POLAROGRAPHIC DETERMINATION OF TRACES OF PHOSPHORUS, ARSENIC AND SILICON USING SOLVENT EXTRACTION OF MOLYBDENUMHETEROPOLY ACIDS

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Introduction

We know that phosphoric acid has been determined polarographically after phosphomolybdic acid complex was extracted with organic solvent and a homogeneous electrolyte solvent was prepared directly from the extract without further treatment such as evaporation or re-extraction.[1,2] Nevertheless, no other method has been proposed to determine micrograms of phosphoric acid with a high sensitivity in spite of the existence of the d.c. polarograph for measuring the maximum wave[3] produced by a molybdenum-hydrogen peroxide system in such a mixed solvent. The present author found perchloric acid to have the following unique property. A system of water-*iso*-butanol giving two phases can be homogenized to a single phase by adding a much smaller amount of the acid than sulfuric acid. It can then determine indirectly traces of phosphoric, arsenic and silicic acids by recording the maximum wave in a mixed solvent prepared by adding perchloric acid, hydrogen peroxide solution and water to one part of *iso*-butanol with which molybdenumheteropoly acids of phosphorus, arsenic and silicon were extracted. The present paper is an outline of the experimental results announced previously in Japanese.[4,5,6]

Reagents and Apparatus

All chemicals used were analytical reagent grade. Standard solutions of phosphorus, arsenic and silicon were prepared from suitable salts and stored in polyethylene bottles.

A Shimadzu polarograph, Model RP-2, was used. The electrolysis cells employed were H-type cell provided with a sintered glass disk between the two compartments. An aqueous saturated calomel electrode served as the reference electrode. The electrical connection between the S.C.E. and the solution in the H-cell was made by a KCL agar salt bridge. The height of the mercury reservoir was 76 cm. The experiments were carried out in a water thermostat at 25°C±0.2°C. The capillary used had a drop time of 4.58 seconds at 0.2 V and *m* value of 1.38 mg per second in the deaerated base solution composed of 0.5 *M* perchloric acid-*ca.* 0.2 *M* hydrogen peroxide-*ca.* 0.8 *M* *iso*-butanol.

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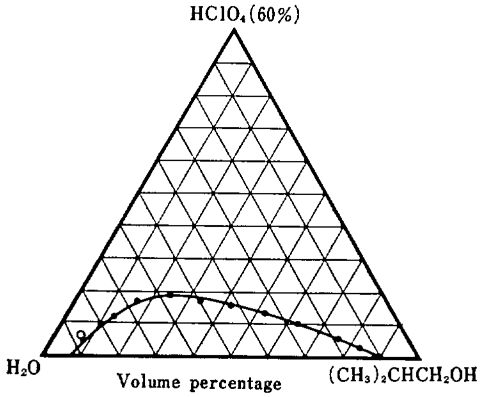
Experiments and Results

Phase diagram of iso-butanol-perchloric acid-water system

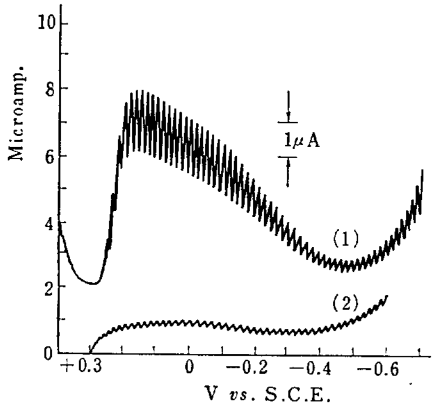
In order to determine the mutual solubility of the three components, *iso*-butanol, water and perchloric acid, perchloric acid (60%) was added dropwise from a burette into a vessel containing certain amounts of *iso*-butanol and water in varying proportions. The exact amount, in terms of volume of perchloric acid necessary to form a homogeneous solution was determined and plotted in the triangular phase diagram as shown in Fig. 1. The amount of

FIG. 1. PHASE DIAGRAM OF THE TERNARY SYSTEM



The recommended composition indicates the vicinity of the open circle point.

FIG. 2. POLAROGRAM OF MOLYBDATE IN AN AIR FREE SUPPORTING ELECTROLYTE OF 0.5 *M* PERCHLORIC ACID—*ca.* 0.2 *M* HYDROGEN PEROXIDE—*ca.* 0.8 *M* *ISO*-BUTANOL



(1) Molybdenum concentration: $5.2\times10^{-6}M$.
(2) Residual current.

perchloric acid sufficient to bring about a homogeneous solution was less than that of sulfuric acid.

