THE DETERMINATION OF FLUORINE IN NICKEL PLATING SOLUTIONS AND IN CHROMIC ACID PLATING SOLUTIONS

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A THESIS

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THE DETERMINATION OF FLUORINE IN NICKEL PLATING SOLUTIONS AND IN CHROMIC ACID PLATING SOLUTIONS

The object of the work described in this paper was to determine quantitatively the amounts of fluorine present in nickel plating solutions and in chromic acid plating solutions.

Methods which have been used to determine fluorides and fluosilicates are:

Honig (1) in which the strength of fluosilicic acid solutions is determined volumetrically. The method depends upon the fact that fluosilicic acid with methyl orange as indicator requires an amount of sodium hydroxide sufficient to neutralize the acid, but if phenolphthalein is used as indicator four additional molecules of sodium hydroxide per molecule of fluosilicic acid are required. The fact that the nickel plating and chromic acid plating solutions are both colored makes it impossible to use this method.

Mayer (2) determined fluosilicic acid gravimetrically as potassium fluosilicate. To the fluosilicic acid was added water and a solution of potassium chloride, then a volume of ethyl alcohol sufficient to make the solution fifty percent alcohol, precipitating potassium fluosilicate. The precipitate is filtered through weighed filtering crucibles and dried at 100°C. in an electric oven and the potassium fluosilicate weighed.
The objection to this method is that nickel sulfate is

quite insoluble in solutions of fifty percent alcohol.

Kurtenacher and Jurenka (3) and Batchelder and Meloche (4) determined fluorine volumetrically by adding a measured volume of cerous nitrate and titrating the excess with potassium permanganate or by a direct titration using methyl red as indicator. This method is eliminated because it is inaccurate in the presence of the sulfate ion.

Guyot (5), Greeff (6) and Bellucci (7) determined fluorine in neutral solutions of alkali fluorides by the addition of ferric chloride obtaining a complex sodium salt.

Deladrier (8), Pisani (9) and others determined fluorine in soluble fluorides by precipitation as thorium fluoride with thorium chloride or thorium nitrate. They ignited the precipitate to the oxide under suitable conditions, and calculated the amount of fluorine present. This method requires the presence of alcohol to make the thorium fluoride insoluble and this causes nickel sulfate to precipitate.

Gooch and Kobayashi (10) used this method and also tried dissolving and titrating the thorium fluoride.

deBoer (11) and others and later Pavelka (12), Feigl (13) and Alamarin (14) determined fluorine colorimetrically by the use of a zirconium alizarine mixture, the color of which faded in the presence of fluorine.

Schrenk and Ode (15) determined silica in substances containing fluorine by volatilizing the fluorine as hydrofluoboric acid by treating the materials with boric acid and either perchloric or sulfuric acid and evaporating.

Willard and Winter (16) discovered that the zirconium alizarine dye mixture was suitable to use as an indicator in the titrating of soluble fluorides with a standard solution of thorium nitrate. They suggested determining fluorine in insoluble fluorides by an adaptation of Schrenk and Ode's method for the determination of silica. They reported erratic results when they tried to volatilize the fluorine as hydrofluoboric acid. They obtained good results when they volatilized fluorine without any boric acid present.

EXPERIMENTAL.

A standard solution of fluosilicic acid was made up. Baker's C.P. fluosilicic (30% solution) acid was diluted one part of acid to three parts of water. This solution was stored in a large wax coated bottle.

The fluorine content was determined volumetrically by Honig's method and gravimetrically by Mayer's method.

Honig's method is as follows: Methyl orange is added to a known volume of the solution of fluosilicic acid which is titrated with normal sodium hydroxide. The solution is then heated to boiling, phenolphthalein added, and titrated again with normal sodium hydroxide. The number of cubic

centimeters of sodium hydroxide solution added in the second titration indicated the amount of fluosilicic acid as well as the sodium fluosilicate originally present in the solution. Other acids which might be present in the solution are neutralized in the first titration.

Equations are as follows:

With methyl orange:

$$2NaOH + H_2SiF_6 \longrightarrow Na_2SiF_6 + 2H_2O$$

With phenolphthalein:

$$4NaOH + Na_2SiF_6 \longrightarrow 6NaF + Si(OH)_4$$

Results obtained by Honig's method are shown in Table I

TABLE I

Trial number	1	2	3	4
Volume of H_2SiF_6 used (cc.)	20.00	20.00	20.00	20.00
Volume 1.1600N-NaOH 2nd titration + 2 (cc.)	21.80	21.85	21.91	21.93
Weight H_2SiF_6 / cc. calculated (mg.)	91.1	91.3	91.6	91.6

Average 1 cc. fluosilicic acid solution contains 91.4 mg. fluosilic acid.

Mayer's method: To five cc. of fluosilicic acid solution was added 20 cc. of water; 5 cc. of 30% solution of potassium chloride and 30 cc. of ethyl alcohol (enough to make the solution 50% alcohol) to precipitate potassium fluosilicate. The precipitate was allowed to stand over night; then filtered through weighed filtering crucibles and washed with a solution of water and ethyl alcohol (1-1).

