

the author's sincerest thanks for many suggestions and comments, both as to matter and methods, especially in respect to the problem of injury caused by the solid emanations.

UNIVERSITY OF UTAH,  
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## PAPERS ON SMELTER SMOKE.

(FIRST PAPER)

### The Determination of Arsenic and Other Solid Constituents of Smelter Smoke, with a Study of the Effects of High Stacks and Large Condensing Flues.

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The determination of the constituents of smelter smoke is important for two reasons: many of the constituents have considerable commercial value, while a large number are poisonous in varying degrees to plant and animal life. Under the first class will come sulphur dioxide, sulphuric acid, copper, lead, zinc, arsenic, antimony, and certain other substances. It will be seen that these same substances belong in some degree to the second class as well, so that the solution of the problem of recovering the economic values from the smoke will also solve the problem of lessening or preventing its injurious action.

It will be the purpose of a series of articles, of which this is the first, to point out the chemical facts which make the solution of these problems so essential to the welfare of many extensive districts in the west, as well as to some in the east and south of our country. The work which led to the publication of this special article, was the estimation of the amount of arsenic expelled from the greatest of the world's smelters—a plant which has a capacity of ten thousand tons of ore per day, and the output of which for 1906 was estimated as eleven and one half per cent. of the world's production of copper. Compare with this the Freiburg smelters at the time of the work of Haubner<sup>1</sup>, Sussdorf<sup>2</sup>, Freytag<sup>3</sup>, taking the date 1870. At this time the two smelters, the Mülden and Halsbrücken, treated daily about seventy tons of ore. According to Haselhoff and Lindau<sup>4</sup>, all the smelters of the Lower Hartz use annually only sixty-three thousand tons, this being the amount for the year 1899. In this country, the Garfield Beach smelter, Utah, is to be enlarged to a capacity of eight thousand tons per day, while the Great Falls, Montana, smelter has now a capacity of three thousand five hundred tons

<sup>1</sup> Haubner, Die durch Hüttenrauch veranlassten Krankheiten des Rindviehes im Hüttenrauchsbezirke der Freiburger Hütten (Arch. f. wiss. u. prakt. Tierheilk. 1878, 4, 97-136; 241-260.)

<sup>2</sup> Sussdorf, Allg. Deut. Naturhist. Ztg., Hamburg, I (1855), No. 3, 97.

<sup>3</sup> Freytag, M., Jahrb. f. d. Berg-u. Hüttenwesen im Königr. Sachsen auf da. Jahr. 1873, Abl. 3. —, (l. c. 1875, Abl. 3).

<sup>4</sup> Haselhoff und Lindau, Rauch-Beschädigung, p. 147.

per day, and will soon be made much larger. In Nevada, the Ely smelter is to treat from ten to twenty thousand tons of ore per day. Many other great plants could be named, but these examples are sufficient to show that the problem of injury by smoke is a much more important one in this country than it is in Germany, at least in so far as the magnitude of the smelting operations themselves is concerned.

During the last few years there have been numerous complaints from smelter districts, that the trees and grass are not only injured in their growth by the sulphur dioxide and sulphuric acid of the smoke, but in some way the grass is also rendered poisonous for horses and stock, probably as the result of the deposition of mineral poisons. This calls to mind the investigations made in Germany in the year 1849 by Stockhardt,<sup>1</sup> and in 1853 by Stockhardt and Frange,<sup>1</sup> who decided that the poisoning caused by smelter smoke was due to the action of lead. However, the later investigations of Sussdorff and Haubner, as referred to above, show conclusively that the principal damage was caused by arsenic, and not by lead.

The investigations which led to the publication of this series of articles on smelter smoke, were begun by one of us (Harkins) in the year 1902, about ten months after the completion of the smelter. The smoke and the grasses of the district were found to contain considerable arsenic, while small quantities of this element were found in the organs of herbivorous animals living in the vicinity of the smelter. For many years previous the ore had been treated in a plant which cost in all about six million dollars, but in January 1902 this was abandoned for the present smelter, in order to reduce the cost of smelting by the adoption of improved methods. The stone and brick settling flues, which in the old works served to carry the smoke to the tops of the hills upon which the stacks were built, were in the new works replaced by large condensing chambers of brick. These chambers averaged about forty feet wide, forty feet high, and two hundred and sixty feet long; but the volume utilized in settling the flue dust was somewhat less than this, since ten feet of the height was taken up at the bottom by a passageway for the cars that carry the dust to the reverberatory furnaces. The volume of each chamber was therefore about three hundred thousand cubic feet. One was attached to the roaster building, one to the blast, and one to the converters, and each was provided with a separate steel stack, twenty-two feet in internal diameter, and two hundred twenty-five feet high. The smoke from the reverberatory furnaces was discharged directly into a stack of the same dimensions.

Whether or not the settling chambers were less effective than the long flues of the old works, is very difficult to say; but it certainly is

<sup>1</sup> Opinion transmitted to the Royal Minister of the Interior, 1854.

a fact, that during the year after the erection of the new works the loss of animals in the valley became very much greater than before. This was due in part to a difference in the location of the smelters, since the new smelter was built closer to the valley lands, and in such a position that the prevailing winds carried more of the smoke across the farms of the district. Even if it is possible that some of the increased poisonous action of the fields upon the animals was due to a difference in the composition of the smoke, owing to a change in the methods of smelting, still it is certain that much valuable material, somewhat poisonous, was thrown out by the old works. The ground surrounding them became so rich in copper that a very large amount of this metal was obtained by smelting the top soil of a considerable area.

As a result of the operation of the new smelter, the losses of stock in the valley during the year 1902 were so heavy, and the hay and grass, on analysis, showed so much arsenic, that a great system of flues was built in order to settle the copper, and to condense the arsenic trioxide. The latter escaped in large quantities as a gas, especially from the blast and McDougall roasting furnaces. The system of flues built at this time, is the largest in the world, and a study of its effects in settling different compounds presents many interesting chemical problems, only a few of which can be touched upon here.

This first set of flues joins all the furnaces to one great flue, the smoke from three of the buildings passing through the settling chambers before entering the flues at all. Of the connecting flues the blast furnace flue is 1653 feet in length; the reverberatory flue, 842 feet; the roaster flue, 488 feet; and all are twenty feet wide and twenty feet high. The converter flue is at present 703 feet long, 18 feet wide, and 10 feet high. All these join in one great flue, and for twelve hundred feet this is sixty feet in width, with twenty foot side walls. The bottom slopes down on both sides to hoppers in the middle, which open into cars underneath. It is 36 feet from the top of the flue to the bottom of the excavation, and the area of the cross section of this portion is 1600 square feet. Above this there are two parallel sections, each 1000 feet long, and of the same dimensions as the single flue, making a double flue, 120 feet wide, with a cross section of 3200 square feet.

The volume of the original settling chambers is about 900,000 cubic feet, while that added in 1903, in the form of new flues, is about 6,000,000 cubic feet, making the volume available for settling the solids of the smoke practically seven and one half times as great as before. In order to cool the gases, the 120 foot flue is covered with a roof made of thin pieces of sheet steel, supported by I beams underneath. This flue lies on a steep mountain side, and ends at the top in a big stack, 31.33 feet in internal diameter, 44.5 feet external diameter at the bottom, 30 feet internal

diameter at the top, and three hundred feet high. The smoke is admitted to the stack by two openings on opposite sides, each 12.5 feet wide by 34.5 feet high. The elevation of the top of the stack is 6,186 feet, and of the reverberatory furnaces, 5,442 feet, or a difference of seven hundred feet. The top of the stack is eleven hundred feet above the valley below.

The great flues and stack were built in order to settle the arsenic and copper, and to prevent the damage to the forests and crops from the sulphur dioxide of the smoke. After a year and a half of operation, it was claimed by the smelter company that these results were accomplished, and that practically all of the arsenic was deposited in the flue and chambers, while the stack raised the smoke to such a height that the sulphur dioxide did little damage to vegetation. The farmers of the district asserted on the other hand, that their animals were poisoned, and their crops damaged in the same way as before, though the distribution of the damage was somewhat different.

The velocity determinations and analyses of smoke which follow, and the more recent of the investigations in regard to the crops and animals, as given in the later papers, were undertaken to determine the real efficiency of this flue and stack.

*The Determination of Velocity.*—In sampling and analyzing smoke, among the most difficult problems is one which may seem to belong to the engineer, but which, our experience has shown, cannot be left to the ordinary man in this profession. Since the results of his analyses depend entirely for their calculation upon the volume of the smoke given off, it becomes the duty of the chemist to make these volume or velocity measurements

In the determination of the velocity of moving gases there are only two methods which have any claim to accuracy. These are the determination by the Pitot tube, and that by the ordinary wheel anemometer. A method much used by smelter men consists in releasing a piece of charred paper, and noting the time which it takes to rise to the top of the stack. This is manifestly a very crude method, and is not applicable in the case of very large stacks, since it is impossible to see the charred paper when it first leaves the top of the stack. Another method sometimes used is to obtain the difference in pressure between the outside and the inside of the chimney.

The Pitot tube was devised by Pitot<sup>1</sup> in 1732, and was used for the determination of the velocity of water. It consisted of an L tube with the ends of the two arms open, but with the horizontal arm drawn down to a small opening. When turned with the horizontal arm pointing up stream, the impact of the stream on its mouth balanced a column of

<sup>1</sup> Pitot, *Histoire de l'Académie des Sciences* (1732), p. 376.

water in the vertical arm of a height equal to the square of the velocity divided by twice the coefficient of gravity. When the plane of the mouth of the tube was placed parallel to the motion of the stream, the level of the water inside and outside the stream was practically the same. When two tubes are placed thus at right angles with each other and connected with a differential manometer in which the liquid is the same as the moving liquid, the difference of level in the two arms of the manometer is the same as that given above, or  $h = \frac{v^2}{2g}$ . An instrument of this kind was devised by Darcy, and is known as a Darcy gauge, or a modified Pitot tube.

