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**SUMMARY OF THE APDA
SODIUM TECHNOLOGY PROGRAM**

J. E. Meyers

United States Atomic Energy Commission

Contract No. AT(11-1)-865

Project Agreement No. 11

JUNE 1970

**ATOMIC POWER
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APDA

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ABSTRACT

This document summarizes an eight-year program conducted in the APDA Sodium Technology Loop in the following areas of sodium technology:

- Impurity monitoring devices such as the UKAEA Rhometer, the UNC oxygen meter, the APDA hydrogen detector, and the APDA variable-orifice plugging meter
- Impurity removal processes such as cold-trapping, hot-trapping, and operation of the APDA-developed sodium centrifuge
- The physical and chemical behavior in sodium of impurities such as hydrogen and sodium carbonate
- Sampling and analysis procedures, including a sampling reliability study for oxygen and hydrogen; a round robin program for measuring oxygen in sodium; a uranium gettering technique for measuring the oxygen content of sodium; and analytical methods for determining oxygen, total carbon, carbonate carbon, and hydrogen.

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INTRODUCTION

A. BACKGROUND

In 1962, a 4-inch sodium loop consisting of a plugging meter, retention tank, cold trap, and zirconium-packed hot trap was built primarily for use as a test facility in a program of evaluating the Blake sodium resistivity meter, or Rhometer, under contract agreement with the U. S. Atomic Energy Commission. The evaluation program was later broadened to include other monitoring devices such as a variable-orifice plugging meter, UNC oxygen meters, and an in-line hydrogen detector.

In 1963, a gas chromatograph and an injection port for the introduction of solid impurities into the loop sodium were added on the loop.

In 1965, the scope of work was further broadened to include (1) the development and refinement of analytical techniques for the quantitative determination of impurities in sodium, (2) investigation of the chemical and physical behavior of impurities in sodium, (3) the development and evaluation of instruments for the detection and determination of impurities in sodium, and (4) the development and evaluation of sodium purification techniques. At that time, the loop capability was further enhanced by the addition of a 1-inch loop equipped with a thermal decomposition tank, a filter cascade, two hydroclones, a through-flow sodium sampling station, two Rhometers, and four UNC oxygen meters.

In 1967, two major improvements were made to the Sodium Technology Loop: a cold trap was installed in the 1-inch loop for performance evaluation, and an inert-atmosphere glove box was enclosed around the new sodium sampling and impurity injection stations to prevent atmospheric contamination of sodium samples and the chemical impurities being injected into the loop. At that time also, refinements were made to the loop heater circuits to obtain better temperature control and to eliminate impurity hideout and feedback; packed valves were replaced with bellows seal valves to prevent contamination of the sodium.

In 1968, improvements to the test facility included automatic control of loop temperatures, an automatic flow control system, and a continuous gas chromatograph. In 1969, a sodium centrifuge which had been previously evaluated in a nonsodium environment was installed in the Sodium Technology Loop for performance evaluation in a sodium system. The APDA-designed hydrogen detector was installed on a bypass section of the 1-inch loop and connected to the 1-inch loop by an economizer. This installation includes a flowmeter, diffusion coil for the injection of hydrogen, and a precision heater to maintain the detector at 900 F.

As an adjunct to the Sodium Technology Loop as well as for fundamental research in the area of sodium technology, a modern chemistry laboratory capable of handling radioactive sodium samples was built. The laboratory equipment includes gas chromatographs and recorders, spectrophotometers, metallurgical and stereo microscopes, high-vacuum glass racks, a sodium still, a sodium purification system, specialized dry boxes and gas purification system, combustion furnaces, induction furnaces, vacuum ovens, optical pyrometers, radiochemical laboratory hoods, and assorted ventilation systems.

The additions and modifications over an 8-year period have resulted in a reliable and efficient facility for research and development in the field of sodium technology. The APDA Sodium Technology Loop is shown schematically and photographically in Figures 1 and 2. The work carried out in this facility and summarized herein falls into the following categories:

- Evaluation of impurity monitoring devices: Rhometers for detecting a variety of impurities, oxygen and hydrogen meters, and plugging meters
- Impurity removal processes such as cold-trapping, hot-trapping, and operation of the APDA-developed sodium centrifuge
- The physical and chemical behavior of such impurities as hydrogen and sodium carbonate
- Sampling and analysis procedures, including a sampling reliability study, a round robin program for measuring oxygen in sodium, a uranium gettering technique for oxygen, and analysis techniques for oxygen, carbon, and hydrogen.

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FIG. 1 SCHEMATIC DIAGRAM OF SODIUM TECHNOLOGY LOOP

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FIG. 2 SODIUM TECHNOLOGY TEST LOOP

SECTION I

IMPURITY MONITORING DEVICES

I. A - RHOMETER EVALUATIONS

The objective of this job is the development of an in-line impurity monitoring instrument for detecting, monitoring, and controlling impurities in high-temperature sodium.

1. Development Program

APDA has conducted a preliminary evaluation of an improved automatically temperature-compensated version of the Blake-type Mark I Rhometer.* Concurrently, response of the Mark I Rhometer to sodium impurities such as sodium monoxide, sodium hydride, water, carbon monoxide, and carbon dioxide as well as the effect of gas bubbles, sodium flow rate, and gamma radiation on meter output, was established.

The original Mark I Rhometer was equipped with manual temperature compensation in the range of 400 F to 600 F. It soon became apparent that if the Rhometer were to become a useful instrument for monitoring impurities in the primary and secondary systems of liquid-metal-cooled fast breeders, not only should the temperature compensation range be broadened but such compensation should be automatic.

In 1965 when the development program for an automatic temperature compensator was initiated, the state of the art for electronic components such as signal conditioners, operation amplifiers, diode function generators, zener diodes, and integrated circuits was such that the prospects for an all-electronic compensator were promising, and this course was pursued (see Figure 3).

The APDA prototype Rhometer output exhibits a short-term (24 hour), nonaccumulative, low-frequency oscillation of 0.01 %R (± 2.5 ppm oxygen), a long-term band width of ± 0.04 %R (± 10 ppm oxygen) and a high-frequency noise level of ± 0.005 %R (1.3 ppm oxygen). To achieve these conditions, it was necessary to extensively modify the control circuitry, to construct a special power supply, to house the sensing element (toroid) in an ambient-temperature-controlled enclosure, and to sense the sodium temperature at the toroid by means of a resistance temperature detector (RTD) probe.

All components of the APDA prototype have thus far exhibited very good maintenance-free histories. The three toroid transformers which were part of the three Mark I Rhometers procured by APDA, one of which was used

* An improved version of this Rhometer (Mark II) is commercially available from English Electric Company, Cambridge Road, Whetstone, England.

in the APDA prototype, have operated without attention for over 30,000 hours; the function generator, power supply, and control circuitry have operated continuously for a period of one year; the RTD, for 7 months.

