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TECHNOLOGY — FEED MATERIALS

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ABSTRACTS

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CHEMISTRY OF FEED MATERIALS

Moving Bed Green Salt Process. Modifications of existing laboratory processes for the extrusion, dehydration and denitration of hydrated uranium trioxide pellets are discussed.

Present start-up procedures for both the reduction and hydrofluorination moving bed reactors are described.

A joint operation is described wherein the consecutive reduction and hydrofluorination of dehydrated uranium trioxide pellets was accomplished in a single multi-stage reactor. One lot of material analyzed 1.07 weight percent uranyl fluoride, 1.12 weight percent ammonium oxalate insoluble (UO_2), the remainder being uranium tetrafluoride. This material had gone through the reduction reactor before the hydrofluorination reactor was put on stream.

Low temperature uranium dioxide (reactor temperatures 500°C or less) was made continuously for at least one volume change of the reductor during this joint run.

About 200 pounds of better than 90 per cent by weight uranium tetrafluoride pellets were rehydrofluorinated in the moving bed using 150 per cent of the theoretical anhydrous hydrofluoric acid rehydrofluorination requirement. After five hours of exposure the extent of improvement was such as to lower its ammonium oxalate insoluble content from 10.2 to 2.9 per cent by weight. The relative non-reactivity of this material was ascribed to high temperatures (arbitrarily defined as greater than 500°C) encountered in the bench scale production of the uranium dioxide feed material used. Sorted samples of a particular lot of the rehydrofluorinated material showed ammonium oxalate insoluble contents as high as 7.9 and as low as 0.4 weight percent.

Steady state operation has been attained in the bench scale equipment during the rehydrofluorination runs. Although this goal has not as yet been realized during the direct hydrofluorination of uranium dioxide feed materials, numerous hydrofluorination runs have been operated continuously for long periods of time. The greatest difficulty experienced appears to be the bridging tendency of this material during hydrofluorination in the bench scale unit.

Heat of Compression of Dimethyl Ether-Boron Trifluoride Complex. The adiabatic compression of dimethyl ether-boron trifluoride complex from 1.0 to 1.25 atmospheres pressure will cause a temperature rise of 7°C . (from $128-135^\circ$). The adiabatic heat of compression was calculated from the heat capacity at constant volume, C_v , which was determined using a flow type calorimeter.

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MOVING BED GREEN SALT PROCESS

R. LeGassie and E. Roszkowski

A process for the production of uranium tetrafluoride by a continuous operation possesses a number of technical and economic advantages^{1,2} and has for the past year and a half been of interest to the New Brunswick Laboratory. A moving bed operation is adaptable to such a continuous process and the developmental work carried out at the laboratories has been reported previously^{3,4,5}. This report will cover the work carried out since the last summary report⁵

The continuous process as proposed consists of four parts. The first is the conditioning of uranium trioxide into pellet form. The second involves the dehydration and denitration of the pellet to reduce the difficulties encountered in the subsequent laboratory treatments. The third is the reduction of the trioxide to the dioxide. The last step is the conversion of the dioxide to the tetrafluoride.

The proper operation of a moving bed depends on a feed material with the proper physical and chemical characteristics. Pellets of hydrated uranium trioxide were prepared at the New Brunswick Laboratory by a process which simulated a continuous operation. This material was then successfully reduced and hydrofluorinated in a moving bed reactor without an excessive amount of attrition.

Preparation of a Feed Material for the Moving Bed Reactor

Pelleting

The large scale production of uranium trioxide pellets was an obstacle to be overcome before extensive developmental work on the moving-bed process could be attempted. The extrusion of hydrated uranium trioxide presented so many technical and economic advantages that the production of pellets by an extrusion process became the primary objective of this early work. The partially successful pellet extrusion tests, at the laboratories of an extrusion equipment supplier, indicated the technical feasibility of such an operation. Since arrangements for the large scale production of pellets could not be made with any outside sources, it became necessary to install at the New Brunswick Laboratory a process for the extrusion of pellets.

A process was developed and installed at the New Brunswick Laboratory with which pellets were made in operations which simulated a continuous operation. Sufficient quantities of 3/16 inch pellets with satisfactory characteristics were produced so that work on the other phases of the moving bed green salt process could be pursued.

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Experimental

The principle items of equipment used in the process consisted of a Welding Engineers Series 2000 Dual Worm Extruder, a Charles Ross Planetary Type Paddle Mixer and an Island Equipment Corporation Moving Belt Conveyor. These items have been described with more detail in previous work⁶.

Uranium trioxide as supplied by the Mallinckrodt Chemical Works was extruded in a manner described in the last summary report⁶. The nitrate content of this material by weight was 0.65% as NO_3^- and the water content was 0.64%. Lots of 15 pounds of this powder, mixed with 650 cc of 25°C water, were used as feed material for the extruder. At shutdown the extruder was purged of the hydrated uranium trioxide by the introduction of some slightly damp Eagle Pitcher Asbestos Insulating Cement after the last quantities of the hydrated uranium trioxide had been fed to the extruder.

Results

The 750 pound lots of uranium trioxide were extruded in two individual runs. The recoveries of 3/16 inch diameter pellets amounted to 420 pounds in the first run and 440 pounds in the second run. During the shutdown at the end of the first run, the material remaining in the extruder set up before the extruder could be taken apart. This set-up in the extruder was the first such experience encountered in making 3/16 inch pellets with the equipment at the New Brunswick Laboratory. During the shutdown, at the end of the second run, when the asbestos cement was used to follow up the hydrated uranium trioxide, the extruder continued to operate and the hydrated uranium trioxide was purged from the extruder to such an extent that no difficulty was encountered in dismantling the extruding mechanism.

Conclusions

The process as described for the production of hydrated uranium trioxide pellets is satisfactory for use as a supply of material for the studies of the other phases of the moving bed green salt process.

An inert purging material can be successfully used to purge the extruder of hydrated uranium trioxide. This prevents the set-up of the undischarged oxide which otherwise would be present in the unit at the end of operations. Thus the use of a purge simplifies the dismantling operation.

