Measurement and Evaluation of Residual Disinfection by Products in Tap Water from Xiamen

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Abstract. This paper has tested typical anions including F⁻, Cl⁻, NO₃⁻, BrO₃⁻, ClO₃⁻, SO₄²⁻ in tap water from Xiamen in order to understand the residual status of disinfection byproducts. Ion chromatography is used to analyze anionsconcentrations from residential and industrial zones in six Districts of Xiamen. The results demonstrate that: (1)BrO₃⁻ is not detected in all samples, (2) NO₃⁻ and SO₄²⁻ exceed 4.046mg/L and 2.223mg/L, the peakconcentrations are 14.342mg/L and 39.345mg/L, respectively, (3) NO₃⁻ and SO₄²⁻ are quite high in Haicang, Siming and Huli districts, which exceed 14.031mg/L and 36.708mg/L, respectively, (4) Smallerresidual disinfection byproducts are found in the tap water near the industrial areas of Jimei, Tongan and Xiangan Districts compared to other districts, all criteria meet the national standard, which means water quality is in a good condition in these three areas.

1. Introduction
According to the WHO survey: 50% of the world's children’s death, and 80% of the disease is more or less related to the quality of tap water[1]. Therefore, it is self-evident to control the effluent quality of tap water. Typically, most of the anions in tap water are closely related to physical health, including fluoride ion, chloride ion, bromate, nitrate, sulfate and hypochlorite ion[2]. These ions are also the routine hygienic indexes of drinking water[3]. The main water source in Xiamen is JiuLong River water[4], and the water quality of primary water supply, secondary water supply, and tap water near the industrial areas in six districts are mainly analyzed in this paper.

2. Materials and Methods

2.1. Instruments and Reagents

2.1.1. Instrument Ion chromatograph (metrohm 883), analytical balance, pipette, ultra pure water machine, suction machine.

2.1.2. Main Reagent Sodium chloride (analytical purity), sodium nitrate (analytical purity), sodium bromate (analytical purity), sodium fluoride (analytical purity), sodium sulfate (analytical purity), sodium hypochlorite (analytical purity), sulfuric acid, sodium carbonate, sodium bicarbonate, 0.22 M filter membrane.

2.2. Methodology
2.2.1. Ion chromatography Chromatographic conditions[5-7]: Swiss Wantong type 883 chromatograph, chromatographic column is Metrosep ASUPP 5150 anion chromatographic column, eluent 3.2mmol/L Na₂CO₃+1mmol/L NaHCO₃, 1mL/min flow rate, 27 degrees column temperature, 20 L injection volume.

2.2.2. Sampling point distribution principle According to the characteristics of six districts in Xiamen, the principle of random sampling was adopted to ensure that sampling points should have a certain representation and could reflect the water quality of the region. The distribution of sampling point can be shown in Figure 1.

Figure 1. Water Sampling

Primary water supply sample, secondary water supply sample, and tap water sample near the industrial areas were collected in six districts. Primary water supply sample was collected in the residential areas(50% of the whole). In Siming and Huli Districts, the software parks or various office buildings were considered as the water sample points of the Industrial areas, while the water samples from the center of the entire industrial areas are the figure of the rest of the industrial areas from the other four districts. The secondary water supply was defined as centralized water supply mode, which must be stored again before entering the household, and then with pressure and disinfection or advanced treatment, transferring water into the users’ residence through pipes or containers[8].

2.2.3. Establishment of standard curve Standard solution preparation: accurately weighting NaCl, NaNO₃, NaBrO₃, NaF, Na₂SO₄ and NaClO each 1g in 6 dry beakers, placed in dryer drying 2h. Took out the beaker and cooled it. Dissolved in ultrapure water, then moved into 1000mL capacity bottle, diluted to the capacity bottle mark, shook well. The concentration of the reserve solution of the anion was 1g/L, and the solution was the reserve one. The standard solution of six anions was diluted from the stock solution.

Linear equation: Linear regression was carried out for six different anionic standard solutions. After the ion chromatography conditions were selected. Taking the concentration as abscissa, the peak area
as ordinate， drew the linear regression equation of different anions.

3. Results and Analysis

3.1 Result and deviation of standard curve
When the eluent concentration was 3.2mmol/LNa$_2$CO$_3$+1mmol/LNaHCO$_3$，the flow rate was 1mL/min, the column temperature of the Swiss Wantong type 883 ion chromatography was generally set to 27°C，and the injection volume was generally set to 20 L. The linear equation and correlation coefficient are shown in Table 1.

