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THE ATOMIC WEIGHT OF LEAD OF RADIOACTIVE ORIGIN.

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It has been pointed out by many of the workers upon radioactivity, especially by Boltwood, Ramsay, Rutherford and Fajans, that the most conclusive test concerning the recent theory of the degeneration of radioactive elements is to be found in the determination of the atomic weights. If each α-transformation involves the loss of an atom of helium and nothing else which is weighable, the atomic weight of the product should be just 3.99 less than that of the original substance, because 3.99 is the atomic weight of helium evolved during the α-transformation. Thus, if radium has an atomic weight of 225.97,[1] its emanation ("niton") should have an atomic weight of 221.98, radium D (which is supposed to involve three more α-transformations) should be 210.01; and radium G (yet another α-transformation) should be 206.02.

Still more recently, a further theory, which has been independently proposed by Fajans, and by Soddy,[2] indicates that some of the places in the periodic table, corresponding to high atomic weights, should perhaps each include several elements, different in atomic weight but very

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[1] Hönigschmid, *Monatsh.*, **33**, 253 (1912).

[2] K. Fajans, *Ber.*, **46**, 422 (1913); F. Soddy, *Chem. News*, **107**, 97 (1913); see "The Chemistry of the Radio-Elements," Soddy, II, 3 (1914).

similar in other properties. Thus, in the place which we usually assign to lead, we should expect to find a mixture of ordinary lead, radium B, D, and G, and perhaps, also at least one other radioactive product from thorium and one from actinium. These different substances, according to the hypothesis, should have identical spectra and be inseparable by chemical means, but, coming from different sources, they should have different atomic weights. The theory supposes that each α-transformation involves a loss of valence of two, and each β-transformation a gain of valence of one. The β-transformation involves no change of weight. Thus radium D (supposed to have an atomic weight of 210) after two β- and one α-transformations returns again as radium G to the same place in the periodic system with an atomic weight of only 206. This place is that assigned to lead (which some suppose to be primarily radium G), the only one of the radium series possessed of a long life and not highly radioactive.

The problem is one capable of a decisive gravimetric test; specimens of lead, consisting of different mixtures, obtained from different sources, should have different atomic weights. On the generous suggestion of Dr. Fajans this matter was taken up in the autumn of 1913 at Harvard.[1] In order to glean as much knowledge as was within reach, we have endeavored to obtain as many different samples of radioactive lead as possible and to determine the atomic weights of the possibly composite element by precisely comparable methods, so as to discover if any variation might exist in the chemical equivalents of the different products.

It is a pleasure, at the outset, to express our deep gratitude to many workers in radioactivity who have furnished us with material. Without this general coöperation, it would not have been possible for us to accomplish anything in so short a time, and we cannot express too highly our appreciation.

In brief, the method of analysis was essentially similar to that used so successfully by Baxter and Wilson in their work upon the atomic weight of ordinary lead.[2] The chloride was in each case prepared in a state of great purity by recrystallization in quartz and platinum vessels, after extensive preliminary treatment to eliminate foreign substances. This

[1] Mr. Max E. Lembert, Dipl. Ing., a pupil of Dr. Fajans, was sent by him and the Technische Hochschule of Karlsruhe, with the support of Professor Bredig, to Harvard University especially for this purpose. Sir William Ramsay, also, at about the same time, had urged on behalf of Dr. Soddy that the atomic weight of radioactive lead should be studied in the Wolcott Gibbs Memorial Laboratory. It is needless to say that the opportunity was welcomed; indeed, the matter would have been taken up here before, except for a fear of trespassing upon a field which might properly be considered as belonging to the proposers of the theory. A brief announcement of this work was made by Dr. Fajans at the meeting of the Bunsen Gesellschaft in Leipzig on May 21st, and a brief notice was published in "Science" on June 5, 1914.—T. W. R.

[2] Baxter and Wilson, *Proc. Am. Acad.*, 43, 363 (1907).

chloride was carefully dried in a desiccator and heated to fusion in a stream of hydrochloric acid gas and nitrogen, in the quartz tube of the well-known bottling apparatus which has served in so many similar cases.[1] The lead chloride was then dissolved in much water, and the chlorine precipitated by silver nitrate. Both the weight of silver required and the weight of the precipitate were determined in the usual Harvard fashion.

As a further check upon the work, control analyses giving the atomic weight of ordinary lead were carried out in precisely the same way. These yielded essentially the same value as that found by Baxter and Wilson, and more recently, by Baxter and Grover in work as yet unpublished.

The outcome was striking. There can be no question that the radioactive samples contain another element having an atomic weight so much lower than that of ordinary lead as to admit of no explanation through analytical error, and yet so nearly like ordinary lead as not to have been separated from it by any of the rather elaborate processes to which we had subjected the various samples.

