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Evaluation of Methods for Determining Nahcolite and Dawsonite in Oil Shales

By Charles W. Huggins, Thomas E. Green, and T. L. Turner

College Park Metallurgy Research Center, College Park, Md.

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CONTENTS

ILLUSTRATIONS

TABLES

EVALUATION OF METHODS FOR DETERMINING NAHCOLITE AND DAWSONITE IN OIL SHALES

by

Charles W. Huggins,[1] Thomas E. Green,[1] and T. L. Turner[1]

ABSTRACT

To determine the nahcolite and dawsonite content in oil shales, the Bureau of Mines compared X-ray diffraction, infrared spectroscopy, thermal methods, and a previously published method by Smith and Young based on the selective solubility of sodium compounds. The Smith and Young method and a new method based on the weight of carbon dioxide produced by thermal decomposition are recommended for determining nahcolite. X-ray diffraction and the Smith and Young method are recommended for determining dawsonite. X-ray diffraction, infrared spectroscopy, and differential thermal analysis were useful for identifying other minerals in the samples.

INTRODUCTION

The specific determination of minerals in naturally occurring materials is generally a more complex problem than conventional elemental chemical analysis. The quantitative determination of the mineral requires measuring some property that is unique. Such a property may be determined by selective extraction, X-ray diffraction, infrared spectroscopy, etc. Serious positive errors will be encountered if other minerals, whose presence in the sample is not known, also have the property used for the determination. To guard against positive errors of this type, it is necessary either to know all the minerals in the sample that would interfere with the determination or to have a confirming analytical method based on a different property of the minerals to be determined. The confirming method may also be subject to positive errors produced by other minerals present. However, if two methods that measure different properties of the desired minerals are used, the probability of both methods being subject to the same interference to the same extent is rather remote.

A problem of this type was encountered in determining nahcolite ($NaHCO_3$) and dawsonite ($NaAl(OH)_2CO_3$) during a Bureau of Mines study on a recovery of soda and alumina associated with oil shales. One method for determining these minerals, described by Smith and Young (<u>11</u>),[2] is based on calculating the

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[1] Research chemist.

[2] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

nahcolite content of the sample from the quantity of sodium released by a cold water leach and then calculating the dawsonite content from the sodium released by a hot acid leach. Because halite (NaCl) is present in many oil shale samples, a chloride determination is performed on a separate water extract, and the nahcolite sodium is corrected by substracting the quantity of sodium required to combine with the chloride to form NaCl. A positive error in determining nahcolite by the Smith and Young method can be caused by the presence of water-soluble sodium compounds other than nahcolite and halite. The presence of water-soluble chlorides other than halite can cause a negative error. An error in the dawsonite determination would be produced by the presence of acid-soluble sodium compounds other than dawsonite.

Availability of alternate methods is especially important when nahcolite and/or dawsonite determinations are required on intermediate products of engineering processes.

The purpose of this Bureau of Mines report is to describe the investigation of methods for quantitatively determining nahcolite and dawsonite.

ACKNOWLEDGMENTS

The authors are indebted to John Ward Smith, Laramie Petroleum Research Center, Laramie, Wyo., for samples of oil shale and single crystals of nahcolite, and to American Chicle Co., Long Island City, N.Y., for a sample of synthetic dawsonite.

MATERIALS STUDIED

The following naturally occurring and synthetic minerals were used in the present investigation:

1. Composite oil shale.--Samples representing 1- to 3-foot sections of core between the depths of 1,936 and 2,761 feet of the Colorado Corehole No. 3, drilled by the Bureau of Mines and the Atomic Energy Commission in Rio Blanco County, Colo. (11), were obtained from the Bureau of Mines Laramie Energy Research Center, Laramie, Wyo. Material equivalent to 100 grams per foot of core was riffled from these samples and combined to prepare a composite representing 825 feet of core.

2. Outcrop oil shale sample.--A surface sample was obtained from a 3-foot outcrop on Piceance Creek Road 2 miles south of the White River in Rio Blanco County, Colo.

3. Individual oil shale samples, Colorado Corehole No. 3 (11) identified as Laramie No. 3, Laramie No. 18, etc.

4. Wyoming oil shale sample, a special oil shale sample containing less than 5 percent nahcolite and no dawsonite.

5. Single crystal nahcolite containing small amount of absorbed oil.

6. Olduvai dawsonite from Olduvai Gorge, Africa.

7. Synthetic dawsonite prepared at College Park Metallurgy Research Center (5).

8. Synthetic dawsonite prepared by American Chicle Co.

X-RAY DIFFRACTION

Quantitative Theory

Quantitative phase analysis by X-ray diffraction has been performed for a number of years and has been discussed in detail by Azaroff (1) and Klug and Alexander (6). A more recent paper by Braun and Ramspott (2) discusses the problems and accuracy of phase analysis of rocks. The intensity of a particular phase in a mixture of other phases depends on the concentration of that phase in the mixture and on the matrix of the mixture; that is,

$$I_A = K_A \frac{\nu A}{\mu}, \quad (1)$$

where I_A is the intensity of selected diffraction peak of phase A, K_A is a constant, νA is the volume percentage of A in the mixture, and μ is the linear absorption coefficient, which varies with changing composition of the mixture. The difficulty of evaluating μ is eliminated by adding a known amount of substance not already present in the mixture and determining the percentage weight fraction of any component in terms of the weight of the added substance. The relationship between relative intensities and relative percentage weight fraction is linear; that is,

$$w_A = K \frac{I_A}{I_S}, \quad (2)$$

where I_A is the intensity of the desired phase, I_S is the intensity of the internal standard, K is a constant, and w_A is the weight fraction of A in the sample.

Quantitative Procedure

Standard materials used in this investigation were natural single crystals of nahcolite from Colorado, synthetic dawsonite, and reagent-grade CaF_2. All materials were crushed and gently hand-ground in a mortar to minus 100 mesh. The CaF_2 powder was annealed at 600° C for 18 hours. Figure 1 illustrates the necessity for annealing the powdered CaF_2. In addition to greater intensity of the X-ray peak, annealing also reduces the width of the base of the peak and thus reduces any chance of errors from overlapping peaks from other phases present in the oil shale samples.

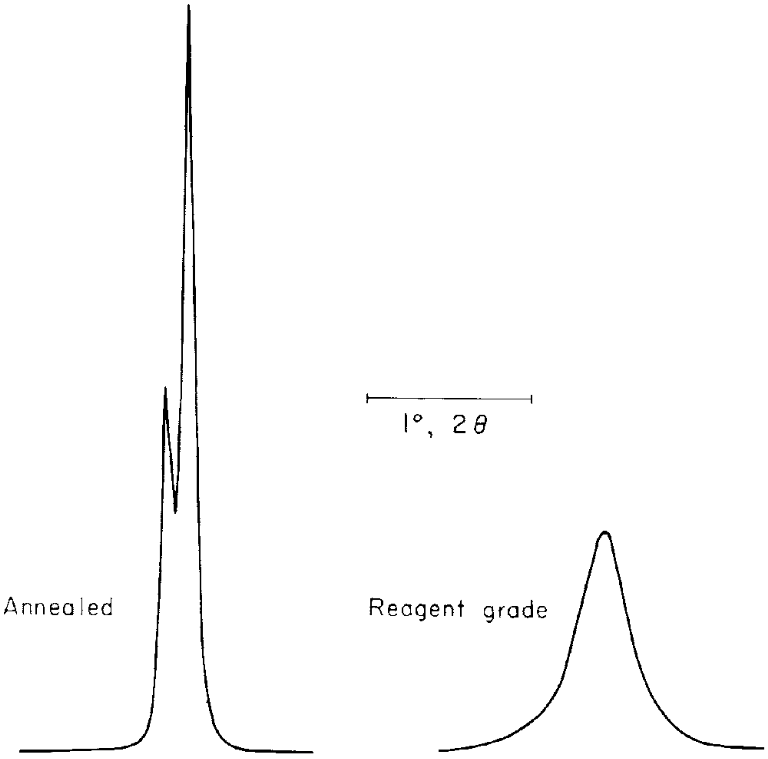

FIGURE 1. - Comparison of 1.931 A peaks in annealed and reagent-grade CaF_2.

Powder diffraction charts were obtained with the Norelco[3] wide-angled X-ray diffractometer using a gas proportional counter coupled to an ORTEC 109 PC preamplifier that was then interfaced with other ORTEC solid-state NIM bin components. Instrumental settings for the diffractometer were as follows: 406 single-channel analyzer, NOR, lower level, 1.0 volt, upper level, 10.0 volts; 485 amplifier, coarse gain 4.0, fine gain 6.5; 441 ratemeter, standard deviation 3 percent, multiplier 2×10^3; 446 high-voltage power supply, 1,900 volts; divergence and scatter slits, 1°; receiving slit, 0.003 inch; scanning speed, ¼° 2θ per minute; chart speed, ½° per inch; tube voltage, 40 kilovolts; tube amperage, 15 milliamperes; nickel filtered CuKα radiation.