Dehydration

The presence of water and nitrate in the extruded pellets of the hydrated uranium trioxide constitutes a potential hazard to a successful countercurrent reduction of uranium trioxide in a moving bed green salt process. As indicated in previous work ^{7,8}, nitrates in the feed material for the moving bed countercurrent reductor are not desirable. Their presence led to a condition wherein the nitrate content built up due to its continued recycling in the cooler parts of the reductor. The resulting uranyl nitrate hexahydrate, formed from the reaction of the nitrate and the feed material, produced bridges in the reactor due to the chemical reconstitution of the surface material of the pellets. This restriction on the feed material to the countercurrent reductor was further emphasized by the successful reductions without chemical bridge formation of low nitrate materials produced after batch dehydration and denitration. On this basis, a continuous moving bed dehydrator for cocurrent operation as described in previous reports ^{9,10}, was developed.

Experimental

The moving bed dehydrator previously described ^{9,10}, has been used in this work with the following modifications:

Rockwell slide valves were replaced by cock valves.

Micro-klean air filter, Cl-2230, was replaced by Micro-klean air filter 1BIG

Moore pressure controller was replaced by 1/2 inch Crane pressure regulator with a 5-30 pound pressure range.

Orifice and Manometer flow indicator was replaced by a Taylor Flowrator No. 3F 3/8-16-5/70 with a 3/8 inch stainless steel ball float.

The diameter of the off gas line has been increased by use of 1/2 inch copper tubing.

The dehydration and denitration of the hydrated uranium trioxide pellets were conducted in the manner discussed in a previous report ¹⁰ with the exception that the reactor wall temperature for one run was reduced to 750°F. The power to the unit was shut off for overnight periods so that the materials in the reactor overnight would not be subjected to continued high temperatures.

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Results

Two lots of material were dehydrated. One lot of 422 pounds of material was dehydrated with a wall temperature of 800°F and a solids rate of about 12 pounds per hour. This run was made before the above listed modifications were made and the weight loss amounted to 8.6%. A second lot of 400 pounds of material was treated after the above modifications were made with a wall temperature of 750°F and a solids rate of about 12 pounds per hour. The weight loss in this case amounted to 7.8%. The product of the second run had a more uniform color thus indicating the greater consistency of treatment afforded to the various portions of the material. This uniformity of treatment was assured because of the gas phase control obtained by the modifications discussed above.

Conclusions

Feed material satisfactory for reduction in a moving bed reactor has been successfully prepared by the dehydration and denitration of hydrated uranium trioxide pellets. The concurrent flow of the gas and solid phases constitutes a satisfactory arrangement. The process as arranged at the New Brunswick Laboratory appears to be satisfactory.

Chemical Conversions in the Moving Bed Reactor

The chemical conversions of single pellets of dehydrated uranium trioxide to uranium dioxide and thence to uranium tetrafluoride have been extensively studied on a laboratory scale^{3,4,5}. As previously reported, a bench scale moving bed reactor has been built at the New Brunswick Laboratory to investigate operational problems associated with larger scale conversions of bulk quantities of pellets. The basic problems being considered in the operation of this equipment include:

- (1) the attainability of continuous and uniform flow of solids in the reactor,
- (2) the controllability of reaction rates and reaction temperatures,
- (3) the completeness of conversion as a function of other variables in the process.

In an attempt to isolate some of the variables involved, the process, although conceived as a continuous operation in a single reactor, has been broken down into separate steps. During the period covered by this report, however, one continuous run was made in which the reduction and

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hydrofluorination steps were carried out consecutively in a multi-stage reactor. A repetition of this run is not planned because of the limitations of the available equipment. It was intended merely as a demonstration of the possibilities and problems of such a combined operation.

Also included in this report are descriptions of two runs in which "upgrading" or additional hydrofluorination of below specification grade uranium tetrafluoride pellets was attempted.

The work covered here is part of a continuing developmental program on the process^{1,2}. Earlier reports^{3,4,5} are available to provide such additional background material and detail on the process and equipment as may be desired.

Experimental

The present moving bed reactor consists of a two-foot high reacting zone made of four-inch Schedule 40 nickel pipe. Above this is a two foot high solids preheater made of two-inch Schedule 40 nickel pipe. Heat can be supplied by zoned heating coils and can be removed through external air cooling coils wound around the reactor. Inlet and exit gas lines are provided as needed with their associated inlet gas preheaters and exit gas disposal facilities.

For the combined run in which the uranium trioxide was progressively reduced and then hydrofluorinated in a single passage through the reactor system, this equipment was modified as shown in Figure 1. An additional unit was mounted above the reactor and solids preheater. This new unit became the new solids preheater. The former preheater was used as the new reduction reactor. The unit below that was used as the hydrofluorination reactor.

The gas flow systems were as shown on the drawing. A differential manometer reading in inches of water was connected across the hydrogen inlet and HF exit lines (pressure taps A and B on the drawing). Operation of the unit was predicated on the assumption that the directions and ratios of the various gas flows inside the reactor could be controlled by controlling the inlet gas pressures. The differential manometer, plus another manometer reading the pressure on the reductor exit gas line (pressure tap C on the drawing), thus would serve as an indication to the operator as to where the gases being fed to and being generated in the reactor were going.

Solids flow was controlled as usual by a variable speed vane meter at the bottom of the hydrofluorination section. This continually removed product from the bottom of the reactor. Normal gravity flow was relied upon to keep the reactors full and to bring new feed down into the re-

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FIGURE 1. MOVING BED REACTOR FOR JOINT REDUCTION AND HYDROFLUORINATION OF DEHYDRATED UO_3 SHOWING ARRANGEMENT OF GAS LINES AND PRESSURE TAPS

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acting zone. If the flow of pellets downward in any section of the reactor stopped, the unit was said to have bridged. Since control of the reaction depended upon a steady and consistent composition gradient in the bed of pellets, any factor which tended to disrupt this gradient, as bridging did, was very undesirable.

Six thermocouples were provided along each reactor so that reaction temperatures could be observed and controlled.

Product lots were withdrawn from the reactor storage hopper each hour and individually sampled and packaged.

For the joint reduction and hydrofluorination run the reactor shown in Figure 1 was loaded with 1/4 inch tabular alumina balls up to the reductor exit gas line. Dehydrated uranium trioxide pellets were loaded as feed material from that point upwards to the top of the pre-heater. After the reactor reached operating temperatures (400-500°C), the bed movement downwards was started and a gas stream of hydrogen and water was fed to the bottom of the reduction section. Inasmuch as the hydrofluoric acid exit gas line was closed off, the reductant gas flow proceeded normally up the reductor and countercurrent to the slowly falling solids.

