The value of the density of aluminum oxide, employed in these calculations, was checked against two Jena glasses¹ which contain large percentages of Al_2O_3 . The results are as follows:

No.	Observed.	Calc. ²	Calc. ³	Error. ² Per cent.	Error. ³ Per cent.
4.....	2.480	2.60	2.471	4.8	0.3
9.....	2.588	2.69	2.612	3.9	0.9
Average, 4.35				0.6	

In both cases the use of the new factors gives more accurate values for the densities.

These new factors present some interesting variations from those originally proposed. From the following table, which shows the old and new factors and the densities of the pure oxides, it appears, as Winkelmann observed, that the oxides in general show a higher density in the glass than in the uncombined condition.

	Winkelmann.	Modified.	Density of pure oxide.
CaO.....	3.3	4.1	3.316 ⁴
MgO.....	3.8	4.0	3.614 ⁵
Al_2O_3	4.1	2.75	3.85 ⁶
Li_2O	...	3.7	2.102 ⁶

Especial attention should be called to the condensation of lithium oxide which amounts to a seventy-five per cent. increase in density. Aluminum oxide appears to be an exception to this generalization and shows an expansion of 40 per cent. Although deductions may not be drawn from these figures, they appear to indicate a peculiar molecular condition, perhaps association, in the aluminum oxide, which is not characteristic of the other oxides in question.

Although these differences are interesting and suggestive, they are not truly indicative of real differences, since the method by which they are obtained rests upon incomplete assumptions. Only the oxides are considered and no account is taken either of the compounds which are present or of their constitution. That this is an important item in any theoretical relationship between the chemical composition of a substance and its density, or any other physical property, is well known in the case of organic compounds, and, even among the silicates, polymorphic forms⁷ of the same chemical composition, but of different density, have been described. A knowledge of the different compounds which exist, together with knowledge of the compounds which are stable at the temperature at which the glass may be formed, will aid materially in solving the numerical relationship between the chemical composition of a glass and its density. Until such information is at hand resort must be had to empirical factors which represent not the true density, but the true density plus or minus an element which is characteristic of the nature of the compound which is formed. Since, in all the pos-

sible mixtures of glass-forming oxides, the field in which glasses are formed is rather limited, the constitution of the more common glasses is more or less similar, and it therefore becomes possible to find factors which hold to a limited degree.

SUMMARY.

1. The density of some pure and mixed silicates have been calculated, using the method and factors suggested by Winkelmann and Schott, with unsatisfactory results.

2. New factors have been derived, which appear to be more satisfactory. These are CaO 4.1, MgO 4.0 and Al_2O_3 2.75.

3. A factor has been derived for lithium oxide, Li_2O 3.7.

4. Although the method is not theoretically correct, it is capable of giving, for large variety of glasses, results which are not more than one or one and one-half per cent. in error.

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THE DETERMINATION OF VOLATILE MATTER IN COAL.

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The variable results obtained in volatile matter determinations on coal have been ascribed to (a) mechanical loss and (b) to different forms of decomposition as a result of varying methods of applying heat. With lignites, as shown by Somermeier,¹ the first-named difficulty is especially pronounced; but we find also in this laboratory that there are numerous coals of the Illinois type which suffer mechanical loss to an appreciable extent when subjected to the usual method for volatile matter determination. This is evident from the sparks that frequently accompany the discharge of the volatile matter and seems also to be indicated by Table II, which gives values for ash as derived from the coke resulting from the official method of determining the volatile matter (column B) as compared with the ash as derived by the official method. In any study, therefore, of the effect of varying temperatures, it is essential that variations due to mechanical loss be first eliminated before conclusions can be safely drawn as to the effect of varying degrees of heat. Moreover, the method employed must admit of the application of the maximum of heat in the minimum space of time in order that variations due to different sorts of decomposition may be brought within a narrow range. This precludes, of course, the application of a slow preliminary heating as suggested for lignites, at least with Illinois coals.

In our experiments it has seemed well to bear in mind certain other sources of variation. First on account of the great avidity of freshly mined coal for oxygen, it is possible that this element, mechanically held or absorbed by the finely ground material, accentuates or adds to the normal content of oxygen

¹ Winkelmann and Schott, *Loc. cit.*

² Using Winkelmann's factors.

