Studies on Nickel and Cobalt in Mineral Springs. I. Nickel Content of Acid Vitriol Springs in Japan.

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(Received April 15, 1943.)

Minute quantities of nickel and cobalt are often detected in mineral springs by various methods. For instance, Prof. Kenjiro Kimura(1) found in Japan some twenty mineral springs with nickel and cobalt by the spectroscopic method. But their accurate determination is regarded to be almost impossible on account of their being accompanied by a large amount of iron, as is usually the case.

The possible methods for common determinations of nickel and cobalt include purely chemical, colorimetric, spectrographic, and polarographic determinations. In the present case, the most desirable method, without separating these two elements either from others or from one another, is the spectrographic method. But the usual optical ray method is not so convenient because of the absence of available determination line, as is well known. Prof. K. Kimura and his co-workers(2) (the author was one of them) adopted, with great success, the variable internal standard method by x-ray spectroscopy for determination of minute quantities of nickel and cobalt, as previously reported. And applying that method to Kinkei Mineral Spring, Totigi Prefecture, the results of 68 γ Ni/l. and 7.2 γ Co/l. were obtained.

K. Heller, G. Kuhla and F. Machek(3) succeeded in determining nickel contents of some mineral springs polarographically, such as "Marienbader Quellen", "Karlsbader Quellen" and "Curiequelle", but failed in the case of cobalt, even to estimate it by the same method. K. Kuroda(4) also obtained the value of the nickel content of a mineral spring in Japan by the same polarographic method. However, as for cobalt he succeeded only in estimating it by spectroscopy.

While working on nickel and cobalt in mineral springs with an idea to determine them colorimetrically, the author came across the report by E. B. Sandell and R. W. Perlich(5), in which they described the method for these elements contained in silicate rocks. On the application of Sandell's method for nickel to mineral springs, especially to acid vitriol springs characteristic of our country, satisfactory results were obtained, the report of which is as follows.

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(1) Not yet published.

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

(3) K. Heller, G. Kuhla and F. Machek, *Mikrochemie*, **23**(1937), 78.

(4) K. Kuroda, this Bulletin, **16**(1941), 234.

(5) E. B. Sandell and R. W. Perlich, *Ind., Eng. Chem., Anal. Ed.*, **11**(1939), 309.

Determination Method.

E. B. Sandell used Rollet's method⁽⁶⁾ which is considered the most excellent of colorimetric methods for nickel. This method is to compare the colour of an unknown solution developed in nickelic state by dimethylglyoxime with that of the standard solution treated in the same manner, by using Duboscq colorimeter. On the other hand, the method of extracting nickel is due to his own idea, which is based on the extraction of nickel dimethylglyoxime with chloroform from the ammoniacal citrate solution of the sample. The author tried to modify this method, by using Pulfrich photometer instead of Duboscq colorimeter, and to find the optimum condition for determining a minute quantity of nickel in the presence of others.

Standard Solutions and Reagents. Nickel standard solution: Nickel chloride (The Kahlbaum for Analysis) contained a small amount of cobalt, which was detected by x-ray spectrographic method. It was removed by repeating precipitation three times with dimethylglyoxime. The stock solution prepared is 0.536 mg. Ni per c.c. in concentration.

Ferric chloride solution: By five reprecipitations with ammonium chloride and ammonium hydroxide, nickel and cobalt detected x-ray spectrographically in ferric chloride were removed. The concentration of the stock solution is 4.46 mg. Fe per c.c.

Dimethylglyoxime reagent: 1 per cent alcoholic solution.

Dimethylglyoxime and other reagents were assured to contain a negligible amount, if present, of nickel.

Procedure. The determination procedure adopted was as described by E. B. Sandell and R. W. Perlich⁽⁵⁾, except that the concentration of ammonium hydroxide in the final solution was increased, and that the final colorimetric measurement was done objectively, using Pulfrich photometer. This procedure is as follows.

(a) Extraction of nickel.—Remove copper and other elements of the hydrogen sulphide group in mineral waters by hydrogen sulphide, remove thoroughly hydrogen sulphide from the filtrate, and oxidize ferrous iron by nitric acid. Add sufficient amounts of ammonium citrate solution, neutralize the cold solution with concentrated ammonium hydroxide using litmus paper, and add a few drops in excess.