The start-up of the reduction process, based upon past experience consisted of feeding 30% of the stoichiometric hydrogen required for the reaction at a concentration of about 20 mole percent, the diluent being water. As the reductor was gradually filled with reacting pellets, the feed gas composition was slowly increased to 130% of the stoichiometric hydrogen required at 100 mole percent hydrogen. This should have established the composition gradient in the bed and prevented the reaction from running out of control since fresh uranium trioxide feed would never have been in contact with a highly concentrated hydrogen gas phase.

As the converted uranium dioxide pellets left the reductor and entered the top of the hydrofluorinator, the hydrofluoric acid exit gas line was opened and the hydrofluorinating gas feed stream was admitted to the bottom of the reactor. In a similar manner, its composition at first consisted of 50% of the stoichiometric hydrofluoric acid required at a concentration of 40 mole percent. Water was again used as the diluent. The gas feed stream gradually changed to the final operating quantity of 110 to 120 percent of the stoichiometric hydrofluoric acid requirement at a concentration of 85 mole percent.

The production rate of uranium tetrafluoride was held to about 4.0 pounds per hour and was partially limited by the capacities of the heat transfer apparatus available to control the reactor body temperature for both the reductor and hydrofluorinator. The temperature ranges of the reacting materials desired in this particular run were from 400 to 500°C.

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Another factor influencing the setting of the solids flow rate was the retention time of the pellets in the two reactors. A rate of 4.0 pounds per hour of uranium tetrafluoride was sufficient to provide a retention time for the solids of about 3.5 hours in the reductor and 7 hours in the hydrofluorinator. These retention times are thought at present to be on the conservative side and should, therefore, allow for any end cooling effects in the reactor arising from insufficient insulation or failure of the bottom heating coils.

Kinetic data indicates that the temperature at which the uranium trioxide is reduced has an appreciable effect on the rate of hydrofluorination of the resulting uranium dioxide. Present efforts have been centered on limiting the maximum temperatures obtained in reduction to 500°C. Under uncontrolled conditions they have reached 1000°C. Using 500°C as the dividing line, the last two separate hydrofluorination runs produced two batches of uranium tetrafluoride, one made from low temperature and one from high temperature uranium dioxide. These are listed as Runs 1 and 2 respectively in Figure 2.

The two runs (3 and 5), in which below specification grade uranium tetrafluoride was upgraded, were started up with alumina balls in the reactor. Because the pellets being fed were already highly converted, no start-up procedure with a diluent was used. Instead the feed gas was introduced immediately at a concentration of 100 mole percent hydrofluoric acid at a rate equivalent to 150 percent of the amount theoretically required to completely convert the low grade material. The feed rate was 11 pounds per hour and sufficed for a retention time of 2.5 hours.

The off gases from the hydrofluorinator were analyzed as often as it was thought to be necessary, at least once an hour. If the feed rates were steady, fluctuations in the off gas composition could indicate a change in the degree of conversion in the bed.

In the second of these rehydrofluorination runs, all of the feed was screened before being charged. Material passing through a 20 mesh screen was discarded. The sources of the various feeds for this run are shown in Figure 2. It will be noted that three separate feed materials were charged into the hydrofluorinator in Run 5, the second rehydrofluorinating operation. The first charge was a composite of poor material from the joint run previously discussed. The second charge was a mixture of uranium tetrafluoride pellets previously made from uranium dioxide, produced in both high and low temperature reductions. The third charge was a recycle of the product obtained in this run from the rehydrofluorination of the first batch of feed material.

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Results and Conclusions

Joint Operation The joint reduction and hydrofluorination run was started off successfully. For 2.5 hours no trouble was encountered in the reduction process and temperatures were steadily maintained below 500°C. Then a temporary jamming of the product withdrawal meter caused the reaction to get out of control for a short period of time after the solids flow was resumed.

The hydrofluorination reaction was similarly started off successfully. The third lot of material produced from the joint reactor assayed as specification grade uranium tetrafluoride. The actual analysis showed 1.07% uranyl fluoride and 1.12% ammonium oxalate insoluble as impurities. This material had gone through the reductor before the hydrofluorination section was put on stream.

Thereafter, with both units running simultaneously, the internal distribution of gas flows could not properly be maintained. The differential manometer did not prove to be sufficiently sensitive to permit the proper adjustments of inlet gas pressures to be made. The unit operated in one of two ways:

1. In one, most of the hydrogen feed left the reactor through the hydrofluoric acid exit gas line. Thus, insufficient reduction of the uranium trioxide was obtained. When this unreduced material entered the hydrofluorinator, uranyl fluoride was produced.
2. In the other, sufficient hydrogen was supplied to the reductor and the proper hydrogen flow was maintained. However, some of the hydrofluoric acid and water produced in the hydrofluorinator entered the reductor. This not only diluted the reducing stream but, because of the water content, served to depress slightly the forward force of the reduction potential. The hydrofluoric acid in this contaminant stream may also have formed uranyl fluoride in the reductor.

The product produced from this joint run, therefore, with the exception of the one good lot described above, varied in uranyl fluoride content from 0.5 to 15.0 percent and in ammonium oxalate insoluble content from 3.2 to 19.1 percent.

Sensitive control of gas flows could undoubtedly be obtained with additional modifications of the apparatus. At present no further plans for other joint runs have been made. However, additional reduction and hydrofluorination runs will be made separately, as before, so that the problems of each operation may be studied in a single environment with better control of the variables involved.

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An important fact could be seen in this joint run. Material containing uranyl fluoride was extremely soft and productive of fines. These caused frequent mechanical bridging of the pellets in the hydrofluorinator.

Finally, the single batch of specification grade uranium tetrafluoride made (1 hour's product, 6.5 pounds) may be indicative of the product that could have been obtained if gas flows could have been controlled.

Rehydrofluorination Table 1 shows the average benefactions experienced in the two rehydrofluorinating runs. All of the data is based on a retention time of 2.5 hours using 150% of the theoretical anhydrous hydrofluoric acid requirement. Reactor temperatures varied from 400-500°C.

TABLE 1

REHYDROFLUORINATION OF URANIUM TETRAFLUORIDE IN THE MOVING BED REACTOR
(Material Analysis)

Run No.	UF ₄ ^(a)	UO ₂ F ₂ ^(b)	UO ₂ ^(c)	Total
3 Feed	89.1	0.6	10.2	99.9
Product	93.8	0.2	5.8	99.8
5 Feed	86.5	2.0	11.4	99.9
Product	91.3	0.7	6.8	98.8
5 Feed	93.8	0.2	5.8	99.8
Product		< 0.1	2.9	

(a.) based on U⁺⁴ analysis.

