ART. XXXII.—*On the Qualitative Separation of Nickel from Cobalt by the action of Ammonium Hydroxide on the Ferricyanides*; by PHILIP E. BROWNING and JOHN B. HARTWELL.

[Contributions from the Kent Chemical Laboratory of Yale University—XCVII.]

SOME years ago F. W. Clarke* suggested a method for the separation of nickel from cobalt depending upon the solvent action of ammonium hydroxide upon the precipitated ferricyanides. The method may best be described by quoting from the original article: "To the slightly acid solution containing the two metals, I first add an excess of ammonium chloride. This causes the cobalt precipitate, which otherwise would run through the filter, to fall in a denser state, and also of a much darker color, often nearly black. I then add the potassium ferricyanide until the precipitation is complete, and afterwards agitate strongly with a considerable excess of ammonia. Upon filtering, all the cobalt remains upon the filter, being recognized by the characteristic color of the precipitate, and the nickel is readily detected in the filtrate, by means of ammonium sulphide. If, upon filtering, the portion at first running through is turbid, it may be disregarded, or returned to the filter, that which filters through subsequently being almost invariably clear."

In making a study of this method we found two serious objections; first, the practical impossibility of obtaining a good filtration from the cobalt ferricyanide, even in the presence of the ammonium chloride, and, second, the large amount of sulphur thrown down when ammonium sulphide was added to the filtrate containing the nickel with the excess of ferricyanide.

Our first attempt was to secure, if possible, a complete separation of the precipitated cobalt ferricyanide and the dissolved nickel by filtration. This we were able to accomplish by the addition of a small amount of a solution of an aluminum salt to the original solution which held back the cobalt, and, as experiment showed, allowed the complete solvent action of the ammonium hydroxide upon the nickel salt. Amounts of nickel as small as 0.0001 gm. were detected, when mixed with the aluminum salt, by precipitating as ferricyanide, extracting with ammonium hydroxide, and testing in the manner to be described.

On turning our attention to a possible improvement in the method for the detection of the nickel, it was found that when the ammoniacal solution of the nickel ferricyanide was treated

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with strong sodium or potassium hydroxide solution, in the presence of an excess of potassium ferricyanide, a black flocky precipitate formed which gave no test for ferro or ferricyanide, and gave every indication of being nickelic hydroxide. This reaction we found to afford us a most delicate test for nickel.

The method as modified by us may be described as follows: Dissolve not more than 0.1 gm. of the salts of the two elements in about 5^{cm}³ of water, add a few drops of a saturated solution of alum, destroy any free mineral acid by neutralizing with ammonium hydroxide, and make faintly acid with acetic acid. To this solution add about 0.5 gm. of potassium ferricyanide and agitate to effect the solution of the ferricyanide and the complete precipitation of the nickel and cobalt salts. Then add about 5^{cm}³ of strong ammonium hydroxide and filter. To the filtrate, which should have no reddish color, add a piece of sodium or potassium hydroxide about the size of a pea and boil. The appearance of a black precipitate, in case of very small amounts of nickel showing first as a dark coloration, indicates nickel.

The tables following give a record of the experimental results. With the precautions indicated, this method may be applied very satisfactorily.

TABLE I.

CoSO ₄ ·7H ₂ O gram.	NiSO ₄ · 7H ₂ O gram.	KAl(SO ₄) ₃ saturated sol. cm ³	K ₃ FeC ₆ N ₆ gram.	NH ₄ OH (conc.) cm ³	NaOH, solid, about size of a pea.	Result.
1. ----	0.0100	2	0.5	5.	"	Heavy ppt.
2. ----	0.0050	"	"	"	"	"
3. ----	0.0010	"	"	"	"	"
4. ----	0.0003	"	"	"	"	Distinct
5. ----	0.0001	"	"	"	"	Plain

TABLE II.

1. 0.10	----	"	"	"	"	None
2. 0.10	0.0100	"	"	"	"	Heavy
3. 0.10	0.0050	"	"	"	"	Distinct
4. 0.10	0.0030	"	"	"	"	Very faint
5. 0.05	----	"	"	"	"	None
6. 0.05	0.0100	"	"	"	"	Heavy
7. 0.05	0.0050	"	"	"	"	Distinct
8. 0.05	0.0030	"	"	"	"	Plain
9. 0.05	0.0010*	"	"	"	"	Faint

* Equivalent to 0.0002 of the metal.