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## HYDROLOGIC PROPERTIES AND ORIGIN OF THE SULFURIC WATER OF THE SPLIT BATHS

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# HYDROLOGIC PROPERTIES AND ORIGIN OF THE SULFURIC WATER OF THE SPLIT BATHS

by

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This paper has grown out of the need to have the fundamental chemical properties of the sulfuric water of the Split Baths systematically examined during a year's period and thus to obtain a complete picture of the hydrology of the water emerging from this spring, which would enable us possibly to solve the questions of its origin and of salt content.

Our work was mainly carried out during the period of time extending from 14th April 1952 to 28th August 1953, but occasional examinations occurred also after August 1953. The contents of chlorides and sulfured hydrogen were determined in the course of our investigations. At the same time temperatures of water were measured at the spring and the port alike, and the temperature of the air above the spring was also recorded. The chlorinity of the spring water was determined side by side with the chlorinity of the sea water in the port. Moreover a few informative analyses were made in order to have an idea of the content of  $\text{PO}_4$ , total ammonia, iron, and pH of the spring water. Analyses of sulfates and total sulfur contained in the water of the spring took also place for a period of time, in the summer 1953.

## *Methods*

The *chlorides* were determined by means of Mohr's method, i. e. by the titration with  $\text{Ag NO}_3$  and with  $\text{K}_2 \text{CrO}_4$  as indicator, using Knudsen's normal water. When applying this method, the bromides actually present and the iodides possibly present are included, then, in the chlorides.

*Sulfured hydrogen* and other *reductive matter* were determined in the following way. Samples of water were taken in oxygen bottles (Winkler bottles of known volume, amounting to about 250 ml, with an obliquely ground stopper).



(a) A quantity of about 0,1 gr  $\text{Cd Cl}_2$  (a nip of knife) is put into an Erlenmeyer flask. Then the water which is being examined is added, followed by a few droplets of N  $\text{Na HCO}_3$  solution, whereupon the mixture is stirred (not shaken) and filtrated through a dry filtering paper on a quantitative funnel.

An aliquot part of the filtrate is taken (e. g. 100 ml) to which 10 ml of N/100  $\text{J}_2$  and 1 ml of concentrated  $\text{HCl}$  are added and then covered with glass in order to prevent the  $\text{J}_2$  vapours to escape. After 30 minutes the remaining  $\text{J}_2$  is titrated with N/100  $\text{Na}_2 \text{S}_2 \text{O}_3$  with 0,2% starch solution as indicator. From the volume of thiosulfate we find out the amount of the consumed  $\text{J}_2$  on reductive matter without  $\text{H}_2\text{S}$ .

(b) The liquid contained in one sample bottle is poured off into the Erlenmeyer flask and a sufficient quantity of the N/100  $\text{J}_2$  solution is added to enable the water to retain its dark brown colour deriving from the surplus of  $\text{J}_2$  (usually 40 ml). Then 1 ml of concentrated  $\text{HCl}$  is added to the liquid which is covered with a watch glass and after a quarter of an hour the remaining  $\text{J}_2$  is titrated with a N/100 solution of thiosulfate.

From the volume of thiosulfate we find out the total of the consumed  $\text{J}_2$  on total reductive matter.

The difference between the consumption of  $\text{J}_2$  during the two procedures (b minus a) shows the amount of  $\text{J}_2$  consumed for the destruction of  $\text{H}_2\text{S}$ . One ml of N/100  $\text{Na}_2\text{S}_2\text{O}_3$  solution corresponds to 0,17043 mg  $\text{H}_2\text{S}$ . The normality of the  $\text{J}_2$  solution is determined as follows. A stock of sea water of about 2 to 3 litres is taken to which some 5 ml of n/100  $\text{J}_2$  solution is added from time to time, the water being thus light yellowish in colour.

(A) A quantity of 50 ml of this »stock-water« is titrated with thiosulfate with starch solution as indicator.

(B) 10 ml of our N/100  $\text{J}_2$  solution is added to the 50 ml of »stock-water« and this solution is titrated. The difference B-A gives the consumption of thiosulfate pro volume of the  $\text{J}_2$  solution and thence the normality of our N/100  $\text{J}_2$  solution.

The normality of thiosulfate was determined by means of the N 10  $\text{K}_2\text{Cr}_2\text{O}_7$  standard solution. A quantity of 3 ml N/10 solution of potassium bichromate, 2 ml KJ 10% solution, 1 ml of concentrated  $\text{HCl}$ , and 50 ml of distilled water is put into a bottle having a ground stopper. The bottle is then stopped, shaken, and left for 30 minutes to wait in order to obtain  $\text{J}_2$  completely free. Thereupon the substance is titrated with our N/100 thiosulfate solution. The consumption of thiosulfate gives the required normality of thiosulfate solution.



The amount of *sulfates* was determined in the following way. A quantity of about 50 ml of spring water was exactly weighed. Then 0,5 ml of concentrated HCl and 150 ml of distilled water were added and brought to the boiling point. At the same time a quantity of 10 ml of 5% solution of  $\text{Ba Cl}_2$  was poured off into 30 ml of distilled water and separately brought to the boiling point, then *quickly* added to the former liquid and allowed to boil a few minutes. After being removed from the fire, the liquid was left to wait until the next day when it was filtrated through a Schleicher-Schüll No. 589, blue ribbon («Blauband») and the filter and sediment washed with boiling distilled water until the chloride reaction disappeared. Thereupon the filtering paper containing  $\text{BaSO}_4$  was glowd and weighted until the constant weight.

In order to obtain the amount of *total sulfur* some  $\text{Cd Cl}_2$  solution was poured off into the Erlenmeyer flask and weighed. Then a quantity of 50 ml of the sulfuric water sample was added and weighted again. To this liquid 0,5 ml of concentrated HCl and 9 ml of  $\text{Br}_2$  water were added and while left waiting for about 15 minutes, the solution was slightly stirred. Thereupon a quantity of 150 ml of distilled water was poured in and boiled as to cause  $\text{Br}_2$  to escape, and finally the precipitation of  $\text{Ba SO}_4$  was obtained by means of  $\text{Ba Cl}_2$  as above. Beside the free sulfates, all the organic sulfurous compounds, free sulfur produced by bacteria,  $\text{H}_2\text{S}$ , and the products of its partial oxidation, are included in the total sulfur.

