

## REFERENCE.

- (1) Nekrasova, *Arch. Pharm.*, 266, 595 (1928); through *C. A.*, 23, 474 (1929).

The author takes this opportunity to acknowledge the help of Mr. Robert F. Ervin in determining the constants in this work.

## A NOTE ON THE MAGNESIA MAGMA HEAVY METALS TEST.\*

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The U. S. P. XI test for heavy metals in magnesia magma is as follows:

"To 5 cc. of Magnesia Magma, add 10 cc. of diluted hydrochloric acid and 10 cc. of distilled water, mix thoroughly, and filter if necessary. Warm the solution to 50° C., add 25 cc. of freshly prepared hydrogen sulfide T.S., and allow the mixture to stand at room temperature for ten minutes. When viewed in a Nessler tube, looking downward through the column of liquid above a white surface, the solution does not show a deeper coloration than that produced by 25 cc. of distilled water, to which 0.5 cc. of lead nitrate solution, containing 0.1599 Gm. of lead nitrate in 1000 cc. of distilled water, has been added, and treated as directed in the foregoing procedure for the Magnesia Magma."

If one follows the directions for the preparation of the standard lead sulfide sol literally he would add 0.5 cc. of lead nitrate solution to 25 cc. of distilled water, followed by 10 cc. of diluted hydrochloric acid, 10 cc. more of distilled water and, after heating to 50° C., 25 cc. of hydrogen sulfide T.S. As the volume of a standard prepared in this manner is slightly over 70 cc. the analyst, realizing that something is wrong, may simply add 25 cc. of hydrogen sulfide T.S. to a mixture of 0.5 cc. of lead nitrate solution and 25 cc. of distilled water, or he may reason that 5 cc., rather than 25 cc., of distilled water is to be mixed with the lead nitrate solution and then "treated as directed in the foregoing procedure for the Magnesia Magma," *i. e.*, adding diluted hydrochloric acid, distilled water and hydrogen sulfide T.S. In consequence of the ambiguity of the official directions at least three different methods of preparing the standard solution have been used. Briefly, the outcome has been that the test is either too stringent or too lenient, for the color produced in an acidified standard is almost imperceptible and very few magmas pass the test, while the light brown color of the non-acidified standard is sufficiently pronounced to allow practically all magmas, some of which may contain excessive quantities of heavy metals, to meet the requirements.

It may be stated here that the correct procedure in preparing the standard, according to a communication from the Chairman of the Sub-Committee on Inorganic Chemicals, is to add 0.5 cc. of lead nitrate solution to 25 cc. of distilled water and, after warming to 50° C., to add 25 cc. of hydrogen sulfide T.S.

Because of the variation in color of the sulfide sol produced by the presence of acid it was decided to investigate the effect of the free acid in the magma solution upon the accuracy of the test. The quantity of free acid in the solution remaining after the neutralization of the magma is approximately 5 cc. of diluted hydrochloric

\* Scientific Section, A. PH. A., Dallas meeting, 1936.

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acid. Varying quantities of lead nitrate solution were added to distilled water containing 5 cc. of diluted hydrochloric acid in a total volume of 25 cc. and, after the addition of hydrogen sulfide T.S., the color of the resulting sol was compared with that produced in an acid-free solution containing 10 parts per million of lead, *viz.*, the U. S. P. XI standard. In this way it was found that about 50 parts per million of lead could be present in the acid solution before an approximate match was obtained. It is emphasized that the comparison was an approximate one for the color produced in the acid sol was grayish whereas that of the non-acidified standard was light brown, thereby making it impossible to make an accurate comparison. By similar experiments it was found that 30 and 50 parts per million of lead, respectively, could be added to two different samples of magnesia magma before the intensity of color was judged to exceed that of the non-acidified standard.

Experiments were then made to determine whether the test could be made accurate by equalizing the acidity in the magma solution and in the standard. Colorimetric tests had shown that the reaction of the non-acidified standard sol corresponded to a  $p_H$  of about 3.2 while that of the acid magma solution was approximately 0.6. If these were equalized it is conceivable that the variation in color might be eliminated. The results of tests along this line indicated that more accurate comparisons could be made if both solutions were adjusted to the same  $p_H$  value, say 1.2, but that the color produced in a standard of this acidity was still not sufficiently pronounced to be entirely satisfactory. Reduction of acidity to  $p_H$  values above 1.2 could not be made readily because of the extensive ionization of hydrochloric acid.

