Determination and Analysis of Fluorine Ion in Surface Water by Ion Chromatography

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Abstract. Determination of fluorine ion in surface water by ion chromatography is simple and rapid. It can well reflect the change of fluorine ion concentration in a certain period of time. In this experiment, the seven rivers of Jingbian, Qingping, White Tower, Sailong, Quanmin Reservoir Dam, Hulu Island and Lingyun Bridge in Guang’an City were monitored for four months. The results showed that from the perspective of watershed and river flow, due to the enrichment of fluorine ions in the downstream reaches, the fluorine ion concentration of the Lingyun Bridge is higher than that of other rivers, but they are all within the limits of 1mg/L which meets national standards of surface water (GB 3838-2002). From the time distribution, the maximum of $F^-$ average concentration of the seven rivers appeared in December, which may be due to the concentration of rainfall in October and November in Guang’an. To a certain extent, it has a certain dilution effect on fluorine ion concentration.

1. Introduction
When the fluoride in the environment exceeds a certain concentration, it will affect the organism. The migration of fluorine in the water will mainly affect the organisms and soil in the runoff area. According to the relevant statistics, there are as many as 1306 counties (cities) that have prevalence of fluorosis in China. Drinking water fluorosis is the most important type of fluorosis in China, and the number of patients is also the most. According to a national survey published in 1990, about 7.9 percent of the population had fluoride in drinking water exceeding the national drinking water standard of 1.0mg/L. The number of patients with dental fluorosis and skeletal fluorosis was about 26.94 million and about 1.035 million, respectively [1, 2]. It can be seen that the impact of pollution of fluoride in water on human health is quite common and quite serious. It should be brought to the attention of the society and prevented actively and effectively.

At present, methods for measuring fluorine in water mainly include ion chromatography, fluorine ion selective electrode, polarography, high performance liquid chromatography and so on. Among them, ion chromatography has great advantages in the determination of anions: multi-component simultaneous determination; fast detection speed; good selectivity; less sample dosage and so on. Currently, ion chromatography is determined as the standard method for ion detection by many standards organizations, including the International Organization for Standardization (ISO), the
American Society for Testing and Materials (ASTM), the American Water works Association (AWWA), and the Chinese Drinking Water Hygiene Standard [3-5]. In this experiment, the concentration of fluorine ion in surface water was determined by ion chromatography, and the fluoride pollution in several major rivers in Guang'an City was investigated.

2. Materials and Methods

2.1. Instruments and Reagents
ICS 1100 ion chromatography (with conductivity detector); chromatographic column (anion separation column and anion protection column); micromembrane suppressor; recorder; eluent; regeneration liquid storage tank; microporous filter; microinjector; vacuum filter.

KOH, Na₂CO₃, NaHCO₃, F⁻ standard solution of 1mg/ml (all analytically pure); adsorption resin (50-100 mesh); cation exchange resin (100-200 mesh); The reagent water is secondary deionized water having a conductivity of less than 0.5 us/cm and filtered through a 0.45 um microporous membrane.

2.2. Chromatographic Conditions
AS11-HC column; mobile phase was Na₂CO₃(0.0024mol/L)-NaHCO₃(0.0030mol/L) (flow rate 1.5ml/min); injection volume was 200ul; suppressor was ASRS 4mm; suppressor current was 90mA.

2.3. Sample Collection and Preservation

2.3.1. Sample Collection.
Sample collection was performed in accordance with the relevant regulations of HJ 494, HJ/T 91 and HJ/T 164. For a relatively stable water body, or a component of a water body does not change much over a relatively long period of time and a considerable spatial extent, the acquisition of transient samples is well represented [6, 7]. Therefore, the instantaneous sampling method is applied to the sampling of the fixed river in Guang'an city.

2.3.2. Preservation of Samples.
The collection of water samples was stored in polyethylene plastic bottles and kept in a dark place. Surface water contains a lot of organic matter and heavy metal ions, which will cause great damage to chromatographic column after flowing through chromatographic column and affect the experimental process and results. Therefore, pretreatment of water samples is very necessary [8, 9].

Pretreatment is a treatment column composed of an adsorption resin and a cation exchange resin. The adsorption resin is in the upper layer, while the cationic resin is on the lower layer. Samples were collected after washing with deionized water, filtered through 0.45um microporous membrane, and finally analyzed with microinjector.

