one and two α-particles by hydrogen ions. The latter are not lost in the radioactive disintegration and increase correspondingly the atomic weight of the lead finally resulting. It is interesting to note that in the actinium series (with presumably an *odd* number of hydrogens in the atomic nucleus) the tendency shown in the uranium and thorium series for β-particles to come off in successive transformations is replaced by a tendency to come off in alternate transformations.

As Soddy and Cranston have pointed out[1] the actinium series differs from the uranium series so markedly,—particularly in the constant of the Geiger-Nuttall relationship between period of transformation and range of α-particles emitted,—as to favor the "suggestion that the actinium and radium families may be quite distinct."

Summary.

1. The assumption (made by Piccard) that the actinium series is derived neither from uranium I nor from uranium II, but from a third isotope (actino-uranium) does not require (as Soddy supposed) the identity of period of the first and third.

2. The relation of the 3 series (uranium, actinium and thorium) becomes more symmetrical if a hypothetical isotope of protactinium (= eka-tantalum = uranium Z) be assumed as the parent of actino-uranium by a β-ray transformation.

3. This element, and likewise actino-uranium are predicted to have an atomic weight 235, corresponding to protactinium 231, actinium 227 and actinium-lead 207.

4. This last value agrees well with Hönigschmid's value of 206.05 for the atomic weight of uranium-lead containing approximately 3% of actinium lead.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

PERCHLORIC ACID AS A DEHYDRATING AGENT IN THE DETERMINATION OF SILICA.

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In the determination of silica the latter is usually rendered insoluble by evaporating the hydrochloric acid solution to dryness and dehydrating the residue at 100° to 120°. This method requires considerable time, and a small amount of silica passes into solution when the salts are dissolved out by acid. Efforts have been made to dehydrate the silica in other ways which would be more rapid and equally or more effective. Drown[2] first suggested the use of hot conc. sulfuric acid as a dehydrating

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[1] *Loc. cit.*

[2] Drown, *J. Inst. Min. Eng.*, 7, 346 (1879).

agent for the determination of silicon in steel, where rapidity is essential, and this method is widely used at the present time. It has several disadvantages, however. Insoluble ferric sulfate separates, causing bumping unless great care is taken, and this sulfate often does not readily dissolve after the solution is diluted. The use of acetic anhydride was suggested by Gooch, Reckert, and Kuzirian[1] but offered no advantages and was no more effective than evaporation to dryness.

The dihydrate of perchloric acid, $HClO_4.2H_2O$, boils at 203° and at this temperature is a powerful dehydrating agent. It seemed probable, therefore, that it could replace sulfuric acid in the method mentioned above, and to great advantage, since its salts are nearly all readily soluble both in the concentrated acid and in water. This was found to be true. Without danger of forming insoluble salts it can be used with all silicates, metals and alloys which are soluble in acids, while sulfuric acid is utterly useless in the presence of lead, barium, strontium and calcium, and is difficult to use in many other cases. Moreover, it is more effective in rendering the silica insoluble than the usual method of evaporation to dryness, and it is extremely rapid. It is, however, without action on those silicates which are not decomposed by hydrochloric acid.

The method in general consists in dissolving the metal or silicate in hydrochloric or nitric acid, adding perchloric acid, or dissolving directly in perchloric acid, evaporating to dense fumes of the latter, boiling gently for 15 or 20 minutes to dehydrate the silica, cooling and diluting with water. All salts are instantly soluble and the silica is filtered off and determined as usual. It contains less impurity than when separated by the usual methods.

The perchloric acid used in this work was prepared from ammonium perchlorate by the method described by one of the authors,[2] and purified by distillation under reduced pressure. If distilled under atmospheric pressure there is some decomposition which is greater the slower the rate of distillation. When 500 cc. of acid containing 67% of perchloric acid was distilled in 50 minutes, the loss by decomposition was about 3.5%. When the time was extended to 135 minutes, the loss was 13%. In the method referred to above it should be noted that the proportions of ammonium perchlorate, hydrochloric acid and nitric acid there recommended are satisfactory when a fairly pure salt is used, but the commercial perchlorate requires 10 to 20% more of the acids.