The precipitate was dried at 100-10°C. in an electric oven, weighed and the weight of fluosilicic acid per cubic centimeter calculated from the weight of potassium fluosilicate found. The results obtained by this method are shown in Table II.

TABLE II.

Trial number	1	2	3	4
Volume H_2SiF_6 used (cc.)	5.00	5.00	5.00	5.00
Weight K_2SiF_6 found (mg.)	459.5	458.2	455.2	457.0
Weight H_2SiF_6 per cc. (mg.) calculated	91.9	91.6	91.0	91.4

Average:-- 1 cc. fluosilicic acid contains 91.5 mg. of fluosilicic acid.

By Honig's method we find 91.4 mg. fluosilicic acid per cubic centimeter and by Mayer's method we find 91.5 mg. fluosilicic acid per cubic centimeter. A mean of these determinations is taken to be 91.5 mg. of fluosilicic acid per cubic centimeter. The chemical factor for fluorine in fluosilicic acid is 0.7912; so by calculation the fluorine content of the standard fluosilicic acid solution is:

91.5 X 0.7912 = 72.4 mg. fluorine per cubic centimeter of the standard solution.

This value was used in all of the subsequent work undertaken.

The nickel plating solution contained the following: Nickel sulfate (149.82 grams per liter);

nickel chloride (14.98 grams per liter); boric acid (23.47 grams per liter); hydrogen peroxide (none to 1.5 grams 30% solution per liter); the ammonium ion is present in varying amounts. The fluosilicic acid was added in known amounts for this work.

The chromic acid plating solution contained: Chromium trioxide (250 grams per liter); Less than 0.1% of the chromium trioxide is chromic sulfate. Fluosilicic acid in known amounts was added to this solution. The usual amount present is from five to fifteen cubic centimeters of a 30% solution of fluosilicic acid per liter of solution.

Guyot, Greeff and Bellucci worked on a method in which neutral aqueous solutions of alkali fluorides with the addition of ferric chloride form a precipitate of the general formula $(FeF_6)X_3$ or

$6NaF + FeCl_3 \longrightarrow Na_3FeF_6 + 3NaCl$. This precipitate does not form $Fe(CNS)_3$ with thiocyanates so KCNS makes a good indicator. When enough ferric chloride has been added to react with the alkali fluoride the excess ferric chloride forms $Fe(CNS)_3$ which is red and serves as an indicator. The sample of fluoride is placed in an iodine flask and two grams of sodium chloride added, then ferric chloride is added until the solution becomes a straw yellow color. The sodium chloride is added to decrease the solubility of Na_3FeF_6 and to sharpen the endpoint. The endpoint is made still sharper by the addition of an alcohol and ether layer, in which the red color of $Fe(CNS)_3$ appears on the addition of an excess of ferric chloride. The solution must be shaken vigorously in order to obtain an accurate endpoint.

The method gave good results with both sodium fluoride and neutralized fluosilicic acid. Results with sodium fluoride are shown in Table III.

TABLE III.

Trial number	1	2	3
Sodium fluoride (grams)	0.2012	0.2014	0.1990
Ferric chloride used (cc.)	19.95	20.11	19.67
1 cc. ferric chloride = sodium fluoride (mg.)	10.085	10.015	10.117

Average:-- 1cc. ferric chloride = 10.101 mg. sodium fluoride
= 4.560 mg. fluorine.

However when boric acid was added to solutions of sodium fluoride erratic results were obtained. Some results with known amounts of fluorine present and with and without any boric acid present are shown in Table IV.

The results obtained from direct titrations of a solution of sodium fluoride with ferric chloride are shown in Table V.

The fact that very erratic results were obtained when boric acid was present made this method useless insofar as the determination of fluorine in a nickel plating solution containing boric acid was concerned.

TABLE IV

1 cc. ferric chloride = 4.560 mg. fluoride.

Trial number	1	2	3	4	5	6
Fluorine present (mg.)	22.80	22.80	22.80	22.80	22.80	22.80
Ferric chloride used (cc.)	4.99	4.97	5.00	11.23	7.37	6.55
Boric acid present (grams)	none	none	none	1.00	1.00	1.00
Fluorine found (mg.)	22.75	22.66	22.80	51.21	33.61	29.87
Error (mg.)	-0.05	-0.14	none	-18.41	-10.81	-7.07

TABLE V.

Fluorine present - 60.55 Mg. (as NaF)
1 cc. ferric chloride = 4.634 mg. fluorine

Trial number	1	2	3	4	5
Ferric chloride used (cc.)	13.12	13.04	13.08	13.11	13.21
Fluorine found (mg.)	60.81	60.43	60.61	60.75	61.21
Error (mg.)	+0.26	-0.12	+0.06	+0.20	+0.66

Finally it was decided to attempt to adapt Schrenk and Ode's method for the determination of silica to the determination of fluorine in nickel plating solutions which contain boric acid. Following Willard and Winter's work it was decided to volatilize the fluorine as hydrofluoboric acid, convert the hydrofluoboric acid in the distillate to sodium fluoride and titrate with a standard solution of thorium nitrate using as an indicator a zirconium alizarine dye mixture.

