Determination of Fluoride by Precipitation of Lead Chlorofluoride: Comparison of Classical and Homogeneous Precipitation Methods

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Optimal conditions for the homogeneous precipitation of lead chlorofluoride were investigated and the method was compared with the classical procedure. The most suitable reagent for the pH control of the homogeneous solution was found to be urea with ammonium acetate buffer. If the precipitate obtained by both procedures was allowed to stand overnight, homogeneous precipitation resulted with more accurate data.

INTRODUCTION

Since its original description by Starc[1], the precipitation of lead chlorofluoride for the gravimetric determination of fluoride has been frequently examined and improved[2-5] because of the non-stoichiometry and significant solubility of the precipitate formed. However, due to the crystalline nature of the precipitate and the small gravimetric factor the gravimetric method is still favoured for the fluoride determination, although an indirect finish by titration of the chloride in the dissolved precipitate is repeatedly recommended[6,7].

The purity and crystalline nature of precipitates obtained by precipitation from homogeneous solutions is well known[8] and Willard and Tang[9] first made use of this approach for the precipitation of lead chlorofluoride.

In the present paper the precipitation from homogeneous solution of lead chlorofluoride was investigated with slow increase of pH achieved by hydrolysis of various reagents. Further, the optimal conditions for the precipitation were studied and the method was compared with the classical one.

EXPERIMENTAL

Procedures

Investigation of the Hydrolysis of Various Reagents. Reaction solution were prepared as described earlier[7]. Instead of sodium acetate, urea or acetamide or urea with ammonium acetate buffer was added in a total volume of 250 ml. The concentrations of the reagents were: 0.7 M urea; 0.7 M acetamide; 0.7 M urea and 0.1 M ammonium acetate. A series of precipitations was carried out by digestion on a steam bath. Samples were withdrawn from the solution at timed intervals, cooled to stop the hydrolysis, filtered and the pH measured.

Investigation of the pH Effect on the Completeness of Prepicitation. Reaction solutions were prepared as cited above[7]. Instead of sodium acetate, urea and ammonium acetate buffer were added. During the reaction aliquots were taken at timed intervals, cooled, allowed to stand overnight, filtered and the pH values

measured. The fluoride in the supernatant was determined by titration with thorium nitrate[10].

Homogeneous Precipitation of Lead Chlorofluoride

Reagents. The reagents used were analytical grade chemicals and were used without further purification. A fluoride stock solution was prepared by dissolving 2.00 g of sodium fluoride (dried overnight at 105 °C) in 1 l of demineralised water and stored in a polythene bottle.

Procedure. The fluoride solution containing approximately 50 mg of sodium fluoride had a volume of 250 ml, 4 drops of bromophenol blue indicator solution were added and followed by 3 ml of 6 M hydrochloric acid. After heating to 80 °C, 5 g of lead nitrate were added and heating and stirring continued until complete dissolution of lead nitrate was achieved. While stirring, 10 g of urea were introduced and when dissolved, 2 g of ammonium acetate was added. The reaction on a steam bath was performed with occasional stirring. The precipitation stage lasted approximately 3,5 hours and its completion was indicated by the change of the supernatant's colour to deep blue. The beaker was removed from bath and the solution allowed to cool to room temperature for about 1 hour. The temperature of the solution should not fall below 15 °C to avoid the crystallization of lead chloride. The precipitate was transferred together with a saturated lead chlorofluoride solution without stirring to a No. 4 sintered glass crucible. The precipitate was washed 3 times with 10 ml portions of saturated lead chlorofluoride solution and finally with 10 ml of cold water. Drying at 105 °C for 30 minutes and cooling for 30 minutes was repeated to constant weight.

The following modifications of the homogeneous precipitation method were worked out:

A — The procedure described above was followed in all details, and the precipitate transferred to the filter without stirring.

B — The precipitate was allowed to stand in contact with the supernatant overnight before transferring to the filter without stirring.

C — Ammonium acetate was not added in this modification, whereas 2 ml of 6 M hydrochloric acid and 3 ml of 10% sodium chloride solution were added instead of 3 ml of 6 M hydrochloric acid only (according to the classical method[7]), so that the concentration of Cl^- in both procedures was the same. The precipitate was transferred to the filter either with or without stirring.

