VOL. XXX. JUNE, 1908. NO. 6.

THE JOURNAL

OF THE

American Chemical Society

PAPERS ON SMELTER SMOKE.

[SECOND PAPER.]

ARSENIC IN VEGETATION EXPOSED TO SMELTER SMOKE.[1]

BY R. E. SWAIN AND W. D. HARKINS.

Received January 28, 1908.

In a previous paper[2] there were presented the results of a study of the smoke emanating from a copper smelter now in operation near Anaconda, Montana. It was estimated that at the time the examination was made this plant was discharging daily from its main chimney an average of 59,270 pounds (26,880 kilograms) of arsenic trioxide, along with notable quantities of copper, antimony, lead, zinc, and other substances. The smelter is situated at the base of a ridge which descends steeply from Mt. Haggin, a perennially snow-capped peak rising near the main crest of the Rocky Mountains. On one side of this ridge is the valley of Warm Springs Creek in which the city of Anaconda is situated, and on the other side is Mill Valley, each typical of a number of narrow valleys and ravines leading down from the main range into a broad basin thirty-five miles long and four to six miles wide, the Deer Lodge Valley. The present paper will deal with the distribution of certain of the more notable constituents of the smoke, particularly arsenic, over the district in the vicinity of the smelter. This is a region of variable winds which often blow with great velocity, so the section affected by the solid or gaseous components of the smoke is not confined to a narrow tract nor to any closely circumscribed area. There are prevailing wind directions for each season of the year, but these are not so constant as to restrict the action in any considerable

---

[1] The work on this paper was begun in 1902 by W. D. Harkins, and was presented in abstract at the New York meeting of the American Chemical Society, December, 1906.

[2] THIS JOURNAL, 29, 970.

degree. Pouring out of the stack a thousand feet above the valley floor, the smoke stream can be traced as far as the eye can reach in that normally clear atmosphere, trailing down the valley for thirty miles toward Garrison, or often eastward in the direction of Butte, or sweeping over into Mill Valley and filling the narrow ravines which lead down from the Continental Divide, fourteen miles to the south. In spite of the height at which it is discharged the smoke may be seen very frequently to strike the valley within less than a mile from the base of the stack, while on quiet days it may rise to a considerable height and hang as a haze over the valley.

The basis of the work herein described has been the vegetation of the Deer Lodge Valley and adjacent territory, and especially the hay and wild grasses, for the primary incentive to the investigation, part of which preceded the examination of the smoke itself, was the claim on the part of the farmers residing in the vicinity of the smelter that they were suffering abnormal losses of live-stock, which they attributed to smelter fumes. The first appearance of the peculiar symptoms of disease in the stock were noticed only a few months after the smelter began to operate; the quick recovery of the milder cases upon removing them to distant pastures, and the recurrence of the disorder on their return; and the fact that the greatest disturbance was observed in those sections over which the smoke drifted most frequently, suggested that the trouble was a local one and in some way connected with the smelter.

In all cases the samples analyzed were collected by one of us or by both of us together, either in stoppered bottles or in heavy glazed jute sampling bags. With very few exceptions the results obtained are from air-dried samples, this being deemed a more reasonable and practical basis to which to refer the analyses than the more complete drying at 100°.

From each of these samples a weighed quantity (30–200 grams) was taken for analysis, placed in a large casserole covered with a watch glass and concentrated nitric acid allowed to stream over it from a pipette. Destruction of the tissue begins at once without the application of heat, and in the case of samples with many leaves which present extensive surfaces for action, the mass may ignite[1] and burn, if not carefully watched during the first stage of the decomposition. Excessive action must be checked promptly by floating the vessel in cold water or, if that is insufficient, by diluting the acid with water. By stirring it occasionally with a glass rod the sample is soon reduced to a thick, yellow, semi-liquid mass after which heat may be applied to the casserole until the most of the acid is expelled. Five to 8 cc. of concentrated sulphuric acid are then added, drop by drop. A rapid decomposition of nitro-compounds fol-

---

[1] If a large amount of acid is added there is no danger of ignition even if concentrated nitric acid is used.

lows and thereafter the mass is reduced to a charred and crisp condition by heating in an air bath to a temperature not exceeding 180°.[1] If the destruction of the tissue is not perfect enough after the addition of the sulphuric acid, successive small portions of nitric acid may be added during the subsequent heating, taking the precaution to cool the casserole to 100° or less before each addition. This method, which is essentially an application to plant tissue of the Chittenden-Donaldson method for the destruction of animal tissue, yields a final residue capable of easy extraction with acidified water. The extract thus obtained was filtered into a graduated flask and an aliquot part taken for analysis.

