

number of times, and has shown its ability to melt copper and brass readily, and with more difficulty, cast iron.

It has been observed in the use of this furnace, that paper pasted on the outside of the outer container was charred only to a light brown, even when the furnace was maintained for several hours at the melting point of copper or even cast iron, during a part of which time a portion of the flame played about the outside of the flame-opening at the bottom; the powder lining in this case was an inch and a quarter thick. On the other hand, a furnace with solid clay walls one and one-quarter inches thick (Hoskins No. 2), when maintained at a similar temperature for an hour, completely blackened paper pasted on the outside.

For small work, a convenient size for the outside container is that of a 5-pound ether can, six inches in diameter by seven inches high, while the sheet-iron lining may be made two and one-half to three inches in diameter, and seven inches high. The same principles of construction may be applied to furnaces of practically any size and shape.

The drawings are self-explanatory.

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## SULFITE METHOD FOR SEPARATING AND IDENTIFYING CALCIUM AND STRONTIUM.

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The difficulty which beginners in qualitative analysis experience in the separation and identification of calcium and strontium has led me to seek a method which might be easier and more satisfactory than those now in use. By study of the table of aqueous solubilities we learn that strontium sulfite is sparingly soluble (0.033 gram to the liter), while calcium sulfite is quite soluble (1.2 gram to the liter), and that strontium sulfate is considerably less soluble than strontium sulfite (0.11 gram to the liter). As to barium and strontium sulfites, the difference in solubility is small and not sufficient for separation. All these solubilities are increased in acid solutions, but not to the same degree. In the presence of sufficient hydrochloric acid barium ion is precipitated by sulfite ion, while strontium ion is not; in dilute acetic acid solution barium and strontium ions are precipitated, while calcium ion is not.

In this investigation I used a freshly prepared concentrated (nearly saturated) solution of sodium sulfite. If the solution is kept long, the sulfate in it is increased by oxidation and the reactions are not typical. In finding the precipitation limits I used standard solutions of calcium and strontium chlorides.

In order to compare the efficiency of the commonly used calcium sulfate with that of sodium sulfite, which I propose as the precipitant, I

diluted the strontium solution to various degrees of concentration with water containing a slight excess of acetic acid and a sufficient quantity of the reagent, in the one case calcium sulfate and in the other sodium sulfite, bringing the mixture to boiling and letting it stand for a few minutes. The following results were obtained:

Concentration of strontium solution.	Reagent.	
	Calcium sulfate.	Sodium sulfite.
0.0005 Normal	No precipitate	Faint cloud
0.0001 Normal	No precipitate	Precipitate
0.0005 Normal	No precipitate	Precipitate
0.001 Normal	No precipitate	Precipitate
0.004 Normal	Faint cloud	Precipitate
0.005 Normal	Precipitate	Precipitate

It is thus seen that the sulfite ion in the presence of a slight excess of acetic acid will give a precipitate in a ten-thousandth normal solution of strontium ion (0.004 gram to the liter), while calcium sulfate requires a concentration 0.005 normal (0.2 gram to the liter); that is, the sulfite is about fifty times as sensitive as the sulfate in grams of strontium ion to the liter. In solutions more strongly acid the difference is greater, though the sensitiveness is diminished.

The calcium and strontium solutions yielded with ammonium oxalate the following results:

Concentration.	Calcium.	Strontium.
0.0005 Normal	No precipitate	No precipitate
0.007 Normal	Faint cloud	Faint cloud
0.001 Normal	Precipitate	Precipitate

The sensitiveness of the calcium and strontium ions to the oxalate ion thus appears to be about the same and the precipitation limit is not far from that of strontium sulfite. This relationship is but little changed in the presence of acetic acid, though the sensitiveness is diminished.

The precipitation limits for the sulfites of calcium and strontium were then determined under four conditions: (1) With the sulfite solution alkaline by hydrolysis, cold. (2) The same with the mixture boiled. (3) The sulfite solution made slightly acid with acetic acid and the mixture boiled. (4) The sulfite solution made more strongly acid and the mixture boiled.

