Studies on Analytical Methods for Trace Elements in Metals by Using Radioactive Isotope. III

Determination of Tantalum by Means of Isotope Dilution Method*

Hiroshi AMANO

The Research Institute for Iron, Steel and Other Metals

(Received June 20, 1959)

Synopsis

The determination of tantalum by isotope dilution method in the presence of niobium was investigated by the use of radioactive isotope tantalum-185. Tantalum was separated from niobium as tantalum-tannin precipitate under the optimum condition of pH 1.9~2.5 and tantalum/niobium ratio up to 1/50. If niobium had been present 100 times or more of tantalum, reprecipitation would have been needed. The reciprocal of the specific activity of tantalum pentoxide preciptiate was in a linear relation to the change in the amount of tantalum added. The recommended method gave an accurate result in the determination of tantalum in steel.

I. Introduction

In determining the contents of niobium and tantalum in steel separately, they are generally estimated first as the sum of the two, then the one is determined, and finally the other is calculated from these two values. To separate niobium and tantalum from each other, or to estimate one of them in the presence of the other, the tannin method[1], the volumetric method[2],[3] and the photometric method[4]~[7] have been reported. Usually, the contents of niobium and tantalum in steel are determined separately by the photometric method[4].

The radiometric titration method for determining the sum of niobium and tantalum was reported[8]. Following the previous paper, the method of isotope dilution technique for the tantalum determination in the presence of niobium is reported in the present paper.

* The 947th report of the Research Institute for Iron, Steel and Other Metals. Reported in Japanese in the Journal of Japan Institute of Metals, 23 (1959), 222.

(1) W. R. Schoeller, Analyst, 57 (1932), 750.

(2) Z. Hagiwara, J. Chem. Soc. Japan, Pure Chem. Section, 69 (1948), 129.

(3) Y. Oka and M. Miyamoto, ibid., 69 (1948), 133.

(4) H. Gotô and Y. Kakita J. Japan Inst. Metals, 11 (1948), 33.

(5) A. E. O. Marzys, Analyst, 80 (1955), 194.

(6) J. L. Kassner, A. Gracia-Porrata and E. L. Grove, Anal. Chem., 27 (1955), 492.

(7) P. C. Stevenson and H. G. Hicks, Anal. Chem., 25 (1953), 1517.

(8) H. Amano, J. Japan Inst. Metals, 22 (1958), 625 : Sci. Rep. RITU, A, 11 (1959), 304.

II. Apparatus and reagents

1. Radioactive tracer solution

(i) Tantalum-182 tracer solution

Tantalum-182 tracer solution was made from the tantalum-182 irradiated unit (tantalum wire). Proper amount of tantalum wire was dissolved in the mixture of sulfuric acid and hydrofluoric acid; the solution was evaporated to fume and then diluted with oxalic acid solution.

(ii) Niobium-95 tracer solution

Niobium-95 was separated from the irradiated unit of zirconium oxide containing niobium-95 as daughter element of zirconium-95. The method of separation of niobium-95 was the one used by Willkinson and Grummitt[9]. The medium for niobium-95 solution was a mixture of sulfuric acid and oxalic acid.

2. Scaler and counting tube

To measure the radioactivities of the samples, the decimal scaler combined with β-counting Geiger-Müller tube was used.

3. Reagents

(i) Standard tantalum solution

The metallic powder of tantalum (99.9 per cent purity) was dissolved in the mixture of sulfuric acid and hydrofluoric acid; the solution was heated until it showed dense fume, and after cooling to room temperature, it was diluted with oxalic acid solution. The medium was finally adjusted 3.6 N for sulfuric acid and 2 per cent for oxalic acid. 1 ml of this solution contained 0.26 mg of tantalum.

(ii) Standard niobium solution

The standard niobium solution was prepared from metallic powder of niobium of 99 per cent purity in the same way as tantalum solution. This solution contained 0.25 mg of niobium in 1 ml.

(iii) Tannin solution

The tannin solution was prepared from chemically pure tannin as 2 per cent aqueous solution, and the reagent was freshly made in each experiment.

All the other reagents used were of pure grade either chemically or analytically.

III. Experiments and results

1. Separation of niobium and tantalum by tannin method

(i) Effects of pH

Schoeller[1] has reported that in the sulfuric acid-oxalic acid medium tantalum gives yellow precipitate in low pH range, and that with increasing pH, the color of the precipitate becomes orange because of contamination with niobium caused by the formation of scarlet precipitate. Further, it has been reported by H.

