

# CHEMICAL STAINING METHODS USED IN THE IDENTIFICATION OF CARBONATE MINERALS

Tamer AYAN

*Mineral Research and Exploration Institute of Turkey*

## INTRODUCTION

Carbonate minerals are the major constituents of sedimentary rocks; however, they are also found in igneous and metamorphic rocks, either as primary or as secondary minerals. In carbonate rocks formed either by chemical or mechanical deposition, these minerals constitute the main rock-forming components. Sometimes they are also found in great abundance in pelitic, psammitic and psephitic rocks.

According to their crystallographic characteristics, carbonate minerals may be subdivided into two main groups :

- 1) Calcite group : Hexagonal-rhombohedral system.
- 2) Aragonite group : Orthorhombic system «pseudo-hexagonal».

Of the calcite group of minerals, calcite ( $\text{CaCO}_3$ ) and dolomite [ $\text{CaMg}(\text{CO}_3)_2$ ] are the two minerals which are dominantly found in sediments. Depending on its purity, or iron and magnesium content, calcite may be found in states of pure calcite, ferro-calcite, or slightly to abundantly magnesian calcite. Similarly, according to the iron content percentage, dolomite may also be regarded as having been composed of two end members, pure dolomite and ferrous dolomite, in varying proportions. The other calcite group minerals are ankerite «ferro-ferric dolomite» [ $\text{CaFe}(\text{CO}_3)_2$ ], magnesite ( $\text{MgCO}_3$ ), siderite ( $\text{FeCO}_3$ ), smithsonite ( $\text{ZnCO}_3$ ), rhodochrosite ( $\text{MnCO}_3$ ) and spherocobaltite ( $\text{CoCO}_3$ ).

The most important mineral of the aragonite group is aragonite ( $\text{CaCO}_3$ ); the others, in decreasing order of importance, are witherite ( $\text{BaCO}_3$ ), strontianite ( $\text{SrCO}_3$ ), cerussite ( $\text{PbCO}_3$ ) and alstonite [ $(\text{Ba}, \text{Ca})\text{CO}_3$ ]. Apart from their refractive indexes (R.I.), the optical and crystallographic characteristics of carbonate minerals are very similar to each other. Therefore identification of carbonates on hand specimens or even in thin sections, is rather difficult. The determination of the R.I.'s, on the other hand, can only be carried out by oil-immersion methods.

The identification and discrimination of carbonate minerals in hand specimens or thin sections, are made easier by the use of simple chemical staining methods, without losing a great<sup>4</sup> amount of time in chemical analyses or optical investigations. Studies in this field have begun towards the end of the 19<sup>th</sup> century and are continuing at the present time. The production of dependable results in a short time by using simple techniques, has made this method fairly popular. Numerous workers have contributed a wealth of knowledge to this field, In purely scientific or economic studies, it

proves to be useful and successful to sturdy sedimentary, especially carbonate, rock specimens by staining methods, before engaging other microscope techniques.

It is hoped that the following list of descriptions of staining methods will be useful to those who intend to carry out some more research in this field.

#### PROCEDURES BEFORE STAINING

It is recommended that the thin section or the cut and polished surface of the hand specimen be etched with diluted HCl acid before staining. Diluted acetic acid or formic acid may also be used in place of HCl acid (Williams, Turner, Gilbert, 1954). Different carbonate minerals in a rock specimen, immersed in an appropriate HCl solution for an appropriate period of time, will show different reactions. When this specimen, after being thoroughly washed with distilled water, is inspected under a binocular or polarizing microscope, the textural and mineralogic features of carbonate minerals may be observed in detail. In Table 1, acid densities and the periods of time for each test employed by various workers are indicated. However, it will be more appropriate to determine the exact acid density and the duration of test, according to the lithological characteristics of each specimen to be tested. All acid solutions shown in Table 1 have been used cold (at room temperature). However, Warne (1962) points out that in tests carried out with cold acid solutions, calcite, aragonite and witherite fizzes quickly, rhodochrosite, ankerite, cerussite, smithsonite and strontianite show a weak fizzing, whereas siderite, dolomite and magnesite do not react at all. He suggests that minerals that show a weak reaction should be treated with warm HCl acid for about 30 seconds to 1 minute.