In all but a few cases the arsenic was estimated by applying the Marsh-Berzelius method and weighing the mirrors which resulted. In no case in which results are given was an estimate based upon comparative mirrors.

Copper was determined by evaporating another portion of the solution to dryness in a porcelain dish, igniting to destroy all organic matter, and after dissolving the residue in dilute nitric acid, precipitating the copper electrolytically. The following table gives the results of the analysis of vegetable tissue collected in the Anaconda region:

TABLE I.—ARSENIC AND COPPER IN GRASS AND HAY.

Number.	Sample.	Month.	Distance and direction.	Parts per million.[2]	
				As_2O_3.	Copper.
		1902			
1	G[3]	Nov.	0.25 E	1551	1800
2	G	Nov.	3.0 W	166	871
3	G	Nov.	4.0 W	88	708
4	H	Nov.	1.5 S	283	...
5	H	Nov.	3.0 W	36	216
		1903			
6	G	Oct.	4.0 E	10	128
6a	G	Oct.	2.0 S	11	...
6b	G	Oct.	4.0 SE	13	...
7	H	Oct.	5.0 SE	13	...
8	G	Nov.	15.0 NNE	52	164
9	M	Nov.	15.0 NNE	405	237
		1905			
10	G	Jan.	3.0 N	122	...
11	G	Jan.	5.0 E	100	563
12	G	Jan.	5.0 ESE	90	
13	G	Jan.	2.0 SSE	79	176

---

[1] Another method used by one of the writers will be described in a subsequent paper.

[2] Parts per million are equivalent to ten-thousandths of 1 per cent., and multiplied by 0.7 give the number of grains in 100 pounds of substance.

[3] H denotes a sample of hay taken from the stack; G, a sample of grass cut from the field; L, leaves of trees; B, bark of trees; C, leaves of the cedar; and V, leaves of the lily-of-the-valley.

TABLE I (*Continued*).

Number.	Sample.	Month.	Distance and direction.	Parts per million.	
				As_2O_3.	Copper.
14	G	Jan.	4.0 SE	50	80
15	H	Jan.	2.0 SSE	23	11
16	G	Jan.	2.5 SW	87	81
17	G	Jan.	4.0 ESE	68	150
18	H	Jan.	3.0 SE	8	51
19	G	Jan.	6.0 NE	170	226
20	H	Jan.	4.2 NE	85	
21	H	Jan.	3.0 NE	96	326
22	G	Feb.	3.0 N	77	112
23	G	Feb.	2.0 N	220	119
24	G	Feb.	4.5 N	217	407
25	H	Feb.	4.0 SE	22	...
26	H	Feb.	4.0 SE	21	...
27	H	Feb.	5.0 ESE	50	46
28	G	Feb.	6.0 N	30	112
29	G	Feb.	5.0 N	263	470
30	G	May	35.0 N	35	...
31	H	June	4.5 N	89	161
32	G	June	6.0 N	67	...
33	H	June	12.0 NNE	35	190
34	H	June	2.0 W	15	...
35	H	June	14.0 NNE	34	221
36	G	Sept.	6.0 N	61	...
37	L	Sept.	0.5 W	427	...
		1906			
38	G	Feb.	5.0 SE	140	
39	G	Feb.	5.5 N	180	
40	H	June	3.0 W	14	
41	G	June	4.0 W	99	
42	H	June	3.0 E	107	
43	H	June	4.0 E	18	
44	G	July	4.2 N	12	
45	G	July	8.0 NNE	111	
46	G	July	5.0 W	38	
47	G	July	3.0 SE	21	
48	G	July	1.5 SW	157	
49	G	July	2.0 S	10	
50	G	July	2.0 SW	359	
51	G	July	1.5 SW	460	
52	G	July	1.7 SW	293	
53	V	July	1.7 SW	583	
54	B	July	1.5 SW	350	
55	B	July	1.7 SW	376	
56	G	July	6.0 N	18	
57	C	July	2.0 SW	508	
58	G	July	0.7 SW	431	
59	H	Aug.	6.0 E	31	
60	B	Aug.	1.5 SW	300	
61	L	Aug.	1.7 SW	683	

TABLE I (*Continued*).