1. The sulfite solution alkaline, cold, the mixture well shaken:

Concentration.	Calcium.	Strontium.
0.0005 Normal	No precipitate	No precipitate
0.001 Normal	No precipitate	Faint cloud
0.0015 Normal	No precipitate	Precipitate
0.002 Normal	No precipitate	Precipitate
0.006 Normal	No precipitate	Precipitate
0.008 Normal	Faint cloud	Precipitate
0.01 Normal	Precipitate	Precipitate

## 2. Sulfite solution alkaline and the mixture boiled :

Concentration.	Calcium	Strontium.
0.0005 Normal	No precipitate	Faint cloud
0.001 Normal	No precipitate	Precipitate
0.005 Normal	Faint cloud	Precipitate
0.001 Normal	Precipitate	Precipitate

We thus see that the alkaline sulfite makes a rather complete precipitation of both the calcium and the strontium.

## 3. The sulfite solution slightly acid with acetic acid, the mixture boiled :

Concentration.	Calcium.	Strontium.
0.005 Normal	No precipitate	Faint cloud
0.001 Normal	No precipitate	Precipitate
0.003 Normal	No precipitate	Precipitate
0.005 Normal	Precipitate	Precipitate

## 4. The sulfite solution strongly acid with acetic acid, the mixture boiled :

Concentration.	Calcium.	Strontium.
0.0005 Normal	No precipitate	No precipitate
0.001 Normal	No precipitate	No precipitate
0.0015 Normal	No precipitate	Precipitate
0.01 Normal	No precipitate	Precipitate
0.1 Normal	No precipitate	Precipitate
1.0 Normal	No precipitate	Precipitate
1.2 Normal	Cloud	Precipitate
1.3 Normal	Precipitate	Precipitate

With acid of this strength the concentration of the filtrate is only 0.001 normal in strontium while it is 1.3 normal in calcium. If the solution is not higher than this in calcium, the separation of calcium and strontium is almost complete. If the solution is stronger, more acid may be added and still the separation will be good, since the strontium is practically all precipitated when the mixture is boiled, even in the presence of much acid. When the salts are mixed, some calcium remains in the precipitate, possibly because of oxidation to sulfate which seems to be less soluble in the acid than the sulfite.

The quantity of strontium which remains in the solution after the precipitation with the sulfite in the presence of acetic acid is just at the precipitation limit of strontium oxalate and the filtrate will give no precipitate with ammonium oxalate, or only a faint cloud. If it be diluted with an equal quantity of water, no precipitate falls. On the other hand, the calcium has largely remained in solution and will be precipitated by the oxalate ion. Calcium is thus sharply and easily separated from strontium. The strontium precipitate may contain some calcium from which it is not easily separated. The strontium will generally be satisfactorily identified by the flame reaction as described below.

Guided by the above facts, I have devised a modified method of analy-

sis for the barium group which in repeated trials by myself and my students has been found to be eminently practical and easy.

1. Precipitate the elements of the group as carbonates, wash, and dissolve in the least quantity of warm, dilute acetic acid in the usual way.

2. Preliminary testing.

*a.* Add to 1 cc. of the solution in a test tube a few drops of hydrochloric acid, then 1 cc. of a freshly prepared concentrated solution of sodium sulfite. A precipitate is barium sulfite and proves the presence of barium.

*b.* Add to 1 cc. of the solution a few drops of dilute acetic acid, then 1 cc. of the sulfite solution. A precipitate is barium or strontium sulfite; in the absence of barium, it can only be strontium.

*c.* If barium and strontium are absent, add to 1 cc. of the solution 1 cc. of the sulfite solution. A precipitate is calcium sulfite, easily soluble in acetic acid.

3. Remove barium ion, if present, with dichromate ion and free the filtrate from dichromate ion by precipitation as carbonate and solution in dilute acetic acid in the usual way. The removal of the dichromate ion is generally not necessary, since the reactions are not seriously disguised by it.

