

The Quantitative Spectrochemical Analysis of Magnesium, Iron, Manganese and Silicon in the Titanium Sponge*

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In connection with the author's 1st and 2nd report of "Quantitative Spectrochemical Analysis of Silicon and Vanadium in Titanium Tetrachloride",⁽¹⁾ the spectral line pairs for determination of magnesium, iron, manganese and silicon in titanium sponge were studied by 5×5 Graeco-Latin square experiments, bifactorial experiment and standard deviation, which was calculated from 50 repeated analysis.

The titanium sponge sample was dissolved without boiling in dilute hydrochloric acid (5g Ti/50 cc HCl (1:1)) on a hot plate. All of the analytical conditions and procedures, except the sample preparation were identical to those described in the author's 1st report. The variation coefficient and the limits of these line pairs for quantitative analysis are shown in Table 7.

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1. Introduction

In the author's previous papers⁽¹⁾ on "The Application of Quantitative Spectrochemical Analysis to the Titanium Refining Industry", methods for quantitative spectrochemical analysis of silicon and vanadium in crude and refined titanium tetrachloride

were reported.† The present paper is concerned mainly with a study of the quantitative spectrochemical method of analysis of magnesium, iron, manganese and silicon in titanium sponge.

Several specifications for impurities in titanium sponge have been published and Table 1 is a typical

Table 1 Classification of titanium sponge (ASTM B 299-58 T)

Grade	Mg (%) max	Fe (%) max	Mn (%) max	Si (%) max	N (%) max	H (%) max	Cl (%) max	C (%) max
MD-120	0.08	0.15	0.05	0.04	0.02	0.005	0.12	0.025
MD-160	0.10	0.45	0.20	0.10	0.03	0.005	0.15	0.05

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(1) N. Oda, S. Tsunoo, T. Hashimoto: Nippon Kinzoku Gakkaishi, 22 (1958) 468, 23 (1959), 86.

† The spectrochemical analytical method described in the author's first report is useful for the quantitative analysis of crude and pure distilled titanium tetrachloride, if the amounts of Si and V are greater than 0.001% and 0.008%, respectively.

The titanium tetrachloride sample was dissolved in dilute hydrochloric acid (2.5 cc TiCl₄/10 cc HCl (1:1)) using an injection syringe. Standard sample solutions for spectrochemical analysis were prepared by adding silicon tetrachloride and a hydrochloric acid solution of V to a dilute hydrochloric acid (1:1) solution of purified titanium tetrachloride.

The various factors (impurity concentration, arc-current, spacing of the analytical gap, diameter of carbon electrodes, exposure time, and the relative position of carbon electrodes), and the effects of its levels (0.1 to 0.0012% of Si, and 1 to 0.012% of V, 7 to 16A, 3 to 7 mm, 1 to 5 mm, 15 to 25 sec, and five different kinds of relative positions, respectively), which affected the precision and sensitivity of this method were studied by duplicated (5×5) Graeco-Latin square experimental designation.↗

↗The determination of impurities in the sample solution is completed in four steps: (1) Loading of the solution (approx. 50~100 mg) on the pointed (3 mm in diameter at excitation area) carbon electrode, (2) Volatilizing and exciting by a direct current arc, (3) Recording of the resulting spectra on a process-hard type photographic plate and (4) Calculation of the per-centage of impurities in the sample solution by the conventional relative-intensity method.

Apparatus and analytical conditions are as follows;

Spectrograph: Carl Zeiss Qu 24. with slit width 15/1000 mm.
 Densitometer: Carl Zeiss non-recording spectral-line photometer.
 Arc current: 12 A. (short-current)
 Analytical gap: 6 mm.
 Carbon electrodes: 5 mm in diameter and 30 mm in length pointed by a pencil sharpener to 3 mm in diameter at the excitation area, and purified by pre-arcing (10A. for 10sec.)
 Exposure time: 20 sec.
 Development: Fuji. FD-31 developer (1:1). 20 C for 6 min.

Line pair A	Analytical range (in TiCl ₄)	Coefficient of variation
Si 2516.12-Ti 2932.16	0.1-0.001%	10.6%
V. 3092.72-Ti 2641.1	0.3-0.008%	7.9%

example⁽²⁾ of them. Although these specifications generally specify non-metallic impurities like nitrogen, oxygen, hydrogen, chlorine and carbon as well as metallic impurities such as magnesium, iron, manganese and silicon, the metallic impurities mentioned above are the main subjects of study in the present paper.

