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ABSTRACT

The distillation method (Argonne Sampler) for the analysis of sodium oxide in NaK was used to calibrate a plug indicator. The description of the equipment, procedure, and experiences with the Argonne Samplers are presented in great detail to aid future users of this method. Although this method is not very precise, it has been thoroughly checked out and is recommended as a standard means for sampling and analysis for oxide in liquid metal systems.

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INTRODUCTION

Various methods for the sampling of liquid metals and chemical analysis of sodium oxide have been tested over a period of years in a continuing attempt to perfect an accurate and reliable "standard method." One of the first methods tested was used during a plug indicator calibration test, as described in Reference 1. This method piped the hot NaK sample from the DANA pump bowl into a hydrogen fired nickel bottle and allowed the NaK to cool before taking several aliquots from the bottle using the three-bulb glass thief tube. The NaK in the glass tubes was analyzed for sodium oxide content by using the butyl-bromide method. The results of this test showed that, although the plug indicator gave good qualitative agreement with the chemical analyses, these analyses were usually unaccountably high, probably due to the difficulty of preventing contamination of the NaK by mere traces of air or water.

In late 1955, Humphreys of ANL presented a radically different method for sampling and analysis for sodium oxide using the Argonne Sampler. As described in Reference 2, this method kept the NaK sample in only one container, the nickel-foil lined cup inside the Sampler, until the NaK was distilled off leaving only an inert residue which included the oxide. This residue was then analyzed by standard chemical methods. This Argonne Sampler method, also called the Distillation Method, was tested, modified slightly, and released by the Analytical Chemistry Division with a detailed procedure, Reference 3. In all, seven technicians have been trained in this method and have participated in calibration tests on various plug indicators. Since this experience was favorable, the test reported partially herein was run to calibrate another plug indicator.

The Analytical Chemistry Division has also released a second sampling method using a modified NEA Sampler, Reference 4. Attempts to use this method in the calibration tests on the plug indicators have been unsuccessful. The difficulty experienced was in attaining the degree of vacuum tightness required to prevent visible contamination of the NaK sample.

The description of the equipment, procedure, and experiences with the Argonne Samplers will be presented with a great amount, perhaps excessive, detail in this report. The reason is this: although this method is not very precise, it has been thoroughly checked out and is recommended as a standard means for sampling and analysis for oxide in liquid metal systems. These details then are to aid future operators of this equipment.

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DESCRIPTION OF ARGONNE SAMPLER EQUIPMENT

Although the Argonne Sampler equipment described in Reference 3 was adequate to run analyses, a number of modifications were made to facilitate assembly and operation. These modifications involved the design of the samplers and NaK valves; use of quick-connect couplings on NaK transfer lines; portable sampler stands; and instrumentation.

The basic sampler unit is shown in the schematic, Figure 1. A brief description of its use facilitates the discussion of the equipment. While sampling, NaK (or sodium) flows from the transfer line (sampling line) and valve into the unit where a fixed volume of the liquid metal is retained on a removable cup. The excess NaK, used to clean the line-valve-cup, falls into the overflow receiver flask. With the valve shut, the NaK retained in the cup is distilled off under vacuum at 800°F leaving a residue of inert sodium oxide. The cup can then be removed from the unit, the oxide dissolved in water and titrated with standard solutions of hydrochloric acid to determine the initial concentration of oxide in the fixed volume of NaK. A complete analysis requires 7 hours.

Four sampler units were used during the test. Two of the samplers, No's. 1 and 2, were supplied by the Analytical Chemistry Division. Another sampler unit, No. 3, was made according to the drawings listed in Reference 5. The only important difference among these samplers was in the construction of the vent part on the drain line, as shown in Figure 2. The last sampler, No. 5, made using the drawings given in Reference 6, was a special design which provided a window for observing the sample cup during sampling and vacuum distillation operations. This window worked very satisfactorily.

The sample cup used in the sampler units is shown in Figure 3 along with an insert, insert heater, and wall type thermocouple. These sample cups were pressed out of soft nickel sheet, 0.010 inches thick. The folds in the cup tended to retain minute amounts of NaK even after a long distillation time. Several perfectly smooth cups had been made by plating nickel onto aluminum cups which were then eaten away by caustic. However, these plated cups were very brittle and broke in use. If the plated cups were made thicker (they were only 0.010 inches thick) and annealed, they would be better than the pressed cups.

The inserts were not interchangeable between sampler units and were marked corresponding to the mating units. The mark, the number of the unit, served to index the insert as there was a tendency for the NaK to leak down along the side of the insert and accumulate in the sump at the bottom if the insert was not clamped straight into and on the index mark of the unit. The glassware used on the sampler units was custom made, as shown on Figure 4.

The NaK valve on the transfer line operated under severe conditions. While sampling, the valve controlled the flow of 1200°F NaK into the sampler unit. During the vacuum distillation, the valve had to be leak tight because drip leaks would result in either high or ruined analyses, depending on whether the drip NaK evaporated off before or remained in the cup when the cup was removed from the unit. The valves used were modified Hoke bellows valves, No. 1197.

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These Hoke valves were made of 316 stainless steel except for the seamless bellows which were of 317 stainless steel. The body was provided with integral 1/4 inch Swagelok connections and the seat diameter was 5/32 inch. The modification, shown in Reference 7, provided a much longer bonnet and positive opening-closing of the valve. This modification operated satisfactory although the set screws on the handle and jam nuts tended to work loose. Special Lavite spacers were made so that a pair of standard clam shell heaters (2-3/8 inch inside diameter, 4 inches long, 290 watt, 57 volt) could be clamped around the body of the valve for heating. The Swagelok connections on the valve tended to develop leaks, so standard practice was to weld the 1/4 inch diameter transfer line to the Swagelok nuts which in turn were welded to the valve body.

This modified Hoke valve had a limited life; after a number of samples, a drip leak through the valve developed. Standard practice was to provide two valves in series and to use first one and then the other until both were leaking. As it was a difficult chore to replace valves on a contaminated line (the services of a welder, inspector, mechanic, electrician, insulator, and instrument man were required), the sampler units and valves were assembled into portable stands which could be connected into the transfer line and replaced as necessary. A pair of safety valves were placed in the transfer line between the connection and the sump of the Cold Trap Test Stand so that the test stand could remain in operation as sampler units were replaced.

Although another modification of the Hoke 1197 valve was available, Reference 8, it was not used during the test. Previous experience with a similar modification of the Fulton Slyphon Model 315 bellows valve, Reference 9, showed that this valve was completely unsatisfactory because of bellows failures.

A quick connect coupling was used to connect the various sampler units to the NaK transfer lines. This coupling, shown on Figure 5, worked very well as long as the coupling was kept at the temperature of the sampled NaK. A pair of standard clam shell heaters (2-3/8 inch inside diameter, 4 inches long, 290 watt, 57 volt) were clamped around the coupling for heating. The coupling was insulated with a strip of Thermoflex blanket.

After using a sampler unit for a sequence of analyses, the oxide formed each time the unit was opened to atmosphere to remove the sample cup would build up and plug the inside of the unit and the drain line. Also the transfer valves would develop drip leaks as explained above. The use of portable sampler assemblies mitigated the difficulties involved in removing, cleaning, replacing the sampler unit and valves by providing duplicate, replaceable, plug-in sampler stands. The time necessary to replace a sampler stand was only an hour and the craft help required were a mechanic, electrician, and an instrument man.

The portable sampler stand was assembled according to the drawings in Reference 10. Figures 6 and 7 show two views of an assembled stand. The male end of the quick connect coupling on the transfer line is clearly shown on Figure 6. The gas panel controlled the helium pressure, and the air flow to the two air cooling coils on the sampler unit. Plugging in a portable stand involved connecting 12 thermocouples, 5 heaters, and 3 gas lines (helium, air, vacuum). Figure 8 shows two sampler stands connected to Cold Trap Stand 1. The handles of the safety valves are visible to the right of the two transfer valves on the right hand sampler stand. Valve tags were used to indicate the position of the

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valves. On the left hand stand, the upper valve is tagged open; the lower valve is being used to take samples. On the right hand stand, the lower transfer valve is tagged open, it leaks; the upper transfer valve is being used to take samples. Not shown are the vacuum pumps which were removed for the photograph. The stand on the left is in Sampler I position while the stand on the right is in Sampler II position. The difference in the positions was the instrument controls attached to the sampler.

The instrument cabinets for the Argonne Samplers are shown in Figure 9. Sampler I position had only the rudimentary controls described in Reference 3. Although these controls (largely manually operated) were satisfactory, their operation was time consuming as the technician had to check the progress of the sampler unit frequently and make the indicated changes in the control settings. A different set of controls for Sampler II position was evaluated during the test. These controls, mostly automatic, were mounted in a single portable cabinet which with the replaceable-portable sampler stands were to form an assembly that could be transported around the laboratory to sample NaK or sodium from any test stand for oxide analysis. This cabinet was assembled using the drawings listed in Reference 11. These automatic controls functioned very satisfactorily during the test. The temperature controllers maintained the important temperatures at the desired values for sampling and distillation without the variability noted in the operation of Sampler I. Although the Foxboro controller on the insert heater tended to raise the temperature of the NaK in the cup too rapidly and overshoot at the beginning of the distillation period (which might result in low oxide analyses because the NaK would bump out of the cup), this minor difficulty was solved by raising the set point of the controller in periodic steps instead of a single large step.

Basic in either system of controls was the 12-point temperature recorder which made a continuous record of the thermocouples, shown in Figure 10, mounted on the sampler units. A typical record of a sampler run is shown in Figure 11.

The pressure in a sampler unit during the vacuum distillation period was measured by a thermocouple gage mounted on the manifold of the vacuum pump. These gages were the Model GV-3 made by the Hastings Instrument Company. The two vacuum pumps used for the sampler units were the Duo-Seal pump made by the M. W. Welch Manufacturing Company, Serial Numbers: 807-97 and 811-97. These pumps were run with 3/4 hp electric motors made by General Electric Company.

The control point values, temperature and pressure, are tabulated in Table I along with a comparison of the control operators and devices for the two sampler positions.

OPERATION OF THE ARGONNE SAMPLERS

The procedure followed in operating the Argonne Samplers differed in some respects from that given in Reference 3. A major difference was in maintaining the safety valves, transfer valves, and transfer line at 1000°F instead of heating and cooling these parts for each sample. As a previous test (unpublished) indicated that the life of the valves was not apparently shortened by maintaining them at the high temperature, this change in procedure was made to reduce

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the technicians' control tasks during the preheating period. The detailed procedure used for the test is quoted from Reference 12 in the Appendix.

Five technicians and the writer participated in running the test on a 24-hour basis. The first letter of the surname will be used to distinguish the analysis run by these six operators. These letter designations are: A, F, L, P, T, and W. During the first part of the test, each operator was responsible for taking and titrating complete samples on his shift. In the second part of the test, one man, P, assumed the responsibility of titrating the samples as they came out of the units. The other operators took the samples and ran them through the distillation step. Slightly more samples were run each day in this latter period as the technicians would begin a new sample as soon as the previous sample was cleared of the unit instead of waiting for the technician on the next shift to begin it.

A total of 82 samples were taken for oxide analysis. A listing of the samples taken, samples run through the titration step, and reasons for replacing each sampler in the sequence used, is given in Table II below:

Table II

Sampler Position I

<u>Sampler Unit No.</u>	<u>Samples Taken</u>	<u>Samples Run Through Titration</u>	<u>Reason for Removing Sampler Unit</u>
5	28	22	Both transfer valves leaked
2	14	11	Not removed, test terminated

Sampler Position II

5	13	7	Both transfer valves leaked
1	2	1	Top calrod burnt out
5	1	0	Unit oxidized up (inadequately cleaned from previous use)
2	2	0	Top calrod burnt out
1	22	20	Not removed, test terminated

The data recorded in the log book did not detail the life histories of the individual transfer valves. However, it is apparent that the pair of transfer valves on each sampler unit lasted from 13 to 28 samples. The calrods on top of two samplers burnt out because of operation errors on the part of different technicians.

The major difficulty encountered with the sampling units before the sampling step was in ensuring that the various lines on the sampler unit were open. The check step detailed in the procedure was, with reference to Figure 10, to close

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the vacuum valve, open the helium and vent valves, and to check that helium could flow through the glassware, sampler body, drain line, and out the vent valve. This check step was done twice, once before the preheat step and once before the sampling step. Failure to do these check steps could result in flooding the glassware with NaK if the drain line was plugged when the transfer valve was opened. This mistake occurred once during the test. When the check step is unsuccessful, the procedure calls for rodding the lines. The horizontal line connected to the glassware was seldom plugged. The drain line was sometimes plugged and was rodded only by removing the glass receiver flask. The vent valve was frequently plugged and was usually replaced with a new valve. About 25 of the Hoke Company's M482 valves were used as vent valves during the test. The bottom portion of the drain pipes was frequently plugged. This area is shown in Figure 2. Although the new design on units 3 and 5 featured a trap to prevent the NaK from backing up and flowing out the vent line, the feature didn't work. Instead, the trap prevented effective rodding of the vent hole as compared to the old design. When this area was plugged with oxide, the effective recourse was to remove the glass receiver flask and the glass-pipe joint and wash the accumulated NaK and oxide out of the flanged area of the drain line with water. The area was dried with a propane burner and allowed to cool before the joint and flask were replaced. A constant flow of helium down the drain pipe was maintained during this operation. Although this recourse was relatively hazardous, the only alternative was to change out the portable sampler unit.

The major difficulty encountered during the sampling and distillation steps was in preventing the NaK from bumping out of the sample cup and thereby losing part of the sample. NaK could be bumped out by the vibration of the mechanical vacuum pump, accidental jars of the sampling stand, flashing of the hot NaK when the vacuum was first applied, heating to distillation temperature too rapidly, and by other unknown reasons. Care was maintained throughout the test to isolate and prevent the vibration of the vacuum pump from being transmitted to the sampler stand. The possibility of accidentally jarring the sampler stands was aggravated by the close quarters about the two stands as shown in Figure 8; there was barely enough room to move between the two stands for the work required. Flashing of the hot NaK when the vacuum was applied never occurred when observations were made of samples through the window of sampler unit No. 5. The procedure called for the cup to be heated to the distillation temperature in 30 to 45 minutes and the strip chart records of each sample showed that this step was almost universally followed to prevent the NaK from bumping out by too rapid heating. Some flashing may occur during the distillation period, after vacuum has been applied and the cup heated to 800°F, if the observation of White, Reference 13, is correct.

