of the charged colloids is the most complete at the isoelectric point, the free valence is at a minimum, the seat of the base exchange capacity is then at a minimum, and the quantity of combined water is at a minimum for a given colloid.

Summary

The cation exchange capacity of seven iron phosphate precipitates varying from the electropositive to the electronegative combinations was investigated. The data presented indicate that high base exchange accompany high electrokinetic potential, whereas low base exchange is characterized by a low electrokinetic potential.

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

The Atomic Weight of Lead from Bedford Cyrtolite

BY GREGORY PAUL BAXTER AND CHESTER M. ALTER

The lead–uranium ratio in a specimen of cyrtolite from Bedford, N. Y., U. S. A., has recently been determined by Muench[1] to be 0.0513 (Pb 0.374, U 7.29, Th 0.0?). In estimating the age of this mineral it is important to discover by the determination of its atomic weight whether this lead was wholly derived from the disintegration of uranium. An added interest to this determination comes from the fact that the mineral is nearly if not quite free from thorium.

Since cyrtolite consists chiefly of zirconium silicate and is extremely refractory, the extraction of the lead was a matter of some difficulty. The method finally adopted after some exploration was that of treatment with hydrofluoric acid. About 1250 grams was available.

The lumps were first crushed in a previously cleaned jaw crusher. The material was then finely ground in a Quaker grinding mill which had been cleaned by grinding in it several hundred grams of marble. Prolonged digestion in 100-g. portions with hydrofluoric acid in a platinum dish followed. Removal of the hydrofluoric acid was effected by repeated evaporation with concentrated nitric acid. The portion soluble in hot dilute nitric acid was then separated from the very considerable residue of undissolved zirconium silicate.

The lead was next separated and purified by the following processes: (1) double precipitation as sulfide; (2) solution of the sulfide in nitric acid and precipitation of lead chromate in ammonium acetate solution; (3) solution of the chromate in nitric acid and precipitation of lead sulfate; (4) conversion of the sulfate to carbonate by boiling with sodium carbonate

(1) Muench, Am. J. Sci., 21, 356 (1931).

solution; (5) solution of the carbonate in nitric acid and three recrystallizations of the nitrate from concentrated nitric acid in quartz; (6) conversion of the nitrate to chloride by repeated evaporation with hydrochloric acid in quartz; (7) recrystallization of the chloride, once in quartz and three times in platinum; (8) distillation of the chloride in a current of hydrogen chloride in a quartz tube. All the acids used in the foregoing operations were freshly distilled and other reagents were proved to be free from lead before use. All the material resulting from this purification was used in Analysis 1.

As soon as the first analysis was completed, the resulting lead nitrate solution was evaporated, freed from silver with a small amount of hydrochloric acid and, after combination with the mother liquors of the first set of crystallizations and conversion to nitrate, the product was three times crystallized as nitrate in quartz and three times as chloride, once in quartz and twice in platinum. The final step was distillation in hydrogen chloride as before. This material was used in Analysis 2.

For the next analysis (3) the combined lead salt was five times crystallized as nitrate in quartz, and five times as chloride, twice in quartz and three times in platinum.

The final analysis with cyrtolite lead was performed with material which had been three times crystallized as nitrate and four times as chloride.

For purposes of comparison experiments were carried out with common lead and with lead extracted from Swedish kolm by Baxter and Bliss.[2] Ordinary lead nitrate was three times crystallized from nitric acid in quartz and after conversion to chloride the latter was crystallized once in quartz and three times in platinum. The kolm lead was crystallized six times as nitrate and six times as chloride. All the samples were finally distilled in a current of hydrogen chloride in a quartz tube.

The distilled lead chloride was prepared for weighing by fusion in a current of hydrogen chloride while contained in a weighed quartz boat in a quartz tube. After cooling in nitrogen, the boat and contents were transferred to a weighing bottle by means of a Richards bottling apparatus. In Analysis 4 the fusion atmosphere was a mixture of one part hydrogen chloride to ten of nitrogen.

Comparison of the lead chloride with silver was effected nephelometrically. In Analyses 2 and 3 the lead chloride solution was added to the silver nitrate solution; in all other analyses the reverse method of precipitation was employed. In three analyses the end-point was approached from one side, in three from the other. The precipitation and testing were both done at room temperature. In Analyses 2 and 7, after the end-point had been found at room temperature, the solutions were cooled with ice. When again tested nephelometrically no change could be detected.

(2) Baxter and Bliss, THIS JOURNAL, **52**, 4848 (1930).

Because of the small amounts of material available in the experiments with cyrtolite and kolm lead the weighing bottle, boat and bottling apparatus were made of small size in order to increase the accuracy of weighing.

