BNWL-1407
UC-4

CHEMICAL ANALYSES OF SODIUM SYSTEMS
FINAL REPORT

W. O. Greenhalgh,
W. H. Yunker and F. A. Scott

June 1970

AEC RESEARCH &
DEVELOPMENT REPORT

BNWL-1407

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

PACIFIC NORTHWEST LABORATORY

RICHLAND, WASHINGTON

operated by

BATTELLE MEMORIAL INSTITUTE

for the

UNITED STATES ATOMIC ENERGY COMMISSION UNDER CONTRACT AT(45-1)-1830

ERRATA

CHEMICAL ANALYSES OF SODIUM SYSTEMS

W. O. Greenhalgh, W. H. Yunker, and F. A. Scott

ABSTRACT

BNWL-1407 summarizes information gained from the Chemical Analyses of Sodium Systems Program pursued by Battelle-Northwest over the period from July 1967 through June 1969. Tasks included feasibility studies for performing coulometric titration and polarographic determinations of oxygen in sodium, and the development of new separation techniques for sodium impurities and their subsequent analyses.

The program was terminated ahead of schedule so firm conclusions were not obtained in all areas of the work. At least 40 coulometric titrations were carried out and special test cells were developed for coulometric application. Data indicated that polarographic measurements are theoretically feasible, but practical application of the method was not verified. An emission spectrographic procedure for trace metal impurities was developed and published. Trace metal analysis by a neutron activation technique was shown to be feasible; key to the success of the activation technique was the application of a new ion exchange resin which provided a sodium separation factor of 10^{11} . Preliminary studies on direct scavenging of trace metals produced no conclusive results.

3 3679 00061 6930

BNWL-1407
UC-4, Chemistry

CHEMICAL ANALYSES OF SODIUM SYSTEMS

FINAL REPORT

W. O. Greenhalgh

W. H. Yunker and F. A. Scott

Chemistry Research Department
Chemistry and Metallurgy Division

June 1970

BATTELLE MEMORIAL INSTITUTE
PACIFIC NORTHWEST LABORATORIES
RICHLAND, WASHINGTON 99352

Printed in the United States of America
Available from
Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U.S. Department of Commerce
Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.65

CHEMICAL ANALYSES OF SODIUM SYSTEMS

FINAL REPORT

W. O. Greenhalgh, W. H. Yunker, and F. A. Scott

ABSTRACT

BNWL-1407 summarizes information gained from the Chemical Analyses of Sodium Systems Program pursued by Battelle-Northwest over the period from July 1967 through June 1969. Tasks included feasibility studies for performing coulometric titration and polarographic determinations of oxygen in sodium, and the development of new separation techniques for sodium impurities and their subsequent analyses.

The program was terminated ahead of schedule so firm conclusions were not obtained in all areas of the work. At least 40 coulometric titrations were carried out and special test cells were developed for coulometric application. Data indicated that polarographic measurements are theoretically feasible, but practical application of the method was not verified. An emission spectrograph procedure for trace metal impurities was developed and published. Trace metal analysis by a neutron activation technique was shown to be feasible. Key to the success of the activation technique was the application of a new ion exchange resin which provided a sodium separation factor of 10 in. Preliminary studies on direct scavenging of trace metals produced no conclusive results.

TABLE OF CONTENTS

LIST OF FIGURES	vii
LIST OF TABLES	viii
PROGRAM INTRODUCTION	1
PROGRAM SUMMARY	1
PROGRAM FACILITIES	2
TASK 1: OXYGEN-ION COULOMETRY IN LIQUID SODIUM	4
Introduction	4
Summary and Conclusions	6
Experimental Development	8
Description of Development Program	9
Apparatus	14
Yttria-Thoria Electrolytes	19
Coulometric Titrations	20
Titration Procedure	20
Discussion of Titration Curves and Titration Results	21
Titration Related Problems	27
Future Work	31
Recommended Studies	31
Titration Considerations	32
TASK 2: OXYGEN-ION POLAROGRAPHY IN LIQUID SODIUM	33
Introduction	33
Experimental	36
Apparatus	36
Procedure	36
Results	38
Conclusions	38
TASK 3: DEVELOPMENT OF NEW SEPARATION TECHNIQUES	39
Subtask A. Spectrographic Analysis of Metallic Sodium	39
Subtask B. Sodium-Ion Separation	41
Introduction	41
Experimental Procedure	42

Results	43
Interaction of Impurities with Resin	44
Conclusions	48
Subtask C. Impurity Gettering from Metallic Sodium	49
Introduction	49
Experimental Procedure	50
Results	52
Conclusions	55
ACKNOWLEDGEMENT	56
REFERENCES	56

LIST OF FIGURES

1	Inert Atmosphere Facility	3
2a	Liquid Sodium Coulometric Cell	7
2b	Simple Coulometry Circuit	7
3	Current Temperature Curve	10
4	Coulometric Titration of Oxygen in Liquid Sodium, UN Probe Number 2	12
5	Nickel Coulometer Apparatus	16
6	Hermetically Sealed Feedthrough Connector	18
7	Coulometric Titrations	22
8	Coulometric Current Versus Time Curves for Na,Na ₂ O//15 wt% Y ₂ O ₃ -ThO ₂ //Na,Na ₂ O	24
9	Coulometric Titrations of Working Standards	26
10	Reverse Coulometric Titrations	28
11	Coulometric Titrations in Various Containers	30
12	Coulometric Titration Current	34
13	Current-Voltage Curve at High Oxygen Concentration	35
14	Expected Oxygen Polarographic Curve	37
15	Nickel Filtration Apparatus	51

LIST OF TABLES

Coulometric Titration Results	25
Elements Determined in Sodium by Emission Spectroscopy and Their Lower Determination Limits	40
Results of Neutron Activation Analysis of Sodium Metal and Related Materials	43
Nitric Acid Analysis	45
Retention Properties of ERBA-RAI Ion-Exchange Resin in 8N HNO ₃	45
Analysis of NaNO ₃ Stock Solution by Neutron Activation Analysis	46
Metal Impurities in Solution	47
Estimated Limits of Detection for an Integrated Neutron Flux of 6×10^{17}	48
Typical Analysis of Baker and Adamson ACS Grade Sodium	50
Concentration of Impurities Added to Sodium in ppm	53
Ratio of Impurity Content of Sodium	54
Ratio of Impurity Content of Trial Getter	55

CHEMICAL ANALYSES OF SODIUM SYSTEMS

FINAL REPORT

W. O. Greenhalgh, W. H. Yunker and F. A. Scott

PROGRAM INTRODUCTION

The purpose of this report is to summarize information gained from the Chemical Analyses of Sodium Systems program over a 2-year period from July 1967 through June 1969. Tasks included feasibility studies for performing coulometric and polarographic titrations of oxygen in sodium, and the development of new separation techniques for sodium impurities and their subsequent analysis. The program was terminated ahead of schedule, and for this reason some of the experimental data are preliminary or incomplete, and firm conclusions could not be made in all areas of the work.

PROGRAM SUMMARY

The concept of conducting direct coulometric titrations of oxygen-ions in sodium has been demonstrated using oxygen-ion permeable ceramics. At least 40 successful titrations have been carried out. Titration techniques and special test cells have been developed specifically for coulometric application. The remaining problem areas have been defined and program plans prepared for their investigation.

A small effort was made to develop oxygen-ion polarography in liquid sodium. Characteristic polarographic curves were not obtained but much of the data developed in the coulometric investigation indicate that polarographic measurements are possible.

An emission spectrographic procedure for the determination of trace metal impurities in metallic sodium has been developed and published. The procedure is based on a lanthanum hydroxide carrier precipitation followed by direct arc emission spectrography on a solution of the precipitate.

The problems normally encountered during the thermal neutron activation analysis of trace metals in sodium have been largely overcome through the use of an ERBA-RAI resin to remove the activated sodium matrix. The activation analysis of trace metals in metallic sodium has been demonstrated to be technically feasible. The technique shows promise and its development should continue, particularly for use in analysis of irradiated loop or FFTF samples. The resin separation should also prove useful when combined with atomic absorption or colorimetric procedures. Additional work is required to completely define the limits of its usefulness with these procedures.

Preliminary studies were made on the direct scavenging of trace metal impurities from molten sodium using solid sorbants. The data obtained are not sufficient to indicate the technical feasibility of the approach. Improved analytical capabilities are needed for significant progress to be made in this portion of the program.

Laboratory facilities for the development of methods for the analysis of metallic sodium have been established. These facilities center around an 18 ft², high purity, inert atmosphere glove box.

PROGRAM FACILITIES

The handling of pure sodium for experimental purposes requires a high purity atmosphere with oxygen and water vapor concentrations in the low ppm range. A conventional inert atmosphere glove box facility was set up for this purpose. It is shown in Figure 1 and consists of the following Vacuum Atmosphere Corporation components:

- Two Model HE-43-2 stainless steel glove boxes bolted together and one evacuable lock all held on an angle-iron stand of our construction.

Neg 0690266-9

FIGURE 1 Inert Atmosphere Facility

- One Model HE-93 purification-recirculation unit which contains a full-flow catalyst bed (dual, parallel beds) with the normal capacity to recover a contaminated box (500 ppm) in 3 to 4 hr.
- Two Model HE-173 refrigeration units of 3,500 Btu/hr capacity, used to remove the heat produced by furnaces operating in the box.

