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THE CONSTRUCTION AND OPERATION
OF A SODIUM PURIFICATION APPARATUS

AEC Research and Development Report

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THE CONSTRUCTION AND OPERATION
OF A SODIUM PURIFICATION APPARATUS

By

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ABSTRACT

An apparatus for purifying sodium by a process involving hot gettering and distillation through a fractionating column has been constructed and operated with success. Gettering is accomplished by the use of zirconium foil at 650°C. The gettered sodium is distilled at 550°C through a packed column equivalent to two theoretical distillation plates. The product sodium has fewer and lower concentrations of metallic impurities than does a 99.999% pure spectroscopic grade sodium chloride standard. The oxygen content of the sodium product ranges downward from 5 ppm to 0.6 ppm, the latter value having been obtained in the latest preparation.

I. INTRODUCTION

Experimental studies of the interactions of materials must be carried out using well-characterized materials of known purities. This is particularly necessary for basic work involving liquid sodium as a solvent medium.

The presence of impurities in sodium has been observed to affect markedly the corrosion rates of metals and alloys.^(1, 2, 3) For example, dissolved oxygen increases corrosion by the formation of compounds of the $\text{Na}_x\text{M}_y\text{O}_z$ type. In the program presently under way, the immediate goal is to perform studies of binary systems such as Na-Fe and Na-Ni, and it is therefore necessary to purify the sodium used to the highest degree. The impurities of concern in their general order of importance are: oxygen, iron, chromium, nickel, other nonmetals, and other metals. Unfortunately, it is difficult to specify in advance the maximum allowable levels for the various impurities. It was found by Mausteller and Batutis⁽²⁾ that there was a marked decrease in the rate of attack of stainless-steel constituents exposed in sodium when the oxygen content of the sodium was reduced from 100 to 30 ppm. An oxygen level of 10 ppm is the generally accepted goal of present-day sodium-cooled reactor systems.⁽⁴⁾ Therefore, the goal of oxygen impurity level for sodium to be used in the present basic research study has been set at <5 ppm. It is also desired that the concentrations of the metallic impurities be as low as can be attained.

The need for achieving minimum concentrations for the metallic impurities precludes the use of a simple gettering treatment. The only practical method of reducing the concentrations of the various metallic impurities is to use a distillation technique. Support for this decision is obtained from Horsley's report.⁽⁵⁾ Horsley discusses in some detail the theoretical considerations affecting the separation from sodium of hydrogen (as NaH and NaOH), of oxygen (as Na_2O , Na_2O_2 , Na_2CO_3 , and NaOH), of chlorine, of sulfur (as Na_2SO_4), of phosphorus (as Na_3PO_4), of arsenic (as Na_3AsO_4), and of the metallic elements. Horsley shows that, with the exception of potassium, all of the usual metallic impurities in sodium are less volatile than sodium. Because of the nature of the usual impurities in sodium, good separations by distillation can be readily achieved. For example, the potassium content of the product sodium can be reduced by discarding the first fraction of the distillate, in which the potassium

(as well as rubidium and cesium) is enriched because its volatility is greater than that of sodium. The less volatile materials tend to remain in the still, so that by saving the middle fraction of the distillate as product, and discarding the first and last portions, a purification can be effected. That this procedure is effective in preparing a highly purified alkali metal has been shown by McKisson, et al.⁽⁶⁾ for potassium. Product material prepared after their still unit had been well conditioned by distilling and discarding several potassium batches showed the only detected metallic elements to be magnesium, sodium, and silicon. Because of the success of the potassium purification, the same technique has been examined for purifying sodium as is described below.

II. DESIGN CONSIDERATIONS

In the foregoing section, it was noted that earlier workers have not only predicted that alkali metals can be purified by distillation, but that substantial purifications have indeed been achieved in particular cases. The present problem is to devise a suitable method of preparing purified sodium from a given starting material. The analysis of the starting material obtained from the Systems Quality Sodium Loop is given in Table 1. The particular design problem is to define a separation process which will prepare the purest possible sodium from such a starting material.

The separation of impurity elements in a distillation process is rather straightforward and is readily analyzed. However, the behavior of impurity compounds which may exist in the sodium is a more difficult analytical problem. That such compounds can exist is shown by work performed at Argonne National Laboratory where researchers report they were unable to remove carbon from

TABLE 1
STARTING MATERIAL ANALYSIS

Element	Analysis (ppm)	Element	Analysis (ppm)	Element	Analysis (ppm)
Ag	<1 D*	Cr	1	Ni	6
Al	3	Cs	<10 ND	O	15
B	<1 ND†	Cu	17	Pb	7
Ba	<5 ND	Fe	4	Rb	<5 ND
Be	<1 ND	H	<1 ND	Si	60
Bi	<5 ND	K	50	Sm	<5 ND
C	35	Li	<1 ND	Ti	<5 ND
Ca	10	Mg	<5 D	V	<1 ND
Cd	<1 ND	Mn	<1 ND	Zn	<100 ND
Co	<5 ND	Mo	<1 ND	Zr	<10 ND

*D = Detected

†ND = Not Detected

sodium by distillation.^(7, 8, 9) These workers found that their product distillate had ~50 ppm carbon but they were not able to establish the mechanism by which the transport into the distillate occurred. One possibility is that carbon and oxygen exist as a CO complex in sodium, and during the distillation the complex is destroyed to form gaseous CO, which is then re-absorbed in the distillate. The compound hexasodium hexacarbonyl (the hexa-sodium salt of hexa-hydroxybenzene) is known to exist.^(8, 10) Also, other addition compounds of CO and sodium have been identified and studied at Dounreay by Sinclair, et al.⁽¹⁰⁾ These are sodium carbonyl, $\text{Na} \cdot \text{O} \cdot \text{C} \cdots \text{C} \cdot \text{O} \cdot \text{Na}$; tetra-sodium tetra-oxy quinone, $(\text{NaO})_4\text{C}_6\text{O}_2$; and some ill-defined linear compounds such as $\cdot \text{CO} \cdot \text{C}(\text{ONa}) \cdots \text{C}(\text{ONa}) \cdot$. In no case were the Dounreay workers able to find evidence of a Na-C bond. Therefore, it does not seem unlikely that compounds of this type would decompose to yield CO gas during a vacuum distillation.