All the materials used in the work were purified with the care usually employed in work of this kind. The silver was made by the precipitation of very pure silver nitrate by ammonium formate, and fused upon boats of the purest lime in hydrogen. The hydrochloric acid gas used for fusion and precipitation was obtained by dropping pure sulfuric acid into chemically pure concentrated hydrochloric acid, furnished by a trustworthy firm and known to be very pure. It was carefully dried and freed from spray by many towers of glass pearls, drenched with sulfuric acid. For precipitation this acid was dissolved in pure water in a quartz flask. The water, and also the nitric acid and other substances used in the work, were purified according to the methods usually employed at Harvard for this purpose.

The description of the preparation of the various samples of lead demands further elaboration. For the first sample of common lead, used as control material, a commercially pure specimen of non-radioactive lead acetate was three times recrystallized from acetic acid solution and the chloride was precipitated, after considerable dilution, by pure hydrochloric acid gas. After the chloride had been many times washed and recrystallized from water, its aqueous solution was filtered through a Gooch-Munroe crucible to eliminate threads of filter paper and other solid impurities. The lead chloride was then twice more recrystallized in a platinum dish and dried over potassium hydroxide (Sample A).

A second sample of ordinary lead chloride was prepared from the purest lead nitrate of commerce in a similar manner. This salt was crystallized three times in glass and twice in platinum, and its aqueous solution was

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[1] Richards, "The Faraday Lecture of 1911," *J. Chem. Soc.*, **99**, 1203 (1911).

precipitated by pure hydrochloric acid gas in a quartz flask. The salt was thoroughly washed with many treatments of wash water, centrifuged, and finally crystallized three times from a solution weakly acidified with hydrogen chloride in a quartz dish (Sample E).

In order to test the efficiency of crystallization of lead nitrate as a means of freeing this salt from bismuth (the impurity most to be feared in our radioactive material), a sample of this salt was mixed with about one-tenth of its weight of bismuth nitrate. After three recrystallizations only a trace of bismuth remained in the crystals, and the fourth removed all that trace which could be detected by qualitative means. There is no doubt, also, that crystallization of the chloride likewise is a very efficient means of purifying lead.

Our first sample of radioactive lead was very kindly furnished by Dr. Fajans; indeed his generous initiative in this way made it possible for us to begin. It was from Colorado carnotite and came to us as chloride, containing doubtless traces of iron, bismuth, and other substances. It was, in the first place, recrystallized eight times from the aqueous solution, but even after this treatment was not absolutely white in color, containing still a trace of iron. Three more crystallizations from hydrochloric acid solution yielded a product of pure whiteness, but because of the slow elimination of the impurities, this sample, C, could hardly be considered as a final product. Therefore, all the remainder of the material was dissolved in a great volume of water, acidified with nitric acid, and saturated with hydrogen sulfide. The carefully washed sulfide was dissolved in nitric acid, and the nitrate was thrice crystallized (once in platinum) from acid solution. That part of the sulfide oxidized to sulfate was dissolved in ammonium acetate and again precipitated by sulfureted hydrogen, this process being repeated until practically all of the sulfide had been converted into nitrate. The purified and recrystallized nitrate was precipitated as chloride by purified hydrochloric acid gas as before, and the product was recrystallized twice from dilute hydrochloric acid, and once from pure water in a quartz dish (Sample D).

A second source of radioactive lead was very kindly provided by Sir William Ramsay, consisting of residues from pitchblende mined in Cornwall. The brown-gray powder contained ferrous carbonate and many other substances besides lead. This latter element we separated in the first place by the solution of the material in nitric acid, and precipitation with pure sulfuric acid (free from lead) with the addition of alcohol. The sulfate was washed by decantation until practically free from iron, and was dissolved in ammonium acetate and tartrate. That portion of the original residue which refused to dissolve in nitric acid was also treated with ammonium acetate to dissolve any lead which might remain as sulfate. This again was precipitated as sulfide. As before, the sulfide was converted into the nitrate, and this salt was treated exactly as in the case of Sample D. The resulting product was designated Sample F, and similar material, prepared later from the same substance with somewhat greater care, was designated as Sample G.

A sample of radioactive lead from Ceylonese thorianite, furnished through the great kindness of Professor Boltwood, had already undergone considerable purification. From 25 kg. of the thorianite (which contained about three times as much thorium as uranium), 1100 g. of lead nitrate had been prepared in a state of considerable purity, and 100 g. of this precious material were placed at our disposal. In its preparation, the thorianite had been dissolved in concentrated nitric acid, and the neutralized solution had been precipitated, when moderately dilute, with hydrogen sulfide. The sulfide, after filtration, was then dissolved in hydrochloric acid with the addition of potassium chlorate, and the lead chloride twice recrystallized, converted into nitrate, twice more recrystallized, and came to us at this state. We crystallized it four times more in a quartz dish and finally converted it into the chloride, which was twice recrystallized from acid solution and once from pure water.