One refrigeration unit was installed in the gas line downstream from the purifier. The condenser coils for the other unit were located in the box and the unit was thermostatically controlled. Monitoring instruments included: one Thermox single probe oxygen detector, a dual probe Panametrics hygrometer for the box atmosphere and a Consolidated Vacuum Corporation Pirani gage for measuring the vacuum lock pressure. Four electric furnace outlets were wired to allow all control equipment to be located outside the box. Other services, i.e., gas, vacuum, electrical and instrument leads, were brought in through appropriate feedthrough connections. During normal operation, the box atmosphere contained a maximum of 1 ppm each of oxygen and water vapor. The atmosphere was continuously mixed by the 30 scfm recirculation blower, and by a fan in the box.

TASK 1. OXYGEN-ION COULOMETRY IN LIQUID SODIUM

INTRODUCTION

The objective of this task is to develop a technique for the direct coulometric determination of oxygen in liquid sodium using an oxygen-ion permeable ceramic.

There are several methods currently in use for the determination of oxygen (oxygen-ion concentration) in sodium. The more commonly applied methods include mercury amalgamation, vacuum distillation, high energy photon activation analysis, and potentiometric cell measurements. Of the laboratory methods, mercury amalgamation and vacuum distillation share a

common problem in that neither is specific for oxygen-ion or even total oxygen. The residues left from both processes are assumed to be Na_2O but in fact may contain many additional impurities which are reflected in erroneous values. Vacuum distillation has the additional disadvantage of requiring relatively complex apparatus. High energy photon activation is specific for oxygen but has very limited availability because of the costly equipment required.

The only widely used technique for the in-line measurement of oxygen-ion concentrations in sodium is the potentiometric cell. The instrumentation required is available commercially from United Nuclear Corporation. The technique is based on the measurement of the potential of an activity (concentration) cell. One half of the cell is a copper, copper oxide mixture with a fixed oxygen-ion activity. This is located inside a 15 wt% Y_2O_3 - ThO_2 electrolyte tube which is an oxygen-ion conductor and serves as the electrolyte. The second half of the activity cell is the sodium of unknown oxygen-ion activity. Measurements are made with a high impedance voltage measuring device (electrometer). The test sodium flows around the outside tip of the probe and an EMF develops as a result of the difference in oxygen activity between the test sodium and the copper, copper oxide reference material. The EMF produced is monitored continuously and the oxygen concentration of the sodium can be estimated by calibrating the instrument initially against cold trapped sodium (oxygen solubilities) or chemical analyses.

The potentiometric oxygen probe has been found to be quite useful in routine continuous operation; however, it has a number of disadvantages and limitations. Some of the disadvantages are:

- The probe must be conditioned at operating temperature for a considerable time before use.

- It is highly sensitive to temperature variation.
- It is often sluggish initially and, in general, response time could be better.
- It is affected by changes in ambient conditions.
- Its calibration is usually affected by sodium loop shut-down and other major system changes.
- Its calibration does not generally agree with theory so in-line chemical standardization is necessary.

These problem areas are under investigation and some progress is being made toward their solution.

Another way of overcoming these difficulties might be through the application of other electroanalytical techniques using the same type of oxygen-ion ceramic electrolyte. One of the more promising electroanalytical techniques is coulometry. A schematic drawing showing the reaction involved and the basic operation of a liquid sodium coulometric cell is shown in Figure 2a. Such a cell could potentially eliminate electrode preconditioning, liquid sodium temperature effects, chemical calibrations on large sodium systems, and ambient condition effects. Also coulometric cell measurements would give directly oxygen-ion concentrations with minimal interference from other ion species. Investigation may even reveal a possible means for the measurement of individual oxygen containing impurity species through the control of the potential or the observation of reaction rates. The basic circuit used for coulometry is shown in Figure 2b.

SUMMARY AND CONCLUSIONS

The coulometric titration of oxygen in liquid sodium systems has been demonstrated. Techniques and test cells permitting the direct titration of oxygen have been developed and at least 40 coulometric titrations have been performed. The titrations were carried out under a constant applied potential

FIGURE 2a. Liquid Sodium Coulometric Cell

FIGURE 2b. Simple Coulometry Circuit

and sharp, well defined curves were generally obtained. Oxygen concentrations obtained by the coulometric titration were often inconsistent with oxygen values obtained by other means such as the mercury amalgamation method. However, in later titrations qualitative agreement was achieved in many instances and it was concluded that a better characterized sodium system or improved sodium sampling technique would probably provide good comparative analyses.

The characteristics of cells suitable for coulometric titrations have been shown to be significantly different from those in use as potentiometric devices. Required characteristics have been defined and acceptable cells developed. Many areas of investigation are apparent which could result in further improvement in cell performance.

Much work remains before a practical oxygen coulometric apparatus and a corresponding optimum titration procedure can be developed. The coulometric concept has been verified, the bulk of the problem areas have been defined, basic titration conditions have been established, and actual experimental titrations have been carried out.

EXPERIMENTAL DEVELOPMENT

The present in-line oxygen analytical techniques are based on the measurement of the potential of relatively high impedance activity (concentration) cells. Cells designed for this purpose are available commercially. Coulometric measurements require cells with significantly different characteristics such as high current carrying capabilities, high current efficiencies, and small sample volumes. The initial phases of this task therefore involved the development of cells and procedures specifically designed to meet coulometric requirements.

Description of Development Program

The initial and crucial problem confronting the program was to define the conditions under which adequate oxygen-ion transport could be obtained in electrolyte tubes without destroying the integrity of the ceramic. In describing the United Nuclear Oxygen Probe, Minushkin and Kolodney⁽¹⁾ indicated that it responds well to oxygen activity at a temperature of 600 °F and lower. McKee⁽²⁾ obtained actual oxygen transport at temperatures between 600 and 1200 °F using various stabilized zirconia or thoria electrolyte tubes in liquid sodium. Alcock and Belford^(3,4) developed a technique for titrating oxygen in molten lead and tin coulometrically between the temperatures of 900 and 1300 °F using either stabilized zirconia or thoria electrolytes.

Oxide electrolytes are attacked chemically by molten sodium. The rate of this attack increases rapidly as the temperature increases. It is therefore desirable to conduct coulometric titrations at the lowest temperature that permits adequate current flow. An effort was made to define this temperature by applying six volts to a cell at 650 °F and measuring the current passed by the cell as the temperature was raised to 1000 °F at approximately 1 °F/min. The measured current values are plotted in Figure 3.

Two regions are apparent in the curve. They are the logarithmic increase in current from 650 °F to approximately 900 °F and the rapid drop in current above 900 °F. The latter drop is undoubtedly caused by the limited availability of oxygen in the small volume of sodium in the titration cell and represents the coulometric removal of oxygen from the cell. If adequate oxygen had been available the curve would have followed the dotted extension shown. This experiment indicated that the minimum temperature at which coulometric titration of

FIGURE 3. Current Temperature Curve (Run Conditions: Applied Potential 6.0 Volts, Approximate Scan Rate $+1 ^\circ\text{F}/\text{min.}$)

the sodium is practical is in the region of 900 °F. Experience gained in subsequent titrations has confirmed this value.

A rough estimate of the current efficiency which can be anticipated can also be obtained from the data in Figure 3. Transport of oxygen ions reduced the current from 1.0 to less than 0.2 milliamperes indicating a current efficiency of greater than 80% at the point where the coulometric effect became apparent. The current efficiency for numerous test coulometric titrations has been determined in a like manner by computing the ratio of the initial current to that of the difference between the initial and final current levels. The initial titration current as illustrated in Figure 4 is the sum of the ionic and electronic (blank) levels, whereas the final titration current approaches the electronic or blank current level. The current efficiency for most titrations with yttria-thoria electrolyte cells was found to be 80% or better. It was observed to be a function of the applied potential, electrolyte characteristics, titration size, temperature, and time. An effort was made to determine actual current efficiencies by measuring the magnitude of the ionic and electronic current components with an oscilloscope detector. The method was abandoned when it failed to resolve the two types of current adequately.

The first successful coulometric titration was obtained with a Na, Na₂O//15 wt% Y₂O₃-ThO₂//Cu, Cu₂O cell operated at about 930 °F. The cell consisted of a United Nuclear Oxygen probe as the electrolyte and anode compartment, and a sodium sample from a test engineering loop as the cathode and material being titrated. The cell, which was contained in a sealed stainless steel tube, exhibited an initial current efficiency of 80%. The titration of the 10 cm³ volume was essentially complete after 2 hr at a potential of 6 V (see Run No. 2, Figure 4). The coulometric titration carried out on the

FIGURE 4. Coulometric Titration of Oxygen in Liquid Sodium, UN Probe Number 2

laboratory bench gave an oxygen value of 30 ppm; which is in the range expected considering the loop sodium contained 10 to 15 ppm before handling. Five other titrations were successfully carried out with the United Nuclear probe, but the probe broke after addition of oxygen to the sodium system on the sixth titration. The electrolyte portion of the probe that had been in the sodium had undergone a color change from white to greyish brown during the course of the titrations. Tube breakage and the brown coloration were probably caused by the addition of oxygen. The grey coloration as well as some tube deterioration was thought to be the result of the applied potential, and it was concluded that whenever possible a lower titration voltage should be used.

