

3 drops of 0.05 *M* triphenylsulfonium bromide or 0.04 *M* tetraphenylarsonium bromide solution). Approximately 1 ml. of chloroform was added and the mixture was shaken. The extent of interference in the cobalt test was investigated by repeating each of the tests in the presence of cobalt, using solutions in which cobalt and the foreign test constituent were present at concentrations of 5 and 500 micrograms per ml., respectively.

Triphenylsulfonium bromide and tetraphenylarsonium bromide when used as reagents in the cobalt test were found to be subject to the same interferences.

Zn(II) and Sn(IV) give slight negative interference, preventing full development of the blue color. This interference is minimized by using a large excess of thiocyanate and onium reagent.

Masking interference was observed in the presence of U(VI), Fe(III), Ru(III), Pd(II), Pt(IV), Cu(II), and Bi(III). The nature of these interferences and methods of preventing them are indicated in Table VI.

The very pronounced interference by Fe(III) and slight interferences by Bi(III) and U(VI) are easily prevented by adding to the solution to be tested 1 or 2 drops of 10% ammonium fluoride. (The bismuth thiocyanate complex unlike BiI_4^- is readily decomposed by fluoride.)

Cu(II) interference is prevented by reducing to Cu(I) with iodide. Thiosulfate serves to remove the iodine formed. One drop each of 10% potassium iodide and 10% sodium thiosulfate are added to the solution to be tested.

The feasibility of employing the onium-thiocyanate-chloroform extraction procedure for the separation and colorimetric determination of cobalt has been demonstrated (1). Studies on applications of the procedure are in progress.

CONCLUSIONS

Triphenylsulfonium and tetraphenylarsonium chlorides and bromides used in conjunction with iodide are particularly suitable reagents for the detection of bismuth. They are fully as sensitive as the commonly used cinchonine reagent and are somewhat less subject to interferences. They possess an advantage over cinchonine of being water-soluble. The same compounds used with

thiocyanate serve as sensitive and, under properly controlled conditions, highly specific reagents for the detection of cobalt.

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Determination of Hydrogen Peroxide in Small Concentrations

A Spectrophotometric Method

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A sensitive method of peroxide analysis which allows not only the detection but the quantitative determination of hydrogen peroxide in concentrations as small as 10^{-6} molar is described. The determination of the optimum wave length for the spectrophotometric determination is described. A typical standardization curve is given.

A SENSITIVE method of peroxide analysis, which provides not only for the detection but the quantitative determination of hydrogen peroxide in concentrations as small as 10^{-6} molar, involves the oxidation of iodide ion to iodine, in the peroxide solution to be determined, and the estimation of the free iodine thus formed by measurement of its light absorption on a spectrophotometer. In order to make the rather slow iodide ion-peroxide reaction go rapidly to completion, use is made of the

catalytic action of molybdic acid discovered by Brode (1) and employed by Kolthoff (2). The method is limited to solutions which do not contain other constituents that either oxidize iodide ion or absorb in the same spectral range as triiodide ion.

A standardization curve is obtained by diluting an approximately 1.0 molar solution of hydrogen peroxide to about 0.01 molar and then analyzing this solution accurately by thiosulfate determination of liberated iodine according to standard procedure.

Table I. Transmittance and Absorption Values^a

Wave Length	% Transmittance	% Absorption
8.00 ml. of 1.31×10^{-3} molar hydrogen peroxide. 1.00 ml. of 1 M sulfuric acid, 10^{-3} F ammonium molybdate. 1.00 ml. of 1 F potassium iodide.		
3200	74.0	26.0
3300	68.9	31.1
3400	60.5	39.5
3500	56.5	43.5
3600	58.3	41.7
3700	65.0	35.0
3800	73.5	26.5
3900	81.0	19.0
4000	87.1	12.9
8.00 ml. of 6.35×10^{-3} molar hydrogen peroxide. 1.00 ml. of 1 M sulfuric acid, 10^{-3} F ammonium molybdate. 1.00 ml. of 1 F potassium iodide.		
3200	86.5	13.5
3300	83.5	16.5
3400	78.2	21.8
3500	75.8	24.2
3600	76.8	23.2
3700	80.7	19.3
3800	85.7	14.3
3900	90.0	10.0
4000	93.1	6.9
8.00 ml. of 3.17×10^{-3} M hydrogen peroxide. 1.00 ml. of 1 M sulfuric acid, 10^{-3} F ammonium molybdate. 1.00 ml. of 1 F potassium iodide.		
3200	95.0	5.0
3300	93.0	7.0
3400	90.1	9.9
3500	88.1	11.9
3600	88.8	11.2
3700	90.8	9.2
3800	93.2	6.8
3900	95.5	4.5
4000	97.0	3.0
8.00 ml. of 1.31×10^{-3} M hydrogen peroxide. 1.00 ml. of 1 M sulfuric acid, 10^{-3} F ammonium molybdate. 1.00 ml. of 1 F potassium iodide.		
3200	97.0	3.0
3300	96.2	3.8
3400	95.1	4.9
3500	95.0	5.0
3600	95.0	5.0
3700	96.0	4.0
3800	97.4	2.6
3900	98.4	1.6
4000	99.1(?)	0.9(?)

