water, and readily so in dilute nitric acid. Mercurous and lead nitrates formed yellow to orange-red precipitates. Copper sulphate caused green precipitates, while cadmium sulphate had no action. Barium chloride had no immediate effect, but there gradually separated reddish crystalline precipitates with usually an orange colored fluorescent precipitate in the supernatant liquid.

The silver salts corresponding to the ammonium salts in 2, 5 and 7 were made and analyzed. The ratios of the acid oxides were preserved in these new compounds.

No study of the limits of concentration leading to the formation of any single member of the series was made. Such a study should be preceded by a systematic investigation of each of the three and four component systems which may be present in this very complicated five-component system. It is proposed to begin such an extended research of the many complexes which have already been prepared.

UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

DOUBLE FLUORIDES OF TITANIUM.[1]

BY JOHN A. SCHAEFFER.

Received August 31, 1908

In the course of a study of titanium the following double fluorides with certain alkaloids were prepared. It was thought a knowledge of them would prehaps lead to better methods than now exist of separating titanium from columbium and tantalum.

Quinine Titanium Fluoride, $(C_{20}H_{24}N_2O_2)(H_2TiF_6)_2.H_2O$.—This salt separated on mixing an alcoholic solution of quinine with a hydrofluoric acid solution of titanium hydroxide. It was recrystallized three times from alcohol and dried in the air. It had a white, velvety appearance. It dissolved readily in water, showing a slight opalescence. In its analysis the titanium was precipitated with ammonium hydroxide and weighed as dioxide. To obtain the fluorine content the water solution of the salt was boiled and titrated with a 0.2 normal solution of sodium hydroxide. Phenolphthalein was the indicator. Fairly concordant results in the estimation of the water were obtained by drying the salt to constant weight at 120°.

Calculated: Ti, 9.67; F, 22.93; H_2O, 1.81.
Found: Ti, 9.53; F, 23.55; H_2O, 1.80, 1.92.

Strychnine Titanium Fluoride, $(C_{21}H_{22}N_2O_2)_2H_2TiF_6.3H_2O$.—It consisted of small lustrous white needles when recrystallized from water. The crystals retained their luster for months. They were quite soluble in

---

[1] From the author's thesis for the Ph.D. degree.

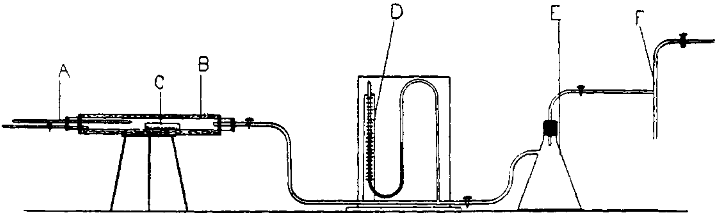
hot water. They were obtained by mixing a hydrofluoric acid solution of the alkaloid with hydrofluotitanic acid in the proportion of two to one.

Calculated: C, 56.87; H, 5.19, ; F, 12.86, ; Ti, 5.42; H_2O, 6.09.
Found: C, 56.82; H, 5.23, 5.16; F, 13.17, 13.01; Ti, 5.45; H_2O, 6.11.

Quinidine Titanium Fluoride, $(C_{20}H_{24}N_2O_2)H_2TiF_6.4H_2O$.—This salt formed large rhombic, yellow colored crystals, readily soluble in hot and cold water. They effloresced on exposure to the air. After six months the water content had entirely disappeared.

Calculated: Ti, 8.58; F, 20.35; H_2O, 12.85.
Found: Ti, 8.96; F, 20.93; H_2O, 13.13.

Brucine Titanium Fluoride, $((C_{23}H_{26}N_2O_4)_2H_2TiF_6)_2.13H_2O$.—It was made just like the strychnine salt. It dissolved in hot water from which it separated on cooling in cream colored crystals. The air-dried salt was used for analysis. The titanium and fluorine were estimated as in previous examples. The water content was determined in the little device shown in the accompanying sketch: *C* is a weighing bottle, containing the salt. This bottle rests in a glass cylinder surrounded by the water jacket *B*. The thermometer is placed so as to register the temperature of the inner tube. *D* is a manometer, and *E* a safety bottle to prevent water entering the apparatus from the suction pump *F*. On using an ordinary faucet pump the pressure was reduced to 30 mm., while the temperature was maintained at from 95° to 100°. The estimation of the water content in all the salts subsequently described was carried out in this way.



Calculated: Ti, 4.50; F, 10.66; H_2O, 10.94.
Found: Ti, 4.72; F, 10.59; H_2O, 10.78, 11.17.

Cinchonidine Titanium Fluoride, $(C_{19}H_{22}N_2O)H_2TiF_6.2H_2O$.—This salt was made by mixing an alcoholic solution of the base with one of hydrofluotitanic acid, evaporating to dryness and extracting the residue with hot 96 per cent. alcohol. On cooling the salt separated in white finely divided needles. It dissolved with difficulty in cold alcohol, but readily in hot alcohol and water.

Calculated: Ti, 9.73; F, 23.08, ; H_2O, 7.29.
Found: Ti, 9.96; F, 23.38, 23.27; H_2O, 7.31.

