SPECTROPHOTOMETRIC DETERMINATION
OF MICRO QUANTITIES OF GOLD WITH
CETYLTRIMETHYLAMMONIUM BROMIDE IN
PRESENCE OF IODIDE

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The reagents [Fe(phenanthroline)³⁺]¹, tetrathenyl-
arsonium chloride², diethyl ether³, Rhodamine B⁴,
mesityl oxide⁵,⁶ or primaquine phosphate⁷ have
been used in spectrophotometric methods for
determination of gold. In the present investigation
we noted that gold(III) forms an yellow ion-associa-
tion complex with cetyltrimethylammonium bromide
(CTAB) in presence of potassium iodide and is
extractable into chloroform. Based on this a simple
spectrophotometric method for the determination of
gold is reported.

A stock solution of Au(III) was prepared by
dissolving gold chloride (Johnson and Matthey) in
distilled water and standardizing⁸. Solution of lower
concentration of the metal was prepared by
appropriate dilution of the stock. Aqueous solutions
of CTAB (0.025 M SISCO) and potassium iodide
(0.03 m BDH) were used. KH₂PO₄-NaOH buffer
was employed to adjust the pH of the aqueous
solution. Standard solutions of diverse ions were
prepared from their salts. Chloroform and other
solvents were distilled before use. All other reagents
used were of analytical grade.

Absorbance measurements were made with a
Shimadzu PRI model recording spectrophotometer.
Stopped quartz cells of 10 mm optical path length
were used for all measurements. An ECL 5651
digital pH meter was used to measure the acidity of
the aqueous solution.

To an aliquot containing Au(III) (70 µg) were
added potassium iodide (1 ml) and CTAB (0.1 ml).
The mixture was adjusted to pH 7.0 with buffer. The
volume of the aqueous phase was made up to 10 ml.
The mixture was then equilibrated (30 sec) with
chloroform (10 ml). The separated organic layer was
dried over anhydrous sodium sulphate. Finally the
absorbance of the chloroform extract was measured
at 290 or 360 nm against a blank prepared in a
similar manner. The amount of gold was computed
from a calibration curve. To test for interference by
other ions, the ions were added to the system before
addition of the reagents.

When potassium iodide was added to a neutral or
slightly acidic solution containing gold(III), a yellow
coloration due to the formation of [AuI₂]⁻ was
formed. This complex anion was not extractable into
chloroform. On addition of an aqueous solution of
CTAB to the coloured solution, an ion-association
complex, probably of the type [CTA⁺][AuI₄]⁻,
was formed. This was extractable into chloroform.
Other solvents like ethyl acetate, benzene and 1,2-
dichloroethane were also tested as extracting
solvents, but these offered no special advantages
over chloroform (table 1). The complex was not
extractable into carbon tetrachloride.

The reagent blank itself shows absorption max-
imum at 250 nm and the absorption becomes
Table 1  Absorption maxima and molar absorptivities of Au(III)–I–CTAB complex extracted into different solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Absorption maxima (nm)</th>
<th>Molar absorptivity (1 mol⁻¹ cm⁻¹ × 10⁻⁴)</th>
<th>Sensitivity (µg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>290</td>
<td>2.14</td>
<td>0.009</td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>1.29</td>
<td>0.015</td>
</tr>
<tr>
<td>Benzene</td>
<td>298</td>
<td>1.97</td>
<td>0.010</td>
</tr>
<tr>
<td></td>
<td>365</td>
<td>1.32</td>
<td>0.014</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>220</td>
<td>2.08</td>
<td>0.009</td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>1.13</td>
<td>0.017</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>295</td>
<td>1.77</td>
<td>0.011</td>
</tr>
<tr>
<td></td>
<td>365</td>
<td>1.07</td>
<td>0.018</td>
</tr>
<tr>
<td>Carbon tetrachloride*</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

*Complex not extractable.

Table 2  Analysis of synthetic mixtures

<table>
<thead>
<tr>
<th>Composition with amounts taken in µg</th>
<th>Recovery of gold (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au(III) 70, Ag(I) 100, Cu(II) 100, Zn(II) 100</td>
<td>98</td>
</tr>
<tr>
<td>Au(III) 70, Fe(III) 100, Co(II) 100, Ni(II) 100</td>
<td>98</td>
</tr>
<tr>
<td>Au(III) 70, Pd(II) 100, Pt(IV) 100, Rh(III) 100</td>
<td>101</td>
</tr>
</tbody>
</table>

Ag(I) and Bi(III) could be tolerated. U(VI) interfered. Among the anions tested, 200-fold excess of borate, phosphate, tartrate, citrate, fluoride, bromide, phthalate, oxalate, acetate and nitrate, and lower concentrations of ascorbate and EDTA did not interfere in the estimation of gold. Thiocyanate, thiosulphate, thiourea and arsenate interfered.

In the absence of real samples, the applicability of the method was tested by analysing some synthetic mixtures containing Au(III), Ag(I), Cu(II), Zn(II), Fe(III), Co(II), Ni(II), Pd(II), Pt(IV) and Rh(III). The compositions of the mixtures and percentage recovery of gold are given in table 2. The results show that recovery of gold was highly satisfactory. Average of three determinations was taken in each case.

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It was further studied by various workers\textsuperscript{2-5}. Photodecomposition of aldrin and dieldrin was reported by Henderson and Crosby\textsuperscript{6}, whereas Benson et al.\textsuperscript{7} characterized the photoproducts of chlordane. Photodecomposition of the chlorinated hydrocarbon endosulfan was observed by Archer et al.\textsuperscript{8,9}, while Dureja and Mukerjee\textsuperscript{10} did not observe any photosensitization product.

Endosulfan (technical grade) (6, 7, 8, 9, 10, 10-hexachloro-1,5, 5a, 6, 9, 9a-hexahydro-6, 9-methano-2, 4, 3-benzodioxathiepin-3-oxide), 1,4-diazobicyclo-(2, 2, 2)-octane (DABCO), methylene blue (CI-52015) and methanol (BDH) were used. All other chemicals used were of SM grade. Endosulfan was used after recrystallization (m.p. 95°C). A 200 W tungsten lamp was used for irradiating the reaction mixture; IR radiations were cut off using a water filter. The reaction mixture was prepared by adding four drops of methylene blue (2 x 10^{-6} M) in methanolic solution of endosulfan (8% v/v) and was aerated for 5 h in the presence of light. The progress of the reaction was followed by TLC. Some suspension was observed in the reaction mixture after 3 h.

A white substance that settled in the reaction mixture after 5 h was separated by decantation. The methylene blue was removed by the addition of activated charcoal. Dureja and Mukerjee\textsuperscript{10} did not observe any photoproduct in methanolic solution with methylene blue in the presence of light from a tungsten lamp while we have obtained a photoproduct, which has been characterized as the sulphate derivative (recrystallized, m.p. 178°C). The following were the results of elemental analysis: found...