Determination of Solubilities. Solubility losses were determined from fluoride content of the supernatants. When the precipitation was completed in a relatively short time, as in the homogeneous precipitaiton, fluoride in the supernatant was determined by the radiometric method previously applied by the authors[10] in the study of calcium fluoride precipitation. Where the time required for the precipitation precluded the use of radioactive flurine-18 (half-life = 1.83 hours), the fluoride content of the supernatant was determined by titration with thorium nitrate[11].

Determination of the Composition of the Precipitates. The washed precipitates were dissolved with warm 3 M nitric acid and the lead content was determined by titration with EDTA using methylthymol blue indicator[12]. An aliquot part of the solution was analysed for chloride content by titration with ammonium rhodanate[10]. The fluoride content in the precipitate was taken to be the difference between the theoretical value and the amount of fluoride found in the supernatant.

RESULTS AND DISCUSSION

Homogeneous Precipitation

A convenient procedure for the homogeneous precipitation of lead chlorofluoride is to increase slowly the pH of the solution after addition of the reagents. The characteristics of the pH increase by hydrolysis of urea and acetamide in the precipitating solution were investigated by taking aliquot samples of the supernatant at various times during digestion, terminating the

hydrolysis by cooling, and measuring the pH value. The results are shown in Fig. 1. It can be seen that when urea is used (curve A) the rate of pH increase
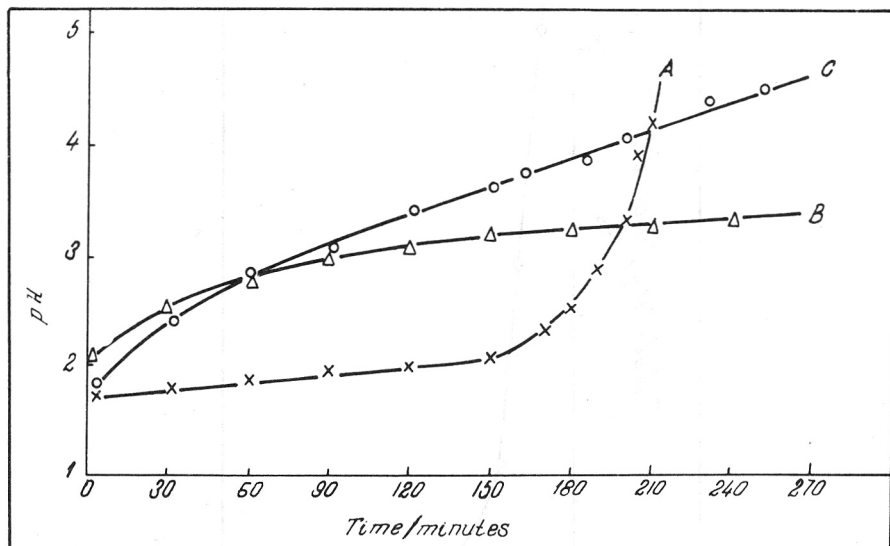

Fig. 1. Effect of various reagents on the rate of pH increase. A, urea 0.7 M; B, acetamide 0.7 M; C, urea 0.7 M and ammonium acetate 0.1 M. Temperature 80 °C.

is very slow in the early stages of precipitation and faster subsequently. The rapid hydrolysis of urea at the end of the precipitation process makes the controlling of the rate of change of the final pH impossible and supersaturation cannot be avoided (resulting in excessive yields of precipitate). When acetamide is used (curve B), a final pH greater than 4 cannot be achieved. After digestion on a steam bath for four hours, the final pH was about 3.3, under which circumstances some fluoride would remain in the solution. An attempt was made to reduce the rate of hydrolysis of urea by the addition of ammonium acetate buffer (curve C). It can be seen that in this case the pH increases at a steady rate and that the optimal pH of 4.5 for completeness of precipitation is reached after approximately 3.5 hours. Qualitative investigations showed that this time could not be shortened by the use of higher reagent concentrations; at reduced concentrations the final pH od 4.5 was not attained. In view of the foregoing, buffered urea was considered to be the most suitable reagent for controlling pH during the homogeneous precipitation of lead chlorofluoride, and this reagent was therefore subjected to a more detailed investigation.

