NOTE ON THE J. LAWRENCE SMITH METHOD FOR THE ANALYSIS OF SAMARSKITE[1]

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The mineral samarskite and several closely related species have long been known to offer analytical problems quite different from those met in the analysis of silicates. These minerals contain columbium, tantalum, the rare earths, uranium, and a considerable number of the more common elements, such as iron, manganese, calcium, lead, zinc and titanium. The principal methods that have been proposed for the decomposition of such minerals are: (1) heating with sulfuric acid;[2] (2) fusion with potassium or sodium hydrogen sulfate;[3] (3) treatment with hydrofluoric acid;[4] (4) heating in the vapor of sulfur monochloride.[5]

The method of J. Lawrence Smith, involving the use of hydrofluoric acid, has considerable historical interest and still presents important analytical problems. It has the advantage of accomplishing a rapid decomposition of the mineral without introducing any alkali salts. Silica, if present, must be estimated separately, but it is seldom found in samarskite itself.

Outline of the Method

A brief outline of Smith's method may assist the reader. He used 5 g. portions but with present-day facilities 2 g. portions are probably sufficient.

The finely powdered mineral is weighed, placed in a platinum dish, covered with hydrofluoric acid and allowed to stand or heated on the steam-bath until decomposition is complete, as evidenced by the disappearance of all dark specks. Decomposition is assisted by stirring with a platinum rod. After standing overnight, cold, the insoluble portion, A, is filtered on a paper supported by a platinum cone or rubber funnel, well washed with dilute hydrofluoric acid, finally transferred to a platinum dish and heated with a moderate excess of sulfuric acid until nearly all of the sulfuric acid is evaporated. Taken up in water, this portion is supposed to contain the rare earths and uranium.

The filtrate, B, soluble in hydrofluoric acid is also evaporated with an excess of sulfuric acid and finally taken up in water with a little hydrochloric acid. On diluting and boiling, if not before, this solution deposits columbium and tantalum oxides. Titanium, tin and tungsten are sup-

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[1] Published with the permission of the Director of the U. S. Geological Survey.

[2] Hoffman, *Am. Jour. Sci.*, [3] **24**, 475 (1882).

[3] Nilson, *Ber.*, **13**, 1430 (1880).

[4] Smith, *Am. J. Sci.*, [3] **13**, 359 (1877); and especially *Am. Chem. J.*, **5**, 44, 73 (1883).

[5] Hicks, This Journal, **33**, 1492 (1911).

posed to accompany the columbium. The filtrate from the "acid earths" carries iron, manganese and most of the other bases that may be present.

Several helpful comments on this method of analyzing samarskite have been made by Hillebrand[6] whose paper should be consulted for some alternative procedures and additions.

The scheme of analysis finally adopted and discussed in this paper is shown in the accompanying diagrammatic form.

Scheme for the Analysis of Samarskite

<table>
<tr><td colspan="7">Moisten 2 g. of the finely powdered mineral, add HF, stir or heat until decomposition is complete.</td></tr>
<tr><td colspan="4">A. Insoluble: Rare Earths, Pb, U, (Fe, Mn), Ca, etc. Fume with H_2SO_4. Saturate with H_2S.</td><td colspan="3">B. Soluble: Cb, Ta, Ti and most of the bases. Fume with H_2SO_4. Evaporate. Take up in a little HCl and considerable SO_2. Boil.</td></tr>
<tr><td rowspan="4">Precipitate: PbS and insoluble.</td><td colspan="3">Filtrate: Boil. Acidify with HNO_3. Boil. Add NH_4Cl and NH_4OH.</td><td rowspan="3">Precipitate: Cb, Ta, Ti (Sn, W). Weigh. Dissolve in $NaHSO_4$. Pass a portion through a reductor and titrate the Cb.</td><td colspan="2">Filtrate: Oxidize iron, add NH_4Cl and NH_4OH. Filter.</td></tr>
<tr><td colspan="2">Precipitate: Dissolve in HNO_3. Evaporate and pour solution into $H_2C_2O_4$</td><td rowspan="2">Filtrate: Combine with similar filtrate in B portion.</td><td rowspan="2">Precipitate: Dissolve. Treat with $(NH_4)_2CO_3$. Filter. Add filtrate to that from FeS in A.</td><td rowspan="3">Filtrate: Determine Mn, Zn, Ca, Mg, K and Na in usual way.</td></tr>
<tr><td rowspan="2">Precipitate: Th and Rare Earths.</td><td>Filtrate Add $(NH_4)_2CO_3$. Remove Fe, etc., with $(NH_4)_2S$.</td></tr>
<tr><td colspan="4">Solution: U. Evaporate, ignite, dissolve in HNO_3, filter, precipitate with NH_4OH, filter, ignite.</td></tr>
</table>

