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Abstract

High purity fluorapatite (FAP) was prepared by solid state reaction, in flowing argon gas, at 1370°C for 60 min. For chemical characterization of $Ca_{10}(PO_4)_6F_2$, the accuracy and reproducibility of different analytical methods were assessed. Methods with a good accuracy for the determination of Ca, P and F content were: titrations with EDTA for Ca determination (accuracy: −0.8%), spectrophotometric method for P determination (accuracy: +0.6%) and measurements with fluoride-selective electrode (accuracy ±5.4%) for F determination. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Fluorapatite; Preparation; Chemical characterization

1. Introduction

Synthetic fluorapatites are important materials for different applications like: preparation of phosphor for fluorescent lamps, laser host for neodymium, biocompatible materials. They are also used as humidity sensors, ion exchangers and dispersive additives for suspension polymer polymerization. For all these applications high purity fluorapatite is needed. This requirement can be assured by a well controlled preparation method and a sound and secure quality controlling of the final product. It is known that stoichiometric apatite powders with high crystallinity could be prepared by solid state reaction by heating a mixture of $Ca_3(PO_4)_2$ and CaF_2 of 1:3 molar ratio at temperatures between 1100 and 1370°C and the reaction times could be about 1 for 4 h [1,2]. There is no data in the literature for optimal heat treating procedure (heat treating temperature and heat treating time). On the other hand, for the quality controlling of these materials is important to identify the most adequate analytical methods for their chemical characterization. Different authors refer to different methods, but the various methods used for determination of Ca, P and F content differ in their accuracy and precision, which depends strongly on the nature of analyzed samples. The aim of present study is to demon-

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strate a solid state preparation method of good reproducibility and to compare, based on statistical calculations, the different analytical methods for each element, in terms of their accuracy and precision.

2. Experimental

2.1. Preparation

$Ca_{10}(PO_4)_6F_2$ (fluorapatite) was prepared by solid state reaction, by heating a stoichiometric (3:1 molar ratio) mixture of $Ca_3(PO_4)_2$ (Merck, 96.2% purity) and CaF_2 (Merck, 99.2% purity), in the presence of some CaF_2 upstream, to minimize volatilization of fluorine (as CaF_2) from the reaction mixture. Homogenization of raw materials was made using ethanol (abs. alcohol). The mixture of raw materials was heated at five different temperatures (1000, 1100, 1200, 1300, 1370°C) for two different heat treating times (30, 60 min). The furnace was first rinsed with H_2O- and CO_2-free Ar gas (99.998%) and than a flush rate of 20 l h^{-1} of Ar was maintained during the heat treatment. Water-free character of the heating atmosphere was checked by scrubbing the gas leaving the furnace in P_2O_5 and by detecting the mass increase (if any) after the heating period. Prevention of CO_2 contamination was done by flowing the Ar gas through a KOH trap. Mineralogical composition of the samples was determined with a Philips PW 1825 type X-ray diffractometer. For identification of samples the following designations were made: FAP, T (°C), t (min), where FAP is fluorapatite.

2.2. Chemical analyses

2.2.1. Determination of Ca content

The calcium content of samples was determined by two different methods: by ICP [3] and by EDTA-titration in the presence of Fluorexon indicator [4]. Stock solutions were prepared as follows: the samples (approx. 0.1 g) were dissolved in 10 ml 1:1 HNO_3 solution and than were diluted to 100 ml (for ICP) and to 500 ml (for EDTA titrations). The measurements were carried out at 317.993 nm, with an ARL 3410 MINITORCH type ICP.

