

	Per cent.
Peroxide, PbO_2	26.4
Litharge, PbO	69.7
Impurities.....	3.5
	99.6

Since the formula Pb_3O_4 is accepted, and this compound is the essential part of a red lead, no matter what may be the views held as to whether the excess of PbO is a mere admixture, or in weak chemical combination; it would seem more satisfactory for commercial work to state an analysis as follows:

	Per cent.
Peroxide of lead, PbO_2	26.4 per cent.
Equivalent to red lead.....	75.6
Lead monoxide (litharge).....	20.5
Impurities.....	3.5
	99.6

If the acetate method is used, we obtain the red lead figure directly; if methods yielding the peroxide or its equivalent, the amount of peroxide found should be multiplied by the factor 2.866 to give the corresponding quantity of red lead.

DISCUSSION.

In regard to the lead monoxide removable by digestion of red lead in solution of lead acetate, Professor Sabin said that in making a cement of litharge and glycerine, considerable inert material, as sand or powdered glass, might be mixed with it without affecting the setting qualities; while on the contrary, red leads would not make a cement when mixed with glycerine. This would seem to indicate that the litharge is not in the same condition as if in simple admixture.

SODIUM PEROXIDE AS A THIRD GROUP REAGENT.

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SODIUM peroxide as a reagent has properties of a very unusual and striking character. These properties are no less valuable than peculiar, and indicate for this substance a prominent place in analytical work. The immediate object of this paper is to note the advantages and adaptability of sodium peroxide to qualitative analysis. By this means its numerous characteristics can be best illustrated. The specific data indi-

cating its use in certain lines of quantitative analytical work will be given later. The methods herein set forth have been employed in this laboratory during the past year by large classes in qualitative analysis. This practical test of the processes involved has abundantly demonstrated their value.

In the ordinary procedure for the separation of the metals the greatest difficulty arises in the third or iron group. These complications may be briefly enumerated as follows :

(*a*) The separation of zinc in the presence of chromium.

(*b*) The unsatisfactory separation of cobalt and nickel from the other members of the group by the action of dilute hydrochloric acid on their sulphides.

(*c*) The variations arising from the presence of phosphates, etc.

It is not necessary to enlarge upon these difficulties. The one most commonly ignored in methods as usually outlined and yet a very serious obstacle, is the one designated under (*a*). Zinc and chromium enter into a combination which to a very large extent resists the action of ammonia and ammonium salts. The use of barium carbonate to obviate this difficulty is cumbersome. By use of sodium peroxide we may oxidize the chromic compounds present to sodium chromate, and thus completely eliminate it as a factor in any precipitation likely to be employed, excepting of course such as would involve a reduction and return to the condition of a chromic salt.

The method of procedure is as follows: The solution should be slightly acid. A small porcelain spoonful of the peroxide is slowly sifted in with constant stirring. The solution is then heated to complete the decomposition of the peroxide and finally boiled for some minutes after the oxygen seems to be all driven off. The completeness of the oxidation may be easily tested by filtering from any insoluble constituents, acidifying, boiling, and making ammoniacal. A precipitate may be aluminum or unoxidized chromium. Filter and wash free from all sodium chromate, redissolve in a little nitric acid and treat as before with a small amount of sodium peroxide. A yellow coloration is due to the chromium which escaped oxidation by the first treatment. However, if properly conducted, the first operation should be complete. Similarly, the insoluble residue on the filter, if suspected of being a zinc-chromium compound, may be

washed free from chromate, dissolved in dilute nitric acid, and treated again with the peroxide. The only condition so far governing the completeness of the transformation to the chromate form is the necessity of starting the oxidation with the chromium entirely in solution. Precipitated chromium hydroxide will undergo this transformation, but less readily, and especially if the precipitate is the double one of zinc and chromium. Hence the advisability of beginning the oxidation with the solution containing some free acid, preferably nitric. The quantity of free acid is immaterial, less than one cc. being sufficient. It should be noted, however, that the amount of sodium peroxide should cause the solution to pass quite beyond the neutral condition since the oxidation is only partial while in the acid state. It might be expected that the moment the addition of sodium peroxide passed the neutral point the precipitation of chromium would commence and the completeness of the oxidation be lessened in consequence, but I have not found this to be the case. The oxidizing action of the peroxide is so pronounced that it precedes the precipitating action, hence the reason for using the dry sodium peroxide. A cold saturated solution of the peroxide will operate but incompletely. Hydrogen peroxide will also act similarly, but even less completely than the solution of sodium peroxide. For obvious reasons also the operation is performed on the solution before heating, and it is better to shake the powder in gradually than to drop the reagent in at once.

We are ready now to note the effect of such treatment as above indicated, upon the other members of this group, assuming that any or all may be present, including cobalt and nickel. The results are as follows :

(a) Aluminum compounds are in solution in the form of sodium aluminate, not different from the ordinary result from using sodium hydroxide in excess. It is assumed of course that the sodium peroxide has exceeded the free acid in sufficient amount to provide sodium hydroxide in excess.

(b) Zinc is similarly in solution as zincate.

(c) Iron precipitates as a very dense, reddish-brown precipitate, the exact composition of which is being made a matter of investigation. The precipitation is complete, no re-resolution being effected upon boiling. The filtration is performed with great

facility. The precipitate is almost insoluble in concentrated nitric acid; soluble in dilute acids on heating. If phosphates are present, none are precipitated with the iron, but all pass through and are found in the filtrate.