The apparatus used in the distillation of samples is shown in Figure I. (A) is a 125 cc. Claisen flask, (B) 250°C. thermometer, (C) separatory funnel, 150 cc. (D) is a micro burner, (E) condenser, and (F) receiving beaker.

For the titration the apparatus and reagents required are: (1) A twenty five cubic centimeter burette. (2) Indicator, (a) zirconium nitrate, 1 gram of $Zr(NO_3)_4$ $5H_2O$ dissolved in 250 cc. of water. (b) Alizarine red, 1 gram of sodium alizarine fulfonate in 100 cc. of ethyl alcohol. Filter off the undissolved residue and add 150 cc. of ethyl alcohol to the filtrate. These two solutions are mixed three parts of zirconium nitrate to two parts of alizarine red as needed. The color should be violet-red when mixed. (3) A standard sodium fluoride solution with which to standardize the thorium nitrate titrating solution. (4) Thorium nitrate solution for titrating. Standardized against a known fluoride solution. (5) Dilute sodium hydroxide solution. (6) Solution

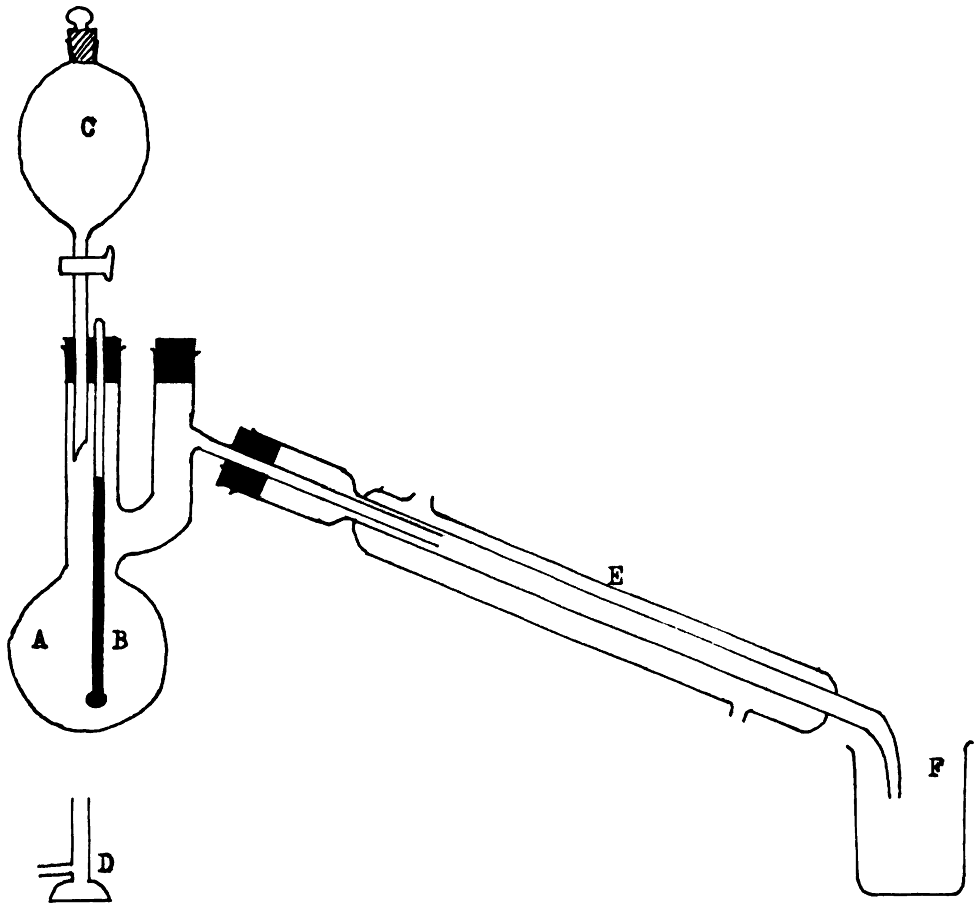

FIGURE I.

of hydrochloric acid (1-25), (7) ethyl alcohol.

Before distilling any samples it was necessary to standardize the thorium nitrate solution. The first method tried was to weigh out known samples of pure potassium fluozirconate, dissolve in water, make neutral and add ethyl alcohol so that the solution was fifty per cent alcohol. Five drops of the zirconium alizarine indicator was added and the solution titrated with thorium nitrate to the endpoint which is pink. If this endpoint lasts for one minute with stirring it is permanent. Because of the insolubility of the potassium fluozirconate it was necessary to dissolve the samples in warm water and the results then obtained were very erratic. It was then decided to use a fluoride which would be more soluble in water, and for this purpose sodium fluoride was used. Both the sodium fluoride and the thorium nitrate were made up very carefully. The results obtained are shown in Table VI.

TABLE VI.

