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**RAPID MEANS OF MONITORING
THE THERMAL DECOMPOSITION OF
MAGNESIUM PERCHLORATE • CHLORIDE DETERMINATION**

K. F. SUGAWARA

DIRECTORATE OF MATERIALS AND PROCESSES

DECEMBER 1961

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K. F. SUGAWARA

DIRECTORATE OF MATERIALS AND PROCESSES

DECEMBER 1961

**PROJECT No. 7360
TASK No. 736005**

**AERONAUTICAL SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO**

FOREWORD

This report was prepared by the Physics Laboratory. The work was initiated under Project No. 7360, "Compositional, Atomic and Molecular Analysis", Task No. 736005 "Rapid Means of Monitoring the Thermal Decomposition of Magnesium Perchlorate Chloride Determination". It was administered under the direction of the Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division with Mr. K.F. Sugawara as the project engineer.

The work was accomplished between May 1961 and July 1961.

The author wishes to acknowledge the technical assistance of Mr. C.D. Houston.

ABSTRACT

A rapid procedure by which the thermal decomposition of magnesium perchlorate can be monitored, is discussed. The method, based upon the spectrophotometric measurement of the iron (III) chloride complex, is quite simple and accurate.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



FREEMAN F. BENTLEY
Chief, Analytical Branch
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Directorate of Materials and Processes

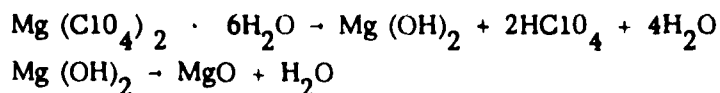
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INTRODUCTION

Although perchlorates were prepared and identified over a century ago, their general use did not materialize until about the last two decades. Presently, these compounds are employed quite extensively by industry and are being utilized in numerous research and experimental projects. This report pertains to a developmental study dealing with the determination of chloride as a means of monitoring the thermal degradation of magnesium perchlorate samples. These samples are expected from a forthcoming investigational study.

Various workers in the past have investigated the thermal decomposition of magnesium perchlorate. In 1922, Willard and Smith (1) reported that at 170°C the greater portion of water, as the hydrate, is volatilized and that at 250°C, the material fuses but does not decompose. At slightly higher temperatures, there exists the tendency of oxides and chlorides to form through decomposition. However, when the temperature attains 400°C, decomposition is rapid and the residue consists primarily of magnesium oxide. Marvin and Woolaver (2), in 1945, indicated that at elevated temperatures the hydrate exhibits a gradual transformation into the hydroxide through hydrolysis in the following manner:



In 1956, Zinovév and Cludinova (3) reported on the thermal decomposition of this same compound. Their data shows that the solid residue from the decomposition of magnesium perchlorate could be represented as a mixture of MgCl_2 and MgO in addition to the compound MgCl-O-MgCl . The over-all exothermal decomposition of $\text{Mg}(\text{ClO}_4)_2$ occurs in the temperature range of 410°C to 547°C.

Since these reports vary somewhat with regard to the decomposition temperature, as well as the composition of the final products, they appear to indicate that the degradation is governed, partially at least, by the exact experimental conditions applied to the experiment. It seems quite plausible to expect the formation of a magnesium compound involving chloride as one of the constituents.

Numerous methods have appeared in the literature relative to the determination of micro amounts of chloride. Some general methods include potentiometric, amperometric, turbidimetric, flame photometric, and others. In addition, various spectrophotometric procedures have been investigated. Gordon (4) determined chloride by utilizing permanganate to oxidize the chloride and quantitatively decolorize a portion of the fast green dye solution with the liberated chlorine. Lambert and Yasuda (5) determined chloride by passing the solution through a column consisting of solid silver iodate. The chloride was quantitatively exchanged for iodate ions which were reacted with cadmium iodide-linear starch reagent to form the blue linear starch triiodide ion complex. The color was then measured spectrophotometrically. Zall and workers (6) based their procedure upon the

displacement of thiocyanate from mercuric thiocyanate by the chloride ion. The liberated thiocyanate was then reacted with Fe (III) to form the colored complex $[\text{Fe}(\text{SCN})]^{+2}$ which could be measured spectrophotometrically. Barney and Bertolacini (7) utilized mercuric chloranilate to determine chloride spectrophotometrically.

This report is based upon a procedure developed by West and Coll (8), which is ideally suited to this study because the method is rapid, simple, accurate, and is carried out in a perchloric acid medium. The purpose of this report is to determine whether chlorides are formed during the thermal decomposition of magnesium perchlorate, and to ascertain whether the chloride is present as a water soluble or water insoluble compound. In addition, we shall determine whether any adverse conditions might exist during the experiment which would affect the accuracy of the procedure.

