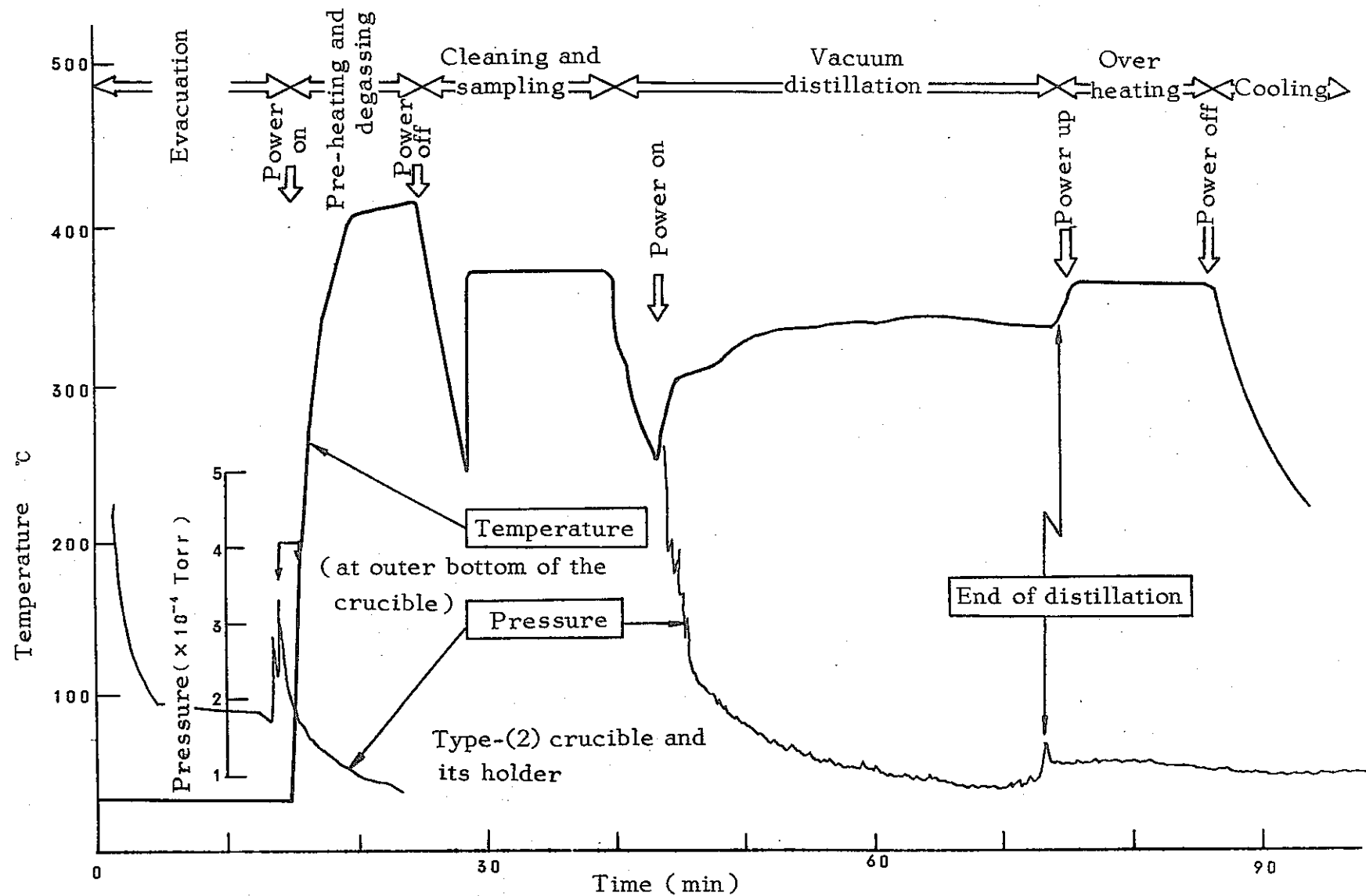
Fig.-19. Profile of Temperature and Pressure during Vacuum Distillation

Fig.-20. Oxygen Solubility in Sodium (analytical values)

Cold trap temperature (℃)

Oxygen meter EMF (volts)

$$E = 1.014 + \frac{75}{T}$$

E : Oxygen meter voltage
T : Cold trap temperature
(in oxygen saturated state)

