Studies on Nickel and Cobalt in Mineral Springs. II. Nickel and Cobalt Contents of Tentoku Mineral Spring, Saga Prefecture.

By Nobuyuki TANAKA.

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In the preceding paper⑴ the colorimetric determination method for nickel and its application to some acid vitriol springs in Japan have been reported. The method was proved to be most satisfactory for the mineral springs containing a minute quantity of nickel. Of some fifteen samples that were treated by this method Wakesui in Okayama Prefecture proved the richest in nickel. However, there are some more springs in which this element is determinable. X-ray examination, for example, clearly shows them to contain a determinable amount of nickel—not only nickel but also cobalt or both of them. In these springs Tentoku in Saga Prefecture seems predominant, concerning the quantity either of nickel or of cobalt. One of the purposes of the present paper is a brief description of it and the other is to show whether or not the deposit of an ocherous ferric oxide could be accompanied by cobalt while it precipitates from mineral waters. As for nickel an experiment was carried out with a result that it was accompanied by almost no nickel, as already related in the preceding report. The same experiment was tried again in this study with the same result.

If the mineral water, especially of acid vitriol springs, is kept on standing some precipitates generally appear in it. In this regard the spring in question, Tentoku Mineral Spring, makes no exception to other springs. Therefore, the parts "filtrate" and "precipitate" were treated separately, and this treatment contributed to the investigation of the distribution of elements between these two parts.

The Filtrate Part: At first the filtrate was taken to be analysed. A spectroscopic examination by the arc method was made prior to the chemical treatment to ascertain all the main elements contained in the sample. The result is shown in Table 1. From the given result the determinations of nickel, cobalt and the major constituents were made. Nickel was precisely determined gravimetrically by the α-benzildioxime method⑵ after estimated colorimetrically by the improved Sandell's method⑴. It would go without specifying anything for the latter method, but for the former some explanations are required.

Table 1.

Fe, Al, Ca, Mg, Mn, Ni, Co, Si, Cu.

A practical application of α-benzildioxime was adovocated by F. W.

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(1) N. Tanaka, this Bulletin, **18**(1943), 201.

(2) F. W. Atack, *Analyst*, **38**(1913), 318, 448.

Atack and he claims that this reagent is very convenient for both qualitative and quantitative analyses of nickel. The fact was confirmed also by H. Grossmann *et al*. According to these investigators, nickel can be more easily separated from cobalt by this reagent than by dimethylglyoxime, which is usually employed for separating or determining the former element. The author adopted this α-benzildioxime for the determination of nickel in mineral waters, and followed the procedure described in Grossmann's report. It will be briefly mentioned.

Taking suitable volume of mineral waters, remove copper and other members of the hydrogen sulphide group by hydrogen sulphide. Expel hydrogen sulphide thoroughly and oxidize ferrous iron completely to ferric. Add the hot alcohol solution of α-benzildioxime reagent (150 c.c. of the saturated solution must be used for 0.01 g. Ni), after the sample solution was treated with ammonium citrate enough to prevent, when the solution is made ammoniacal, ferric iron from precipitating. Then make the solution slightly ammoniacal and heat it on a water-bath for a few minutes. Filter the precipitate with a glass-filter, wash it with hot 50% alcohol (more concentrated alcohol should not be used if ammonium citrate is present) and dry at 110–120°C. The temperature for the drying can be allowed up to about 180°C.

Cobalt was estimated by the nitroso-R-salt method⁽³⁾, one of the colorimetric methods for cobalt. It could be only estimated, but not determined, owing to an interference considered to be caused by one or more of the elements in the given samples. As the present investigation is imperfect for the detailed discussion, it will not be gone into here. It, however, is necessary to mention that the various aliquots of the sample solution, taken to be determined colorimetrically, gave discordant cobalt contents as a result, and that the highest of these was adopted as giving the value nearest to the true one. Copper was thoroughly removed with hydrogen sulphide because it interferes with the determination. Although nickel, of course, is present in the sample, the procedure for removing it was omitted for only a reason that the nickel content is not so large compared with that of cobalt that its interference hardly requires to be taken into account. Anyway it could not be found what interferes with the cobalt determination. The matter, therefore, remains for the subsequent studies. Here will be only shown the estimated content of cobalt in Tentoku, which is remarkably large.

The determinations of the major constituents were carried out in the usual way. Table 2 shows in the first column the contents of nickel, cobalt and major constituents in the filtrate, and in the second column the percentage of these elements in total residue.

Table 2.

	Content (g./l.)	Content (% in total residue)
Ni	0.00927	0.0308
Co	0.00218	0.0073
Fe ($Fe^{++}+Fe^{+++}$)	4.903	16.27
Al	0.6019	2.00
Ca	0.4306	1.43
Mg	0.8462	2.81
H_2SiO_3	0.2021	0.67

Total residue 30.143 g./l.

