ON THE OCCURRENCE OF HYDROGEN SULPHIDE IN THE NATURAL GAS OF POINT ABINO, CANADA; AND ON A METHOD FOR THE DETERMINATION OF SULPHUR IN GAS MIXTURES.[1]

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Received July 19, 1898.

On the northern shore of Lake Erie, ten miles west from Buffalo, a narrow promontory extends for a distance of about two miles out into the lake. This promontory, known as Point Abino, forms the southern extremity of an important region of natural gas production from which a large part of the gas used in Buffalo at the present time is derived.

In 1892 a well was drilled by the Provincial Natural Gas Company near the extremity of Point Abino, to a depth of 600 feet. Gas was found in this boring at 550 feet below the surface, and again fifty feet deeper, or at the base of the Niagara limestone. The well has maintained its productiveness with little loss of pressure since the date of its drilling.

As regards chemical composition, the gas derived from this limestone at Point Abino differs in a remarkable manner from that which is usually found in the Devonian rocks of western Pennsylvania in the fact that it contains hydrogen sulphide, easily recognizable by its strong odor, by its action upon polished surfaces of silver and copper, and by the presence of sulphur dioxide among the products of its combustion. Two other wells on Point Abino yield gas of similar character (known locally as "sulphur gas") from the same geological formation.

It is common in drilling wells into the Niagara limestone in this region to find natural gas impregnated with hydrogen sulphide, sometimes occurring in small quantities, apparently stored in cavities from which it soon escapes and is exhausted; in other cases the sulphur gas, when once it is tapped, may continue to flow for an indefinite period.

In cutting a sewer tunnel through the limestone, fifty to sixty feet under the city of Niagara Falls, and extending about one mile from Twenty-third street to the river, hydrogen sulphide

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[1] Read at the Washington meeting of the American Chemical Society, December, 1897.

was frequently encountered, and was the cause of much inconvenience to the workmen, requiring the construction of ventilating shafts for its removal. The occurrence of this gas was always accompanied by a strong flow of dark-colored water.

Mr. W. A. Brackenridge, resident engineer for the Cataract Construction Company, informs me that hydrogen sulphide was found at a depth of about sixty feet in excavating for the wheel pit and tunnel shaft of this company at Niagara Falls. Patches of gypsum were often found about ten feet above the gas-bearing stratum. If this gas is allowed to come in contact with the polished metal surfaces about the power house they are rapidly blackened. Natural gas of the same character has been found near Fort Erie, at several places between Buffalo and Point Abino, and also at Port Colborne on Lake Erie, twenty miles west from Buffalo. Water well drillers state that they often strike sulphur gas at Chippewa, south of Niagara Falls. Southeast from Buffalo, from four to six miles, hydrogen sulphide occurs in the Niagara limestone of the West Seneca field, and at Alden, eighteen miles east from Buffalo. The sulphur gas is found in wells distributed over a territory extending irregularly for about forty miles east and west, and about twenty miles north and south.

Natural gas occurs in the region at three other horizons below the Niagara limestone; namely the Clinton limestone, the Medina sandstone, and the Trenton limestone, which latter rock was reached at a depth of 2940 feet in a well drilled six miles north of Point Abino. The Niagara limestone seems, however, to be the only one of these formations which yields gas containing hydrogen sulphide.

On September 2, 1896, I visited the well at Point Abino, and by the courtesy of Mr. E. Coste, engineer for the Provincial Natural Gas Company, was enabled to conduct some tests of the gas upon the spot and to collect samples for analysis. Of these tests made at the well and the results obtained, the following is a brief summary:

On leading the gas through an alkaline lead acetate solution, a heavy black precipitate was at once produced.

An ammoniacal cadmium chloride solution yielded a bright yellow precipitate. The odor of hydrogen sulphide was very strong.