Concerning quantitative spectrochemical analyses⁽³⁾ of impurities in metallic titanium or sponge titanium, Peterson investigated the spectrochemical analysis of iron, magnesium and manganese up to 0.08, 0.05 and 0.08% respectively with about 7% of the variation coefficient by using the spark method with a porous-cup electrode by dissolving the titanium metal sample in dilute sulfuric acid. Heller et. al.⁽⁴⁾ also analysed magnesium, iron, manganese and silicon up to 0.04, 0.03, 0.01 and 0.02% respectively with about 5% of the variation coefficient by employing the spark method with a rotating carbon disk electrode by using a dilute solution of hydrochloric acid. The sensitivity of these methods is not adequate for industrial process controls and the analytical methods are complicated taking too much time, owing to the deviation of the exciting conditions for magnesium from those other impurities.

Another method⁽⁵⁾ have been also tried where titanium dioxide converted from the sample is analysed spectrochemically. According to the ASTM, E-2 SM-7.8, method metallic titanium is converted to titanium dioxide to which sodium chloride is added. Then, impurities are vaporized together with sodium by a D.C. arc method to determine quantitatively the amounts of respectively iron, magnesium and manganese up to 0.0003, 0.0006 and 0.0003% with about 20% the variation coefficient by three time repetition of experiments. As the results of the author's study, the sensitivity and precision of this methods were confirmed to be nearly sufficient, but the procedure was found unsuitable for routine analysis as it required cumbersome sample preparation, taking much time, and especially the method itself is low in sensitivity for silicon analysis, and analyses had to be repeated to obtain the accuracy required by the authors.

The results of the studies reported this paper, together with the previous papers on the method for titanium tetrachloride, constitutes a part of the routine spectrochemical analysis for process and

quality control of the production of titanium tetrachloride by the method of the Kroll-process. In this study, samples of titanium sponge were dissolved in hydrochloric acid and spectral line pairs were investigated under the same excitation and spectrographic conditions as reported for titanium tetrachloride sample in the previous paper to determine magnesium, iron, manganese and silicon contained in titanium up to 0.001, 0.002, 0.003 and 0.005% respectively with about 9% variation of coefficient.

The results of these studies have been employed in routine analysis since 1953 in this laboratory.

2. Preparation of Analytical Sample and Standard Sample

(a) Sampling of analytical specimen

It is rather difficult to take out an analytical specimen from which the average content of impurities in a product lot can be estimated correctly, as titanium sponge commercially available has a particle distribution of 2~20 mesh and impurities like iron or magnesium is not rather evenly distributed. From these reason, most specifications for titanium sponge specify sampling methods for the analytical specimens and the authors have also made statistical investigations⁽⁶⁾ on the sampling methods for obtaining a correct estimation of the per-centage of impurities in a production lot, considering from the point of view of titanium sponge producer.

Analytical samples mentioned in this paper were taken during the packing of titanium sponge by the following sampling method, a total lot of the product was reduced with the automatic sampler (Ajax Flexible Coupling Co., V. V-8, -4, -8, sampler), the material was further reduced with a riffle and mixed with the V-type blender (Twin Shell Dry Blender Co., 3 liter capacity), pressed under 5 t/cm² pressure to form a briquet, and then the compacts thus formed was drilled to obtain about 50 grams of drillings for the analytical sample.

(b) Preparation of analytical sample

5.00 grams of the titanium sponge sample was weighed in a 200 cc beaker, 50 cc of dilute hydrochloric acid (1 : 1) was added, the beaker covered with a watch-glass was placed on a hot plate to dissolve the titanium sponge sample. Precautions were taken to prevent the solution from boiling and overheating the inside of the beaker, as the deposit formed on the surface might cause precipitation of white insoluble matter in the solution. Hydrochloric acid (1 : 1) was added occasionally to keep the volume of solution a little bit larger than 40 cc. When the sample was almost dissolved, nitric acid was added drop by drop to oxydize Ti⁺⁺⁺ to Ti⁺⁺⁺⁺.