By taking advantage of recent advances in the state of the art in electronic components which comprise the subsystems of the prototype Rhometer, a long-term stability and repeatability of ± 0.005 %R resistivity (± 1.3 ppm oxygen) with a sensitivity of ± 0.002 %R (± 0.5 ppm oxygen) appears to be an attainable goal for a commercial Rhometer.

Preliminary gamma radiation exposure tests (a 28-curie iridium-192 source placed just outside the metal enclosure of the toroid assembly for 5 minutes) showed that Rhometer output was unaffected by such radiation.

In parallel with the development of the prototype automatically temperature-compensated Rhometer, an extensive program was conducted at APDA to determine the response coefficients of the Rhometer to sodium impurities. This work progressed through three phases of evaluation (1) cold trap injections using the plugging temperature and solubility curves to establish concentration changes, (2) specific impurity injections (H_2O , Na_2O , $NaOH$, NaH , CO_2) using material balances to determine the quantity of material injected, and (3) specific impurity injection (NaH , Na_2O , $NaOH$) using chemical analysis of sodium samples to establish concentration changes. The latter technique was deemed to be the most accurate. For example, by thorough chemical analysis, Rhometer response coefficients were established for Na_2O and NaH . The response of the Rhometer to $NaOH$ was then accurately predicted by assuming that the $NaOH$ was completely converted to Na_2O and NaH and that each of these species contributed independently to the resistivity change of sodium.

Not only does the Rhometer respond to small changes in the sodium resistivity due to dissolved impurities as mentioned above (see Figures 4 and 5), but it also responds to changes in sodium resistivity caused by bubbles of insoluble gases and by particles of insoluble solids, as indicated by a significant increase in the noise level of the output signal as the gas and particulates pass through the Rhometer toroid.

2. Conclusions

Although the Rhometer does not discriminate among types of dissolved impurities nor among types of particulate matter, it is a reliable instrument for continuously monitoring sodium impurities to indicate deviations from normal operating conditions. It is not affected by radiation; moreover, the stainless steel toroid is the only component of the instrument in contact with the sodium. The capability of on-line calibration of the response of the Rhometer by means of inducing a step change in resistivity of the toroid (the cut-wire technique), coupled with its versatility and reliability, leads to the

conclusion that the Rhometer is an instrument which could be commercially developed as a plant instrument for both primary and secondary sodium systems.

3. Documentation

This work is documented in the APDA quarterly progress reports; in APDA-149, "Evaluation of the Blake Sodium Resistivity Meter"; in APDA-163, "Operation of the Sodium Technology Loop for Contamination Meter Evaluations"; in a paper, "Impurity Monitoring in a Large Sodium Test Loop," given at the Conference on Sodium Technology and Large Fast Reactor Design at Argonne, Illinois (reported in ANL-7520, pp 235-237), November 7-9, 1968; and in APDA-247, "Design, Development, and Testing of a Temperature-Compensated Rhometer for Monitoring Impurities in Sodium."

Digital Voltmeter

Recorder

Function Generator

Isolated 60-cycle
Power Supply

Output Voltage
Controller

FIG. 3 ELECTRONIC COMPONENTS OF RHOMETER AUTOMATIC TEMPERATURE COMPENSATING SYSTEM

Xenon Gas Injection into
Pump Discharge

Sodium Conditions = 200 GPM @ 570 F
Resistivity Decade = 104.449 % R
Cold Trap and Hot Trap Isolated

FIG. 4 RECORDER TRACE OF RHOMETER RESPONSE TO XENON INJECTION

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FIG. 5 RESPONSE OF AUTOMATIC TEMPERATURE-COMPENSATED PROTOTYPE RHOMETER TO INJECTIONS OF HYDROGEN GAS IN SODIUM

I. B - EVALUATION OF UNC OXYGEN METERS

The scope of this work is the in-sodium evaluation of the oxygen meters (electrochemical cells) developed by United Nuclear Corporation (UNC) for the purpose of detecting oxygen activity in the sodium. The sensitivity of the meter, its accuracy, response time, and drift were studied, along with the effects of sodium and ambient temperature and gamma radiation on meter performance. In an effort to improve the instrument's performance, the variables causing operating problems were identified.

1. Test Program

Since 1965 twelve of the UNC meters have been evaluated in the APDA Sodium Technology Loop. The evaluation included studies of (1) the meter response to injections of impurities such as sodium monoxide, sodium hydride, and sodium hydroxide, (2) sodium and ambient temperature coefficients, and (3) the effects of gamma radiation on the meter's performance.

a. Response to Impurities

To evaluate oxygen meter response to impurities, injections of sodium monoxide, sodium hydride, and sodium hydroxide were made to the Sodium Technology Loop with the sodium maintained at $600\text{ F} \pm 5\text{ F}$. A typical oxygen meter response to a sodium monoxide injection is presented in Figure 6. The conclusions drawn from these evaluations are (1) that the meters respond to concentration changes in sodium monoxide in a quantitative and reproducible manner, (2) that the calibration constant varies from meter to meter, (3) the time response increases with in-sodium service, and (4) the meters respond to sodium hydroxide injections in sodium at 600 F, although response to sodium hydride injections is inconclusive based on data obtained in this test program.

b. Sodium and Ambient Temperature Coefficients

During these tests, the sodium and ambient temperature coefficients of the oxygen meters were determined in an effort to remove the effects of temperature fluctuations from the output of the instruments. It was found that the sodium temperature coefficient of the meters varied from 0.56 mv/F to 0.04 mv/F, indicating that in sodium systems having temperature fluctuations at a given meter, the temperature coefficient for that meter must be known in order to correctly interpret the meaning of meter output.

The ambient temperature response factors of the oxygen meters were obtained at two oxygen concentrations (10 and 41 ppm) and with the meters mounted in boxes having a controlled environment ranging from 66 to 113 F. From these tests it was determined that the ambient temperature response of the meters was -1.16 to 0.0 mv/F and that the oxygen concentration did not significantly affect the ambient temperature coefficient.

c. Gamma Radiation

In an effort to determine the response to radioactivity, four meters installed in the Sodium Technology Loop were subjected to radiation from a 73-curie iridium-192 source and a 12-curie cobalt-60 source. Gamma radiation caused response changes from 0 to 50 mv, depending on the meter.

d. Improvement of Readout

Due to the excessive zero drift incurred on the tube-type electrometers originally installed to continuously monitor the oxygen meters, a decision was made in April 1968 to obtain a more stable unit. The unit, Keithley Model 602, is a battery-operated solid-state amplifier utilizing a field effect transistor as the input stage. The input resistance is as high as the tube-type units ($<10^{14}$ ohms); the zero drift specification is approximately an order of magnitude better than the tube-type unit.

The unit was tested and found to operate well within its drift specification of 1 mv/day after a 30-minute warmup, after which it was installed to monitor oxygen meter No. 4 in August 1968. Since that time it has continued to operate as specified, i. e., within ± 0.3 mv of zero. It is concluded that the Keithley Model 602 solid-state electrometer is entirely adequate for continuously monitoring the oxygen meters.

e. Cell Life at 900 F

The life of oxygen meter 3 (UNC TPE-1/216 - the only meter tested above 600 F) in 900 F sodium was 18 days, following a successful operating life of 18 months in 600 F sodium.