Polarograms of molybdenum in perchloric acid-hydrogen peroxide-iso-butanol mixed solvent

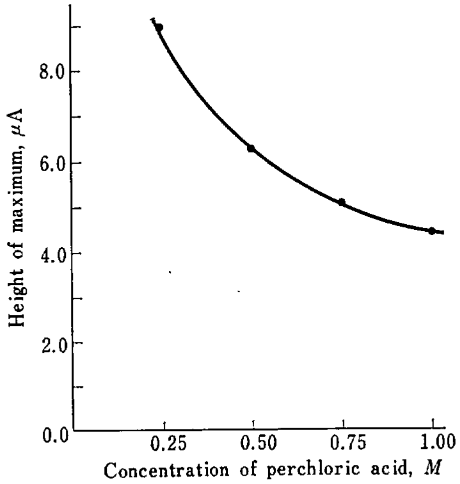
A definite volume of the molybdenum standard solution, 1.4 m*l* of perchloric acid, 2.0 m*l* of *iso*-butanol and 5.0 m*l* of hydrogen peroxide solution (3%), were taken into a 25 m*l* volumetric flask. The combined solution was made up to about 20 m*l* with water and shaken thoroughly to achieve a homogenized solution; the solution was then diluted exactly to 25 m*l* with water. An aliquot of the solution was poured in a polarographic cell, and the polarogram was recorded after deaeration for 10 minutes with purified hydrogen gas. Fig. 2 shows the

TABLE 1. RELATION BETWEEN THE HEIGHT OF MAXIMUM WAVE AND MOLYBDENUM CONCENTRATION

Molybdenum concentration ($\times 10^{-6} M$)	Height of maximum wave (μA)	$K = i_k/C$ ($\mu A/10^{-6} M$)
0.26	0.28	1.0
0.52	0.56	1.0
0.78	0.87	1.1
1.04	1.19	1.1
2.60	2.90	1.1
5.20	6.25	1.2
7.80	8.84	1.1
10.4	12.5	1.2
20.8	24.5	1.1
41.6	42.3	1.0
		Average 1.1±0.1

Supporting electrolyte: 0.5*M* perchloric acid-0.18*M* hydrogen peroxide-0.87*M* *iso*-butanol.

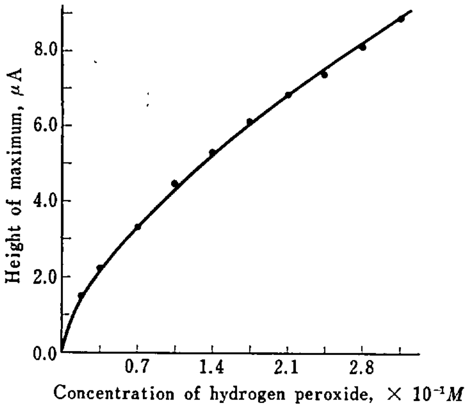
FIG. 3. EFFECT OF THE CONCENTRATION OF PERCHLORIC ACID ON THE MAXIMUM WAVE



Concentrations of molybdenum, hydrogen peroxide and *iso*-butanol were $5.2 \times 10^{-6} M$, 0.18*M* and 0.87*M*, respectively.

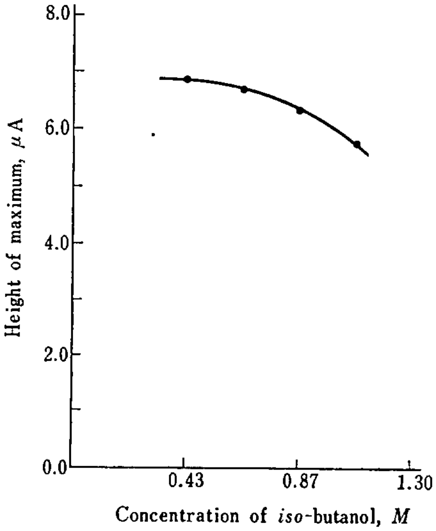
polarograms obtained. The wave did not run smoothly and first approached a trough near +0.3V before reaching its peak near +0.2V. As shown in Table 1, the relation between the concentration and the height of the maximum wave was in the form of direct proportionality below about $2\times10^{-5}M$ Molybdenum.