The principal of the Pitot tube was developed from the proposition of Toricelli<sup>1</sup> by Daniel Bernoulli<sup>2</sup>, who used as a basis of his development the principle of the *conservatio virium vivarum*. He proved that in a steady stream of a frictionless liquid, loss of energy of motion is accompanied by an equivalent gain of head, and gain of motion energy by an equivalent loss of head. The head may be in the form of elevation of the liquid or of pressure, or of both combined. In other words, when kinetic energy is converted into potential, or potential into kinetic, the loss of kinetic energy is accompanied by an equal gain in potential energy, and the gain of kinetic energy by an equal loss of potential energy. Expressed in symbols:

$$mgh = \frac{1}{2} mv^2$$

or

$$v = \sqrt{2gh}$$

This is the last formula of the Pitot tube, and is the same as the well known formula for the efflux of liquids.

Although there has been considerable dispute as to the practical formula of the Pitot tube, the experiments of Darcy, and also of most of the modern writers, show that in the formula  $v = c \sqrt{2gh}$  the factor  $c$  is unity within the limits of experimental error, where the tube is of the proper construction. This is the view expressed by Freeman,<sup>3</sup> White,<sup>4</sup> Williams,<sup>5</sup> Robinson,<sup>6</sup> and Gregory,<sup>7</sup> in recent articles upon this subject. The Pitot tube, when properly constructed, has proved an accurate instrument for the measurement of the velocity of either gases or liquids when the velocities are not too low. Nearly all the early applications of

<sup>1</sup> Toricelli, *De Motu gravium Projectorum* (1643).

<sup>2</sup> Bernoulli, *Hydronamica* (1738).

<sup>3</sup> Freeman, J. R., *Trans. Am. Soc. Civil Engineers*, 21 (1889).

<sup>4</sup> White, W. M., *J. of Assoc. Eng. Soc.*, 25 (1900), p. 161, and 27, (1901), pp.

35-67.

<sup>5</sup> Williams, G. S., *Pr. Ann. Soc. Civil Eng.*, May, 1901.

<sup>6</sup> Robinson, S. W., *Trans. Am. Soc. Mech. Eng.*, 25 p. 208-211 (1903).

<sup>7</sup> Gregory, W. B., *Trans. Am. Soc. Mech. Eng.*, 25 (1903).

this apparatus were made in the determination of the velocity of liquids, usually the velocity of streams or of ships<sup>1</sup>.

The tubes used for our work, as shown in Figure 1, consists of two

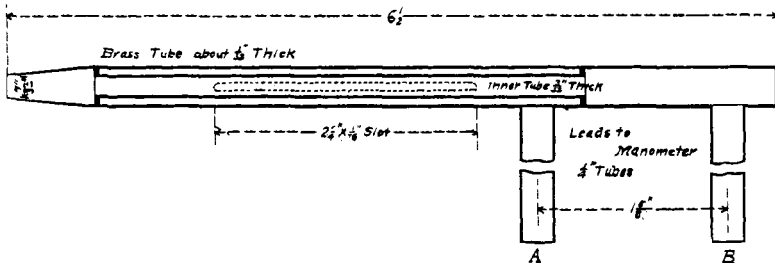


FIG. 1. Pitot tube as modified by Captain D. W. Taylor.

These tubes were made from a design furnished by Captain D. W. Taylor,<sup>2</sup> Naval Constructor at Washington. Tubes of this design had been used by him to test the ventilating fans of the battleship Missouri, and were previously tested by Prof. A. F. Zahm, of the Catholic University, Washington. Using the formula  $v = \sqrt{2gh}$ , the latter found that the results agreed with very accurate independent measurements of the volume of the air.

concentric tubes, each connected to one arm of a differential manometer, so that the latter gives the difference of pressure of the gas in the two tubes. The axis of the tube is placed parallel to the direction of motion of the smoke, and the inner tube has an opening 0.553 centimeters in diameter with its plane at right angles to the axis. The outer tube has a slot 5.71 centimeters long by 0.16 centimeters wide on each side, so that it gives to the manometer the static pressure of the gas. The inner tube corresponds to the original Pitot tube, and gives the static pressure plus the pressure caused by the impact of the gas upon its mouth, or what is often called the velocity pressure. The use of slots instead of the circular openings usually employed to obtain the static pressure, prevents the aspirating effects noticed in the ordinary form of the tube. The two tubes (A) and (B), each 0.63 centimeters in diameter, are provided with screw threads at the ends, and on these tubes iron pipes of the same diameter are fastened. In the velocity determinations these pipes varied in length up to twenty-three feet, and served to support the Pitot tubes in the stack and to connect it with the manometer. To make the support rigid they were stiffened by a band of steel, 1.3 centimeters thick and 4 centimeters wide, which fitted exactly between the two pipes (A) and (B). The pipes and the steel band were bound at distances of 60 centimeters by clamps of heavy steel, bolted together by 1.3 centimeter

<sup>1</sup> Berthon, E., *The Engineer* (1850); Pendred, Vaughn, *The Engineer*, Dec. 17, 1869; Rankine, W. J. M., *The Engineer*, Jan. 1870.

<sup>2</sup> Taylor, D. W., *Eng. News*, 52, 18, p. 387-89, Nov. 3, 1904.

bolts. It was essential that these supports should be rigid, since the portions inside the wall of the stack had to be entirely self-supporting.

The manometer<sup>1</sup> used for this work was the simplest form possible and proved perfectly satisfactory. It consists of a glass U tube of a small even bore, laid upon the slant of a triangle having a base of 23.74 centimeters, a vertical side of 2.5 centimeters, and a slanting side of 25 centimeters. This was built of well seasoned wood, very carefully cut, and was fastened upon a broad horizontal base into which two levels were set. The U tube was bound down by copper wires, and a steel scale, accurate at 15<sup>2</sup>, was placed between the two arms. The two sides should be connected at the bottom by a horizontal spiral of the same glass tube, in order to lengthen the natural period of vibration of the ether column. The liquid used was ether, which responds freely to any change of pressure. It had a specific gravity of 0.7300 at a temperature of 17°. The manometer was connected to the Pitot tube pipes through two two-way cocks; and on reversing both of these, the impact arm of the manometer became the static pressure arm, so that the effect of any slight difference of level between the two side tubes was eliminated. Great care was taken to set the instrument in such a way that the two ends of the base of the triangle should be at the same level. For each reading the stopcocks were reversed several times, the average taken, and reduced to velocity by the formula,  $V = \sqrt{\frac{2gh D_{\text{ether}}}{120 D_{\text{gas}}}}$ , where  $h$  is the reading expressed in inches.

*Comparison of a Pitot Tube with an Anemometer.*<sup>2</sup>—In order to see how the results obtained by the Pitot tube would compare with those given by a wheel anemometer, the two instruments were placed side by side, as shown in Figure 2. The pipe (A), running just beneath the concrete floor, connects a large fan, placed some distance from the section shown in the cut, with one of the main flues of the building where the tests were made. The Pitot tube (P) and the anemometer (M) were supported by the two 0.64 centimeter iron pipes (C), which connect with the two arms of the Pitot tube—the static pressure arm (S), and the impact arm (I). The tubes (C) were connected by the rubber tubes (R) to the differential ether manometer. The anemometer was stopped or started by the lever (L'), which was turned by means of a series of levers and rods (L, D, L' and D'), arranged so that the recording mech-

<sup>1</sup> Seger's manometer may be used if a vertical form of instrument is desired.

<sup>2</sup> The anemometer was the property of the Department of Mechanical Engineering of Stanford University, and was the best instrument which could be purchased. The apparatus used for this purpose was designed for us by Professor W. R. Eckhart, Jr.

anism could be turned on or off without removing the apparatus from its place. The Pitot tube (P) and the anemometer (M) were set so that their axes were at equal distances from the axis of the pipe. The whole