It seemed to be of interest to ascertain whether organic sulphur compounds were present among the hydrocarbons of this gas. Accordingly, a stream of the gas was caused to bubble through an alkaline lead acetate solution, in order to absorb hydrogen sulphide, and then through an alcoholic solution of mercuric chloride. The experiment was continued for six hours at the well. Methyl, as well as ethyl sulphide would have caused a precipitation in the mercuric chloride solution, if present even in very small quantity. The solution was found to remain clear. The absorbent solutions were returned to the laboratory to be further tested. The alkaline lead acetate solution was warmed upon a water-bath while a current of nitrogen was passed through the flask and into an alcoholic solution of mercuric chloride. In this latter solution no precipitate appeared, nor was any odor attributable to a sulphur ether observed. These tests seemed necessary, as a volatile sulphur ether might have condensed unchanged in the lead acetate solution during the passage of the gas in the trials which were made at the well. The nitrogen stream was used in order to evaporate any traces of such condensed sulphur compound, should there be any such, and carry its vapor over into the reagent solution.

In order to test for methyl mercaptan advantage was taken of the fact that its vapor is readily absorbed by an alkaline lead acetate solution and is again evolved when the liquid is acidulated and warmed. If the escaping vapors are led (by a nitrogen stream) into a solution of palladium chloride a cinnamon-colored precipitate is produced. This test was performed but the results were negative. The odor of mercaptans was not noticeable. It is of course possible that experiments with still larger volumes of gas might have disclosed the presence of traces of such organic sulphur compounds.

The vapors of methyl and ethyl sulphide, even if present in a gas in quantity insufficient to produce a precipitate in mercuric chloride solution, are absorbed by the solution, and impart to it their characteristic odor, so that this reagent may in such manner serve for the detection of very slight traces not otherwise recognizable.

In order to test for the presence of carbon monoxide the gas, as it flowed from the well, was passed (1) through lead acetate solution containing a large excess of sodium hydroxide to remove carbon dioxide and hydrogen sulphide, (2) through lime-water, in order to maintain control of the efficiency of the first solution, (3) through palladium chloride solution, and (4) through lime-water. When present in a gas mixture, even in traces, carbon monoxide is easily recognized by this method, the second lime-water becoming milky as a result of the oxidation of the carbon monoxide by the palladium chloride. The palladium chloride is simultaneously reduced, yielding a black precipitate of finely divided metal.[1]

In testing for free hydrogen the method I have described in the *American Chemical Journal*, **16**, 259, was used. The gas freed from hydrogen sulphide and dried by phosphoric anhydride, was passed through a tube containing dry palladium chloride and then into silver nitrate solution. Dry palladium chloride is quickly reduced in the cold by free hydrogen, with formation of hydrogen chloride, which then produces its characteristic effect upon the silver nitrate solution.

The results of these tests, conducted at the well during about six hours, were negative, and the conclusion seems justified that carbon monoxide and free hydrogen do not occur in the Point Abino natural gas in recognizable quantity.

Tests for ethylene were made in small portions of the gas brought back to the laboratory for the purpose, but with negative results. Determinations of hydrogen sulphide were made by agitating a measured volume of the gas with an alkaline solution of lead acetate, in a bottle fitted with a rubber cork, traversed by inlet and outlet tubes having stop-cocks, and by a burette for the introduction of the reagent solution. This part of the work was carried out at the well, due account being taken of the temperature and barometric pressure. The bottle used was of 1890 cc. capacity. The precipitated lead sulphide was returned to the laboratory, its sulphur oxidized to sulphuric acid, and from the weight of barium sulphate obtained the proportion of hydrogen sulphide in the original gas was calculated.

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[1] For details of this method as applied to natural gas see *American Chemical Journal*, **16**, 275.

The results of four determinations made in this manner were 0.76, 0.73, 0.75, and 0.72 per cent.

Nitrogen was determined by combustion of a measured volume of the gas (about 150 cc.) over copper oxide, and measurement of the residual gas over mercury. This residue may include other inert gases besides nitrogen, but these have been classed together in the present analysis. The method used for collection of this inert residue is one requiring a somewhat complicated form of apparatus. Its details will be described in a later paper.

