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UNITED STATES ATOMIC ENERGY COMMISSION

ANALYSIS OF DIMETHYL ETHER-BORON TRIFLUORIDE

By
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Whiting, Indiana

Technical Information Extension, Oak Ridge, Tennessee

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ERRATA FOR REPORT A-2359

The following changes should be made to report A-2359, "Analysis of Dimethyl Ether-Boron Trifluoride", by Charles M. Judson, October 26, 1945:

1. On pages 11 and 12 modification number 9 should follow number 8 directly.

2. On page 12 in the third line of the next to the last paragraph "constructed" should be changed to "constricted".

3. On page 25 in the third line of the fourth paragraph, "or dioxane" should be "in dioxane".

4. On page 33 at the end of the fifth paragraph add the words "of Figure 3" to read "curve I and curve IV of Figure 3".

5. The third paragraph on page 42 should be changed to read:

"Two ml. of the $(CH_3)_2O:BF_3$ to be analyzed are added to a 100 ml. volumetric flask with a ST 13 stopper. Ten ml. of Baker's reagent grade glacial acetic acid are added from an automatic burette. The drying tube containing Drierite is attached to the flask with a ST 14/35 joint. The flask is placed in an electric oven at 70°C. for two hours and removed. The flask is cooled to room temperature, then placed in ice water. When cool, 4 ml. of pyridine are added and the solution is titrated with Karl Fischer reagent in the usual way."

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ANALYSIS OF DIMETHYL ETHER-BORON TRIFLUORIDE

I. SUMMARY

The methods used for laboratory control analyses in the operation of a unit for the separation of boron isotopes by the fractionation of dimethyl ether-boron trifluoride complex are described and evaluated.

Procedures developed at the S.A.M. Laboratories of Columbia University for the determination of boron, fluorine, and dimethyl ether in this complex have been applied with only minor modifications. Procedures for the determination of impurities in the complex have been developed. Hydroxyl and alkoxyl groups are determined by methods employing the Karl Fischer reagent. Metals are determined by the conventional methods of colorimetric, volumetric, and gravimetric analysis. Conductivity measurements are also used in analytical control. Consideration has been given to other impurities which might be expected to appear in the complex.

Data have been presented to show the precision and accuracy of the methods. Consideration has been given to the chemical information obtainable from the analyses.

Most of the methods are capable of further improvement. A great deal of further information is required before the chemical reactions of the impurities in dimethyl ether-boron trifluoride complex are completely understood. Some suggestions have been made as to the directions which further investigations might take.

II. INTRODUCTION

In connection with the operation of a large scale unit for the separation of boron isotopes[1] by fractionation of dimethyl ether-boron trifluoride, several analytical methods for the routine chemical analysis of dimethyl ether-boron trifluoride were developed by the S.A.M. Laboratories during the initial stages of the project. After construction was complete and operation of the fractionation unit was started, difficulties were encountered due to contamination of dimethyl ether-boron trifluoride with water. This was caused by leakage of water from tubes which were part of the steam heating and water cooling systems, and leakage of air into the unit due to the fact that it was operated under vacuum. As a result of these difficulties, it was necessary to develop analytical methods for determination of impurities in the dimethyl ether-boron trifluoride. These methods were developed largely at the initiative of the S.A.M. Laboratories, although a considerable amount of work was also necessary at this laboratory. It is the purpose of this report to present all of the analytical procedures which have been used in the operation of the fractionation unit at this location.

In determining the purity of $(CH_3)_2O:BF_3$, the sodium hydroxide titration method developed by Judson and Turner[2] for the determination of boron and fluorine has been found satisfactory. By making suitable blank corrections, the evolution method developed by Kirshenbaum[3] for the determination of dimethyl ether has been found satisfactory.

Methods for the determination of impurities which might be expected to be present have been investigated. These impurities might be present in the $(CH_3)_2O$ or the BF_3 used to prepare the $(CH_3)_2O:BF_3$, or they might come from thermal decomposition of the $(CH_3)_2O:BF_3$, from the reaction of H_2O with $(CH_3)_2O:BF_3$, or from the corrosion of metals by $(CH_3)_2O:BF_3$ and its hydrolysis products.

The use of the Karl Fischer reagent to titrate H_2O in $(CH_3)_2O:BF_3$ was suggested by Kirshenbaum.[4] This titration has been found useful for estimating the extent of contamination by H_2O even though the constituent determined is not H_2O but the sum of H_2O plus B-OH or B=O compounds which react with CH_3OH in the reagent to form H_2O. Evidence has been obtained to indicate that all B-OH and B=O compounds are titrated in the procedure used.

A procedure based on that of Bryant, Mitchell and Smith[5] for the determination of alcohols with the Karl Fischer reagent has been developed for the determination of B-OCH$_3$ groups plus CH_3OH. This determination is intended for following the decomposition of $(CH_3)_2O:BF_3$ in which a compound with the empirical formula $(BF_2OCH_3)_3$ is formed.

Conductivity measurements have been used for control analyses as suggested by Sabi.[6] The measurement is easily made, although the significance of the observed conductivity is, unfortunately, not clearly understood. Although a number of substances other than water are known to contribute to the conductivity of $(CH_3)_2O:BF_3$, the conductivity at a given point in the fractionation unit is reasonably constant and a sudden increase in the conductivity at any point may be taken as an indication that contamination is taking place. Furthermore, the absolute value of the conductivity at any point should be a measure of certain not entirely identified impurities present in the complex at that point.

An etch test for hydrogen fluoride depending on the reaction of HF with glass has been suggested by Kirshenbaum.[7] The method does not appear to be applicable to the systems encountered in the plant.

The metals found in plant $(CH_3)_2O:BF_3$ are determined in order to estimate the rate of corrosion. Iron is always present in considerable amounts and is determined regularly. Nickel is always present in traces from the corrosion of monel, but the copper concentration is generally negligible. When $(CH_3)_2O:BF_3$ is handled in brass instead of monel, zinc is found in solution rather than nickel.

Together with the analyses of the vent gases[8] and the determination of the isotopic concentrations[9,10], these chemical analyses provide the data necessary for control of the operation of the fractionation unit. From the chemical analyses made on samples taken regularly from each operating column, information is obtained concerning the extent and nature of the decomposition, the leakage of water, and the corrosion of the equipment. The chemical analyses are also used for a determination of the purity of the $(CH_3)_2O:BF_3$ used as feed, and of the final redistilled product, and for determining the total boron concentration in solution in connection with the rapid method used for the determination of isotopic concentrations.[10]

It is possible that other impurities not accounted for are present in the $(CH_3)_2O:BF_3$ used. Analyses of the BF_3 and the $(CH_3)_2O$ used[11,12] to make the $(CH_3)_2O:BF_3$ used as feed for the fractionation unit show that SO_2, SO_3, SiF_4, amines, aldehydes and unsaturated hydrocarbons may be present. No analyses for these constituents in $(CH_3)_2O:BF_3$ have been made.

Each of these procedures is described in detail below. A general description of the method is given first. This is followed by a detailed description of the manipulations involved. Finally a critical examination of the method is presented. The reliability of the method, possible variations in the procedure, and the significance of the analyses obtained by the method are considered in detail.

The casual reader will find it possible to obtain a general idea of the methods by reading the introductory section to each of the analytical procedures.

III. SAMPLING

A. Introduction

Sample valves must be provided at regular intervals on the fractionation unit. Since the system operates under reduced pressure these valves must be equipped so that samples can be withdrawn into a bottle evacuated to a still lower pressure, or the sample valves must be located where the pressure is greater than atmospheric.

These sample valves must be located so that representative samples can be obtained without draining large amounts of material. They must be protected when not in use so that access of water is minimized. The location, construction, and use of sample valves which fulfill these requirements are described in detail below.

DEVICE FOR SAMPLING UNDER VACUUM

To Sampling Valve

3-Way Cock

To High Vacuum

Thread for Pipe Cap

Tapered To fit Sample Bottle ₿ 29/12

To Atmosphere
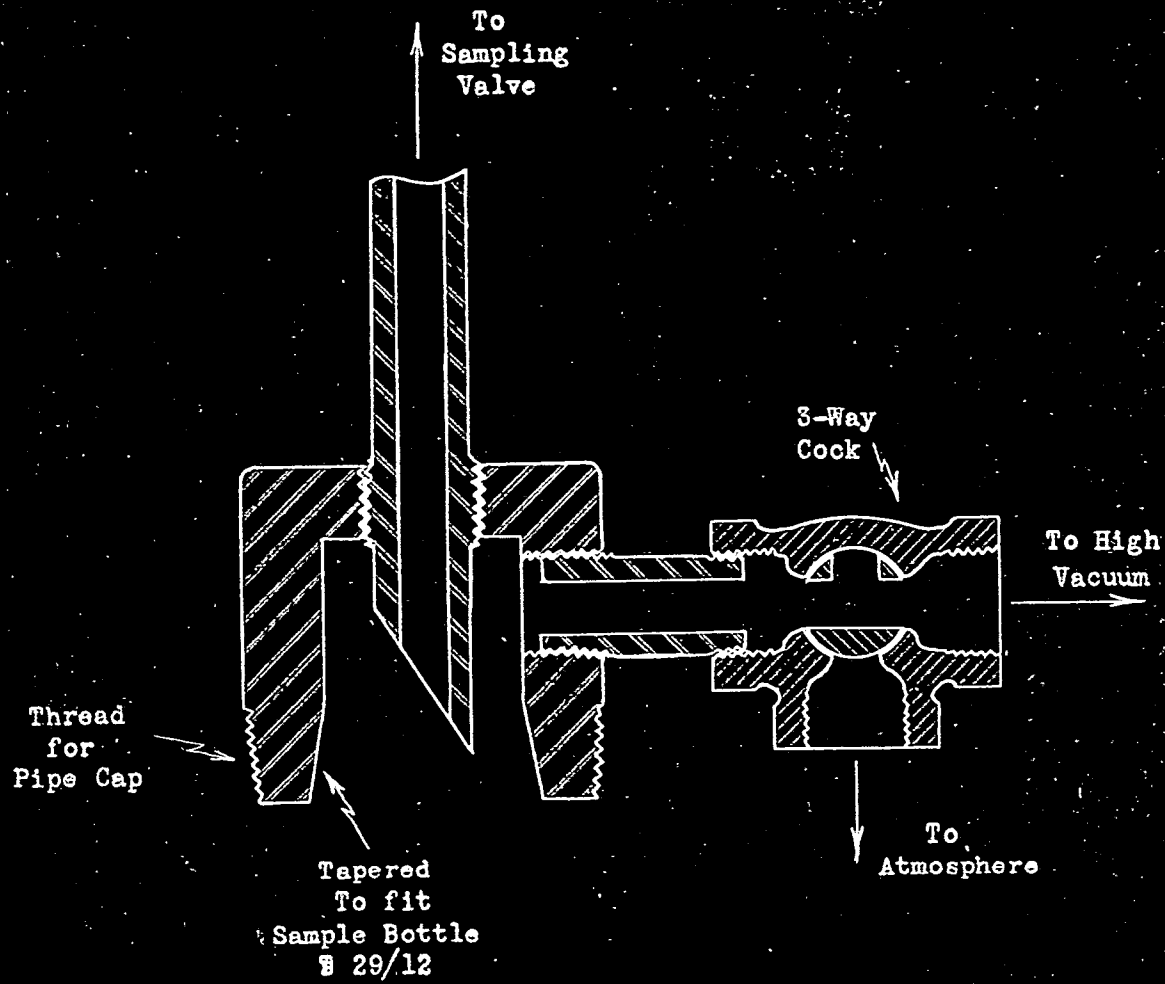
Figure 1

10-19-45
J.W.

B. Description of Sample Points

Location of sample valves.—Each column of the fractionation unit is equipped with three sample valves, one on the reflux line from the condenser at the top of the column, one on the liquid return line from the bottom of the column to the reboiler, and one on the discharge from the pump which transfers the liquid from the reboiler to the top of the next column and at the same time circulates the liquid in the reboiler. Provisions were originally made so that sample valves could be attached to each redistributor plate, and connections are available for this purpose. The redistributor sample valves, however, have not been used in regular operation of the unit.

Except for the pump discharge sample point, these valves are constructed so that a sample can be removed from the column when it is under reduced pressure. The pump discharge sample point has a simple valve since the pressure at this point is above atmospheric.

The top and bottom sample points are used only in testing the column. When the columns are in cross-flow operation these sample points are plugged off and the valves coated with glyptal to prevent potential air leaks. The bottom sample points are preferentially used instead of the pump discharge points in testing a column because the samples from the pump discharge points contain considerable amounts of impurities and consequently the determination of isotopic concentrations is more difficult.

In normal operation only the pump discharge sample points are used. In addition, a sample valve is located on the overhead draw-off line from the first column, the line through which the more volatile $(CH_3)_2O:B^{11}F_3$ is withdrawn. This point is located at the lowest point in the line so that the liquid is under pressure and a vacuum sample valve is not required. Sample valves are also located on the tank in which the feed $(CH_3)_2O:BF_3$ is evacuated to remove excess $(CH_3)_2O$, the pot of the still from which the product, $(CH_3)_2O:B^{10}F_3$, is redistilled,[13] and the mixing tank from which the redistilled product is taken for shipment.

The locations of sample valves on the fractionation unit are shown on the flow chart of the report describing the construction and operation of the unit.[14] The location of the sample points in the feed system and the product still are described in separate reports on these units.[13,15]

Construction and operation of sample valves.—The sample point used for removing samples from evacuated parts of the fractionation unit is shown in Figure 1. The sample point is machined to fit a 29/12 standard taper ground glass joint. A 25 x 50 mm. weighing bottle with a 29/12 ST joint can therefore be attached as shown in the diagram. Two inch pipe threads are provided so that a cover can be screwed onto the open end to prevent access of moisture to the inside of the sample point when it is not in use. A three-way brass plug valve is provided so that the sample bottle can be evacuated to a pressure lower than that of the part of the unit to be sampled. A 1/4 inch steel needle valve connecting to the unit may then be opened to permit the liquid being sampled to flow into the sample bottle. The needle valve is closed and the three way valve is afterward turned to admit atmospheric air into the bottle, thus breaking the vacuum and permitting removal of the sample bottle.

A weighed sample of $(CH_3)_2O:BF_3$ is dissolved in water and a suitable aliquot taken. Calcium chloride is added so that the fluorine will be removed as calcium fluoride as rapidly as fluoride ion is formed. The solution is titrated with standard 0.3 N. sodium hydroxide to a methyl red end point. After 30 minutes reflux, the solution is again neutralized, one cc. of 0.3 N. sodium hydroxide added in excess, and the reflux continued for three hours. In this way the boron trifluoride is quantitatively hydrolysed. By back titrating to the methyl red end point, the total amount of sodium hydroxide consumed is determined. Mannitol is added converting the boric acid to a stronger complex acid which is titrated to phenolphthalein end point in the absence of carbon dioxide, using 0.1 N. sodium hydroxide solution.

Modifications in procedure.—A few modifications of the S.A.M. procedure[2] have been introduced as a matter of convenience but the method as originally written is still accepted as a standard.

1. The empty weighing tube is more conveniently weighed before filling than after dissolving the sample.

2. It has been found that it is not necessary to cool the water before dissolving the sample.

3. It has been realized that 0.3 N. hydrochloric acid is not necessary and that 0.1 N. acid can be used as runback for both 0.1 N. and 0.3 N. sodium hydroxide solutions.

4. Filtration of the calcium fluoride has been omitted. This step was optional in the procedure specified by the S.A.M. Laboratories.

5. The original procedure specified that the solution be titrated hot after the first 30 minutes refluxing period. This was intended to mean that it was permissible to titrate hot, not that it was required. It has been general practice to cool the solution before titrating.

6. The calculated values of the per cent $(CH_3)_2O:BF_3$ are corrected for the isotopic weights of boron as determined separately.

7. Small corrections are subtracted from the observed titers when iron is found to be present.

8. Modified techniques for weighing the sample have been developed for routine determinations, but these are not considered a part of the official method.

The details of the procedure followed are described below. The precision of the method has been shown by duplicate determinations to be ± 0.1%. In evaluating the method, the various modifications introduced are discussed. The basis of determining the corrections for isotopic concentrations and for the presence of iron is shown. Another modified procedure which led to unsatisfactory results is described. The difficulty encountered is used to emphasize the importance of following the specified procedure rigorously. Methods

The valve used for taking samples where the liquid is under a positive pressure is simply a 1/4 inch steel needle valve fitted with a 1/4 inch cap to prevent access of moisture when the valve is not being used.

In all cases the sample points are located so that the pipe between the sample valve and the line being sampled is as short as possible. This reduces holdup in the line and makes it possible to obtain representative samples without draining large quantities of material.

C. Sampling Procedure

In order to obtain representative samples, it is necessary that moisture be kept out of the sample line and valve, and sufficient material must be drained before taking the sample.

On the other hand it is important that the amount of sample be kept to a minimum because of the value of the product. It is also necessary that any excess of the concentrated B^{10} over that needed in analyses be saved. The analytical procedures used have been developed with these points in mind. Actually the procedures used do not use up a significant amount of material as long as a small conductivity cell is used and the sample left from the conductivity measurement is saved.

