mixture, on dialysis, will yield a practically clear sol. The reversibility in this case is due to the greater diffusion velocities of manganese and potassium chlorides as compared with ferric chloride. As the manganese and potassium chlorides diffuse, the residual ferric ion peptizes the coagulated colloid, and the sol is again formed.

Summary.

The stoichiometric relations in the permanganate-ferrous sulfate and permanganate-ferrous chloride reactions are the same with or without the addition of acid. In the permanganate-ferrous chloride reaction, the collateral oxidation of chloride ion is practically avoided by adding the permanganate gradually and with vigorous stirring.

The products of the permanganate-ferrous chloride reaction are the chlorides of potassium, manganese and ferric iron, and colloidal hydrous ferric oxide, while in the permanganate-ferrous sulfate reaction, the corresponding sulfates are formed, and also hydrous ferric oxide, which is precipitated by the sulfate ion.

A gram equivalent of permanganate, dissolved in about 600 cc. water, was slowly added to a gram equivalent of ferrous chloride, dissolved in about a liter of water, and the resulting clear, deep brownish red solution diluted to two liters. This solution remained perfectly clear for several weeks, then gradually became more and more turbid, until finally a suspension settled out. Until the latter stage is reached, dialysis yields a perfectly clear brownish red hydrosol of hydrous ferric oxide. After a suspension settles out, dialysis will give a hydrous ferric oxide hydrosol which is slightly turbid in reflective light, but perfectly clear in transmitted light.

PITTSBURGH, PA.

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

FURTHER STUDY OF THE ATOMIC WEIGHT OF LEAD OF RADIOACTIVE ORIGIN.

BY THEODORE W. RICHARDS AND CHARLES WADSWORTH, 3D.

Received October 20, 1916.

The recent independent and almost simultaneous investigations upon the atomic weights of lead from radioactive minerals have proved with very little room for doubt that the substance derived from this source has a much lower atomic weight than ordinary lead.[1] This conclusion is so important in its theoretical relations that its every aspect should be carefully investigated. Accordingly, the present paper represents further

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[1] Richards and Lembert, THIS JOURNAL, 36, 1329 (1914); Hönigschmid and St. Horovitz, *Compt. rend.*, 158, 1798 (1914); M. Curie, *Ibid.*, 158, 1676 (1914); Soddy and Hyman, *J. Chem. Soc.*, 105, 1402 (1914); also especially, Hönigschmid, *Sitzb. k. Akad. Wiss, Wien, IIa*, 123, 1 (Dec., 1914).

research in this direction, embodying determinations of the atomic weight of new samples of varied origin. The outcome entirely supports the earlier conclusion.

Four samples from widely separated sources were studied in the present research, namely, radio-lead from Australian carnotite, from American carnotite, from Norwegian cleveite, and Norwegian bröggerite.

The first of these samples was obtained in large quantity from the Olary mines of South Australia, through the kindness of Mr. S. Radcliff and Mr. E. R. Bubb, of the Radium Hill Company, of Sydney, New South Wales. The carnotite, an impure vanadate of uranium and potassium, mixed with much ilmenite and mica, was crushed and fused with excess of salt cake. The powdered product was extracted with cold water in agitators, dissolving the uranium and rare earths and leaving a suspension of barium, radium and lead sulfates, which was allowed to settle in lead-lined vats. After digestion with sulfuric acid to remove the iron, the separated sulfates were converted into carbonates by boiling with 20% sodium carbonate solution. The carbonates were dissolved in hydrochloric acid and the metals were reprecipitated as sulfates, which, after washing, were fused with sodium carbonate in graphite crucibles. Two kilograms of metallic lead thus reduced served as the basis of one of our present samples, as well as of the work now being continued in this laboratory.

The preliminary purification above described was carried out in Australia.[1] Our subsequent work with the sample is briefly described in a recent paper on the density of radio-lead,[2] but because so much depended upon the purification of materials in work of the sort under consideration, further details are desirable. Three different purified samples derived from the Australia lead were prepared as follows: In each case the metallic lead was dissolved in nitric acid, leaving practically no residue. Two portions of the nitrate thus obtained were taken; the first for the preparation of Samples A and B, and the second for the preparation of Sample C.

