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Analytical Report

on

THE ALKALINE PEROXIDE COLORIMETRIC DETERMINATION OF URANIUM

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Department of Chemistry, Purdue University

by

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DISCLAIMER

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Analytical Report
on
Research at Purdue University
by
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THE ALKALINE PEROXIDE COLORIMETRIC DETERMINATION OF URANIUM

Abstract

A Beckman spectrophotometer was used to determine the effect of reagent concentration, order of addition of reagents, pH, temperature, stability of color, uranium concentration, and interfering substances on the yellow coloration produced by the uranyl ion in the presence of alkaline hydrogen peroxide.

Selection of wavelength for measurement, sensitivity, range, calibration, Beer's law conformity, precision and accuracy are discussed. Precipitation, electrolysis, and extraction separations are described.

The procedure recommended is simple and reproducible. The color develops immediately in a pH range of 11-14. As little as 1 p p m can be measured in 10 cm cells with an accuracy of 1-3%.

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For The Atomic Energy Commission
H. R. Carroll
Chief, Declassification Branch

THE ALKALINE PEROXIDE COLORIMETRIC DETERMINATION OF URANIUM

INTRODUCTION

Several colorimetric methods have been proposed for determining small amounts of uranium. The method generally accepted as the most reliable is the alkaline peroxide method proposed by Hackl(1). Arnold and Pray (2) used this method for the indirect determination of sodium through the sodium, magnesium, uranium acetate precipitate. Sandell(3) also includes this method in his collection of colorimetric procedures. Although not as sensitive as many other colorimetric procedures for uranium, the alkaline peroxide method has the advantage of possessing a straight line calibration curve since it conforms to Beer's law. It is also less sensitive to iron contamination than most other methods.

Experimental Work

Apparatus and Reagents. Measurements were made with a Beckman quartz spectrophotometer using about one $m\mu$ band width. One cm and 10 cm matched absorption cells were used. Reagents used consist of 30% H_2O_2, a 10% solution of NaOH, and a 20% solution of Na_2CO_3.

The Color Reaction. Hydrogen peroxide reacts with the uranyl carbonate complex, $UO_2(CO_3)_3^{-4}$, in alkaline solution to produce a yellow colored system whose optical density at any wavelength is directly proportional to the amount of uranium present. The spectral transmittancy curves for this yellow system are shown in Figure 4.

1. The Effect of Reagent Concentration. The spectral transmittancy curves for all reagents are shown in Figure 1 as measured against a

