Study on the Practical Problems of Routine Spectrochemical Analysis of Impurities in Titanium Sponge

By Nakaaki Oda,** Sadayuki Tsunoo** and Toshio Hashimoto**

Practical problems concerning the application of our previously reported spectrochemical method for routine industrial analysis were studied. The differences and variation of the components between the sponge titanium sample solution and the spectrochemical standard solution of titanium tetrachloride and hydrochloric acid, and the evaporation of impurity elements while titanium sponge was dissolved were negligible. The change in the percentage of Si in the spectrochemical standard solution while standing was found by observation of relative intensity for 6 months, and correction procedures are proposed. Various physical properties of carbon electrodes for spectrochemical analysis were evaluated. The effect of the quality of carbon electrodes on the analytical accuracy and precision are described. Finally, some methods for increasing the analytical range are described.

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I. Introduction

In connection with the study on the industrial refining of titanium sponge by the Kroll process, the authors have been doing research on quantitative spectrochemical analyses of vanadium, magnesium, iron, manganese and silicon contained as impurities in titanium tetrachloride(1) and titanium sponge,(2) and the results obtained have been adopted for routine analyses since 1953. In this paper, the result of investigations on various problems concerning the routine analyses are reported.

The improvements of the author’s method are principally to make available standardized analytical samples for titanium tetrachloride and titanium sponge by dissolving them in dilute hydrochloric acid (1:1), and standard solutions for spectrochemical analysis were prepared by adding silicon tetrachloride and a hydrochloric acid solution of magnesium, iron, manganese and vanadium to purified titanium tetrachloride, standardized conditions were employed for D.C. arc excitation and exposure with carbon electrodes impregnated with the solutions. As a result, routine analysis can be make quickly and easier with better sensitivities and precision for various kinds of samples encountered in refining research, better operation control and specification analysis of the products have been improved.

Dissolving the titanium sponge and the preparation of standard solutions differed in many ways, and for this reason their effects on the analytical results were studied in detail. In the case of routine analysis, because of the conditions change and aging of solutions procedure and the investigation must be continued for a long time, there are many problems to be discussed, though the study of the analysis can be done in a short time without any serious change in conditions.

According to investigations to the present, the most important problems are the increase of the silicon content in the standard sample solutions due to aging and effects on the analytical results of varying change of quality in carbon electrodes used for spectrochemical analysis and fluctuations in properties of the same manufacturers products. The above points were studied and the results are reported in this paper.

Furthermore, analyses with higher precision and sensitivity than can be expected by routine analysis are frequently requested when cooperating in a study on industrial refining processes, and some studies and discussions are also described in this paper.

II. Preparation of Analytical Sample

As stated in the introduction, the author’s method consists of routine analyses from titanium tetrachloride to titanium sponge, the standard samples are basically a dilute hydrochloric acid (1:1) solution of titanium tetrachloride. The method of preparation of the standard solution does not differ substantially from that of the titanium tetrachloride samples, however, there is a difference in the procedure and composition from that of the titanium sponge sample. Therefore, the component changes in sample solutions caused by the method of preparation and the possibility of partial evaporation of impurities during dissolving are discussed.

1. Effect of composition change

According to the method of preparation of the sponge titanium sample solutions mentioned in Chap.
II, 3rd report, the final concentration of titanium is 1g/10cc, however, the concentration of hydrochloric acid is not exactly (1:1) and it varies during heating addition of the acid while dissolving and adjustment of the final volume of the sample solution. Furthermore, the concentration of titanium changes within the range of precision for the final volume adjustment. It is necessary to carry out this procedure under carefully controlled specified conditions when dissolving the samples and using more improved apparatus, but it is more sensible for routine analysis to determine the tolerance of the processes capable of keeping the precision with the requested limit than specifying more complicated processes and improved apparatus.

Therefore, 20 beakers of 200cc capacity were marked at 50cc in which sample solutions were prepared under conditions reported previously. The volumes of sample solutions were measured accurately to find the average values as 52.0cc within 2.1cc of the standard deviation. It was also found that the volume was 56.4 ~ 47.6cc and the titanium concentration was 1.05 ~ 0.89g/10cc at 95% of the confidence limit.

From a sample solution analyzed by a wet-chemical method and formed to contain 1.15g/10cc of titanium, two series of the analytical sample solution were prepared with addition of water or hydrochloric acid (1:1) to adjust their titanium concentrations to 1.15, 1.04, 0.95, 0.88, 0.82 and 0.76g/10cc respectively.