The 25 x 50 mm. weighing bottles used for vacuum type sample points are also used for taking samples from the pressure type sample points. One bottle full is ordinarily drained before taking a sample for analysis. When the isotopic concentration is sufficiently high to warrant it, the drainings are saved and eventually returned to the unit. If, for special reasons, larger samples are required, 250 ml. flasks are used. A 29/12 ST joint suitable for use with the vacuum sample point may be made by shortening a 29/42 ST joint. This joint may be sealed to a 250 ml. flask or attached to a ST glass stoppered flask through another joint.

IV. BORON AND FLUORINE DETERMINATIONS

A. Introduction

The procedure which has been used is essentially that developed at the S.A.M. Laboratories by Judson and Turner.[2] In this procedure fluorine is determined by quantitative hydrolysis of boron trifluoride with sodium hydroxide, and boron is determined after the addition of mannitol by a sodium hydroxide titration of the boric acid in the hydrolyzed solution. The procedure for fluorine is based on the Harshaw Company fluorine determination in boron trifluoride as developed by Swinehart and Flisik.[11] These investigators did not attempt to determine boron.

used by other investigators for the analysis of BF_3 are evaluated. Consideration is given to possible further modifications in the method described. The conclusion is reached that further modifications are not called for and that the accuracy of the procedure used is satisfactory. A correction in the data presented in Report A-1299[2] to show the error introduced by allowing the BF_3 solutions to stand is noted. The conclusions originally drawn are not affected.

9. Nitrogen is bubbled in to remove CO_2 before adjusting the indicator for the beginning of the second titration.

B. Procedure for Determination of Boron and Fluorine

Reagents and equipment.--The reagents required are:

0.1 N. standard carbonate free sodium hydroxide
0.3 N. standard carbonate free sodium hydroxide
0.1 N. standard hydrochloric acid
20% solution of reagent grade calcium chloride
0.02% methyl red indicator in 60% ethanol
0.1% phenolphthalein indicator in 50% ethanol

The procedure used for the preparation and use of carbonate free sodium hydroxide for boron titrations is that described by Judson.[16] Fifty per cent sodium hydroxide is filtered with a Buchner fritted disc filter and diluted with carbon dioxide free water. Baker's reagent grade sodium hydroxide and calcium chloride are recommended.

Kimble exax pipets and burets are used. Pyrex brand volumetric flasks are used. Calibration of the volumetric glassware has not been found necessary. Geissler type aide-filling burets are used with A. H. Thomas Co. Lubriseal stopcock lubricant.

Analysis of sample.--A 20 cm. length of 10 mm. pyrex glass tubing is sealed at one end and blown out slightly into a bulb. This weighing tube is dried in an electric oven, cooled, and weighed. The tube is constructed about 5 cm. from the open end and pulled out to a capillary. This capillary is bent into the form of a U. The sample of $(CH_3)_2O:BF_3$ is taken by cooling the tube with liquid nitrogen while the end of the capillary is submerged in the liquid to be analysed. The tube is filled so that it contains about 2.8 grams, the amount required to give a 25 cc. titer with 0.30 N. and 0.10 N. sodium hydroxide solutions. The tube is removed from the liquid nitrogen and the expanding air is permitted to drive out the liquid remaining in the capillary. The capillary is warmed to remove the remaining liquid and then sealed off. The tube and the two sealed off pieces are allowed to cool, wiped with a towel, and weighed.

The sample tube is scratched with a glass cutter, about 9 cm. from the end, the liquid frozen with liquid nitrogen, and the tube opened by breaking between the fingers. Both pieces are immediately dropped into a 500 ml. ST stoppered iodine flask containing 100 ml. of distilled water. The flask is stoppered, a little water is placed in the lip of the flask, and the flask is shaken gently until evolution of ether around the stopper has ceased. The pieces of the sample tube are removed with a glass rod, and washed quantitatively. The solution is transferred quantitatively to a 250 ml. ST stoppered volumetric flask. The flask is filled to the mark and the solution mixed. The titration should be started within an hour of the time the sample is dissolved.
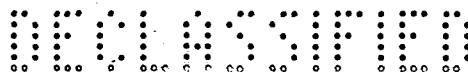
Twenty five ml. of 20% calcium chloride solution are placed in a 500 ml. Erlenmyer flask having a 24/40 ST joint. Four drops of 0.02% methyl red solution are added. The solution is acidified, and then made barely alkaline with 0.1 N. sodium hydroxide. A sample of 25 ml. of the 250 ml. in the volumetric flask is transferred with a pipet to the Erlenmyer containing the neutralized calcium chloride. This solution is titrated to the appearance of a red color with standard 0.3 N. carbonate free sodium hydroxide. The flask is attached to a 300 mm. pyrex Graham spiral condenser having a 24/40 ST joint, and refluxed for 30 minutes ± 5 minutes. A Silex electrical heating element is used to heat the solution. The solution is cooled immediately with running cold water and again titrated to the appearance of a red color, this time adding 1.0 ml. in excess. The solution is then refluxed for three hours ± 10 minutes. If the color has faded, methyl red is again added until the intensity of the color is as nearly as possible the same as at the beginning of the analysis. The solution is then back titrated with 0.1 N standard hydrochloric acid solution to the first appearance of the red color. An excess of acid must not be added. Finally the solution is titrated to the alkaline side of the indicator. From the amount of acid and alkali added to this point, the fluorine present as boron trifluoride is calculated.

The solution is made slightly acid and nitrogen is bubbled through the solution for ten minutes to remove carbon dioxide. The nitrogen bubbling is continued during the titration and the wash water used must have been boiled just before use to remove carbon dioxide. More acid is added if necessary, and the solution is again adjusted to the alkaline side of the indicator with 0.1 N. sodium hydroxide solution. The initial buret reading for the boron titration is taken at this point.

One gram of mannitol is added for every 10 mg. of boron present as calculated from the fluorine titration. This generally amounts to 3 grams. After the addition of mannitol, 6 drops of 0.1% phenolphthalein indicator are added. The solution is titrated to the first appearance of the pink phenolphthalein color. It will probably not be necessary to use a run-back acid solution in this titration, but the 0.1 N. hydrochloric acid may be used if necessary. The amount of sodium hydroxide used in this second titration is a measure of the boron present.

Standardization of solutions.—Mallinckrodt primary standard potassium acid phthalate is dried at 110°C. and kept in a desiccator over P_2O_5. The acid phthalate should be satisfactory without drying, but it is advisable to take every possible precaution. For the standardization of 0.3 N. sodium hydroxide, 1.8 grams of acid phthalate are weighed into a 125 ml. Erlenmyer flask, and dissolved in 25 ml. of water. Nitrogen is bubbled through the solution for ten minutes, 4 drops of 0.1% phenolphthalein are added and the solution is titrated with the standard sodium hydroxide to the appearance of a faint pink color. Freshly boiled wash water is used during the titration and the nitrogen bubbling is continued. Standard hydrochloric acid is used as a run-back if necessary. For 0.1 N. sodium hydroxide, 0.6 gram of acid phthalate is used.

Figure 2
Corrections for Iron
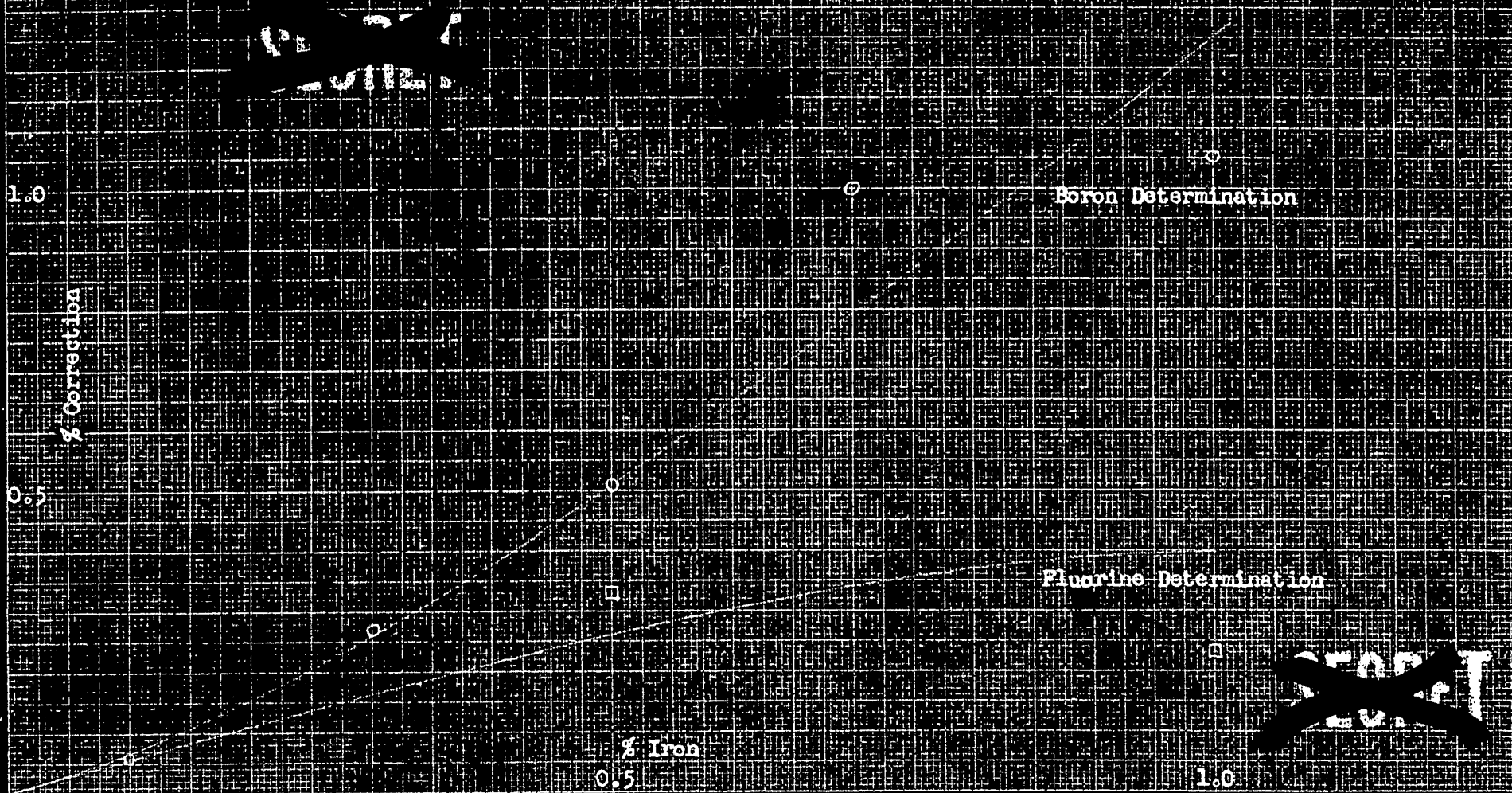
To compare the 0.1 N. sodium hydroxide with 0.1 N. hydrochloric acid, 30 ml. of hydrochloric acid are measured out into a 125 ml. Erlenmyer flask, and titrated with sodium hydroxide using 3 drops of 0.02% methyl red indicator. No precautions to exclude carbon dioxide are necessary.

Calculations--correction for isotopic concentration.--In calculating the per cent boron, the atomic weight to be used must be corrected by an isotopic analysis. It has been the general practice in this laboratory to calculate the per cent purity as $(CH_3)_2O:BF_3$ from the boron and from the fluorine determinations and to use these values in the records rather than the per cent boron and per cent fluorine. The molecular weight of $(CH_3)_2O:BF_3$ used in calculating must be corrected by isotopic analysis. In Table I are shown the atomic and molecular weights used.

TABLE I

Molecular and Atomic Weights

Atom % B^{10}	Atomic Weight B	Molecular Weight $(CH_3)_2O:BF_3$	Ratio $\dfrac{(CH_3)_2O:BF_3}{(CH_3)_2O}$
0	11.01	114.08	2.476
10	10.91	113.98	2.474
20	10.81	113.88	2.472
30	10.71	113.78	2.470
40	10.61	113.68	2.468
50	10.51	113.58	2.465
60	10.41	113.48	2.463
70	10.31	113.38	2.461
80	10.21	113.28	2.459
90	10.11	113.18	2.457
100	10.01	113.08	2.455

Interpolation from the values in the table can be used for accurate atomic and molecular weights for any known isotopic abundance of boron.

Analysis in the presence of iron.--Corrections to be applied to the observed analyses when the titrations are made in the presence of iron are shown in Figure 2. The observed titer or the calculated per cent purity is corrected by subtracting a correction which is a known per cent of the value to be corrected. These corrections are valid only for titration of samples of about 2.5 milli-equivalents of boron.

When larger amounts of iron are present, they must be removed by precipitation with sodium hydroxide. Boron can be titrated in the filtrate but fluorine must be determined gravimetrically.

TABLE II

Duplicate NaOH Titrations

Analysis of pure $(CH_3)_2O:BF_3$

Material	Designation	% $BF_3 \cdot CH_3OCH_3$ by F Titration	% $(CH_3)_2O:BF_3$ by B Titration	% B^{10}
Pure Complex	D-195	100.0 100.0 <u>100.0</u> 100.00±0.00	100.1 100.0 <u>100.1</u> 100.07±0.04	19
Column 2	D-265	99.9 <u>99.8</u> 99.85±0.05	99.9 <u>99.9</u> 99.90±0.00	33
Column 2	D-780	100.0 <u>100.0</u> 100.00±0.00	100.0 <u>100.0</u> 100.00±0.00	28
Column 7	D-785	99.8 <u>99.9</u> 99.85±0.05	99.9 <u>100.0</u> 99.95±0.05	92
Column 7	D-346	99.9 <u>99.9</u> 99.90±0.00	99.9 <u>99.9</u> 99.90±0.00	94

Analysis of product (95% B^{10})

Material	Designation	% $BF_3 \cdot CH_3OCH_3$ by F Titration	% $(CH_3)_2O:BF_3$ by B Titration	% B^{10}
Shipment	Lot 66	99.9 <u>99.9</u> 99.90±0.00	99.9 <u>99.9</u> 99.90±0.00	96
Shipment	Lot 67	99.9 <u>99.9</u> 99.90±0.00	99.9 <u>100.0</u> 99.95±0.05	96
Shipment	Lot 68	99.9 <u>100.0</u> 99.95±0.05	99.9 <u>100.0</u> 99.95±0.05	96
Shipment	Lot 69	99.9 <u>100.0</u> 99.95±0.05	100.0 <u>100.0</u> 100.00±0.00	96

$13D^{81}$

14a

C. Evaluation of Procedure

Accuracy and precision.--In the use of this method for routine analyses during the period of over a year since the original S.A.M. report[2] on the method was written, considerable data have been obtained concerning the accuracy of the method.

The original tests of the accuracy of the method were made by analysing samples of pure $(CH_3)_2O:BF_3$ prepared in the laboratory and distilled at room temperature in a high vacuum by application of liquid nitrogen to the receiver. The pure $(CH_3)_2O:BF_3$ now used in this laboratory for testing is made by the reaction between BF_3 and $(CH_3)_2O$ condensed together in a vacuum system by the application of liquid air. This $(CH_3)_2O:BF_3$ is evacuated thoroughly and used without further purification. In all cases the complex has been made from Harshaw BF_3 and duPont $(CH_3)_2O$.

Since a unit for the fractionation of the boron isotopes in $(CH_3)_2O:BF_3$ is available, it is possible to compare samples which have been separated by fractional distillation in a unit which is capable of separating the isotopes and should therefore be capable of separating any chemical impurities present in the feed $(CH_3)_2O:BF_3$. Samples for testing the titration are taken from the bottom of the second and the seventh column in a system of eight columns operating in series. The end columns are avoided because of possible accumulation of impurities. The analyses which have been made for the purpose of testing the titration procedure are shown in the first five entries of Table II. The excellent agreement of these values with the theoretical value of 100.0% may be used as evidence for a claim that the accuracy of an average of a number of determinations is within $\pm 0.1\%$.

Basis for modifications.--1. The empty weighing tube is weighed before filling in order to avoid difficulties due to small pieces of glass breaking off when the sample tube is broken open.

2. The water is not cooled before dissolving the sample because the $(CH_3)_2O$ liberated by the reaction of H_2O with $(CH_3)_2O:BF_3$ will escape around the stopper whether or not the water is cooled.

3. The elimination of 0.3 N. HCl is an obvious simplification.

4. It has been found that omission of the CaF_2 filtration introduces a considerable simplification in routine determinations. The object of filtering was to improve the end point by providing a clear solution. The increased volume resulting from the filtering operation tends to make the end point as difficult as ever. The relative merits of the two methods are at best, debatable. In routine determinations, the analyst learns to detect the end point even though it is not sharp, and the simplest method is advisable.

5. The procedure used at S.A.M. actually involved cooling the solution before titrating, the statement in the report[2] notwithstanding.