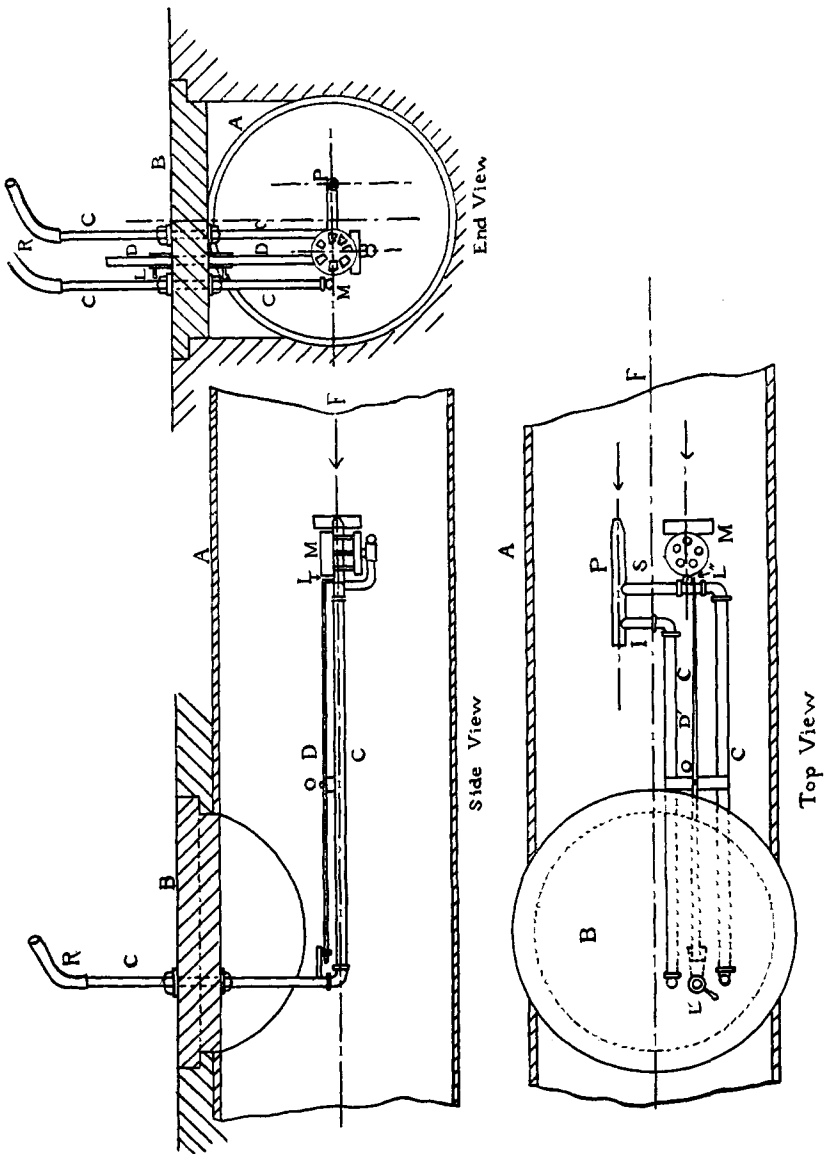


FIG. 2.

apparatus being supported by the tubes (C), which were fastened in the removable cover (B) of the manhole, could be removed in a moment to read the anemometer. The instruments were set several feet from



the manhole so that the slight irregularities in the pipe at the latter would cause no eddies near the instruments.

The apparatus was put in place, and the fan regulated until the manometer of the Pitot tube indicated that the velocity of the air had become as nearly constant as possible. The recording mechanism was then turned on, and the readings of the Pitot tube manometer taken for a certain time, usually five minutes. The recording mechanism of the anemometer was then stopped, the apparatus taken out, and the dial read. The fan was run at the highest and lowest velocities possible, as well as at numerous intermediate velocities. The determinations as shown in Table 1<sup>1</sup>, are not given in the order in which they were made, but are rearranged in the order of the increasing velocity.

The column "Ft. per Second Corrected" gives the results as determined by the anemometer, corrected by the calibration curve of the instrument maker. Under  $\frac{V_{\text{anemometer}}}{V_{\text{pitot}}}$ , the first column gives the anemometer velocity as obtained directly by reading the dial, divided by the velocity as determined by the Pitot tube. In the second column the anemometer reading has been corrected by its calibration curve.

On account of this rise of reading with the velocity, the easy corrosion of its parts, the fact that in the smoke the vanes become loaded with flue dust, and its high original cost, the wheel anemometer is a very poor instrument for the determination of the velocity of smelter smoke. The cost is of importance, since a number of instruments should be used.

*Determination of the Velocity Curve.*—The sampling hole, through which all our apparatus was introduced into the stack, was 5.75 inches in diameter, formed by an iron pipe extending through the five-foot wall, and projecting one foot on the outside of the stack. It was 53 feet from the ground, at an altitude of 5935 feet, and about 13 feet above the top of the baffle wall, which extends across the middle of the stack. At the time our measurements were made, we believed that the top of the baffle wall was very much lower than it really is, so at that time we were not able to understand why our curve of velocity showed a velocity considerably lower at the center of the stack than at four feet from the inner wall. The sampling hole was the highest opening in the stack, and also the only opening at this height, so that we were able to secure no other support for our apparatus than its walls. Not only the small size of this opening, but also its length, and the fact that it was round, made it difficult to insert, and keep vertical, any large amount of apparatus for the velocity determination. When no smoke sample was being drawn off, it was possible to insert four tubes for the

<sup>1</sup> The calculations in this table, and all the other calculations in this paper, were made on a slide rule.

TABLE I. Comparison of an Anemometer and a Pitot Tube.

$$V_{\text{Pitot}} = \sqrt{2gh \frac{D_{\text{Dettler}}}{D_{\text{Air}}}}$$

$2g = 64.28$      $b = 759 \text{ mm}$      $e = 12.7 \text{ mm.}$

No.	Anemometer			Pitot.							1 + .003665 t	.0012934 1 + .003665 t × $\frac{759 - 3.16e}{60}$ D <sub>Air</sub>	Dettler D <sub>Air</sub>	Velocity by Pitot Ft Sec	V anemometer by Pitot	
	2nd Reading Anemom- eter	1st Reading Anemom- eter	Time Min utes	Difference	Ft. per minute	Ft. per second	Ft. per second correct- ed	Pitot Man- ometer aver- age	Pitot pres- sure in feet vertical	Tem- pera- ture °C.					Read- ings	Cor- rected
1	97,606	97,030	576	1	576.0	9.60	9.55	0.312	-.00260	16.5	1.0605	.001209	603.0	10.03	0.957	0.952
2	101,108	97,606	3,502	5	700.4	11.67	11.55	0.383	-.00319	15.8	1.0578	.001213	602.5	11.15	1.047	1.036
3	291,046	286,554	4,492	3	1497.3	24.95	24.45	1.547	-.01289	22.0	1.0807	.001188	615.0	22.52	1.107	1.085
4	286,554	280,905	5,649	3	1883	31.38	30.75	2.320	-.01933	22.0	1.0807	.001188	615.0	27.49	1.142	1.118
5	124,813	112,924	11,888	5	2377	39.63	38.84	3.437	-.02864	18.4	1.0674	.001203	608.0	33.42	1.186	1.162
6	272,947	265,075	7,872	3	2624	43.73	42.86	4.375	-.03646	22.5	1.0824	.001189	616.0	37.92	1.153	1.130
7	280,905	272,947	7,958	3	2653	44.22	43.34	4.445	-.03704	22.5	1.0824	.001189	616.0	38.28	1.156	1.132
8	154,580	140,030	14,550	5	2910	48.50	47.54	4.954	-.04128	20.8	1.0762	.001193	612.0	40.30	1.203	1.179
9	169,142	154,580	14,552	5	2910	48.50	47.54	5.023	-.04186	20.8	1.0762	.001193	612.0	40.58	1.196	1.172
10	184,005	169,142	14,863	5	2972	49.53	48.54	5.198	-.04332	21.3	1.0781	.001190	614.0	41.28	1.200	1.176
11	199,463	184,005	15,458	5	3092	51.53	50.50	5.682	-.04735	22.8	1.0836	.001185	616.8	43.30	1.190	1.167
12	140,074	124,813	15,261	5	3952	50.87	49.84	5.940	-.04950	21.1	1.0773	.001191	613.1	44.12	1.153	1.130
13	218,219	208,730	9,487	3	3162	52.70	51.65	5.922	-.04935	22.8	1.0836	.001185	616.8	44.30	1.190	1.166
14	208,730	199,463	9,267	3	3089	51.48	50.45	5.917	-.04931	23.0	1.0843	.001184	617.0	44.21	1.164	1.142
15	238,555	228,516	10,039	3	3346	55.77	54.66	6.813	-.05677	22.8	1.0836	.001185	616.8	47.42	1.176	1.153
16	228,516	218,219	10,297	3	3432	57.20	56.16	6.877	-.05731	22.8	1.0836	.001185	616.8	47.63	1.201	1.178
17	254,096	243,128	10,968	3	3656	60.93	59.71	7.553	-.06294	23.0	1.0843	.001184	617.0	49.93	1.236	1.211
18	265,075	254,096	10,979	3	3659	60.98	59.76	7.677	-.06397	23.4	1.0857	.001183	617.3	50.36	1.211	1.197

determination of the velocity curve. The region near the wall of the stack is by far the most important in this determination. Thus one-half of the area of the cross section, with its radius of 15.67 feet, is within 4.66 feet of the wall, and also includes all that portion in which there is any great variation in the velocity. Measurements were made at the following distances from the inner wall of the stack, the numbers being given in feet: 0.0, 0.25, 0.50, 0.75, 1.0, 1.50, 2.00, 2.50, 3.00, 4.00, 10.00, and 15.67.

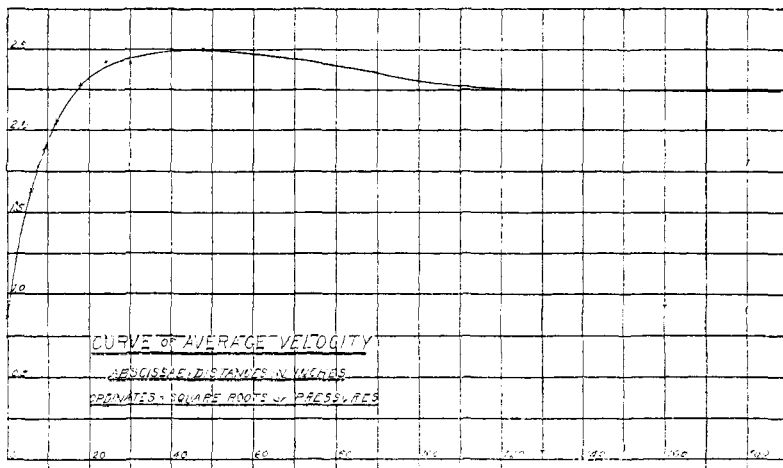


FIG. 3.

