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A METHOD FOR THE DETERMINATION OF WATER IN FLUORIDE SALTS

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J. C. White

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A METHOD FOR THE DETERMINATION OF WATER IN FLUORIDE SALTS

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September 8, 1953

ANALYTICAL CHEMISTRY DIVISION

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ABSTRACT

The removal of water by extraction with xylene and its subsequent determination by titration with Karl Fischer reagent has been successfully adapted to the determination of traces of water in alkali metal fluorides. The method was also applied to the determination of water in other solids containing larger concentrations of water. It is of particular value for the determination of water in thermally unstable solids.

If a large sample (10 to 20 grams) is used, the limit of determination is of the order of 0.01 per cent.

A METHOD FOR THE DETERMINATION OF WATER IN FLUORIDE SALTS

INTRODUCTION

Methods for the determination of water in solids can be classified in two general groups: (1) desiccation to constant weight and (2) extraction as an azeotrope by means of some solvent.

Feibig and Warf[2] used a modification of the desiccation technique to determine water in alkali fluorides. The main difficulty in this technique is to convert hydrogen fluoride, which has been formed by hydrolysis, to water before capture of the exhaust gases. Feibig allowed the gases to pass over heated sodium carbonate, which neutralized hydrogen fluoride and, in so doing, liberated water. Other approaches to this particular problem have been the use of lead oxide as a scrubber by Rose and Jannasch[8] and the use of sodium carbonate, intimately mixed with the fluoride, by Gooch[9]. Solvent extraction of water has an inherent advantage over desiccation in that hydrolysis is usually not a factor. Using this procedure, Penfield[5] has determined water in macro amounts volumetrically.

This study was initiated to determine water in alkali metal fluorides which had been subjected to desiccation at various temperatures. In general, it was considered sufficient to ascertain if the water content were less than 0.1 per cent. Ignition and extraction techniques were investigated for application to this problem. Past experience had indicated that the direct titration with Karl Fischer reagent was not generally applicable to solids. During this investigation Hibbitts and Zucker[4] reported a method which in essence combines both desiccation and titration with Karl Fischer reagent.

Their study was confined to the determination of adsorbed moisture on uranium metal and uranium oxides. The sample is heated in a stream of dry nitrogen to drive off the water and the exhaust gases are passed through a cell containing Karl Fischer reagent.

REMOVAL OF WATER BY DESICCATION

Determination of traces of water by desiccation was investigated by three methods: (1) loss in weight on heating the solid in an oven or furnace; (2) capture of evolved gases in absorption tubes; (3) loss in weight on heating in vacuo. Appraisals of these techniques are included in the following paragraphs.

Loss in Weight by Heating in Oven or Furnace

Determinations of water in solids can be carried out very easily by determining the loss in weight after heating the solid. The degree of hydrolysis of the salt can be evaluated approximately by this technique if the basicity of the ignited solid is also measured.

These tests consisted of heating 5 to 10 grams of reagent grade sodium fluoride in an open porcelain or nickel crucible for four hours at selected temperatures. A drying oven was used to attain a temperature of 110° C while temperatures above 110° C were achieved by means of an electric muffle furnace. The changes in weight in addition to the pH of aqueous saturated solutions (0.5 g per 50 ml solution) of the heated samples were obtained. The results are shown in Table 1.

Table I

Loss in Weight On Ignition of Sodium Fluoride
Heated at Various Temperatures
and pH of Saturated Aqueous Solutions

NaF Sample	Temperature °C	Loss in Weight Per Cent	pH
1	30	-	7.0[a]
2	110	0.06	8.1
3	200	0.08	8.7
4	400	0.27	8.9
5	500	0.33	9.5
6	650	0.39	9.9
7	1030	- [b]	10.3

(a) The original salt contained 0.11 per cent free hydrogen fluoride as determined by titration.

(b) Fused NaF partially destroyed nickel crucible.