TABLE III

Correction for Iron in F Analysis

Iron Present	Titer, ml. 0.3 N. NaOH	Error in Titer, ml.	Error in Fluorine Determination
0.0%	17.68	0.00	0.00%
0.5	17.75	0.06	0.34
1.0	17.72	0.04	0.23

TABLE IV

Correction for Iron in B Analysis

Iron Present	Titer, ml. 0.1 N. NaOH	Error in Titer, ml.	Error in Boron Determination
0.0%	34.51	0.00	0.00%
0.1	34.53	0.02	0.06
0.3	34.60	0.09	0.27
0.5	34.68	0.17	0.51
0.7	34.84	0.33	1.00
1.0	34.86	0.35	1.05

TABLE V

Variation in Sampling Procedure

Sample	Designation	Weighing Method	% $(CH_3)_2O:BF_3$ By F Titration	% $(CH_3)_2O:BF_3$ By B Titration
Shipment	Lot 28	Sealed Tube	99.5	100.0
		Weighing Bottle	99.6	100.1
Shipment	Lot 29	Sealed Tube	99.9	100.2
		Weighing Bottle	100.2	100.2
Column 2	D-780	Sealed Tube	100.0	100.0
		Stoppered Tube	100.0	100.0
Column 7	D-785	Sealed Tube	99.9	99.9
		Stoppered Tube	99.9	99.9

15a

6. The corrections for isotopic concentrations shown in Table I were calculated using the mass spectrometer value for the normal abundance ratio $B^{11}/B^{10} = 4.31$ (18.8% B^{10}) obtained by Inghram,[17] and the accepted mass spectrograph values[18] for the weights of the individual isotopes ($B^{10} = 10.01605$, $B^{11} = 11.01286$). The 1943 atomic weights[19] for carbon (12.01), hydrogen (1.0080), oxygen (16.00), and fluorine (19.00) were used, these being the latest available values and agreeing with the most recent International Atomic Weights. Negligible fractionation of carbon, oxygen, and hydrogen was assumed.

7. The corrections for the presence of iron were made by titrating samples of pure $(CH_3)_2O:BF_3$ containing various amounts of added ferric sulfate. The data used to construct the graph in Figure 2 were taken from Tables III and IV. A titer of 25 ml. of sodium hydroxide solution was assumed in calculating the per cent corrections.

8. The use of a stoppered weighing tube instead of a sealed weighing tube involves a simplification. The weighing bottle technique in which the $(CH_3)_2O:BF_3$ is poured into the water involves an even greater simplification. Although some white fumes escape on pouring the $(CH_3)_2O:BF_3$, the data in Table V indicate that accurate analyses can be obtained by the careful use of this technique.

9. The effect, if any, of starting the nitrogen bubbling before making the final adjustment of the indicator is small.

The rapid method for isotopic concentrations[10] is generally carried out with solutions containing 5.00 ml. of $(CH_3)_2O:BF_3$ in 250 ml. of water. Ten ml. samples taken from these solutions are suitable for titration. The amount of BF_3 titrated is approximately equal to that obtained in the regular procedure. For routine determinations in which boron and fluorine determinations are to be made in conjunction with rapid isotopic analyses, 5 ml. samples are taken in a weighing bottle.

The determinations in Table V, all made with 2.8 gram samples, indicate that the three methods are equivalent. The weighing bottle procedure has, however, not been accepted except for routine determinations. The stoppered tube procedure is accepted as entirely satisfactory, although the determinations reported in the study of the accuracy and precision of the method (Table I) were all made by the sealed tube procedure.

Modifications 1 to 5 inclusive are believed not to have introduced any detectable change in the results obtained. Modifications 6 and 7 involve corrections which are known to be necessary. Modification 8 does not show any detectable change, but has not been accepted as official.

Methods reported in the literature.--Procedures for the determination of boron and fluorine in addition compounds of boron trifluoride have been described by several authors. Kraus and Brown[20] determined boron by titration and fluorine by the lead chlorofluoride method in addition compounds of amines without taking any precautions to hydrolyse the borofluoride bond. The precision obtained in the boron titrations was poor.

TABLE VII

Comparison with Recipient's Analyses

Lot No.	% $(CH_3)_2O:BF_3$ by F Analysis			% $(CH_3)_2O:BF_3$ by B Analysis		
	Recipient	This Laboratory	Diff.	Recipient	This Laboratory	Diff.
28	99.3	99.5	+0.2	99.3	99.9	+0.6
29	100.0	100.0	0.0	100.0	100.2	+0.2
30	99.9	99.6	−0.3	99.3	99.4	+0.1
31	99.7	99.7	0.0	99.3	99.9	+0.6
32	99.9	100.1	+0.2	99.4	100.0	+0.6
33	99.9	100.0	+0.1	99.3	100.1	+0.8
34	99.7	99.9	+0.2	99.4	100.0	+0.6
35	99.7	100.0	+0.3	99.0	99.9	+0.9
36	99.5	99.7	+0.2	99.3	99.8	+0.5
37	99.8	100.2	+0.3	99.0	100.0	+1.0
38	99.7	100.1	+0.4	99.5	99.9	+0.4
39	99.6	99.7	+0.1	99.5	100.0	+0.5
40	99.6	100.0	+0.4	99.2	99.9	+0.7
41	99.5	100.0	+0.5	99.1	99.9	+0.8
42	99.9	100.0	+0.1	99.4	100.0	+0.6
43	99.8	99.9	+0.1	99.4	99.8	+0.4
44	100.0	100.0	0.0	99.5	99.9	+0.4
45	99.9	99.7	−0.2	99.3	99.5	+0.2
46	99.8	99.8	0.0	99.8	99.9	+0.1
47	99.7	99.8	+0.1	99.7	99.9	+0.2
48	99.8	99.7	−0.1	99.8	99.9	+0.1
49	99.7	99.9	+0.2	99.7	99.8	+0.1
Avg.	99.74	99.88	+0.13	99.42	99.90	+0.48
a.d.	± 0.14	± 0.15	±0.15	± 0.19	± 0.09	±0.23

16a

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TABLE VI

Analyses from Published Literature

Author	Method	Compound	Purity F anal.	B anal.	C anal.	H anal.	N anal.
Kraus & Brown	K & B	$NH_3:BF_3$	-	98	-	-	100.1
			-	110	-	-	100.4
		$Et_3N:BF_3$	99.9	-	-	-	100.6
			99.1	-	-	-	98.4
		$EtNH_2$	100.4	-	-	-	112
			101.1	-	-	-	100
Bowlus & Nieuwland	B & N	$(MeCOOH)_2:BF_3$	-	98.4	101.8	102.6	-
		$(EtCOOH)_2:BF_3$	-	96.4	97.7	104.0	-
		$(MeCOOMe):BF_3$	-	107.2	99.4	111.3	-
		$(MeCOOEt):BF_3$	-	98.6	99.7	100.8	-
Pflaum & Wenzke	P & W	$NH_3:BF_3$	102.1	99.3	-	-	-
			100.3	100.0	-	-	-
		$(MeCOOMe):BF_3$	99.8	99.6	-	-	-
			101.1	99.8	-	-	-
		$(MeCOOEt):BF_3$	99.6	102.1	-	-	-
			100.3	101.4	-	-	-
Laubengayer & Finlay	P & W	$Me_2O:BF_3$	98.8	109	-	-	-
			100.1	99	-	-	-
		$Et_2O:BF_3$	97.8	114	-	-	-
			100.5	120	-	-	-
	*	$MeOEt:BF_3$	99.3	94	-	-	-
			101.4	104	-	-	-

* (Boron determination by method of Pflaum and Wenzke, fluorine determination by method of deBoer & Basart.)

$2 < R^{81}$

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Bowlus and Nieuwland[21] used a Carius tube decomposition to decompose organic addition compounds. They obtained slightly better results for boron titrations in this way. The only procedure appearing in the published literature for which precise quantitative results have been claimed is that of Pflaum and Wenzke.[22] These authors decomposed the compound with sodium peroxide in a Paar bomb, removed the alkali by boiling with ammonium salts, precipitated the fluorine as calcium fluoride, and titrated the boron after removing the ammonia by boiling in alkaline solution. Laubengayer and Finlay[23] reported that they used the method of Pflaum and Wenzke using a sodium hydroxide hydrolysis. The precision obtained was not as good as that reported by Pflaum and Wenzke although it is not certain just how closely the procedure of Pflaum and Wenzke was followed. Laubengayer and Finlay also used a zirconium titration[24] for one of their fluorine determinations and found this as satisfactory as the gravimetric method of Pflaum and Wenzke.

The data reported by these workers is shown in Table VI. The values are calculated as per cent purity to provide a comparison with the $(CH_3)_2O:BF_3$ analyses described in this report. Carbon and hydrogen determinations made by Bowlus and Nieuwland and nitrogen determinations made by Kraus and Brown are also shown. The carbon determinations apparently can be made with fair precision.

Although considerable work has been done with boron trifluoride addition compounds in recent years, most of the investigations have not depended on chemical analyses to establish the identity of the compounds prepared. The papers mentioned above are the only recent ones which have seriously considered the problem of chemical analysis of BF_3. The best procedure in the published literature is that of Pflaum and Wenzke. Their procedure, judged by the analyses which they reported, is not capable of the precision obtained by the S.A.M. method.

Procedure used by recipient of product.--The product prepared in this laboratory has been analysed by the recipient of the material and his analyses have been reported to this laboratory for purposes of comparison. The procedure used by the recipient for these analyses is a modified form of the Judson and Turner method[2] in which a larger sample is used, no excess sodium hydroxide is added, and a blank correction is applied. In Table VII are recorded all of the data available for comparison of the recipient's analyses with the analyses made in this laboratory according to the procedure described in this report. The description of the procedure used by the recipient[25] and the analyses reported[26] were transmitted through Capt. Chapman of the Chicago Area Office.

The agreement of the fluorine analyses reported by the two laboratories is excellent. The boron analyses show a definite and reproducible discrepancy. Average values have been calculated for the 22 samples reported and average deviations calculated. Since the samples are not all identical, the deviation is a measure of the variation in samples as well as in the analysis. However, the calculated deviations do show that the difference between the boron analyses reported by the two laboratories is considerably larger than the deviations in the analyses, implying the existence of a reproducible discrepancy. If the evidence presented in this report establishes sufficiently the validity of the original Judson and Turner procedure, then a slight but definite error (0.5%) would have to be attributed to the modified procedure used by the recipient for boron analyses.

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Desirability of further modifications.—1. Modified procedure leading to erroneous results.—An attempt was made in this laboratory to simplify the S.A.M. procedure further. When the amount of BF_3 present in solution is known, it would appear that the theoretical amount of sodium hydroxide could be added in one step with a slight definite excess, and that a single reflux period of three hours should complete the hydrolysis. A procedure was tried in which a slight excess over the calculated amount of sodium hydroxide was added in one step. The results obtained by using this procedure were, however, in considerable error as shown in Table VIII.

TABLE VIII

Modified NaOH Titrations

Sample	Designation	Procedure	% $(CH_3)_2O:BF_3$ By F Titration	% $(CH_3)_2O:BF_3$ By B Titration
Shipment	Lot 33	S.A.M.[2]	100.0	100.1
		Modified	102.5	100.2
Shipment	Lot 31	S.A.M.	99.7	99.9
		Modified	101.9	99.8
Feed	C-581	S.A.M.	99.2	99.7
		Modified	102.4	100.0
Feed	C-790	S.A.M.	99.4	99.7
		Modified	101.8	99.9
Sample with added HF		S.A.M.	101.2	99.6
		Modified	103.4	100.0

The explanation of the cause of this error is not immediately obvious although a detailed investigation of the problem was made. The data are presented only to emphasize the necessity of following a proven procedure explicitly. It is recommended that any analyst using this procedure for precise work should check carefully with the purest available $(CH_3)_2O:BF_3$. If the slightest modification is made at any time, it is necessary that careful checks be made to show that agreement can be obtained with the original procedure.

In spite of the necessity for following an empirical procedure, excellent precision can be obtained as was shown in Table II.

2. Original Harshaw procedure.—In the procedure originally suggested by the Harshaw Company[11], and in the procedure reportedly followed by the recipient[25], the fluorine titrations were carried out in a large number of steps never adding an excess of alkali. From a theoretical standpoint this procedure might have some advantages, although it would not be convenient for routine analyses. Since the Hawshaw Company's procedure is much more laborious and since entirely satisfactory results have been obtained by the S.A.M. Laboratories procedure[2], no investigation comparing the two procedures has been attempted.

3. **Blank corrections.**—Careful consideration has been given to possible methods of calculating a blank correction. The conclusion has been reached that no direct method can be developed for calculating a correction for the blank due to the attack of the hydroxyl or fluoride ion on glass vessels, or to the failure of the borofluoride bonds to be completely hydrolysed. The extent to which glass is attacked by various amounts of excess alkali has been suggested as a method of studying this effect, but the action in the presence of boron trifluoride is not necessarily the same. The fact that, in the method used, the blank required is negligible must be based on the titrations shown in Table II in which 100.0% analyses were obtained.

4. **Use of larger samples.**—It was suggested by Judson and Turner[2] that a procedure might be preferable in which a larger sample is used. Experiments at that time had shown that satisfactory results could not be obtained when larger samples were used in the procedure described. It was thought that by using a longer hydrolysis period, larger samples could be used and the difficulty of estimating the end point decreased. It appears probable that a blank would be required in such a titration as was found in the method used by the recipient. The high precision attained with the present procedure as shown in Table II indicates, however, that further modifications are not required. Since any procedure for using larger samples would necessarily be more involved, there is no apparent advantage to such a modification. If such a method is used, the blank must be determined by analysis of 100% $(CH_3)_2O:BF_3$.

5. **Analyses in the presence of iron.**—For accurate analyses in the presence of considerable iron, the iron must be removed by sodium hydroxide precipitation. Boron can be determined in the filtrate in the usual way. Fluorine must be determined gravimetrically as calcium fluoride. It is probable that a modification of the Pflaum and Wenzke method using the Harshaw hydrolysis procedure would be the most satisfactory method of accomplishing this.

6. **Fractionation of oxygen, hydrogen and carbon.**—Fractionation of the isotopes of oxygen, hydrogen and carbon also takes place during the fractionation of boron. Consideration must be given to the possibility that this affects the molecular weights. McCaulay[27] has come to the conclusion that the separation in the boron fractionation takes place primarily in the dissociation of the boron-oxygen bond. The isotopic fractionation of oxygen would therefore be expected to be greater than that of carbon, and probably greater than that of hydrogen.

It was reported by Schutz[28] that the ratio of O^{18} to O^{16} in the product containing 95 atom % B^{10} was only four times the normal ratio. Since the normal ratio[29] is 0.0020, the ratio in the product is therefore 0.008 changing the molecular weight of $(CH_3)_2O$ from 46.07 to 46.08. Thus the effect of oxygen fractionation on the values in Table I is negligible.

7. **Use of other values for abundance of boron isotopes.**—The abundance ratio used differs slightly from the accepted literature value[29] which is $B^{11}/B^{10} = 4.44$ (18.4% B^{10}). Still another value can be calculated from the accepted 1943 atomic weights as determined chemically[19] (B = 10.82). The value on this basis is $B^{11}/B^{10} = 4.17$ (19.4% B^{10}) assuming as before the mass spectrograph value for the weights of the individual isotopes.[18] Errors due to the assumed value of the abundance ratio would not affect the atomic weights in Table I by more than 0.005 atomic weight units.

D. Correction in Report A-1299

An error was made in section V.c. on page 10 of S.A.M. report A-1299[2] in which the sodium hydroxide titration was originally described. The table showing the effect of standing in pyrex on the observed titration should appear as shown in Table IX below.

TABLE IX

Change in Boron Titer with Time of Standing

Solution	Date Analysed	%F	%B	% SiF$_4$
1	5/19/44	49.3	9.4	-
	5/31/44	49.4	10.17	-
2	7/22/44	50.0	9.52	.00
	7/24/44	49.9	9.70	.42

The error was made in the calculation of per cent fluorine. The conclusion drawn that the apparent boron titer increases as does the silicon concentration while the fluorine titer remains essentially unchanged, in still valid.

V. DIMETHYL ETHER DETERMINATION

A. Introduction

A method for the determination of dimethyl ether with an accuracy of 2% was described by Kirshenbaum, Sabi, and Schutz.[3] Following suggestions made by this laboratory,[30] a modified procedure was described by S.A.M.[31] The latter procedure has been followed in all essentials. The method consists essentially in the measurement of the loss in weight when sodium fluoride is added to a mixture of $(CH_3)_2O:BF_3$ and water. A compound is formed between boron trifluoride and sodium fluoride and the ether is evolved as a gas. It has been found that reproducible determinations can be made if 20 minutes are allowed after the addition of the sodium fluoride before the final weighing is made.

Kirshenbaum found that a correction term was required for the solubility of dimethyl ether in water. Actually the correction due to solubility of the dimethyl ether is partly compensated by a correction in the opposite direction due to the boron trifluoride which escapes mechanically from the bottle during the addition of sodium fluoride. It has been found necessary to have each analyst periodically determine his own correction term using pure $(CH_3)_2O:BF_3$. Redeterminations of the correction term should be made regularly. Redistilled $(CH_3)_2O:BF_3$ taken from the second column of the fractionation unit has been used as a standard for making this correction.

The detailed procedure is described below. Experiments are described in which the time required for equilibrium was determined. The data used for determining the correction term, and for evaluating the accuracy and precision are presented. It is believed that a precision of 0.5% is attainable with extreme care.