Effect of pH on Completeness of Precipitation

The amount of fluoride remaining in the supernatant of the buffered urea system was determined as a function of pH and the results are shown in Fig. 2. It can be seen that the solubility of lead chlorofluoride is pH dependent under the given conditions. The amount of fluoride remaining in solution decreases rapidly as the pH increases from 2.8 to 3.8. No significant change occurred above pH value 4.
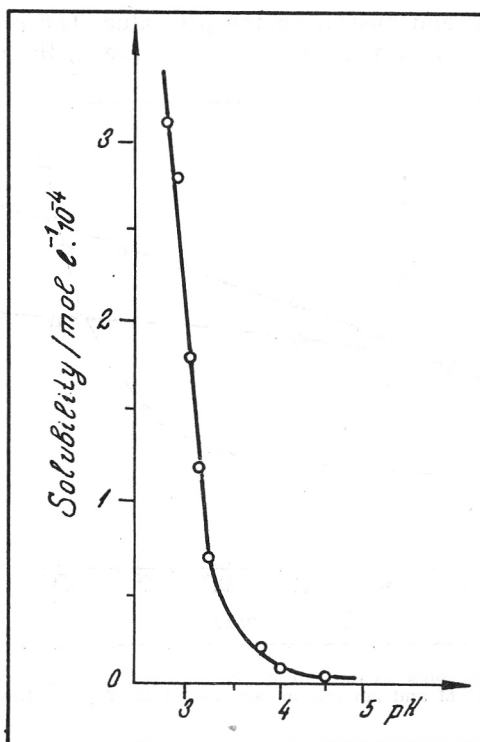
Fig. 2. Effect of pH on the solubility of lead chlorofluoride at a temperature of 20 °C.

Applying these results to the acetamide system, where the pH does not exceed 3.3, it can be seen that in this case the amount of fluoride remaining in solution is equivalent to about 2% of the finally weighed precipitate. This was confirmed by gravimetric determinations where the final precipitates were found to be 2.3% lower than the expected theoretical value.

Comparison of Classical and Homogeneous Precipitation Methods

A number of precipitations were carried out following the classical method[7] and following the described modifications of the homogeneous precipitation procedure with urea and ammonium acetate buffer. Methods were compared concerning the accuracy of results, fluoride solubility and precipitate stoichiometry.

Results are given in Table I. Accuracy in assessed by comparing the measured weights with the theoretical value expected from the stock solution (0.3116 g).

It can be seen that both better accuracy and better precision are obtained by the homogeneous precipitation following modification B, where the precipitate is allowed in contact with the supernatant overnight before filtration. The high results obtained with the classical method are attributed to coprecipitation, as found by Starc[1] and Hammond[13]. The lower results obtained if

TABLE I

Accuracy

Method	Classical	Homogeneous precipitaion		
		A	B	C Without Stirring
No. of determinations	8	10	10	6
Average wt. of ppt./g	0.3149	0.3015	0.3108	0.3087
Standard deviation/g	0.0014	0.0018	0.0011	0.0042
Accuracy, %	+ 1.1	— 3.24	— 0.26	— 0.93

modification A of the homogeneous precipitation precedure is followed, are attributed to solubility losses.

Bournique and Dahmer[5] have attained an improved accuracy by precipitation at pH = 2 with sodium formate buffer but the authors presumed that it might be an artifact due to compensation of errors.

Whilst particular attention has been given to the stoichiometry of the final precipitate[3,4,5], the efficiency of the precipitation process was not previously investigated. The solubility of precipitated lead chlorofluoride was determined[4] but not under the precipitating conditions. In the present investigation unprecipitated fluoride was determined by titrimetric and radiometric procedures, and the results are given in Table II.