The first portion was precipitated with 20% hydrochloric acid from dilute solution, the precipitate being separated from the mother liquor by suction and dissolved in pure warm water to which enough acid had been added to prevent precipitation of the basic salt. Lead sulfide was precipitated from this solution by thoroughly scrubbed hydrogen sulfide gas, and after separation and washing was dissolved in pure nitric acid. The small portion oxidized to sulfate during this latter process was boiled with sodium carbonate for several hours, and the precipitate of lead carbonate, washed free from sodium, was dissolved in nitric acid and united to the

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[1] A fuller description of the details is to be found in the paper by S. Radcliff, *Jour. and Proc. of the Roy. Soc. of New South Wales*, 47, 145 (1913).

[2] THIS JOURNAL, 38, 223 (1916).

main portion of the nitrate, which was recrystallized four times from pure water and precipitated as chloride from a warm solution in a quartz dish with hydrogen chloride. The precipitate was centrifuged, dissolved in water in a large platinum can and recrystallized four times, each time having added a few drops of hydrochloric acid to prevent the formation of basic salt. The second mother liquor gave no test for nitrate. This chloride, dried over caustic alkali, formed Sample A, and after two additional recrystallizations a smaller specimen constituted Sample B.

The second portion of the original nitrate made from the Australian sample was purified in a much simpler fashion. Avoiding the troublesome precipitation with hydrogen sulfide, we recrystallized the nitrate five times successively by adding concentrated nitric acid to its aqueous solution; then the radio-lead was converted into chloride, and by precipitation with excess of hydrochloric acid this salt also was recrystallized five times. This was Sample C of the chloride, a portion of which before the last crystallization had served to prepare Sample D of the metallic radio-lead used for determining the density.[1]

The next sample, designated F, was prepared from American carnotite by the Standard Chemical Co., of Pittsburgh, and came to us through the kindness of Dr. C. H. Viol, of this company, and of Professor W. D. Harkins, of the University of Chicago. After one or two recrystallizations as nitrate and three consecutive separations as chloride, this material had been reduced to metal by fusion with alkaline tartrate and carbonate, and reached us in this form. Harkins had determined its grating spectrum, and found no lines foreign to ordinary lead. Recrystallization as nitrate and chloride having been so efficacious in the case of Sample C, we continued the same method here, recrystallizing this sample thrice successively in the form of each of these salts. The limitation in the amount of material prevented further purification.

Two other samples of especial value and significance were obtained through the kindness of Dr. Ellen Gleditsch, of Kristiania. Both came from primary rocks—Norwegian pegmatite dykes. The purification of one of these, from cleveite, has already been described;[2] the source of this material, which occurred in cubic crystals and was carefully selected, was near Langesund, Norway. It was recrystallized first as nitrate and then as chloride three times each, in the usual manner; and the pure substance, dried in a vacuum over caustic alkali, was designated as Sample G.

Yet another sample, designated H, was prepared from lead sulfide, also kindly sent by Dr. Gleditsch, obtained from selected crystals of Norwegian octahedral bröggerite from Roade, near Moss, Norway. This was purified in precisely the same way as lead from cleveite.

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[1] *Loc. cit.*, p. 224.

[2] Richards and Wadsworth, THIS JOURNAL, **38**, 1659 (1916).

In addition to these four samples of radio-lead enough ordinary lead was carefully purified to serve as the basis of control-analyses. The purest "test lead" of commerce, free from silver, was dissolved in nitric acid, and recrystallized four times as nitrate and four times as chloride.

Throughout this work the usual care taken in atomic weight investigations was not forgotten. The nitric acid, hydrochloric acid, water and silver were all purified in methods already often described, and throughout the work on the nitrate and chloride of lead (except in the preparation of the nitrate for Sample A), the material was treated exclusively in vessels of platinum or quartz. In the case of Sample A, vessels of a good modern, slightly soluble glass, were employed.