Sodium temperature
at oxygen meter 315±1℃
Flow rate of sodium at oxygen meter 0.76 ~ 0.51 ℓ/min
UNC oxygen meter TP-1 Serial №351
Cold trap temperature 250 ⟶ 200 ⟶ 150 ⟶ 120℃ Equilibrium

Reciprocal cold trap temperature 1000/T (°K)
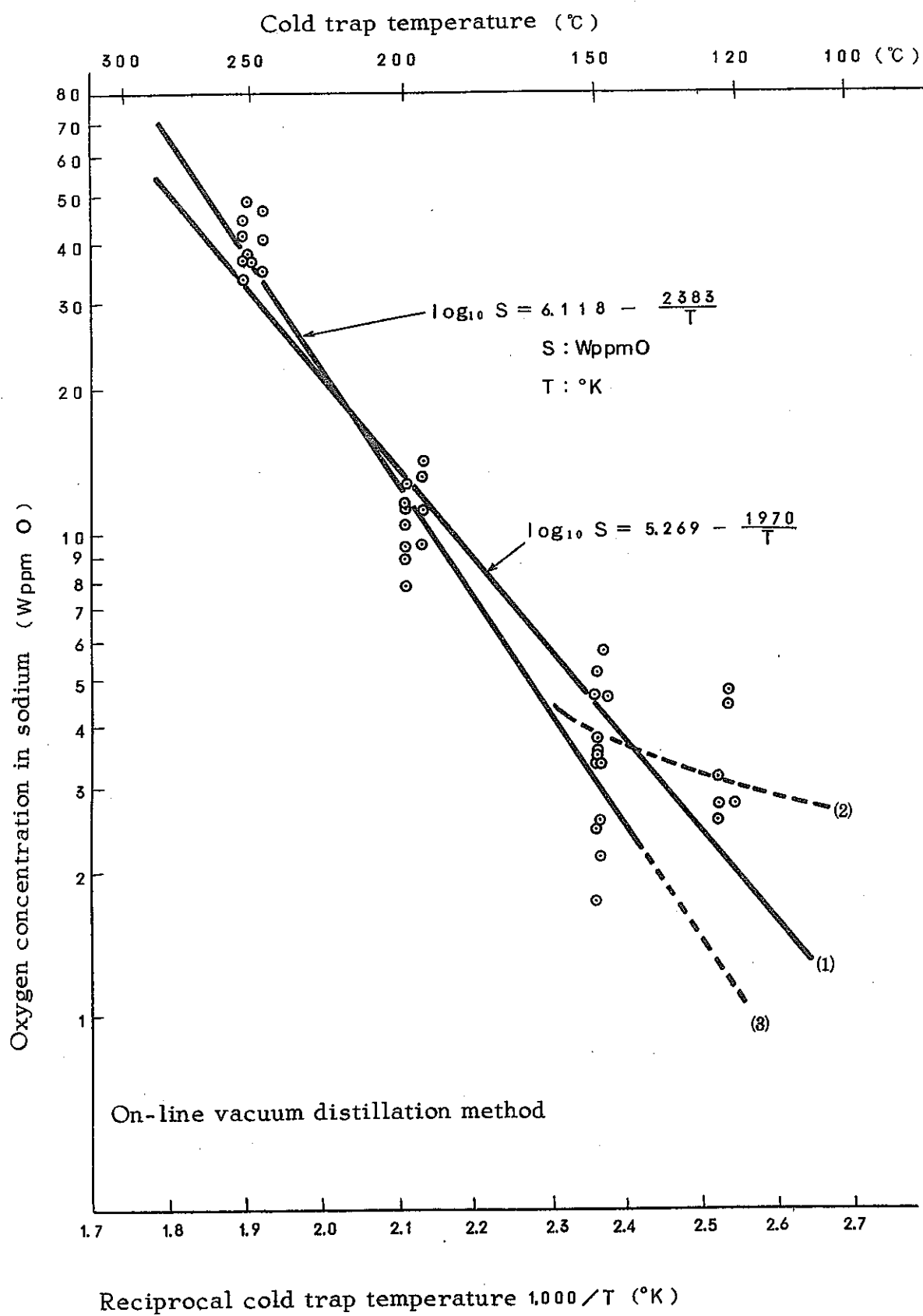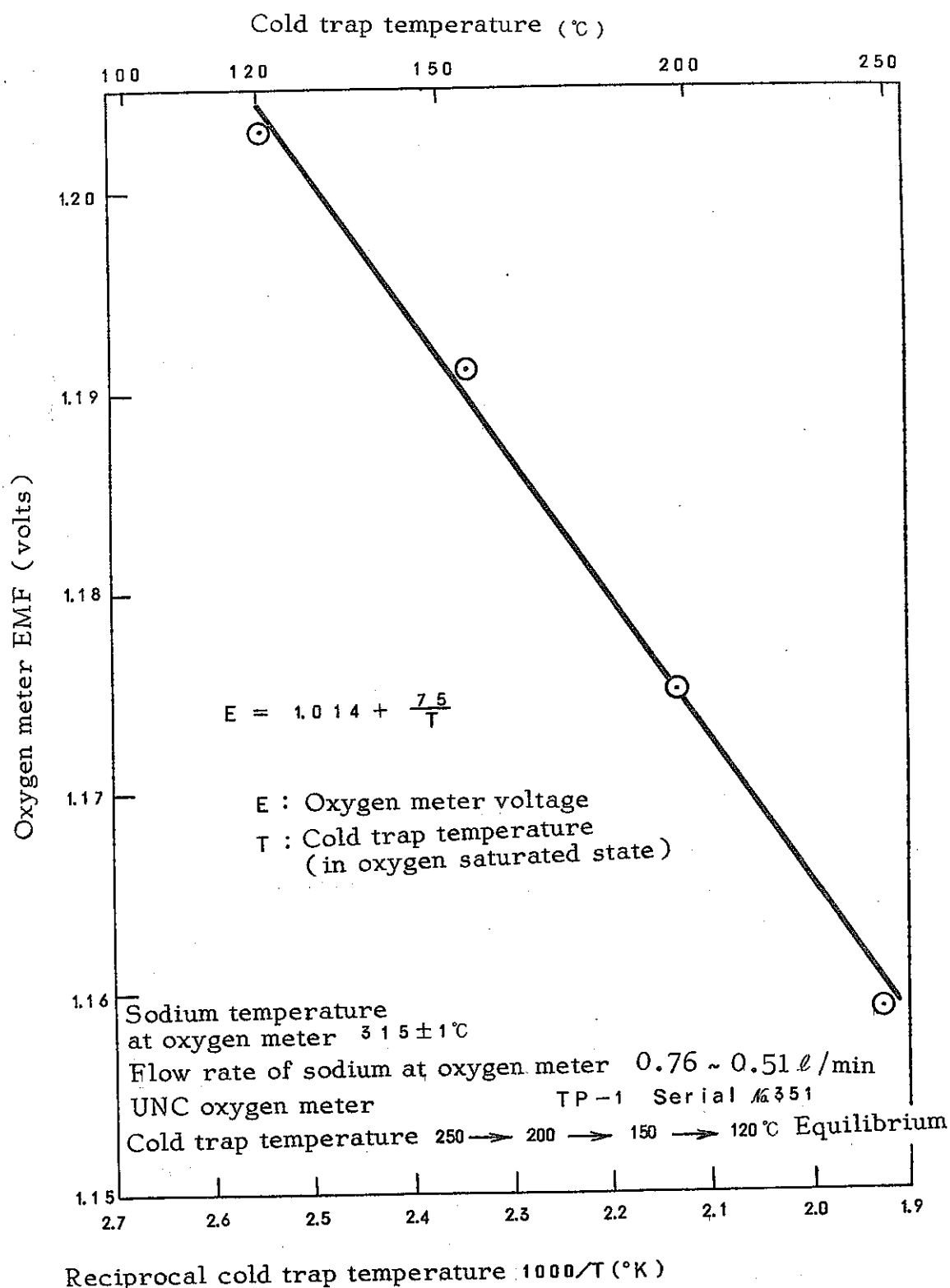
