INDIRECT A. C. POLAROGRAPHIC DETERMINATION OF NIOBIUM USING SOLVENT EXTRACTION*

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1. *Introduction*

Niobium has been colorimetrically determined by formation of molybdoniobphosphoric acid (MNPA).1)~4) In these methods the MNPA is reduced to heteropoly blue after the selective decomoposition of the excess of binary molybdophosphoric acid (MPA) by increasing the acidity of the solution with sulfuric acid. Strict adherence to the time of addition of the acid must be observed in this procedure, because the MNPA is apt to decompose at the same time. Therefore, the procedures of these methods contain critical operation. Kirkbright et al.5) have solved this problem by selective extraction of the MPA with isobutyl acetate at first, then extracted the MNPA with butanol and determined niobium indirectyl with a high level of sensitivity by using this extract and atomic absorption spectroscopy.

The author has determined indirectly some elements until now by using formation of the MPA complex and polarographic method.6) Then, the author has studied to applicate Kirkbright's method to polarograph.

This paper concerns the results of examination of polarographic application.

2. *Reagents and Apparatus*

2. 1. *Reagents*

Niobium standard solution: A reagent grade niobium pentoxide (0.7153g) was fused with 5 g of potassium pyrosulfate in a platinum crucible, the melt was leached with a 3% oxalic acid solution and then the solution was diluted to 1 *l* with the oxalic acid solution. In experiments this solution was diluted to ten fold with the 3% oxalic acid solution. It corresponds 50μg of niobium per m*l*.

Molybdate solution: 10.69 g of ammonium heptamolybdate tetrahydrate was disolved in water and diluted to 1 *l*.

Phosphate solution: 1.098 g of potassium phosphate monobasic was dissovled in water and diluted to 1 *l*.

Isobutyl acetate and isobutanol: Reagents of commercially available E. P. grade were used, without further purification.

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All other reagents and chemicals used were commercial extra pure grade or analytical reagents grade.

Apparatus:

Polarograms were recorded with a Shimadzu Recording Polarograph, RP-50, equipped with a.c. attachment BF-50.

The characteristics of the D.M.E. were m=1.01mg/sec., t=6.54 sec., (h=60cm) in water.

All experiments were carried out at 25±0.2°C.

3. *Experimental*

3.1 *Preparation of calibration graph for niobium*

To each of a series of five 100 m*l* beakers, adopt 0, 0.2, 0.4, 0.6, and 0.8 m*l* of the niobium solution, and add 3 drops of 6*N* sulfuric acid to each, then evaporate on sand bath to fumes of sulfar trioxide to decompose oxalic acid. After cooling, to the each beaker, add 2.5 m*l* of 6*N* hydrochloric acid, 0.5 m*l* of (1+50) hydrofluoric acid solution, 1.0 m*l* of phosphate solution, 10.0m*l* of molybdate solution and water to make the final volume 25 m*l*. Mix the solutions by stirring, allow to stand for about 5 minutes, and proceed with each as follows, after transfer the solution to 100 m*l* separatory funnel, extract the MPA into two 25 m*l* portion of isobutyl acetate by shaking each time for 1 minute and discarding the organic phase. Add 10 m*l* of isobutanol to the remaining aqueous phase and shake for 1 minute to extract the MNPA and discard the aqueous phase. After the organic phase is washed twice 10 m*l* of 0.5 *N* hydrochloric acid, transfered in 25 m*l* volumetric flask. 8 m*l* of ethanol and 2 m*l* of 6 *N* sulfuric acid are added to it, then the solution is filled with water to the mark of 25 m*l*. After mixing well, transfer a portion of the solution into an electric cell, then record the polarogram appeared from −0.2 to −0.6 V vs. Hg. Measure the height of maximum peak which appears at the vicinity of −0.36 V vs. Hg. Plot the measured heights for the concentrations of niobium, respectively.

3.2 *A. c. polarogram of MNPA*

Fig. 1 shows the a.c. polarogram of MNPA formed under the procedure described at 3.1. This polarogram is produced by the reduction of molybdenum which is contained in the MNPA complex, therefore the polarogram is the same as the one of the MPA. Although the polarogram shown in Fig. 1 is recorded without deaeration, it is the same as the deaerated polarogram. The peak heights are independent of the electrode distance. The polarogram consists of two a.c. peaks, the summit potential of the first, and the second are −0.20 and −0.36 vs. Hg, respectively. The corresponding height of the first peak is obscure as the concentration of niobium is low; therefore, it is not a good measure of the height.

Table 1 shows the relation between the second peak height and niobium concentration. The relation is linear less than the concentration of 2μg of niobium per milliliter, and precision of reproducibility of the calibration graph was an average height 20.5 mm, and the standard deviation was 0.82mm (n=4) or 4 per cent.