³ Using modified factors.

⁴ Day and Shepherd, *Am. J. Sci.*, [4] **22**, 265 (1906).

⁵ Larsen, *Ibid.*, [4] **28**, 273 (1909).

⁶ Van Nostrand's Chemical Annual.

⁷ "The Lime-silica Series of Minerals," Day and Shepherd, *J. Am. Chem. Soc.*, **28**, 1089 (1906). "Minerals of the Composition Mg_2SiO_5 : A Case of Tetramorphism," Allen, Wright and Clement, *Am. J. Sci.*, [4] **22**, 385 (1906).

¹ *J. Am. Chem. Soc.*, **28**, 1003 (1906).

of the crucible and may thus furnish an initial oxidation of appreciable amount. To guard this point and at the same time prevent mechanical loss, numerous experiments were undertaken wherein a liquid was added to the dry coal which would have non-oxidizing properties and whose vapor would tend to carry out the oxygen content of the crucible at a temperature below that where oxidation would begin and at the same time promote adhesion and prevent the blowing out of the particles as a result of the moistening throughout of the mass. Such a liquid, of course, must be completely volatile and be distilled without decomposition by the subsequent heat.

TABLE I.—VOLATILE MATTER IN COAL.

Table No.	Lab. No.	Kind of coal.	A.	Variation	B.	Variation
			Standard method.	+ or — from av., Column A.	Standard with kerosene, Column B.	+ or — from av., Column B.
1	117	Vermilion Co., Ill.	38.90	+0.21	38.40	+0.07
			38.48	—0.21	38.26	—0.07
			Average,	38.69	0.21	38.33
2	128	Saline Co., Ill.	36.41	—0.14	36.61	—0.03
			36.69	+0.14	36.68	+0.04
			Average,	36.55	0.14	36.64
3	214	Lignite, Mississippi.	47.09	+1.06	44.87	+0.58
			45.70	—0.33	44.35	+0.06
			45.25	—0.78	43.95	—0.34
			46.09	+0.06	43.99	—0.30
Average,	46.03	1.11	44.29	0.64		
4	1762	Sangamon Co., Ill.	40.48	—0.74	40.05	+0.01
			41.72	+0.50	40.03	—0.01
			41.67	+0.45	..	..
			41.00	—0.22	..	..
Average,	41.22	0.95	40.04	0.01		
5	1809	Williamson Co., Ill.	37.24	+0.03	37.41	—0.05
			37.18	—0.03	37.52	+0.06
			Average,	37.21	0.03	37.46
6	1810	Franklin Co., Ill.	34.65	—0.32	34.78	+0.10
			35.30	+0.33	34.59	—0.09
			Average,	34.97	0.32	34.68
7	1870	Christian Co., Ill.	41.12	+0.68	39.41	+0.10
			39.76	—0.68	39.21	—0.10
			Average,	40.44	0.68	39.31
8	1878	Jackson Co., Ill.	34.32	—0.12	34.72	+0.19
			34.55	+0.11	34.70	+0.17
			..	..	34.43	—0.10
			..	..	34.26	—0.27
Average,	34.42	0.11	34.53	0.36		
9	2902	Williamson Co., Ill.	33.29	—0.18	33.78	0.00
			33.65	+0.18	33.77	0.00
			Average,	33.47	0.18	33.77
10	4035	Sangamon Co., Ill.	40.47	+0.07	41.35	+0.01
			41.33	—0.07	41.33	—0.01
			Average,	41.40	0.07	41.34
11	4085	Vermilion Co., Ill.	35.85	—0.08	36.54	—0.04
			36.01	+0.08	36.63	+0.05
			Average,	36.93	0.08	36.58
12	4130	Franklin Co., Ill.	37.06	+0.05	36.72	+0.16
			36.96	—0.05	36.41	—0.15
			Average,	37.01	0.05	36.56
Average variation.			0.33		0.13	

Numerous vehicles were tried, such as ether, alcohol, carbon tetrachloride, petroleum ether, kerosene, etc. Of these substances, kerosene seemed to be the best adapted, besides being readily available. The procedure was very simple. One gram of the air-dried sample, ground to 80 mesh, was weighed into the crucible and ordinary kerosene, from 10 to 15 drops, added, sufficient in amount to completely penetrate and saturate the coal. The cover was then put in place, the crucible supported on a platinum or nichrome triangle and placed directly in the usual Bunsen flame, 20 cm. high as prescribed by the Committee on Coal Analysis.