In an attempt to decompose compounds which may exist in the sodium used in the preparation of purified product for the present program, a hot gettering step was included in the process sequence. Zirconium metal is used, the gettering process is operated at 650 to 700°C, and the sodium is treated for a minimum of 16 hours. Under these conditions, the following typical reactions are possible:

At 900°K (627°C) the free energies of formation of the various compounds are: ZrC, -42 kcal/mol;⁽¹¹⁾ ZrO₂, -220 kcal/mol;⁽¹¹⁾ Na₂O, -69 kcal/mol;⁽¹¹⁾ Na₂O (10 ppm O), -79 kcal/mol;⁽¹²⁾ and Na₂O (1 ppm O), -83 kcal/mol.⁽¹²⁾ An estimated value for $(\text{NaO})_6\text{C}_6$ is -290 kcal/mol [$\Delta F_f(\text{CO})(900^\circ\text{K}) = -46 \text{ kcal/mol}$]. Using these values, one finds for the reactions shown above, $\Delta F(\text{Rx 1})(900^\circ\text{K}) = -622 \text{ kcal}$, $\Delta F(\text{Rx 2})(900^\circ\text{K}) = -529 \text{ kcal}$ (for Na₂O at 10 ppm O), and $\Delta F(\text{Rx 3})(900^\circ\text{K}) = -436 \text{ kcal}$ (for Na₂O at 10 ppm O).

These large negative ΔF -values indicate that at equilibrium, zirconium will indeed decompose the Na-CO complexes. The remaining uncertainties are the rates at which the zirconium can react in this fashion, and the capacity of zirconium for absorbing carbon and oxygen. The operating temperature level of 650°C was chosen as being high enough to permit a reasonable rate of diffusion of oxygen into the body of the zirconium, but the rate of diffusion of carbon into zirconium at 650°C is expected to be quite small. In order to maximize the amount of carbide which can be formed, the zirconium getter was made of 0.002-in. thick foil. The total surface area exposed in the getter chamber is 21,000 cm².

After undergoing the hot zirconium gettering treatment, the sodium is ready for the distillation step. A batch process is considered, and one must therefore provide for the removal of the elements more volatile than sodium as well as the less volatile ones. This is most easily achieved by taking three "cuts." The first portion of the distillate, which is discarded, contains the materials more volatile than the sodium. The second cut is the middle portion of the distillate, which becomes the purified product. The third cut is the "bottoms" of the distilland, and will be discarded by draining it from the still pot. Referring to Tables 1 and 2, one sees that of the detected impurities, only potassium is more volatile than the sodium, and of the remainder, only the Group II elements have sufficiently high vapor pressures to warrant consideration in the analysis of the distillation process. This is further illustrated in Table 3, in which the relative volatilities of the elements are tabulated, with sodium as a reference. Thus the elements which must be separated from sodium by discarding the first cut of distillate are potassium, rubidium, and cesium. The remainder must be separated from sodium by becoming concentrated in the still pot while the sodium product cut is distilled off. Either a simple pot still or a still and distillation column can be used to effect the separation. The choice between the two alternates was made as described below.

The batch distillation process was first analyzed by Rayleigh,⁽¹³⁾ and more recently, by Kirschbaum.⁽¹⁴⁾ In its most simple form, the process simply involves loading the distilland into a pot still, and distilling a portion of it into a

TABLE 2
VAPOR PRESSURES OF SELECTED ELEMENTS

T (°K)	P ^o _{Cs} (atm)	P ^o _{Rb} (atm)	P ^o _K (atm)	P ^o _{Na} (atm)	P ^o _{Li} (atm)	P ^o _{Mg} (atm)	P ^o _{Ca} (atm)	P ^o _{Ba} (atm)	P ^o _{Sr} (atm)
600	4.6×10^{-3}	2.9×10^{-3}	8.6×10^{-4}	4.8×10^{-5}	4.1×10^{-9}	1.1×10^{-7}	2.9×10^{-10}	1.7×10^{-10}	3.5×10^{-9}
700	3.6×10^{-2}	2.5×10^{-2}	9.5×10^{-3}	9.1×10^{-3}	3.5×10^{-7}	7.2×10^{-6}	4.3×10^{-8}	2.2×10^{-8}	3.5×10^{-7}
800	0.17	0.13	5.6×10^{-2}	8.1×10^{-3}	9.7×10^{-6}	1.6×10^{-4}	1.7×10^{-6}	8.8×10^{-7}	1.1×10^{-5}
900	0.54	0.44	0.22	4.3×10^{-2}	1.3×10^{-4}	1.9×10^{-3}	2.9×10^{-5}	1.5×10^{-5}	1.5×10^{-4}

TABLE 3
RELATIVE VOLATILITY VALUES
 $\alpha = P(\text{Metal})/P(\text{Na})$

T (°K)	Cs	Rb	K	Na	Li	Mg	Ca	Ba	Sr
600	96.0	60.0	18.0	1.00	8.5×10^{-5}	2.3×10^{-3}	6.0×10^{-6}	3.5×10^{-6}	7.3×10^{-5}
700	39.6	27.5	10.5	1.00	3.9×10^{-4}	7.9×10^{-3}	4.7×10^{-5}	2.4×10^{-5}	3.8×10^{-4}
800	21.0	16.0	6.9	1.00	1.2×10^{-3}	2.0×10^{-2}	2.1×10^{-4}	1.1×10^{-4}	1.4×10^{-3}
900	12.6	10.2	5.1	1.00	3.0×10^{-3}	4.4×10^{-2}	6.8×10^{-4}	3.5×10^{-4}	3.5×10^{-3}

collector. In this case, there is only one liquid-vapor interface at which the distillation process can effect a separation. For a simple two-component distillation system (which is reasonably approximated for each pair consisting of an impurity element and sodium so long as the impurities do not interact), Rayleigh's simple batch distillation equation applies:

$$\int_{B_2}^{B_1} \frac{dB}{B} = \int_{X_2}^{X_1} \frac{dX}{Y - X} = \ln \frac{B_1}{B_2} , \quad \dots(4)$$

where B is the amount of sodium in the still, X is the concentration of the more volatile constituent in the still, Y is the concentration of the more volatile constituent in the vapor entering the condenser, subscript 1 refers to the initial conditions, and subscript 2 refers to the final conditions. For very dilute solutions in which α , the relative volatility ($\alpha = P_M/P_{Na}$), is constant,

$$Y = \alpha X . \quad \dots(5)$$

Substituting Equation 5 in Equation 4 and integrating, one finds,

$$\ln \frac{B_1}{B_2} = \frac{1}{\alpha - 1} \ln \frac{X_1}{X_2} , \quad \dots(6)$$

which relates the initial and final total amounts of liquid in the still to the initial and final concentrations of the more volatile component.