The chemically pure acid has been on the market for some time, so that it is no longer necessary to prepare it. The price is still rather high, but if there is sufficient demand, it can be produced cheaply.

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[1] Gooch, Reckert and Kuzirian, *Am. J. Sci.*, **186**, 598 (1913).

[2] Willard, THIS JOURNAL, 34, 1480 (1912).

The following procedures are recommended for the differnt classes of materials and these were followed in obtainin the results tabulated below.

Procedure for Metals and Alloys.

Weigh out a sample corresponding to about 10 mg. of silica, using a 100 or 150 cc. beaker. Dissolve it in either nitric or hydrochloric acid, depending on which reagent is more suitable for effecting solution. For steel, 20 to 40 cc. of dil. nitric acid (sp. gr. about 1.17) will be found convenient. After the action has ceased add 8 to 10 cc. of perchloric acid (60 to 70%) for each gram of metal dissolved. The amount of acid required depends upon the solubility of the metal perchlorate in hot conc. perchloric acid. In the case of aluminum and its alloys it is necessary to use as much as 15 cc. of perchloric acid per gram of sample. Support the cover glass on glass hooks to facilitate evaporation, place the beaker on the hot-plate and evaporate to copious fumes of perchloric acid. Remove the glass hooks to prevent unnecessary loss of acid and boil 15 to 20 minutes, so that the acid refluxes down the side of the beaker. Especial care must be taken never to allow the boiling contents of the beaker to become solid, since if this occurs the separation of silica is always incomplete. If there is a tendency for much insoluble perchlorate to separate out, either the heating is not properly regulated or insufficient acid is present. In the case of aluminum, however, there is always a considerable amount of insoluble perchlorate. As the solution cools it usually becomes completely solid. Dilute with 4 or 5 times its volume of water, heat to boiling, filter off the silica, wash it with very dilute hydrochloric acid and finally with water, ignite and weigh as usual. Treat the precipitate with hydrofluoric and sulfuric acids, ignite and weigh the residue to determine the weight of pure silica. This correction is usually very small.

The metal may be dissolved directly in hot conc. perchloric acid but the action is often so violent as to be almost explosive. For this reason it is usually advisable to use some other acid, but dil. perchloric acid may be used if the action is rapid enough.

If a liberal amount of perchloric acid is used, the process is more satisfactory and the separation of silica more certain. The amount suggested is a minimum to economize acid as much as possible.

High per cent. ferrosilicon is not decomposed by perchloric acid.

Procedure for Limestone and Soluble Silicates.

In a 100 to 150 cc. beaker dissolve about 0.5 g. of the material in a mixture of 5 cc. perchloric acid and 10 cc. of water. If the silica content is very high, it is advisable to use more acid. Evaporate to dense fumes of perchloric acid and follow the procedure for metals described above. Insoluble silicates must first be fused with sodium carbonate as usual.

In order to test the accuracy of the process several experiments were carried out using a known weight of silica in the form of quartz sand containing only 0.025% of impurity. It was fused in a platinum crucible with sodium carbonate, the melt dissolved in water in a platinum dish and perchloric acid added. The silica was separated as described above. The filtrate was evaporated to dryness and taken up with hydrochloric acid to recover any silica remaining in solution. The residue left after treatment with hydrofluoric and sulfuric acids was obviously sodium sulfate and was, therefore, converted into its equivalent of oxide before subtracting from the weight of the impure silica. The results appear in Table I.

TABLE I.

Expt.	Weight SiO_2 taken. G.	Weight impure SiO_2. G.	Weight pure SiO_2. G.	Error. Mg.	Weight SiO_2 from filtrate.[a] Mg.
1	0.3613	0.3626	0.3615	0.2	0.0
2	0.1553	0.1545	0.1541	1.2	0.6
3	0.1716	0.1710	0.1708	0.8	0.7
4	0.1400	0.1395	0.1394	0.6	0.4
5	0.1503	0.1496	0.1494	0.9	1.1
6	0.3152	0.3140	0.3138	1.4	1.3

[a] Not used in calculating error.