^a All figures are given for 20 Å. band width around wave length indicated.

The solution is then diluted accurately to the range of concentrations given in Table I, and in each case to 8.00 ml. of the resultant solution are added 1.00 ml. of a 1 M sulfuric acid, 10^{-3} F ammonium molybdate solution, and 1.00 ml. of a 1 F potassium iodide solution, the latter freshly prepared. The absorption spectra were in all cases determined within 20 minutes after addition of the potassium iodide solution to avoid any oxidation of the iodide ion by the oxygen of the air, and were determined over the range 3000 to 4000 Å. in order to find the optimum wave length for use with an unknown. In making an actual determination on a solution of unknown peroxide concentration it is necessary to make only one reading at the selected wave length.

All the per cent transmittance values in Table I and Figures 1 and 2 are based upon the value of the blank (8 mm. of distilled water plus reagents as above) taken as 100%. The readings taken on the various solutions in the spectrophotometer (Beckman quartz cell spectrophotometer) remain nearly constant for an hour or more after the fresh iodide reagent is added. After longer periods, however, there is a considerable increase in absorption shown by the solution due to air oxidation of the iodide ion.

It is seen from Figure 1 that the maximum per cent absorption is obtained at a wave length of 3500 Å. This wave length was accordingly taken as the standard for the subsequent analyses performed.

In order to test the applicability of Beer's law, $\log I/I_0$ (at 3500 Å.) for the various hydrogen peroxide (H_2O_2) concentrations used for standardization are tabulated in Table II and plotted in Figure 2.

Because the solutions corresponding to these concentrations were diluted from 8 to 10 ml. by the addition of the reagents, the concentrations actually existent in the absorption cell at the time of measurement are actually only eight tenths of those shown. In Figure 2 it is seen that $\log I/I_0$ versus concentration does not give exactly a straight line, showing that Beer's law is not obeyed, in accord with Winther (3). The plot in Figure 2 serves, however, as a standard curve for this procedure of analysis.

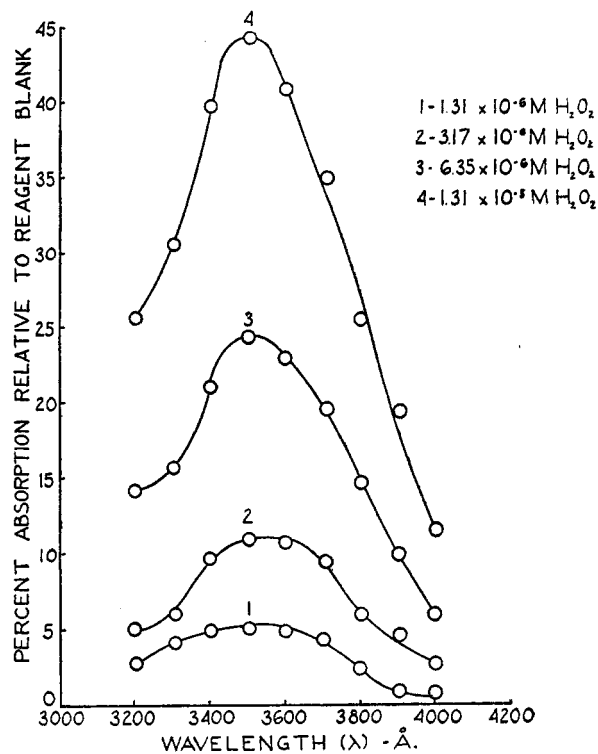


Figure 1

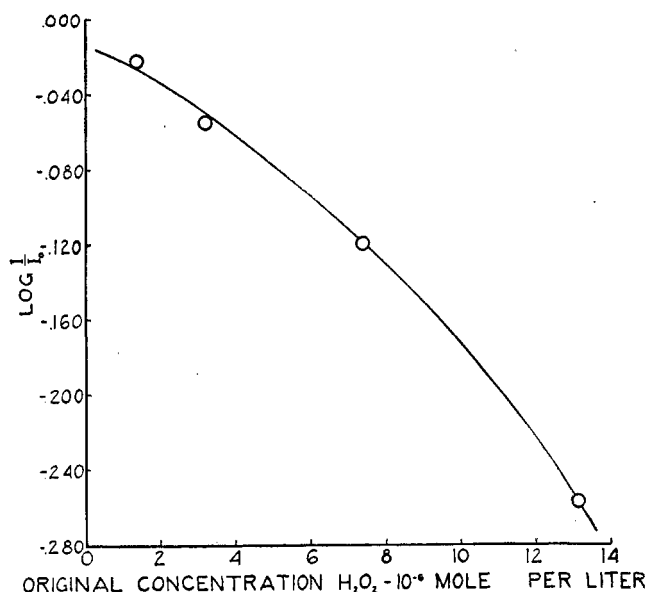


Figure 2. Standardization Curve

Table II. Concentrations Used for Standardization

I/I_0	$\log I/I_0$	H_2O_2 (I_0) Molarity ($\times 10^3$)
0.565	-0.248	13.1
0.758	-0.120	6.35
0.881	-0.055	3.17
0.950	-0.022	1.31

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