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(3) A. M. M. Davidson and R. L. Mitchell, *J. Soc. Chem. Ind.*, **59** (1940), No. 10, 232; H. T. MacPherson and J. Stewart, *Biochem. J.*, **32** (1938), 763, etc.

The Precipitate Part: The precipitate from the mineral waters was separated from the filtrate, and dissolved in concentrated hydrochloric acid. The residue was filtered, washed, ignited, and weighed as silica. The solution, on the other hand, was worked concerning the same elements as those of the filtrate. Nickel was determined only colorimetrically because of its minute quantity. The content of cobalt was obtained by the colorimetric method using nitroso-R-salt as the reagent. All results are given in Table 3, reduced to the form of oxides.

Table 3.

	Content in the precipitate from 1 l. of the water (g.)
NiO	0.0001411
CoO	0.0000138
Fe_2O_3	0.86272
Al_2O_3	0.01048
CaO	0.00772
MgO	0.00422
SiO_2	0.00159

Table 4.

	Content in the original water (g./l.)
Ni	0.00938
Co	0.00219
$Fe(Fe^{++}+Fe^{+++})$	5.506
Al	0.6075
Ca	0.4363
Mg	0.8488
H_2SiO_3	0.2042

On the Analytical Results: The data of two parts were combined to obtain the contents in the original water, which are given in Table 4. As a result it became clear that this mineral water is the richest in Japan either in nickel or in cobalt; as for the former element Wakesui, Okayama Prefecture, has predominated. Concerning the determination of the latter element in mineral springs a little has been published before this study. In our country only Kinkei Mineral Spring was the example(4); it is estimated by the arc spectroscopic method to be less than $10\,\gamma$ Co/l. and determined by the X-ray method to be $7.2\,\gamma$/l. The present investigation, however, suggested that there could be found mineral springs containing a fairly large amount of cobalt. The percentages of nickel and cobalt in total residue(5) correspond to 0.0302% and 0.0071% respectively, the former of which is far higher than the mean nickel content of acid vitriol springs in Japan. As for the latter, on the other hand, only a comparison with Kinkei is possible, showing far higher value. Moreover, the atomic ratios, Ni/Fe, Co/Fe and Co/Ni are calculated to be 16.21×10^{-4}, 3.77×10^{-4} and 0.232 respectively, as shown in Table 5. The first is also higher than the average of Ni/Fe that is represented in the last paper of this series. Co/Fe shows far and Co/Ni somewhat higher when compared with those of Kinkei.

Table 5.

	Ni/Fe	Co/Fe	Co/Ni
Atomic ratio	16.21×10^{-4}	3.77×10^{-4}	0.232

If the content of iron is assumed to be 100 the other elements analysed

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(4) K. Kimura, M. Nakamura and N. Tanaka, *J. Chem. Soc. Japan*, **64**(1943), 349.

(5) 31.030 g./l. (calculated).

give the figures in Table 6. The first column is concerned with the contents in the filtrate and the second, those in the precipitate. Leaving aside the question of the major constituents, the distributions of nickel and cobalt between the filtrate and the precipitate will be taken up here. Ni/Fe in the filtrate is about ten times higher than that of the precipitate. The fact gives a full explanation to the behaviour of nickel to the ocherous ferric oxide that precipitates from mineral waters, and it proves the experience gained in the case of Kinkei to be true. The next problem is concerned with the behaviour of cobalt, which is demonstrated by the fact that Co/Fe is about twenty-five times lower in the precipitate than in the filtrate. The element, therefore, proves to remain mostly in solution, part of it migrating to the precipitate. After all, no difference can be found between nickel and cobalt regarding its remaining in solution. If there were any differences, it would be a matter of degree—the difference between the atomic ratio Co/Ni in the filtrate and that in the precipitate. The former is 0.24 and the latter 0.10. Would nickel have a somewhat closer affinity to such a deposit than cobalt? The question requires so many examples that it will be discussed in the subsequent papers.

Table 6.

	Filtrate	Precipitate
$Fe(Fe^{++}+Fe^{+++})$	100	100
Al	12.28	0.921
Ca	8.78	0.936
Mg	17.26	0.426
SiO_2	3.18	0.264
Ni	0.189	0.0184
Co	0.044_5	0.00180

Summary.

The determinations of nickel, cobalt and the major constituents in Tentoku Mineral Spring, Saga Prefecture, typical of the acid vitriol springs in Japan, have bee made. The result is that this spring contains such a remarkable amount both of nickel and cobalt that it proves to be the richest in our country in either element, showing 9.38 mg. Ni/l. and 2.19 mg. Co/l.

The distributions of these two elements between the filtrate and the precipitate have been investigated. Either of these mostly remains in the filtrate and partly migrates to the precipitate. In this regard a difference between nickel and cobalt, if it could be found, seems to be a matter of degree, that is, a problem as to which element has closer affinity to the precipitate of ferric hydroxide.

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Chemical Institute, Faculty of Science,
Imperial University of Tokyo.