Carbon and hydrogen were determined gravimetrically, by weighing the carbon dioxide and water produced when a measured volume of the gas was burned over copper oxide. For this purpose glass cylinders holding from 350 to 400 cc. were filled with the gas at the well.

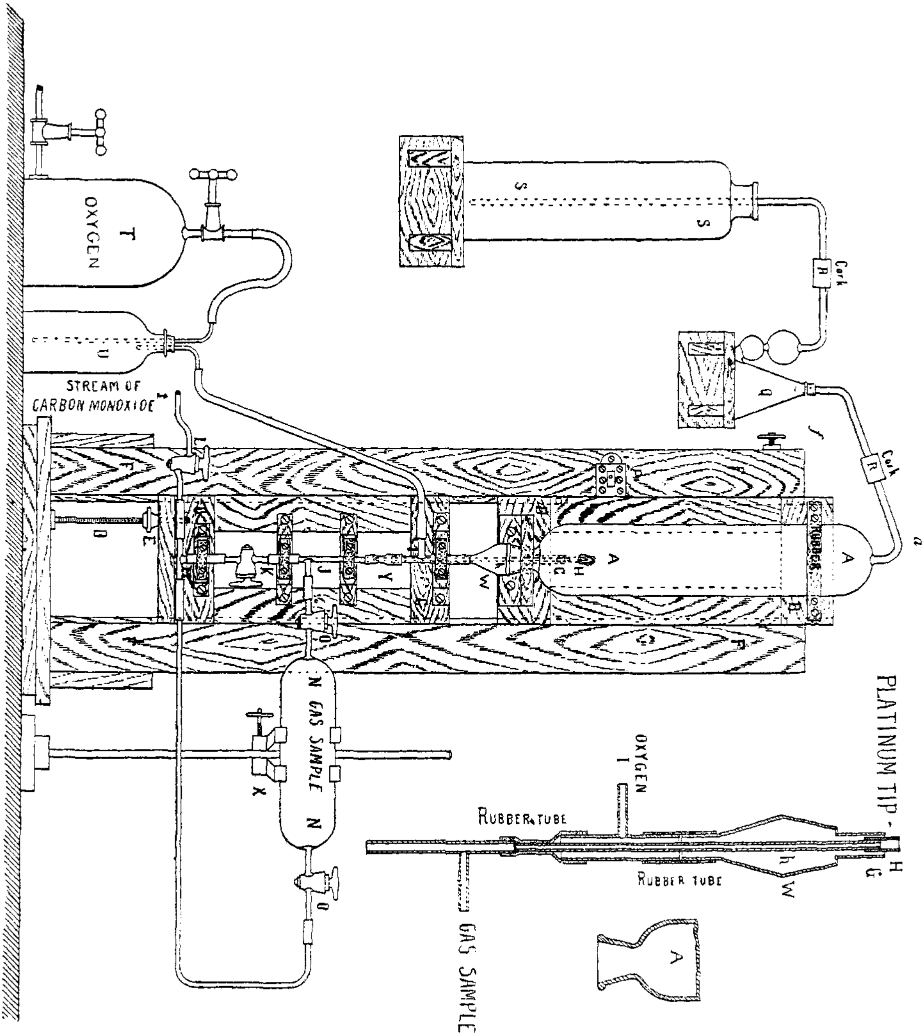
Results of analysis of natural gas from the Point Abino well.

