

Determination of Fluoride in Fertilizers by Means of the Ion-Selective Electrode

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Bestimmung von Fluorid in Düngemitteln mit Hilfe der Ionen-selektiven Elektrode

Zusammenfassung. Ein Verfahren wird beschrieben zur Bestimmung des säure- und wasserlöslichen Fluorids in einigen handelsüblichen Düngemitteln. Die gemahlene Probe wird mit Wasser oder Salzsäure verschiedener Konzentration gerührt, filtriert, mit Citrat als Komplexbildner versetzt und dann mit Hilfe einer Ionen-selektiven Elektrode gemessen. Bei den meisten Proben ergab sich, daß bei höherer Säurekonzentration (bis 1,0 M HCl) mehr Fluorid gefunden wurde, was dann dem Gesamtfluorid entsprach.

Die relative Standardabweichung lag im allgemeinen zwischen 0,5 und 1,5%. Die Wiederfindung an zugesetztem Fluorid lag zwischen 97 und 100%. Die Ergebnisse wurden mit den nach einer Referenzmethode erhaltenen verglichen, und es ergab sich eine gute Übereinstimmung.

Summary. A method is described for the determination of acid and water soluble fluoride in some commercial fertilizers. The ground samples are stirred with water or with hydrochloric acid of different concentrations, filtered, citrate added as complexing agent, and then measured with an ion-selective electrode. With most of the investigated samples it was seen that the more concentrated the acid (up to 1.00 M HCl) the more fluoride was found in the solution, and this was supposed to be the same as the total amount.

The relative standard deviation was usually between 0.5 and 1.5%. The recovery of added fluoride to some samples was between 97 and 100%. The results from this method were compared with the results from a reference method, and there was good correlation between them.

Introduction

In recent years there has been interest in determining fluoride in commercial fertilizers, both because it is an interesting analytical problem, and because it is useful to keep a certain control of the fluoride addition to the soil with fertilizers. AOAC [8] describes a procedure for the determination of fluoride in inorganic matrices as calcium phosphate. They recommend distillation from perchloric acid, followed by visual or potentiometric titration. We found this method very tedious, and we also wanted to avoid the use of perchloric acid.

Determinations of fluoride in vegetation and in soils have been described previously [5, 6]. We wanted to try a modification of these procedures for fertilizers. The methods described for fluoride determination in fertilizers and other inorganic matrices depend on whether it is the total or extractable fluoride which is to be determined. To measure soluble fluoride different diffusion techniques have been used [7, 12, 13, 14]. Some authors have determined the total amount by sintering with KNaCO_3 [2] or by decomposition with a high-frequency induction furnace or in a quartz tube [3, 10]. The determination of fluoride in egg shells by dissolving in 1 M HCl [4] has also been described. Larsen and Widdowson [11] have shown that the solubility of fluoride in rock phosphate increases with decreasing pH. But to the author's knowledge any comparative review of different extracting solutions has not been published. In this work a method for the determination of soluble fluoride in commercial fertilizers is developed. The method has been used for the determination of fluoride in samples extracted with various extracting solutions. In addition, the total amount was determined after fusion with NaOH [5, 6], and by a distillation/titration method proposed by AOAC and the Royal Society of Chemistry, Analytical Methods Committee [1, 8]. These measurements were performed at Norsk Hydro, Porsgrunn Fabrikker, Norway.

Experimental

Apparatus

Orion fluoride electrode (Model 90-01) filled with saturated potassium chloride solution. All measurements were made with Orion Model 901 microprocessor ionalyzer.

Reagents

All chemicals were of analytical grade. Water used for dilution was deionised.

Stock solution of fluoride, 1000 ppm. Sodium fluoride from C. B. Baker was dried, and 2.210 g was dissolved in water and diluted to 1000 ml. Standards of 1–5–10 ppm F^- were made by diluting this solution. The standards were diluted with blank solution to keep the ionic strength the same in both standards and samples. TISAB II buffer solution was made as described in Orion's manual [9] with the exception that CDTA was replaced by EDTA, and pH adjusted to 5.7. TISAB was added to all standards and samples, and usually

Table 1

Content of some elements in the various fertilizers used

Sample type	No. of samples	% P	% N	% K	% Ca	% S	% Cl
Calcium nitrate	1	—	16	—	19	—	—
PK fertilizer	2	6.8 5.0	— —	13 16	16 13	9—10	13 15
Complex fertilizer	A	6.0	14	16	2.6	2.7	12
	B	5.5	13	16	2.6	8.0	0.3
	C	6.6	16	12	3.0	1.6	11
	D	4.8	20	9.1	2.2	1.6	8
	E	2.7	18	15	1.8	2.8	11
NaCa phosphate	3	18	—	—	31	—	—
Potassium sulphate	1	—	—	42	0.6	18	1
Potassium chloride	1	—	—	50	—	—	47

contained 2 ppm F^- to be sure all measurements were higher than 1.00 ppm when mixed (1 + 1) with sample.