Observations and Suggestions

Experience with this method has shown that it is not as simple or clean-cut in its separations as the original description might lead one to suppose. Some suggestions and additions are given in the following paragraphs, relating chiefly to work done on a specimen of samarskite collected from a pegmatite about two and a half miles southwest of Petaca, New Mexico, by Mr. F. L. Hess, of the Bureau of Mines, U. S. Department of Commerce. The results given here refer only to an average lot of certain picked portions that was first analyzed. Later tests showed that the mineral was not of uniform composition throughout. The genetic relations of the different portions and the geological features will be considered elsewhere.

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[6] Hillebrand, *Col. Sci. Soc. Proc.*, 3, 38 (1888).

1. The paper on which the fluorides are filtered should be carefully treated for a small quantity of earths invariably retained by it, by gently igniting and adding the residue to the main A portion before all the sulfuric acid is evaporated.

2. Practically all of the lead, which is of interest now-a-days on account of its supposed genetic relation to uranium and thorium—their ratio permitting a determination of the "age of the mineral"—may be filtered off from the solution of the rare earth sulfates as $PbSO_4$. If small in amount, it is separated as PbS and eventually determined by the Fairhall method,[7] which consists in separating the lead as $PbCrO_4$, and titrating the chromate iodimetrically with thiosulfate; or the lead may be weighed as $PbCrO_4$. It is of historical interest to note that Smith supposed the insoluble in sulfuric acid to be Cb_2O_5 and added its weight to the main Cb_2O_5. On the other hand, Hillebrand considered it to be all $PbSO_4$, which it is not always. A small fraction of the lead may escape determination as $PbSO_4$, but only a trace will be found in the B portion when hydrofluoric acid alone is used to decompose the mineral.

3. On account of the almost certain contamination of the rare earth oxalates by calcium, manganese, zinc and sometimes uranium, if they are precipitated with oxalic acid immediately after removing lead, it is advisable to make two or more precipitations first with sufficient ammonia and ammonium chloride, dissolve the hydroxides in nitric acid, evaporate the excess and then precipitate the rare earths as oxalates.

4. It is unnecessary to describe the determination of manganese, zinc, calcium, magnesium and the alkalies here except to say that it is advisable to evaporate the main filtrate somewhat to recover any uranium that may have been washed through the filter in the absence of an electrolyte in the wash water.

5. In regard to the precipitation with oxalic acid the fear expressed by Hauser[8] that uranium and iron may carry considerable rare earths into the filtrate was found to be groundless when dilutions appropriate to analytical work were used. Thorium is separated from the other rare earths by the well-known thiosulfate method. The remaining earths are separated by means of several treatments with sodium sulfate into two groups, the insoluble cerium-terbium group and the soluble yttrium group. Cerium is determined by oxidation in sulfuric acid solution with ammonium persulfate and titration with hydrogen peroxide.[9] A very little, apparently, remains in the "yttrium group."

6. Iron is separated from uranium in the A portion by means of ammonium carbonate (about 2 g. to 15 ml. of ammonia) and ammonium sulfide (considerably more than the "few drops" recommended in some books, to avoid colloidal effects). The uranium solution is evaporated and the residue ignited. After dissolving in nitric acid and filtering off the residue of platinum, etc.—probably all derived from utensils and reagents—the operation is repeated. Blank tests showed that beryllium remains with the uranium in this treatment, if present. Uranium is then precipitated by ammonia and weighed as U_3O_8. The weight so obtained was very close to that obtained by titration with permanganate. The uranium solution cannot be ignited directly to U_3O_8 on account of the presence of sulfates, as uranyl sulfate does not go to U_3O_8 on ignition.

