An Improved Method for Measuring Phosphorus Using Spectrophotometry

By J.L. Mullen

An improved method for the measurement of phosphorus, using spectrophotometry, is described. This method makes use of selective optical absorption at wavelengths of 704 μm. This absorption results from the formation of a phosphorus-molybdenum complex. It is shown that this optical technique has significant advantages over previously used techniques in terms of speed and long stability (24 hr) of the complex. The method is especially suitable for the measurement of phosphorus in nickel-phosphorus (Ni-P) alloys.

Electrochemically produced alloys of Ni-P are widely used in industry. Their structure and properties are closely linked to the phosphorus content. It is important, therefore, to have an accurate, rapid way of determining this value. These alloys are crystalline if the phosphorus content does not exceed 7 or 8 weight percent.[1] The phosphorus concentration is inversely proportional to the hardness and directly proportional to corrosion performance and contact resistance.[1,2] Nickel-phosphorus alloys with less than two atomic percent are used for low contact resistance to replace gold when contact resistance values up to 50 mΩ are desired.[3] For these reasons, it is important to have a quick and accurate means of measuring phosphorus concentration.

Typical conventional phosphorus measurements include alkalimetric, gravimetric, inductively coupled argon plasma (ICAP), and spectrophotometry. Another method occasionally used is an indirect technique in which the nickel content is determined by an analytical method, and the phosphorus content is determined by the difference. This technique requires the alloy to be a pure binary.

In the usual alkalimetric method,[4] phosphorus is separated as a yellow ammonium phosphomolybdate complex. This precipitate is collected and dissolved in a standardized sodium hydroxide solution; the excess is back-titrated with a standardized nitric acid solution. This method requires a considerable amount of time, and is very tedious.

The gravimetric method[5] is similar to the alkalimetric method in that the precipitate of ammonium phosphomolybdate is collected and weighed, and the amount of phosphorus is determined by the weight of the precipitate. The accuracy and precision of this method are influenced by the environmental conditions of the yellow precipitate. Slight changes in pH, temperature, and the amount of ammonium molybdate as a precipitant will produce similar changes in the composition of the precipitate; therefore, the sample size is directly proportional to the accuracy of the measurement. Because the phosphorus atoms are not chemically combined ($(NH_4)_3PO_4 \cdot 12MoO_3 \cdot H_2O$) with the molybdenum atoms, the ideal ratio of 1:12 is not always the same.

The ICAP method[6] is considered to be the most reliable for phosphorus analysis. Because this method requires very expensive analytical equipment, it is not practical for every laboratory. The precision of the method is about one percent. As the detection limit is approached, however, the precision ca decrease to as much as five percent. The accuracy of th method is limited chiefly by the precision because interference can be reduced to a minimum.

The molybdivanadophosphoric acid and the phosphomolybd acid methods[7,8] are the two most commonly used spectroph tometric methods, and both are similar, but this paper will de only with the improvement of the phosphomolybdic acid metho When the molybdivanadophosphoric method was publishe precision and accuracy were not required in the report, and th original data are no longer available. In the phosphomolybd acid method, precision is not mentioned, but the maximu error is 0.003 percent.

A new spectrophotometric procedure utilizes the formati and reduction of phosphomolybdic acid. This procedure i volves an acid molybdate solution containing ascorbic acid. phosphomolybdenum blue color, rapidly formed by addition antimony to the solution, lends itself to accurate spectrophot metric determination of phosphorus. The maximum error ass ciated with this method has been shown to be one percent.

Experimental Procedure

Phosphorus can be quantitatively determined by finding t optical density measured at 704 μm (absorbance) phosphomolybdenum blue formed by the reduction phosphomolybdic acid with ascorbic acid. The maximum inte sity of the blue color is formed within eight min, and the colo stable for at least 20 hr. The phosphomolybdenum blue produced by a single reagent, and antimony causes this ra color change. A typical absorption spectrum made with spectrophotometer is shown in Figure 1.

