

Exploration and Application of Ion Selective Electrode Method for the Determination of Fluoride in Soil

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Abstract

The water-soluble fluoride in soil samples was determined by ion-selective electrode method, and good results were obtained. The detection limit was 0.314 mg/kg and the lower limit was 1.26 mg/kg. The relative standard deviation (n=7) between 3.82% and 6.28%, and the relative error (n=7) between 1.6% and 5.8% were obtained by the precision and accuracy analysis of standard materials (GBW07412a, GBW07414a, GBW07459). The test results show that the relative standard deviation and relative error of the test sample are within the allowable range.

Keywords

Ion selective electrode method, Soil, Water soluble fluoride.

1. Introduction

Fluoride in the soil is an important source of fluoride in water and food, which can affect human health through drinking water, precipitation and dusting[1]. The presence of fluorine in soil is extremely complex, and water-soluble fluorine is highly effective for plants, animals, microorganisms and humans[2], and is listed as one of the important control indicators of soil inorganic pollutants by the Ministry of Environmental Protection[3]. At present, pretreatment methods for soil water-soluble fluorides include oscillation, ultrasonic, hot water bath and distillation. The detection methods include fluorine reagent colorimetry, fluoride ion selective electrode method, ion chromatography, etc.[4-6], and there is no uniform National standard method. The pretreatment temperature of hot water bath and distillation method is very high, and there is a big difference between the water-soluble fluorine leaching conditions under natural environment, and the interference factors of fluorine reagent colorimetry and ion chromatography are more. Therefore, it is preferred to select ultrasonic, oscillating leaching for pre-treatment, fluoride ion selective electrode method, using different quality levels of soil certified standard samples for accuracy and precision testing, to determine the optimal pretreatment conditions and instrumental analysis conditions, The method of ultrasonic leaching-ion selective electrode method for determining water-soluble fluorine in soil has good applicability.

2. Experimental Part

2.1 Drugs and instruments

drug: Trisodium citrate, hydrochloric acid, fluorine standard solution (1000 μg / mL).

Instruments: ion meter, centrifuge, ultrasonic cleaner, fluoride ion composite electrode.

2.2 Experimental methods

Accurately weigh 5.00 g of soil sample in a polyethylene bottle, add 50.0 mL of deionized water, cover, ultrasonically extract for 30 min, let stand, take the supernatant in a polyethylene centrifuge

tube, centrifuge for 5~10 min (speed 4000r /min), to be tested. A blank experiment was performed along with the sample. Transfer 0.00 mL, 0.10 mL, 0.20 mL, 0.40 mL, 1.00 mL, 2.00 mL, 4.00 mL of fluorine standard solution (50 $\mu\text{g/mL}$) to a 50 mL volumetric flask, and add 10.0 mL of total ionic strength adjustment buffer solution to water. Dilute to the mark and mix. The standard series solution was transferred from a low concentration to a high concentration in a polyethylene beaker, inserted into the electrode, stirred, and the curve was calibrated with an ion meter. Accurately remove 10.0 mL of the sample supernatant into a 50 mL volumetric flask, add 10.0 mL of total ionic strength adjustment buffer solution, dilute to the mark with water, and mix to determine the water-soluble fluoride in the sample. The blank sample was measured in the same manner as the sample measurement.

Curve equation: $f(x) = 57.904x - 343.72$, correlation coefficient $r = 0.9991$

3. Results and Discussion

3.1 Method detection limit and lower limit of measurement

Table 1 Detection limit, lower limit verification data record

Numbering	Measured value (mg/kg)
Sample 1	2.50
Sample 2	2.40
Sample 3	2.35
Sample 4	2.60
Sample 5	2.35
Sample 6	2.55
Sample 7	2.40
Average value (mg/kg)	2.45
Standard deviation S (mg/kg)	0.100
t	3.143
Detection limit (mg/kg)	0.314
Lower limit of determination (mg/kg)	1.26

From Table 1, the detection limit was 0.314 mg/kg, and the lower limit of the method was 1.26 mg/kg.

3.2 Method precision and accuracy

Table 2 Tested Reference Material/Standard Sample Test Data

Parallel sample number		Certified reference material/standard sample		
		ASA-1a (GBW07412a)	ASA-3a (GBW07414a)	ASA-8 (GBW07459)
The measurement results (mg/kg)	1	5.40	5.24	9.99
	2	4.95	5.34	11.64
	3	5.14	5.55	10.79
	4	5.35	5.49	10.25
	5	5.24	4.94	11.34

	6	5.34	5.25	11.83
	7	5.65	5.20	10.94
Average value (mg/kg)		5.30	5.29	10.97
Certified reference material/standard concentration (mg/kg)		5.1±0.6	5.0±0.6	10.8±1.3
Relative error(%)		3.9	5.8	1.6
standard deviation		0.22	0.20	0.69
RSD/%		4.12	3.82	6.28

The precision and accuracy analysis of the standard materials (GBW07412a, GBW07414a, GBW07459) were applied in this method for 7 times, and the corresponding relative standard deviation (RSD) was calculated. The relative standard deviation of the measured values (n=6) Between 3.82 and 6.28%, the relative error of the measured values (n=7) is between 1.6 and 5.8%. The test results show that the relative standard deviation and relative error of the test samples are within the allowable range. The results are shown in Table 2.

3.3 Exploration and discussion

1. When the sample is ultrasonically extracted, the water temperature rises. At this time, the circulating water can be used to cool the leaching temperature at 25 ± 2 °C.
2. If the sample composition is more complicated, the supernatant is not clear enough after centrifugation for 5~10 min (speed: 4000r/min). At this time, the centrifugation time (10min) and the increase of the rotational speed (8000r/min) can be appropriately extended. The sample was uniform and stable.
3. After measuring the sample with high fluorine content, the fluorine electrode should be rinsed with deionized water until the measured potential value is close to the potential value of the blank solution. After the memory effect is eliminated, the next sample can not be measured.
4. The linearity of the working curve requires a correlation coefficient of 0.999 or more, and the slope of the curve is 58.0 ± 2 . The intensity of the sample detection must be within the calibration curve.

4. Summary

The sample was extracted by pure water at room temperature (40 kHz), and the ion-selective electrode method for the determination of water-soluble fluorine in soil has good applicability. The method has good linearity in the range of 5.00~200μg of fluorine, and the detection limit is 0.314 mg /kg. The RSD of soil water-soluble fluorine parallel test results is 3.82~ 6.28%, and the fluorine mass ratio is 5.0~10.8 mg /kg. The test results of the soil certified standard samples were all qualified, and the RE was 1.6~5.8%. It can be seen that the ion-selective electrode method for the determination of water-soluble fluorine in soil has a wide linear range, less interference factors, good reproducibility, high accuracy, easy operation, easy to obtain equipment, and low chemical reagent usage. Etc.

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