B. Procedure for Dimethyl Ether Determination

A 40 x 80 mm. weighing bottle with a standard taper stopper fitted on the outside of the body is dried in the oven along with a stirring rod just long enough (95 mm.) to fit inside the bottle with the cap on the bottle. These are cooled, and weighed. Approximately 3.0 grams (2.4 ml.) of $(CH_3)_2O:BF_3$ to be analysed are added to the bottle using a graduated pipet which has been dried by washing with acetone and removing the acetone with a stream of dry air. The $(CH_3)_2O:BF_3$ is delivered slowly to the bottom of the bottle. The stoppered bottle is again weighed to determine the amount of $(CH_3)_2O:BF_3$ added. The bottle is cooled in a Dewar flask containing ice water. While the weighing bottle is cooling, a weight buret filled with water is weighed. An Eck and Krebs No. 778 weight buret of 10 ml. capacity is very convenient in that it will stand up without the necessity of wires for suspension. A 3 inch watch glass is weighed empty and again with 3.0 grams of reagent grade sodium fluoride. Two ml. of water from the weight buret are poured drop by drop down the side of the weighing bottle containing the cold $(CH_3)_2O:BF_3$. The mixture is again cooled. Another sample may be started at this time. The sodium fluoride is then carefully added to the cold $(CH_3)_2O:BF_3$ with a camel's hair brush. The bottle is removed from the ice water and the outside of the bottle wiped dry. The mixture is stirred until bubbles are no longer evolved. This should take about five minutes. The bottle is stoppered and left for twenty minutes ±1 minute from the time when the addition of the sodium fluoride was completed. During this time the weight buret is weighed again to determine the amount of water which was removed from the buret. After exactly twenty minutes the cover of the weighing bottle is removed, the mixture is stirred again, the cover replaced, and the final weighing made.

From the weight of the bottle and the $(CH_3)_2O:BF_3$, water, and sodium fluoride added, and the final weight, the loss in weight is calculated. The correction term is added to the loss in weight to obtain the corrected amount of ether present. From this the per cent dimethyl ether can be calculated. To calculate the per cent $(CH_3)_2O:BF_3$ from this determination, molecular weights corrected for isotopic concentration should be used. The correction term is obtained periodically by each analyst by analysing the purest obtainable $(CH_3)_2O:BF_3$ and finding what correction must be added to give an analysis of 100.0%.

Values of the factor for converting from per cent $(CH_3)_2O$ to per cent $(CH_3)_2O:BF_3$ are recorded in Table I.

C. Evaluation of Procedure

Time allowed for equilibrium.--Experiments were carried out to determine the time interval which should elapse between the addition of sodium fluoride and the final weighing. As shown in Table X the rate of loss in weight becomes less than 1 mg. per minute after about 20 minutes. A time interval of 20 minutes ± 1 minute has been selected as the optimum time. The loss in weight will continue longer, but after 20 minutes should be reproducible to ± 1 mg. or better.

TABLE X

Approach to Equilibrium in Ether Evolution

Time Minutes	Loss in Weight Grams	Rate of Loss in at Grams/Min.
5	1.224	.24
11	1.246	.004
15	1.252	.0015
21	1.2572	.0003
27	1.2575	.00005
41	1.2578	.00002

Correction term.--A correction term must be determined by reference to an assumed 100.0% product. The correction term originally used was determined separately for each analyst by carrying out duplicate determinations on a sample of the feed stock from the fractionation unit which was purified by pumping off the excess $(CH_3)_2O$ with a Hyvac pump. The correction term required to be added to the weight of $(CH_3)_2O$ evolved in order to make the analysis 100.0% was calculated. This correction was then applied to each sample analysed, assuming that if the amount of $(CH_3)_2O:BF_3$, H_2O, and NaF are kept constant the required correction term is a constant.

It was later decided that for the most accurate application of the method the correction term should be regularly determined to compensate for changes in technique which may occur from time to time in routine determinations. From the data shown in Table XI, all obtained by the same analyst using the correction factor determined as described above, it was decided to use $(CH_3)_2O:BF_3$ from column 2 as a standard. This material has nearly the same $(CH_3)_2O$ content as the evacuated feed used previously as a standard, and it has a $(CH_3)_2O$ content intermediate between that of the feed which is known to have an excess, and the redistilled product which is known to be slightly impure. Routine analyses of the $(CH_3)_2O$ in the $(CH_3)_2O:BF_3$ from column 2 are made and the correction factor is periodically revised on the basis of these analyses. For the analysis of the final redistilled product, duplicate determinations of $(CH_3)_2O:BF_3$ from column 2 are made at the same time as the duplicate determinations of the product being analysed. Although, due to the limitations in the precision of the method, it is difficult to estimate the absolute purity of the standard used for corrections, it is believed that the corrections obtained by the procedure described are as accurate as can be obtained using the evolution method in its present form.

TABLE XI

Ether Determination with Various Products

Column 2	Column 7	Feed	Redistilled Product
99.8	99.1	100.7	99.6
100.1	99.0	100.3	100.1
99.7	98.4	100.5	99.8
98.7	98.7	100.9	99.7
100.0	99.2	100.8	99.6
100.1	99.6	101.7	99.7
100.9	99.4	100.8	99.4
99.9±0.4	98.6	100.7	99.7
	99.0±0.3	100.2	99.6
		100.8±0.3	99.6±0.2

TABLE XII

Duplicate Ether Determinations of Shipments

Lot	Analysis	Average	Lot	Analysis	Average
34	99.4 99.4	99.4±0.0	44	100.0 100.2	100.1±0.1
35	100.0 99.0	99.5±0.5	45	99.9 99.4	99.7±0.3
36	99.3 99.4	99.4±0.1	46	100.8 100.0	100.4±0.4
37	99.0 99.7	99.4±0.4	47	101.3 101.1	101.2±0.1
39	99.8 100.1	100.0±0.2	48	100.1 99.8	100.0±0.2
40	100.3 98.9	99.6±0.7	49	99.1 99.3	99.2±0.1
41	100.0 98.8	99.4±0.6	66*	99.5 98.5	99.0±0.5
42	99.9 99.8	99.9±0.1	67*	99.3 99.2	99.3±0.1
43	100.3 100.4	100.4±0.1	68*	98.9 98.8	98.9±0.1

Accuracy and precision.—Data obtained with the method are shown in Tables XI and XII. Table XI shows values obtained at several points over a three week period. All data were obtained by the same analyst. The original corrections made from the analysis of evacuated feed stock were applied.

Table XII shows the data which are available for duplicate determinations of redistilled product. The three samples designated by * were compared with $(CH_3)_2O:BF_3$ from column 2, and the other samples were analysed using the correction determined with evacuated feed stock.

The average deviation for a set of two samples rarely exceeds 0.5%. The high values from 100.0 to 101.2% reported for redistilled product appear to be partly due to errors in the correction factor as it is doubtful whether any of this product could have had more than 100.0% of the theoretical amount of $(CH_3)_2O$. It is hoped that improved method of obtaining correction factors now used should make it possible to keep the accuracy within ±0.5% for the duplicate determinations used for the final product and within ± 1.0% for ordinary single determinations.
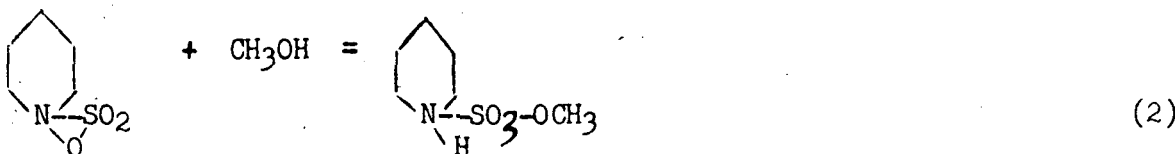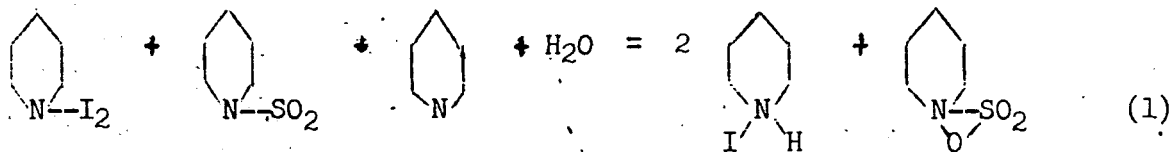
Possibility of further improvement.—It is not clear whether the ultimate limit of the precision and accuracy of the method has been reached. It would appear that it might be possible to develop a technique based on this method such that the loss in weight due to ether evolution could be measured to ± 1 mg. which would correspond to a precision of 0.1%. This would require extreme care in avoiding loss of material, in making sure that all complex reacts, and in allowing time for complete equilibrium to be reached.

Bowlus and Nieuwland[21] used carbon and hydrogen determinations in the analysis of organic addition compounds of BF_3. Such determinations might be useful for accurate measurements of the $(CH_3)_2O$ content of $(CH_3)_2O:BF_3$.

VI. KARL FISCHER HYDROXYL DETERMINATION

A. Introduction

The Karl Fischer reagent as developed by Smith, Bryant, and Mitchell[32] is used for the determination of hydroxyl groups present in $(CH_3)_2O:BF_3$. The Karl Fischer reagent, consisting of a mixture of pyridine, iodine, and sulfur dioxide, in a methanol solvent was used by Smith for the titration of water in accordance with reactions (1) and (2) using the appearance of the iodine color as the end point.

$$N{\cdot}I_2 + N{\cdot}SO_2 + N + H_2O = 2\ N(I)(H) + N{\cdot}SO_2(O) \tag{1}$$

$$N{\cdot}SO_2(O) + CH_3OH = N{\cdot}SO_3{-}OCH_3\ (H) \tag{2}$$

3/

The iodine reacts with water in the presence of sulfur dioxide, pyridine, and methanol in accordance with the reactions shown. When the water has all reacted, the red color of unreacted iodine appears.

The procedure used for the determination of water in $(CH_3)_2O:BF_3$ was developed by Kirshenbaum.[4] A thorough investigation of the determination was described in a report by Kirshenbaum.[33]

The presence of BF_3 causes the premature appearance of the iodine color, presumably because of the reaction of BF_3 with water or sulfur dioxide or both. To eliminate this difficulty Kirshenbaum added pyridine to remove the BF_3 by forming the pyridine complex. This method of removing BF_3 had been used by Bryant, Mitchell, and Smith,[5] although the problem encountered by Bryant was different. In the case encountered by Bryant acetic acid was present and the BF_3 had already been converted to the acetic acid complex. Acetic acid in the presence of $(CH_3COOH)_2:BF_3$ reacts with the methanol in the Karl Fischer reagent liberating water which is titrated. Pyridine was added to remove the BF_3 catalyst and prevent esterification of the methanol solvent.

Kirshenbaum used dioxane as a solvent for $(CH_3)_2O:BF_3$. Experiments in this laboratory have shown that either methanol or dioxane may be used.

The procedure used is described in detail below. In evaluating the procedure detailed consideration is given to the meaning of the observed Karl Fischer titers. The results are calculated in terms of per cent H_2O, although it is known that B-OH and B=O groups are determined as H_2O by this procedure.[5,34] H_3BO_3, for instance, reacts with the methanol solvent in the Karl Fischer reagent to form H_2O.

$$B(OH)_3 + 3 \ CH_3OH = B(OCH_3)_3 + 3 \ H_2O \qquad\qquad (3)$$
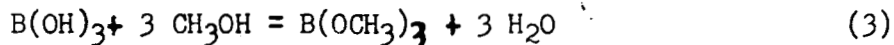
Although Taylor[35] has questioned the assumption that all B-OH and B=O groups will be titrated, evidence is presented to indicate that this assumption is valid. The procedure is therefore referred to as a hydroxyl determination. The compound $HBF_2(OH)_2$ which Taylor maintained would show only one hydroxyl group by Karl Fischer analysis was shown to have two titratable hydroxyl groups.

It is known[33,36] that the observed Karl Fischer titer of $(CH_3)_2O:BF_3$ decreases on heating. Data are presented to show that the mechanism used by Taylor[35] to explain this is incorrect. All available evidence points to the conclusion that the hydroxyl groups which disappear are no longer present as hydroxyl groups. Another mechanism for the disappearance suggested by Hiebert's experiments[36] in which the formation of CH_3OH is postulated has been investigated by a methoxyl determination described below.

The development of a Karl Fischer reagent not containing methanol was suggested for distinguishing H_2O from B-OH compounds. Experiments are described showing that Karl Fischer reagent in dioxane is not satisfactory for analyses of $(CH_3)_2O:BF_3$.

B. Procedure for Hydroxyl Determinations

Reagents.—The Karl Fischer reagent is prepared in accordance with the directions of Smith.[32] This is the same reagent used by Kirshenbaum.[33] Instead of weighing liquid SO_2, the SO_2 is measured volumetrically by bubbling into CH_3OH, following a suggestion in the Belle Works Control Laboratory Procedure[37] for the determination of H_2O in $(CH_3)_2O$.

Approximately 2 liters of reagent are made by dissolving 156 grams of Mallinckrodt A.C.S. reagent iodine in 500 ml. of Baker's analytical reagent pyridine in the Karl Fischer bottle. A two liter graduate is filled to 1250 ml. with Baker's A.C.S. reagent absolute methanol. Sulfur dioxide is bubbled into the methanol solution under a hood until the volume has been increased by 80 ml. (115 grams). The methanol solution is added to the pyridine solution and the mixture shaken. The reagent is allowed to stand 24 hours before use. The reagent is kept in an all glass automatic filling buret protected by drying tubes containing drierite.

Similar burets filled with anhydrous dioxane and pyridine are required. Anhydrous dioxane is obtained from The Carbide and Carbon Chemicals Corporation. No purification of the dioxane is required. The pyridine is the same as that used in making the reagent. Neither reagent requires drying.

The reagent is standardized daily by means of a standard solution prepared by dissolving a weighed amount of H_2O in absolute methanol or dioxane. Twenty-five ml. of a solution containing 4 grams per liter of water or dioxane are used. A correction for the amount of water present in the original methanol or dioxane is determined by titration. Pyridine must be used in determining the blank for dioxane.

Analysis of samples.—The procedure used for titration of $(CH_3)_2O:BF_3$ with Karl Fischer reagent is identical with that used by Kirshenbaum.[33] The weight of the sample is obtained by measuring the volume and assuming a density of 1.23, the value reported by S.A.M. for 25°C.[3] For routine analyses of $(CH_3)_2O:BF_3$ from the fractionation unit in which the water content is generally under 0.30% variations in density may be neglected. The 100 ml. volumetric flasks used as titration vessels are dried in an electric oven over night at 150°C. along with the weighing bottles used for taking samples. Twenty five ml. of dioxane are added to the flask from an automatic buret. Five ml. of the $(CH_3)_2O:BF_3$ to be analysed are added to the flask with a dry pipet. The flask is stoppered and the mixture is cooled in ice water. The pipet is washed with water, then acetone, and dried with a stream of air for use with the next sample. The compressed air in this laboratory is fortunately dry enough for this purpose. Ten ml. of pyridine are added slowly from an automatic buret. The Karl Fischer reagent is added slowly until a red color lasting for 30 seconds appears.

A blank titration of a mixture of 25 ml. of dioxane and 10 ml. of pyridine is made each day. This blank is subtracted from the observed titer.

The result is calculated as per cent H_2O.

TABLE XIII

Karl Fischer Analyses

Representative Data

Day	1st Column		2nd Col. Reb.	3rd Col. Reb.	4th Col. Reb.	5th Col. Reb.	6th Col. Reb.	7th Col. Reb.	8th Col. Reb.
	Top	Reboiler							
Typical Week October,1945									
1	0.11%	0.03	0.04	0.08	0.01	0.06	0.02	0.04	0.07
2	0.07	0.02	0.04	0.03	0.02	0.02	0.02	0.01	0.04
3	0.08	0.02	0.02	0.03	0.02	0.02	0.04	0.02	0.04
4	0.05	0.02	0.01	0.02	0.02	0.02	0.01	0.02	0.02
5	0.06	0.03	0.02	0.05	0.02	0.02	0.02	0.02	0.04
6	0.08	0.03	0.02	0.07	0.03	0.02	0.03	0.02	0.04
Average	0.08	0.03	0.03	0.05	0.02	0.03	0.02	0.02	0.04
	±.02	±.01	±.01	±.02	±.00	±.01	±.01	±.01	±.01
Typical Week July,1945									
Average	0.14	0.05	0.03	0.03	0.04	0.03	0.05	0.09	0.09
	±.01	±.03	±.01	±.01	±.02	±.02	±.03	±.03	±.02
Typical Week March,1945									
Average	0.23	0.04	0.05	0.04	0.05	0.10			
	±.02	±.01	±.01	±.01	±.02	±.02			
Typical Week January,1945									
Average	0.27	0.16	0.20	0.16	0.21	0.15			
	±.10	±.05	±.06	±.06	±.13	±.04			

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Some samples of impure $(CH_3)_2O:BF_3$ have been obtained which were so dark in color that the titration was impossible with 5 ml. in 25 ml. of dioxane. This was remedied by using 2 ml. of $(CH_3)_2O:BF_3$ instead of 5 ml., or by using larger volumes of dioxane in a larger titration flask.

