# METHODS OF DETERMINING NICKEL AND COBALT IN METEORIC IRON.

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ABSTRACT. Different analyses on the same iron meteorite frequently show a wide variation in composition. This may be due to the methods of sampling the meteorite or to the method followed in determining iron, nickel and cobalt.

(1) Iron should always be determined volumetrically; (2) nickel can be precipitated by dimethylglyoxime in the presence of iron by holding the iron in solution with tartaric acid; (3) nickel and iron can be separated by four precipitations of iron with strong ammonia and the nickel determined in the combined filtrates after the excess ammonium salts are expelled and (4) cobalt is not as completely separated from the iron as is nickel by the strong ammonia. A high degree of accuracy is not claimed for this method of separating cobalt from iron.

ANYONE studying the literature of iron meteorites is annoyed by the poor agreement between analyses of meteorites that have almost identical structures and even between analyses of the same meteorite. Much of the confusion is caused by the separation of nickel from iron, which, although appearing to be a simple problem, is rather a difficult one. However, it must be remembered also that some of the difficulty is traceable to the manner of sampling of the specimen. Their heterogeneous character makes the selection of an easily removable protruding knob a questionable procedure, since it cannot be assumed that this knob does not contain a sizable inclusion of one of the extraneous compounds.

As a rule a specimen of the octahedrite class does not vary greatly in coarseness of its structure from one place to another in the same meteorite, but inclusions are distributed at random throughout the mass. Hence, unless the sample selected is studied after it is polished and etched, the homogeneous nature can certainly not be assumed. The slice selected should be thin and its etched face compared with a larger section of the meteorite to make certain it is of average character.

Hexahedrites are more uniform in texture than octahedrites, though they may contain irregularly distributed schreibersite or troilite inclusions. The chemical composition of hexahedrites should be very definite, at least more so than is now reported, if there is a close relationship between chemical composition and

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structural pattern. The reported finding of a wide range in compositions of the hexahedrite class suggests that the data on the methods employed in analyzing iron meteorites should be examined more closely.

*Preparation of the sample*: In the past samples for analyses have often been prepared from iron meteorites by taking the saw cuttings as a slice was being made or by drilling out a small core from the meteorite. Frequently it has been convenient to remove a protruding knob and use this portion for chemical analysis. However, such procedures are not recommended.

In this work it is recommended that a thin slice be removed, polished, and etched on both sides to make certain it is free from sizable foreign inclusions. If the meteorite is to be further sliced, it is better to delay the selection of the sample until one or more representative slices have been removed and examined, then the sample for the chemical investigation can be chosen with more confidence.

It was found convenient to select samples weighing from 10 to 20 grams, but smaller ones could be used. The sample was dissolved in mixed hydrochloric and nitric acid and after complete solution was effected, the solution evaporated to expel the nitric acid, hydrochloric acid added, the insoluble material filtered off, and the filtrate diluted to volume.

*Analytical methods*: *Iron.* It is recommended that only volumetric methods be used for the determination of iron. Regardless of whether or not all the nickel and cobalt can be separated from the iron, gravimetric methods give high results, which partly explains why many old meteoric iron analyses are incorrect. Many chemists relied on repeated reprecipitations of the iron to free it from nickel and cobalt. Prior[2] in discussing the methods of chemical analysis said: "For the separation of nickel, precipitation of the iron with ammonia, repeated four or even five times was used." Less than a year later he[3] made this correction: "Almost immediately after the publication of that paper, however, it was found that the separation of iron and nickel by means of ammonia had been by no means complete, and that it could not be made so even after as many as six or seven precipitations." In the investigations reported in

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[2] Prior, G. T.: Min. Mag., v. 17, no. 78, p. 25, 1913.

[3] Ibid., v. 17, no. 80, p. 132, 1914.

this paper the iron when precipitated by ammonia was reprecipitated only four times. When gravimetric determinations were employed the results were always high, sometimes by several per cent. Phosphorus will be retained in the iron, but in cases investigated a correction was made for the phosphorus. Undoubtedly, the chief reason for such high results is due to the retention of nickel and cobalt in the iron.

It was pointed out by Allen and Johnston[4] that gravimetric methods for iron gave high results. These authors found that iron may be high by as much as two per cent of the total iron present. Some of the error was directly traceable to the reaction of the ammonia on the glass containers and when platinum vessels were used satisfactory results were obtained.

Since platinum vessels are not available to all chemists, and no real reason exists why iron must be determined gravimetrically, no investigation was undertaken to learn what proportion of the high percentages was traceable to the impurities dissolved from the glass containers.