The *averages of temperature* and the *averages of salinity* were obtained by the integration of annual curves by means of a planimeter.

Some of the computations were made by means of a slide-rule.

In this paper the name for the Split Bath Sulfuric Spring has been sometimes shortened e. g. in «Sulfuric spring», «Split Baths», or «Thermal Baths». In the same way the water of this spring is sometimes named as «sulfuric water», «spring water», or as «water of the Thermal Baths».

The author is greatly indebted to Dr Dinko Mirošević, director of Split Thermal Baths, for encouraging these investigations and his kind giving of information and facilities during the work. His thanks are also due to Prof. Dr. S. Miholić (Zagreb) and Prof. A. Vuletić (Split) who have seen the manuscript and made useful remarks. Useful assistance in the preparation of some of the analyses was also rendered by abs. techn. chem. Joško Špan, students of techn. chem. Nada Ružić, Ivo Pavičić, Igor Armada, and technical assistant Davor Ratković, to whom the author expresses his thanks.

### Results:

The data resulting from the investigations carried out from April 1952 to May 1953 are shown in Table I, while the data obtained during the Summer 1953 are contained in Table II.

*The chlorinity of the spring water.* It is evident from the data shown in Table I that during the year 1952/53 the chlorinity of the spring water was ranging from a maximum reaching up to 19,48 pro mille Cl (18. XII.) to a minimum amounting to 1,33 pro mille Cl (12. I.) — see picture 1. If the period of the profuse freshwater influx into the spring, occurring between December 8th 1952 and March 10th 1953, is left aside, the chlorinity of the spring water was all the time higher than 13,75 pro mille Cl. The chlorinity of the spring water was above 16 pro mille Cl during the period extending from July to December 1952, and in April 1953. From April 14th 1952, when the investigations were started, to December 9th 1952 the average contents of chlorides amounted to 16,24 pro mille,

Table 1

Results of observations made from April 1952 to May 1953, relative to Split sulfuric water and sea water in the port of Split.

Date	Air		Sulfuric water of the Split Baths					Water from the port of Split	
	Temp. C°	Temp. C°	Consumption of J <sub>2</sub> n/100/l		H <sub>2</sub> S mg/l	Cl g/kg	O <sub>2</sub> ml/l	Temp. C°	Cl g/kg
			for H <sub>2</sub> S	for other reductive matter					
<i>1952.</i>									
14. IV.	16,10	18,45	23,78	8,46	4,05	13,75	—	15,34	15,07
21. IV.	20,98	18,65	20,12	9,50	3,43	14,27	—	16,42	18,30
28. IV.	21,06	19,50	51,08	13,60	8,70	—	—	18,00	—
12. V.	20,64	19,90	116,05	25,95	19,78	14,98	—	—	17,74
20. V.	17,40	20,40	195,17	1,98	33,26	—	—	16,40	20,32
26. V.	19,60	20,45	134,35	3,95	22,88	15,20	—	16,14	20,67
2. VI.	22,70	20,58	171,58	6,62	29,25	15,16	0,0	20,08	19,42
9. VI.	22,15	20,78	179,89	8,91	30,60	15,21	—	19,65	15,07
16. VI.	27,14	20,93	149,78	14,52	25,52	15,90	—	22,90	19,24
23. VI.	27,50	20,98	116,75	6,69	19,88	16,25	—	24,30	16,25
30. VI.	26,95	21,10	98,35	14,45	16,77	15,85	—	22,40	20,63
22. VII.	30,00	21,50	140,32	14,45	23,85	16,44	—	26,40	20,32
5. VIII.	—	21,60	129,91	6,39	22,11	—	—	24,50	—
27. VIII.	25,40	21,60	152,68	8,32	26,01	17,27	0,0	23,85	19,88
15. IX.	26,00	22,70	137,54	6,95	23,43	17,32	—	22,30	20,94
30. IX.	23,90	23,75	115,80	4,00	19,74	16,39	—	21,80	19,73
13. X.	14,55	21,40	119,71	9,69	20,40	16,91	—	19,80	20,51
27. X.	16,20	22,40	177,31	6,19	30,25	16,38	—	18,40	13,32
12. XI.	12,40	20,90	114,22	12,78	19,51	16,59	—	14,60	19,64



(Table 1 continued)

Date	Air		Sulfuric water of the Split Baths					Water from the port of Split	
	Temp. C°	Temp. C°	Consumption of J <sub>2</sub> n/100/1 for H <sub>2</sub> S for other reductive matter		H <sub>2</sub> S mg/l	Cl g/kg	O <sub>2</sub> ml/l	Temp. C°	Cl g/kg
26. XI.	14,20	21,70	161,35	19,05	27,40	—	—	14,60	—
8. XII.	12,20	21,10	65,62	17,58	11,18	19,48	0,0	13,40	20,40
11. XII.	—	—	—	—	—	5,49	—	—	—
16. XII.	14,60	16,80	0,00	0,00	0,00	4,50	—	—	—
29. XII.	13,50	14,90	0,00	0,00	0,00	2,20	—	12,10	15,17
1953.									
12. I.	8,50	14,30	0,00	0,00	0,00	1,33	4,88	10,80	19,90
19. I.	8,80	14,60	0,00	0,00	0,00	1,95	5,13	11,60	19,55
26. I.	8,50	15,30	0,00	0,00	0,00	2,72	4,04	11,10	19,01
2. II.	8,90	16,40	0,00	0,00	0,00	6,30	1,61	10,90	19,47
9. II.	1,00	16,80	0,00	0,00	0,00	12,23	1,50	10,10	20,20
16. II.	9,80	16,25	0,00	0,00	0,00	13,59	1,13	11,20	19,85
23. II.	12,20	16,75	0,00	0,00	0,00	12,88	0,75	10,20	17,53
10. III.	8,40	19,90	51,10	6,17	8,81	14,71	0,00	11,40	20,75
16. III.	9,80	20,45	107,29	1,16	18,28	15,44	0,00	10,80	20,38
23. III.	13,00	20,65	89,58	17,52	15,27	15,40	—	11,95	19,56
30. III.	15,10	20,85	128,13	1,07	22,00	15,83	—	13,05	19,42
5. IV.	15,25	20,60	90,39	3,26	15,48	16,04	0,00	15,25	17,92
13. IV.	17,10	21,40	118,53	1,37	21,90	16,17	—	14,10	15,93
16. IV.	15,10	20,40	115,40	0,00	19,66	16,44	—	13,40	18,50
17. IV.	13,65	20,18	96,28	0,72	16,42	16,82	—	14,00	19,48
18. IV.	16,40	20,00	86,44	0,36	14,74	16,08	0,00	14,45	18,86
19. IV.	17,84	19,95	77,50	0,00	13,21	15,65	—	15,30	19,65
20. IV.	18,00	20,25	94,20	0,00	16,05	16,23	—	15,30	19,93
21. IV.	18,70	20,20	94,88	9,47	16,17	16,50	—	15,60	20,07
22. IV.	17,75	20,25	102,32	6,68	17,43	16,47	0,00	15,80	17,87
23. IV.	18,10	20,50	109,56	0,34	18,66	16,52	—	16,00	14,76
27. IV.	17,20	20,95	114,39	1,06	19,48	16,27	0,00	—	—
28. IV.	18,60	20,80	130,15	0,15	22,18	16,50	—	20,40	12,73
29. IV.	18,50	20,90	146,53	7,20	24,97	16,50	—	18,95	19,63
4. V.	18,20	21,10	125,24	5,38	21,34	16,39	—	17,60	19,28