Four reagents are mixed to make the final reagent. T mixed reagent is not very stable, and should be used within hours. These reagents are shown in Table 1.[9]

Table 1
Reagents Required

70 mL conc. H_2SO_4 in 500 mL H_2O
20.0 g $(NH_4)_6\,Mo_7\,O_{24} \cdot 4H_2O$ in 500 mL H_2O
(Ammonium molybdate)
1.32 g $C_6H_8O_6$ in 75 mL H_2O
(Ascorbic acid)
0.2743 g $K(SbO)C_4H_4O_6 \cdot {}^1\!/_2\,H_2O$ in 100 mL H_2O
(Potassium antimonyl tartrate)
Mixed reagent for test:
a. 125 mL H_2SO_4 and 37.5 mL ammonium molybdate, thoroughly mixed.
b. Add 75 mL ascorbic acid and 12.5 mL potassium antimonyl tartrate. Total volume of the mixed reagent: 250 mL.

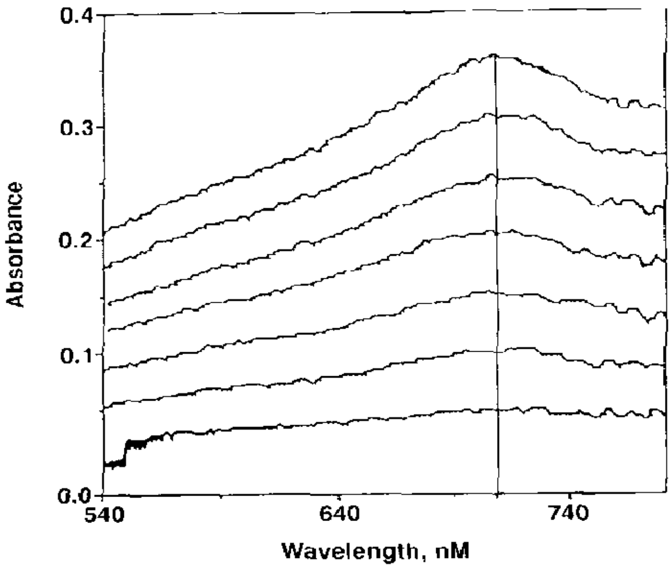

Fig. 1—Typical spectrum of phosphorus from 0 to 35 µg/mL.

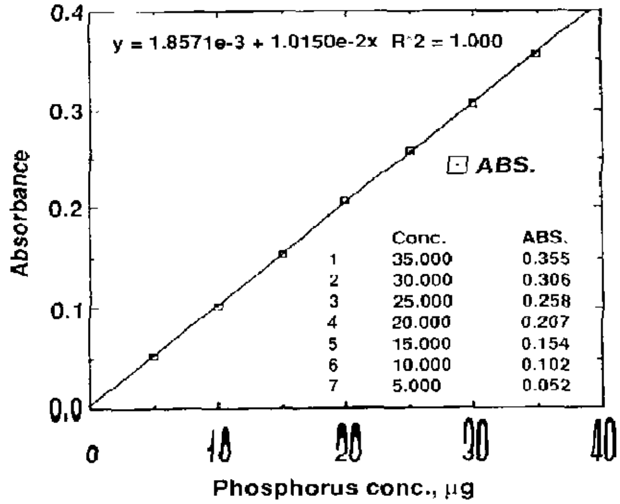

Fig. 2—Calibration curve of phosphorus made from fresh solutions.

A standard solution is prepared by first dissolving 4.386 g of potassium dihydrogen phosphate (KH_2PO_4) in one liter of water. This solution contains 1.000 g of phosphorus as orthophosphate (PO_4^{-3}). The solution is then diluted (1:100), so that the resulting concentration of phosphorus is 10 µg/mL. Initially, an unknown sample with a known weight is placed in a 250-mL Erlenmeyer flask. The sample is dissolved in 4 mL of 1:1 HNO_3 and 1 mL of three-percent H_2O_2 added to ensure that all the phosphorus has been oxidized to orthophosphate (PO_4^{-3}). The sample is heated to near dryness to expel all NO_2. The flask is thoroughly rinsed, and the rinse solution is diluted to the mark in a 200-mL volumetric flask. This 200 mL represents the stock unknown solution to be analyzed.

