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SUMMARY

A method which is applicable to most solids has been developed for the determination of carbonate present in the surface of sodium chloride. It entails the liberation of carbon dioxide by a reaction with hydrogen chloride vapors in a previously evacuated chamber and the analysis of the resulting gas mixture mass spectrometrically. The carbon dioxide liberated at room temperature originates in the surface layer while at elevated temperatures some may come from subsurface layers. Comparison with an earlier method in which water was used to liberate carbon dioxide demonstrates the greater reliability of the hydrogen chloride method.

INTRODUCTION

A recent study (ref. 1) of the reactions occurring between sodium chloride (NaCl) crystals and carbon dioxide (CO_2) indicates that carbonate or bicarbonate is formed in the crystal surface. If these reactions are to be studied, a method of analyzing for such substances is required. In an analysis of this type, problems are posed by the required sensitivity, the possible interferring substances, and the need to differentiate the surface carbonate from that of the bulk.

The first two problems have already been solved by using mass spectrometry to determine the CO_2 liberated from crystals when heated to 400° C in the presence of water vapor (H_2O)(ref. 1). Other methods that could be used for the determination of such small quantities of CO_2 include the measurement of the volume of CO_2 by ultramicroanalytical techniques (ref. 2) as well as measurements involving chromatographic techniques (ref. 3). However, such methods do not yield all the required information (e.g., the identification of the gaseous species involved) as readily as does mass spectrometry.

In order to distinguish surface carbonate from bulk carbonate, an appropriate new analytical method or an appropriate set of standard samples must be developed. A lack of standard samples is not too serious if the analytical technique liberates for analysis all the CO_2 in the exposed lattice. The investigation of reference 1 evaluated this approach and demonstrated that virtually all the surface CO_2 could be liberated by a single water treatment. These analytical results were consistent with conclusions obtained in a study of the mechanical properties of NaCl (ref. 4) even though the CO_2 found (ref. 1) included some from impurities containing CO_2 which were originally part of subsurface lattice layers. Research in this vein was continued since it was deemed reasonable that slight modifications in the analytical technique might allow the desired surface analysis to be accomplished.

This report presents such a modification. The method described makes use of hydrogen chloride (HCl) vapors at room temperature to liberate CO_2 from the salt surface. To determine whether the reaction was complete at room temperature, the liberation is also studied at elevated temperatures. The method is compared with the earlier one that uses H_2O as the reagent (ref. 1), and the advantages of the new method are discussed.

MATERIALS

The reagent grade NaCl used was obtained in two lots. Previous work (ref. 1) indicated a need for greater homogeneity of the samples. In order to achieve this for the present tests, each lot of granules was well mixed and stored in a dry atmosphere (relative humidity less than 5 percent). Samples used for the evaluation of the reproducibility of the analytical method required even greater homogeneity. The additional precautions used included removal of salt dust, mixing before taking each sample, and completing all the work on a given lot in 1 day. The surface area of the salt was estimated to be about 80 square centimeters per gram (as calculated from the weight of a given number of granules and the density of NaCl).

The single crystals of NaCl used were melt-grown optical grade. Unlike the samples composed of granules, there was no assurance that the surface carbonate concentration of the single crystals did not vary. An attempt was made to overcome this difficulty in some of the work by repeatedly using the same specimen after identical exposures to moist CO_2 (60 percent relative humidity). The areas of these single crystal samples were calculated from their gross dimensions and ranged from 18 to 42 square centimeters.

PROCEDURE

The apparatus was described in reference 1. It consisted of a gas collection system of borosilicate glass, having a main and a side chamber which could be isolated from one another (fig. 1). The collection system was connected to the inlet of a cycloidal focusing mass spectrometer. Before the collection system was used, it was cleaned by being rinsed first with hydrochloric acid and then with distilled water, and finally it was dried. The side chamber was used to hold a mixture of concentrated phosphoric acid and NaCl granules. The gas above the mixture contained HCl and some H_2O vapor. This mixture was care-

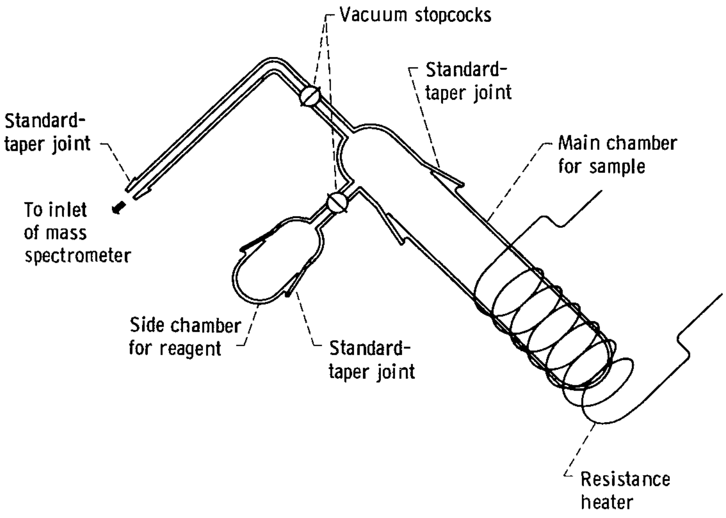

Figure 1. - Gas collection system.