The removal of silica is remarkably complete considering the amount present, and in all but the most accurate work the amount remaining in solution can be disregarded. In the usual method the latter amounts to several milligrams.[1]

Table II gives the results obtained with limestone and silicates.

TABLE II.

Expt.	Material.	Weight of sample. G.	Weight of impure SiO_2. G.	Weight of pure SiO_2. G.	SiO_2 found. %.	SiO_2 usual method. %.	SiO_2 in filtrate.[a] G.
7	Cement A	0.3337	0.0756	0.0747	22.38	22.48	0.0001
8	Cement A	0.3507	0.0797	0.0790	22.50	22.48	0.0003
9	Cement B	0.6205	0.2244	0.2238	36.07	36.10	......
10	Limestone	0.6693	0.0356	0.0346	5.18	5.20	......
11	Limestone	0.5915	0.0316	0.0306	5.18	5.20	......
12	Willemite[b]	1.5199	0.3911	0.3743	24.63	24.70	0.0010
13	Willemite	1.3331	0.3433	0.3289	24.62	24.70	0.0009

[a] Not used in calculating per cent. of SiO_2.

[b] Contained a little gangue.

The silicon present in iron and steel separates out as the gelatinous precipitate of silicic acid, while in the case of aluminum part of the silicon is precipitated in the form of brown amorphous silicon which is not oxidized by perchloric acid. This is converted on ignition to silicon dioxide.

Table III shows the results obtained with metals.

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[1] Hillebrand, THIS JOURNAL, 24, 366 (1902).

TABLE III.

Expt.	Material.	Weight of sample. G.	Weight of impure SiO_2. G.	Weight of pure SiO_2. G.	Silicon found. %.	Silicon present. %.
14..........	B. of S. Iron D	1.0675	0.0603	0.0600	2.64	2.64
15..........	B. of S. Iron D	0.6496	0.0369	0.0368	2.66	2.64
16..........	B. S. Steel 1% C	3.0897	0.0103	0.0101	0.153	0.153
17..........	B. S. Steel 1% C	3.0406	0.0102	0.0100	0.153	0.153
18..........	B. S. Steel 30*a*	5.1190	0.0265	0.0259	0.238	0.228
19..........	B. S. Steel 30*a*	5.1659	0.0272	0.0259	0.235	0.228
20..........	B. S. Steel 30*a*	2.0565	0.0110	0.0106	0.237	0.228
21..........	Steel 5% W.	2.1036	0.0592	0.0068	0.147	0.135
22..........	Steel 5% W.	2.0120	0.0405	0.0061	0.142	0.135
23..........	"99%" Aluminum	1.1417	0.0076	0.0072	0.28	0.28
24..........	"99%" Aluminum	2.0621	0.0144	0.0124	0.28	0.28
25..........	Nickel wire	3.3265	......	0.0157	0.22	0.21[a]
26..........	Nickel wire	3.1486	......	0.0145	0.22	0.21

[a] Drown's method.

It was noticed that some tungsten steels formed a clear solution in nitric acid and that in a few of these cases the tungsten remained in solution after evaporation with perchloric acid. This allowed the method to be applied to the determination of the silicon in such steels. The steel used in Expts. 21 and 22 was of this character. The silica was contaminated with both ferric oxide and tungsten trioxide. Much more perchloric acid was required in this case to prevent the precipitation of tungstic acid. This method is applicable only in comparatively few cases, since with most tungsten steels the tungstic acid precipitates.

Summary.

1. The silica in metals and silicates can be rendered insoluble by boiling the conc. perchloric acid solution (60 to 70%) for a short time.

2. Less silica remains in the filtrate than by the usual method of evaporating the hydrochloric acid solution to dryness, and the process is far more rapid.

3. The perchlorates formed are dissolved instantly upon dilution with water, leaving pure silica, uncontaminated by difficultly soluble salts.

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