The results of a number of determinations are given in Table I, along with results obtained by the official method.

The values at the foot of the columns indicated that by the use of kerosene the variations are reduced from an average of 0.33 per cent. to 0.13 per cent.

As further evidence tending to show absence of mechanical loss when kerosene is applied, the results in Table II show the ash as obtained by the official method in column A, with which may be compared column C, showing the results for ash as derived from the coke obtained when kerosene was added as above described.

TABLE II.—MECHANICAL LOSS AS INDICATED BY ASH DETERMINATIONS.

Table No.	Lab. No.	Kind of coal.	A.	B. Ash	C. Ash
			Ash by official method.	from coke residue by official method.	from coke residue using kerosene.
1	117	Vermilion Co., Ill.	8.74	8.66	8.82
2	1162	Christian Co., Ill.	11.32	11.15	11.26
3	2902	Williamson Co., Ill.	10.12	9.75	10.07
4	2952	Pittsburg, Pa.	16.95	16.92	16.89
5	4035	Sangamon Co., Ill.	9.44	9.31	9.40
6	4085	Vermilion Co., Ill.	23.58	23.70	23.50
7	4130	Franklin Co., Ill.	4.87	4.79	4.80

It seems fair to conclude, therefore, that an advantage attends the use of kerosene and that the matter of mechanical loss is thereby eliminated. This brings us to a consideration of that phase of the matter which relates to variations due to differences in the application of heat. Fieldner and Davis¹ have shown that variations in heat as derived from burners of different sizes, different types of gas, etc., yield different values. Their discussion of the results would lead one to infer that in their opinion the various temperatures employed produced a varying speed of decomposition which resulted in the fixation of varying amounts of carbon. With bituminous coals at least it would seem essential to first eliminate the possibility of mechanical loss. But, aside from this feature of the case, there are many evidences that in the main the variations due to different temperatures are the result of a more or less complete driving off of the residual hydrogen, to variations in the amount of carbon deposit on lid and sides of the crucible, to the oxidizing or reducing character of the flame immediately above and around the lid of the crucible, the extent of leakage or care with which the lid of the crucible is made to fit, etc.

¹ THIS JOURNAL, 2, 304 (1910).

Further uniformity of results might be expected if we could locate more precisely the point wherein the variation occurs. This feature of the case is receiving further study.

As bearing somewhat on the case, the following table is submitted. If any interpretation can be attempted from these results it would seem to be that the higher results are not always to be credited to the larger burner and the higher temperature. It is more likely that coals vary as to the ease or completeness with which they part with their last residuum of gas.

I am indebted to Mr. F. W. Whittum and Mr. J. M. Lindgren for the analytical results accompanying this paper.

TABLE III.

Table No.	Lab. No.	Kind of coal.	A. Standard method with kerosene, Sargent burner.	B. Standard method with kerosene, Fletcher burner.	B compared with A variation + or —.
1	117	Vermilion Co., Ill.	38.33	39.44	+1.11
2	128	Saline Co., Ill.	36.64	37.11	+0.47
3	214	Lignite, Mississippi.	44.29	44.35	+0.06
4	1762	Sangamon Co., Ill.	40.04	39.84	—0.20
5	1809	Williamson Co., Ill.	37.46	37.78	+0.32
6	1810	Franklin Co., Ill.	34.68	35.18	+0.50
7	1870	Christian Co., Ill.	39.31	39.65	+0.34
8	1878	Jackson Co., Ill.	34.53	34.22	—0.31
9	2902	Williamson Co., Ill.	33.77	34.16	+0.39
10	4083	Vermilion Co., Ill.	36.58	36.29	—0.29
11	4130	Franklin Co., Ill.	36.56	36.99	+0.43

In column A, the burner used is illustrated as No. 1000 in Sargent's catalogue. It has an internal diameter of 9 mm.

