118. *Substituted Benzidines and Related Compounds as Reagents in Analytical Chemistry. Part V. New Indicators for the Microvolumetric Determination of Gold.*

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Two new indicators, 3-methyl- and 3 : 3′-diethyl-benzidine, are recommended for use in the microtitration of gold with quinol. End-points are sharper than those obtained with *o*-dianisidine, the indicator normally used in this determination. Titration may be carried out in neutral or slightly acid solution.

Pollard (*Analyst*, 1937, **62**, 597) has used *o*-dianisidine to indicate the end-point in the titration of gold salts with quinol. Good results were obtained for the range 0·5—2 mg. of gold. Jamieson and Watson (*ibid.*, 1938, **63**, 702) have extended the method to the determination of gold in urine, where smaller amounts of the element were present.

In the above method the neutral or faintly acid gold solution was buffered with potassium bifluoride and titrated with standard quinol solution until the red colour of the indicator was discharged. We have confirmed Pollard's results but did not obtain very satisfactory end-points, the colour change being red-violet to violet. When one drop of a 1% solution of *o*-dianisidine in glacial acetic acid (rather than in dilute hydrochloric acid) was used as indicator improved end-points were obtained, but were still not entirely satisfactory.

Pollard also used *o*-tolidine as indicator in this titration but preferred *o*-dianisidine.

Some substituted benzidines and the related compound naphthidine have been used in the titration of zinc with ferrocyanide (preceding paper), and it was thought that these compounds might be substituted for *o*-dianisidine in the titration of gold salts. The following compounds gave sharper and more easily detectable end-points than *o*-dianisidine; benzidine and its 3-methyl and 3 : 3′-diethyl derivatives and 2 : 7-diaminofluorene. With the first three, the quinol solution should be added slowly near the end-point owing to the slow reaction between the gold salt and the indicator. An indication of the approach of the end-point is given by the discharge and restoration of the indicator colour. The end-point is reached when the indicator colour is not restored within 30 seconds. 2 : 7-Diaminofluorene gives a satisfactory end-point, but the indicator colour is discharged and restored with each drop of titrant, hence the titration is somewhat slower than with the other indicators.

The gold solution should be titrated immediately on addition of the indicator, because, after the solution had stood for 10 minutes, the indicator would not function. *o*-Dianisidine was found to behave similarly.

3-Methylbenzidine gave the best colour change, that with 3 : 3′-diethylbenzidine being almost as good. End-points with benzidine and 2 : 7-diaminofluorene were sharper than those obtained using *o*-dianisidine, though the discharge of the 2 : 7-diaminofluorene indicator colour during titration is a disadvantage. Results obtained are included in the table.

Indicator (and end-point).		Au present, mg.	Au found, mg.	Au present, mg.	Au found, mg.	Au present, mg.	Au found, mg.	Au present, mg.	Au found, mg.
3-Methylbenzidine (Green ⟶ pale violet)	{	2·00	1·98	1·50	1·50	1·00	0·98	0·50	0·50
	{	2·00	2·00	1·50	1·50	1·00	1·02	0·50	0·50
3 : 3′-Diethylbenzidine (Yellow-green ⟶ pale violet)		2·00	2·00	1·50	1·50	1·00	1·00	0·50	0·50
Benzidine (Yellow ⟶ pale violet)		2·00	1·99	1·50	1·50	1·00	1·00	0·50	0·50
2 : 7-Diaminofluorene (Yellow ⟶ pale violet)		2·00	2·00	1·50	1·50	1·00	0·98	0·50	0·49

Gold solutions of acid concentrations between 0·025N. and 0·25N. were also titrated. Good results were obtained, but when the acid concentration reached 0·25N., the titration had to be done very slowly owing to the slow reaction between the gold salt and the indicator. With decreasing acidity the titration could be carried out more quickly, until at 0·05N. a fairly fast drop-rate could be used. In 0·025N-acid the reaction was immediate, and titration could be effected in the usual way.

In alkaline media, a sparingly soluble compound separated, the indicator change was not easily detected, and low results were obtained.

Experimental.—Indicator solution. 1% Solution of the compound in glacial acetic acid.

Quinol solution. 0·8375 G. of quinol was dissolved in 400 ml. of water, 20 ml. of concentrated hydrochloric acid were added, and the volume was adjusted with distilled water to 1000 ml. (1 ml. $\equiv$ 1 mg. of Au).

Gold solution. 1 G. of pure gold was dissolved with warming in 12 ml. of concentrated hydrochloric acid and 4 ml. of concentrated nitric acid. Volatile gases were then removed by bubbling air through the solution, and the volume was adjusted with distilled water to 1000 ml.

Potassium bifluoride solution. 20 G. of the salt were dissolved in distilled water, and the volume adjusted to 1000 ml. The solution was stored in a polythene bottle.

General titration procedure. Amounts of gold solution, containing between 0·5 and 2 mg. of gold, were delivered from a graduated pipette into a 150-ml. conical flask, 50 ml. of potassium bifluoride solution added, then 1 drop of indicator, and the solution titrated with standard quinol solution from a microburette until the permanent discharge of the indicator colour.

Titration of gold solutions of different acid concentrations. The gold solution was measured into a 150-ml. conical flask, 1 g. of solid potassium bifluoride added, and the volume adjusted to 50 ml. with hydrochloric acid of appropriate concentration.

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