Additional titrations were also carried out successfully with copper-copper oxide anode cells prepared in this laboratory, but a significant irreversibility or battery effect was observed in these cells. The effect tended to prolong the measurements by decreasing the effective applied potential. In an effort to define the problem, a cell $\text{Cu,CuO (2000 ppm O) // 15 wt\% Y}_2\text{O}_3\text{-ThO}_2\text{ // Cu,CuO (2000 ppm O)}$ was constructed, a potential applied, and the current observed. Upon interruption of the current, the cell exhibited a significant potential, the magnitude of which increased with the amount of current passed. This potential indicated the creation of an oxygen activity cell with large concentration differences. The amount of current required to create this cell was not sufficient to significantly alter the bulk composition of copper-copper oxide within the cell. This fact was also confirmed by chemical analysis of the mixture. Large oxygen concentration gradients must therefore exist at or very near the membrane surface. Such gradients indicate that the diffusion rate of oxygen in copper-copper oxide material is inadequate at 930 °F for prolonged use in coulometric electrodes.

Other anode materials such as graphite and tungsten-tungsten oxide were tested. Coulometric titrations were successfully carried out with a graphite anode, but carbon contamination became a problem. Tungsten material was then tried but the internal cell resistance was found to be excessive. Molten bismuth and lead have been considered but were deemed impractical because their high melting points would create handling difficulties.

An ideal reference electrode material would act as a good oxygen-ion acceptor, wet the electrolyte wall, and readily transport oxygen. Sodium oxide-liquid sodium was selected as a material to satisfy these requirements. Initial attempts to use sodium in the program were unsuccessful because of internal electrical shorting of the cells from condensation of metallic sodium in the cooler portions. Subsequent work has been much more successful and the shorting problem has been eliminated by keeping the hot zone well below the seals. All of the later work was conducted with sodium anode systems.

Apparatus

The simple circuit shown in Figure 2b was set up for the purpose of measuring the cell current and the applied cell potential. It consisted of a calibrated **Weston Model 980** analyzer for measuring titration current, a **Simpson Test Meter** for measuring the applied potential, a wire-wound **500 ohm** pot for adjusting the potential, and a **9-v** heavy duty **Eveready** battery for a ripple-free dc power supply. In some of the early experiments, a Tektronix Model 564 oscilloscope was put into the coulometric circuit to look at wave forms.

Early experiments were not carried out in a glove box but in a sealed hardware on the laboratory bench. Later the inert-atmosphere glove box described in the Program Facilities Section became available and the bulk of the experiments have

been carried out in this facility. Electrical penetrations through the box were made with Dage hermetically sealed feed-throughs. The hardware used for supporting the electrolyte tubes was that obtained from United Nuclear Corporation and was designed for the operation of their potentiometric cells. The hardware was complete with electrical leads but these were removed and sealed nickel leads were used instead. The hardware was used repeatedly but was never taken out of the glove box after initial bake out in a vacuum furnace. This hardware was incorporated into the small nickel thermal convection system shown in Figure 5. The bulk of the titrations were made in this apparatus.

The nickel thermal convection apparatus was designed to permit consecutive analyses of sodium samples of known oxygen content. It consisted of a small thermal convection loop containing two compartments, each having an electrode. The larger compartment contained a United Nuclear type oxygen probe, a thermocouple, sparge tube, and an oxygen getter. The other compartment contained an experimental coulometer cell. While the hardware was equilibrating, the sodium was to be circulated through the system including the coulometry section by thermal convection. After equilibration, positive argon pressure was to have been applied to the coulometric compartment and the sodium level lowered, leaving a standard volume of sodium in contact with the electrode for titration. Provisions were made to take samples for confirmatory chemical analysis but, in general, concentration measurements made with the coulometric cell were to be verified by determining the oxygen activity before and after titration with the potentiometric oxygen probe.

Unfortunately, after a little use the system would no longer seal. One problem was gas leakage by the Dage hermetically sealed electrical feedthrough connectors. Leakage was not detected when the connectors were tested initially.

FIGURE 5.- Nickel Coulometer Apparatus

Use under conditions in which the seal temperature cycled up to approximately 100 °C apparently broke the seal. Photographs of a typical feedthrough connector as used are shown in Figure 6. Note that in the view identified as 6a a tight metal glass seal protects the center electrical lead, but a wide gap is present between the glass seal and the electrical ground. The sealant has broken down with thermal cycling causing gas leakage up through the plastic spacers shown in the second view of this figure. A silicone rubber seal prevented leakage between the connector and the electrode hardware.

The electrode hardware used in the nickel coulometric apparatus, including the Dage connector, was that furnished by United Nuclear Corporation with their oxygen probes. As mentioned in an earlier section, some problems with so-called "ambient effects" have been experienced with the UN oxygen probes. It seems likely that the electrical feedthrough leakage problem described above could be the basis of this "ambient effect". A leak in the hardware would make the oxygen activity of the reference material a function of air leakage rather than the constant activity of oxygen induced by the copper-copper oxide material. Some progress toward solving the "ambient effect" problem in the commercial probes has been made; however, should the effect be noticed on a probe, replacement of the old feedthrough connector would be rapid and might solve the problem.

Feedthrough connectors were replaced in the nickel apparatus and no leakage was observed with the new seals during leak testing. Unfortunately, gas leakage because of thermal stress cracking in the nickel occurred shortly thereafter with the apparatus, so the original titration plan was abandoned.

Most later titrations were made by using the coulometer cell in a reverse configuration by placing the unknown inside of the electrolyte tube. This offered the advantage of a small

FIGURE 6. Hermetically Sealed Feedthrough Connector

sample volume (2 to 5 cm³) and, correspondingly, a shorter titration time. However, it posed a mechanical problem of transferring analytical samples to the coulometer without contamination as they now had to be pipeted through the long narrow neck of the thimble without loss., It also posed a mechanical problem in taking an appropriate sample for amalgamation confirmational analysis.

Yttria-Thoria Electrolytes

Yttria-thoria electrolyte tubes used in this work were purchased from Zirconium Corporation of America. The as-received tubes were brown in color and were slightly **hyperstoichiometric** in oxygen. To prevent contamination of the samples by the hyperstoichiometric electrolyte tubes and to ensure the proper electrical conductivity, tubes were fired at 600 °C in an 8% hydrogen-argon gas mixture until they were white in color.

Although they looked good, initial attempts to use these locally prepared tubes in coulometric titrations were not successful. Cell current increased with time rather than decreasing and oxide contamination was found in every test cell during post-titration examination. Differential thermal analysis (DTA) of the hydrogen-fired electrolytes indicated substantial loss of material by volatilization, as much as 1 **wt%**. Most of the loss occurred at a temperature of about 700 °C and was attributed to release of chemically bound water. To eliminate this problem the hydrogen firing temperature was raised to 900 °C and a new firing furnace was fabricated that would force the gas to sparge both the inside and outside of the tube before being exhausted from the furnace. Unfortunately, the 900 °C firing temperature introduced some surface metallic impurities into the tube from the stainless steel furnace. To avoid this the temperature was reduced to 800 °C. All subsequent electrolyte tubes have been hydrogen fired at the 800 °C temperature with generally good results.

Extensive effort is presently being made in other programs to improve the performance of the electrolyte used for potentiometric oxygen measurements. The need for this information is supported by observations made in this program and some evidence has been obtained which indicates that improvement is possible. In a couple of rare instances, electrolytes were tested that simply would not work, and no reason or explanation for this could be discovered. The unexplained performance of these, apparently normal tubes, shows that we do not have a complete understanding of the variables controlling the behavior of the electrolyte in either the coulometric or potentiometric application. An important step in any extension of this work or in the program to improve the existing **potentiometric** electrode will be the characterization of these "**non-performing**" electrolytes, the discovery of an explanation for their behavior, and the development of a preparative technique to attain adequate control over their behavior. One area for investigation might be their stoichiometry.

COULOMETRIC TITRATIONS

Titration Procedure

A sample of liquid sodium is taken with a 25 ml **tipless** glass pipet from a pot of low temperature (140 °C) liquid sodium. An accurately measured weight (~2 to 5 g) is used for a coulometric sample and at least two other similar portions are used as comparison samples for oxygen analysis by the mercury amalgamation method. The coulometric sample is placed either on the inside or outside of the electrolyte tube for titration and the apparatus is sealed by a Conoseal flange and gasket. The comparison samples are placed in 5 cm³ vials, plugged, placed into a jar that can be sealed, and then are transferred to the amalgamation dry box.

The titration is carried out as soon as the apparatus has had time to become thermally equilibrated at the pre-selected temperature (1020 °F). The electrical connections are made and the 500 ohm potentiometer is adjusted to give the desired current; the voltage drop across the cell is sufficiently small to ensure that little fluctuation in the applied potential occurs during the period of the titration. Cell current values are recorded as a function of time and a current-time curve plotted. The area under the curve is integrated after subtracting the residual electronic current blank, and the quantity of oxygen passed by the cell is calculated. Coulometric oxygen values have been found to be equal to or greater than values determined by the mercury amalgamation method or the known oxygen concentrations prepared by standard gas additions.