Number.	Sample.	Month.	Distance and direction.		Parts per million. As_2O_3.
62	G	Aug.	1.7	SW	482
63	G	Sept.	2.5	NW	81
64	G	Sept.	2.5	SW	100
65	G	Sept.	6.0	N	33
66	G	Sept.	4.2	N	34
67	G	Sept.	1.0	N	101
68	G	Sept.	1.0	E	236
69	G	Oct.	10.0	SW	64
70	G	Oct.	13.0	SW	38
71	G	Oct.	35.0	N	29
72	G	Oct.	34.0	N	21
73	G	Nov.	4.2	NNE	121
74	G	Nov.	6.0	NNE	73
75	G	Nov.	1.5	E	705
		1907			
76	G	Jan.	1.0	NE	265
77	G	Jan.	2.0	SE	97
78	G	Jan.	3.0	SSE	51
79	G	Jan.	4.0	SE	86
80	G	Jan.	4.0	SE	76
81	G	Jan.	6.0	SSE	47
82	G	Jan.	6.5	SE	98
83	G	Jan.	8.0	SE	79
84	G	Jan.	100.0	NW	00
85	G	Jan.	75.0	W	00
86	G	Oct.	100.0	NW	00

A few of the above samples were analyzed by each of us, using the same balance sensitive to 0.005 mg., but otherwise independently, and the mean of the results obtained taken for the table above. The complete data for each joint determination are given as follows:

TABLE II.

No.	Sample.	Per cent. As_2O_3. H.	Per cent. As_2O_3. S.	Difference. Per cent.
11	Grass	0.0103	0.0097	0.0006
16	Grass	0.0089	0.0085	0.0004
19	Grass	0.0169	0.0170	0.0001
20–31	Hay	0.0089	0.0085	0.0004
22	Grass	0.0079	0.0075	0.0004
23	Grass	0.0219	0.0220	0.0001
29	Grass	0.0264	0.0261	0.0003
33–35	Hay	0.0034	0.0035	0.0001

In all but two cases of those cited above the results given are merely duplicate determinations made on a single sample, but samples 20 and 31 and samples 33 and 35 were instances where each of us took a sample from a stack independently of the other and conducted a separate determination.

The first samples taken from this district were collected in November, 1902, but the record of all except nine of the results of the analyses made on this material and that of the following year was accidentally destroyed. The smelter started early in 1902 and continued without interruption throughout that year, so the results for grass represent a deposition of arsenic extending over a period of six months, while the hay, cut in July, was exposed less than three months. Samples 2 and 5 were taken from the same farm, but one was left exposed in the field during the whole period while the other was removed and stacked as hay. The difference here shown in the two values, 166 and 36, respectively, is fairly representative of a condition which will be found to prevail with notable uniformity throughout the analyses. An interesting exception is found in the data for 1903, where samples 6 and 7 show quantities which are not only relatively very low, but nearly equal. During 1902 and a part of the following year the smoke from the smelter was delivered from four smaller stacks which were erected near the center of the plant. But in June, 1903, the smelter was shut down until late in September in order to permit certain modifications to be made, chief among them being the final work of construction upon the present high stack and extensive settling flue. At the time these samples were collected, one from a haystack and the other of grass from the open field, the smelter had barely begun operations after the summer's inactivity, so that the two samples had been exposed to smoke only during the period of growth until the time of the closing down of the smelter in June, and both were exposed equally long. Sample 8 shows the result of an added exposure of over a month during the dry season of the year. The moss sample from the same locality gave a remarkable result which is to be explained only on the assumption that owing to its peculiar matted growth the moss may have collected the arsenic which fell upon it like a natural filter, and held on to it from the previous year. During the year 1904 no collections were made, though the hay samples taken in the early part of 1905 were from the 1904 crop. The average amount of arsenic in these hay samples collected up to May, 1905, is 41.9 parts per million, while the average of the results for grass is 120.4.