(b.) determined by solubility in methanol.

(c.) AOI, ammonium oxalate insoluble.

As can be seen the conversion rates obtained are self consistent for these materials.

In an attempt to determine the reason for the low conversion rates obtained, one batch of material was divided into two different lots. The color of the pellet was used as the criterion. Those pellets that appeared uniformly colored were placed in one lot. Those which were heavily marked with darkish regions were placed in the other. The analyses are given in Table 2.

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TABLE 2

ANALYSES OF SORTED LOTS OF URANIUM TETRAFLUORIDE PELLETS

<u>Sample No.</u>	<u>Description</u>	<u>Weight % AOI</u>
5 SG 1	All green	0.4
5 SG 2	Green and darker	7.9
5 CG 18	Original lot	2.7

The material was originally a mixture of uranium tetrafluoride pellets made from two separate batches of uranium dioxide, one being low temperature and the other high temperature material. It is postulated that the highly unreactive pellets, those that show local surface markings, are derived from the high temperature reduction. It may be noted that, mathematically, the two extremes must be combined in the ratio of 2.1 to 1.0 in order to produce the average analysis of the original lot. The ratio of low to high temperature material in the original feed material is about 1.6 to 1.0. This figure may serve as a tentative indication of the differences in reactivity to the hydrofluorination step which may be realized as a result of temperature variations in the reduction step.

The fines in any given batch of product were found to be consistently less highly converted. This indicates that a natural sifting downward of the smaller size particles in the reactor may be experienced. If their retention time is less than that of the major portion of the material, it is natural to expect a lower degree of chemical conversion. For this reason, excessive attrition of the pellets or excessive pounding or vibrating of the apparatus can be detrimental to the process as a whole, especially as regards the quality of product being produced. In addition, in the bench scale reactor at least, a large accumulation of fines is conducive to mechanical bridging and thus the disruption of the solids and gas phase composition gradients.

With low temperature uranium dioxide as a feed material, the sorted sample cited above indicates the possibility of obtaining specification grade uranium tetrafluoride using present operational techniques in the bench scale moving bed reactor.

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Summary

Attempts to consecutively reduce and hydrofluorinate uranium trioxide pellets in the bench scale **multi-stage moving bed reactor** were unsuccessful because of limitations of the available equipment. The production of one lot of specification grade uranium tetrafluoride from this joint reactor early in the run suggested the feasibility of the operation if proper control of the gas phase compositions in the reactor could be realized. At present, no further joint runs of this nature are projected.

Attempts to upgrade some 260 pounds of uranium tetrafluoride (about 10% uranium dioxide by weight) revealed that the material was relatively unreactive when compared to the uranium dioxide utilized in kinetic studies of the hydrofluorination reaction. This was probably due to uncontrolled high reaction temperatures encountered in the moving bed reduction runs. Analysis of one lot of rehydrofluorinated moving bed uranium tetrafluoride pellets showed a range of uranium dioxide content, from 0.4 to 7.9 weight percent. These fractions corresponded roughly to the amount of uranium dioxide present in the raw material which was produced at reduction temperatures below and above 500°C respectively. The average value of this particular lot was 2.7 weight percent uranium dioxide.

Work planned for the immediate future will include the attempted reduction and hydrofluorination of uranium trioxide in the temperature range of 400-500°C only. These two reactions will be carried out separately so as to provide better control and evaluation of the many factors which influence the physical and chemical characteristics of materials encountered in these moving bed operations.

Moving Bed Green Salt Process - Summary

Although the effect of all the variables has not been completely evaluated, the following operations have been successfully performed at the New Brunswick Laboratory.

1. A commercial extruder has been able to provide sufficient uranium trioxide pellets to supply the requirements of the bench scale moving bed reactor.
2. A moving bed dehydrator has produced uranium trioxide acceptable for use as a feed material for the bench scale reductor.
3. Uranium dioxide pellets have been produced assaying 98% by weight or better.

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HEAT OF COMPRESSION OF DIMETHYL ETHER-BORON TRIFLUORIDE COMPLEX

L. C. Nelson and J. E. Hudgens

INTRODUCTION

In the design of distillation equipment for the fractionation of boron isotopes, two methods of transferring the dimethyl ether-boron trifluoride complex from one column to the next were considered: (1) the transfer of the dimethyl ether-boron trifluoride complex from one tower to the next by condensation of the vapor and pumping the liquid, in which case the heat required to revaporize the complex was known or (2) by pumping the vapor directly. In the second case the pressure of the vapor must be increased to 1.25 atmospheres to overcome the pressure head of the second tower. It was necessary to determine the heat which would be obtained from such an adiabatic compression. This calculation required a determination of heat capacity at constant volume, C_v , for the temperature range 128-137°C.

Heat capacity can be determined by using infrared spectrometer data and quantum mechanical calculations. However, for the dimethyl ether-boron trifluoride complex no data was available and assumptions concerning the dissociation of the complex would make the calculations difficult ^{1,2}.

A heat conductivity apparatus has been used to determine the heat capacity of gases from their thermal conductivity at low pressures. The apparatus, however, must be accurately made and an accurate resistance thermometer used.

Heat capacity measurements at constant pressure, C_p , are made extensively by means of a flow calorimeter. With these calorimeters, the temperature and the flow rates of the gases must be rigidly controlled ³. However, a flow calorimeter designed by Bennewitz and Schulze ⁴ offered the simplest method of determination and this apparatus does not require accurate temperature and flow control to achieve a reasonable accuracy.