Several special experiments on the Argonne Samplers were run during the last part of the test to demonstrate that bumping or flashing of the NaK may have occurred almost consistently throughout the latter part of the test. These experiments included the taking of cup samples as a means of determining the amount of NaK retained in the cup after the sampling step. A pair of cup samples were taken on 12-13 using the procedure of Reference 3 which follows the normal steps of preheating and sampling. However, once the vacuum is applied, the heat is turned off and the unit is allowed to cool instead of heating to the distillation conditions. The cup and insert are removed after the NaK has been frozen with a jet of carbon dioxide from a fire extinguisher. The amount of NaK retained in the cup is determined using standard wet analysis techniques. A second

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pair of cup samples were taken on 12-14 with the vacuum step omitted. Two samples were also run for oxide on 12-14 (0555-0557 hrs) by allowing the cup to cool to 300°F before the vacuum was applied, whereas the usual procedure applied the vacuum with the cup at 400 to 600°F. The water solutions of the four cup samples were sent to the Analytical Chemistry Division for the following analysis: Na, K, Ca, Ni, Cr, and Fe.

The cup temperature (insert temperature) when vacuum was applied depended primarily on the quantity of NaK flowed through the unit on sampling. Before sampling, the cup temperature ranged from 160° to 210°F due to preheating the top of the unit to between 400°F and 500°F. Upon sampling, the hot NaK falling from the transfer line heated the cup. The resulting cup temperatures ranged from 320°F to 790°F. Normally the vacuum was applied very soon after the transfer valve was shut before the cup could cool appreciably except in the experiment described above. The procedure, Reference 3, called for about 200 ml of NaK to flow through the unit. The procedure used here called for flowing 2 inches of NaK into the receiver flask using the 2 inch rings marked on the flask as a guide. These rings, shown in Figure 8, were equivalent to about 250 ml of NaK per ring. The variability in cup temperatures resulted from different flow rates (higher flows didn't heat as much) and different quantities of NaK used by the several technicians. As larger quantities of NaK probably helped make cleaner samples, the technicians tended to flow more than the quantity called for in the procedure. When the glass receiver flasks were filled with NaK, they were removed and stored under kerosene in a large G.I. can to await disposal. New glass flasks were used to replace full flasks because they could not be cleaned economically.

In contrast to the bumping which loses part of the sample, three effects were observed which tend to increase the size of the sample. One such effect is a surface tension phenomenon which permitted the cup to hold more NaK than would be the case if the surface of the NaK lay flat across the cup edges. This was observed first using the window of unit No. 5, but one of the cup samples taken on 12-14 also demonstrated this effect. All the cup samples had NaK in the depression of the insert under the cup. This NaK had leaked up under the eaves of the cup edge shown in Figure 3. When the oxide of this NaK adhered to the cup, it was titrated in the analysis in addition to the oxide inside the cup. Lastly, the transfer line tended to drip NaK after a transfer valve was shut, particularly when the lower valve was left open and the upper valve was used. When this dripping continued very long, the drips fell into partly distilled cups of NaK and would, of course, add more oxide for the titration.

Due to all the different effects noted, there was considerable variability in the exact quantities of NaK in the samples. This variability manifested itself in the cup samples which usually are regarded as the primary standard for measuring the amount of NaK sampled. In lieu of the cup samples, a secondary standard was employed which involved titrating water into individual cups until they were full. Care was taken so that the surface of the water did not rise above the edge of the cups due to the same exact surface tension effect noted above with NaK.

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Various other difficulties were experienced during the distillation period. With one sample, the insert heater burnt out and had to be replaced midway through the 3-hour period. With another sample, the technician forgot to open the vacuum valve until the distillation temperature was reached. Another sample was distilled at 900°F instead of 800°F because of a thermocouple error. This type of thermocouple error was due to a difference between the two thermocouples in the insert wall shown in Figure 3. These thermocouple assemblies were specially made and were not calibrated until the latter part of the test. The error was not easy to pick up on the instruments because one of the thermocouples indicated on a controller while the other indicated on the recorder. As the controllers had different calibrations than the recorders, the error was not observed unless it was large. Some of the errors detected are shown in Table III below:

Table III

<u>One Thermocouple</u>	<u>Other Thermocouple</u>	<u>Difference</u>
600°F	1000°F	400°F
775	910	135
680	805	120
740	815	75
790	840	50
705	740	35

As the individual errors were detected, the walls were removed and broken to keep from using them again. The 12 samples which were not completely distilled were partly due to this thermocouple error. Once the calibration procedure was instituted, this error was eliminated.

After the distillation was complete... the unit had cooled, the insert was removed and the cup placed in the beaker of distilled water. One cup was dropped at this step ruining the sample. An aggravating trouble was the tendency for NaK to leak down the side of the insert and accumulate in the wall at the bottom. Gloves were required to protect the hands in case the NaK in the wall or along the sides fell off while handling the insert. These NaK leaks, which do not hurt the sample, were usually prevented by clamping the insert straight into and on the index mark of the sampling unit. A blank insert was clamped into the unit to prevent the entrance of air into the helium filled unit while the numbered insert was being drained and cleaned of NaK.

The titration step was straight forward except in the interpretation of the methyl orange end point. Reference 3 describes the end point as the change from a clear yellow solution to a permanent red although it appears to the writer as a change from a clear yellow to orange to a light pink. The use of the blank mitigated the difference in interpretations by various technicians. Also a full size colored photograph of the titration color changes in similar beakers, Reference 14, was used as a standard.

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For the first 45 samples, the technician who took the sample was responsible for running the titration. Six of these 45 samples were discarded before the correlation because the technicians used too much acid in the back titration step (volume of acid denoted by V_2 in Table 12). This back titration is made after the first titration and after the solution has been boiled and allowed to cool. Only a small amount of acid is necessary to reattain the methyl orange end point which was lost by boiling off the carbon dioxide in the solution. The use of too much acid in the back titration step results from an uncertainty about the end point color. Due to this and other apparent differences among the five technicians in doing the titration steps, the last 37 samples were titrated by only one man, P, with the technicians taking and running the samples through the distillation step as before.

Three different strengths of standard hydrochloric acid solution were used in titrating the various samples. The different strengths, 0.01 N, 0.005 N, and 0.001 N, were made up in volumetric flasks from a primary solution of 0.1 N acid supplied by the Analytical Chemistry Division. This primary solution was checked by the writer against a standardized acid solution also supplied by the A.C.D. and found to be correct within a 2% maximum error. Three different buretts were used, one for each solution. These buretts were in the standard sizes, 0 to 25 ml or 0 to 50 ml with a least division of 0.1 ml. The buretts were read to an accuracy of only 0.05 ml. The strength of solution used was selected to make the reading error less than 1% of the titration and was based on the amount of acid used for the previous sample. One pair of samples was ruined by the writer by mixing 0.1 N acid solution into the 0.01 N acid burett solution before the titrations were made.

One detail in the assembly of the portable sampler stands is important in assuring full cups of NaK after sampling. This detail is the position of the end of the transfer line above the cup. The correct position is shown in Figure 12 from Reference 10. When the end of the line is inside the Swagelok nut, the NaK tends to flow along the top of the sampler instead of falling into the cup. Each portable sampler assembly was checked before installation for this detail.

EXAMINATION OF ARGONNE SAMPLER DATA

The difficulties of running the Argonne Sampler analyses through the titration step have been described. The quantity of oxide in the sampled NaK is calculated from the amount of titrated hydrochloric acid using a conversion factor. This conversion factor was based on the secondary standard previously described. The amounts of water measured into the cups are listed below. As the cups were used interchangeably in all sampler units and as no record was kept relating the cups to the samples, the water measurements were lumped in determining the conversion factor.

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Table IV

Volumes of Sampler Cups Determined by Water Measurement

<u>Cup Number</u>	<u>Volume Capacity, mls</u>
1	4.85
1	4.90
2	4.65
3	4.50
4	4.75
Average	4.73 with a standard deviation of 0.1605

The 95% confidence limits on this volume are: 4.39 ml to 5.07 ml or a range of $\pm 7.2\%$. The weight of NaK at 500°F represented by 4.73 ml is 4.0 gm. The conversion factor calculated using the equation of Reference 3 is:

$$CF = \frac{1000 N_1 (8.00)}{\text{(Weight of NaK sample, gm)}}$$

Or:
$$CF = \frac{1000 (0.01 N) (8.00)}{(4.0 \text{ gm})} = 20$$

Where: CF, ppm O_2 /ml Acid, is the conversion factor
 N_1 , gm of Acid in 1000 ml solution, is the Normality of acid (0.01 N)
8.00, is the equivalent weight of oxygen

Thus: (Oxygen, ppm) = 20 (Amount of 0.01 N Acid titrated, mls net)

The conversion factors for the three strengths of acid used are tabulated below:

Table V

Conversion Factors for Various Hydrochloric Acid Solutions

<u>Acid Strength normality</u>	<u>Conversion Factor ppm O_2/ml Acid</u>
0.01	20
0.005	10
0.001	2 0

The 95% confidence limits for these conversion factors, being directly derived from the measured volumes of water, are also $\pm 7.2\%$.

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There appears to be a decided difference between the sampler units in addition to a bumping or flashing effect when vacuum is applied. This is further borne out in the special test when the NaK was allowed to cool after sampling before applying the vacuum as shown in the following table:

Table VI

Argonne Sampler Oxide Analysis

Date	Time, Hours	Sampler Position-Unit	Sampling Temperature °F	Temperature on Application of Vacuum, °F	Volume of 0.01 N Acid titrated, net ml	Equivalent Oxide concentration, ppm O ₂
12-13-56	1411	I-2	520	520	5.50	110
	1415	II-1	500	500	2.05	41
12-14-56	0555	I-2	520	300	11.65	235
	0557	II-1	470	300	2.75	55

The cup samples taken on 12-13 and 12-14 also showed wide variation. These samples are tabulated below along with their corresponding conversion factors:

Table VII

NaK Cup Samples Taken Directly From Argonne Sampler Units

Date	Time, Hours	Sampler, Position-Unit	Sampling Temperature, °F	Procedure	Weight of NaK, gms	Conversion Factor for 0.01 N Acid, ppm O ₂ /mls Acid
12-13-56	2125	I-2	790	Sampled, applied vacuum, then cooled	2.13	38
	2130	II-1	510	Sampled, applied vacuum, then cooled	0.28	280
12-14-56	1307	I-2	(not measured)	Sampled, then cooled, no vacuum	6.68	12
	1309	II-1	(not measured)	Sampled, then cooled, no vacuum	3.65	22

The cup with 6.68 gm. NaK was over full, demonstrating the tendency for surface tension to hold more than capacity amounts of NaK in the cup. The cup with only 3.65 gm. NaK was observed to be not quite full.

An attempt was made to assess the significance of the vacuum-bump effect on the Argonne Sampler analysis. A model was hypothesized which presumed that low oxide analysis result from applying the vacuum at high cup temperatures. As shown on Figure 13, this model does not fit much of the data amenable to plotting, 30 of the possible 41 samples, as many of the constant break temperature lines do not show lower analysis at higher vacuum application temperatures. A statistical correlation for this model was inconclusive. The reliability of the model was checked by an analysis of variance on the eight natural classes of data, seven of which had duplicate or repeated oxide analysis at certain vacuum

application temperatures and provided opportunities to estimate the precision of the data. This check suggested that the model was satisfactory with respect to the fit, which was poor, only because the precision within the various classes was also very poor.

In addition to the vacuum application temperature-bump, many other difficulties have been described. These difficulties introduce variables which possibly invalidate the statistical tests above. A critical examination was made on the data to assess the impact and importance of these other variables. The major and obvious variables are listed below:

1. Sampler Positions, there were two, I and II involving instrumentation differences.
2. Sampler Units, there were four, 1, 2, 3, and 5, involving the interchangeable units.
3. Technician Combinations, there were ten, A, F, L, P, and T, who ran complete analysis including titration; and A-P, F-P, L-P, T-P, and V-P where the technicians took the sample and a common man, P, did the titrations.

Unfortunately, this examination was instituted after the data had been gathered so the experimental design was very poor for attempting to appraise these variables. The examination was made by Mr. D. A. Gardiner, Mathematics Panel, and the results which follow are taken from Reference 15.

The data were divided into five groups depending on the range of plug indicator break temperatures taken in conjunction with the Argonne Sampler analysis. The method of examination was to form sets of orthogonal comparisons (individual degrees of freedom) which would reflect as many as possible the differences between the variables enumerated above in each group. Standard analysis of variance techniques were then used to assess the significance of these differences.

A summary of the conclusions from these groups for the variables of sampler position and unit is given in Table VIII below:

Table VIII

Summary, Analysis of Variance Tests on Argonne Sampler Position and Unit Variables

<u>Group</u>	<u>Sampler Position</u>	<u>Sampler Position</u>	<u>Conclusions</u>
	<u>I</u>	<u>II</u>	
	<u>Unit Number</u>	<u>Unit Number</u>	
I	3	5	No test possible
II	3	1	No test possible
III	2 and 3	-	No significant difference
III	2 and 3	1	A difference may be conjectured
IV	2	1	No significant difference
V	2	1	No significant difference

Thus, there is no apparent difference in the analysis resulting from the differences in instrumentation of the positions or differences among the interchangeable units.

A summary of the conclusions about the technician variables is given in the following table:

Table IX

Summary, Analysis of Variance Tests on Technician Variables

<u>Group</u>	<u>Technician Variables Tested</u>	<u>Conclusions</u>
I	A vs P, AMP vs F, F vs L, F&L vs T	No test possible
II	A vs P, L vs T, AMP vs L&T, A vs T, AMT vs F	A is significantly higher than the others. No differences shown among the other three technicians.
III	A-P vs L-P vs T-P, L-P vs W-P, A-P vs L-F vs T-P vs W-P	No test possible
IV	F-P vs W-P	No significant difference
V	F-P vs T-P vs W-P	No significant difference

The details of this examination are given in the Appendix.

Thus, except for the one technician, A, all the technicians apparently run the Argonne Samplers alike and give similar results. The one man, A, tends to give high analysis. There is no direct comparison possible to test if the titrations made by P helped to make the analysis more consistent.

The standard deviations calculated in the analysis of variance tests are compared to the sample averages on Figure 14 and in the following table.

Table X

Averages and Standard Deviations of Argonne Sample Analysis

(listed in increasing magnitude of sample average)

<u>Group</u>	<u>Position, Unit</u>	<u>Technician</u>	<u>Degrees of Freedom</u>	<u>Sample Average Net ml acid</u>	<u>Standard Deviation net ml acid</u>	<u>Ratio of Std. Dev. to Avg.</u>
IV	II,1	F-P	1	0.46	0.085	0.185*
		W-P	1	0.74	0.11	0.149*
	I&II,1&2	F-P	2	0.85	0.24	0.286
		W-P	3	0.92	0.42	0.459
III	II,1	A-P	2	1.06	0.037	0.035*
IV	1,2	W-P	1	1.09	0.64	0.587*

Table X - contd.