but when the salinity of the spring water decreased (from about December 9th 1952 to April 14th 1953), the mean amounted to 9,20 pro mille Cl only. The average content of chlorides in the water of this spring amounted to 13,80 pro mille Cl during the period extending from April 14th 1952 to May 4th 1953. But if we take the data from Table 4, covering the Winter of 1953/54, when there was no drop of salinity in the spring water, and if we put them together with the data covering the remaining part of the year (from Table 1), we shall see that the average chlorinity of the spring water in its normal saline aspect reached up to 16,26 pro mille Cl.

The chlorinity of the sea water in the port of Split (in front of the Naval Officers' Club), at the same time, permanently showed higher values of chlorides in comparison to those recorded for the water of the Thermal Baths (with the exception of 4 out of 46 findings). The maximum value of chlorides in the port water was found on September 15th 1952, being as high as 20,94 pro mille Cl, while the minimum value was found on April 20th 1953, amounting to 12,73 pro mille Cl. For a period covering more than a year's time the average amount of chlorides found in the water of the port of Split was 18,97 pro mille Cl.

During the Winter 1952/53 the fluctuations of chlorinity of the spring water were, then, considerably bigger than those recorded for the sea water of the Split port.

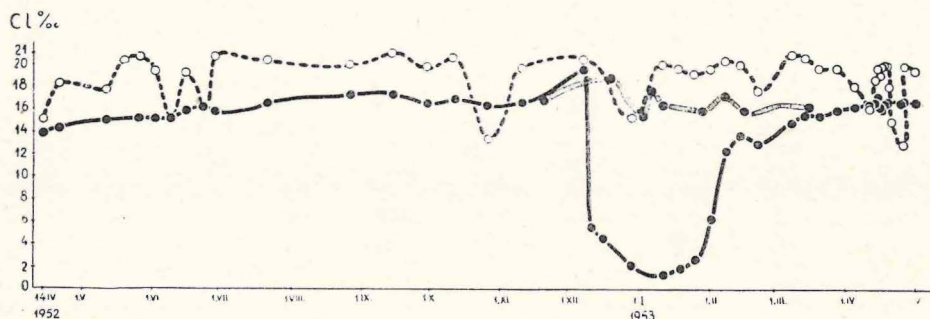


Fig. 1. — Annual fluctuation of chlorinity in the Split area. — White dots for Split Port water, black dots for Split sulfuric water. The short gray line connecting some of the black dots shows the chlorinity of the sulfuric water during the period from November 1953 to March 1954.

The causes of that decrease of chloride concentration in the water of the Sulfuric Spring will be dealt with later. The relative stability of chloride contents recorded in the course of our investigations for the sulfuric water during the Spring, Summer, and Autumn 1952, may be unbalanced by abundant rainfalls, as evident from the data covering July 1953 (Table 2). But it would not be correct to deduce that big decreases of salinity, of the extent as found from December 9th 1952 onward, are regular yearly occurrences. On the contrary, such a decrease did not occur either in December 1953 or in January and February 1954, as shown by our observations and measurements covering that period.

*Temperature.* The maximum temperature of the Sulfuric Spring water amounted to 23,75° C (September 30th) and the minimum one was found



to be  $14,30^{\circ}\text{C}$  (January 12th). The annual mean amounted to  $20,00^{\circ}\text{C}$ . (Table 1 and fig. 2). By considering the data obtained in the Winter 1953/54 until the 17th of March 1954 when there was no fall of salinity and no fall of temperature of the spring water, the annual mean temperature of Spring water changes to  $21,06^{\circ}\text{C}$ .

The *air temperature above the spring* (which is situated in a locality shut in on all sides by houses, but not covered) yielded a maximum of  $30,00^{\circ}\text{C}$  (July 22nd 1952), which *preceded* the maximum temperature of the spring water for two months. The minimum temperature of the air amounted to  $1,0^{\circ}\text{C}$  (February 9th 1953), and appeared about a month *later* than the minimum temperature of the spring water.

The measurements of the *sea water* in the port yielded a maximum temperature of  $26,40^{\circ}\text{C}$  (July 22nd 1952) and a minimum temperature of  $10,10^{\circ}\text{C}$  (February 9th 1953). The annual mean temperature amounted to  $17,20^{\circ}\text{C}$ .

The maximum temperature of the sea water in the port of Split *preceded* the maximum temperature of the water of the Sulfuric Spring for more than two months, while the minimum temperature of the sea water came for about one month *after* the minimum temperature of the spring water.

