

In each of the following experiments 20 cc. of the potassium iodide solution in a 250 cc. glass-stoppered bottle were treated with different amounts of hydrochloric acid and five cc. of chloroform. The bromate solution was run in until, after violent shaking, the chloroform had lost its pink color. The results obtained are given in the following table:

| A.              |                  |                          |                                |                   |                   |         |
|-----------------|------------------|--------------------------|--------------------------------|-------------------|-------------------|---------|
| KI soln.<br>cc. | HCl (1:1)<br>cc. | H <sub>2</sub> O.<br>cc. | KBrO <sub>3</sub> soln.<br>cc. | I taken.<br>Gram. | I found.<br>Gram. | Error.  |
| 20              | 40               | 0                        | 19.92                          | 0.2523            | 0.2530            | +0.0007 |
| 20              | 30               | 10                       | 19.94                          | 0.2523            | 0.2532            | +0.0009 |
| 20              | 20               | 20                       | 20.00                          | 0.2523            | 0.2539            | +0.0016 |

  

| B. <sup>1</sup> |                   |                          |                                |                   |                   |         |
|-----------------|-------------------|--------------------------|--------------------------------|-------------------|-------------------|---------|
| KI soln.<br>cc. | Conc. HCl.<br>cc. | H <sub>2</sub> O.<br>cc. | KBrO <sub>3</sub> soln.<br>cc. | I taken.<br>Gram. | I found.<br>Gram. | Error.  |
| 20              | 40                | 0                        | 19.87                          | 0.2508            | 0.2523            | +0.0015 |
| 20              | 40                | 0                        | 19.87                          | 0.2508            | 0.2523            | +0.0015 |
| 20              | 40                | 0                        | 19.81                          | 0.2508            | 0.2516            | +0.0008 |
| 20              | 20                | 20                       | 19.87                          | 0.2508            | 0.2523            | +0.0015 |
| 20              | 30                | 10                       | 19.90                          | 0.2508            | 0.2527            | +0.0019 |
| 20              | 40                | 0                        | 19.80                          | 0.2508            | 0.2514            | +0.0006 |
| 20              | 40                | 0                        | 19.85                          | 0.2508            | 0.2521            | +0.0013 |
| 20              | 40                | 0                        | 19.80                          | 0.2508            | 0.2514            | +0.0006 |

In all cases a slight positive error could be observed, probably due to the fact that the end point was less sharp with the iodine and chloroform than with the starch iodine indicator.

If a bromide is substituted for an iodide, while a reaction takes place and the chloroform is colored, still complete bleaching is not obtained even by adding an excess of the bromate; so we cannot determine in this way what reaction takes place between bromides and bromates in the presence of strong hydrochloric acid. With ferrous salts there is no coloration of the chloroform at all.

#### Summary.

This work has shown that like the iodate the bromate will oxidize the iodide, but the bromate is a more powerful oxidizer in that the bromine itself will react with one atom of iodine. Further, iodides may be easily and rapidly determined by titrating the iodide solution with standard bromate solution in the presence of twice its volume of hydrochloric acid.

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### COMPOSITION OF SEA WATERS NEAR BEAUFORT, NORTH CAROLINA.

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Clarke, in his "Data of Geochemistry," reports no analyses of sea waters along the coasts of North America. Possibly no careful analyses have

<sup>1</sup> Solutions of different strengths than those used in A were taken.

been made. These analyses were undertaken owing to the increasing interest which biologists are taking in the chemical composition of sea water as a feature of the environment of sea life. The work was done during the summer of 1909 at the U. S. Biological Laboratory at Beaufort, North Carolina, and for the U. S. Bureau of Fisheries. I wish to express here my thanks to the Commissioner of Fisheries, Mr. George M. Bowers, for his courtesy in permitting the publication of my report.

*Sodium and Potassium.*—The most careful investigation of sea water was made by Dittmar, reported in the "Report of the Scientific Results of the Exploring Voyage of H. M. S. Challenger, 1873-1876," Vol. I, Physics and Chemistry. This work was not at hand when this investigation was undertaken and the usual methods for determining sodium and potassium were adopted. These are given in "Mineral Waters of the United States," *Bull.* 91, Bureau of Chemistry, by J. H. Haywood and B. H. Smith. The determination of sodium came out low, the total bases being insufficient for the total acids. This experience is in agreement with the statement of Dittmar that "the routine method adopted in mineral salt analysis, *i. e.*, the elimination of lime and magnesia and subsequent joint determination of soda and potash as sulphates or muriates, would never give sufficiently precise results." My determinations were therefore corrected by employing Dittmar's method of "total sulphates." Ten cubic centimeters of water were weighed out in a glass-stoppered weighing bottle and evaporated to dryness in a platinum dish with a small excess of sulphuric acid, a dilute solution of known strength being employed. After evaporation to dryness over steam, the residue was heated on a sand bath and finally ignited to dull redness to constant weight. The following figures show the value of the method. The values for sodium sulphate by the total sulphate method and by calculation from the determinations of the other constituents differed by two parts in a thousand. On the other hand, the values obtained experimentally, after elimination of sulphuric acid, lime and magnesia, and by calculation from the determinations of the other constituents, differed anywhere from thirteen to thirty in a thousand.