Following this step, 40 mL of H_2O are pipetted into a 50-m volumetric flask. One mL of the stock unknown solution an eight mL of the mixed reagent are added and diluted to 50 m with distilled water. After mixing, within eight min the solutio will turn a bright blue color because of formation of th phosphomolybdenum blue complex. A calibration curve i constructed in this same manner by using the standard stoc solution. Because each mL contains 10 µg of phosphoru increments of the standard stock solution are added to the 5C mL volumetric flasks until the unknown sample is within th concentration of the known.

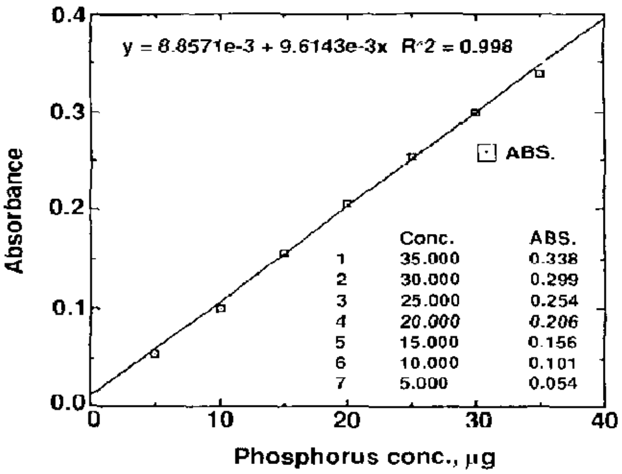

Fig. 3—Calibration curve of phosphorus made from the solutions of Fig. 2 afte 20 hr.

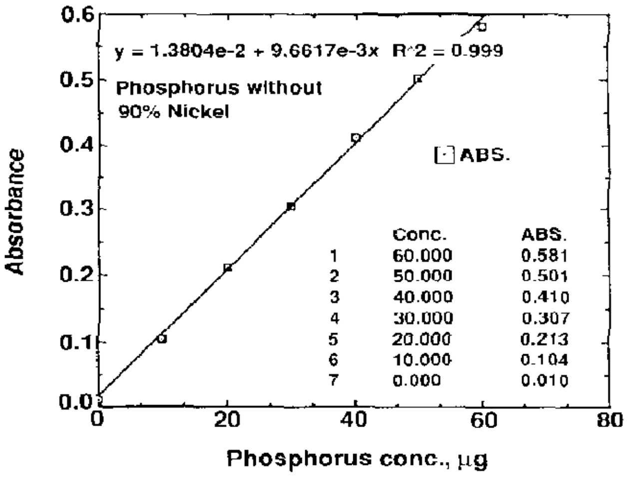

Fig. 4—Calibration curve of phosphorus from 10 to 60 µg/mL (first data set).