(*d*) Manganese behaves exactly as iron, precipitating presumably as the hydrated dioxide, $\text{MnO}_2 \cdot x\text{H}_2\text{O}$, having all the properties of that compound as to color, solubilities, etc. Similarly also, phosphates are not precipitated. It should also be noted that from this precipitate can most readily be obtained the delicate test for the presence of manganese by formation of permanganic acid by means of nitric acid and lead peroxide or Pb_3O_4 .

(*e*) Cobalt precipitates also a black hydrated cobaltic oxide with solubilities the same as in the case of iron and manganese. No phosphate is precipitated with the cobalt. The precipitate, in conjunction with dilute acid and potassium iodide, liberates free iodine, imparting an intense blue to starch solution. This latter property, however, is common to the precipitates of iron and manganese under (*e*) and (*d*).

(*f*) Nickel precipitates, as the ordinary green nickelous hydroxide, $\text{Ni}(\text{OH})_2$, easily soluble in acid, either concentrated or dilute. As to phosphates, in the case of nickel, if present in large amounts, small quantities are found in the precipitated nickel. A re-solution and reprecipitation with sodium peroxide, however, eliminates all the phosphate from the precipitate. The behavior of nickel in thus precipitating as the nickelous compound indicates for its higher form of oxidation a less degree of stability than exists in the case of cobalt. This property suggests the readiest and most delicate method for the detection of nickel, even in the presence of the three precipitates enumerated above, thus: boiling this precipitate of nickel with bromine water converts it at once into the black nickelic hydroxide, which has the property of decomposing potassium iodide with water alone, no acid being required, as in the case of iron, manganese, and cobalt. It is necessary, of course, to boil off the free bromine, which is readily accomplished. The action upon a potassium iodide starch solution is very marked.

The above facts suggest a method for the iron group which is

indicated by the following table. It is given here to illustrate the adaptability of some of the well-known but more positive and satisfactory tests for the several metals.

The precipitate obtained in the ordinary method by means of ammonium hydroxide and ammonium sulphide contains, as hydroxides and sulphides, iron, manganese, cobalt, nickel, aluminum, zinc, and chromium, and is brought into solution by means of ten to fifteen cc. of concentrated nitric acid with heat. Nearly neutralize with sodium hydroxide, then sift in slowly with stirring sodium peroxide in excess. Boil.

Precipitate A contains iron, manganese, cobalt, and nickel.

(a) Test for iron by dissolving a small portion of the precipitate in dilute hydrochloric acid and adding potassium thiocyanate. The blood red coloration is due to ferric thiocyanate.

(b) For manganese, to five cc. water add five cc. concentrated nitric acid and five to ten grams Pb_3O_4 . Stir into the warm mixture a little of the precipitate and let stand. A purple solution is permanganic acid.

(c) In absence of iron or manganese, stir a little of the precipitate into dilute hydrochloric acid and add solution of potassium iodide and starch. In presence of iron and manganese use the bead test.

(d) Boil some of the precipitate with bromine water till all bromine is expelled, add water and solution of potassium iodide and starch, $Ni(OH)_3 + KI = Ni(OH)_2 + KOH + I$, imparting the blue to the solution.

Solution A contains all the aluminum, zinc, and chromium. The yellow color is evidence of chromium. Acidify with hydrochloric acid, boil, and add ammonium hydroxide.

Precipitate B consists of aluminum hydroxide, and any chromium hydroxide that may have escaped oxidation. Dissolve in nitric acid and repeat the precipitation with sodium peroxide, or apply the blowpipe and cobalt test for aluminum.

Solution B contains zinc and chromium.

(a) Test for zinc by adding to a portion a few drops of potassium ferrocyanide. A heavy white precipitate indicates zinc.

(b) If further verification of chromium is needed, make the solution acid with hydrochloric acid and boil with a little alcohol added. The chromium reverts to the green chromic chloride.

In the presence of phosphates the method so far employed has been as follows: Upon dissolving the precipitate from the ammonium sulphide in concentrated nitric acid a very little of the solution is tested for phosphoric acid in the usual manner. If

present, granulated tin is added and the boiling continued. Filter from the insoluble tin phosphate, make ammoniacal, reprecipitate with ammonium sulphide, and proceed as with phosphoric acid absent. Any method not involving the use of tin and depending upon the non-formation of the phosphates of iron, manganese, and nickel, is as yet unsatisfactory. Having removed the barium and strontium with sulphuric acid before the precipitation with ammonium sulphide, the oxidation and precipitation by means of sodium peroxide may be performed as usual, but before filtering, the solution is made acid with acetic acid and boiled a little further and filtered. The filtrate now may contain besides the aluminum, zinc, and chromium, the nickel which is readily soluble in acetic acid, and the calcium and magnesium which has been brought along by means of the phosphoric acid. A little of the cobalt, however, dissolves with the acetic acid and a solvent has not been found thus far for the calcium phosphate and nickel hydroxide that will not dissolve traces of the other three metals of the precipitate.

One other application to qualitative analysis may be mentioned as having proved valuable. In testing for acids a ready method for distinguishing between carbon dioxide and sulphur dioxide when both are present is found in the use of a solution of sodium peroxide. Conducted into this solution, the above gases form sodium carbonate and sodium sulphate respectively. With lime-water the solution will give a copious precipitate if the carbonate has been formed, and with an acidulated solution of barium chloride the sulphate test is obtained.

Many other features incidental to the properties above outlined have developed, mainly of interest in quantitative methods. It is hoped that the data will be of sufficient value to warrant further notice.