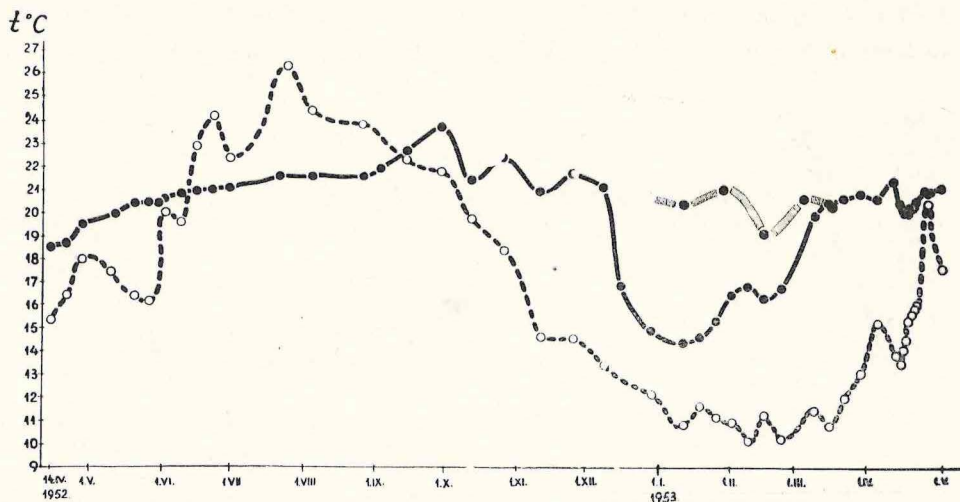


Fig. 2. — Annual oscillation of temperature in the Split area. — White dots for Split Port water, black dots for Split sulfuric water. The short gray line connecting some of the black dots shows the temperature of the sulfuric water between January and March 1954,

While the maxima and minima of temperatures of the water in the port and of the air concurred during the Winter 1952/53, the maximum temperature of the spring water came after them for more than two months and its minimum temperature preceded them for about one month. It seems that this early occurrence of the minimum temperature of the Sulfuric Spring water was caused by the influx of larger quantities of fresh water of a relatively low temperature during the period of particularly abundant rainfalls in the late Autumn 1952, and just a few days before the spring water suddenly grew cooler in the first half of December 1952. The sudden presence of that freshwater of a low temperature made itself felt in a number of ways: it caused the temperature curve to sink rapidly; the minimum temperature of the spring water to appear all of a sudden; the chlorinity of the spring water to grow less at once; sulfuretic hydrogen to disappear from the spring water and oxygen to appear in it.

*Sulfuretic hydrogen.* The amount of  $H_2S$  in the spring water was ranging from a minimum 0,00 mg/l at the end of 1952 at the beginning of 1953 to a maximum 33,26 mg/l on May 20th 1952. (The maximum involved a consumption of iodine amounting to 195,17 ml  $J_2$  N100).  $H_2S$  was present in quantities larger than 10 mg/l, corresponding to 58, 70  $J_2$  N/100 solution pro litre during the periods of time extending from May to December 1952, and from the middle of March to the beginning of May

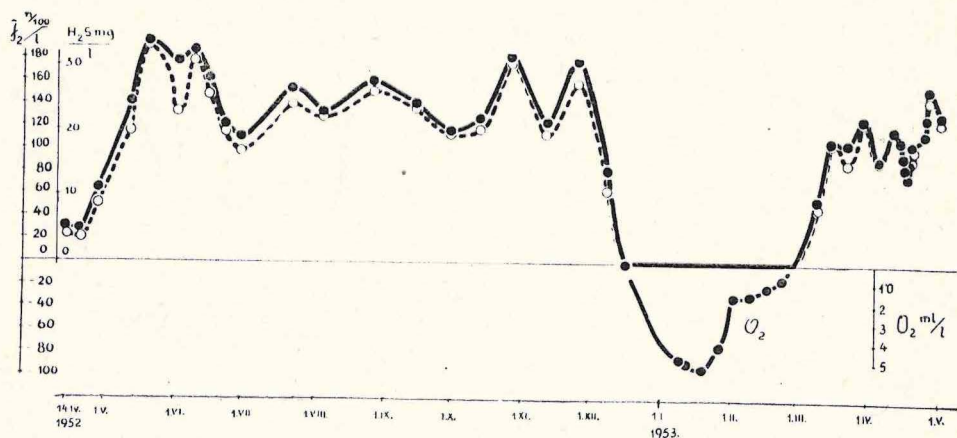


Fig. 3. — Annual fluctuations of  $H_2S$  content (white dots), of total reductie matter reacting with  $J_2$  — solution (black dots), and of  $O_2$  (black dots) in the sulfuric water of Split.



1953. (Table 1 and fig. 3). The amount of other reductive matter, absorbing the iodine solution — expressed as consumption of ml  $J_2$  N/100 pro litre — ranged from a maximum 29,95 ml to a minimum 0,00 ml. The amount of these reductive water shows a close concurrence with the occurrence of sulfuretic hydrogen in the spring water, so when  $H_2S$  was absent there was no reductive matter either. (Table 1 and fig. 3). We are obviously met here by some products of a partial oxidation of sulfuretic hydrogen such as thiosulfates, sulfites. etc.

*Oxygen.* No  $O_2$  was present in the water of the Sulfuric Spring during the Summer and Autumn 1952. Oxygen was found in this water only after the disappearance of  $H_2S$ .

Oxygen was found on January 12th for the first time since our investigations were started in a quantity of 4,88 ml  $O_2$ /l, corresponding to a 58,4% saturation of water with oxygen.  $O_2$  in the spring water was present until February 22nd 1953. During the month of December 1952 and at the beginning of January 1953, however, the amount of  $O_2$  was not determined. The maximum content of  $O_2$  — amounting to 5,13 ml/l — was found on January 19th, corresponding to a saturation of 63,90%. The occurrence of oxygen in the water of the sulfuric springs goes hand in hand with the period of the lowest chlorinity of that water. (Table 1 and fig. 3). This was caused, in our opinion, by an abundant influx into the system of the spring of surface fresh water of a relatively lower temperature and rich in oxygen.

