Distribution of Fluorine in Various States in Terrestrial Waters

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Introduction

Despite an accumulation of the fluorine studies in terrestrial waters, the distribution of the element in its various states remains untouched, a problem particularly important from the viewpoint of its pathology and hygienics. Filling in the lack of knowledge is the primary motive for the present study.

In effect, the author applied Sanchis' method[1] of fluorine determination in four different ways to thirty-nine samples of various kinds of terrestrial waters in Japan and established the distribution of the element in the three following different states:

(A). The fluorine, which can be determined when Sanchis' method is applied to the supernatant water obtained by keeping the sample still until the suspended matter settles down. This comprises the fluoride ions pre-existent as well as those which can be liberated from certain kinds of complexes such as the ions of silicofluoride or aluminofluoride under the conditions of the application of the method.

(B). Other kinds of dissolved fluorine, which can be converted into silicofluoric acid when the supernatant water is condensed into a smaller volume and treated with concentrated sulfuric or perchloric acid.

(C). The fluorine of the suspended matter, which can be converted into silicofluoric acid when the original sample is evaporated nearly to dryness and treated with concentrated sulfuric or perchloric acid.

Experimental

The sample is cautiously shaken so that the suspended matter is uniformly distributed, and then divided into two fractions.

Fraction 1 is left still until the suspended matter completely settles. The supernatant water is siphoned out into a separate vessel. To a measured portion (50-100 ml.) Sanchis' method is applied directly (a). Another portion is made slightly alkaline with sodium carbonate solution and evaporated nearly to dryness. Then it is distilled with the addition of sufficient amounts of solid silver sulfate and powdered quartz or glass, and some 5 ml. of concentrated sulfuric or perchloric acid. The fluorine in the distillate is determined

1) J. M. Sanchis, *Ind. Eng. Chem.*, Anal. Ed., **6**, 134 (1934).

by Sanchis' method[2,3] (b).

Fraction 2 is shaken again and Sanchis' method is applied to a measured portion of the uniformly distributed suspension (c). Another portion of the same suspension is processed similarly as in (b), and the fluorine content of the distillate is finally determined (d).

By the following equations, the individual amounts of the element in the three different states can be calculated from the data, (a), (b), (c), and (d).

Fluorine in state (A) (a)
" " " (B) (b)—(a)
" " " (C) (d)—(b)

Results

The samples vary one from another in the distribution of the element in its three different states, but can be classified into the four following states, as given in Table I.

TABLE I

DISTRIBUTION OF VARIOUS FORMS OF FLUORINE IN TERRESTRIAL WATERS

Sample	Source	a mg/L	b mg/L	c mg/L	d mg/L
	Waters of Type 1, (a=b=c=d)				
No. 1	Well, Gamagori, Aichi Pref.	0.15	0.15	0.15	0.15
2	Well, Gamagori, Aichi pref.	0.15	0.15	0.15	0.10
3	Well, Oi, Gifu Pref.	0.25	0.35	0.30	0.30
4*	Well, Kasamatsu, Gifu Pref.	0.45	0.50	0.45	0.45
5*	Well, Sendanbayashi, Gifu Pref.	3.8	3.9	3.8	3.8
6	Well, Sendanbayashi, Gifu Pref.	0.10	0.10	0.10	0.10
7	Well, Sendanbayashi, Gifu Pref.	0.10	0.10	0.10	0.10
8	Well, Kamioka, Gifu Pref.	0.10	0.10	0.10	0, 10
9	Spring "Kikusuisen", Yōrō, Gifu Pref.	0.25	0.30	0.25	0.30
10	Thermalsprings "Sakakibara-onsen", Sakakibara, Mie Pref.	3.5	3.5	3.5	3.4
11	The botten water of Lake "Kizaki-Ko", Kitaazumi, Nagano Pref.	0.40	0.35	0.40	0.40
12*	River "Wada-gawa", Shimizubara-mura, Nagano Pref.	0.75	0.75	0.75	0.75
13(a)	River "Yumata-gawa" just up its confluence with River "Mizumata-gawa", Nagano Pref.	2.0	2.0	2.0	2.1
14	River "Toyo-kawa" Miya, Aichi, Pref.	0.45	0.40	0.45	0.40
15	River "Sugo-gawa", Okazaki, Aichi Pref.	0.10	0.10	0.10	0.10
	Waters of Type 2, (a=c<b=d)				
No. 16	Well, Gamagori, Aichi Pref.	0.25	0.50	0.25	0.50
17*	Well, Higashikata, Ehime Pref.	0.35	0.60	0.35	0.55
18*	Well, Ōsato, Aichi Pref.	1.7	2.1	1.6	2.1
19	Thermalsprings "Kinryu-onsen" Nagashima, Gifu Pref.	2.0	2.4	1.9	2.4
20	River, Shimecha, Hokkaido.	0.20	0.30	0.15	0.25
	Waters of Type 3, (a=c<b<d)				
21*	River "Takase-gawa", Motoki, Tokiwa-Mura, Nagano Pref.	0.70	1.0	0.75	1.1