For practical purposes, each impurity in the sodium can be considered as one component of a binary system with sodium. Then one can use Equation 6 to compute the fraction of the original still-pot charge which must be discarded to obtain any desired purification ratio, $r = (X_1/X_2)$, for the more volatile components. This is given by the ratio D'/B_1 , where D' is the amount of distillate to be discarded,

$$D' = B_1 - B'_2 . \quad \dots(7)$$

Then the second "cut" of the distillate,

$$D'' = B'_2 - B''_2 \quad , \quad \dots (8)$$

will contain essentially all of the remaining more-volatile component, and its average concentration $\bar{Y}$ in D'' will be closely approximated by,

$$\bar{Y}D'' = X_2(B'_2 - B''_2)/B'_2 = X_2D''/B'_2 = X_1D''/rB'_2 \quad . \quad \dots (9)$$

For the separation in question, Table 3 shows that the α -values for potassium vs sodium range from 5 to 18 at the temperatures of interest, and that those for rubidium and cesium vs sodium are larger. Equation 6 has therefore been evaluated for α -values in the range of 2 to 20 and for r -values of 2 to 20. The results, in terms of D'/B_1 , are shown on Figure 1. This figure shows that for α -values greater than 20, a purification ratio r of at least 20 can be effected in a simple pot still by discarding the first 15% of the distillate. However, for an 800°K distillation and for an r of 20 for potassium, D'/B_1 is seen to be 38% ($\alpha = 7$), while, for $r = 10$, D'/B_1 is 31%. These D'/B_1 values are quite large. However, by using a fractionating column in conjunction with the batch still, one can markedly reduce these values for any combination of α and r .

A simple analysis of a limiting-case distillation plate column can be made. If α is constant throughout the column, and there is an infinite reflux ratio (i. e., total reflux or no product), then the following analysis applies for a two-component system. At steady state, the flow of liquid down the column and the flow of vapor up the column are equal, and a steady-state composition is set up on each plate. The vapor leaving plate i will have a composition given by

$$Y_i = \alpha X_i \quad , \quad \dots (10)$$

where Y_i is the concentration of the lower boiling component in the vapor, X_i is the composition of the lower boiling component in the liquid on the plate, and α is the relative volatility. Further, the liquid on plate $(i+1)$ will have the same composition as the vapor coming to it,

$$X_{i+1} = Y_i \quad \dots(11)$$

A steady-state condition is thus set up when the moles of vapor arriving at a plate are equal to the moles of liquid leaving the plate. Under this limiting-case condition, the vapor leaving the top plate (the n th plate) will have the composition $Y_n = \alpha^{(n+1)} X_B$. Now, consider a material balance when a differential amount of product dD is removed from the condenser. As product is removed, both the amount and the concentration of the more volatile component of the distilland liquid in the boiler are reduced, thus:

$$Y_n dD = B X_B - (B - dB)(X_B - dX_B) \quad \dots(12)$$

Expanding Equation 12, noting that $dD = dB$, and neglecting differentials of second order,

$$Y_n dB = B dX_B + X_B dB \quad \dots(13)$$

Now, substituting for Y_n , rearranging, and integrating, one finds

$$\int_{B_2}^{B_1} \frac{dB}{B} = \ln \frac{B_1}{B_2} = \int_{X_{B_2}}^{X_{B_1}} \frac{dX_B}{(\alpha^{(n+1)} - 1) X_B} \quad \dots(14)$$

or,

$$\frac{B_1}{B_2} = \left(\frac{X_{B_1}}{X_{B_2}} \right)^{\frac{1}{\alpha^{n+1} - 1}} = r^{\left(\frac{1}{\alpha^{n+1} - 1} \right)} \quad \dots(15)$$

Equation 15 provides a good approximation of the separation attainable in a distillation using an enriching column provided the reflux ratio (the ratio of the amount of liquid returned to the column as reflux to the amount of product drawn off) is, say 10 or greater. Figures 2 and 3 show the D/B_1 ratios required to

Figure 1. D'/B_1 Values for the Simple Pot Still for $\alpha > 1$

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Figure 2. D'/B_1 Values for Simple Pot Still with a One-Theoretical Plate Distillation Column for $\alpha > 1$

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effect the various r -values for α -values of 2 to 20 for $n = 1$ and $n = 2$ plates, respectively. A comparison of Figures 1, 2, and 3 for $r = 20$ and $\alpha = 5$ shows the marked decrease in the D'/B_1 -values in going from zero to two plates: for no plate, $D'/B_1 = 0.53$; for one plate, $D'/B_1 = 0.12$; and for two plates, $D'/B_1 = 0.025$. For larger α -values, the D'/B_1 -values are lower than those noted above. Therefore, it was concluded that a distillation column having two theoretical plates would be required to adequately separate potassium at the 50 ppm level from sodium. With such a still column, one can theoretically effect at least a 50-fold decrease in the potassium (and rubidium and cesium, as well) by discarding the first 10% of the distillate.

Now, let us consider the separation of the components less volatile than sodium. An examination of Table 3 shows that the α -values for the less-volatile components are all smaller than 5×10^{-2} , so that their separations from sodium should be quite readily effected. Equation 6 applies, but it is most conveniently evaluated in the form,

$$\left(\frac{X_1}{X_2}\right)^{\frac{1}{\alpha-1}} = \left(\frac{X_2}{X_1}\right)^{-\frac{1}{\alpha-1}} = \frac{B_1}{B_2} \quad \dots(16)$$

Because sodium is more volatile than the elements of present interest, the separation to be effected here involves leaving the less volatile elements in the "bottoms." Thus the applicable separation factor is the ratio $X_1/\bar{Y}$, where $\bar{Y}$ is the average concentration of the impurity element in the distillate, and X_1 is the concentration of the impurity element in the starting material distilland. This ratio is obtained as follows. The overall material balance for a simple pot still and distillate is

$$X_1 B_1 = X_2 B_2 + \bar{Y} D \quad \dots(17)$$

Dividing all terms by $X_2 B_1$, and simplifying,

$$\frac{X_1}{X_2} = \frac{B_2}{B_1} + \left(\frac{\bar{Y}}{X_2}\right)\left(\frac{D}{B_1}\right) \quad \dots(18)$$

Figure 3. D'/B_1 Values for a Simple Pot Still with a Two-Theoretical-Plate Distillation Column for $\alpha > 1$

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Figure 4. D/B_1 Values for the Simple Pot Still for $\alpha < 1$