These sample solutions were spectrochemically analysed by the methods reported previously and the results were processed by a bifactorial experiment as shown in Table 1. According to the author's investigation, the effect of changes in the titanium content and acid concentration on the analytical results of element were not great, and it was proved that a change of ±4 cc in volume for the preparation of 50 cc sample solutions is allowable.

The coefficient of variation shown in the 5th column of Table 1 were calculated from the residual variance in the 4th column, which shows the precision of the analysis. However, as the original data were converted numerically to carry on the variance analysis, it is impossible to obtain any definite conclusion directly from Table 1. (this relation is also applicable to the results shown in the 7th column in Table 5)

2. Difference in composition of the standard sample and analytical sample

The standard sample solution used in this method was basically a hydrochloric acid (1:1) solution of titanium tetrachloride, however, the sample solutions differed from the standard ones as sponge titanium dissolved in hydrochloric acid formed dark purple Ti++, and the concentration of hydrochloric acid differed also from that of the standard solution.

Though the difference in ionic state of the major constituent in the solution had been thought to cause no effect on the analytical result if the solution was excited in a D.C, arc, this point was further studied in the experiment. The original solution containing Ti+++ and another one containing Ti++++ (light yellow) in color prepared by heating with a small amount of nitric acid were both analysed on photographic dry plates and the differences in analytical results were statistically examined for the purpose of observing the significant differences (t-test).

From the results obtained, it was confirmed as had been expected that the oxidation of Ti+++ to Ti++++ was not needed. However, this oxidation procedure turns the color of the solution to light yellow and is very effective for analytical control, since an insoluble part of the sample retained in the solution can not be observed when the solution is a dark purple color.

As the spectrochemical analysis of sample solutions having different compositions from the standard solutions were made under identical excitation conditions, statistical deviations of the analytical results had been considered to occur.

Table 1 Variance analysis summary table. (Sample preparation)

<table>
<thead>
<tr>
<th>Impurity element %</th>
<th>Mean square</th>
<th>Variation Coefficient %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Addition of HCl or H2O</td>
<td>Ti conc.</td>
</tr>
<tr>
<td>Mg 0.015</td>
<td>10</td>
<td>2.6</td>
</tr>
<tr>
<td>Mn 0.005</td>
<td>7</td>
<td>34.8</td>
</tr>
<tr>
<td>Si 0.024</td>
<td>48</td>
<td>21.6</td>
</tr>
<tr>
<td>Degree of freedom</td>
<td>1</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 2 Comparison of results between chemical and spectrochemical analysis.

<table>
<thead>
<tr>
<th>Analytical method</th>
<th>Mg %</th>
<th>Fe %</th>
<th>Mn %</th>
<th>Si %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical method X</td>
<td>0.002</td>
<td>0.042</td>
<td>0.0020</td>
<td>0.005</td>
</tr>
<tr>
<td>JIS H(1961) X max</td>
<td>0.003</td>
<td>0.047</td>
<td>0.0030</td>
<td>0.011</td>
</tr>
<tr>
<td>X*</td>
<td>0.003</td>
<td>0.045</td>
<td>0.0024</td>
<td>0.008</td>
</tr>
<tr>
<td>Spectrochemical X**</td>
<td>0.027</td>
<td>0.043</td>
<td>0.0027</td>
<td>0.008</td>
</tr>
</tbody>
</table>

* Calculated from 80 analysis.
** Calculated from 4 analysis.

Therefore, a titanium sample analysed very carefully by a wet-chemical method was spectrochemically analysed and the result is shown in Table 2 for comparison. The sample used was the "common sponge titanium powder" which was distributed to members by the "JIS Committee for Titanium Analysis" on October, 1956. Thirteen JIS members analysed the sample following the analytical specification JIS H 1601 (1957), and the values shown in Table 2 represent the total average.

maximum ($\bar{X}_{\text{max}}$) and minimum ($\bar{X}_{\text{min}}$) of the results obtained by the members, who repeated the analysis six times. (As the analysis contains errors caused by sampling, the difference between maximum and minimum does not necessarily indicate the preciseness of the chemical analyses). The spectrochemical data are the mean values of analyses repeated 4 times. The spectrochemical results closely agree with those of the chemical analysis based on the total mean values, so that the difference in composition between standard and analytical sample solutions is considered to have no effect on the analytical result. This relation was confirmed also for a spectrochemically analysed sample solution by comparing the results of the analysis obtained spectrochemically and by the wet chemical process.

