

*A. A. Breneman*: My impression is that Seger says there seems to be a connection between the peculiar light gray of salt-glazed stoneware, a color which is unique, and the presence of titanium. That is a very interesting statement, because that peculiar form of whitish or bluish gray stoneware is very characteristic, and I see nothing in the presence of iron alone in the clay sufficiently to account for it.<sup>1</sup>

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CASE SCHOOL OF APPLIED SCIENCE.]

## XXV. COMPOSITION OF CERTAIN MINERAL WATERS IN NORTHWESTERN PENNSYLVANIA.<sup>2</sup>

BY A. E. ROBINSON AND CHARLES F. MABERY.

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THE therapeutic qualities of mineral springs throughout northwestern Pennsylvania have long been recognized, and recently some of these springs, notably those at Saegertown and Cambridgeboro, have come into prominence through the enterprise of persons interested in hotels and sanitariums. The desirable qualities of these waters are doubtless dependent on

<sup>1</sup> NOTE ON TITANIUM IN CLAYS.—In the course of a discussion of Prof. Mabery's paper on American clays at the Buffalo meeting I alluded to the peculiar color of salt-glazed stoneware, and ascribed to Seger the suggestion that it was due to the presence of titanium. On referring to Seger's article (Wagner's *Jahresbericht*, 1883, p. 625), I find that he says that titanitic acid (13.3 per cent.) heated with a very pure kaolin to a temperature between the melting points of wrought iron and platinum fuses, and that titanitic acid is, under similar conditions, more of a flux for clay than silicic acid is. In the proportion of 6.65 per cent. of  $TiO_2$ , the mass became only semi-fused, and exhibited a dark-blue gray color. He says this color suggests the tint given by many clays when strongly heated.

Morgenroth (Wag. *Jahr.*, 1884, 638) says, however, that rutile gives to clay ware a gray color under the glaze when impure ferruginous clays are used, but a yellow, ivory-like tint with pure clays. As rutile was used in the proportion of only 0.4 per cent., the minute proportion of iron which it carries (1.5 to 2.4 per cent.  $Fe_2O_3$ ) would have little effect.

The interpretation of these facts to explain the peculiar gray color of salt-glazed stoneware, was probably a suggestion of my own, made at the time of reading these articles a dozen years ago. It was ascribed in the course of the discussion to Seger, as my "impression."

Nevertheless, in view of the peculiarity of this color, the gray of salt-glazed ware which is uniform throughout the body and becomes more bluish in overburned pieces, and in view also of the presence of iron in the rather crude clays used for the ware, and the fact that iron alone tends to escape as volatile chloride in presence of the salt used for glazing, the suggestion is worthy of note.

A. A. BRENNEMAN.

<sup>2</sup> This work, with a study of the methods of analysis, was offered by Mr. Robinson in a thesis for the degree of Bachelor of Science. Read at the Buffalo Meeting, August, 1896.

iron and certain other salts, especially on the bromides, and it is a popular view that lithium salts sometimes present impart valuable medicinal qualities. A quantity of water was collected from one of these surface springs at Conneautville by one of us (Robinson) and its composition as shown by analysis may serve as a representative of the springs in this region. The total solids in this water is equivalent to 6.586 grains per imperial gallon, or 9.83 parts per 100,000. Evidently the combination of bases and acids is to a certain extent arbitrary, but this distribution accounts for the total quantities of the various elements given by analysis :

	Grains per gallon.
Potassium carbonate.....	0.985
Lithium carbonate.....	0.002
Sodium chloride.....	0.925
Calcium bicarbonate.....	2.879
Calcium sulphate.....	1.291
Magnesium chloride.....	0.204
Ferrous carbonate.....	0.743
Silica .....	0.233
Hydrogen sulphide.....	trace

The specific gravity of this water was found to be 1.0002 at 20°. Evidently the analysis shows the composition of a good potable water. Any medicinal qualities it possesses must be referred to the iron and perhaps to a less extent to the lithium.