FIG. 4. EFFECT OF THE CONCENTRATION OF HYDROGEN PEROXIDE ON THE MAXIMUM WAVE



Concentrations of molybdenum, perchloric acid and *iso*-butanol were $5.2\times10\ ^{6}M$, $0.5M$ and $0.87M$, respectively.

FIG. 5. EFFECT OF THE CONCENTRATION OF *ISO*-BUTANOL ON THE MAXIMUM WAVE



Concentrations of molybdenum, perchloric acid and hydrogen peroxide were $5.2\times10^{-6}M$, $0.5M$ and $0.18M$, respectively.

With increasing concentrations of perchloric acid, the height of the maximum wave decreased as shown in Fig. 3. At more than 1.5 M the shape of the wave became poorly developed. At less than 0.25 M the height of the maximum wave was extremely tall, but widths of recorder oscillations were too large to measure them. Although the wave height increased with increasing concentrations of hydrogen peroxide, the relation of the concentration of hydrogen peroxide to the wave height had no linear function as shown in Fig. 4. The effect of the concentration of *iso*-butanol on the maximum wave is shown in Fig. 5. The most suitable concentration of *iso*-butanol was at the range of 0.4 to 0.9 M in 0.5 M perchloric acid; the shape of the wave became very poorly developed in concentrations less than 0.2 M and more than 1 M. Although it was not necessary to remove the disolved oxygen from the solution in measuring the height of the maximum wave, which appeared in the vicinity of +0.2V, deaeration made the shape of polarogram better so all test solutions were deaerated in subsequent experiments. When polarograms were recorded repeatly after insertion of the electrode, the wave height decreased gradually, and this decrease was about 3% for 15 minutes. This phenomenon seemed to be due to the decomposition of the solution when brought in contact with mercury. The temperature coefficient of the wave height was 6.9% at the range of 20° to 30°C.

Extraction of phosphoric, arsenic and silicic acids with iso-butanol

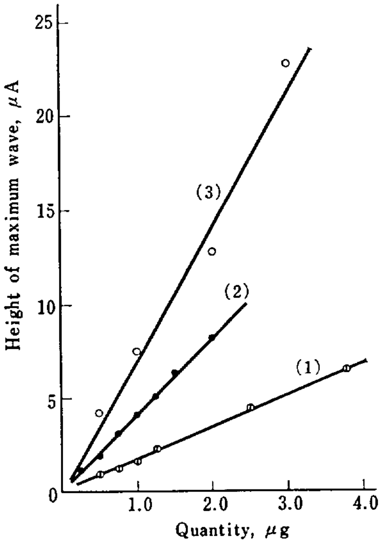
Various organic solvents have been used to extract the molybdenumheteropoly acids. Krjukowa *et al.*[1] used *iso*-butanol to extract the phosphomolybdic acid complex in 1 N sulfuric acid solution, and this method was then further studied in order to apply to arsenic and silicic acids.

A 10 ml of aqueous sulfuric acid solution containing a definite quantity of phosphoric or arsenic acid was taken into a 50 ml separatory funnel. After addition of 1 ml of ammonium molybdate solution (5%), the solution was shaken with 10 ml of *iso*-butanol for one minute and left to form two layers. The organic layer was separated and washed four times with 5 ml of 0.5 N sulfuric acid solution. A 2 ml portion of the extract was transferred into a 25 ml volumetric flask and after addition of 1.4 ml of perchloric acid and 5 ml of hydrogen peroxide solution (5%), a mixed solvent was prepared by the procedure above mentioned. An aliquot of the solution was taken into the polarographic cell, deoxygenated by hydrogen gas and the polarogram was recorded. The wave heights of maximum for phosphoric and arsenic acids were constant within the range of about 0.5 to 1 N and 0.4 to 0.7 N sulfuric acid concentration, respectively. The conditions for extraction of silicic acid with *iso*-butanol were first studied with an aid of colorimetry, and resultant conditions were adopted for the polarographic method. The procedure was as follows. 1 ml of ammonium molybdate solution (5%) was added to 20 ml of aqueous sulfuric acid solution containing silicic acid, and the solution was left to stand for 15 minutes. Then, after addition of 10 ml of 9N sulfuric acid solution, the solution was transferred into a 50 ml separatory funnel immediately and shaken with 10 ml of *iso*-butanol for one minute to extract the complex formed. Using a 2 ml of aliquot of the extract, washed four times with 5 ml of 2 N sulfuric acid solution in a 25 ml volumetric flask, a mixed solvent was prepared by the above-mentioned procedure. The silicomolybdic acid complex in this solvent did not transform instantly into peroxymolybdic acid under room temperatures different from the heteromolybdic acids of phosphorus and arsenic, therefore the mixed solvent prepared needed to be heated by dipping into a water bath of 70° to 80°C for 30 minutes in order to finish the transformation. The maximum wave height for silicon was only constant when the formation of the complex was carried out at the range of pH 1.20 to 1.75. The molybdate ion added to form those complexes produced the same maximum wave; therefore it was mostly necessary for successful determination of phosphorus, arsenic and silicon to remove the free molybdate ion in the extract by washing. The maximum wave caused by the free molybdate ion was negligible by washing out four times with 5 m*l* of 0.5 or 2 *N* sulfuric acid solution.