As noted by Hillebrand, the uranium is not all found in the A portion, but it seems doubtful whether the distribution between the A and B portions gives the UO_2 and UO_3 of the mineral exactly. Several factors, such as the insolubility of uranous fluoride, the ionization of ferric fluoride and the proportion of ferric iron present, come

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[7] Fairhall, *J. Ind. Hygiene*, **4**, 9 (1922); also Kehoe and others, *J. Am. Med. Assocn.*, **87**, 2081 (1926).

[8] Hauser, *Z. anal. Chem.*, **47**, 677 (1908).

[9] Schoeller and Powell, "The Analysis of Minerals and Ores of the Rarer Elements," Griffin and Co., London, **1918**, p. 73.

into play here. A consideration of these factors makes it appear advisable to express the reducing power of the mineral, as determined by solution in sulfuric acid in a sealed tube and titration with permanganate, first as UO_2 and any remaining as FeO.[10]

7. The small precipitate of iron in the A portion is tested for SiO_2, Mn, Zn, Ti, Al, Cb and other elements. Aluminum could not be found in samarskite and SiO_2 was very doubtful.

8. The sulfates obtained from the B portion are evaporated short of dryness, moistened with about 2 ml. of hydrochloric acid and about 10 ml. of saturated SO_2 solution, diluted to about 400 ml. and boiled to hydrolyze the acid earths. This process is repeated until the earths are free from iron and their recovery from the filtrate is as complete as possible. They are then weighed as $Cb_2O_5 + Ta_2O_5 + TiO_2$. The titanium is then determined colorimetrically, and Ti + Cb volumetrically by means of a Jones reductor and titration with $KMnO_4$.[11] This method even if somewhat approximate is far preferable to the method of Marignac. Sears' method[12] proved unreliable as a quantitative method.

9. The filtrate from the hydrolysis of the acid earths is analyzed as has been described for the A portion, except that iron is separated by ammonium carbonate without the use of ammonium sulfide, bringing the solution just to boiling. When the distribution of the elements between the A and B portions is of no consequence the uranium portions, the iron portions and the manganese portions can be combined with a great saving of time.

TABLE I

ANALYSIS OF SAMARSKITE FROM PETACA, NEW MEXICO

	Insoluble in HF	Soluble in HF	Total		Insoluble in HF	Soluble in HF	Total
Cb_2O_5	..	41.00	41.00	MnO	0.20	0.47	0.67
Ta_2O_5	..	4.62	4.62	ZnO	.06	.03	.09
TiO_2	..	2.20	2.20	Ba, Sr	..	..	Traces
SnO_2	..	.04	.04	CaO	2.57	.05	2.62
WO_3	..	.02	.02	MgO	.13	.04	.17
UO_2	5.83	..	6.14[a]	PbO	.84	.02	.86
UO_3	..	2.41	2.08[a]	K_2O	.10	.11	.21
Ce_2O_3	.20	..	.20	Na_2O	.04	.06	.10
$(La, Tb)_2O_3$, etc.	4.56	..	4.56	H_2O	..	1.31	1.31
Y_2O_3, etc.	27.54	..	27.54	Undetermined	.30	.25	.55
ThO_2	1.55	..	1.55	He	..	..	Present
ZrO_2	..	.02	.02				——
Fe_2O_3	.71	2.33	3.04	Total, per cent.			99.69

[a] Stage of oxidation based on titration with $KMnO_4$.

Physical and Optical Data

Determination of the density of some mineral fragments in the pycnometer at 25° gave 5.670. Another lot of fragments of somewhat different

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[10] There is scarcely any reason why we should not write Mn_2O_3 and CeO_2 but it is not conventional in these minerals.

[11] One mg. TiO_2 = 0.1247 ml. of 0.1 N $KMnO_4$. My latest experience is that 1 ml. of 0.1 N $KMnO_4$ = about 7.55 mg. Cb_2O_5, although Metzger and Taylor found 7.052 mg. Cb_2O_5 [*Columbia School of Mines Quart.*, **30**, 323 (1909)]. Further details are given in a dissertation by David Hart, Columbia Univ., **1926**.