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A purification ratio r' can be defined as $r' = X_2/X_1$ ($r' > 1$) to be analagous to the r used for the materials more volatile than sodium. Using the r' expression, Equation 18 can be rearranged to give the desired ratio,

$$\frac{X_1}{\bar{Y}} = \frac{D/B_1}{1 - r'(B_2/B_1)} \quad \dots(19)$$

When Equation 19 was evaluated for an α -value range of 0.001 to 0.1 it was found that the value of $X_1/\bar{Y}$ varied from $1/\alpha$ for $D/B_1 = 0$ to 1 for $D/B_1 = 1.00$. In order to more readily show the data in graphical form, the quantity D/B_1 is plotted against $\alpha(X_1/\bar{Y})$ in Figure 4. An examination of this graph shows that for $\alpha = 0.001$, an $(X_1/\bar{Y})$ of 500 is effected by retaining 20% of the distilland as bottoms ($D/B_1 = 0.80$), and for $\alpha = 0.01$, the corresponding $X_1/\bar{Y}$ is 50. There is only a nominal decrease in $X_1/\bar{Y}$ if α is 0.001 or smaller when only 10% of the distilland is retained as bottoms ($D/B_1 = 0.90$); i. e., for $\alpha = 0.001$, $X_1/\bar{Y}$ is still 380, as compared with 500 for $D/B_1 = 0.80$. Because the $(X_1/\bar{Y})$ -values for the desired separations are quite large even for a simple-pot still, and will be substantially greater if a column is used, no further analysis of the distillation separation is necessary. The preferred still system consists of a two-plate column or equivalent. The first 20% of the distillate is to be discarded, the product cut is the next 60 to 70% of the distillate, and the bottom cut is thus the last 20 to 10% of the still charge.

The decision was made to use a packed column rather than to attempt to build a tray column. The required height of the column was estimated using the Height Equivalent to a Theoretical Plate (H. E. T. P.) concept as described by Perry.⁽¹⁵⁾ Based upon reported measurements for saddle-shaped packing materials in 1/4 and 1/2 in. sizes, and an extrapolation based upon the expected mass flow rate of 30 lb/hr-ft² in a 1-1/2-in. pipe packed column, an H. E. T. P. value of 0.7 ft was estimated. Thus a packed column depth of 1.4 ft is indicated. In order to provide a modest contingency, a packed depth of 20 in. was chosen. The remaining design selection to be made was the amount of distilland to be treated. This value was based upon the desired amount of product per run, 400 $\pm$ 50 gm. For a 60% yield, about 650 gm is the amount of sodium needed per batch.

Figure 5. Sodium Purification Unit

Figure 6. Liquid Level Indicator Detail

The apparatus designed to meet these requirements is shown in Figure 5. It consists of a metering pot in which the batch volume is measured by means of the liquid level sensors, a gettering pot packed with 0.002-in. zirconium foil, and the still-pot-and-distillation column unit. The distillation column is lined with 0.005-in. tantalum foil and is packed with pieces of $1/4 \times 1/2 \times 0.030$ -in. tantalum, bent into a V or saddle-like shape. The basic construction material is 304 stainless steel. The distillate is condensed in a tantalum-foil-lined $3/8$ -in. SS tube. The movement of the sodium through the unit is monitored by the use of the level sensors, whose construction is shown in Figure 6. The unit is simply a small inconel-clad heater wound on the bottom inch of a 2-hole thermocouple insulator, and a pair of thermocouple wires which extend through the bottom of the insulator and are welded to the bottom plate of the probe assembly. When the sodium level is high enough to cover the end of the probe, the thermal conductivity of the sodium prevents the temperature of the bottom plate from rising appreciably, even though the heater may be running at a several-watt rate. However, when the end of the probe is not immersed in sodium, this heating rate is sufficient to cause the probe-end temperature to rise rapidly. The unit is thus a "go-no-go" type of sensor, but it has been found to be very useful. In all, there are four of these mounted in the metering pot, two in the gettering pot, and three in the still pot.

A second device which has proven to be reliable and very useful is the freeze-seal valve shown in Figure 7. The sodium transfer lines are all fitted with these valves, which are made by simply winding a $1/8$ - or a $3/16$ -in. copper tube on a $1/4$ - to $3/8$ -in. pitch around the sodium line to be valved. Then a sheathed heater wire is wound on the sodium tube between the turns of the copper tubing. When the valve is to be "closed," cooling water is run through the coil to freeze the sodium. When the valve is to be opened, the water is turned off and the heater wire is heated. Care must be taken to ensure that the drain side of the water line is open, to avoid building up steam pressure in the coil as the temperature rises above the melting point of the sodium and the boiling point of the water. A thermocouple is mounted on each end of the valve to monitor the tube temperature and the open-or-closed condition of the valve. These have been very successful units, but the degree of success in using such a valve may be dependent upon the oxygen content of the sodium being transferred

Figure 7. Freeze Valve Detail

Figure 8. Sodium Purification Unit Assembly Before Installation of Heaters, Thermocouples, and Insulation

through the 1/4-in. sodium line. If the material is pure as ours has been, there is little or no tendency for a plug to form and valve action is easily maintained.

Figure 8 shows the basic hardware of the purification unit before the control instrumentation was installed. Figure 9 shows the locations of the heaters, whose power levels are adjusted to maintain the desired temperatures within the system. Figure 10 shows the locations of the thermocouples installed on the purification unit. An attempt to have a reasonable redundancy was made, so that, for example, if thermocouple No. 9 were to fail, the reading of the equivalent thermocouple, No. 11, could be used in its place.

Figure 11 shows the assembled unit with the heaters, valves, thermocouples, and insulation in place. The product passes out of the unit toward the rear through a line which penetrates the circular plate shown just behind the top of the still column. In operation, these elements of the purification unit are enclosed in a roughing pump vacuum under the cover arrangement as shown on Figure 12. The figure also shows the power console which consists of 14 Variacs which are used to control heater power inputs during operation of the unit. The panel in the foreground shows the rectangular connectors for the unit's thermocouples. (There are six thermocouples in each of the connectors.) Groups of thermocouple readings can be displayed on a multipoint recorder by using appropriate intermediate cables with matching connectors. The bank of 24 sockets supplies the heaters on the unit. Individual heaters are energized by connecting power cords from the power console to the appropriate socket. In general, only a few of the thermocouples and heaters need be used for each operation, so that we can make the appropriate plug-in connections quite easily.

The product sodium, after it is condensed in the tantalum foil-lined condenser flows into the product collector, an extruder. The construction of this unit is shown in Figure 13. Basically, it is a simple unit consisting of a heavy-walled barrel, and a piston. The liquid sodium product flows into the extruder and at first is allowed to flow through and out the discharge tube. This tube is fitted with a freeze-valve unit larger in size but similar in concept to the unit of Figure 7. The first distillate D' passes into a container held in an ion-pumped vacuum of $\sim 10^{-7}$ torr in the discharge collector vessel (Figure 14). Then the freeze valve is closed and the liquid sodium product collects in the extruder.