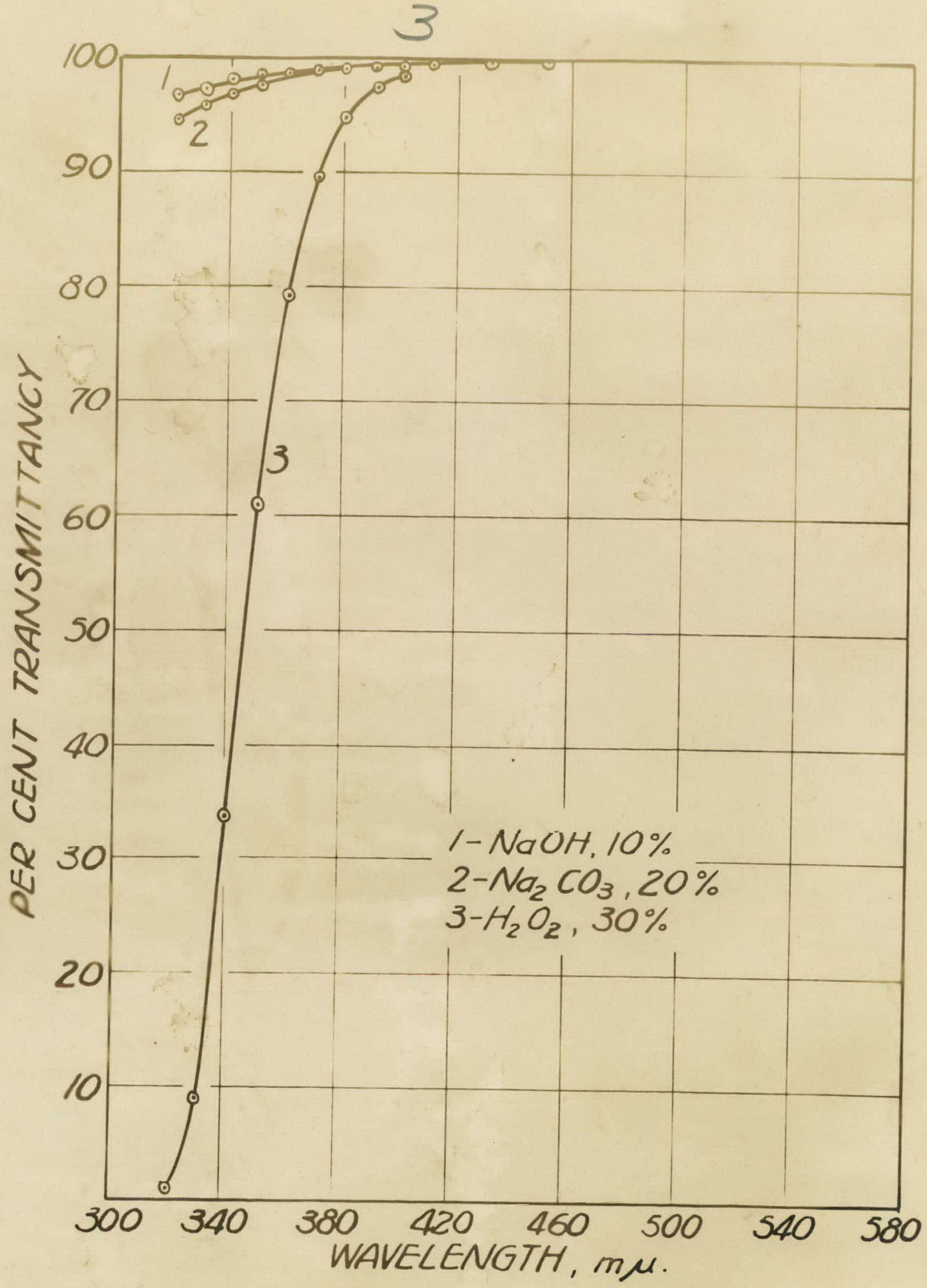

FIGURE 1-SPECTRAL TRANSMITTANCY FOR REAGENTS