**Table - 1**  
**Acid solutions and test duration times used by various workers**

<i>Worker</i>	<i>Acid solutin</i>	<i>Duration</i>
LAMAR, 1950	8-10 cc HCl + 100 cc distilled water	5 min.
WILL., TUR., GILBERT, 1954	10 cc HCl + 100 cc distilled water	—
IVES, 1955	8-10 cc HCl + 100 cc distilled water	8 min.
FRIEDMAN, 1959	8-10 cc HCl + 100 cc distilled water	2-3 min.
WARNE, 1962	8-10 cc HCl + 100 cc distilled water	3 min.
DICKSON, 1965	%1.5 HCl (1.5 cc HCl + 98.5 cc distilled water)	10-15 seconds

#### STAINING METHODS

For the identification of various carbonate minerals, the following available tests may be listed:

I - Discrimination between aragonite and calcite :

- (1) Meigen test; (2) Feigl test; (3) Rhodizonic acid test.

## II - Discrimination between calcite and dolomite :

(1) Lemberg hydroxide test; (2) Lemberg test; (3) Fairbanks test; (4) Lemberg silver chromate test; (5) Copper nitrate test; (6) Trypan blue test; (7) Harris hematoxilin test; (8) Alizarin red test; (9) Friedman test; (10) Potassium ferricyanide test; (11) Alizarin red and potassium ferricyanide composite test; (12) Mann test; (13) Ramsden test.

## III - Discrimination between magnesite and smithsonite :

(1) Friedman test; (2) Magneson test; (3) Tropaeolin 00 test.

## IV - Discrimination between ankerite and siderite :

(1) Kirchberg test; (2) Hydrogen peroxide-potassium hydroxide test.

## V - Discrimination of rhodochrosite :

(1) Benzidine test.

The outlines of each test are given below :

**I. 1 - Meigen test**

This test was first described by Meigen (1901). The rock specimen is boiled in cobalt nitrate solution (Holmes, 1921; Twenhofel and Tyler, 1941).

*Solution.* — Cobalt nitrate  $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ .

*Test.* — Specimen is boiled in cobalt nitrate solution for 20 minutes (Twenhofel and Tyler, 1941; Williams, Turner and Gilbert, 1954). Togari has carried out this test (1955) by boiling 0.2 gr rock specimen in 2 cc 0.1 N cobalt nitrate solution and filtering the specimen off.

*Result.* — During the test aragonite first takes a lilac color, which slowly turns into purple. On the other hand, in calcite such coloring is either not present or slow developing. In the latter case, this color disappears within a few hours after the test (Twenhofel and Tyler, 1941; Le Roy, 1950; Williams, Turner and Gilbert, 1954; Friedman, 1959).

The disadvantages of this test are illustrated by the following :

Jirova (1956) carried out a Meigen test on three foraminifera species which indicated aragonite; yet later an X-ray analysis showed calcite. Another difficulty arises in the investigation of fine-grained specimens: since cobalt nitrate solution spreads over both minerals to the same degree, discrimination becomes difficult. However, sensitivity of the method can be increased by the application of ammonium sulphide to the stained surface. In this case aragonite appears as black spots (cobalt sulphide= $\text{Co}_2\text{S}_3$ ), while the color of calcite remains greyish.

## I2- Feigl test

This test has been arranged by Feigl (1937) and is based on the slightly different dissolution rates of calcite and aragonite in water.

*Solution.* — To prepare the solution, 1 gr  $\text{Ag}_2\text{SO}_4$  is added to a mixture of 11.8 gr  $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$  and 100 cc distilled water. The whole mixture is boiled, cooled and filtered, before adding one or two drops' of diluted NaOH. After letting it settle for two hours the solution is re-filtered and kept in a dark-colored bottle (Feigl, 1946).

*Test.*—The rock specimen is soaked in the solution for 10 minutes.

*Result.*—Aragonite becomes black, while no change of color is observed in calcite, dolomite and witherite (Warne, 1962).