2. Conclusions

Further development is required to produce oxygen meters with meter characteristics in a narrower band than those evaluated by APDA. Without such development, each meter must be individually calibrated for its response to oxygen, sodium temperature, ambient temperature, and gamma radiation in order to interpret the meaning of its output.

3. Documentation

This work is reported in a paper, "Impurity Monitoring in a Large Sodium Test Loop," presented at the International Conference on Sodium Technology and Large Fast Reactor Design, Argonne National Laboratory, November 7-9, 1968, and in APDA quarterly progress reports, particularly APDA-242. A topical report, "Experience with UNC Oxygen Meters in APDA Sodium Technology Loop," APDA-245, was published at the close of the program.

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FIG. 6 TYPICAL RESPONSE OF OXYGEN METER TO INJECTION OF 16 PPM OXYGEN AS SODIUM MONOXIDE

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FIG. 7 BASIC CIRCUIT OF OXYGEN METER

I. C - HYDROGEN DETECTOR

The objective of this job was to develop an in-line detector for monitoring hydrogen in sodium. The development effort proceeded in two phases:

- Phase I - A laboratory feasibility study
- Phase II - Loop evaluation of a palladium-plated sensor coil

1. Test Program

a. Phase I - Laboratory Feasibility Study

As a result of this study, the feasibility and design considerations which apply to a hydrogen detector based on the diffusion of hydrogen through a nickel-palladium membrane followed by the catalytic oxidation of the hydrogen on the palladium surface to water and its subsequent detection by a moisture monitor were determined. Three types of sensor coils were evaluated: a palladium-plated nickel coil, a nickel-plated palladium coil, and a coil formed from codrawn nickel and palladium tubing. The sensors were evaluated by injecting such hydrogen-containing species as hydrogen gas, sodium hydroxide, sodium hydride, and water into a container of sodium; they were responsive to each of these forms of hydrogen-containing compounds. It was demonstrated that the experimental detector would respond to a change of hydrogen concentration in sodium as low as 2 parts per billion. The response time required to detect a step change in hydrogen concentration in the experimental equipment was as low as 15 seconds. The hydrogen detector coil is shown in Figure 8.

b. Phase II - Loop Evaluation

A palladium-plated sensor coil was installed in the APDA Sodium Technology Loop to evaluate this type of hydrogen detector in a dynamic sodium system. The evaluation consisted of (1) a determination of the response of the detector to injections of hydrogen-containing compounds (NaH, H₂ gas, and H₂O) and subsequent cold-trapping, (2) the effect of sodium flow rate, (3) the effect of sweep gas flow rate, (4) the effect of loop temperature, (5) the effect of sensor temperature, (6) response time, and (7) suitability of the moisture-sensing equipment.

Response to Hydrogen Impurities - The detector responded to each of the types of hydrogen impurities mentioned above. The injection of sodium hydride equivalent to an increase of 1 ppm hydrogen in the loop sodium caused the readout to increase from a base level of 8 ppm H₂O to

105 ppm H₂O. The response to water injections equivalent to an increase of 0.75 ppm hydrogen in the loop sodium demonstrated the capability of the hydrogen detector to detect water leaks in either a cover gas space or below sodium. The detector output increased to 30 ppm H₂O from a base level of about 1 ppm H₂O for a water injection above the sodium level in the APDA Sodium Technology Loop surge tank (see Figure 9). Gaseous hydrogen injections accomplished by diffusing hydrogen through a nickel coil constituted the major portion of the impurity injection evaluation. Hydrogen injection ranged from 0.020 ppm to 3.0 ppm, giving a response coefficient which ranged from 27 to 79 ppm H₂O per ppm H₂.

Effect of Sodium Flow Rate - The sodium flow rate through the sensor coil was viewed over the range of 1 to 2.5 gpm with no effect on the hydrogen detector output.

Effect of Sweep Gas Flow Rate - A limited amount of test data indicated that the hydrogen detector output appeared to be inversely proportional to the flow rate of the sweep gas, a mixture of 5% oxygen in argon. This gas contained the oxidant for diffusing hydrogen and carried the water to the moisture detector.

Effect of Loop Temperature - Sufficient data were not obtained to make a definitive statement with regard to this variable. No significant differences were obtained when injections of hydrogen were made at previous loop temperatures. On the other hand, in some cases changing the loop temperature at a given loop hydrogen concentration produced changes in the hydrogen meter readout and in other cases it did not.

Effect of Sensor Temperature - The effect of the sensor temperature was studied over the range of 800-900 F. The effect of sensor temperature was in fair agreement with that predicted by the activation energy for diffusion.

Response Time - It was not possible to make an accurate measure of the response time of the instrument. The overall system response time was approximately 5 minutes. Of this 5 minutes, 2 minutes are accounted for in the hydrogen injection, 2 minutes for the sodium transport time, and 1/2 minute in the sweep gas system transport time. It is estimated from these data that the response time of the APDA hydrogen detector is less than 1/2 minute.

Panametric Hygrometers - APDA experience with the Panametric hygrometer has demonstrated the need for a more precise calibration of the individual moisture-sensing probe than is available from the manufacturer. Probes now on hand appear to differ in calibration by a factor of 3.

2. Conclusions

The APDA hydrogen detector has been demonstrated to be a candidate instrument in the LMFBR program for monitoring hydrogen in sodium and as a leak detector for monitoring leaks in steam generators.

3. Documentation

Feasibility Study of In-Line Detector for Hydrogen in Sodium - APDA-222, 1968.

Evaluation of an In-Line Hydrogen Detector in the APDA Sodium Technology Loop - APDA-252.

FIG. 8 APDA HYDROGEN DETECTOR COIL

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FIG. 9 HYDROGEN METER RESPONSE TO WATER INJECTIONS

I. D - PLUGGING METER

The APDA intermittent plugging meter was used primarily as a guide in the operation of the Sodium Technology Loop to indicate when purity levels had changed significantly from cold-trapped conditions and to indicate when to terminate clean-up operations. However, during the evaluation of other impurity monitoring devices such as the Rhometer, UNC oxygen meter, and the APDA hydrogen detector, the behavior of the plugging meter was observed and analyzed.

1. Plugging Meter Installation

The instrument used for this study is a variable-orifice, air-cooled plugging meter installed in a side loop of the 4-inch loop. The unit consists of a special 1/2-inch bellows-seal globe valve with a seat ground to a 15-degree angle for close control of clearance. A special fine thread on the stem and position indicator permits clearance settings to a tolerance of 1 mil. The temperature ramp is controlled by controlling forced air flow past the 1/2-inch finned sodium line by a hand-operated slide valve (see APDA-163 for installation diagram).

