Hydrogen peroxide photometric analysis of titanium in vanadium alloy

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Abstract: The hydrogen peroxide photometric method for analyzing main constituent titanium in vanadium alloy were investigated in the paper, including the sample digestion method, chromogenic conditions, Lambert-Beer's law range, matrix interferences, method precision, recovery of standard addition, sample analysis and comparison analysis. The method precision in RSD% was 2.6%, the recoveries of standard addition were from 98.7%-99.4%. The experimental results indicated that the proposed method for determination of titanium in vanadium alloy was simple, fast, accurate, and easy to operate, which was suitable for quality control of vanadium alloy.

Introduction

Vanadium alloy is a kind of important material with important application, its quality must be ensured, in which its chemical constituents and mechanical properties are important parameters which must be controlled, in which titanium is one of the main constituents which must be controlled and determined [1].

The determination method of titanium includes FAAS method [2], GFAAS method [3], ICP-AES method [4], indirect AAS method [5], derivative spectrophotometry [6], hydrogen peroxide-photometric method [7], alternating current voltammetry method [8], gravimetric method [9], titration method [10] and etc.. In the above methods, the hydrogen peroxide photometric method was widely used in determination of titanium in various metal or alloy materials, which had advantages of being fast, accurate, cheap and easy to operate. But in analysis of vanadium alloy, matrix vanadium seriously interfered with the signal of titanium in the hydrogen peroxide photometric method. The later method could not be directly used in determination of titanium in vanadium alloy. Therefore it was needed to study how to remove the interference from vanadium during the determination of titanium in vanadium alloy.

In the present study, titanium in vanadium alloy was determined by H_2O_2 spectrophotometric method with subtraction of matrix signal, and the results indicated that the proposed method was simple, accurate, and easy to operate, which was suitable for quality control of vanadium alloy.

Experimental

Instrumentation

A model 721 Spectrophotometer (Shanghai No.3 analytical instruments factory, China) was employed in determination experiments.

Reagents

HCl(1+1), H_2O_2, HNO_3(1+1), H_2SO_4(1+1), sulfuric and phosphorus acids mixture (SP hybrid acids) used in the experiments were all analytical reagents grade and purchased from market.

Titanium standard solution ($1000mg \cdot L^{-1}$), Chromium standard solution ($1000mg \cdot L^{-1}$) was prepared by high purity metal. Vanadium standard solution ($1000mg \cdot L^{-1}$) was prepared by dissolving NH_4VO_3 (AR, 99.0%) in pure water.

Analytical procedure

0.1000g of vanadium alloy sample was digested in 10ml 1+1 H_2SO_4 under slightly heating, and 1+1HNO_3 was added dropwise into the solution to remove purple color, and boiling was used to drive off NO_x. After cooling, the solution was transferred into a 100ml volumetric flask, and adjusted to the mark. 5ml of sample solution was pipetted to make chromogenic solution , and then the solution's absorption was determined at a wavelength of 410 nm by a spectrophotometer. Absorption of titanium was equal to that of sample chromogenic solution minus that of matrix calibration solution. The content of titanium was then calculated by calibration curve.

Matrix calibration solution: pipetting 4.5ml of 1000mg/L V solution+2.5ml of 100mg/L Cr solution, adding 5ml 1+1 H_2SO_4, shaking it, and then adding 2ml H_2O_2, adjusting to 50ml.

Sample chromogenic solution: pipetting 5ml of sample solution, adding 5ml 1+1 H_2SO_4, shaking it, and then adding 2ml H_2O_2, adjusting to 50ml.

Calibration curve

A three points calibration curve of titanium was plotted according to the determination results from a series of titanium standard calibration solutions, including 0, 10.00, 20.00 $mg \cdot L^{-1}$ three concentration levels. 5ml 1+1 H_2SO_4 in 50ml total volume was used as reference solution (RS).

Results and discussion

Selection of digestion method

The solubility of vanadium alloy in different acids was still not completely known, therefore we carried out digestion method experiments, and selected suitable acid according to experimental results. The result of the digestion method experiments was given in table 1.