A somewhat similar sample, also from Ceylon, came to us through the kindness of Mr. Miner, chief chemist of the Welsbach Light Co., of Gloucester City, N. J., U. S. A. The source was a kilogram of thorianite. This, after solution in dilute nitric acid (the solid residue being separated), was precipitated with oxalic acid to eliminate the thorium, and the filtrate, made alkaline with ammonia, was precipitated with hydrogen sulfide. But much of the lead had gone into the oxalate precipitate, so that Mr. Miner very kindly recovered this also for us, treating the precipitate with sodium hydroxide and extracting with hot water. From this lye, hydrogen sulfide precipitated a mixture of sulfides which contained much more lead. These two samples of sulfides we now united, dissolved in nitric acid and crystallized four times as nitrate. The product was converted in the usual manner into the chloride and designated Sample M. A further product, made from lead oxidized to sulfate by the action of nitric acid, gave another sample N.

When the work was well advanced, a new sample of Bohemian uranium-lead was prepared especially for us through the kindness of Dr. Fajans in the following way: "Das geröstete Erz wurde mit einem Gemenge von H_2SO_4 und HNO_3 (zur Oxydation der vorhandenen Sulfide) behandelt, und dadurch das Uran in Lösung gebracht. Der Rückstand enthielt das Blei als Sulfat, und wurde ihm durch Behandlung mit Aetznatron entzogen, durch Ansäuern wieder ausgefällt, und mittelst Soda in Karbonat verwandelt. Dieses war dann in HNO_3 aufgelöst und das Nitrat kristallisiert worden. Das Präparat wurde unter Ausschluss der Möglichkeit einer Verunreinigung durch Blei anderer Provenienz gewonnen." This nitrate (which contained lead oxide and traces of iron) was purified in two different ways. One part was precipitated like Sample F twice as sulfide. This was converted into the nitrate, and was three times recrystallized in quartz, being finally turned into the chloride as usual (Sample I). Another part was recrystallized only three times as nitrate, then turned into chloride, and again recrystallized (Sample K), but according to the results of the analyses it appeared to be as pure as the most carefully treated product. From the lead sulfate which appeared during the solution of the sulfide (Sample I), yet another fraction, L, was made.

Perhaps the most valuable of all our samples (because it came from very pure ore) was a small amount of 3.8 g. of lead chloride very kindly given us by Professor Boltwood and Dr. Ellen Gleditsch, of Christiania, Norway, now collaborating with Professor Boltwood. This product came from the analysis of 110 g. of the purest selected uraninite from North Carolina, U. S. A. The material was practically of pure radioactive origin, no other lead except that from uraninite itself being included. The sulfides, which had been precipitated from an acid solution of the mineral, were dissolved in nitric acid and the lead separated as chloride. This was crystallized three times from hydrochloric acid solution, and, finally, once more from aqueous solution in a quartz dish, and was designated sample O.

Another sample, P, was prepared from the filtrates of all the analyses of Sample D. Silver (in addition to other slightly electropositive elements, if present) was removed by slow fractional electrolysis. The residual electrolyte was repeatedly recrystallized as chloride. It will be noticed that the atomic weight was essentially unchanged.

One of the samples provided by Dr. Fajans came originally from Professor Giesel, and the other had been prepared with a subsidy from the Heidelberger Akademie der Wissenschaften. We wish to express our grateful thanks to these helpers also. A list of the sources of these various samples may facilitate comparison.

Sources of Samples of Lead Chloride.

Sample A.	Commercial lead acetate, Germany.
Sample B.	Carnotite, Colorado, U. S. A. (impure) (Fajans).
Sample C.	Carnotite, almost pure.
Sample D.	Carnotite the most carefully purified.
Sample E.	Commercial lead nitrate, America.
Sample F.	Pitchblende, Cornwall, England (Ramsay).
Sample G.	Pitchblende, the most carefully purified.
Sample H.	Thorianite, Ceylon (Boltwood).
Sample I.	Pitchblende, Joachimsthal, Bohemia, purest (Fajans).
Sample K.	Pitchblende, preliminary product.
Sample L.	Pitchblende, same as I.
Sample M.	Thorianite, Ceylon (Miner).

Sample N. Thorianite, later fraction.
Sample O. Uraninite, North Carolina, America (Gleditsch).
Sample P. Extremely careful purification of sample D.
Sample R. Sample O, further purified.

The consistent method according to which all these samples were analyzed has already been briefly described but perhaps a few points concerning the details deserve discussion.