Averages and Standard Deviations of Argonne Sampler Analysis
(listed in increasing magnitude of sample average)

Group	Position Unit	Technician	Degrees of Freedom	Sample Average Net ml acid	Standard Deviation net ml acid	Ratio of Std. Dev. to Avg.
IV		F-P	1	1.24	0.33	0.266*
V	II,1	F-P	1	2.20	0.21	0.096*
III	II,1	L-P	1	2.69	0.37	0.138
II	II,1	F	1	3.30	0.56	0.170
V	II,1	W-P	2	3.33	0.88	0.264*
II	I,3	L	2	4.07	0.90	0.221*
		F	3	4.16	1.81	0.435*
V	IA&II,1&2	F-P	2	4.98	2.26	0.454
		W-P	3	6.03	1.72	0.285
II	I,3	ASPHALT	9	6.59	1.97	0.299
I	I,3	F	1	6.8	3.82	0.562
II	I,3	T	1	7.45	3.61	0.485
V	I,2	F-P	1	7.75	3.18	0.410*
I	II,5	F	1	9.05	3.61	0.399
V	I,2	W-P	1	10.08	2.23	0.221*
II	I,3	A	3	10.48	1.87	0.178*
I	II,5	T	2	11.5	1.50	0.135

(* Denotes samples that were pooled for several estimates of standard deviation)

The standard deviations are usually large and, as would be expected, are a function of the size of the sample means. There is apparently very little increase in precision through the use of more than two samples in the sample average. This is shown on Figure 14 where the points with 2 or more degrees of freedom (means 3 or more samples in the average) fall in the same scatter of points with only one degree of freedom (only 2 samples in the average). The ratio of the standard deviation to the sample average ranges from 0.035 to 0.587. This ratio is assumed to be a population for the purposes of predicting future ratios to be expected on Argonne Sampler analysis. In this calculation, those samples that are pooled (denoted by * in Table X) are not used as they are represented by the pooled result. Also, each ratio was weighed by the degrees of freedom available after calculating the standard deviation; to tend to give more weight to the ratios that should be more precise. The results of this calculation are shown in Table XI.

Table XI

Population Values for Argonne Sampler Analysis Ratio	Standard Deviation Sample Average
Name	Value
Number of ratios in population	27
Ratio average	0.297
Standard Deviation for ratio	0.130
High end of Ratio population mean, 99% confidence range	0.348
Low end of Ratio population mean, 99% confidence range	0.246

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While these ratios do not directly indicate confidence limits of error in the sample averages, they do indicate that these confidence limits will be wide.

SUMMARY AND CONCLUSIONS

The detailed description of the many difficulties encountered in using the Argonne Samplers was not written to discourage their use for oxide analysis. The samplers are the best means for sampling and chemical analysis that the writer has had experience with. It is a good method, although it may appear tedious and not always precise. The future use of the Samplers, in pairs where possible to take advantage of the increased accuracy by taking two samples, is recommended.

Much of the material covering the description and operation of the Argonne Samplers was written to aid the technician who might be responsible for operating the Samplers. These three sections can be summarized by saying, "treat the Samplers like a baby."

The operation of the Samplers should be the responsibility of only a few technicians as the procedure is difficult and requires care. This would be a full time job as the complete analyses require about 7 hours. These men cannot, of course, be color blind to red and yellow, the end points of the methyl orange indicator used in the titration. The few technicians should be checked statistically one against another, to avoid the possibility of one man tending to sample high, as was the case for technician A.

There was no apparent differences among the sampler units or controls in the net results of the analysis. The automatic controls used on position II facilitated the operations and can be recommended. Of the samplers, unit 5, the unit with the window, is the most interesting one to run because of the opportunity to observe the effect of many of the operating variables. Indeed, this unit could be used to provide the answers to the effect of such variables as: the vacuum-bump, rapid heating after sampling, and distillation at other than 800°F.

Fifty per cent of the samples taken during the calibration test were lost for one reason or another. This mortality rate can be reduced by strict attention in avoiding the difficulties enumerated. The interchangeable plug-in sampler stands increase the reliability of the sampler method during an extended sequence of samples by making it easy to change out a Sampler quickly.

The standard deviation of Argonne Sampler analysis is high compared to the average of the analysis. The 95% confidence limits on the population of standard deviation ratios experienced during the test are 0.245 to 0.348. These analysis average limits indicate that the errors in the method are large and that several samples are required to give reasonable confidence in the oxide analysis.

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- 20 -

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6. Assembly - Sodium Sampler Type "B", Dwg. E-2-02-054-4802, parts: C-4796, B-4797, B-4798, B-4799, B-4800, B-4801, D-4803, B-4804, B-4805, B-4806, B-4807, B-4808.
7. Assembly - Hoke 1197 Valve Modification II, Dwg. D-2-02-054-4884-A, parts: B-4885, B-4886, B-4887, B-4889.
8. Assembly - Hoke 1197 Valve Modification, Dwg. D-4440, parts: B-4441, B-4442, B-4443, B-4444, B-4445, B-4446.
9. Assembly - Fulton Siphon Model 315 Valve Modification, Dwg. D-5205, parts: B-5206, B-5207, B-5208, B-4209.
10. Assembly - Portable Argonne Sampler, Dwg. (E) SK-RFP-864, parts: SK-RFP-845, SK-JWK-863.
11. Control Cabinet Panel Layout for Argonne Sampler, Dwg. D-2-02-054-5426, parts: D-5401, D-5402, D-5427, D-5428.
12. Cold Trap Stand 1, Operations Manual, 9-21-56, R. D. Peak.
13. Personal Communication with J. C. White, 12-5-56.
14. Colored Photograph, Y-12, 26274.
15. Personal Communication, D. A. Gardiner, February 7, 1957.

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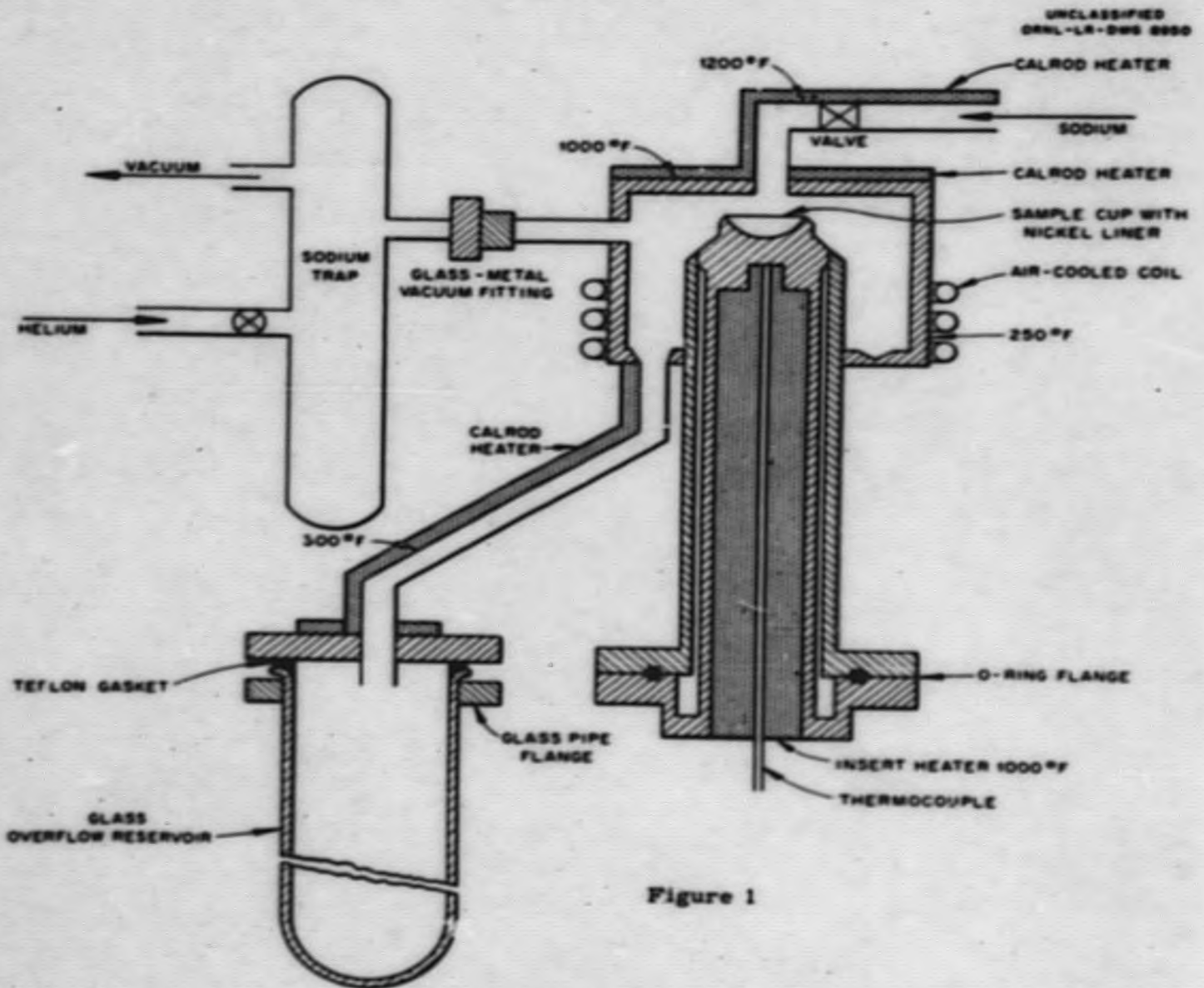
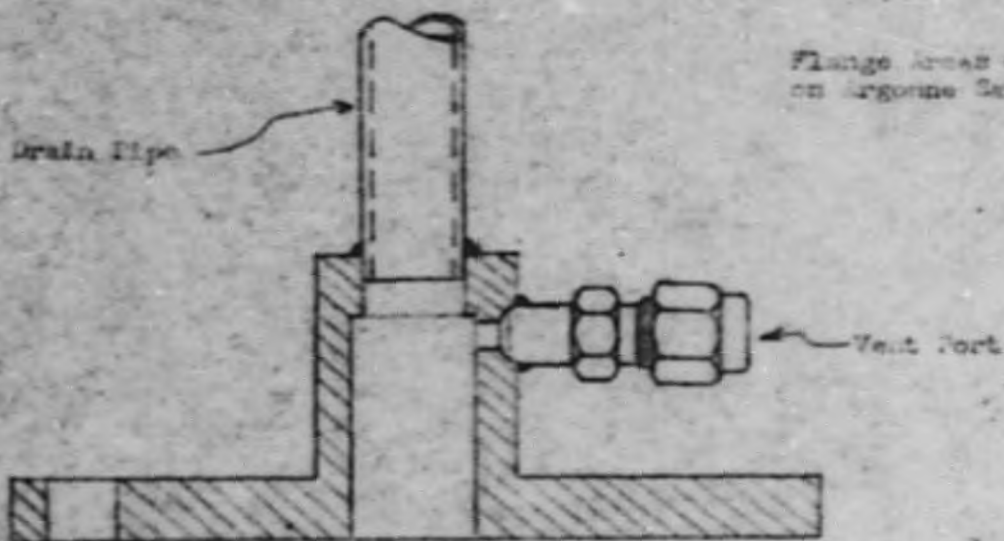
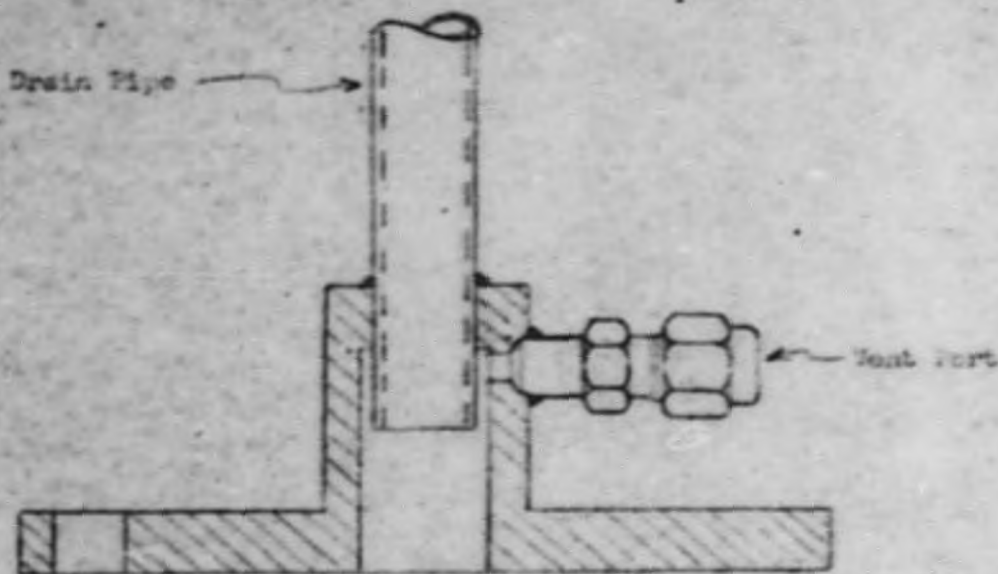


Figure 1

Figure 2



Sampler Units 1 and 2 supplied by the Analytical Chemistry Division
The Design is such that it is Very Easy to Rod out and Unplug the Vent Port



Sampler Units 3 and 5 made to Drawing D-3-02-154-4794
The design is such that it is very difficult to rod out and unplug the vent port.