3. The effects of evaporation of impurities during the dissolving process

As mentioned above, this method has nearly the same accuracy as the JIS method, however, the amount of titanium dissolved in hydrochloric acid is nearly 10 times larger than that used for sample solution prepared usually for routine chemical analysis.

On the other hand, it has been considered that, Ti$^{+++}$ has a strong reductive property, and the boiling points of compounds like Fe$^{++}$ are rather low.

Therefore, small quantities of iron present as impurities may be evaporated during the dissolving of the sample.

In order to clarify these points, 4 grams of the titanium sample was heated in 60 cc of hydrochloric acid (2:1) and about 20 to 30 cc of the distillate obtained in 6 hours using the apparatus shown in Fig. 1 and under the same conditions used for routine chemical analysis. Iron in the distillate was determined by the potassium rhodanate colorimetric method as well as qualitatively by spectrochemical analysis, and the result is shown in Table 3. Judging from this result, the evaporation of iron is small enough to be negligible, but the fact that negligible amounts of iron are evaporated must be considered.

The lower limits of sensitivity for the qualitative spectrochemical analysis of iron, magnesium, manganese, silicon, copper and titanium were nearly 0.1, 0.01, 0.01, 0.05, 0.001, and 0.01 mg/10 cc, respectively. And, therefore, as Fig. 3 shows there is no difference in the analytical results of iron obtained with qualitative spectrochemical methods and those obtained with colorimetric methods.

4. The aging characteristics of the standard sample

When plotting analytical working curves by photographing a series of samples on dry plates, a standard sample stock solution was prepared and an aliquote part was used for each test. Change in the impurity concentration caused by aging will cause a change of shape, position and angle of the analytical curve, and this aging of the standard sample stock solution has considerable effects on the analytical results of samples used for routine analysis.

After a three year investigation, the authors found the silicon content changed as the standard sample solutions used of silicon content in standard sample solutions for routine analyses aged. An example is shown in Fig. 2, in which a is an analytical working curve plotted for a newly prepared standard sample while b is for a standard sample solution aged six months. This change of concentration did not always occur, but the change of working strength shown in Fig. 2 could usually be confirmed with only small variations in the working strength. The curves show that the silicon content become lower in the high concentration of silicon percentage and higher at a dilute range when aged. The reasons may be that silicon mainly may precipitate of adhere to the wall of the beaker in a concentrated solution and contamination by silicon dissolving out of the
wall may occur in a dilute solution, but these points have not yet been confirmed.

To avoid this effect, the relative intensity of silicon must be calibrated at regular intervals. Fig. 3 is a plot of the mean relative intensity of a 0.11% silicon standard solution representing three values taken separately during a week, and the arrow indicates the renewal time of the standard sample solution. This result proves that standard sample solutions can be used for routine analyses if relative intensities of the standard sample series are calibrated once a week throughout the entire silicon range in reference to the values obtained previously.

Using another method, this checking of a standard sample may be replaced by determining a photographic emulsion calibration curve and by omitting standard samples for each photographic plate, but care must be taken not to plot an original analytical working curve based on an aged standard sample solution.

Other impurities did not cause this effect when aged standard sample solution were used.

### III. Carbon Electrode for Spectrochemical Analysis

In order to carry out routine analysis over a long period of time, variations in the properties of photographic dry plates and the qualities of the carbon electrodes used for spectrochemical analysis are the main problems to be considered. As the effect caused by the properties of carbon electrodes on analytical results are not yet known well, a study was made of this subject. Table 4 gives data showing the properties of carbon electrodes which since 1953, when the method described in this report was first used by the authors for routine analysis. The data in Fig. 4 shows that some problems still remain to be determined regarding their relations as to the accuracy and precision of spectrochemical analysis, but the results of this investigation and the data shown in Fig. 4 should be enough to classify the present domestic supply of carbon electrodes for spectrochemical analysis. This investigation will be reported in detail in a separate paper to be published later.

As to items in the table, the absorbed amount of solution, shown in column 8 is defined as the amount of solution absorbed when a carbon electrode having the size mentioned in Table 2 of the author's previous report is baked with a 12 A pre-arcing.
and immersed in a sample solution for 5 seconds for a distance of 10 mm from the end; the amount consumed by the arc, shown in column 9 is the amount of consumption of an electrode of the same size when it was treated with a 10 A arc-current for 30 seconds; and the qualitative analyses, shown in column 10 are the results of 20 second exposures after 10 seconds of pre-arcing. The effect of the properties of these electrodes on blackness and relative intensities were analysed with a bifactorial experiment taking impurities concentration in samples (5 levels for 0.44~0.027%) as one factor and 5 kinds of electrodes mentioned above as the other factor, and the results are shown in Table 5.