Standard calibration samples for the determination of nahcolite were prepared by adding known amounts of nahcolite to samples of oil shale that contained no nahcolite. Oil shale samples free of nahcolite were obtained by leaching with water. Removal of the other soluble phases such as halite has little if any matrix effect because these phases were generally present in concentrations below 5 percent. The mixtures were blended for 10 minutes in a Spex mill using three plastic balls and a plastic container. Total weight was 3½ grams. The blended mixtures of nahcolite standards were then briquetted at 30,000 psi into 1-inch disks.

Calibration standards for dawsonite are more difficult to make as naturally occurring nondawsonite oil shales have a matrix slightly different from that of the dawsonitic oil shales, but this problem is overcome by using CaF_2 as an internal standard. Calibration standards for dawsonite are prepared by adding ½ gram of annealed CaF_2 to 4½-gram mixtures of nondawsonitic oil shale and synthetic dawsonite. The crystallinity of this synthetic dawsonite, according to Jackson, Huggins, and Ampian (5), is quite similar to that of the natural material.

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[3] Reference to specific equipment does not imply endorsement by the Bureau of Mines.

Integrated intensities were used in both nahcolite (34.00° to 35.00° 2θ) and dawsonite (15.00° to 16.00° 2θ) determinations because this minimizes any minor errors caused by differences in crystallinity. The 220 reflection of the internal standard was integrated from 46.5° to 47.5° 2θ. Background values were determined from measurements on both sides of the peak being integrated, and the average was used for the background correction. As a rule, it is a good practice to identify all the major phases present before quantitative determinations are attempted; peak superposition errors are greatly reduced by this procedure.

Calibration Data

It is desirable to use the strongest peak in order to get the greatest sensitivity; however, this is not possible in the nahcolite determination because the 30.45° 2θ peak nearly always has interference from dolomite. The most sensitive dawsonite peak at 15.65° 2θ is nearly always free of interference except on rare occasions when analcite is present. The peaks selected

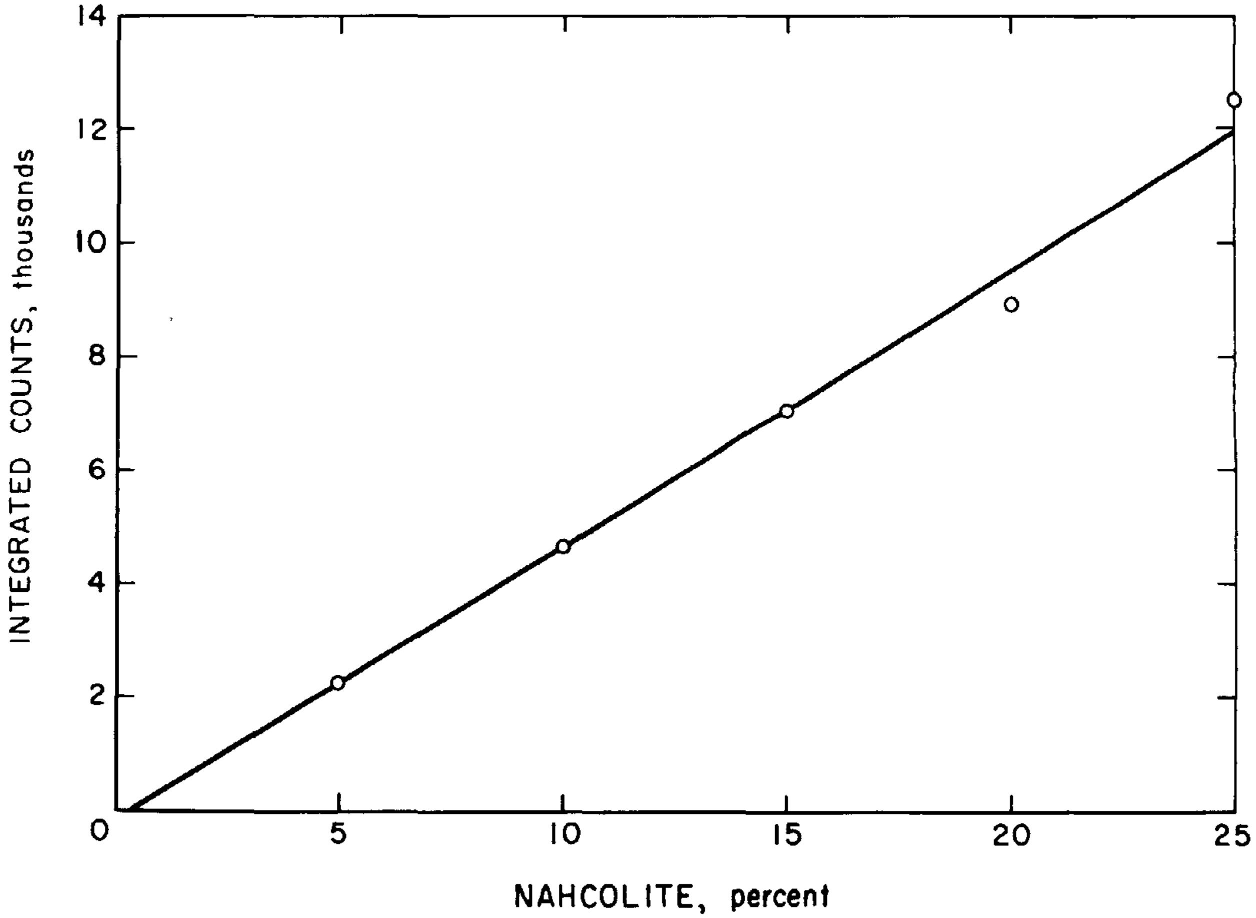


FIGURE 2. - Nahcolite analysis by the integrated intensity method.

are listed in table 1. Calibration curves for nahcolite and dawsonite are shown in figures 2-3.

TABLE 1. - Diffraction peaks used for quantitative determinations of nahcolite and dawsonite

Phase	Diffraction plane (hkl)	d-value, A	2θ, degrees
Nahcolite......	121	2.60	34.51
Dawsonite......	110	5.67	15.65
CaF_2...........	220	1.93	47.05

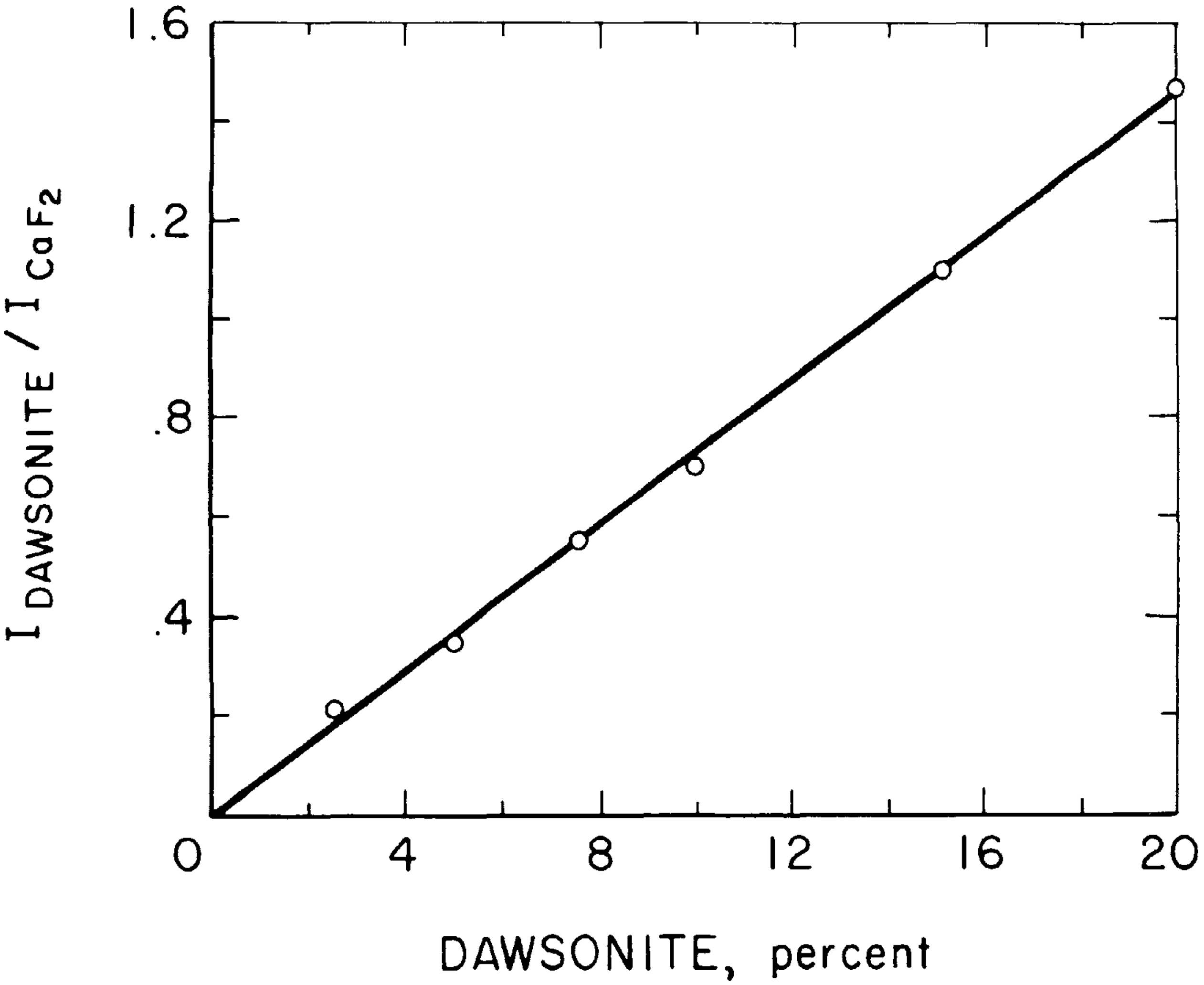


FIGURE 3. - Dawsonite analysis by the integrated intensity and internal standard method.