4. To 5 cc. of the solution of 3 (or of 1, if barium is absent) add about 3 cc. of the sulfite solution, or enough for complete precipitation. A precipitate may be calcium or strontium sulfite. No precipitate does not indicate their absence. In either case, add about 1 cc. of dilute acetic acid, or just enough to dissolve or nearly dissolve the precipitate. Avoid much excess. If much strontium is present, it will not dissolve. Heat to boiling and set aside until the precipitate has mostly subsided. Pour the liquid on a filter leaving the bulk of the precipitate in the test tube. If the filtrate is cloudy, pass it through the filter again and again until it is perfectly clear.

The filtrate will contain most of the calcium and very little strontium.

The precipitate is strontium sulfite, but may contain some calcium sulfite.

5. Add to 5 cc. of the filtrate of 4 a little ammonium oxalate solution. A precipitate is calcium oxalate. If there is only a faint cloud, it may be due to strontium. In this case, dilute another portion of the filtrate with an equal volume of water and add the oxalate. The precipitate now must be calcium oxalate, since the strontium concentration has been reduced below the precipitation limit of strontium oxalate.

6. Cover the precipitate of 4 in the test tube with hydrochloric acid and heat to boiling. Test on platinum wire in the flame for strontium. If much calcium is present, there may be enough in the precipitate to mask the strontium flame. In this case, a very sharp distinction can be made

as follows: Use two platinum wires, dipping one in a pure hydrochloric acid solution of a calcium salt and the other in the solution to be tested. Insert the middle of the wires in opposit sides of the Bunsen flame near its base and draw them slowly forward until the looped ends are in the flame. The sodium (and potassium if dichromate has been used) burns off first and leaves the more persistent calcium and strontium in the flame. A decided difference in the flame colors thus brought side by side is caused by even a trace of strontium.

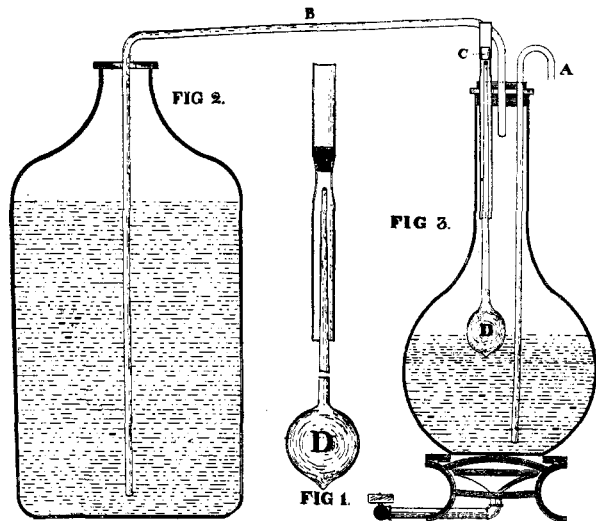
7. For further confirmation of strontium add calcium sulfate solution to a portion of the solution of 3 and boil. A slowly forming precipitate indicates strontium.

The chief advantage of this method lies in the easy and unmistakable identification of calcium in the presence of strontium.

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### NOTES.

*A Wash Bottle for Continuous Hot Water Supply.*—It is often found very desirable, where a large amount of routine analytical work is done, to have a more convenient means of washing precipitates than that furnished by the common wash bottle. A wash bottle which has given



very good satisfaction in this laboratory is described below in detail.

It consists of a heavy, 5-liter boiling flask (Fig. 3) connected with a large supply bottle (Fig. 2). The boiling flask has a tight-fitting three-holed rubber stopper as shown in the diagram. Through one hole passes a glass tube, A, which is connected by rubber tubing

to the washing-jet. The tube B connects the supply bottle with the boiling flask. As the liquid in the boiling flask is lowered, there is a partial vacuum created which causes water from the supply bottle to pass through B into the boiling flask, thus maintaining the supply.

To allow the escape of steam from the boiling flask and to prevent