For the year 1905 a noteworthy sample is that of grass (No. 30) from Garrison, thirty-five miles north of the smelter, which carried 35 parts of arsenic trioxide per million. Two samples (Nos. 71 and 72) collected in October of the following year from the same locality carried 29 and 21 parts, respectively, per million. The former sample was old grass collected in May, at which time the grass from the preceding year usually attains its maximum content of arsenic.

It must be admitted that, whatever the amount of arsenic discharged daily with the smoke, we have, without further evidence, no satisfactory measure of its distribution. If arsenic and copper and other toxic constituents of smelter smoke were not to be found in the soil, their appearance in the vegetaton of the smoke zone could be attributed at once to atmospheric deposition. But it may be claimed that the arsenic and copper found in these samples are not deposited from the smoke stream, but absorbed from the soil itself. It is a fact that growing plants may absorb small amounts of copper from the soil, and a review of the literature would seem to leave no doubt that the same is true, in a very slight degree, for arsenic.

Voelcker[1] experimented with grass grown on soils to which arsenical superphosphate had been added, and Hehner, who made the analyses for him, found on an average 0.0045 grain of arsenic per pound of straw (0.7 part per million). Swedes under the same conditions gave no arsenic in the bulbs, and in one case only 0.02 grain per pound of dried tissue (2.8 parts per million) in the leaves and stems. Barley straw grown on soil manured heavily with superphosphate containing 0.5 per cent. arsenic trioxide carried 0.007 grain per pound (1 part per million) while the leaves of swedes and mangels grown on ordinary soils containing about 0.0002 per cent. of arsenic trioxide were found to contain 0.002–0.004 grain of arsenic per pound (0.3 to 0.6 part per million). Angell[2] analyzed a large variety of cereals and table vegetables which were grown on soil to which superphosphate carrying 0.5 per cent. of As_2O_3 was added. Of thirty-two samples examined twenty-two showed not a trace of arsenic while the rest are reported as containing slight traces. Since, however, only an acid extract of the plant in dilute hydrochloric acid was made, with no effort to destroy organic matter before adding it to the Marsh generator, and since only fifteen minutes were allowed for the arsenic mirror to appear, the results are open to very serious question. Gautier[3] found arsenic in many vegetable foodstuffs; in wheat (0.000,007 per cent.), bread (0.0000071 per cent.), and in potatoes (0.000,0112 per cent.), but not a trace in cabbage and beans. He also claims to have found it in marine and fresh water algae.

Copper in traces has been shown repeatedly to be present in plants grown on coppery soils. In fact the occasional presence of copper in plants has been admitted for nearly a century.[4] Verdrödi[5] found notable amounts of copper in buckwheat (0.87 per cent. CuO), maize (0.06–0.39 per cent.) and other cereals. These results, however, have been criticized

---

[1] *Report Royal Arsenical Commission*, Vol. II, p. 174.

[2] *Ibid.*, p. 10.

[3] Gautier, *Compt. rend.*, **139**, 101 (1904).

[4] See Meissner-Schweigg, Journal, **17**, 340 (1816); Phillips, *Ann. chim. phys.* [2], **19**, 76 (1821).

[5] Verdrödi, *Chem. Z.*, **17**, 1932 (1894); and **20**, 399 (1896).

by Lehmann,[1] who points out that they are ten times those obtained by Tscherch from soils very rich in copper, and justly criticizes the method adopted by Verdrödi for the estimation of copper, *viz.*, ashing the plant, extracting the residue with nitric and hydrochloric acids, precipitating with hydrogen sulphide, and without further treatment weighing the precipitate as copper sulphide. Lehmann's own results, however, show that minute quantities of copper may be present in certain plants which subsist on a soil containing copper salts.