---

(9) G. W. Willkinson and W. E. Grummitt, Nucleonics, 9 (1951), 52.

Bhatta Charya[10] that tantalum is precipitated by the tannin solution at pH of 4.0, followed by the precipitation of niobium at pH of 4.6. But this is not in agreement with the preliminary experiments, and so, in the present study, the effects of pH on the precipitation of tannin complexes of niobium and tantalum were examined.

10 ml of standard tantalum solution (Ta : 2.6 mg) and 10 ml of standard niobium solution labeled with niobium-95 (Nb : 2.5 mg, radioactivity 80 cpm/ml) were taken , pH of the solution being adjusted by hydrochloric acid and ammonium hydroxide, and the sample solution was heated to boiling state. 10 ml each of saturated ammonium chloride solution and 2 per cent tannin solution were added. After boiling for 2 minutes, the solution was cooled to room temperature.

The precipitate was filtered off, washed with 2 per cent ammonium chloride solution containing small amount of tannin, charred and ignited. From the amount of ignited precipitate the amount of niobium and tantalum was calculated as the tantalum value, and the contamination of niobium was calculated from the activity measured with the precipitate. As shown in Table 1, above the

Table 1.   Effect of pH on the separation of Ta from Nb
with tannin method.

pH	Nb contamination (counts %)	Weight of Ta_2O_5 (mg)	*Weight of Ta (mg)
1.9	0.0 0.16	1.5 1.6	1.1 1.1
2.0	0.20 0.23	2.0 2.0	1.4 1.4
2.3	0.00 0.23	2.2 2.1	1.5 1.5
3.5	4.06 4.03	5.6 5.8	3.9 4.1
4.5	69.2 66.6	6.3 6.0	4.4 4.2
8.0	white ppt.was appeared.		

Used Ta 2.6mg, Nb 2.5mg in $3N\text{-}H_2SO_4 + 2\% H_2C_2O_4$ solution.
*   Calculated from the weight of Ta_2O_5.

pH of 3.5, the tantalum values found were higher than theoretical values, and the amount of contaminated niobium calculated from the counting values increased. From the experimental results mentioned above, tantalum was precipitated below pH of 2.3.

(ii)   The effect of amount of niobium on tantalum precipitation

The optimum pH range for the tantalum precipitation was found by using the sample solution containing tantalum and niobium in the ratio of 1 to 1 in weight. The ratio of niobium to tantalum was varied and the effect of niobium amount was studied.

(10)   H. Bhatta Charya, Science and Culture, 16 (1950), 69.

To the standard tantalum solution which was labeled with radioactive tantalum (Ta : 2.5 mg) were added the niobium solutions (Nb : 0~750 mg), and experiments were carried out under the above-mentioned condition. The specific activity of each precipitate was measured, and it was seen that the precipitates were not contaminated with niobium provided that the specific activities of precipitates were constant.

As shown in Table 2, niobium did not contaminate the precipitate up to the

Table 2. Effects of Nb amounts on the purity of Ta-tannin precipitate.

Ta : Nb (weight to weight)	Weight of Ta_2O_5 (mg)	Specific activity (cpm/mg)	Weight of Ta_2O_5 after reprecipitation (mg)	Specific activity after reprecipitation (cpm/mg)
1 : 0	1.5	525 2	...	...
1 : 1	1.1	529.2	...	...
1 : 2	1.0	521.2	...	...
1 : 5	1.3	528.4	...	...
1 : 10	1.8	523.2	...	...
1 : 20	1.2	519.2	...	...
1 : 50	1.1	523.5	...	...
1 : 100	1.4	510.1	0.9	524.3
1 : 200	1.0	480.1	0.6	528.6

ratio of tantalum to niobium 1 to 50, but below the ratio of 1 to 100 the precipitate showed low specific activity, which might be caused by the contamination of niobium. When the precipitate showing low specific activity was dissolved on the filter and the reprecipitation was carried out, pure tantalum precipitate could be obtained. So, it was decided that in the presence of large amount of niobium, which was recognized by the color change of the precipitate from pale yellow to orange, double precipitation method had to be applied.

2. Examination on the isotope dilution method

As a high specific activity was desirable for the tracer solution used in the isotope dilution method, the tracer solution was prepared to have about 21,000 cpm/ml. To determine the amount of tantalum from the results obtained, the graphical method used by T.R. Sweet et al.[11] for the determination of cobalt was adopted instead of the computation method, and the calibration curve once prepared could be used for a fairly long time because of a long half life of tantalum-182.