*Nickel*: Undoubtedly the chief reason why wide variations in the nickel contents are reported in analyses of even the same meteorite is due to the difficulties of completely separating the nickel from iron. Many of the old analyses were made before the introduction of dimethylglyoxime. Some variations in nickel content on a particular meteorite may be traceable to the use of different samples, some of which contain perhaps more of the high nickel compounds than others. This may be a partial explanation for high nickel values, but almost certainly low nickel values result from nickel being retained in the iron.

*Nickel in the presence of iron*: The method as outlined in Hillebrand and Lundell[5] in which tartaric acid is used to prevent precipitation of iron by ammonia hydroxide is very satisfactory. Repeated determinations by this method gave consistent results and qualitative tests on the dimethylglyoxime precipitate showed it to be free from iron.

In all perhaps 25 determinations by this method have been run. In two cases a turbidity developed which appeared to be a basic tartrate of iron. It formed after the iron hydroxide

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[4] Allen, E. T., and Johnston, John: Jour. Ind. & Eng. Chem., v. 2, no. 5, May 1910.

[5] Hillebrand, W. F., and Lundell, G. E. F.: Applied Inorganic Analysis, p. *316*, 1929 edition.

had been dissolved by additions of tartaric acid and the solution then made slightly ammoniacal. On heating, a light-colored precipitate formed which is almost clay-like in consistency. The solution was about 300 ml. in volume and even on diluting to 500 ml. and boiling, the turbidity did not disappear and a slight addition of hydrochloric acid did not clear it. The exact nature of the precipitate was not investigated nor were the conditions under which it forms. When this turbidity was encountered, the solution was discarded and another portion taken from the flask containing the dissolved meteorite.

*Nickel in the filtrate from iron after several reprecipitations with a slight excess of ammonia*: Although it has been shown by others that nickel cannot be separated from iron by precipitation with a slight excess of ammonia, it was found desirable to run a series of determinations to learn the order of magnitude of the inaccuracies of the method. In Table I is contrasted the results where nickel was determined after four reprecipitations of iron with a slight excess of ammonia and where the nickel was determined in the presence of iron, using tartaric acid.

The filtrates from the four iron precipitates were combined, evaporated to dryness, and the excess of ammonium salts expelled, the residue taken up in hydrochloric acid and reevaporated, so as to remove any silica that may have been dissolved from the glass containers, after which the nickel was then determined in the regular manner by using dimethylglyoxime.

From these data it is evident that very serious errors result

TABLE I.

Comparison of results for the two methods of determining nickel.

| | Puripico | | Sierra Gorda | Rio Loa | Coye Norte | Cedar-town | Negrillos | Glorieta (Santa Fe) | Iquique | Grant |
|---|---|---|---|---|---|---|---|---|---|---|
| Fe .... | 93.40 | | 93.19 | 93.33 | 93.74 | 94.02 | 93.94 | 87.06 | 83.80 | 88.63 |
| Ni[1] .... | 5.75 | 5.80 | 5.58 | 5.70 | 5.51 | 5.48 | 5.32 | 11.67 | 15.91 | 9.35 |
| Ni[2] .... | 3.57 | 5.12 | 4.12 | 5.33 | 4.58 | 4.63 | 2.67 | 8.33 | 11.70 | 6.26 |
| [3] .... | —2.18 | —.68 | —1.46 | —.37 | —.93 | —.85 | —2.65 | —3.34 | —4.21 | —3.09 |

[1] Nickel determined in the presence of iron, by using tartaric acid.

[2] Nickel determined in combined filtrate from 4 reprecipitations by slight excess of ammonia.

[3] The erratic but consistently low results obtained by one method compared with another.

The values given for Fe are all volumetric determinations.

in the separation of iron from nickel by the use of dilute ammonia, even after repeated precipitations. Any analysis made by this frequently used method is totally unreliable.

*Separation of Nickel from Iron by Strong Ammonia. Made by mixing one part standard reagent ammonium hydroxide with two parts water*: A solution of ammonia is heated and into it is slowly added the solution of the iron meteorite under investigation. It was found convenient to have about 300 ml. of the strong ammonia and that the solution being analyzed be only slightly acid and of about 100 ml. volume or less. Iron precipitated in this manner coagulates nicely and after a few minutes of heating settles readily.

This precipitate is again washed into the beaker and the filter cleaned with hydrochloric acid. The second precipitation is carried on precisely as the first and the filtrates containing the nickel and cobalt are combined. Four such reprecipitations are made and each time the backwards precipitation is followed as above described.

The combined filtrates are evaporated to dryness, the ammonium salts removed by repeated acid treatments and the residue then taken up in about 100 ml. of ten per cent hydrochloric acid and filtered. Some silica from the glassware is always present but this can be rejected. This solution now contains the nickel and cobalt; the nickel can be easily precipitated from a slightly ammoniacal solution by adding dimethylglyoxime.