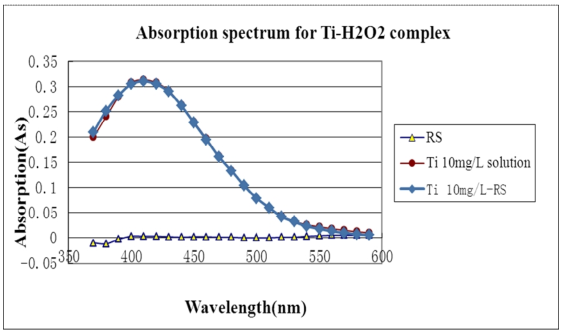
Table 1 Effect of digestion method on determination results

Digesting acid	1+1 $HCl+H_2O_2$	1+1 HNO_3	1+1 H_2SO_4	SP hybrid acids
Sample weight(g)	0.1000	0.1000	0.1000	0.1000
Acid Volume(ml)	10+12.5	10+10	10	10
Digestion time(min)	30	10	10	15
Digestion effect	partially dissolved	Completely dissolved	Completely dissolved	Completely dissolved
Solution color	Light green	Light green	Deep blue	Deep green
Remark	Not good	Good	Good	Good

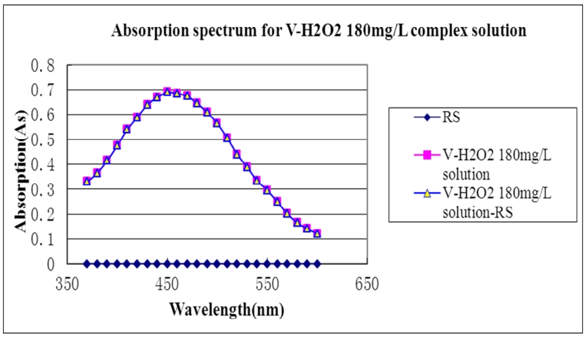
According to table 1, 10ml 1+1H_2SO_4 was selected for further experiments.

Selection and optimization of determination conditions

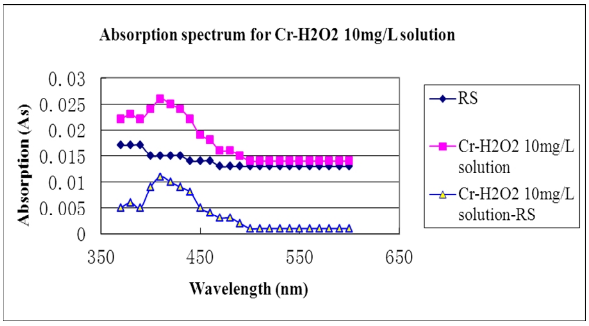
Absorption Spectrum



(a)



(b)



(c)

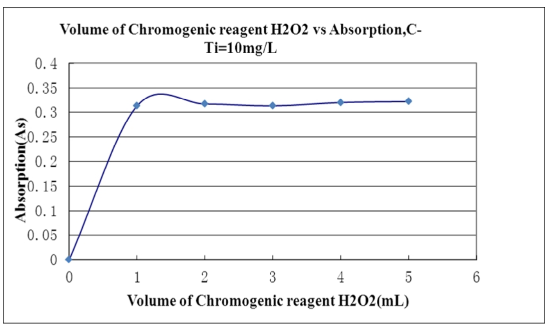
Figure 1 Absorption spectrum for Ti-H_2O_2 complex solution (a) and V-H_2O_2 complex solution (b) and Cr-H_2O_2 complex solution (c)

From figure 1, we knew that the absorption maximum for Ti-H_2O_2 complex solution appeared at a wavelength of 410nm, therefore we chose 410nm as determination wavelength for further experiments. Vanadium-H_2O_2 complex had strong interference on absorption on Ti-H_2O_2 complex at 410nm, and Cr-H_2O_2 complex also had slight interference on Ti- H_2O_2 complex at 410nm, which should be subtracted as background from total absorption.

Selection of volume of Chromogenic reagent

Experimental conditions were as following：[Ti]=10mg/L, volume of 1+1H_2SO_4=10ml,

volume of chromogenic reagent H_2O_2：1.0, 2.0, 3.0, 4.0, 5.0ml.