The desiccator-dried lead chloride was always fused in a current of hydrochloric acid gas, as already stated, in order to be sure that the water was expelled as completely as possible. There was reason to expect that lead chloride thus fused should be neither basic nor containing an important amount of dissolved hydrochloric acid. In support of this conclusion we may cite the neutrality of other chlorides thus fused, as determined by the alkalimetric testing of the dissolved material.[1] It is true, of course, that the specific nature of each chloride is different, and reasoning from analogy is not always safe.

After the lead chloride had been cooled within the bottling apparatus in nitrogen, and this gas had been displaced by air, the fused salt in its platinum boat was pushed into a weighing bottle, in which it was weighed with great accuracy. It was then slowly dissolved in a large bulk of warm water (about 40°) contained in a large Erlenmeyer glass-stoppered precipitating flask. We verified the experience of Baxter that no chlorine is lost during this process.

In spite of our precautions, our samples of lead chloride always exhibited on solution in water a small amount (three or four milligrams) of white precipitate, which was shown by its immediate solution in a trace of acid to be a basic salt. This may have been partly due to alkali dissolved from the glass. The literature concerning lead chloride suggested that it may be somewhat hydrolyzed in aqueous solutions.[2] If this is the case, and the trace of basic precipitate came from this cause, it would of course have no effect whatever on the result, provided that it was dissolved in a drop of nitric acid before adding silver nitrate. On the other hand, if the basic salt had been formed during fusion, its presence would signify a real loss of chlorine, and the resulting atomic weight of lead would be too high. We obtained from ordinary lead essentially the same values as those found by Baxter and Wilson (and later by Baxter and Grover); therefore the error (if it exists) must apply equally to both sets of determinations. Because lack of time prevented our solving the question, we strove only for comparative results; our problem was not so much to find the true atomic weight of lead, but rather merely to find if the atomic weight of radioactive lead is like that of ordinary lead. The suitable

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[1] See for example Richards and Hönigschmid, THIS JOURNAL, 33, 28 (1910); *Sitz. b. Akad. Wiss. Wien*, 119 (1910); *Chem. News*, 104, 182, 190 (1911).

[2] See for example Abegg's "Handbuch," III, 2nd part, pp. 648–653; also p. 657 (1909).

correction, if any is needed, can be applied at any time, by subtracting a small quantity from each of our values, which were obtained under precisely similar conditions. Professor Baxter and his students have previously met with this difficulty in the cases of both lead chloride and lead bromide and they have been for some time engaged in experiments directed towards solving the problem.

One other correction is involved in three of these analyses, Nos. 21, 25, and 28. In these analyses a combustible black residue, chiefly carbon, of appreciable amount, was left upon dissolving the lead chloride, due doubtless to organic matter taken from the filter paper during purification. In each case this was very carefully filtered off and weighed on a Neubauer crucible, and the weight subtracted from the original weight of lead chloride. These three corrections were, respectively, 0.83, 0.66 and 0.20 milligram. None of the other analyses was entirely free from this carbonaceous substance, but the amount was in every other case less than the least of those just mentioned and was neglected. Its presence would tend to increase very slightly the observed atomic weight determined from the ratio of lead chloride to silver, but would have no appreciable effect on that referred to silver chloride.

The lead chloride which has been thus weighed and dissolved was precipitated by a weighed amount of silver in the usual way. No unusual precautions were necessary, except that we found that when the solutions were concentrated, lead chloride is more easily occluded by the silver chloride than many other salts.[1] Working, however, with solutions so dilute that only 1 g. of lead chloride was contained in 500 cc. of the solution, we were but little troubled from this source. According to Franke[2] the salt must be about 80% dissociated at this dilution. The precipitate after several days comes to a definite and consistent end point, unchanged by further standing. In order to establish the end point with greater exactness, the solubility of the silver chloride was reduced by cooling the solution almost to 0° before removing the samples to be tested. As usual, silver was added to the very nearly precipitated mixture until 25 cc. portions of the supernatant liquid showed, in the nephelometer, the same cloudiness with excess of added chloride in one test tube as with excess of added silver in the other. The amount of silver exactly equivalent to the chlorine having this been found, an excess of dissolved silver was added in order to precipitate the dissolved silver chloride, and the whole was filtered with the usual precautions on a carefully weighed Gooch-Munroe crucible with a mat of platinum sponge. The precipitate was dried to constant weight at about 180°; and then transferred to a porcelain crucible and fused, in order to dislodge the small remaining trace of water.

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[1] This confirms the experience of Baxter.