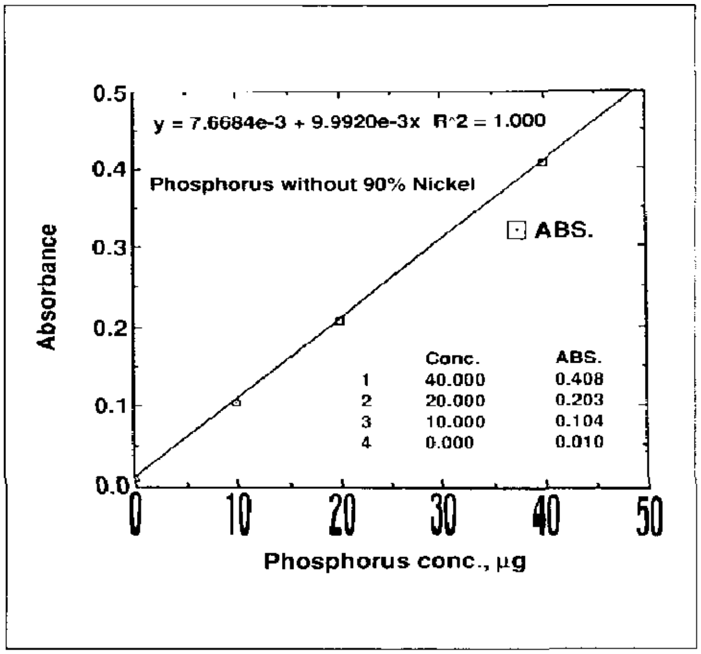

Fig. 5—Calibration curve of phosphorus from 10 to 40 μg/ml (second data set).

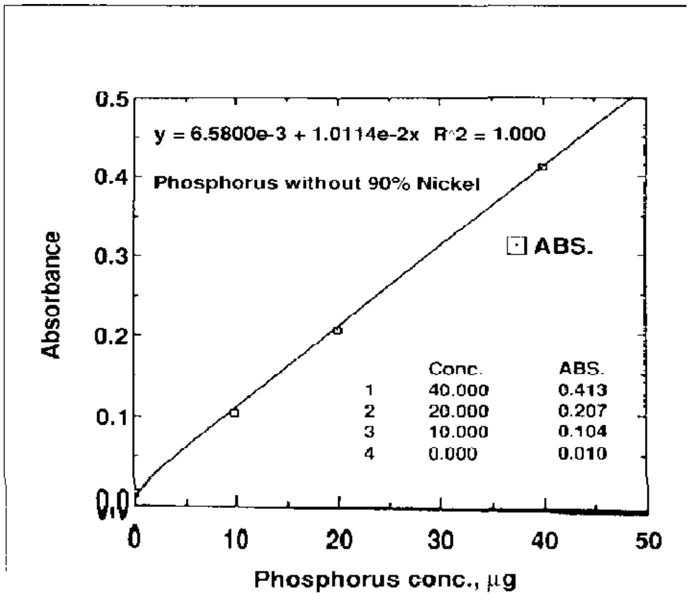

Fig. 6—Calibration curve of phosphorus from 10 to 40 μg/mL (third data set)

Results and Discussion

A calibration curve made from fresh standard stock solution is shown in Fig. 2. A calibration curve made from the same solutions after 20 hr is shown in Fig. 3. The data indicate that a reliable analysis can be made from solutions prepared for at least 20 hr. To test interference by nickel, solutions of 90 percent nickel-10 percent phosphorus were made, inasmuch as the standards will contain approximately 90 percent nickel. Three sets of solutions, consisting of four solutions each, were made to complete this test. The results are shown in Figs. 4, 5 and 6. Figure 4 shows the concentration of the first six sets of phosphorus samples without nickel. Figure 5 shows the results of the second set of data without nickel. Each of these two sets was made from entirely different solutions.

Figure 6 shows the results of the third set of data with the 90-percent nickel solution, and the 10, 20, and 40 μg/mL concentrations are also common to the first set of data. The absor bance value for the third set of data at 40 μg/mL is slightly highe at 0.413. Because the first and second sets of data were 0.41 and 0.408 respectively, there is strong evidence of a dilutio error other than the error resulting from the presence of nickel Such an error is indicative of the sensitivity of the method.

