

from Caracas, Venezuela, and from St. Denis, Reunion. In the former the mean proportion of nitric nitrogen was found to be 0.578 part per million, in the latter 0.69 part.

These results are far in excess of the quantities found by us, although, from time to time, instances have occurred to us in which the nitrogen present as nitric acid has approached or even exceeded these amounts.

Possibly, the results obtained by Müntz and Marcano were from rainfalls lower in quantity than those which occurred during our present investigation, whilst probably the composition of rain-water may be materially affected by the prevalence or not of the trade-winds.

Briefly our somewhat extended investigation leads to the conclusion that the rainfalls of certain tropical climates whilst containing a higher relative proportion of the nitrogen as nitric acid, do not supply to the soil a larger quantity of nitrogen as nitric acid and as ammonia than is supplied by the rain-water of temperate climates.

ANALYSIS OF AN IRON RAIL TAKEN FROM A GALLERY OF AN UNUSED COAL MINE.

BY H. P. TALBOT AND A. G. WOODMAN.

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THE section of the rail in question was taken from a gallery of the "Hub Mine," at Glace Bay, Cape Breton. The gallery was allowed to fill with water in 1872, and was pumped out by the Dominion Coal Company last year. The rail had, therefore, lain unused in the gallery for over twenty years, most of the time under water which is reported to be "impregnated with acid," and, as indicated by the analysis, had undergone an entire change in composition. The rail was initially, presumably, of cast iron, and it is interesting to record the report which has come to us, that utensils of steel, and articles of wrought iron, did not undergo material change during the same length of exposure to the same conditions. So far, the writers have not had opportunity of examining any of these samples of wrought iron or steel.

After the mine had been pumped out, the rail was found to have lost its initial density and strength, and was easily broken or cut into fragments.

In the sample which came into our possession, there was a well-defined demarcation between the inner core, which was gray and very soft, and the outer shell, which was black and relatively hard, although this too could be readily cut with a knife and powdered in a mortar. The two portions were easily separated by running a knife blade along the line of demarcation. The outer and inner portions were examined separately.

Before presenting the results, the writers wish to state that the analytical work has been done at irregular intervals, and that the results are given solely for the interest which the figures seem to possess in themselves, and with the consciousness that, considered as an investigation, the report would be incomplete.¹

The results are as follows :

	Outer shell.	Inner core.
Specific gravity (compared with water at about 20° C.)	2.45	2.16
	Per cent.	Per cent.
Lost on ignition at a red heat	7.50	8.75
Total iron	42.00	38.10
Total silicon	5.85	10.60
Total phosphorus	3.60	3.75
Sulphur evolved by treatment with acid.	2.30	0.73
Sulphur in the residue after evolution method	2.35	0.68
Carbon corresponding to graphitic carbon	9.50	16.00

Manganese and aluminum were present in very small quantities. The former could not be precipitated in weighable quantities, except by using so large a sample that determination was not attempted.

No silicon, as such, was detected by ignition of the sample in dry chlorine. The presence of metallic iron was plainly indicated by the deposition of metallic copper, when fragments of the rail were placed in copper sulphate solution. The amount is distinctly larger in the outer shell than in the inner core. During solution in acids, a distinct odor of hydrocarbons was detected, but a combustion of the residue after treatment with copper potassium chloride, yielded a lower percentage of carbon

¹ Shortly after the transmission of the manuscript of this paper to the editor, a detailed description of the properties and analysis of other specimens from the same source, by F. W. Durkee, appeared in the *Am. Chem. J.*, 18, 849. Interesting information concerning the mine-water, and the possible steps in the transformation of the iron, are also presented.

than was found in the residue after treatment with nitric acid (as given above). This may possibly be explained by the incomplete decomposition of the substance by the copper-ammonium salt, with the consequent protection of some of the carbonaceous by the mineral matter.

The loss on ignition at a red heat does not probably represent any definite quantity, but is given as having some possible interest.

The statement was made to us by one who had had opportunity to handle a fragment of the rail of considerable size, and during an interval of a year or more, that its density perceptibly increased with length of exposure to the air. The determinations of specific gravity already cited, were made about April 15, 1896. New determinations, made November 14, gave as results, for the outer shell 2.83, and for the inner core 2.23. While these results confirm the general statement, we do not feel that they are above criticism, as they were obtained from small fragments. They are comparable, however, with the earlier specific gravity determinations.

In connection with the foregoing statements, it is interesting to note the results reported by Herting,¹ of an analysis of a similar fragment of rail, which not improbably came from the same source, as he mentions it as coming from a mine in Cape Breton, in which the rail had remained for twenty years. His results are as follows :

Specific gravity, 2.053; silicon, 14.20 per cent.; graphitic carbon, 24.20 per cent.; phosphorus, 5.85 per cent.; total sulphur, 1.00 per cent.; manganese, 1.93 per cent.; iron, metallic, 31.50 per cent.

He finds that approximately one-half of the sulphur is volatile with acids, as in the results cited in this paper, and considers that the iron is otherwise present as Fe_2O_3 . His percentages, upon recalculation, yielded the following: Ferrous sulphide, 1.37 per cent.; ferrous sulphate, 2.38 per cent.; manganese monoxide, 2.50 per cent.; phosphorus pentoxide, 13.37 per cent.; magnetic oxide (Fe_3O_4), 39.34 per cent., which with the carbon and silicon, yields a total of 97.36 per cent. It would appear, however, from our results, that the silicon was probably present as silica in his samples as well, at least in some measure.

¹ *Chem. Ztg.*, 20, 54.

Our analytical examination has not been, and cannot well be continued further than to afford the results cited above; hence we prefer not to express a positive opinion as to the probable combinations of the constituents as they occur in the rail, nor do we feel able to offer any explanation as to how the changes in composition have been brought about. Merely for comparison with Herting's results, we present our own, calculated upon the same basis, except that the silicon is calculated as oxide.

They are as follows :

	Outer shell. Per cent.	Inner core. Per cent.
Carbon	9.50	16.00
Silica.....	12.45	22.55
Phosphoric anhydride	8.25	8.60
Ferrous sulphide.....	6.30	2.00
Ferrous sulphate.....	11.15	3.20
Magnetic oxide (Fe_3O_4).....	46.80	49.20

The writers wish to express their obligations to Mr. J. B. Dil-
lingham, and Prof. W. H. Niles, through whose courtesy they
came into possession of the fragment of the rail, and to whom
they are indebted for information as to its history.

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[CONTRIBUTIONS TO THE CHEMISTRY OF ZIRCONIUM, No. 6.]

THE OXALATES OF ZIRCONIUM.

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THE text-books of chemistry make either very little or no reference to the oxalates of zirconium. Beyond an occasional reference to the oxalate or basic oxalate gotten by precipitating with oxalic acid or an oxalate, we can find little mention of these compounds. Behrens, in his microchemical work, speaks of an oxalate prepared as colorless pyramids by precipitating a solution of zirconium sulphate with potassium binoxalate, but no analyses are given, and the crystals could scarcely have been the pure oxalate. Paykull¹ speaks of double oxalates being prepared with the alkaline oxalates (1:2) and of his failure to prepare the neutral oxalate. His methods, and indeed full results, are unknown to us, as we did not have access to the original paper.

We may summarize the work which follows in the succeeding pages by saying that we found it possible to prepare the basic oxalates by precipitation. This was usually in the form of

¹ *Ofv. af. Vet. Ak. Förrhandl. ref. in Ber. d. chem. Ges.*, 12, 1719.