Citrate Buffer Solution. The solution contained 0.65 M trisodium citrate and 0.35 M citric acid. 10 ml of this solution was added per 100 ml sample. The samples were filtered through "Faltenfilter No. 595 $\frac{1}{2}$ " from Schleicher and Schüll.

Extracting Solutions. The samples were extracted with water, 0.01 M $CaCl_2$ and HCl solutions with concentrations of 0.01—0.1—1.0—2.0 and 4.0 M.

Total Fluoride. The samples were fused with NaOH in a muffle furnace, dissolved in hydrochloric acid, citrate added and measured after mixing with TISAB.

The Samples

Thirteen various fertilizers were investigated, i.e. NaCa phosphate (3 samples), calcium nitrate, potassium sulphate and -chloride, potassium phosphorous fertilizer (2 samples), and 5 complex fertilizers. A brief description of them is given in Table 1. In addition, one sample of rock phosphate was extracted with water, 0.01 M $CaCl_2$ and 1.0 M HCl. Two additional complex fertilizers and one calcium nitrate sample were also extracted with 1.0 M HCl and analysed according to a reference method.

Procedure

1. Weigh 1.000 g of ground sample into a suitable container.
 2. Add 50 ml of extracting solution and stir for 15 min with a magnetic stirrer.
 3. Filter through filter paper into a glass to which 25 ml 1.0 M citrate solution is added.
 4. Adjust the pH to about 5.7 with 10 M NaOH.
 5. Dilute to 250 ml with water and leave the solutions for at least 2 h before measuring.
 6. Calibrate the electrode against standards of 1.00 and 10.0 ppm F^- .
 7. Pipette 5 ml each of sample and TISAB II into a small container and stir while measuring.
- Prepare 3—4 blanks according to the given procedure.

Results and Discussion

The samples were extracted with the different extracting solutions, and measured against the corresponding standard solutions. The results are given in Table 2.

NaCa Phosphate. These samples contained very little water soluble fluoride. Also the $CaCl_2$ and dilute HCl extracts contained small amounts. When the concentration of HCl was 1.0 M or higher, however, almost all of the fluoride was extracted. The amount was found to be 0.13—0.25 % F. Some of the samples were found to contain a considerable less amount of total-fluoride than found in the extracts with 1.0 M HCl. This was probably due to loss of inorganic salts during the fusion.

Calcium Nitrate. About 20 % of the total amount of fluoride was water soluble. The more concentrated the HCl the more fluoride is extracted (up to 1.0 M HCl). The content was found to be about 0.09 % F. Extraction with 4.0 M acid showed a somewhat lower result, both for this sample and some others. One possible explanation could be that with such concentrated acid some fluoride was lost as volatile HF.

Potassium Sulphate and -Chloride. These samples contained very small amounts of fluoride. There was no difference between dilute or more concentrated extracting solutions.

P-K Fertilizers. About 30 % of the total amount of fluoride was water soluble. The more concentrated the acid the more fluoride was extracted (up to 1.0 M HCl). These samples contained about 1.4—1.9 % F.

Complex Fertilizers. Common for all five samples was that just a small amount of the fluoride was water soluble (14—23 % of the total). The maximum amount was extracted at an acid concentration between 0.1 and 1.0 M HCl. The total amount was about 1 % F.

Rock Phosphate. This sample contained more acid soluble fluoride than the other samples, about 3 % F, indicating that most of the fluoride originated from the rock phosphate. It contained a somewhat smaller amount of water and 0.01 M $CaCl_2$ soluble fluoride than the complex fertilizers.

Table 2. Extraction of samples with different extracting solutions, and total-fluoride

Sample	Measured fluoride concentration, % F in the sample								
	Water sol.	0.01 M CaCl ₂	0.01 M HCl	0.1 M HCl	1.0 M HCl	2.0 M HCl	4.0 M HCl	Total F ^a	
NaCa phosphate	0.004	<0.001	0.004	0.007	0.237	0.253	0.255	0.275	
	0.004	<0.001	0.004	0.004	0.128	0.129	0.124	0.125	
	0.004	<0.001	0.004	0.004	0.150	0.151	0.142	0.084	
Calcium nitrate	0.019	0.014	0.063	0.092	0.092	0.092	0.085	0.068	
Potassium sulphate	0.003	<0.001	0.002	0.002	0.002	0.002	0.002	0.002	
Potassium chloride	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	
PK fertilizer	0.607	0.563	0.840	1.41	1.86	1.74	1.69	1.65	
	0.427	0.370	0.580	1.30	1.37	1.35	1.32	1.40	
Complex fertilizer	A	0.231	0.120	0.430	1.18	1.27	1.24	1.17	1.18
	B	0.227	0.130	0.440	1.20	1.21	1.14	1.06	1.10
	C	0.229	0.130	0.410	1.13	1.13	1.01	0.920	0.890
	D	0.254	0.125	0.370	0.960	1.01	0.920	0.810	0.990
	E	0.117	0.073	0.380	0.770	0.800	0.790	0.610	0.540
Rock phosphate	0.021	0.010	—	—	3.12	—	—	—	