2. Results and Discussion

Initial evaluation of this meter in 1964 (see APDA-163) produced plugs from 213 to 670 F under tests with reproducibility to ± 5 F and furnished consistent values for sodium hydride contamination. This order of reproducibility was demonstrated in more recent tests described in a paper, "Impurity Monitoring in a Large Sodium Test Loop," ANL-7520, Part I, pp 233-253. Plugging temperatures obtained under sodium monoxide contamination agreed with accepted solubility data when loop oxygen concentrations were calculated by means of material balances. Sodium hydroxide contamination plugging temperatures were higher than anticipated. Later tests, based on chemical analysis of sodium samples (ANL-7520, p 244), showed that the plugging temperature increases resulting from the injection of sodium hydroxide or sodium hydride to cold-trapped sodium indicated only the increase in the sodium hydride concentration of the sodium.

A common practice is to use plugging temperatures with data on sodium monoxide solubility in sodium to infer the amount of oxygen impurity in sodium. Experience at APDA has shown, however, that this practice may lead to erroneous conclusions. For example, in a 12-day test span with the loop sodium at 600 F, the plugging temperature increased steadily from 264 F to 304 F, whereas sampling and analysis results

indicated essentially the same oxygen concentration (11.3 ± 1.8 ppm) over the same period.

The APDA Sodium Technology Loop is usually operated at 600 F. At this temperature, the loop is easily cleaned up to a plugging temperature of 225 F; upon termination of the cold trapping operation, the plugging temperature remains fairly constant. However, at loop temperatures of 700 to 900 F, under conditions of relatively clean sodium (<10 ppm oxygen and <4 ppm total hydrogen), the plugging temperature increased without a corresponding change in the measured oxygen or hydrogen concentration. The maximum plugging temperature observed was 620 F when the loop temperature was 900 F (see APDA-242).

Efforts to reduce the plugging temperature by cold-trapping or hot-trapping were only successful during the cold- or hot-trapping operation. Within 24 hours the plugging temperature had increased to over 500 F. By lowering the loop temperature to 600 F, the plugging temperature decreased and in 6 days reduced to 240 F. These test results suggest that the high plugging temperatures are caused by chemical species other than hydrogen or oxygen.

3. Conclusions

- The plugging meter is a reliable instrument for indicating the temperature at which impurity saturation occurs
- Plugging temperatures near the freeze point of sodium are a reliable indication that the sodium has reached a purity that is usually less than 10 ppm oxygen or 2 ppm total hydrogen
- Inference with regard to the level of impurities in sodium when the plugging temperature is greater than 270 F is frequently erroneous.

4. Documentation

Operation of the Sodium Technology Loop for Contamination Meter Evaluations - APDA-163, March 1964.

Quarterly Technical Progress Report on AEC-sponsored Activities, April-June 1969 - APDA-242.

SECTION II

EVALUATION OF MECHANICAL PURIFICATION CONCEPTS

II. A - SODIUM CENTRIFUGE

The scope of this program is the investigation of mechanical purification devices capable of removing very small particles from the sodium systems of LMFBRs. The work includes a review of the performance characteristics of standard devices as well as novel concepts, and determination of the optimum combination of methods for effective and economic particle removal.

1. Test Program

A functional specification for a high-speed sodium centrifuge was prepared and submitted to several manufacturers, all of whom declined to bid. Subsequently, a conventional centrifuge was selected for adaptation to the functional specification; and, in consultation with Sharples Division of Pennsalt Chemicals Corporation, APDA finalized the design of a sodium centrifuge featuring a bottom-fed, top-discharge bowl suspended from a spindle driven at speeds up to 50,000 rpm by a turbine producing a centrifugal force of 62,000 g at the bowl wall (see Figure 10). The bowl is enclosed in an insulated, heated housing and all components except the turbine drive are contained in an argon-filled glove box to maintain an inert atmosphere over the free surface of the sodium in the bowl and the collecting chamber. The centrifuge and piping components are arranged to facilitate removal of the centrifuge bowl for examination of its contents. Safety devices were installed on the centrifuge and piping system to shut down the turbine drive, electromagnetic pump, and sodium loop valves in the event of mechanical or control problems.

A program of tests was initiated to determine the dynamic characteristics of the unit, to become familiar with its operation prior to modification, and to individually test the modified components of the centrifuge. Concurrently, work was done on a design concept for installation of the centrifuge in the Sodium Technology Loop (see Figure 11). Environmental control around the centrifuge was investigated from the standpoint of avoiding contamination of the sodium being processed and in terms of manipulation of the equipment required.

a. Developmental Tests

The final design centrifuge was assembled in its spherical glove box and a series of tests was performed in water to demonstrate the unit's readiness for sodium operation. In this series of tests, only minor problems were encountered, and the glove box containing the centrifuge was connected to the APDA Sodium Technology Loop. The system was operated

at 350 F in an argon atmosphere without sodium flow. The centrifuge was operated at 50,000 rpm for 15 hours, during which time no unusual events occurred and the rotational speed remained relatively constant.

b. Initial Operation in Sodium

The sodium line valve was opened and a flow of 350 F sodium was established at 1/4 gpm. The centrifuge was then operated for 24 hours, during which period the only problem was a very slow leak of sodium from the housing. The sodium flow was shut off; the centrifuge was allowed to cool to room temperature and was then disassembled, placed in a plastic bag, and moved to a very pure atmosphere glove box in the chemistry laboratory for analysis of the problem.

Examination of the bowl contents revealed a higher concentration of impurities adjacent to the bowl wall, and it was decided to core out the purer sodium and leave an annulus of approximately 0.010 inch of impurity-containing sodium on the lower 1-1/2 inch of the bowl. This section of the bowl was sent to Battelle Memorial Institute for detailed analysis of particle size, elemental composition, and identification of compounds through optical and scanning microscopy, electron microprobe, optical emission, spectroscopy, and X-ray diffraction analysis. These analyses revealed an adherent film containing no discernible particles and an area containing 1 to 3 micron particles. X-ray diffraction identified carbon and silicon dioxide as being present in the sample. No other elements or compounds were present in sufficient quantity that diffraction patterns could be seen. Optical emission spectrographic analysis revealed silicon to be the largest constituent detectable by this means. Carbon analysis revealed a 13.6% content by weight.

c. Long-Term Operation

Following the initial operation, a test was conducted to demonstrate the ability of the centrifuge to operate over an extended period of time. The operating conditions were 50,000 rpm with a sodium flow rate of 1/4 gpm and sodium temperature at 480 F. At the end of a 93-hour period, the sodium flow was shut off, the centrifuge slowed to 4000 rpm with the heat turned off to allow the sodium remaining in the bowl to solidify. The total period of uninterrupted rotation was 120 hours. No serious damage was found when the unit was disassembled and examined.

2. Conclusions and Recommendations

Based on the demonstrated successful operation of the centrifuge, two avenues for further development are apparent: one is to make several improvements to the design of the present unit and test a number of the

improved units; the second is to design a larger improved model for testing as a prototype in-line sodium purification device for reactor systems.