TABLE II.

Comparison of the Nickel Determinations using Strong Ammonia and the Tartaric Acid Method.

| | Mt. Joy | Grant | Sandia Mts. | Coahuila | Maria Elena | Farmington | Glorieta (Santa Fe) | Iquique |
|---|---|---|---|---|---|---|---|---|
| $NH_4OH$ .... | 5.74 | 9.25 | 5.87 | 5.58 | 7.75 | 6.61 | 11.91 | 16.007 |
| Tartaric acid ..... | 5.84 | (9.27)<br>(9.35) | 5.97 | 5.60 | 7.89 | 6.71 | 11.67 | 15.91 |

All determinations made by E. P. Henderson.

A satisfactory separation of iron from nickel can be made by this method in which a great excess of ammonia is always present, a condition achieved by slowly adding the test solution to the strong ammonia reagent. This method may be preferred where the sample is very limited, but care should be taken in the case of a complete analysis on a single sample to remove completely the silica derived from the glassware.

Evidently it is optional which method one selects for the determination of nickel. If cobalt is to be determined, the strong ammonia method seems preferable.

Ardagh and Broughall[6] describe a method that separates nickel from iron by precipitating the iron with concentrated $NH_4OH$ in a solution of small volume and almost saturated with $NH_4Cl$. The precipitated iron hydroxide is then washed in a solution of $NH_4Cl$ in $NH_4OH$ instead of water. These authors report that all the nickel can be separated from the iron by this method. In six separate determinations 100 per cent of the nickel present was recovered. Any investigator wishing to use this procedure should read their technique given in their description. Moreover, a series of references on methods of separating nickel from iron by various methods is also given.

*Analytical Methods for Cobalt*: The difficulties in the determination of cobalt in meteorites lie in the failure to find any successful method for the separation of this metal from iron.

It has been pointed out[7] that after a double precipitation with ammonium hydroxide, a solution containing .1 gram of $Al_2O_3$ and .05 gram of Co, that .0012 gram of the Co was still retained by the aluminum hydroxide. Since nickel was found to be so well separated from iron by the use of strong ammonia, it was hoped that cobalt could likewise be as completely separated.

A known amount of cobalt was taken from a prepared standard solution and precipitated by passing hydrogen sulphide gas into it after it had been made slightly ammoniacal. The precipitate was then filtered off, ignited, and weighed as cobalt oxide. After several direct cobalt determinations were made in this manner and the results found to agree with each other a solution containing both cobalt and nickel was prepared. The nickel was precipitated by dimethylglyoxime. The organic salts in the filtrate were removed by evaporating to dryness and adding mixed nitric and hydrochloric acid. Finally the residue was taken up in dilute hydrochloric acid, filtered if neces-

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[6] Ardagh, E. G. R., and Broughall, G. M.: Canadian Chemistry and Metallurgy, v. 7, no. 8, p. 199, 1923.

[7] Lundell, G. E. F., and Knowles, H. B.: Jour. Amer. Chem. Soc., v. 45, p. 680, 1923.

sary, and the cobalt precipitated in the manner as described above. It was found that nickel precipitated in this manner did not contain any appreciable quantity of cobalt, as the results obtained agree perfectly with those from the cobalt standard solution.

Next a solution was prepared which contained iron in excess of cobalt. It so happened that this particular solution contained nine times as much iron as cobalt. The iron was precipitated by strong ammonia as previously outlined and after four such precipitations the filtrates were evaporated to dryness and the ammonia salts expelled and the cobalt afterwards determined.

Three separate determinations were made, each with four precipitations of iron and in each case cobalt was found to be retained in the iron. Thus it can be seen cobalt does not behave like nickel.

From solutions containing known quantities of cobalt and nickel, the following figures were obtained for cobalt: .01694 gram; .01687 gram; .01694 gram.

From solutions containing iron and the same quantity of cobalt the following results were obtained: .01539 gram; 0.1407 gram. This shows that in one case 8.93 per cent of the cobalt was retained in the iron and in the other 16.7 per cent was held back. Since such variable results were found, it is possible that even a more complete separation of cobalt might sometimes be had, but the method is not reliable.

The cobalt determined in meteorites by this method can always be expected to be low and perhaps by a wide margin.

It has been proposed to use lead peroxide[8] to separate iron from nickel and cobalt. Walker found that 99.5 per cent of the nickel could be recovered by this method. He also found that the accuracy for the separation of cobalt from iron was much lower. Walker recovered 89.5 per cent of the cobalt. This method, although interesting, does not seem to lend itself to analyses of meteorites.

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[8] Walker, T. L.: On the Separation and Determination of Nickel and Cobalt. Trans. Roy. Soc. Canada, Series III, no. 9, p. 93, 1915.

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