The color of the solution was changed from dark

(2) A.S.T.M. Designation B 299-58 T, Tentative Specification for Titanium Sponge, (1958).
 (3) P. R. Perry, R. W. Lewis, T. A. Sullivan : U. S. Ber. Mines Rept. Invest. 5168 (1955), 45 pp. N. M. Kagen, L. N. Filimonov : Zavodskaya Lab., 33 (1957) 185.
 (4) M. J. Peterson : Anal. Chem., 22 (1950) 1398 : A.S.T.M. E-2 SM-8 : H. A. Heller, R. W. Lewis : Anal. Chem., 25 (1953) 1038. A.S.T.M. E-2 SM8-10.
 (5) N. H. Nachtreib, D. H. Johnson, K. S. Dress : Ind. Eng. Chem. Anal. Ed., 15 (1943) 734 : A.S.T.M. E-2 SM-8. 7 : Sh. G. Melamed : Zavodskaya Lab., 21 (1955) 1066. Sh. G. Melamed, M. A. Notkina, S. M. Rolodovnik : Izvest Akad. Nauk. U. S. S. R. Ser Fiz, 19 (1955) 179. K. Kurosaki and T. Nakashima : Bunko Kenkyu, 3 (1955) 16. D. C. Spindler : Appl. Spectroscopy, 11 (1957) 28.

(6) N. Oda, S. Tsunoo, M. Kubo : Report for "JIS Committee for Titanium Analysis" No. 40, 41 (1957).

purple to clear light yellow. After being checked for insoluble residue in the beaker, the solution was cooled to room temperature and the volume was adjusted to $50 \text{ cc} \pm 3 \text{ cc}$ with hydrochloric acid (1:1).

The reasons for using the dilute hydrochloric acid solution as sample solution is the preparation of metallic electrode directly from sponge titanium is quite difficult in procedure, and there are high possibility of the change of the per-centage of impurities by such preparation.

The analytical results obtained by using such kind of electrode may give the poor representation of the composition of specimen as the impurities do not distribute evenly in the specimen and the surface area for the excitation is small.

The solution method, on the other hand, has the advantage that the homogeneous sample solution for the spectrochemical analysis is prepared simply by dissolving a large amount of sponge titanium and an excellent reproducibility of analytical result for the specimen can be obtained. Highly reliable standard solution is easily prepared and the standard solution for the spectrochemical analysis of titanium tetrachloride can be also be used in this case.

As to the procedure of preparing titanium solution, a concentration change of a certain component may be taken place and also the evaporation of impurities during the procedure must be considered. The results of the author's further studies on these problems being reported in the future, however, the procedure describes above has been confirmed to be a satisfactory condition for the preparation of analytical samples.

(c). Preparation of standard sample

Standard sample solutions for spectrochemical analysis were prepared by adding silicon tetrachloride and hydrochloric acid solutions of vanadium, magnesium, iron, and manganese to a dilute hydrochloric acid (1:1) solution of purified titanium tetrachloride, as described in 2. (b) (Standard Sample) in the author's first report.

In that case, the composition of standard solutions was not identical with the solution of titanium sponge sample. However, the effect due to the differences of the compositions of the solutions proved to be negligible and the study on this point will be discussed in succeeding report.

3. Selection of Optimum Analytical Line Pairs

(a) Apparatus and excitation conditions

The experiment was carried out for the purpose of finding out optimum line pairs for the analysis of magnesium, iron, manganese and (silicon) with the same conditions for determining impurities in titanium tetrachloride, and the equipment, materials and conditions are shown in Table 2, which were the same with ones mentioned on Tables 1 and 6, of the author's first report.

(b) Selection of spectral lines

As the per-centage of impurities in the sample were rather small only about between of 0.01~0.001% and their spectral lines were very weak, only two or three lines could be selected for each impurity element. Table 3 shows two favorable lines for

Table 2 Apparatus materials and analytical conditions.

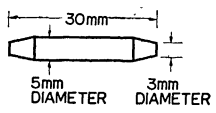
Spectrograph	Carl Zeiss Qu 24. with slit width of 15/1000 mm.
Densitometer	Carl Zeiss non-recording spectral line photometer.
Arc current	12 A. (short current).
Analytical gap	6 mm.
Carbon electrodes	5 mm in diameter and 30 mm in length pointed by a pencil sharpener to 3 mm in diameter at the excitation area, and purified by pre-arcing (10 A. 10 sec.).
	
Exposure time	20 sec.
Development	FD-31 developer (1:1), 20°C 6 min.

Table 3 Impurities and internal standard lines studied in this report.