Table 1
Ca% (wt) content of the samples determined by ICP method at 317.993 nm

Sample	Ca% (wt)
FAP,1100,60	39.0 ± 0.6
FAP,1200,60	39.1 ± 0.7
FAP,1370,60	38.3 ± 0.7
FAP,1370,30	38.7 ± 0.7

2.2.2. Determination of P content

Two different methods were used for the determinations: ICP [3] and spectrophotometric method [5]. ICP measurements were carried out at 213.618 nm, with an ARL 3410 MINITORCH type ICP. The reagents used for spectrophotometric determinations were as follows:

1. 0.25% NH_4VO_3 pur. spec. solution
2. 5% $(NH_4)_6Mo_7O_2 \cdot 4H_2O$ pur. spec. solution
3. 1:1 HNO_3 a.r. solution
4. 1 mg ml^{-1} KH_2PO_4 pur. spec. stock solution

The stock solutions were prepared as follows: the samples (approx. 0.07 g) were dissolved in 10 ml 1:1 HNO_3 solution and than the volume of solutions were adjusted to 200 ml. Measurements were done at 400 nm with a LAMBDA 20 UV/VIS, Perkin Elmer type spectrophotometer.

Table 2
Ca% (wt) content of the samples determined by EDTA titration in the presence of Fluorexon indicator

Sample	Ca% (wt)
FAP,1000,60	39.5 ± 0.4
FAP,1100,60	39.2 ± 0.7
FAP,1200,60	39.1 ± 0.4
FAP,1300,60	39.1 ± 0.4
FAP,1370,60	38.1 ± 0.4
FAP,1370,30	38.9 ± 0.7

Table 3
F-test for comparison between standard deviations of determinations of Ca, P content by two different methods

Samples	*F*-test for comparison between standard deviations of determinations of Ca content by ICP and EDTA titrations		*F*-test for comparison between standard deviations of determinations of P content by ICP and spectrophotometric method	
	F(95)	$F_{calculated}$	*F*(95)	$F_{calculated}$
FAP,1100,60	19.00	1.36	19.00	1.27
FAP,1200,60	19.00	3.06	19.00	1.30
FAP,1370,60	19.25	1.30	19.25	5.23
FAP,1370,30	19.00	1.00	19.00	1.27

2.2.3. Determination of F content

The methods used for fluoride determination were as follows:

1. Pyrohydrolytic method (distillation at 1000°C in the presence of Al_2O_3) [6]
2. Distillation with conc. H_2SO_4 (water vapor distillation at 165 ± 2°C) [7]. In both cases the fluoride content of the condensate was measured by thorium nitrate titration [8].
3. By ionchromatographic method [9]. The samples were dissolved in 4 ml 10% H_2SO_4 solution at 50°C. Ionchromatographic determinations were done with a DIONEX (DX 1000) ionchromatograph, using Na_2CO_3/$NaHCO_3$ eluent and AS9 column.
4. With fluoride selective electrode [10]. The samples (approx. 0.1 g) were dissolved in 10 ml 1:1 HNO_3 solution. The solutions were adjusted to pH = 5–6 using 1:1 NaOH solution, than 100 ml of TISAB was added and diluted to 500 ml.

According to some authors [11] the use of TISAB as buffer in fluoride determinations leads to an apparently lower result than by other methods. The use of citrate–hydrochloric acid buffer appears to avoid the fluoride loss that occurs with TISAB. The measurements were carried out using citrate–hydrochloric acid buffer too, but no differences were observed in the results. The pF values were obtained with the help of an OP-F-07 fluoride-selective electrode connected to a pH/ion Analyser OP-271 Radelkis. The reference electrode was a double-junction silver/silver chloride OP-0820P electrode (Radelkis).

3. Results and discussion

The following results were calculated based on 3–5 parallel measurements. The confidence intervals were determined considering a 95% confidence level and the convenient values of standard deviations and Student's *t*-test. The different analytical methods were compared based on *t*-test. The normal distribution of the results was supposed. Comparison of the standard deviations was done using *F*-test.

3.1. Ca determination

The theoretical value of calcium content was found to be 38.4% (wt), which value was calculated considering the purity of raw materials. Determination of Ca and P content of apatites by ICP is a routine method. The accuracy of this method is already mentioned in the literature to be ±1–3% both for the Ca and the P determination [3]. However, for evaluation of the method's reproducibility and comparison with other methods, parallel measurements were necessary (Table 1).