2) H. H. Willard and O. B. Winter, *Ind. Eng. Chem.*, Anal. Ed., **5**, 7 (1933).

3) H. Okuno, *J. Faculty Sci., Hokkaido Imp. Univ.*, **3**, (3), 101, (1942).

Waters of Type 3, (a=c<b<d)

Sample	Source	a mg/L	b mg/L	c mg/L	d mg/L
No.22(b)	Well, Sakae-machi, Nagoya City.	0.15	0.40	0.15	1.2
23*	Well, Yokomichi, Ehime Pref.	0.30	0.45	0.30	0.60
24	River "Aki-gawa", Ōi, Gifu Pref.	0.30	0.40	0.25	0.75
25	River "Ibi-gawa", Wakino, Gifu Pref.	0.10	0.30	0.15	0.50

Waters of Type 4, (a=b=c<d)

Sample	Source	a mg/L	b mg/L	c mg/L	d mg/L
No. 26	Well, Ōi, Gifu Pref.	0.35	0.40	0.40	0.90
27	Thermalsprings "Yunoyama-Onsen", Yunoyama, Mie Pref.	12.0	12.5	12.0	20.0
28	The surface water of Lake "Kizaki-ko", Kitasazumi, Nagano Pref.	0.40	0.35	0.40	0.60
29	Swamp "Nakano-sawa", Tokiwa-mura, Nagano Pref.	0.60	0.65	0.60	0.90
30	River "Kago-gawa" just up its confluence with River "Takase-gawa", Nagano Pref.	0.25	0.25	0.25	0.70
31	River "Kashima-gawa", Ōide, Nagano Pref.	0.25	0.25	0.25	0.75
32	River "Titi-gawa" at the foot of Mt. Shiroyama, Nagano Pref.	0.40	0.45	0.45	0.60
33*	River "Takase-gawa", Kutsukake, Tokiwa-mura, Nagano Pref.	0.75	0.80	0.75	1.25
34(c)	River "Takase-gawa" near Kuzu-onsen, Nagano Pref.	2.2	2.2	2.2	3.6
35*	River "Takase-gawa" about 2.5 km. down streem from Kuzu-onsen, Nagano Pref.	0.80	0.80	0.85	1.6
36	River "Mizumata-gawa" just up its confluence with River "Yumata-gawa", Nagano Pref.	2.1	2.0	2.1	2.5
37	River "Kiso-Gawa", Enakyo, Gifu Pref.	0.25	0.25	0.25	0.55
38	River "Togi-Gawa", Togi, Ishikawa Pref.	0.30	0.30	0.25	0.40
39	Water-fall "Yōrō-no-taki". Yōrō, Gifu Pref.	0.30	0.30	0.35	0.50

* Cases of mottled enamel of teeth were found among the people, usually using this water for drinking.

(a), (c) Sample contaminated with thermalsprings water.

(b) Turbid.

Type 1. This type of water dissolves one or more kinds of the ions belonging to (A), but contains no other fluorine compound either dissolved or suspended.

Type 2. This type of water contains the fluorine of (B) in addition to one or more kinds of the ions belonging to (A), but no suspended fluorine compound.

Type 3. This type of water contains one or more kinds of the ions belonging to (A) as well as the fluorine belonging to (B) and (C).

Type 4. This type of water contains one or more kinds of the ions belonging to (A) as well as fluorine (C), but none of (B).

From the result it may be seen that the

statistic exploration of fluorisis cases can be successful only when it is done simultaneously with a differential determination of fluorine in various states in the water, which if ever has seldom been the case in the foregoing studies.

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