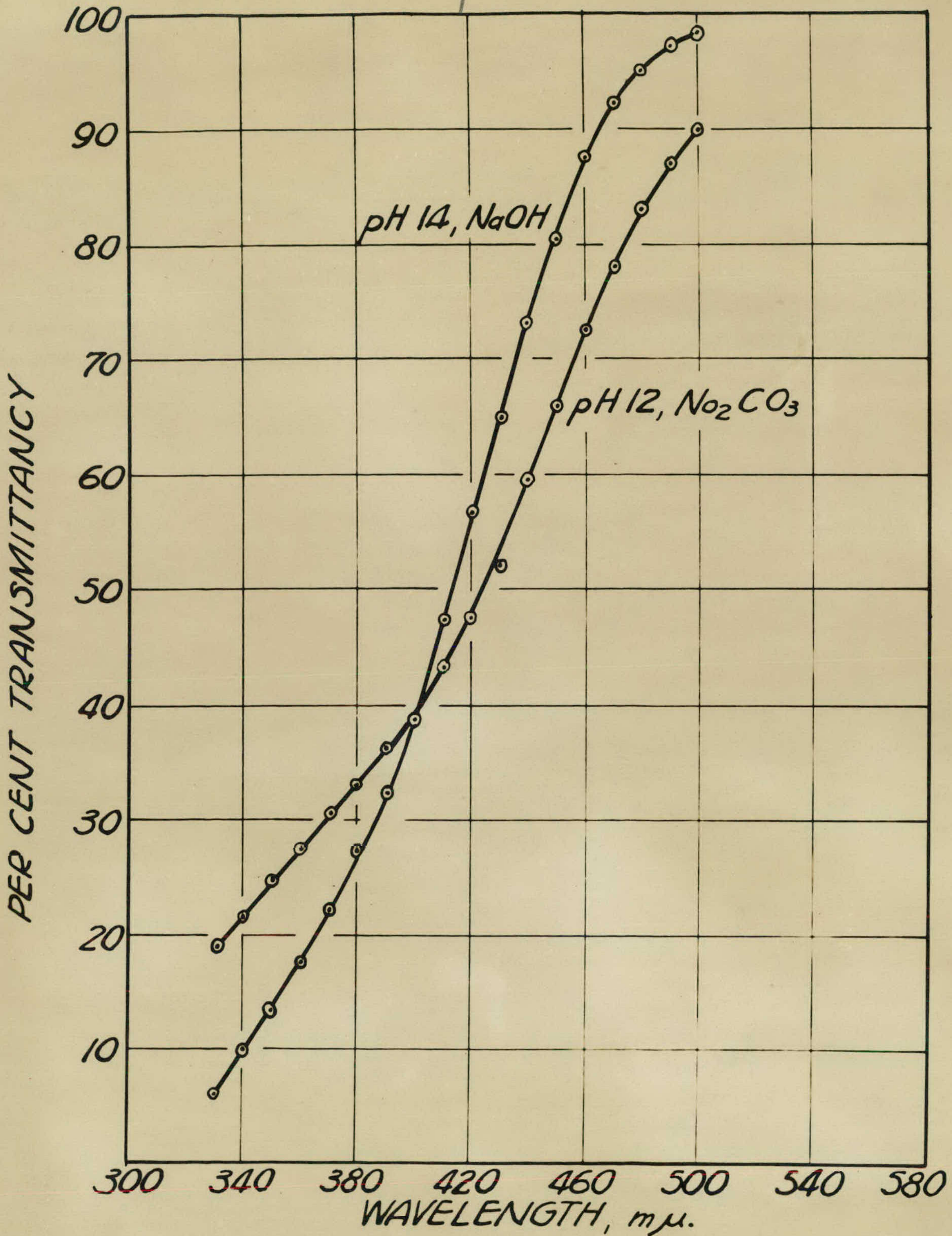

FIGURE 2 - SPECTRAL TRANSMITTANCY FOR
5 mg. U IN 50 ml. SOLN.