Effects of Grinding on X-Ray Intensities

Great care must be exercised in grinding if quantitative results for nahcolite are to be obtained by X-ray diffraction. Nahcolite begins to break down to sodium carbonate, water, and carbon dioxide,

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2, \tag{3}$$

at temperatures as low as 90° C. In addition to the heat problem, the crystalline structure of nahcolite is easily altered in grinding. Table 2 shows the variation of peak area with particle size. Hand grinding did not affect the dawsonite peak areas but had a pronounced effect on the nahcolite peak areas.

TABLE 2. - The effect of hand grinding on nahcolite and dawsonite integrated-peak areas of composite oil shale

Ground to mesh	Nahcolite counts	Dawsonite counts
100	6,700	5,200
150	5,800	5,000
200	5,000	5,200
270	4,600	5,300
325	4,300	5,200

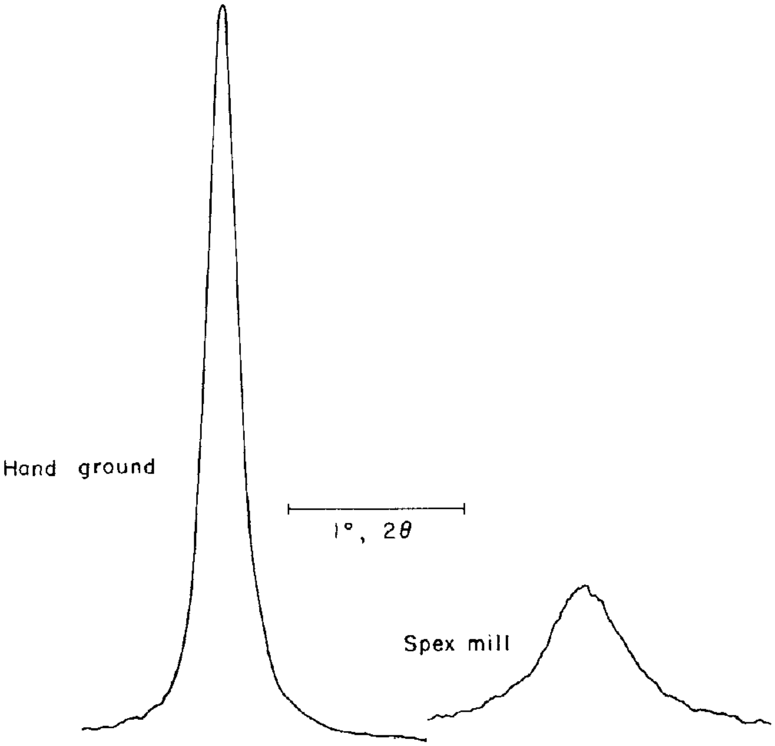


FIGURE 4. - Comparison of 5.67 A dawsonite X-ray diffraction peaks resulting from hand grinding and further grinding in the Spex mill.

The weight loss data given in table 4 in the "Thermal Analysis" section shows nearly identical values for minus 100- and minus 325-mesh samples of composite oil shale. The great difference in the X-ray peak areas is therefore not due to decomposition of the nahcolite but to alteration of the crystalline structure caused by grinding. Figure 4 compares the results on a sample of dawsonite from Olduvai Gorge, east Africa, by hand grinding to minus 100 mesh and then further grinding for 20 additional minutes in a Spex mill using a hardened steel container and two steel balls. The authors also checked the mixing and blending procedure and found the dawsonite peak at 15.64° 2θ did not change after blending for 20 minutes in the plastic containers. Hand grinding in a mortar and blending with plastic balls presents no problem for quantitative dawsonite determinations by X-ray diffraction; however, grinding with steel balls in a Spex mill must be avoided.

The only quantitative nahcolite determination by X-ray diffraction was done on the composite oil shale sample. Grinding problems affecting the peak intensities as previously discussed are very hard to cope with, and extreme care must be taken in order that the standards and unknowns are processed identically. The percent nahcolite found in the composite oil shale sample is given in table 5 in the "Thermal Analysis" section.

Quantitative dawsonite values obtained by X-ray diffraction are given in table 3 along with determinations made on the same samples using the wet chemical method of Smith and Young (11).

TABLE 3. - Dawsonite determinations in oil shale samples

Sample No.	Dawsonite (X-ray method), weight-percent	Dawsonite (wet chemical method), weight-percent
3..................	5.4	4.9
17..................	.3	.7
18..................	6.0	5.2
43..................	4.0	3.7
60..................	10.8	9.2
61..................	9.5	6.5
63..................	16.4	14.8
70..................	6.4	5.4
75..................	10.0	8.3
78..................	9.1	8.5
Composite sample....	9.4	7.5
Outcrop sample......	9.8	11.0

THERMAL ANALYSIS

Weight Loss Methods

Methods based on loss of weight of the sample on heating can be of two general types. A weighed sample can be heated at a specified temperature for a specified time and reweighed, as in the open dish procedure described later in this report and in the method reported by Dyni, Mountjoy, Hauff, and Blackmon (4). Alternately, the loss in weight can be recorded continuously as the sample is heated at a specified rate as in conventional thermogravimetric methods. High results can be caused by loss of adsorbed water or water of crystallization, distillation of organic matter from the sample, decomposition of inorganic or organic compounds other than the species sought. The oxidation of other components of the sample can cause low results.

Open Dish Procedure

In the present investigation, samples of minus 100- and minus 325-mesh composite shale and minus 100-mesh single crystal nahcolite were treated as follows. Approximately 2-gram samples of material, which had been dried overnight at room temperature in a desiccator containing Anhydrone, were placed in 58-millimeter-diameter weighing dishes and accurately weighed. Use of these larger diameter weighing dishes instead of the 15-millimeter-diameter crucibles used by Dyni, Mountjoy, Hauff, and Blackmon (4) permits the samples to be spread in a thinner layer and thus facilitates the escape of CO_2 and H_2O. The open dish method is more rapid than Dyni's method, which requires 14 hours heating at 105° C, and the open dish method does not require the use of an empirical equation as employed by Dyni.

Table 4 shows the weight loss of samples of composite shale and single-crystal nahcolite heated at various temperatures. From these results, the conditions of 1 hour heating at 116° C were deemed adequate. The percent nahcolite was calculated from the weight loss using the factor 2.709 derived from equation 3.

TABLE 4. - Results of open dish technique for various times and temperatures

Heating conditions	Composite oil shale		Single-crystal nahcolite minus 100 mesh
	Minus 100 mesh	Minus 325 mesh	
	Weight loss, percent		
1 hour at 68° C.......	0.20	0.20	0.22
1 hour at 86° C.......	.37	.39	1.97
1 hour at 96° C.......	5.27	2.32	11.02
1 hour at 109° C......	6.26	6.20	36.28
3 hours at 116° C.....	6.23	6.16	36.26
	Calculated nahcolite, percent		
3 hours at 116° C.....	16.9	16.7	98.2

The open dish technique was not attempted for the determination of dawsonite because volatilization of organic matter in the oil shales would have seriously interfered at the temperature required for the decomposition of dawsonite.

Dynamic Thermogravimetric Procedure

Thermogravimetric determinations were performed on 20- to 100-milligram samples of minus 100-mesh composite shale, single-crystal nahcolite, synthetic dawsonite, Olduvai Gorge dawsonite, and four shale samples. Weight losses were measured on a Cahn model RH microbalance using a heating rate of 6° C per minute. Controlled atmospheres of nitrogen or carbon dioxide were used; both produced the same results.