Discussion of Titration Curves and Titration Results

Three types of current versus time titration curves were obtained, linear, exponential, and a combination of these which resulted in a step shaped curve. An example of each is shown in Figure 7. The linear or sloping curve was obtained under the conditions of either a low applied potential, or a high oxygen concentration or both. The ideal or exponential curve was obtained under the condition of either a high applied potential, or a low oxygen concentration. The step-type curve was typical of most samples and is a combination of the linear and exponential plots. The **horizontal** portion represents a situation in which the oxygen-ions are plentiful so that the cell current is limited only by the IR drop across the membrane and the applied cell potential. The second portion of the curve represents the situation in which the concentration of oxygen-ions is depleted so that cell current is limited by the diffusion of the available oxygen-ions to the membrane surface. Under these conditions the concentration of oxygen-ions decreases exponentially and therefore the current decreases

FIGURE 7. Coulometric Titrations

- A. Titration Curve Under Typical Conditions; Cell Na, Na₂O // 8 wt% Y₂O₃-ThO₂ // Na, Na₂O, T = 550 °C, E = 0.3 Volts.
- B. Titration Curve with a Low Applied Potential.
- C. Titration Curve with a High Applied Potential.

exponentially. Another typical titration curve which exhibits these effects is shown in Figure 8. Both the main step-like titration and a manipulation blank of similar shape are shown. A compilation of the data obtained during these and all other coulometric titrations is given in Table 1.

Initial attempts to obtain a correlation between coulometrically measured oxygen concentration and mercury amalgamation values using the sample handling and titration procedures described above have not been successful. Coulometric values have been consistently higher than amalgamation values probably because of oxide or moisture contamination to the sample and hardware. Also, sampling techniques have not worked out as well as expected. Very low oxygen concentrations were anticipated in the samples because of the manner in which they were taken (vacuum thieved at low temperatures). Concentrations in the 20 to 40 ppm range were frequently observed both coulometrically and by mercury amalgamation. These observations throw doubts on the quality of the sample handling technique. Plans were underway to obtain a correlation between coulometric and amalgamation values by placing the titration cell in-line in a small forced circulation loop which would permit sampling of the bulk sodium. These plans were abandoned when the program was terminated.

There have been a few examples of confirmational analyses that have checked semiquantitatively. Run 39 (Figure 9a) shows a coulometric analysis of a 22 ppm sodium sample with the oxygen being added by means of an oxygen standard gas sparge. Coulometric analysis of the 22 ppm sample gave an oxygen value of 25 ppm. Likewise, Run 40 (the titration shown in Figure 9b) gives a value of 35 ppm oxygen for sodium analyzed by the amalgamation method to be 30 ppm.

A second method of adding known quantities of oxygen that eliminates contamination problems is through direct coulometric

FIGURE 8. Coulometric Current Versus Time Curves for $\text{Na,Na}_2\text{O//15 wt\% Y}_2\text{O}_3\text{-ThO}_2\text{//Na,Na}_2\text{O}$

TABLE 1. Coulometric Titration Results

Run No.	Type of Run or Objective	Temperature (°F)	Apparatus Set Up	Applied Voltage (Volts)	Current (ma)		Type of Electrode	Type of Electrolyte	Initial Current Efficiency (%)	Titration Time	Sodium Weight (g)	(μ eq)	(ppm)	Oxygen Comparison Analyses (ppm)	Observations and Conclusions
					Initial	Final									
1	Scan to determine minimum temp.	670-940	Sealed stainless steel tube	6.0			UNC probe	15 wt % $\text{Y}_2\text{O}_3\text{-ThO}_2$			10				900°F required for oxygen coulometry Coulometric titration successful
2	Test coulometric titration	930		5.0	1.04	1.18			83	140 min.	10	35	28	No data	
3		920		6.2	2.07	0.80			61	160 min.	25	62	20	48 by gas sparge	
4a	Reverse coulometric titration	925		6.2	0.80	1.64				30 min.	25	11	3		
4b	Reverse coulometric titration				1.40	0.80				60 min.		10	3		
5	Current level variation with oxygen	930		6.2	0.30	1.10			63 (final)	30 min. addition	25			20 μ eq/min oxygen added by gas sparge	Note! UNC Probe broke after Run No. 5 Current level increases with increase in oxygen conc.
	Blank tube resistivity measurements	840-970		5.7	<0.001	0.003	Thoria probe	100% ThO_2							No blank contribution by thoria ceramic.
	Test coulometric titration for calcia-zirconia electrolytes	930		5.7	0.30 2.8 14.0	15.6 23.6 78.0	Prepared with Cu, CuO anode	74 wt % CaO-ZrO_2	None	4 hrs. 7½ hrs. 6 hrs.	20	-	-		Use of calcia-zirconia electrolytes for coulometric titrations is very doubtful; the tube appears to be chemically attacked and mechanical strength is gone.
10-13	Coulometric titrations with Oscilloscope detector	930		6.1	Increased with time		Prepared with Cu, CuO anode	15 wt % $\text{Y}_2\text{O}_3\text{-ThO}_2$	Little or None	6-7 hrs.	20	-	-		Runs failed due to faulty system set up
14	Temperature scan with oscilloscope to determine current efficiency	825-1110		1.4	0.04	8.0	Prepared with Na, Na ₂ O anode	New 15 wt % $\text{Y}_2\text{O}_3\text{-ThO}_2$		8	20				Wave form did not differentiate ionic and electronic currents.
15	Test coulometric titration (CaO-ZrO_2)	1040		2.7	0.66	22.0	Na, Na ₂ O anode	1/8" wide 7½ CaO-ZrO_2	None		20				Probe broke at sodium-gas interface.
16	Test coulometric titration						Na, Na ₂ O anode	8 wt % $\text{Y}_2\text{O}_3\text{-ThO}_2$			15				Run discontinued, tube has a substantial moisture content.
17	Test coulometric titration	985		4.5	0.30	0.078	Carbon anode	New 8 wt % $\text{Y}_2\text{O}_3\text{-ThO}_2$	61	12 hrs.	5	340	900		Performance of carbon test electrode is poor.
18		990		5.5	1.0	-				84 hrs.	5				Probe broke after 8-1/2 hours.
19	Test coulometric titration	935		3.6	1.0	0.60*	Cu, CuO anode	New 8 wt % $\text{Y}_2\text{O}_3\text{-ThO}_2$		55 hrs.	10				Results are erratic due to temperature control problems and possibly oxygen contamination.
20		930		4.4	1.02	0.66*			-	29 hrs.					The intended operation was a failure.
	Nickel coulometric apparatus put into operation														
21	Test Coulometric titration	1020	Cathode inside tube	3.45	0.60	0.10	Na, Na ₂ O anode	15 wt % $\text{Y}_2\text{O}_3\text{-ThO}_2$	83	60 min.		16	25	19 initial sodium	Titration is successful; steplike curve obtained.
22				0.30	0.55	0.06			89	95 min.		22	35	7 thief sample	Titration looks good, but oxygen comparison is poor.
23		1025		0.25	0.60	0.06			90	115 min.	3½	36	81	sample contaminated	Titration looks good.
24		1020		0.32	0.47	0.02			95	85 min.	2-3/4	14	41		Titration looks good.
25				0.32	0.63	0.04			94	55 min.	2-3/4	13	38	5	Titration looks good, but oxygen comparison is poor.
26a				0.28	0.68	0.05			93	65 min.	2.9	16	43		Titration and blank looks good, oxygen in leakage is small.
26b	Test coulometric titration on overnight blank			0.28	0.44	0.06			87	10 min.	2.9	1.6	4.3		
27a	Test coulometric titration			0.05	0.64	0.07		8 wt % $\text{Y}_2\text{O}_3\text{-ThO}_2$	89	170 min.	2.5	40	129	Analysis is no good	Titration and blank looks good, oxygen in leakage is small.
27b	Test coulometric titration on overnight blank				0.30	0.02			93	60 min.		3	10		
28	Test coulometric titration			0.10	0.62	0.02			98	80 min.	2.0	15	60	30	Titration plot almost fits the ideal coulometric curve
29				0.07	0.60	0.04			93	175 min.	2.4	28	94	5	Oxygen comparison values poor.
30				0.15	0.89	0.07			92	80 min.	3.1	16	42	10	
31				0.20	1.02	0.08			92	50 min.	1.8	25	109	60	
32				0.28	1.00	0.10			90	60 min.	2.0	26	105	Sample contaminated	
33				0.22	1.10	0.10			91	50 min.	2.7	20	60	14	
34	Ideal Coulometric Titration (Test Extent of Polarization)		Reversed oxide migration Cathode inside tube	3.00	0.72	0.07			90	50 min.	2.7	4	13		Excess oxygen capacity of electrolyte is at least 4 μ eq.
35	Test coulometric titration				0.15	1.06			35	40 min.	2.6	15	40	15	Oxygen comparison values poor.
36					0.25	1.20			32	90 min.	3.2	27	90	17	
37					0.14	1.63			88	200 min.	3.2	110	270	100	
38					0.15	1.22			33	40 min.	3.2	19	47	15	
39				0.15	1.04	0.13			88	30 min.	3.2	9	22	25	Oxygen comparison values good.
40				0.15	1.08	0.14			37	35 min.	3.2	12	30	25	
41		1025		0.69	0.75	0.14		New 8 wt % $\text{Y}_2\text{O}_3\text{-ThO}_2$	82	60 min.	3.0	11	29	16	Oxygen comparison values poor.
42		1020		0.46	0.55	0.09			84	55 min.	3.5	15	34	19	
43				0.33	0.62	0.06			90	60 min.	1.5	14	75	13	
44	Test coulometric titration in nickel container		Cathode outside tube	0.12	0.82	0.15			82	24 hrs.	25	350	110	23	No oxygen buffering affects, but titration was lengthy
45	Test coulometric titration in stainless steel container			0.20	1.30	0.22			93	30 hrs.	20	525	210	110	Oxygen buffering affects seem present
46	Reverse coulometric Titration in a magnesia crucible			0.45	0.32	0.08			75	4-1/2 hrs.	3.0	53	normalized 140	135	
47			Cathode inside tube	0.80	0.48	0.08			83	7 hrs.		62	165		In qualitative terms, oxygen ions can be transferred reversibly. No adverse affects from the ceramic crucible were observed.
48					0.88	0.20			77	5 hrs.		49	130		
49	Test coulometric titration in steel crucible		Cathode outside tube	3.43	0.37	0.07			81	80 min.		7	18	21	Oxygen comparison value good and no adverse affects from oxygen buffering were observed
50					0.32	0.86			83	5 hrs.		47	125	Analysis contam.	
51				0.40	0.68	0.11			84	75 min.		18	50	42	Oxygen comparison values good
52	Reverse coulometric titration of No. 51		Cathode inside tube		1.04	0.09			91	125 min.		21	55		
53	Test coulometric titration				0.46	0.04		15 wt % $\text{Y}_2\text{O}_3\text{-ThO}_2$	91	120 min.	3.5	17	40	20	Oxygen comparison values poor