Using EDTA titration method for Ca determination was mentioned in the literature [12], but no data for accuracy were available. To estimate the accuracy of the method, determination of the Ca content of a standard sample was needed. Selection of the most relevant standard was troublesome. It was necessary to find a standard sample containing all the elements which were present in the analyzed samples and having the same dissolution properties in 1:1 HNO_3 solution. Because

Table 4
t-test for comparison between determinations of Ca, P content by two different methods

Samples	t-test for comparison between determinations of Ca content by ICP and EDTA titrations		t-test for comparison between determinations of P content by ICP and spectrophotmetric method	
	$t(95)$	$t_{calculated}$	$t(95)$	$t_{calculated}$
FAP,1100,60	2.776	0.931	2.776	2.501
FAP,1200,60	2.776	0.000	2.776	2.430
FAP,1370,60	2.447	0.884	2.447	0.000
FAP,1370,30	2.776	0.873	2.776	0.364

of the different dissolution properties, the stoichiometric mixture of the raw materials was ruled out. The same problem was faced also with $Ca_3(PO_4)_2$. In both cases the measured values of Ca and P contents were lower than the theoretical values. Based on the X-ray diffractograms of the samples prepared at different heating temperatures, unit cell parameters were calculated [13]. Unit cell parameters of sample FAP, 1000, 60 were found to be $a = 9.35 \pm 0.00296$ Å, $c = 6.86 \pm 0.00267$ Å, whereas those of the sample FAP, 1370, 60 were $a = 9.36 \pm 0.00243$ Å, $c = 6.87 \pm 0.0022$ Å, respectively. In Kanazawa's monography [1] $a = 9.36$–9.37 Å, $c = 6.87$–6.89 Å parameters were given. Relying upon these findings, the sample prepared by heating at 1370°C for 60 min had a composition which best approaches the stoichiometric composition of fluorapatite. This sample was used as a standard for different analytical methods. Dissolution properties of the standard sample were identical to those of the other samples.

Using the sample mentioned above as a standard, the accuracy of the Ca content determination by EDTA titration method were found to be -0.8% (Table 2), better than that of the ICP method. For a comparative evaluation of these two methods statistical calculations were done. Based on F-test was established that no differences among the standard deviations of the two methods, $F_{calculated} < F(95)$ (see Table 3). The results of t-test showed with an uncertainty at 95% confidence level that no differences among the average values of the two determinations, $t_{calculated} < t(95)$ (see Table 4). This results show that both of the methods (ICP and EDTA titration) are suitable for determination of Ca content if their accuracy is taken into consideration.

Table 5
P% (wt) content of the samples determined by spectrophotometric method at 400 nm

Sample	P% (wt)
FAP,1000,60	17.7 ± 0.8
FAP,1100,60	17.7 ± 0.9
FAP,1200,60	17.9 ± 0.8
FAP,1300,60	17.7 ± 0.9
FAP,1370,60	17.8 ± 0.8
FAP,1370,30	17.7 ± 0.9

3.2. P determination

The theoretical P content was found to be: 17.7% (wt). The accuracy of the spectrophotometric method was found to be $+0.6\%$ (Table 5), better than experienced with ICP, ± 1–3% (Table 6). Results of F-test and t-test showed no differences among the standard deviations and average values of P content determination by two different methods. Difference between the two methods was found only in their accuracy as compared to the standard sample.

Table 6
P% (wt) content of the samples determined by ICP at 213,618 nm

Sample	P% (wt)
FAP,1100,60	18.4 ± 0.8
FAP,1200,60	18.5 ± 0.7
FAP,1370,60	17.8 ± 0.7
FAP,1370,30	17.8 ± 0.8

Table 7
F% (wt) content of the samples determined with fluoride-selective electrode

Sample	F% (wt)
FAP,1000,60	3.6 ± 0.2
FAP,1100,60	3.4 ± 0.2
FAP,1200,60	3.5 ± 0.2
FAP,1300,60	3.4 ± 0.3
FAP,1370,60	3.5 ± 0.2
FAP,1370,30	3.4 ± 0.2

