Analysis of titanium content in titanium tetrachloride solution

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Abstract. Strontium titanate, barium titan and lead titanate are new type of functional ceramic materials with good prospect, and titanium tetrachloride is a commonly used in the production such products. Which excellent electrochemical performance of ferroelectric temperature coefficient effect. In this article, three methods are used to calibrate the samples of titanium tetrachloride solution by back titration method, replacement titration method and gravimetric analysis method. The results show that the back titration method has many good points, for example, relatively simple operation, easy to judgment the titration end point, better accuracy and precision of analytical results, the relative standard deviation not less than 0.2%. So, it is the ideal of conventional analysis methods in the mass production.

1. Introduction
Strontium titanate (SrTiO3) ultrafine power has already became a key material of electronic industry and ceramic industry. The performance of an application is superior to the traditional materials, it in many areas (high voltage capacitor, grain boundary layer capacitor, pressure sensitive ceramics, temperature sensor, etc.). Strontium titanate powder is also a raw material of strontium titanate monocristalline. Strontium titanate single crystal is one of the perfect used widely high temperature superconducting single crystal substrate. It is well matched with the lattice of high temperature superconducting materials, such as Abacus, which has no twin structure and owns, good physical and mechanical properties. Using a variety of the membrane technology (such as magnetic sputtering, pulsed laser deposition, laser molecular beam epitaxy, etc.) productively a variety of high temperature superconducting thin film (Y -, Bi -, La - system, etc.) own obtain some index data such as TCO acuity 90° K, JCO acuity 106 a/cm².

SrTiO3 is also the preferred monocristalline material for high-temperature superconducting junction technology (using twinning substrate or step substrate) and substrate step-cutting and heat treatment at a specific angle. Strontium titanate and its derivative applications have a broad prospect, so the preparation of strontium titanate ultrafine powder is focused for a long time.

SrTiO3, including of BaTiO3 and PbTiO3 and similar products, traditionally composed by using for solid phase. The cost of solid phase method is low, and the preparation process is simple and was big, but the particle size of powder and it was prepared by solid phase method, chemical homogeneity was poor, easy to cause pollution, and it was hard to get a single phase, which was far away from the demand of high purity materials. In recent years, liquid phase synthesis technology, including chemical co precipitation, sol gel is development rapidly, are generally four isopropyl titanium, titanium source four butyl titanate and titanium tetrachloride, in which titanium tetrachloride is relatively cheap, is the industrial production for the most ideal choice. Therefore, the determination of...
titanium tetrachloride water solution is one of the key technologies for SrTiO$_3$ or BaTiO$_3$, PbTiO$_3$ powder synthesis$^{[1]}$. The determination of titanium tetrachloride (TiCl$_4$) water solution is rarely reported. The classic method of determination of titanium (HGB 3252-1960) is the oxidation reduction titration method of ammonium sulfate. Of this method measuring results are accurate and reliable, but the experiment has many steps, taking a long time, the oxidizing atmosphere requires. For this experiment it is difficult to control, and it requires special glass or instrument, it is hard to be used in the conventional test for the production process. Gravimetric analysis method$^{[2]}$ is also considered to be a more reliable method, but the gravimetric analysis method needs about three working days, which is either not suitable for mass production. EDTA-complexometric titration was reported by more researchers in the reference of titanium compound, titanium alloy and titanium content analysis. Although titanium and EDTA can form stable complexes, the reaction rate is slow. Therefore, the back titration method$^{[3-5]}$ or replacement titration method$^{[6, 7]}$ are usually adopted by researchers. The former uses lactic acid, malice acid, bitter almond acid, tart rate, citrate, phosphate, etc. As the release agent, which can quantitatively replace EDTA complexed with titanium. The latter is in the presence of hydrogen peroxide to makes the titanium and EDTA complex, titrate excess EDTA after a short time.

This article in view of the high purity titanium tetrachloride configuration solution method of calibration. According to the report in the reference the back titration method, the replacement titration method and the gravimetric analysis method three by the specific traget of this article in view for calibration samples of titanium tetrachloride solution. The results show that titanium tetrachloride solution method of calibration using the EDTA complexes with titanium ions, zinc standard solution titrate excess EDTA, has many good points, for example, relatively simple operation, easy to judgment the titration end point, better accuracy and precision of analytical results, the relative standard deviation (RSD) not less than 0.2%. So, it is the ideal of conventional analysis methods in the mass production.

2. Experiment
The chemical reagents used for the experiment were all analytically pure agents while ultrapure water was also used.

2.1 Back titration method
Add the 25.00 ml EDTA standard solution to the conical flask. Add 1ml hydrogen peroxide in the mixing condition, and quickly add 2.500 ml titanium tetrachloride solution and place 10 min. In stirring conditions, add 25 ml sodium acetate (2 mol/L) and a few drops of dimethylphenol orange solution, and use ammonia water (1 + 1) to the solution appearing red, and to pH=5.65 with hydrochloric acid (1 + 1). The concentration of TiCl$_4$ was calculated by using zinc standard solution to return the excess of EDTA and recording the volume of consumption.