### I. 3 - Rhodizonic acid test

Feigl (1946, 1954) used this test for the detection of the presence of barium and strontium in solutions.

*Solution.*—It is prepared by dissolving 2 gr disodium rhodizonate in 100 ml distilled water. Sodium potassium rhodizonate may also be used for the same purpose.

*Test.*—Previously etched specimen, after having been washed with distilled water is placed in this solution for 5 minutes.

*Result.*—Witherite takes a color between orange and red, while no change is observed in calcite (Warne, 1962).

### II. 1 - Lemberg hydroxide test

This test has been devised by Lemberg (1887) for discrimination between calcite and dolomite (Rodgers, 1940).

*Solution.*—1 part of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  is mixed with 10 parts of distilled water.

*Test.*—The specimen is kept in the solution for about 1 minute (fine-grained specimens for a shorter period), washed with distilled water and then immersed in  $(\text{NH}_4)_2\text{S}_x$  solution (the strength of the solution and the length of time are not important).

*Result.*—Prior to immersing in  $(\text{NH}_4)_2\text{S}$  solution, the color of calcite—due to  $\text{Fe}(\text{OH})_3$ —would be pale brown; after immersion, it will turn black. If the specimen is kept in the second solution for a long time, dolomite assumes a light green color.

The disadvantages of this test are: the color is not stable, it is easily scratched off and, in time, locally cracks and flakes off.

With a slight modification this test has been adapted by Keller and Moore (1937) in the following way, for using on bore-hole samples and fragmentary specimens: Freshly broken or cut face of the specimen, after being wetted with water, is placed in  $\text{FeCl}_3$  solution (2.5 %) for about 5-10 seconds. After being washed thoroughly in distilled water, the specimen is immersed in  $(\text{NH}_4)_2\text{S}$  solution for the same period of time. Once again it is rinsed and dried. While calcite becomes black, no color change will be observed in dolomite.

### II. 2 - Lemberg test

This test was first described by Lemberg (1887) and slightly modified later by Steidtmann (1917) (Rodgers, 1940).

*Solution.*—4 gr  $\text{AlCl}_3$  and 6 gr logwood chips are boiled in 60 cc distilled water for 20-25 minutes. The amount of loss due to evaporation is replaced by the addition of some more distilled water. After cooling the solution is filtered and kept in a bottle.

Steidtmann, slightly modifying the formula, has used 6 gr of logwood spirit (hematoxilin) instead of logwood chips and has diluted the solution with 1200 cc distilled water before making the tests (Rodgers, 1940).

*Test.*—The specimen is kept immersed in the solution for about 5-10 minutes.

*Result.* — During this time calcite acquires a purple color as opposed to dolomite, which does not change color within the first 20 minutes. However, after 20 minutes, dolomite turns into pale blue (Rodgers, 1940; Twenhofel and Tyler, 1941). The outstanding disadvantages of this test are the instability of the solution and the ease of scratching and flaking of the acquired color.

### II. 3 - Fairbanks test

This is essentially a Lemberg test, improved by Fairbanks (1925).

*Solution.* — 0.24 gr of hematoxin and 1.6 gr of  $\text{AlCl}_3$  are boiled in 24 cc of distilled water. After cooling, a little amount of hydrogen peroxide is added to the solution after which it is filtered and kept in a dark-colored bottle.

*Test.* — Specimen is immersed in the solution for about 30 seconds, then washed carefully.

*Result.* — Calcite acquires a dark purple color, while there appears to be no change in the color of dolomite. As far as the stability of the solution and the results are concerned, this test in general is considered to be quite satisfactory.

### II. 4 - Silver chromate test

This test was first described by Lemberg. (1892) for the discrimination between calcium minerals and magnesium minerals. Some details of this test have been given later by Rodgers (1940) (Friedman, 1959).

*Solution.* — 10 % silver nitrate ( $\text{AgNO}_3$ ) and potassium chromate ( $\text{K}_2\text{CrO}_4$ ).

