Table I. Determination of Rhenium in Tungsten Alloys

Rhenium, Nominal, %	Rhenium, Found, %			Average, %
10	10.2	10.0	10.3	10.2
5	4.95	4.92	4.90	4.92
3	2.78	2.76	2.79	2.78
1	0.97	0.98	0.96	0.97
1/4	0.28	0.29	0.28	0.28

column were obtained by taking an aliquot from the solution of a 0.4- to 0.5-gram sample while the values in the third column were obtained with duplicate individual samples which ranged from <0.02 gram for the 10% alloy to 0.3 gram for the 1/4% alloy. The precision of the determination is within 3% of the rhenium content, over the range of alloy compositions tested.

DISCUSSION

The Na_2WO_4 serves as a preservative for the tartaric acid, but is used to provide a minimum of 0.5 gram of tungsten per 100 ml. in the final solution, and thus minimize errors due to slight changes in the absorbancy with changes in tungsten concentration. This effect is greatest at low concentrations of tungsten. Thus, a solution of 1.00 mg. of rhenium in 100 ml. appeared to contain 1.05 mg. when 0.2 gram of tungsten was added, and 1.06 mg. with 1 gram of tungsten. The calibration curve departed slightly from Beer's law in exhibiting a small degree of curvature, but was closely fitted by two straight lines over the 0 to 1 and 1 to 2 mg. per 100 ml. of rhenium ranges. The yellow color of the rhenium complex develops rapidly and is stable for at least 2 hours. Transmittance measurements were made at 385 mμ instead of at the 400-mμ absorbance peak (*4*) to extend the range of rhenium concentration.

ACKNOWLEDGMENT

The author thanks Lutfi Amra of this laboratory for supplying the alloy samples.

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Spectrophotometric Determination of Phosphorus as Molybdovanadophosphoric Acid. Application to Air-Borne Particulate Matter

Sir: In an effort to apply the nitric-perchloric acid, wet-ashing technique of Rogers (*2*) to air-borne compounds of phosphorus collected on membrane filters and filter papers, difficulties were experienced in obtaining reproducible results by the subsequent colorimetric procedure outlined by Rogers. The discrepancies in the results appeared to be related to the amount of perchloric acid present at the time of color development.

A study of the effect of acid concentration failed to support the conclusions of Rogers and of Quinlan and DeSesa (*1*) that a final perchloric acid concentration of $0.4M$ is optimal for color development by the molybdovanadophosphoric acid method, but shows rather that a concentration of 1 16M is more appropriate.

On the basis of this study, a modified procedure is presented for the determination of phosphorus by the molybdovanadophosphoric acid method directed primarily to the analysis of samples requiring ashing such as are obtained when air-borne organic and inorganic phosphorus compounds are collected by means of membrane filters or filter papers.

APPARATUS AND REAGENTS

All measurements were made with a Beckman Model DU spectrophotometer.

Perchloric Acid, $2.8M$.

Nitric-Perchloric Acid Mixture. Dilute 162 ml. of 70% perchloric acid to 1 liter with concentrated nitric acid.

Vanadate Reagent, $0.02M$ in $0.4M$ perchloric acid. Dissolve 1.17 grams of ammonium metavanadate in 400 ml. of water. Add 17.2 ml. of 70% perchloric acid and dilute to 500 ml. with water.

Molybdenum Reagent, $0.2M$. Dissolve 35.3 grams of ammonium molybdate tetrahydrate in water and dilute to 1 liter.

Standard Phosphorus Solution, 50 μg. of P per ml. Dissolve 0.2236 gram of National Bureau of Standards potassium dihydrogen phosphate in water and dilute to 1 liter.

PROCEDURE

Standard Curve. To a series of 25-ml. volumetric flasks, add increments of the standard phosphorus solution to provide a range up to 300 μg. of P. Add in order, mixing after each addition: 10 ml. of $2.8M$ perchloric acid, 2.5 ml. of $0.02M$ vanadate reagent, and 5 ml. of $0.2M$ molybdenum reagent. Add water to the 25-ml. mark of the flasks, mix, and allow to stand at least 4 minutes. Measure the absorbance in a 1-cm. cuvette at 400 mμ using a reagent blank as reference.

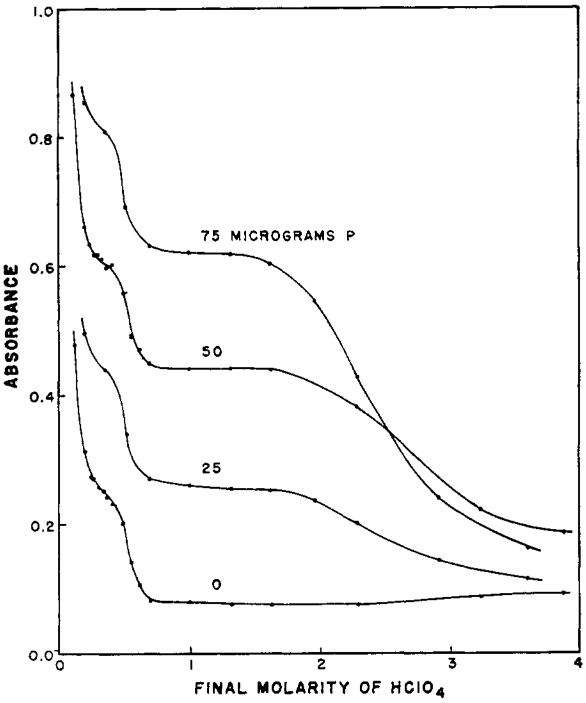
Samples. Transfer the membrane filter or filter paper containing the sample to a 125-ml. conical, Phillips beaker, and add 20 ml. of the nitric perchloric acid mixture. Heat at the boiling point on a hot plate until all of the nitric acid has been volatilized and the white fumes of perchloric acid appear. The volume of acid remaining in the beaker at this point should be about 3 ml. Cool and add about 5 ml. of water. Repeat the evaporation to fumes of perchloric acid to assure complete removal of the nitric acid.