None of our preparations after ignition in hydrochloric acid was entirely free from a trace of the insoluble black residue usually left by even carefully purified fused lead chloride when it is dissolved in water. This difficulty has been already met with by Baxter and his assistants, as well as in the earlier work on radio-lead.[1] In many cases the amount of contamination was almost if not wholly negligible; in others, on the other hand, it was appreciable. The amounts found in the two analyses of ordinary lead detailed below were, respectively, 0.26 and 0.30 mg., whereas the amounts found in the nine analyses of radio-lead were, respectively, 0.84, 0.21, 1.95, 0.00, 0.05, 0.47, 0.04, and 0.00 mg. These quantities, found by collecting the black residue on a Gooch-Munroe crucible before precipitation of chlorine with silver, were subtracted from the initial weight of the fused lead chloride. It is noticeable that in general those preparations which contained appreciable amounts of the residue were slightly lower than the others as regards the final atomic weight obtained, but this conclusion rests on only a few cases and may have no significance. In any case the error produced by this slight residue (which consisted mainly of carbon, with a trace of silica) could not have been important. The residues were of a much smaller order than the differences between the atomic weights of the various samples, and the main outcome of the work would have been unaffected if they had been entirely disregarded.

The black residue may be entirely eliminated by adopting a method which has been in use for a long time for freeing fusible salts from silica, namely, the preliminary fusion of the salt, filtering off the residue, and recrystallizing before the analysis is commenced.[2] Hönigschmid and St. Horovitz[3] have shown also that by distillation in quartz this residue remains behind, a fact which we have recently verified.

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[1] Richards and Lembert, THIS JOURNAL, 36, 1336 (1914).

[2] See Stas, "Untersuchungen Über die Gesetze der Chemischen Proportionen. Über die Atomgewichte und Ihre Gegenseitigen Verhältnisse," Leipzig, 1867, p. 275; Richards, THIS JOURNAL, 24, 376 (1902); see also Baxter and Hartmann, *Ibid.*, 37, 117 (1915).

[3] Hönigschmid and St. Horovitz, *Sitzb. k. Akad. Wiss, Wien, IIa*, 123, 16 (1914).

The method of analysis was essentially similar to that so often described. The lead chloride was fused in a platinum boat in pure hydrogen chloride; this gas was displaced by nitrogen while the substance was cooling; and finally the pure dry salt in its boat was pushed into the weighing bottle, stoppered in pure dry air with the help of the familiar "bottling apparatus," and weighed at leisure. The weighed salt was placed in a large Erlenmeyer flask with glass stopper very carefully ground. Enough water was then added to form a fiftieth-normal solution of the salt and the flask and contents, with the addition of a drop of pure nitric acid to prevent the formation of basic salt,[1] were gently warmed on an electric stove, at about 50°, until complete solution was obtained. The boat was then removed, and the residue filtered off, both boat and residue being carefully washed and the filtrate being collected directly in the precipitating flask.

The chlorine contained in this solution was then precipitated in the usual fashion by an amount of silver calculated as nearly as possible to correspond with it. Especially in the early determinations of a previously untested sample the exact amount was not attained, and more silver or more chloride had to be added, but in most of the subsequent cases the precipitation was found at once to be almost complete. These small quantities of silver, or those corresponding to the additional chloride, were, respectively, added to or subtracted from the weight of silver originally taken in each case, and the finally corrected weight is given in the table. As the magnitudes of these small quantities are purely accidental, their detailed recital is unnecessary. The precipitation was carried on in a dark room, under red light, and the usual precautions were taken. The attainment of exact equivalence of silver and chlorine was tested in a nephelometer in the customary fashion.

The balance used was a good one, and the weights were, of course, carefully standardized. All the weighings were reduced to the vacuum standard (adding 0.060 mg. for each gram of lead chloride and subtracting 0.030 mg. for each gram of silver) and all other precautions usual in this sort of work were carefully maintained.

The first two determinations on ordinary lead were only preliminary, in order to gain practice with the method, and are not included in the table below. They yielded as values for the atomic weight, respectively, 207.15 and 207.16. All the other analyses which were brought forward to conclusion are recorded in the tables. Probably the first analysis in the second table of Sample A of Australian carnotite was somewhat erroneous, but the effect on the average, in which it was included, is unimportant. The tables are self-explanatory. The atomic weights of silver and chlorine are taken as 107.88 and 35.459, respectively.