At the suggestion of Joseph Rosin, of Merck and Co., experiments were made with acetic acid as a substitute for hydrochloric acid. Not only was it found that the resulting color was very pronounced and, in nearly all cases, of the same quality as that produced in the U. S. P. XI non-acidified standard but it developed that the standard sol could also be prepared with acetic acid without producing any perceptible change in its color. The desirability of adding the same reagents to the test and to the standard is obvious. Applying the modified test to twelve samples of magnesia magma it was found that only four of them passed the test whereas all of them met the requirements specified by the U. S. P. XI. However, by increasing the volume of lead nitrate in the standard to correspond to 20 parts per million of lead all of the samples but one passed the modified test. In preparing a solution of the magma 5 cc. of 36 per cent acetic acid was used to dissolve the magnesium hydroxide. The same quantity of acid was used in preparing the standard sol. Before heating to 50° C. and adding the hydrogen sulfide T.S. both solutions were diluted to 25 cc. After the addition of hydrogen sulfide the colors of the resulting sols were immediately compared because of the obscuring effect produced by the gradual formation of a precipitate resembling colloidal sulfur in the sol containing the magma. The amount of sulfur produced is not appreciable if the comparison is made within five minutes but if it is delayed to ten minutes some difficulty is occasionally experienced. It does not appear to be objectionable to make the comparison immediately after preparing the sols, this in fact being the procedure recommended by Yoe (1).

The  $p_H$  of magma-containing sols prepared with 5 cc. of 36 per cent acetic acid was approximately 4.5, whereas that of the standard sol containing the same quan-

tity of acid was 4.3. Although 5 cc. of acid constitutes an excess this quantity was used in order to minimize the buffering effect of the magnesium acetate and thereby equalize as much as possible the reactions of the two sols.

The explanation of the apparently anomalous behavior observed when hydrochloric acid is used in preparing the solution of the magma may be found in the variation of the particle size of insoluble sulfides with change in hydrogen-ion concentration. According to Thomas (2), acids are potent precipitants of colloidal sulfides, probably because such additions repress the ionization of hydrogen sulfide and drive back the hydrolysis of the metallic sulfide. If one assumes that the adsorption of hydrosulfide ion is responsible for the stabilization of sulfide sols it would follow that the stability of the sols will be decreased by an increase in hydrogen-ion concentration and vice versa, the decreased stability being evidenced by coagulation of the sulfide particles to form aggregates having, according to Rayleigh's formula (3), lower light-scattering power. Another effect which would appear to be important is the increased solubility of sulfides in acid solution due to the repression of the ionization of hydrogen sulfide by strong acids. That this effect is not of quantitative importance may be proved by calculations involving the solubility product of lead sulfide and the dissociation constant of hydrogen sulfide. Neither of the two factors enumerated above influence the sols prepared in an acetic acid medium for the ionization of this acid is insufficient to produce any significant effect.

On the basis of the experiments reported here the authors are of the opinion that the U. S. P. XI heavy metals test for magnesia magma can be improved by using 5 cc. of 36 per cent acetic acid both in dissolving the magma and in preparing the standard sol. If the change is considered desirable it will also be necessary to increase the quantity of lead present in the standard sol to, probably, 20 parts per million. This, of course, does not imply that 20 parts per million of lead will be present in magmas which just meet the requirements of the test for the latter is in fact a test for a number of heavy metals.

#### SUMMARY.

It has been shown that the difference in acidity between a solution of the sample being tested and the standard sol permits of the inclusion of larger quantities of heavy metals in magnesia magma than is anticipated from the lead content of the standard.

Acetic acid is demonstrated to be better suited for use in dissolving the magma.

A theoretical consideration of the variation of sensitivity of the test with acidity is presented.

#### REFERENCES.

- (1) Yoe, J. H., "Photometric Chemical Analysis," Vol. 1, 251, 253 (1928).
  - (2) Thomas, A. W., "Colloid Chemistry," 185 (1934).
  - (3) *Ibid.*, 35.
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