The results of these measurements are given in the form of a curve in Figure 3. Instead of plotting the velocities themselves, the square roots of the Pitot readings, multiplied by four, are given as ordinates, and distances from the inside wall as abscissæ. The extreme right of the curve represents the center of the stack. In computing the velocity for the time while samples of smoke were being taken for analysis, determinations were recorded at only one point, the point of maximum velocity, or four feet from the inside wall. This series of determinations was corrected by the velocity curve in order to give the average through the whole cross section. In computing this the method of sections was used. The radius of the stack was divided beginning at the center, into divisions of ten inches each; and the area of the ring formed by each segment, on rotating the radius in a plane about the center of the stack as an axis, was multiplied by the average velocity for that ring as shown by the curve.

Let  $a = 10''$   $r_0 = 188''$   $r = 180''$   $V =$  average velocity. Then since  

$$V \pi r^2 = V_0 \pi [188^2 - 180^2] + V_1 \pi [r^2 - (r-a)^2] + V_2 \pi [(r-a)^2 - (r-2a)^2] + \dots + V_n \pi [r - (n-1)a]^2 - (r-na)^2]$$

$$V = \frac{1}{\pi r^2} [V_0 (188^2 - 180^2) + a \{ V_1 (2r-a) + V_2 (2r-3a) + V_3 (2r-5a) + \dots + V_n (2r - (2n-1)a) \}]$$

The calculation according to this formula is shown in Table 2.

TABLE 2

	V	$2r - (2n - 1)a$	Product.	Product times $a$
$V_0$	6.00			17760.
$V_1$	8.40	350	2940.	29400.
$V_2$	9.53	330	3146.	31460.
$V_3$	9.83	310	3046.	30460.
$V_4$	9.95	290	2885.	28850.
$V_5$	9.92	270	2678.	26780.
$V_6$	9.77	250	2442.	24420.
$V_7$	9.53	230	2192.	21920.
$V_8$	9.31	210	1955.	19550.
$V_9$	9.18	190	1744.	17440.
$V_{10}$	9.08	170	1544.	15440.
$V_{11}$	9.01	150	1352.	13520.
$V_{12}$	8.98	130	1167.	11670.
$V_{13}$	8.96	110	986.	9860.
$V_{14}$	8.94	90	805.	8050.
$V_{15}$	8.93	70	625.	6250.
$V_{16}$	8.93	50	446.	4460.
$V_{17}$	8.93	30	268.	2680.
$V_{18}$	8.93	10	89.	890.
			<u>Total</u>	<u>320880.</u>

$320880 \times \frac{1}{r^2} = \frac{320880}{35360} = 9.076$ , or four times the average square root

of the Pitot reading for the whole cross section of the stack. The average square root of the Pitot reading therefore = 2.269.

These measurements covered a period of eight and one-half hours. The average velocity corresponding to the average square root of the Pitot reading (2.269) is 55.80 ft. per second, which gives a volume of 3,721,000,000 cu. ft. in twenty-four hours under the conditions assumed to exist in the stack: temperature = 174.7° C, and pressure = 612.2 mm. Under external conditions of  $t = 17^\circ$  C, and  $p = 612.2$  mm., the volume would be 2,411,000,000 cubic feet; and under standard conditions, 1,828,000,000 cubic feet. Although the results have been calculated to the same internal and external pressures, the external pressure exceeded the internal by about 5 mm. Other tests will be given later which covered a greater period of time. The curve at 4 feet from the inside wall shows 9.95 as four times the square root of the Pitot reading. The average for the whole cross section of the stack, 9.076 divided by 9.95, the value at 4 feet, gives the factor 0.912. The average velocity over the whole cross section of the stack is therefore 0.912 of the maximum velocity, or the velocity at a distance of 4 feet from the inside wall. This factor is used later in converting velocity at this point into average velocity.

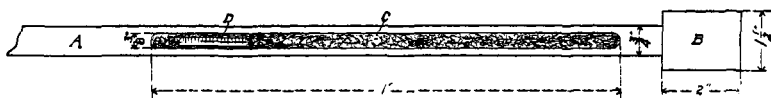
It had been planned to use sixteen tubes in the determination of the

velocity of the smoke, but this method had to be abandoned on account of the small size of the opening through which the tubes were introduced. However, the arrangement will be described as it was planned, since it is a somewhat better method than the one we were forced to use. Sixteen tubes are placed in one cross section of the stack in the form of a spiral, each tube at an angle of seventy-two degrees from its neighbors on the spiral. On account of the much greater area of the outer rings when the cross section is divided into concentric rings of equal width, the greater part of the tubes should be near the wall of the stack. In order to obtain the true average Pitot pressure ( $h$ ), allowance should be made for this fact by some method which depends upon the law, that the area of a circle is proportional to the square of its radius. If the radius is squared and this square divided into fifteen equal parts, the proper distance of the tubes from the center are found by extracting the square root of each of the numbers obtained in this way. For example, in the case of a stack with a radius of fifteen feet the numbers would be: 0, 15, 30, 45, 60, 75, 90, 105, 120, 135, 150, 165, 180, 195, 210 and 225. When the square roots of these numbers are taken, the distances of the tubes from the center are found to be as follows: 0, 3.87, 5.48, 6.71, 7.74, 8.66, 9.48, 10.24, 10.95, 11.62, 12.24, 12.83, 13.40, 13.95, 14.48, and 15. It would be even better to use nineteen tubes at distances of eighty degrees. All the tubes are connected through large air chambers (one for each arm of the manometer) to a differential manometer, or floating manometers may be used according to the method given by Captain Taylor. When this plan is followed, a mechanical average of the pressure through the stack is obtained, taking into account the greater area of the outer rings. The air chambers should be connected to the Pitot tubes so that there are separate connections provided with stop cocks for each tube. In this way readings may be taken on any one, or on all at the same time. The pressure given by the tube in contact with the wall of the stack is so low that it should not be connected with the manometer when the mechanical average is being taken, for it influences too greatly the pressure in the chambers. The greatest error in this method of obtaining a mechanical average is due to the fact that the average velocity obtained is not the true average velocity, but the square root of the average of the squares of the velocities. Still, the results obtained are so nearly correct that they are satisfactory for most purposes. If the relation between these quantities is desired, it can be determined by the apparatus as described above. Since the method would be obvious to a worker who could do work sufficiently accurate to need such a relation, only a bare outline of the procedure will be given. The readings of the separate tubes should be taken in order, one at a time, as rapidly as possible, and this procedure repeated a number of times. After each is

read separately, a reading should be taken with all the tubes connected, except those that have not been included in the mechanical average. The single readings should then be calculated to velocity, and curves drawn showing its variation with the distance from the wall of the stack. From these can be calculated the average velocity by the method given later, or by any other satisfactory method. These results should then be compared with the results from the mechanical averages which were obtained under the same conditions. The ratio will serve for the correction of all the mechanical averages obtained during the drawing off of smoke samples. A simpler method would be to use the tubes singly in determining the velocity curve according to the method given by Figure 3 and the accompanying description.

*Measurement of the Temperature.*—The temperature was measured by the simplest means possible, which, while not so satisfactory as a good self-recording instrument<sup>1</sup>, gave accurate measurements for the times that the readings could be taken. An accurate chemical thermometer was put in a long iron pipe A, Figure 4, with the bulb of the

FIGURE 4 Scale  $\frac{1}{2}$  Size



thermometer wrapped carefully in asbestos. The bulb was protected by an iron cap (B), two inches long and one and one-half inches in diameter. The whole stem of the thermometer, except the portion to be read, was wrapped in asbestos, and then the small exposed portion of the scale was covered with a loose layer of the same material. The scale of the thermometer could be read through a long slot (C) in the wall of the pipe. Before beginning the readings, the bulb (B) was put in the desired location in the stack, and left there for one hour. The pipe was then very quickly partially withdrawn, until the portion of the thermometer to be read (D) was just outside the sampling hole. This portion was quickly uncovered and the reading taken; then the scale was at once recovered and the instrument immediately inserted in the stack. Subsequent readings could be taken every fifteen minutes.

*Velocity Measurements for the Smoke Samples.*—Sample 4 was taken during a period of twenty-eight hours. Preparations had been made for a seventy-two hour run, but a violent thunderstorm stopped the work at the end of twenty-eight hours. The data and results of the velocity determinations for this sample are given in Table 3.

<sup>1</sup> A recording resistance thermometer may be used near the wall of the stack.

TABLE 3.  
VELOCITY OF THE SMOKE.

$$V = \sqrt{\frac{2gh D_{ethier}}{D_{gas}}}$$

Density of Ethier = 0.7300  
Density of Gas = 1.018 Density of Dry Air.

