Extraction of Copper from Sodium Salicylate & Its Spectrophotometric Determination with 4-(2-Pyridylazo)-resorcinol

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A method is described for the extraction and separation of microgram amounts of copper(II) from sodium salicylate solution using mesityl oxide as an extractant. The metal ion is stripped from the organic phase with water and determined photometrically as its 4-(2-pyridylazo)resorcinol complex. The method is applicable to the analysis of synthetic mixtures and pharmaceutical samples.

Copper is associated with iron, aluminium, nickel, manganese, lead, zinc, chromium and molybdenum in industrially important copper-base alloys. It is also found in a number of pharmaceuticals. Separation and quick estimation of copper is thus desired. We report here a method for the extraction of microgram amounts of copper with mesityl oxide from sodium salicylate solution (0.1 M; pH 4-4.5). The metal ion is stripped from the organic phase with water and determined photometrically as its 4-(2-pyridylazo)resorcinol complex at 540 nm. The method permits separation of copper from Zn(II), Cd(II), Mn(II), Fe(III), Al(III), Ti(IV), V(V), Cr(VI) and Mo(VI) and has been successfully applied to the analysis of steel, brass, aluminium alloy and pharmaceutical samples.

The extraction of copper was studied at various pH values (3.5-9.0), sodium salicylate concentrations (0.025-0.2 M) and mesityl oxide concentrations (20-100%, using benzene as the diluent). A single extraction for 45 sec with 10 ml of undiluted mesityl oxide was found to be adequate for quantitative extraction of copper from 0.1 M salicylate solution of pH 4.0-4.5. Beyond pH 4.5, the extraction decreased and the distribution ratios were calculated as usual.

The log-log plots of distribution ratio vs salicylate concentration (at fixed pH and mesityl oxide concentration) or vs mesityl oxide concentration (at fixed pH and salicylate concentration) gave a slope of 1.9 indicating molar ratio of 1:2 with respect to both extractant and salicylate. Hence, the probable nature of the extracted species is Cu(HOC₆H₄ COO)₂·2 Meo where Meo stands for mesityl oxide. 2500 μg each of Ag(I), Mn(II), Hg(II), Pb(II), Cd(II), Ni(II), Ca(II), Sr(II), Ba(II), Cr(III), Sc(III), La(III), Y(III), In(III), Ga(III), Sb(III), Au(III), Al(III), As(III), Th(IV), Ce(IV), Pt(IV), V(V), Cr(VI), U(VI), Mo(VI), thiocyanate, thiourea, ascorbate, perchlorate, Cl⁻, Br⁻, NO₃⁻, PO₄³⁻ and tartrate; 1000 μg each of Be(II), Sn(II), Ir(III), Ti(IV), Os(VIII) and citrate; 500 μg of Fe(III); 200 μg each of Pd(II) and Rh(III) did not interfere in the estimation. However, Co(II), Bi(III) and EDTA interfered severely and must be absent.

Extraction of copper (25 μg) by the recommended procedure facilitates its separation from ions such as Zn(II), Mn(II), Cd(II), Fe(III), Al(III), Ti(IV), V(V), Cr(VI) and Mo(VI) as they do not extract into mesityl oxide. The recoveries were > 99.0% from the binary mixtures.

Extraction procedure

An aliquot containing 25 μg of copper was taken and to it was added 400 mg of sodium salicylate (0.1 M) and the pH was adjusted to 4.0-4.5 in a total volume of 25 ml. Extraction was carried out for 45 sec with 10 ml of undiluted mesityl oxide. The organic phase was collected, copper stripped with two 10-ml portions of water and the metal ion was determined in the combined aqueous phase spectrophotometrically with PAR at 540 nm.

The extraction of copper was studied at various pH values (3.5-9.0), sodium salicylate concentrations (0.025-0.2 M) and mesityl oxide concentrations (20-100%, using benzene as the diluent). A single extraction for 45 sec with 10 ml of undiluted mesityl oxide was found to be adequate for quantitative extraction of copper from 0.1 M salicylate solution of pH 4.0-4.5. Beyond pH 4.5, the extraction decreased and the distribution ratios were calculated as usual.

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Synthetic mixtures containing either Mn(2.5 mg), Ni(0.5 mg), Cr(0.5 mg), Mo(1 mg), Fe(200 μg), Cu(25 μg) or Ni(0.5 mg), Fe(200 μg), Zn(2.5 mg), Mn(2.5 mg), Cu(25 μg) or Al(2.5 mg),
Table 1 — Analysis of Standard Samples

<table>
<thead>
<tr>
<th>Sample/Item</th>
<th>Composition of Alloy</th>
<th>Copper %</th>
<th>Rel. error, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 33 d NBS</td>
<td>C, 2.4; Si, 1.63; Mn, 0.63; Ni, 2.38; Cr, 0.32; Mo, 0.48; rest iron (90.3)</td>
<td>1.54</td>
<td>1.3</td>
</tr>
<tr>
<td>2 41 Brass (NML)</td>
<td>Pb, 2.35; Zn, 40.65; Fe, 0.009</td>
<td>56.9</td>
<td>0.9</td>
</tr>
<tr>
<td>3 Aluminium alloy</td>
<td>Ni, 2.12; Mn, 1.7; Fe, 0.031, rest Al</td>
<td>4.0</td>
<td>1.2</td>
</tr>
<tr>
<td>4 Multivite FM capsules</td>
<td>Vitamin A, 5000 IU; Vitamin D₃, 200 IU; Vitamin E, 7.5 mg; Vitamin B₁, 2.5 mg; Vitamin B₂, 2.5 mg; Nicotinamide, 25 mg; Folic acid, 500 mcg; Ferrous fumarate, 25 mg; Calcium dibasic phosphates, 35 mg; Copper sulphate, 0.1 mg; Manganese sulphate, 0.01 mg; Zinc sulphate, 50 mg; Potassium iodide, 0.025 mg; Magnesium oxide, 0.15 mg</td>
<td>0.1 mg</td>
<td>—</td>
</tr>
</tbody>
</table>

Fe(200 μg), Ni(0.5 mg), Mn(0.5 mg), Cu(25 μg) or Pb(1 mg), Zn(2.5 mg), Cu(25 μg) were analysed by the recommended procedure. The results show that the detection and determination of copper is possible in presence of these metal ions with greater than 99% recovery of copper (Table 1).

The method also permits separation and determination of copper in 33 d cast iron steel (NBS), 41 Brass (NML), aluminium alloy and in multivite FM capsules.

The reproducibility of results was satisfactory and the results were found to be accurate within ± 0.5% with a standard deviation of ± 0.004 from the mean. The 95% confidence limit for the mean is 0.0042.

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References