CALCULATIONS

Flow calorimeters of the type used by Bennewitz and Schulze give the heat capacity at constant pressure, C_p , but as we can see from equation [2] the heat capacity at constant volume, C_v , must be calculated.

$$C_p - C_v = R$$

[1]

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The heat of compression was calculated by the equation,⁶

$$\ln T_2 = - \frac{R}{C_v} \ln \left(\frac{V_2}{V_1} \right) \ln T_1 \quad [2]$$

where R is the gas constant in liter atmospheres, C_v is the heat capacity at constant volume in calories/mole/°C, V₁ and V₂ are the initial and final volumes in liters, and T₁ and T₂ are the initial and final temperatures in degrees K respectively. Equation [2] also requires a knowledge of V₂ the final volume of the gas but under the conditions of the problem only the final pressure is known. Therefore, a simple application of Boyle's and Charles' laws gives an equation for these conditions:

$$1.0 \frac{V_1}{V_2} \times \frac{T_2}{T_1} = 1.25 \quad [3]$$

Solving for V₂ and substituting in equation [2] gives the following which can be used to solve for T₂ if C_v and T₁ are known.

$$\ln T_2 = \frac{\frac{R}{C_v} \ln 1.25 T_1 + \ln T_1}{\frac{R}{C_v} + 1} \quad [4]$$

EXPERIMENTAL

A flow type calorimeter similar to that designed by Bennewitz and Schulze as shown in Figure 1 was constructed and operated as follows. The liquid was vaporized in the boiler using an electric heating mantle to maintain constant boiling. The vapor was passed up the side tube past thermocouple F, through the brass blocks, past thermocouple E, was condensed in the condenser, and returned to the boiler via the three way stopcock and trap. The temperatures of the brass blocks C and D were measured by thermocouples, and were maintained at 137° and 128°C. respectively by means of heating coils. In order to determine the flow rate, the condensate was collected in the weighing bulb for measured time intervals.

If no gas was flowing through the tube, the temperature changed linearly with the distance along A. When, however, gas was flowing, the temperature drop was measured with considerable precision by the multijunction thermocouple between the calorimeter tube and "blind tube" B, which was constructed of the same material. The temperature drop, zero with no gases flowing, was proportional to the flow rate and heat capacity of the gas if the temperature between the brass blocks was constant.

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FIGURE 1
FLOW CALORIMETER

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Using steam as a standard⁷, a series of runs were made and the total energy W for each run was calculated using

$$W \text{ (calories/sec)} = c_p \text{ (cal/g)} \Delta T(^{\circ}\text{C}) \times F \text{ (g/sec)} \quad [5]$$

where F is the flow rate. The energy W was plotted against the temperature drop as read directly in millivolts, between points A and B and gave the curve as shown in Figure 2.

Then the complex was run at a known constant flow rate. The temperature difference was measured between A and B, the total energy W was found from Figure 2 and the heat capacity calculated using equation [5].

RESULTS

The results are shown in Table 1 along with the calculated probable error. Air and a constant boiling 20% hydrochloric acid solution were run to check the accuracy of the calibration and results. The data are shown in Table 1.

CONCLUSIONS

The heat capacity of dimethyl ether-boron trifluoride complex was determined over the temperature range 128-137°C to be 0.42 ± 0.07 calories per gram, per degree centigrade at constant pressure and 0.40 ± 0.07 calories per gram, per degree centigrade at constant volume. The probable errors given for these determinations were calculated from the statistical spread of the determination and were not less than the combined errors contributed by the experimental measurements. The temperature increase for a compression of the vapor at 128°C from 1.00 to 1.25 atmospheres was calculated to be 7°C.

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FIGURE 2. CALIBRATION CURVE FOR STEAM

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TABLE 1
HEAT CAPACITY DATA

<u>Material</u>	<u>C_p (cal/g/°C)</u>	<u>Probable Error</u>	<u>Temperature °C</u>
Complex	0.50	--	128-137
Complex	0.34	--	128-137
Complex	0.42	--	128-137
Average	0.42	±0.07	
Air	0.236	--	128-137
Air	0.244	--	128-137
Air (literature) ⁸	0.240	--	120
20% <chem>HCl</chem>	0.163	--	128-137
20% <chem>HCl</chem> (literature) ⁹	0.185	--	10-190

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ISOTOPIC ANALYSIS OF BORON

J. C. Hasson and J. E. Hudgens

Studies concerning the enrichment of the dimethyl ether-boron trifluoride complex in the B^{10} isotope by means of countercurrent isotope separation distillation columns are now being made. In order to determine the conditions under which the column operates most efficiently and also to make routine production checks, it is necessary to have a fairly rapid method for analyzing the products of this column for percent B^{10} .

An isotope exchange method which was developed by Judson¹ was previously used in this laboratory². However, this method becomes increasingly inaccurate as the concentration of impurities increases (i.e. the boron trifluoride added to the samples reacts with the impurities instead of participating in an isotope exchange) and this makes it impossible to determine the value of A in the formula:

$$\%B^{11} = \left(\frac{Z}{1+Z} - \frac{Y}{1+Y} \right) 100A + \left(\frac{Z/K}{1+Z/K} \right) 100$$

Z is the B^{11}/B^{10} ratio in the added boron trifluoride after it has been equilibrated with the sample. Y is the B^{11}/B^{10} ratio in the added boron trifluoride before it has been equilibrated with the sample. A is the number of moles of added boron trifluoride divided by the number of moles of dimethyl ether-boron trifluoride, and K is the equilibrium constant for the reaction:

Consequently a new procedure was needed so that routine samples, which usually contain decomposition and corrosion products, could be analyzed.

The recovery of boron trifluoride from organic complexes by precipitating the ammonia boron trifluoride complex, originally described in a patent by Gleason³ and investigated in early work by Kirshenbaum, Sabi, and Schutz⁴, was investigated and finally adopted at the New Brunswick Laboratory. Since Kirshenbaum, et al. had to use concentrated sulfuric acid to obtain 80-85 % yields, they did not think the process had any advantage over the calcium fluoride method³ from which they obtained 95-98 % yields. However, the calcium fluoride method required incubation times of 24 hours to form the calcium fluoride-boron trifluoride complex, and this was much too long for the present needs.

The object of this investigation was to find a method of analysis which would be satisfactory when impurities were present. The Gleason procedure³ seemed to meet this requirement. It was therefore investigated with particular attention given to the following three considerations:

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1. Fractionation in the chemical steps, which could cause the ratio B^{11}/B^{10} to be different in the compound to be introduced into the mass spectrometer than it was in the original sample compound. If the difference between the samples containing a high and low percent B^{10} is to be an accurate gauge of the amount of separation of the isotopes in the production process the fractionation in the analytical procedure should be small (i.e. the plot of the percent fractionation versus percent B^{10} can only be considered linear over a small range and, therefore, the high and low percent B^{10} material will both be affected to the same extent only if the fractionation is small).
2. The time of analysis should be as short as possible so that if the column is running inefficiently it can be readjusted as quickly as possible on the basis of an analysis.
3. The yield of boron trifluoride would be as large as possible as greater yields reduce the effect of fractionation. Consequently a small tendency to fractionate (i.e. the B^{10} compounds reacting slightly faster than the B^{11} compounds) can be compensated for by large yields.

