(8) Chromium does not interfere with either method, but more accurate results are obtainable by the hydrogen sulphide method, using pressure.

(9) The sulphide precipitation, followed by reduction and titration with potassium permanganate, not only gives accurate results, but has the great advantage that nothing which is present in steels, ferromolybdenum, or molybdenum metal, interferes with the accuracy of the results.

QUANTITATIVE LABORATORY,
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SOME METHODS FOR THE DETECTION OF COBALT AND NICKEL.[1]

BY STANLEY R. BENEDICT.

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BECAUSE of the great similarity of chemical behavior between cobalt and nickel, the detection of these two elements in the presence of each other, particularly of small amounts of either, is a problem which presents peculiar difficulties. Many solutions of this problem have been proposed.

For comparison with the methods I wish to propose, I mention what are, so far as I have been able to learn, the most delicate methods yet offered for the detection of cobalt and nickel when both are present in one solution. The one for the detection of cobalt was proposed by Vögel.[2] A saturated solution of ammonium sulphocyanide is added, then a mixture of amyl alcohol and ether added and the solution shaken. If cobalt be present, the alcohol-ether layer has a blue color. This method is very sensitive, and will detect 0.5 per cent. of cobalt in nickel solutions.

The detection of traces of nickel in an excess of cobalt is a more difficult problem. The most delicate method, up to the present time, is probably the one suggested by Parr,[3] which de-

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[1] Read before the Cincinnati Section of the American Chemical Society, February 10, 1904.

[2] *Ber. d. chem. Ges.*, 12, 2314 (1879).

[3] This Journal, 19, 341 (1897).

pends upon the fact that freshly precipitated nickelic hydroxide will liberate iodine from potassium iodide, while cobaltic hydroxide will not. The procedure is as follows: Bromine water is added to the solution, which is then warmed, next an excess of sodium carbonate added, and the solution brought to boiling. Both the cobalt and nickel are oxidized and precipitated in the trivalent condition by this treatment. The precipitate is well washed upon a filter and hot potassium iodide poured upon it. Free iodine in the filtrate is evidence of the presence of nickel. This test is not as delicate as Vögel's method for cobalt, yet it will detect nickel in many commercial cobalt salts.

My work comprises two methods, one for the detection of nickel only, the other for the detection of both elements. The first of these, *viz.*, for the detection of nickel only, depends upon the fact that if a mixture of nickelous hydroxide and cobaltic hydroxide be treated upon a filter with a cold, saturated solution of oxalic acid, the cobalt dissolves to form a complex cobaltioxalate compound, which is only very slowly precipitated by sodium hydroxide, whereas the nickel dissolves as a nickelous compound. The procedure is as follows: Treat the solution with an excess of sodium peroxide and warm to boiling. This, as was mentioned by Kassner,[1] oxidizes the cobalt but not the nickel. Filter, wash the precipitate until perfectly cold, and pour upon the filter a cold, saturated solution of oxalic acid. Pour this through the filter two or three times. To the filtrate add a few drops of a dilute solution of potassium ferricyanide and then a slight excess of sodium hydroxide. If nickel be present, it is oxidized by the ferricyanide and a heavy black precipitate of nickelic hydroxide appears, or if only a small amount of nickel be present, the solution darkens considerably. This test is very delicate, detecting as small an amount of nickel as 2 per cent., with comparatively little trouble.

Although nickel forms no compound corresponding to the cobaltioxalate compound mentioned above, it has nevertheless been found advisable to use such a reagent as sodium peroxide, which oxidizes only cobalt, in preference to bromine or chlorine water, which would oxidize both elements, because in the decomposition of the oxalic acid by nickelic hydroxide some of the cobalt salt is reduced to the bivalent condition.

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[1] *Arch. Pharm.*, **232**, 226-240 (1894).

It may be stated that the cobaltioxalate compound formed in this test is of some interest. It has never been made in this way before, its only method of formation having been by electrolysis, and by leaving a mixture of cobalt hydroxide and potassium tetroxalate made up to a paste with water, for a period of from fourteen to twenty-one days (Kehrmann[1]). It is a green compound, the aqueous solution resembling the solution of a nickel salt in color. In a manner similar to that outlined above, I have been able to form some new complex salts of other metals, which will be described later.

The second method which I propose is one by means of which either or both elements can be detected, even if one be in great excess, by a single operation in a test-tube. The procedure is extremely simple. It consists in adding an excess of 5N sodium hydroxide (ordinary reagent strength) to the solution, and agitating for half a minute. The results depend upon these facts. If sodium hydroxide be added in excess to a cobalt solution, a dark blue precipitate is at first formed, which is usually regarded as a basic salt. If nickel be entirely absent, this salt changes almost instantaneously to a bright pink compound, *viz.*, the normal cobaltous hydroxide. If, however, nickel is present, this change of color is retarded, the length of time increasing with the amount of nickel present. As will be seen, this test is extremely rapid, yet its rapidity is fully equaled by its delicacy. If sodium hydroxide be added in excess to each of two cobalt salts, one being an ordinary C. P. salt, and the other a sample of Kahlbaum's "nickel-free" cobalt, a decided difference in the length of time required for the change of color is evident. In testing for traces of nickel, it is well to have a check tube containing a nickel-free sample for comparison. In this way mere traces of nickel can be detected. In fact, there is every reason to believe that this is the most delicate method so far proposed for the detection of nickel, as well as the most rapid. Its delicacy considerably exceeds that of the potassium iodide test outlined above, as has been determined by making comparative tests. In 10 cc. of normal cobalt solution containing 1 per cent. of nickel solution, the potassium iodide fails absolutely to reveal the presence of nickel, whereas the test outlined above will, in the same strength of solution, detect 0.5

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[1] *Ber. d. chem. Ges.*, **19**, 3101 (1886); **24**, 2324 (1891).

per cent. of nickel, and if the amount of cobalt be increased without decreasing the actual amount of nickel, 0.3 per cent. of this element can be detected.