There are good reasons for believing that the values given for arsenic and copper in the previous table are not due to absorption from the soil. Plants do not absorb so much arsenic or copper as is there shown. The writers have grown cereals on several soil samples which were collected in the Deer Lodge Valley. These were taken outside the range of the smelter smoke and planted to barley and timothy. In no case have they found more than 0.0002 per cent. of arsenic trioxide in the matured plants, where values as high as 0.0263 per cent. had been obtained from grass grown on the same soil five miles from the smelter. Moreover, above everything else the length of time the plant is exposed to the free atmosphere in the smelting district is the determining factor in connection with its arsenic content. A few cases illustrating this have already been cited in connection with some of the earlier results, and many others could be selected. Nos. 53 and 61, samples of wild lily-of-the-valley, were collected by one of us from the same spot about one and three-quarter miles from the smokestack and in a section over which the smoke blows much of the time in the summer months. The first one was cut July 3rd and the other August 14th, or six weeks later. During this time the arsenic content of the plants increased from 583 to 682 parts per million. At the same time these were taken a kind of wild grass (*agripirons divergens*) growing at the same place was sampled. These are designated as Nos. 49 and 62. When the first of these was collected the grass was already dead, so the increase in arsenic trioxide from 293 to 482 parts per mllion cannot be ascribed to processes of absorption from the soil. Nos. 44, 66 and 73 are meadow grass samples taken from the same field in the months of July, September and November, respectively. The July sample, covering the period of most rapid growth and most frequent rainfall, carried 12 parts of arsenic trioxide per million. The September sample more than covered the rest of the growing period and carried 34 parts, while the November sample carried 121 parts per million, thus collecting an added 87 parts after all growth had ceased.

A striking proof that the arsenic is deposited from the smoke was found by a study of the wind currents. The Mill Valley district southwest of the smelter is the one toward which the smoke blows most during the early

---

[1] *Arch. Hyg.*, **24,** 3; and **27,** 1 (1896).

summer, while late in August the air currents begin to go northward down the Deer Lodge Valley, and from this time until the snow covers the ground the greater part of the smoke blows in this direction. The analyses show that the grass of Mill Valley contains more arsenic than any other district during the early summer. Thus samples 48, 50, 51, 52, 53 and 58, which were gathered in July, 1906, contained respectively 157, 359, 460, 293, 583 and 431 parts of arsenic trioxide per million. North of the smelter, sample 12, taken in July 1906, from the Bliss ranch, contained 18 parts, one taken in September 33 parts, and one taken in November 73 parts of the trioxide per million. In 1905 the Bliss grass in June contained 67 parts, in September 61 parts, and in February, 1906 (grass of the season of 1905) it contained 180 parts per million. Hay from the same ranch cut in August, 1904, contained only 30 parts to the million, while by the next April the grass in the same field had increased its arsenic content to 263 parts. During 1906 the Para ranch gave 12 parts in July, 34 parts in September, and 121 parts in November. There is, of course, some objection to a comparison of the grass with the hay, since a certain portion of the arsenic of the latter is shaken off by the cutting and stacking. Even with the grass it is difficult to obtain the original arsenic content, since the sample must be cut, put into containers, and transported to the laboratory.

These results show very plainly that the greatest accumulation of arsenic generally occurs after the period of growth is ended and the plant is dead. There is little doubt that the rains during the early summer wash much of the arsenical deposit from the vegetation, while in winter the grass is protected by snow. The most favorable time then for the arsenic to accumulate on the tissue is during the late summer and fall; and during that period, in fact when absorption through the roots is out of the question, since when the grass is dead the accumulation is most rapid.

That this is deposited arsenic rather than absorbed arsenic is evidenced further by the fact that by shaking dry hay or grass grown in the vicinity of the smelter a finely divided dark-gray powder, running notably higher in arsenic than the tissue from which it came, is obtained. Various samples of this dust were collected by shaking the hay or grass on a fork over a glazed cloth and separating leaves and fragments of the tissue by means of an 80-mesh sieve. This dust accumulates in quantity on the floors and rafters of hay lofts and in the mangers of feeding barns where it can be swept up in large amounts. Several samples of dust were also obtained from parts of threshing machines and analyzed for arsenic. Complaints are often made by men working on these machines that the thresher dust from grain in the smoke zone irritates the skin and the mucous membrane of the eyes and nasal passages,

TABLE III.—ARSENIC IN DUST FROM HAY AND GRAIN.