Figure 5 shows thermogravimetric curves for single-crystal nahcolite, synthetic dawsonite, and composite shale, which are replotted on a weight loss versus temperature basis. These curves demonstrate that the thermogravimetric

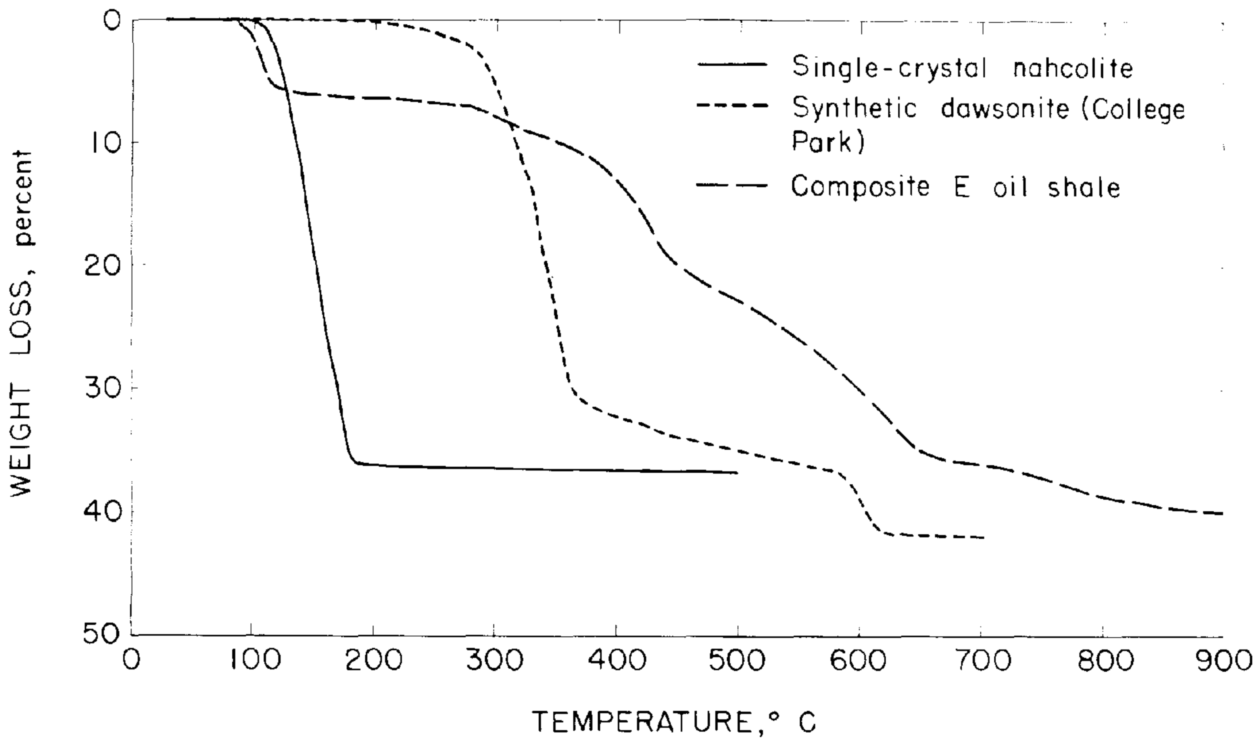


FIGURE 5. - Thermogravimetric curves for nahcolite, dawsonite, and composite oil shale.

method is satisfactory for the determination of nahcolite in samples free of extraneous moisture. The data in figure 5 indicates 98.7 percent nahcolite in the single-crystal nahcolite and 16.0 percent nahcolite in the composite shale. The thermogravimetric method also gave satisfactory results for dawsonite in the synthetic dawsonite sample and Olduvai Gorge dawsonite. Thermogravimetric data indicated 97.5 percent dawsonite in the synthetic dawsonite sample. The interference of organic matter at temperatures below the decomposition temperature of dawsonite is demonstrated by the thermogravimetric curves for composite oil shale in figure 5. Attempts to remove the organic matter by solvent extraction as recommended by Müller-Vonmoss (7) were unsuccessful.

Figure 5 also shows that the thermal decomposition of dawsonite is a two-step procedure. The second step in the curve at 600° C accounts for approximately 17 percent of the total weight loss. This second step of the reaction is not mentioned by Müller-Vonmoss (7). Evidence of such a two-step reaction is indicated in the thermal decomposition procedure described in the next section.

Results of nahcolite determinations obtained by the thermogravimetric method are compared with results obtained by other methods in table 5 in the "Thermal Analysis" section.

Thermal Decomposition

Methods based on total weight loss, either those using heating at a fixed temperature for a specified period of time or dynamic methods such as thermogravimetric analysis (TGA), are not specific. They do not differentiate between weight losses due to decomposition products, water of hydration, and volatile organic matter.

The thermal decomposition method can be made specific by collecting the decomposition products separately in weighable form. Thus, H_2O and CO_2 can be collected in absorption tubes for the determination of nahcolite and dawsonite, which decompose on heating according to the following reactions suggested in the literature:

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2; \tag{3}$$

$$NaAl(OH)_2CO_3 \rightarrow NaAlO_2 + H_2O + CO_2 \ (\underline{8}); \tag{4}$$

$$2NaAl(OH)_2CO_3 \rightarrow Na_2CO_3 + Al_2O_3 + 2H_2O + CO_2. \tag{5}$$

Apparatus

The apparatus used to heat the samples and collect the H_2O and CO_2 is shown in figure 6. The parts of the apparatus within the dashed line, including the Vycor sample tube (A) and absorption train, were attached to a metal rod so they could be moved as a unit when the sample tube was placed in the vertical tube furnace.

Nitrogen carrier gas entering the system is held at a pressure of approximately 1 inch of water by a bubbler (B). The vacuum at the exit end of the system is maintained at approximately 5 inches of water by a bubbler (C). The bubblers also provide a bypass for the nitrogen and vacuum relief when stopcocks in the train are in the closed position.

Procedure

Two sets of H_2O and CO_2 absorption bulbs are required so that one set is connected to the apparatus at all times. At the beginning of each day, each set of bulbs is put on the apparatus with an empty sample tube and run for 30 to 45 minutes at a flow rate of 200 milliliters per minute to obtain an initial weight. The bulbs are turned to the closed position before disconnecting them from the apparatus and are allowed to stand near the balance for 15 to 20 minutes before weighing. Each bulb is wiped with a soft cloth, opened to the atmosphere for a moment to equalize the pressure, then weighed to the nearest 0.1 milligram.

The following stepwise procedure is used for each determination.

1. Connect the weighed absorption bulbs in the train and leave them in the closed position.

2. Close stopcock (K), and replace the previous sample tube with the sample tube containing the weighed sample.

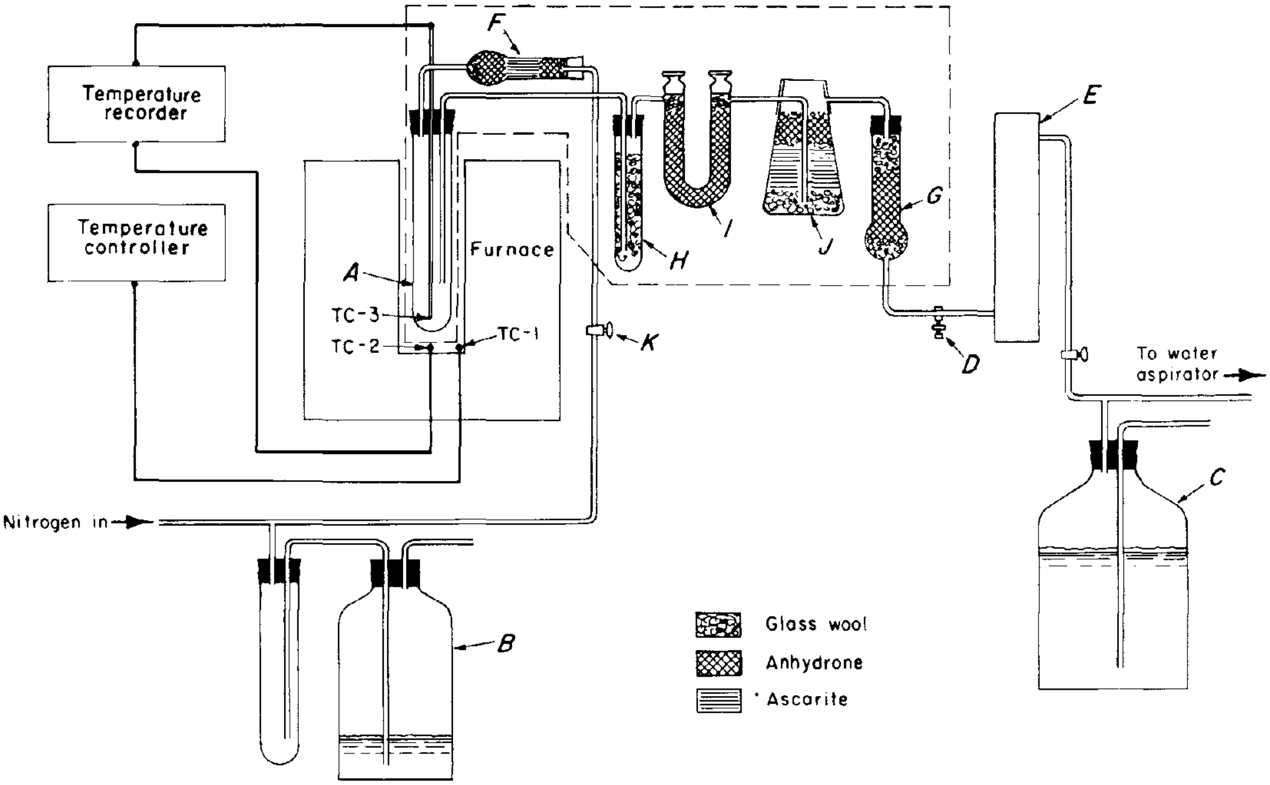


FIGURE 6. - Apparatus for measuring products of thermal decomposition: *A*, Reaction tube; *B*, relief bubbler for nitrogen inlet; *C*, relief bubbler for vacuum; *D*, screw clamp for controlling gas flow rate; *E*, flowmeter; *F*, guard tube to absorb H_2O and CO_2 from incoming gas stream; *G*, guard tube at exit end; *H*, trap containing glass wool; *I*, H_2O absorption bulb; *J*, CO_2 absorption bulb; *K*, stopcock to interrupt nitrogen flow.