*Sulfates.* A number of analyses of sulfates, total sulfur, and chlorinity of the spring water were made during the Summer 1953. Comparative analyses of sulfates and chlorides contained in the water of the adjoining Bay of Kaštela were also made (Table 2).

The amounts of sulfates ( $SO_4$ ) ranged between the minimum 1,4414 gr/kg and the maximum 2,2932 gr/kg of the spring water and the amounts of total sulfur (S calculated as  $SO_4$ ) amounted to 1,4509 (minimum) and 2,4672  $SO_4$  gr/kg (maximum) of that water. These varying amounts of sulfates and total sulfur went along with the fluctuation of chloride contents, the ratio  $SO_4/Cl$  being 0,1363 to 0,1443 for the free  $SO_4$  in the spring water averaging with 0,1386 for twelve analyses, and 0,1411 to 0,1528 for the free sulfur averaging with 0,1448, in the same water, expressed as sulfate. The ratio  $SO_4/Cl$  for sulfates contained in the sea water of Kaštela Bay amounted to 0,1387.

Table 2

Content of sulfates and total sulfur in the Split sulfuric water as found in Summer 1953.

Date	Cl g/kg	Free sulfate		Total sulfur	
		SO <sub>4</sub> g/kg	SO <sub>4</sub> /Cl	SO <sub>4</sub> g/kg	SO <sub>4</sub> /Cl
10. VII. 53	9,99	1,4414	0,1443	1,4509	0,1451
21. VII.	13,78	1,8895	0,1372	1,9593	0,1422
24. VII.	12,67	1,7532	0,1383	1,8159	0,1433
28. VII.	15,40	2,1085	0,1369	2,2246	0,1444
31. VII.	16,06	2,2047	0,1373	2,2928	0,1428
3. VIII.	16,40	2,2745	0,1386	2,3341	0,1423
10. VIII.	15,89	2,1881	0,1372	2,2584	0,1421
13. VIII.	16,53	2,2533	0,1363	2,3323	0,1411
17. VIII.	16,57	2,2932	0,1384	2,4134	0,1456
20. VIII.	16,29	2,2882	0,1404	2,3991	0,1472
24. VIII.	15,59	2,1510	0,1411	2,3823	0,1528
27. VIII.	16,56	2,2800	0,1376	2,4672	0,1490
Water from Kaštela Bay 8.VII. 19533.	19,98	2,7728	0,1387		

Note: All these results are based on double analyses.

#### *Other data relative to the water of the Sulfuric Spring.*

The pH was 7,46 (April 28th 1952) and 7,35 (November 12th 1952). Sulfuretic hydrogen was present in both cases. It is instructive to note that the pH of the water of the Adriatic Sea, which is well aerated, amounts to 8,20, whereas the pH of the sea water which contains H<sub>2</sub>S, as e. g. the bottom water of the Little Mljet Lake amounts to about 7,50 (according to the yet unpublished data obtained by the author).

The amounts of free iron were 64 mg/t on September 15th 1952 and 47 mg/t on March 10th 1953.

The amounts of total phosphorus were 35,0 mg/t on November 12th 1952 and 57,0 mg/t on December 29th 1952. Free phosphates were investigated only once and the amount ascertained was 1,6 mg/t P — PO<sub>4</sub> (November 12th 1952).

An analysis was also made to find out the N-NH<sub>3</sub> content and it resulted in 150 mg/t.

#### DISCUSSION OF RESULTS

The following conclusions illustrating the character of the water of the Thermal Baths at Split, can, in our opinion, be drawn from our findings.

In its normal saline aspect, the water of the Sulfuric Spring is made up of two components:



a) of sea water, and b) of a mineral water poor with chlorides, belonging to the type of water found at the spring of Slana Jaruga (Glavice) in the vicinity of Sinj (Miholić, 1952, a). When the water of the Sulfuric Spring grows less salty, a third component joins the other two, i. e. c) surface freshwater.

The first two components, mingled together, come into contact with a deposit of some fossil organic matter such as bitumen, asphalt, lignite. The Cretaceous and Eocene strata along the eastern coast of the Adriatic are frequently bituminous, particularly in their lower parts (Miholić, 1952, b), and layers of asphalt are not uncommon in this region. The origin of  $H_2S$  in the water of the sulfuric spring might be explained by the reduction of sulfates in this water by means of that organic matter stored in its land deposits under the sea level, this making the contact with sea water possible and causing a wet combustion. (The vein, which normally conveys the mineral water (b) comes to the place containing sea water where the two waters mingle and proceed to the deposit where wet combustion takes place.)

The mineral water (b) component amounts to 1/9 of the spring water at the time of its normal aspect. The mineral water (b) is rich with soluble sulfates even before it mingles with the sea water. These conclusions are drawn from the following facts.

The total sulfur ratio  $SO_4/Cl$  — (sulfur expressed as sulfate) of the spring water is somewhat higher than the ratio  $SO_4/Cl$  for the sea water of the Bay of Kaštela (Table 2). There are data at our disposal resulting from analyses of the  $SO_4$  content in the waters of both the high and inshore Adriatic. The mean obtained from 31 analyses amounted to  $SO_4/Cl$  — 0,1382. The maximum value of the ratio  $SO_4/Cl$  in the Adriatic was 0,1398 (Station »Hvar« 1/22).

(From the paper in preparation Buljan M.: »Sulfates in the Adriatic«.)