Impurity lines (Å)	Internal standard line (Å)			
Fe I 2488.15	Ti II 2531.25	Ti I 3000.87	Al I 3082.16	
Fe I 3020.64	Ti II 2534.62	Ti II 3078.65	Al I 3961.53	
Mg II 2795.53	Ti I 2604.15	Ti I 3100.67	Sn I 2839.99	
Mg I 2852.13	Ti I 2619.94	Ti II 3106.23	Bi I 2897.98	
Mn 2801.06	Ti I 2641.10	Ti II 3234.52	Bi I 2897.98	
Mn II 2605.69	Ti I 2644.26	Ti II 3242.00	Bi I 3067.72	
Si I 2516.12	Ti I 2805.70	Ti II 3244.31	Cu I 3247.54	
Si I 2881.58	Ti II 2832.16	Ti I 4017.77	Ca I 3698.47	
	Ti II 2891.07		Ni I 3414.77	

each element which were selected through careful examination of the whole spectrum-range. For the selection of these lines from the titanium spectrum under the conditions of this analytical procedure, strong and continuous spectra from visible to 3000 Å were excluded, as much as possible. Some lines in a certain elements were found to have higher sensitivities than those of so-called *raies ultimes*. (Fe 2488.15 Å, Mn 2801.06 Å for example)

In order to select the internal standard lines, 17 lines from titanium, the main component, and 8 lines from spectra of the elements like about 1% of aluminium, tin, nickel and copper which are contained titanium, were studied. These lines selected among ones having the wave-lengths of 2500~4000 Å have comparatively strong intensities and favorable photographic-photometry effects, and most of these lines were measured by their intensities after being reduced through a three-step neutral filter. Internal standard elements were selected from those which are hardly possible to find in titanium and small in number of spectrum lines. (Table 3)

(c) Blackness of spectral lines

There are many factors affecting the intensity of spectral lines of impurities elements and those of the

internal standard elements in case of quantitative spectrochemical analysis by the D.C. arc method. Among them, the important ones are such factors as the arc-current, analytical-gap, relative position of the carbon electrodes (fluctuation of arc-column) and the exposure time for photograph. The behavior of each line shown in Table 3 was analysed in a 5 × 5 Graeco-Latin square experiments in the various level changes of these factors described above. In this experimental designation, 25 experiments were carried out in total, so that the degree of freedoms is 24. Furthermore, as 4 kinds of factors were employed and each factor changed in 5 levels (as shown in Table 4 and Fig. 1), having each 4 degree of freedoms, total degree of freedoms for these factors is 4 × 4 = 16. Therefore, the degree of freedoms for the error is 24 - 16 = 8.

Table 4 Source of variation and level of condition in (5 × 5) Graeco-Latin square experiment.

Source of variation		Level of condition				
Arc current	A	7.0	8.0	9.5	12.0	16.0
Anal. gap	mm	3	4	5	6	7
Exp. time	sec	15	17	20	23	25
Relative position*	A	B	C	D	E	

* Shown in Fig. 1.

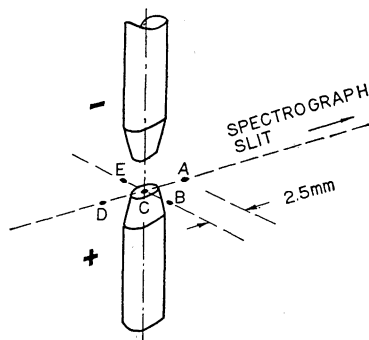


Fig. 1 Relative position of anode and cathode electrodes.

Experimental sample solutions were prepared by the addition of the above mentioned internal standard elements to the standard sample solution containing 0.033% of magnesium, iron, manganese and silicon. The experimental results were obtained by the measurement of the intensities of the spectral lines as shown in Table 3, the calculation of blackness and the variance analysis of the usual ways (* and ** show the significance). Since the results obtained in this experiment are too much in volume to describe them all in this paper, only the data for the behavior of manganese are shown in Table 5 and Fig. 2 as an example.

The mean square for each factor shown in Table 5 is considered to be the representative of the varied amounts of blackness by the change of "the factor level", and is able to be used for the direct comparison of behaviours among each factor or blackness of each spectral line if the change in blackness caused by the change of the factor level would satisfy a 1-st order orthogonal polynominal function being

introduced by the statistical inference. Practically, as noted from Fig. 2 the change in blackness of each line caused by the change of factor levels was considered to satisfy a 1-st order equation, and this fact was ascertained by checking with an orthogonal analysis method.

Table 5 Variance analysis summary table (Blackness).