[2] See Abegg's Handbook, *Loc. cit.*

In the first place, a number of preliminary analyses were made in order to acquire experience in the method. Of course some of them failed for one reason or another, but they yielded important consequences nevertheless. They showed that the method in our hands yielded with common lead essentially the same results as those obtained by Baxter and Wilson—our values averaging about 207.15 for the atomic weight of lead when it did not contain radioactive material. They showed, moreover, that Colorado carnotite contained lead (Samples C, D) having an atomic weight not far from 206.6 by the same method and that the lead extracted from English pitchblende (Sample F) had an atomic weight of about 206.9. The preliminary analyses of the radioactive material need not be recounted in detail because the chloride was not thoroughly purified and the analytical procedure was not wholly without fault. The analyses of common lead may be briefly recounted.

In four closely agreeing analyses, 16.2966 g. of fused lead chloride, after complete solution, required 12.6458 g. of silver for complete precipitation. Thus 100 parts of silver are equivalent to 128.87 parts of lead chloride, and if the atomic weight of silver is taken as 107.88, lead becomes 207.14. Again in two closely agreeing analyses 8.17662 g. of fused lead chloride yielded after due correction, 8.4293 g. of silver chloride. Hence, 100 parts of silver chloride correspond to 97.002 parts of lead chloride, and on the same basis as before, lead becomes 207.16. The mean between these two results, 207.15, may be taken as the experimental value for the atomic weight of ordinary lead as observed under these conditions. This result is about halfway between that found by Baxter and Wilson and that more recently found by Baxter and Grover, but not yet published. Therefore the results indicate that the method had been mastered and that it had been giving sufficiently satisfactory results throughout. The agreement of our results by the two methods shows that no important amount of impurity was occluded by the precipitated silver chloride, in agreement with Baxter's outcome.

Most of the analyses thus summarized were made before the radioactive lead was attacked. In the last one, made at the very end of the work, 5.0089 g. of lead chloride, were fused and dissolved as usual, but before precipitation an amount of the nitrate of radium D (kindly sent by Dr. Fajans) was added, sufficient to make the radioactivity of the mixture correspond approximately to that of Sample D. This was in order to discover whether or not the presence of radioactivity produces serious effect upon precipitation. As the atomic weight calculated from this last result (207.14) was exactly like the average, it is evident that the analytical process is not affected by the mere presence of radioactivity.

Let us now turn to the final results for material obtained from radioactive sources. The work was done with great care, and because of the experience gained in the preliminary trials, the results were more satisfactorily concordant. All the figures concerning these final series are given in the table below, no experiment having been omitted except a single analysis of Sample O, which was made before it was fully purified, and was therefore rejected. Table III contains, the weight of silver needed for each specimen of lead chloride, and Table IV the weight of silver chloride obtained. The last two columns of each table record, the ratios of

TABLE III.—FINAL RESULTS.

Series 1. 2Ag : $PbCl_2$.

Number of analysis.	Sample PbCl.	Ag.	Corrected wt. of fused PbCl in vacuum.	Corrected wt. equivalent Ag in vacuum.	Ratio $PbCl_2$:Ag.	Atomic weight.
16......	D	X	3,87082	3,00984	1,28606	206,56
18......	D	X	5,57331	4,33300	1,28625	206,60
26......	P	Z	5,49412	4,27157	1,28621	206,59
Sum..................			14,93825	11,61441	Av. 1,28618	**206,59**
17......	H	X	3,88228	3,01600	1,28723	206,81
19......	H	Y	4,05550	3,15061	1,28722	206,81
20......	H	X, Y	4,05168	3,14788	1,28712	206,79
Sum..................			11,98946	9,31449	Av. 1,28719	**206,81**
24......	M	Y	2,80814	2,18162	1,28718	**206,81**
21......	I	X	3,95052	3,07209	1,28594	206,54
22......	K	X, Y	2,95726	2,29951	1,28604	206,56
			6,90778	5,37160	Av. 1,28598	**206,55**
23......	G	Y	4,05702	3,15153	1,28732	206,84
29......	R	Z	2,01795	1,56952	1,28563	206,47

TABLE IV.—FINAL RESULTS.

Series 2. $PbCl_2$: 2AgCl.

Number of analysis.	From Series No. 1.	Sample of $PbCl_2$.	Corrected wt. of fused in vacuum.	Corrected wt. of fused AgCl in vacuum.	Ratio PbCl:AgCl.	Weight Ag = 107.33
40..........	16	D	3,87082	3,99879	0,96799	206,59
42..........	18	D	5,57331	5,75707	0,96808	206,61
50..........	26	P	5,49412	5,67573	0,96800	206,58
Sum..................			14,93825	15,43159	Av. 0,96803	**206,59**
41..........	17	H	3,88228	4,00703	0,96886	206,84
43..........	20	H	4,05168	4,18265	0,96870	206,78
Sum..................			7,93778	8,18968	Av. 0,96877	**206,81**
46..........	24	M	2,80814	2,89816	0,96894	**206,85**
45..........	22	K	2,95726	3,05475	0,96809	206,61
47..........	23	G	4,05702	4,18670	0,96903	**206,88**
51..........	29	R	2,01795	2,08663	0,96767	206,32

the substances concerned and the atomic weights of lead computed in the usual fashion from these ratios, assuming the atomic weights of silver and chlorine to be 107.880 and 35.458, respectively.