To this ammoniacal citrate solution of the sample add 2 c.c. of 1 per cent alcoholic dimethylglyoxime solution, and shake vigorously for half a minute with two or three portions of chloroform, each having a volume of about 10 c.c. Combine all the chloroform extracts and shake vigorously with 10 c.c. of dilute ammonium hydroxide (1:50). Draw off the chloroform, taking care that no drops of the aqueous phase accompany it, and shake the water layer with a few c.c. of chloroform to recover any suspended drops of chloroform solution.

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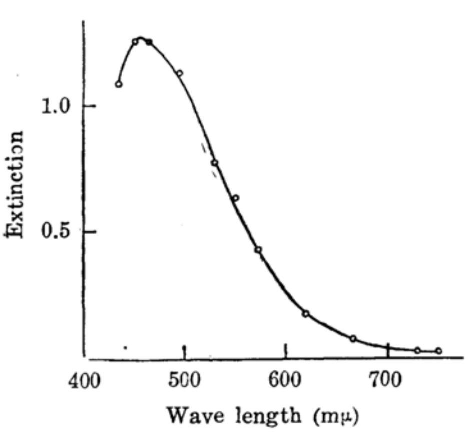
(6) A. P. Rollet, *Compt. rend.*, **183** (1926), 212.

Shake the chloroform solution of nickel dimethylglyoxime vigorously for 1 minute with two portions of 0.5 N hydrochloric acid, each having a volume of 5 c.c.

Transfer the hydrochloric acid solutions to a volumetric flask of suitable size, taking care that no appreciable amount of chloroform is carried over. For colour measurement in a Pulfrich photometer the nickel concentration of the final solution should be at least 0.05 p.p.m.

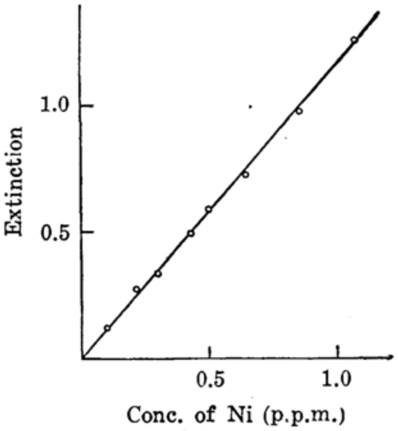
(b) Colour development (standard solution is treated in the same manner as mineral waters from this point).—To the solution to be determined in the volumetric flask, add 5 drops of freshly prepared saturated bromine water, mix, and then add concentrated ammonium hydroxide dropwise shaking until the colour of bromine disappears. Next, add 0.5 c.c. of 1 per cent alcoholic dimethylglyoxime solution, and mix. Finally, add as much concentrated ammonium hydroxide as needed to get a 2.8 per cent concentration of ammonium hydroxide in the final solution, and dilute to volume with water.

(c) Photometric determination.—The colour should not be measured immediately, but after half an hour at least. The colour intensity of the solutions increases slowly on standing, reaching to the almost constant intensity within half an hour from the colour development, and showing neither increase nor decrease of extinction value for twenty four hours afterwards. The filters employed were S45 (450 mμ) because the extinction maximum of nickelic dimethylglyoxime solution exists near 450 mμ in wave length, as shown by the extinction curve of Fig. 1. 50 mm.-cells were used.



Concentration of Nickel: 1.072 p.p.m.
Stratum length of Cell: 50 mm.

Fig. 1.



Filter: S 45 (450 mμ)
Cell: 50 mm.

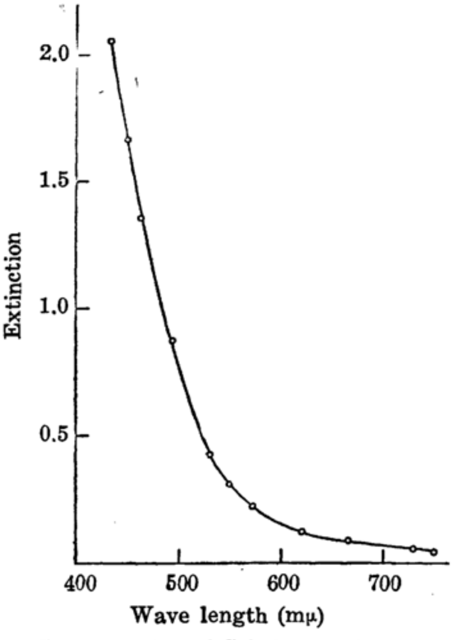
Fig. 2.