Narcotine Titanium Fluoride, $(C_{22}H_{23}NO_7)_2H_2TiF_6.3H_2O$.—Colorless crystals were obtained which dissolved more readily in alcohol than in water. The salt also dissolved freely in hydrofluoric acid.

Calculated: Ti, 4.59 ; F, 10.92 ; H_2O, 5.17.
Found: Ti, 5.26, 5.05, 5.00, 4.94; F, 11.50, 11.36; H_2O, 4.89.

The results for titanium and fluorine are high, due to a slight impurity in the alkaloid.

Cinchonine Titanium Fluoride, $(C_{19}H_{22}N_2O)H_2TiF_6$.—This salt, made practically like the preceding salt, is an anhydrous white crystalline mass. It is extremely soluble in water, but not soluble in absolute alcohol.

Calculated: Ti, 24.89 ; F, 10.49.
Found: Ti, 25.13, 25.21; F, 10.65.

Narceine Titanium Fluoride, $(C_{23}H_{27}NO_8)_3H_2TiF_6.5H_2O$.—This salt was obtained like the brucine salt. It dissolved quite freely in hot water and crystallized on cooling in colorless needles.

Calculated: Ti, 3.03 ; F, 7.17 ; H_2O, 5.66.
Found: Ti, 2.57, 2.57; F, 7.17, 6.99; H_2O, 5.57.

Morphine Titanium Fluoride, $((C_{17}H_{19}NO_3)_2H_2TiF_6)_2.5H_2O$.—Small yellowish white, well defined needles, soluble with ease in cold and hot water, with a yellow color.

Calculated: Ti, 6.17; F, 14.63 ; H_2O, 5.77.
Found: Ti, 6.24; F, 14.68, 14.93; H_2O, 5.75.

Codeine Titanium Fluoride, $((C_{18}H_{21}NO_3)_2H_2TiF_6)_4.3H_2O$.—White needles, readily soluble in alcohol and in hot hydrofluoric acid, but very slightly soluble in cold hydrofluoric acid and in hot and cold water.

Calculated: Ti, 6.20; F, 14.69 ; H_2O, 1.74.
Found: Ti, 6.25; F, 14.39, 14.50; H_2O, 1.88, 1.67.

Papaverine Titanium Fluoride, $((C_{20}H_{21}NO_4)_2H_2TiF_6)_6.3H_2O$.—Extremely soluble, small yellow prisms. Alcohol proved the best solvent from which to obtain the salt pure.

Calculated: Ti, 5.62; F, 13.32 ; H_2O, 1.58.
Found: Ti, 5.66; F, 13.43, 13.49; H_2O, 1.53, 1.64, 1.70.

Apomorphine Titanium Fluoride, $(C_{17}H_{17}NO_2)_2H_2TiF_6.4H_2O$.—A brown precipitate separated on the addition of a hydrofluoric acid solution of apomorphine to a similar solution of titanium. On standing, the precipitate rapidly changed to a deep-red, gummy mass. It dissolved instantly in water. The solution was next evaporated to dryness and the residue extracted with much hot alcohol from which liquid the salt crystallized on standing.

It was found impossible to titrate the fluorine directly, owing to the deep red color which the alkaloid gave to the solution, so an excess of sodium hydroxide was added to the liquid. This caused the precipitation of the alkaloid and after filtration the colorless filtrate was titrated with standard acid.

Calculated: Ti, 6.24; F, 14.80; H_2O, 9.30.
Found: Ti, 6.56; F, 15.24; H_2O, 9.54.

Aniline Titanium Fluoride, $(C_6H_5NH_2)_2.H_2TiF_6.H_2O$.—Pink colored needles, readily soluble in water and in alcohol. The salt became perfectly anhydrous after standing for a period of three months, exposed to the air.

Calculated: Ti, 13.05; F, 30.96.
Found: Ti, 12.99; F, 30.88.

Piperine and santonine apparently do not form double fluorides with titanium.

Numerous attempts were made, both by the boiling point and freezing point method, to arrive at the molecular magnitudes of these several double salts but the results were quite discordant.

In conclusion, it may be mentioned that the titanic acid used in this study was derived from rutile from Magnet Cove, Arkansas, and that this particular sample of mineral contained quite a considerable quantity of vanadium.[1]

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

THE USE OF THE ROTATING ANODE IN ELECTROLYTIC SEPARATIONS.[2]

BY MARY E. HOLMES.

Received September 3, 1908.

This investigation was undertaken with the view of learning what advantages could be had with the rotating anode, when using low currents. Heretofore, currents of from three to five amperes have been employed when using the rotating anode. The most exhaustive contribution to the subject of metal separations, employing the rotating anode, was made by Ashbrook in 1904.[3] All his work was done with high currents, five amperes being generally used. Other separations were later recorded by Miss Langness (Thesis, 1906), in which low currents and rotation were successful. The results would seem to indicate the possibility of obtaining other separations with low currents in comparatively short periods of time.

Criticism of the rapid methods of electrolytic work has often been made to the effect that while the methods employed may be adequate for the determination of single metals, the introduction of more than one metal

---

[1] *Compt. rend.*, **53**, 161 (1861); *Astrophysical Jour.*, **6**, 22 (1897).

[2] From the author's thesis for the Ph.D. degree.

[3] THIS JOURNAL, **26**, 1285.