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A RAPID METHOD FOR DETERMINATION OF WATER IN  $TO_3$

By

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SUMMARY

A set of conditions is described for a ten minute determination of water in  $TO_3$  by ignition and absorption of the evolved water in magnesium perchlorate. Complete conversion to  $T_2O_3$  is obtained under these conditions, so that total loss on ignition and total  $T_x$  (plus non-volatile impurity) content may also be obtained.

It has been found unnecessary to employ copper foil to prevent interference by nitrates, which may be present with a nitrate/water ratio as high as 5, and in an amount that does not exceed 100 mg. (auth)

INTRODUCTION

As a control on the production of  $TO_3$  by the calcination of hydrated  $TO_4$ , a simple and rapid method for the determination of water in  $TO_3$  was required. Simplicity is necessary so that a technician or operator can perform the analysis. Rapidity is required if the results are to be accurate, for the sample picks up an inconstant and indeterminate amount of water between the times of sampling and analysis.

Consequently, an investigation was begun to find a suitable method. As previously reported (1) no success was met in the attempts to determine accurately the moisture content of  $TO_3$  by either the Karl Fischer Titration Method or the acetic anhydride temperature rise method. Work was then begun to improve the combustion method, currently in use, to allow it to meet the standards set. The efforts in this direction were successful.

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EXPERIMENTAL

A. Proposed Procedure for Determination of Water in  $TO_3$ .

1. Apparatus.

The apparatus and procedure were similar to those employed by Beacham and Hubbard, (2). The apparatus included: a cylinder of oil pumped nitrogen with the flow rate controlled by a nitrogen valve.

A U-tube containing calcium chloride and some indicating drierite.

A U-tube containing magnesium perchlorate.

A calibrated mercury manometer.

A McDanel combustion tube of high temperature alundum; length of 70 cm., bore of 3 cm., with the outlet end constricted to 0.5 cm.

A multiple type Hoskins combustion furnace controlled by a variac.

Several porcelain boats, coors NO. 6 A, 15 mm. by 100 mm.

A double stopcock U-tube with 12 mm. bore containing 10-12 grams of magnesium perchlorate. A copper wire was attached to each end.

A U-tube containing calcium chloride.

A test tube containing mercury to serve as a safety valve.

2. Procedure.

When the apparatus has been out of use for an appreciable length of time, the furnace is heated and nitrogen is blown through for 20-30 minutes to remove water from the apparatus.

- (a) The magnesium perchlorate collector is tared, the weight recorded, and the tube placed in the train at the outlet end of the combustion tube. At all times when the collector is off the train the stopcocks must remain closed. The collector is only handled by the copper wire.
- (b) Weigh the boat and record the weight. All weights should be made to a tenth of a milligram.
- (c) Add approximately a one gram sample to the boat, weigh, and record. *li*
- (d) Quickly place the boat in the combustion tube and push it into the hot section of the tube with a metal rod hooked through the lip of the boat.

- (e) Leave the rod attached to the boat, stopper the end of the tube, open the collector stopcocks, and turn on the gas stream.
- (f) After the specified time, turn off the gas stream, close the collector cocks, and remove the collector, touching only the copper wire. Stopper the outlet end.
- (g) Place the collector in the balance case. Remove the boat from the combustion tube by pulling out the metal rod. Stopper the tube. Place the boat in a desiccator.
- (h) Weigh the collector in the balance case. Record the weight. Return it to the train.
- (i) Calculate the results for water: gain in collector weight/wt. of sample  $\times 100 = \% \text{ water}$ .
- (j) Weigh the boat when cool. Record the weight, and calculate "T" content and percent loss on ignition:

$$\text{"T" Content: } \frac{\text{wt. of residue} \times 0.8460}{\text{wt. of sample}} \times 100 = \% \text{ T}$$

$$\text{L.O.I. } : \frac{\text{loss in sample weight}}{\text{wt. of sample}} \times 100 = \% \text{ L.O.I.}$$

#### B. Effect of Variation in Temperature and Flow Rate.

The answers to two major questions were sought in the experimental plan. First, what temperature could give an adequately rapid evolution of the combustion materials. And, Second, what gas rate would quickly sweep the moisture into the magnesium perchlorate. The latter should be the pivotal point in a rapid analysis and is limited to the maximum rate at which none of the sample will be blown out of the boat.