*Test.* — Specimen is soaked in silver nitrate solution at a temperature of  $60^\circ\text{--}70^\circ\text{C}$  for about 2-5 minutes (Rodgers, 1940; Twenhofel and Tyler, 1941; Friedman, 1959). After washing with distilled water, the specimen is immersed in potassium chromate solution for about 1 minute.

*Result.* — Calcite and aragonite acquire a chocolate or red-brown color, while dolomite and magnesite do not show any change in color.

### II. 5 - Copper nitrate test

This test was first described by Hinden (1903) as a means of identification of calcite by the use of  $\text{FeCl}_3$ . Mahler (1906) and Spangenberg (1913), who also worked on this subject, have considered it more suitable to use copper salts [ $\text{CuSO}_4$  or  $\text{Cu}(\text{NO}_3)_2$ ], instead of  $\text{FeCl}_3$ . Lately, Rodgers (1940) has further developed this test and has given some more details, which have bearing on the results of the test, such as duration of test, density of the solution, degree of acidity, temperature and the calcite percentage of the specimen tested.

*Solution.* — Copper nitrate molar solution. Prepared by mixing 188 gr of  $\text{Cu}(\text{NO}_3)_2$ , 225 gr of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  — or, 332 gr  $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  — and 1000 gr distilled water. In addition there should be a sufficient amount of  $\text{NH}_4\text{OH}$  available.

*Test.* — Specimen is soaked in copper nitrate molar solution for about 5-6 hours. Care must be taken that the particular surface of the specimen to be stained

should not be in contact with the walls of the vessel containing the solution, and also that no bubbles should accumulate on this surface. After the treatment, the specimen is washed, dried and immersed in  $\text{NH}_4\text{OH}$  solution for a few seconds. Once again the specimen is washed carefully.

*Result.* — Calcite acquires a green or bluish-green color, while dolomite does not show any change in color (Rodgers, 1940).

## II. 6 - Trypan blue test

*Solution*— There are two different sets of formula available (Friedman, 1959).

a) 10 gr of potassium aluminium sulphate  $[\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}]$  is dissolved in 100 cc of warm water and this solution is mixed with the solution obtained by dissolving 0.25 gr trypan blue in 5-8 cc methanol. Also 8 cc of 10 %  $\text{HCl}$  is added.

b) Preparation of the other solution is much easier : 6 cc of 10 %  $\text{HCl}$  is added to the solution obtained by dissolving 0.1-0.2 gr of trypan blue.

*Test* — Specimen is soaked in the solution for an unspecified period of time.

*Result.* — As a result of this test, both calcite and dolomite acquire colors. Color of calcite becomes dark blue, while dolomite becomes pale blue

## II. 7 - Harris hematoxilin test

*Solution.* — Harris hematoxilin may be either obtained commercially in a ready-made form or prepared in the following way as described by Gurr (1956): «5 cc of hematoxilin ( $\text{C}_{16}\text{H}_{14}\text{O}_6$ ) solution (10 % hematoxilin in pure alcohol) and 100 ml of potassium aluminium sulphate solution are mixed and heated. When the mixture reaches boiling point, 0,25 gr of mercury oxide ( $\text{HgO}$ ) is added. Heating is stopped when the color of the solution becomes dark lilac. After cooling, 4 ml of acetic acid ( $\text{CH}_3\text{COOH}$ ) is added to the solution.»

For the test, a mixture of 50 cc Harris hematoxilin solution and 3 cc 10 %  $\text{HCl}$  is used. Hematoxilin bottle must be well shaken before use.

*Test.* — Specimen to be inspected is soaked in the solution for 3-10 minutes. With freshly prepared solutions the results are obtained in 9-10 minutes. When the solution is re-used, the test duration must not exceed 3 minutes.

*Result.* — Color of calcite changes to lilac, while there is no corresponding color change in dolomite (Friedman, 1959).

## II. 8 - Alizarin red test

Alizarin red was first used by Huegi (1945) to discriminate between ankerite and siderite. Later, Friedman (1959) has successfully applied this technique to other carbonate minerals. Warne (1962), Evamy (1963) and Dickson (1965) have all contributed to the development of this test.