The concentration of the solutions before precipitation was not far from 0.02 normal, and the total volume of the solutions in the cyrtolite experiments about one liter. Under these circumstances the uncertainty in determining the end-point with the nephelometer is not over 0.05 mg. of silver or the equivalent amount of chloride, a quantity which would affect the observed atomic weight of lead by 0.02 unit in an experiment in which somewhat less than one gram of lead chloride was used. The range of the cyrtolite analyses is about double this, but three of the four analyses are essentially identical.

Three different specimens of silver were employed, all of which had been purified by the same processes.[3]

All weighings were made by substitution with calibrated weights. Vacuum corrections of +0.058 mg. and −0.031 mg. per gram, respectively, were applied to the air weights of lead chloride and silver.

THE ATOMIC WEIGHT OF LEAD

Ag = 107.88   Cl = 35.457

Analysis	Sample of $PbCl_2$	$PbCl_2$ in vacuum, g.	Ag in vacuum, g.	Ag added, g.	Corr. wt. of Ag, g.	Ratio $PbCl_2$: 2Ag	At. wt. of Pb
1	Cyrtolite	0.99965	0.77881	+0.00025	0.77906	1.28315	205.938
2	Cyrtolite	.99219	.77286	+ .00039	.77325	1.28314	205.936
3	Cyrtolite	.76907	.59951	− .00005	.59946	1.28294	205.893
4	Cyrtolite	.73596	.57368	− .00010	.57358	1.28310	205.928
					Average	1.28317	205.924
5	Common	2.47843	1.92263	+ .00011	1.92274	1.28901	207.203
6	Common	2.80252	2.17405	.00000	2.17405	1.28908	207.218
					Average	1.28905	207.211
7	Kolm	3.42063	2.66525	− .00010	2.66515	1.28347	206.007

The analyses of common lead chloride were performed first and although the average atomic weight found is slightly lower than the more probable value, 207.22, the difference was so small that it did not seem a matter of concern. Since the results of the experiments with cyrtolite lead were unexpectedly low, the experiment with kolm lead was undertaken. The outcome of this experiment is reassuring, since Baxter and Bliss[2] obtained an almost identical result, 206.013.

One conclusion seems certain, that the cyrtolite lead is essentially free from common lead so that the lead–uranium ratio obtained by Muench may be confidently employed in computing the age of the mineral.

The explanation of the low value for cyrtolite lead is not so obvious. Aston finds the lead isotopes integral with the mercury isotopes, which on the physical scale, O^{16} = 16.0000, were found to have values 0.01 per cent.

(3) See Baxter and Ishimaru, THIS JOURNAL, **51**, 1730 (1929).

higher than integral, the accuracy claimed being 0.01 per cent. In converting from the physical to the chemical scale, if the higher factor of Mecke and Childs, 1.00022, is used, the atomic weight of radium lead falls between 205.96 and 206.00. However, if the latter is always accompanied by actinium lead, Pb^{207}, in the proportions found in Katanga lead by Aston[4] (93.3:6.7) the average atomic weight of uranium lead should be 0.07 unit higher, a difference far outside the apparent accuracy of our experiments. This suggests the possible presence in uranium lead of lead isotopes of lower atomic mass than 206. An alternative is that the atomic weight of lead as found by us is too low, or that the packing fraction of lead determined with the mass spectrograph is incorrect.

The experimental result of this research is that the atomic weight of uranium lead from a specimen of cyrtolite is 205.92 ± 0.02.

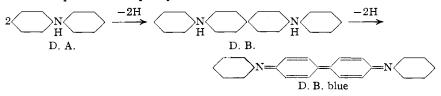(4) Aston, *Nature*, **129**, 649 (1932).

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Diphenylamine Sulfonic Acid as a Reagent for the Colorimetric Determination of Nitrates

BY I. M. KOLTHOFF AND G. E. NOPONEN

Since first suggested by E. Kopp,[1] the use of diphenylamine for the colorimetric determination of nitrates has been studied by numerous investigators.[2] Diphenylamine, mainly for the following reasons, is far from being an ideal reagent in the colorimetric determination of nitrates.

1. The blue color developed by nitrate in the presence of much sulfuric acid and some hydrochloric acid is to be attributed to the formation of an oxidation product of diphenylbenzidine, the latter being the first oxidation product of diphenylamine.

Diphenylamine therefore is not a specific reagent for nitrate, but the blue color is also developed by other oxidizing agents, such as ferric iron, nitrite, dichromate, etc.

(1) E. Kopp, *Ber.*, **5**, 284 (1872).

(2) See especially the more extensive investigations of Tillmans and Sutthoff, *Z. anal. Chem.*, **50**, 473 (1911); L. Smith, *ibid.*, **56**, 28 (1917); Riehm, *ibid.*, **81**, 353 (1930); for bibliography compare J. H. Yoe, "Photometric Chemical Analysis," Vol. I, Colorimetry, John Wiley and Sons, New York, 1928, pp. 638–659.