Fig.-21. Relation between Cold Trap Temperature and Oxygen Meter Voltage
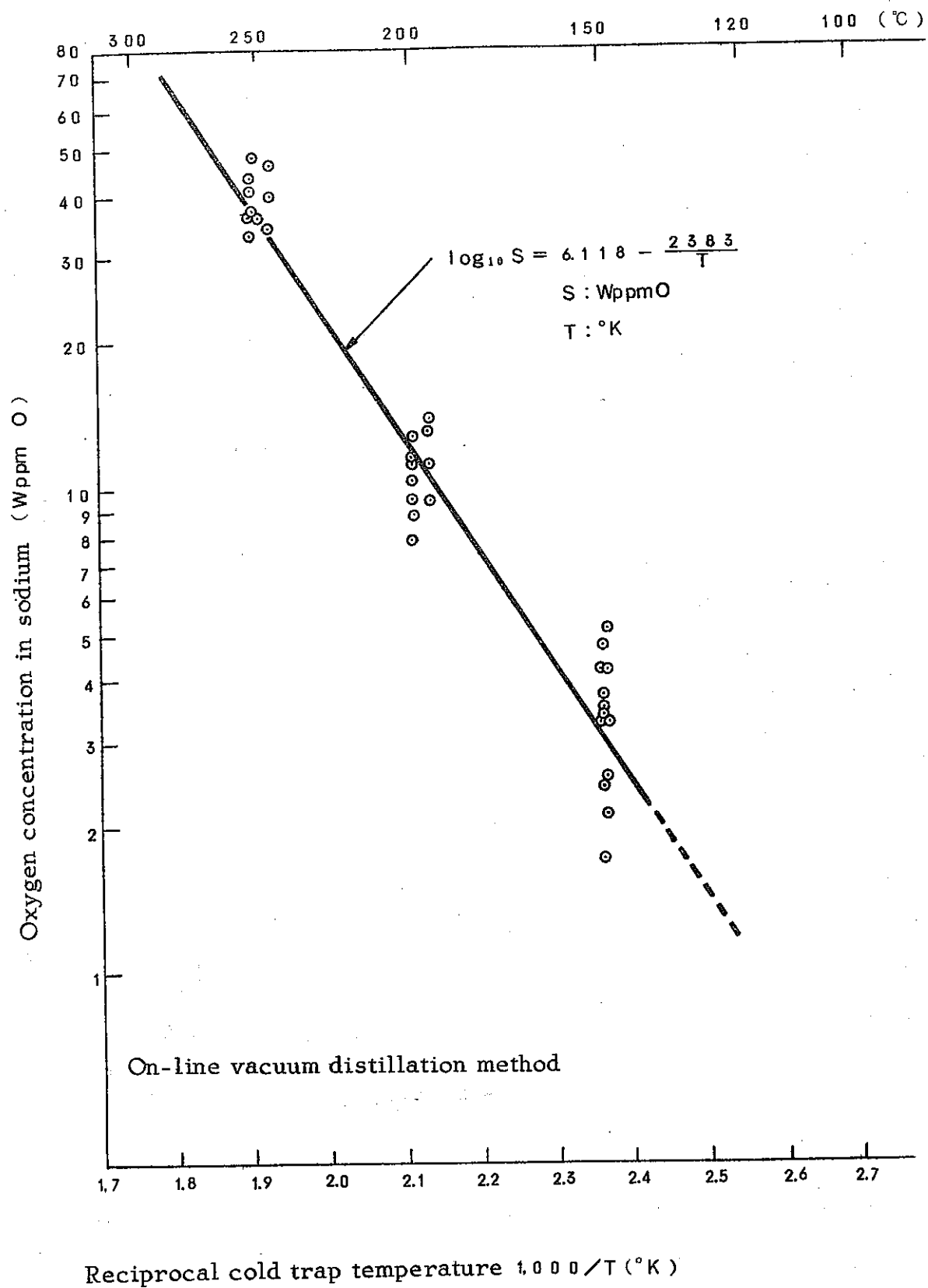
Fig.-22. Oxygen Solubility in Sodium