*Solution.* — According to Friedman, the solution is obtained by dissolving 0.1 gr of alizarin red [sodium alizarin sulphonate =  $\text{CO.C}_6\text{H}_4\text{CO.C}_6\text{H}(\text{OH})_2\text{SO}_3 \text{Na} + \text{H}_2\text{O}$ ] in 100 ml of 0.2% cold  $\text{HG1}$ . 0.2 %  $\text{HCl}$  can be prepared by adding 2ml conc.  $\text{HCl}$  to 998 ml distilled water.

The same formula has also been used by Warne.

Evamy has obtained the solution by mixing 0.2 % HCl with 0.2 % alizarin red.

Dickson has slightly altered formula by dissolving 0.2 gr of alizarin red in 100 cc of 1.5 % cold HCl.

Tests carried out by the author were made with a solution obtained by dissolving 0.1 gr of alizarin red in 100 cc 2 % cold HCl.

*Test.* — Previously etched and washed specimen is soaked in the solution for a certain period. This period has been determined as 5 minutes by Warne, 2-3 minutes by Friedman, 1 minute by Evamy, 10-15 seconds by Dickson and as 3 minutes by the author. Care should be taken that no accumulation of air bubbles occurs on the surface of the specimen. After the test, specimen is washed lightly with distilled water. If tap water has to be used, damage due to the pressure of water can be prevented by holding the opposite side of the specimen of thin section against the water.

*Result.* — Color of calcite will turn into red-brown, whereas dolomite will not be affected (Friedman).

Evamy states that calcite and ferrocalcite will be colored red, while no change will take place in the color of dolomite, ferrodolomite and ankerite.

Dickson states that calcite and ferrocalcite will acquire a color between pink and red, whereas dolomite and ferrodolomite will acquire no color.

According to the observations made by the author, calcite and ferrocalcite acquire a color between light and dark-pinkish red, as opposed to dolomite and ferrodolomite which do not acquire any color at all.

According to Warne, as a result of this test calcite, abundant magnesium-bearing calcite, aragonite and witherite acquire a dark red color, while ankerite, ferrodolomite, strontianite and cerussite acquire a lilac color. On the other hand, the colors of siderite, dolomite, rhodochrosite, magnesite and smithsonite are not affected at all.

## II. 9 - Friedman test

This test has been described by Friedman (1959).

*Solution.* — 0.2 gr of an organic dye (titan yellow, eosin Y, Congo red, alizarin red, etc. may be used) is boiled in 25 cc methanol, while 15 cc of 30 % sodium hydroxide (30 gr NaOH + 70 cc distilled water) are added.

*Test-* — Specimen is soaked in boiling solution for about 5-10 minutes.

*Result.* — Dolomite acquires a color depending on the organic dye used. Thus, with :

Titan yellow — dark orange-red  
Eosin Y — dark pink  
Congo red — red  
Alizarin red — lilac

Faded colors may be restored back by reheating the specimen with diluted NaOH.

## II. 10 - Potassium ferricyanide test

Lemberg has first used potassium ferricyanide  $[K_3Fe(CN)_6]$  in determining FeS in the hydroxide test. The same compound was used by Krech (1909) for the staining of  $Fe^{++}$  in dolomite. Later it was used by Heegel (1913) for discriminating between dolomite and calcite, according to their iron content. Also Rodgers (1940), Twenhofel and-Tyler (1941), Friedman (1959), Warne (1962) and Evamy (1963) have all contributed to the development of this test.

*Solution* — It can be prepared in different ways according to different workers:

Krech has obtained his solution by acidizing freshly prepared potassium ferricyanide solution by the addition of one or two drops of HCl.

Heeger has mixed a couple of drops of potassium ferricyanide with diluted HCl.

Henbest (1913) has added 10 parts of  $K_3Fe(CN)_6$  to 2 parts of concentrated HCl and 88 parts of distilled water.

Twenhofel and Tyler have added one or two drops of potassium ferricyanide to diluted hydrochloric acid (1 part conc. HCl+100 parts of distilled water).