	Pitot Reading.	Temper- ature.	h Feet	Density	Velocity ft. per sec. = V
Aug. 23, '05					
A.M. 11.45	5.00	177	.04167	.0006312	55.95
12.45	4.75	177	.03960	.0006312	53.75
P.M. 1.45	5.25	173	.04375	.0006365	56.22
2.40	5.25	173	.04375	.0006365	56.22
3.00	7.00	173	.05833	.0006365	64.96
3.50	5.50	173	.04583	.0006365	57.60
4.30	6.00	173	.05000	.0006365	60.16
4.45	5.50	174	.04583	.0006350	57.64
5.00	6.50	177	.05416	.0006312	62.88
5.20	6.50	178	.05416	.0006298	62.96
3.40	6.25	174	.05208	.0006350	61.41
6.00	6.00	177	.05000	.0006310	60.43
6.10	7.00	176	.05833	.0006324	65.20
6.30	6.50	174	.05436	.0006350	62.76
6.50	7.00	180	.05833	.0006266	65.45
7.20	6.50	170	.05436	.0006406	62.52
7.55	7.50	172	.06250	.0006379	67.19
8.05	8.00	172	.06667	.0006379	69.40
8.20	8.25	176	.06867	.0006417	70.75
8.45	7.75	174	.06460	.0006350	68.42
9.15	7.00	173	.05833	.0006365	64.95
9.45	7.00	174	.05833	.0006350	65.00
10.00	7.00	174	.05833	.0006350	65.00
10.20	7.00	175	.05833	.0006329	65.13
11.15	6.00	180	.05000	.0006265	60.56
11.40	6.25	170	.05208	.0006409	61.16
A.M. 12.05	6.50	175	.05416	.0006329	62.75
12.15	6.50	180	.05416	.0006265	63.07
12.30	6.25	175	.05208	.0006329	61.54
12.50	6.50	174	.05416	.0006350	62.66
1.30	7.25	180	.06040	.0006265	66.70
2.00	8.00	175	.06667	.0006329	69.49
2.30	8.00	179	.06667	.0006283	69.95
3.30	7.00	174	.05833	.0006350	65.03
4.20	7.25	170	.06040	.0006409	65.86
4.45	7.50	171	.06250	.0006398	67.15
5.15	7.25	169	.06042	.0006423	65.82
5.45	7.00	165	.05833	.0006481	64.41
6.20	6.50	160	.05416	.0006557	61.65
6.40	6.00	158	.05000	.0006585	59.17
7.10	7.00	165	.05833	.0006484	64.41
7.25	8.00	166	.06667	.0006470	68.87

Time.	Pitot Reading.	Temperature.	4 Feet	Discharge	Velocity ft. per sec. = V
8.05	8.50	173	.07083	.0006363	71.58
8.25	9.00	173	.07500	.0006363	73.65
9.20	8.50	175	.07083	.0006265	71.76
9.55	9.25	180	.07708	.0006329	75.22
10.45	9.50	185	.07916	.0006200	76.63
10.55	9.40	180	.07837	.0006265	75.84
11.05	9.40	180	.07837	.0006265	75.84
11.15	8.50	175	.07083	.0006329	71.75
11.20	9.50	175	.07916	.0006329	75.84
11.30	9.75	185	.08124	.0006200	77.64
12.00	8.75	178	.07294	.0006296	73.40
P.M. 12.25	9.00	177	.07500	.0006310	74.01
12.40	9.25	185	.07708	.0006200	75.65
1.00	8.75	183	.07294	.0006245	73.36
1.30	9.00	187	.07500	.0006175	74.78
2.00	8.50	171	.07083	.0006394	71.42
2.15	8.50	171	.07083	.0006394	71.42
2.32	9.00	180	.07500	.0006265	74.22

$g=32.158$  Average Gas Pressure= $612.2\text{mm.}^1$

Pitot tube at 48 inches from the inside wall of the stack.

The average velocity was obtained by plotting the results given in this table as ordinates and the time in hours as abscissæ, which gave the curve shown in Figure 5. The average velocity was found by obtaining

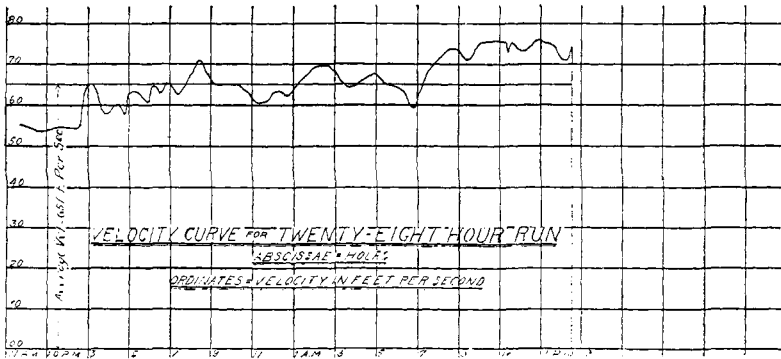


FIG. 5

the area of the curve with a planimeter, and dividing this area by the horizontal distance across it. The result obtained in this way is 65.00 feet per second. From this the average velocity for the whole cross section of the stack is 59.24 feet per second, or 65.00 multiplied by 0.912, the factor for conversion into average velocity, and the volume per day at the temperature of the stack, 3,098,000,000 cubic feet. At the temperature of  $17^\circ$  (the average temperature of the surrounding air) the volume would be 2,007,000,000 cu. ft., and under standard conditions, 1,523,000,000 cu. ft.

<sup>1</sup>On account of the breaking of our standard barometer during transit by express, an aneroid barometer had to be used in taking the pressures.



The average velocity for smoke sample 2 was found in exactly the same way, the data being given in Table 4. On account of an accident to the velocity determination apparatus, there is a considerable break in the readings between 8.30 and 12 A. M.

TABLE 4 (Sample 2). VELOCITY OF SMOKE.

July 23, 1905.		p = 613.4 mm.			
Time.	Pitot.	T.	h Feet	Density	V.
A.M. 1.00	7.25	182	.06038	.0006264	66.64
1.15	7.00	182	.05828	.0006264	65.45
2.00	6.75	182	.05624	.0006264	64.34
2.50	6.50	182	.05414	.0006264	63.14
3.30	6.25	182	.05204	.0006264	61.84
4.10	5.50	182	.04580	.0006264	58.01
5.10	5.50	182	.04580	.0006264	58.01
6.10	5.25	182	.04372	.0006264	56.63
6.46	5.00	182	.04165	.0006264	55.36
8.30	4.75	181	.03957	.0006276	53.85
12.00	3.25	181	.02708	.0006276	44.58
P.M. 3.15	3.00	181	.02500	.0006276	42.85
3.35	3.20	181	.02666	.0006276	42.29
3.50	3.50	181	.02956	.0006276	46.28
4.00	4.00	181	.03332	.0006276	49.44
5.10	3.00	181	.02500	.0006276	42.85
6.00	2.50	181	.02092	.0006276	39.10
7.15	3.25	180	.02708	.0006294	44.57
7.50	4.00	179	.03332	.0006306	49.37
8.15	4.50	178	.03750	.0006308	52.34
8.45	5.00	177	.04165	.0006334	55.04
9.15	5.00	176	.04163	.0006340	55.03
9.45	4.50	175	.03750	.0006361	52.15
10.00	4.00	174	.03332	.0006370	49.10
10.25	4.50	174	.03748	.0006376	53.07

The average velocity as calculated from the curve, Fig. 6, is 50.90

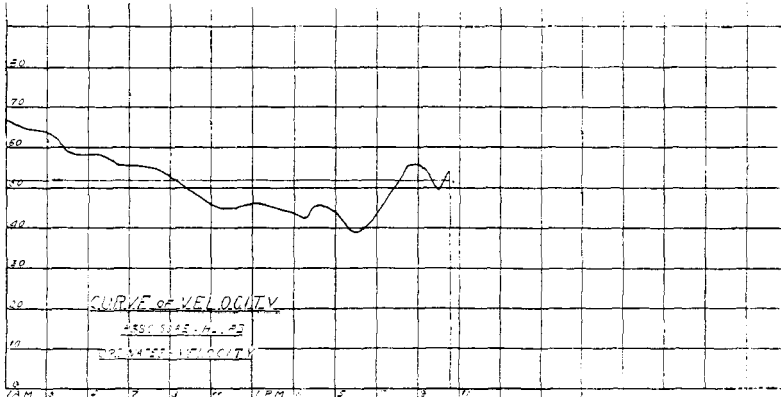


FIG. 6

feet per second; this multiplied by the factor 0.912, gives the average velocity for the whole cross section of the stack as 46.43 feet per second. The volume at the temperature of the stack in cubic feet per day is 3,098,000,000; under the conditions of the outside air, 2,007,000,000; and under standard conditions, 1,523,000,000.

Another smoke sample was taken on July 27, 1905, the measurements being made four feet from the inner wall of the stack, and under an average pressure of 616 mm. The results of the velocity measurements are given in Table 5.

TABLE 5 (Sample 3).—VELOCITY OF SMOKE.

July 27, 1905.		p = 616 mm.				
Time.	Pitot inches	T	h Feet	D <sub>dry air</sub>	v	
A. M. 8.40	4.00	189	.0333	.0006187	49.80	
8.55	4.00	189	.0333	.0006187	49.80	
9.30	4.25	189	.0354	.0006187	51.38	
10.00	4.50	189	.0375	.0006187	52.85	
10.35	4.75	189	.0396	.0006187	54.32	
11.10	4.75	190	.0396	.0006076	54.40	
11.45	5.00	189	.0416	.0006187	55.63	
P. M. 12.45	5.00	188	.0416	.0006292	55.58	
1.30	5.00	187	.0416	.0006018	55.55	
2.20	5.50	188	.0458	.0006202	56.44	
3.10	4.75	189	.0396	.0006187	54.32	
3.45	4.75	191	.0396	.0006148	54.46	
5.00	5.25	189	.0437	.0006191	57.02	
6.00	5.25	188	.0437	.0006292	56.98	
6.15	5.00	187	.0416	.0006018	55.58	

The average velocity is 54.86 feet per second, or 50.04 feet per second for the whole cross section of the stack. The volume of the smoke per day is 3,337,000,000 cubic feet at the temperature of the stack; 2,092,000,000 cubic feet at the temperature of the outer air ( $17^{\circ}$ ); and 1,595,000,000 cubic feet at standard conditions.

A summary and average of the volume determinations will be given later in the paper.

*Standardization of the Meter.*—A recording wet meter would have been used for this work if it could have been procured in time, but the best instrument available was of the type of dry meter used for measuring the volume of illuminating gas.