*Calcium and Magnesium.*—Forty cubic centimeters of water were weighed out and transferred to a beaker. One cc. 5 *N* hydrochloric acid was added and the mixture boiled to expel carbon dioxide. After cooling, four cc. 5 *N* ammonium hydroxide and five cc. *N*/2 ammonium oxalate solution were added. The next day the supernatant liquid was decanted upon a filter, the residue redissolved in dilute hydrochloric acid and reprecipitated with ammonium hydroxide and a little ammonium oxalate solution. The following day the calcium oxalate was filtered upon the filter already used, washed with hot water and ignited in a platinum crucible to constant weight. The combined filtrates were

concentrated to a volume of 150 cc., cooled, mixed with ten cc. normal disodium phosphate solution and ten cc. strong ammonium hydroxide. The next day the precipitate was filtered off, washed with dilute ammonium hydroxide and finally with water. It was ignited in an open platinum crucible.

*Chlorine.*—Eight cc. sea water were weighed out and transferred to a beaker. Titration was conducted with a standard solution of silver nitrate (one cc. = 0.003555 gram Cl), using potassium chromate as indicator. In order to better observe the change of tint, a standard of comparison was made by precipitating a sodium chloride solution with excess of silver nitrate and re-establishing the yellow color with a little more salt. The silver nitrate solution was standardized by means of two samples of sodium chloride: 1. A sample labeled "Sodium Chloride, C. P., Eimer and Amend" was dissolved in pure water and reprecipitated with hydrochloric acid. It was filtered off, washed with water, and ignited. 2. A sample labeled "Sodium Chloride, C. P. Special. Baker's Analyzed Chemicals." The impurities were  $\text{CaO} = 0.001$  per cent.,  $\text{Fe} = 0.0001$  per cent.,  $\text{SO}_3 = 0.001$  per cent.

*Sulphuric Acid.*—To 25 cc. sea water, which had been weighed, were added, while hot, 2 cc. dilute hydrochloric acid and 3 cc. *N* barium chloride solution. The next day the barium sulphate was filtered off, washed with hot water and ignited in a platinum crucible.

*Carbon Dioxide.*—The determination of carbon dioxide was carried out by titrating 100 g. of water with 0.05 *N* hydrochloric acid, using phenolphthalein as indicator for normal carbonates and then methyl orange for bicarbonates. The results were checked by titrating with 0.05 *N* acid potassium sulphate as recommended by Cameron.

*Specific Gravities.*—The specific gravities were determined by the use of a pycnometer of U-form. The temperature employed was that of the laboratory, in order to avoid the unusual condensation of moisture on the pycnometer if lower temperatures were used.

*The Waters.*—Five samples of water were analyzed. The localities were marked upon a chart of Beaufort Harbor which accompanies my report to the Bureau of Fisheries: A. Taken in Beaufort Inlet. B. At the laboratory dock where water is taken for the laboratory aquaria. C. In Bogue Sound, opposite Moorehead, where *Toxopneustes* are abundant. D. At a point between the eastern end of Beaufort and Bird Island shoal. E. At Green Rock, in Newport river, near the entrance to Core Creek.

The results are given below in four tables. Comparison is made with Dittmar's results. Challenger water No. 924, a deep sea water, is given in three tables, because this is the only water whose composition is reported in parts per thousand of water. It does not, of course, represent the average. For example, the value for chlorine is 55.396 per cent. of

the total salts whereas the average for the 76 analyses is 55.420. Comparison is also made with the analysis of a water mentioned in an article by Curt Herbst in *Archiv für Entwickelungs mechanik der Organismen*, 5, 651. This water is from the Mediterranean sea below Naples, Italy.