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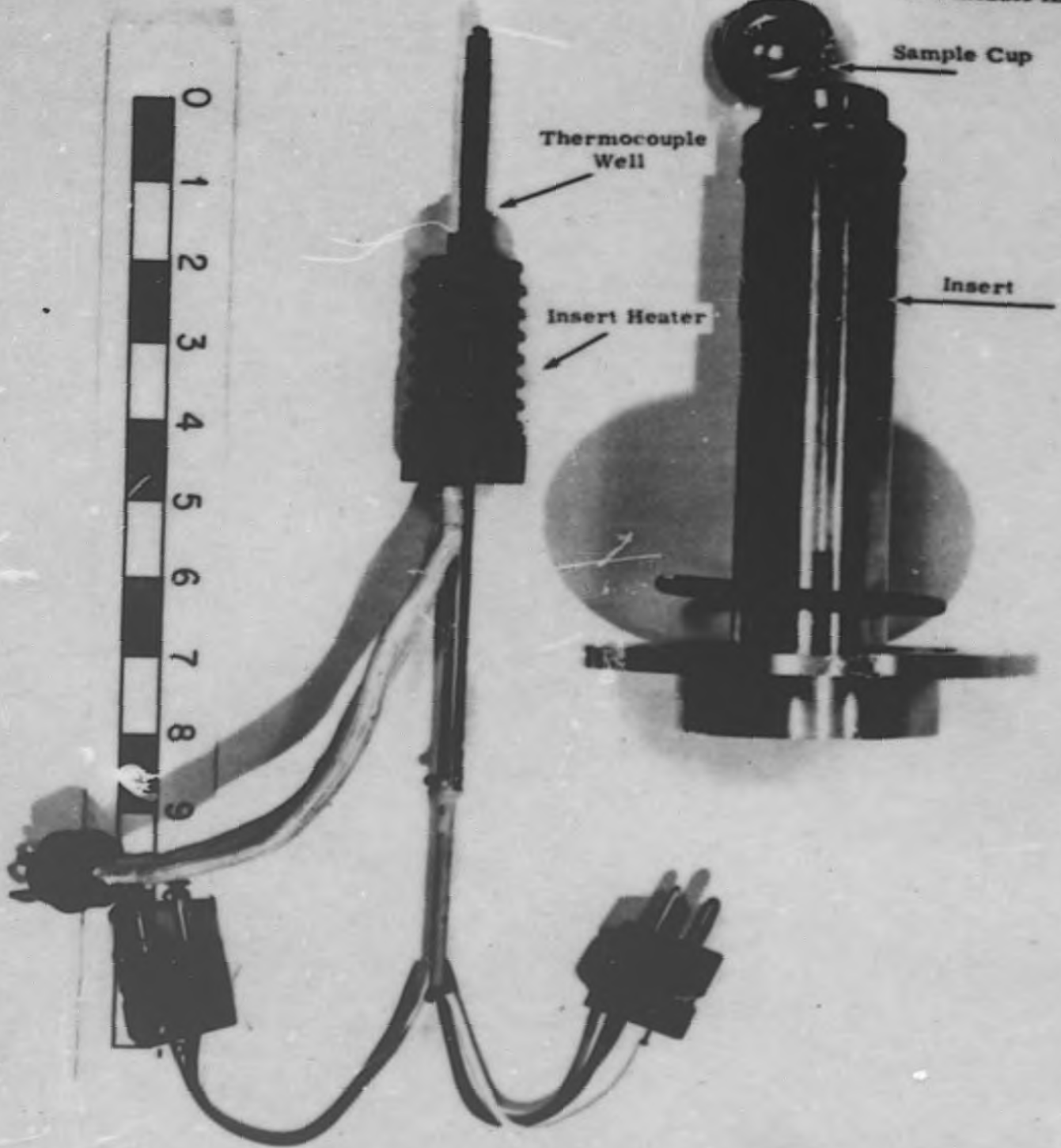


Figure 3 Parts for Argonne Sampler Units

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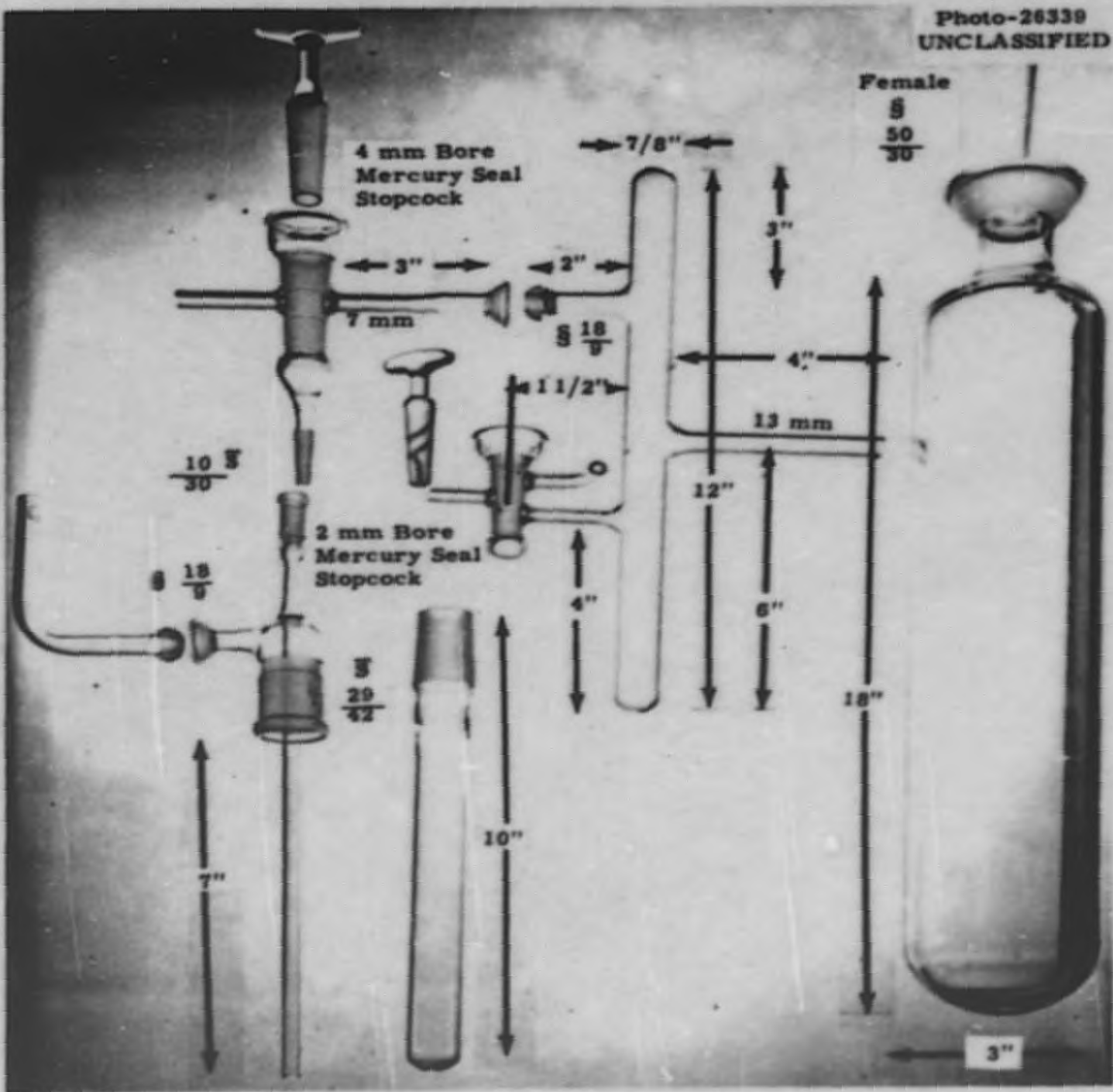
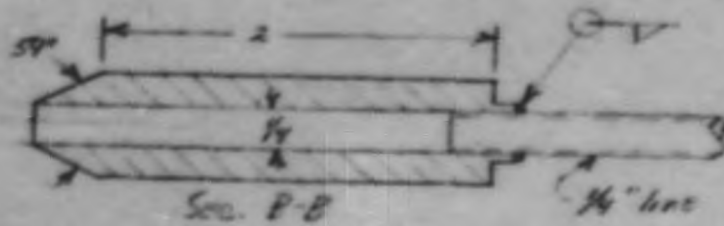
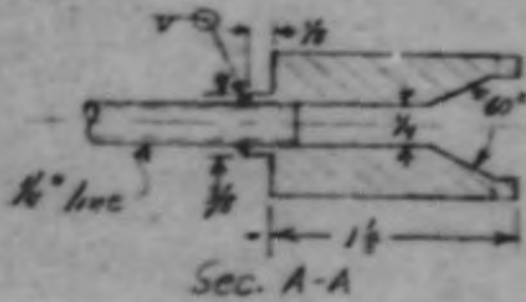
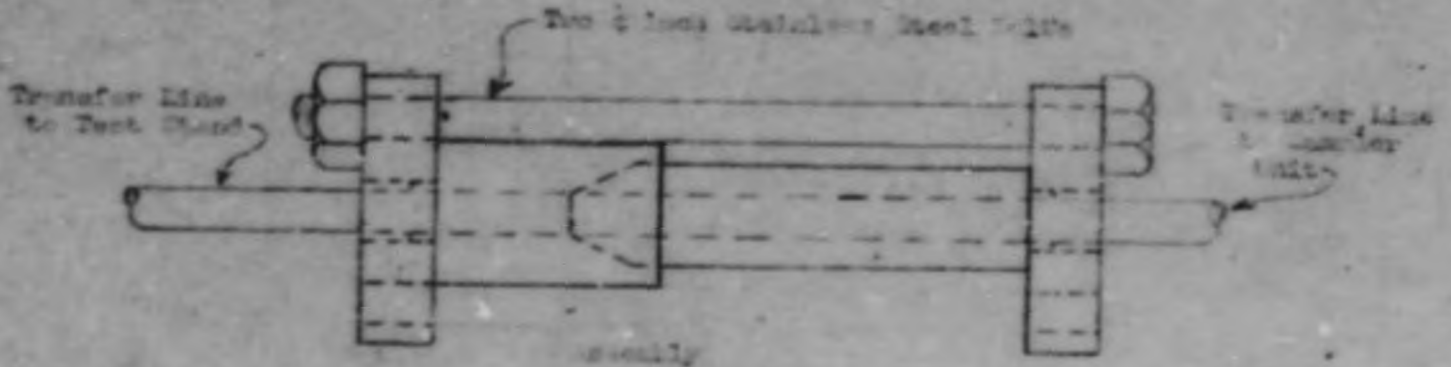


Figure 4 Glass Ware Used on Argonne Sampler Units

Figure 5

Quick Connect Coupling used
on Port No. 2 of the Amplifier
Head



SR-RDP-1394
3-22-57

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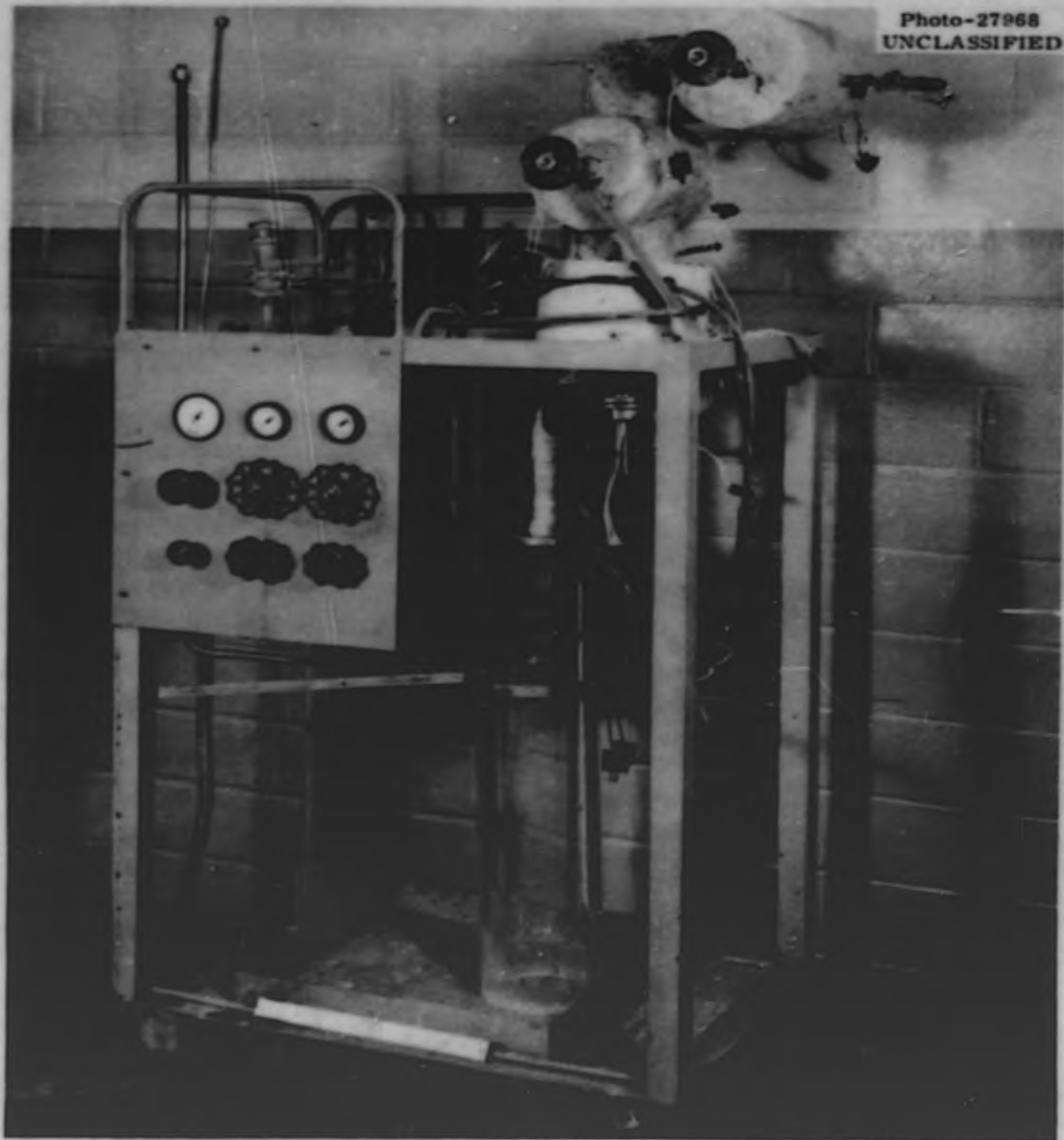