2.2 Replacement titration method
(1) put 10.00 mL titanium standard solution into conical flask, (2) add 20.00 mL EDTA solution and 5 mL masking solution (sulphur succint acid- acetyl acetone solution), (3) heat to boil for 2 min, (4) cooling to 60 °C ~ 70 °C, (5) add 10 mL acetate buffer medium of pH 5.5, several drops PAN - Brij - 35 mixed indicator. (6) Titration with Zn standard solution from bright yellow to red (excluding reading). (7) Add 15 ml tartrate solution (release agent), (8) heat to boil 2 min, (9) cooling and 60 °C ~ 70 °C. (10) Titration with Zn standard solution titration from bright yellow to purplish red, calculate the content of TiCl$_4$.

2.3 Gravimetric analysis method:
Excessive ammonia water was used to fully hydrolyze TiCl$_4$ completely into TiO$_2$. Ash free filter paper was used for filter washing. The constant heavy crucible was put into the maf furnace to reach constant weight, was calculated at last TiCl$_4$ content.
3. Results and discussion
The three batches of titanium tetrachloride aqueous solution were calibrated by back titration method, replacement titration method and gravimetric analysis method (parallel experiment 5 times). The experimental results were showed in table 1. From the results, the date obtained by the three methods are similar. It shows that the three methods all can be used to analyze the concentration of titanium tetrachloride solution. The back titration method and gravimetric analysis method have relatively high precision, RSD is no more than 0.2% and 0.3% respectively. The replacement titration method date is slightly higher, RSD is less than 1.0%. According to the reference and experimental results, the gravimetric analysis method is more reliable, but the process cycle is too long, which is recommended to be used as a comparison and reference analysis method in mass production. The RSD values of replacement titration method is higher than other two methods, So it is speculated that this is mainly due to the experiment process. For example, the replacement titration method operation is relatively complicated, and replacement which is not fully completed. Changing color is not sharp, is difficult to determine. By analysing the references, the main advantage of this method can undergo with the exist of a large number of interference ions titanium content analysis, this paper, analysis object is high purity titanium tetrachloride of aqueous solution. So the replacement titration method should not be the best choice.

| TiCl₄ solution | Analysis method      | Average value/mol/L | Relative standard deviation |
|---------------|---------------------|----------------------|----------------------------|
| NO. 1 ~2.2 mol/L | Back titration     | 2.186                | 0.11%                      |
|               | Replacement titration | 2.184               | 0.82%                      |
|               | Gravimetric analysis | 2.188               | 0.24%                      |
| NO. 3 ~2.0 mol/L | Back titration     | 2.025                | 0.18%                      |
|               | Replacement titration | 2.030               | 0.95%                      |
|               | Gravimetric analysis | 2.028               | 0.20%                      |
| NO. 3 ~1.8 mol/L | Back titration     | 1.174                | 0.16%                      |
|               | Replacement titration | 1.171               | 0.78%                      |
|               | Gravimetric analysis | 1.175               | 0.26%                      |

For the back titration method, complexation reaction of titanium and EDTA with in the presence of H₂O₂, are as follows: TiO(H₂O)₂²⁺ + Y⁴⁻ ⇌ TiOY₂⁻(H₂O)₂. The stable constant complex of the Ti-H₂O₂-EDTA is 2.7×10²⁰. In this paper, the stability of the complex, H₂O₂ and excessive EDTA standard solution are added into aqueous solution, which can stop the hydrolysis of titanium, after a short time, zinc standard solution to titrate excessive EDTA standard solution for determining the content of titanium. The analysis method is relatively simple and easy to judge. The accuracy and precision of the analytical results are good, which is the ideal method for conventional analysis in mass production.

At the same time, the experimental data got by back titration method seems to have a very small systematic bias compared with the gravimetric analysis method in the experiment. This may be due to the fact that the hydrolysis of titanium tetrachloride which hydrolysis is quite complicated. Although it is relatively stable under the high concentration conditions, very slow hydrolysis still exists. The hydrolysis product was negative in the analysis of the back titration method, which the hydrolysis was positive in the gravimetric analysis method. Therefore, regular back titration and gravimetric analysis method can be used to supervise the quality of titanium tetrachloride solution by comparing.

4. Conclusions
The back titration method, the replacement titration method and the gravimetric analysis method are used to calibrate the samples of titanium tetrachloride solution. The results show that the three
methods can effectively analyze the concentration of TiCl₄ solution. Among the three methods, the back titration method has many good points, for example, relatively simple operation, easy to judge the titration end point, better accuracy and precision of analytical results, the relative standard deviation not less than 0.2%. So, it is the ideal of conventional analysis methods in the mass production. The replacement titration method is more suitable for the analytical method in the complex composition sample and the gravimetric analysis can be used as the comparing experimental method.

Acknowledgments
Authors wishing to acknowledge assistance financial support from the fund of the Education Department of Liaoning Province (ZXLGL-1614).

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