Separation and determination of fluoride in plant samples

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Abstract

A simple and rapid separation method is described for the determination of fluoride in plant samples. Fluoride is separated by distillation in the presence of H_2SO_4 and H_2O_2 in a dry air stream. The variables that influence the distillation quantitation were optimized. The fluorides separated were subsequently determined by a spectrophotometric method of the $\text{La(III)}-\text{F}^-$ -alizarin complexone system. The precision of the procedure was significant, and the RSD was 3.7%. The accuracy of the method was statistically satisfactory, and the recovery was from 95.9 to 104.4%. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Fluoride; Separation; Distillation; Determination; Plant sample

1. Introduction

The effect of fluoride on human beings has a dual role as an essential trace element and at high levels as a toxic substance. Therefore, fluoride has received much attention with regard to medicine, pharmacy, public health and environmental protection. It is important and necessary to determine fluoride of plants because fluoride is known to affect various types of plants and, thus, both man and animals are susceptible to poisoning by fluoride-contaminated food or feedstuffs.

Fluoride determination can sometimes be carried out in the presence of matrix compounds and by adding, if necessary, a complexing agent. Generally, however, fluoride must be separated to avoid interference. The separation methods for plant samples are mainly distillation after mineralization in an alkaline medium [1,2], and diffusion, either with or without ashing [3,4]. The distillation is time-consuming and the volume of the distilled fraction is too large. Diffusion allows the separation of a large number of samples at the same time. However, it also takes a long time when only a few samples need to be handled.

In this paper, a simple and rapid method to separate fluoride from plant samples is developed.

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2. Experimental

2.1. Apparatus

A 721 spectrophotometer (Shanghai No.3 Analytical Instrument Factory) was used.

2.2. Reagents

NaF, H_2SO_4 , H_2O_2 , NaOH and HCl were all commercially available (made in China) and were used without any further purification except where it is stated. All reagents were puprapure or analytical pure grade. Deionized water was used throughout. Concentrated H_2SO_4 was heated till sulfur trioxide white smoke was produced in order to get rid of fluoride. The standard sodium fluoride solution was $1000 \mu\text{g ml}^{-1}$. A stock solution of the fluoride ion ($1000 \mu\text{g ml}^{-1}$) was prepared by dissolving 0.2210 g sodium fluoride, maintained under well-dried conditions, in 100 ml water and stored in a polyethylene bottle. The

working solution was prepared by suitable dilution of the stock solution with water.

2.3. Procedure

The plant samples were put into a round-bottom flask. The apparatus was installed as shown in Fig. 1. NaOH solution was added preliminarily into the gas-washing bottle in order to get rid of the fluoride in the air. NaOH solution was added in advance to the collector. Phenolphthalein was added as an indicator if determined by spectrophotometry. The operating process used the following steps: The tap to fill the separating funnel with water was turned on. Then the piston of the separating funnel was turned on to add water to the glass bottle so that the air was forced out. The air entered the round-bottom flask through the gas-washing bottle. Carrying with HF and SiF_4 , it arrived at the collector. H_2SO_4 was added by the sample-adding apparatus. Then H_2O_2 was dripped into the round-bottom flask by

Fig. 1. Separating apparatus: (A) separating funnel; (B) glass bottle; (C) three-way pipe; (D) gas-washing bottle; (E) sample-adding apparatus; (F) thermometer; (G) round-bottom flask; (H) oil bath; (I) collector.

Table 1
Results of collecting fractions of tea

Temperature ($^{\circ}\text{C}$)	Time (min)				Total value ($\mu\text{g g}^{-1}$)
	10	20	30	40	
150	108.6	17.5	7.0	— ^a	134.0
160	143.3	10.8	—	—	154.2
170	176.5	—	—	—	176.5
180	178.0	—	—	—	178.0

^a Nothing was detected.

Table 2

The precision of the method for mulberry leaf samples

Sample No.	1	2	3	4	5	6	7	8	9	10	$\bar{X}$	SD	RSD (%)
F found ($\mu\text{g g}^{-1}$)	31.2	28.5	30.5	32.5	29.8	30.1	30.9	29.5	32.0	31.5	30.7	1.1	3.7

Table 3

The recovery of the method for mulberry leaf samples

Sample No.	1	2	3	4	5	6	7	8	9	10
Mass (mg)	348.2	461.3	401.8	362.1	487.3	422.8	367.9	413.4	390.6	403.4
F found (μg)	12.1	12.5	11.3	11.9	12.7	12.9	11.8	11.4	12.6	12.4
F added (μg)	12.0	12.0	12.0	12.0	12.0	24.0	24.0	24.0	24.0	24.0
F found (μg)	23.6	24.3	23.8	24.0	24.6	36.8	36.0	35.2	36.9	36.1
Recovery (%)	95.9	98.4	104.4	100.8	99.2	99.2	101.7	98.2	102.4	97.6

the sample-adding apparatus. The temperature of the glycerin bath was controlled with an adjustable transformer. If the air was supplied by a pump and an electrothermal cap was used, the operation process was simpler and easier.

Dried plant samples (0.3–0.5 g) (such as tea leaves, tobacco leaves, and mulberry leaves) were placed into the distillation bottle and linked to every part as shown in Fig. 1. Concentrated H_2SO_4 (5 ml) was added at 110°C and 8 ml 30% H_2O_2 solution was added dropwise. The samples were distilled at 175 – 180°C for 10 min. Then the distillation was continued for 5 min after 2 ml 30% H_2O_2 was added dropwise. The flow rate of the carrier gas was 0.4 l min^{-1} . The Time to add concentrated H_2SO_4 and H_2O_2 was 10 min followed by distillation at 175 – 180°C for 15 min. Therefore, it took about 25–30 min to process a sample.