First, the examination was carried out on the volume of tracer solution. The volume of tracer solution which was added to the standard tantalum solutions was varied to 5 or 10 ml. The sample solutions were adjusted below pH of 2.3 and heated. To the solution were added 10 ml of 2 per cent tannin solution and 10 ml of saturated ammonium chloride solution, and the solution was boiled for 2 minutes. The precipitates were converted to tantalum pentoxide, and then

(11) D. Salyer and T.R. Sweet, Anal. Chem., **28** (1956), 61.

the specific activities were measured. From the reciprocal of the specific activities and the amount of non-radioactive tantalum which was added to the tracer solution, calibration curves were ob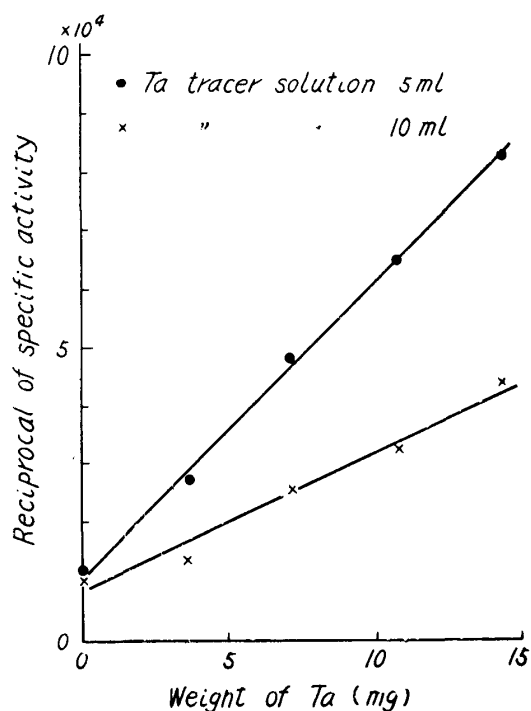tained. As shown in Fig. 1, it is most convenient to use 5 ml of tracer solution because of the steep gradient of calibration curve. Second, the amount of tantalum added to 5 ml of tracer solutions was varied, and it was found that when tantalum used was below 0.5 mg, the value differs from theoretical one in some cases. So, it was decided to take the sample sufficient to give more than 0.5 mg of tantalum in total amount.

Fig. 1. Effects of Ta-tracer solution volume to the dilution.

3. The effects of diverse ions

In studying the interference of other elements on the isotope dilution method, only the effect of iron was examined because the interferences of other elements could be eliminated sufficiently at the first step of separation of niobium and tantalum by acid hydrolysis method. Various amounts of iron were added to the solution containing 5.0 mg of tantalum and 2.5 mg of niobium, and the specific activities of tantalum precipitates were measured. As shown in Table 3, iron did not affect the method up to the amount equal to that of tantalum.

Table 3. Effects of Fe^{3+}.
(Ta 5.2 mg, Nb 2.5 mg in $3N-H_2SO_4 + 2 \% H_2C_2O_4$ solution)

Fe^{3+} added (mg)	Weight of Ta_2O_5 (mg)	Color of ignited ppt.	Specific activity of ignited ppt. (cpm/mg)
0	2.1	white	621
	2.2	//	622
1	2.0	white	620
	2.1	//	630
2	1.9	white	619
	2.3	//	622
5	2.1	brown	618
	2.2	white	622

4. Preparation of calibration curve and analysis of synthetic samples

The calibration curve was prepared as follows: To several 5 ml portions of tantalum tracers olutions were added standard tantalum solutions by the amount of 0, 1.3, 2.6, 5.2, 7.8, and 10.4 mg of tantalum respectively. The pH of the solutions were adjusted from 2.5 to 1.9. 10 ml of tannin solution, and 10 ml of saturated

ammonium chloride solution were added while heating and boiled for 2 minutes. The precipitate was filtered and washed with 2 per cent ammonium chloride solution containing a small amount of tannin. The precipitate was charred and ignited to be converted into oxide.

The weight and the radioactivity of each precipitate was measured. From the reciprocal of specific activities and the amounts of tantalum added, the calibration curve was made. As shown in Fig. 3, the amount of tantalum and the reciprocal of specific activities showed good linear relation.