The data indicate that the determination of water in sodium fluoride by desiccation is complicated by the hydrolysis of the salt at high temperatures to form the metal hydroxide and gaseous hydrogen fluoride. That hydrolysis is a real factor at elevated temperatures is evidenced by the pronounced increase in basicity of the saturated aqueous solution with increasing temperature due to the formation of alkali metal hydroxide. The equilibrium of reaction (1) is shifted further to the right with increasing temperature.

$$NaF + H_2O \xrightarrow{200^\circ C} NaOH + HF \qquad (1)$$

It also appears that free hydrogen fluoride is not completely removed until the temperature exceeds 200° C. It is thus obvious that the determination of water in alkali metal fluorides by merely determining the loss in weight of the salt on heating is not feasible.

Capture of Evolved Gases

The results of the foregoing experiments revealed that hydrolysis occurs at high temperatures. An attempt was made to capture the evolved gases selectively and determine not only water but also hydrogen fluoride.

A quartz combustion tube was fitted at the outlet with a 3-inch loose "plug" of sodium carbonate enclosed in glass wool. Absorption tubes containing Ascarite and Anhydrone were connected to the outlet to capture the gases evolved when the sample, contained in a nickel boat, was heated to 900° C. Moisture-free argon was used as a sweep gas. The apparatus was so arranged that gaseous hydrogen fluoride was converted by the sodium carbonate to water and carbon dioxide, which were absorbed in the absorption tubes. The results of this test proved conclusively that hydrolysis occurred since an increase in the weight of the ascarite was found, which meant that CO_2 had been liberated by the reaction between sodium carbonate and hydrogen fluoride. For example, a typical weight increase in the ascarite tube was 0.3 per cent calculated as hydrogen fluoride.

Although this procedure was satisfactory in principle, a number of difficulties were encountered in actual practice. Chief among these difficulties was the amount of time consumed in conditioning the apparatus and absorption tubes. A contributing factor was the process of eliminating water in the sodium carbonate trap. Feibig and Warf[2] met this particular problem by keeping the sodium carbonate at 300° C, but the improvement was negligible with respect to reducing the conditioning time.

In order to determine 0.1 per cent water it is necessary to weigh 1 mg of water per gram of solid taken, which would require a micro technique. In addition, the use of larger-sized samples is not practical by this technique.

Heating in Vacuo

Cursory attempts were made to evaluate the technique of drying in a vacuum oven, which would obviate the use of high temperatures. When a sample of NaF was heated at 110° C for four hours under a pressure of 100 mm of mercury, 0.03 per cent loss in weight was found. The pH of the saturated aqueous solution was 8.2 as compared with pH 7.1 of the original salt solution, once again evidence of hydrolysis. Experiments using conditions of longer periods of heating, lower pressures, and combinations of the two factors showed no further significant losses in weight

REMOVAL OF WATER BY EXTRACTION

Many techniques have been devised for the removal of water from solids or liquids by refluxing the solid or liquid with an inert, azeotrope-forming solvent whereby the water is removed with part of the solvent and collected separately from the solid. Xylene, toluene, benzene, and other solvents have been used for this purpose. The separated water is finally determined by different methods, usually volumetrically in macro determinations. A successful example of this technique is the Dean-Stark method[1] for the determination of water in petroleum oils and other materials.

A procedure was formulated embodying the principle of separation of water from the solid by extraction and its ultimate determination by titration with Karl Fischer reagent. In brief, dried xylene in contact with the solid, was refluxed for one hour and the azeotrope formed by xylene with water was removed by distillation. To insure complete removal of the water, all of the xylene was distilled and collected. The water in the distillate

was titrated with Karl Fischer reagent and the end point determined electrometrically using the "dead stop"[3] end point. A blank test was made to determine the water in the reagents and on the glassware.

Reagents

Reagent grade xylene and absolute methanol were used. The xylene was dried over sodium then distilled and stored over aluminum oxide. Desiccation or purification of the methanol was not attempted.