C. Evaluation of Procedure

Accuracy.—Kirshenbaum reported[33] an absolute accuracy of 0.02% for amounts of water from 0.0 to 2.0%. Applicability in the presence of HF was also shown. Most of the analyses in this laboratory are done with samples from 0.02% to 0.2% water. The blank for the dioxane and pyridine is about 7 ml. The strength of the reagent is about 3 mg. H_2O per ml. reagent. The titers therefore for a blank of 7.0 ml. vary from 7.4 ml. to 11 ml. The desired accuracy of 0.02 absolute % or 0.4 ml. of reagent is easily obtainable for these samples if the blank measurements are carefully made.

The major source of errors is in the sampling technique, removing the sample from the fractionation unit and transferring the sample with a pipet. In Table XIII are shown values for routine analyses over one week periods. It is evident that amount of water present has been gradually decreasing over the period from January to October, 1945. To what extent the variations over a period of one week are due to sampling error and to what extent to actual variations in the water content of the $(CH_3)_2O:BF_3$ is difficult to say.

The density generally lies between 1.23 and 1.25 in the samples analysed. The error due to assuming a constant density is therefore less than 2% relative error. When higher accuracy is required, the sample may be added to a dry volumetric flask and weighed, and the dioxane added after weighing.

Titration of B-OH groups.—Bryant, Mitchell and Smith[5] showed that H_3BO_3 is quantitatively determined by the Karl Fischer reagent due to reaction with the methanol solvent according to reaction (3) even without a BF_3 esterification catalyst.

$$B(OH)_3 + 3 \ CH_3OH = B(OCH_3)_3 + 3 \ H_2O \qquad (3)$$

A similar reaction was found by Mitchell, Smith, Ashly, and Bryant[34] for B_2O_3 and HBO_2, $B(OCH_3)_3$ being the final product in both cases. It would appear that any hydroxyl group or any double bond oxygen atom attached to boron should be titrated quantitatively by the Karl Fischer reagent.

Taylor[35] has reported that in the compound $Ni(BF_3OH)_2 \cdot 6H_2O$ only 6 of the 8 hydroxyl groups are titrated. He concludes from this observation that not all OH groups attached to boron atoms are titrated with the Karl Fischer reagent. Specifically, he concludes that in the compound $HBF_2(OH)_2$ only one hydroxyl group would be titrated. Experiments described with $HBF_2(OH)_2$ below showed that both of the hydroxyl groups in this compound are titrated. The conclusion has been drawn that in all hydroxy substituted derivatives of BF_3 and HBF_4, the Karl Fischer reagent will titrate all of the hydroxyl present. No explanation is offered for the situation encountered by Taylor with the nickel salt.

Disappearance of OH groups.—It is known that the initial reaction of H_2O with $(CH_3)_2O:BF_3$ forms $(2H_2O):BF_3$ according to reaction (4).[36]

$$(CH_3)_2O:BF + 2H_2O = (2H_2O):BF_3 + (CH_3)_2O:BF_3 \qquad (4)$$
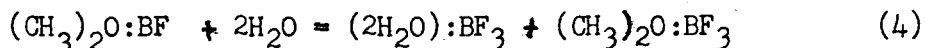
It has been observed that on heating the amount of "water" determined by Karl Fischer reagent decreases slowly until it reaches a constant value depending only on the amount of water originally present. This reaction was studied in detail by Kirshenbaum[33] and later by Hiebert.[36] It appears that some of the water is converted into a form in which it is not titrated.

One explanation offered for this disappearance of water on heating was that of Taylor[35] who suggested the reaction (5), believing that the product $HBF_2(OH)_2$ would show only one molecule of water in the Karl Fischer titration.

$$(2H_2O):BF_3 = OH_3BF_3OH = HF + HBF_2(OH)_2 \qquad (5)$$
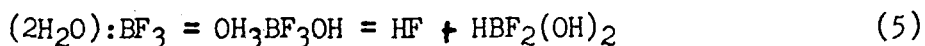
While the reaction (5) is the reaction shown by McGrath, Stack, and McCusker[38] for the thermal decomposition of $(2H_2O)BF_3$ it is shown below that both hydroxyl groups of $HBF_2(OH)_2$ are titrated so that this reaction cannot be the explanation for the decrease in hydroxyl content.

The conclusion drawn is that the hydroxyl groups which appear to have disappeared are no longer present as hydroxyl groups. The most obvious mechanism for the removal of hydroxyl groups is the reaction to form methoxyl groups according to equation (6).

$$(2H_2O):BF_3 + (CH_3)_2O:BF_3 = 2\ CH_3OH:BF_3 + H_2O \qquad (6)$$
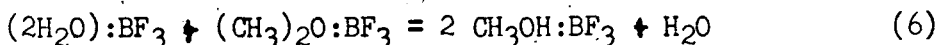
This equation is in agreement with the evidence obtained by Hiebert[36] that 1 mol of $(CH_3)_2O$ disappeared along with each mol of H_2O.

Preparation and analysis of dihydroxy fluoboric acid.—Dihydroxy fluoboric acid, $HBF_2(OH)_2$ was prepared to show that both hydroxyl groups are titrated. One of the methods suggested by Sowa, Kroeger, and Nieuwland[39] was used.

$$2BF_3 + 4B(OH)_3 = 3HBF_2(OH)_2 + 3HBO_2 \qquad (7)$$
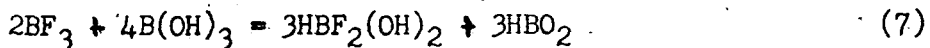
H_3BO_3 was treated with BF_3 at room temperature. When the reaction had become very slow the temperature was elevated somewhat by the application of heat. The amount of gas taken up was still less than theoretical. The product was distilled. When a solid suspension started to appear in the distillate, the distillation was cut, and the distillate redistilled, this time taking about 1/2 of the first distillate into the second distillate. The product was a liquid identified as $HBF_2(OH)_2$ by boron and fluorine analyses. Calculated, 12.79% B, 44.8% F; found, 12.63% B, 44.3% F.

The Karl Fischer hydroxyl determination was carried out on this material to show that all of the hydroxyl present is determined in the Karl Fischer titration: Calculated for 2 OH groups, 42.5% H_2O; found, 41.3, 43.2% H_2O.

Use of the method.—The Karl Fischer titration of hydroxyl has been shown to provide a quantitative measure for H_2O, H_3BO_3, HBO_2, $(2H_2O):BF_3$ and $HBF_2(OH)_2$. It seems reasonable to assume that other compounds with B=O or B-OH groups will be measured. The values are reported as per cent H_2O, realizing that the determination actually made is the total oxygen present as water or convertible to water by reaction with methanol. It is generally referred to as a hydroxyl determination, although B=O compounds are also titrated. It should be noted that C-OH groups are not hydroxyl groups in this sense but are determined by the methoxyl determination described below.

As far as is known the only way in which hydroxy compounds can be formed in the fractionation unit is by reaction with H_2O. Although part of the H_2O entering the system is converted into a form which does not appear in the Karl Fischer titration, and part of it is converted into a volatile constituent (formula not established) which passes out the top of the distillation column[40] these determinations are of value in following the leakage of water into the fractionation unit.

Karl Fischer reagent in the absence of methanol.—It was hoped that a reagent made in dioxane instead of methanol could be used to distinguish H_2O from B-OH compounds. Smith, Bryant, and Mitchell[32] studied the reaction of Karl Fischer reagent with H_2O in non-alcoholic solvents. They reported that titrations were possible although the reaction involved was somewhat different.

A solution of Karl Fischer reagent made up in the usual way using dioxane for a solvent instead of methanol was prepared and standardized with a solution of water in dioxane. It was not found possible, however, to titrate dioxane solutions containing BF_3 with this reagent. An end point developed immediately in the presence of BF_3 even though pyridine was added. It would appear that the pyridine does not tie up the BF_3 sufficiently under these circumstances.

The further investigation of this problem using other non-alcoholic solvents, and using other reagents to remove the BF_3 would be well worth investigating.

VII. CONDUCTIVITY MEASUREMENTS

A. Introduction

Sabi[6] suggested the use of conductivity measurements to determine the H_2O present in $(CH_3)_2O:BF_3$. The addition of H_2O to pure $(CH_3)_2O:BF_3$, which is practically non-conducting, results in an increased conductivity which is a function of the amount of H_2O added. This method seemed at first to be particularly valuable since it was believed that conductivity measurements could be made without removing samples from the fractionation unit. Conductivity cells were therefore installed in each column of the fractionation unit and connected to a micromax recorder so that a continuous record could be obtained. However, the installation has not been entirely satisfactory, due to a number of difficulties,[14] and samples have therefore been withdrawn regularly for laboratory measurement of conductivity.

Conductivities of solutions of $(CH_3)_2O:BF_3$ containing various impurities have been studied in some detail by S.A.M.[7,33] Other substances besides H_2O were found to contribute to the conductivity of $(CH_3)_2O:BF_3$. It was hoped, however, that conductivity measurements could be used to detect sudden increases in the water content of $(CH_3)_2O:BF_3$.

Conductivity data obtained from the fractionation unit during the past year have been studied in detail. The observation was made that material causing high conductivity collects in the bottom of the column and that the Karl Fischer titratable material tends to separate into two parts, one more volatile and one less volatile than $(CH_3)_2O:BF_3$. Systems containing H_2O were studied in more detail by Hiebert[40] who obtained concrete evidence for these conclusions, independently.

In the operation of columns in cross flow an equilibrium state is attained in which the conductivities gradually increase throughout the system as the bottom column is approached. The conductivity of the material in the bottom reboiler is quite high as compared with the very small amount of Karl Fischer hydroxyl found.

It has not been found possible to satisfactorily account for these observations, nor is it even possible to state what substance is being measured by conductivity.

The apparatus used for laboratory measurements of conductivity is described below. The automatic recording apparatus is described elsewhere.[14]

A summary of the information obtained concerning conductivity measurements with $(CH_3)_2O:BF_3$ from the experiments at S.A.M. and from the operation of the fractionation unit in this laboratory is presented. Consideration is given to all of the hypotheses which have been proposed to explain the meaning of the observed conductivities. The obvious explanation in terms of hydrogen ions is not acceptable because the corresponding anions cannot be detected.

Figure 3

Effect of Heating on Conductivity

I. Unheated $(CH_3)_2O:BF_3$ - Original Conductivity
II. Heated $(CH_3)_2O:BF_3$ - Original Conductivity
III. Heated After Adding H_2O - Original H_2O Concentration
IV. Heated After Adding H_2O - Karl Fischer H_2O Analysis

(From SAM Reports M-1184 and M-1405)

The usefulness of conductivity measurements for detecting leaks is discussed. The conclusion is reached that the conductivity measurement is probably the least valuable of the analyses which have been used to detect leaks.

B. Laboratory Measurements of Conductivity

An Ostwald pyrex conductivity cell obtained from E. H. Sargent has been found the most satisfactory of the several cells tried for routine measurements. The cell has a cell constant of about 1. The electrodes were platinized according to the standard procedure. Instead of using the cell in its original form it was found that the 25 x 50 mm. weighing bottles used for taking samples could be filled to a fixed level and used as conductivity cells by inserting the electrodes of the Ostwald cell. Calibration was made with 0.01 N. KCl solution. Measurements are made with the Industrial Instruments Conductivity Bridge, model RC-1B. An external condenser is available for use when necessary to obtain a sharp balance. The calibration must be checked from time to time, and the platinization may need to be repeated. The platinization and calibration of the cell used were made by Hiebert in connection with his studies of conductivity.[40]

The temperatures are measured by inserting a dry thermometer into the solution immediately after measuring the resistance. The resistance is corrected to 25°C. by using cell constants calculated for each temperature. These cell constants were calculated using a temperature coefficient for the resistance of 0.014 ohms/degree, calculated from the data obtained at the S.A.M. Laboratories.[41]

The data are reported as specific resistance at 25°C. The specific conductance has been found more suitable for the purpose of day by day plotting.

C. Study of the Significance of Conductivity Measurements

Summary of data obtained by S.A.M. Laboratories.--Kirshenbaum[7,33] studied the effect of a number of compounds on the conductivity of $(CH_3)_2O:BF_3$. H_3BO_3, HF, and CH_3OH in $(CH_3)_2O:BF_3$ gave molar conductivities lower than but comparable with those of H_2O in this medium. The metal salts which were studied by Kirshenbaum were only slightly soluble in $(CH_3)_2O:BF_3$ and did not affect the conductivity significantly.

Effect of heating.--Kirshenbaum also studied the effect on the conductivity of $(CH_3)_2O:BF_3$ containing H_2O of heating in a closed system. Just as the amount of Karl Fischer titratable H_2O decreases to a constant value on heating, the conductivity of the $(CH_3)_2O:BF_3$ increases to a constant value. In Figure 3 the conductivities taken from Report M-1405 (Figure 4)[7] and Report M-1184 (Figure 7)[33] are plotted. Curve I represents the conductivity observed on adding weighed amounts of H_2O to unheated $(CH_3)_2O:BF_3$. Curve II represents the conductivity observed on adding H_2O to previously heated $(CH_3)_2O:BF_3$. On heating the $(CH_3)_2O:BF_3$ for 15 hours at 100°C. the conductivity decreases to a constant value shown by curve III, the H_2O concentration plotted being the amount of H_2O which had been added. At the same time the amount of H_2O as shown by the Karl Fischer analysis has decreased. The relation between the conductivity and the amount of H_2O still determinable by Karl Fischer analysis is shown in curve IV. This is the curve which should be used to estimate
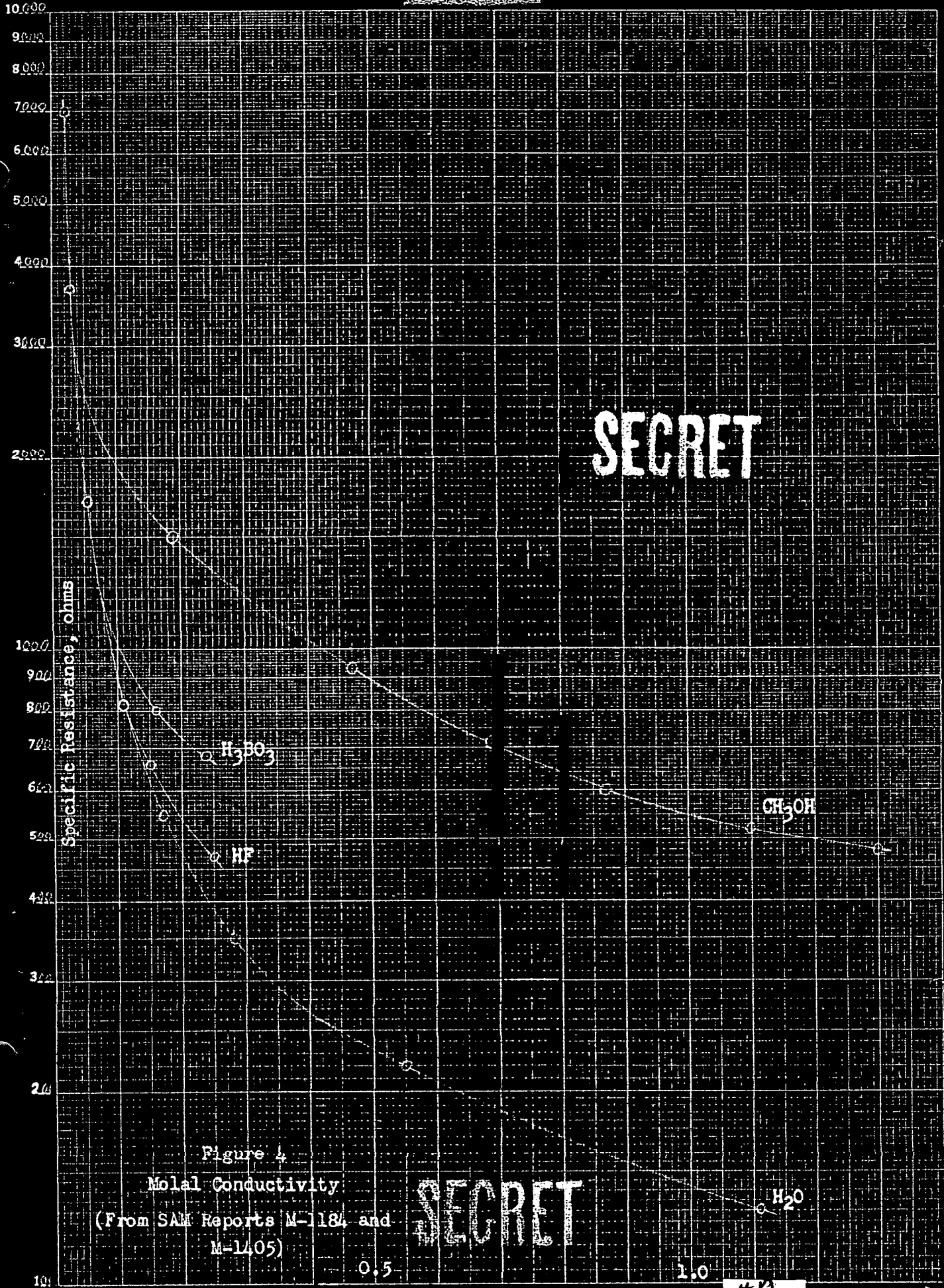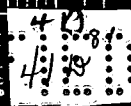
Figure 4
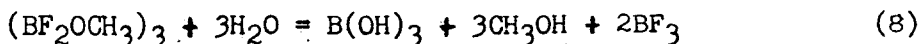Molal Conductivity
(From SAM Reports M-1184 and M-1405)

41

H$_2$O concentrations from conductivity measurements. Curve III may also be used to estimate from conductivity measurements the total amount of H$_2$O added including that present as H$_2$O and that which has been converted into some other form but which is still present in the (CH$_3$)$_2$O:BF$_3$ as an impurity of some sort. The values in curves I, II, and IV were taken directly from Kirshenbaum's data. Curve III was calculated using Kirshenbaum's values for the relation between the amount of H$_2$O added and the Karl Fischer analysis at equilibrium as shown in Report M-1405 (Figure 3).[7]

Comparative effects of H$_2$O, H$_3$BO$_3$ and CH$_3$OH on conductivity.--The data reported by Kirshenbaum for the conductivity of H$_2$O, H$_3$BO$_3$ and CH$_3$OH in Report M-1405 (Figure 9)[7] and of HF in Report M-1184 (Figure 9)[33] in solutions of unheated (CH$_3$)$_2$O:BF$_3$ are shown in Figure 4 with the concentrations expressed in mols solute/1000 g. solvent. Unfortunately no measurements have been made in which solutions of HF, CH$_3$OH, and H$_3$BO$_3$ in (CH$_3$)$_2$O:BF$_3$ were heated to constant conductivity.