In column B, the Fletcher burner had an internal diameter of 11 mm.

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SOME NEW FEATURES IN THE ELECTROLYTIC DETERMINATION OF LEAD.

By JOHN G. FAIRCHILD.

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It has been found that good deposits of lead peroxide, free from flakes and of close texture, can be obtained on a smooth platinum cylinder in two hours' time without rotation, and as much as 100-200 mg. in weight. This can be raised to 300 mg. but there is danger of flaking off. The secret of success is a low amperage to begin with and a hot solution, 50°-60° C.

For alloys high in lead two grams or more are weighed out and an aliquot taken to represent about 0.1 gram of metallic lead. The volume of electrolyte is 200 cc. in a 250 cc. beaker, and contains 30 cc. strong HNO₃. Heat to 50°-60° C., using an anode of 25 sq. in. surface with a cathode cylinder of 12 sq. in. The anode should be burnished frequently and ignited previous to placing in the electrolyte. This ignition removes any greasy film adhering to the cylinder. Split cover glasses are used to prevent loss through

evaporation of the hot solution, which just completely immerses the edge of the anode cylinder. The current is started at 0.25 am. for one hour and a half when it is raised to 0.5 am. for half an hour longer to remove the last traces of lead, and the cover glasses are rinsed down. At the end of two hours deposition is complete, as shown by the newly immersed stem remaining bright. The beaker is lowered and removed, being replaced by one containing clean water for rinsing the cylinders, which are then disconnected, the anode being rinsed in a glass of alcohol, drawn through a flame to burn off what adheres while holding the cylinder in a vertical position. It is then held for a few seconds about a foot above the flame to dry thoroughly, and weighed. On adding ammonia to the electrolyte and passing H₂S, no more than a mere brownish color should show.

To prove the accuracy of this method, purified lead sulphate was taken as the standard. An amount equal to 0.7335 gram was put into a 500 cc. flask and dissolved in just enough hot am. acetate solution, 100 cc. being taken for analysis by means of a pipette standardized to the flask. After adding 30 cc. HNO₃ of 1.42 sp. gr., this aliquot was made up to 200 cc. The electrolyte is best kept hot throughout the run by means of a hot plate or burner. The results for lead sulphate and test lead were as follows:

PbSO ₄ .	PbO ₂ equiv.	PbO ₂ found.	Pb. Per cent. ¹
0.1467	0.1157	0.1156	99.92
0.1467	0.1157	0.1160	100.26
0.1467	0.1157	0.1155	99.83
0.1467	0.1157	0.1159	100.17
Test lead.			
0.1000	0.1157	0.1145	98.92
0.1000	0.1157	0.1143	98.72
0.1000	0.1157	0.1142	98.63
0.1000	0.1157	0.1147	99.14
0.1000	0.1157	0.1145	98.92
0.1000	0.1157	0.1146	99.04

Whenever a weight was low the lead was found to be not all deposited, due to faulty manipulation which is not likely to occur. If the electrodes short-circuit re-solution occurs with some lead flaking off.

Lead scrap and furnace dross can be treated thus: About 5 grams are dissolved in HNO₃ + H₂SO₄ in a Kjeldahl flask and evaporated till fumes appear. After cooling, the impure PbSO₄ is filtered off, the paper punctured and the precipitate rinsed back into the flask. It is then treated with just sufficient hot saturated am. acetate solution, which is warmed till solution is complete, then filtered into a 500 cc. flask, a proper portion being taken for electrolysis.

On comparison with pure lead it will be seen that material relatively low in lead will require only about half an hour at 0.5 am., a small percentage of lead being given a higher amperage. In this way can lead be readily separated from copper, manganese, silver, antimony, etc.? When a relatively large amount of copper is present, as in blister copper, only 20 cc. nitric acid may be present. The presence or absence of am. nitrate seemed to have no effect on the results.

This method gives lower results than the chromate method; thus, by the latter 59.25 per cent. lead was

¹ Conversion factor 0.866.