Calibration Curve and Single Determination. A calibration curve, covering the range from 0.05 to 1 p.p.m. of the final solution, was prepared, and it is almost linear (Fig. 2). The mean error of single determinations of standard solutions did not exceed ±2 per cent, as shown in Table 1.

Table 1.

Ni present p.p.m.	Scale reading	Ni found p.p.m.	Error p.p.m.
0.100	0.121	0.107	+0.007
0.161	0.193	0.168	+0.007
0.161	0.192	0.167	+0.006
0.214	0.275	0.239	+0.025
0.300	0.337	0.291	−0.009
0.375	0.433	0.373	−0.002
0.375	0.425	0.369	−0.006
0.429	0.492	0.424	−0.005
0.500	0.594	0.511	+0.011
0.643	0.728	0.627	−0.016
0.858	0.974	0.839	−0.019
1.072	1.251	1.079	+0.007

Discussions on Some Interfering Substances and Extraction of Nickel. The improvement made to Rollet's method was in concentration of ammonium hydroxide in the final solution to be measured. The reproducibility was increased and the colour due to copper which can not be avoided according to Rollet's method with low ammonium hydroxide concentration, is extinguished, as a result of the improvement. But the presence of a large amount of copper interferes with or decreases the colour development of nickelic dimethylglyoxime, so that if any solution to be analysed contains such an amount of copper as above mentioned, hydrogen sulphide must be used to remove it. Some elements of the hydrogen sulphide group are also necessary to be treated in the same manner as for copper.



Concentration of Cobalt: 31.60 p.p.m.
Stratum length of Cell: 50 mm.

Fig. 3.

Cobalt is another element influencing the nickel determination by nickelic dimethylglyoxime method. The extinction maximum of cobalt dimethylglyoxime solution ranges less than 434 mμ, as is shown by the extinction curve for cobalt (Fig. 3), which is prepared by using Pulfrich photometer in the same manner as for nickel. As its degree in the case of the filter S45, however, is about one-eighteenth of that for nickel, so much consideration is not required for cobalt in the case of mineral springs.

Generally speaking, any element which interferes with the determination by Rollet's method, interferes more or less in the case of this improved method too, but less than the former.

Some tests were made of Sandell's method for extracting nickel from the solutions containing a large amount of iron, which were artificially prepared with the standard solutions of iron and nickel. As shown in Table 2, the results were as satisfactory as Sandell's work.

Table 2.

Ni present γ	Fe added mg.	Ni found γ	Error γ
0	45.5	1.8	+1.8
0	45.5	1.6	+1.6
0	45.5	0.6	+0.6
13.4	45.5	13.8	+0.4
26.8	45.5	25.8	−1.0

Determination of Nickel in Acid Vitriol Springs.

The author determined the nickel content of some acid vitriol springs in Japan, which are given in Table 3. Iron in them was determined gravimetrically or colorimetrically, and for copper the colorimetric or polarographic method was applied. These results are also given in Table 3. Determinations of iron or copper, some of the values thereof are gratefully taken from the papers by K. Kuroda(4)(7), were made with the intention of comparing them with nickel and drawing out something interesting from them.

In Table 4 are shown the percentage of nickel in the total residue and the atomic ratio Ni/Fe, both calculated from analytical results represented in Table 3. The percentage of nickel ranges from 0.00026 to 0.0087% of total residue. The average is 0.0024%, which is far less than either Clarke number for nickel or the mean nickel content of igneous rocks. Clarke number for nickel is 0.01%, whilst F. W. Clarke(8) gave 0.031% Ni for the latter. Even the highest is below them.

As regards the values of the atomic ratio Ni/Fe, it is seen that the maximum is $8.5_9\times10^{-4}$, while the minimum is 0.67×10^{-4}. Any and every value of Ni/Fe, therefore, falls between 0.67×10^{-4} and $8.5_9\times10^{-4}$, the average being $2.6_8\times10^{-4}$. The ratio Ni/Fe for either Clarke number or the mean content of igneous rocks is far more than that of acid vitriol springs described in the present paper; according to Clarke number it is 2.02×10^{-3}, and for igneous rocks, for example, 5.81×10^{-3} is given(9).

It is supposed that the ratio in acid vitriol springs is similar to that in iron sulphide ores such as pyrite or arsenopyrite, although the exact comparison has been difficult so far for lack of accurate determinations of nickel there.

Further generalization, however, must be avoided because of lack of analysis and the partial selection of samples.