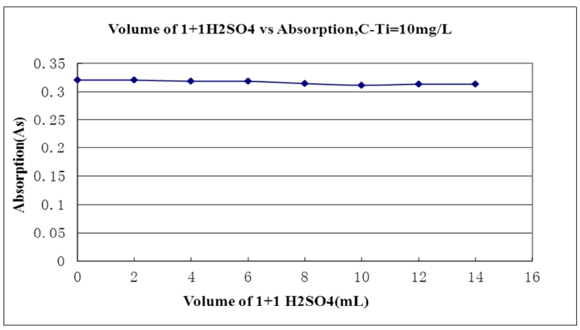


Figure 2 Effect of volume of chromogenic reagent H_2O_2(left) and chromogenic acid 1+1 H_2SO_4 (right) on absorption of titanium-H_2O_2

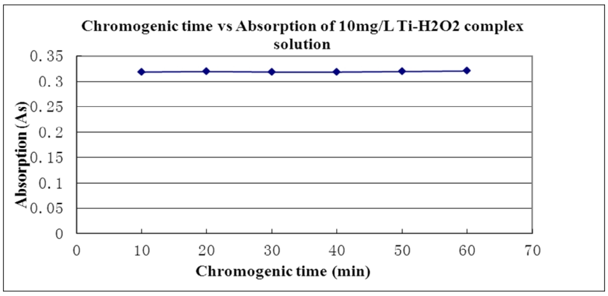
From figure 2(left), we known that the absorption basically kept unchanged when the volume of chromogenic reagent H_2O_2 was between 1.00 to 5.00ml, to save chromogenic reagent, we chose 2ml as the volume of chromogenic reagent H_2O_2 for further experiments.

Selection of chromogenic acidity (volume of 1+1H_2SO_4)

From figure 2(right), we known that the absorption of titanium basically kept unchanged when the volume of chromogenic acid 1+1 H_2SO_4 was between 2ml to 14ml, to make analysis easy and to prevent Ti ion from hydrolysis, we chose 5ml as the volume of chromogenic acid 1+1 H_2SO_4 for further experiments.

Selection of chromogenic time

We carried out stability (chromogenic time) experiments, the concentration of Ti solution was 10mg/L, and the main result within 1h was given in figure 3. The absorption of the same chromogenic solution after 17h was 0.316As, slightly decreased compared to that within 1h.



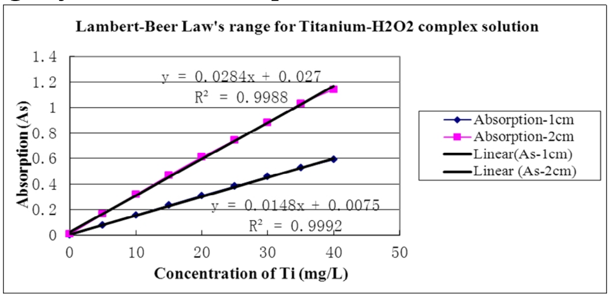


Figure 3 Selection of chromogenic time Figure 4 Lambert-Beer's law range at 410nm

From figure 3, we saw that the absorption almost kept unchanged within 60 min, to make the absorption stable enough, we chose 20-30min as the chromogenic time for further experiments.

Lambert-Beer's law range

From figure 4, we knew that lambert-beer's law was best obeyed from 0 to 40 mg/L for 1cm cell, and from 0 to 35mg/L for 2 cm cell. For vanadium alloy, the calibration graph practically used for 1cm cell was in concentration range from 0 to 20mg/L.

Matrix interference experiments

The main constituents of vanadium alloy are vanadium, chromium and titanium. After 0.1000 gram sample was digested and adjusted to 50ml and had a dilution of 10, the concentration of vanadium, chromium and titanium in test solution were ca. 180 $mg{\cdot}L^{-1}$,10 $mg{\cdot}L^{-1}$, 10 $mg{\cdot}L^{-1}$, respectively. After matrix interference experiments, we found that the vanadium had serious interference on the absorption of Ti- H_2O_2 solution, and chromium also had slight interference on the absorption of Ti- H_2O_2 solution.