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Figure 9. Heater Locations

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Figure 10. Thermocouple Locations

Figure 11. Sodium Purification Unit Assembly with Heaters, Thermocouples, and Insulation in Place

Figure 12. Sodium Purification Unit Enclosed in Cover, Power Console, and Thermocouple and Power Distribution Panel

8-4-66 UNC

7650-4005

Figure 13. Extruder

Figure 14. Extruder in Place on Sodium Purification System

The barrel is kept at about 125 °C to prevent the sodium from freezing during the product-collection period. By maintaining the sodium as liquid, mixing occurs due to the inevitable convection currents and the product sodium becomes essentially uniform in composition. When the product-collection is complete, the extruder is allowed to cool and when the sodium is frozen, the piston is run down against it. This effectively seals the purified sodium in the unit and closes off the inlet tube. Then, a cover is placed over the discharge end of the extruder, and the joint in the product line is broken and re-sealed with a cover-plate to seal off the extruder in preparation for removing it from the fill position at the rear of the purification unit (Figure 14) and mounting it in its use- or discharge-position on the ultrahigh vacuum chamber as shown in Figure 15. In use, the sodium is extruded into the chamber under a vacuum in the high 10^{-9} torr range. This extrusion is effected by the use of the drive unit, a worm-gear and jack-screw arrangement shown in Figures 13, 14, and 15. The mechanical advantage of the drive unit is 3240, and a force of about 50 lb on an 18-in. lever-arm is required to extrude the sodium.

Figure 15. Extruder in Place for Delivery of Sodium

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III. EXPERIMENTS

The sodium purification unit has been operated to produce three batches of purified sodium to date. In each case, at least one preliminary clean-up batch was run through the system and collected as liquid in the extruder to "wash" the extruder surfaces. The ram was then moved down to touch the surface of the molten sodium in order to wash the ram face. After moving the ram back to its fill position, the entire preliminary batch was drained out of the extruder.

The procedure used in carrying out the preparation process was the same for the preliminary batches as for the product-producing batches. The stock sodium obtained from the Systems Quality Sodium Loop is transferred from the 5-gal transfer container into the metering pot using 99.999% pure argon (J. T. Baker Chemical Corp. - "Ultra-Pure" Argon) at about 10 in. Hg absolute pressure (250 torr abs.) and with the freeze valve (Thermocouples 7 and 8, Figure 10) closed. The metering pot is previously pumped to <1 torr during the discharge of the still-pot bottoms from the previous batch. This discharge is performed by first introducing pure argon into the metering pot and opening the freeze valves to allow communication of all three pots. Then the drain valve is opened and the bottoms are pumped out. The transfer is essentially complete when the argon gas first appears at the vacuum pump. Pumping is continued until a vacuum of 10^{-3} torr or less is developed in the receiver. Under these conditions, it is estimated that the residual argon pressure in the metering pot is below 1 torr. This is the pressure into which the new batch of sodium is delivered during the filling operation. The filling is monitored by observing the temperature behavior of the level probes. The lowest one of the four was found to be too close to the bottom of the vessel (design clearance of 0.18 in.) and the surface tension of the sodium maintains a small amount of sodium between the probe and the bottom of the pot so that even when the metering pot is empty, an "uncovered" response of Thermocouple No. 56 (Figure 10) is not observed. Figure 16 shows a typical response of a liquid level probe during the metering pot filling operation. The heater power input (No. 13, Figure 9) is 8 watts, and the equilibrium temperature of the end of the probe is about 75 to 100°C above the average temperature of the metering pot. The usual fill time is about 10 minutes. The sodium flow is controlled by setting a needle valve in the feed

6-17-67 UNC

7708-4711

Figure 16. Probe Temperature Response During Loading of Metering Pot

6-16-67 UNC

7708-4712

Figure 17. Probe Temperatures During Sodium Transfer from Metering Pot to Gettering Pot

line. The sodium is moved from the metering pot by melting the appropriate freeze seal and the transfer is monitored by observing the behavior of the level probes. Figure 17 shows the probe data for a typical transfer. It can be seen that the rate of transfer is quite rapid, once the freeze valve opens. This is to be expected because there is very little resistance to the flow through the "valve." Note that the response of Probes 47, 48, and 49 as they become uncovered is rapid enough to give a certain indication in a matter of 30 to 45 sec, but that the response of No. 20 is virtually instantaneous. The volume of the getter pot is 965 ml and the sodium normally just covers the top of the zirconium getter coil. Gettering is performed at 650°C as an overnight operation so that the exposure time is 16 to 18 hours.

After gettering, the sodium is moved to the still pot. The volume of the still pot is approximately 1 liter. The distilland is initially about 3-1/3 in. deep, and covers all three of the level probes. As the distillation proceeds, the probe temperatures are recorded. The time at which each probe becomes uncovered is noted to obtain a measure of the distillation rate, and therefore an estimate of the amount of distillate discarded, or collected. Normally, the distillation is terminated shortly after the lowest probe becomes uncovered, leaving a nominal 100 ml of sodium in the still as bottoms.

During the distillation, it is found that the temperatures at the top of the still tend to rise as the liquid level drops. Table 4 shows the time sequence of the still and distillation column temperatures observed during Run No. 3. The temperature of Thermocouple No. 16 dropped 5°C during the run, but that of Thermocouple No. 43 rose 35°C during the last three hours of the run. The reason for this temperature rise is that the heat is applied rather uniformly along the cylindrical side of the pot, but as the sodium level drops, the heat path to the sodium lengthens, and the temperature of the top of the pot rises.

The temperatures of the level probes behaved very much as one would expect them to, in that they followed the sodium temperature until they became uncovered. Then they rose about 50°C in a few minutes, each in turn, as one would expect.

In addition to observing the rate of loss of sodium from the still pot, the distillation rate is monitored by observing the pressure gauges on the vacuum line which leads to the still and column. As the sodium condenses, it collects

TABLE 4
STILL AND DISTILLATION COLUMN TEMPERATURE
HISTORY DURING RUN NO. 3

Time (4/27/67)	Volume of Product (ml)	Temperature (°C)											
		No. 16 *	No. 43	No. 41	No. 39	No. 37	No. 35	No. 33	No. 31	No. 45	No. 23	No. 24	No. 21
0945	0 (a)	550	550	550	545	540	540	535	530	500	550	550	550
1005	0 (a)	550	550	550	545	540	540	535	530	500	550	550	550
1020	0 (a, b)										555	555	555
1115	0 (c, d)	550	550	550	545	540	540	535	530	500	555	560	555
1145	40 (d, e)										575	560	555
1220	(d)	550	555	550	545	545	540	535	530	495	600	560	555
1335	220 (d, f)										620	585	555
1340	225 (d)	545	565	550	545	545	540	535	530	495	620	610	555
1513	420 (d, g)	545	590	545	540	540	535	530	525	490	640	635	600
1520	430 (h)	545	590	545	540	540	535	530	525	490	635	635	630

*Thermocouple Numbers.