Friedman recommends that the solution - be prepared by adding one or two drops of potassium ferricyanide to diluted HG1 (1:50 - 100).

Warne has considered it best to use a solution obtained by mixing equal parts of 2 % HCl acid and potassium ferricyanide (0.01 gr  $K_3Fe(CN)_6$  + 100 ml distilled water).

Evamy has used a mixture of 0.2 % HCl and 0.5-1.0 % potassium ferricyanide.

In tests made by the author this mixture was prepared by adding 2 cc of concentrated HCl and 98 cc distilled water into the solution of 2 gr of potassium ferricyanide in 100 cc of water. However, since the solution is not stable, it should be used up within one or two days. Otherwise it changes into HCN and acquires a dark color.

*Test*- — Specimen is immersed in cold potassium ferricyanide solution, for a certain period of time. The author has found 3 minutes to be sufficient for this. Evamy recommends 1 minute. After the test, specimen is carefully washed with distilled water.

*Result*- — According to Twenhofel and Tyler, at the end of this treatment dolomite will acquire a blue color, while calcite will remain unaffected. This reaction is due to Turnbull blue  $[Fe_3(FeC_6N_6)_2]$  formed by the combination of the ferrous iron in dolomite with potassium ferricyanide. Although from the test results it may be concluded that the ferrous iron component is more abundant in dolomite and less abundant in calcite, this of course, may not always be true; because in some cases dolomites may have very little or no ferrous components; on the other hand this component may be quite abundant in some types of calcite.

According to Friedman, while dolomite with ferrous iron acquires a blue color, no coloring is observed in calcite.

Warne points out that after tests carried out with cold solution, ankerite and ferrodolomite acquire a dark blue color; whereas dolomite and siderite may acquire



color only after treatment with a warm solution. During heating tests change of color occurs in siderite earlier than in dolomite.

Evamy reports that ferrocalcite, ferrodolomite and ankerite acquire a light or dark blue color (depending on the amount of  $Fe^{++}$  component), while neither pure calcite nor pure dolomite will show any change of color.

In tests carried out by the author, ferrodolomite and ferrocalcite have acquired a blue color, while no change appeared in pure calcite and pure dolomite. The degree of darkness of blue is proportional to the iron content of the minerals.

## II. 11 - Alizarin red and potassium ferricyanide composite test

This test is used for discriminating between four different types of carbonates (calcite, ferrocalcite, dolomite and ferrodolomite) in a single series of operation. The test and results were described by Evamy (1963) and Dickson (1965).

*Solution.* — Evamy has obtained the solution by mixing 0.2 % HCl, 0.2 % alizarin red, and 0.5-1.0 % potassium ferricyanide.

According to Dickson, two solutions are prepared separately :

a) Alizarin red solution: This solution is obtained by dissolving 0.2 gr of alizarin red in 100 cc of 1.5% hydrochloric acid (98.5 cc distilled water + 1.5 cc concentrated HCl).

b) Potassium ferricyanide solution : 2 gr of potassium ferricyanide is dissolved in 100 cc 1.5 % HCl.

The mixed solution, to be used in the test, is prepared by mixing 3 parts of alizarin red solution and 2 parts of potassium ferricyanide solution.

Solutions for the tests carried out by the author have been prepared in the following way :

a) 0.1 gr of alizarin red is dissolved in 100 cc of 2 % HCl.

b) To the mixture of 2 gr of potassium ferricyanide and 100 cc distilled water, 100 cc of 2 % HCl is added.

These two solutions are mixed in equal parts for obtaining the mixed solution to be used in the test.

*Test* — Specimen is soaked in cold solution for 3 minutes (according to the author). Evamy considers 1 minute as sufficient, while according to Dickson a period of 30-45 seconds is adequate. After the test, specimen is carefully washed and dried.

*Results-* — According to Evamy, the results of the test are as follows :

Calcite : Red.

Ferrocalcite, (low ferrous iron content) : lilac «red dominant».

Ferrocalcite (high ferrous iron content) : scarlet «blue dominant».

Dolomite: no coloring.

Ferrodolomite: pale blue.