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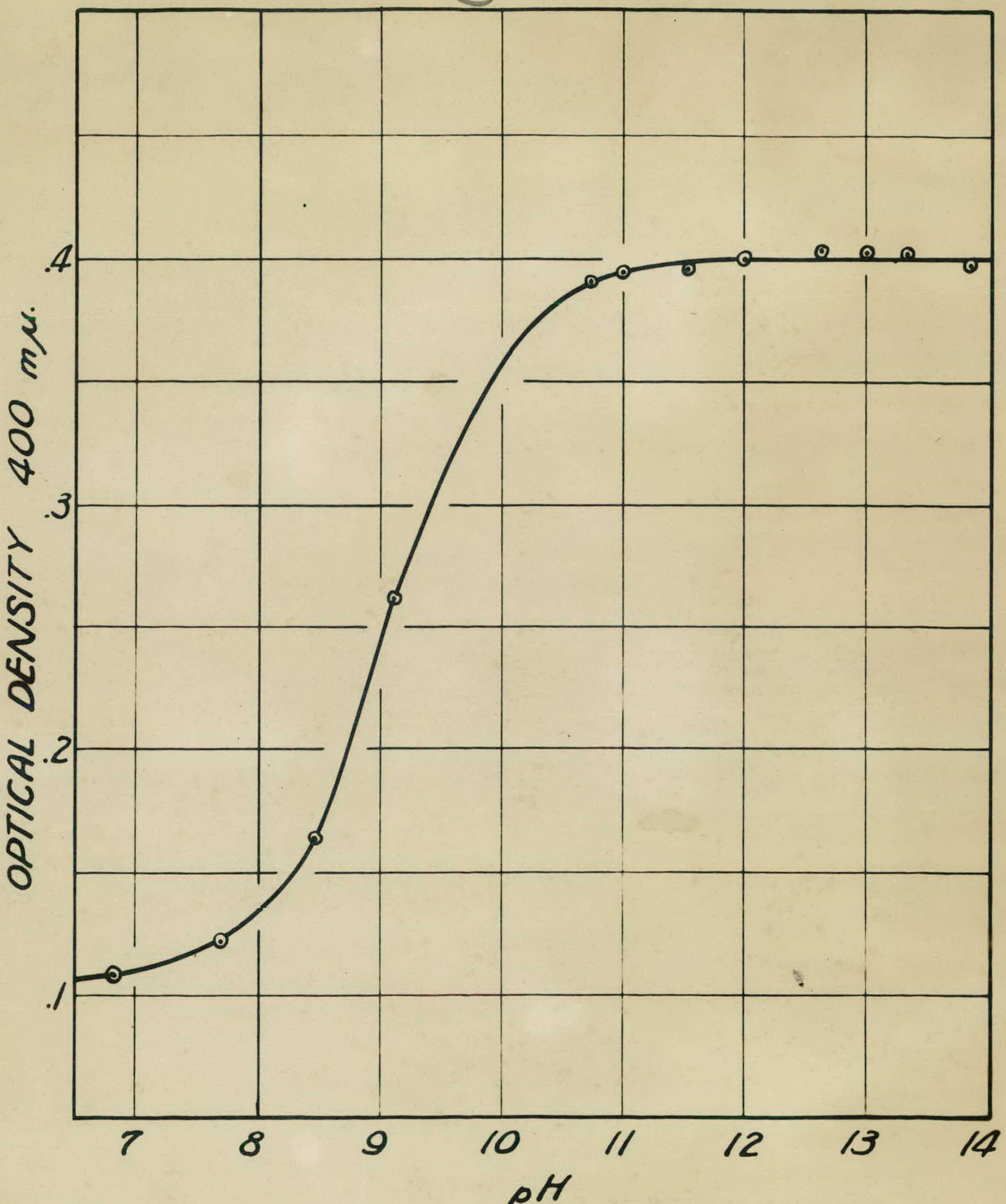