The question naturally arises why nickel in such minute quantities retards the change of the blue basic salt to the pink normal hydroxide. This is evidently difficult to answer, and the explanation put forth below is merely offered as a possible one.

This explanation is that when the basic salt, which would have some such formula as $Co(OH)NO_3$, loses its NO_3 and begins to take up another OH radical, *i. e.,* becomes, so to speak, nascent, the nickel combines with it to form a nickel cobaltite, which is even more blue than the basic salt. Then, as more of the basic salt changes over, the nickel is finally all taken up, the normal cobaltous hydroxide begins to form, and when a sufficient quantity of this has been formed to hide the blue of the nickel cobaltite, the pink color makes its appearance. It may also be that the nickel cobaltite is formed immediately upon precipitation, and being unstable, soon breaks up, forming the hydroxides of the two metals.

The reasons for suggesting the formation of nickel cobaltite are as follows: Firstly, the nickel produces an effect which cannot be accounted for by the physical properties of its hydroxide; secondly, cobalt is shown to form some cobaltites by the following facts: (1) The hydroxide is somewhat soluble in a concentrated solution of potassium hydroxide, forming a dark blue solution. I have found that the hydroxide is also considerably soluble (upon warming) in a 5N sodium hydroxide solution in the presence of considerable quantities of salts of some other metals, among which are aluminum, lead, sodium and lithium. (2) The solutions of these cobaltites are intensely blue, much more so than the original basic salt, a very small amount of cobalt in solution sufficing to give a very intense blue color. It is, therefore, possible, if not probable, that the formation of a corresponding nickel compound, which is insoluble and deep blue in color, may be the cause of the interference with the change of color of the cobalt precipitate.

As was mentioned, the presence of very small amounts of cobalt can be detected by this method in presence of an excess of nickel. This test depends upon the formation of the blue compound mentioned above, and on the further fact that this color makes itself evident in a great excess of nickel. For this reason, when sodium hydroxide is added to a solution which contains nickel in excess, if cobalt is present (even somewhat under 1 per cent.), this blue color makes itself visible, especially upon standing a moment, *i. e.*, the hydroxide, instead of being a pure, pale green, will have a bluish tinge, more or less deep, depending upon the amount of cobalt present.

In a test of this delicacy it is only natural that certain conditions must be fulfilled lest the results lead to incorrect conclusions. These conditions are as follows:

(1) Other metals besides nickel and cobalt should be absent, since many of these interfere with, or give the reaction outlined above. This is easily accomplished by following the ordinary course of analysis.

(2) The solution in which the test is made should be roughly normal (or somewhat stronger) in order that the color reactions may be best observed.

(3) The solution should not contain much free acid (a small amount makes no difference), since the salt formed upon the addition of the hydroxide may interfere somewhat, because, as was mentioned above, the salts of the alkali metals tend to form cobaltites.

The procedure for the detection of the two metals is, therefore, as follows: Dissolve the sulphides in concentrated nitric acid, evaporate to dryness, heat gently to expel free acid and dissolve in a little water. To about 3 cc. of this solution in a test-tube add 6 to 8 cc. of sodium hydroxide, cover the mouth of the test-tube with the thumb, mix thoroughly by shaking, and note the result. If cobalt be in excess, the precipitate will have a dark blue color; if nickel be present in very small amount, the color will not change immediately, *i. e.,* within four to five seconds, to a bright pink. If, however, the nickel be present in large amount, the change of color will be retarded for half an hour or more, the color never becoming a bright pink, but changing to a dirty gray. If nickel be absent, the change of color is practically instantaneous.

If nickel be in excess, the precipitate will not be dark blue, but will have a green color, which will show more or less bluish tinge, depending upon the amount of cobalt present. If cobalt be absent, the precipitate will be a pale green, and will remain so upon standing.

It will, therefore, be evident that by this test, which is practically instantaneous and requires no manipulation, it is possible in one operation, carried on in a test-tube, to detect both elements, even if either element be in exceedingly small amount, in a great excess of the other, the test for cobalt being probably as delicate as any hitherto proposed (with the exception of Vögel's test, outlined above, which requires the use of ammonium sulphocyanide, amyl alcohol and ether), while that for the detection of nickel is considerably more delicate than anything hitherto proposed for this purpose.

For use in ordinary qualitative analysis in college laboratories where nickel-free cobalt salts are not supplied to students, the test may be modified in one of two ways in order to slightly decrease its delicacy. (1) The students may be told that unless the change of color is retarded over a minute nickel may be regarded as absent, or (2) by using, instead of a 5N sodium hydroxide solution, a 10N or 15N solution, when the delicacy is so decreased as to give practically no reaction for nickel in ordinary cobalt salt solutions.

I desire to express my sincere thanks to Dr. J. F. Snell for the valuable advice he has rendered during the progress of this work.

SYNTHESES OF DERIVATIVES OF QUINOLINE.

BY EDWARD BARTOW AND ELMER V. MCCOLLUM.

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THE best method for the synthetical preparation of quinoline and its derivatives is that of Skraup,[1] which consists in heating an aromatic amine with glycerin, an aromatic nitro compound (usually nitrobenzene), and sulphuric acid. A quinoline ring is formed by the combining of the aromatic amine and the glycerin with loss of water and hydrogen. The nitro compound serves as an oxidizing agent, and is itself reduced to an amine from which quinolines are also formed, sometimes making mixtures that are difficult to separate.

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[1] Wien. Acad. *Ber.*, **2**, 593 (1881); **2**, 1089 (1883).