fully preevacuated until bubble formation became very slow. Next, the main chamber was vented and the sample of NaCl inserted in it. (After a cleaning, the first few analyses using NaCl samples were discarded in order to avoid uncertainties due to unconditioned glass surfaces (see ref. 1, p. 2). The weight of the granular samples was 1 or 2 grams. Single crystals had estimated surface areas of 18 or more square centimeters. In order to remove the physically adsorbed gases, the main chamber containing the sample was evacuated to 0.1 micron for 15 minutes.

The main chamber was then isolated from the pump, and the stopcock to the side chamber was opened for 15 seconds. This allowed the HCl to reach a pressure of about 0.2 torr in the reaction (main) chamber. Thus, a reaction of the following type was permitted to occur on the surface of the sample:

$$2\ HCl + Na_2CO_3 \rightarrow 2\ NaCl + CO_2 + H_2O$$

After a 30-minute collection period, the gas was introduced into the expansion volume of the inlet system of the mass spectrometer. The reaction chamber was isolated from the expansion chamber only after no further pressure change was indicated by a micromanometer. The gas was analyzed by using typical mass spectrometric techniques. Up to 500 nanomoles could be determined with an average deviation of 2 nanomoles.

Some of the samples (without exposure to air) were repeatedly exposed to HCl in the same manner at room temperature to determine the completeness of the liberation of CO_2. Moreover, the same samples (again without exposure to air) were subsequently exposed to HCl at elevated temperatures ($200^\circ \pm 20^\circ$ C and $400^\circ \pm 20^\circ$ C) to determine the effect of temperature on the reactions involved.

Additional experiments were performed at 400° C to compare the results with HCl to those with H_2O as a reagent; the method with H_2O was described in reference 1. The comparison was made at 400° C because liberation of CO_2

TABLE I. - LIBERATION OF CARBON DIOXIDE FROM SODIUM CHLORIDE IN PRESENCE OF HYDROGEN CHLORIDE

Sample	Carbon dioxide collected at various temperatures, nanomoles (a)					
	25° C		200° C		400° C	
None	1		1		1	
2 g granulated sodium chloride; lot 1[b]	52		3		30	5
	47		1		31	2
	51		0		38	7
2 g granulated sodium chloride; lot 2[b]	106		27		113	40
	123	7	22	2		
	100	10	21	0		
	107	5	19	0		
1 g granulated sodium chloride; lot 2[c]	56		13		42	16
	35		16		61	11
	56		12		42	12
Single crystal A[d]	16	2	6		24	4
Single crystal B[e]	10	1	4		16	5

[a] Each row presents a series of results from an individual sample. Gas collections were made in the order they are presented without exposing the sample to the air between gas collections. In some instances, two collections were made at a given temperature.

[b] Estimated surface area, 160 sq cm.

[c] Estimated surface area, 80 sq cm.

[d] Estimated surface area, 42 sq cm.

[e] Estimated surface area, 31 sq cm.

by H_2O at room temperature is very slow. The source of H_2O was slightly dehydrated copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$). For single crystals the results were obtained in the following manner. Freshly cleaved crystals (surface area about 18 sq cm) were analyzed using H_2O as the reagent. They were then aged 16 hours in moist CO_2 (relative humidity about 60 percent). This sequence was repeated until two consecutive analyses gave the same results for CO_2. Work in reference 1 indicates that such treatments do eventually lead to consistent consecutive analyses. Finally the sample was analyzed (after aging in CO_2) using HCl as the reagent.

RESULTS

Table I lists the amounts of CO_2 liberated from the salt samples analyzed successively at 25°, 200°, and 400° C with HCl vapor as the reagent. The results of a typical blank show that the HCl reagent was essentially free of CO_2 and that CO_2 from other possible sources would not interfere with the analysis. For each type of NaCl, at least 90 percent of the carbonate "available" at room temperature was liberated during the initial 1/2 hour. For the NaCl from lot 1, virtually no additional CO_2 was liberated, even at 200° C.

TABLE II. - COMPARISON OF TWO REAGENTS FOR LIBERATION OF

CARBON DIOXIDE FROM SODIUM CHLORIDE AT 400° C

Sample	Reagent	
	Water	Hydrogen chloride
	Amount of carbon dioxide found, namomoles	
2 g granular sodium chloride; lot 1[a,b]	22,19,21,19, 20,21,19	29,28,26,29,30
2 g granular sodium chloride; lot 2[a,b]	47,40,39	87,87
Single crystals[c]	19,21	19
	17,16	16
	15,17	30
	22,23	19
	16,17	24

[a] Each result listed for granular sodium chloride was obtained from a different sample of well mixed material.