Ankerite: dark blue.

Dickson lists the following results :

Calcite : between very pale pink and red. (The tone of the color depends on the optical orientation of the crystal. Stained surfaces parallel to c-axis are darker than those which are at right angles to the axis.)

Ferrocaltite: between lilac (pinkish purple)-scarlet and royal blue, derived from the mixture of very light pink-red group and pale blue-dark blue group.

Dolomite: shows no coloring.

Ferrodolomite: Light to dark turquoise. Tone of the color depends on the ferrous iron content.

The following results were observed in tests carried out by the author:

Calcite: pinkish red.

Ferrocaltite: lilac-mauve or light scarlet.

Ferrodolomite: blue-green.

Dolomite: No change of color observed.

With staining on thin sections, a mixture of Durofix and amilacetate (1:3) should be applied to the stained surface, before the cover glass is placed. In this way the colors will be protected during heating operation.

## II. 12 - Mann test

Mann (1955) has used alkali p-nitrobenzene-azoresourcenol solution to differentiate between pure and MgO-bearing limestones. This solution was first described by Feigl (1946) and used by him to determine the Mg content in solution.

*Solution-* — 10 % HCl and solution of 0.002 gr p-nitrobenzene-azoresourcenol in 100 cc 2N NaOH.

*Test-* — First one drop of 10 % HCl is placed on the specimen's surface. When the fizzing stops, one drop of p-nitrobenzene-azoresodrcenol is placed on the same spot.

*Result* — If within 30 seconds the color changes to blue, there is a high concentration of MgO in the specimen. Purple or scarlet color is indicative of no MgO present. The tone of the blue color is proportional to the percentage of MgO present.

This method can be used successfully by the field geologist in places where the lithological boundaries are not visible or difficult to detect. Boundaries between limestones and dolomitic limestones may easily be determined in the field by the geologist.

## II. 13 - Ramsden test

This test was described by Ramsden (1954) for the discrimination between calcite and dolomite.

*Solution* — It is prepared by dissolving 2.5-3.0 gr of  $AlCl_3$  and 1 gr methyl red in 1000 cc of warm water. This is a stable solution.

*Test* — In a small beaker, 2 parts of solution are mixed with one part of powdered specimen.

*Result.* — In less than 30 seconds, pure calcite is observed to acquire a color between pink and pale yellow. Dolomitic limestone shows very little coloring. No change is observed in dolomite.

### III. 1 - Friedman test

This test has been described by Friedman (1959). 0.2 gr of one of the organic dyes shown in II.9 is boiled in methanol and in the meantime 15 cc of 5 % NaOH is added. The test and results are similar to those explained in II.9.

### III. 2 - Magneson test

This test is based on the determination of Mg content in solutions (Feigl, 1946 and 1954; B. D. H., 1946 and 1963).

*Solution.* — 0.5 gr of magneson [p-nitrobenzene-azoresourcenol =  $\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{N}=\text{N}-\text{C}_6\text{H}_3(\text{OH})_2$ ] is dissolved in 100 ml of 0.25 N (1.0 %) NaOH (B. D. H., 1946).

For the same purpose magneson I [4-p-nitrophenyl-azoresourcenol =  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}=\text{N} \cdot \text{C}_6\text{H}_3(\text{OH})_2$ ] or magneson II [4-p-nitrophenyl-azo-1-naphthol =  $\text{C}_6\text{H}_4 \cdot \text{NO}_2 \cdot \text{N}=\text{N} \cdot \text{C}_{10}\text{H}_6\text{OH}$ ] may also be used (B. D. H., 1963).

*Test and result.* — Equal parts of 30 % NaOH and magneson solution, prepared as described above, are mixed. The specimen is soaked in this solution for a certain period. Magnesite, after 1 minute becomes blue; after 2-3 minutes, dark blue. Smithsonite, on the other hand, becomes slightly bluish only after 5 minutes. After this treatment, if the specimen is thoroughly washed and heated in 30 % NaOH solution (without attaining boiling point), it will be observed that only the blue color on magnesite will remain stable, while the color on smithsonite will disappear (Warne, 1962).