Figure 6 Portable Argonne Sampler Stand

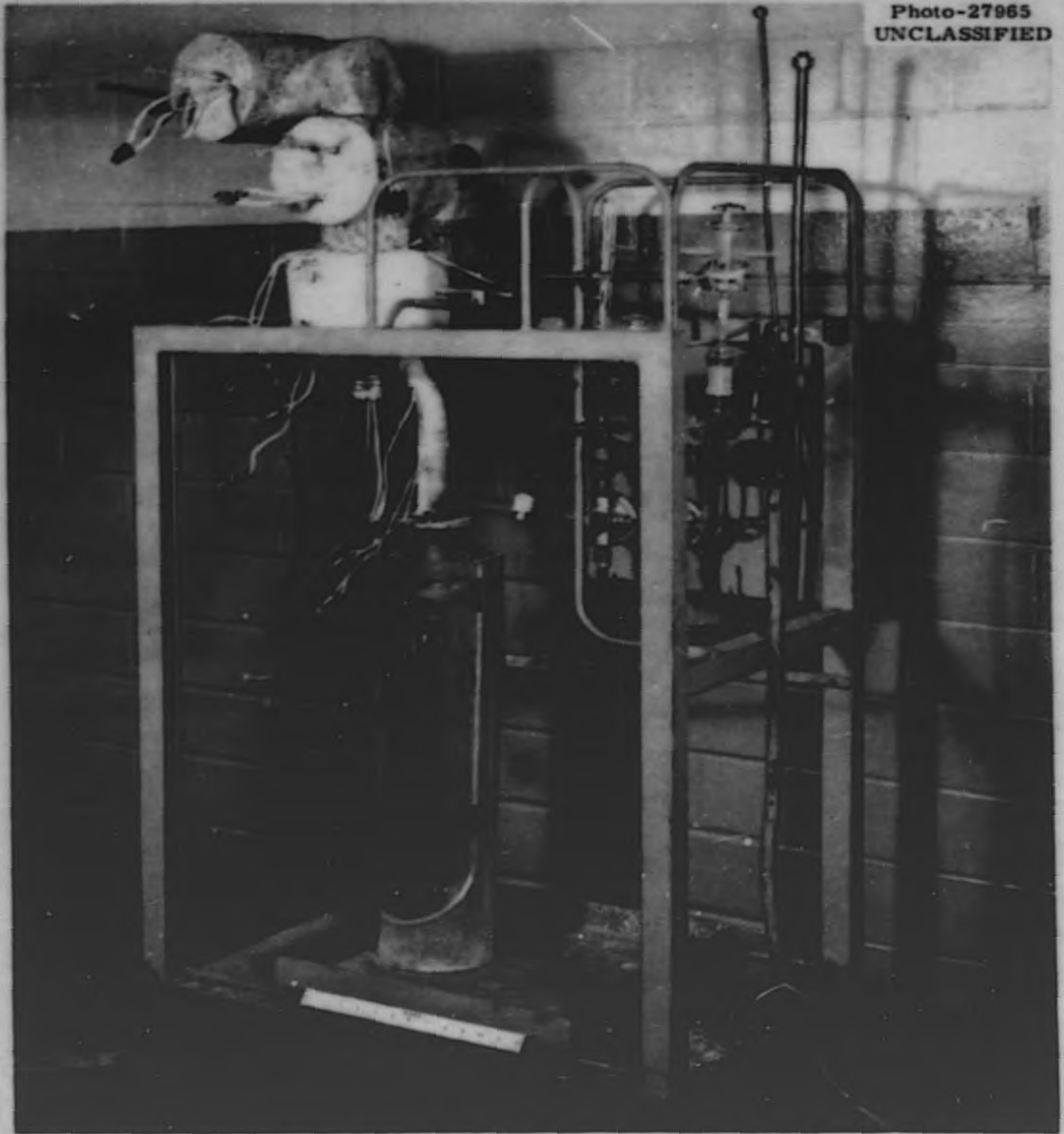


Figure 7 Portable Argonne Sampler Stand

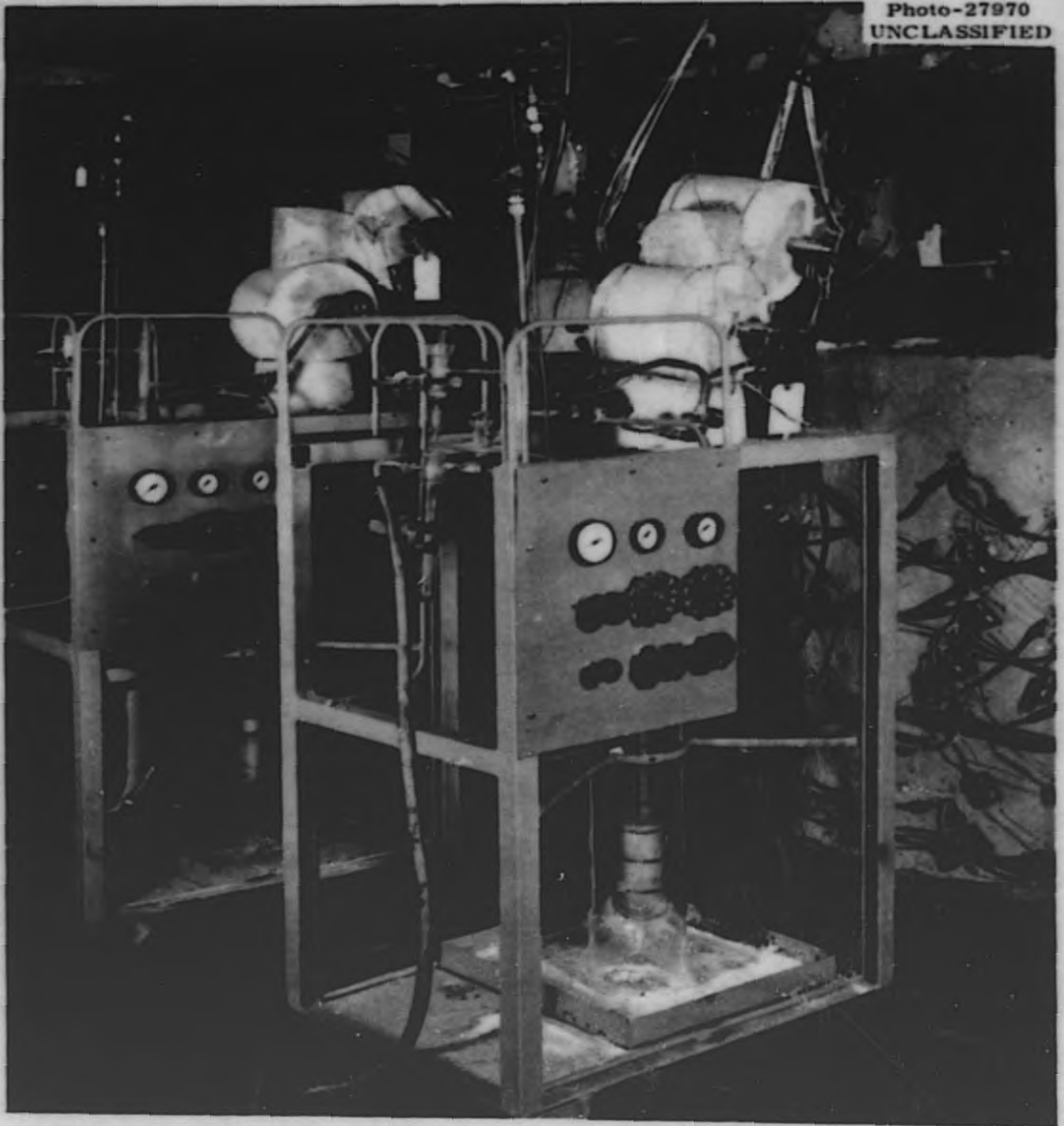


Figure 8 Installation of Portable Argonne Sampler Stands on
Cold Trap Stand 1



Figure 9 Instrumentation for Argonne Sampler Units
Cold Trap Stand 1

Figure 10

Electric Heater and Thermocouple Locations on Argonne Sampler Units

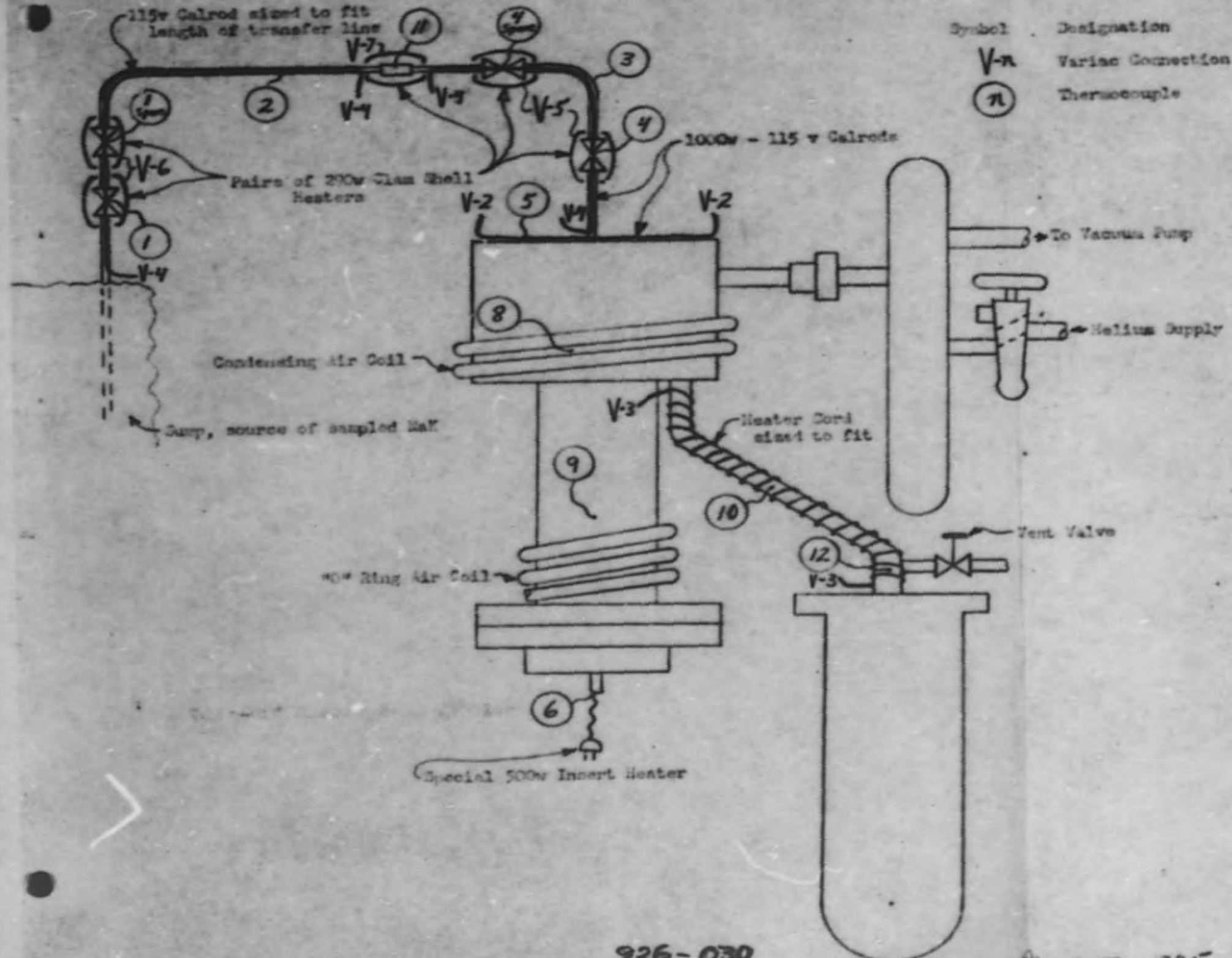
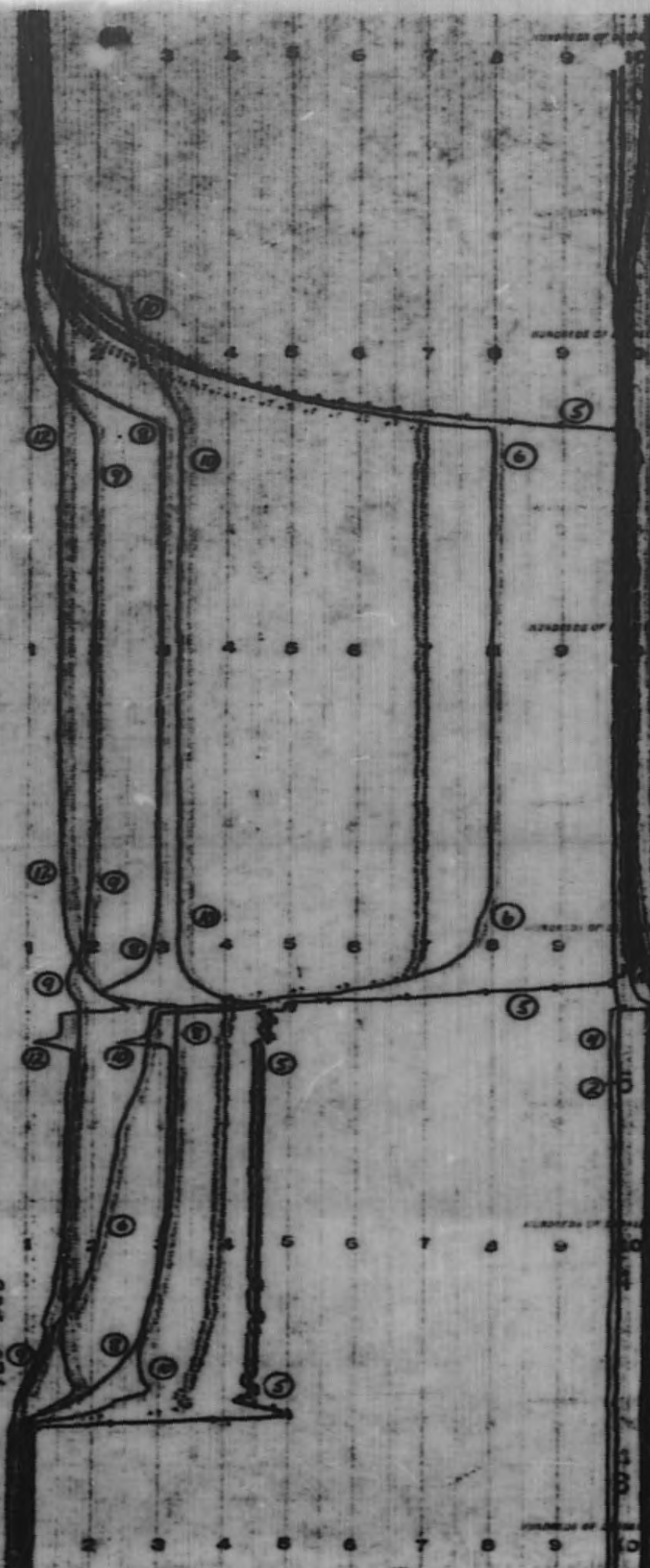