Thus the final analyses yielded results essentially like the preliminary ones. The situation will become clearer if the results are all collected and averaged in a summarized table (V) giving the values of the atomic weight corresponding to each kind of lead.

TABLE V.—FINAL VALUES FOUND FOR ATOMIC WEIGHT OF LEAD FROM DIFFERENT SOURCES.

Lead from North Carolina uraninite (Sample R)	206.40
Lead from Joachimsthal pitchblende (Sample I, K)	206.57
Lead from Colorado carnotite (Samples D and P)	206.59
Lead from Ceylonese thorianite (Samples H, M)	206.82
Lead from English pitchblende (Sample G)	206.86
Common lead	207.15

The result is amazing. Evidently then the chemical equivalents of these different specimens are markedly different from one another. Because the method of analysis was the same in each case, one cannot help thinking that there is a real variation in the chemical equivalents of these samples of lead. Either a large amount of some element having a chemical equivalent nearly as great as lead, or a small amount of an element having a low chemical equivalent, must be present, mixed with the substance which we ordinarily call lead. The fact that all the analyses were carried out by the same method, and that each sample gives consistent results, seems to exclude the effect of analytical error. The nature of this admixture it would be perhaps premature to decide. Clearly it has reactions very much like those of lead, if not exactly identical; for the various processes to which our material was subjected would have eliminated any element widely different. Moreover, the fact that protracted purification had no effect on the atomic weight of any one sample is evidence in the same direction.

A word should be said concerning the determination of the radioactivity of these various samples, which is an important item in the consideration. The determination was made by means of a quantitative gold-leaf electroscope of the usual type—a square brass box with mica windows, containing a gold-leaf suspended from a flat rod passing through amber. The box was grounded and the electroscope was charged by means of rubbed sealing wax. The material to be investigated was placed on a wooden slide beneath the instrument. The β-rays (which alone were studied) were measured, being allowed to come into the box through a screen of thin tinfoil and aluminum foil. In the first place the time taken for the gold-leaf to fall between two definite points in the micrometer eyepiece of the observing telescope was noticed when no radioactive substance was present; then the times for the various portions were studied under precisely like conditions and compared with the same weight of uranium trioxide. From these times of fall the rates were easily computed, and on subtracting from the rates with radioactive substances, the rate when nothing was present, the comparative values for the various substances were obtained. Immediately after purification, of course, the specimens were practically non-radioactive, because during crystallization radium E, which is the chief source of the β-rays, goes into the mother liquor. As is shown by the figures for our Sample D at the top of Table VI, the radioactivity of freshly prepared crystals steadily increased in the usual curve until the maximum was attained in about thirty days. Radium E is then in equilibrium with radium D. The table gives, in its lower part, a comparison of the radioactivity of the different samples. It will be seen that Sample D was the most radioactive, sample O next, and Samples F and G the least. An old sample of uranium trioxide is included to give an idea of the magnitude of the effect.

TABLE VI.

Sample of $PbCl_2$. 1.5 g.	Time in days elapsed since crystallization.	Time in seconds of fall of gold-leaf with preparation.	Rate of fall per minute.	Natural fall of leaf per minute.	Corrected rate of fall with preparation.
D..............	0.2	472	0.127	0.043	0.084
D..............	1.2	203	0.296	0.035	0.261
D..............	2.0	144	0.417	0.035	0.378
D..............	4.1	91	0.659	0.036	0.623
D..............	5.2	78	0.769	0.041	0.728
D..............	6.1	71	0.845	0.042	0.803
D..............	7.0	69	0.870	0.043	0.827
D..............	8.9	64	0.942	0.037	0.905
D..............	12.1	56	1.072	0.039	1.033
D..............	14.3	53	1.133	0.043	1.090
D..............	16.3	49	1.220	0.039	1.188
D..............	18.0	49	1.220	0.039	1.188
D..............	27.0	43	1.396	0.046	1.350
D..............	40.0	43	1.396	0.045	1.351
B[1]..............	>200	47	1.278	0.031	1.247[1]
1.27 g.					
D..............	59.0	53.0	1.132	0.045	1.087
F..............	40	265.0	0.226	0.045	0.181
G..............	24	270.0	0.222	0.045	0.177
H..............	35	204.0	0.294	0.045	0.249
I..............	?	182.5?	0.329?	0.045	0.284?
M..............	29	257.5	0.234	0.045	0.189
O..............	20±	85.0	0.707	0.045	0.662
UO_3 standard....	>1000	628.0	0.095	0.045	0.050

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[1] This sample was taken from the impure original lead chloride from carnotite, as we had received it. The slightly lower value is probably due to another size of crystals and the non-radioactive impurities.