At greater depths in this section of Pennsylvania and in certain portions of Ohio, water may be found that partakes in a greater degree of the qualities imparted by the constituents of bittern. Wells sunk to depths of 1,000 to 3,000 feet have penetrated strata enclosing, frequently under great pressure, large quantities of bittern waters. While in general conforming in composition to the salts contained in bittern, occasionally these wells have yielded peculiar results on analysis. Such an aqueous stratum was reached several years ago at Conneautville, Crawford County, Pa., in an endeavor to obtain oil or gas. The drill penetrated the formation enclosing water at a depth of 2,667 feet and the drilling tools were forced upwards to a height of 1,800 feet by the water which prevented further drilling. This

level was maintained notwithstanding vigorous attempts to clear the well by pumping. A slight examination then showed that this water possessed peculiar qualities, but the well received no further attention until within a few months ago when it was cleared and a quantity of the water was procured for a more thorough examination. The total solids is equivalent to 21,334.34 grains per gallon or to 30,536 parts per 100,000. The specific gravity of the water is 1.205 at 15°. Its composition as shown by the results of analyses is as follows :

	Grains per gallon.	Parts per 100,000.
Potassium chloride .....	528.577	755.6
Lithium " .....	56.422	80.3
Ammonium " .....	151.879	216.6
Sodium " .....	9902.578	14430.0
Potassium bromide .....	137.010	245.7
" iodide.....	2.078	2.96
Magnesium chloride .....	2172.499	3096.0
Calcium " .....	8335.537	11880.0
" sulphate.....	7.886	11.1
Ferrous carbonate.....	114.836	163.5
Aluminum chloride.....	21.816	31.1
Silica.....	3.220	4.6
Hydrogen sulphide .....	0.033	0.05

There are certain features of this water that deserve especial mention. The large proportion of ammonium chloride is quite unusual in waters from such depths. Lithium chloride is frequently found in surface springs, and in brines from deep wells, but rarely, if ever, in such quantities as this water contains. If lithium salts impart to spring water the therapeutic qualities claimed for them, it is not difficult to account for the beneficial effects that have been observed in the use of this water. No doubt the large proportion of potassium bromide has much to do with the marked sedative effect. The large percentage of potassium iodide is also phenomenal, and it must intensify the mineral characteristics of the water. Besides the characteristics of a bromo-lithia water the large percentage of iron assures the desirable qualities of an iron water. The peculiar composition of this water, especially in the large quantities of the rarer elements, offered a favorable opportunity to ascertain whether these

bittern deposits contain also the elements, cesium and rubidium, which are rarely found in springs. Forty-five liters of the water were evaporated to a small volume, removing the great quantities of salt as they separated. When the volume was reduced to less than fifty cc. this solution as well as the lixiviated salts that had separated during evaporation were carefully examined in the spectroscope. But not a trace of rubidium nor cesium could be detected. It is therefore safe to conclude that the bittern deposits from the ancient sea do not contain these rarer elements.

It may not be out of place to remark that the chemical composition of this water explains the remarkable therapeutic qualities especially for rheumatism and nervous diseases that it has been found to possess.

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## SOME ANALYTICAL METHODS INVOLVING THE USE OF HYDROGEN DIOXIDE.<sup>1</sup>

BY B. B. ROSS.

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THE use of hydrogen peroxide as a laboratory reagent, although originally restricted to a few operations of minor importance, has within recent years met with a much wider extension, and its numerous applications in both qualitative and quantitative analysis, render it at present almost indispensable in every well-equipped analytical laboratory.

Among the more interesting applications of this substance in quantitative estimations are those which are based on the reaction which takes place when an excess of hydrogen dioxide is brought in contact with an acid solution of chromic acid, and Baumann<sup>2</sup> several years since described quite fully a number of analytical processes growing out of the reaction referred to.

In the process for the estimation of chromic acid in soluble chromates as outlined by Baumann, the substance under examination is first brought into a state of solution, and the not too concentrated liquid is transferred to a generating flask of special construction.

<sup>1</sup>Read at the Buffalo meeting, August 22, 1896.

<sup>2</sup>*Ztschr. anal. Chem.*, 31, 436.