Table 12
Summary of Data

Date	Time	Technician-Sampler		Argonne Sampler Data				Plug Indicator Data				Cold Trap Data								
				Temp. on Applying Vacuum °F	Htg. Time Min.	Titration Volumes T ₃ - T ₁ ml. acid	Titration net ml. acid T ₁ +T ₂ +T ₃ +T ₄	Hydrochloric Acid concentration Normalcy	Oxygen ppm	Remarks	Time at Break	Total Cooling Rate °F Min.	Cooling Rate During 2 min. prior to break °F/min.	Starting Flow gpm	Dread Temperature °F	Reading Time	Flow gpm	Thermo-Couple - Temp.		
11-19	0925	T	II-5	400	3	2.1 11	12.6	.01	252	Distillation temp. reached in 3 min.	1635	420	7	-	.41	680	1040	0	80	720
11-27	0940	T	II-5	400	30	1.5 11.6	12.1	.01	242		1530	390	8	-	.35	660	1010	0	80	690
11-28	0850	F	I-3	450	20	0.6 5.2	5.3	.01	202		1350	450	7	-	.30	690	0900	0	5	515
11-30	1515	F	I-3	400	30	0.8 9.6	9.8	.01	196	Used CF of 38	1025	400	5	-	.49	680	1340	0	5	580
12-1	1525	F	II-5	350	10	0.8 11.2	11.6	.01	190	Distillation temp. reached in 3 min. Insert heater burnt out during distillation	1355	300	8	-	.39	680	0940	0	5	630
12-1	0812	L	II-5	360	6	0.5 8.6	8.9	.01	232		1635	420	11	-	.52	68	1640	.70	80	740
12-1	0730	A	I-3	450	60	5.0 8.4	12.7	.01	178		0210	380	6	-	.55	690	0030	.36	70	755
12-1	1635	F	I-3	550	30	0.1 4.4	4.1	.01	156	Titration wrong	0905	370	9	-	.50	675	0920	.64	80	705
12-2	1630	F	II-5	470	7	0.4 6.5	6.5	.01	130	Used CF of 38	1625	440	16	17	.54	660	1600	1.12	84	665
12-2	0905	A	I-3	360	20	1.5 1.0	2.4	.01	-		0208	440	14	18	.54	640	0130	.96	84	620
12-2	0900	A	II-5	330	12	0.1 .5	0.8	.01	-	Solution wrong	0920	460	24	15	.55	645	0920	1.06	84	615
12-2	1720	F	I-3	550	20	0.5 9.7	9.7	.01	-	Solution wrong										
12-3	0740	L	I-3	600	20	1.5 6.4	7.0	.005	97		1702	480	17	17	.55	620	1630	.96	84	625
12-3	0735	A	I-3	370	30	5.6 16.2	21.1	.005	70		0609	470	19	14	.55	615	2030	.95	84	620
12-3	1600	F	I-3	410	20	0.1 5.5	5.1	.005	-	Titration wrong	0818	470	28	8	.54	610	0750	.86	84	600
12-3	1730	F	II-1	670	70	0.3 5.9	5.8	.005	51		1554	490	21	11	.53	615	1520	.88	84	630
12-4	0825	L	I-3	520	20	1.7 6.5	7.2	.005	58		2352	470	18	14	.56	620	2330	.91	84	630
12-4	0810	A	I-3	410	20	6.6 17.3	23.4	.005	72	Titration wrong	0845	470	19	13	.53	610	0820	.83	84	610
12-4	1705	F	I-3	460	20	0.3 6.0	5.7	.005	57		1435	470	20	12	.53	610	1425	.93	84	625
12-5	0105	L	I-3	550	40	1.4 9.3	10.2	.005	102		1650	480	24	8	.53	615	1625	.90	84	622
12-5	2325	A	I-3	450	30	2.1 7.6	23.5	.005	102		0035	480	20	11	.51	610	0005	.85	84	625
12-5	0730	T	I-3	500	50	4.4 4.4	10.0	.01	-	Not used	1534	500	13	29	.54	610	0940	.83	84	624
12-5	1600	F	I-3	650	40	0.4 6.2	6.4	.01	-	Titration wrong	0012	500	19	12	.53	600	1510	.70	84	607
12-5	1605	F	II-1	630	20	0.4 3.7	3.7	.01	128		0809	470	13	33	.51	615	0700	.97	84	610
12-5	2335	A	I-3	370	10	0.5 7.6	7.8	.01	141	Used CF of 38	1532	470	15	17	.48	610	1515	1.04	84	620
12-5	2345	A	II-1	520	30	0.3 2.1	2.3	.01	-	Not used	0056	470	15	17	.50	610	0030	1.02	84	620
12-7	0740	T	I-3	490	25	2.1 3.3	4.9	.01	-	Not used										
12-7	0825	T	II-1	450	4	5.1 1.3	15.8	.005	-	Titration wrong	0901	450	11	41	.50	625	0840	1.04	84	630
12-7	1625	L	I-3	550	20	.45 3.1	3.2	.005	30	Distillation temp. reached in 4 min. Titration wrong										
12-7	2330	L	I-3	500	18	.75 7.9	8.0	.005	80	Distilled at 900°F	1548	500	20	12	.47	570	1515	.88	84	530
12-8	0720	T	I-3	410	20	.25 2.1	2.1	.005	21		0055	540	16	14	.50	550	0430	.87	84	540
12-8	1610	L	II-1	480	14	.35 2.75	2.75	.005	28	Used CF of 38	0827	540	15	47	.50	530	0805	.70	84	540
12-8	2312	A	II-1	390	17	.25 2.20	2.30	.005	22		1545	510	24	9	.48	530	1515	.81	84	540
12-8	0735	A	II-1	500	6	.4 1.9	2.05	.005	21		2137	540	10	30	.48	530	2145	.72	84	535
12-8	1330	T	II-1	490	25	.1 2.7	2.6	.005	26		0009	520	13	28	.48	540	2350	.74	84	530
12-8	2040	L	I-3	550	50	.75 4.7	5.2	.005	52	Distillation temp. overshoot by 50°F.	0844	550	16	23	.50	510	0750	.65	84	520
12-10	2045	L	II-1	380	20	.4 3.7	3.9	.005	39		1312	600	20	18	.50	460	1245	.64	84	490
12-10	0110	L	I-3	550	15	.3 3.25	3.4	.005	34		2001	560	23	8	.48	550	1920	.79	84	530
12-10	0325	L	II-1	490	30	.2 2.25	2.3	.005	23		0215	560	25	13	.49	560	0230	.76	84	520
12-11	0830	L	I-3	-	-	.35 1.95	2.0	.005	20		0439	540	5	81	.49	550				
12-11	0830	F	II-1	-	-	.2 1.95	1.05	.005	11		0548	530	5	75	.49	550				
12-11	1437	F	I-3	490	20	2.15 13.55	14.7	.001	19		1630	700	20	24	.48	390	1600	.70	84	390
12-11	1438	F	II-1	440	26	.75 4.4	4.8	.001	20		2031	700	20	13	.48	395	2000	.72	84	400
12-11	2320	L	I-3	570	35	1.4 15.45	15.45	.001	31		0016	700	12	25	.48	395	0000	.72	84	390
12-11	2315	L	II-1	470	25	1.25 6.45	6.6	.001	13		0410	720	11	25	.44	400	0400	.72	84	390
12-11	0830	L	I-3	-	-	.35 1.95	2.0	.005	20	T/O trouble	0811	750	12	23	.43	385	0755	.71	84	390
12-11	1437	F	I-3	490	20	2.15 13.55	14.7	.001	19		1434	850	14	26	.52	385	1417	.76	84	415
12-11	2320	L	I-3	570	35	1.4 15.45	15.45	.001	31		2250	830	16	15	.50	395	2225	.65	84	385
12-11	2315	L	II-1	470	25	1.25 6.45	6.6	.001	13		0055	800	16	15	.52	395	0030	.72	84	390



Safety Valves, Transfer-Control Valves,
Transfer Line, and Connection remain hot

End of Distillation, All Sampler Unit Heat
turned off, 1230 hours

t/c 6 reaches 800°F, Distillation Period
begins, 7950 hours

Helium Sample Transferred, 0925 hours

t/c's 10 and 12 cool due to helium flow,
check that the Drain Pipe and Vent Valve
are open

Preheat Started on Sampler Unit, 0715 hours

Safety Valves, Transfer-Control Valves,
Transfer Line, and Connection remain hot
from previous sample.

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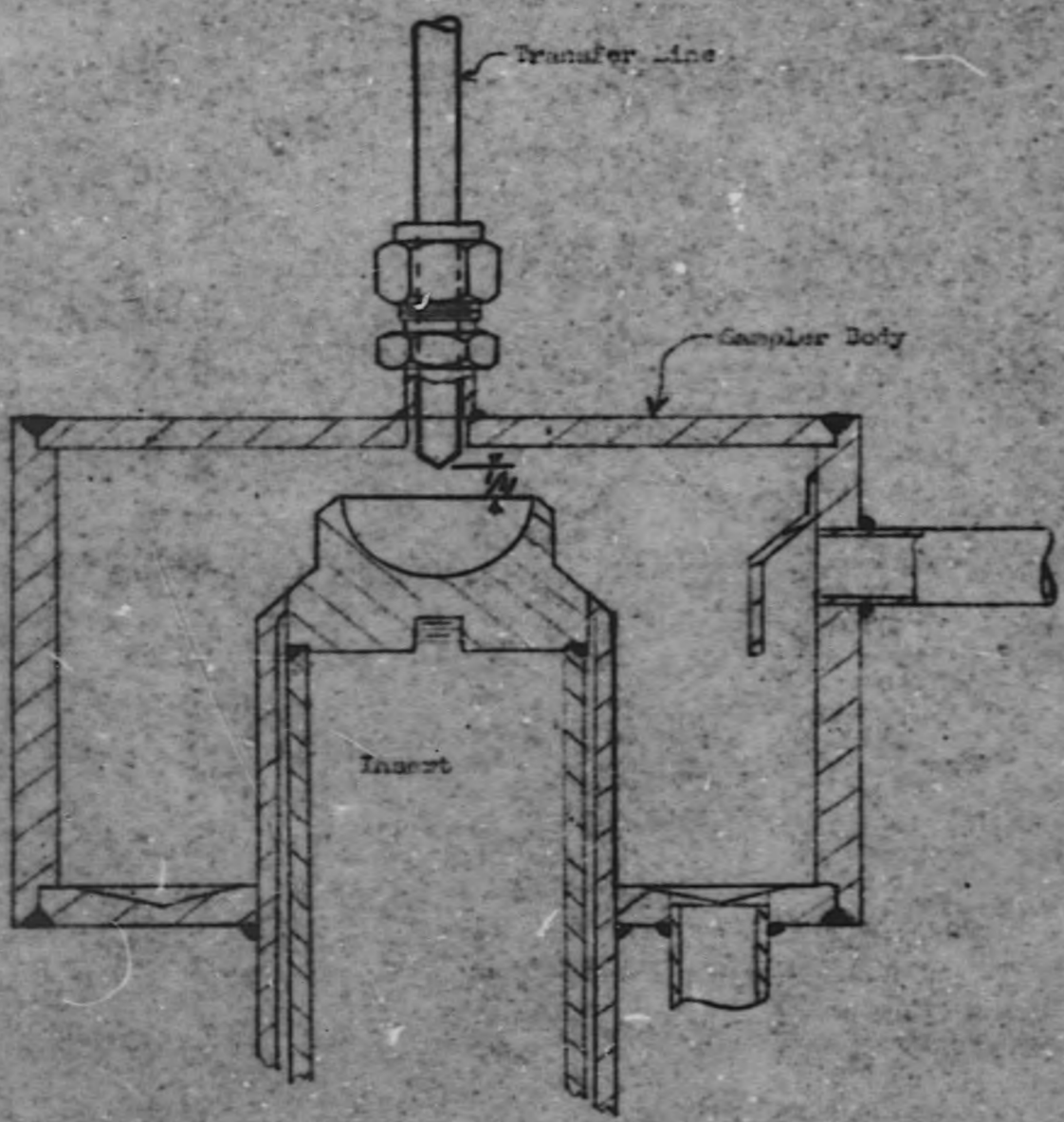
Typical Helium Sampler Line
Drawing No. 1996

Figure 11

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Figure 12

Detail Showing Correct
Position for End of
Transfer Line in Sampler

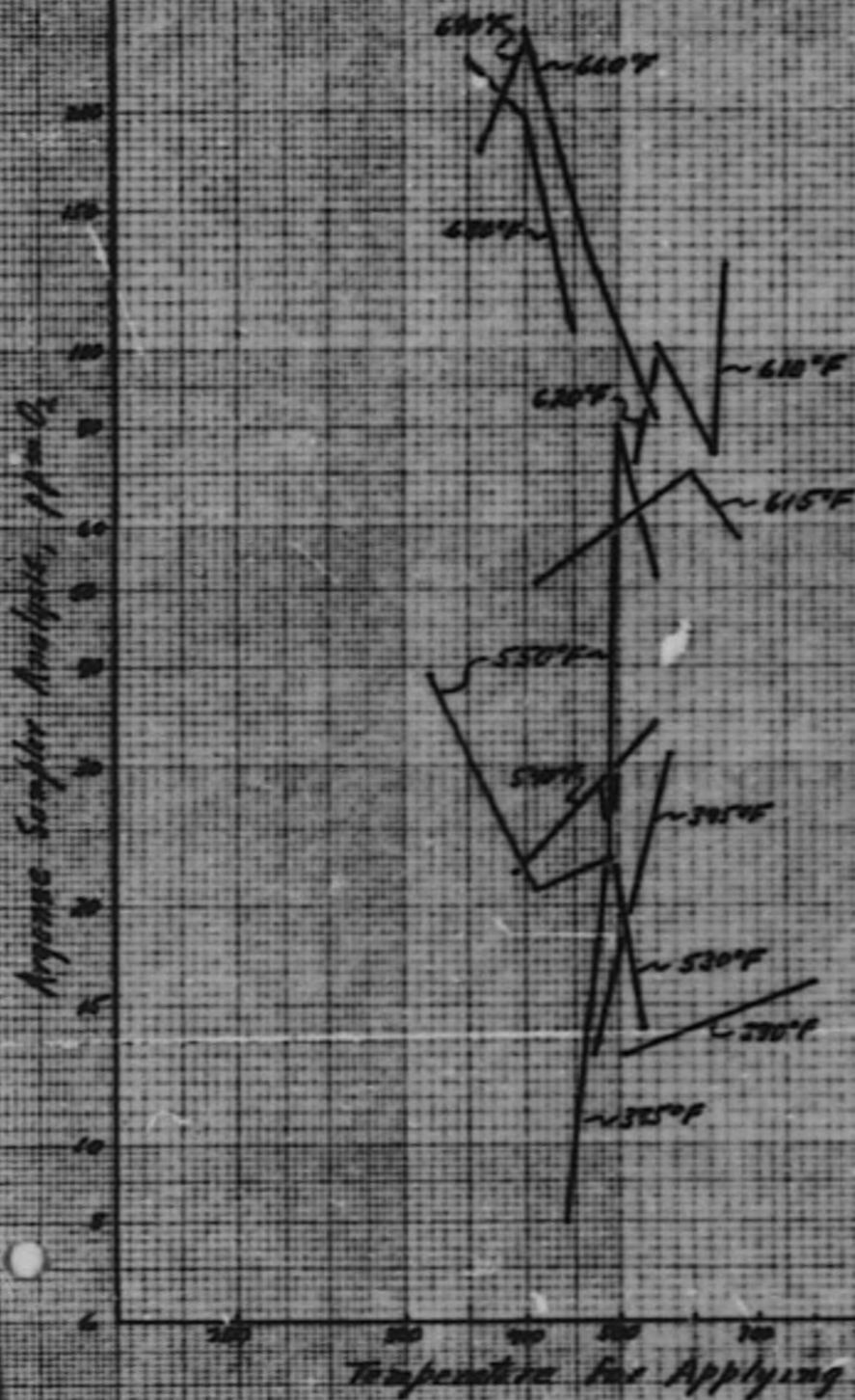


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OR-REP-1397

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Oxide Analysis
vs
Vacuum Application Temperature
at
Constant Break Temperatures