The great inconvenience of this type is that for small volumes it is necessary to keep track of the movement of the hand which gives the number of cubic feet and fractions, since the recording hands do not move with sufficiency accuracy. This is not so great an inconvenience as it seems, for in any case it is necessary to note constantly the velocity at which the smoke is passing through the sampling apparatus. The meter was tested by displacing the air from a large gas holder by the

addition of water. Several tests were made in this way, the gasholder being connected with the meter, and the latter to a filter pump. The meter was tested at various pressures, the pressure in the apparatus being determined and kept constant by means of a T tube which was interposed between the meter and the gas holder. The lower arm of this T tube was graduated in millimeters, and dipped into a cup of mercury. In the later experiments the gasholder was replaced by a fifty gallon tank, into which measured amounts of water were introduced from a large carboy. The results are shown in Table 6.

TABLE 6.—AIR DRAWN THROUGH METER.

Test	Pressure.	Meter	Gasometer	Correction	
		Cu. Feet.	Cu. Ft.	Cu. Ft.	Per Cent.
1	580 mm.	14.25	14.44	+ 0.19	+ 1.31
2	430 "	22.00	22.32	+ 0.32	+ 1.43
3	500 "	16.00	16.19	+ 0.19	+ 1.17

The average correction of the meter reading was taken as 1.3 per cent. Experiments at pressures slightly over 760 mm. gave practically the same correction.

*Apparatus for Collecting Samples of Solids.*—In sampling smoke for solids there are a few general principles which should be observed in the design of the apparatus for the work. The apparatus recommended for this purpose is shown in Fig. 7, of which the apparatus used by us in our work is a modification. The gas should pass through the opening (O) of the sampling tube at the same velocity as that of the surrounding smoke, which may be as great as 75 feet per second, or 4,500 feet per minute, according to the data given in Table 3. The flue dust tends to collect to some extent around the edge of the opening (O), and if this is very small, may change the diameter so materially that it is difficult to calculate the velocity through it. If this factor alone were considered, the opening (O) would be made large; but, since the volume of the smoke which passes through the sampling apparatus varies as the square of the diameter of the tube, the practical limit must be small, unless the apparatus is made exceedingly large. The apparatus as shown in Figure 6 is intended for an opening 0.60 to 1.00 centimeter in diameter. When the opening is of this size, the apparatus must be large, if the velocities encountered are as great as those in our experiments. The tube (B) through which the smoke first passes after leaving the stack, is shown as eight centimeters in diameter, and the rest of the apparatus in proportion; though if convenient, it would be better to have this one tube (B) even larger.

In the case of sample Number 4, (A) was a Jena hard glass tube, 24 feet long, supported and protected by an iron pipe in which it was placed. A porcelain lined iron tube was tried in the case of sample 1 (which has not been given), but this was unsatisfactory as the porcelain

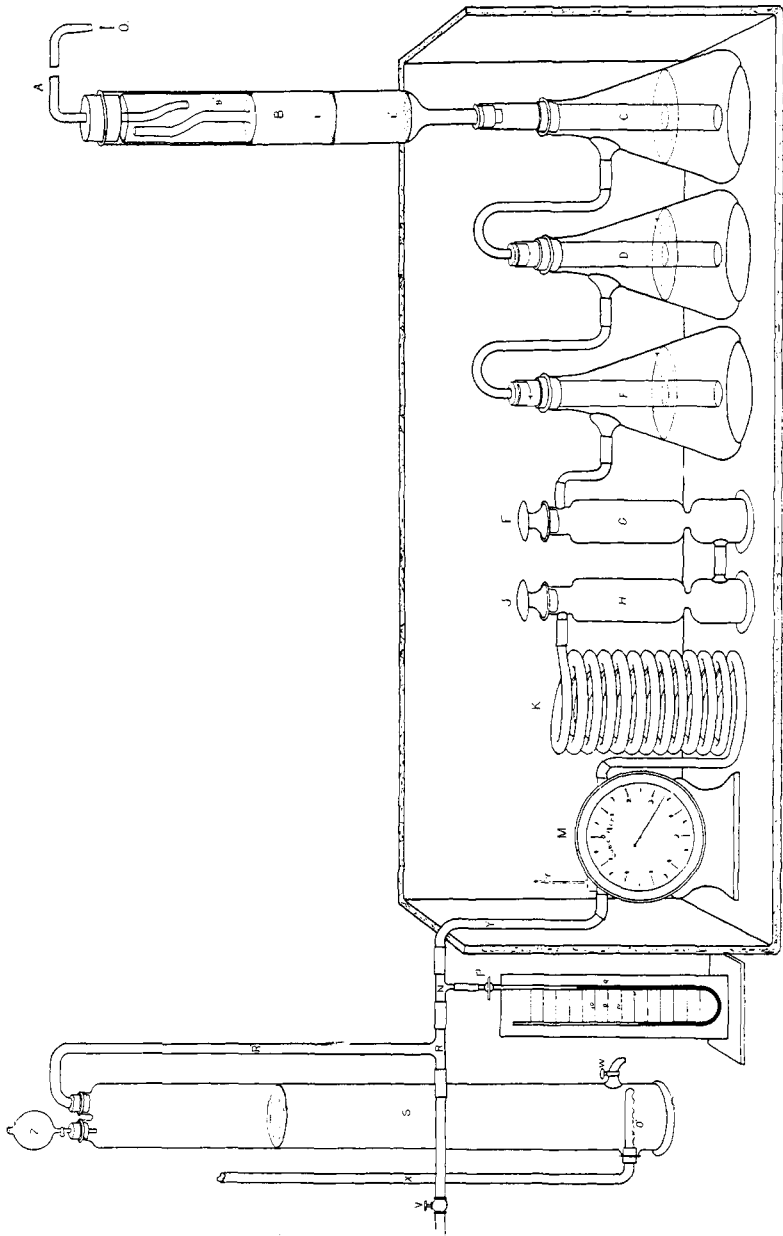


FIG. 7. Apparatus for Collecting the Solids of Smoke.

lining cracked. (B) is a large tube of thin glass, having projections on the inside for the support of other apparatus; B', a glass cup<sup>1</sup>, de-

<sup>1</sup> This is omitted, if the total weight of dust is not desired. A simple cup, without the inside tube, would serve as well and be less fragile. It is supported by platinum wires.

signed to catch any heavy dust which may pass through the tube A; L and L' are porcelain discs upon which ash free absorbent cotton is piled loosely. The gas next passes through three large filter flasks (C, D, and E), then through two bottles (G and H) filled with absorbent cotton; and finally, just before entering the meter, through a coil of thin copper tubing in order to equalize the temperature. This apparatus, including the meter, is contained in a box in which all the apparatus may be carried. The box is made water tight, so that water may be kept running through it in order to maintain a constant temperature. A window just in front of the dial of the meter, makes the reading of the latter easy, while a cover having openings for the tubes (B) and (Y), protects the apparatus while in use and during its transportation. After passing the meter, the gas is drawn off through an iron pipe. The pressure is partially regulated by the valve (V) in the pipe, and is measured by the manometer (Q), being finally determined by the height of the liquid (mercury or water) in the regulating tower (S). The exhaust through the valve (V) is always kept just strong enough to cause a small amount of air to pass down the tube (X), through the openings (O'), the column of liquid in (S), and the tube (K) into the T tube which forms a portion of the main exhaust pipe. Liquid may be added to the tower (S) by the dropping funnel (Z), or drawn off through the outlet (W). The three filter flasks contain water or some other liquid absorbent; and although not shown in the drawing, the lower portions of the tubes (C), (D), and (E), are pierced by a large number of small holes. The connections are made by rubber stoppers and by rubber tubes which have been first soaked in strong caustic potash solution, then in water, and finally in paraffin. Glass stoppers are not so satisfactory, since they sometimes begin to leak suddenly; and they weaken the apparatus, making it less flexible. Large rubber stoppers have the base covered by a disc of glass. Other parts may easily be added to the apparatus, such as a large trap to catch the solids just before they pass into B, in order to decrease the clogging of the absorbent cotton by dust.

It will be found, on using a properly constructed apparatus, that the greater portion of the heavy solids will deposit before reaching the absorbent cotton; however, it will be necessary to insert the trap in (A) if high velocities are to be used.

In our work we used a smaller opening (O) of the sampling tube, and found that in a short time the maximum amount of flue dust collected at its mouth, the high velocity at this point keeping it from filling up to any extent. Still, the larger opening is advised, since its free diameter can be calculated with more certainty. The opening should be of platinum foil, or of a sharpened glass tube. If it is desired that the mouth of the sampling tube should be placed in different portions of the cross section

of the stack for different periods of the time of sampling, this may be accomplished by making the portion of the sampling tube (A) which lies outside the stack in several joints.

It will often be advisable to use the apparatus in a simplified form, in which case the tube (B) may be made from a condenser jacket simply filled with cotton. This was the form of apparatus used in the work given in this paper, and it proved very satisfactory. However, the glass tube (A) was so long that it rendered the use of a cup or a trap unnecessary, as will be shown by the data on Sample 4.

*Determination of the Total Weight of the Solids.*—In determining the total weight of the solids contained in a certain volume of the smoke, as great a quantity of the dust as is possible should be collected before the smoke reaches the absorbent cotton. Asbestos fiber may be used in the place of the cotton, but the latter is more efficient in stopping the finer particles. A large amount of the solids can be shaken out from the tubes (A) and the cup (B') and weighed without further treatment. The whole inside of the apparatus should then be washed<sup>1</sup> with water, the solution filtered and evaporated. The residue from the evaporation and that on the filter paper (or better, in the Gooch crucible) is first dried and then weighed. The remainder of the solids may then be washed out by aqua regia, the solution evaporated, the residue dried and weighed. The cotton, which should be of a known weight and ash content and as ash free as possible, is decomposed by nitric and sulphuric acids until the organic matter is entirely destroyed, then the solution is evaporated, and the residue dried and weighed. Although a portion of the dust is changed somewhat in chemical composition by the action of the solvents, the results are sufficiently accurate. The total weight of the dust may be checked by a complete analysis of the residues.<sup>2</sup>

*The Collection and Analysis of the Samples.*—Sample 4, the velocity determinations for which are given in Table 3, was taken from the center of the stack through a tube (A) of Jena glass 23 feet in length and one-half inch in diameter, with a small opening (O) through which the smoke was drawn. The sampling was begun August 23 at 10.55 A. M., and continued, with an hour's intermission, until the next day

<sup>1</sup> To aid in the washing, the tube (A) may be cut into sections, and a glass rod with a rubber end used to loosen the adherent particles.

