

DETERMINATION OF PHOSPHORUS AND FLUORINE IN POLYMERS AND ORGANIC COMPOUNDS WITH Nd^{3+} *

XIE Zhengqiu (谢正秋)

(Department of Chemistry, Wuhan University, Wuhan)

ABSTRACT

Percentages of P or/and F in polymers and organic compounds are found by using Nd^{3+} as precipitant and subsequent titration of excess Nd^{3+} with EDTA after decomposing sample in oxygen flask. The errors of determination are for $\text{P} < \pm 0.20\%$ and $\text{F} < \pm 0.30\%$ except fully fluorinated compounds.

INTRODUCTION

In order to determine phosphorus and fluorine in polymers or organic compounds, usually two steps are taken. First transform the sample into PO_4^{3-} and F^- , then determine the content of PO_4^{3-} and F^- . Decomposing organofluorine compounds with oxygen flask is a simpler and more rapid method than others such as combustion-pyrohydrolysis^[1], pyrolysis with AlI_3 ^[2]. Usually the oxygen flask is made of quartz^[3,4] because F^- reacts with B and Al in glass^[5,6]. Although decomposing organophosphorus compounds with oxygen flask suffers reproach^[7,8] for damaging platinum wire, but most analysts still like to use this method because it is very convenient. About determinations of F^- and PO_4^{3-} , direct titration with metal ion or complexometric titration with M-EDTA in the presence of precipitate is simpler than others, such as with La^{3+} ^[9,10], Th^{4+} ^[9,11], La-EDTA, Pr-EDTA^[12] and so on for F^- and La^{3+} ^[13,14], Ce^{3+} ^[15], Pb^{2+} ^[16], Ce-EDTA^[17], Mg-EDTA^[18] and the rest for PO_4^{3-} .

Nevertheless, the methods described above are merely suitable for determining F^- or PO_4^{3-} . If the sample contains both fluorine and phosphorus, it is usually necessary to remove one of them and determine the other. So far, no report on the using of a single reagent to determine both F^- and PO_4^{3-} appeared in the literature.

In this paper, a simple and accurate method using Nd^{3+} is presented for determining phosphorus or/and fluorine content in polymers and organic compounds. In this method, Nd^{3+} solution in a hard glass oxygen flask serves as an absorbing liquid. After absorbing, F^- is transformed into NdF_3 to prevent F^- from reacting with Al and B in glass.

EXPERIMENTAL

Apparatus

Hard glass oxygen flask. 500 ml.

* Received July 8, 1985

Filter paper. Approximately 50 mg of ashless paper with about 20 mg of adhesive paper.

Conical flask. 100 ml.

A set of filter, including a fused silica filter about 30 ml and 100 ml filter flask.

Reagents (All reagents are analytical-grade)

0.01M EDTA, standardized with standard Zn.

0.01M $\text{Nd}(\text{NO}_3)_3$, containing 0.5 ml concentrated hydrochloric acid/L, standardized with EDTA.

0.01M ZnCl_2 standardized with EDTA.

pH=5.5 buffer solution, aqueous 20% hexamethylene-tetramine solution, adjust the pH to 5.5 with hydrochloric acid.

0.015% methyl orange, 0.015% xylene orange in 80% ethanol.

Powder anhydrous sodium acetate.

Concentrated hydrochloric acid.

Concentrated nitric acid.

0.1M BaCl_2 and 1N NH_4OH .

Procedure

(1) Determination of fluorine

Weigh the sample corresponding to about 0.8—1.2 mg fluorine onto an ashless paper with adhesive paper. Decompose according to usual procedure, put it in a 500 ml hard glass oxygen flask, add an excess of 1 ml 0.01M $\text{Nd}(\text{NO}_3)_3$ and make up to 20 ml with distilled water as absorbent beforehand. After shaking and absorbing, rinse the head and wall of the flask with distilled water into the bottom of flask and control the volume to about 30—35 ml. Gently boil for 3 minutes. After cooled, add 5 ml of pH=5.5 buffer. In the presence of xylene orange, titrate with 0.01 M EDTA from red to yellow color.