Table 1. Six anionic linear regression equation

| anion   | Range/ (mg/L) | linear equation | correlation coefficient/ R |
|---------|---------------|-----------------|---------------------------|
| F       | 0.01-0.5      | y=4.7741x-0.0403 | 0.9995                    |
| BrO$_3^-$ | 0.5-1.5      | y=0.5364x-0.253  | 0.9998                    |
| ClO$_2^-$ | 0.1-2        | y=3.7678x-0.2414 | 0.9997                    |
| Cl$^-$  | 0.1-5         | y=0.1164x+0.0062 | 0.9999                    |
| NO$_3^-$ | 0.25-10       | y=0.0709x-0.0039 | 0.9999                    |
| SO$_4^{2-}$ | 0.2-16       | y=0.0629x+0.0968 | 0.9997                    |

Table 2. The detection limit of six anions

| anion   | detection limit / (mg/L) |
|---------|--------------------------|
| F       | 0.001                    |
| BrO$_3^-$ | 0.002                  |
| ClO$_2^-$ | 0.004                  |
| Cl$^-$  | 0.001                    |
| NO$_3^-$ | 0.002                  |
| SO$_4^{2-}$ | 0.001                 |

Different concentrations of anions were analyzed in the same chromatographic conditions. It was not difficult to observe the test results through the standard curve of Table 1 and various anions: F$^-$ at 0.01-0.5mg/L, BrO$_3^-$ at 0.5-1.5mg/L, ClO$_2^-$ at 0.1-2mg/L, Cl$^-$ at 0.1-5mg/L, NO$_3^-$ at 0.25-10mg/L, SO$_4^{2-}$ had a good linear relationship in the range of 0.2-16mg/L. The correlation coefficients of each ion were 0.9995-0.9999.

Detection limit: the concentration of the standard solution was close to the blank value. Injected the solution continuously for 10 times, the detection limit, was the standard deviation of 3 times response value. The results are shown in Table 2.

The experimental results showed that the detection limit of the anion was nearly 10 times lower than that of the national drinking water standard (GB/T5750.5-2006) [9].

Accuracy: the 1.00mg/L standard mixture solution was used to calculate the relative standard deviation of anions. The final results are shown in Table 3.

Table 3. Accuracy

| anion   | Measured value (mg/L) | relative standard deviation / (%) |
|---------|------------------------|----------------------------------|
| F       | 1.032 1.025 1.013 1.025 1.003 1.007 1.032 1.026 | 1.10 |
| BrO$_3^-$ | 0.994 1.011 0.998 1.012 1.015 1.027 1.012 1.015 | 1.02 |
| ClO$_2^-$ | 0.998 0.987 1.005 1.028 1.032 1.011 1.013 1.002 | 1.49 |
| Cl$^-$  | 1.026 0.987 0.998 1.003 1.015 1.036 1.019 1.021 | 1.58 |
| NO$_3^-$ | 1.024 1.008 1.036 1.003 1.027 1.002 1.024 1.015 | 1.21 |
Through the table above, it was found that the method which was used in this paper met the requirements of drinking water according to GB/T 5750.5-2006.

### 3.2. Overview of residual disinfection byproducts in tap water

After the pretreatment of collected eighteen samples, making use of suction filtration with 0.22μm membrane to filter the water. The filtrationsamples were analyzed by ion chromatography and the anions concentrations were determined by the peak height, peak area and peak time of the six anions. The analysis results are shown in Table 4.