<sup>2</sup> The use of several large porcelain filters (six inches in diameter) has proved satisfactory in preliminary experimental work on the determination of the total solids. The first filters are covered with coarse, and the last with finely shredded asbestos. No liquid absorbent is used, but the tubes leading to the filters must be cleaned carefully. The weight is determined by direct weighing after drying. This method may be used where the more complex apparatus of our standard method is too cumbersome. Filter paper may be used for low velocities in cases where the smoke does not have a chemical action upon the paper.

at 2.32 P. M. The total volume of the sample at 17° was 123.2 cubic feet, this being the meter reading, corrected for the error of the meter, and for the solubility of the gases in the absorbing liquid. Since in this case the opening (O) was so small that the sampling velocity did not need to be very great, it was decided to ascertain how much of the sample would deposit in the glass tube (A) (Figure 6). The tube (B) was omitted, but in its place, the tubes (C), (D) and (E) were filled with absorbent cotton. The velocity of the gas through the sampling tube itself was approximately one and one-half feet per second, the first fifteen feet of the tube from the opening having a temperature of 174.7° on the average, while in the remaining eight feet, the temperature fell gradually to about 25°.

The deposit in the tube was washed with water, and the water solution analyzed for arsenic, giving 0.009496 grams of arsenic trioxide per cubic foot, or 53,580 pounds per day of soluble arsenic trioxide for the portion of the sample which settled in the tube. The solution in the flasks was filtered, and the filtrate added to the water washings of the cotton. On analysis, this gave 0.001446 grams of arsenic trioxide to the cubic foot, or 8,200 pounds per day, which shows that 87.7 per cent. of the soluble arsenic was collected in the glass tube (A). The insoluble portions were analyzed together, and gave 6,000 pounds per day of water insoluble arsenic calculated as arsenic trioxide. This sample gave as a result, 61,780 pounds of water soluble arsenic trioxide; 6,000 pounds of water, insoluble; and a total of 67,780 pounds of arsenic trioxide per day as the amount sent out in the smoke.

In the case of Sample 2 (See Table 4 for the velocity determination), the sample was divided into two parts; the water soluble and the water insoluble. The sample was taken from a point four feet from the inner wall of the stack, beginning July 23, 1905, at 1 A. M., and stopping at 10.35 P. M. the same day. Of this time there were four hours during which the sampling apparatus was not running. The results of this test are shown in Table 7, which gives the results for the more impor-

TABLE 7.

APPROXIMATE AMOUNTS OF SUBSTANCES EXPELLED IN THE SMOKE, AS DETERMINED FROM SAMPLE 2.<sup>1</sup>

Substance.	Water Soluble.		Water Insoluble.		Total.	
	Grams per cu. ft.	Pounds per day.	Grams per cu. ft.	Pounds per day.	Grams per cu.ft.	Pounds per day.
Arsenic trioxide	0.01212	52.650	0.001428	6,204	0.01355	58,854
Antimony trioxide	0.000650	2,800	0.000321	1,400	0.000971	4,200
Copper	0.00071	3,100	0.00046	2,000	0.00117	5,100
Lead	trace		0.00110	4,800	0.00110	4,800
Zinc					0.0013	5,500
Iron and Aluminum Oxides	0.00318	13,800	0.00221	9,600	0.00539	25,400
Bismuth					0.00021	880

<sup>1</sup> Volume of smoke per day for Sample 2 = 2,007,000,000 cu. ft. under the conditions of the meter. Volume of sample (corrected) = 72.53 cu. ft.

tant metals. Where only the total is given, the soluble and insoluble portions were united before making the determination.

The analysis of Sample 3 (velocity of determination, Table 5) is given in the form of a table of the same kind (Table 8).

TABLE 8.

APPROXIMATE AMOUNTS OF SUBSTANCES EXPELLED IN THE SMOKE, AS DETERMINED FROM SAMPLE 3, JULY 27, 1905.

Substance.	Water Soluble.		Water Insoluble.		Total.	
	Grams per cu. ft.	Pounds per day.	Grams per cu. ft.	Pounds per day.	Grams per cu. ft.	Pounds per day.
Arsenic trioxide	0.00988	47,000	0.00089	4,210	0.01077	51,210
Antimony trioxide					0.00093	4,400
Copper	0.00058	2,700	0.00023	1,080	0.00081	3,780
Lead			0.00100	4,750	0.00100	4,750
Zinc	0.00137	6,480			0.00137	6,480
Iron and Aluminum Oxides	0.00109	5,280	0.00162	7,680	0.00271	12,960
Silica					0.00219	10,260
Manganese	0.000040	180			0.000040	180

Volume of Smoke per day under the conditions of the meter = 2,161,000,000 cu. ft. Volume of sample (corrected) = 72.40 cu. ft.

In obtaining the above results, standard analytical methods were used, the arsenic determinations being made, as a rule, in triplicate, using different methods. The arsenic and antimony were separated from the lead, bismuth, and copper, by the use of chemically pure sodium sulphide, using in each case a fresh solution. The arsenic was separated from the antimony by a fusion method, by distillation, or by precipitation of the pentasulphide in a strong hydrochloric acid solution, the last method being preferred. In this case the pentasulphide was first weighed in a platinum Gooch crucible, then dissolved in caustic potash, oxidized by chlorine, acidified with hydrochloric acid, the chlorine boiled off, and the arsenic finally precipitated in an ammoniacal solution as magnesium ammonium arsenate. The solution was then filtered through a platinum Gooch crucible, and the precipitate heated by a Bunsen flame, the platinum crucible being protected from too high a temperature by a large porcelain crucible in which it was placed. The antimony was precipitated as antimony trisulphide, filtered through a Gooch crucible, and the precipitate heated in a stream of carbon dioxide in a Paul's drying oven. The lead was determined as sulphate, and by electrolysis; the bismuth, separated by repeated precipitations with ammonium carbonate; and the copper determined by electrolysis.

*Sulphur Dioxide.* Five determinations of sulphur dioxide, made August 25, 1905, will be given here to show something of the amount of sulphur dioxide which is thrown off by the smelter. Other determinations were made at different times, but will not be reported, since there is some uncertainty due to a loss of a portion of the notes. The gas



itself was drawn through tenth normal iodine solution, from ten to forty cubic centimeters being used for each test. The results were calculated from the formulas:

$$V_1 = \frac{V(B-w) \times 273}{760 \times (273 + t)} + 11.19 \quad \text{where } B = 613.4$$

$$w = 14.4$$

$$t = 17^\circ\text{C}$$

$$\% \text{ SO}_2 = \frac{11.19}{V_1}$$

The results of these determinations are shown in Table 9, where the probable value is calculated from the formula,  $v = 0.6745 \sqrt{\frac{v^2}{n-1}}$  where  $v$  is the variation of the probable value from the determined average.

TABLE 9.--PERCENTAGE OF SULPHUR DIOXIDE.

No.	Volume sample.	Vol. = 10 cc. l.	V <sub>1</sub>	Per cent. SO <sub>2</sub>	v	v <sup>2</sup>
1	2100 cc.	1030	790.2	1.417	-.076	.005776
2	900	900	679.0	1.648	-.155	.024025
3	1020	1020	768.0	1.458	-.035	.001225
4	3815	953.7	718.2	1.558	-.065	.004225
5	3225	1075	809.0	1.384	-.109	.011881
Average per cent. by volume of SO <sub>2</sub> = 1.493 ± .0732.						

Gravimetric determinations of sulphuric acid were made on the remaining solutions, and the sulphuric acid determined by difference. The average percentage by volume was 0.114.

A summary of the volume determinations and analyses of the smoke, is given in Table 10, where all the results for volume are given as calculated to uniform temperatures and pressures. The results for sulphur dioxide are obtained by taking the average percentage, and calculating the amount for each volume as given for the separate volume determinations.

TABLE 10.--SUMMARY OF THE VOLUME DETERMINATIONS.

Sam- ple.	Velocity ft. per sec.	Cu. ft. per day at temp. of stack = 174.7° p = 612.2 mm.	Cu. ft. per day at temp. surrounding air = 17° C.	Cu. ft. per day standard conditions.	Tons Sul- phur dioxide per day
2	46.43	3,098,000,000	2,007,500,000	1,523,000,000	2,038
3	50.04	3,337,000,000	2,161,000,000	1,641,000,000	2,195
4	59.24	3,951,000,000	2,561,000,000	1,942,000,000	2,597
5	55.80	3,721,000,000	2,411,000,000	1,828,000,000	2,443
Average	52.88	3,525,800,000	2,285,100,000	1,753,500,000	2,318

AVERAGE IN POUNDS PER DAY OF SUBSTANCES THROWN OFF IN THE SMOKE.

Arsenic trioxide	59,270
Antimony trioxide	4,320
Copper	4,340
Lead	4,775
Zinc	6,090
Oxides of Fe and Al	17,840
Bismuth	880
Manganese	180
Silica	10,260
Sulphur trioxide	447,600
Sulphur dioxide	4,636,000

These results show that while the great flue, previously described, may be fairly efficient in settling the copper from the smoke, still a considerable amount escapes, while the amount of arsenic given off is very great. The greater part of this arsenic is in the form of the trioxide, though the crystals are somewhat rounded. A small amount exists as the trisulphide, and in the form of complex minerals containing iron. No attempt was made to identify the latter, but, judging from the ore, there was undoubtedly some enargite present.