FIGURE 9. Coulometric Titrations of Working Standards

- A. Confirmational Analysis of a 22 ppm Sample
- B. Confirmational Analysis of a 30 ppm Oxygen Sample

addition. By reversing the polarity of the cell, oxygen in the anode compartment can be electrically transferred back to the cathode section and the titration repeated. An attempt was made to establish the usefulness of this technique as a means of instrument calibration through repeated transport of a fixed amount of oxygen through a cell membrane. Sodium containing approximately 50 micro equivalents of oxygen was placed in a cell, approximately one-third inside of the ceramic tube and the rest outside. Current was passed until all of the oxygen was inside the tube. The potential was reversed and the current necessary to move all of the oxygen to the outside of the tube measured. The potential was again reversed and the current necessary to transport all of the oxygen through the membrane was measured. The results are presented in Table 1, Runs No. 46, 47, and 48, and shown in Figure 10. The analytical figures should be identical. They are in general agreement but the observed precision is poor (± 10). Additional work will be required to establish the feasibility of adding precisely known quantities of oxygen to sodium coulometrically.

Titration Related Problems

One anticipated problem is the life expectancy of the electrolyte tubes in liquid sodium at the high operational temperature of about 1000 °F. This has not been specifically studied because Sodium Compatibility studies carried out by the BNW Metallurgy and Ceramics Department should provide the required information when the studies are completed. Experience in the Sodium Systems Program has led us to believe that chemical attack will not be a problem, however, because with rare exception electrolyte breakage to date has occurred from causes other than chemical attack. Most tubes broke from thermal shock during analytical sampling at 400 °F. Mechanical shock has also been responsible for some breakage. One of the electrolyte tubes used logged 75 intermittent hr at 1000 °F

FIGURE 10. Reverse Coulometric Titrations

- A. Titration No. 1 (140 ppm)
- B. Titration No. 2 (165 ppm)
- C. Titration No. 3 (130 ppm)

with 17 titrations completed before being voluntarily retired and examined. The tube showed no outward signs of deterioration or change and only slight changes were observed during microstructure analysis. It is believed that tubes protected from thermal and mechanical shock by such things as protective metal sleeves, and minimal handling after installation will provide coulometric cells with a practical life expectancy. This conclusion is supported by the work of Berkey and Cleary⁽⁵⁾ who have recently operated yttria-thoria cells continuously at 930 °F for more than two months.

Concern for possible oxygen buffering in sodium exposed to metal hardware prompted further titrations in sodium contained in either nickel or stainless steel systems. Run 44 (Figure 11a) shows a titration of a 25 g sodium sample contained in and exposed to a nickel vessel. No apparent titration interference nor oxygen buffering effect was observed. Run 45 (Figure 11b) contained the only indication that a buffering effect exists. It is a titration of a 20 g sodium sample contained in a stainless steel container. In this titration oxygen buffering is indicated by the very low initial current and by the long time required to titrate an apparently low concentration of oxygen (3 ppm). Other experiments carried out in a newly-machined, small volume stainless steel crucible showed no such effects but gave typical coulometric curves. The establishment of appropriate hardware cleaning and handling procedures should prevent any such problem. The titration of sodium contained in a magnesia crucible was also successful as shown in Figure 11c, Run 46, establishing the possibility of using ceramic materials in the construction of coulometric cells.

FIGURE 11. Coulometric Titrations in Various Containers

- A. Titration of Sodium Contained in Nickel Metal
- B. Titration of Sodium Contained in Stainless Steel Metal
- C. Titration of Sodium Contained in a Magnesia Crucible

FUTURE WORK

Recommended Studies

A good correlation between coulometrically and chemically measured oxygen concentrations should be obtained through the construction of a cell for in-line operation on an engineering scale sodium loop. It would be placed in operation on a well-characterized loop where oxygen titration values obtained by coulometry could be compared with reliable values from other oxygen methods and plugging meter readings. Deficiencies and limitations of the cell would be defined and corrected where possible. Other work suggested includes the following procedures:

- Reduce the required titration time by defining optimum operational cell temperatures and applied potentials; also determine the maximum operational cell temperature and cell potential that can be used without detrimental electrolyte effects.
- Determine the life expectancy of electrolytes under coulometric operational conditions and work to improve the electrolyte tube where performance is inadequate or limits cell application.
- Determine the best hardware material to contain the titration sample - stainless steel, nickel, or ceramic liner materials.
- Establish a quality control test procedure for non-destructive pre-operation testing of electrolyte tubes.
- Establish the most convenient ways to take this type of coulometric data and to automate the system as much as possible.
- Study electrolyte electronic conductivity as a function of its composition and establish methods of lowering electronic blank levels.

- Establish a procedure and design a prototype instrument for rapid routine coulometric analyses in sodium systems.

Titration Considerations

The following items ought to be considered in the test design and planned procedure for future oxygen coulometers in sodium systems:

- Instrumentation - Coulometers should be designed to provide a measure of both current and integrated current and to feed this information directly to a dual pen recorder.
- System design - A means of taking repetitive calibrated volumes of sodium in an otherwise closed system should be devised. Titration volumes of 5 cm³ or less would be preferred.
- Metal hardware - Nickel construction material would be preferred, but it is more important that the surface of the design hardware be free of oxides.
- Electrolyte hardware - Either 15 or 8 wt% yttria-thoria tubes can be used. The 8 wt% is probably the better electrolyte. Precautionary measures must be taken to prevent thermal shock and a protective metal sleeve should be installed around the electrolyte. Installation of coulometric cells should be carried out at a temperature of about 250 °F.
- Procedure - A titration temperature of 1000 °F and an applied potential of 1.0 V or less should be used until titration variables are better understood.
- Stirring devices - Methods of stirring the sodium during the titration should be investigated. Stirring should reduce significantly the titration time and provide improved accuracy.

TASK 2. OXYGEN-ION POLAROGRAPHY IN LIQUID SODIUM

INTRODUCTION

The objective of this task is to demonstrate that polarographic techniques can be applied to the analysis of oxygen in liquid sodium.

Polarography is an electroanalytical technique that has potential use for the direct measurement of the oxygen-ion concentrations in liquid sodium. Polarography would offer fast response to changes in oxygen concentration, eliminate most variations induced by temperature changes, eliminate electrode preconditioning, eliminate ambient effects, and it could be readily adapted as a continuous monitoring device.

Application of polarography should be possible when the cell current becomes limited by the diffusion of oxygen-ions to the anode surface. It seems apparent from the coulometric titrations described in the previous section that the diffusion of oxygen-ions become rate determining at the low oxygen concentrations represented by the exponential portion of the curves. The current level starts dropping off rapidly (exponentially) when all oxygen-ions in the immediate vicinity of the anode have been discharged. At this point the reduced form of Fick's law applies, hence the level of current is directly proportional to the concentration of oxygen-ions in the cathode or sample compartment.

A schematic drawing of coulometric titration which exhibits typical ionic, diffusion, and electronic currents is shown in Figure 12. As discussed in the previous section, at high oxygen concentrations the number of oxygen-ions moving through the electrolyte is limited solely by the potential applied. Current-voltage curves obtained for this portion of the curve obey Ohm's law and are linear as expected. Such a curve is shown in Figure 13. Current-potential measurements

FIGURE 12 Coulometric Titration Current

FIGURE 13. Current-Voltage Curve at High Oxygen Concentration

for the "exponential," or portion of polarographic interest, have been somewhat erratic and ill defined; future work will surely need to be directed to this component of the curve. As expected, the lower electronic portion of the curve also conforms with Ohm's law.

Figure 14 shows the type of polarogram that would be expected in the diffusion limited system. The current would rise sharply with increases in applied cell potential until the current limiting voltage was reached. At this point a distinct change in slope would be observed for all measurements at higher potentials until the electrolyte itself began to be reduced. The diffusion current would be determined by extrapolating this line back to zero voltage and, correspondingly, zero ionic current. The electronic current at any point is merely the total current minus the diffusion current.

EXPERIMENTAL

Apparatus

The equipment used was essentially the same as for the coulometric work except a null balance potentiometer was used for measuring cell voltages. Attempts to prepare micro electrodes were unsuccessful as it is currently difficult to obtain and work with micro size stabilized thorium tubes.