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(7) K. Kuroda, this Bulletin, **16** (1941), 69.

(8) F. W. Clarke, "Data of Geochemistry," 5th Ed., p. 29, Washington (1924).

(9) Calculated from data represented in (8).

Table 3.

Sample No.	Mineral spring (Prefecture)	Date when the water was taken	Temp. °C.	pH	Total residue g./l.	Ignition residue g./l.	Ni content γ/l.	Fe content g./l.	Cu content mg./l.
1	Wakesui (Okayama)	Nov. 2, 1934	—	—	85.94	27.39	2080	17.3474	—
2	Anizaka (Okayama)	Nov. 3, 1934	—	2.0	13.281	4.313	172	2.0310	—
3	Sudōriyama (Okayama)	Nov. 3, 1934	—	2.2	4.444	1.444	69	0.5124	—
4	Ōhira-kōzan Naka-kō (Okayama)	Nov. 3, 1934	—	2.2	8.980	6.545	299	0.3391	—
5	Isiyama (Okayama)	Nov. 3, 1934	—	2.0	4.01	1.40	43	0.6096	—
6	Aoki (Yamanasi)	Nov. 11, 1940	—	2.9	15.24	4.29	94	0.6330	4.3
7	Aoki (Yamanasi)	Jun. 1941	—	2.9	22.45	6.34	133	1.6968	14.6
8	Aoki No. 1 (Yamanasi)	Sep. 28, 1941	11.2	4.0	4.18	1.35	44	0.3347	—
9	Aoki No. 2 (Yamanasi)	Sep. 28, 1941	14.0	2.9	11.63	3.39	231	0.9373	—
10	Aoki No. 3 (Yamanasi)	Sep. 28, 1941	14.2	2.9	9.18	2.93	173	0.6275	—
11	Kinkei (Totigi)	May 5, 1940	10.0	2.4	—	—	53	—	1.033
12	Kinkei (Totigi)	Jun. 2, 1941	8.8	2.4	3.62	1.13	62	0.5182	2.2
13	Kinkei a. (Totigi)	Nov. 6, 1942	8.0	2.4	2.230	0.770	194	0.291	—
14	Kinkei b. (Totigi)	Nov. 6, 1942	5.8	2.4	2.123	0.756	170	0.236	—
15	Yoemon-Yu Yunohanazawa (Kanagawa).	Dec. 11, 1938	78.0	2.3	1.72	—	4.4	0.0392	—
16	Tyōsinokuti (Totigi)	Nov. 7, 1942	9.0	3.3	0.3296	0.1569	4.1_5	0.0104	—

Table 4.

Sample No.	Mineral spring (Prefecture)	Date when the water was taken	Ni content % (in total residue)	Fe content % (in total residue)	Ni/Fe (atomic ratio) $\times 10^{-4}$
1	Wakesui (Okayama)	Nov. 2, 1934	0.0024	20.18	1.1_4
2	Anizaka (Okayama)	Nov. 3, 1934	0.0013	15.29	0.81
3	Sudōriyama (Okayama) ..	Nov. 3, 1934	0.0016	11.53	1.2_8
4	Ōhira-kōzan Naka-kō (Okayama)	Nov. 3, 1934	0.0033	3.78	8.5_9
5	Isiyama (Okayama)	Nov. 3, 1934	0.0011	15.20	0.67
6	Aoki (Yamanasi)	Nov. 11, 1940	0.00062	4.15	1.4_1
7	Aoki (Yamanasi)	Jun. 1941	0.00059	7.56	0.75
8	Aoki No. 1 (Yamanasi) ..	Sep. 28, 1941	0.0011	8.01	1.2_5
9	Aoki No. 2 (Yamanasi) ..	Sep. 28, 1941	0.0020	8.06	2.3_5
10	Aoki No. 3 (Yamanasi) ..	Sep. 28, 1941	0.0019	6.83	2.6_2
11	Kinkei (Totigi)	May 5, 1940	—	—	—
12	Kinkei (Totigi)	Jun. 2, 1941	0.0018	14.32	1.1_4
13	Kinkei a. (Totigi)	Nov. 6, 1942	0.0087	13.05	6.3_4
14	Kinkei b. (Totigi)	Nov. 6, 1942	0.0080	11.11	6.8_6
15	Yoemon-yu Yunohanazawa (Kanagawa)	Dec. 11, 1938	0.00026	2.28	1.0_7
16	Tyōsinokuti (Totigi)	Nov. 7, 1942	0.0013	3.16	3.8_0

Details on Some Mineral Springs.