The conductivities of HF, CH$_3$OH, H$_3$BO$_3$, and H$_2$O in (CH$_3$)$_2$O:BF$_3$ appear to be due to dissociation to form solvated hydrogen ions and the corresponding anions. The data in Figure 4 indicate that if this is the case the number of hydrogen ions produced by one mol of these different acids is not constant. Kirshenbaum studied the conductivities of mixtures of H$_3$BO$_3$ and H$_2$O in (CH$_3$)$_2$O:BF$_3$ and suggested a mechanism for a reaction between these two molecules to account for the observed effects.[7]

Conductivity of solutions containing (BF$_2$OCH$_3$)$_3$.--Kirshenbaum also studied the conductivity of (CH$_3$)$_2$O:BF$_3$ containing methoxy-boron difluoride, a compound with the empirical formula (BF$_2$OCH$_3$)$_3$ to which Kirshenbaum, Sabi, and Schutz[3] attribute the structure of a trimethyl borate-boron trifluoride complex, B(OCH$_3$)$_3$:2BF$_3$. Admitting that the compound shows the reactions of B(OCH$_3$)$_3$ and BF$_3$, there are some reasons for preferring the empirical formula (BF$_2$OCH$_3$)$_3$. Kirshenbaum found that (BF$_2$OCH$_3$)$_3$ caused only a slight change in the conductivity of dry (CH$_3$)$_2$O:BF$_3$ but that it decreased the conductivity of (CH$_3$)$_2$O:BF$_3$ containing H$_2$O considerably.[7] This observation was explained qualitatively, if not quantitatively, by the reaction (8).

$$(BF_2OCH_3)_3 + 3H_2O = B(OH)_3 + 3CH_3OH + 2BF_3 \qquad (8)$$

These experiments establish the fact that in the presence of (BF$_2$OCH$_3$)$_3$ relatively small increases in conductivity can be caused by the addition of H$_2$O because of the hydrolysis reaction (8).

Data obtained by analysis of samples from fractionation unit, single column operation.--Conductivity data obtained from the fractionation unit during the past year have been studied from time to time. In the early operations in which single columns were being tested for fractionation of (CH$_3$)$_2$O:BF$_3$, it was observed that the amount of H$_2$O determined by Karl Fischer titration was higher at the top of the column than at the bottom. It was further observed that the Karl Fischer titer at the top of the column could be greatly reduced by withdrawing material from the top, and that the Karl Fischer titer at the bottom was reduced slightly at the same time.

TABLE XV

Representative Specific Resistances
January, 1945

Date					Column Sampled					
	2T	2B	3T	3B	4T	4B	5T	5B	6T	6B
1-1	4400	1370	4100	510	4600	640	1000	490	560	240
1-2	4800	1460	6300	470	5400	360	1720	540	690	210
1-3	4600	1400	7600	710	6400	600	1740	360	630	240
1-4	5000	1490	3400	610	5400	640	1330	570	670	230
1-5	6400	1300	4700	980	4900	650	1800	530	510	490
1-6	5200	1490	5600	1300	6300	670	4900	530	530	430
1-7	7500	580	5800	850	4000	650	2500	500	580	560

Date	2T	2R	3T	3R	4T	4R	5T	5R	6T	6R
1-8	5200	550	940	370	5400	320	4200	270		200
1-9	4700	500	5500	370	6700	350	4500	310		170
1-10	4700	490	6000	330	6100	300	3300	290		180
1-11	4100	530		370		320		280		160
1-12	3000	480		340		300		270		200
1-13	2500	430		310		300		300		170
1-14	3100	460		320		300		290		150

T = Top of column
B = Bottom of column
R = Reboiler (pump discharge)

TABLE XVI

Representative Specific Resistances
September, 1945

Date				Column Sampled					
	1T	1R	2R	3R	4R	5R	6R	7R	9R
9-10	5200	800	740	290	290	210	180	200	140
9-12	4900	810	780	380	260	220	200	200	120
9-14	5400	920	760	430	340	280	190	270	150
9-17	5200	890	750	420	310	240	180	270	150
9-19	5300	840	720	390	360	290	190	280	130
9-21	5300	920	740	420	320	220	210	300	150

31a

A considerable amount of data on the H_2O analyses in single column operation was collected by Schutz[42] for the period November2 - November 15, 1944. Another example of single column operation studied was the testing operation with column 1 during March, 1945. Water analyses for this test are shown in Table XIV. Analyses in this case were made on the sample taken from the pump discharge where in the cases described by Schutz, only column bottom samples were analysed. There is considerable doubt whether the column bottom sample is a valid test for the amount of H_2O present in the reboiler.

TABLE XIV

Water Analyses
Tests of Column 1

| Date | Time | Karl Fischer Analyses | | Specific Resistance | | Total Withdrawn |
		Top	Reboiler	Top	Reboiler	Overhead
3-3-45	3 PM	1.25%	----	1180 ohms	----	3/4 gal.
3-4-45	8 AM	1.25	0.19%	1500	380 ohms	5 gal.
3-5-45	8 AM	0.87	0.10	1800	390	6 1/2 gal.
3-6-45	8 AM	0.23	0.06	3800	380	11 1/4 gal.

The observations on single column operation suggested that H_2O in $(CH_3)_2O:BF_3$ is separated into two parts on long continued distillation. One of the products appears to be a compound less volatile than $(CH_3)_2O:BF_3$, with Karl Fischer titratable hydroxyl groups and with a low conductivity. The other product, a less volatile constituent than $(CH_3)_2O:BF_3$, has a high conductivity and a low Karl Fischer titer.

Cross-flow operation.--The data obtained in the operation of a number of columns in cross flow provided additional information concerning the use of conductivity measurements. First it was found that the Karl Fischer titrations showed small amounts of H_2O present throughout the system, the amount being about the same for each column when no serious leaks were present, except for the top and bottom ends of the system. The $(CH_3)_2O:BF_3$ continuously withdrawn from the top and the bottom under steady state conditions showed larger amounts of water, particularly in the top. Some average values are shown in Table XIII. The conductivity on the other hand was found to increase from the top of a column to the bottom and from the column containing the more volatile material to the column containing the less volatile material. Typical data are shown in Tables XV and XVI.

Operation of the product still.--The data obtained in the operation of the product still used for redistilling the product withdrawn from the bottom[13] show further that the H_2O present in the bottoms draw-off material is relatively non-volatile. The Karl Fischer analysable H_2O and the conductivity material both appear to remain in the residue on redistillation.

81

TABLE XVII.

Anions Estimated from S.A.M. Conductivity Values (Figure 4)

Material	Spec. Res.	% OH Calc. I	% OH Calc. IV	% OH Obs.	% OCH_3 Calc.	% OCH_3 Obs.	% F Calc.	% F Obs.
Column 9 (last column)								
E-112	150	1.5	0.8	0.07			3.	<0.1
E-190	200	1.0	0.43	0.07	>5.	0.10		
E-218	250	0.8	0.32	0.04			1.2	<0.1
Column 7								
D-346	380	0.43	0.18	0.14			0.6	<0.1
D-785	410	0.39	0.16	0.03			0.5	<0.1
D-189	370	0.45	0.18	0.02	>5.	0.07		
Column 6								
D-958	220	0.89	0.37	0.07				
D-986	200	1.0	0.43	0.03				
E-7	250	0.76	0.31	0.04				
Redistilled Product								
Lot 40	280	0.65	0.28	0.11	>5.		1.0	0.1
Lot 41	280	0.65	0.28	0.16	>5.		1.0	<0.1
Lot 66	430	0.37	0.15	0.03	5.		0.6	<0.1
Lot 68	640	0.20	0.06	0.05	2.5		0.3	<0.1

$H4D^{81}$

32a

45

Data obtained in laboratory column.--A more detailed study of the distillation of the $(CH_3)_2O:BF_3$--H_2O system was made by Hiebert[40] in a glass laboratory column. He arrived independently at essentially the same conclusions which were suggested by the analysis of plant data, that water separates into two parts, one more volatile containing hydroxyl with a low conductivity, and one less volatile having a high conductivity and a low Karl Fischer titer.

D. Evaluation of Procedure

Attempts to explain the observed conductivities.--The material causing the conductivity is apparently present in equilibrium concentrations at each point, and is being drawn off from the last column at a rate equal to the net rate at which it is being formed. Since it has been observed that the non-volatile iron salts appear to settle very quickly to the bottom of the system, and that H_2O formed by leaks is rapidly transferred to the top of the system, it is difficult to understand why the conductivity material is distributed throughout the unit in the observed manner. It seems unlikely that the compound causing conductivity has a separation factor for distillation with $(CH_3)_2O:BF_3$ which is comparable with the isotopic separation factor. It would appear that the explanation must be the existence of a chemical equilibrium involving the ions which cause conductivity.

The observations described so far are all consistent with the theory advanced above that a non-volatile material causing conductivity and a volatile hydroxy fluoride are formed from the $(2H_2O):BF_3$ when it breaks down. Unfortunately neither of the products formed has been definitely identified, and the exact nature of the reaction is not known. However, any reaction which can be written to form hydroxy fluorides from $(2H_2O):BF_3$ would involve the formation of a compound which would be expected to have a dissociable hydrogen ion.

Assuming that, as indicated, a considerable concentration of hydrogen ion must be present in the lower reboilers of the fractionation unit, a search was made for corresponding anions. The analytical data showing the absence of the required amounts of fluoride, methoxyl, and hydroxyl ions, are shown in Table XVII.

The curves in Figure 4 were used to calculate the amount of fluoride, methoxyl, or hydroxyl from the specific resistance, assuming in each case that all of the conductivity is caused by a single acid. The hydroxyl values are calculated from both curve I and curve IV.

From the data shown, it can only be said that if the conductivity is a measure of hydrogen ions, the corresponding anions have not been identified. The possibility must be considered that hydrogen ions are not present in the concentrations indicated by the conductivity measurements.

Consideration must be given to other possible cations which might be present. Organic cations with the charge residing on the carbon atom might be postulated. Recent work[43] has shown that the conductivity of transformer oils is due to such ions and not to hydrogen ions as expected. An electrometric study of the system could be used to measure more directly the hydrogen ion concentrations as was done with the transformer oils. All indications are that the effect of metallic ions on the conductivity is small. The metallic ions are

TABLE XVIII

Detection of Leaks

Date	K.F. Anal.	Specific Resistance	% Fe	Explanation
5-14-45	1.8	135 ohms	0.57	Air leak detected and repaired
5-7-45	0.19	160	0.38	
4-10-45	0.57	130	0.39	High K.F. analysis—location of leak
4-3-45	0.16	175	0.39	not known.
3-8-45	0.09	135	1.6	Air leak—corrosion in reflux loop—
3-1-45	0.09	125	0.8	column shut down
2-9-45	0.06	210	0.62	Leak in overhead line—column shut
2-2-45	0.15	215	0.26	down

47

almost entirely concentrated in the bottom reboiler while the conductivity is distributed throughout the system. Further, the conductivities of all metal salts which have been studied in $(CH_3)_2O:BF_3$ have been small.[7]

It would appear that there are present compounds of an unidentified nature which either cause conductivity in themselves or markedly increase the conductivity of the known compounds containing dissociable hydrogen ions. If these compounds do not result from reactions with H_2O they may be caused by the thermal decomposition of $(CH_3)_2O:BF_3$ which has been shown to cause a dark color in the less volatile fraction, or they may possibly result from reactions involving impurities present in the BF_3 and $(CH_3)_2O$ used. It is known that carbon compounds collect in the less volatile fraction.

Use of conductivity for detecting leaks.--Although the identification of the material causing the conductivity has not been accomplished, the conductivities are in any case a measurement of undesirable impurities. The conductivities which may be permitted in operation of the fractionation unit are much higher than was originally expected, but exceptionally high conductivities are still considered potentially dangerous until it has been demonstrated to the contrary. As far as is known, the danger from high conductivities would be in a high corrosion rate, which is much better measured directly by the concentration of dissolved iron.

The object of the automatic recording conductivity cells was to detect the sudden appearance of water in case of a serious leak, particularly a steam or condenser leak. There is no question that conductivity measurements would provide an indication of such a state of affairs, although it may be that in a large H_2O leak, the temperature, pressure, or flow instruments would show the effect even more rapidly. For air leaks, the conductivity measurements are of limited value. In the course of plant operations carried out since December 30, 1944, it has been necessary twice to shut down a column because of serious leaks in the overhead line. On two other occasions high Karl Fischer titers in the bottom reboiler were observed, presumably due to leakage. In both cases, measures taken to stop leakage were successful, although in one case the location of the leak was not found. The analytical data for these columns at the time of the leak and the analyses reported 7 days previous are shown in Table XVIII. The Karl Fischer analysis and the iron analysis appear to be better indications of a leak than conductivity measurements. All of the cases presented in the table concern the last column in the series. Leaks in other columns are not so readily detected by any chemical analyses, but there has been no evidence to show that a leak not detected by Karl Fischer analyses would be detected by conductivity measurements.

In the operation of a single column, when the conductivity of the bottom is not very high, conductivity measurements offer more possibility for detecting the appearance of water. Data tabulated by Schutz[41] showed that both Karl Fischer analyses and conductivity measurements were useful in detecting a leak which necessitated shutting down a column.

VIII. DETERMINATION OF METALS

A. General Introduction

Methods for the rapid colorimetric determinations of iron, nickel and copper in $(CH_3)_2O:BF_3$ were developed by the S.A.M. Laboratories.[31] Modified forms of these methods have been used in this laboratory. These colorimetric procedures were found particularly valuable when a number of single columns were being tested separately and metal analyses were required regularly on each column. A volumetric method for copper was found to be more satisfactory than the S.A.M. colorimetric method. A volumetric method for zinc was also developed. Under routine operating conditions, the corrosion takes place primarily with iron, and only small amounts of the other metals are dissolved. Only the bottom column needs to be analysed for metals. A volumetric determination of the iron replacing the colorimetric determination is suggested as the most reliable test for corrosion. A gravimetric determination of nickel should also be considered. The advantages of the colorimetric method are greatly reduced when only occasional analyses are required.

In the procedures described by the S.A.M. Laboratories,[31] the determinations of iron, nickel, and copper were all made on aliquot fractions of the same sample. The routine procedures now in use do not involve any separations and independent samples are used. If desired, the procedures described below could be modified to use aliquot fractions of a single sample.

In the procedures described below, the samples are measured volumetrically, assuming a density of 1.23 as was done in the Karl Fischer analyses. Weighed samples can be used if desired.

B. Sampling for Metal Determinations

The raw product from the reboiler of the bottom column, which is the only sample containing enough metal to require analysis, sometimes contains a precipitate which is insoluble in $(CH_3)_2O:BF_3$. The technique which has been followed in this case is to take as nearly as possible a representative sample including the suspended solids, shaking the sample bottle before removing the sample with a pipet. Any portion of the sample taken which is not soluble in cold water is discarded. In this way satisfactory analyses for routine determination can be readily obtained.

For strictly quantitative analyses a more rigorous procedure is required. Fortunately during the normal operation of the fractionation unit, the product has a homogeneous appearance and is entirely soluble in water. In this case no problem is involved.

Sampling of solutions containing suspended solids.—When there is an excessive amount of corrosion taking place, a suspended solid will be present and further precautions must be taken to secure a representative sample. The $(CH_3)_2O:BF_3$ could be filtered through a sintered glass filter crucible taking precautions to prevent the access of water. The amount of dissolved solids could then be determined in the filtrate.

On the other hand if it is desired to measure the total metal content, a representative sample of the suspension must be taken and an attempt made to dissolve the entire sample. The insoluble residue might be dissolved by heating with strong acid or might require a carbonate fusion.

The precipitates found in $(CH_3)_2O:BF_3$ are generally of two kinds. One is a white iron salt which has a limited solubility in $(CH_3)_2O:BF_3$ but is readily soluble in water. The second type is primarily carbonaceous material, insoluble in $(CH_3)_2O:BF_3$ and in water, containing only a trace of metal. Serious difficulties are therefore not likely to result from neglect of water insoluble precipitates in routine analyses.