EXPERIMENTAL

In this procedure, the strong absorption band of Fe (III) chloro complex is measured in the region of 350 m μ . West and Coll, (8) recommend two procedures, the second of which is a modification of the first. The second procedure was chosen for this study because it is more rapid and the accuracy is satisfactory. One change was incorporated in the procedure, namely, the preparation of the iron (III) perchlorate reagent from iron (II) perchlorate. This was done for the sake of expediency rather than necessity, because of the availability of ferrous perchlorate in the laboratory. The final product possessed a slightly lower blank than that reported in the literature.

PREPARATION OF REAGENT - IRON (III) PERCHLORATE

1. To a warm solution of dilute perchloric acid (75 ml HClO_4 + 40 ml H_2O) in a 600 ml beaker, gradually add 50 grams of ferrous perchlorate while stirring the solution on a hot plate. Add more distilled water if necessary to dissolve the crystals.
2. Cover the beaker with a ribbed watch glass and evaporate the solution to strong fumes. Continue fuming until traces of iron (III) perchlorate begin to crystallize from the solution.
3. Remove the beaker from the hot plate, cool, and filter through a dry, clean, sintered glass filtering crucible. Any trace of moisture will transform the white (tinted purple) crystals to a yellow color.
4. Wash the salt with about 100 ml of perchloric acid which has previously been fumed.
5. Recrystallize the salt in a manner similar to the above procedure using the same amount of perchloric acid mixture. For the second filtration, the crucible should be tared.
6. Dissolve 60 grams of the moist recrystallized salt (dried by vacuum) in a mixture of 270 ml HClO_4 plus 230 ml H_2O . Any amount of reagent can be prepared providing the same proportions are adhered to.

PREPARATION OF CALIBRATION CURVE

In graph 1, the calibration curve adheres consistently to Beer's law, and the ratio, concentration versus optical density, is constant. In checking the stability of the color at 350 m μ using 1 cm cells, it was found to be quite stable showing no observable drift. However, on endeavoring to increase the sensitivity by employing 5 cm cells, it was evident that slight drifting was occurring during the measurements. Hence, it was necessary to limit all optical density readings to 1 cm cells. Also, the stability of the reagent was checked by carrying out a second absorbance measurement after a period of three weeks. This experiment proved that there was only a very slight decrease in the optical density. Thus, unless extreme accuracy is desired, one can assume the reagent to be stable for at least several weeks. The procedure used for the calibration curve is as follows:

1. Into each of five 25.0 ml volumetric flasks, transfer 13.0 ml of the iron (III) perchlorate solution.
2. Add aliquots containing 50 to 400 micrograms Cl to four of the volumetric flasks. Dilute the solutions in all five volumetric flasks to volume. The one flask not containing any chloride is the reagent blank.
3. Determine the optical density of the standard solutions versus the reagent blank at 350 m μ using 1 cm corex cells.

To determine the possible effects which chlorates may have on the procedure, perchlorate samples and standard chloride solutions were spiked with 10.2 mg of chlorate as barium chlorate. The absorbance measurements indicated no interference whatsoever.

As a further check on the procedure, approximately two grams of magnesium perchlorate was spiked with standard amounts of chloride to verify the percent recovery. An average of 98.2 percent recovery on the spiked samples was made for two different experiments.

DETERMINATION OF CHLORIDE IN FUSED MAGNESIUM PERCHLORATE

In order to establish whether this procedure for the determination of chloride could be satisfactorily employed for monitoring the degradation of fused magnesium perchlorate, the following experiment was conducted. A sample of chloride free magnesium perchlorate (dehydrite) was heated in a test tube on a sand bath until the material barely commenced to fuse. On the second sample, the temperature of the sand bath was increased to approximately 300°C, at which temperature the sample fused completely. The salt was maintained in this molten state for about thirty minutes, cooled, and then analyzed. Chloride was determined in the water soluble portion as well as on the water insoluble residue in the following manner. The water insoluble residue was filtered, dried at 110°C and then dissolved in the minimum amount of perchloric acid. After diluting with a little water, it was neutralized with dilute sodium hydroxide and made up to volume. Upon analysis, this solution presented no detectable amount of chloride. The analysis of the water soluble portion of the sample resulted in a determinable amount of chloride. The results are summarized in table 2.

ANALYSIS OF SAMPLE

1. Using a tared eye dropper (pyrex), sample the hot magnesium perchlorate bath and place the sample (2 - 3 grams) in a tared weighing bottle. Cool the sample in a dessicator and then determine the weight to the nearest milligram.
2. Dissolve the sample in approximately 20 ml of distilled water (chloride free) and mix well. If the sample does not go into solution completely, warm the mixture over a hot plate for about five minutes, cook, and filter into a 50.0 ml volumetric flask. Wash the residue well with hot distilled water and dilute the solution to volume.
3. Transfer a 10.0 ml aliquot to a 25.0 ml volumetric flask and add 13.0 ml of iron (III) perchlorate reagent. Dilute to volume and mix well.
4. Determine the optical density of the solution versus a reagent blank at 350 m μ using 1 cm corex cells. The optical density of the sample should be determined at the same temperature as the standards in the preparation of the calibration curve.
5. If the optical density reading is too low, step 2 should be modified so as to bring the final volume to 25.0 ml instead of 50.0 ml. This is easily done if there is very little residue to filter and wash.