$$\log_{10} S = 6.118 - \frac{2383}{T}$$

S : Wppm O
T : °K
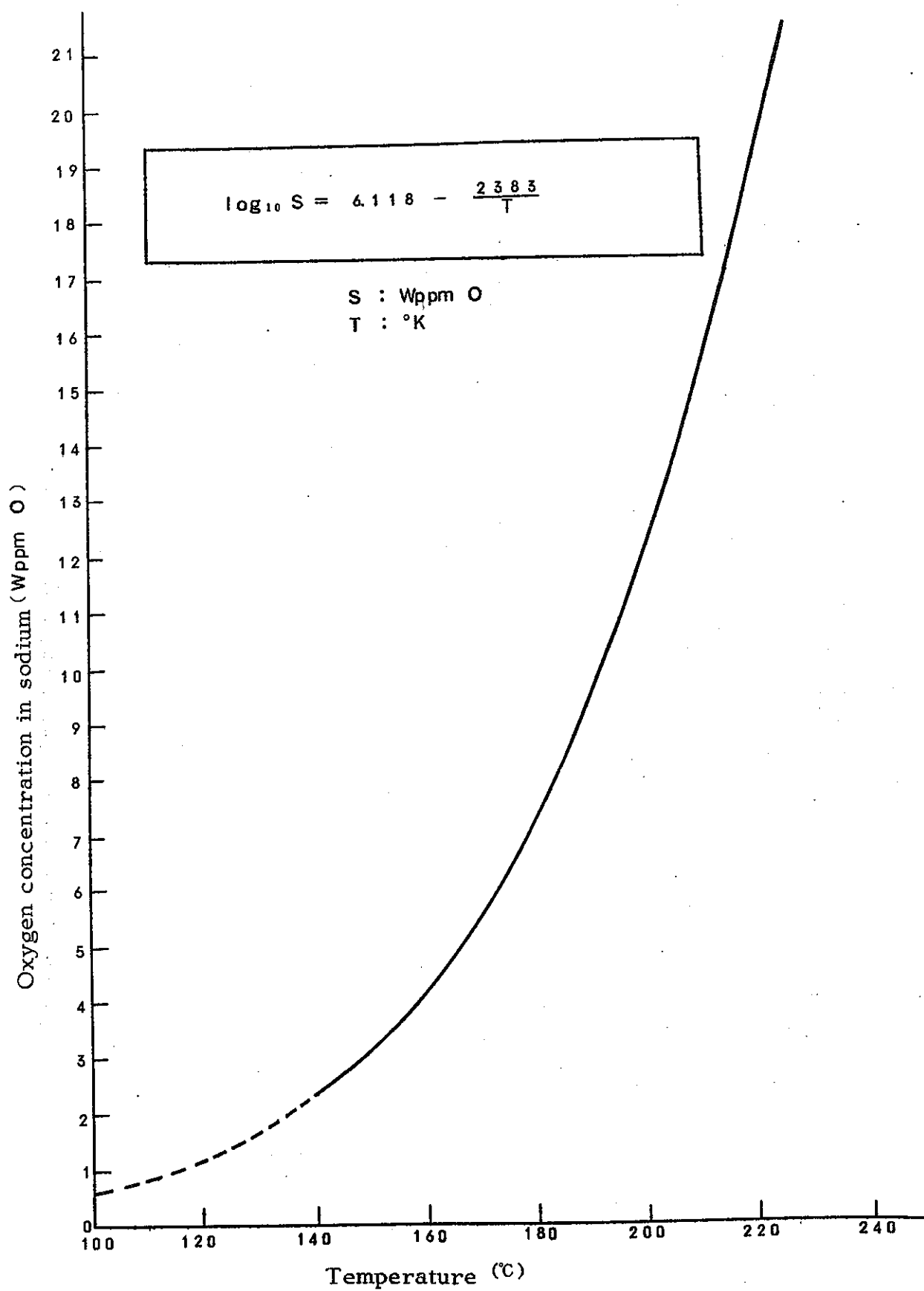
Fig.-23. Oxygen Solubility in Sodium

Fig.-24. Comparison of Oxygen Solubility in Sodium

The figure shows the comparison of oxygen solubility equations:

1. This work : $\log_{10}S = 6.118 - \dfrac{2383}{T}$

2. Claxton[6] : $\log_{10}S = 5.21 - \dfrac{1777}{T}$

3. Noden[5] : $\log_{10}S = 6.1579 - \dfrac{2384.2}{T}$

4. Eichlberger[3] : $\log_{10}S = 6.239 - \dfrac{2447}{T}$

5. Rutkauskas[7] : $\log_{10}S = 8.25 - \dfrac{3499}{T}$

S : Wppm O
T : °K
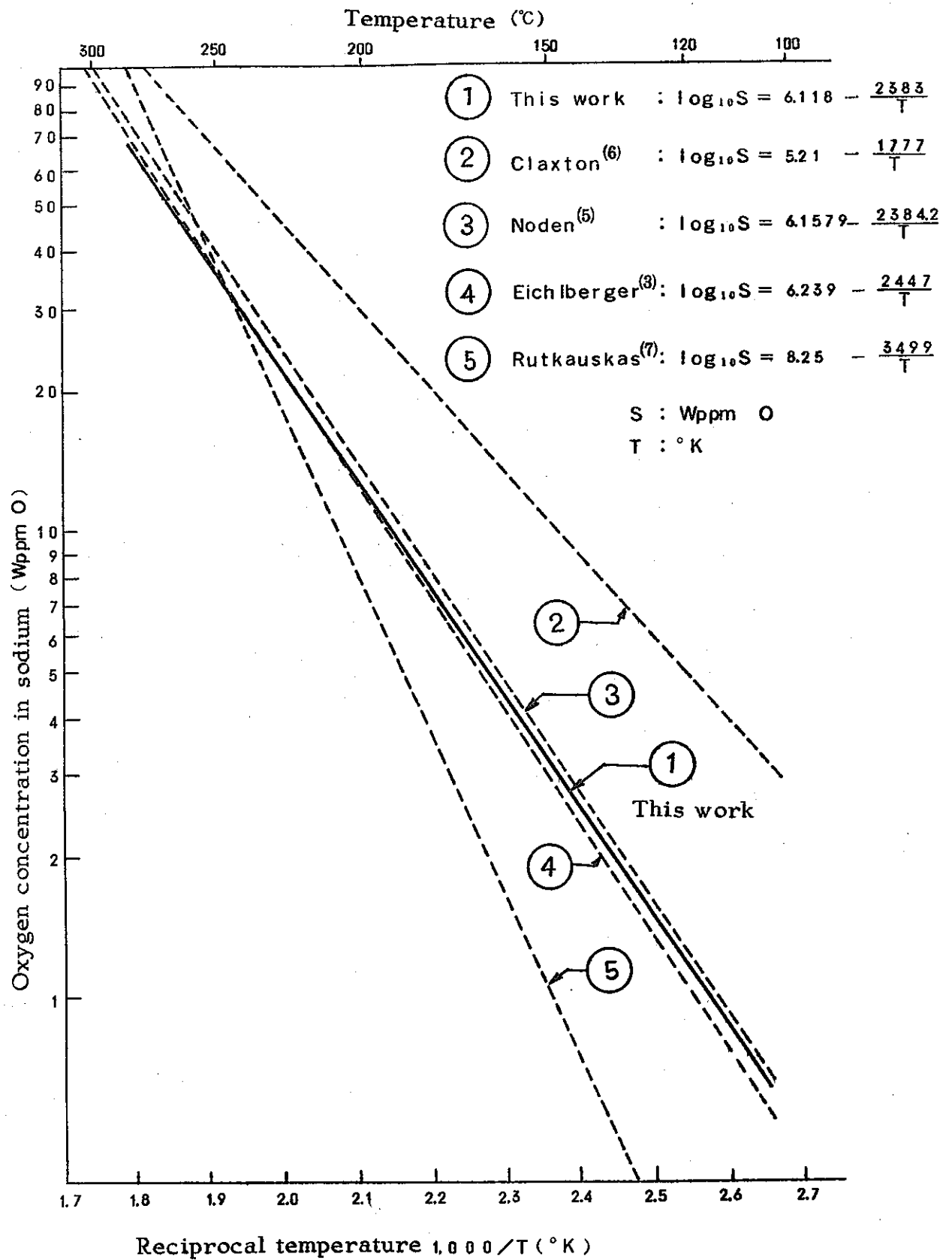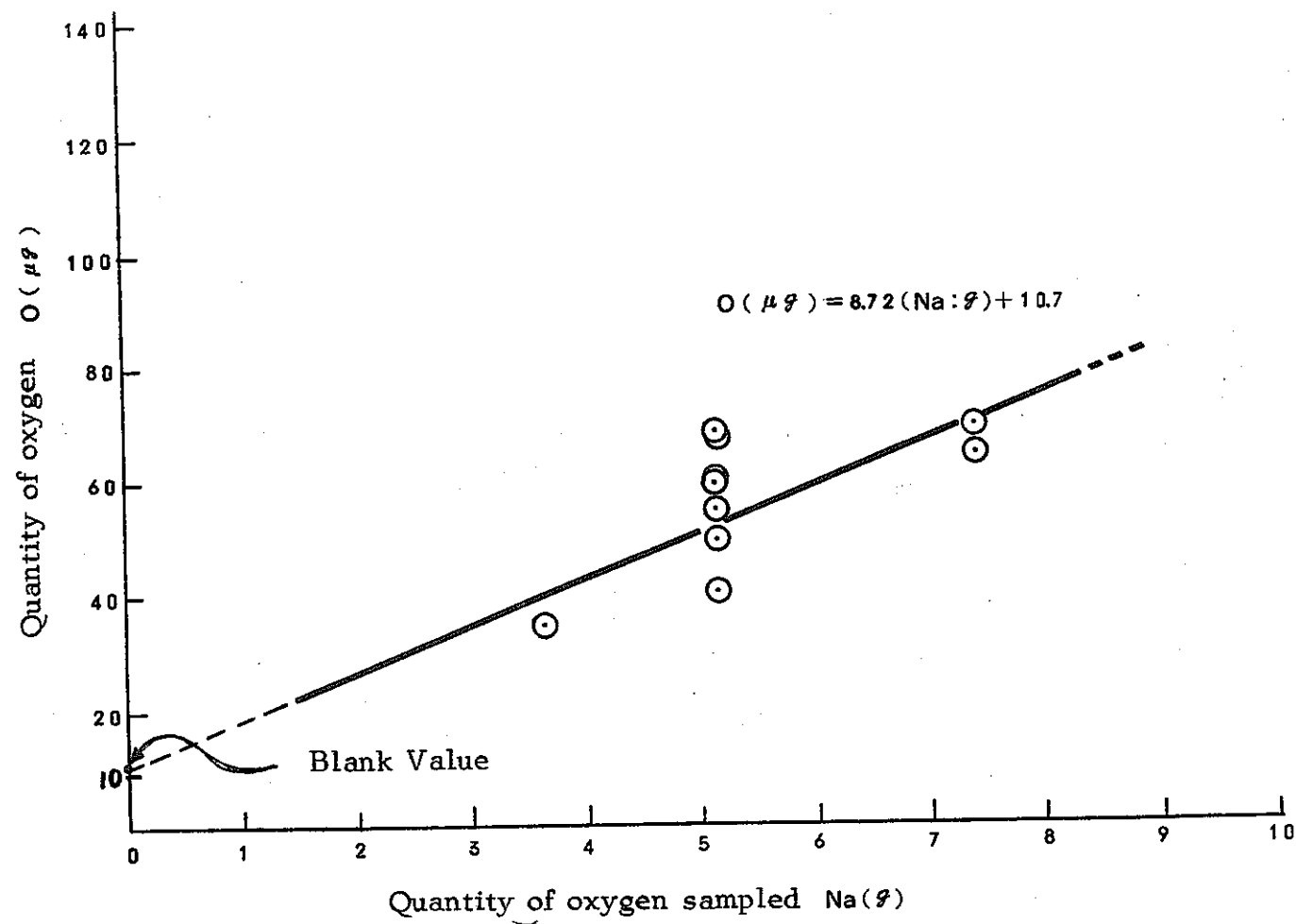
Fig.-25. Blank Value Obtained by means of Exterpolation