A sample of Mallinckrodt  $\text{TiO}_2$  was used throughout. It was kept in a ground-glass stoppered bottle and was weighed into the boat. The weight pickup on this slight exposure was found repeatedly to be negligible. The sample was run a number of times at high temperatures and for extended periods to accurately determine its water content. This was found to be 2.60%.

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Since the same  $\text{TO}_3$  batch was used throughout, some moisture pickup was to be expected, because the bottle was frequently opened to remove samples. The amount of moisture pickup appeared in the increased loss on ignition which could be corrected back to the starting figure for loss on ignition and % water. These changes were accurately determined by ignition for an hour in a muffle furnace at  $850^\circ\text{C}$ .

In all the following tables of data, the last column lists the corrected percent water by means of which a comparison of results may be made. The accurate value is 2.60%. A deviation of plus or minus 0.1% is tolerable for the desired analysis. Correct analyses are starred.

The first series of experiments was performed at relatively low temperatures for varying lengths of time with the results shown in Table I.

**TABLE I**

**THE EFFECT OF TIME OF IGNITION OF  $\text{TO}_3$  AT LOW TEMPERATURE**

Run	Hot Time (min)	Temp. ( $^\circ\text{C}$ )	Rate (cc/min)	Determined $\text{H}_2\text{O}$ (%)	L.O.I. (%)	Corrected $\text{H}_2\text{O}$ (%)
(1)	15	600	750	2.18	2.89	2.18
(2)	15	650	700	2.23	4.75	2.23
(3)	15	650	700	2.18	4.77	2.18
(4)	30	600	750	2.37	2.88	2.37
(5)	30	650	700	2.80	4.77	2.80
(6)	45	600	750	2.57	2.91	2.57*

Some interesting conclusions may be reached from the data in Table I.

- (a) A temperature of  $600^\circ\text{C}$  was insufficient to yield conversion to  $\text{TiO}_2$  in a period of 45 minutes, so that the percent loss on ignition is much lower than the value 4.77% obtained by muffle ignition at  $850^\circ\text{C}$ . The average value obtained by ignition at  $650^\circ\text{C}$  was 4.75%.
- (b) A period of 15 minutes at 600 to  $650^\circ\text{C}$  is too short to

allow collection of all the water with gas flow of 700-750 cc/min. A 30 minute period was likewise insufficient. The slightly high result obtained in (5) was probably due to the water picked up from (4).

- (c) Although 15 minutes is an insufficient length of time at these flow rates for an accurate moisture determination, still it may be seen that the loss on ignition at 650°C is quite accurate, i.e., all volatile material was driven from the sample.
- (d) Using the flow rates and temperature specified in Table I, 45 minutes would appear to be a safe period for a water determination.

In the next series of experiments reported in Table II, the temperature was raised to 850°C and the rate of gas flow was lowered to 400 cc/min.

TABLE II  
THE EFFECT OF IGNITION TIME AT 850°C AND A FLOW RATE  
OF 400 cc/min

Run	Net Time (min)	Determined H <sub>2</sub> O (%)
(7)	10	2.46
(8)	10	2.40
(9)	10	2.50
(10)	10	2.40
(11)	20	2.57*
(12)	20	2.57*

At the higher temperature of 850°C a significant decrease in the time required for accurate water determination was effected. Conversion to  $T_3O_3$  brings about rapid evolution of the oxygen and moisture, and 20 minutes is sufficient to give an accurate result.