Trial number	NaF solution used (cc.)	$Th(NO_3)_4$ used (cc.)
1	5.00	4.23
2	5.00	3.95
3	5.00	4.19
4	5.00	3.94
5	5.00	3.93
6	5.00	3.95
7	5.00	3.95

These results seemed favorable so a new solution of thorium nitrate was made up and a series of direct titrations was run to standardize the thorium nitrate. The results of this standardization are shown in Table VII.

TABLE VII.

Fluorine present = 4.750 mg. (present as NaF).

Trial number	Thorium nitrate used (cc.)	Fluorine (mg.) per cc. $Th(NO_3)_4$
1	4.16	1.142
2	4.12	1.153
3	4.14	1.147
4	4.15	1.145
5	4.09	1.161
6	4.10	1.158
7	4.15	1.145
8	4.15	1.145

Average:-- 1 cc. thorium nitrate = 1.150 mg. fluorine.

The determination of fluorine in the nickel plating solution was tried by direct titration but the color of the solution completely obscured the endpoint.

It was decided to try and check the results shown in Table VII by running a series of distillations of known amounts of sodium fluoride using boric and perchloric acids as recommended by Schrenk and Ode.

The procedure used was as follows: Place the sample in the distilling flask and add the water, boric acid (solid) and perchloric acid then distill until the temperature reached about 200°C. The condenser was then washed with distilled water and the distillate was ready to prepart for titration. The volume of the distillate was doubled by the addition of ethyl alcohol and then five drops of the zirconium alizarine indicator was added. Next the solution was neutralized with sodium hydroxide and a small amount of hydrochloric acid (1-25) was added to destroy the color if necessary. The solution was then titrated with standard thorium nitrate. Results obtained are shown in Table VIII. The results, while they vary, do show promise because some of the trials gave results which checked with the direct titrations. It was thought that if the temperature were run higher better results might be obtained. In order to distill at a higher temperature it was necessary to discontinue the use of perchloric acid which boils at 200°C. Sulfuric acid (1-1) was substituted and the results are shown in Table IX. While using such a high temperature trouble was encountered with the boric acid condensing in the side arm of the distilling flask and plugging up the outlet. On trial #4 (Table IX) the side arm of the distilling flask became completely closed and at 247°C. the stopper blew out of the flask, ruining the determination and showing that the method was not safe to use. The results obtained did look favorable and seemed to warrant a continuation of the volatilization method using sulfuric acid in place of perchloric acid. It was thought that perhaps if a larger volume of water were used in the distillation and the temperature kept at a lower point that the fluorine could be distilled over as hydrofluoboric acid. The water was not all added directly to the distilling flask at first but was added a drop at a time through a separatory funnel keeping the temperature at a constant point.

A new solution of thorium nitrate was made up and standardized against a known solution of sodium fluoride and the amount of fluorine titrated by 1 cc. of thorium nitrate calculated. The results of this standardization (Table X) show 1 cc. thorium nitrate = 2.433 mg. fluorine.

Several samples of the nickel plating solution were distilled with known amounts of fluorine added. The conditions were varied somewhat in an attempt to find a set of conditions which would work successfully in the running of a series of distillations. The amounts of the various substances used together with the results obtained are shown in Tables XI and XII. From this series of distillations we find good results were obtained from trial #6 through trial #10 (Table XI) excepting #7 which was partially lost and also from trial #11 through trial #16 (Table XII) omitting trial #14 which was wrong because of bumping in the distilling flask. Of the others only trial #9 (Table XI) does not check reasonably close.

In trials number 17-19 (Table XII) no boric acid was added to the distilling flask, the only boric acid present being that which was in the nickel plating solution. It was thought possible that the fluorine might be distilled over as fluosilicic acid instead of hydrofluoboric acid, but the low results obtained when the distillation was carried on below 130°C. (the boiling point of hydrofluoboric acid) together with the fact that some boric acid was known to be present tended to show that the fluorine was partially held by the boric acid and that it was necessary to distill this fluorine over as hydrofluoboric acid.

Different series of distillations of nickel plating solutions with a known fluorine content of from 2.90 to 23.2 milligrams of fluorine in five cubic centimeters of nickel plating solution were now run. The method of procedure used is as follows:

Part I Distillation.

1. The sample is added to the flask after which the separatory funnel and thermometer are placed in position as shown in figure I.

2. The nickel plating solution is added through the separatory funnel. (In the case of unknowns this would be part of step 1.)

3. Seven cubic centimeters of sulfuric acid (1-1) are added through the separatory funnel.

4. 1.5 grams of boric acid are dissolved in ten cubic centimeters of hot water and are added through the separatory funnel.

5. From ten to fifteen cubic centimeters of water is added through the funnel to be sure that all the boric acid is in the distilling flask.

NOTE: In steps 2-5 be sure and have a closed system with the only outlet being through the condenser into the receiving beaker.

6. Add whatever amount of water that is to be used in the distillation to the separatory funnel.

7. Distill off the fluorine keeping the temperature between 130 and 150°C. by the addition of water from the separatory funnel a drop at a time. Distill until the volume of distillate is 125 cc. or more.