The peak height is decreased gradually as the electrolyte-solvent is allowed to stand,

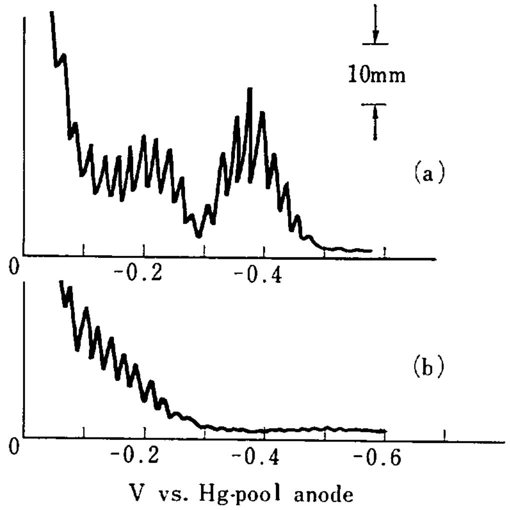

FIG. 1. A. C. POLAROGRAM OF MOLYBDONIOBOPHOSHORIC ACID

Electrolyte solvent: a mixture of isobutanol, ethanol, sulfuric acid and water. (a) a.c. polarogram of Nb 25μg/25m*l* (1.06×10^{-5} M) (b) a. c. polarogram in blank test. Each polarogram, not deaerated. RP-50, Range 100μA/200mm, Damp. 3, BF-50, a.c. Voltage, 25 mV, Sensitivity 1, Compen. Cap. 0.3μF.

and it diminishes after standing one night, but the gradual decrease of the peak height is negligible for about 30 minutes after preparation of the electrolyte solvent. The extraction of MPA with isobulty acetate is best when the acidity of the solution is 0.60 to 0.75 *N*. As the solution deviates from this region of acidity, the amount of MPA left increases, and the results obtained become large; hence, special attention is needed for adjustment of the acidity of the solution. When ethanol and sulfulic acid added for preparation of the electrolyte solvent are 6 to 10 m*l* and about 0.5 *N*, respectively, they do not affect the polarogram and peak height.

The extractability of free MPA from isobutyl acetate is better in hydrochloric acid solution than in a sulfuric acid solution. Polarograms due to MPA are negligible when

TABLE 1. RELATION BETWEEN CONCENTRATION OF NIOBIUM AND PEAK HEIGHT

No.	Nb concentration ($\times 10^{-6}$ *M*)	peak height (mm)
1	4.30	9.0
2	8.61	16.0
3	10.76	20.5
4	12.92	23.0
5	17.22	33.0

RP-50, RANGE: 50μA/200 mm, Damp. 3, BF-50, a.c. Voltage: 25 mV, Senstitivity 1, Compen. Cap. 0.3μF blank tests are carried out by the procedure mentioned in 3.1; however, when the hydrochloric acid solution is replaced by the sulfuric acid solution, a polarogram due to MPA appears distinctly. The polarogram due to free molybdic acid is a low wave which has a maximum peak at near —0.6 V vs. Hg, and the polarogram of MNPA is not disturbed as far as the amount of molybdic acid is not especially large; hence, it does not disturb the determination of niobium. This fact is an advantage of the polarographic method as compared with the atomic absortion method.

4. *Influence of Diverse Elements*

All elements, which form a complex with phosphomolybdic acid and are extracted to isobutanol, disturb the determination of niobium carried out by the recommended procedure mentioned in 3.1. Kirkbright et al. examined influence of 28 diverse ions, under the condition that when $30\mu g$ of niobium added 0.1 mM of an ion was determined, and an error in the absorbance of less than twice the standard deviation of the determination of niobium alone (4.8%) was produced, the ion was considered not to interfere. According to the examination, as follows reported, that Al^{3+}, Ag^{1+}, Bi^{3+}, Be^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Ni^{2+}, Mg^{2+}, Mn^{2+}, Sb^{5+}, Zn^{2+}, SO_4^{2-}, NO_3^-, F^- and EDTA did not interfere, in addition, the presence of a 1m*l* of 10^{-1} *M* solution of the important refractory elements Ta, W and Zr produced no interference when taken through their procedure, an equal amount of Ti was tolerable. V^{5+} and Cr^{6+} were tolerable up to 3 fold and 45 fold excess by weight, respectively.

The author has examined polarographically the influence of diverse ions which are commonly contained in commercial iron and steel, under the condition that when the measurement do not exceed the precision of the calibration graph for Nb, the ion is considered not to interfere. Table 2 shows results.