APPARATUS

A Consolidated-Nier Isotope Ratio Mass Spectrometer was used to analyze the released boron trifluoride. Some changes were made in this instrument in order to adapt it to the analysis of boron trifluoride. The thermionic emission source which had been used for solid samples was replaced by an electron bombardment ion source. The D. C. collector amplifier was replaced by an A. C. vibrating reed electrometer which has greater stability, due to its amplifying of an A. C. rather than a D. C. signal, and which was more sensitive than the D.C. amplifier. A Brown Recorder was attached to the vibrating reed output. The all metal leak was replaced by a glass leak to reduce the effect of "memory" due to boron trifluoride forming coordination compounds on the metal parts of the spectrometer.

In addition to the mass spectrometer a glass high vacuum system was needed to collect and measure the released boron trifluoride. This system is shown in Figure 1. In the glass vacuum system E was a dry ice trap used to keep sulfur trioxide out of the system; F was a refluxing condenser packed with glass beads to keep the fuming sulfuric acid from distilling out of the reaction flask G; H was a liquid air trap used to protect the Cenco Hy-vac pump, and B, a mercury manometer, was used to measure the yield of boron trifluoride. Equilibration flask D and the manifold above all the stopcocks constituted a known volume used

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FIGURE 1. GLASS VACUUM SYSTEM

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for measuring the yield in conjunction with the manometer B. C was the sample flask for the mass spectrometer. G was the reaction flask in which the ammonia boron trifluoride and the sulfuric acid were heated. A was a thermocouple gauge which was used to measure the vacuum (below 100 microns was considered sufficient).

EXPERIMENTAL

Twenty cubic centimeters of diethyl ether were added to 0.5 ml of unknown sample. The solution was centrifuged to remove the solid impurities. Ammonia was added above the surface of the solution, as the solution was shaken, until the solution became turbid. The solution was then boiled in a water bath at 55°C. to remove the diethyl ether. Fuming sulfuric acid was added to the resulting white precipitate in the reaction flask while the reaction flask was immersed in liquid air to prevent the reaction from starting.

The reaction flask was attached to the vacuum system which was pumped on, while the reaction mixture was held at liquid air temperature, until the vacuum was less than 100 microns. The flask was then heated gently at first and then more vigorously until no more gas was evolved as indicated by the manometer. During the heating, D was immersed in liquid air to trap the evolved boron trifluoride. When the evolution of boron trifluoride had ceased the yield was measured and recorded. The percent B^{10} was determined by the mass spectrometer.

The preceding method was carried out with varying amounts of 6N, 36N and fuming sulfuric acid so that a combination of these two factors (i.e. concentrations and amount) giving the greatest yield of boron trifluoride could be determined.

Since the mass spectrometer showed memory effects even with the glass leak it was necessary to adopt a standard procedure in deciding when the measured percent B^{10} was correct. It was decided that successive introductions of a new sample were to be made with three ratios being taken for each introduction until a constant ratio, within experimental error, was obtained.

The mass spectrometer was flushed with ammonia between introductions to aid in the removal of boron trifluoride which was causing the memory. The strongest addition compound of boron trifluoride is the ammonia boron trifluoride compound, and ammonia has been reported⁵ to aid the removal of memory by replacing the metal oxide which holds boron trifluoride to the wall of the apparatus with ammonia.

Once a constant ratio was reached, ten B^{11} and ten B^{10} peaks were taken. The average ratio of these ten readings was then converted to percent B^{10} and taken as the final value for that particular sample

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aliquot. The boron trifluoride for the next sample aliquot was then introduced after the system had been flushed with ammonia. Ten readings were then taken. The same procedure was followed for the third and last sample aliquot. The average value of the three sets of readings was taken as the result for that sample.

RESULTS

At least three aliquots of each sample were taken. The largest yields were obtained using 5 ml of fuming sulfuric acid. These yields were between 70% and 80%. Part of this variation in the yield can be attributed to the fact that the sample was not 100 % dimethyl ether-boron trifluoride so that the theoretical yield calculated by assuming that the aliquot taken was 100 % dimethyl ether-boron trifluoride was in many cases too high.

A plot of yield versus percent B^{10} normalized to the percent B^{10} at 65% yield gave a random scatter of points about the abscissa 1.000 indicating freedom from measurable fractionation. This plot is shown in Figure 2.

Agreement of the results between different aliquots of the same sample was much better in the present method than that in the Isotope Exchange Method. The probable error was calculated by averaging the ratios of the three aliquots and calculating the probable error of the determination of a single aliquot. This was equal to or less than ± 0.2 atom percent for all the samples.

The time required for the analysis is at the present determined by the memory effect in the mass spectrometer. The total time for all the steps involved in releasing the boron trifluoride from the dimethyl ether-boron trifluoride including the cleaning of trap E and condenser F in between different samples is about an hour. Trap E and condenser F must be cleaned between different samples to eliminate memory effect.

DISCUSSION

The fact that a random scatter was obtained in the plot of yield versus normalized percent B^{10} was taken to indicate that measurable fractionation did not occur. If measurable fractionation had occurred the plotted points would have aligned themselves in a band (a band rather than a curve due to the tendency of the normalizing process to flatten out the data) with a slope different from zero which would have crossed the abscissa 1.000 at 65 percent yield.

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FIGURE 2.

In the Isotopic Exchange Method the difference in results between different aliquots of the same sample was in many cases too large to be accounted for by the limits of precision of the mass spectrometer alone. This larger difference was probably due to small amounts of impurities. Although no measurable fractionation occurs in the process of removing the boron trifluoride from the dimethyl ether-boron trifluoride, this does not mean that the ratios obtained by the mass spectrometer are the accurate isotope ratios, although they are precise. The value which is accurate is the amount of separation between the products of the bottom and the top of the column for any particular run; this conclusion assumes that fractionation effects the high and low percent B^{10} 's equally, which would seem reasonable considering the small range (76-84%) over which we are working. One of the reasons for fractionation is the leak. The exact amount of this fractionation need not be known, for by making the leak long enough (i.e. long enough to prevent back diffusion) it can be kept at a constant value, thus this will introduce a systematic error which will cause the same change in the high and low B^{10} percent material and, therefore, not effect the difference between them.

CONCLUSIONS

A procedure has been described which makes it possible to analyze samples of dimethyl ether-boron trifluoride containing large amounts of impurities. Since some of the samples from actual operation of the boron isotope separation column may contain large amounts of decomposition and corrosion products the accurate analysis of the samples resulting from the operation of these columns can be more easily accomplished by using this method.