FIGURE 3 - EFFECT OF pH ON THE OPTICAL DENSITY AS MEASURED AT 400 mμ.

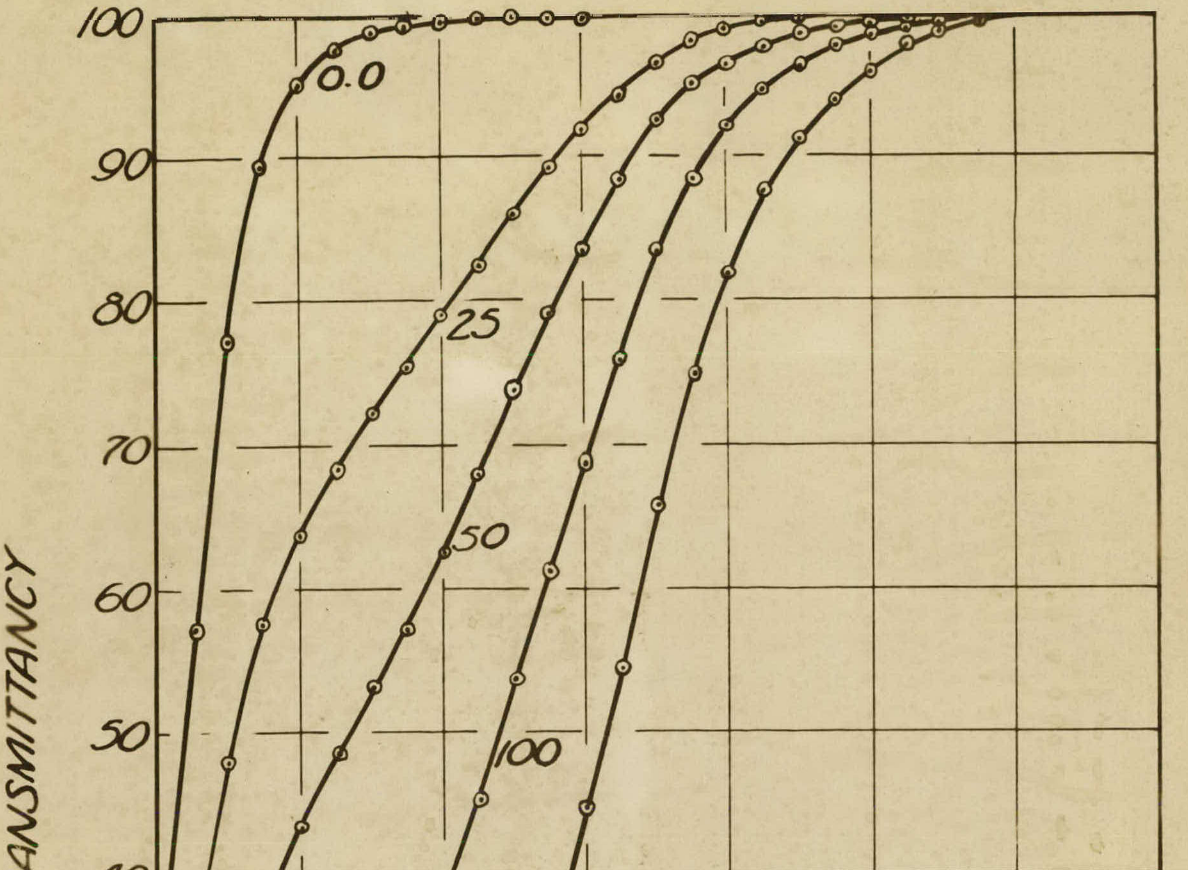

FIGURE 4 - PER CENT TRANSMITTANCY, CONCN. OF U IN mg. PER LITER

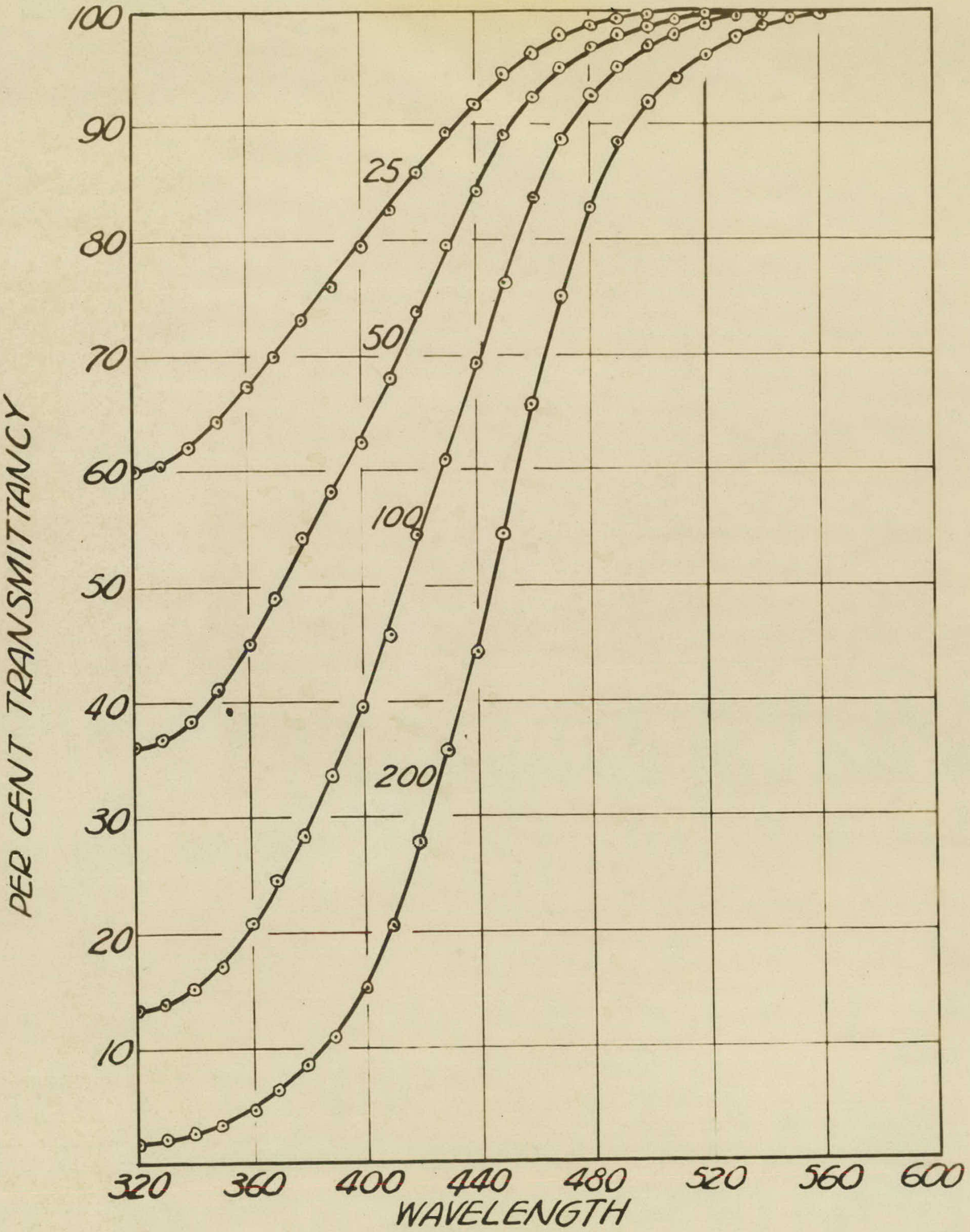

FIGURE 5-PER CENT TRANSMITTANCY, CONCN. OF U IN mg. PER LITER CORRECTED FOR REAGENTS

water blank in 1 cm cells, at 1 $m\mu$ band width. None of the reagents absorb in the visible region of the spectrum. In the ultra-violet region hydrogen peroxide has an appreciable absorption. Any measurements made in this region would vary with the hydrogen peroxide concentration as well as the uranium concentration. Reagent blanks can be avoided by making measurements at 400 $m\mu$.

The sodium carbonate serves to complex the uranium and prevent its precipitation in alkaline solution. Although not absolutely necessary for amall amounts of uranium it is added routinely. The concentration of this reagent is not critical.

The sodium hydroxide is added to adjust the pH. Within the allowable limits of pH, the concentration of this reagent is not critical.

One tenth milliliter of 30% hydrogen peroxide per 100 ml brings about nearly complete color development. The recommended 1 ml per 100 ml allows a safe excess. Ten milliliters per 100 ml does not cause any further change in transmittancy at 400 $m\mu$, although the tendancy for bubble formation from peroxide decomposition increases.

Table 1

EFFECT OF H_2O_2 CONCENTRATION

5 mg. U, 5 ml 20% Na_2CO_3, 5 ml 10% NaOH per 100 ml; 1-cm cells against H_2O reference blank.

Ml 30% H_2O_2/100 ml	0.1	0.5	1.0	10.0
Transmittancy 400 $m\mu$	61.3	60.5	60.5	60.6
Transmittancy 320 $m\mu$	29.0	16.0	10.3	5.4

2. Order of Addition of Reagents. The order of addition of reagents apparently makes little difference as long as the sodium carbonate is added to complex the uranium before the sodium hydroxide is added. The system can be made alkaline either before or after the addition of the hydrogen peroxide.