Then, the method was applied in determining tantalum in synthetic samples. First, 3 g of the steel sample containing 0.89 per cent of niobium was taken and niobium + tantalum was separated by the perchloric acid hydrolysis method. The separated precipitate was redissolved in sulfuric acid + hydrofluoric acid medium, and was heated to expel hydrofluoric acid. The residual solution was diluted with oxalic acid solution, and finally the solution was made up in 3 N sulfuric acid and 2 per cent oxalic acid solution. To this solution was added 5 ml of tantalum tracer solution, and the tantalum was determined in the same way as in the preparation of calibration curve. As shown in Table 4, tantalum could not be detected. So, the amount of sample was varied to 5 g and 10 g, but they gave the same result. To this sample was added 0.54, 1.80 and 3.60 mg of tantalum, and the synthetic samples were analyzed. As shown in the lower columus of Table 4, the method led to the good results.
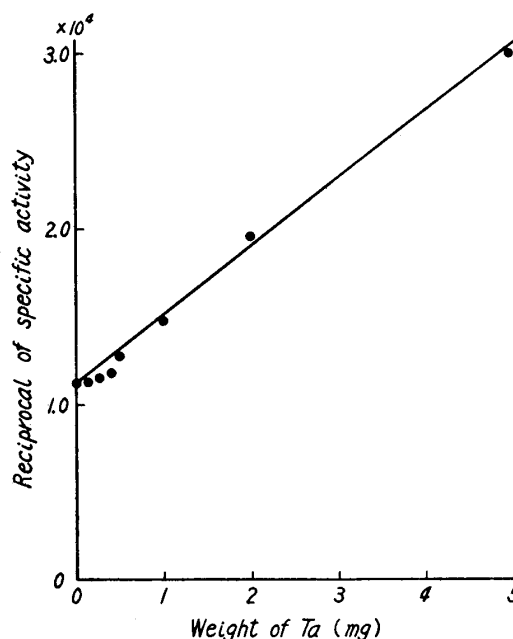

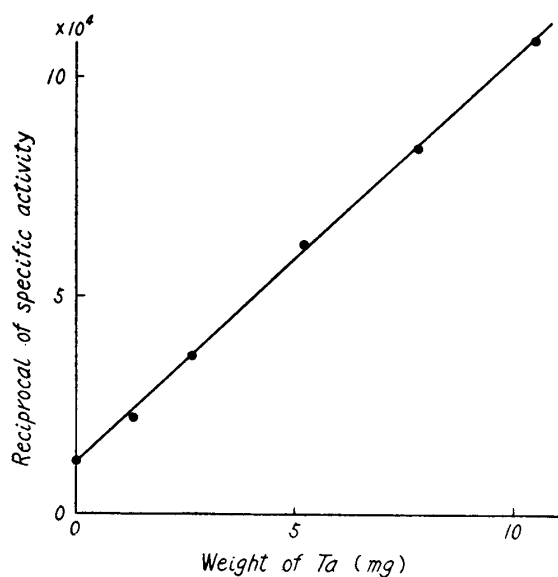Fig. 2. Effects of dilution on the small amounts of Ta.

Fig. 3. Calibration curve of Ta with Tannin isotope dilution method.

Table 4. Results of actual analysis.

Ta added (mg)	*Sample taken (g)	Reciprocal of specific activity ($\times 10^4$)	Ta found (mg)
0	3.0	1.2_3	0
	5.0	1.3_2	0
	10.0	1.1_8	0
0.54	10.0	1.7_1	0.5_3
1.80	10.0	3.0_5	1.9_1
3.60	10.0	4.6_2	3.5_2

* Sample : Fe-Nb steel (Nb=0.89 %)

Summary

(1) The isotope dilution method for the determination of tantalum in the presence of niobium was studied by tannin-precipitating method.

(2) The tannin precipitate of tantalum occurred in pH range from 1.9 to 2.5, and was not contaminated with niobium.

(3) The presence of niobium did not affect the purity of precipitate up to the ratio of tantalum to niobium 1 to 50, but below this ratio it was necessary to carry out double precipitation.

(4) The reciprocal of specific activity and tantalum amount showed good linear relation, but when tantalum was present below 0.5 mg, it became uncertain. So, it was necessary to take a sufficient amount of sample.

(5) The method was applied in determining tantalum in the synthetic samples, and it gave accurate results for the amount of tantalum from 0.54 to 3.6 mg.