3. Open the stopcocks on the absorption bulbs, and check the reading on the flowmeter. It should show zero flow indicating that there are no leaks in the system.

4. Open stopcock (K), and move the sample tube-absorption train assembly to the position that places the sample tube in the preheated furnace.

5. After the sample temperature reaches the' desired level, allow the system to run for 1 hour.

6. Turn the stopcocks of the absorption bulbs to the closed position, and move the sample tube-absorption train assembly to a position with the sample tube out of the furnace.

7. Replace the absorption bulbs with the other set of bulbs, and repeat the procedure for the next sample.

Results

A series of tests using the aforementioned apparatus and procedure were performed on samples of single-crystal nahcolite, synthetic dawsonite, and dawsonite from Olduvai Gorge. The results for the nahcolite and synthetic dawsonite, expressed as millimoles of H_2O and CO_2 per gram of sample, are shown in figure 7. The results for the Olduvai dawsonite were similar to those shown for the synthetic dawsonite. The data for nahcolite show a small excess of H_2O over CO_2 instead of the 1:1 mole ratio indicated by the reaction

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2. \tag{3}$$

This excess H_2O can be interpreted as mechanically bound water. Decomposition of nahcolite begins at approximately 100° C and is essentially complete by 170° C. The initial decomposition temperature of dawsonite is 220° C, and H_2O released below this temperature can be designated as mechanically bound water. The H_2O curve for synthetic dawsonite resembles the H_2O and CO_2 curves for nahcolite and is typical of a single-step reaction; however, the CO_2 curve for dawsonite indicates that CO_2 release is a two-stage process. X-ray diffraction patterns of the residue produced by heating synthetic dawsonite to temperatures between 300° and 600° C showed no crystalline phases. The diffraction patterns were typical of amorphous material.

For the determination of nahcolite, the region of approximately 170° to 220° C provided a range in which the nahcolite was quantitatively decomposed, but dawsonite had not started to decompose. Therefore, 195° C was used in the

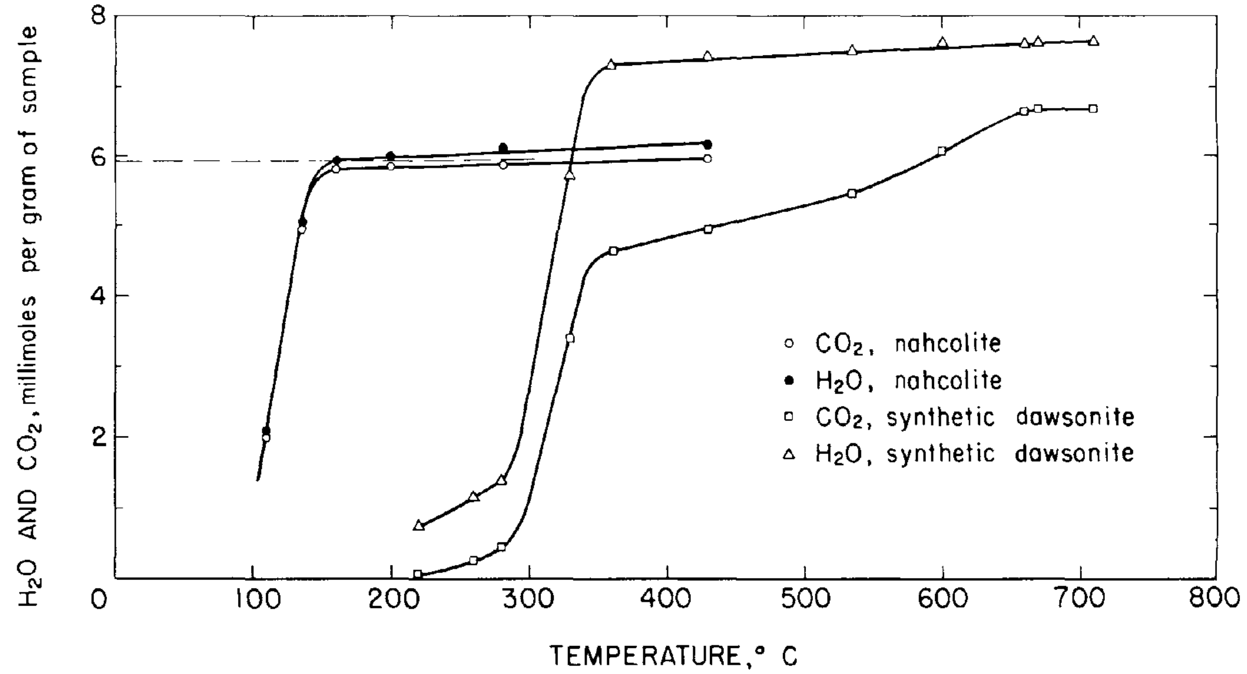


FIGURE 7. - Evolution of H_2O and CO_2 from nahcolite and dawsonite during thermal decomposition.

procedure, and the percent nahcolite was calculated from the weight of CO_2 collected. Results of this procedure, the wet chemical method, thermogravimetric method, and X-ray diffraction are compared in table 5. At temperatures above 400° C, cracking products of the organic matter in the sample contaminated the absorption train as far as the CO_2 absorption bulb and made the procedure unsatisfactory for the determination of dawsonite. An attempt was made to eliminate the effect of organic matter on the dawsonite determination by absorbing the CO_2 in NaOH solution and precipitating the carbonate as $BaCO_3$. In some tests the $BaCO_3$ was ignited, in others the $BaCO_3$ was converted to $BaSO_4$ and ignited. Results of these tests showed that the technique was suitable for nahcolite, but the results for dawsonite were too high.

TABLE 5. - Comparison of nahcolite analysis methods

Sample	Nahcolite content of oil shales, weight-percent			
	X-ray diffraction	Wet chemical method	Thermal decomposition	Thermo-gravimetric procedure
Composite sample........	16.7	16.4	15.7	16.0
Laramie No. 18..........	-	33.9	34.1	36.3
Laramie No. 43..........	-	52.6	51.9	53.8
Laramie No. 70..........	-	43.4	42.7	44.0
Laramie No. 75..........	-	21.1	21.3	22.2
Single-crystal nahcolite	-	97.7	98.2	98.7

Removal of interfering organic matter by extraction with a mixture of methanol and benzene as recommended by Müller-Vonmoss and Bach (7) was ineffective.

Differential Thermal Analysis

Differential thermal analysis (DTA) was applied to single-crystal nahcolite, synthetic dawsonite, Olduvai Gorge dawsonite, and a series of oil shales. All samples were ground to minus 100 mesh and placed in platinum crucibles. They were not dried in an oven, since this would markedly affect the nahcolite peak. The differential thermal analyzer was a Du Pont Model 900 that used high-purity Al_2O_3 as the reference material. The sample weight was 35 milligrams, and the heating rate was 6° C per minute. A ΔT scale factor of 0.008 millivolt per inch was used for all oil shales, and a ΔT scale factor of 0.02 millivolt per inch was used on the remaining samples.

Typical results on oil shales are shown in figure 8. The endotherm at 140° C provides an indication of the nahcolite content in oil shales. Sample 1 (fig. 8) contains 16.5 percent nahcolite, sample 2 has no nahcolite, and sample 3 has less than 5 percent nahcolite as determined by the wet chemical method. Speil (12) has used DTA for quantitative measurements of clays, and similar circumstances should apply to oil shales. The area of the peak is a measure of the total heat effect, and if the conductivity is constant, the peak area is proportional to the amount of thermally active material present. Quantitative nahcolite values versus the area of the peaks are shown in figure 9. This area is measured by a planimeter or by simply cutting out the endotherms and comparing the weight with that of a standard area as done by the authors.