TABLE 2. INFLUENCE OF DIVERSE IONS

Element	Amount coexisted	Note
Al^{3+}	0.1 m*M*	not disturb
Ca^{2+}	〃	〃
Co^{2+}	〃	〃
Cu^{2+}	〃	〃
Ni^{2+}	〃	〃
Mg^{2+}	〃	〃
Mn^{2+}	〃	〃
Zn^{2+}	〃	〃
Cr^{3+}	〃	〃
Cr^{6+}	〃	〃
Fe^{3+}	〃	〃
V^{5+}	0.02	disturb
Ti^{4+}	〃	〃
Zr^{4+}	〃	〃
Si^{4+}	0.1	not disturb
Ge^{4+}	0.05	〃
As^{5+}	〃	disturb

Nb $25\mu g$ (1.07×10^{-2} m*M*)

The results agreed in general with those obtained by other students, although there were some differences. Zr was reported not to interfere by Kirkbright and associates, but interruption of Zr for the Nb determination was serious according to my observation. W less than 200 mg was harmless, but when it was greater than this, it deposited and hindered the extraction. The obstruction due to arsenic was most serious; this was solved by evaporation with hydrobromic acid.

5. *Application for Determining Niobium in Steels*

5.1 *Procedure*

A 0.1g sample of the steel is dissolved in 5m*l* of concentrated nitric acid and 5m*l* of 45% hydrofluoric acid in a platimun crucible by heating on a sand bath, then the solution is evaporated to fumes of sulfric trioxide after addition of 1.5m*l* of (1+1) sulfuric acid. After cooling, 5m*l* of 48% hydrobromic acid is added to the syrupy residue and again the solution is evaporated to fumes of sulfuric trioxide in order to expel arsenic. After the crucible has cooled, the deposited salts are dissolved with 25 m*l* of 6*N* hydrochloric acid by gentle heating, then 5 m*l* of (1+50) hydrofluoric acid solution is added to the resulting soluton. The solution is transferred into a 100 m*l* volumetric flask and filled up to the mark with water. After a 10 m*l* aliquot of the solution is taken into a 100 m*l* beaker, 1 m*l* of phosphate solution and 10m*l* of molybdate solution are added to it, then the solution is diluted with water to a final volume of 25 m*l* and allowed to stand off for 5 minutes. Then, the solution is transferred into a 100 m*l* separatory funnel, and niobium is determined by carrying out from the process of extraction of the MPA described in 3.1.

5.2 *Analytical results*

Table 3 shows the analytical results obtained with synsetic samples which are prepared by adding the niobium standard solution to various Japan Standard Steels. The results are

TABLE 3. DETERMINATION of NIOBIUM in PREPARED SAMPLES

No.	Nb added μg per 10 mg	Nb found μg	Sample used
1	12.5	15.0 13.5 12.0	J.S.S. No. 1 (d) Carbon steel
2	25.0	25.5 21.0 23.0	J.S.S. No. 4 (c) Carbon steel
3	37.5	37.5 38.5 39.0	J.S.S. No. 8 (a) Cr steel
4	25.0	27.5 27.5 28.0	J.S.S. No. 9 Cr-W-V steel V 0.64% W 19.3%

satisfactory considering precision of the calibration graph. High results of No. 4 sample seem to be due to mainly the high content of vanadium.

6. *Discussion*

Kambara et al.7) had already studied a.c. polarograms of MPA in the ternary mixture of methylisobutylketone-water-methylcellosolve containing a suitable electrolyte; that is,

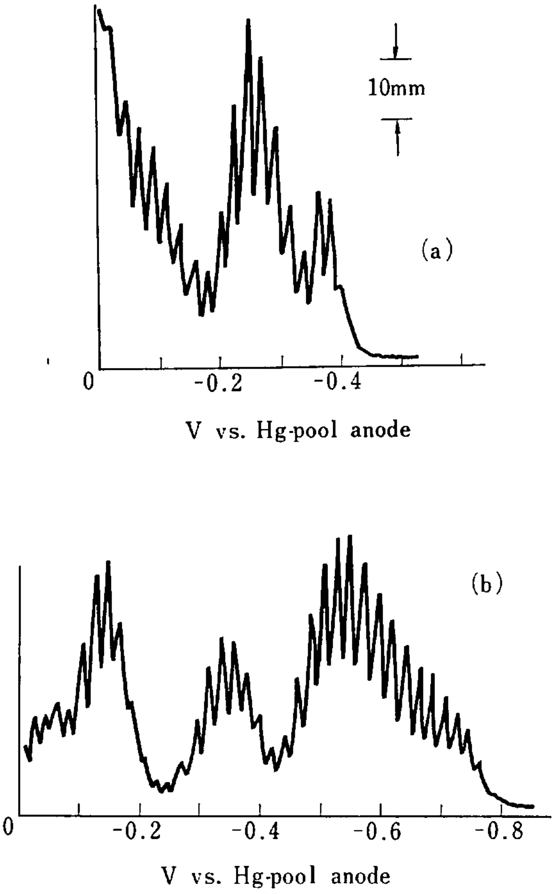

FIG. 2. A. C. POLAROGRAMS OF MOLYBDOPHOSPHORIC ACID COMPLEX

(a) P $25\mu g/25ml$; electrolyte solvent: a mixture of isobutanol, ethanol, hydrochlroic acid and water.
(b) Nb $25\mu g/25\,ml$; electrolyte solvent: same as Fig. 1. (polarograms not deaerated)