3. Documentation

Design, Development, and Evaluation of a Continuous Flow Sodium Centrifuge - APDA-243, December 1969. The work is also reported in the APDA quarterly progress reports.

FIG. 10 CROSS SECTION OF SODIUM CENTRIFUGE

Legend

Existing Cold Trap Lines	Sodium Return Lines
Existing Economizer Lines	By-Pass Lines
Sodium Supply to Centrifuge	Drain Lines

099569

FIG. 11 SODIUM TECHNOLOGY AND CENTRIFUGE LOOP

II. B - MOVABLE BED GETTERING

The scope of this work is the compilation of information on insoluble getter materials, the selection of candidate materials for a test program, and a program to design, build, and test model hot traps using the candidate getter materials for removing oxygen, carbon, nitrogen, or hydrogen from primary and secondary sodium during recovery or steady-state operation. The proposed process consists of eliminating impurities by introducing small spherical particles of getter materials to the system, transporting the spheres in conventional sodium plumbing by sodium flow, separating the spheres from the mainstream of the sodium, and regenerating the spheres.

1. Test Program

Several getter materials were examined with respect to their affinity for carbon, hydrogen, and oxygen impurities in sodium, and their regeneration characteristics and compatibility with sodium. The availability of the materials in quantities needed for testing purposes was also investigated.

The final selection for the gettering materials was zirconium and tantalum for hydrogen impurities; titanium and tantalum for oxygen; and Type 304 stainless steel for carbon. The regenerative process for hydrogen and carbon was selected, although no decision was reached regarding the process for oxygen. Particle specifications were prepared and quotations obtained indicating the average cost of the materials would be between \$300 and \$400 per pound.

Concurrently, preliminary work was done on the second phase of the program. This was concerned with the design for modifications to an existing loop which had been used in the study of a paste blanket concept for fast reactor application.

Further work on this project was precluded by reduction in the FY-68 budget.

II. C - COLD-TRAPPING

Cold-trapping was used exclusively as an operational cleanup device to purify the loop sodium in preparation for evaluation of such on-line impurity monitors as the Rhometer, oxygen meter, and hydrogen detector. The reference point of purity was well cold-trapped sodium, i. e., loop sodium that had been cold-trapped until the plugging temperature was less than 215 F. No fundamental studies of the cold-trapping operation were undertaken to provide engineering design data. The intention here is to record pertinent information obtained during the operation of the APDA cold traps.

1. Cold Trap Installation

There are two cold traps in the APDA sodium technology facility (shown in Figure 1), one for the 4-inch sodium loop and one for the 1-inch loop. Both are air cooled. The 4-inch loop cold trap consists of a 30-gallon vertical tank with a 4-inch downcomer inlet. Sodium exits from the downcomer near the bottom of the 30-gallon tank and flows up on the outside of the downcomer through Yorkmesh packing and then through a 5-micron-frit filter before it is discharged from the cold trap.

The 1-inch loop cold trap consists of a 52-gallon vertical tank which contains a shell open at the bottom and containing Yorkmesh in its interior. Sodium flows down the 3/4-inch annulus formed by the two shells to within 4 inches of the bottom, up through the Yorkmesh packing, and is then discharged from the cold trap. The technology loop inventory is about 110 gallons and both cold traps are operated at approximately 1 to 2 gpm.

2. Conclusion

The purification capability of both cold traps as determined by the analysis of sodium samples taken is essentially the same. When the plugging temperature is less than 215 F, the oxygen and hydrogen concentrations, as determined by the mercury amalgamation method, are approximately 7 ppm oxygen and 1.5 ppm total hydrogen.

It is interesting to note that the hydrogen level for cold-trapped sodium predicted by the APDA hydrogen detector is 0.02 ppm. The discrepancy between the hydrogen concentration as determined by the two different techniques led to the belief that there is significant blank contribution from the sampling tubes in the mercury amalgamation determi-

nation. Some very preliminary experiments on sampling tubes free of sodium supports this conclusion.

3. Documentation

Quarterly Progress Report on AEC Activities (APDA-206) and "Impurity Monitoring in a Large Sodium Test Loop," a paper presented at the International Conference on Sodium Technology and Large Fast Reactor Design, held at Argonne, Illinois, November 7-9, 1968, ANL-7520, Part I, p 233.

II. D - HOT-TRAPPING

The hot trap located in the APDA Sodium Technology Loop facility was used very infrequently throughout the sodium technology program conducted at APDA. There was no planned program to study conventional hot-trapping as an impurity removal process. A program was undertaken, however, to study movable bed gettering as a cleanup process for sodium (see Section II. B for a summary of this task). APDA's hot trap was used on two occasions: to study the performance of the UNC oxygen meter in hot-trapped sodium and to determine the effectiveness of hot-trapping on reducing the high plugging temperature observed whenever the loop sodium temperature was raised more than a hundred degrees above the normal operating temperature of 600 F. A summary of these studies is presented below.

1. Hot Trap Installation and Operation

The location of the hot trap in the APDA Sodium Technology Loop is shown in Figure 1. It is constructed from Type 304 stainless steel Schedule 40 pipe 6 feet 8 inches long and packed with 1/2-inch zirconium chips. The sodium flows downward through the zirconium bed and then through a 5-micron metallic-frit filter located at the bottom of the hot trap and exits from the hot trap through a piece of 1/2-inch stainless steel tubing connected to the filter. At the normal supply rate of 1 gpm to the hot trap, the residence time of the sodium is approximately 9 minutes. The hot trap is operated in the range of 800-1000 F.

The best measure of the hot trap performance was obtained during a program designed to check the response of the UNC oxygen meter to hot-trapped sodium. The sodium technology loop was operated isothermally at 600 F, with the exception of the hot trap which was operated for 56 hours at 1000 F and then for 83 hours at 800 F. The entire loop sodium inventory was processed through the hot trap approximately 30 times during the first hot-trapping operation and 45 times during the second hot-trapping operation.

2. Conclusions

As determined by the mercury amalgamation procedure, oxygen concentration was 12 ppm before the first hot-trapping, 8 ppm after the first hot-trapping, and 8 ppm after the second hot-trapping; however, extrapolation of the output of a UNC oxygen meter, which had been calibrated at 12 ppm oxygen and higher, indicated 2.3 ppm oxygen following the first hot-trapping and 0.7 ppm oxygen following the second hot-trapping. The hydrogen concentration (also determined by mercury amalgamation), which

was initially 2.5 ppm total hydrogen, dropped to 1.6 ppm hydrogen after the first hot-trapping operation with no significant change after the second hot-trapping operation.

It appears that following the hot trap operation, the oxygen concentration was below the detectable limit of the analytical chemical method used. The best estimate of the oxygen concentration following hot-trapping is that obtained from the oxygen meter measurements.