3.3. F determination

The analysis of fluoride is one of the most difficult in analytical chemistry. The experiments demonstrated a strong dependence between the applicability of the methods and the nature of the samples as well as the quality of sample preparation. The difference between the first two methods (i.e. pyrohydrolytic method and distillation with conc. H_2SO_4) were merely in the sample preparation. Fluoride content of the solutions was determinated by thorium nitrate titration. The results showed that neither of the methods is adequate for fluoride analysis, because the total fluoride content can not be extracted. The measured values were 45% (wt) less than the theoretical value 3.72% (wt).

3.3.1. F determination by ionchromatography

The precision of this method was satisfactory, but the accuracy was poor: −23%. This poor accuracy could be explained by the non-adequate sample preparation. The samples were dissolved in H_2SO_4 at 50°C, when a part of the fluoride content could be evaporated in the form of HF. Sample preparation by dissolution using an other acid (e.g. HNO_3) was not applicable because of the disturbing effect of NO_3^- ions for the fluoride determination in this method.

3.3.2. F determination with a fluoride-selective electrode

Accuracy of the method was found to be: ±5.4%. This method was of good precision but a moderate accuracy (Table 7). Nevertheless this latter method seems to be an acceptable compromise between precision and accuracy, especially in comparison with the formerly listed methods.

4. Conclusions

Fluorapatite with a composition (Ca:P:F = 10:6:1.9) which best approximates the theoretical stoichiometry (Ca:P:F = 10:6:2) was prepared by solid state reaction, heating a mixture of $Ca_3(PO_4)_2$ and CaF_2 of 3:1 molar ratio. Heating run was performed in flowing argon gas (20 l h^{-1}) with some CaF_2 upstream, at 1370°C for 60 min. Considering that this sample had the same unit cell parameters as the theoretic values, this one was selected for reference for Ca, P and F determination. Accuracy and precision of different analytical methods were determined. Methods with a good accuracy for the determination of Ca, P and F content were: titrations with EDTA for Ca (accuracy: −0.8%), spectrophotometric method for P (accuracy: +0.6%) and measurements with fluoride-selective electrode (accuracy: ±5.4%) for F determination. Statistical results (t-test) demonstrated that all of the presented analytical methods (ICP, EDTA titrations, spectrophotometric method) were suitable for determination of Ca and P content in fluorapatites provided their accuracy, as compared to a standard sample, is considered during evaluation of results.

References

[1] T. Kanazawa, Mater. Sci. Monogr. 52 (1989) 64.
[2] J.R. Lehr, E.H. Brown, A.W. Frazier, J.P. Smith, R.D. Thrasher, Crystallographic properties of fertilizer compounds, National Fertilizer Development Center, Alabama, 1967, p. 11.
[3] W.P. Rothwell, J.S. Waugh, J.P. Yesinowski, J. Am. Chem. Soc. 102 (1980) 2637.
[4] I. Sajó, Complexometry, Mûszaki Kiadó, Budapest, 1973, p. 194.
[5] Z. Marczenko, Spectrophotometric determination of elements, Halsted Press, Toronto, 1976, p. 424.
[6] P. Fodor, T. Tamás, Analytical Methods in Silicate Chemistry, Építésügyi Tájékoztatási Központ, Budapest, 1986, p. 37.
[7] Hungarian Patent, MSZ-13-158-1990.
[8] H. Monma, T. Kanazawa, Bull. Chem. Soc. Jpn. 49 (1976) 1421.
[9] Dionex Product Selection Guide, 1994–1995.
[10] D.J. Pietrzyk, C.W. Frank, Analytical Chemistry, Ed. Technica, Bucuresti, 1989, p. 533.
[11] E.J. Duff, J.L. Stuart, Anal. Chim. Acta 52 (1970) 155.
[12] D.R. Simpson, Am. Mineralogist 53 (1968) 432.
[13] A. Boultif, D. Louer, J. Appl. Cryst. 24 (1991) 987.