[12] Sears, THIS JOURNAL, **48**, 343 (1926).

composition gave 5.656. The hardness and other physical properties of the mineral agree with Dana's description of samarskite. Its index of refraction, determined by Dr. C. S. Ross, of the U. S. Geological Survey, is somewhat variable between 2.18 and 2.20. It is isotropic. Unfortunately the pieces of mineral give no indication of external crystal form. The rock surrounding them is stained somewhat brown. After the above analytical work was completed radiographs of polished sections of the mineral and rock showed some unhomogeneities and zoning and further analyses of certain portions will probably assist in making the geologic relations clear, but this work may not be completed for some time and will be published elsewhere.

Test for Helium

Helium was identified spectroscopically by the method used for brannerite[13] in 1920. In fact, by means of a direct-reading Hilger spectroscope, the spectrum tube used in 1920 was reëxamined more carefully and compared with one containing gas from samarskite, with the results shown below. There is no doubt that the yellow line 5876 is slightly removed from the two sodium lines, and several other helium lines were observed. Some lines, however, are still not classified with certainty.

TABLE II

DATA ON HELIUM LINES

Gas from brannerite observed in 1920	Observed more accurately in 1927	Gas from samarskite observed in 1927	Gas from brannerite observed in 1920	Observed more accurately in 1927	Gas from samarskite observed in 1927
	He lines			Other lines	
6660		6698 (N_2?)	7000	6081 very faint	
5880	5875	5876		6067 very faint	
5030	5013	5014	6070	6020 very faint	
		4923		5981 very faint	
4720		4715		5972 very faint	
4470		4472		5938 very faint	
	H_2 lines		5620	5931	
6545	6569	6569		5812	
4870	4863	4863	5470	5610 green band	5609
					5462
			5200	5198 green band	5199
					5044

Age of the Mineral

The approximate age of the material analyzed, based on Pb = 0.80, U = 7.14, and Th = 1.36, computed by the equation

$$\text{Age} = \frac{\text{Pb}}{\text{U} + 0.38\ \text{Th}} \times 7900 \text{ million years}$$

gives 1040 million years, but this is only an average, as the mineral is not homogeneous and it is accordingly difficult to evaluate what weight

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[13] Hess and Wells, *J. Franklin Inst.*, **189**, 225 (1920).

should be attached to this figure. It is hoped, however, that the preparation of radiographs may assist in indicating the less altered portions of the material and, if so, an age determination of the unaltered portion may have greater significance.

Summary

A study of the J. Lawrence Smith method of analyzing samarskite has been made, showing how the different elements distribute themselves in the treatment with hydrofluoric acid. Precautions to be observed in completing the different determinations are given.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF PITTSBURGH]

THE HYDROLYSIS OF SUCROSE BY HYDROCHLORIC ACID IN THE PRESENCE OF ALKALI AND ALKALINE EARTH CHLORIDES[1]

BY C. F. KAUTZ AND A. L. ROBINSON

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The Influence of Neutral Salts on the Acid Inversion of Sucrose

Introduction

It has long been known that neutral salts exert an accelerating influence on reactions of substances subject to catalytic decomposition in acid solutions. Since the original discovery of this phenomenon in the case of sugar hydrolysis by Löwenthal and Lenssen,[2] a large amount of work has been done and a rather extensive literature has resulted. A summary of the earlier work, especially that concerning sugar hydrolysis, is given by Caldwell.[3] A discussion of later work, giving an account of some of the theories which have been proposed to explain this phenomenon, will be found in a recent paper by Bowe.[4] An excellent review of the present status of the problem is given by Schmid and Olsen.[5]

In recent years there have been many attempts made to explain the phenomenon in terms of the activity of the hydrogen ion in the reacting mixture, and the present view of several recent investigators is that the rate of decomposition of a compound by hydrogen or hydroxyl ion catalysis in salt solutions is related to the activity coefficients of these ions. Quali-

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[1] This paper is an abstract of the thesis submitted by C. F. Kautz to the Graduate School of the University of Pittsburgh in partial fulfilment of the requirements for the degree of Master of Science in Chemistry.

[2] Löwenthal and Lenssen, *J. prakt. Chem.*, **85**, 321 (1862).

[3] Caldwell, *Report Brit. Assoc. Adv. Sci.*, **1906**, p. 267.

[4] Bowe, *J. Phys. Chem.*, **31**, 297 (1927).

[5] Schmid and Olsen, *Z. physik. Chem.*, **124**, 97 (1926).