Temperatures listed are
Break Temperatures, °F

926-033

Paul
11-1-52

Figure 14.
 Standard Deviation vs
 Argonne Sample Average
 Cold Trap Stand 1

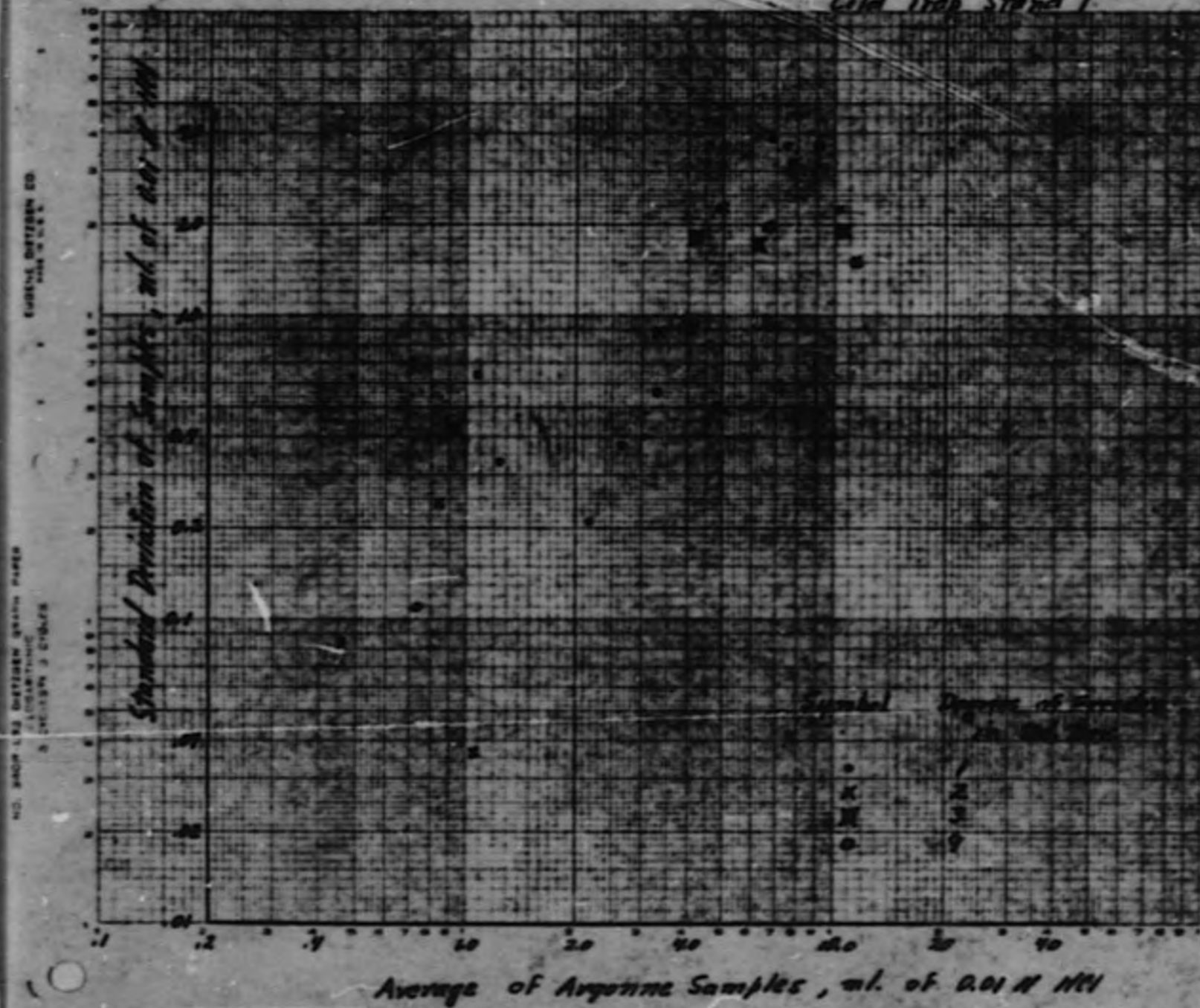


Table I
Argonne Sampler Controls

<u>Control Points</u>	<u>Transfer Line (T/C 2)</u>	<u>Safety Valves (pair) (T/C 1)</u>	<u>Transfer Valves (pair) (T/C 3)</u>	<u>Top of Sampler (T/C 5)</u>	<u>Side of Sampler (Condensing Coil) (T/C 8)</u>
Controlled function	Temperature	Temperature	Temperature	Temperature	Temperature
Required function values	1000°F	1000°F	1000°F	80°F, 500°F, 1000°F	80°F, 300°F
Variable controlled	Electric power to Calrod Heater	Electric power to Glass Shell Heaters	Electric power to Glass Shell Heaters	Electric power to Calrod Heater	Air flow to Cooling Coil
Typical variable values	62 W/ft.	130 W/valve	130 W/valve	off, 55 W, 500 W	off, 4.7 SCFH at 35 psig
Stand I					
Control Operator	Manual	Manual	Manual	Manual	Manual
Control Device	Variac	Variac	Variac	Variac	Air pressure regulator
Stand II					
Control operator	Proportional temp. controller	Proportional temp. controller	Proportional temp. controller	Pneumatic temp. recorder-controller	Pneumatic temp. recorder-controller
Control link	-	-	-	Thermocouple-air converter	Thermocouple-air converter
Control device	Variac	Variac	Variac	Air motor driven variac	Pneumatic air control valve

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Table I - contd.

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<u>Control Points</u>	<u>Insert (Sample Cup) (T/C 6)</u>	<u>Drain Line (T/C 10)</u>	<u>Insert Joint ("O" Ring Coil) (T/C 9)</u>	<u>Transfer Line Connection (11)</u>	<u>Pressure in Sampler (vacuum) (Pressure at Pump)</u>
Controlled function	Temperature	Temperature	Temperature	Temperature	pressure
Required function values	80°F, 800°F	80°F, 300°F	80°F, <150°F	1000°F	<5 microns
Variable controlled	Electric power to special heater	Electric power to heater cord	Air flow to cooling coil	Electric power to Clam Shell heaters	leaks
Typical variable values	10 W	off, 125 W	off, 10.4 SCFH at 80 psig	175 W	1 - 25 microns
Stand I					
Control operator	Manual - on-off temp. controller	Manual	Manual	Manual	Essentially no control
Control device	Variac	Variac	Air pressure regulator	Variac	
Stand II					
Control operator	Pneumatic temp. recorder-controller	Proportional temp. controller	Manual	Manual	Essentially no control
Control link	Thermocouple-air converter	-	-	-	
Control device	Air motor driven Variac	Variac	Air pressure regulator	Variac	

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Table 12 - contd.

Argonne Sampler Data										Plug Indicator Data							
Date	Time	Tech-nician-Sampler		Temp. on Applying Vacuum °F	Htg. Time Min.	Titration Volume ml. acid		Titration net mlg. acid		Hydrochloric acid Concentration Normalcy	Oxygen ppm	Remarks	Time at Break	Total Cooling Rate		Cooling Rate During 2 min. prior to break °F/min.	Starting Flow gpm
						T ₂ - T ₁	T ₁ - T ₂	T ₁ + T ₂	T ₂ - T ₁					°F	Min.		
12-12	0630	M-F-F	I-2	510	60	1.55	6.2	6.4	.001	13		0457	800	9	38	.53	
	0610	M-F-F	II-1	800	50	1.9	7.5	8.25	.001	16	Vacuum late	1825	400	8	56	.48	
12-13	2100	T-M-F	I-2	600	30	.2	3.7	3.75	.01		Not used						
	2103	T-M-F	II-1	510	20	.2	3.75	3.8	.01	323	Used CF of 38	0222	380	3	93	.49	
	0245	M-F-F	I-2	390	50	.25	8.4	8.5	.01		Not used						
	0230	M-F-F	II-1	350	22	.15	4.3	4.35	.01	385	Used CF of 38	0829	420	4	84	.5	
	0832	F-F	I-2	500	30	.4	9.85	10.05	.01		Not used						
	0835	F-F	II-1	500	16	.2	2.3	2.35	.01		Not used	1407	320	4	91	.52	
	1411	F-T-F	I-2	520	40	.25	5.4	5.5	.01		Not used						
1415	F-T-F	II-1	500	40	.15	2.1	2.05	.01				2116	310	9	43	.52	
12-14	0010	M-F	II-1	410	10	.25	2.85	2.9	.01		Distillation temp reached in 10 min.	2400	280	2	140	.53	
	0555	M-F-F	I-2	300	40	.35	11.45	11.65	.01	445	Used CF of 38	0536	300	2	138	.53	
	0957	M-F-F	II-1	300	40	.25	2.65	2.75	.01		Not used						
												0720	300	8	29	.52	
												0819	300	4	-	.53	

Cold Trap Data				
Break Temperature °F	Reading Time	Flow gpm	Thermo-Couple - In.	Temp.
390	0450	.72	84	400
800	1805	.65	84	855
730	2045	1.13	84	860
770	0200	1.13	84	850
800	0820	1.21	84	845
810	-	1.16	84	840
815	2100	1.13	84	935
850	2400	3.3	84	860
830	0530	3.3	84	860
820			84	873
840				
820				
820				

Date	Time	Tech-nician-Sampler		Temp. on Applying Vacuum °F	Htg. Time Min.	Titration Volume ml. Acid - Normalcy		Sample Weight, gm		Remarks
						T ₂ - T ₁	T ₁ - T ₂	Weight	Normalcy	
12-13	2125	T-F	I-2	700	-	-	12.95	.10	2.13	Cup 1/2 full
	2130	T-F	II-1	510	-	-	1.7	.10	.28	Just a drop
12-14	1307	F-F	I-2	-	-	-	40.6	.10	6.6	Cup over full
	1309	F-F	II-1	-	-	-	27.2	.10	3.65	Cup just under full

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APPENDIX

Procedure Used for Argonne Sampler Analysis. (Quoted from Reference 12.)

"Follow the instructions given in this manual.

Remember that the technicians running the stand are responsible for the correct installation and repair of the sampling equipment.

Remember that the sampler parts are not interchangeable. The inserts are marked corresponding to the sampler they fit in.

Use the different strengths of acid solutions according to the following: for convenience, use the acid strength which will use less than one buret fill of acid; for accuracy, use the acid strength which will use more than 5 milliliters for titrating the sample. Base your decision on which strength to use on the previous results given in the log book.

Use only one transfer valve at a time, leaving the other open and labeled as open. When the transfer valve leaks under vacuum, as shown by H₂K being left in the cup after the distillation; mark that valve as leaky and leave it open and labeled as open. Then use the other transfer valve. When both transfer valves leak under vacuum, then close the safety valve next to the sampler and change out the sampler stand. Don't use the safety valve except when changing out the samplers.

Procedure

A. Preheating Period

1. Assume that the sampler was left set up by the previous technician and that the cup and insert are in place, insert heater and thermocouple are screwed in, and that the sampler is all set to go.
2. Prior to turning on the preheat, shut the vacuum stopcock and open the helium stopcock (set at about 2 to 3 psi).
3. Open the pressure relief valve and check that there is helium venting through the valve. If there is no helium venting, take the valve off. If helium vents out the connection, replace the valve. If helium doesn't vent out the connection, then rod lines are necessary, based on past experience, until there is helium venting out the pressure relief valve.
4. Close the helium stopcock and open the vacuum stopcock.
5. While the sampler is being evacuated, adjust the variacs to heat the top of the sampler to 400-500°F, and the discharge line to 300°F. It is assumed that the variacs controlling the transfer valves, safety valves, and transfer line are set to hold these at 1000°F.
6. While the sampler is being heated to these operating temperatures, flush the sampler alternately with helium and evacuate it to the best vacuum attainable at least three times.

The rate of heating should be such that the preheating period takes an hour or less.

B. Transfer of Sample

1. Prior to transferring the sample, shut the vacuum stopcock and open the helium stopcock slowly.
2. Open the pressure relief valve slowly and check that there is helium venting out the relief valve. If there is no helium venting, unplug the sampler before proceeding further.
3. Open the transfer valve and allow about 2 inches of NaK to flow through the sampler into the glass overflow receiver.
4. Close the transfer valve slowly and immediately close the pressure relief valve.

C. Distillation of Sample

1. Open the air valve for the condensing coil (300°F coil), and the air valve for O ring coil (150°F coil).
2. Close the helium stopcock and slowly open the vacuum stopcock.
3. Adjust the variac heating the top of the sampler to maintain a temperature of 1000°F during the distillation period.
4. Adjust the variac heating the insert heater so that the distillation temperature of 800°F is reached within 30 to 45 minutes. Set the controller for the insert heater and adjust the variac so that the 800°F is held within 20°F or less.
5. Adjust the air valve for the condensing coil to maintain a temperature of 300°F within 20°F.
6. Adjust the air valve for the O ring coil to maintain as low a temperature as possible at the flange.
7. Continue the distillation at 800°F for at least 2.5 hours, preferably for 3 hours, counting the start of distillation as that time the insert first reached 800°F.
8. At the end of the distillation period, shut off the variacs to the insert heater and the calrod at the top of the sampler.