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[1] See Baxter and Grover, THIS JOURNAL, **37**, 1027 (1915).

THE ATOMIC WEIGHT OF ORDINARY LEAD.

Sample.	Corrected weight $PbCl_2$.	Corrected wt. Ag added.	Ratio $PbCl_2 : Ag$.	Atomic weight Pb.
3	3.72918	2.89325	1.28892	207.179
4	5.35111	4.15151	1.28896	207.188
			Average,	207.183

THE ATOMIC WEIGHT OF RADIO-LEAD.

Sample.			Corrected weight $PbCl_2$.	Corrected wt. Ag added.	Ratio $PbCl_2 : Ag$.	Atomic weight Pb.
1	A	Carnotite, Australia	4.64010	3.61118	1.28493	206.318
2	B	Carnotite, Australia	5.35517	4.16711	1.28512	206.359
3	B	Carnotite, Australia	6.15608	4.79072	1.28500	206.334
4	C	Carnotite, Australia	4.14770	3.22748	1.28512	206.359
					Average,	206.342
5	F	Carnotite, U. S. A.	5.31585	4.12670	1.28816	207.015
6	F	Carnotite, U. S. A.	4.65899	3.61707	1.28806	206.994
					Average,	207.004
7	H	Bröggerite, Norway	4.29104	3.34187	1.28402	206.122
8	G	Cleveite, Norway	3.92736	3.05913	1.28382	206.079
9	G	Cleveite, Norway	4.45270	3.46818	1.28387	206.090
					Average,	206.084

The results of these analyses show that the different samples of radio-lead all give lower values for the atomic weights than ordinary lead, but that the material from each source gives a different value, precisely as had been previously found in the earlier investigations in this and other laboratories. Summarized, the results were as follows:

ATOMIC WEIGHT OF RADIO-LEAD.

Ore.	Geographical origin.	Atomic wt.
Galena (?)	American ordinary lead	207.18
Carnotite	Colorado, U. S. A. (?)	207.00
Carnotite	Radium Hill, N. S. W., Australia	206.34
Bröggerite	Moss, Norway	206.12
Cleveite	Langesund, Norway	206.08

In this table results have been arranged in order of the atomic weight. Ordinary lead gave the maximum value (essentially equal to that found by Baxter and Grover[1]; and Norwegian cleveite gave the minimum value (essentially equal to that found by Hönigschmid in bröggerite,[2] 206.06).

It seems reasonable to suppose that the other samples were composed of mixtures of these two kinds of lead, but that is by no means certain, for there may be yet a third variety. The Norwegian bröggerite gave a result so near to that of the cleveite that we may assume the substance to be almost of the same kind, with but very slight admixture of an im-

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[1] Baxter and Grover, THIS JOURNAL, **37**, 1027 (1915).

[2] Hönigschmid and St. Horovitz, *Sitzb. k. Akad. Wiss, Wien, IIa,* **123**, 1 (Dec., 1914).

purity; but the two carnotites give widely divergent results. The lead from Australian carnotite was known to have originated partly from an admixture of galena; therefore it was to be expected that the atomic weight would be greater than the minimum value for radio-lead. Its value, 206.34, would be given approximately by a mixture of three parts of radio-lead like that obtained from Norwegian cleveite with one part of ordinary lead—a reasonable supposition, since, as stated above, the Australian carnotite was known to have contained galena. The American carnotite, Sample F, represented by Analyses 5 and 6, is more puzzling. This has an atomic weight which would be given by a mixture of only one part of radio-lead with 5 or 6 of ordinary lead, a condition which seems to indicate the admixture of very large amounts of galena with the sample in question. Since the source is uncertain one cannot say whether or not this inference is satisfactory. The alternative would be the assumption of an admixture of a third kind of lead with yet higher atomic weight, such as that possibly indicated by the work of Soddy and Hyman.[1]

Two physical properties of the several preparations under consideration have especial interest, namely, the magnitude of the radioactivity and the nature of the spectrum.