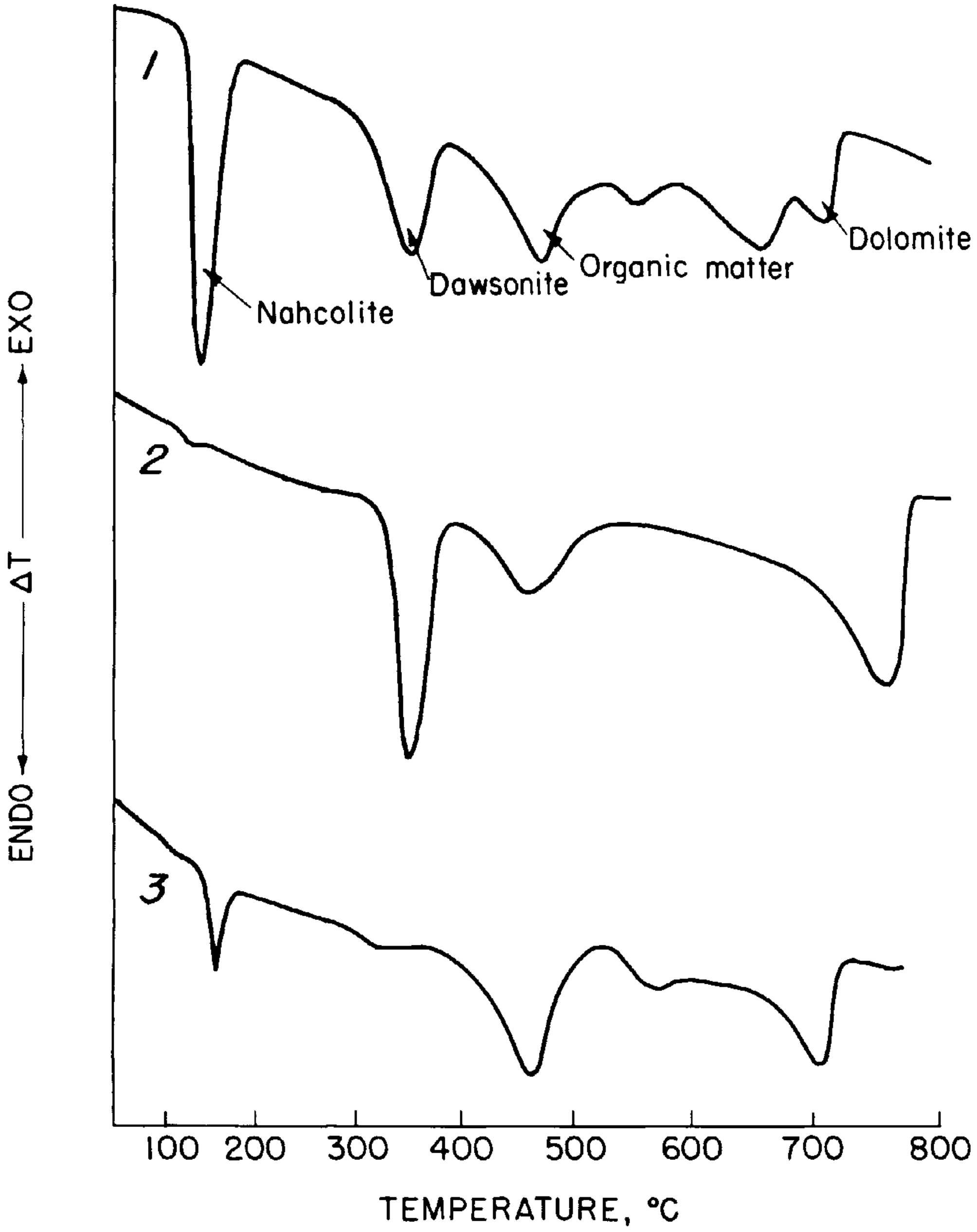


FIGURE 8. - DTA tracings of three oil shales showing the presence and absence of both nahcolite and dawsonite: *(1)* Composite shale; *(2)* outcrop shale; *(3)* Wyoming oil shale.

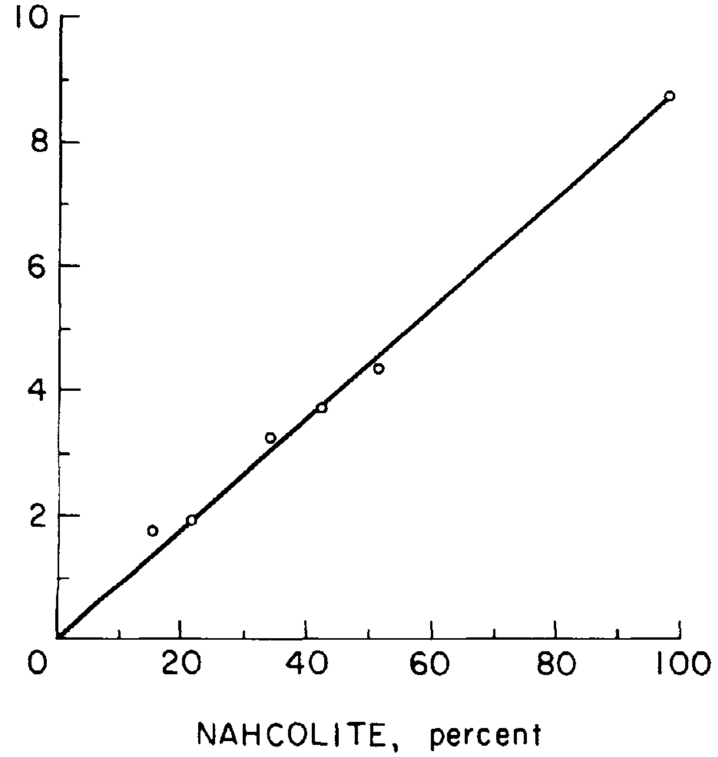
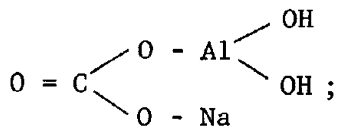


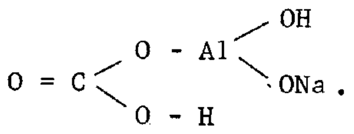
FIGURE 9. - Nahcolite determination by DTA.

The dawsonite endotherm at 350° C (fig. 8) provides an indication of the dawsonite content in oil shales. This endotherm, however, cannot be used for quantitative determinations as the endotherm is seldom symmetrical. Colorado oil shales usually have a shoulder on the low-temperature side of the dawsonite endotherm. The shoulder could be caused by a mixture of poorly crystallized dawsonite with well crystallized dawsonite or result from degradation of another phase in the shale. Smith (10) attributes the shoulder to nordstrandite, $Al(OH)_3$. However, a similar shoulder can be produced in the absence of $Al(OH)_3$, as shown in figure 10. This endotherm is from a mixture of 40 percent poorly crystallized dawsonite and 60 percent well crystallized dawsonite. Schmidt-Collerus (9) raises still another question as he claims the following two forms of dawsonite exist in the Colorado oil shales:

(A)



(B)



According to Schmidt-Collerus (9), form A would degrade at about 357° C, and form B would degrade at about 327° C. A mixture of the two forms (A and B) would produce a dawsonite shoulder. The shoulder on the low-temperature side of the dawsonite endotherm illustrates that a complex situation can exist. The presence or absence of $Al(OH)_3$ can be handled by infrared spectroscopy. No attempt was made to evaluate the other minerals present in the oil shales by DTA.