	Per cent.
Hydrogen sulphide	0.74
Nitrogen	2.69
Carbon dioxide	trace
Carbon monoxide	0
Hydrogen	0
Ethylene	0
Hydrocarbons of the paraffin series	96.57
	100.00

The percentage composition of these paraffins by weight was :

	Per cent.
Hydrogen	24.10
Carbon	75.90
	100.00

With a view to greater certainty in the determination of hydrogen sulphide it seemed desirable to employ a method by which the gas could be burnt, and the sulphur collected as barium sulphate. Accordingly, a process was devised for the combustion of a measured volume of the gas in an oxygen atmosphere, absorption of the sulphuric or sulphurous acid produced, and weighing of the sulphur as barium sulphate. Such a method is not new in principle, having been proposed by various authors for the determination of sulphur in gases. As adopted for use in the present instance the method may be described as follows :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RUBBER TUBE
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The gas sample is contained in the vessel *N* (which may be replaced by a larger vessel if necessary). It is burnt from a narrow glass tube *h* surmounted by a roll of thin platinum foil *H*, in a light blown glass cylinder *A*, which is about forty cm. long and about ten cm. wide. The cylinder is closed below by a ground stopper *W*. This stopper is hollow and carries the narrow tube of about one and one-half mm. bore supplying the gas to be burnt. The narrow tube passes up through one of larger diameter which receives oxygen by way of the side tube *I* from a holder *T* and delivers it just below the flame of burning gas. As is shown in the sketch of the stopper *W* and its connections, the burner tubes are arranged concentrically, the oxygen issuing from the wide tube *G* and encircling the flame of the gas burning at the tip *H*. The rate of flow of the oxygen is approximately indicated by the rapidity of its bubbling through water in the bottle *U*. It seemed desirable to effect the expulsion of the gas from the sample vessel into the cylinder where it is to be burnt without the use of water, which by reason of its solvent power might absorb and partially remove those constituents of the gas which are to be determined. Mercury is out of the question. A gas appeared preferable and carbon monoxide was employed for the purpose. The carbon monoxide is contained in a gasholder and enters by the tube *L*, passing upward by *K* and *h* to the platinum tip *H*, where it is ignited. The combustion cylinder, which is mounted on the movable frame *BB*, is then lowered over the ignited carbon monoxide jet and clamped in position by the screw *f*. The outlet tube *a* is connected with the flask *Q* containing a solution of sodium carbonate to which some bromine has been added. The lower sliding frame *CC* can be raised or lowered by the nut *E* moving upon the fixed screw *D*. The carbon monoxide jet being ignited and the oxygen supply by way of *I* being adjusted so as to insure a steady flame, the stop-cocks *OO* are opened and then *K* is closed. The carbon monoxide then goes by way of the gas sample vessel to the jet, driving out the contained gas and carrying it into the combustion cylinder, where it is burnt. Many liters of gas may be burnt in this manner without danger of the flame becoming extinguished. The sodium hypobromite solution into which the products of the combustion have passed contains the sulphur as sodium sulphate, and, after acidulation and evaporation, may be used for the determination of sulphur as barium sulphate. After the combustion is finished the apparatus is tilted down, the cylinder is rinsed, and the rinsings added to the contents of the flask *Q*. The large bottle *S* containing a few drops of bromine water, which is renewed from time to time during the process, is used to insure complete absorption of products of combustion of the sulphur. The connections *RR* consist of corks soaked in melted paraffin or spermaceti, rubber being objectionable on account of the sulphur which it contains.

The combustion of natural gas, or other gas rich in hydrogen, leads necessarily to the production of much water. This water is partly condensed at first, but as the temperature of the cylinder rises and evaporation is accelerated, the water vapor increases, and impairs the stability of the flame, which may flicker and become extinguished, even when the oxygen supply is apparently sufficient. The carbon monoxide, by diluting the products of combustion, tends to prevent condensation of steam and renders the flame more steady and more easily controlled. If very large volumes of gas are to be burned carbon monoxide cannot be used as it renders the process too slow, and in such case measurement of the gas must be effected by meter. No carbon monoxide is then required. Natural gas may be burned in this apparatus at the rate of a liter in twelve minutes.

Experiments have shown that the position of the gas sample vessel, whether vertically or horizontally placed, makes little difference, as the carbon monoxide rapidly mixes with the gas in the sample vessel and the two emerge together at the burner.