Symbol

⊙ : B　－V.D	B : By-pass flow through sampling method		
● : G.V－AM	SV : Vacuum thief sampling method using stainless steel tube		
△ : S.V－AM	GV : Vacuum thief sampling method using glass tube		
▲ : B　－AM	AM : Analytical method of separation by amalgamation process		
⊡ : S.V－V.D	V.D : Analytical method of separation by vacuum distillation		

Solubility curve obtained in this work

$$\log_{10} S = 6.118 - \frac{2383}{T}$$

Dipping cup-vacuum distillation method

Name of loop

a : General purpose sodium test loop
b : Low-purity material test loop
c : Medium-purity material test loop
d : Activated material test loop
e : Endurance test loop
f : 50MW steam generator test loop

Oxygen concentration in sodium (Wppm O)

1.8　　1.9　　2.0　　2.1　　2.2　　2.3　　2.4　　2.5　　2.6

Reciprocal cold trap temperature 1000/T (°K)

Fig.-26.　Comparison between Oxygen Concentration in various Sodium Test Loops of Oarai Engineering Center and Oxygen Solubility

Table-1: Loop operating conditions

Sodium capacity	192
Flow rate of cold trap line	3 ℓ/min.
Flow rate of plugging meter line	0 - 3 ℓ/min.
Flow rate of flow through sampling line	2 ℓ/min.
Flow rate of V8-8 line	5 - 2 ℓ/min.
Cold trap temperature	120 - 250 $^{\circ}$C
Temperature of heater (H8-1)	400 $^{\circ}$C
Temperature of heater (H9-1)	400 $^{\circ}$C
Temperature of impurities tank (expansion tank)	375 - 400 $^{\circ}$C
Piping and values	over 315 $^{\circ}$C

Table-2 Oxygen solubility in sodium (analytical values)

1) Tem- perature (°C)	2) Analytical values (ppm)	3) Mean values (ppm)	4) Standard deviation (ppm)	5) Relative standard deviation (%)
121 122 "	2.7 4.4 4.6	- -	- -	- -
124	2.5 3.1 2.7	2.8	-	-
150 "	2.1 5.1 2.5 4.2 3.3	3.4	1.2	3.5
151	3.5 1.7 3.4 2.4 4.7 4.2 3.3 3.7	3.3	0.9	2.7
196	13.1 9.4 14.0 11.2 13.0	12.1	1.8	15
201	11.6 11.4 7.8 10.3 9.4 12.7 8.8 7.8	10.0	1.8	18
246 "	34.8 40.1 46.1	- 36.7	- -	- -
251	36.7			
252 252	37.5 47.9	-	-	-
252 253	41.0 33.4 41.0 36.5 43.8	39.1	4.1	18

1) Cold trap temperature at sampling time.
2) More than 5 analytical values under same condition were statistically treated.

Table-3: Recommended equations and experimental equations of oxygen solubility

Original worker or reviewer	Number of literatures used ※	Number of data used	Temperature range °C	Recommended equation or experimental equation $\log_{10} S(wppmo) =$
(6) Claxton review	4	88	110~555	$5.21 - \dfrac{1777}{T}$
(3) Eichelberger (review)	6	107 Selected	125~555	$6.239 - \dfrac{2447}{T}$
(5) Noden review	11	217 Selected	114~555	$6.1579 - \dfrac{2384.2}{T}$
(7) Rutkauskas Experiment	—	52	125~300	$8.25 - \dfrac{3499}{T}$
This work	—	37	150~250	$6.118 - \dfrac{2383}{T}$

※ For the original data and authors, refer to the Review in which they are introduced.

Table-4: Oxygen concentration in various sodium test loops

Loop name	Cold trap temperature	Analytical value, w ppm o note(1)	Mean value	Note(2) analytical method	Note(3) sampling method
General Purpose Sodium	1 5 0	4. 9, 4. 9, 5. 0, 6. 2,	5.3	A.M	B
Low-purity sodium material test loop	1 8 9	8. 7. 10.2, 10.1, 9. 7, 1.1.2, 8. 3	9.7	A.M	S V
	1 8 5	10.8, 6. 0, 9. 0, 8. 6	8.6	A.M	G V
Medium-purity sodium material test loop	1 4 4	5. 0, 6. 8, 3. 9, 6. 2	5.5	A.M	S V
Activated material test loop	1 9 0	9. 0, 10.6, 10.3, 9. 5, 9. 7	9.8	A.M	G V
	2 0 0	6. 6, 6. 5, 8. 1	7.0	A.M	G V
	2 0 5	1 3.7, 10.8, 10.7	11.7	A.M	G V
	2 6 0	4 0.1	40.1	V.D	S V
Endurance test loop for "Joyo"	1 4 7	3. 9, 3. 7	3.8	V.D	B
	1 5 0	2. 7, 3. 0, 3. 5, 3. 8	3.3	V.D	B
	1 9 0	1 1.0, 10.2	10.6	V.D	B
50MW steam generator test loop	1 2 0	− 2. 0	2.0	V.D	B
	1 2 0	1. 7	1.7	V.D	B

Note (1):   Analytical blank value is corrected

Note (2):   A.M.:   Amalgamation method
V.D. :   Vacuum distillation method

Note (3):   B   :   By-pass flow through sampling method
SV   :   Vacuum thief sampling method using stainless steel tube
GV   :   Vacuum thief sampling method using glass tube