Wakesui, Okayama Prefecture. This mineral water contains a tremendous amount of inorganic salts, most of them being ferric and ferrous sulphates. The present analyses show the total residue, the iron and nickel contents in the water, to be the richest in Japan, as represented in Table 5. The last of these, above all, is the most interesting subject.

Table 5.

	Wakesui (Okayama Prefecture)	The richest content which has been published up to the present		
		Content	Spring (Prefecture)	Determined by
Total residue	85.94 g./l.	77.1 g./kg.	Arima-Sin Onsen (Hyōgo)	Chemical Institute, Faculty of Science, Imperial University of Tokyo.
$Fe^{++}+Fe^{+++}$	17.3474 g./l.	16.214 g./kg. (sp. gr. 1.0683)	Mituisi (Okayama)	The Ōsaka Imperial Hygienic Laboratory.
Ni	2080 γ/l.	68 γ/l.	Kinkei (Totigi)	Chemical Institute, Faculty of Science, Imperial University of Tokyo.

Aoki, Yamanasi Prefecture. The mineral water of Aoki is considered to be a kind of mine water, because it emerges halfway up Mt. Tubakuroatamayama, where a zinc mine is located. In the previous paper, K. Kuroda and the present author(10) reported on it, as containing remarkable amounts of magnesium and zinc. There are three springs in a row, named No. 1, No. 2, and No. 3. The comparison of the conditions and of the constituents of these springs are represented in Tables 6a. and 6b., all samples being taken at the same time. From the view-point of similarity in the temperature, pH value and the percentage in the total residue, it is presumable that springs No. 2 and No. 3 might have the same source, while the water of spring No. 1 might come through a different path, as pH value and other conditons of it differ from the others to some extent. The determination of the heavy water content of this spring shown in Table 6a. is by courtesy of S. Oana, and according to him, it seems that the water of Aoki does not originate in rain water, but in a river, as is inferred from its density difference of $-0.13\ \gamma$.

Table 6a.

Spring	No. 1	No. 2	No. 3
Temp. (–C)	11.2	14.0	14.2
pH	4.0	2.9	2.9
Flow of water (l./min.)	3.7	0.70	0.25
Total residue (g./l)	4.18	11.63	9.18
Ignition residue (g./l.)	1.35	3.39	2.93
Heavy water content (density difference)	—	-0.13γ	—

Table 6b.

	Content in g./l.			Content in % (in total residue)		
	No. 1	No. 2	No. 3	No. 1	No. 2	No. 3
Ca^{++}	0.1258	0.0679	0.0679	3.01	0.58	0.74
Mg^{++}	0.2207	0.3676	0.4689	5.28	3.16	5.11
Fe^{++}	0.3306	0.7452	0.5923	7.91	6.41	6.45
Fe^{+++}	0.0041	0.1921	0.0352	0.098	1.65	0.38
Al^{+++}	0.1523	0.3750	0.3506	3.64	3.22	3.82
Zn^{++}	0.0367	0.1434	0.0561	0.88	1.23	0.61
Ni^{++}	0.000044	0.000231	0.000173	0.0011	0.0020	0.0019
H_2SiO_3	0.0811	0.2232	0.2161	1.94	1.92	2.35

Kinkei, Totigi Prefecture. Analytical results of this mineral water which is typical of the kind, are comparatively abundant, most of them being credited to K. Kuroda. He detected or determined many elements in it, including nickel, by various methods. In one(4) of his papers we find 0.000066 g./l. as the nickel content of this spring, which was determined by the polarographic method. As described before, the value of nickel in the same sample determined x-ray spectroscopically is 68 γ/l., or 0.000068 g./l., and colorimetrically 62 γ/l. (0.000062 g./l.). These results

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(10) K. Kuroda and N. Tanaka, this Bulletin, **17** (1942), 1.

indicate a slight difference between the findings by the three methods, and this fact tends to prove that this water contained 60–70 γ of nickel per litre, and that the values by different methods described above are comparable with each other.

Analytical results of nickel are so far too incomplete for discussing changes of its content, of the percentage in the total residue and of the atomic ratio of iron to nickel, wrought in a long course of time. It may be said, however, that the augment of salinity does not necessarily mean the augment of nickel content, no less the augment of iron and the kind, and also that the nickel content, the percentage in the total residue and the atomic ratio Ni/Fe cover respectively a certain definite range, so far as the same condition continues.