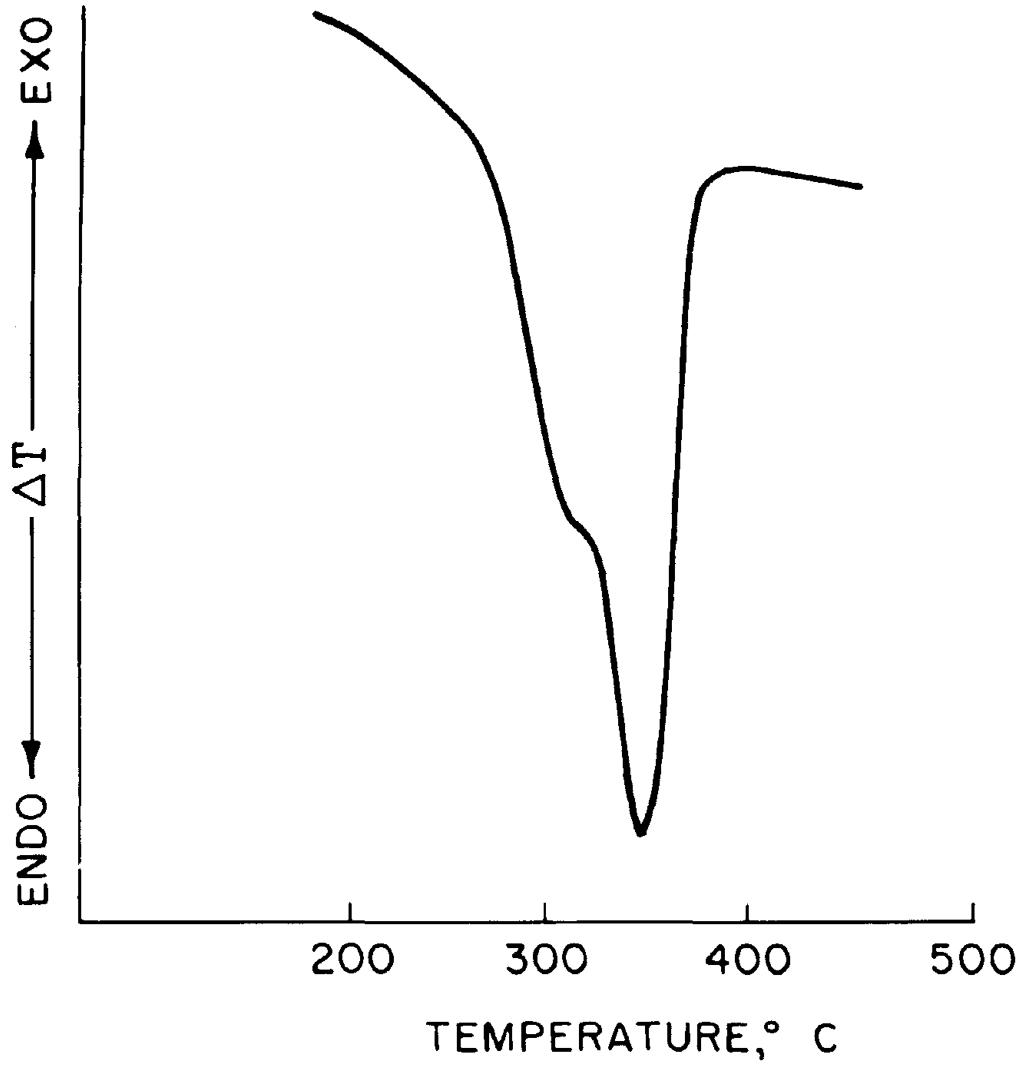


FIGURE 10. - DTA tracing of a mixture of poorly crystallized dawsonite and well crystallized dawsonite.

INFRARED SPECTROSCOPY

Experimental Procedure

Samples for infrared spectroscopy were prepared using a procedure similar to that used by Coles (3). Eight drops of isopropyl alcohol were added to 50 milligrams of sample in an agate mortar and hand ground until dry. Two and one-half milligrams of this material was weighed on a microbalance and blended with 1,000 milligrams of KBr in a Wig-L-Bug for 1 minute. One hundred and seventy-five milligrams of this mixture was then pressed into a 13-millimeter-diameter disk using a Perkin-Elmer evacuation die and a pressure of 8,000 psi. The infrared spectrum was then scanned on a Perkin-Elmer 225 infrared grating spectrophotometer from 4,000 to 200 cm^{-1}. The following instrumental settings were used: scale factor, 4.0; scan speed, fast--2.0; pen traverse time, 3.0 seconds; suppression, 2.0; slits, manual 0, program 4.0; gain, 8.0; response, 0; intensity, 4.0.

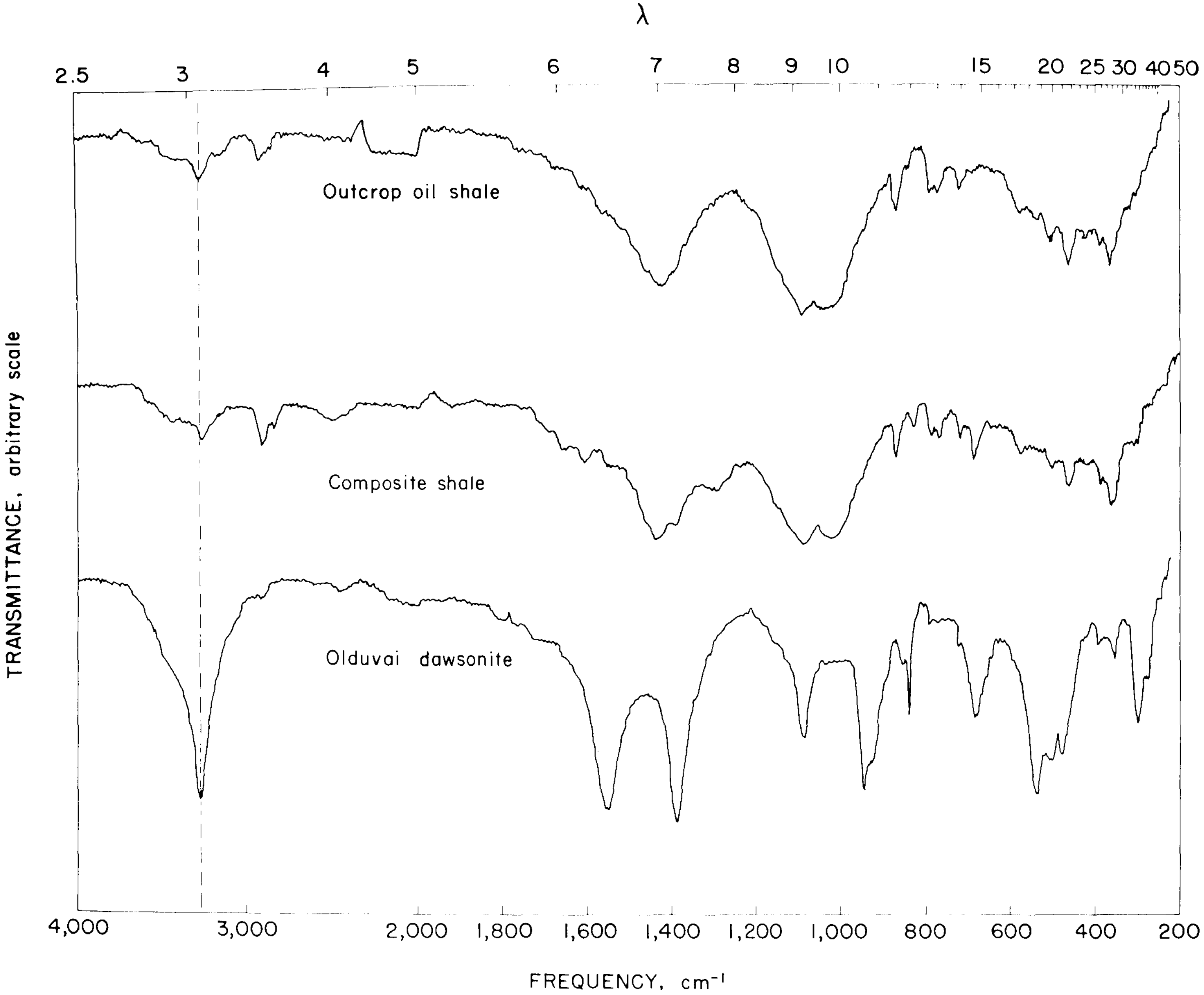


FIGURE 11. - Infared spectra showing the presence of dawsonite.

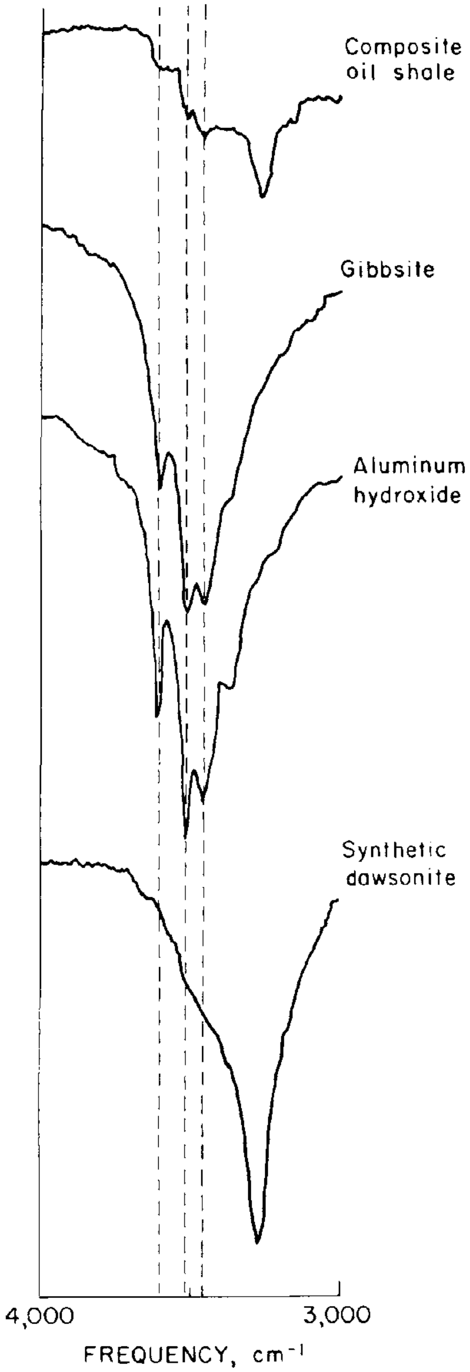


FIGURE 12. - Infrared spectra showing the presence of hydroxyl absorption bands.