There appeared to be some danger that carbon monoxide made from oxalic acid by heating with sulphuric acid might contain volatile sulphur compounds. Carbon monoxide, prepared from chemically pure sulphuric acid and recrystallized oxalic acid, was found after passage through sodium hydroxide solution, to yield no sulphuric acid when ten liters were burned in the apparatus described.

Nitrous oxide may be substituted for oxygen in the process, and being readily obtainable in liquefied form, proves more convenient. During combustion in nitrous oxide higher oxides of nitrogen are formed in quantity sufficient to give a bright orange color to the gaseous contents of the combustion cylinder. The conditions are then very favorable to the complete oxidation of gaseous sulphur compounds.

The Point Abino gas well was visited again on September 3, 1897, when the tests made a year ago were repeated, and other samples taken. Determinations of sulphur were made by the method of combustion above described. Determinations of hydrogen sulphide were also made by treatment of a known volume of gas at the well with alkaline lead acetate solution. The precipitated lead sulphide having been returned to the laboratory, its sulphur was converted by oxidation by means of potassium chlorate and hydrochloric acid into sulphuric acid, and precipitated and weighed as barium sulphate.

	By combustion in oxygen and weighing as barium sulphate. Percentage by volume.	By precipitation as lead sulphide and conversion into barium sulphate. Percentage by volume.
Hydrogen sulphide	0.80	0.77
	0.83	0.86
	0.82	0.80
	0.82	
	0.83	

The only important difference as regards composition between the natural gas from the Niagara limestone and that from the Devonian measures of western Pennsylvania consists, apparently, in the hydrogen sulphide which the former gas contains. If the sulphur compound be removed the residual gas is hardly distinguishable in composition from the natural gas of other regions. There appears to be reason for regarding the sulphur gas of Point Abino as natural gas which has received an addition of hydrogen sulphide derived from some local source. The same process which has produced natural gas in other regions has probably yielded this gas but the hydrogen sulphide which it contains may be derived from a different source, and may have been of more recent origin.

The occurrence of hydrogen sulphide in the Niagara limestone is no doubt connected with that of gypsum, which abounds so largely throughout the region. Gypsum has been quarried near Buffalo and is often found scattered through the limestone in cavities. In artesian borings many alternations of limestone and gypsum are often encountered. Considerable masses of this mineral are found near Sherkston, north of Point Abino, and near Niagara Falls it occurs abundantly in the limestone.

If a genetic relationship exists, as is suggested by their association, it is difficult to determine whether the hydrogen sulphide, by oxidation in presence of limestone, has produced gypsum, or whether the gypsum has by decomposition yielded hydrogen sulphide. If hydrogen sulphide has undergone oxidation there seems to be reason to suppose that the process must have occasionally remained incomplete when occurring at great depths, and have resulted in the setting free of sulphur. Sulphur does not appear to occur native in the region. If the hydrogen sulphide has penetrated from greater depths to undergo oxidation in the higher strata it should be found more abundantly in the lower gas-bearing rocks, instead of being confined to the uppermost of these, the Niagara limestone.

On the other hand, the production of hydrogen sulphide from gypsum would seem to require an exposure to high temperature in presence of hydrocarbons—conditions which cannot have occurred. No one of the constituents of natural gas could, at temperatures existing in the stratified rocks of the region, have produced hydrogen sulphide by its action upon gypsum.

The Point Abino well produces, according to Mr. E. Coste, engineer for the Provincial Natural Gas Company, 1,000,000 cubic feet per day, and of this amount 7,000 cubic feet are hydrogen sulphide, corresponding to 600 pounds of sulphur, or 115 tons in one year. It is true that the well is not being drawn upon constantly up to its full capacity, but as it represents only one among the many outlets from which the sulphur gas escapes, it is evident that a very large quantity of sulphur, either in form of hydrogen sulphide, or burnt in furnaces to sulphur dioxide, is making its way annually into the atmosphere in the region of Buffalo and Niagara Falls.

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