3. Effect of pH. The spectral transmittancy curves for a solution containing 5 mg of uranium with 10 ml of 20% sodium carbonate and 0.5 ml of 30% hydrogen peroxide per 50 ml having a pH of 12 and another containing the same amount of uranium with 20 ml of 10% sodium hydroxide and 0.5 ml of 30% hydrogen peroxide per 50 ml having a pH of 14 are shown in Figure 2 measured against water in 1 cm cells with 1 mμ band width. The sample containing sodium hydroxide shows less absorption in the visible region and more absorption in the ultra-violet region than the sample containing only sodium carbonate. The only wavelength which is independent of the type of base and which is apparently free from pH effects is 400 mμ. Figure 3 shows the effect of pH on the optical density at 400 mμ for a solution containing 5 mg U per 50 ml measured against water in 1 cm cell with 1 mμ band width. As can be seen, a pH of from 11 to 14 gives satisfactory results.

4. Effect of Temperature. Above normal room temperatures decomposition of hydrogen peroxide is pronounced and the bubbles formed made optical measurements difficult. In very hot weather it is advisable to cool samples to 15-20°C to avoid excessive decomposition.

5. Stability of Color. The yellow color is stable for several hours if the peroxide is not destroyed by high temperature or the catalytic action of impurities, particularly mixtures of iron and copper.
6. Effect of Uranium Concentration. The effect of concentration of uranium on the transmittancy measured against water in 1 cm cells at one mμ band width is shown in Figure 4. Figure 5 shows the same set of curves corrected for reagent blank. Concentrations as low as 0.05 mg per 50 ml (1 ppm) can be measured in 10 cm cells giving a 90.9% transmittancy. Beer's law holds up to at least 20 mg/100 ml (200 ppm) in a 1 cm cell at narrow band widths. It may be noted that if the light is far from monochromatic, Beer's law may not apply.