C. Determination of Iron

Two methods for the colorimetric determination of traces of iron are in standard use.[44] The potassium thiocyanate method was used by the S.A.M. Laboratories.[31] The orthophenanthroline method would perhaps have been more satisfactory although this method has not been investigated for analysis of $(CH_3)_2O:BF_3$. Fluorine interferes with volumetric and colorimetric determinations of iron. Instead of separating the iron from fluorine by precipitating with ammonia and redissolving as was done in the S.A.M. method, the calibration is carried out with known amounts of fluorine present.

Under routine operating conditions, only a few iron determinations are required. The rapid colorimetric method is therefore not necessarily the most suitable method. A more accurate volumetric method would probably be preferable. The Jones reductor method used at S.A.M. for the determination of traces of iron[45] in which 0.01 N. ceric sulfate solution was employed is nearly as sensitive as the colorimetric method. This method has not been used for analyses of $(CH_3)_2O:BF_3$ but its employment should improve the usefullness of the iron determination.

Procedure for colorimetric determination of iron.--The raw undistilled product from the fractionation unit generally contains between 0.1% and 2.0% iron. This product may be analysed taking 0.05 ml. of $(CH_3)_2O:BF_3$ in 100 ml. water.

One ml. of the $(CH_3)_2O:BF_3$ to be analysed is dissolved in 50 ml. of water. Four ml. of saturated bromine water are added and the solution warmed to oxidize the iron. The solution is filtered if not perfectly clear and the precipitate washed with distilled water. The filtrate is caught in a 100 ml. volumetric flask and the volume made up to 100 ml. Five ml. of this solution are transferred with a pipet to another 100 ml. volumetric flask. Five ml. of 3 M. potassium thiocyanate and 5 ml. of 6 M. hydrochloric acid are added from burets. The volume is made to 100 ml. and the flask shaken. The transmittance is measured with a Cenco-Sheard-Sanford "Photolometer", industrial type B-2 operated from a 6 volt storage battery. A blue filter is used for measuring the red solution of ferric thiocyantate.

Figure 5
Colorimetric Determination of Iron

I. No Fluoride
II. 720 mg. BF₃/100 ml.
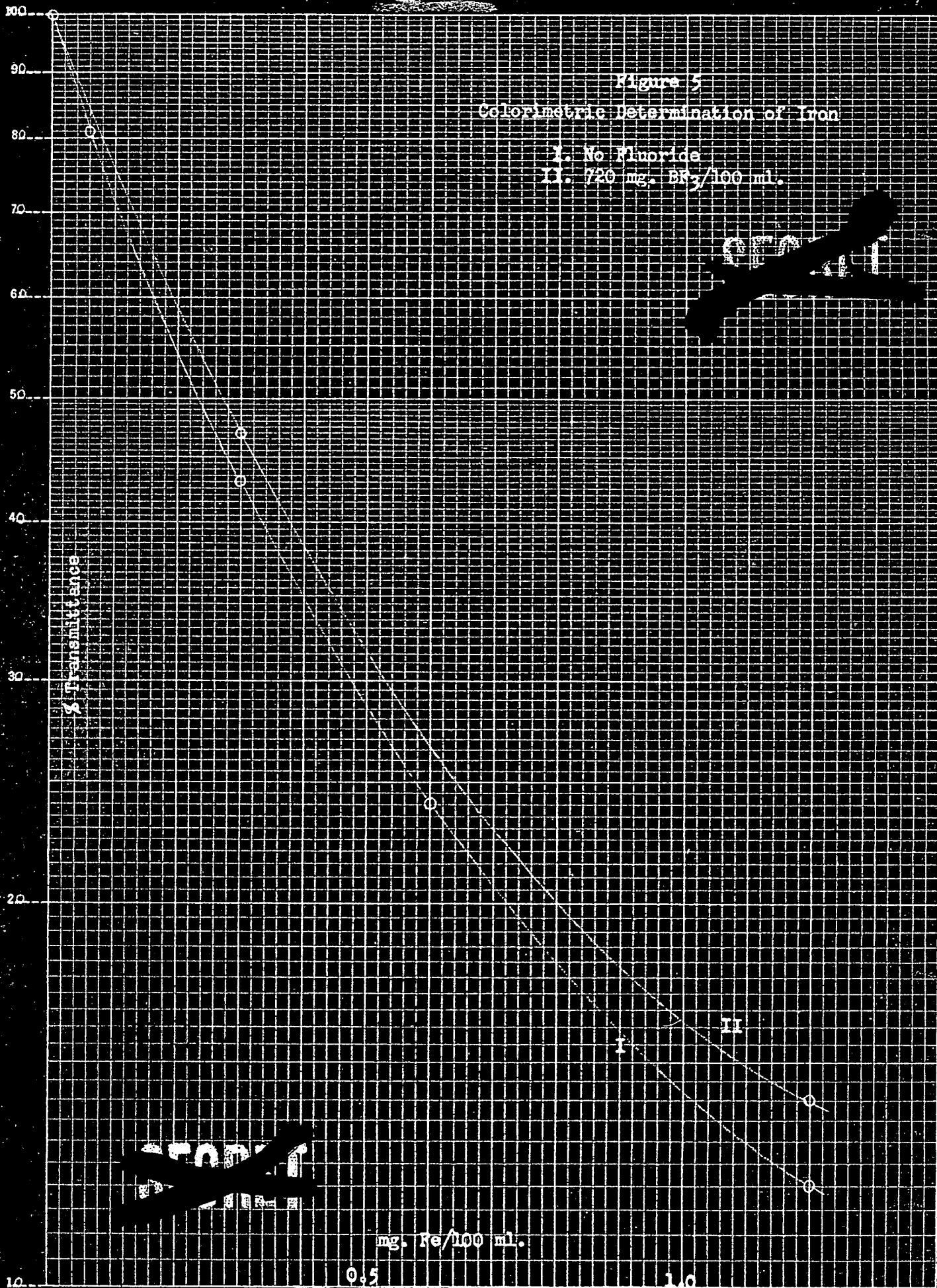
% Transmittance

mg. Fe/100 ml.

The concentration of the iron in the measured solution is determined from the calibration curve in Figure 5, using curve I. The amount of iron in the original $(CH_3)_2O:BF_3$ is calculated taking into account the dilution of the solution made.

$$\% \text{ iron} = \frac{\text{mg. Fe/100 ml.}}{0.05 \times 1,230} \times 100 \qquad (9)$$

Procedure for determination of very small amounts of iron.—For amounts of iron less than 0.1%, a larger sample must be taken. Instead of making the filtrate to a volume of 100 ml. and removing a five ml. sample for further dilution, the potassium thiocyanate and hydrochloric acid are added directly to the filtrate before making to volume. The calibration curve for solutions containing 720 mg. BF_3/100 ml. must be used.

$$\% \text{ iron} = \frac{\text{mg. Fe/100 ml.}}{1 \times 1,230} \times 100 \qquad (10)$$

This modified procedure can be used for concentrations down to 0.001% iron, and is used for analyses of redistilled product.

Calibrations for colorimetric iron determinations.—The calibrations in Figure 5 were made with standard solutions of ferrous sulfate analysed gravimetrically by oxidation with bromine, precipitation with ammonia, and weighing as the oxide.[46] Calibrations made in the presence of a measured amount of BF_3 are shown along with a curve made in the absence of fluoride. The transmittances of solutions containing 36 mg. BF_3/100 ml. of solution, the concentration generally used in analysis, could not be distinguished from transmittances in the absence of fluoride.

Volumetric determination of iron.—In the S.A.M. iron titration the standard Jones reductor procedure was followed[47] and the reduced iron was titrated with 0.01 N. ceric sulfate using ortho-phenanthroline ferrous indicator. Standardization is best carried out by comparing with recrystallized potassium dichromate through a standard ferrous sulfate solution. Standard potassium dichromate of 0.01 N. concentration could probably be used similarly, with ortho-phenanthroline ferrous complex or diphenylamine indicator. Fluorine must be separated by precipitating the iron with ammonia and redissolving. Copper will be separated from iron in the ammonia precipitation unless present in considerable quantity. In this case a preliminary separation of copper as sulfide is required.[31,47] The precision of the colorimetric method using the industrial type colorimeter is quite limited. For any precise work, either the volumetric method should be used or a colorimeter capable of higher precision should be employed.

D. Determination of Nickel

The standard dimethylglyoxime colorimetric method[48] for the analysis of nickel was used in the S.A.M. procedure.[31] Iron was separated by precipitation with ammonia and nickel determined in the filtrate. A modification of the S.A.M. procedure was developed in this laboratory in which the iron is kept in solution with tartrate. Some difficulty was encountered with fading of the red color.
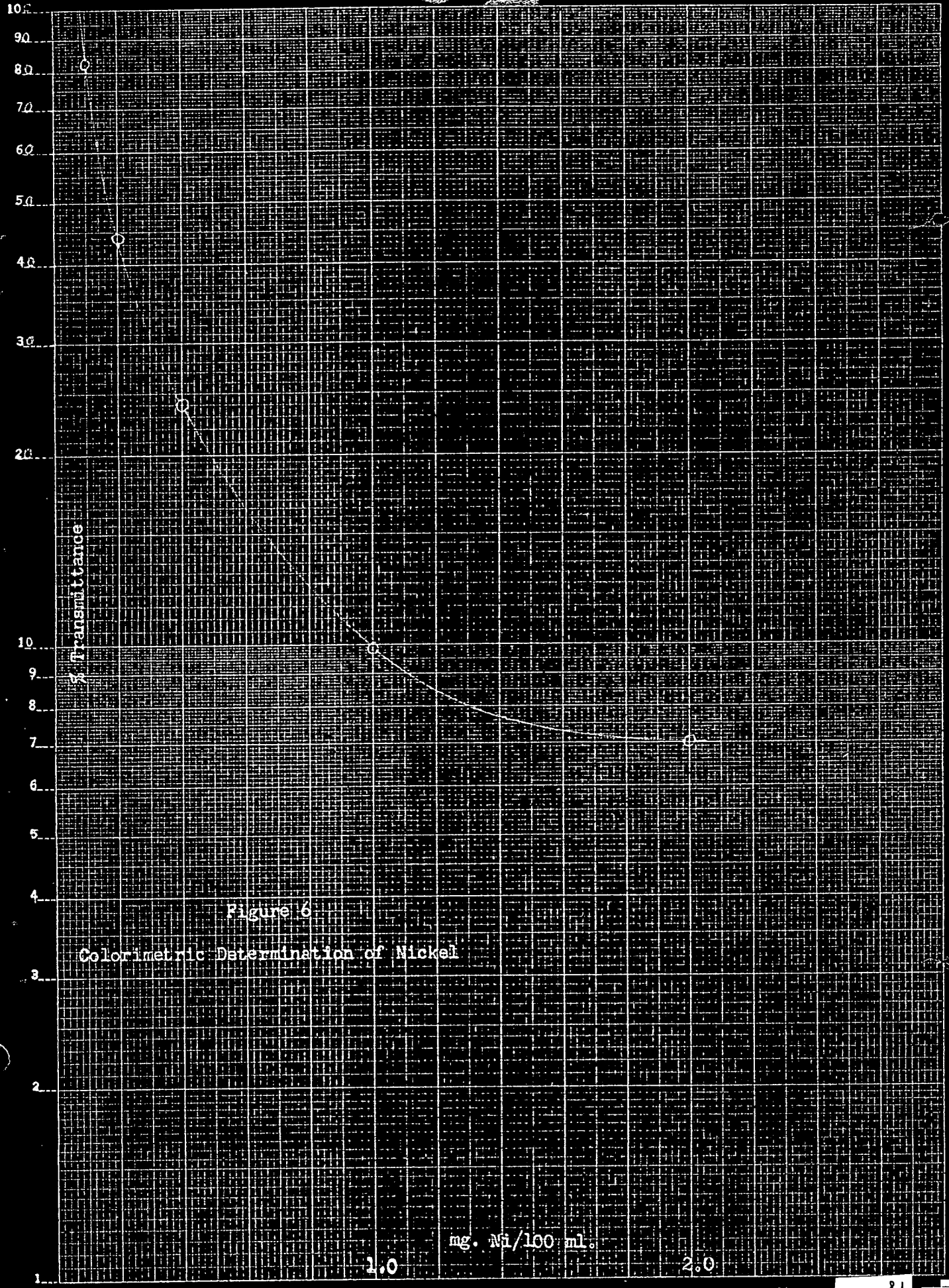
Figure 6

Colorimetric Determination of Nickel

% Transmittance

mg. Ni/100 ml.

The procedure of Makepeace and Craft[49] has recently been adopted and has been found more satisfactory. In this procedure tartrate is used in a strongly alkaline medium.

Although the intensity of color is not as great as in methods using a less alkaline medium, this method has the advantages that iron interference is eliminated without encountering any difficulties due to fading.

The calibration of the colorimeter for nickel determinations was made with a standard solution of nickel sulfate standardized by the conventional gravimetric procedure[47] in which the dimethylglyoxime compound is weighed. If only occasional analyses are being made, the routine determinations could be made by the gravimetric method. This method must be used whenever high precision is required.

Colorimetric procedure for nickel.--One ml. of the $(CH_3)_2O:BF_3$ to be analysed is transferred with a pipet to a 100 ml. volumetric flask. About 15 ml. of water are added. Five ml. of 20% tartaric acid are added, then 5 ml. of saturated bromine water, then 10 ml. of concentrated ammonia (sp.gr. 0.90), and finally 5 ml. of 1% dimethylglyoxime in methanol, mixing the solution after each addition. After 1 minute, 10 ml. of 6 N. sodium hydroxide solution are added. After 5 minutes the transmittance is measured using the industrial "photolometer" mentioned above, with a blue filter.

From the calibration curve shown in Figure 6, the concentration of nickel in the solution is determined and the amount of nickel in the $(CH_3)_2O:BF_3$ calculated.

$$\% \text{ nickel} = \frac{\text{mg. Ni/100 ml.}}{1,230} \times 100 \qquad (11)$$

The procedure described is useful for concentrations from 0.02% to 0.2% nickel. The amount of nickel in the undistilled product obtained from the fractionation unit generally lies in this range. For analyses outside of this range the concentration of $(CH_3)_2O:BF_3$ in water must be varied.

It was found that the presence of BF_3 in concentrations as large as 1 ml. $(CH_3)_2O:BF_3$ per 100 ml. water affects only slightly the observed transmittance of the nickel-dimethylglyoxime solutions. Calibration could be carried out in the presence of known amounts of BF_3, but this has not been considered necessary. The results are accurate to within 20% for concentrations of 1 ml. $(CH_3)_2O:BF_3$ per 100 ml. of water or less.

Gravimetric procedure for nickel.--The standard dimethylglyoxime procedure is used.[47] The interference of iron is avoided by adding tartaric acid[46] or by precipitating the iron. Copper does not interfere in moderate quantities. If zinc is present a modified procedure in an acetate medium is preferred.[47] If a volumetric iron determination is to be made, the nickel determination is made on the filtrate from the iron precipitation.

A 5 ml. sample of $(CH_3)_2O:BF_3$ containing 0.01% nickel would give a precipitate of 2.5 mg. of nickel so that the method is easily capable of application to the determination of traces of nickel in $(CH_3)_2O:BF_3$.

Procedure.--A suitable sample of $(CH_3)_2O:BF_3$ containing not more than 30 mg. of nickel is dissolved in water. Iron, if present, is oxidized with bromine, the excess bromine removed, and 7 grams of tartaric acid added to form a complex with the iron. The volume is made to 200 ml., the solution made ammoniacal, and any precipitate filtered. The solution is acidified with HCl, heated to 80°C., 5 ml. of 1% dimethylglyoxime solution added for each 10 mg. of nickel present, and excess ammonia added. The solution is digested for 1 hour, filtered through a sintered glass pyrex crucible, and the precipitate weighed after drying for one hour at 110°C.

E. Determination of Copper

In the early tests in which considerable corrosion was observed, copper analyses were also required. A colorimetric procedure[48] using ferrocyanide was suggested by the S.A.M. Laboratories.[31] The iron and nickel must both be removed carefully. Small traces of iron interfere by causing a blue precipitate. An iodimetric method was found to be preferable. Actually using 0.01 N. sodium thiosulfate solution the sensitivity of the iodimetric method is greater than that of the colorimetric method. An additional advantage is that interference due to iron which is generally present in quantities considerably greater than the copper is eliminated. The interference of iron in the iodimetric titration is avoided by the use of potassium fluoride which forms a complex with ferric iron. The procedure is similar to that described by Kolthoff and Sandell[46] except that 0.01 N. thiosulfate is used instead of 0.1 N. Under routine operating conditions the amount of copper dissolved in $(CH_3)_2O:BF_3$ is negligible compared to the iron, and is considerably smaller than the amount of nickel dissolved. Occasional analyses should be made to check the copper concentration of the raw product, however.