The iodine, pyridine, methanol, and sulfur dioxide used in the preparation of the Karl Fischer reagent were reagent grade. The reagent was prepared by adding 169 grams iodine to 533 ml pyridine, and diluting with 1333 ml of methanol. Liquid sulfur dioxide (90 ml) was added to the cold solution, which was shaken well, and allowed to stand protected from light for 12 hours. The reagent was standardized against a standard methanol-water solution. This solution was prepared by adding a calculated volume of water from a calibrated buret to absolute methanol so as to yield a final water concentration of approximately 2.5 mg per ml. The water concentration of absolute methanol which was determined by titrating with Karl Fischer reagent, was subtracted before calculating the exact concentration of the standard solution. A volume of 25 ml of the standard water solution was added to approximately 25 ml of absolute methanol in which the water had been previously consumed with Karl Fischer reagent. Successive titrations were repeated until agreement of successive 0.05 ml portions had been obtained. The "water titer" was calculated by dividing the weight of water in the standard by the volume of reagent required for titration.

Apparatus

A drawing of the apparatus is shown in Figure 1. The apparatus is so designed as to permit all steps in the procedure to be conducted without exposure of the sample to the atmosphere. All outlets are protected with drying tubes filled with anhydrous magnesium perchlorate. A significant feature of the apparatus is the design of the condenser which has a 6-inch elbow covered with asbestos and fitted with a standard tapered joint. The condenser outlet is controlled by a No. 10 stopcock to regulate the flow of liquid into the titration flask. The titration flask is fitted with a buret and an amber-colored reservoir to contain the Karl Fischer reagent. The buret is treated with "desiccote" to prevent holdup of liquid. All glass-to-glass connections are lubricated with a thin film of graphite and are wetted by the addition of a drop of xylene immediately before the connections are made. Commercial lubricants were readily attacked by xylene. The titration flask is fitted with platinum electrodes to permit the titration to be conducted potentiometrically. The end point can be obtained either electrometrically, "dead stop" end point[3] or visually. The former is more convenient; however, during the course of this investigation it was demonstrated that reproducible results can be obtained visually by the same operator by detecting the appearance of the iodine color at the end point.