Hot-trapping at 1000 F was effective in reducing the plugging temperature of 900 F loop sodium from 620 F to 265 F after 48 hours of operation; however, the rise in plugging temperature was very rapid after the hot trap was secured, with the plugging temperature increasing to 490 F in six hours. The zirconium chips in the hot trap were not examined and there is no available information as to impurities that might have been picked up by it.

3. Documentation

Quarterly Progress Reports on AEC-Sponsored Activities APDA-212 and APDA-242.

SECTION III

PHYSICAL AND CHEMICAL
BEHAVIOR OF SODIUM IMPURITIES

III. A - SOLUBILITY OF HYDROGEN IN SODIUM

This study had two basic objectives:

- To determine the solubility of hydrogen in sodium over the temperature range of 550 to 750 F at pressures less than 1 mm of mercury
- To determine the hydrogen equilibrium pressure for an unsaturated sodium system as a function of temperature, especially that region of the system containing more than 1 ppm of hydrogen in sodium.

1. Experimental Program

The closed-cell technique (see Figure 12) used by APDA consisted of equilibrating hydrogen gas with sodium of controlled purity contained in a thin-walled nickel capsule at isothermal conditions. Figure 13 illustrates the experimental apparatus used for system pressures greater than 1 mm of mercury.

2. Conclusions

The present data represent the best direct experimental agreement with Sievert's law reported to date and indicate that Sievert's law is most exactly obeyed at hydrogen pressures greater than 10^{-2} cm Hg (see Figure 14).

Sievert's law constant varies slightly with temperature ranging from 14.3 to 17.7 ppm $H_2 \times (P_{H_2}, \text{cm Hg})^{-1/2}$ over the temperature range of 297 to 401°C. The hydrogen solubility is expressed by

$$\log H_2 \text{ solubility (ppm)} = -\frac{3180}{T(^{\circ}\text{K})} + 6.52$$

and the equilibrium hydrogen pressure at saturation by

$$\log P_{H_2}, \text{ cm} = -\frac{6400}{T(^{\circ}\text{K})} + 10.82$$

over the temperature range of 296 C to 406 C for systems containing less than 25 ppm oxygen (see Figures 15 and 16).

3. Documentation

The Solubility of Hydrogen in Liquid Sodium - APDA-241.

128170

FIG. 12 TYPICAL SEALED NICKEL CAPSULES AND QUARTZ HOLDER

127970

FIG. 13 SCHEMATIC OF PHASE 1 SYSTEM-PRESSURE > 1 mm

128570

FIG. 14 HYDROGEN SOLUBILITY IN LIQUID SODIUM

FIG. 15 SOLUBILITY OF HYDROGEN IN SODIUM AS A FUNCTION OF TEMPERATURE

FIG. 16 EQUILIBRIUM HYDROGEN PRESSURE FOR SATURATED SODIUM AS A FUNCTION OF TEMPERATURE

III. B - THE SOLUBILITY OF SODIUM CARBONATE IN SODIUM

As part of the program to determine the physical and chemical behavior of sodium and its impurities, studies of the solubility of sodium carbonate in liquid sodium were conducted at 150°C, 275°C, and 400°C.

1. Test Program

About 3 pounds of commercial grade sodium was melted and introduced to the still; the entire apparatus was sealed and evacuated. Distillation time was 2 to 3 hours. Thereafter the distilled sodium was recycled for distillation several times before introduction to the solubility apparatus.

One gram of the Na_2CO_3 thus prepared was introduced into the solubility apparatus (corresponding to 1000 ppm of Na_2CO_3), stirred overnight, and the sodium sampled. Total alkalinity and sodium carbonate determinations were performed on the mercury-insoluble residue from the amalgamation by a differential titration technique using a recording titrimeter.

2. Conclusions

Results of these determinations indicated the solubility of carbonate sodium to be 24.4 ppm at 150°C, 37.9 ppm at 275°C, and 51.0 ppm at 400°C with standard deviations of 4.8, 5.2, and 1.6, respectively.

3. Documentation

This work is documented in the APDA quarterly reports and in APDA-184, "The Solubility of Sodium Carbonate in Sodium," published in August, 1968.

III. C - COVER GAS IMPURITIES--HYDROGEN GETTERING IN GAS SAMPLE LINES

The objective of this job was to determine the quantity and composition of deposits collected in the cover gas sampling line of APDA's Sodium Technology Loop in order to estimate the error in the cover gas analysis for hydrogen as determined by a gas chromatograph.

1. Test Program

A schematic of the sampling system is presented in Figure 17. After 82 days of operation this sampling system was removed and analyzed for sodium and hydrogen.

The total amount of hydrogen in the sampling system was equivalent to not more than 22 ppm hydrogen in the sample stream when averaged over the 82 days the system was in operation. Over the same period, the time-averaged hydrogen concentration of the gas reaching the chromatograph was approximately 29 ppm. The maximum error involved in the sampling system averaged over this period was 43%. The source of error is in the final filter section where the sample gas cools to room temperature; 95% of the hydrogen is estimated to be in this section.

2. Conclusions

Sampling of the cover gas above the sodium is extremely difficult because of the gettering of hydrogen by sodium in the gas sample lines.

3. Documentation

This work is reported in the following Quarterly Technical Progress Reports on AEC-Sponsored Activities: APDA-232, APDA-234, APDA-236, and APDA-242.

010268

FIG. 17 ARRANGEMENT OF THE GAS SAMPLE LINE FOR THE SODIUM TECHNOLOGY LOOP

SECTION IV

SAMPLING AND ANALYSIS OF SODIUM

IV. A - ANALYTICAL METHODS

1. Determination of Oxygen in Sodium

a. APDA Technique

The development of a suitable analytical method for the determination of oxygen in sodium involves care in sampling to reduce contamination, the development of methods to quantitatively separate oxygen-containing compounds from an approximate ten thousandfold excess of sodium, and development of a sensitive, reliable method for quantitatively measuring the oxygen.

The APDA method consists of separating the oxygen from insoluble residues by amalgamation and extraction with mercury. The oxygen-bearing residue is dissolved in deionized water, titrated with sulfuric acid in the presence of excess sodium hydroxide using a modified methyl red indicator, and the oxygen concentration is calculated from the total alkalinity. The procedure is applicable to the determination of 10 to 100 ppm oxygen in metallic sodium with a relative standard deviation of 10%.

This method is described in the APDA Quarterly Progress Reports and in a topical report (see Documentation).

b. Uranium Gettering Technique

APDA conducted a program to evaluate the proposed Brookhaven National Laboratory technique for measuring oxygen in sodium using uranium as a getter metal in the APDA Sodium Technology Loop.

(1) Test Program

Twelve uranium specimens which had been exposed to static sodium for 1 hour at 500°C were obtained from BNL. The specimens, designated A₁, B₂, C₃, E₂, F₃, and G₁, were cleaned by electropolishing and weighed prior to experimentation. All the specimens were 0.508 cm thick by 1 cm wide by 12.5 cm long with a net surface area of 26.3098 cm², with the exception of Specimen C₃, which was 0.508 cm thick by 1 cm wide by 12.35 cm long and had a net surface area of 25.9946 cm².