For this test Feigl (1946) has used a mixture of 0.001 gr p-nitrobenzeneazoresourcenol or p-nitrobenzeneazo-a-naphthol and 100 ml of alkali.

### III. 3-Tropaeolin 00 test

This test was first described by Vogel (1945) for the determination of zinc in solutions. It was later used by Warne (1962) to discriminate between smithsonite and magnesite.

*Solution.* — This is a mixture of 1 part tropaeolin solution [0.01 gr tropaeolin 00(4-p-sulphophenyl-azo-dyphenylamin) dissolved in 100ml of distilled water], 1 part N sulphuric acid ( $\text{H}_2\text{SO}_4$ ) and 3-5 parts freshly prepared 2 % potassium ferricyanide solution [2 gr of  $\text{K}_3\text{Fe}(\text{CN})_6$  + 100 cc of distilled water].

*Test.* — Specimen is soaked in the solution for 5 minutes.

*Result.* — While no change is observed in magnesite, smithsonite acquires a yellow color.

### IV. 1 - Kirchberg test

This test was first used by Kirchberg (1940,41) for the determination of ankerite (ferroferric dolomite) (Friedman, 1959; Warne, 1962).

*Solution*- — 10 % copper sulphate ( $\text{CuSO}_4$ ) solution, and also ammonium sulphide  $[(\text{NH}_4)_2\text{S}]$  solution.

*Test*- —The polished face of the specimen is kept in 10 % hydrofluoric acid [80 cc distilled water + 48 % HF) for 2 minutes, after which it is washed and dried. This-time specimen is immersed in ammonium sulphide solution for about 1 minute, washed and then soaked in copper sulphate solution for about 5 minutes. After being washed thoroughly the specimen is once again immersed in ammonium sulphide solution, for a time. If necessary, this procedure may be repeated several times.

*Result*.— Ankerite acquires a gray-black color

In the preparation of the solution, sodium sulphide may be used instead of ammonium sulphide. In this case, while ankerite and ferrodolomite become almost black after a few repetitions, siderite presents very little coloring (Warne, 1962).

#### **IV. 2 - Hydrogen peroxide - potassium hydroxide test**

This test was used by Hallimond (1925) for the determination of ankerite and siderite by staining (Warne, 1962).

*Solution*. — Concentrated potassium hydroxide (KOH) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ).

*Test*.—Specimen is immersed in warm KOH solution, for about 5-10 minutes, during which time drops of  $\text{H}_2\text{O}_2$  are added to the solution. After removing the specimen, it is washed with distilled water and dried.

*Result*. — After the test ankerite acquires an orange color, while no coloration is observed in dolomite (Friedman, 1959). Siderite, on the other hand, is stained brown (Warne, 1962). According to Taylor (1948), the tone of darkness of the color depends on the amount of ferrous iron.

#### **V. 1 - Benzidine test**

This is based on the determination of Mn in solutions (B.D.H., 1946; Warne, 1962).

*Solution*. — It is obtained by adding and mixing 2 gr of pure benzidine ( $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ ) into 100 ml of distilled water containing 1 ml 10N of HCl.

*Test*. — Specimen is immersed in diluted sodium hydroxide solution (1-3 % NaOH) for about 1.5 minutes. After airing for approximately 1,5 minutes, it is colored with benzidine solution.

*Result*. — Rhodochrosite acquires a blue color, while no color change is observed in dolomite.

### **CONCLUSIONS**

The identifications of some of the carbonate minerals becomes fairly easy time-saving, when the simple chemical staining tests described above are used. Some of these tests can be carried out in a small laboratory set up near a drilling operation, which would facilitate the study of core specimens and small fragmentary chips of

boreholes. Also, some of the more easily preparable and relatively stable solutions can be easily carried by the field geologist in strong bottles. Simple tests carried out in the field may enable the field geologist to recognize his lithological boundaries or important marker horizons in sedimentary—especially carbonate—areas. Thus, the geologist may have some idea about the lithological and mineralogical details on his maps and sections, even before final chemical analyses and sedimentary petrographic determinations are concluded.

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