(2) Determination of phosphorus

Idem, but, the weight of sample correspond to 0.5—1.0 mg of phosphorus; take 20 ml of distilled water as absorbent; distilled water for rinsing the flask head and wall is about 30 ml; after absorbent boils for 3 minutes, add excess of Nd^{3+} , 5 ml of pH=5.5 buffer and reheat to boil; after cooled, continue the determination.

If the sample contains sulfur, after boiling, add 1 ml of 0.1M BaCl_2 at once and allow to cool. Filter BaSO_4 by number 4 fused silica filter. Continue the determination of the filtrate.

If the sample contains fluorine, take 20 ml of distilled water and 1—2 ml of concentrated nitric acid as absorbent. Boil the absorbent and evaporate to 10 ml and then transfer into a 100 ml conical flask. Continue to evaporate to dryness on steam bath. Add 1 ml of distilled water and evaporate to dryness again. After dissolution, continue the determination.

If the sample simultaneously contains fluorine and sulfur, first remove the former and then the latter.

If the sample contains boron and nickel, the sample mixes with 2 times of anhydrous sodium acetate powder before decomposition and the absorbent contains 1 ml of concentrated

hydrochloric acid. After boil and subsequently allow to cool, add 2 drops of methyl orange and neutralized with 1N NH_4OH . Then add 5 ml of pH=5.5 buffer and an excess* of EDTA (for complexing Ni^{2+}). In the presence of xylenol orange, titrate with 0.01M ZnCl_2 to red color and subsequently titrate with 0.01M EDTA to yellow color again. Add an excess of Nd^{3+} and reheat to boil, continue the determination as 2.

(3) Determination of the total content of fluorine and phosphorus

Operation is similar to 1. The weight of sample correspond to 0.8 — 1.2 mg of fluorine, but the quantity of Nd^{3+} absorbent is 2 ml of 0.01M $\text{Nd}(\text{NO}_3)_3$ more than the total equivalent of fluorine and phosphorus and make up to about 30 ml with distilled water. After rinsing the flask head and wall, the volume is about 50 ml. The absorbent boils for 3 minutes, then add 5 ml of pH=5.5 buffer. After cooled, titrate as determined fluorine.

Calculation

$$\text{F}\% = \frac{(\text{MV})_{\text{Nd}^{3+}} - (\text{MV})_{\text{EDTA}}}{W} \times 57 \times 100 \quad (1)$$

$$\text{P}\% = \frac{(\text{MV})_{\text{Nd}^{3+}} - (\text{MV})_{\text{EDTA}}}{W} \times 30.97 \times 100 \quad (2)$$

From the determination of the total content of fluorine and phosphorus:

$$\text{F}\% = \frac{(\text{MV})_{\text{Nd}^{3+}} - (\text{MV})_{\text{EDTA}} - (W \times \text{P}\% / 30.97)}{W} \times 57 \times 100 \quad (3)$$

In (3), P%: found value.

RESULTS AND DISCUSSION

Analytical values of a part of compounds are arranged in Table 1.

(1) Combustion-supporting agent. It is difficult to transform quantitatively high fluorine, $-\text{CF}_3$ containing or fully fluorinated compounds into F^- . In order to solve this problem, mix sample with some combustion-supporting agent such as KClO_3 , KNO_3 , NH_4NO_3 , grape sugar, paraffin etc. or wrap sample in filter paper with adhesive paper^[10] before combustion. In that way, an improved analysis value may be obtained. After the literature^[10], we determined some of fully fluorinated compounds, the values obtained approximately 0.40—0.50% lower than that from calculation.

(2) Reaction temperature. At room temperature, Nd^{3+} reacts with F^- to form NdF_3 , with PO_4^{3-} to form NdPO_4 when pH=3—6 and 5—6 respectively. But the stability of the precipitates is so low that during titrating the excess of Nd^{3+} , xylenol orange and EDTA can substitute F^- and PO_4^{3-} from the precipitates and the determination fails. If precipitation reaction is carried out at 80—100°C, titrating reaction is stoichiometrical.

