agreement with those reported in the literature[20] for 1,1-diphenylethylene. The higher boiling fraction consisted of a resinous material which distilled at 250–260° at *ca.* 1 mm. From this resin, which probably consisted of a mixture of polymers of 1,1-diphenylethylene, no crystalline compounds could be isolated.

Condensation of Triphenylcarbinol and Phenol.—Five grams of aluminum chloride was added, with stirring, to a mixture of 20 g. of triphenylcarbinol and 20 g. of phenol. After heating for ten minutes on the steam-bath, 75 ml. of 50–70° petroleum ether was added, the reaction mixture refluxed an additional fifty minutes and then decomposed by heating with 200 ml. of 5% hydrochloric acid. This heating removed the volatile solvent. The solid matter was filtered off, the lumps crushed and washed first with hot water then with two 75-ml. portions of alcohol. After drying, the yield of *p*-triphenylmethylphenol was 24.5 g. (95%); m. p. 281–283.5°.

We wish to acknowledge our indebtedness to J. R. Adams and J. K. Wolfe for the carbon, hydrogen and nitrogen determinations.

Summary

1. Dimethylphenylcarbinol, methyldiphenylcarbinol and triphenylcarbinol have been condensed with phenol in the presence of aluminum chloride.

2. Mechanisms for these condensations have been postulated.

3. The methyl ether, diphenylurethan and aryloxyacetic acid of *p*-(α,α-dimethylbenzyl)-phenol have been prepared.

COLLEGE PARK, MD. RECEIVED NOVEMBER 1, 1937

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[20] Beilstein, "Handbuch der organischen Chemie," 4th ed., 1922, Vol. V, p. 639; Supplement, 1930, Vol. V, p. 308.

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

I. The Atomic Weight of Lead from a Specimen of St. Joaquimsthal Pitchblende. II. The Lead–Uranium Ratio of this Pitchblende

BY GREGORY P. BAXTER AND WALLACE M. KELLEY

I. The Atomic Weight

Although it has been clear from earlier work[1] that St. Joaquimsthal (Bohemia) pitchblende is badly contaminated with common lead, since we had the opportunity of examining a fine specimen of pitchblende stated to be from this locality it seemed worth while to determine the atomic weight of the lead and the lead–uranium ratio on identical material. The results correspond to earlier evidence with pitchblende from the same source.[1]

The original specimen, which weighed over a kilogram, was streaked with veins of colored calcite. The search for galena in a polished section was negative.

About 450 g. of this mineral was crushed in a clean chipmunk crusher and then finely ground in a nutmeg mill. A sample of about 25 g. of the powder was set aside for analysis. Treatment with 1% hydrochloric acid removed most of the calcite. A small amount of lead sulfide (± 50 mg.) was obtained from the solution. Treatment of the pitchblende with hot nitric acid left a considerable residue, a large part of which dissolved in hot aqua regia. The material remaining insoluble was then evaporated with redistilled hydrofluoric acid in platinum, and then again with sulfuric acid. After removal of the excess sulfuric acid by fuming, the lead sulfate was extracted with ammonium acetate and precipitated as sulfide. Lead was recovered from the nitric acid and aqua regia solutions either by crystallization as chloride or by precipitation as sulfide. All the lead was at least once converted to sulfate by evaporation with excess sulfuric acid. This was washed with dilute sulfuric acid, and dissolved in ammonium acetate. After filtration lead sulfide was precipitated, converted to chloride and crystallized (13 g.). Conversion to nitrate by evaporation with nitric acid followed.

The nitrate was then recrystallized from nitric acid five times, twice in glass and three times in quartz. To convert the nitrate to chloride it was evaporated to dryness with 20% hydrochloric acid three times. Five crystallizations as chloride from 10% hydrochloric acid in quartz and two distillations in quartz in a current of dry hydrogen chloride completed the purification.

In the course of the purification it early became evident that the lead contained bismuth as chief impurity. The final product when examined with a quartz spectrograph on pure carbon electrodes seemed to be free from this element as well as copper and silver.

This material was used in Analyses 4, 5 and 6. For Analyses 7 and 8 the residues from the first purification were further purified as sulfide and sulfate and combined with material contained in the lead nitrate solutions resulting from Analyses 4–6. The combined material was crystallized as nitrate and chloride and distilled in hydrogen chloride as before.

To prepare the lead chloride for weighing it was fused in a current of nitrogen and hydrogen chloride in a small quartz boat contained in the quartz tube of a Richards bottling apparatus. After sweeping out the bottling apparatus with nitrogen followed by air, the weighing

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(1) Bull. Nat. Res. Council, The Age of the Earth, 305 (1931).

bottle containing the boat and salt was weighed against a counterpoise. Solution in hot water containing a trace of nitric acid followed. After dilution to 0.05 *N* concentration a 0.05 *N* solution of a weighed very nearly equivalent amount of pure silver was added, and the end-point was found by the equal opalescence method in the usual way. The end-points remained constant over a period of several months.