2.4. Drawing of Fluorine Ion Standard Curve
A series of standards of 0.5 mg/L, 1 mg/L, 2 mg/L, 5 mg/L, 10 mg/L, and 20 mg/L were prepared using standard solution of fluorine ion. The peak height was determined according to the established chromatographic conditions, and each standard sample was manually injected twice with a micro syringe. Regression equation of calibration curve was calculated by least square method with peak height as ordinate and fluorine ion concentration as abscissa [10, 11]. The standard curve is shown in Figure 1.
3. Results and Analysis

3.1. Sample Determination

Seven fixed rivers of Liemian, Qingping, White Tower, Sailong, National Reservoir Dam, Hulu Island and Lingyun Bridge in Guang'an city were monitored for four months from September to December in 2017. And the concentration of fluorine ion in these four months was determined. The results are shown in Table 1.

| Point position     | Fluorine ion concentration(mg/L) |
|--------------------|----------------------------------|
|                    | Sep     | Oct    | Nov    | Dec    |
| Liemian            | 0.188   | 0.190  | 0.224  | 0.240  |
| Qingping           | 0.170   | 0.130  | 0.137  | 0.253  |
| White Tower        | 0.210   | 0.110  | 0.112  | 0.165  |
| Sailong            | 0.183   | 0.120  | 0.130  | 0.226  |
| National Reservoir Dam | 0.280  | 0.182  | 0.184  | 0.303  |
| Hulu Island        | 0.282   | 0.203  | 0.212  | 0.307  |
| Lingyun Bridge     | 0.533   | 0.221  | 0.230  | 0.676  |

The data from Table 1 show that the content of fluorine ion in the above-mentioned rivers is lower than that in the national standard "Groundwater Quality Standard (GB/T 14848-93)", and all meet the standard limit of fluorine ion concentration (1mg/L) [12]. The above data is drawn into a diagram, and the result is shown in Figure 1.
It can be seen from Fig. 2, the change trend of fluorine ion concentration in the seven rivers from September to December is basically the same. Because Liemian and Qingping belong to the Jialing River basin, and the flow direction of the river is from Qingping to Limian, the concentration of fluorine ion is higher than that of Qingping. Because White Tower and Sailong belong to the Qujiang River basin, and the flow direction of the river is from the White Tower to Sailong, the concentration of fluorine ion is higher than that of the White Tower. Because the National Reservoir Dam, Hulu Island and Lingyun Bridge belong to the Xixi River Basin, and the flow direction of the river is from the National Reservoir Dam to Hulu Island to Lingyun Bridge, the fluorine ion concentration increases in turn.

3.2. Horizontal Comparison

By arranging the fluorine ion concentrations monitored by the seven rivers from September to December, the average concentration of these four months can be calculated, as shown in Table 2.

| Section               | Average concentration of fluorine ion (mg/L) |
|-----------------------|---------------------------------------------|
| Liemian               | 0.210                                       |
| Qingping              | 0.172                                       |
| White Tower           | 0.149                                       |
| Sailong               | 0.165                                       |
| National Reservoir Dam| 0.237                                       |
| Hulu Island           | 0.251                                       |
| Lingyun Bridge        | 0.415                                       |

From Table 2, it can be seen that from the perspective of watershed and river flow, the maximum concentration of fluorine ion in the seven rivers is 0.415 mg/L for Lingyun Bridge, and the minimum is 0.149 mg/L for White tower. The maximum concentration difference between rivers is 0.226 mg/L. The main reason may be that Lingyun Bridge belongs to the downstream section of Xixi River Basin, and there are many tributaries in this basin. Fluorine ions are enriched in the downstream reaches, which result in the concentration of Lingyun Bridge is higher than that of other rivers.
3.3. Vertical comparison

After the monthly measurement of the above-mentioned rivers in real time, the average concentration of the seven rivers in each month was calculated, and the average concentration of fluorine ions in the fixed rivers from September to December was obtained. The results are shown in Table 3.

| Months     | Average concentration of fluorine ion (mg/L) |
|------------|---------------------------------------------|
| September  | 0.264                                       |
| October    | 0.165                                       |
| November   | 0.176                                       |
| December   | 0.310                                       |

From Table 3, it can be seen that from the time distribution, the average concentration of fluorine ion of the seven rivers appears in December, and the smallest is in October. The difference between them is 0.145 mg/L. This may be due to the fact that the rainfall in Guang'an City is relatively concentrated in October and November. To a certain extent, there is a certain dilution effect on the fluorine ion concentration. Therefore, the concentration is lower than that in September and December.

4. Conclusion

According to the national standard of groundwater quality (GB/T 14848-93), the monitoring of fixed rivers in Guang'an city from September to December found that the concentration of fluorine ions was below the limit of standard concentration (1mg/L);

From the river basin and flow direction, fluorine ion concentration increased in turn from the National Reservoir Dam to Hulu Island to Lingyun Bridge. The results show that fluorine ions are continuously enriched with the flow of rivers, and the concentration is increased. Therefore, it is necessary to increase the monitoring of the downstream river sections;

From the time distribution analysis, the rainfall in Guang'an City is more concentrated in October and November. Therefore, to a certain extent, there is a certain dilution effect on the fluorine ion concentration, and the concentration is lower than that in September and December.

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