For the series reported in Table III, the temperature was kept at 850°C for rapid evolution and the flow rate was increased to 750 cc/min. to give more rapid collection.

The results obtained for water content within 10 minutes appear to be fairly satisfactory, that is, within 0.1%. A five minute combustion at this flow rate yields low results. The seeming discrepancy between loss on ignition figures is due to the fact that the samples were run on different days and are not chronologically listed in the table. The corrected percent water is not based on these figures, but on values determined by an hours ignition in auffle furnace.

TABLE III

THE EFFECT OF IGNITION TIME AT 850°C AND A FLOW RATE OF  
750 cc/min.

Run	Net Time (min)	Determined H <sub>2</sub> O (%)	L.O.I. (%)	Corrected H <sub>2</sub> O (%)
(15)	5	2.34	-	2.30
(14)	5	2.33	-	2.29
(15)	5	2.31	-	2.23
(16)	10	2.54	-	2.48
(20)	10	2.70	4.90	2.62*
(21)	10	2.74	4.97	2.66*
(24)	10	2.65	4.90	2.57*
(25)	10	2.74	-	2.69*
(19)	20	2.62	4.86	2.54*
(22)	20	2.53	-	2.45
(23)	30	2.60	4.90	2.52*
(26)	30	2.84	5.03	2.69*
(27)	30	2.85	4.93	2.70*
(28)	30	2.93	-	2.78
(29)	30	2.75	4.95	2.60*
(18)	45	2.68	4.86	2.60*
(17)	45	2.65	4.82	2.57*
(30)	60	2.93	4.99	2.78
(31)	60	2.87	4.96	2.70*

The next series of runs was made with the object of determining whether 5 minutes could suffice to yield accurate results at an increased flow rate of 1700 cc/min.

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TABLE IV  
EFFECT OF IGNITION TIME AT 850°C AND A FLOW RATE OF  
1730 cc/min.

Run	Net Time (min)	Determination H <sub>2</sub> O (%)	L.O.I. (%)	Corrected H <sub>2</sub> O (%)
(32)	5	2.82	5.09	2.56*
(33)	5	2.90	5.11	2.64*
(34)	5	2.76	5.05	2.50*
(35)	5	2.88	5.08	2.62*
(36)	10	2.78	5.09	2.52*
(37)	10	2.92	5.08	2.66*
(38)	10	2.65	5.06	2.39
(39)	11	2.94	5.03	2.68*
(40)	12	2.84	5.08	2.53*
(41)	20	2.72	-	2.46
(42)	30	2.83	-	2.57*
(43)	30	2.97	-	2.71

The results in Table IV show that an ignition time of 5 minutes is as satisfactory as the longer ignition times; however, the precision of these data is somewhat low.

To determine whether the results would be more consistent and whether the oxide could still be kept in the boat at a higher rate of flow, 3000 cc/min. was chosen as the next rate. The data is in Table V.

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TABLE V

THE EFFECT OF IGNITION TIME AT 850°C A FLOW RATE OF

3000 cc/min

Run	Net Time (min)	Determined H <sub>2</sub> O (%)	L.O.I. (%)	Corrected H <sub>2</sub> O (%)
(44)	5	2.77	5.08	2.51*
(45)	5	2.78	5.08	2.52*
(46)	5	2.87	5.07	2.61*
(47)	5	2.81	5.07	2.55*
(48)	5	2.91	-	2.58*
(49)	5	2.93	5.08	2.60*
(50)	10	2.91	5 -	2.60*
(51)	10	2.91	-	2.60*
(52)	10	3.04	-	2.73
(53)	10	2.94	5.04	2.61*
(54)	10	2.95	5.00	2.62*
(55)	20	2.93	5.02	2.60*
(56)	20	2.93	-	2.60*
(57)	30	2.89	5.13	2.56*
(58)	30	3.18	5.05	2.85*
(59)	30	2.85	5.04	2.52*

From Table V it is seen that the results obtained within 5, 10 and 20 minutes are fairly consistent. The results from L.O.I. agree well with those obtained by ignition for one hour in a muffle. The muffle result being 5.10% on duplicates. No oxide is blown out of the boat, since this would lead to high results for the % L.O.I., and those obtained are slightly low.