One of us, in collaboration with Dr. Lembert, had already concluded that the radioactivity is not proportional to the decrease in atomic weight in samples of radio-lead coming from different sources, and our present experience fully confirms this conclusion. The radioactivity of the several samples was determined by the rate of fall of a gold-leaf spectroscope arranged in the usual fashion so as to measure quantitatively the rate of fall of the gold leaf by means of a small telescope. Equal weights of the several samples of lead chloride spread out in a thin layer were tested in succession. The rate of the fall of the instrument in the absence of any radioactive substance was subtracted from that in the presence of each. Alpha radioactivity was excluded by thin aluminum foil; that which was measured was due almost entirely to beta-rays. The results are given by the following table:

TABLE.

Source of radio-lead.	Time of fall in seconds.	Rate of fall.		Corrected.
		Per minute.	Natural.	
Australian Carnotite.........	9.45	0.1053	0.0287	0.0766
Norwegian Bröggerite........	4.02	0.2487	0.0287	0.2200
Norwegian Cleveite..........	....	....	....	0.1638[2]
American Carnotite..........	1.79	0.5587	0.0287	0.5300
Uranium Oxide.............	11.73	0.0850	0.0287	0.0563

If the radioactivity were dependent upon the presence of radium G (the supposed end product of the decomposition, a form of metallic lead),

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[1] *Loc. cit.*

[2] Calculated from data from another electroscope.

the rate of fall for cleveite would be the greatest and that for American carnotite the least. But the results are precisely the other way about. There can be little question, then, that radioactivity is not due to the isotope which gives the low atomic weight. Probably it is due to radium E, since in all of our samples the half-value of the radioactivity was attained in about five days—the half life of radium E. The maximum value, approached asymptotically, is nearly reached in a month.

The spectrum of radio-lead as thus far studied by Hönigschmid, by Merton and by Harkins, as well as by Baxter (who kindly photographed the ultraviolet spectrum of one of the samples of lead prepared by one of us with the help of Dr. Lembert) has always been found to be essentially like that of ordinary lead. In the present research we thought it worth while once more to test this question and especially to extend the inquiry to the visible portion of the spectrum—most of the tests in the past having been made in the ultraviolet region. We found difficulty in eliminating traces of copper, silver and calcium too small to be detected by ordinary analysis, either quantitative or qualitative. The extreme delicacy of the spectrum in a Féry spectrometer was shown by the fact that Sample C of Australian lead, which gave distinct silver lines, nevertheless showed no trace of this metal when dissolved in nitric acid and tested nephelometrically with bromide for the presence of silver, although the latter test is a very sensitive one. The amount of silver giving these strong lines must, therefore, have been at least as small as is represented by the very slight solubility of silver bromide in the presence of excess of bromine ion—far too little to affect the atomic weight. After eight recrystallizations as nitrate and two as chloride, the product gave in every respect precisely the same spectrum as the purest ordinary lead prepared by Baxter and Grover, except for a vanishingly small trace of two of the most prominent silver lines.

The details of the spectroscopic testing were as follows: To make the electrodes, electrolytic crystals were dried on pure filter paper and fused in a current of pure hydrogen in a hard glass (or silica) tube constricted at one end to the desired size. The molten metal was allowed to run into the constricted part of the tube. If the glass adheres to the metal the surface of the lead must be carefully freed from fragments when the glass is removed, preparatory to use in the spectroscope.

Between two electrodes thus prepared, 2 mm. apart, were flashed sparks from a large induction coil. As usual, a large condenser, placed in parallel with the coil, increased the strength of the spark; and a small self-inductance (consisting of a number of turns of coarse insulated wire) served to eliminate air lines. The spark must be intermittent, otherwise the leaden electrodes will melt; its light was focused on the slit of the spectroscope by means of a double convex spherical-cylindrical lens, of quartz or glass, as the need required.

The photographs of the ultraviolet region in the Féry spectrometer were very kindly made by Professor Baxter. Photographs of the visible portion of the spectrum were made by us in the Gibbs Laboratory (by means of a less technically complete, but nevertheless fully satisfactory, spectrometer). The range of this latter spectroscope was between wave lengths 3300 and 7800—the permeability of glass limiting the effect on one end and the sensitiveness of the specially prepared plate on the other. All the latter work of loading and developing had to be done in complete darkness. To make assurance doubly sure, a further study of the visible spectrum was made, in collaboration with Mr. Norris F. Hall, with the help of the Hilger wave-length spectrometer, comparing visually in the same field of view the spectra of pure ordinary lead and the best purified specimen from Australian carnotite. Every line was scrutinized between the range 4000 and 7600, especial pains being taken in the red and yellow portions, the least satisfactory from a photographic point of view. No discernible differences between the two spectra were observed.