Although this colorimetric method is rather insensitive, it does not present a serious problem since the uranium in samples can be concentrated by ammonia precipitation or by evaporation and ether extraction. A precision and accuracy of better than ±1% can be attained by this method on pure samples using a Beckman spectrophotometer, as evidenced by the series of determinations shown in Table 2. However, under routine conditions, on impure samples which must undergo separation, an average error of ±3% should be expected.

Interference. Ions such as ammonium, sodium, potassium, lithium, acetate, chloride, nitrate, phosphate, perchlorate, and sulfate do not interfere appreciably. The interfering ions can be classified into those which possess a yellow color or which develop one with hydrogen peroxide, those which precipitate in sodium carbonate, sodium hydroxide

TABLE 2

Precision and Accuracy

Sample No.	True Value mg U	Experimental mg U	Error mg	Per cent error
1	8.70	8.70	0.00	0.00
2	8.70	8.76	+0.06	+0.69
3	9.45	9.37	-0.08	-0.85
4	9.45	9.36	-0.09	-0.94
5	10.63	10.68	+0.05	+0.47
6	10.63	10.68	+0.05	+0.47
7	11.92	11.93	+0.01	+0.08
8	11.92	11.90	-0.02	-0.16
9	12.78	12.69	-0.09	-0.70
10	12.78	12.66	-0.12	-0.94

Average per cent error ±0.53

or hydrogen peroxide solution, and those which catalyze the decomposition of hydrogen peroxide.

Of those which possess a yellow color, chromium is the most likely to interfere, since in the presence of alkaline hydrogen peroxide it is oxidized to the yellow chromate ion. Cerium and molybdenum develop yellow colors in alkaline hydrogen peroxide solution. Titanium, vanadium and columbium develop yellow colors with hydrogen peroxide in acidic solution but also develop a definite though weaker yellow color in alkaline solution which may interfere.

Many ions are precipitated in alkaline solutions. Most frequently encountered in this list are Cr^{+3}, Fe^{+3}, Cu^{+2}, Ni^{+2}. Others include Al^{+3}, Be^{+2}, Bi^{+3}, Cd^{+2}, Ce^{+3}, Co^{+2}, Ga^{+3}, Ge^{+2}, In^{+3}, La^{+3}, Pb^{+2}, Mg^{+2}, Mn^{+2}, Hg^{+2}, Pt^{+2}, Sm^{+3}, Sc^{+3}, Ta^{+5}, Th^{+4}, Ti^{+4}, Y^{+3}, and In^{+2}. In addition the carbonate ion precipitates Ba^{+2}, Ca^{+2}, Sr^{+2}, Ra^{+2}, Dy^{+3}, Pr^{+3}, and Ag^{+1}. Thorium will precipitate from its carbonate complex with hydrogen peroxide. Although these precipitates can be filtered off, there is danger of coprecipitation of the uranium especially with gelatinous precipitates such as those of iron and aluminum.

Many impurities catalyze the decomposition of hydrogen peroxide. In alkaline solutions containing a mixture of copper and iron salts it is impossible to obtain full color development due to rapid destruction of the hydrogen peroxide.

It should be stressed that the accurate colorimetric determination of uranium depends upon good separation from interferences. Separation, then, is the most important part of the determination and the source of greatest error. Separation can seldom be avoided.

Methods of separation. Three procedures are analytically practical: precipitation, electrolysis, and extraction. Extraction is very effective especially for large amounts of impurities. It is difficult to remove all interferences by precipitation or electrolysis alone.

Precipitation. In order to separate uranium by precipitation methods, solutions are acidified with nitric acid, and boiled to remove all the carbon dioxide. The solutions are cooled somewhat and an excess of carbonate free ammonia added. Uranium will precipitate along with iron, chromium (III) and many other ions. Most of the copper and nickel will remain in solution as an ammonia complex. The precipitate is dissolved in a small amount of hydrochloric acid. Thorium, if present, can be removed from this solution by precipitation with oxalic acid. Then the iron and chromium (III) can be precipitated with an excess of ammonium carbonate, digested at 80-90°C and filtered. The uranium remains in the filtrate as a carbonate complex.