Although in general the samples of lead having greater radioactivity show less atomic weight, the decrease in the atomic weight is not exactly proportional to the radioactivity. For example, preparation O (the same material as preparation R) is distinctly less radioactive than Sample D, although the atomic weight exhibited by O is decidedly more divergent from the usual value than that exhibited by D. The rates of fall for 1.27 g. of O and D, both twenty days old, were respectively 0.66 and 0.99, whereas the deficiencies in the atomic weights of these samples were respectively 0.75 and 0.56. The irregularity suggests the presence of more than two variables. More data are clearly necessary for a definitive conclusion. The attempt to explain the relationship will therefore be deferred.

The spectroscopic examination of one of these samples (Sample D) was conducted with the generous help of Professor Baxter in his admirable Féry quartz spectrograph. Very well-defined photographs of the ultraviolet portion of the spectrum of our Sample D (after it had been recovered from an analysis, and therefore contained a trace of silver) were taken on a film, side by side with similar photographs of Baxter's purest lead. The parallelism of the two, both as regards the number of lines and the intensity of the lines was complete throughout the whole field, from wave length 0.4μ to the extreme ultraviolet visible in this instrument (about 0.200μ) except that the characteristic silver lines 0.3281μ and 0.3383μ were clearly depicted and the prominent copper lines 0.3248μ and 0.3274μ were faintly visible. The latter had an intensity corresponding, on a very conservative estimate, to 1 part of copper in 100,000 parts of lead, determined by comparison with the spectrum of lead containing known traces of copper—an amount far too minute to have any effect on the atomic weight. The silver doubtless came from the analytical operations, as already said; and its manifest appearance is good evidence of the great sensitiveness of the spectrometer. No shifting or obvious broadening of any of the lines was observed, but it would not have been possible to see a very slight effect of this kind.

Thus it appears that the lead from radioactive sources, having an atomic weight of 206.6, gives essentially the same ultraviolet spectrum as ordinary lead, having an atomic weight (determined by the same method in parallel analyses) of 207.15.

The obvious inference to be drawn from this amazing result is that one of four alternatives must hold true. Either the unknown substance, which is mixed with ordinary lead and produces the lower atomic weight, has the same spectrum as lead itself; or else it gives no lines whatever in the ultraviolet range of this photograph; or else the presence of a large bulk of lead hides or aborts the spectrum of the foreign admixture; or else ordinary lead is a similar medley in somewhat different proportions. It is perhaps premature to decide between these alternatives, but all are of interest, the first and last of course being the most revolutionary.

That lead should be composed of a mixture of substances of different origin but similar properties is, after all, possibly not so revolutionary a proposition as might appear at first sight. Rare earths are often very similar in properties, and large amounts of material and very patient fractionation are necessary to separate them. Why should not the same thing be true of several of the commoner elements? The only practical difference besides the presence of radioactivity seems to lie in the fact that in the present case the intruders produce no obvious change in the ultraviolet spectrum. But if all lead is a mixture, this might be expected.

At first sight one might be inclined to feel that the irregularity in the quantitative results above described should diminish one's respect for the significance of atomic weights in general, but further thought shows that this is a superficial view. If the results which we have obtained really indicate that several kinds of lead having the same properties and spectrum may be mixed together and not separated chemically, it is evident that the atomic weight becomes almost the only criterion, except radioactivity, capable of detecting the admixture and tracing the factors to their source. Thus the study of atomic weights is shown to be not less but more significant than it had been before. To emphasize this point, we may perhaps quote two paragraphs, written seven years ago, long before the theory under discussion had been proposed, and when such ideas were of a rather heretical character.

"Are the supposed constant magnitudes to be measured in chemistry really variable......? If they are thus variable, is it worth while to expend much labor in determining the values which they happen to possess at any one time under any one set of conditions?