An accurate water determination can thus be obtained by ignition for five minutes, and with an experienced person at the balance, the total time from receipt of sample to submission of results should be no more than 15 minutes and may be as low as 8 minutes.

Allowing an additional 15 minutes for the boat to cool, total T plus non-volatile impurities and loss on ignition may be determined in addition to the water.

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### C. Effect of Copper Mat.

In the analysis as done in the area, a copper mat was placed at the outlet end of the combustion tube. The purpose of this was to remove the oxides of nitrogen. (For details, see report by Beachan and Hubbard, loc. cit.)

To determine whether the mat is necessary, a number of runs were made with it interspersed between determinations in which it was absent. Results for these latter are included in Table V. Loss on ignition was not determined on the copper series. The results of the copper series are given in Table VI.

TABLE VI

RESULTS USING COPPER PCL AT 3000 cc/min. AND 850°C.

Run	Net Time (min)	Determined H <sub>2</sub> O (%)	Corrected H <sub>2</sub> O (%)
(70)	5	2.97	2.64*
(61)	10	2.83	2.52*
(62)	10	3.03	2.72
(63)	10	2.79	2.48
(64)	(20) (x)	2.95	2.64*
(60)	10	2.94	2.63*
(65)	10	2.91	2.60*
(66)	10	2.98	2.67*
(67)	5	2.86	2.55*
(68)	(15) (x)	2.95	2.64*
(69)	30	2.95	2.64*
(71)	30	2.84	2.51*
(72)	30	2.74	2.41
(73)	40	3.07	2.74

(x) - In these cases the samples were run for an additional ten minutes and picked up the amount of water noted.

From this data it was concluded that the copper mat adds nothing to the accuracy of the determination; that is, the oxides of nitrogen do not interfere with the reaction in the amounts normally found in Mallinckrodt TO<sub>3</sub>. The sample contained about 1% nitrate. Moisture is sometimes held up by the copper giving low results for one determination and high results for the following one.

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## D. Effects of Nitrates.

The effect of nitrates on the determination of moisture in  $\text{TC}_2$  by combustion was next investigated. To do this it seemed desirable to add varying amounts of tubanyl nitrate to  $\text{TC}_2$  in order to increase the  $\text{NO}_2/\text{H}_2\text{O}$  ratio, and then to determine the water and the effect of the added nitrate.

The weight ratio of  $\text{NO}_2/\text{H}_2\text{O}$  is almost exactly one in tubanyl nitrate hexahydrate. Therefore, any addition of tubanyl nitrate would serve only to increase the absolute amounts of these constituents but not the ratio. In order to increase the ratio, some tubanyl nitrate hexahydrate was recrystallized from ether and heated at  $100^\circ\text{C}$ . This was then placed in a ground glass stoppered bottle kept in a desiccator.

The first series of runs was made on this tubanyl nitrate alone. From the weight of the ignition residue the weight of tubanyl nitrate (anhydrous) was calculated, and the difference between this weight and the sample weight was taken as calculated percent water. The ignition was run at  $850^\circ\text{C}$  for 5 minutes with a gas rate of 3000 cc/min.

TABLE VII

THE EFFECT OF NITRATE ON THE DETERMINATION OF WATER AT  
 $850^\circ\text{C}$  AND A FLOW RATE OF 3000 cc/min.