CONCLUSION

This study, although not exhaustive, shows quite conclusively that the degradation of fused magnesium perchlorate involves the formation of chloride. A rapid means of determining chloride can then be utilized to monitor the decomposition of the salt. Experiments were limited to commercial grade magnesium perchlorate and did not include any specially purified salt.

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TABLE I

CONCENTRATION OF CHLORIDE VERSUS CHANGE IN ABSORBANCE			
Cl (mg/25.0 ml)	Absorbance (Optical Density Versus Blank)	Factor (Cl/O.D.)	Deviation
0.050	0.054	0.926	-0.006
0.075	0.082	0.915	-0.017
0.100	0.108	0.926	-0.006
0.125	0.131	0.954	+0.022
0.125	0.134	0.933	+0.001
0.250	0.269	0.929	-0.003
0.300	0.325	0.923	-0.009
0.400	0.422	0.948	+0.016
		Mean = 0.932	Av. Dev. = ± 0.010

CHART I
CHLORIDE DETERMINATION
CALIBRATION CURVE

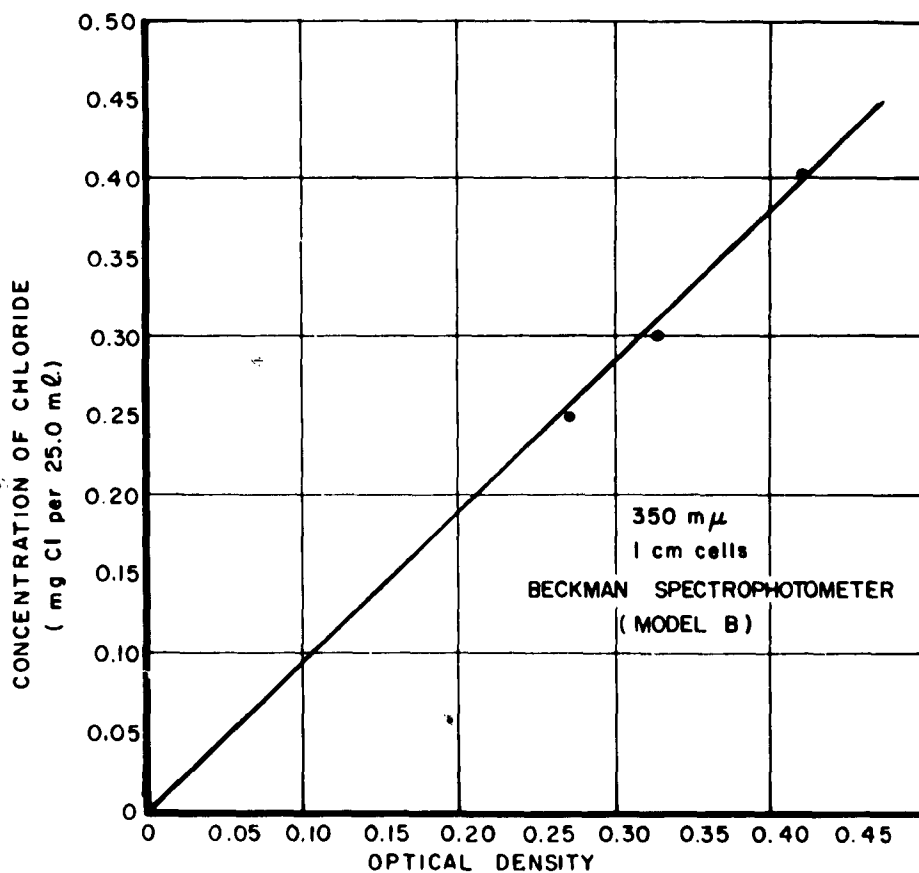


TABLE 2

ANALYSIS OF FUSED MAGNESIUM PERCHLORATE		
Sample No.	Absorbance (O.D.)	Chloride Conc. (%)
1	a (w.s.e.)	0.000
	b (w.i.r.)	0.000
2	a (w.s.e.)	0.231
	b (w.i.r.)	0.000

Note:

Sample No. 1 was barely fused

Sample No. 2 was fused completely

w.s.e. = water soluble extract

w.i.r. = water insoluble residue

Calculation:

$$\% \text{ Cl} = \frac{(0.856) (0.231) (10) (10^2)}{(2.4089) (10^3)} = 0.082$$

Where 0.856 = factor (mgCl/O.D.) for this batch of iron (III) perchlorate reagent

0.231 = optical density

2.4089 = sample weight

 10^2 = percentage factor

10 = dilution factor

 10^3 = mg to gm conversion factor

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