D. Titration of Sample

1. When the insert temperature is less than 200°F, shut the vacuum stopcock and slowly open the helium stopcock.
2. Shut off the variac on the discharge line heater.
3. Close the air valves on the condensing coil and on the O ring coil.
4. Place an estimated 25 ml of distilled water into each of two 150 ml breakers and add one drop of methyl orange indicator to each breaker.

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5. Remove the insert from the sampler and transfer the cup from the insert into one of the breakers.
6. Place a clean cup back on the insert and replace the insert in the sampler.
7. From a buret titrate HCl solution to the breaker with the sample cup until the color of the solution becomes pink. This volume of HCl is (V_1).
8. Repeat step 7 with the second breaker containing only the water. This volume of HCl is (V_2).
9. Place both breakers on a hot plate, heat the solutions to a boil and then remove and allow the breakers to cool to about room temperature.
10. Add additional HCl to both solutions until the pink color of the breakers match. Record the volume of HCl added to the sample cup breaker as (V_3) and the volume added to the water breaker as (V_4).
11. Record the information requested in the log book and compute the oxide content of the NaK as shown and using the factor given in the log book.
12. Leave the sampler under vacuum with everything hooked up ready for the next technician.

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D. A. Gardiner's Examination of the Argonne Sampler Data, Reference 15.

The data were divided into five groups depending on the range of plug indicator break temperatures taken in conjunction with the Argonne Sampler analysis.

These groups will be examined in the sequence that they occurred. The net amount of hydrochloric acid titrated for each sample was used in this examination after placing all samples on the equivalent base of using 0.01 N acid. The corresponding oxide content can be calculated for any sample with the conversion factor of 20 ppm O_2 /net ml. acid.

The first group, in the break temperature range of 660°F to 690°F, consists of 10 samples taken between 11-23-56 (0925 hours) and 12-1-56 (1635 hours). Each titration was performed by the same technician who had taken the sample. The data and analysis of variance are as follows:

Table 13

Group I, Argonne Sampler Analysis in Break Temperature Range 660°F to 690°F

Technician	Sampler Position, I Sampler Unit, 3 Net ml. Acid Titrated	Break Temperature °F	Sampler Position, II Sampler Unit, 5 Net ml. Acid Titrated
A	12.7	685	-
F	4.1	660	6.5
F	9.5	680	11.6
L	-	690	8.9
T	-	660	12.6
T	-	680	9.6*
T	-	690	12.1
P	5.3*	680	-

(* run concurrently)

Table 14

Group I, Analysis of Variance of Data in Break Temperature Range 660°F to 690°F

Source	Degrees of Freedom	Mean Squares
Within Position I		
Technician F		
660°F vs 680°	1	14.58000
Among Technicians		
A vs P	1	27.38000
A and P vs F	1	4.84000
Combined estimate	2	16.11000
Within Position II		
Technician F		
660° vs 680°	1	13.00500
Technician T		
660° vs 690°	1	.12500
660° vs 690° vs 680°	1	4.33500
Combined	2	2.23000

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Table 14 - contd.

Source	Degrees of Freedom	Mean Squares
Among Technicians		
F vs L	1	.01500
F and L vs T	1	9.37500
Combined	2	4.69500
Between Sampler Positions (Junk)	1	13.25400
Total	9	

The pertinent features of this group are:

1. Technician F performed as consistently on position I, unit 3 (14.6) as on position II, unit 5 (13.0).
2. The two mean squares reflecting the differences between three samples (0.13, 4.3) for technician T can be pooled because they are not outside the range of random fluctuation with a hypothesis of no real difference among analyses in a temperature range of 30°F. The standard deviation for F on position II, unit 5, is 1.49.
3. No estimate of the variability for all technicians can be made so it is impossible, mathematically, to assess the significance of the observed differences among the technicians. However, these differences are not believed to be significant.
4. The remaining comparison between sampler positions is called "junk" because it has the differences among technicians hopelessly mixed up with it. It reveals nothing of value.

The second group, in the break temperature range of 600°F to 630°F, consists of 17 samples taken between 12-2-56 (0900 hours) and 12-7-56 (0805 hours). As with the first group, each titration was performed by the same technician who took the sample. The data and analysis of variance are as follows:

Table 15

Group II, Argonne Sampler Analysis in Break Temperature Range 600°F to 630°F

Technician	Sampler Position, I Sampler Unit, 3 Net ml. Acid Titrated	Break Temperature °F	Sampler Position, II Sampler Unit, 1 Net ml. Acid Titrated
A	11.8	600	-
A	10.6	610	-
A	11.7	610	-
A	7.8	610	2.5
F	6.4	610	3.7
F	2.55	615	2.9
F	4.85	620	-
F	2.85	630	-
L	5.1	610	-
L	3.5	615	-
L	3.6	620	-
T	10.0	615	-
T	4.9	625	7.9

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Table 16

Group II, Analysis of Variance of Data in Break Temperature Range 600°F to 630°F

Source	Degrees of Freedom	Mean Squares
Within Position I		
600° vs 610°	1	2.34083
Within A at 610°	2	4.04033
Pooled estimate of A variability	3	3.47583
Technician F		
630° vs 615° (average)	1	2.29688
610°, 615°, 620° - linear	1	1.20125
610°, 615°, 620° - quadratic	1	6.30375
Pooled Estimate of F variability	3	3.26729
Technician L		
610°, 615°, 620° - linear	1	1.12500
610°, 615°, 620° - quadratic	1	.48167
Pooled estimate of L variability	2	.80334
Technician T		
615° vs 625°	1	13.00500
Among Technicians		
A vs F	1	79.69531
L vs T	1	13.73633
A and F vs L and T	1	11.09308
Combined estimate	3	34.84157
Within Position II		
A at 610° vs T at 625°	1	15.68000
F at 610° vs F at 615°	1	.32000
A and T vs F	1	3.24000
Combined	3	6.41333
Between Sampler Positions (Junk)	1	17.44982
Total	16	

A more detailed examination is possible because of the greater number of samples. The pertinent features of this second group are:

1. The four samples for technician A, position I, can be pooled because the mean square which reflects the differences among the three 610°F samples (4.04) is larger than the mean square which compares the average of the three 610°F samples with the 600°F sample (2.34). The resulting estimate of the variability for technician A is 3.48 (3 degrees of freedom). The standard deviation for A on position I, unit 3, is 1.86.

2. The four samples for technician F, position I, can be pooled because the mean squares reflecting the various differences (2.30, 1.20, 6.30) are not

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outside the range of random fluctuation with an hypothesis of no real difference among analyses in a temperature range of 20°F. The pooled estimate of the variability for technician F is 3.27 (3 degrees of freedom). The standard deviation for F on position I, unit 3, is 1.81.

3. The three samples for technician L, position I, can be pooled similarly. The two mean squares (0.48, 1.15) combine to make the pooled estimate of the variability of L of 0.80 (2 degrees of freedom). The standard deviation for L on position I, unit 3, is 0.90.

4. Not much reliance can be placed on the estimate of the variability for technician T, position I, of 13.01 (1 degree of freedom). The standard deviation for T on position I, unit 3, is 3.61.

5. These four estimates of the standard deviations of the technicians, 1.86 (A), 1.81 (F), 0.90 (L), and 3.61 (T), cannot be shown to be significantly different. Therefore, the technicians perform about the same with L being most consistent, and T the least consistent. The combined estimate of variability for all four technicians is 3.869 (9 degrees of freedom). The standard deviation for position I, unit 3, is 1.967.

6. With respect to the size, not variability, of the samples, the comparisons noted are a convenience for position I. The mean square for the comparison A vs F (79.70) is certainly not a random fluctuation of the other comparisons, L vs T (13.74) or ASF vs LAF (11.09), which in themselves are not significantly different. Table 15 shows that technician A's samples are higher than those of the other technicians and apparently are significantly so.

7. Not much reliance can be placed on the estimate of the variability for technician F, position II, of 0.32 (1 degree of freedom). The standard deviation, 0.57, is not significantly different from that obtained for F on position I, 1.81.

8. The three comparisons shown within position II do not test significantly different one from another (0.32, 3.24, 15.7).

9. The remaining comparisons between samplers is called "junk" for the same reason as for the first group.

The third group, in the break temperature range of 460°F to 570°F, consists of 12 samples taken between 12-7-56 (1625 hours) and 12-10-56 (0325 hours). With this group, the four technicians took the samples while a common man, P, did all titrations. The data and analysis of variance are as follows:

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Table 17

Group III, Argonne Sampler Analysis in Break Temperature Range 460°F to 570°F

Technician	Sampler Position I net ml. acid titrated		Break Temperature °F	Sampler Position II Sampler Unit 1 net ml. acid titrated
	Unit 2	Unit 3		
A-P	-	-	510	1.02
A-P	-	-	540	1.10
A-P	-	4.0	550	1.05
L-P	-	-	530	1.42
L-P	2.6	-	550	1.95
L-P	-	1.6	570	-
T-P	-	-	460	1.5
T-P	-	0.68	530	-
W-P	1.7	-	545	1.15

Table 18

Group III, Analysis of Variance of Data in Break Temperature Range 460°F to 570°F

Source	Degrees of Freedom	Mean Squares
Position I		
Rig 2		
Between Technicians	1	.40500
Rig 3		
Among Technicians	2	2.95813
Between Units	1	.00385
Position II		
Technician A variability	2	.00142
Technician L variability	1	.14045
Among Technicians	3	.16495
Between Sampler Positions	<u>1</u>	<u>2.01760</u>
Total	11	

Although the break temperature range for this group is excessive, 110°F, no examination is possible unless it is assumed that the size of this range has no effect on the analyses of variance. The pertinent features of this group are:

1. Within position I, there appears to be no difference between units 2 and 3 (0.0038).
2. The source of greatest variability in position I is the difference among the technicians (2.94), particularly with A's tendency to sample high as noted before in group two.

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3. Within position II, the greatest variability is due to differences among technicians (0.16). There is insufficient data to test whether this variability is significantly different from the variability of the individual technicians (0.0014, 0.14).

4. The variability due to differences between the two samplers is large (2.02) and would appear to be significantly so, however, this can only be conjecture.

The fourth group, in the break temperature range of 385°F to 395°F, consists of only 8 samples taken between 12-11-56 (0630 hours) and 12-12-56 (0630 hours). The reliability of the samplers was remarkable because no samples were lost in this group. The two technicians took the samples with the common man, P, doing all the titrations. The data and analysis of variance are as follows:

Table 19

Group VI, Argonne Sampler Analysis in Break Temperature Range 385°F to 395°F

Technician	Sampler Position I Sampler Unit 2 Net ml. acid titrated	Break Temperature °F	Sampler Position II Sampler Unit 1 Net ml. acid titrated
F-P	1.0	385	0.52
F-P	1.47	385	0.40
W-P	0.64	390	0.82
W-P	1.54	395	0.66

Table 20

Group VI, Analysis of Variance of Data in Break Temperature Range 385°F to 395°F

Source	Degrees of Freedom	Mean Squares
Technician F		
Between Sampler Positions	1	.600625
Between Duplicates	1	.030625
Interaction	1	.087025
Pooled estimate of F variability	2	.058825
Technician W		
Between Sampler Positions	1	.122500
Between Temperatures	1	.136900
Interaction	1	.280900
Pooled estimate of w variability	3	.180100
Between Technicians	1	.009125
Total	7	1.2676875

The pertinent features for this fourth group are:

1. The difference between sampler positions within technicians F (0.60) and W (0.12) is not significant.

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2. For technician F, the mean squares (0.60, 0.031, 0.087) can be pooled to give a variability of 0.059 (2 degrees of freedom). The standard deviation for F on position I and II, units 1 and 2, is 0.243.

3. Similarly for technician W, the mean squares (0.12, 0.14, 0.28) can be pooled to give a variability of 0.18 (3 degrees of freedom). The standard deviation for W on positions I and II, units 1 and 2, is 0.43.

4. The difference between the two technicians (0.0091) hardly exists in this group.

The fifth group, in the break temperature range of 730°F to 850°F, consists of 11 samples taken between 12-12-56 (2100 hours) and 12-14-56 (0957 hours). Again, the three technicians took the samples with the common man, F, doing all the titrations. The data and analysis of variance are as follows:

Table 21

Group V, Argonne Sampler Analysis in Break Temperature Range 730°F to 850°F

Technician	Sampler Position I	Break Temperature °F	Sampler Position II
	Sampler Unit 2		Sampler Unit 1
	Net ml. Acid Titrated		Net ml. Acid Titrated
F-P	10.0	800	2.35
F-P	5.5	810	2.05
T-P	3.75	730	3.8
W-P	8.5	770	4.35
W-P	11.63*	830	2.75*
W-P	(8.21)**	850	2.9

(* This pair of samples were cooled to 300°F before the vacuum was applied.)

(** This number was supplied to facilitate the analysis. It in no way biases the results.)

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Table 22

Group V, Analysis of Variance of Data in Break Temperature Range 730°F to 850°F

Source	Degrees of Freedom	Mean Squares
Between Sampler Positions	1	72.09126
Among Technicians	2	5.92178
Technician F		
Between Temperatures	1	5.76000
F variability	<u>1</u>	<u>4.41000</u>
Pooled estimate of F variability	2	5.08500
Technician W		
Among Temperatures	2	1.35452
W variability	<u>1</u>	<u>6.13270</u>
Pooled estimate of W variability	3	2.94725
Sampler Position x Technician Interaction	<u>2</u>	<u>7.45160</u>
Total	10	

With this group also, the range of break temperatures is excessive, 120°F, but the assumption will be made that this range will not affect the results of the examination. The pertinent features of this group are:

1. Although the mean square for the comparison between sampler positions (72.09) is large, it is not larger than would be expected from random fluctuation considering that the sampler-position x technician interaction (7.45) is also large.
2. The sampler-position x technician interaction (7.45) is not significantly high.
3. For technician F, the mean squares of the two comparisons (5.76, 4.41) are enough alike so that they can be pooled to give an estimate of variability of 5.09 (2 degrees of freedom). This is a standard deviation for F on positions I and II, units 1 and 2, of 2.26.
4. Similarly for technician W, the mean squares of the two comparisons (1.35, 6.13) can be pooled to give a variability of 2.95 (3 degrees of freedom). The standard deviation for W on positions I and II, units 1 and 2, is 1.72.
5. If there is a difference among the three technicians, F, T, W, this difference (5.92) is masked by the size of the variability for the technicians F (5.09) and W (2.95).

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6. The variability between technician F and W is not significantly different, so they can be combined to give a pooled estimate of technician variability of 3.80 (5 degrees of freedom). This corresponds to a standard deviation of 1.95.
7. It appears obvious that the magnitude of the break temperature range did not affect the examination of this group.

END

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