Notes:

- (a) Discard distillate.
- (b) Begin to cool freeze seal on extruder.
- (c) Extruder seal made. Begin collecting product.
- (d) Collect product.
- (e) Top level indicator uncovered, Thermocouple No. 23.
- (f) Second level indicator uncovered, Thermocouple No. 24.
- (g) Bottom level indicator uncovered, Thermocouple No. 21.
- (h) End of Run No. 3.

on the wall of the condenser tube until there is enough sodium to form a plug across the diameter of the condenser. The sodium then continues its slow movement down the collector tube to the drop counter, from which it drains into the tube leading to the extruder. The still vacuum is applied to the upper end of the drop counter and the vacuum gauge shows the influence of the formation and discharge of the drop of sodium. Just after the sodium falls, there is an increase in the pressure level as the added volume of the still and the distillation column are opened to the vacuum. The pressure decreases and continues to decrease slowly until a new drop forms. When this happens, the vacuum pumps have less volume to evacuate, and the pressure quickly falls until the sodium drop clears the condenser tube to start the cycle again. This technique of drop counting was adopted after it was found that the original method was unreliable. The drop counter unit has a sheathed thermocouple mounted in it so that the drop of sodium which runs down the condenser tube falls on it. The idea was that the temperature of each new drop would cause a response in the thermocouple, thereby giving a means of estimating the distillation rate. It was found during the first run that the response of the thermocouple was initially

as expected, but that after a few hours, it became sluggish and failed to give a good indication. This is thought to be due to the sodium wetting the exposed surfaces of the drop counter, and the subsequent development of a sodium bridge from the thermocouple to the adjacent wall. The combination of the internal geometry and the high surface tension of sodium makes this the most plausible explanation for the observed behavior. However, the response of the vacuum gauge to the drops has been rather consistent during all of the runs, and it is now used instead of the drop-counter thermocouple.

Another finding that still causes some concern is that the freeze seal "valve" at the discharge end of the extruder acts very sluggishly. This was observed in all of the runs, and in Run No. 3 the cooling water to the valve was turned on at 10:30 a.m., but it wasn't until 11:15 a.m. that the seal was made, and the sodium stopped passing through. An estimated 125 ml was discarded as D', about 430 ml was collected as product, and 100 ml was discarded as bottoms. In all, about 555 ml was distilled in the 335-min run, which amounts to an average distillation rate of 1.6 ml/min.

The only data obtained from the first two sodium product runs were the composition of the starting material and of the extruder product. However, in Run No. 3 samples were also taken of the first few distillate drops, the middle of the first cut, the end of the first cut (beginning of the product cut), and the end of the product cut. Table 5 shows the analyses of the sodium samples taken at various times during the preparation of Batch No. 3. The data are quite interesting in that they generally confirm the analytical studies of the distillation process. However, because the absolute concentrations of so many of the metallic impurities are below the limits of detection, there are only a few elements whose concentration levels change enough to permit analysis. Further, it is not possible to obtain an accurate value of any purification ratio because the product analyses all show "less than" figures (except for chromium, whose detection at the <1 to 1 ppm level is quite marginal). However, it is interesting to examine the potassium concentrations in the various cuts and to compare these with the predictions of the distillation analysis. One cannot expect to get any more than a qualitative agreement between the predictions and the observations because of the manner in which the still must be operated. For example, the column is never completely free of sodium when a new batch is loaded to be

TABLE 5
SODIUM SAMPLE ANALYSES, RUN NO. 3, IMPURITIES (ppm)

Elements	Starting Material	First Distillate	Middle of Discard Portion	Begin Product Cut	Product No. 3	End Product Cut
Ag	<1 D*	<1 D	<1 D	<1 D	<1 D	<1 D
Al	3	<1 ND	<1 ND	<1 ND	<1 ND	<1 ND
B	<1 ND [†]	<1 ND	<1 ND	<1 ND	<1 ND	<1 ND
Ba	<5 ND	<5 ND	<5 ND	<5 ND	<5 ND	<5 ND
Be	<1 ND	<1 ND	<1 ND	<1 ND	<1 ND	<1 ND
Bi	<5 ND	<5 ND	<5 ND	<5 ND	<5 ND	<5 ND
C	35	-	-	-	8	-
Ca	10	<10 ND	<10 D	<10 D	<10 D	<10 D
Cd	<1 ND	<1 ND	<1 ND	<1 ND	<1 ND	<1 ND
Co	<5 ND	<5 ND	<5 ND	<5 ND	<5 ND	<5 ND
Cr	1	<1 ND	<1 ND	<1 ND	1	<1 ND
Cs	<10 ND	<10 ND	<10 ND	<10 ND	<10 ND	<10 ND
Cu	17	<5 D	<5 D	<5 D	<5 D	<5 D
Fe	4	<1 ND	1	2	<1 ND	1
H	<1 ND	-	-	-	-	-
K	50	100	30	10	<10 D	<10 D
Li	<1 ND	<1 ND	<1 ND	<1 ND	<1 ND	<1 ND
Mg	<5 D	<5 ND	<5 ND	<5 ND	<5 ND	<5 ND
Mn	<1 ND	<1 ND	<1 ND	<1 ND	<1 ND	<1 ND
Mo	<1 ND	<1 ND	<1 ND	<1 ND	<1 ND	<1 ND
Ni	6	<5 ND	<5 ND	<5 ND	<5 ND	<5 ND
O	15	-	-	-	0.6	-
Pb	7	1	<1 ND	<1 ND	<1 ND	<1 ND
Rb	<5 ND	<5 ND	<5 ND	<5 ND	<5 ND	<5 ND
Si	60	<10 D	<10 D	<10 D	<10 D	<10 D
Sn	<5 ND	<5 ND	<5 ND	<5 ND	<5 ND	<5 ND
Ta	-	-	-	-	<1 ND	-
Ti	<5 ND	<5 ND	<5 ND	<5 ND	<5 ND	<5 ND
V	<1 ND	<1 ND	<1 ND	<1 ND	<1 ND	<1 ND
Zn	<100 ND	<100 ND	<100 ND	<100 ND	<100 ND	<100 ND
Zr	<10 ND	<10 ND	<10 ND	<10 ND	<10 ND	<10 ND