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THE DETERMINATION OF EXTREMELY LOW CONCENTRATIONS OF BORON IN URANIUM

H. G. Yuster and H. R. Mullin

The need for a more sensitive quantitative spectrographic method for the determination of boron in uranium has long been realized. The present routine procedure has fair accuracy to approximately 0.15 parts per million, but samples now being analyzed might possibly be a factor of ten lower than this figure in boron concentration. This procedure utilizes the carrier distillation method of Scribner and Mullin¹ which serves to suppress the complex uranium spectrum so that trace impurities can be evaluated. Sensitivity improvement, with this method, would include the use of a larger sample, a shorter sample burning time to decrease the amount of background, a change in carrier material, and improvement in the densitometry of the photographic plate. It should be emphasized that all of these variations in the standard procedure, with the exception of densitometry, will limit the use of the photographic plate for the analysis of elements other than boron. Therefore, it appears that improvement in the means of determining the degree of blackness of spectral lines is the most advantageous method of acquiring improvement in sensitivity.

Improvement in densitometry would include not only an increase in sensitivity of the measuring instrument, but also a means of differentiating between spectral line and background blackness - - - a definite necessity when estimating small amounts of impurities by the photographic plate method. The average microdensitometer measures the maximum blackness of a line, but does not permit simultaneous viewing of line and background so that reasonably accurate corrections for background contributions can be made. Furthermore, the lack of sensitivity of this type of densitometer would limit its use.

With the publication of work by Davis and Webb², it appeared that the boron sensitivity problem might possibly be closer to a solution. These investigators described the conversion of a commercial densitometer to one capable of tracing line and background peaks on the face of a cathode-ray tube. In addition it was possible to evaluate extremely weak spectral lines on a photographic plate.

The reasons for this work were to find the lowest boron concentration obtainable when using routine procedures and the cathode-ray tube densitometer, and then to establish the lower limit of quantitative determination when using special procedures.

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APPARATUS AND MATERIALS

In the work reported at this time, a cathode ray tube densitometer described in a previous report³ was used. This type of instrument has good sensitivity, traces both line and background on a long persistence screen, and permits rapid estimations of true peak heights.

A Baird 3 meter grating spectrograph was used throughout the work and the spectrographic procedure followed that recommended by Scribner and Mullin which utilizes a carrier distillation method. In the methods using indium oxide in place of gallium oxide as a carrier, the pre-arc and exposure time had to be changed in order to fit the difference in burning characteristics. When a sample of more than 100 mg. was used, for the purpose of increasing sensitivity, it was necessary to vary pre-arc and exposure time for the two different carriers. It was necessary to devise an electrode of larger dimensions so that a larger sample could be used in the sensitivity work. This also meant that a new sample punch had to be made for the larger electrode. Dimensions of the larger electrode are shown in Figure 1. The pedestal hole is of the same size as in the electrodes used for the routine procedure.

Electrode For 225 mg. Sample

FIGURE 1.

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The preparation of standards required very careful control to avoid contamination. First, it was necessary to find a base material which was extremely low in boron content. This was accomplished by selecting a black uranium oxide in which the boron could not be detected visually and checking this sample on the cathode-ray tube densitometer. The standards were prepared by first making a master standard containing 1 ppm of boron by the addition of sodium borate in solution form to the base material. This standard was dried and ignited in a platinum dish at 700°C for two hours. The resulting master standard was used to make the other standards of lower concentrations by dilution with the pure base material. (The master standard, base material, and later carrier materials, were ground together in an agate mortar until uniformity resulted.) At least five grams of each standard were made so that contributions due to contamination would be low due to the amount of the standard handled. The carrier materials were examined on the spectrograph, before using, to determine their boron purity.

EXPERIMENTAL

It was decided to investigate spectral line saturation and amplifier linearity because of the possibility of their occurrence in the case of high background and low line intensities. This might easily occur when gallium oxide is used as a carrier, because of the presence of a heavy gallium line close to the boron line to be measured. Generally, amplifier non-linearity results from line saturation and is due to amplifier overloading. Regardless of which effect predominates, the end effect is the same, i. e., a non-linear plot of peak height versus concentration is obtained. Therefore, it was decided to make a study of the combined effects, with no attempt made to separate the two phenomena.

Since the usable portion of the cathode ray tube face had a scale measuring only 40 divisions, it was sometimes necessary to make measurements which were off-scale. When off-scale readings occurred a factor of two decrease in sensitivity could be obtained with (1) the use of dimming switch on the light source, or (2) with an appropriate setting of the gain control. In this manner a factor of four decrease would be obtained and on-scale readings equivalent to 160 could be realized.

At present gallium oxide is being used in the New Brunswick Laboratory as a carrier material in the quantitative estimation of trace impurities in uranium. The standard procedure was first employed to see if sufficient sensitivity were possible. This would not necessitate the preparation of new mixes or making of special runs, and the resulting plate could be used for visual or densitometric estimations of the other elements in the routine manner. A special procedure (modified-1) was then tried, which used the same mix as the first, but conditions

of pre-arcing and total exposure time were changed in order to cut down on the gallium background appearing under the boron line. Both methods used the standard electrode and their comparative conditions are listed in Table 1. A third procedure (modified-2), for a larger size sample, is also listed in this table.

TABLE 1.

<u>Procedure</u>	<u>Pre-arc (sec.)</u>	<u>Exposure (sec)</u>	<u>Sample wt. (mg)</u>
Standard	5	35	100
Modified-1	8	20	100
Modified-2	15	30	225

Indium oxide was first tried as a carrier material in some preliminary work ³ in order to cut down on background near the boron line. Good burning qualities were obtained when a 5% mix was used. The conditions for its use are listed in Table 2.

TABLE 2.

<u>Procedure</u>	<u>Pre-arc (sec)</u>	<u>Exposure (sec)</u>	<u>Sample wt. (mg)</u>	<u>Grating Mask</u>
Modified-3	5	20	100	3/4 "
Modified-4	12	25	225	1/2 "

RESULTS

The results with the use of gallium oxide in the modified-2 method are listed in Table 3. These results were used to illustrate line saturation and amplifier non-linearity in the graph shown in Figure 2. Values are peak height in terms of scale divisions on the face of the cathode-ray tube.

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FIGURE 2.

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TABLE 3.