(3) Absorbent of fluoride and its acidity. Taking Nd^{3+} as absorbent it is possible to use a hard glass flask in place of quartz flask and raises absorption effect and sensitivity of titration. But it must be noticed that when pH>5, absorbent absorbs a large amount of CO_2 liberated from decomposed sample to form so much $\text{Nd}_2(\text{CO}_3)_3$ that the original amount of Nd^{3+} is not enough for precipitating all of F^- , so F^- corrodes glass and evolves on

* Only a part of nickel is transformed into Ni^{2+} .

Table 1 Analytical values of fluorine and phosphorus in polymers and organic compounds after decomposition

Samples	Theory F (%)	Found P (%)	Average error(%)
p-fluorobenzoic acid	13.56	13.41 13.38 13.60	-0.10
4-trifluoromethyl-1,3-phenylene diamine dihydrochloride	22.89	23.01 23.22 22.99	+0.18
β -(5-fluorouracil) propionic acid ethylester	8.26	8.50 8.45 8.56	+0.24
1,3-bis (2,2-diethoxyethyl)-5-fluorouracil	5.24	5.10 5.05 5.00	-0.19
Poly-N-(β -(1-(5-fluorouracil) propionyl) -ethylene imine	4.76	4.53 4.49 4.46	-0.27
Sodium perfluoro-butyrate	56.35	55.84 55.95 55.92	-0.45

Samples	Theory P (%)	Found P (%)	Average error(%)
Triphenyl phosphine	11.82	11.78 11.74 11.68	-0.09
Methylene bis (diphenyl phosphine)	16.13	16.24 16.33 16.20	+0.13
Propylene bis (diphenyl phosphine) + Na ₂ SO ₄ *	15.04	15.15 15.00 15.23	+0.09
Butylene bis (diphenyl phosphine) + Na ₂ SO ₄ *	14.53	14.40 14.35 14.54	-0.10
Poly-N,N-bis (β -chloroethyl)-O-((β -(N'-(N''-(N'''-(β -oxoethyl)-acetylimido)-uracil)-acetylimido))-ethyl)-phosphoamide	5.98	5.85 5.77 5.81	-0.17
Poly-N,N-bis (β -chloroethyl)-O-((β -(N'-(N''-(N'''-(β -oxopropyl)-acetylimido)-5-methyluracil)-acetylimido))-propyl)-phosphoamide	5.72	5.56 5.50 5.70	-0.10
Poly-O-ethyl-O-((β -(N'-(N''-(N'''-(β -oxopropyl)-acetylimido)-5-methyluracil)-acetylimido))-propyl)-phosphate ester	6.67	6.70 6.75 6.81	+0.08
π -cyclopentadienyl bis (triphenyl-phosphine) nickel tetradecahydrooundeca borate	7.94	7.95 7.85 7.79	-0.08
π -cyclopentadienyl ethylene bis (diphenyl-phosphine) nickel decahydrodeca-borate	10.67	10.79 10.85 10.87	+0.17

π -cyclopentadienyl trimethylene bis (diphenyl phosphine) nickel dodecahydrododeca-borate	10.20	10.25 10.02 11.99	-0.11
π -cyclopentadienyl tetramethylene bis (diphenyl-phosphine) nickel octahydrotriborate	10.50	10.60 10.45 10.40	-0.02

Samples	F (%)		Average error	P (%)		Average error
	Theory	Found		Theory	Found	
Poly-N,N-bis (β -chloroethyl)-O- ((β -(N'-(N''-(N'''-(β -oxoethyl)- acetylimido)-5-fluorouracil)- acetylimido))-ethyl)-phosphoamide	3.55	3.28 3.50 3.30	-0.19	5.78	6.00 5.97 5.88	+0.17
Poly-N,N-bis (β -chloroethyl)-O- ((β -(N'-(N''-(N'''-(β -oxopropyl)- acetylimido)-5-fluorouracil)- acetylimido))-propyl)-phosphoamide	3.37	3.40 3.19 3.45	-0.02	5.50	5.55 5.40 5.30	-0.08

* For introducing S.

heating; when $\text{pH} < 2.5$, the solubility of NdF_3 increases or precipitate disappears. The most appropriate acidity is $\text{pH} = 3$, in which the interference of CO_2 is small and the titrating reaction is stoichiometrical.