Procedure

A. Determination of Blank

1. Distill 50 ml xylene through the apparatus to remove moisture and condition the system.

2. Drain the xylene from the system.

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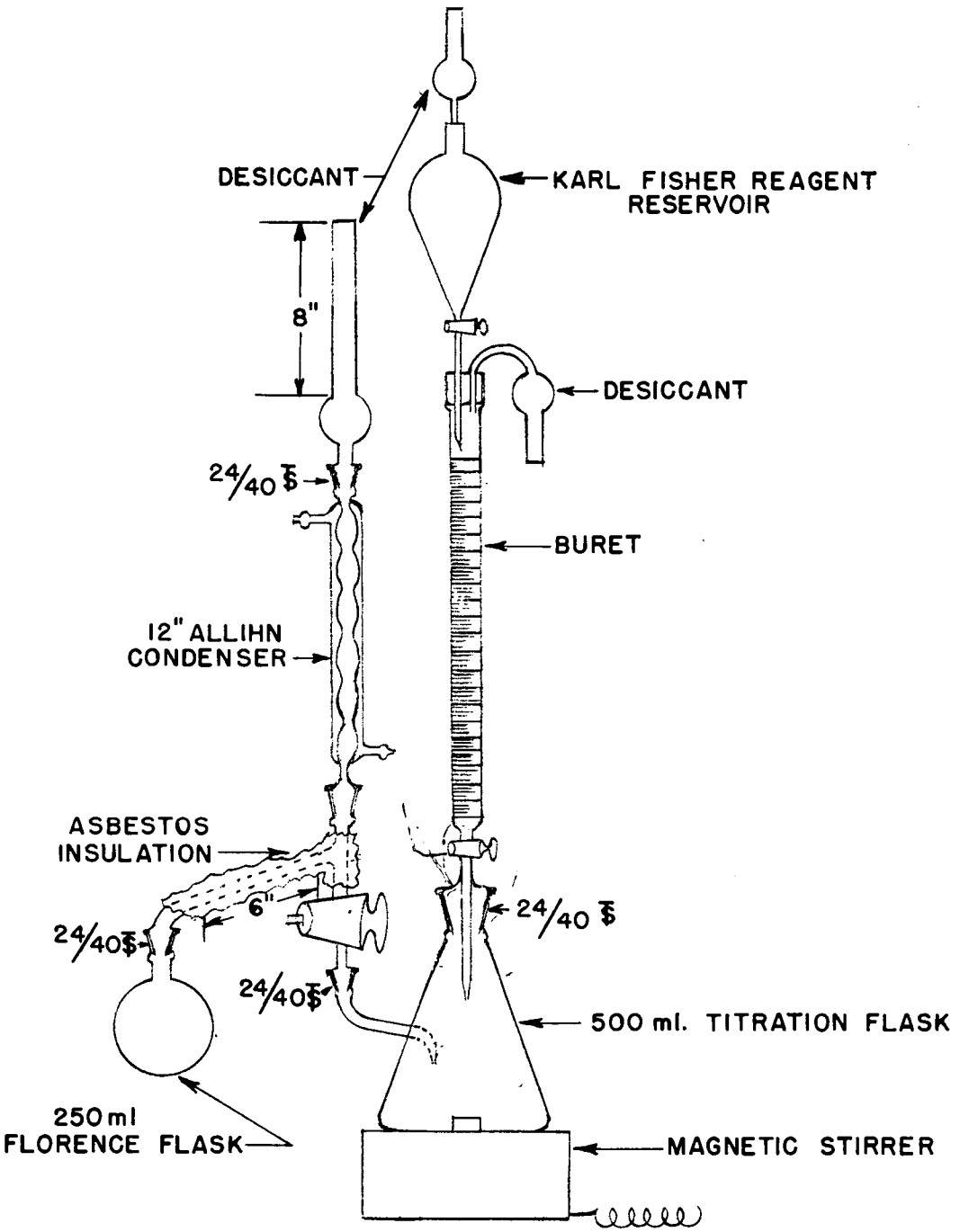

Figure 1
APPARATUS FOR THE DETERMINATION OF WATER IN FLUORIDE SALTS

3. Add 50 ml of xylene to the reflux flask and with the condenser stopcock in closed position connect the flask to the condenser arm.

4. Add 25 ml methanol to the titration flask. Allow the liquid to wash down the sides of the flask to remove any adhering moisture.

5. Place a magnet in the titration flask then connect the flask to the condenser and buret.

6. With the stopcock on the condenser closed, reflux the xylene for one hour at a rate sufficiently slow to prevent the distillate from rising no higher than 4 to 5 cm in the condenser.

7. Consume the water in the alcohol in the titration flask by titrating with Karl Fischer reagent.

8. Remove the condenser desiccant tube, flush the condenser with 10 ml of methanol and replace the desiccant tube.

9. Open the condenser stopcock and distill all the liquid from the flask into the titration flask.

10. When distillation is complete, close the condenser stopcock.

11. Titrate the distillate with Karl Fischer reagent and record the volume.

12. Titrate and use this volume as the blank.

B. Determination of Water in Sample

1. Flush the apparatus by refluxing with 50 ml of xylene for 30 minutes and drain.

2. Transfer a 10 to 20-g. sample, weighed by difference, to a dry 250-ml Florence flask in a dry box.

3. Add 50 ml xylene and proceed exactly as described in the procedure for determining the blank. (Steps 3 through 11). Record the volume of reagent required to titrate the sample.

C. Calculations

Let V_b = reagent for blank, ml.

V_s = reagent for sample, ml.