Caribration Curve

The relation between the amount of phosphorus, arsenic and silicon, each taken in aqueous sample solution and the corresponding molybdenum peak height in the mixed solvent was found to be linear, as shown in Fig. 6. The determinable amount of phosphorus, arsenic and silicon were about 0.1~2 μg, 0.5~13μg and 0.2~5μg, each. The reproducivility of each calibration curve was about 2% for phosphorus and arsenic and 8% for silicon, respectively, as coefficients of variation. For the determination of silicon by the proposed method, the most attention was also payed to the amount of silicic acid which was contained in the water used in experiments. The water used in this experiment was prepared by distilling the water treated with ion-exchange resin, and the amount of silicon in it was about 0.02 p.p.m. It was very difficult to prepare pure water less than this amount.

FIG. 6. CALIBRATION CURVE



Curve (1): As μg/10 m*l*
Curve (2): P μg/10 m*l*
Curve (3): Si μg/20 m*l*.

Influence of Diverse Ions

As neither silicomolybdic acid complex nor germanomolybdic acid complex were formed under the experimental conditions above described, the existence of silicon and germanium were not harmful for determining phosphorus and arsenic. Vanadium (V) and zirconium (IV) hindered the extraction of molybdenumheteropoly acids of phosphorus and arsenic into *iso*-butanol, so the heights of the maximum waves decreased. The allowable quantity of coexisted vanadium (V) was up to each $25\mu g$ for determining phosphorus and 1 mg for arsenic. Zirconium (IV) less than $50\mu g$ was not harmful for either phosphorus and arsenic. Arsenic was removed by the bromide evaporation method and phosphorus was separated by the prior extraction of the sample solution with butylacetate for determining each phosphorus and arsenic. Germanium (IV) behaved in the same fashion as silicon, and interfered with the determining of silicon. Disturbance of phosphorus and arsenic for the extraction of silicomolybdic acid was eliminated by increasing the acidity of the solution at which the complex was formed with concentrated sulfuric acid. The molybdate used to produce the complex was decomposed by the coexisted ferric ion, the solution became turbid, and the extraction was hindered. The turbidity did not occur in less than 5 mg of ferric ion. The decomposition caused by existence of much ferric ion could be prevented successfully by addition of ammouinu sulfate.

Analytical Application of the Method for Steels

(1) *Procedure for phosphorus*

A 0.1 g of sample was dissolved in 10 m*l* of nitric acid (1+2) with the aid of heat and boiled for short time to remove nitrogen gas. Potassium permanganate solution (5%) was added dropwise until oxides of manganese were precipitated, the solution was then cleared by addition of a few drops of sodium nitrite solution (0.5%). After the excess of nitrus acid was driven off by boiling, 9 m*l* of sulfuric acid (1+1) was added to it, and the solution was evaporated to sulfur trioxide fumes. The residue was dissolved by heating with about 10 m*l* of water followed by the addition of 1 g of potassium bromide and evaporation to sulfur trioxide fumes again. The residue was dissolved with water and the solution was diluted to exactly 200 m*l*. A 10 m*l* aliquot of the solution was taken into a 50 m*l* separatory funnel. From this time forth, the electrolyte solvent was prepared by the treatment as described above, and the maximum wave was recorded. 0.03~0.002% of phosphorus were able to be determined by this method.