Of course, the blackness of impurity spectral lines changes significantly with changes of the concentration-factors of the impurities in the standard sample, but highly significant changes caused by different kinds of electrodes will cause a change of the blackness of spectral the lines for impurities of in the electrodes. This fact may be related with the amount of solution absorbed, electro-resistivity of electrodes or the amount consumed by the arcing. The fluctuation of the significance for relative intensities caused by different kinds of electrodes and impure elements is considered to be due to different kinds of impurities and their contents and states of arc excitation.

From these results, it is found to be important for the stabilization and improvement of precision and sensitivity for routine analytical procedure to use carbon electrodes of one brand with a known constant quality. From the stand point of easiness of mechanical finishes, carbon electrodes having 22~25 Shore hardness and 200~300 kg/cm² of compressive strength were satisfactory for the electrodes used as described above.

**IV. Widening of the Spectrochemical Analysis Range**

Generally, the lower limit of spectrochemical analytical ranges may be expressed in various ways in accordance with their procedures, photometry and calculations. The analytical working curves plotted using the method proposed by the authors gave curvetures at ranges under 0.4 of blackness for spectral lines of the element being determined, as they were processed for a difference in blackness, but the spectral lines were satisfactory for the photometry at 0.1~0.05 of blackening and were visible enough to detect.

On the other hand, analytical precisions decrease gradually under 0.4 of blackness, so that average values of repeated analyses have to be used to maintain the analytical range within the requested accuracy. Therefore, the authors define the concentration of impurities at the points of inflexion on the analytical working curves as the lower limits of the analytical range, and the lower limit of sensitivity is expressed as concentrations at which spectral lines on dry plates no longer are visible. (c.f. Table 3, 3 rd report)

If emulsion calibration curves for dry plates are used and conversion of light intensity and back-ground corrections, if necessary, (or defference of the Seidel function) are tried, the curving mentioned above may disappear and the lower limit of the analytical range coincides with the lower limit of sensitivity found by the author's proposed method. Therefore, as the gradual decrease of the analytical accuracy is inevitable under 0.4 of blackness, repeated analyses have to be made and the spectrochemical-addition method mentioned in the author's 2 nd report is effective for improving the accuracy.

It is necessary to increase the blackness of impure element spectral lines to widen the lower limits of sensitivity, and factors having significant effects are arc-currents and the analytical-gap as reported previously (Table 3, Fig. 1, 3 rd report). Among them, the effect of the analytical-gap is composed of so-called cathode-layer effects and increased back-ground radiations by incandescent radiation at the top of the carbon electrodes. The former is very effective for increasing sensitivities, however, their usage is not recommended at present because the arc position is difficult to control, resulting in large errors.

The size of the slit of the spectrograph, was 1.5/100 mm used in the previous report in consideration of the back-ground radiation, and a slit of 2/100 mm increases the sensitivity. It is possible to increase the analytical sensitivity by making a photograph by duplicated exposures, and Table 6 shows the result obtained with this method. However, as this method causes increased intensity of the back-ground radiations, it is desirable to adopt a method of converting the blackness of lines into light intensity with the aid of the emulsion calibration curve and the calculation of the relative intensity after back-ground correction.

In order to widen the concentration of the analytical ranges of the element being analysed, sample

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solutions were diluted with a hydrochloric acid (1:1) solution of pure titanium tetrachloride (Ti 1 g/10 cc). This is a useful way of preparing samples in solution form.

V. Summary

Detailed discussions were made on several problems encountered in the practical applications of the conditions for spectrochemical analysis reported previously to routine analysis.

The standard sample solution was basically a solution of titanium tetrachloride. Though the component differed from that for an analytical sample solution prepared by dissolving titanium sponge in dilute hydrochloric acid, this difference as well as the evaporation of iron chlorides contained in a solution by the dissolving procedure was found to be negligible.

The change of silicon content in the standard sample solution by aging was investigated and its effect on the sensitivity of analytical working curves was clarified to determine a correct procedure.

Properties of carbon electrodes presently available for spectrochemical analyses were examined and the effects of changes in specific properties and qualities on the analytical results were investigated. Furthermore, some methods for expanding the concentration ranges of the elements being determined by the proposed spectrochemical analysis were found.

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