This surplus of sulfur in the spring water, when compared with sea water, makes it clear that the mineral water contains its own sulfate possibly originating from a deposit of gypsum not infrequent in central Dalmatia, or from some secondarily formed gypsum resulting from the oxidation of pyrite. This idea has already been put forth by Vierthaler, but Kerner (1917) did not attach much likelihood to it. Our investigations, however, have positively demonstrated the occurrence of sulfate intake from the mainland by the Sulfuric Spring at Split. The surplus value of  $SO_4/Cl$  for the sea water in the Bay Kaštela, and the difference

Table 3

Reckoning of quantities of sulfates conveyed into Split sulfuric water by the mineral water component

Date	Cl gr/kg in spring water	Cl gr/kg in the sea water	In the sulfuric water			% of mineral water in Spring water	SO <sub>4</sub> g/l conveyed by mineral water
			SO <sub>4</sub> gr/kg of marine origin	Total S as SO <sub>4</sub>	SO <sub>4</sub> conveyed by mineral water (5-4)		
1	2	3	4	5	6	7	8
9. VII. 1953		20,70					
10. VII.	9,99		1,386	1,4579	0,071 <sub>9</sub>	52	0,138
19. VII.		20,83					
21. VII.	13,78		1,905	1,9593	0,048 <sub>3</sub>	34	0,142
23. VII.		20,97					
24. VII.	12,67		1,760	1,8159	0,055 <sub>9</sub>	40	0,139
26. VII.		20,87					
28. VII.	15,40		2,130	2,2246	0,094 <sub>6</sub>	26	0,364
2. VIII.		20,81					
3. VIII.	16,40		2,270	2,3341	0,114 <sub>1</sub>	21	0,543
7. VIII.		20,86					
10. VIII.	15,89		2,201	2,2584	0,057 <sub>4</sub>	24	0,239
13. VIII.	16,53		2,290	2,3323	0,042 <sub>3</sub>	21	0,201
17. VIII.	16,57		2,292	2,4134	0,121 <sub>4</sub>	21	0,578
20. VIII.	16,29		2,260	2,3991	0,139 <sub>1</sub>	22	0,631
24. VIII.	15,59		2,160	2,3823	0,222 <sub>3</sub>	26	0,855
25. VIII.		21,00					
27. VIII.	16,56		2,290	2,4672	0,177 <sub>2</sub>	22	0,805
28. VIII.		21,03					

Note: The data given in column 3 result from measurements of sea water chlorinity at the head of the pier in front of the Institute. The data contained in column 4 were obtained on the basis of the ratio  $SO_4:Cl=0,1387$  for the water of the Kaštela Bay.

between the amounts of chlorinity found in the water of the Sulfuric Spring on the one hand and in the inshore sea water along the Marjan Peninsula on the other hand, enabled us to find out in what per cent. the mineral water is present in the water of the Split Sulfuric Spring, and what is the amount of gypsum conveyed by it (Table 3). So for instance, on July 10th, the sulfate from the mineral water (b), expressed in gypsum  $CaSO_4 \cdot 2H_2O$ , amounted to 0,19 g/l (minimum value found in



Summer 1953), and on August 24th the amount of gypsum was 1,20 g/l (maximum value found during the period of our investigations). By assuming that the temperature of the mineral water, intaken by the Split Sulphuric Spring, was about 14° C, it then saturated with nearly 10%, respectively 62% with regard to its content of gypsum.

It is probable however that a part of the surplus sulfate derives from the reductive matter in the place of wet combustion.

A slow combustion of organic matter either in the total absence of free oxygen or in the presence of very scarce quantities of it is performed in such a place of wet combustion. This process is made possible by the reduction of oxygen from sulfate, as it was found to occur in the Little Mljet Lake and in the Rogoznica Lake (Buljan, 1952), where that oxidoreductive process results in the oxidation of organic matter and in the formation of H<sub>2</sub>S. This phenomenon occurs in the sea under definite hydrographic circumstances only, i. e. when the water is insufficiently aerated, as for instance in the already mentioned Dalmatian marine lakes, in the fjords of Norway, (K. M. Strom, 1936), in the Black Sea, etc.

The third component, common freshwater (c), which was present in the sulfuric spring in the late Autumn 1952 (Fig. 4) is not a frequent appearance. It occurs in the year of exceptionally abundant precipitations only, when larger quantities of freshwater suddenly appear, pushing aside the blend of waters which normally compose the water of the spring [sea water (a) and mineral water (b)] from the place of wet combustion and from the spring, and reducing the Cl content of the spring water to 1/12 of the normal amount occurring in it (January 12th). The freshwater (c), which is of surface origin and of a lower temperature, contains a quantity of O<sub>2</sub>. This is the way in which the water of the Sulfuric Spring changes its hydrologic aspect, its salinity growing less and its H<sub>2</sub>S and other reductive matter completely disappearing, while O<sub>2</sub> becomes present (fig. 4).

The two normal components of the Spring water (a and b) convey only small quantities of oxygen, so a low redox potential is maintained in the region of the organic matter deposit (the place of wet combustion) and a slow oxidation of that organic matter is performed in that midst, rich in chlorides and sulfates, by means of oxygen from the sulfates through the medium of anaerobic bacteria. This circumstance may help us to explain, partially at least, the higher temperature of the spring water in its normal aspect in comparison with the temperature of the sea water in the port of Split.

But when there is a violent influx of freshwater (rainwater) rich in oxygen into the Sulfuric Spring, the place of wet combustion is then aerated, the formation of  $H_2S$  being thus discontinued owing to new conditions, unfavourable for the activity of anaerobic bacteria, and the formerly present  $H_2S$  is then oxidized. In such an aerated midst, exhausted of chlorides and sulfates, the destruction of fossil organic matter is less possible, if there is any at all.

The exceptional freshwater aspect of the sulfuric spring at Split, which occurred during our survey in 1952-53, lasted for three winter months. As already stated, the aspect of this kind is not a frequent occur-