The amount of perchloric acid in 20 ml. of the nitric-perchloric acid mixture is such that the acid concentration on color development will be within the optimal range of 0.7 to $1.7M$ even if 50% of the perchloric acid is fumed off. When the phosphorus content of the sample is known to be within the range of the standard curve, the perchloric acid solution of the sample may be washed into a 25-ml. volumetric flask with 10 ml. of water, and the color developed as for the standards except that the 10 ml. of $2.8M$ perchloric acid is omitted.

If the approximate phosphorus content is unknown, the sample should be transferred to a 10-ml. volumetric flask and 5 ml. should be taken for the analysis. To preserve the correct acidity, 5 ml. of $2.8M$ perchloric acid is added followed by the vanadate and molybdenum reagents—i.e., the volume of sample aliquot and volume of $2.8M$ perchloric acid should total 10 ml.

EXPERIMENTAL

The effect of perchloric acid concentration on the colors which are obtained with the molybdovanadophosphoric acid method was investigated by varying the



◄ Figure 1. Variation of absorbance of molybdovanadophosphoric acid with concentration of perchloric acid

amount of perchloric acid at four different levels of phosphate concentration. The first series represented blanks with no added phosphate, and the other three series contained 25, 50, and 75 µg. of P, respectively, in 25 ml. of final volume. The results of this investigation are given in Figure 1 in which the absorbances obtained are plotted against the final perchloric acid concentration. The data show that an inflection occurs in the region of 0.4*M* perchloric acid, which is the acid concentration stated by Quinlan and DeSesa (*1*) to be optimal, and corroborate the conclusions of these authors in the limited range of acidities investigated (from 0.2*M* to 0.8*M*). The present investigation reveals a broad plateau in the 0.7 to 1.7*M* region of acidity within which the depth of color is essentially independent of variations in acidity. Further tests have shown no changes in the characteristics of the plateau region at phosphorus concentrations as high as 300 µg. in 25 ml. of solution. This region of acidity is also more appropriate from the standpoint of the lower blank absorbance which is one third of the absorbance of a blank at an acid concentration of 0.4*M*.

The existence of this broad plateau has additional significance in that perchloric acid may be used in wet-ashing of samples without the necessity for exacting control of the amount of perchloric acid fumed off.

The amount of perchloric acid selected for the preparation of the standard curve provides an acid concentration of 1.16*M*, the midpoint of the plateau region, while the amount of perchloric acid in the nitric-perchloric acid mixture would correspond to a final perchloric acid concentration of 1.54*M* if none were volatilized. A variable amount of perchloric acid is volatilized in the ashing process, but a considerable margin of safety is provided by the width of the plateau region.

Beer's law was found to apply at least to an absorbance of 1.41 in a 1-cm. cuvette at a phosphorus concentration of 375 µg. per 25 ml.

Comparative rates of color development at perchloric acid concentrations of 0.44*M* and 1.16*M* were obtained for reagent blanks and solutions containing 1 µg. of phosphorus per ml. The data, presented in Table I, show that the color development at an acid concentration of 1.16*M* is essentially complete within a few minutes and that subsequent drift over a 24-hour period is slight. The color intensity at 0.44*M*, extrapolated to zero time, is the same as at 1.14*M*, but the absorbance values increase with time.

As a test of the comparative precision at the two acid concentrations, 50-µg. amounts of phosphorus were carried through the nitric-perchloric acid digestion according to the present procedure, and the procedure given by Rogers. The mean of the absorbance values obtained in six determinations by the present procedure was 0.4992 with a standard deviation of 0.0029 representing 0.4 µg. of phosphorus. The mean absorbance value of six determinations by Rogers' procedure was 0.8537 with a standard deviation of 0.0644 representing 9.2 µg. of phosphorus.

Table I. Comparison of Rates of Color Development at Different Perchloric Acid Concentrations

Concentration, $HClO_4$	Phosphorus, µg.	Absorbance *vs.* Water in a 4-Cm. Cell			
		2 minutes	15 minutes	3 hours	24 hours
1.16*M*	Blank	0.142	0.142	0.143	0.142
1.16*M*	50	0.496	0.499	0.502	0.494
0.44*M*	Blank	0.186	0.246	0.513	0.700
0.44*M*	50	0.534	0.632	0.848	0.868

RESULTS

A standard curve was prepared using phosphorus concentrations up to 150 µg. per 25 ml. of solution. Matched test tubes (*3*), 22 mm., were used as cuvettes. Computation by the least squares method revealed a slope corresponding to 138.3 µg. of phosphorus per unit absorbance. A similar curve was obtained by adding the identical increments of standard phosphorus solution to 47-mm. membrane filters which were then carried through the ashing process. A slope of 138.6 was found for the second curve; the deviation between the two curves was only 0.2%.

The displacement of the two curves indicated a mean blank value of 6.84 µg. of phosphorus for the membrane filters. The maximum deviation of any of the points in the second curve was 1.2 µg. of phosphorus.

It was evident that membrane filters could be used for sampling of air-borne phosphorus compounds, provided that a representative blank filter was carried through the ashing process and that sufficient sample was collected to override the variation in phosphorus content of the filters.

DISCUSSION

With respect to choice of acid concentration, the experimental data support the earlier work of Willard and Center (*4*) in which the use of perchloric acid was suggested for the reduction of interference by iron. These authors found that the interference of iron could be further reduced by reading the color at 450 mµ but at the expense of sensitivity.

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