For comparison, experiments were carried out with a specimen of lead occurring as cerussite at Wallace, Idaho, U. S. A. This material was crystallized five times as nitrate and five times as chloride exactly as in the case of the St. Joaquimsthal material.

In the following tables vacuum corrections of +0.058 and −0.031 mg., respectively, have been applied to the weights of lead chloride and silver.

TABLE I

THE ATOMIC WEIGHT OF LEAD

Ag = 107.880 Cl = 35.457

Analysis	$PbCl_2$ in vacuum, g.	Ag in vacuum, g.	Ag[a] added, g.	Corrected Ag in vacuum, g.	Ratio $PbCl_2:2Ag$	At. wt. Pb
			Cerussite			
1	4.81912	3.73859	0.00000	3.73859	1.28902	207.205
2	2.45187	1.90208	.00000	1.90209	1.28904	207.209
3	1.55822	1.20876	.00000	1.20877	1.28910	207.222
				Average	1.28905	207.212
			St. Joaquimsthal			
4	1.59548	1.24101	0.00020	1.24121	1.28542	206.428
5	2.75039	2.14118	−.00240	2.13878	1.28596	206.545
6	3.77378	2.93779	−.00280	2.93499	1.28579	206.506
7	2.70109	2.10070	.00000	2.10070	1.28580	206.510
8	4.40976	3.42962	.00000	3.42962	1.28579	206.507
				Average	1.28575	206.500

[a] In Analyses 1, 2, 3, 4, 7 and 8 the end-point once found was upset by adding small measured amounts of silver and redetermined by adding the necessary amount of chloride. The quantities given in this column represent the algebraic sum of such additions.

The atomic weight of the same sample of common lead has been determined by both Baxter and Grover[2] and Baxter, Tuemmler and Faull[3] to be 207.21.

Since this specimen of St. Joaquimsthal pitchblende was found to contain no detectable amount of thorium, it must consist in large part of common lead. With the atomic weights 207.21 for common lead and 206.00 for uranium lead[4] the percentage of common lead may be calculated to be 41.3.

Isotopic analysis of a portion of our material with a mass spectrograph by Dr. A. O. Nier indicates the following proportions of lead isotopes (private communication).

Pb^{208}	21.56
Pb^{207}	11.74
Pb^{206}	66.12
Pb^{204}	0.58

Using the packing fraction for lead of $+0.5 \times 10^{-4}$ and the conversion factor 1.00027 the atomic weight of the St. Joaquimsthal lead is 206.49, a value in close accord with ours. Nier's percentage of Pb^{208} in common lead is 52.3. With this value the percentage of common lead in this sample of St. Joaquimsthal lead is 41.2, again in close agreement with the percentage calculated from the atomic weight.

II. The Lead–Uranium Ratio

The 25-g. sample of the original powdered mineral was finely ground in an agate mortar in small portions and then thoroughly mixed by grinding. In the first two analyses the mineral was digested with hydrochloric acid and the solution evaporated to dryness. After dehydration soluble matter was extracted with hydrochloric acid and the insoluble residue collected. The latter was treated with hydrofluoric acid and sulfuric acids and after evaporation to fuming was extracted with hydrochloric acid. This solution gave a small sulfide precipitate. A small residue from the hydrofluoric acid treatment was fused with sodium carbonate. The solution of the melt in dilute hydrochloric acid gave no precipitate with hydrogen sulfide nor with ammonia.

Lead was precipitated as sulfide from the original hydrochloric acid solution (0.3 *N*) of the mineral and after combination with that from the hydrofluoric acid treatment of the residue was converted to sulfate, collected and weighed. The filtrate yielded a small amount of sulfides, chiefly bismuth sulfide, which was dissolved and converted to sulfate as above.

Both portions of sulfate were then dissolved in ammonium acetate and after filtration of the solution lead chromate was precipitated, collected and weighed. A small quantity of lead chromate separated from the filtrate on long standing. This also was collected and weighed.

In Analyses 3 and 4 the mineral was first treated with nitric acid, and the nitrates were converted to chlorides. After treatment of the insoluble residue with hydrofluoric acid as before the hydrochloric acid solution was added to the main portion. The lead was then precipitated as sulfide and converted to nitrate. Bismuth was eliminated from the nitrate solution by double precipitation as oxychloride. Conversion of the lead to sulfate followed and this after being weighed was dissolved in ammonium acetate and the lead precipitated as chromate.

To determine uranium the filtrates from the lead sulfide were boiled, oxidized with hydrogen dioxide, and treated with an excess of ammonium carbonate. The precipitate after being washed with dilute ammonium chloride was dissolved in nitric acid and reprecipitated with ammonium carbonate. The combined filtrates were boiled and the precipitate of ammonium uranate was dissolved in nitric acid, and reprecipitated. The combined filtrates were digested with concentrated nitric acid for some time to destroy ammonium salts, evaporated to dryness, taken up with nitric acid, and precipitated with ammonia in small volume. These two precipitates were ignited separately.