TABLE II

Fluoride in the supernatant

Method	Classical	Homogeneous precipitation			
		A	B	C With Stirring	Without Stirring
No. of determinations	8	10	10	2	2
Average wt. of PbClF/g determined by titration	0.0040	0.0098	0.0020	0.0510	0.0416
Standard deviation, g	0.0005	0.0011	0.0007		
Average wt. of PbClF/g determined radio-metrically				0.0502	

It can be seen that precipitation is most complete if the precipitate is allowed to stand overnight and filtration performed without stirring. It would appear that the amount of PbClF found in the supernatant is related to the crystal size of the precipitate, as if the solutions were allowed to stand for the same period of time, larger crystals are obtained by the homogeneous precipitation method. The major impurity in the precipitates is considered

to be $PbCl_2$[14,15]. The amounts of Pb and Cl found experimentally were compared with the expected amount of Pb and Cl in PbClF (taking into consideration the solubilities) and the ratios of Pb to F and Cl to F in the different precipitates calculated. The results are shown in Table III, where it can be seen that the ratios Pb : F and Cl : F all exceed unity. The least deviation is shown by modification A of the homogeneous precipitation method.

TABLE III

Composition of precipitates

Method	Classical	Homogeneous precipitation	
		A	B
No. of determinations	6	3	10
Ratio Pb : F	1.042	1.011	1.024
Standard deviation/g	0.0027	0.0016	0.0021
Ratio Cl : F	1.051	1.005	1.019
Standard deviation/g	0.0025	0.0019	0.0024

CONCLUSION

Examination of the results given shows that a more accurate result (in terms of the weighed precipitate) can be obtained in the gravimetric determination of fluoride by precipitation of PbClF when a homogeneous precipitation is carried out in the presence of urea and ammonium acetate than by the classical precipitation procedure. Since the precipitate must stand in contact with the solution overnight before the filtration is performed to reduce the solubility losses, no shortening of the analysis duration could be achieved. In the absence of ammonium acetate, coprecipitation of $PbCl_2$ is severe.

REFERENCES

1. G. S t a r c, *Z. Anorg. Chem.* **70** (1911) 173.
2. F. H o f f m a n and G. E. F. L u n d e l l, *J. Res. Nat. Bur. Stand.* **3** (1929) 589.
3. J. H. S a y l o r, C. H. D e a l I n r., M. E. L a r k i n, M. E. T r a v e n n e r, and W. C. V o s b u r g h, *Anal. Chim. Acta* **5** (1951) 157.
4. L. H. A n d e r s s o n, *Ark. Kemi* **30** (1968) 57.
5. R. A. B o u r n i q u e and L. H. D a h m e r, *Anal. Chem.* **36** (1964) 1787.
6. I. M. K o l t h o f f and P. J. E l v i n g, *Treatise on Analytical Chemistry*, Part II, Vol. 7, Interscience Publ., New York 1961, p. 265.
7. A. I. V o g e l, *Quantitative Inorganic Analysis*, 3rd Ed., Longmans Publ., London 1964, p. 269.
8. L. G o r d o n, N. L. S a l u t s k y, and H. H. W i l l a r d, *Precipitation from Homogeneous Solution*, Wiley Publ., New York 1959, p. 4.
9. H. H. W i l l a r d and N. K. T a n g, *J. Amer. Chem. Soc.* **59** (1937) 1190.
10. I. T c h o l a k o v a and J. E. W h i t l e y, *J. Radioanal. Chem.* **2** (1969) 409.

11. I. M. Kolthoff and E. B. Stenger, *Volumetric Analysis*, Vol. II, Second Revised Edition, Interscience Publ., New York 1947, p. 320.
12. R. Pribil, *Kompleksometria I*, Tehnika Publ., Sofia 1959, p. 56.
13. L. D. Hammond, *Ind. Eng. Chem.* **16** (1924) 938.
14. F. G. Hawley, *Ind. Eng. Chem.* **18** (1926) 573.
15. P. J. Elving, C. A. Horton, and H. H. Willard, *Analytical Chemistry of Fluorine and Fluorine-Containing Compounds,* in: J. H. Simons, Fluorine Chemistry, Vol. II, Chap. III, Academic Press Publ., New York 1954, pp. 51—211.

IZVOD

Određivanje fluorida uz taloženje olovnog hlorofluorida: upoređivanje klasičnog metoda i metoda homogenog taloženja

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Ispitani su optimalni uslovi homogenog taloženja olovnog hlorofluorida i metod je upoređen sa klasičnim metodom. Homogeno taloženje izvršeno je uz hidrolizu karbamida i uz dodavanje amonium-acetata kao pufera. Kada se talog, dobijen na oba načina, ostavi da odleži jednu noć, taloženjem u homogenom rastvoru dobiju se tačniji rezultati .

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