Procedure

Cell current-voltage measurements were taken manually by adjusting the potential and then recording the resulting current. Cell potentials from 0 to 1 V were normally investigated but on occasion higher and negative potentials were tested. Measurements taken in this manner invariably gave a linear or Ohm's law curve when plotted. In some instances coulometric titrations were used to adjust the oxygen-ion concentration in the sodium in preparation for polarographic measurements. A coulometric titration was performed up to the exponential

FIGURE 14. Expected Oxygen Polarographic Curve

portion of the curve and then the current-voltage measurements were taken. Unfortunately the available equipment was not sensitive enough to obtain meaningful results.

Results

Numerous current-voltage curves have been obtained but none have exhibited typical diffusion-limited plateaus. At a given potential, qualitative relationships between current and oxygen concentration have been observed. For example, during coulometric titration measurements with a United Nuclear prepared electrode, a 50% drop in current was observed after the use of a uranium metal oxygen getter to lower the oxygen level of the sample. Current voltage curves are consistently displaced to higher current levels for sodium samples containing higher concentrations of oxygen.

CONCLUSIONS

The conclusions reached concerning the applicability of polarography are preliminary in nature and depend primarily upon the electroanalytical data obtained during the coulometry study. Coulometric curves consistently show a region of diffusion limited current at low oxygen concentrations (<20 ppm). Attempts to obtain characteristic polarograms of cell current as a function of potential have been unsuccessful. Current-potential curves generally showed Ohm's law characteristics even with low oxygen samples that should have exhibited diffusion-limited current.

The relationship of cell current to oxygen concentration indicates that polarography is applicable provided the correct electrode and conditions can be established. If the conditions can be optimized it would make continuous on-line monitoring of the oxygen concentration possible.

TASK 3. DEVELOPMENT OF NEW SEPARATION TECHNIQUES

The objective of this task is to develop techniques for concentrating impurities in sodium prior to their measurement. The three areas of activity are Carrier Precipitation for Spectrographic Analysis of Sodium, Sodium Ion Separation in Aqueous Systems, and Impurity Gettering from Sodium.

SUBTASK A. SPECTROGRAPHIC ANALYSIS OF METALLIC SODIUM

An emission spectrographic method was established in order to provide relatively simple, general chemical analysis of metallic impurities in samples generated by the early impurity gettinger experiments. A detailed write-up of the procedures has been published in Analytical Chemistry.⁽⁶⁾ The method is outlined below.

The procedure is patterned after that developed at Atomics International by Scarborough⁽⁷⁾ et al., where $\text{La}(\text{OH})_3$ carrier precipitation was used for impurity concentration followed by atomic absorption analysis. A comparison of the spectra of lanthanum with those of the impurities revealed that lanthanum precipitation could be also used for emission spectrographic analysis.

The conditions used here for the $\text{La}(\text{OH})_3$ precipitation are those used by Scarborough et al., with slight modifications. After the 1 g sample is dissolved in methanol, a double precipitation is performed in polypropylene test tubes with centrifugation-separation of the precipitates. The final precipitate is dissolved in 6N HNO_3 and an aliquot analyzed by direct current arc emission spectrography.

Quantitative working curves for iron, nickel, chromium, cobalt and manganese were prepared by running spiked sodium chloride solutions through the analysis scheme. Transmittances of selected lines were measured on a densitometer, the readings converted to impurity-to-indium (internal standard) intensity

ratios using the emulsion calibration curves and, finally, the intensity ratios were plotted against concentration. Precision by this method has been measured to be $\pm 13\%$.

Standard reference plates for 30 other impurities have been prepared by varying the quantities taken through the precipitation-spectrographic analysis in steps of 2 from an equivalent of 0.1 ~~ppm~~ through 1000 ppm. Many impurities can be detected down to 0.2 ppm, manganese down to 0.01 ppm, while some have poor sensitivities, notably phosphorus, barium, tantalum and tungsten. Elements detected and their sensitivity are given in Table 2.

TABLE 2. Elements Determined in Sodium by **Emission Spectroscopy** and Their Lower Determination Limits

<u>Element</u>	<u>Detection Limit, ppm</u>	<u>Element</u>	<u>Detection Limit, ppm</u>
Mn	0.01	Y	0.5
In	0.1	Pb	1.
Mg	0.1	Ru	1.
Ag	0.2	Sc	1.
Al	0.2	Si	1.
Au	0.2	Ca	2.
Be	0.2	Sb	2.
Co	0.2	Tl	2.
Cu	0.2	Cd	5.
Ga	0.2	Bi	5.
Ni	0.2	Nb	5.
Ti	0.2	Zn	5.
Cr	0.3	As	10.
Fe	0.5	Zr	10.
Mo	0.5	P	20.
Rh	0.5	W	20.
Sn	0.5	Ta	50.
V	0.5	Ba	100.

The technique is good for the general, semiquantitative analysis of sodium. However, it did not develop to as precise or sensitive method as was hoped and did not adequately meet the needs of the gettering experiments. In particular, the quantitative analysis was only semiquantitative in practice. Had this program continued, other methods would have been developed to support the gettering experiments, such as radio-tracer, atomic absorption, or colorimetric analysis.

SUBTASK B. SODIUM ION SEPARATION

Introduction

One of the problems in analyzing sodium metal for low level impurities is the interference or masking of impurities by the gross quantity of sodium. Also, impurity analysis of irradiated sodium would be simplified if the radioactive sodium could be first removed. Present analytical methods remove the impurities from the sodium solution by standard carrier precipitation or ion exchange techniques. These techniques require extensive sample handling to separate the various groups of elements. Much time and labor is required and the danger of sample contamination is increased. It was recognized at PNL⁽⁸⁾ that the success of an Sb_2O_5 resin for specifically removing Na^+ from aqueous, biological systems might have important application to this problem. A series of tests were run with this resin (produced by Carlos Erba, Italy) using activation analysis. This analytical technique has the extremely high sensitivity needed to measure very large decontamination factors (DF). Properties of the resin studied include (1) sodium DF, (2) retention of impurities by the resin both with and without carrier, and (3) contamination of the sample by the resin. These are discussed in Sections III and IV.

Experimental Procedure

For each analysis, about 3 g of the sodium metal sample were placed in a clean (leached with concentrated HNO_3) 500 ml polyethylene bottle and dissolved in 50 ml of redistilled ethanol. A 20 ml portion of this solution was placed in a 30 ml poly-bottle and the bottle placed in a polyethylene irradiation container. The sample was cooled to dry ice temperature and, with appropriate standards, was irradiated to an integrated neutron exposure of 10^{16} n/cm^2 . The solution was quantitatively transferred to a 1-liter Erlenmeyer flask containing 50 ml of concentrated HNO_3 , 5 ng of each element to be measured and 50 g of Sb_2O_5 inorganic exchanger (ERBA-RAI Resin). The mixture was placed in a water bath for 30 min at 25 °C to destroy the ethanol, then centrifuged and the supernate removed. The resin was washed with several 20 ml portions of 8N HNO_3 . These washings were combined with the supernate and this solution passed through a column of ERBA Resin 1 in. thick by 2 in. in diameter. The column was washed with several 10 ml portions of 8N HNO_3 and the effluent placed in a standard polyethylene bottle for gamma-ray analysis.

A gamma-ray spectrum of the solution was obtained with a 1000 min counting interval on a 20 cm^3 Ge(Li) detector system. This permitted the estimation of the neutron induced activities of: ^{51}Cr , ^{208}Hg , ^{59}Fe , ^{60}Co , ^{24}Na , ^{65}Zn , ^{75}Se , and ^{86}Rb . The solution was evaporated to a volume of several ml, mixed with plaster of paris and placed in a standard counting geometry consisting of a 1-1/2 in. $\times$ 2 in. PVC ring. A second gamma-ray spectrum of the sample was taken with an anticoincidence shielded, gamma-gamma coincidence multidimensional analyzer by counting the source for 1000 min. From this spectrum the additional radionuclides $^{110\text{m}}\text{Ag}$, ^{46}Sc , ^{124}Sb , and ^{134}Cs could be measured. The concentration of each element in the sodium metal was determined by comparing the specific

activity induced in the sample with the specific activity of a standard. To determine the reagent blank contribution, samples of the ethanol used to dissolve the sodium were activated and analyzed in the manner described above. An empty polyethylene bottle accompanied each step of the procedure from sample collection through final sodium analysis to establish an estimate of the total background contamination.

Results

The results from the two samples of sodium metal analyzed by the above procedure are shown in Table 3. The residual ^{24}Na activity was below detection limits of 0.4 d/m compared with an original activity of 6×10^{10} d/m giving a DF of sodium by this procedure of $>10^{11}$. The concentrations of several elements found in the ethanol and the ethanol used to wash these containers are also presented in Table 3. These low concentrations are typical of those determined by activation analysis. The elements detectable by this method will be discussed below.