RP-50, Range $100\mu A/200\,mm$, Damp. 3, BF-50, a.c. Voltage 25 mV, Sens. 1, Compen. Cap. $0.3\mu g$.

mono peak appeared at —0.2 V vs. Hg in hydrochloric acid electrolyte and triple peak appeared at —0.24, —0.50 and —0.70 V vs. Hg, respectively, in a sulfuric acid electrolyte.

Fig. 2 (a) is the polarogram of the MPA obtained using hydrochloric acid in place of sulfuric acid used as the electrolyte in Fig. 1, and two peaks appeared at —0.25 and —0.36 V vs. Hg, respectively. Fig. 2 (b) is the polarogram produced in the electrolyte solvent obtained by the following procedure: the MNPA was formed in a 0.5 *N* sulfuric acid solution using the phosphate and molybdate solutions. After the MPA formed simultaneously was removed by extraction with isobutyl acetate from the solution, the MNPA was extracted with isobutanol, and the electrolyte solvent was prepared by treating the extract with the procedure described in 3.1. This polarogram has three peaks and each peak is at —0.16, —0.36 and —0.53 V vs. Hg, respectively; hence, the polarogram resembles one which Kambara and associates obtained in a sulfuric acid electrolyte. The electrolyte solvent of Fig. 2 (b) do not contain chloric ion at all, but that of Fig. 1 contains it, because extraction of the MNPA was carried out in a hydrochloric acid solution, then the organic solvent used was saturated with hydrochloric acid. When a quantity of hydrochloric acide is added to the electrolyte solvent of Fig. 2. (b), the polarogram of Fig. 2 (b) is changed into the shape of Fig. 2 (a). For the reason mentioned above, the following is decided: although sulfuric acid was apparently used as supporting electrolyte in Fig. 1, three peaks in sulfuric acid electrolyte did not appear and the polarogram produced in hydrochloric acid electrolyte was obtained. This is due to the hydrochloric acid saturated in the organic solvent used for extraction.

It is troublesome to determine niobium in iron and steel either by the gravimetric method or the absorption method, but, although attention is needed for the acidity of the solution to extract the MPA simultaneously formed, the recommended method is comparatively simple because it only consists of operation of selective extraction into an organic solvent, and the sensitivity is as same high as atomic absorption method. In addition, the free molybdic acid does not interfere, which is an advantage of the polarographic method.

After the sample is dissolved, the solution is twice evaporated to fumes of sulfuric trioxide in the recommended method. When the iron salts are evaporated to fumes of sulfuric trioxide with aid of heating, they turn into water insoluble salts, and the following operation is very troublsome, but the time of heating for evaporation is short, the deposited residue is easily soluble in water by gentle heating.

7. *Conclusion*

The MNPA complex was formed in a hydrochloric acid solution, and the MPA formed simultaneously was separated by extraction of isobutyl acetate. Then the MNPA in the aqueous phase was extracted with isobutanol. After the electrolyte solvent of the mono phase was prepared by adding ethanol, sulfuric acid and water to the extract, an a.c. polarogram of the MNPA was recorded, and $5 \sim 50 \mu g$ of niobium in steels was determined.

REFERENCES

1) G. Norwitz, M. Codell, *Anal. Chem.*, **26,** 1230 (1954).

2) A.L. Davydov, Z.M. Vaisberg, I.E. Burkser, *Zavod. Lab.*, **13,** 1038 (1947). C.A. 43, 4177e (1949).
3) K. Mukaewaki, *Japan Analyst*, **8,** 219 (1959).
4) R.M. Veisman, *Zavod. Lab.*, **25,** 552 (1959). C.A. 53, 16821 b (1959).
5) G.F. Kirkbright, A.M. Smith, T.S. West, *Analyst,* **93**, 292 (1968).
6) H. Asaoka, *Hitotsubashi Journal of Arts and Sciences,* Vol. 9, No. 1, p. 35 (1968).
7) T. Kambara, K. Hayashi, Y. Kamiya, *Rev. of Polaro.*, Vol. **12,** 71 (1964).