TABLE I.—PARTS PER 1000 GRAMS OF SEA WATER.

|                       | A.     | B.     | C.     | D.     | E.     | 924.   | Herbst.            |
|-----------------------|--------|--------|--------|--------|--------|--------|--------------------|
| Cl.....               | 19.909 | 19.635 | 19.767 | 19.810 | 17.571 | 19.201 | 21.137             |
| SO <sub>4</sub> ..... | 2.754  | 2.681  | 2.699  | 2.730  | 2.378  | 2.673  | 3.237              |
| CO <sub>3</sub> ..... | 0.132  | 0.129  | 0.129  | 0.129  | 0.129  | 0.143  | 6.080 <sup>1</sup> |
| Na.....               | 11.049 | 10.968 | 11.022 | 11.036 | 9.771  | 10.607 | 11.936             |
| K.....                | 0.442  | 0.390  | 0.394  | 0.394  | 0.368  | 0.380  | 0.409              |
| Ca.....               | 0.433  | 0.429  | 0.440  | 0.436  | 0.392  | 0.483  | 0.473              |
| Mg.....               | 1.353  | 1.301  | 1.313  | 1.323  | 1.177  | 1.301  | 1.362              |
| Total....             | 36.072 | 35.533 | 35.767 | 35.867 | 31.786 | 34.788 | 38.634             |

TABLE II.—PARTS PER 1000 GRAMS OF SEA WATER.

|                        | A.     | B.     | C.     | D.     | E.     | 924.   | Herbst.            |
|------------------------|--------|--------|--------|--------|--------|--------|--------------------|
| NaCl.....              | 28.043 | 27.836 | 27.977 | 28.006 | 24.796 | 26.882 | 30.292             |
| KCl.....               | 0.842  | 0.742  | 0.751  | 0.751  | 0.702  | 0.725  | 0.779              |
| MgCl <sub>2</sub> .... | 3.379  | 3.245  | 3.300  | 3.335  | 2.972  | 3.413  | 3.240              |
| MgSO <sub>4</sub> .... | 2.417  | 2.328  | 2.320  | 2.372  | 2.062  | 1.937  | 2.638              |
| CaSO <sub>4</sub> .... | 1.171  | 1.168  | 1.202  | 1.188  | 1.039  | 1.591  | 1.605              |
| CaCO <sub>3</sub> .... | 0.220  | 0.214  | 0.214  | 0.215  | 0.215  | 0.240  | 0.080 <sup>2</sup> |
| Total....              | 36.072 | 35.533 | 35.767 | 35.867 | 31.786 | 34.788 | 38.634             |

TABLE III.—PERCENTAGE OF TOTAL SALTS.

|                       | A.            | B.     | C.     | D.     | E.     | Dittmar. <sup>3</sup> | Herbst.            |
|-----------------------|---------------|--------|--------|--------|--------|-----------------------|--------------------|
| Cl.....               | 55.191        | 55.257 | 55.270 | 55.231 | 55.280 | 55.292                | 54.710             |
| SO <sub>4</sub> ..... | 7.635         | 7.546  | 7.547  | 7.612  | 7.481  | 7.692                 | 8.380              |
| CO <sub>3</sub> ..... | 0.366         | 0.363  | 0.361  | 0.360  | 0.405  | 0.207                 | 0.207 <sup>3</sup> |
| Na.....               | 30.630        | 30.867 | 30.818 | 30.768 | 30.741 | 30.593                | 30.894             |
| K.....                | 1.226         | 1.098  | 1.102  | 1.099  | 1.157  | 1.106                 | 1.059              |
| Ca.....               | 1.201         | 1.208  | 1.230  | 1.216  | 1.233  | 1.197                 | 1.224              |
| Mg.....               | 3.751         | 3.661  | 3.672  | 3.714  | 3.703  | 3.725                 | 3.526              |
| Total....             | 100 per cent. |        |        |        |        | Br 0.188              |                    |

TABLE IV.—PERCENTAGE OF TOTAL SALTS.

|                        | A.            | B.     | C.     | D.     | E.     | 924.   | Herbst.            |
|------------------------|---------------|--------|--------|--------|--------|--------|--------------------|
| NaCl.....              | 77.743        | 78.340 | 78.229 | 78.083 | 78.010 | 77.274 | 78.408             |
| KCl.....               | 2.334         | 2.088  | 2.100  | 2.093  | 2.208  | 2.085  | 2.016              |
| MgCl <sub>2</sub> .... | 9.367         | 9.132  | 9.227  | 9.300  | 9.350  | 9.811  | 8.386              |
| MgSO <sub>4</sub> .... | 6.700         | 6.551  | 6.487  | 6.612  | 6.487  | 5.569  | 6.828              |
| CaSO <sub>4</sub> .... | 3.246         | 3.287  | 3.361  | 3.313  | 3.269  | 4.572  | 4.154              |
| CaCO <sub>3</sub> .... | 0.610         | 0.602  | 0.596  | 0.599  | 0.676  | 0.689  | 0.208 <sup>3</sup> |
| Total....              | 100 per cent. |        |        |        |        |        |                    |

Specific gravities at 28.7° (corr.).

1.0227 1.0222 1.0226 1.0227 1.0193

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<sup>1</sup> The residue insoluble in water after evaporation to dryness.

<sup>2</sup> Average of analyses of 77 Challenger waters.

<sup>3</sup> Insoluble residue.