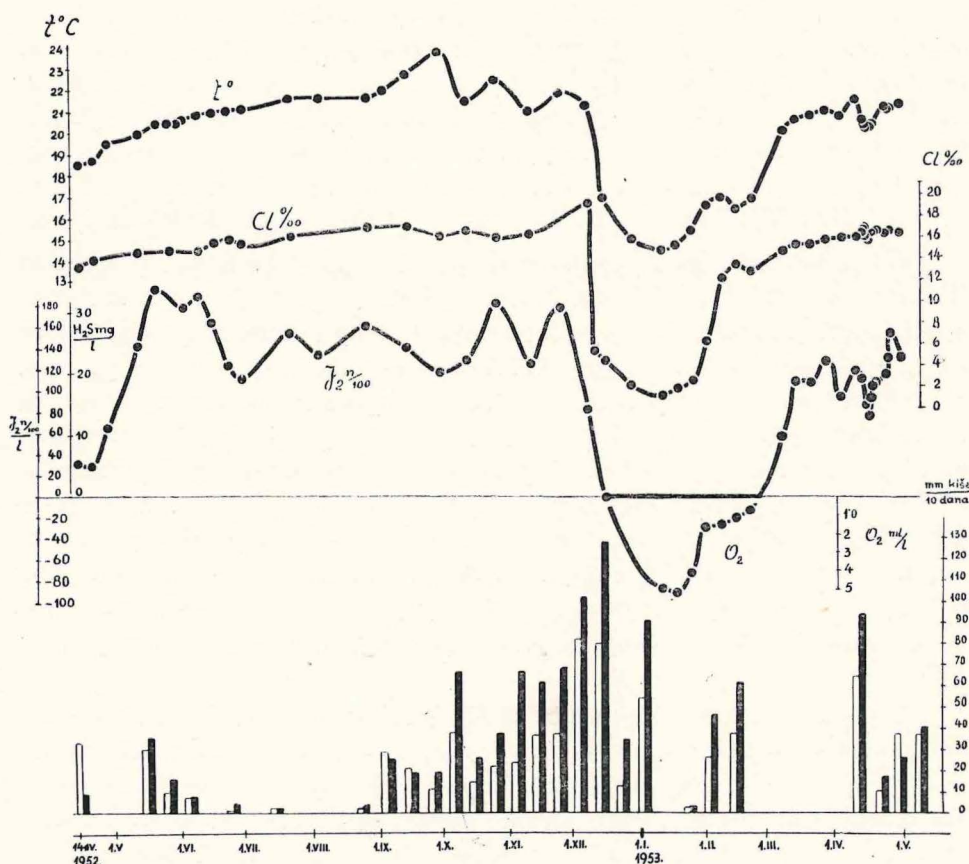


Fig. 4. — Diagram representing the interconnection of fluctuations of rainfalls in the Split area and of observed hydrographic factors of Split sulfuric water. Rainfalls (mm of rain during 10 successive days) are shown by vertical columns in the lower part of the diagram. White columns for Split, and black columns for Klis (a locality some 15 Km farther inland from Split).



rence in this Sulfuric Spring. This is also evident from the fact that such an occurrence was not yet registered. But the personnel employed with the establishment remember a few cases when — at short intervals only — the smell of  $H_2S$  was missing from the water of the Thermal Baths. There is another, likewise infrequent appearance, manifesting itself in the complete drying up of the Sulfuric Spring for a while (Vierthaler, 1867). This occurred in December (12th to 24th) 1907 also (Glaser, 1909), and, according to information from Dr. Mirošević, in 1948 again.

Judging from the foregoing facts we should say that abundant rainfalls are chiefly responsible for the structural change of the water of the Split Sulfuric Spring causing its transit from a form rich with  $Cl$  and  $H_2S$  to a form exhibiting a low salinity and absence of  $H_2S$ . The interconnection and interrelation of various factors is evident from the comparative graph No. 4. The factor responsible for all these changes, i. e. abundant rainfalls, is the first to reach its maximum. The maxima of temperature and salinity drop follow, appearing simultaneously. The last to appear in the succession of time is the maximum degree of aeration of the water of the Sulfuric Spring.

If the amount of precipitations in the surroundings of Split, or at Split itself, is of such an extent that, e. g. at Klis, or at Split itself, there is an excessive deposition of moisture from the atmosphere during two consecutive ten days' periods, — let us give an approximate figure, as for instance more than 100 mm, or more than 80 mm of rainfall, — which were preceded by other rainy decades, the above changes are bound to occur. (The amounts of precipitations recorded at Split and the close by Klis have more or less a parallel course, with the only difference that the deposition of moisture occurring at Klis regularly exceeds Split record for a couple of millimeters).

Possible further observations may yield perhaps more precise information on the conditions under which the salinity values are caused to grow smaller in the Split Sulfuric Spring.

There are, then, several signs by which we can recognise the actual condition of the spring, i. e. whether it has its normal saline aspect or not. The data, obtained during the period of our investigations 1952/53, show that the normal aspect of the water of the Sulfuric Spring is characterized by the following properties:

- Chlorinity exceeding 10 to 14 pro mille,
- Temperature higher than 17 to 19° C,
- $H_2S$  permanently present,
- $O_2$  permanently absent.

All these factors are likely interconnected. The following facts resulted from our sporadic observations made during the winter of 1953/54:

Table 4

Results of sporadic observations made in winter 1953/54, relative to Split sulfuric water and Split Port sea water.

	<i>Water of the Sulfuric Spring</i>			<i>Sea Water in the Port</i>	
	t°C	Cl ‰	H <sub>2</sub> S	t°C	Cl ‰
21. XI. 1953	—	16,63	present	—	—
21. XII. 1953	—	18,61	"	—	—
3. I. 1954	—	15,30	"	—	—
6. I. "	—	17,64	"	—	—
12. I. "	20,45	16,31	"	11,40	20,99
29. I. "	21,20	15,80	"	—	—
8. II. "	20,20	17,19	"	10,80	20,73
16. II. "	19,20	15,76	"	10,90	20,11
5. III. "	20,75	16,73	"	11,70	16,72
17. III. "	20,30	16,06	"	12,20	18,61
30. III. "	19,80	10,04	"	14,10	18,65

We find, then, that recorded values of chlorinity never dropped below 15 pro mille during the winter of 1953/54 and that the temperature of the Sulfuric Spring kept up above the 19° C level. As for H<sub>2</sub>S, it was permanently present in the spring water.

The water of the spring did not prove to contain iodine in quantities quoted in the earlier literature (Vierthaler, op. cit.). The method applied by us was not a sensitive one, but it yielded amounts of iodine not surpassing 5 mg J/l, whereas a value of about 700 mg/l was given in the paper mentioned above. Our datum is in full agreement with the result of analyses made by Glaser (1909.) which did not yield even the least traces of iodine content in the water of Split Baths Sulfuric Spring.

The presence of iodine in the water of the Sulfuric Spring was not mentioned by S. Miholić (1952 a) either.