When the water of a spring emerges into the open air it begins to undergo changes. The following data may suggest what changes will occur to the nickel content and its conditions. The waters of sample number 14 and 15 in Tables 3 and 4 were taken at the same time but in different places; the former marked (a.), was taken where the spring emerges and flows down, while the other marked (b.), some twenty meters below (A).

In order to compare the contents of sample (a.) with those of sample (b.), determinations of some elements in them were made, which are shown in Table 7.

Table 7.

Sample No.	13	14
Spring	Kinkei a.	Kinkei b.
Temp. (°C)	8.0	5.8
pH	2.4	2.4
Total residue (g./l.)	2.230	2.123
Ignition residue (g./l.)	0.7700	0.7555
Fe^{++} (g./l.)	0.2257	0.0892
Fe^{+++} (g./l.)	0.065	0.147
Ni (γ/l.)	194	170
As (γ/l.)	637.6	407.2
$Fe^{++}+Fe^{+++}$(g./l.)	0.291	0.236
$(Fe^{++}+Fe^{+++})/Ni \times 10^{-4}$	6.3_4	6.8_6

Sample (b.) was lower in amounts of all constituents except ferric iron, which is remarkably higher. As the water flowed down, it might have been oxidized by air and subsequently its ferric iron content increased rapidly. The depression of total iron content may be ascribed wholly or partly to deposition of an ocherous ferric hydroxide, a noticeable amount of which is always found around the spring.

The following experiment may demonstrate whether such a deposit accompanies nickel or not. If waters of this kind are kept standing in a laboratory, ferric hydroxide precipitates in a while. The distribution of nickel between the precipitate and the filtrate, both produced in such a way, is illustrated by the atomic ratio Ni/Fe in Table 8. As a result, it

Table 8.

	Ni content	Fe content	Ni/Fe (atomic ratio)
Precipitate	less than 2 γ	0.2333 g.	less than 1/116000
Filtrate	53 γ/l.	0.06495 g./l.	1/1230

is found that the greater part of nickel contained in the original water remains in the filtrate, and that nickel concentrates itself there. This phenomenon of Kinkei Mineral Spring may be found likewise in other waters of the kind, and this phenomenon occurring in a laboratory may also occur in nature.

Summary.

The determination method for nickel in mineral springs and some applications of it have been described. The method of extracting nickel was taken from Sandell's report, which is based on the extraction of nickel dimethylglyoxime from ammoniacal citrate solution using chloroform. For the purpose of obtaining an accurate determination, some improvements were made on Rollet's method; as the concentration of ammonium hydroxide in the final solution was made higher, the reproducibility was increased, and therefore, Pulfrich photometer could be employed instead of Duboscq colorimeter. The mean error of the determinations did not exceed ±2 per cent.

Some fifteen samples of acid vitriol springs were analysed in connection with nickel and a few other elements. The richest in nickel was Wakesui, Okayama Prefecture, with the richest total residue and iron content. The percentage of nickel in the total residue ranged from 0.00026 to 0.0087%, and the average is 0.0024%, showing a far higher value against either Clarke number for nickel or the percentage of the mean nickel content of igneous rocks, while the ratio Ni/Fe of the present analyses covers the range from 0.67×10^{-4} to $8.5_9\times10^{-4}$, the average of which is $2.6_8\times10^{-4}$, far less than either 2.02×10^{-3} of Clarke number or 5.81×10^{-3} of igneous rocks.

Finally, details on some springs,—Wakesui, Okayama Prefecture, Aoki, Yamanasi Prefecture, and Kinkei, Totigi Prefecture—have been related. The distribution of nickel between the ocherous ferric hydroxide precipitated from the water of Kinkei and its filtrate has been represented and the answer to the question whether the deposit of ferric hydroxide from waters of the kind accompanies nickel or not, suggested.

The author wishes to express his hearty thanks to Prof. Kenjiro Kimura for his kind guidance in the course of this study. He is also grateful to Dr. Shinya Oana who has given valuable data and most helpful suggestion in the interpretation of the relationship betwen the spring and its origin. Dr. Kazuo Kuroda has given his kind advice and encouragement on all occasions, and permitted the author to include some of his works in the present paper. His generosity is greatly appreciated. The cost of this research has been defrayed from the Scientific Research Encouragement Grant from the Department of Education, to which the author's thanks are due.

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