*D = Detected

[†]ND = Not Detected

processed because the surfaces have become wetted with sodium and a film tends to remain. This is necessary for good liquid-vapor exchange, but tends to reduce the early efficiency of the column. Nevertheless, it is of interest to estimate the concentration of potassium that should be contained in the first 5% of the distillate. In Run No. 3 the system operated initially at 550°C (823°K) and the α -value for that temperature is about 6. If it is assumed that the column operates as would two theoretical plates, one can use Figure 3 to estimate the value of r which is obtained for $\alpha = 6$ and $D'_1/B_1 = 0.05$. This theoretical r -value is at least 100, which means that 99% of the original 50 ppm potassium should have been removed from the liquid in the still. Thus, the concentration of potassium in the early distillate is, theoretically, $\bar{Y}(2 \text{ plate}) = (49.5 \text{ ppm}/0.05) = 990 \text{ ppm}$. For a one-theoretical-plate column, $r = 5$, and $\bar{Y}(1 \text{ plate}) \cong 40.5/0.05 \cong 810 \text{ ppm}$. These values are the average $\bar{Y}$ -values, $\bar{Y}$, of the first 5% of the distillate produced under the given theoretical conditions. The samples whose analyses are given in Table 5 are instantaneous samples of 2 to 3 grams taken at the indicated times in the distillation. In every case, their potassium analysis should be lower than the $\bar{Y}$ values, but the observed difference, 100 ppm K observed vs 810 or 990 ppm K calculated, is larger than one would expect to find. However, there is a qualitative agreement, and it is of interest to note that the K analysis at the beginning of the product cut was 10 ppm. Therefore, although analytical sensitivity is lacking below 10 ppm K, a purification ratio for potassium of at least 10 is not unlikely.

The analyses reported in Table 5 and 6 were carried out using the following techniques. The metals, except for tantalum and copper, were determined by emission spectrography using Kodak Spectrum Analysis No. 1 and No. 1N emulsions. The values reported are based on comparisons with AI standard plates. Figures 18 and 19 show the emission spectra of the starting material, of the three product batches, and of SPEX 99.999% pure NaCl. The oxygen analyses are performed using the mercury amalgamation technique with a flame photometer measurement of the sodium as the final read-out step. Recently developed blank corrections for the analytical procedure have been applied.⁽¹⁶⁾ The carbon analyses are performed using the high temperature oxidation technique with a gas chromatographic read-out of the evolved CO₂ as the final step. The hydrogen analysis was performed using the permeable iron membrane

TABLE 6
PRODUCT SODIUM ANALYSES, IMPURITIES (ppm)

Elements	Starting Material	Batch No. 1	Batch No. 2	Batch No. 3
Ag	<1 D*	<1 D	<1 D	<1 D
Al	3	<1 ND	<1 ND	<1 ND
B	<1 ND†	<1 ND	<1 ND	<1 ND
Ba	<5 ND	<5 ND	<5 ND	<5 ND
Be	<1 ND	<1 ND	<1 ND	<1 ND
Bi	<5 ND	<5 ND	<5 ND	<5 ND
C	35	14	27	8
Ca	10	<10 D	<10 D	<10 D
Cd	<1 ND	<1 ND	<1 ND	<1 ND
Co	<5 ND	<5 ND	<5 ND	<5 ND
Cr	1	<1 ND	1	1
Cs	<10 ND	<10 ND	<10 ND	<10 ND
Cu	17	<5 D	<5 D	<5 D
Fe	4	1	1	<1 ND
H	<1 ND	-	-	-
K	50	<10 D	<10 D	<10 D
Li	<1 ND	<1 D	<1 ND	<1 ND
Mg	<5 D	<5 ND	<5 ND	<5 ND
Mn	<1 ND	<1 ND	<1 ND	<1 ND
Mo	<1 ND	<1 ND	<1 ND	<1 ND
Ni	6	<5 ND	<5 ND	<5 ND
O	15	5	5	0.6
Pb	7	<1 ND	<1 ND	<1 ND
Rb	<5 ND	<5 ND	<5 ND	<5 ND
Si	60	<10 D	<10 D	<10 D
Sn	<5 ND	<5 ND	<5 ND	<5 ND
Ta	-	-	-	<1 ND
Ti	<5 ND	<5 ND	<5 ND	<5 ND
V	<1 ND	<1 ND	<1 ND	<1 ND
Zn	<100 ND	<100 ND	<100 ND	<100 ND
Zr	<10 ND	<10 ND	<10 ND	<10 ND

*D = Detected

†ND = Not Detected

LEGEND:

1. STARTING MATERIAL
2. PRODUCT BATCH NO. 1
3. PRODUCT BATCH NO. 2
4. PRODUCT BATCH NO. 3
5. SPEX 99.999% NaCl

Figure 18. Spectrographic Plate of Sodium Samples (Kodak Spectrum Analysis No. 1 Emulsion)

1
2
3
4
5

↑ ↑
K K
(7664) (7669)

NAA-SR-12444
38

LEGEND:

1. STARTING MATERIAL
2. PRODUCT BATCH NO. 1
3. PRODUCT BATCH NO. 2
4. PRODUCT BATCH NO. 3
5. SPEX 99.999% NaCl

1
2
3
4
5

↑
Na
(8183-8194)

Figure 19. Spectrographic Plate of Sodium Samples (Kodak Spectrum Analysis No. 1N Emulsion)

technique in which the sodium is heated in an iron container to liberate the hydrogen. The hydrogen passes through the iron wall and its pressure in a known volume is measured. The tantalum analysis is performed colorimetrically using phenylfluorone as the color development agent. The copper was analyzed by atomic absorption spectrometry.

Table 6 shows the analyses of the three products prepared thus far. Batch No. 3 is seen to be quite pure, the major detected impurity being carbon at 8 ppm. This value is approaching the limit of sensitivity of the method, so there is a large relative uncertainty of ± 5 ppm in this value. The carbon analysis of Batch No. 1 is higher than we prefer at 14 ± 5 ppm, but the carbon content of Batch No. 2 is clearly too large at 27 ± 5 ppm C. This value was established as the average of eight separate analyses whose individual values ranged from 14 to 39 ppm C. However, there was a problem in the first attempt to prepare Batch No. 2, in that a short circuit developed in one of the level probes and the resulting arc melted a hole in the probe wall. It was necessary to halt the run and to replace the probe, and, in doing so, the still could have been contaminated, even though an argon purge was used during the repair period. It is therefore concluded that Batch No. 2 was contaminated, even though three washing distillations were made following the repair. That the contamination has been removed, and the system is operating well is shown by the Batch No. 3 analysis, and no further problem with carbon is expected.