Kerner (1917) who found that the temperature of the spring water was 25,5° C, had calculated on the basis of that temperature level that the water of the Sulfuric Spring was coming from a depth of about 300 metres, or even more if there is an afflux of surface water of a lower temperature in the upper layers. Our recordings, covering the period from April to December 1952, yielded an average temperature of the spring water of 21,73° C, and a maximum temperature of 23,23° C. These values were, then, lower than those given by the said author. If our temperature



data are taken to calculate the depth from which the water of the Sulfuric Spring arises, we would arrive at a relative depth of about 230 to 240 metres. In our opinion, however, we must not neglect the heat produced by the oxidation of fossil reductive matter constituting the basis of the formation of  $H_2S$ , and, having this in mind, we should rather avoid the application of the geothermic scale method for the purpose of the depth calculation in this case.

With regard to sea water as a component of the water of the Sulfuric Spring it was stated by *Vierthaler* (1867) and *Kerner* (1917) that it does penetrate into the spring. In our opinion, however, sea water constitutes the dominant part of the spring water, and is not a simple addition to, or a kind of pollution of the water of the Split Baths Sulfuric Spring. Sea water is its essential constituent part, representing as much as 9/10 of the spring water at the time of its normal aspect.

The occurrence of chlorides in the spring water, in our opinion, is directly associated with the sea. Owing to *high values* of chlorides found in the water of the Sulfuric Spring, there is no place for the probability of their being of an indirect marine origin, i. e. of their occurring as a consequence of chlorides extracted from sedimentary rocks. The circumstance that the concentration of chlorides in the water of the Sulfuric Spring has never exceeded the maximum concentration of Cl in the water of the Split port suggests that the process of washing of some hypothetical salt layer is not responsible for the occurrence of chlorides in the spring water. Another argument is the ratio  $SO_4/Cl$  in the Sulfuric Spring which value is very close to that for the sea water.

The idea that a part of the spring water must derive directly from the sea is the more acceptable as we are faced here with a spring coming out at some ten metres from the original waterfront (the present quay is a result of filling up) in a place belonging to the Karst region well known for its porous structure.

Given a direct presence of sea water in the water of the Sulfuric Spring, it is not surprising that, beside some organisms specially adapted to the conditions prevailing in the spring, some purely marine species of chlorophyceae, diatomeae, and cyanophyceae were found by *Z. Klas* (op. cit.) Some expressly marine organisms from the foraminifera and nematoda groups were found in the spring water by *F. Pax* (1940) also.

According to *S. Miholić* and *L. Trauner* (1952) the Split Sulfuric Spring is one of the strongest of its kind in Europe, with an extraordinary concentration of Na Cl.

(1) A particular effect of this kind of springs consists in their distoxicating property in cases of poisoning with heavy metals, e. g. consequences of Hg and Bi cures of syphilis, various professional diseases occurring among printers, miners in mercury mines etc.

(2) Baths of this kind are recommended in cases of chronic rheumatic troubles and skin diseases.

Now when the occurrence of intervals, however short, of lower salinity of the water of the Split Sulfuric Spring and of absence of  $H_2S$  from it has been demonstrated, the practical question arises what are the therapeutic qualities of this spring during those shortlived changes of its hydrologic aspect.



## SUMMARY

The results are given of intensive investigations of the sulfuric water of the Split Baths in the course of 1952/53.

Annual curves cover the fluctuations of temperature, chlorinity,  $H_2S$  content, and other reductive matter, as well as of oxygen found in the spring water. Comparative data are given on the amount of chlorides and on the temperature of the sea water in the port of Split which resulted from parallel examinations of conditions prevailing in the sea water.

The results of analyses covering the  $SO_4$  and total sulfur contents in the water of the Sulfuric Spring, and some other analyses are also published.

It is evident from the data that the spring water is subject to marked fluctuations of all the investigated factors owing to superabundant precipitations occurring in some years. It results from the paper that the water of the Sulfuric Spring is normally composed of (a) sea water, which is deducted from the  $SO_4/Cl$  ratio of both the spring water and sea water, and from biological indications; (b) a sort of mineral water, containing, among others, a large amount of sulfates, which is deducted from the fact that the content of total sulfur is higher in the spring water than in the sea water. A third component (c), i. e. rain water, joins the other two under the influence of heavy rainfalls which occur periodically.

The opinion is given in the attempt to explain the cause of both the normal occurrence of  $H_2S$  in the water of the Sulfuric Spring and its disappearance for a short interval of time, noticed in some years.

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- Fig. 1. Fluctuations of chloride content in the waters of the Split Baths Sulfuric*

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## HIDROLOŠKA SVOJSTVA I PORIJEKLO VODE SPLITKOG SUMPORNOG KUPALIŠNOG VRELA

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### Kratak sadržaj

Iznose se rezultati intenzivnog istraživanja vode vrela u toku 1952/53 g.

Donose se godišnje krivulje kolebanja temperature, kloriniteta, sadržaja  $H_2S$  i drugih redukcionih tvari, te kisika u vodi vrela. Za usporedbu su doneseni i podaci određivanja klorida i mjerenja temperatura vode splitske luke, vršenih usporedno sa onima vode vrela Splitskih toplica.

Doneseni su rezultati analiza  $SO_4$  i ukupnog sumpora vode Splitskih toplica, kao i još neke druge analize.

Iz podataka proizlazi, da vrelo nekih godina podliježe veoma snažnim kolebanjima svih istraživanih faktora pod uplivom izvanredno jakih oborina. Iz svih rezultata je izvedeno, da se voda vrela Splitskih toplica sastoji normalno iz komponenata: a) morske vode, na što je zaključeno iz omjera  $SO_4/Cl$  vode vrela i morske vode, te iz bioloških indicija; b) jedne mineralne vode, koja uz ostalo sadrži i dosta sulfata, što je izvedeno na temelju većeg sadržaja ukupnog sumpora u vodi Splitskih toplica nego li u vodi Jadrana. Neki godina pod uplivom oborina njima se pridružuje i treća komponenta c) slatka voda kišnica.

Dano je mišljenje o uzroku normalne pojave  $H_2S$  u vodi vrela Splitskih toplica i o uzroku nestanka istog, koje se događa nekih godina na kraće vrijeme.

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