[b] Estimated surface area, 160 sq cm.

[c] Each row presents a series of results from one sample.

For the other samples, up to 30 percent additional CO_2 was liberated at 200° C. Thus, there appears to be a definite difference between lots 1 and 2. From all samples, relatively large amounts were again obtained in the collections at 400° C. The single crystals behave more like lot 2 than lot 1.

The reproducibility of the method as determined by using special granular material (see the section MATERIALS) is better than that of earlier work (ref. 1) and even better than that of table I. This improvement can be attributed partially to the greater homogeneity of the samples. An average deviation of about ±6 percent has been observed for the room-temperature collections from samples yielding 50 and 100 nanomoles of CO_2. Some of this remaining scatter is still attributable to variation between samples in spite of the care taken in the sampling process. Thus, the precision of the method may be better than that indicated.

Table II presents the comparison of the effectiveness of the reagents, H_2O and HCl, for the analysis of carbonate from the NaCl surface at 400° C. The agreement between granular samples from a particular lot with a given reagent was good. However, significantly more CO_2 was liberated from granular NaCl by HCl than by H_2O.

As noted in footnote c of table II, each row of data for single crystals was obtained from a single sample. This avoided difficulties caused by differences in the various single crystals. For three of the samples, both reagents appeared to be equally effective for the liberation of CO_2 from the salt surface. For two crystals, the HCl reagent appeared to be more effective than the H_2O.

DISCUSSION

The establishment of this method requires the discussion of subjects that are not usually considered in a report on analysis. Since there are no standard samples, the results must be shown to be reasonable and consistent with other data. This was done by demonstrating the following: the amount of CO_2 found was less than that predicted for the replacement of every chloride ion in the surface by a carbonate ion, the liberation of CO_2 was essentially complete, and there was good agreement with results obtained by other methods.

The amount of CO_2 that should be obtained per unit area of surface can easily be estimated from the size of the unit cell of the NaCl crystal. Such calculations show there is 1 nanomole of NaCl per square centimeter of lattice. If each of the chloride ions (Cl^-) in the surface lattice layer is replaced by a species that liberates CO_2 (e.g., bicarbonate (HCO_3^-)), a maximum of 1 nanomole of CO_2 per square centimeter should be obtained. In lot 1, the amount of CO_2 found indicated that the impurity was substituted for about one-quarter of the Cl^-. In lot 2 and the single crystals, about one-half of the Cl^- was apparently replaced by carbonate.

In some of the analyses carried out at 400° C, the CO_2 found was greater than 1 nanomole per square centimeter. Since true bulk diffusion is reported to occur above 264° C in NaCl (ref. 5), these high values can be explained in terms of impurities containing CO_2 diffusing to the surface. Thus, it is reasonable to assume that the CO_2 found initially at room temperature was essentially from the surface lattice layer of the solid and that the CO_2 obtained in subsequent collections at 400° C was from impurities which had diffused to the surface from subsurface lattice layers.

It is evident from the data for lot 1 in table I that at room temperature a 1/2-hour exposure to HCl vapors liberated all the CO_2 from the surface layer because virtually no CO_2 was liberated in the subsequent collections at 200° C for lot 1. Since the exposed carbonate in all samples would be expected to behave the same, the amounts of CO_2 found in subsequent collections at room temperature and at 200° C on other samples (lot 2 and single crystals) suggest that a hitherto unsuspected surface phenomenon was involved. A preliminary investigation suggests that this phenomenon was due to the slower liberation of CO_2 from an impurity in a semiprotected site. Such a site might be a dislocation pipe or the inner surface of a crack whose width is close to the molecular diameter.

The data in table II indicate that the two reagents, HCl and H_2O, can be equally effective for some samples but that HCl is more effective than H_2O for others. This anamolous behavior is difficult to explain if the H_2O reacts in the same manner as the HCl, that is, directly with the carbonate to release CO_2. However, if the H_2O first hydrolyzes the NaCl to release HCl, which in turn reacts with the carbonate, the low values of CO_2 found for some specimens using H_2O can be attributed to limitations in the hydrolysis step (see appendix of ref. 1). Thus, the present data supply evidence to help distinguish between the two mechanisms presented in reference 1 for the liberation of CO_2 from NaCl by H_2O.

The method using HCl as the reagent has several advantages. Of primary importance is its greater reliability. In addition, the method can be readily applied to the determination of carbonate on the surface of almost any solid because it is not necessary that the sample hydrolyze to form an acid gas which in turn will liberate CO_2. Another advantage lies in the ability of the HCl at room temperature to liberate virtually all of the CO_2 from the salt surface. This means that the CO_2 so liberated is only from the exposed surface layer, and a differentiation can be made between surface carbonate and that from the interior of the crystal.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, January 29, 1965.

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