(4) Elimination of interference factors. SO_4^{2-} does not influence the determination of F^- unless its quantity is large. But SO_4^{2-} , as well as F^- , interfere the determination of PO_4^{3-} , F^- can be removed by adding concentrated nitric acid and evaporating to dryness, while the other by adding BaCl_2 and filtering BaSO_4 . Presence of excess of Ba^{2+} does not interfere the determination. During burning B-containing samples, a by-product, black B_4C is formed, so whether the sample has been completely mineralized is still a question. The author referred to previous work taking powder anhydrous sodium acetate as additive instead of $\text{Na}_2\text{SO}_4^{[19]}$ to avoid the formation of B_4C .

SUMMARY

A simple procedure is described for the quantitative determination of phosphorus, fluorine in polymers and organic compounds through the precipitation of NdPO_4 or/and NdF_3 and subsequent titration of excess Nd^{3+} with EDTA after decomposition in a hard glass oxygen flask.

Nd^{3+} solution serves as absorbing liquid for the determination of F^- or the total content of F^- and PO_4^{3-} .

Interferences of SO_4^{2-} , F^- in determining PO_4^{3-} are eliminated by adding BaCl_2 and filtering BaSO_4 , adding HNO_3 and concentrating solution to dryness, respectively. The error is $\pm 0.20\%$ for P, and $\pm 0.30\%$ for F except fully fluorinated compounds, which give values approximately 0.4–0.5% lower than calculation.

REFERENCES

- [1] Noshiro, M. and Yarita, T., *Jpn. Anal.*, **1977**, 26, 721–723.
- [2] Osadchii, V. D. and Maklakova, A. V., *Zavod. Lab.*, **1977**, 43 (3), 269.

- [3] Nara, A., Kobayashi, N., Hasegawa, K., Honba, K. and Baba, S., *Microchem. J.*, **1975**, *20*, 440.
- [4] Hozumi, K. and Akimoto, N., *Jpn. Anal.*, **1971**, *20*, 467.
- [5] Olson, E. C. and Shaw, S. R., *Microchem. J.*, **1961**, *5*, 101.
- [6] Lévy, R. and Debal, E., *Mikrochim. Acta*, **1962**, 224.
- [7] Friesse, H. J., *Mikrochim. Acta*, **1981**, *1*, 265.
- [8] 陈耀祖、杜棣华, 有机微量定量分析, 科学出版社, **1978**, 214.
- [9] Light, T. S. and Manion, R. F., *Anal. Chem.*, **1969**, *41* (1), 107.
- [10] 王昌益、和海青, 高分子通讯, **1980**, (5), 309.
- [11] Hassan, S. S. M., *Mikrochim. Acta*, **1974**, 889.
- [12] 刘惠英、何云陔、丁自荣、曾昭抡, 化学学报(增刊), **1981**, 153.
- [13] Tysganova, M. F. and Novikova, K. F., *Zh. Anal. Khim.*, **1969**, *24* (2), 272.
- [14] 云南省化工研究所有机微量分析小组, 分析化学, **1976**, *4*(6), 440.
- [15] Puschel, R. and Wittmann, H., *Mikrochim. Acta*, **1960**, 670.
- [16] Hunter, T. L., *Anal. Chim. Acta*, **1966**, *35*, 398.
- [17] Selig, W., *Z. Anal. Chem.*, **1969**, *247*, 294.
- [18] Bennewitz, R. and Tänzer, I., *Mikrochim. Acta*, **1959**, 835.
- [19] 谢正秋、赵明焕、段九菊, 高等学校化学学报, **1983**, *4*(5), 646.