(2) *Procedure for arsenic*

A 0.1~0.2 g sample was dissolved by heating with 10 m*l* of Aqua regia and evaporated nearly to dryness. The residue was dissolved in 20 m*l* of 2.5 *N* hydrochloric acid, and the solution was diluted to exactly 100 m*l* with water, and a 25 m*l* portion of the solution was transferred into a 50 m*l* separatory funnel. Then after addition of 1 m*l* of ammonium molybdate solution (5%), the phosphomolybdic acid formed was extracted three times 5 m*l* of butylacetate. The aqueous layer transferred to a beaker was evaporated to fumes of sulfur trioxide after addition of 0.9 m*l* of 6 *N* sulfuric acid and 1 m*l* of concentrated nitric acid. The residue was dissolved with a few m*l* of water, and the solution was transferred to a separatory funnel with an aid of water followed by the adjustment to about 10 m*l* with water. From this time forth, arsenomolybdic acid was extracted with *iso*-butanol, and the electrolyte solvent was prepared by the above-mentioned procedure. The method was applicable to the samples containing 0.05~0.001% arsenic and up to 0.04% phosphorus. The extraction of phosphorus with butylacetate is said to be hindered by coexistence of Ti, Zr, Sn, etc., and phosphorus remains in the aqueous layer.[7] Therefore, more investigations must be made with regard to the application of the prior extraction of the sample solution with butylacetate in the procedure for arsenic.

(3) *Procedure for silicon*

As quantities of silicic acid contained in reagents and water used were relatively high to the sensitivity of the proposed method, it mattered that they were first purified to give full play to the method. Then, for steels another method, different from Grasshoff's[8,9] and Kemula's,[10] was adopted by which the polarogram of silicomolybdic acid alone was recorded; however the sensitivity of this method was lower than that of the one previously described. A 0.25 g of sample was decomposed with 12 m*l* of sulfuric acid (1+6) and 5 m*l* of hydrogen peroxide solution (15%). The excess hydrogen peroxide was removed by boiling. After addition of 5 g of ammonium sulfate the solution was transferred into a 100 m*l* volumetric flask and filled to the mark with water. A 20 m*l* aliquout of the solution was taken into a 50 m*l* separatory funnel, 4 m*l* of ammonium molybdate solution (10%) was added, and allowed to stand for 4 minutes. After adding 12 m*l* of 9 *N* sulfuric acid, immediately the complex formed was extracted with 10 m*l* of *iso*-butanol. The extract washed with 5 m*l* of 2 *N* sulfuric acid solution four times was transferred into a 25 m*l* volumetric flask and filled with 8 m*l* of ethanol and water to the mark. A portion of the solvent was transferred to a H type-cell, the dissolved air was removed with hydrogen gas, and the polarogram appeared at 0~0.8 V range was recorded. 0.2~0.01% of silicon could be determined.

Analytical Results

The procedures were tested by analyzing some plain and alloy steels supplied by the Japan Iron and Steel Association. The averages of determinations are shown in Table 2.

TABLE 2. DETERMINATION OF PHOSPHORUS, ARSENIC AND SILICON IN STEELS

Element determined	Type of steel	J.I.S.S. No.	Certificate value %	Found %	Number of determination
P	Carbon steel	1a	0.019	0.017	3
	〃	1d	0.037	0.035	2
	〃	5d	0.027	0.025	2
	Ni-Cr steel	10a	0.012	0.012	3
As	Carbon steel	1a	0.0108*	0.0125	2
	〃	1d	0.0259*	0.0238	2
	〃	4c	0.0106*	0.0123	2
	Ni-Cr steel	10a	0.0559*	0.0517	2
Si	Carbon steel	4b	0.145	0.144	4
	〃	5d	0.077	0.075	4
	Cr-W-V steel	9	0.10	0.103	4
	Ni-Cr steel	10a	0.21	0.211	4
	Cr steel	8	0.220	0.231	4

* These figures are the author's experimental values obtained by the colorimetric method of JIS G-1225, and not the certificate values.

Conclusion

The procedures using the maximum wave for phosphorus, arsenic and silicon had as high a sensitivity as the heteropoly blue procedure of colorimetry, the precision was also good. In the polarographic determination of silicon, it was effective to use the extraction method of silicomolybdic acid complex alone.

Aknowledgements

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