The reason for a maximum temperature of 150°C. is that it was noticed that when higher temperatures were used boric acid started to condense on the side arm of the distilling flask and caused danger of stopping up the outlet of the system.

Part II Titration with Standard Thorium Nitrate.

Titrating agent--Thorium nitrate standardized against a known solution of sodium fluoride, using a direct titration for the standardization. Use the same procedure as is given below.

Indicator--Two parts of alizarine red and three parts of zirconium nitrate mixed as wanted.

Procedure:

1. Double the volume of distillate by the addition of ethyl alcohol.

2. Add five drops of zirconium alizarine indicator. (If fluorine is present the pink color will disappear in ablut

a minute.)

3. Add enough sodium hydroxide to make the pink color return.

4. Add very carefully just enough hydrochloric acid (1-25) to just destroy the pink color.

NOTE: This is very important as an excess of hydrochloric acid will tend to give high results. If too much acid is added more sodium hydroxide may be added so as to return the pink color and the solution can again be decolorized with hydrochloric acid.

5. Titrate with standard thorium nitrate until the solution is just pink. This endpoint should last with stirring for a minute. If it lasts that long it will be a permanent endpoint and the pink color will remain.

The equations for a solution containing boric acid are:

1. $2H_2SiF_6 + 3H_3BO_3 \longrightarrow 3HBF_4 + 4H_2O + SiO_2$

2. $HBF_4 + 4NaOH \longrightarrow 4NaF + H_3BO_3 + H_2O$

3. $NaOH\ (excess) + HCl \longrightarrow NaCl + H_2O$

4. $4NaF + Th(NO_3)_4 \longrightarrow ThF_4 + 4NaNO_3$

Results obtained on consecutive distillations of nickel plating solutions containing boric acid are shown in Tables XIII, XIV, XV and XVI.

The results obtained in Tables XIII and XIV were obtained without the addition of more boric acid to the nickel plating solution. When an attempt was made to run a series of distillations in which there was 11.58 mg. of fluorine present in five cubic centimeters of nickel plating solution the results were uniformly low. Boric acid in varying amounts was added to the distilling flask through the separatory funnel after first having been dissolved in ten to fifteen cubic centimeters of hot water. The amount of boric acid finally decided upon was 1.5 grams.

A nickel plating solution was made up containing everything present in the original nickel plating solution with the exception of boric acid which was entirely absent. From some work done with solutions containing no boric acid it was thought that it would be possible to run the distillation at a higher temperature and so lessen the volume of water that must be used. This also tended to cut down the time required for a distillation very materially.

The results obtained on a series of consecutive distillations of this new solution containing 5.79 mg. of fluorine in 5 cc. of the nickel plating solution are shown in Table XVII. In all these series of distillations on the nickel plating solutions it did not seem to make any difference as to whether or not the distillate was trapped under water in the receiving beaker or not.

Claisen distilling flasks are recommended instead of Wurtz flasks because of the fact that the nickel plating solution tends to bump and carry over unwanted acid, which makes the endpoint of the titration less distinct than it should be in order to get good results.

TABLE VIII.

Fluorine present - 4.750 mg. (as NaF)
1 cc. thorium nitrate = 1.150 mg. fluorine

Trial number	1	2	3	4	5	6	7	8	9	10	11	12	13
Sodium fluoride (cc.)	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Boric acid added (grams)	1.50	1.50	1.50	2.00	1.50	1.50	1.50	1.50	1.50	1.50	1.00	0.50	3.00
60% Perchloric acid (cc.)	10.00	10.00	10.00	10.00	10.00	10.00	10.00	15.00	10.00	5.00	2.00	5.00	3.00
Water added (cc.)	20.00	25.00	35.00	30.00	30.00	55.00	25.00	40.00	35.00	30.00	30.00	30.00	35.00
Maximum temperature (°C.)	180	190	195	198	195	195	195	196	200	200	200	200	201
Thorium nitrate for titrating (cc.)	2.86	3.21	4.14	4.19	3.66	3.25	3.52	4.00	3.86	3.83	4.30	3.78	4.20
Fluorine found (mg.)	3.289	3.692	4.761	4.819	4.209	3.738	4.048	4.600	4.439	4.405	4.945	4.347	4.830

TABLE IX.

Fluorine present - 4.750 mg. (as NaF)
1 cc. thorium nitrate = 1.150 mg fluorine

Trial number	1	2	3	4*
Sodium fluoride used (cc.)	5.00	5.00	5.00	5.00
Boric acid added (gram)	3.00	3.00	3.00	3.00
Sulfuric acid (1-1) used (cc.)	10.00	10.00	10.00	10.00
Water added (cc.)	35.00	35.00	35.00	
Maximum temperature (°C.)	225	246	247	247
Thorium nitrate for titrating (cc.)	4.09	4.15	4.18	
Fluorine found (mg.)	4.704	4.775	4.807	

* Sample #4 blew up.

TABLE X.