Run	Wt. Sample (mg)	Nitrate Content (mg)	Content (%)	Calculated $\text{H}_2\text{O}$ (mg)	(%)	Found $\text{H}_2\text{O}$ (mg)	(%)
(74)	0.1645	-	-	-	-	14.3	8.81
(75)	0.1843	52.9	28.70	16.1	8.73*	17.0	8.63*
(76)	0.2635	75.8	28.77	22.6	8.58*	22.8	8.63*
(77)	0.3228	92.9	28.78	27.6	8.55*	28.3	8.77*
(78)	0.3888	111.4	28.65	34.5	8.87	35.1	9.03
(79)	0.3577	114.5	28.72	33.9	8.62*	37.3	9.51
(80)	0.4571	140.0	28.74	42.0	8.62*	43.3	8.89
(81)	0.6035	173.5	28.75	52.1	8.63*	54.1	8.96
(82)	0.6923	199.1	28.76	59.4	8.64	62.3	9.03
(83)	0.7794	223.9	28.73	67.6	8.67*	71.1	9.12
(84)	0.9036	259.9	28.76	77.4	8.57*	80.2	8.88

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Onitting run NO. 79, it may be seen that the difference in milligrams of water between the calculated and the determined values increase as the weight of sample increases. The starred values are considered accurate, and the discrepancy becomes apparent when the weight of nitrate goes over 100 mg., qualitatively considered. This is undoubtedly due to the formation of nitric acid in the collector tube.

Experiments might have been performed to determine whether a copper mat would have alleviated this difficulty; however, the quantity of nitrate which began to interfere was approximately five times that present in a one gram sample of Mallinckrodt  $\text{TiO}_2$  containing an uncommonly high amount of nitrate, so that the question of nitrate effect in the normal samples seemed somewhat obviated.

The ratio of  $\text{NO}_3/\text{H}_2\text{O}$  in these runs was close to 3:1. It is felt, however, that the absolute amounts of nitrate and water, rather than their ratio would be the cause of any difficulty in the analysis. An analogous situation is found in considering the collector tube, which loses its efficiency after a certain number of determinations (dependent upon the amount of water collected, but usually about 50). Results then became high; probably due to formation of nitric acid by reaction of the nitrogen oxides with the free water in the collector.

Another series of experiments was run in which nitrate was added in the form of barium nitrate to a fresh sample of  $\text{TiO}_2$ . The  $\text{TiO}_2$  gave a water analysis of 0.99%, and the barium nitrate gave no water.

These results are all within the accuracy of the determination, showing no interference by the added nitrate.

Run	$\text{NO}_3^-$ (mg)	Theoretical $\text{H}_2\text{O}$ (mg)	Ratio ( $\text{NO}_3/\text{H}_2\text{O}$ )	$\text{H}_2\text{O}$ Found in $\text{TiO}_2$ (%)
(85)	15.2	4.4	3.5	1.05
(86)	23.3	16.7	1.4	0.93
(87)	30.2	12.7	2.4	0.94
(88)	35.8	7.1	5.0	0.94

These results are all within the accuracy of the determination showing a third series was run in which tributyl nitrate hexahydrate was added to  $\text{TiO}_2$ . Both were carefully analysed for water content.

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The results follow:

Run	Grams Sample (oxide & nitrate)	Total NO <sub>3</sub> (mg)	Total H <sub>2</sub> O (mg)	Theoretical H <sub>2</sub> O (%)	H <sub>2</sub> O Found (%)
(89)	0.6519	26.4	26.2	4.02	3.91
(90)	0.7270	17.9	20.4	2.81	2.70
(91)	0.8289	62.0	59.1	7.12	7.06

Here again, it is seen that relatively large amounts of nitrate did not interfere with the accuracy of the water determination.

#### E. Present Status.

The method has been taught to several women operators. Over a period of four days instruction was given in use of the balance, procedure, technique, and method of calculation. A calcined sample was then analysed by each of the three analysts, and the results were:

1.01% H<sub>2</sub>O  
0.96% H<sub>2</sub>O  
and 1.00% H<sub>2</sub>O

The time of analysis was around 30 minutes, and this should improve as familiarity with the balance and the procedure increase.

- (1) Reports CD 2208 and CD 2225
- (2) Report CD 491

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