<u>Boron Conc. (ppm)</u>	<u>Sector Steps</u>			
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
1.44	52	122	128	54
0.92	50	104	92	27
0.62	45	92	62	13.5
0.25	39	50	15	2
0.10	25	27	5	-

A listing of the results with gallium oxide as the carrier in standard determinations is shown in Table 4. A graph of these results is shown in Figure 3.

TABLE 4.

<u>Boron Concentration (ppm)</u>	<u>Peak Height</u>
0.200	48.5
0.100	25.5
0.075	18.5
0.050	14.5

Table 5 shows the results obtained when the modified-1 procedure of pre-arc and exposure was tried in a regular burn, and Figure 4 shows a graph of the results.

TABLE 5.

<u>Boron Concentration (ppm)</u>	<u>Peak Height</u>
0.100	34.5
0.075	27.5
0.050	21.5
0.035	17.5
0.020	12.5
0.010	8 (?)
Blank	6 (?)

When indium oxide was used as a carrier in the modified-3 procedure, the results listed in Table 6 were obtained. The figures in the third column of the table resulted from a different set of standards having a higher boron value in the blank material. Graphs of these two sets of results are shown in Figure 5.

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FIGURE 3.

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Concentration of Boron in ppm.

FIGURE 4.

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FIGURE 5.

TABLE 6.

<u>Boron Concentration (ppm)</u>	<u>B/Sn</u>	<u>B/Sn</u>
0.100	0.83	1.27
0.075	0.62	0.97
0.050	0.44	0.71
0.035	0.33	-
0.020	0.26	0.48
0.010	0.19	0.38
Blank	0.14	0.31

The values obtained when 225 mg of sample having indium oxide as the carrier and burned in a modified electrode, are listed in Table 7. These results are graphically shown in Figure 6.

TABLE 7.

<u>Boron Concentration (ppm)</u>	<u>B/Sn</u>
0.100	1.14
0.075	0.84
0.050	0.63
0.035	0.52
0.020	0.40
0.010	0.28
Blank	0.26

DISCUSSION OF RESULTS

The results of the tests on line saturation and amplifier linearity merely confirms what had been known. The high boron standards and a large size sample were used mainly for emphasis. It is interesting to note that the steps, numbered on the graph when arranged in order gives something resembling a characteristic curve with the toe being represented by step 4 and the heel by step 1. Steps 2 and 3 fall quite closely into their respective positions. In all cases background contributions due to the gallium line were extremely large and corrections for this effect very difficult. The increase in line intensity with the use of a larger sample is completely offset by the heavy gallium background.

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FIGURE 6.

From the results, it appears that the gallium oxide carrier in a standard burn did not increase the boron sensitivity appreciably. None of the runs were usable due to the difficulty in background correction below a concentration of 0.05 ppm, which in reality is 0.07 ppm when the correction for the blank is made. This value is slightly under the limit of visual detection and only a factor of two better than the method using standard densitometry.

The variations of pre-arc and exposure times in the above procedure gave encouraging results though, and all but one of the standards were usable in the preparation of the standard curve shown in Figure 4. The last standard and the blank material gave doubtful readings due to the difficulty in making their background corrections.

When indium oxide was used as a carrier the background problem under the boron line was simplified. It will be noticed that tin was used as an internal standard and boron-tin ratios were used in the drawing of the standard curves. It served two purposes. First, no corrections were necessary if a change in amplifier gain occurred in the densitometer, as both tin and boron lines would be affected equally. Second, its presence helped take care of any differences in burns in that its rate of volatilization approximates that of boron. No background corrections were applied in the reading of both lines, because the slight background that does occur is the result of continuum.

In all cases the data, resulting from the use of indium oxide as carrier material, were good. Considering that the lowest standard went down to 0.01 ppm, which actually was 0.03 ppm when the blank correction is made, there was no necessity of making the runs with 225 mg. of sample. These runs only proved, that if it were necessary, an increase in sensitivity could be realized with the larger samples without increasing the background appreciably. With reference to Figure 5 it is seen that the values for the blank, denoted by an X, fall very close to the curve. In all cases, irregardless of the method, the extrapolated blank reading was approximately 0.02 ppm.

An illustration of how background corrections were made is shown in Figure 7. In this figure ABD is the tracing obtained for the boron line, and ADE is the approximate tracing of the background occurring under the boron line due to the gallium line. The reading of the length of the line BC was taken as the corrected peak height. When taking readings a straight edge was laid across the points A and D and the line BC read from the scale on the face of the cathode ray tube.

A final check of the procedure was made on three uranium metals and three orange oxides samples which had been previously analyzed by the usual routine procedures. The results of these six samples are tabulated in Table 8. The first three samples listed are the metals, and the last three are the orange oxides.

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FIGURE 7. BACKGROUND CORRECTION METHOD

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TABLE 8.

NBL Sample No.	Concentration in ppm	
	Modified-1	Routine Procedure
B-3636	0.14	< 0.2
B-3639	0.08 ₅	< 0.2
B-3640	0.07 ₂	< 0.2
B-3638	0.06 ₂	not detected
B-3650	0.09 ₆	< 0.2
B-3651	0.13	< 0.2

An examination of Table 8 will show that good agreement was obtained with the use of the two methods. It has been standard practice to report results falling between the limits of 0.15 and 0.19 ppm. as 0.2 ppm. Furthermore, any value below 0.15 down to the point of visual detection would be designated as < 0.2 ppm. Any value of 0.20 or above would be reported as such; eg. 0.22 ppm. Sample numbers B 3638 and B 3640 confirms that the limit of visual detection is approximately 0.07 ppm.

SUMMARY

The lowest boron value of 0.15 ppm now reported can be improved upon by a factor of two, when using routine spectrographic techniques and a more sensitive densitometer. Background difficulties can be partially overcome by a special run on the same type of carrier mixture with an increase in sensitivity by a factor of five. Further increases in sensitivity can only be realized by using special techniques and a special carrier material such as indium oxide. All readings must be made with a sensitive densitometer, such as the cathode ray tube type. The difficulty of the preparation and handling of standards cannot be overemphasized. This would also include the securing of clean blank material, and preparation of pure carrier materials.

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SERVICE ANALYSIS OF SPECTROCHEMICAL SECTION

During the quarter ending September 30, 1953, 370 samples were analyzed by the spectrochemical section. On these samples there were 2870 quantitative estimations and determinations made plus several thousand qualitative checks. The types of samples received are shown in the following table:

<u>Material</u>	<u>Samples</u>
U	195
Be	4
Mg	57
Ores	65
Th	6
Misc. incl. R. E.	43

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