Standardization of Thorium Nitrate Solution

Trial number	1	2	3	4	5
Sodium fluoride added (cc.)	10.00	10.00	10.00	10.00	10.00
Fluorine added (mg.)	9.500	9.500	9.500	9.500	9.500
Thorium nitrate for titrating (cc.)	3.92	3.91	3.88	3.92	3.87
Fluorine found (mg.) per cubic centimeter $Th(NO_3)_4$	2.421	2.430	2.442	2.421	2.452
Average 1 cc. thorium nitrate = mg. fluorine	2.433				

TABLE XI.

1 cc. thorium nitrate = 2.433 mg. fluorine

Trial number	1	2	3	4	5	6	7	8	9	10
Fluorine added (mg.)	72.4	14.5	14.5	14.5	14.5	14.5	14.5	14.5	14.5	14.5
Nickel plating solution (cc.)	10.00	10.00	10.00	15.00	25.00	15.00	15.00	15.00	15.00	5.00
Boric acid added (grams)	0.20	3.00	1.00	1.00	2.00	2.50	2.00	2.00	2.50	2.00
Sulfuric acid (1-1) (cc.)	10.00	10.00	10.00	10.00	15.00	20.00	10.00	10.00	10.00	7.50
Water added (cc.)	125	125	125	125	140	150	135	135	135	85
Distilling temperature (°C.)	104	104	117- 123	125- 134	133- 140	135- 141	135- 147	135- 140	135- 145	133- 146
Maximum temperature (°C.)	120	114	125	140	143	145	152	145	151	149
Thorium nitrate for titration (cc.)	8.47	1.30	4.84	5.18	5.72	5.95	5.80*	5.90	5.33	5.93
Fluorine found (mg.)	20.61	3.16	11.78	12.60	13.92	14.48		14.36	12.97	14.43
Error (mg.)	-51.74	11.31	-2.69	-1.87	-0.55	+0.01		-0.11	-1.50	-0.04

* Some of the distillate was lost.

TABLE XII.

1 cc. thorium nitrate = 2.433 mg. fluorine

Trial number	11	12	13	14	15	16	17	18	19
Fluorine added (mg.)	14.47	14.47	14.47	14.47	5.79	11.58	5.79	5.79	5.79
Nickel plating solution (cc.)	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Boric acid added (grams)	2.00	2.00	2.00	2.00	1.50	1.50	none	none	none
Sulfuric acid (1-1) (cc.)	7.00	5.00	5.00	5.00	7.00	7.00	5.00	7.00	7.00
Water added (cc.)	105	95	100	125	115	115	85	110	110
Distilling temperature (°C.)	132-142	130-150	130-150	130-155	130-145	130-150	118-122	118-140	130-135
Maximum temperature (°C.)	155	157	150	155	145	150	123	145	138
Thorium nitrate for titrating (cc.)	5.94	5.98	5.91	5.58	*2.34	4.78	2.20	2.30	2.40
Fluorine found (mg.)	14.46	14.55	14.38	13.58	5.69	11.63	5.35	5.60	5.84
Error (mg.)	-0.01	+0.08	-0.09	-0.89	-0.01	+0.05	-0.64	-0.19	+0.05

* Error caused by bumping of solution in distilling flask

TABLE XIII.

Fluorine present - 2.90 mg. in 5 cc. nickel plating solution.
1 cc. thorium nitrate = 2.433 mg. fluorine

Trial number	1	2	3	4	5	6
Sulfuric acid (1-1) added (cc.)	7.00	7.00	7.00	7.00	7.00	7.00
Boric acid added (grams)	none	none	none	none	none	none
Water added (cc.)	125	115	120	115	105	110
Distilling temperature (°C)	130- 135	130- 140	130- 145	130- 140	130- 140	130- 140
Maximum temperature (°C.)	142	140	147	143	148	143
Thorium nitrate for titrating (cc.)	1.11	1.17	1.20	1.16	1.12	1.14
Fluorine found (mg.)	2.70	2.85	2.92	2.82	2.73	2.77
Error (mg.)	-0.20	-0.05	+0.02	-0.08	-0.17	-0.13

TABLE XIV.

Fluorine present - 5.79 mg. in 5 cc. nickel plating solution.
1 cc. thorium nitrate = 2.433 mg. fluorine

Trial number	1	2	3	4	5	6
Sulfuric acid (1-1) added (cc.)	7.00	7.00	7.00	7.00	7.00	7.00
Boric acid added (grams)	none	none	none	none	none	none
Water added (cc.)	110	115	115	115	105	100
Distilling temperature (°C.)	130-135	130-135	130-135	130-135	130-135	130-135
Maximum temperature (°C.)	138	137	139	137	136	136
Thorium nitrate for titrating (cc.)	2.40	2.32	2.34	2.35	2.41	2.37
Fluorine found (mg.)	5.84	5.65	5.69	5.72	5.86	5.77
Error (mg.)	+0.05	-0.14	-0.10	-0.07	+0.07	-0.02

TABLE XV.