No.	Year.	Month.	Sample.	Direction from smelter.	Distance from smelter.	As_2O_3. Per cent.	As_2O_3. Parts per million.	CuO. Per cent.	Farm.
1	1905	June	H.[1] Dust	N. E.	4.5	0.0987	987	0.5320	Para
2	1905	June	"	"	4.5	0.0969	969	0.5600	"
3	1905	Apr.	"	"	4	0.4380	4380	0.7430	Staffanson
4	1905	Apr.	"	"	4	0.5140	5140	0.7970	"
5	1905	Oct.	T.[2] Dust			0.0887	887		Bowman
6	1905	Oct.	"			0.0594	594		Perkins
7	1905	Oct.	"			0.0448	448		Watts
8	1905	Oct.	"			0.0410	410		Day
9	1905	Oct.	"			0.0941	941		Jones
10	1906	July	H. Dust	E.	1.5	0.3526	3526		Lappin
11	1906	Nov.	"	S. E.	2	0.9190	9190		Allen

These values are uniformly high, the richest of the hay dust samples exceeding any of those for the plant tissues many times over. The thresher dust samples run lower, due in part at least to the fact that the conditions under which that dust was deposited are more apt to cause a loss in arsenic and a concentration of the heavier silicious dusts. The samples of hay dust from the Para farm were collected from the stack from which hay samples 20 and 31 were taken. The hay averaged 87 parts of arsenic trioxide per million, while the dust shaken from it averaged 978 parts. The dust from the Staffanson hay contained 7700 parts of arsenic trioxide per million, while the hay itself carried 261 parts. In the case of Lappin's hay the dust carried 9190 parts and the hay 50 parts per million. Such results indicate clearly that the arsenic is deposited on the surface of the plant and is not distributed throughout the tissue.

A contention which might be raised is that this dust is soil which has been blown upon the hay, or which adhered to it during the process of curing in the field. Some representative analyses of soil taken to a depth of three inches are given in the following table:

TABLE IV.—ARSENIC IN SOILS.

Farm.	Distance.	Per cent. As_2O_3.
Staton	2 miles S.	0.0019
Callan	3 " S. W.	0.0029
Para	4.5 " N. N. E.	0.0043
Bliss	5.5 " "	0.0061
Staffanson	3 " "	0.0107

The Para hay dust then carried 22.7 times as much arsenious oxide as did the soil. The Lappin hay dust carried 483 times as much as the soil sample from the adjoining Staton farm; and the Staffanson hay dust contained 72 times as much arsenic as the soil upon which it grew. It is

---

[1] H = Hay.

[2] T = Thresher.

extremely unlikely that dust from the soil is any large contributor to the quantities of arsenic found in the hay dust. Rather would it appear more reasonable to assume that in so far as the soil is present it is a diluent which diminishes the percentage of arsenic. Originally the soil of this district does not seem to have been arsenical. The top three inches of uncultivated soil will usually afford small quantities of arsenic which rapidly vanish at greater depths. A sample of top soil taken from underneath a well built log house erected long before smelting operations began in that valley carried only a trace of arsenic, while soil from an adjoining field was found to contain 0.0107 per cent. in the top three inches. Soil which had never been plowed contained no arsenic whatever at depths of from twelve to fifteen inches, so the arsenic present in the top soil would seem to be due wholly to the smelter emanations.

Samples of snow were scraped from the surface at a time when the ground for miles was covered with a sheet which had not yet been disturbed by the wind. Considerable amounts of soluble arsenic were found, the arsenic being dissolved in the water formed when the snow melted. The appended table gives the analytical results obtained:

TABLE V.—ARSENIC IN SNOW.

Date, 1906.	Farm.	Distance and direction.			Weight of snow grams.	Sq. ft. surface area.	Time exposed.	As_2O_3 per sq. ft.	Per cent. of dust.
2–5	Para	5	miles	N.	925	6.228	17 days	0.00306	0.1130
2–5	Williams	4	"	N.	955	12.6	17 days	0.00026	0.1690
2–5	Bliss	5.5	"	N.	...	...	17 days	0.00040	0.2810
3–18	Callen	3	"	S. W.	808	13.45	3 days	0.00057	......
3–18	Bliss	5.5	"	N.	604	6.72	3 days	0.00058	......

The figures in the column "Per cent. of dust" include the percentage of soluble arsenic calculated as if it were a component of the water-insoluble dust.