The effect of the separation was studied by a spectrophotometric method of the $\text{La(III)}-\text{F}^-$ –alizarin complexone system. The process was carried out according to Ref. [5].

3. Results and discussion

There were many factors affecting the separation. Here only the concentrations of H_2SO_4 and H_2O_2 , the heating temperature and time were studied. Other factors, such as the flow rate of the carrier gas, 0.4 l min^{-1} , the volume of the round-

bottom flask, 100 ml, the distance from the top of the tube to the bottom of the flask, 0.5 cm, were kept constant.

3.1. Effect of H_2SO_4 concentration

Under the conditions of the addition of 10 ml 30% H_2O_2 , and heating for 20 min at 180°C , for 0.3–0.5 g dried tea samples, no effect was seen on the separation when the volume of concentrated H_2SO_4 was from 3 to 6 ml. However, when the volume of concentrated H_2SO_4 was less than 5 ml, white precipitation was produced in the digested solution. If the volume of concentrated H_2SO_4 was 5 ml or more, then no white precipitation was produced and the digested solution was clear. The white precipitation may be CaSO_4 . When the volume of concentrated H_2SO_4 was more than 5 ml, the precipitation could be turned into soluble $\text{Ca}(\text{HSO}_4)_2$. Consequently, 5 ml concentrated H_2SO_4 was chosen. It was noted that less acid fog was produced if the drop rate of H_2SO_4 to H_2O_2 was controlled properly.

3.2. Effect of H_2O_2 concentration

Under the conditions of the addition of 5 ml concentrated H_2SO_4 , and heating for 20 min at 180°C , for 0.3–0.5 g dried tea samples, the effect of separation was almost constant when the volume of 30% H_2O_2 was more than 8 ml. If the differences

Table 4
Results of the determination of fluorine in tea leaves

Sample No.	Fuding					Mingshan 23						
	1	2	3	4	5	Mean	1	2	3	4	5	Mean
Tender leaves ($\mu\text{g g}^{-1}$)	282.3	302.5	312.7	316.7	269.8	297.0	235.6	219.1	198.9	222.6	197.6	214.8
Older leaves ($\mu\text{g g}^{-1}$)	986.7	998.3	1021.1	1044.5	976.6	1005.4	943.5	911.3	893.0	927.2	889.2	912.8

in plant samples were considered, the volume of 30% H_2O_2 in later experiments should be 10 ml to ensure complete digestion. Furthermore, surplus H_2O_2 decomposed to H_2O and O_2 , which had no effect on the determination of fluoride. So H_2O_2 could be added in excess.

3.3. Effect of temperature and time

Under the conditions of the addition of 5 ml concentrated H_2SO_4 and 10 ml 30% H_2O_2 , for 0.3–0.5 g dried samples, the results for the collected fraction of tea are shown in Table 1. From the data in Table 1, it can be seen that the separation was complete when heated for 10 min at 170°C considering the difference between the parallel samples. Therefore, the heating temperature was controlled at 175–180°C. Considering the diluting effect of collecting at different sections, the heating time should be 10–15 min.

3.4. Blank and absorption

The blank value was found to be almost zero by doing five experiments. Additionally, the second-order water absorption experiment was carried out using 95 $\mu\text{g F}^-$ (five times). That is, two gas-washing bottles were used in tandem and the second bottle absorbed the gas from the first bottle. There was no fluoride detected in the second bottle. Thus, it could be seen that the fluoride compounds can be absorbed completely by first-order water absorption. Because there was little H_2SO_4 acid fog produced in the experiment, the absorption solution containing NaOH was used.

3.5. Precision of the method

Under the above optimum conditions, for 0.3–0.5 g mulberry leaves, the precision of the method was determined and the results are shown in Table 2. The RSD was 3.7%.

3.6. Recovery

The recovery of the method was determined with mulberry leaf samples and the results are shown in Table 3. The recovery was 95.9–104.4%.

3.7. Determination of fluorine in tea leaf

Two kinds of tea leaves produced from two location were processed by the separation method developed. The fluorides separated were determined by spectrophotometry. One sample was of older leaves and tender leaves of Fuding Tea produced on the purple soil of Zheyin Mountain. The other sample was tea from Mingshan 23 produced on the yellow soil of Mingshan county. The tea leaves sample was a gift from Professor Yao in the Department of Chemistry in Sichuan Normal University. The results are shown in Table 4.

The ratio of fluorine in older and tender leaves of Fuding was 3.4:1, and that of Mingshan 4.2:1. The difference in fluorine between the older and tender leaves among the different soils, locations and types was large. Furthermore, fluorine was higher in the older leaves than in the tender because of enrichment of the leaves from the fluorine in the air.

Tea is a popular drink in China. The above results suggest that tea made from the tender leaves should be taken in areas containing high fluorine, and should be drunk less, to prevent chronic poisoning owing to the surplus fluorine absorbed. In areas of low fluorine, tea made of the older leaves, which contain more fluorine, should be taken, thus removing the need to add fluorine to the water to prevent disease from lack of fluorine.

4. Conclusions

A simple and rapid method to separate the fluoride from plant samples has been established. It combines wet digestion (H_2SO_4 and H_2O_2 were used) with distillation using air as the carrier gas. The volume of collected liquid is several millilitres. The procedure to handle a sample takes only 25–30 min. The proposed method is simpler and more rapid than distillation after mineralization in an alkaline medium. Diffusion allows separation of a large number of samples at the same time. However, the proposed method is more

rapid than diffusion when only a few samples need to be handled. That is, diffusion is adopted when a lot of samples need to be handled and the proposed method is adopted when only a few samples need to be handled.

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