Two experiments were conducted at two oxygen levels by exposing the specimens, three at a time, to the sodium of the APDA Sodium Technology Loop using a specimen holder of 3/4-inch stainless steel tubing. The experimental conditions and test results are shown in Table 1.

TABLE 1 - TEST CONDITIONS FOR URANIUM
GETTERING EXPERIMENTS

	<u>Test 1</u>	<u>Test 2</u>
Sodium Conditions		
Flow through Sample Holder, gpm	1/2	1/2
Temperature, °C (F)	485 (905)	485 (905)
Oxygen Level,* ppm	6.7	9.5
Exposure Time of Specimens, hr	2	2
Pretest Weight of Specimens, g	A ₁ 11.3897 B ₂ 11.3588 C ₃ 11.4429	E ₂ 11.7364 F ₃ 11.0974 G ₁ 11.1063
Weight Gain of Specimens, g	A ₁ 0.0050 B ₂ 0.0058 C ₃ 0.0045	E ₂ 0.0112 F ₃ 0.0119 G ₁ 0.0128
Average Weight Gain, μg/hr cm ²	97.3	194.93
Predicted Oxygen Concentration** by Uranium Gettering	6.0	12.0

* Calculated value as Na₂O, as determined by the mercury amalgamation method

**Based on a rate constant of 16.3 μg/hr cm² at 500°C as established by BNL (Reference BNL-50111, pp 41-46, 1968)

(2) Conclusions

This evaluation demonstrated the feasibility of the uranium gettering technique for monitoring the oxygen concentration in a dynamic sodium system. The work is documented in Quarterly Report of AEC-Sponsored Activities, April-June, 1969 - APDA-242.

2. Determination of Hydrogen in Sodium

It is hypothesized that hydrogen can be present in reactor sodium in the form of sodium hydride, sodium hydroxide, dissolved hydrogen, and possibly hydrocarbons. It is imperative, therefore, that sensitive analytical methods be developed to distinguish among the hydrogen species present.

The method used at APDA is a 2-stage vacuum reflux technique utilizing mercury as the refluxing medium (see Figure 18). The evolved hydrogen is measured quantitatively by gas chromatography. The mercury acts as a sequestering agent, removing the highly reactive sodium from the system by amalgamation, thus preventing re-formation of sodium hydride by the liberated hydrogen. By carefully controlling the amalgamation temperature, hydroxide hydrogen, nonhydroxide hydrogen, and total hydrogen can be determined. These results can, in turn, be used to more accurately evaluate the sodium monoxide contents of a sodium sample. The procedure is applicable to the 0.2 to 100 μg of hydrogen in sodium with a relative standard deviation of $\pm 5\%$. (See Documentation).

3. Determination of Carbon in Sodium

The need to monitor the carbon content of large sodium systems used in the LMFBFRs and even in small test loops such as the APDA Sodium Technology Loop has necessitated the development of a reliable method for determining total carbon in sodium. The concentration range is 10 to 100 ppm.

The APDA analytical method for the determination of total carbon in sodium metal is based on a stepwise conversion of the total carbon in the sodium sample to sodium carbonate to carbon dioxide, which is collected at liquid nitrogen temperature and subsequently measured by gas chromatography (see Figure 19). A sample of the sodium is placed in a quartz combustion system and heated to 1100°C within 1 hour, with an additional residence time of 1 hour to ensure complete reaction. An atmosphere of approximately 10.75 ml/min of oxygen in helium is used during the heating process. The sample is protected from atmospheric contamination by loading the combustion tube in an oxygen-free glove box.

A representative series of replicate sodium samples analyzed by this method had a standard deviation of ± 3 ppm and is applicable to the determination of carbon in sodium in the concentration range of 10 to 150 ppm in 0.2 to 0.4 g samples of sodium. The method is thought to be capable of giving reasonably precise results with a relative error estimated at being in the range of ± 5 to 10%. This method is described in a topical report (see Documentation).

4. Determination of Carbonate Carbon in Sodium

The term carbonate carbon refers to the carbon which is present in the form of sodium carbonate, or exists as a chemical species capable of evolving carbon dioxide under the dissolution-evolution conditions of the recommended procedure. Because relatively small quantities of carbonate are present in the sodium from nuclear reactors, the standard methods of detecting this impurity are not suitable.

a. Test Program

The APDA method is based on the carefully controlled dissolution of a sodium sample in water, the evolution and collection of carbon dioxide, and the measurement of the carbon dioxide by gas chromatography. An investigation of the relative merits of water dissolution and alcohol dissolution resulted in the selection of water as the solvent.

b. Conclusions

The analytical results from replicate determinations of carbonate carbon on three samples of sodium metal showed a standard deviation between 0.2 ppm and 0.26 ppm; a relative standard deviation of 4% to 7% would indicate that a reasonably good precision can be obtained at low levels of carbonate carbon in sodium.

This work was documented in a topical report (see Documentation).

5. Documentation

1. The Determination of Oxygen in Sodium Metal - APDA-163, July 2, 1965.
2. The Determination of Hydrogen in Sodium Metal - APDA-183, June 1966.
3. Determination of Carbon in Sodium by a High-Temperature Combustion Method Utilizing Gas Chromatography - APDA-164, November 1964.
4. Determination of Carbonate Carbon in Sodium Metal - APDA-166, January 1965.

143870

FIG. 18 REFLUX VESSEL FOR HYDROGEN DETERMINATION

143970

FIG. 19 COMBUSTION TRAIN FOR DETERMINING CARBON IN SODIUM METAL

IV.B - SAMPLING RELIABILITY STUDIES

Extensive studies were conducted at APDA to determine the sampling and analysis reliability for measuring the oxygen content of loop sodium using the bypass freeze tube sampling technique and the mercury amalgamation procedure for oxygen. This effort was culminated by the publication of two topical reports (see Documentation).

A similar but much less extensive study of the reliability of sampling procedures for hydrogen was also conducted and the results published in APDA Quarterly Progress Report on AEC-Sponsored Activities, APDA-242.

1. Oxygen Sampling and Analysis

a. Test Program

Sodium samples were taken from two sampling stations enclosed in a glove box continuously purged with a stream of purified argon. Both pinched and nonpinched bypass freeze tubes were used.

b. Conclusions

The effect of oxygen segregation along the length of a nonpinched sample tube is more pronounced at Station 1 than at Station 2. At Station 1, impurity segregation was detectable at each of the three nominal oxygen concentration levels (11, 47, and 76 ppm). At Station 2, impurity segregation was detectable only at the high oxygen concentration. It is believed that the segregation of oxygen in the sample tube is caused by a nonuniform cooling rate along the length of the sample tube. There was no detectable site-to-site variation at Station 2 for the 11-ppm and 47-ppm levels of oxygen above the amount which could be attributed to chance alone. This means there was no detectable correlation between the measured oxygen and site location over the length of the sample tube, but does not imply that no segregation occurred - only that the data are not sufficient to detect segregation against the background of random variation.