Spectral lines (Å)	Mean square				
	Analytical gap	Relative position	Arc current	Exposure time	Residual
Mn II 2605.69	628**	24	1018**	70	88
Mn 2801.06	82	24	435**	20	46
Ti I 2641.10	40	25	653**	77	36
Ti II 2832.16	259**	12	1209**	126*	21
Ti II 3078.65	194**	12	325**	219**	12
Ti I 3100.67	372**	7	1312**	87	39
Ti I 3232.00	198**	14	334**	234**	11
Al I 3082.16	416*	22	1064**	30	68
Sn I 2839.99	344	21	344	88	123
Cu I 3247.54	52	12	218**	38	19

* Significance ** Highly significance.

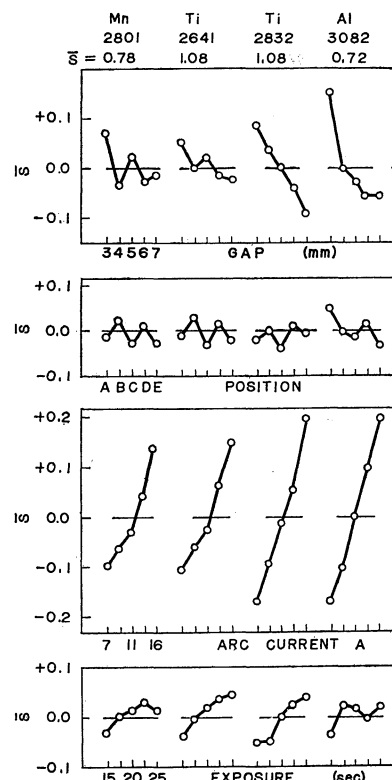


Fig. 2 Graphical representation of (5 × 5) Graeco-Latin square experiment. (Mn 0.033%)

Therefore, line pairs having similar values in their mean square for each factor are considered to be affected in the same way by the level change of each factor, and paralleled lines in Fig. 2 are can be used as optimum line pairs.

From Table 5, it is clear that Mn 2605 Å and Mn 2801 Å are completely different in their characteristics, and furthermore, line pairs like Ti 2832 Å and Ti 3100 Å or Ti 3078 Å and Ti 3232 Å have similar characteristics. As for line pairs for manganese and titanium, it is clear that Mn 2801 Å and Ti 2641 Å are suitable, considering from the paralleled behavior of the both lines shown in Fig. 2.

Though it is generally difficult to pick out line pairs having identical behaviours in this way, this method is a very effective one for finding out prospective line pairs. The following are prospective pairs† obtained through this method.

Mg 2795.53 Å-Ti 2832.16 Å
 Fe 2488.15 Å-Ti 2641.1 Å
 Mn 2801.06 Å-Ti 2641.1 Å
 Si 2516.12 Å-Ti 2832.16 Å

(d) Behaviour of relative intensity

The relative intensities were calculated for line pairs selected by the above process, and the data for manganese and magnesium are shown in Table 6 as

Table 6 Variance analysis summary table (Relative intensity).

Line pairs (Å)	Mean square				Residual
	Analytical gap	Relative position	Arc current	Exposure time	
Mn 2801. Ti 1	43	31	36	27	28.4
Mn 2801. Ti 2	172	50	206	28	25.4
Mn 2801. Ti 3	102	21	26	205	19.5
Mn 2801. Sn	114	8	36	110	44.3
Mg 2755. Ti 1	177	3	13	38	17.6
Mg 2795. Ti 2	13	2	65	40	11.1
Mg 2795. Ti 3	70	21	100	148	26.3
Mg 2795. Sn	13	14	152	145	30.4

* Significance ** Highly significance
 Ti 1=2641Å, Ti 2=2832Å, Ti 3=3232A, Sn=2840 Å

an example. In this case, it is desirable that the results of F-test of the variance analysis would have no significance, and the residual variance would be the minimum. However, even if the value of the F-test would be significant, a practical analysis could be carried out under fixed conditions at a specified level of the factor, consequently, the line pairs adopted are not necessarily improper though the change in relative intensity caused by the whole change in levels of the factor is significantly large. It is clear that, however, as for the line pairs selected among these lines studied, the degree of significance of the effect of variation of the factor will be smaller than that observed in other line pairs. From these examples, the line pairs thus selected are also considered to give excellent results.

In order to ascertain the experimental result shown in Table 6, a bifactorial experiment was made with 5 levels based on two factors, arc-current and analytical gap. In making the analysis of the experiment, two insignificant factors were excluded from the 5 × 5 Graeco-Latin square experimental designation, which was used in the above experiment.