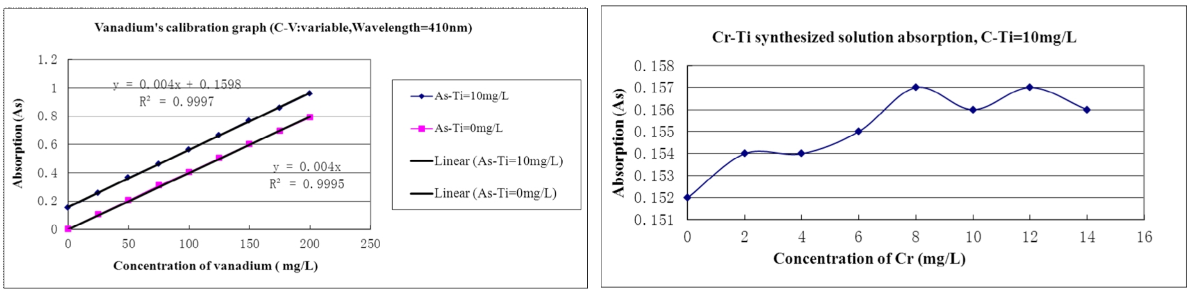


Figure 5 Effect of the V(left) and Cr(right) concentration on absorption of Ti- H_2O_2 complex

（C-Ti=10mg/L）

From figure 5(left) we saw that the two vanadium calibration graphs with titanium and without titanium were parallel to each other, indicating that the absorption of vanadium-H_2O_2 complex and titanium-H_2O_2 complex had good additivity, and the total absorption of sample solution is the sum of that of vanadium and that of titanium. The concentration of vanadium in test solution was about

180mg/L, its absorption should be subtracted from the total absorption when calculating the content of titanium. From figure 5(right) we saw, when Cr's concentration was in range of 8-12mg/L, the delta absorption of Cr-Ti solution was only 0.004-0.005 As. The concentration of Cr in the test solution was about 10mg/L, and its absorption should be subtracted as background from the total absorption when calculating the content of Ti.

Method Validation

Method precision

6 runs of individual determinations (1 sample in each run) were carried out with newly prepared series calibration solutions in each run，and the results were given in table 2. From table 2 we found that the method precision in RSD% was 2.6%.

Table 2 Precision data（n=6）

Sample Number	Averaged determination content($\overline{X}$ /WT%)	Standard derivation (SD/%)	Relative standard derivation (RSD/%)
1#～6#	5.45	0.14	2.6

Recoveries of standard addition

The recovery experiments of standard addition included two groups, group A was carried out with addition of titanium standard solution before sample digestion, and group B was carried out with addition of titanium standard solution after sample digestion, 1 samples was used in each experiment, and the results were given in table 3. From table 3 we knew that the recoveries of standard addition were between 98.7%-99.4%, which could meet the requirement of determination.

Table 3 Analytical results and recoveries

Sample No.	Average content ($\mu g \cdot ml^{-1}$)	Added ($\mu g \cdot ml^{-1}$)	Found ($\mu g \cdot ml^{-1}$)	Recovery (%)
Group A	5.22	5.00	10.19	99.4%
Group B	5.51	10.00	15.38	98.7%

Sample analysis and comparison experiments

6 samples were analyzed by the proposed method, and determination results were listed in table 4. From table 4, we saw that the results determined by the proposed method were in good agreement with the comparison data by ICP-AES method. It indicated that the proposed method has good accuracy enough to satisfying the requirements of determination.

Table 4 sample analysis and comparison experiments

Sample No.	Found by the method (Wt%)	Found by ICP-AES *(Wt%)
1#-6#	5.51，5.53，5.64，5.41，5.41，5.22	5.55，5.44，5.60，5.46

Note*: The content data for comparison by ICP-AES method was provided by National Center of Analysis and Testing for Non-ferrous Metals & Electronic Materials (No.2 Xinjiekouwai Street, Beijing, 100088, China) for the same batch of samples.

Conclusion

The proposed method for analysis of titanium in vanadium alloy was simple, fast, precise and easy to operate, which could practically meet the requirement of quality control of vanadium alloy.

Acknowledgements

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