TABLE 3. Results of Neutron Activation Analysis of Sodium Metal and Related Materials, ppm

Element	Ethanol ^(b)	Container Background ^(b)	Baker and Adamson Sodium ^(a)	Reactor Grade Sodium Sample No. 1 ^(a)
^{124}Sb	0.001	0.002	0.003	<0.0001
^{60}Co	<0.0002	0.0008	0.0007	0.0007
^{134}Cs	<0.0003	0.002	0.010	0.0001
^{46}Sc	<0.00001	0.00007	0.001	0.0003
^{65}Zn	0.25	0.28	12.6	0.67
^{208}Hg	<1	2	88	<1

a. Concentration - ppm based on sodium

b. Concentration - ppm based on ethanol

Interaction of Impurities with Resin

A personal communication with Carlo Erba⁽⁹⁾ stated that the resin was checked for the retention of 60 elements and that only tantalum (other than sodium) was held by the material in significant amounts. Their observations for several elements were checked using pure radionuclides. The isotopes were spiked into 100 ml of 8N HNO₃ containing 1 g of sodium ion. The mixture was contacted with 50 g of ERBA-RAI Resin (with mixing) for 10 min and then filtered. The resin was rinsed twice by a 5-min mixing with 20 ml of 8N HNO₃. The resulting resin was counted by the techniques described above and where high retention occurred the filtrate was counted also. Analysis of the nitric acid (Table 4) showed that only chromium was sufficiently concentrated to act as an eluant during washing. The results presented in Table 5 indicate the resin also retained silver (45%), antimony (35%), iron (16%), and selenium (15%) in addition to sodium. Since these radionuclides contained only a few milligrams of stable element carrier, it is possible that higher concentrations of each carrier would suppress this retention of the activated isotopes. This could be done easily in the analysis of activated sodium loop Samples. However, these resin holdup properties may not necessarily apply when techniques other than NAA are used to analyze the ERBA-RAI eluate, when no carriers are used.

To test the column retention properties without carriers and in the levels of normal sodium contamination, ~20 ppm, a series of scouting experiments were run using the emission spectrographic analysis technique described above. Again, termination of the program prevented improvement of the analytical techniques to the desired precision.

A solution was prepared of strontium, silicon, aluminum, nickel, magnesium, chromium, iron, cesium, and copper at a final concentration of 2 µg/ml each in 0.01N HNO₃ (Solution A).

TABLE 4. Nitric Acid Analysis(8)

<u>Metal</u>	<u>Impurities, ppb</u>	<u>Metal</u>	<u>Impurities, ppb</u>
Zn	10.	Sc	0.0007
Fe	~2.	Cs	<0.01
Sb	~0.03	Ag	~0.24
Co	~0.018	Cu	1.3
Cr	72.	Hf	<0.005

TABLE 5. Retention Properties of ERBA-RAI Ion-Exchange Resin in 8N HNO₃

<u>Element</u>	<u>Isotope</u>	<u>Weight of Element, μg</u>	<u>Amount Retained on Resin, %</u>
Ag	^{110m} Ag	0.07	45
Sb	¹²⁴ Sb	0.67	35
Fe	⁵⁹ Fe	670.	15
Se	⁷⁵ Se	11.	15
Hg	²⁰³ Hg		10
Co	⁶⁰ Co	0.3	3
Cr	⁵¹ Cr	0.62	3
Zn	⁶⁵ Zn	80.	2
Sc	⁴⁶ Sc	0.018	6
Cs	¹³⁴ Cs	0.52	<1
Rb	⁸⁶ Rb	33.	4

A second identical solution was prepared except that it also contained 100 g Na/l (Solution B). Both solutions were analyzed by emission spectrography. The sodium was analyzed by NAA (see Table 6) before being added to Solution B. Solution B was run through an ERBA-RAI batch extraction as described above, and an aliquot was analyzed. The remaining solution was then sent through a column extraction as above and again analyzed. Solutions of 0.01N HNO₃ were also passed through the process and analyzed as blanks. Results are shown in

Table 7. Within the precision of the technique, iron, chromium, nickel, copper, aluminum, and silicon appear to carry through the procedure. There is an unexplained pickup of magnesium, possibly from difficulty encountered in handling those samples. The high copper blank may be from the methanol. Cesium appeared not to be transported. The antimony picked up passed through a 0.5 micron filter. Obviously, the experiment needs to be repeated using analytical techniques with greater sensitivity and precision, and with a greater spectrum of elements. Use of tracers to measure small column retentions is limited because of the high dilution of stable isotopes supplied with most radionuclides, which act as carriers.

**TABLE 6. Analysis of NaNO_3 Stock Solution^(a)
by Neutron Activation Analysis^(b)**

<u>Element</u>	<u>Average Concentration</u>	<u>Number of Measurements</u>
^{86}Rb	<1.0	4
^{134}Cs	<0.005	4
^{46}Sc	<0.01	2
^{65}Zn	9.63	2
^{60}Co	1.20	2
^{124}Sb	<0.1	2

Gamma ray analysis performed with a $20\text{ cm}^3\text{ Ge(Li)}$ detector system.

Estimated experimental error - 20% to 30%.

-
- a. The concentration units of the NaNO_3 stock solution are 100 g Na/1.*
- b. The concentration units of the analysis are nanograms/gram of solution.*

TABLE 7. Metal Impurities^(a) in Solution,^(b) ppm

Elements	Starting Solution		After Batch Extraction		After Column and Batch Extraction	
	Without Na (Solution A)	With Na (Solution B)	Solution	Blank	Solution	Blank
Cs					0.04 ^(c)	<0.1 ^(c)
Fe	2	2	10	5-	5	2
Ni	2	1	5	<0.2	5	0.2
Cr	5	2	10	0.5	10	0.5
Cu	5	2	5	5	5	2
Al	5	2	10	1	10	1
Mg	2	2	50	1	50	0.5
Si	2	1	5	5	5	<1
Sb	Not spiked to original solution				90 to 120 ^(c)	130 ^(c)

- a. Sodium metal impurity ratio equivalent to ~20 ppm of each impurity in metallic sodium.
- b. Precision is $\pm X2$ - original solutions made up to ~2 ppm.
- c. By neutron activation analysis - original calcium spike not verified - sodium stock solution checked.

Conclusions

The technical feasibility has been demonstrated for performing chemical analysis of sodium by neutron activation followed by removal of sodium ions from the impurities with EBRA-RAI resin. The separation factor for sodium is appreciably greater than 10^{11} . For the elements which can be analyzed by NAA, the estimated sensitivities are given in Table 8 for an integrated flux of 6×10^{17} n/cm². The lower flux (2×10^{16} n/cm²) was used here because of laboratory handling requirements. The accuracy of the reported results may be on the order of X2 because the experiments were preliminary. A significant improvement would be expected as the procedures were refined. This technique shows promise and its development should continue, particularly for use in analysis of irradiated loop or FFTF samples.

TABLE 8. Estimated Limits of Detection for an Integrated Neutron Flux of 6×10^{17}

<u>Metal</u>	<u>Detection Level</u>	<u>Metal</u>	<u>Detection Level</u>
Co	0.2 ppb	Cr	20 ppb
Sc	0.02 ppb	Se	50 ppb
Sb	0.1 ppb	K	100 ppm
Cs	0.05 ppb	Mn	1 ppm
Zn	0.1 ppm	Cu	500 ppb
Hg	0.05 ppm	Sr	?
Fe	1 ppm	La	50 ppb

Before a statement can be made regarding the usefulness of this resin in conjunction with atomic absorption or colorimetric methods, more testing is needed on impurity retention by the column and impurity pickup from the column in the concentration ranges of interest.

SUBTASK C. IMPURITY GETTERING FROM SODIUM

Introduction

The objective of this **subtask** is to explore possible techniques for concentrating impurities from sodium directly onto solid surfaces. Such a technique, if developed, would be useful for (1) reducing the chance of external contamination during analysis of the sample by the reagents usually used in removing the sodium (e.g., by amalgamation), hence increased sensitivity over present methods, (2) by avoiding the alterations in the sample which might occur during vacuum distillation, (3) by quickly reducing the gross radioactivity from an irradiated sample, and (4) by permitting the collection of impurities from a much larger sample of sodium than could be normally handled by present techniques. A relatively long term program will be **required** to find and adequately develop the use of such a scavenging agent. The cost of this program is warranted by the several potential uses of the techniques. The program was primarily dependent upon the development of excellent analytical techniques and on the performance of several generations of experiments. The decision to abort the task caught it during the growing and learning phases, so that not much encouraging data have been accumulated. These initial experiments were of an empirical nature and were designed primarily to identify problem areas and to develop laboratory techniques. Until the termination of the program was announced (March 1969) the impurities of primary interest were iron and chromium. Techniques for the analysis and handling needed to follow low concentrations (<0.5 ppm) of these elements were under development. At that time, the activity was switched to a series of simple experiments using existing methods and the elements bismuth, tin, lead, zinc, cadmium, antimony, and magnesium were followed. The information acquired is given in the following pages.

Experimental Procedure

The all nickel reaction-separation apparatus used on this task is shown in Figure 15. Sodium could be moved through the 5 μ sintered nickel filter by controlling the pressure difference between the two chambers. About 10 g of sodium and trial gettering agent were loaded into the upper chamber. If ball milling was used, two 3/16 in. diameter nickel balls were also added. The equipment was rotated about its long axis which was at an angle of ~ 60 degrees to the horizontal. Heat was supplied by a 4 1/2 in. diameter $\times$ 4 in. cylindrical heating coil. Filtration could be accomplished at any temperature above the sodium melting point. After filtration, the reactor was cooled and aliquots of the original sodium, the sodium filtrate and the wash of the reaction chamber were dissolved in methanol and analyzed by emission spectrography. The original trial getter and used getter were analyzed by spark source mass spectrography for changes in concentration of the impurity metals (except for Na_2O which went with the reaction chamber wash).

The sodium used was Baker and Adamson ACS grade which had been decanted and filtered at ~ 150 $^{\circ}\text{C}$ to remove particles of oxide and carbonate. A typical analysis is shown in Table 9.