The lead kindly sent us by Professor Harkins was also found to be identical in every respect to the other two samples, except for a faint trace of copper. The lead made from the Norwegian cleveite had been less often crystallized; it showed a distinct trace of silver, and minute traces of copper and calcium; but (so far as we could tell) no impurity in amount sufficient to affect the atomic weight.

Because no lines were detected between wave lengths 7800 and 2200 in any of the samples which were not due either to ordinary lead or to unimportant traces of well-known impurities, the conclusion previously reached by Richards and Lembert is supported, namely, that radio-lead possesses the same spectrum as ordinary lead. The present confirmation is especially interesting because of the support of the presumably almost pure radio-lead obtained from the preparations of Dr. Gleditsch.

Since the atomic weight is variable, but the spectrum of these samples all the same, one must conclude that a part of the atom exercising an important effect upon the atomic weight is without influence upon the spectrum or the volume. The dual nature thus postulated is, of course, in accord with the interesting hypothetical assumptions which have been advanced on various sides concerning the possible make-up of the atom; but our present research can go no further than support the idea of duality without defining exactly of what the two parts may consist. Nothing in the outcome is in any way inconsistent with the suggestive disintegration hypothesis, independently advanced by Soddy and Russell in England and by Fajans in Germany.

We are glad to acknowledge our indebtedness to the Carnegie Institution of Washington for generous support in this investigation.

Summary.

In this paper the atomic weight of four different samples of radio-lead not hitherto tested, as well as one sample of ordinary lead (used to control the others) was determined. The results were as follows:

Ordinary lead	207.18
Radio-lead (Colorado)	207.00
Radio-lead (Australia)	206.34
Radio-lead (obtained from bröggerite from Norway)	206.12
Radio-lead (obtained from cleveite from Langesund, Norway)	206.08

That the most carefully selected sample should give the lowest result is strong evidence that the higher results obtained from other samples were due merely to the accidental admixture of ordinary lead. As before, no new lines were found either in the ultraviolet or visible spectrum of any of these samples. Hence the atom of lead may be supposed to have a dual structure. Each sample, except the ordinary lead, possessed radioactivity, but the magnitude of this radioactivity seemed to bear no relation to the lowering of the atomic weight.

CAMBRIDGE, MASS., 1914–1916.

[CONTRIBUTION FROM THE LABORATORY OF QUALITATIVE ANALYSIS, COLLEGE OF THE CITY OF NEW YORK.]

THE SYSTEMATIC DETECTION OF THIOCYANATES.

BY LOUIS J. CURTMAN AND BEN R. HARRIS.

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Nature of the Problem.—One of the most striking reactions in qualitative work, is the red color produced when ferric salts and thiocyanates are brought together in solution. While the production of this red color serves as an exceedingly sensitive test for iron, as a test for thiocyanates this reaction is not only of a much lower order of sensitiveness,[1] but is also interfered with by many acids. Arsenates, phosphates, oxalates, tartrates, fluorides[2] and borates[3] hinder the free course of the reaction; ferrocyanides mask the red color, while iodides, acetates and nitrites offer the most serious interferences by forming colorations with ferric salts similar to the color of ferric thiocyanate.

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[1] This was to be expected; for, Kruss and Moraht (*Ber.*, **22**, 2056 (1899)) have demonstrated that the maximum color is produced when ferric chloride and potassium thiocyanate are brought together in the proportion of 1 : 12, respectively, a condition that is not reproducible when unknown and minute amounts of thiocyanate have to be dealt with. Quantities of thiocyanates in excess of this ratio also produce the maximum color, so that in testing for iron it is always possible to produce the deepest color attainable in a given case.

[2] Stokes and Cain, *Bull. Bur. of Standards*, 3, No. 1, 115 (1907).

[3] Prescott and Johnson, *Qual. Chem. Anal.*, 1918, p. 155.