For the low level of oxygen in sodium (nominal 11 ppm), Station 1 is recommended for obtaining reliable sodium samples in nonpinched sample tubes. An arithmetic average of the site analyses was used as an estimate for oxygen concentration of the sampled sodium. At this concentration, an estimated precision for the combined sampling and analysis is about $\pm 8.8\%$ at the 95% confidence level.

For the medium level of oxygen (nominal 47 ppm) in sodium, either of the two sampling stations could be used for obtaining reliable sodium samples in nonpinched sample tubes, although Station 1 is preferable. An arithmetic average of the site analyses was used as an estimate for oxygen concentration of the sampled sodium. An estimated precision for the combined sampling and analyses at this concentration is 5.6% and 10% for Station 1 and 2, respectively, at the 95% confidence level.

For the high level of oxygen (nominal 76 ppm) in sodium, the sampling and analysis technique using a nonpinched sample tube was not adequate for reliable sodium samples at either of the two sampling stations. A significant impurity segregation occurred over the length of the sample tube at both sampling stations (see Figures 20 and 21). A significant difference in the tube averages (arithmetic average computed from individual site analyses) from each station was detectable, and the grand means of the sampling tube averages from the two stations were also significantly different ($\bar{X} = 79.2$ ppm at Station 1 and $\bar{X} = 72.62$ ppm at Station 2).

The technique of hot-pinching the sample tube into segments where the entire sodium is consumed in the chemical analyses was found to be very effective in reducing the scatter in the individual chemical analyses (see Figure 22). Although a segregation effect, or site-to-site variation, was still detectable at both sampling stations for the modified hot-pinched sample tubes at the nominal 30-ppm oxygen level, the extent of variability in the individual analyses was smaller than the estimated precision for the chemical analytical method alone (10% relative standard deviation), showing that the hot-pinching technique of sampling significantly reduced the error due to the sampling procedure. Therefore, for the 7-to-30 ppm oxygen range, the technique of hot-pinching is adequate for obtaining reliable results from either of the two stations. The combined sampling and analysis error lies within the range of the estimated error of the analytical technique alone (10% relative standard deviation) even if an individual site analysis of the hot-pinched sample tube is used as an estimate for the oxygen concentration of the sampled sodium.

Thus, if the sample tube averages computed from at least five individual site analyses are used to estimate the oxygen concentration of the sampled sodium, then for the levels of oxygen evaluated there is no distinct advantage in hot-pinching the sample tube. However, hot-pinching could be used to reduce the number of site analyses used in estimating the concentration of the sampled sodium. Additional studies should be made at higher levels (50-100 ppm) of oxygen with hot-pinched tubes to establish the precision for the combined sampling and analysis procedure.

2. Round Robin for Oxygen in Sodium

A round robin program involving five laboratories selected by the sponsor for their experience with the mercury amalgamation procedure was conducted for measuring oxygen in sodium. The objective of the program was to establish the precision of a revised mercury amalgamation analytical procedure as prepared by a cognizant ASTM subcommittee.

A statistical evaluation of the round robin results using the proposed procedure indicate a relative standard deviation of $\pm 30\%$ at the 7 ppm oxygen level and $\pm 15\%$ at the 30 ppm oxygen level. Results of the round robin program also demonstrated that the pinched tube method of preparing sodium samples (see Figure 23), developed by APDA, resulted in samples which were homogeneous within $\pm 25\%$ at a 95% confidence level.

Graphical analyses of the data indicate that the procedure and its execution in some of the participating laboratories can and should be improved.

The reproducibility of the analytical blank was investigated and results indicate a need for further investigation into the source of its variability. Additional work needed to improve the mercury amalgamation includes analytical blank and mercury purity studies.

A revised amalgamation procedure, based on the experience gained from this round robin, was presented for consideration.

This work was also documented in a topical report (see Documentation).

3. Hydrogen Sampling Reliability

The objective of this test program was to establish the precision of the combined sampling and analysis procedure (bypass freeze tube sampling and mercury amalgamation procedure for hydrogen, APDA-183). Table 2 presents data indicating the reproducibility of the above-mentioned sampling and analysis procedure for the two sampling stations located in the APDA Sodium Technology Loop. Figure 24 illustrates the site-to-site variation of hydrogen along a sample tube taken from Station 2.

As stated in Section II. B, a discrepancy was observed between the hydrogen concentration of cold-trapped loop sodium determined by the APDA hydrogen detector and that determined by the above described sampling and analysis procedure. This has led to the consensus at APDA that there is a significant blank contribution from the sampling tubes in the mercury amalgamation procedure. Some very preliminary experiments in sample tubes free of sodium supports this conclusion, although the precision of

TABLE 2 - DATA FROM HYDROGEN
SAMPLING RELIABILITY STUDIES

	<u>Sample Tube Average, ppm Hydrogen</u>	<u>Standard Deviation of Sample Tube Averages, ppm</u>
<u>First Test Period</u>		
Station 1 (18 Tubes)		
Hydride Hydrogen	0.95	0.46
Hydroxide Hydrogen	1.97	0.53
Total	2.93	0.66
Station 2 (4 Tubes)		
Hydride Hydrogen	0.93	0.32
Hydroxide Hydrogen	1.63	0.22
Total	2.56	0.52
<u>Second Test Period</u>		
Station 2 (11 Tubes)		
Hydride Hydrogen	0.53	0.13
Hydroxide Hydrogen	1.38	0.25
Total	1.90	0.33

NOTE: Three sample sites per sampling tube were used to establish the sample tube average.

the combined bypass tube sampling method and mercury amalgamation method has been measured, no meaningful statement regarding the accuracy can be made at this time.

4. Documentation

1. Sampling and Analysis for Oxygen in Sodium - APDA-246, April 1970.
2. Evaluation of an In-Line Detector for Hydrogen in Sodium - APDA-252.
3. Evaluation of the Proposed ASTM Method for Measuring Oxygen in Sodium Utilizing a Round Robin Program - APDA-238, January 1970.

119069

FIG. 20 OXYGEN CONCENTRATION VERSUS SITE LOCATION FOR SAMPLES FROM STATION 1—NONPINCHED SAMPLE TUBE, HIGH-LEVEL OXYGEN

117969

FIG. 21 OXYGEN CONCENTRATION VERSUS SITE LOCATION FOR SAMPLES FROM STATION 2—NONPINCHED SAMPLE TUBE, HIGH-LEVEL OXYGEN

134070

FIG. 22 RELATIVE STANDARD DEVIATION VERSUS OXYGEN CONCENTRATION FOR PINCHED AND NONPINCHED SAMPLE TUBES FROM STATION 1

118269

**FIG. 23 CAPSULES PREPARED BY THE APDA LABORATORY
FOR ASTM ROUND ROBIN ANALYSIS**

114569

FIG. 24 SAMPLE TUBE SITE AVERAGES – STATION 2

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