The impurity metal contents of these samples are quite low, and only eight metals are detected in the samples (see Figures 18 and 19). These are: silver, which can be detected at a very low level and is virtually always found in spectroscopic samples; calcium, which was detected in all these samples, but was below the calibration limit; chromium, which was found in two cases, but not detected in the third; copper, which is also quite readily detected, but whose concentration levels in the products were below the calibration concentration; iron, which was detected at the 1 ppm level in Batch Nos. 1 and 2, but was not detected in Batch No. 3; potassium, which was detected at below the calibration level; lithium, which was not detected in two cases and barely observed in the third; and silicon, which was detected in all cases, but was below the calibration limit. In no case is the amount of total metallic impurity likely to exceed

25 ppm, and with an estimated nonmetal total of 15 ppm for Run No. 3, one can arrive at an estimated 99.995% purity for that product. This estimate is further supported by a comparison of the spectra shown in Figures 18 and 19. The product sodium of Batch No. 3, in particular, is seen to be at least as pure as the SPEX spectrographic standard with respect to metallic impurities.

IV. CONCLUSIONS

The apparatus for preparing highly purified sodium is quite effective and the impurity content of the product is quite low. This is shown in Figures 18 and 19 in Spectra Nos. 2, 3, and 4, when they are compared with Spectrum No. 5, obtained from SPEX 99.999% standard spectroscopic NaCl. The ability of the apparatus to reduce the concentration of the most abundant impurity, potassium, to, at most, 1/5 of its concentration in the starting material has been demonstrated. The analysis of Batch No. 3 indicates the system to be operating quite well following the probe failure prior to Batch No. 2, which did cause contamination problems in Batch No. 2. The 0.6 ppm O found in Batch No. 3 is a very low value and is at the limit of sensitivity of the mercury amalgamation method. The carbon analysis of Batch No. 3 is relatively low, and is also near the limit of sensitivity of the method. This must be established by subsequent testing of the technique, and by preparing additional batches of purified sodium. Nevertheless, the product sodium prepared in the apparatus described above is quite pure, and is eminently suited for its intended purpose.

REFERENCES

1. J. H. Stang, E. M. Simons, J. A. DeMastry, and J. M. Genco, "Compatibility of Liquid and Vapor Alkali Metals with Construction Metals," DMIC Report 227, p. 2, April 15, 1966
2. J. W. Mausteller and E. F. Batutis, "Effect of Oxygen on the Mass Transport of Stainless Steel Components in Sodium," NP-5583, 1955
3. G. W. Horsley, "The Corrosion of Iron by Oxygen-Contaminated Sodium," AERE-M/R-1441, April, 1964
4. E. W. Murbach, J. E. Bodine, and N. W. Heath, "The Systems-Quality Sodium Loop Design, Construction, and Startup," NAA-SR-12327, 1967
5. G. W. Horsley, "The Purification of Sodium by Vacuum Distillation," AERE M/R 1152, May 12, 1953
6. R. L. McKisson, R. L. Eichelberger, R. C. Dahleen, J. M. Scarborough, and G. R. Argue, "Solubility Studies in Alkali Metals," AI-65-210, March 21, 1966
7. R. C. Vogel, et al., "Chemical Engineering Division, Semiannual Report, January - June, 1964," ANL-6900
8. R. C. Vogel, et al., "Chemical Engineering Division, Research Highlights, May, 1965 - April, 1966," ANL-7175
9. R. C. Vogel, et al., "Chemical Engineering Division, Semiannual Report, July - December 1965," ANL-7125
10. V. M. Sinclair, R. A. Davies, and J. L. Drummond, "Reaction of Carbon Monoxide with Sodium," Paper presented at the International Symposium on the Alkali Metals, Nottingham, England, July 19-22, 1966
11. C. E. Wicks and F. E. Block, "Thermodynamic Properties of 65 Elements - Their Oxides, Halides, Carbides, and Nitrides," Bulletin 605, Bur. Mines, 1963
12. NASA-AEC Liquid Metals Corrosion Meeting, Lewis Research Center, Cleveland, Ohio, October 2-3, 1963, Volume I; paper by J. R. Weeks, "Effects of Impurities, a. Oxygen," NASA-SP-41, p. 49, 1963
13. Lord Rayleigh, Phil. Mag. 8, 534, 1904
14. E. Kirschbaum, Distillation and Rectification. Chemical Publishing Co., Inc., Brooklyn, N. Y., p. 71 ff (1948)

15. J. H. Perry, Chemical Engineers Handbook, Third Edition, McGraw-Hill, New York, N. Y. (1950)
16. J. M. Scarborough and P. DeVries, "Characterization of the Blank Correction in the Determination of Oxygen in Sodium by the Amalgamation Method," Paper given at the 1966 Fall National Meeting of the American Chemical Society, and submitted for publication in Analytical Chemistry

APPENDIX NOMENCLATURE

- d = Differential operator
- ppm = Parts per million by weight
- n = Number of theoretical distillation plates
- r = Purification ratio, X_1/X_2 , applies to cases in which $\alpha > 1$.
- r' = Purification ratio, $X_1/\bar{Y}$, applies to cases in which $\alpha < 1$.
- 1 = Subscript indicating initial condition
- 2 = Subscript indicating final conditions
- B = Amount of distilland, general variable
- B_1 = Initial amount of distilland
- B_2 = Amount of distilland after operation of the still
- B'_2 = Amount of distilland at the end of the discard cut
- B''_2 = Amount of distilland at the end of the product cut
- D = Amount of distillate, general variable
- D' = Amount of distillate discarded (first cut)
- D'' = Amount of distillate in product cut
- ΔF = Free energy of a chemical reaction
- ΔF_f = Free energy of formation
- P^0 = Vapor pressure
- X = Concentration of more volatile component, general variable
- X_1 = Initial concentration of more volatile component
- X_2 = Concentration of more volatile component after operation of the still
- X_B = Concentration of more volatile component in still
- X_{B_1} = Initial concentration of more volatile component in still
- X_{B_2} = Concentration of more volatile component in still after operation of the still
- Y = Concentration of more volatile component in vapor
- Y_n = Concentration of more volatile component in vapor over the n -th distillation plate
- $\bar{Y}$ = Average concentration of the more volatile component in the distillate
- α = Relative volatility, equal to the ratio of the vapor pressure of a metal to that of sodium,
 $\alpha = P^0(\text{metal})/P^0(\text{sodium})$