^a Determined after fusion with NaOH

Table 3. Comparison between 1.0 M HCl extractable fluoride and total fluoride^a

Sample	g F/100g (1.0 M HCl)	g F/100g (AOAC method)
Calcium nitrate	0.092	0.091
PK fertilizer	1.86	1.81
PK fertilizer	1.37	1.33
Complex fertilizer A	1.27	1.23
Complex fertilizer B	1.21	1.11
Complex fertilizer C	1.13	1.00
Complex fertilizer D	1.01	1.07
Complex fertilizer E	0.80	0.70
Rock phosphate	3.12	3.14
NaCa phosphate	0.15 (0.15) ^b	0.13
Complex fertilizer 13–13–21	1.36	1.37
Complex fertilizer 17–17–17	0.645	0.65
Calcium nitrate	0.20	0.18

^a Total fluoride is given as the amount found with the AOAC method [8]

^b F-value given from the producer

Comparison between this Method and a Distillation/Titration Method

As seen from Table 2 extraction with 1.0 M HCl gave the highest results, and was assumed to be the same as the total amount. To investigate whether this was true, some samples were also distilled according to the AOAC [8] and titrated according to the Analytical Methods Committee [1]. A comparison of the results is given in Table 3.

Using Student's *t*-test any significant difference was not found between the values from the AOAC method and the amount of fluoride extracted with 1.0 M HCl (confidence level 95%), indicating that extraction with 1.0 M HCl will give the total amount of fluoride in fertilizers.

Recovery

The accuracy of the method was investigated by studying the recovery of fluoride added to the samples before the extraction with 1.0 M HCl. Usually, the recovery was between 97 and 100%, and was never less than 94% for any of the samples investigated. This indicates a satisfactory accuracy. One of the samples also had a value certified from the producer, and this agreed very well with the value found in this work.

Precision

The method has been used as a routine method at this laboratory for some time. With a fluoride content of about 0.004% or higher the relative standard deviation was never higher than 5%. With fertilizers containing about 1% F the relative standard deviation usually was between 0.5 and 1.5%.

Conclusion

With most of the investigated samples extraction with 1.0 M HCl will give the highest results. The values are about the same as those found after fusion with alkali and subsequent dissolution in acid. This means that most (if not all) of the fluoride in fertilizers is soluble in 1.0 M HCl. The amount of water soluble fluoride was somewhat varying, from 3% of the total amount (NaCa phosphate) to about 30% (the P-K fertilizers). The rock phosphate contained only 0.7% water soluble fluoride. Some of the samples showed a lower total content than 1.0 M HCl soluble. This could probably be due to loss of inorganic fluoride during fusion. Extracting with 1.0 M HCl therefore seems to be a good and convenient way to determine the total amount of fluoride in commercial fertilizers. The comparison between the AOAC method for the determination total-fluoride, and extraction with 1.0 M HCl showed good correlation, also indicating that extraction with 1.0 M HCl gives the total amount of fluoride in the fertilizers.

References

1. Analytical Methods Committee (1972) *Analyst* 97:734
2. Bebeshko GI, Roze VP, Khalizova VA (1979) *J Anal Chem USSR* 34:388
3. Bettinelli M (1983) *Analyst* 108:404
4. Bird DM, Massari C (1983) *Environ Pollut Ser A* 31:67
5. Eyde B (1982) *Fresenius Z Anal Chem* 311:19
6. Eyde B (1983) *Fresenius Z Anal Chem* 316:299
7. Hall RJ (1968) *Analyst* 93:461
8. Horwitz W (ed) (1980) *Official methods of analysis of the Association of Analytical Chemists*, 13th edn. Assoc of Anal Chemists, Washington DC, p 392
9. Instruction manual for fluoride electrode (1977), model 94-09, Orion Research Inc, Cambridge, Mass.
10. Kirsten WJ (1976) *Anal Chem* 48:84
11. Larsen S, Widdowson AE (1971) *Soil Sci* 22:210
12. Stuart JL (1970) *Analyst* 95:1032
13. Wilkeyson JK (1975) *Anal Chem* 47:2053
14. Zimmermann RL, Bertrand HG (1978) *Anal Lett* A11 (7):569

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