Electrolysis. To separate interfering ions from uranium by electrolysis, one can add sulfuric acid and evaporate to fumes of sulfur trioxide, then dilute until the solution is 1 N in sulfuric acid and electrolyze at 5 amps in a water cooled vessel with a coiled platinum wire anode and a stirred mercury pool cathode until free of iron and chromium as shown by spot test. The diphenyl carbazide spot test for chromium and the 2,2'-bipyridine spot test for iron are suggested. Impurities are removed into the mercury, in the order copper, nickel, iron, and chromium, leaving uranium in solution.

Extraction. In order to separate small amounts of uranium from most interferences, one should evaporate the sample solution containing 50 ml of concentrated nitric acid to about 20 ml. Silver nitrate is added to precipitate any chloride ions; some sodium sulfite is added to reduce any chromium to chromium (III). The solution is saturated with calcium nitrate and extracted with several portions of diethyl ether in a separatory funnel or in a continuous extractor. The ether extract should be slowly evaporated to dryness, dissolved in 2 ml of concentrated nitric acid, diluted to about 20 ml with saturated calcium nitrate solution and extracted again with portions of diethyl ether. The second extract containing the uranium is evaporated to dryness in a pyrex beaker and ignited to oxides in the beaker on a wire gauze over a Meker burner to destroy any yellow organic material. The oxides are then dissolved in one ml of nitric acid and analyzed. Traces of many ions extract with the uranium and are removed by the second extraction. Samples containing thorium must also receive an oxalate precipitation.

Recommended Procedure

Sample

Selection. Select a representative portion of the solid or liquid sample to be analyzed.

Measurement. Weigh or measure by volume a portion containing from 1 to 20 mg of uranium.

Treatment. Dissolve solids in nitric acid in so far as possible. Samples insoluble in nitric acid should be dried, powdered, and fused with sodium carbonate. Dissolve the cooled cake in nitric acid, filter off any silica and volatilize it with hydrofluoric acid. Dissolve the residue in nitric acid and add it to the nitric acid solution of the carbonate cake.

Any aqueous samples should be acidified with nitric acid and filtered. Ash the filter paper and work up separately as above. Non-aqueous samples immiscible with water should be extracted with nitric acid in a separatory funnel. Non-aqueous samples miscible with water should be evaporated to dryness and dissolved in nitric acid.

Desired Constituent

Separation. The interfering substances must be removed from the nitric acid solution by precipitation, or electrolysis; or the uranium isolated by ether extraction or other suitable means.

Measurement. To the acidic solution of UO_2^{++} ion free from all interfering substances add enough 10% sodium hydroxide to neutralize most of the acid. Complete the neutralization with 20% sodium carbonate in order to avoid precipitation of uranium. Add 5 ml excess of 20% sodium carbonate to complex the uranium, then 5 ml of 10% sodium hydroxide to obtain a pH of 11-14. Add 1 ml of 30% hydrogen peroxide, and dilute to 100 ml. Measure the transmittancy or optical density at 400 mμ. A blue or violet filter is recommended for a filter photometer. Calculate the amount of uranium present from the Beer's law equation or read it from a calibration curve. If the solution is cloudy, it is caused by incomplete separation. The solution may be filtered, although for accurate work purification should be improved.

SUMMARY

The alkaline peroxide colorimetric method for determination of uranium is described. The effect of reagent concentration, order of addition of reagents, pH, temperature, stability of color, uranium concentration, and interfering ions are discussed. A recommended procedure is presented. The method will determine uranium as low as 0.05 mg per 50 ml (1 p.p m) in 10 cm cells. A precision and accuracy of about 3% can be expected.

Literature Cited

(1) Hackl, Z. Anal. Chem. 119 321 (40).

(2) Arnold and Pray, Ind. Eng. Chem, Anal. Ed. 15, 294 (43).

(3) Sandell, "Colorimetric Determination of Traces of Metals" p 436 New York, N.Y. Interscience Publishers Inc. 1944.

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