The result obtained is almost the same with that

in Table 5 and Table 6. Fig. 3 shows the influences of arc-current and analytical-gap on the relative intensity of selected line pairs. From these results, it is noted that levels of these factors must be as constant as possible during the analysis.

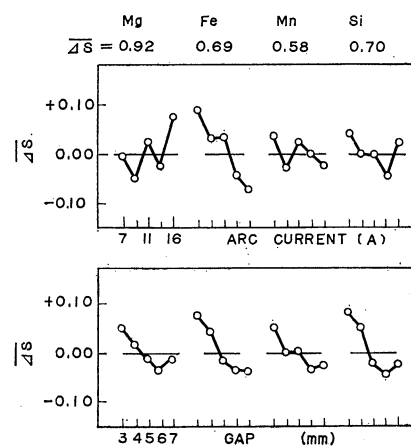


Fig. 3 Influences of arc current and analytical gap on the relative intensity of selected line pairs.

(e) Optimum line pairs and its performance

Line pairs shown in Table 7 are considered to be optimum line pairs for this experiment, and the analytical working curve based on these lines pairs are shown in Fig. 4 as the example. Analytical

Table 7. Variation coefficients and lower limits of analytical line pairs.

Line pair		Variation coefficient (n=50)	Lower limit of analytical range	Lower limit of sensitivity
Impurity	Internal standard			
Mg 2795.53Å	Ti 2832.16 Å	9.4%	0.001%	0.0005%
Fe 2488.15 Å	Ti 2641.1 Å	9.8%	0.02%	0.005%
Mn 2801.06 Å	Ti 2641.1 Å	8.2%	0.003%	0.001%
Si 2516.12 Å	Ti 2832.16 Å	11.0%	0.005%	0.002%

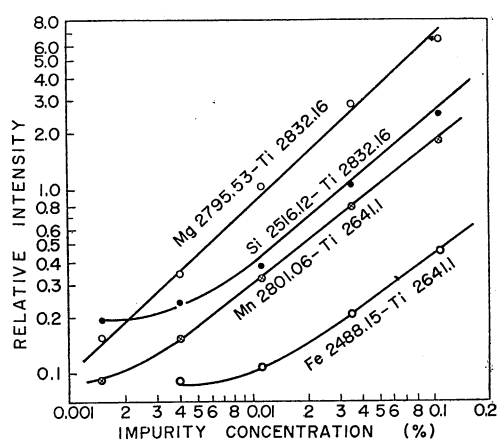


Fig. 4 Analytical curve of this spectrochemical method.

† The authors do not claim that these line pairs consist of the most suitable ones, since whole pairs of spectral lines of titanium have not yet been studied.

As for the line pairs of titanium, they were chosen from ones having the same characteristics and their wavelengths are as close as possible with that of impurities to be paired.

precisions were obtained by repeating the analysis 50 times under conditions reported previously, and the variation coefficient was calculated from the standard deviation of the analytical data.

The concentration at points of inflexion in an

analytical working curve (lower limit of the analytical range) and the concentration where spectral lines for impurities were hardly detected (lower limit of sensitivity) were examined statistically from photographic plates used for the routine analysis. The resulting data are shown in Table 7.

This lower limit of the analytical range may coincide with the lower limit of sensitivity, by converting the blackness (or Seidel function) of the spectral line to the intensity with the aid of emulsion calibration curves, by correcting of background intensity, and by calculating relative intensity, because, the analytical working curve has no point of inflexion in this case.

4. Summary

A spectrochemical analysis of titanium sponge was studied in connection with conditions applied previously for quantitative analysis of silicon and vanadium in titanium tetrachloride.

5×5 Graeco-Latin square experiments were employed to analyse the effect of spectrochemically important factors on blackness and relative intensity of 33 spectral lines composed of 8 impure elements, 17 of titanium and 8 of additional internal standard elements.

Optimum line pairs capable of analysing quantitatively magnesium, iron, manganese and silicon impurities in titanium sponge up to 0.001, 0.02, 0.003 and 0.005 % respectively with about 9 % of deviation (variation coefficient) were found.

Elements like aluminum, tin, bismuth and copper were tested as additional internal standard elements, but they were not so effective like those line pairs selected from titanium lines.

This analytical method can be used for analysing 20 dissolved samples (taking about 6 hrs for dissolving) in about 5 hrs, and has an analytical range of about one tenth lower than the usual limit of specification analysis for titanium sponge with good precision for a control of industrial refining processes.

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