Early in the fall of 1905 vaselined cloths, each presenting a surface of three to eight square feet, were exposed at several points near the smelter. One was fastened to each side of a board tablet, somewhat larger than the cloth, which was set up on poles about twelve feet above the ground and broadside to the direction of the smoke stream at that place. Thus one vaselined cloth faced the smelter and the other faced in the opposite direction. In one case (No. 2) a cloth was stretched horizontally above the other two with its vaselined surface upward. Samples 1 and 2 were set up September 5th and taken down November 21, 1905. No. 3 was set up October 1st and taken down March 18th, but the vaselined surface was frozen hard and smooth for most of the winter and its efficiency as a collecting medium thus greatly decreased. The following data were obtained from this experiment:

TABLE VI.—ARSENIC IN VASELINED CLOTHS.

					As_2O_3 per sq. ft. of cloth.		
No.	Farm.	Direction from smelter.	Distance from smelter.	No. days exposed.	Facing upward, gram.	Facing smelter, gram.	Facing away, gram.
1	Bliss	N.	5.5	77	...	0.00052	0.00024
2	Para	N.	5.0	77	0.01194	0.00700	0.00083
3	Staton	S. E.	5.0	169	...	0.00327	0.00051

The results admit of only one interpretation, which is that the smelter smoke is the source of the arsenic found in such excessive amounts in the vegetation of the region about Anaconda. The question of whether this is a condition for which there is no remedy is difficult to answer. It is doubtful whether the present limited water supply would permit of the installation of wash towers, and the large amount of sulphur trioxide in the smoke would be destructive to a bag-house system. With its present high temperature and velocity the smoke must carry most of the arsenic out of the stack. In spite of the use of dry filters and wash towers and a consequent low velocity of the smoke, in an effort to meet the requirements of the amended Alkali Acts of 1892, the average escape of arsenic trioxide from the chimneys of arsenic plants in England for the past five years has been 0.0028 gram (0.041 grain) per cubic foot.[1]

In the thirtieth annual report[2] the Chief Inspector under the Alkali Acts wrote: "The inspection of these works (*i. e.*, arsenic works) had been much called for by residents in the district where they are found, and the necessity for the adoption of remedial measures was shown by the frequent litigation brought about by the alleged destruction of cattle through eating grass said to be poisoned by the arsenic too freely distributed through the air from the chimneys up which it had been carried by the draught. The arsenic driven off by the heat of the roasting furnace was caught and retained as far as possible, in long flues, culverts, and settling chambers, but although these were often of great extent, reaching in one place, a length of 2895 feet, or more than half a mile, and having a capacity of 60,795 cubic feet, yet arsenic was always liable to pass away. In one case a test of the chimney gases showed the presence of as much as 7.40 grains of arsenic trioxide in a cubic foot of gases passing into the air, and small flakes of it were seen falling continually in a mild snow-shower." The average escape of arsenic trioxide per cubic foot of chimney gases from plants provided with wash-towers, or with dry filters made by packing large chambers with brushwood, for each year since 1896 was as follows:

1896	0.080 grain
1897	0.086 "
1898	0.098 "

---

[1] Annual Reports Chief Inspector under Alkali Acts 1902–6.

[2] 30th Annual Report under Alkali Acts (1893), p. 91.

1899	0.074 gram
1900	0.094 “
1901	0.083 “
1902	0.049 “
1903	0.039 “
1904	0.053 “
1905	0.036 “
1906	0.030 “

These results attest the difficulty of removing all the arsenic from chimney gases even where, as in many of the plants referred to above, the furnace gases are cooled by wash-towers and the velocity of the smoke is reduced by extensive settling chambers. The smoke proceeding from the smelter at Anaconda on the basis of results presented in the first paper carries about 0.200 grain per cubic foot, a considerable velocity even in the settling chambers and a chimney temperature of 180° both interfering strongly with the deposition of the arsenic. The quantity which is given off under the present smelting conditions is not likely to be reduced except by the use of a less highly arsenical ore. As the ore supply for the Anaconda plant in drawn entirely from the mines of the Butte district and the arsenic content of these ores seems to be constantly increasing as greater depths are reached, the prospect of finding a ready solution of the problem is not encouraging. The great value of the products lost in the smoke, as shown by the first paper of this series, should encourage smelter companies to conduct extensive experiments with a view to the mitigation of this evil.

