Determination of Phenylmercuric Compounds in Fungicidal Preparations and in Paint

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Summary. It is shown that phenylmercuric compounds can be determined simply and quickly by reacting the sample with a known quantity of potassium iodide and by back-titrating the surplus with mercuric nitrate.

The method described in this paper is suitable for phenylmercuric compounds (P.M. compounds) soluble in water, e.g., phenylmercuric acetate, or for compounds like phenylmercuric oleate which dissolve in organic solvents. The most frequently used substances are phenylmercuric acetate, oleate, naphthenate, hydroxyquinolate and di-(phenylmercuric)-dodecenyl succinate. Though the procedure proposed here has only been tried for these it is likely to be valid for all organic mercuric compounds in which one valency is attached to a carbon atom and the other is combined with an acid radical.

The method is based on the fact that P.M. compounds react in aqueous solution with potassium iodide according to the equation

\[ \text{C}_6\text{H}_5\text{HgR} + \text{KI} = \text{C}_6\text{H}_5\text{HgI} + \text{RK} \]

giving insoluble phenylmercuric iodide. The surplus potassium iodide formed can be found most conveniently by titration with a standard mercuric nitrate solution using diphenylcarbazone (D.P.C.) as indicator.

The reaction also proceeds when a solution of the phenylmercuric compound in an organic solvent is shaken with an aqueous solution of potassium iodide. The method can also be used for the determination
Determination of phenylmercuric compounds in paint. The P.M. compound is extracted with toluene and the solution obtained is then analysed as already indicated. The various metal salts like cobalt, manganese, lead and zinc usually present as naphthenates in paint and which are also extracted do not disturb the analysis as they do not react with potassium iodide.

Experimental
(a) Solutions needed. D.P.C. 0.25% in ethanol; potassium iodide solution of accurately known concentration; mercuric nitrate solution of approximately the same concentration. Suitable concentrations of these solutions for use with various concentrations of the unknown can be gauged from Table 1.
(b) Standardization. Dilute a known amount of potassium iodide solution to approximately 25 ml and add about 0.1 g of sodium hydrospergencarbonate to achieve a slight buffering action. Adjust to a pH of 5.3–5.6 and add 0.2 ml of the indicator. Titrate this with the mercuric nitrate solution until the colour of the indicator changes from nearly colourless to a slight pink. Keep the pH within the range indicated by adding 0.1 M sodium hydroxide solution if necessary. A direct reading glass electrode pH meter is the most convenient means of keeping a check on the pH during titration. It is preferred to work in the above pH range because the sensitivity of the indicator is very high in this interval and because it proved easy to keep within it. Note that a given quantity of mercury in a P.M. compound reacts with only half as much potassium iodide as the same amount of mercury in mercuric nitrate.
(c) Analysis of Water Soluble Phenylmercuric Compounds. Dissolve a sample in a suitable volume of water, add a known amount (excess) of potassium iodide solution and back-titrated at pH 5.3–5.6 with the previously standardized mercuric nitrate solution.
(d) Analysis of Phenylmercuric Compounds Soluble only in Organic Solvents. Shake a measured quantity of the solution of the P.M. compound in toluene or other suitable solvent with a surplus of standard potassium iodide solution. Separate the layers and check for completion of reaction by adding a drop of D.P.C. to the organic layer. If any P.M. compound remains in the organic layer repeat the procedure until reaction is complete. This was found to be necessary only with phenylmercuric hydroxyquinolate. The aqueous layer is then back-titrated with mercuric nitrate solution as in (c).
(e) Analysis for Phenylmercuric Compounds in Organic Solvents in the presence of Cobalt, Manganese, Lead and Zinc Naphthenates. The presence of cobalt, manganese, lead or zinc does not directly interfere with the determination of the P.M. compound as none of these metals forms a sufficiently insoluble iodide. However, these metals are usually present in paint as naphthenates and small quantities of naphthenates may dissolve in the aqueous layer and react with the indicator causing a reddish colour.

Table 1. Determination of Di-(phenylmercuric) dodecenyl succinate

<table>
<thead>
<tr>
<th>Mercury in sample mg</th>
<th>Mercury found mg</th>
<th>Strength of potassium iodide sol. used mg/ml</th>
<th>Strength of mercuric nitrate sol. used mg/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.0</td>
<td>9.90, 10.1, 9.80</td>
<td>0.800</td>
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<tr>
<td>1.00</td>
<td>0.99, 1.02, 0.98</td>
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<tr>
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<td>0.206, 0.203, 0.195</td>
<td>0.016</td>
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<tr>
<td>0.050</td>
<td>0.055, 0.051, 0.048</td>
<td>0.004</td>
<td>0.004</td>
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