The original solution of 450 g. of mineral from which the lead had been separated was treated with enough

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[2] Baxter and Grover, THIS JOURNAL, **37**, 1057 (1915).

[3] Baxter, Tuemmler and Faull, *ibid.*, **59**, 702 (1937).

[4] See Baxter and Alter, *ibid.*, **57**, 470 (1935).

ammonium oxalate to precipitate a portion of the uranium. The precipitate was ignited, dissolved in nitric acid and again precipitated with oxalate. A precipitate consisting chiefly of bismuth oxalate was obtained, but no thorium could be detected with the peroxynitrate test after removal of the bismuth as sulfide.

TABLE II

LEAD–URANIUM ANALYSES OF ST. JOAQUIMSTHAL PITCHBLENDE

Pb = 206.50

Sample	Sample, g.	$PbSO_4$, g.	% Pb	$PbCrO_4$, g.	% Pb	U_3O_8, g.	% U
1	2.4310	0.1137	3.192	0.1214	3.197	lost	...
2	2.4583	.1175	3.262	.1248	3.251	1.7453	60.21
3	2.0904	.1000	3.265	.1053	3.225	1.4867	60.31
4	2.2388	.1055	3.216	.1125	3.217	1.5896	60.21
		Average	3.234		3.223		60.24

Pb/U = 0.0536

Since 41.3% of the lead in this mineral appears to be common lead, the percentage of uranium lead in the pitchblende is 1.892 and the corrected Pb/U ratio 0.0314. The approximate age on this basis is 239 million years. With the logarithmic formula the age is 234 million years. Lead–uranium ratios from this pitchblende range from 0.10 to 0.02.[5] Specimens with the low ratios may be freer from common lead than this one.

Summary

1. The atomic weight of a specimen of lead from St. Joaquimsthal pitchblende has been found to be 206.50.
2. The percentage of common lead calculated from the atomic weight is 41.3. This agrees with the percentage found by Dr. A. O. Nier from isotopic analysis.
3. The percentages of lead and uranium in the mineral are found to be 3.22 and 60.24, respectively.
4. The percentage of uranium lead is calculated to be 1.89 and the Pb/U ratio 0.0314.
5. The approximate age of the mineral appears to be 239 million years, and the age by the logarithmic formula 234 million years.

[5] Bull. Nat. Res. Coun. No. 80.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Determination of Molybdenum with the Silver Reductor[1]

BY NATHAN BIRNBAUM AND GEORGE H. WALDEN, JR.

A number of oxidimetric methods for the volumetric determination of molybdenum involving reduction to both the quinquivalent and trivalent states have been developed.[2] In the method involving reduction to the trivalent state the reduced solution must be protected from air oxidation by an atmosphere of an inert gas or by collecting the reduced solution in a flask containing excess of an oxidizing agent. No such protection is necessary when the molybdenum is reduced to the quinquivalent state.

Walden, Hammett and Edmonds[3] observed that molybdenum is reduced by the silver reductor to the quinquivalent state and that the reduced solution can be titrated with ceric sulfate using the *o*-phenanthroline ferrous complex indicator. They failed, however, to obtain reproducible results with the method they used.

Furman and Murray[4] recently have developed a method for the determination of molybdenum by reduction with mercury and titration with ceric sulfate. They have shown that quinquivalent molybdenum solutions are stable at room temperature for several hours.

We have found that molybdenum is quantitatively reduced by the silver reductor when the solution is 2 *M* in hydrochloric acid and the temperature of the solution 60–80° during passage through the reductor. The method is precise and the use of a reductor column makes it rapid and convenient.

Apparatus and Reagents.—The silver used was prepared according to the directions of Walden, Hammett and Edmonds.[3] The reductor column was similar to the one they describe except that the length of the glass column was 17 cm. and the length of the silver column 12 cm. About 25 g. of silver was required. Calibrated glassware was used throughout the investigation.

An aqueous ammonium molybdate solution, approximately 0.1 *M* with respect to molybdenum, was prepared from Merck ammonium heptamolybdate (blue label reagent grade). The amount of molybdenum in the solution

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[1] From a dissertation submitted by Nathan Birnbaum in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University.

[2] (a) Bonardi and Barrett, Tech. Paper 230, Bureau of Mines, 1920; (b) Stehlik, *Coll. Czechoslov. Chem. Comm.*, **4**, 418 (1932); (c) Lang and Gottlieb, *Z. anal. Chem.*, **104** (1936).

[3] Walden, Hammett and Edmonds, THIS JOURNAL, **56**, 350 (1934).

[4] Furman and Murray, *ibid.*, **58**, 1689 (1936).