Fluorine present - 11.58 mg. in 5 cc. nickel plating solution
1 cc. thorium nitrate = 2.433 mg. fluorine

Trial number	1	2	3	4	5	6
Sulfuric acid (1-1) added (cc.)	7.00	7.00	7.00	7.00	7.00	7.00
Boric acid added (grams)	1.50	1.50	1.50	1.50	1.50	1.50
Water added (cc.)	115	115	150	125	130	155
Distilling temperature (°C.)	130-135	130-140	130-140	130-140	130-140	130-140
Maximum temperature (°C.)	137	150	142	140	143	146
Thorium nitrate for titrating (cc.)	4.75	4.78	4.71	4.74	4.67	4.70
Fluorine found (mg.)	11.56	11.64	11.46	11.53	11.36	11.44
Error (mg.)	-0.02	+0.06	-0.12	-0.05	-0.22	-0.14

TABLE XVI.

Fluorine present - 23.17 mg. in 5 cc. nickel plating solution.
1 cc. thorium nitrate = 2.433 mg. fluorine.

Trial number	1	2	3	4	5	6	7
Sulfuric acid (1-1) added (cc.)	7.00	7.00	7.00	7.00	7.00	7.00	7.00
Boric acid added (gram)	1.50	1.50	1.50	1.50	1.50	1.50	1.50
Water added (cc.)	120	130	150	140	115	120	125
Distilling temperature (°C.)	130-140	130-140	130-140	130-140	130-150	130-150	130-150
Maximum temperature (°C.)	146	144	144	150	157	156	152
Thorium nitrate for titrating (cc.)	9.37	9.42	9.45	9.60	9.40	9.47	9.45
Fluorine found (mg.)	22.80	22.92	22.99	23.35	22.87	23.04	22.99
Error (mg.)	-0.37	-0.25	-0.18	+0.18	-0.30	-0.13	-0.18

TABLE XVII.

Fluorine present - 5.79 mg. in 5 cc. nickel plating solution.
1 cc. thorium nitrate = 2.433 mg. fluorine

Trial number	1	2	3	4
Sulfuric acid (1-1) present (cc.)	7.00	7.00	7.00	7.00
Water added (cc.)	80	100	85	90
Distilling temperature (°C.)	155-170	150-160	150-165	150-160
Maximum temperature (°C.)	187	168	172	176
Thorium nitrate for titrating (cc.)	2.39	2.35	2.36	2.37
Fluorine found (mg.)	5.82	5.72	5.74	5.77
Error (mg.)	+0.03	-0.07	-0.05	-0.02

Determination of Fluorine in Chromic Acid Plating Solutions

After completing the work on the nickel plating solution it was decided to extend the work and see if the method would apply to chromic acid plating solutions.

Because of the fact that the solution did not contain boric acid it was thought possible that the fluorine could be distilled over as fluosilicic acid instead of hydrofluoboric acid. If this were true it would be possible to run the distillations at a higher temperature and so lessen the amount of water that it would be necessary to use and also shorten the time required to make a distillation.

Several trial runs were made and in almost every one the distillate was a pale yellow color. This made it difficult to see the pink endpoint in the thorium nitrate titration. In one of the trials the chromium was accidently reduced giving a green solution in the distilling flask which when distilled gave a water clear distillate which was easy to titrate. On all subsequent runs the chromium was reduced by the addition of 2 cc. of ethyl alcohol to the distilling flask, the alcohol being added through the separatory funnel.

Equations involved are:

1. $H_2SiF_6 + 6NaOH \longrightarrow 6NaF + Si(OH)_4 + 2H_2O$
2. $NaOH \text{ (excess)} + HCl \longrightarrow NaCl + H_2O$
3. $4NaF + Th(NO_3)_4 \longrightarrow ThF_4 + NaNO_3$

The results obtained when the chromium was not reduced are shown in Table XVIII.

After running a series of distillations in which there was 2.90 mg. of fluorine in 2 cc. of chromic acid plating solution (Results in Table XIX) it was discovered that by distilling at a temperature of from 150-70°C. (safe when no boric acid is present) that the fluorine could all be distilled over in about 35 cc. of water. Actual distillations bore out this assumption and the results obtained are shown in Table XX. There was 4.34 mg. of fluorine in 1 cc. of the chromic acid plating solution.

A short series of distillations was run in which from 50 to 500 mg. of ferric chloride was added to a chromic acid plating solution which contained 4.34 mg. of fluorine in 1 cc. of plating solution. The results showed that ferric iron did not interfere with the determination of fluorine. The results are shown in Table XXI.

Another short series was run on a chromic acid plating solution containing 2.90 mg. of fluorine per cubic centimeter of solution to which was added 200 mg. each of; aluminum sulfate, cadmium nitrate, cupric nitrate, cobaltous nitrate, lead nitrate, manganous chloride, stannous chloride and zinc nitrate. None of the metals present seemed to interfere with the determination of fluorine in the chromic acid plating solution. The results obtained are shown in Table XXII.

TABLE XVIII.