Samples of flue dust were taken from the big flue in August, 1905, beginning at the bottom of the stack, and sampling at approximately equal intervals to the bottom of the sixty foot flue, a distance of about 2,200 feet. The results of the analyses for copper and arsenic as given in Table II, throw some light on the efficiency of the flue, especially when the results of the analyses of the smoke are also considered. The flue collects daily approximately fifty tons of dust, but it seems evident that the amount collected near the stack would be much less than that collected in the portion nearer the furnaces.

TABLE II.—ANALYSES OF FLUE DUST.

Number.	Location.	Per cent. Cu.	Per cent. As <sub>2</sub> O <sub>3</sub> .
1	Near foot of stack	4.64	26.06
2		5.23	22.00
3		5.85	16.40
4 <sup>1</sup>	Bottom of 120' flue	5.89	12.62
5	Near top of narrow flue	6.33	10.32
6		7.37	8.85
7	Bottom of narrow flue	8.00	7.14

Dust collected from the outside of the glass sampling tube in the stack gave 25.7 per cent., and dust which dropped from the top of the stack, 25.63 per cent. of *soluble* arsenic calculated as trioxide.

The flue dust at the top of the big flue is roasted to produce commercial arsenic trioxide, but all of the rest is sent to the reverberatories and smelted for copper, so that the arsenic which it contains must in the end be eliminated in the smoke, excepting only that portion which goes into the reverberatory slag.

The amount of copper deposited is greatest at the bottom of the flue, just as would be expected, since the copper is not in a volatile state; but the amount of arsenic increases rapidly as the stack is approached. The flue evidently ends just where it is beginning to be very effective in the condensation and settling of the trioxide of arsenic, and the greater part of this substance passes out through the stack. However, even at the bottom of the sixty foot flue a considerable amount is deposited. It is evident that a large percentage of the oxide of arsenic which condenses to the solid state while in the flue, is carried along simply be-

cause it is so fine that it will not deposit at the rate the gas is moving, 11.4 feet (3.47 meters) per second. Most of the crystals which were obtained in the stack, were from 0.006 to 0.020 millimeters in diameter, but collected together in larger masses. After withdrawing each sample of smoke the sampling tube (A) (Figure 6) contained considerable loose dust which ran high in arsenic, and on the walls of the tube there was always some of the trioxide which had crystallized from a vapor. The sulphides of lead, bismuth, and arsenic were deposited in definite rings on the walls of this tube. The flue collects the greater part of the heavy metals, but allows the most of the white arsenic to pass as a finely divided solid, and as a gas.

*The General Effects of the High Stack.*—The change from low stacks to a very high one, has given an excellent opportunity to observe the difference in their effects. The result of the change has been to decrease the amount of arsenic deposited near the stack, and to spread it over a greater area. On account of the higher specific gravity of the smoke, it tends finally to fall to the earth, even though it may first be carried to a very great height, often striking the ground at distances of from one to four miles. As a general thing, the sulphur dioxide is more dilute when it reaches the ground than it was in the case of the lower stacks. However, there is often a greater amount of damage done in certain valleys which were previously protected by the mountains, but into which the smoke can now drop. The trees on certain high mountain sides are also acted upon more than before, in some cases showing a streak in the forest where the current of smoke passes, while below this the damage is less noticeable; but usually the gas finally descends into some valley. At times, in a high wind, the smoke will come to the ground at the base of the stack; and the leaves of shrubs in the valley about half a mile from the stack, and 1000 feet lower than its top, show a very high percentage of arsenic.

On the contrary, in still weather, the smoke sometimes rises very high, and seems to be carried away at a great elevation. It is certain, at least, that on level land, near the stack, the action of the sulphur dioxide is less intense than before, and as a result it is easier to raise trees and vegetables. In spite of these beneficial results the building of a high stack cannot always be recommended. Such a case was that of the Keswick smelter, where the smelter lay in a low, narrow valley. The short stacks threw out smoke which killed practically everything within a mile and a half on the low land. This district would have been of little use had a high stack been constructed, and the result would have been to spread the injurious action over an undamaged area, only to protect that which was already ruined.

In order to determine to what extent the smoke was diluted before

striking the ground, one sample of air taken at a distance of two and one half miles was analyzed for arsenic, and gave three thousandths of a milligram of the oxide to a cubic foot. In this case we were in the rapidly passing clouds of dilute smoke only about one fourth of the time. Another analysis at the same distance gave one part of sulphur dioxide to thirteen thousand parts of air. Analysis of cloths, snow, wood, grass, and other substances showed considerable quantities of arsenic: most on surfaces turned upward, slightly less on vertical sides facing the smelter, and very little on vertical sides facing away from the smelter. The arsenic in the smoke as shown by the analyses, was, in the three cases, 91.8 per cent. 91.1 per cent., and 89.4 per cent. soluble in water; and the arsenic in two samples of grass was 92.6 per cent. and 83.6 per cent. soluble in the digestive fluids of the cow. As a rule, the arsenic in the grass is less soluble than that in the smoke, since the rains wash away the more soluble portions. The subject of the deposition of the arsenic will be treated in detail in the second article of this series.

The concentration of the sulphur dioxide in the air of a smelter district is much more variable than in the great cities during the winter. In neither case, however, is much known of the actual percentages present. While the amount present in a concentration of even a few hundredths of a per cent, may easily be determined by absorption in iodine or potassium permanganate, no method is at present known for the determination of the minute amounts of sulphur dioxide present in ordinary or even city air. The best that can be done at present is to approximate the total amount of sulphur gases in the air. A great deal of work has been done upon this subject recently in the smelter regions of the west using a solution of sodium bicarbonate or sodium carbonate as an absorbent. It should be emphasized that such alkaline liquids are wholly unsuitable as absorbents for sulphur dioxide, since even a ten per cent. potassium hydroxide solution does not completely absorb this gas.

In cities, sulphur dioxide is present in the greatest quantities during the winter, when it can have little action upon plant growth. In smelter regions, the amount of sulphur dioxide in the air depends more upon the winds and the humidity than upon the season of the year. The highest results for sulphur gases in city air were obtained by Oliver, who drew London air through dilute hydrogen peroxide. The amounts obtained were as follows:

	Per cubic meter.		Parts per million.
Cloudy weather	1.9 mg. SO <sub>3</sub>	= 1.52 mg. SO <sub>2</sub>	= 1.17 SO <sub>2</sub>
Light fog	2.9	= 2.52	= 1.95
Heavy fog	6.0	= 4.80	= 3.71
Yellow fog	7.2	= 5.76	= 4.45
Black fog	14.1	= 11.28	= 8.73

A comprehensive treatment of this subject is given by Max Rubner.<sup>1</sup> The determination of the amount of sulphur dioxide in the smoke stream is much more simple, since the concentration of the gas is considerable. The principal difficulty where high stacks are in use is that the smoke stream shifts so rapidly that it is usually impossible to follow it. The best time for such a determination is at night, when the smoke often settles in a cloud in the valley.

Many interesting problems have arisen in this work which could not be solved on account of lack of time. It is possible that the flue dust, as assorted by the flues and chambers, would supply a good field for work on the rare elements. An analysis made several years ago gave 0.011 per cent. vanadium, 0.027 per cent. selenium, and 0.016 per cent. tellurium; while a qualitative examination for the ordinary elements showed, in addition, the presence of silver, lead, bismuth, copper, arsenic, iron, aluminium, manganese, zinc, barium, calcium, magnesium, sodium, ammonium, silica, water, sulphuric acid, chlorides, sulphides, sulphites, sulphates and a trace of organic matter. Other elements might have been present in traces. The dust from the flue near the stack, or in the stack itself, contains a considerable amount of concentrated sulphuric acid, while that from near the furnaces contains much less. To this latter, together with the arsenic with which it is associated, is probably due much of the spotting of leaves which is so common in smelter regions. This action of the flue dust is of far less importance than that of the sulphur dioxide<sup>2</sup> in affecting the growth of plants, in spite of some recent opinions to the contrary; but the arsenic of the dust may affect to a greater degree the value of the grasses, since it renders them poisonous.

In conclusion, we wish to express our special indebtedness to Dr. John Maxson Stillman, who has helped us very greatly in all of this work. We wish also to thank Captain D. W. Taylor for the design of the Pitot tube, Professor Robert Sibley for checking the calculations, and Professors W. R. Eckart, Jr., W. F. Durand, and Albert W. Smith, for aid, and for suggestions as to the determination of velocity.

THE UNIVERSITY OF MONTANA AND STANFORD UNIVERSITY, April 22, 1907.

[CONTRIBUTION FROM THE MISCELLANEOUS LABORATORY, BUREAU OF CHEMISTRY, SENT BY H. W. WILEY WITH THE PERMISSION OF THE SECRETARY OF AGRICULTURE.]

## INJURY TO VEGETATION AND ANIMAL LIFE BY SMELTER FUMES

By J. K. HAYWOOD.

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Before taking up the subject of the actual injury to vegetation and

<sup>1</sup> Rubner, *Archiv. für Hygiene*, LVII, 323-378; LIX, 91-149.

<sup>2</sup> For a comprehensive bibliography on the subject of damage by smelter smoke see: Haselhoff und Lindau, *Die Beschädigung der Vegetation durch Rauch*, Leipzig, 1903; Schroeder, J. v., u. Reuss, C., *Die Beschädigung der Vegetation durch Rauch und die Oberharzer Hüttenrauchschäden*, Berlin, 1885.