Results and Discussion

Figure 11 shows the infrared spectra of outcrop oil shale, composite shale, and dawsonite. The OH vibration at 3,175 cm^{-1} caused by the dawsonite is visible in both the outcrop and composite shales. The outcrop shale contains 9.8 percent dawsonite, and composite shale contains 9.4 percent dawsonite as determined previously in the X-ray diffraction procedure. Other absorption bands related to dawsonite are quite difficult to distinguish because of overlapping by the organic components.

Figure 12 gives a comparison of the OH band spectra of composite oil shale, gibbsite, $Al(OH)_3$, and synthetic dawsonite. Smith (10) postulated the presence of $Al(OH)_3$ in oil shale from his DTA data but was not able to confirm the presence of $Al(OH)_3$ as no X-ray diffraction pattern could be obtained--possibly because this phase was of low concentration or poorly crystallized. The infrared data in figure 12 indicates the presence of hydroxyl absorption bands typical of $Al(OH)_3$ in the composite oil shale. The three small peaks at 3,460, 3,520, and 3,605 cm^{-1} are in close agreement to those of $Al(OH)_3$ and gibbsite.

Other minerals in oil shale can be detected by infrared spectroscopy. Figure 13 shows the infrared spectra of composite shale, outcrop shale, and nahcolite. The outcrop oil shale contains no nahcolite and has no absorption bands typical of nahcolite. Composite shale contains 16.5 percent nahcolite as determined in the previously discussed procedures, and the CO_3 stretching modes at 830 and 690 cm^{-1} are visible.

Quantitative mineral determinations by infrared spectroscopy were not attempted because of various problems including the difficulty in obtaining representative (2.5-milligram) samples.

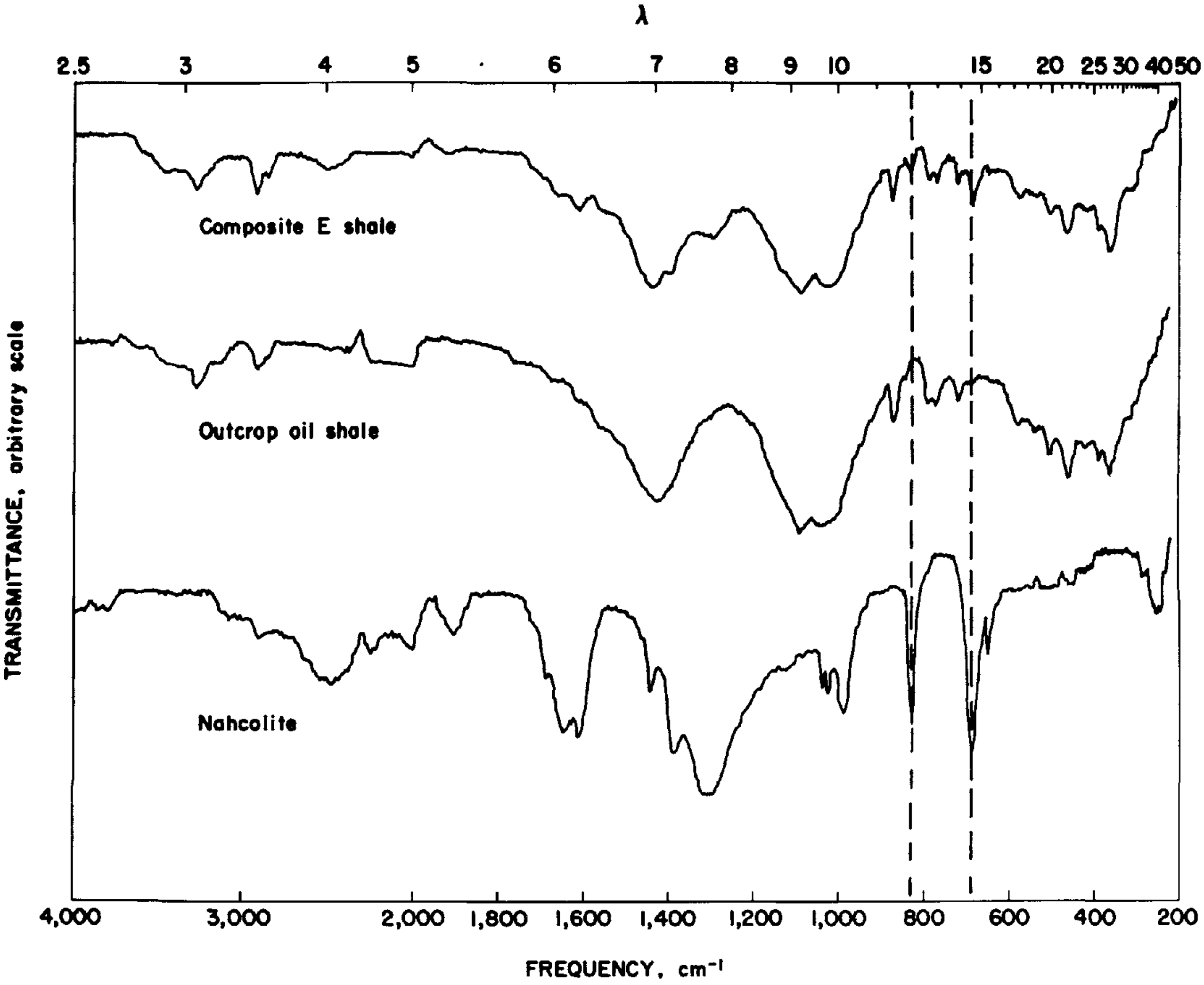


FIGURE 13. - Infrared spectra showing the presence of nahcolite.

CONCLUSIONS

Two methods based on different principles are desired for the determination of a specific mineral in naturally occurring mixtures. The best pair of methods for determining nahcolite is the Smith and Young method and a new method based on the weight of carbon dioxide produced during thermal decomposition. For determining dawsonite, the best combination of methods is X-ray diffraction and the Smith and Young method.

X-ray diffraction is also useful for identifying other mineral species present in the sample, but great care must be exercised in grinding the sample to avoid alteration of the crystallinity of carbonate minerals. Differential thermal analyses and infrared spectroscopy are useful for detecting minor or poorly crystallized minerals present in oil shales.

REFERENCES

1. Azaroff, L. V. Elements of X-Ray Crystallography. McGraw-Hill Book Co., Inc., New York, 1968, 610 pp.

2. Braun, R. L., and L. D. Ramspott. Quantitative Phase Analysis of Rocks by X-Ray Diffractometry. Lawrence Radiation Laboratory, Univ. of Calif., Livermore, Calif., UCRL-50921, 1970, 19 pp.

3. Coles, J. L. A Study of Some Synthetic Apatites. Ph.D. Thesis, Univ. of Utah, Salt Lake City, Utah, June 1963, 70 pp.

4. Dyni, J. R., W. Mountjoy, P. L. Hauff, and P. D. Blackmon. Thermal Method for the Quantitative Determination of Nahcolite in Colorado Oil Shales. U.S. Geol. Survey Prof. Paper 750-B, 1971, pp. B194-B198.

5. Jackson, J., Jr., C. W. Huggins, and S. G. Ampian. Synthesis and Characterization of Dawsonite. BuMines RI 7664, 1972, 14 pp.

6. Klug, H. P., and L. E. Alexander. X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials. John Wiley & Sons, Inc., New York, 1954, 716 pp.

7. Müller-Vonmoss, M., and R. Bach. Thermoanalytic-Mass Spectrochemical Investigations of an Oil Shale Containing Dawsonite. Thermal Analysis, v. 2, 1969, pp. 1229-1238.

8. Savage, J. W., and D. Bailey. Economic Potential of the New Sodium Minerals Found in the Green River Formation. 61st Ann. Meeting, AIChE, Los Angeles, Calif., December 1968, American Institute of Chemical Engineers, New York, Paper 27D, 27 pp.

9. Schmidt-Collerus, J. J., and R. D. Hollingshead. Investigations Into the Nature of Dawsonite in the Green River Formations. Colo. School Mines Quart., v. 63, No. 4, 1968, pp. 143-167.

10. Smith, J. W., and D. R. Johnson. Thermal Analysis of Natural Fuels. Proc. 2d Toronto Symp. on Thermal Analysis, Toronto Sec., Chemical Institute of Canada, Ottawa, Canada, Feb. 27, 1967, pp. 95-116.

11. Smith, J. W., and N. B. Young. Determination of Dawsonite and Nahcolite in Green River Formation Oil Shales. BuMines RI 7286, 1969, 20 pp.

12. Speil, S. Applications of Thermal Analysis to Clays and Aluminous Minerals. BuMines RI 3764, 1944, 36 pp.

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