| Table 4. Water sample |
|-----------------------|
| **region** | **Ion concentration / (mg/L)** |
| | F− | BrO3− | ClO− | Cl− | NO3− | SO4²⁻ |
| Water supply samples of Jimei Industrial Zone | 0.01 | Below detection limit | 0.34 | 0.06 | 5.936 | 5.826 |
| Secondary water supply samples in Jimei district | 0.01 | Below detection limit | 0.31 | 0.06 | 5.569 | 4.270 |
| Primary water supply samples in Jimei district | 0.01 | Below detection limit | 0.43 | 0.09 | 5.795 | 5.089 |
| Water supply samples of Haicang Industrial Zone | 0.02 | Below detection limit | 0.53 | 0.07 | 16.17 | 36.70 |
| Secondary water supply samples in Haicang district | 0.03 | Below detection limit | 0.55 | 0.06 | 16.10 | 38.36 |
| Primary water supply samples in Haicang district | 0.02 | Below detection limit | 0.56 | 0.06 | 16.30 | 39.34 |
| Water supply samples of Siming Industrial Zone | 0.03 | Below detection limit | 0.54 | 0.06 | 14.34 | 38.19 |
| Secondary water supply samples in Siming district | 0.02 | Below detection limit | 0.57 | 0.09 | 14.18 | 38.62 |
| Primary water supply samples in Siming | 0.03 | Below detection limit | 0.56 | 0.06 | 14.03 | 38.26 |
The concentration of F⁻ and BrO₃⁻ was extremely low, so the data of ClO⁻, Cl⁻, NO₃⁻ and SO₄²⁻ were extracted from Table 4. The chart example results are as follows.

### 3.3. Sampling from industrial zones

**Figure 2.** Concentrations of ClO⁻ and Cl⁻ in industrial area

| District | Water Supply Samples of Huli Industrial Zone | Secondary Water Supply Samples in Huli District | Primary Water Supply Samples in Huli District | Water Supply Samples of Xiangan Industrial Zone | Secondary Water Supply Samples in Xiangan District | Primary Water Supply Samples in Xiangan District | Water Supply Samples of Tongan Industrial Zone | Secondary Water Supply Samples in Tongan District | Primary Water Supply Samples in Tongan District |
|----------|-------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
|          | Water supply samples                       | Secondary water supply samples                 | Primary water supply samples                   | Water supply samples                          | Secondary water supply samples                 | Primary water supply samples                   | Water supply samples                          | Secondary water supply samples                 | Primary water supply samples                   |
|          | of Huli Industrial Zone                     | in Huli district                                | in Huli district                                | of Xiangan Industrial Zone                    | in Xiangan district                            | in Xiangan district                            | of Tongan Industrial Zone                     | in Tongan district                             | in Tongan district                             |
|          | 0.02                                       | 0.02                                           | 0.02                                           | 0.01                                          | 0.03                                          | 0.02                                          | 0.01                                          | 0.01                                          | 0.01                                          |
|          | Below detection limit                       | Below detection limit                          | Below detection limit                          | Below detection limit                         | Below detection limit                         | Below detection limit                         | Below detection limit                         | Below detection limit                         | Below detection limit                         |
|          | 6                                           | 9                                              | 7                                              | 2                                             | 1                                             | 6                                              | 2                                             | 3                                             | 3                                             |
|          | Below detection                             | Below detection                               | Below detection                               | Below detection                               | Below detection                               | Below detection                               | Below detection                               | Below detection                               | Below detection                               |
|          | 58                                          | 56                                             | 59                                             | 25                                            | 55                                            | 56                                            | 27                                            | 44                                            | 25                                            |
|          | 0.07                                        | 0.06                                           | 0.00                                           | 0.05                                          | 0.06                                          | 0.06                                          | 0.02                                          | 0.06                                          | 0.04                                          |
|          | 14.31                                       | 14.55                                          | 14.96                                          | 4.766                                         | 13.93                                         | 14.04                                         | 5.767                                         | 5.767                                         | 2.698                                         |
|          | 38.10                                       | 37.39                                          | 37.82                                          | 3.009                                         | 37.29                                         | 39.18                                         | 6.055                                         | 6.055                                         | 2.223                                         |

**Figure 3.** Concentrations of NO₃⁻ and SO₄²⁻ in industrial area

![Concentration Chart](image)
Figure 2 and figure 3 show that the water pollution in industrial areas of Siming, Haicang and Huli Districts was relatively serious. SO$_4^{2-}$ in Siming District was comparatively high (38.198mg/L) compared with other districts. Besides, the highest NO$_3^-$ was found (16.175mg/L) in Haicang District, which had exceeded 50% of the national standard, while the Chlorine was evenly distributed in different industrial areas.

3.4. Sampling of residential areas

Through figure 4 and 5, the lowest concentration of SO$_4^{2-}$ and NO$_3^-$ were found in the secondary water supply samples of Tongan and Jimei districts, which had met the national water quality standard. ClO$_2^-$ and Cl$^-$ in the secondary water supply samples was in average level.