"The question as to whether or not the supposed constants of physical chemistry are really not constants, but are variable within small limits, is of profound interest and of vital importance to the science of chemistry and to natural philosophy in general. If this latter alternative is true, the circumstances accompanying each possible variation must be determined with the utmost precision in order to detect the ultimate reason for its existence. As Democritus said long ago, 'the word chance is only an expression of human ignorance.' No student of natural science who perceives the dominance of law in the physical universe would be willing to believe that such variations in a fundamental number could be purely accidental. Every variation must have a cause, and that cause must be one of profound effect throughout the physical universe. Thus the idea that the supposed constants may possibly be variable, adds to the interest which one may reasonably take in their accurate determination, and enlarges the possible field of investigation instead of contracting it."[1]

This matter has received not only speculative but also experimental treatment at Harvard. For many years the possibility that samples of a given element from different sources might have different atomic weights had been considered, and investigated, but never before with a positive outcome. In the first investigation of the atomic weight of copper undertaken by one of us as long ago as 1887,[2] samples of copper obtained from Germany and from Lake Superior were found to give precisely the same atomic weight for this element. More recently the question was revived and in 1897, specimens of calcium carbonate were obtained from Vermont, U. S. A., and from Italy, in order to discover whether or not the calcium in these two widely separated localities had the same atomic weight. Not the slightest difference was found between them.[3] Again, in a very elaborate investigation on the atomic weight of sodium,[4] silver was obtained from several distinct sources and sodium chloride was obtained partly from several different samples of German rock salt, and partly from the salt pumped from the Solvay Process Company's mines at Syracuse, N. Y. These preparations, differing widely in the steps of manufacture and in geographical source, all yielded essentially the same atomic weights within the limit of error of the process.[5] Yet more recently Baxter and Thorvaldson,[6] with the same possibility in mind, determined the atomic weight of extra-terrestrial iron from the Cumpas meteorite, which gave a result identical with ordinary iron within the limit of error of experimentation. From these researches it would seem probable that even if an unusual eccentricity may be exhibited by lead, most elements do not as a rule differ from any such cause of uncertainty. Baxter and Grover are now engaged in the examination of ordinary lead from different geographical sources. Perhaps this also contains more than one component, as suggested above.

It would perhaps be premature to indulge in further hypothetical reasoning concerning the nature of this extraordinary phenomenon, but the nature of the variation unquestionably points in the direction of the hypothesis of Fajans and of Soddy.

This paper must be looked upon only as a preliminary one. More time, larger amounts of material, and more chemical experimentation are needed in order to be sure that the reactions of the unknown contaminating ele-

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[1] Richards, (Berlin Inaugural), *Science, N. S.*, **26**, 562 (1907); also *Die Umschau*, **13**, 542–543 (1909); translated by F. Haber.

[2] Richards, *Proc. Am. Acad.*, **23**, 179–80 (1887).

[3] Richards, This Journal, **24**, 374 (1902).

[4] Richards and Wells, *Carnegie Instit. Wash. Pub.*, **28** (1905).

[5] Even if both specimens of salt came originally from a Silurian ocean, the time and condition of deposition were probably widely different.

[6] This Journal, **33**, 337 (1911).

ment and lead are wholly identical. We hope and intend to continue the study, and solve the highly interesting questions which it presents.

We are greatly indebted to the Carnegie Institution of Washington for much of the apparatus and material used in this research.

Summary.

In this paper a description is given of parallel experiments determining the equivalent weights of various samples of lead chloride obtained from different sources. It was found that all of the radioactive specimens possess a lower atomic weight than ordinary lead, as determined under identical conditions, the deficiency in one case amounting to as much as 0.75 of a unit.

No simple linear quantitative relationship between the exact amount of radioactivity and the atomic weight was found. The radioactivity of the various samples was compared by means of the quantitative electroscope.

The ultraviolet spectrum of a typical radioactive sample was compared with that of ordinary lead, with the help of G. P. Baxter, in a quartz spectrograph. No difference was found between the spectra of these specimens, except for a trace of copper too small to affect the result, and a negligible trace of silver known to have been present. The inference seems to be that radioactive lead contains an admixture of some substance different from ordinary lead, and very difficult to separate from it by chemical means. This substance cannot be identified in the ultraviolet spectrum of the material, either because it has the same spectrum as lead, or because it has no spectrum in that part of the field, or because its spectrum is masked or aborted by that of lead.

This amazing outcome is contrary to Harvard experience with several other elements, notably copper, silver, iron, sodium, and chlorine, each of which seems to give a constant atomic weight, no matter what the geographical source may have been. No attempt is made here to discuss the theoretical aspects of the facts presented, but attention is called to their qualitative agreement with the hypothesis of Fajans and of Soddy.

CAMBRIDGE, MASS.

TWO NEW MODIFICATIONS OF PHOSPHORUS.

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The two new modifications of phosphorus to be described here were obtained during an investigation of the effect of high pressure on the melting point of ordinary white phosphorus. The two new forms have perfectly distinct characteristics; in this they are different from the questionable modifications of red phosphorus often announced. The first of these modifications is a new form of white phosphorus, which changes