The absorbance for the third set of data at 20 μg/mL is slightl lower at 0.207 than the first and second data, indicating that th presence of nickel does not interfere with the phosphoru analysis. Because the absorbance of all three 10 μg/mL solu

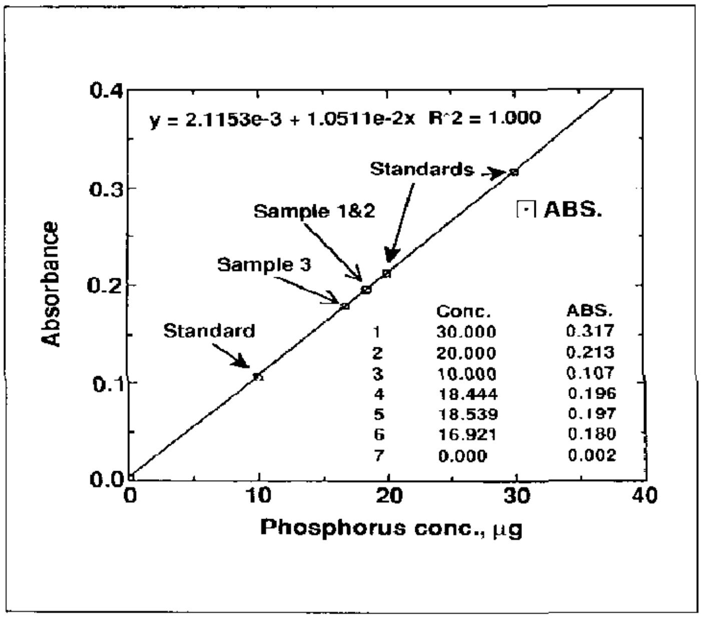

Fig. 7—Calibration curve of phosphorus with three samples.

Table 2
Results of Spectrophotometric Analysis

A. Spectrophotometry (P)

1. $$\text{Sample 1} = \frac{(18.444\ \mu g/mL)(200\ mL)(10^{-6})(100)}{\text{Wt. of sample } (0.04124)} = 8.94\%\ P$$
2. $$\text{Sample 2} = \frac{(18.539\ \mu g/mL)(200\ mL)(10^{-6})(100)}{\text{Wt. of sample } (0.04160)} = 8.91\%\ P$$
3. $$\text{Sample 3} = \frac{(16.921\ \mu g/mL)\ (200\ mL)(10^{-6})(100)}{\text{Wt. of sample } (0.04286\ g)} = 7.9\%\ P$$

B. Atomic absorption (Ni)

1. $$\text{Sample 1} = \frac{(3.762\ \mu g/mL)(50)(200\ mL)(10^{-6})(100)}{\text{Wt. of sample } (0.04124\ g)} = 91.22\%\ N$$
2. $$\text{Sample 2} = \frac{(3.773\ \mu g/mL)(50)(200\ mL)(10^{-6})(100)}{\text{Wt. of sample } (0.04160)} = 90.70\%\ N$$
3. $$\text{Sample 3} = \frac{(3.957\ \mu g/mL)(50)(200\ mL)(10^{-6})(100)}{\text{Wt. of sample } (0.4286\ g)} = 92.32\%\ N$$

C. Total Nickel and Phosphorus

Sample 1: 100.16%
Sample 2: 99.61 %
Sample 3: 100.22%

tions was the same (0.104), the conclusion is that nickel does not interfere. J. Murphy and J.P. Riley reported that no interference is caused by 500 µg of copper, 2500 µg of iron, or 500 µg of silicate in the presence of 10 µg of phosphorus,[9] which is well within the working experimental range. This suggests that this technique may be suitable for determining phosphorus in steels.

In order to check the accuracy of this technique, three deposit samples were analyzed for their phosphorus and nickel contents, and the sum of their weights was 100 percent.[10] The phosphorus results of the spectrophotometric analysis are shown in Fig. 7; the nickel content was determined by atomic absorption. The amounts of phosphorus and nickel of the three different samples are shown in Table 2.

Conclusions

The advantages of this procedure, compared to previous phosphorus determinations, are:

1. Lack of interference with the analysis by other elements.
2. Heat is not required for rapid production of the phosphomolybdenum blue color.
3. More than one analysis of a sample can be made.

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