TABLE 9. Typical Analysis^(a) of Baker and Adamson ACS Grade Sodium

Element Detected	Concentration, <u>ppm</u>	Element Detected	Concentration, <u>ppm</u>
Al	0.1	Mg	<0.1
B	<10	Mn	<0.1
Bi	<3	Mo	<0.5
Co	<0.2	Ni	<0.2
Cr	<0.3	Pb	<1
Cu	<0.1	Sc	<1
Fe	<0.5	Si	1
Ga	<0.1		

a. By emission spectrography for elements listed in Table 1.

- A. Removable Filter Holder
- B. Press Fit Sintered Nickel Filter,
5 Micron Mean Pore Size
- C. Hollow Metal "O" Rings -
Nickel Plated Stainless Steel
- D. Typical Hold Down

FIGURE 15. Nickel Filtration Apparatus

Results

Results of the first two experiments are shown below. In one of the two experimental runs, the Na_2O content was approximately 1000 ppm, in the second it was approximately 30 ppm. The systems were equilibrated for approximately 1 1/2 hr at 450 °C and then cooled to 150 °C and filtered. The concentrations of the elements listed were found to be sufficiently high to be treated. The sums and differences, however, are within the experimental deviations of the analytical procedures used. The fact that all changes were made in the direction of purifying the sodium and are about X2 indicates either a systematic error in the analysis or the existence of a tendency for separation.

Metal Concentrations, ppm

	<u>High Oxide Exp.</u>		<u>Low Oxide Exp.</u>	
	<u>Before</u>	<u>After</u>	<u>Before</u>	<u>After</u>
<u>Accuracy of Measurements X2</u>				
Al	1.1	0.5	0.7	0.3
Si	0.3	0.1	---	---
Mg	0.5	0.2	0.6	0.5
<u>Accuracy of Measurements $\pm 30\%$</u>				
Fe	0.4	0.3	0.2	0.04
Ni	1.6	0.9	0.4	0.2
Cr	Some sign of chromium in residue, but the blank is too high to estimate separation.			

Separations of this type can also be inferred from the analysis of cold trap data such as Hansen's.⁽¹⁰⁾ However, the possibility of co-precipitations and filtration of metal oxides and sodium oxide at high temperatures should be investigated further as a means of concentrating these impurities directly from the sodium, particularly where there is evidence of complex oxide formation at higher temperatures and oxygen

concentrations such as with iron and chromium. Pursuit of this idea was halted since results could not be expected before the termination of the program.

For the second set of experiments, a 500 g supply of sodium was prepared which contained the impurities listed and at the concentrations shown in Table 10. The sodium was stored at 150 °C in a closed stainless steel vessel in the glove box, during the entire series of experiments. Samples were obtained by syphoning from a fixed stainless steel tank. Contact time in the experiments was 3 1/2 to 4 hr at ~ 400 °C ± 25 °C. Trial gettering agents used were Na₂O and -100 +200 mesh powders of Type 314 SS, graphite, Al₂O₃, SiO₂, and Sm₂O₃ which had been vacuum outgassed at 10⁻⁴ torr at 500 °C for several hr.

TABLE 10. Concentration of Impurities Added to Sodium in ppm

<u>Element</u>	<u>Amount Added</u>	<u>Present by Analysis^(a)</u>
Bi	780	200
Sn	550	120
Pb	800	200
Zn	240	10
Cd	510	200
Sb	650	2
Mg	72	60

a. These numbers were checked with each experiment run. Analysis by emission spectrography. Accuracy $\pm X2$.

The criterion used for a useful separation for these experiments was a concentration change of X10 in either the sodium impurity level or in the impurity buildup on the trial gettering agents. This could be seen with the analytical precision of X2 for sodium impurities and X3 for the trial getter impurities.

The observed changes in impurity content of the sodium are summarized in Table 11. There appears to be a general reduction of bismuth in the sodium by 1/3. Magnesium shows more reduction, as might be expected, and zinc shows some occasionally. Cadmium, lead, and tin showed no tendency for change. The loss of antimony and zinc from the stock solution (see Table 10) probably indicates that they slagged out during the decantation. Pickup of material by the trial gettering agent is shown in Table 12. Calcium and magnesium have a tendency to be scavenged. The graphite and Sm_2O_3 appeared to be rather active scavenging agents; however, the results need to be verified. These agents may have met the above criteria and warrant more study.

TABLE 11. Ratio^(a) of Impurity Content^(b) of Sodium

<u>Element</u>	<u>Blank</u>	<u>Sm_2O_3</u>	<u>SS</u>	<u>Na_2O</u>	<u>Graphite</u>	<u>Vycor</u>	<u>Al_2O_3</u>
Bi	1/2	1/2	1/5	1/2	1/3	1/3	1
Cd	1	1	1	1	1	1	1
Mg	1/2	1/2	1/20	1/5	1/10	1	<1/20
Pb	1	1	1	1	1	1	1
Sn	2	1	1	1	1	1	1
Zn	--	--	--	--	1/2	1/4	1

-
- a. Concentration after contact/concentration before contact.*
b. Analyzed by emission spectrography. Accuracy ± 2 .

TABLE 12. Ratio^(a) of Impurity Content^(b) of Trial Getter

Element	Sm ₂ O ₅	SS	Na ₂ O	Graphite ^(a)	Vycor	Al ₂ O ₃
K	*(c)	10/1		*(c)	3/1	4/1
Mg	*			*	3/1	
Fe	*			*		
Mn				*		
Cr				*		
Ca	*			*		
Co	*					
Ni	*					
Si	*					
Al	*					

a. Concentration after contact/concentration before contact.

b. Analysis by spark source mass spectrography.
Accuracy $\pm 3\%$.

c. The scavenging agents contained significant quantities of these elements; however, the quantities of impurity reported exceeded the material balance estimates.

Conclusions

Whether this approach is continued is primarily a matter of whether the potential rewards are worth pursuing over an extended period of time. If surface reactions are found, they should be studied in more detail than is required for analytical applications, as they will likely have significant value in analyzing other problems associated with corrosion chemistry, fission product behavior, and fuel element reactions in sodium loops. The data obtained here, in this short period, are not sufficient to indicate the technical feasibility of the approach.

ACKNOWLEDGEMENT

The authors wish to thank L. A. Rancitelli and his associates for the experiments with ERBA-RAI resin.

REFERENCES

1. B. Minushkin and M. Kolodney. Development of a Continuous Electrochemical Meter for Oxygen in Sodium, UNC-5131. United Nuclear Corporation, December 1967.
2. J. M. McKee. Electrolytic Removal of Oxygen from Sodium, APL-TDR-64-93. United Nuclear Corporation, White Plains, New York, August 2964.
3. C. B. Alcock and T. N. Belford. "Thermodynamics and Solubility of Oxygen in Liquid Metals from E.M.F. Measurements Involving Solid Electrolytes," Trans. Farad. Soc., vol. 60, p. 822. 1964.
4. T. N. Belford and C. B. Alcock. "Thermodynamics and Solubility of Oxygen in Liquid Metals from E.M.F. Measurements Involving Solid Electrolytes," Trans. Farad. Soc., vol. 61, p. 443. 1965.
5. E. Berkey and J. G. Cleary. "Developments Pertaining to Electrochemical Oxygen Meters," Trans. Am. Nucl. Soc., vol. 12, no. 1, p. 125. 1969.
6. R. Ko and P. Anderson. "Determination of Impurities in Sodium by Lanthanum Hydroxide Carrier Precipitation and Spectrographic Analysis," Anal. Chem., vol. 41, no. 1, p. 177. 1969.
7. J. M. Scarborough, C. D. Bingham, and P. F. DeVries. "Determination of Trace Metallic Impurities in High Purity Sodium Using Atomic Absorption Spectrometry," Anal. Chem., vol. 39, p. 1394. 1967.
8. D. E. Robertson. "Role of Contamination in Trace Element Analysis of Sea Water," Am. Chem. Soc., vol. 40, no. 7, pp. 1067-1072. June 1968.
9. F. Girardi and E. Sabbioni. "Selective Removal of Radio-Sodium from Neutron-Activated Materials by Retention on Hydrated Antimony Pentoxide," J. Radioanal. Chem., vol. 1, pp. 169-178. 1968.
10. A. E. Hansen. The Effects of Long Term Operation on SRE Sodium System Components, NAA-SR-11396. Atomic International, Canoga Park, California, August 1965.

DISTRIBUTIONNo. of
CopiesOFFSITE

1 AEC Chicago Patent Group
 G. H. Lee

3 AEC Division of Reactor Development and Technology
 Coolant Chemistry Branch
 J. R. Ellwanger
 J. R. Humphreys
 R. A. Hunter

194 AEC Division of Technical Information Extension

3 Argonne National Laboratory
 IMBR Program Office
 J. McKee (2)
 Sodium Technology
 R. J. Meyer (1)

ONSITE - HANFORD

1 AEC Chicago Patent Group
 R. K. Sharp (Richland)

1 AEC Richland Operations Office
 C. L. Robinson

3 Battelle Memorial Institute

4 RDT Assistant Director for Pacific Northwest
 Programs
 A. D. Toth (2)

29 Battelle Northwest

J. W. Bartlett	D. R. Packard
J. L. Bates	L. A. Rancitelli
R. L. Bunnell	V. J. Rutkauskas
W. H. Caplinger	F. A. Scott
D. R. de Halas	D. W. Shannon
R. L. Dillon	W. R. Wykoff
W. O. Greenhalgh (5)	W. H. Yunker (2)
J. N. Judy	Technical Information (5)
R. Ko	Technical Publications (2)
J. J. McCown	