Table VI.[1]

No.	Collected.	Sample.	Source.	As_2O_3. Per cent.	As_2O_3. Parts per million.
1	July 12, 1907	Grass	Everett, 300 ft. S.E. from smelter	1.3000	13,000
2	July 12, 1907	Grass	Everett, ¼ mile S. E. from smelter	0.9400	9,400
3	July 12, 1907	Poplar leaves	Everett, 50 ft. W. from smelter	4.4000	44,000
4	July 12, 1907	Grass	Everett, 50 ft. W. from smelter	0.2300	2,300
5	July 12, 1907	Grass	Everett, 100 ft. N. from smelter	0.2300	2,300
6	July 12, 1907	Grass	Everett, ¼ mile N. from smelter	0.0420	420
7	Aug. 11, 1906	Sunflower leaves, ¼ mile from Murray smelter, Utah		0.1072	1072
8	Aug. 11, 1906	Grass, ½ mile from Highland Boy smelter, Utah		0.0062	62
9	Aug. 12, 1906	Alfalfa, 1 mile from Highland Boy smelter, Utah		0.0038	38
10	Aug. 12, 1906	Grass, 2 mile from Bingham smelters, Utah		0.0021	21
11	Aug. 12, 1906	Grass, 1 mile from Bingham smelters, Utah		0.0045	45
12	Aug. 12, 1906	Milkweed, 3 miles from Highland Boy smelter, Utah		0.0027	27

Incidental to this work in connection with the smelter at Anaconda samples of plant tissue have been collected from two other prominent

---

[1] A large number of grass samples from other smelter districts have been analyzed since the completion of this paper. Many of these contain arsenic in large quantities.

smelting centers, from Everett, Washington, about thirty miles north of Seattle, and from the region a few miles south of Salt Lake City, Utah, where several large smelters are in operation.[1] At both of these places complaints of injury to live stock have arisen from time to time. Only a few of these samples have been analyzed with the above results.

The writers wish to express their indebtedness to Dr. John Maxson Stillman for suggestions in regard to this work.

THE UNIVERSITY OF MONTANA, MISSOULA, MONTANA, AND STANFORD UNIVERSITY, CALIFORNIA,
December 28, 1907.

THE CHRONIC ARSENICAL POISONING OF HERBIVOROUS ANIMALS.[2]

(PAPERS ON SMELTER SMOKE, THIRD PAPER.)

BY W. D. HARKINS AND R. E. SWAIN.

Received April 1, 1908.

The two outbreaks of supposed arsenical poisoning which have led to the most investigation from a scientific standpoint, are the one in Manchester, England, in the year 1900, and that in the district surrounding Anaconda, Montana, during the year 1902-1903. The former was confined to human beings, the latter almost entirely to cows, horses, and sheep. As yet very few data have been obtained to show whether or not the effects of the arsenic in the latter case extended to the human beings who resided in the district.

During the latter part of November, 1902, it was the fortune of one of us to travel over about one hundred square miles of the territory surrounding the new Washoe smelter at Anaconda. At that time the carcasses of several hundred animals that had recently died lay scattered over various ranches of the valley, and one ranch was visited where approximately sixty carcasses, mostly horses, were seen in a group in one corner of the field. A very large number of the animals were dissected, and practically all of them gave evidence of arsenical poisoning, either acute or chronic.

As has been explained more in detail in a former paper, what was called the "Old Works" had been in operation for many years on the north side of the valley of Warm Springs Creek, in which the city of Anaconda is located. In January, 1902, smelting operations were transferred to the "New Works," which are located on the south side of the same valley, on a ridge extending down from the foot-hills. This ridge projects into the Deer

---

[1] See Ebaugh, Gases *vs.* Solids, THIS JOURNAL, **29**, 951, 970 (1907).

[2] At the New York meeting of the American Chemical Society, December, 1906, W. D. Harkins presented a similar paper including only his own work. The first paper of this series deals with the amount and character of the smoke given off by the smelter, and the second treats of the arsenic content of the vegetation.