Fluorine present - 2.90 mg. in 2 cc. chromic acid plating solution.
1 cc. thorium nitrate = 2.433 mg. fluorine

Trial number	1	2	3
Sulfuric acid (1-1) added (cc.)	7.00	7.00	7.00
Water added (cc.)	115	120	100
Distilling temperature (°C.)	120-130	120-130	120-130
Maximum temperature (°C.)	150	155	158
Thorium nitrate for titrating (cc.)	1.09	1.15	1.16
Fluorine found (mg.)	2.65	2.75	2.82
Error (mg.)	-0.25	-0.15	-0.08

TABLE XIX.

Fluorine present - 2.90 mg. in 2 cc. of chromic acid plating solution.
1 cc. thorium nitrate = 2.433 mg. fluorine

Trial number	1	2	3	4	5	6
Sulfuric acid (1-1) added (cc.)	7.00	7.00	7.00	7.00	7.00	7.00
Ethyl alcohol added (cc.)	2.00	2.00	2.00	2.00	2.00	2.00
Water added (cc.)	110	110	130	120	110	105
Distilling temperature (°C.)	120-150	120-130	120-130	120-150	120-140	120-135
Maximum temperature (°C.)	134	136	132	152	143	152
Thorium nitrate for titrating (cc.)	1.15	1.14	1.13	1.17	1.16	1.18
Fluorine found (mg.)	2.80	2.77	2.75	2.85	2.82	2.87
Error (mg.)	-0.10	-0.13	-0.15	-0.05	-0.08	-0.03

TABLE XX.

Fluorine present - 4.34 mg. in 1 cc. of chromic acid plating solution.
1 cc. thorium nitrate = 2.433 mg. fluorine

Trial number		1	2	3	4	5	6
Sulfuric acid (1-1) added	(cc.)	7.00	7.00	7.00	7.00	7.00	7.00
Ethyl alcohol added	(cc.)	2.00	2.00	2.00	2.00	2.00	2.00
Water added	(cc.)	50	70	65	65	70	75
Distilling temperature	(°C.)	150-160	150-170	150-160	150-165	150-160	150-160
Maximum temperature	(°C.)	165	175	176	174	165	170
Thorium nitrate for titrating	(cc.)	1.84	1.74	1.82	1.79	1.82	1.79
Fluorine found	(mg.)	4.48	4.23	4.43	4.36	4.43	4.36
Error	(mg.)	+0.14	-0.11	+0.09	+0.02	+0.09	+0.02

TABLE XXI.

Fluorine present - 4.34 mg. in 1 cc. chromic acid plating solution.
1 cc. thorium nitrate = 2.433 mg. fluorine

Trial number		1	2	3	4
Sulfuric acid (1-1) added	(cc.)	7.00	7.00	7.00	7.00
Ethyl alcohol added	(cc.)	2.00	2.00	2.00	2.00
Ferric chloride added	(mg.)	50.00	500.0	500.0	500.0
Water added	(cc.)	80	90	95	85
Distilling temperature	(°C.)	150-170	145-160	150-160	150-160
Maximum temperature	(°C.)	182	166	171	176
Thorium nitrate for titrating	(cc.)	1.74	1.77	1.75	1.80
Fluorine found	(mg.)	4.23	4.32	4.26	4.38
Error	(mg.)	-0.11	-0.02	-0.08	+0.04

TABLE XXII.

Fluorine present - 2.90 mg. in 1 cc. chromic acid plating solution.
1 cc. thorium nitrate = 2.433 mg. fluorine

Trial number		1	2	3	4	5	6
Sulfuric acid (1-1) added	(cc.)	7.00	7.00	7.00	7.00	7.00	7.00
Ethyl alcohol added	(cc.)	2.00	2.00	2.00	2.00	2.00	2.00
Water added	(cc.)	90	100	95	90	90	95
Metals present* each	(mg.)	200	none	none	200	200	200
Distilling temperature	(°C.)	145-160	150-170	150-160	150-160	150-160	150-165
Maximum temperature	(°C.)	168	197	165	168	166	178
Thorium nitrate for titrating	(cc.)	1.17	1.19	1.17	1.17	1.18	1.15
Fluorine found	(mg.)	2.85	2.90	2.85	2.85	2.87	2.80
Error	(mg.)	-0.05	none	-0.05	-0.05	-0.03	-0.10

* Metals present are: Aluminum, cadmium, copper, cobalt, lead, tin, manganese and zinc.

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CONCLUSIONS

A method is described for volatilizing fluorine quantitatively as hydrofluoboric acid and the fluorine in the distillate titrated with standard thorium nitrate solution using a zirconium alizarine mixture as indicator for determining the endpoint.

This method has been applied to nickel plating solutions containing 2, 4, 8 and 16 cc. of 30% solution of fluosilicic acid per liter of solution.

The method has also been applied to chromic acid plating solutions containing from 5 to 15 cc. of 30% solution of fluosilicic acid per liter of solution.

The presence of ferric iron, aluminum, cadmium, copper (cupric), cobalt (ous), lead, manganese (ous), tin Stannous, and zinc did not interfere with the determination of fluorine in a chromium solution.

When boric acid is not present in the unknown solution the fluorine can be determined more rapidly than if it is present.

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