T = titer of reagent

W = weight of sample, g.

$$\frac{(V_s - V_b) \times T}{10\ W} = \text{water, per cent}$$

Results

A blank test was first made to condition the apparatus, then followed by a careful determination of the blank. This procedure was adopted when it was observed that the initial blank was always considerably higher than succeeding blanks, which were reproducible to within less than one per cent when the same reagents were used. A typical blank was of the order of 10 mg of water. The salts, sodium tartrate dihydrate, $Na_2C_4H_6O_4 \cdot 2H_2O$, and barium chloride dihydrate, $BaCl_2 \cdot 2H_2O$, both of which are considered standard[7] materials for use in the determination of water were used to test the method. The known value was determined by drying a sample to constant weight at 110° C. A comparison of the results is shown in Table 2.

Table 2

Determination of Water by
Desiccation and Extraction Procedures

	Water, mg		
	Drying at 110° C A	Extraction* B	Difference A-B
$Na_2C_4H_6O_4 \cdot 2H_2O$	22.83	22.36	0.47
	29.06	29.49	0.43
	37.24	36.27	0.93
	12.61	12.61	0.00
	19.87	19.60	0.27
	32.66	32.07	0.59
$BaCl_2 \cdot 2H_2O$	41.01	40.77	0.34
	41.07	41.82	-0.75
	43.75	44.28	-0.53
	43.75	43.53	0.22
	29.43	29.40	0.03
	29.65	28.81	0.84

* less water present in the blank

The standard deviation of the differences was 1.4 per cent; the relative standard error was one per cent.

A number of fluoride salts in addition to mixtures of fluorides and other solids were analyzed for water. Some of the test results on compounds that have been tested are listed in Table 3.

Table 3

Water Content of Some Fluorides

Fluoride	Previous Treatment	Water, per cent
NaF	None	0.18
	500° C, in vacuo, 48 hrs.	0.01
		0.01
		0.01
		0.04
KF	500° C, in vacuo, 48 hrs.	0.01
		0.01
		0.02
		0.03
		0.05
		0.09
		0.11
AlF_3	None	0.09
NH_4F	None	0.27
		0.83
KHF_2	None	0.62
NH_5F_2	None	12.33
		13.21
K_2FeF_5	100° C, 16 hrs.	0.18
		0.18
NiF_2	450° C	0.48
		0.67
$NaF-ZrF_4-C$	Dried materials mixed in dry box	0.12
		0.15
		0.28

DISCUSSION

The success of the method is dependent primarily upon two factors, blank and sample size. A preliminary flushing of the apparatus with xylene and methanol eliminated nearly all of the adsorbed water on the walls of the apparatus. The blank, therefore, consisted mainly of water from the

reagents, xylene and absolute methanol, of which the former can be dried and maintained with a low water content. Dehydration of methanol to reduce the blank to quite low values did not prove practical. The problems involved in storing and keeping methanol free from water overcame, for this purpose, any advantages gained by dehydration. Further, it was found that by means of a preliminary "flush," the water content of the blanks could be reproduced to within less than 0.2 mg of water, 0.1 ml of Karl Fischer reagent.

To counteract the effect of the blank, a large-size sample was used when only traces of water were known to be present. The apparatus was designed to permit the use of samples of the order of 10 to 25 grams in order to have available a measurable quantity of water. A 5-ml microburet that is graduated in 0.01 ml increments was used whenever possible.

Although the intent of this investigation was to develop a method for the determination of traces of water in alkali fluoride salts, the method can, of course, be applied to other solids. For example, hydrated salts containing as much as 50 per cent by weight of water can be determined by use of a small-size sample.

Application was also made to thermally-unstable compounds. Examples of the type listed in Table 3 are ammonium fluoride, NH_4F, all of which decompose with evolution of HF at temperatures below 150° C. The method seems of particular value for application to unstable compounds and can be used efficiently to determine water in any type of solid sample in which the water exists in such a state that extraction can be accomplished by refluxing.

SUMMARY

The removal of water by extraction with xylene and its subsequent determination by titration with Karl Fischer reagent has been successfully adapted to the determination of traces of water in alkali metal fluorides. The method was also applied to the determination of water in other solids containing larger concentrations of water. It is of particular value for the determination of water in thermally unstable solids.

If a large sample (10 to 20 grams) is used, the limit of determination is of the order of 0.01 per cent.

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