In particular, little difference of parameters can be found in water samples between primary water supply and secondary water supply.

3.5. Distribution characteristics of anions in different districts

1) In Jimei District, the disinfection byproducts were much less, all the indexes met standard, water quality was in good condition;

2) In Haicang District, the concentration of SO$_4^{2-}$ and NO$_3^-$ in primary water supply was relatively high, up to 39.345mg/L and 16.302mg/L, respectively, while NO$_3^-$ exceeded the standard (10mg/L);

3) In Siming District, the concentration of four kinds of anions was in average level, but SO$_4^{2-}$ was comparatively high, three samples were all above 38.194mg/L;

4) In Huli District, Cl$^-$ in primary water supply was much lower (0.08mg/L), which was suitable for residents as drinking tap water. But the number of NO$_3^-$ was still higher than 10mg/L, overtaking the standard;

5) In Xiangan District, Industrial Zone, where 4 kinds of ions had low amount of SO$_4^{2-}$ (3.009mg/L) and NO$_3^-$ (4.766mg/L), which illustrated that the water quality was much better than the figure for primary or secondary water samples;

6) In Tongan District, SO$_4^{2-}$, NO$_3^-$ and Cl$^-$ detected in secondary water supply samples were significantly higher than that of primary water supply and industrial zone.

3.6. Reasons for the difference in distribution

Research shows that the concentration of ClO$_2^-$ and Cl$^-$ is more reasonable, this is may due to the fact that the tap water is disinfected by the amount of Cl which is controlled by the waterworks, and then through the network transmission, the secondary compression process, residual chlorine is consumed...
in the interaction of chemical conversion, but not less than 0.05mg/L, which can reach the standard of drinking water.

SO$_4^{2-}$ detected in Haicang, Siming and Huli district is significantly high, which may be caused by: these three districts was developed relatively early, the pipeline buried in the construction areas had been damaged to a certain extent. It could cause the waste water and some special materials infiltrate into the pipeline. At the same time, SO$_4^{2-}$ as industrial waste, by the form of atmospheric deposition, is discharged into the water body, which lead to a significant number of SO$_4^{2-}$ in these three districts.

The three districts of NO$_3^-$ is much higher which may be caused by: The main tap water sources of Haicang, Siming and Huli District originate from 40km outside of JiuLong River water, mainly for surface water supply. And there is a little NO$_3^-$ in this type of water, which is difficult to remove in purification.

4. Conclusion

Under the evaluation of the residual status of disinfection by-products including F$^-$, Cl$^-$, NO$_3^-$, BrO$_3^-$, ClO$_3^-$, SO$_4^{2-}$ in tap water of main districts, in Xiamen city, by using ion chromatography, the results of the figure illustrate that: the disinfection byproducts in three kinds of water samples in all districts of Xiamen show the trend: SO$_4^{2-}$ > NO$_3^-$ > ClO$_3^-$ > Cl$^-$ > F$^-$ > BrO$_3^-$. 

1) the concentrations of BrO$_3^-$ in all sampling sites of six districts are less than the detection limit, which means BrO$_3^-$ in Xiamen city meet the standard. 2) The residual chlorine in tap water is free residual chlorine (ClO$_3^-$), the concentration of which should be controlled at 0.05~0.8mg/L, and the test results are in line with the standard. 3) Although SO$_4^{2-}$ is quite high, especially in Haicang, Siming and Huli districts, where all the figure exceed 36.708 mg/L, and one of which reach its peak at 39.345 mg/L in Haicang District, all SO$_4^{2-}$ detected in these areas are within the standard value of 250mg/L. 4) F$^-$, BrO$_3^-$, ClO$_3^-$, Cl$^-$, SO$_4^{2-}$, these five kinds of ions are within the standard range, while NO$_3^-$ overtakes the national standard concentration (10 mg/L) in Haicang, Siming and Huli districts, which exceeds 14.031mg/L, and the peak concentration is 14.342mg/L. 5) Smaller residual are found in the tap water near the industrial areas of Jimei, Tongan and Xiangan Districts compared to other districts, all criteria meet national standard, which means water quality is in good condition in these three areas.

Therefore, from the result of test, the relevant departments should attach importance to it, who shall arrange personnel to renovate and manage pipe network regularly, so as to reduce the possibility of tap water pollution. Besides, dispatching appropriate water sources in different areas to ensure the water safety should be taken seriously.

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