Procedure for iodimetric copper determination.--A sample of 1 ml. of $(CH_3)_2O:BF_3$ to be analysed is transferred to a 100 ml. Erlenmyer flask containing 50 cc. of H_2O. The solution is treated with 4 cc. of bromine water and boiled vigorously for five minutes. Two grams of potassium fluoride are dissolved in the solution. The solution is then cooled and 20 cc. of 10% potassium iodide solution added. One ml. of fresh 1% starch solution is added and the solution titrated to the disappearance of the blue starch-iodine color with 0.01 N. standard sodium thiosulfate solution.

The method is sensitive to 0.01% Cu which will give a titer of 0.10 ml. of thiosulfate solution. The thiosulfate solution may be standardized against potassium dichromate solution.[46]

For analyses of the highest precision the iron should be separated from the copper. The iron may be precipitated with ammonia and the copper determined in the filtrate. The precipitation of copper with H_2S as used in the S.A.M. procedure[31] is better. The CuS is redissolved and titrated iodometrically. The filtrate may be used for iron and nickel determinations. The addition of 1 g. of potassium acid phthalate as a buffer might also improve the iodometric titration.

F. Determination of Zinc

Some research work was done using brass packing in the columns instead of monel packing. In these experiments small amounts of zinc were found to be dissolved in the $(CH_3)_2O:BF_3$. The titration with potassium ferrocyanide[46] was used for the determination of zinc. Iron, nickel, and copper were removed by precipitation with sodium hydroxide although nickel will not interfere. It was found that the titration was not satisfactory for very small quantities of zinc. It was therefore necessary to add an excess of standard zinc solution to the unknown solution and determine the amount of zinc in the unknown solution by difference.

Procedure for determination of zinc.--Five ml. of $(CH_3)_2O:BF_3$ are dissolved in water. The iron and copper are removed by precipitation with sodium hydroxide.[47] The filtrate is neutralized and made acid with 10 ml. of 6 N. sulfuric acid. Two drops of 1% potassium ferricyanide and two drops of 1% diphenylamine indicator in sulfuric acid are added. At least 2 ml. of standard 0.1 M. zinc solution is added. The solution is titrated with 0.05 M. potassium ferrocyanide solution to the appearance of a green color. The solution is back titrated with standard zinc solution to a blue color.

The standard zinc solution is made by dissolving weighed amounts of metallic zinc. The standard ferrocyanide solution is standardized against the zinc solution.

If the amount of zinc being determined is small, the procedure should be checked by the analysis of $(CH_3)_2O:BF_3$ known to be free from zinc. The procedure has only been used occasionally and no experiments with zinc free $(CH_3)_2O:BF_3$ have been carried out.

IX. HYDROGEN FLUORIDE DETERMINATION

A detailed study of the etch test in which hydrogen fluoride is determined in $(CH_3)_2O:BF_3$ by the rate of reaction with standardized strips of soft glass was described by Kirshenbaum.[7] It was reported that the extent of etching was a function of the water concentration as measured by Karl Fischer titrations as well as the hydrogen fluoride concentration. In samples of $(CH_3)_2O:BF_3$ taken from the fractionating unit, not only are there several different compounds which contribute to the observed Karl Fischer titers, but there are also other substances not measured by the Karl Fischer determination but causing a relatively high conductivity which might very well affect the etching reaction. The method is therefore not satisfactory for plant analyses. No satisfactory method for the determination of hydrogen fluoride in plant $(CH_3)_2O:BF_3$ has been found except the sodium hydroxide titration. This titration in which boron and fluorine are determined will show excess fluorine in amounts of a few tenths of one per cent..

# X. KARL FISCHER METHOXYL DETERMINATION

A. Introduction

In connection with the search for a mechanism for the disappearance of Karl Fischer titratable H_2O, the presence of $CH_3OH:BF_3$ was postulated. This compound might be formed by reaction (6) suggested above.

$$(2H_2O):BF_3 + (CH_3)_2O:BF_3 = 2\ CH_3OH:BF_3 + H_2O \qquad (6)$$
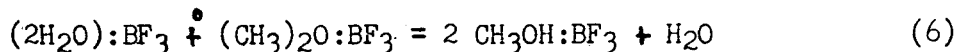
The compound $CH_3OH:BF_3$ has been described in the literature,[50] the existence of the compound being proved by vapor pressure measurements. The compound was, however, reported to undergo decomposition on distillation.

A procedure for the analysis of alcohols in $(CH_3)_2O:BF_3$ was developed to test the proposed mechanism (6) for the disappearance of H_2O and appearance of CH_3OH. Two standard methods were considered. The acetyl chloride method[51] was considered first. In this method the alcohol is esterified and the acetyl groups used up are measured by the decrease in acid titer. BF_3 interferes with the acidimetric titration. Although the BF_3 can be separated, this procedure is not very satisfactory for the detection of small amounts of alcohol in the presence of BF_3.

The method of Bryant, Mitchell, and Smith[5] in which the alcohol is esterified with glacial acetic acid and the water liberated is titrated with the Karl Fischer reagent offers much better possibilities.

$$ROH + CH_3COOH = CH_3COOR + H_2O \qquad (12)$$
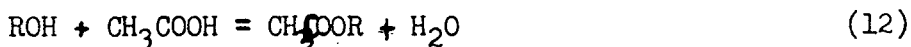
This procedure is normally carried out using BF_3 as an esterification catalyst so that the procedure is easily adapted to $(CH_3)_2O:BF_3$ analysis. Pyridine is added just before the Karl Fischer titration to remove the BF_3 and prevent esterification of the CH_3OH in the Karl Fischer reagent. The only modification required for $(CH_3)_2O:BF_3$ analysis is that the esterification flask cannot be stoppered because pressure is developed by the $(CH_3)_2O$ evolved on heating. Drying tubes filled with drierite are connected to the esterification flasks with ST ground glass joints.

Just as the Karl Fischer H_2O analysis was found to determine H_3BO_3 as well, the Karl Fischer CH_3OH analysis was found to determine $B(OCH_3)_3$. CH_3COOH reacts with $B(OCH_3)_3$ in much the same way that H_2O does.

$$B(OCH_3)_3 + 3\ CH_3COOH = B(OH)_3 + 3\ CH_3COOCH_3 \qquad (13)$$

$$B(OCH_3)_3 + 3\ HOH = B(OH)_3 + 3\ HOCH_3 \qquad (14)$$
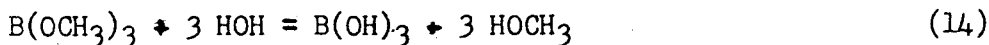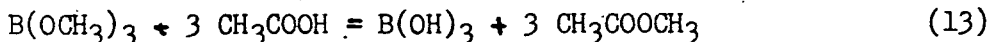
The decomposition product, methoxyl boron difluoride, $(BF_2OCH_3)_3$ and other mixed methoxy fluorides react similarly. The H_3BO_3 formed by reaction (13) is titrated by the Karl Fischer reagent as if it were H_2O.

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Tests were carried out to show that CH_3OH and $B(OCH_3)_3$ could be determined quantitatively. Measurements were then carried out to show the amount of $CH_3OH + B(OCH_3)_3$ formed on heating $(CH_3)_2O:BF_3$ containing H_2O. Finally, experiments were carried out in an attempt to identify CH_3OH as the product which causes the high conductivity of the product withdrawn from the bottom of the fractionation unit.

The most useful application of this analytical procedure would be for the determination of B-OCH_3 groups in the overhead draw off from the fractionation unit. This should be a better method of determining the amount of decomposition than the purity analyses which have been used in the past to calculate the amount of $(BF_2OCH_3)_3$ indirectly.

B. Procedure for Methoxyl Determination

Two ml. of the $(CH_3)_2O:BF_3$ to be analysed are added to a 100 ml. volumetric flask with ST 13 stopper. Ten ml. of Baker's reagent grade glacial acetic acid are added from an automatic buret. A drying tube containing drierite is attached to the flask with a ST 14/35 joint. The flask is cooled to room temperature, then placed in ice water. When cool, 4 ml. of pyridine are added and the solution is titrated with Karl Fischer reagent in the usual way.

A blank containing the same amounts of acetic acid and pyridine is titrated at the same time. A separate analysis of Karl Fischer hydroxyl in the $(CH_3)_2O:BF_3$ must also be made. The amount of CH_3OH is calculated after subtracting the blank for the water in the pyridine and acetic acid and another blank for the water present in the $(CH_3)_2O:BF_3$.

The method of preparing and handling reagents, of standardizing the Karl Fischer reagent, of drying the glassware, and of carrying out the titration are identical with those described for the Karl Fischer hydroxyl determination. From the standardization made with a H_2O standard the concentration in terms of mg. CH_3OH/ml. reagent is calculated.

For determinations of small amounts of CH_3OH the size of the sample can be increased to 5 ml., the amounts of pyridine and acetic acid being increased proportionately. For larger amounts of CH_3OH the amount of Karl Fischer reagent would more than fill the 100 ml. flask if a 5 ml. sample were used.

The result is expressed as per cent CH_3OH but it must be realized that methoxyl groups in $B(OCH_3)_3$ and $(BF_2OCH_3)_3$ are included in this determination as well as any other B-OCH_3 groups.

C. Evaluation of Methoxyl Procedure

Accuracy and precision of methoxyl determination.--The data obtained in analyses of solutions containing weighed amounts of CH_3OH and of $B(OCH_3)_3$ are shown in Table XIX. The $B(OCH_3)_3$ used was analysed for boron, fluorine, and hydroxyl since it was known to be impure. The equivalent amount of methoxyl was calculated by subtracting the equivalents of fluorine and of hydroxyl from the equivalents of boron. The agreement with the theoretical is not entirely satisfactory but indicates that the method can be used for approximate determinations.

$5 \cancel{A}^{81}$

This concentration corresponds to a partial pressure of 240 mm. of mercury for $(CH_3)_2O$ in the vapor phase. Since the total pressure at the top of an operating column is 150 mm. of mercury, it is not likely that appreciable concentrations of $(CH_3)_2O$ or $B(OCH_3)_3$ are present in the $(CH_3)_2O:BF_3$ drawn from the top of the column. Not enough is known about the reactions of CH_3OH in $(CH_3)_2O:BF_3$ to decide whether CH_3OH could be present in these samples.

The data obtained are shown in Table XX. A great deal of data is available for comparing the $(CH_3)_2O$ determination with the boron and fluorine determinations. The results calculated from boron and fluorine determinations are nearly always higher, indicating that the solutions are not simple mixtures of $(BF_2OCH_3)_3$ and $(CH_3)_2O:BF_3$. Such data as are available for methoxyl determinations also indicate that the amount of $(BF_2OCH_3)_3$ is less than that calculated from the boron and fluorine titrations.

It is for accurate analyses of methoxyl in the overhead decomposition product that the development of a more accurate procedure should be considered.

TABLE XX

Determination of Decomposition Product

| Date Sample	CH_3OH Anal.	% $(BF_2OCH_3)_3$ B & F Anal.	$(CH_3)_2O$ Anal.
Avg. May, 1945		12.8	8.2
9-17-45		10.9	5.7
9-19-45		10.9	7.3
9-21-45		10.5	6.9
9-24-45		10.1	6.2
9-27-45	6.6	11.8	7.6
10-5-45	4.2	7.5	2.1

Application to determination of $CH_3OH:BF_3$.--Analyses were made for CH_3OH in samples taken from the reboilers of the fractionation unit. The data previously presented in Table XVII show that no significant amounts of CH_3OH could be detected by this method in the high conductivity products from the reboilers containing the less volatile material, indicating that the high conductivities are not a measure of CH_3OH. The methoxyl determination would probably have little value for analyses of the reboiler samples.

Although no CH_3OH could be found in significant amounts in the reboilers, an attempt to identify CH_3OH in the products formed during the disappearance of Karl Fischer water on heating $(CH_3)_2O:BF_3$ was made.

Samples containing H_2O were analysed for hydroxyl H_2O and for methoxyl groups and were then heated at 100°C. and analysed again. The results from two experiments with 5 and 12 hours heating are shown in Table XXI. The amount of CH_3OH found was greater than that required to account for the H_2O which has disappeared. This may be explained by the methoxyl resulting from the $(BF_2OCH_3)_3$ formed by the thermal decomposition according to equation (19).

$$3 (CH_3)_2O:BF_3 = (BF_2OCH_3)_3 + 3 CH_3F \qquad (19)$$
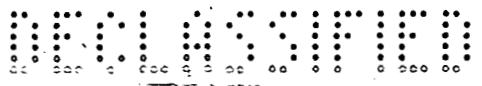
It is known that at least part of the observed methoxyl is due to this decomposition product. It is possible that all of the observed methoxyl results from reaction (19). The reaction (6) for the disappearance of H_2O to form CH_3OH has been neither proved nor disproved. A detailed study of the effect of heating $(CH_3)_2O:BF_3$ containing H_2O along the lines of the experiments carried out by Hiebert[40] would be required to settle the problem of disappearance of Karl Fischer titratable hydroxyl groups.

TABLE XXI

Disappearance of Karl Fischer Water

| Before Heating		After Heating		% CH_3OH	Time
%H_2O	CH_3OH	%H_2O	%CH_3OH	Calculated	Heating
4.68	0.5	3.64	5.3	3.70	5 hrs.
5.24	0.4	3.81	8.3	5.09	12 hrs.

Suggestions for further study.---The method has not been found satisfactory for quantitative analyses. It would appear that either the hydrolysis is not complete, the esterification of the methanol in the Karl Fischer reagent with acetic acid is not entirely blocked, or contamination by water is taking place. It should be possible to improve the technique and develop an accurate quantitative method.

If Hiebert's experiment in which $(CH_3)_2O:BF_3$ containing H_2O was heated in a fractionating column, removing the decomposition product overhead to keep the top temperature constant, were repeated, it should be possible, using the methoxyl determination which was not available at the time Hiebert's experiments were carried out, to definitely determine whether CH_3OH is formed in the disappearance of H_2O. Even with the crude analytical procedure now used for methoxyl it should be possible to obtain the desired information concerning the reaction of H_2O with $(CH_3)_2O:BF_3$ from such an experiment.

XI. DETERMINATION OF OTHER IMPURITIES

In addition to the impurities for which analyses have been described, it is possible that further contamination is introduced by the impurities known to be present in the BF_3 and the $(CH_3)_2O$ used to prepare the feed $(CH_3)_2O:BF_3$. The nature of the impurities present in these gases, estimates of the amounts, and descriptions of the procedures used for analyses have been obtained from the manufacturers. Careful consideration of these data and other available information made it appear likely that only a negligible contamination of the feed $(CH_3)_2O:BF_3$ would occur. This has been confirmed by purity analyses of the feed and by the fact that this $(CH_3)_2O:BF_3$ has been successfully used as feed to the fractionation unit over a long period of time.
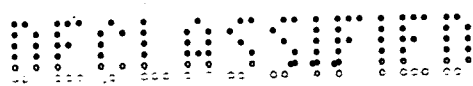
However, it appears likely that small impurities in the $(CH_3)_2O:BF_3$ in the fractionation unit will become of more interest as efforts are made to increase quality and quantity of product. In view of the fact that the methods of analysis of BF_3 and $(CH_3)_2O$ may be of value in setting up methods for determining the impurities in $(CH_3)_2O:BF_3$, these methods are presented below. Consideration is given to the probability of reactions taking place with these impurities which would lead to contamination of the product.

The Harshaw Chemical Company reports the impurities in BF_3 as air, SiF_4, SO_2, and SO_3. Procedures used by the Harshaw Company[11] for the determination of impurities in BF_3 were studied by the author at the S.A.M. Laboratories. The iodimetric procedure for SO_2 used by Harshaw was found satisfactory. Several procedures for SiF_4 were found which were more satisfactory[31] than the NaOH titration used by Harshaw. The molybdate colorimetric method would offer the best application to the determination of SiF_4 in $(CH_3)_2O:BF_3$. SO_3 analyses were not made, as Harshaw claims that only occasional traces are found. An improved procedure for the determination of air was employed at S.A.M.[2] but the Harshaw procedure could be used.

No analyses for these constituents in $(CH_3)_2O:BF_3$ have been made. Kirshenbaum[3] has shown that SiF_4 does not react appreciably at room temperature with $(CH_3)_2O$. SO_2, however, is known to form a compound with BF_3.[53] This compound should be less stable than $(CH_3)_2O:BF_3$. SO_3 is probably less apt to be present in fractionated $(CH_3)_2O:BF_3$ than SO_2.

The impurities known to be present in $(CH_3)_2O$ are H_2O, amines, aldehydes, unsaturated hydrocarbons, and non-volatile residue. Procedures have been developed in other laboratories for the determination of H_2O and CH_3OH using the Karl Fischer reagent,[37] and for the low boiling impurities.[12] Amines are absorbed with H_2SO_4, determined by titration with NaOH, and reported as NH_3. Aldehydes are absorbed with dinitrophenylhydrazine in HCl, determined gravimetrically, and reported as isobutyraldehyde. Unsaturated hydrocarbons are absorbed with Denige's reagent, determined gravimetrically, and reported as isobutylene.

Amines would form BF_3 compounds of low volatility collecting in the B^{10} fraction. In the presence of BF_3 the other organic compounds might undergo reactions and form compounds which would collect in the product. No analyses have been made for any of these constituents in $(CH_3)_2O:BF_3$.

If further research is carried out in order to improve the quality and quantity of product from the fractionation unit, investigation of analytical procedures for the determination of some of these constituents in $(CH_3)_2O:BF_3$ should be made.

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