convenience in transfer with a 1-ml. pipet, 1 ml. of 3% hydrogen peroxide is sufficient for attainment of maximum absorbancy as measured at 342 mμ.

Effect of Diverse Ions. The effect of the diverse ions was studied using 78 p.p.m. of columbium with an acidic mixture of 25 ml. of sulfuric and 5 ml. of phosphoric acid. The absorbancy measurements were taken at 342 mμ in order to ascertain any deleterious effects of the various ions. A negligible error has been obtained with 1000 p.p.m. of aluminum, acetate, arsenate, cadmium, cerium, cobaltous, cupric, citrate, calcium, bismuth, carbonate magnesium, manganous mercuric, malonate, nickelous, oxalate, perchlorate, stannate, tartrate, tetraborate, thiosulfate, silver, lithium, iodate, and zinc ions. It was found that 150 p.p.m. of tantalum did not interfere. The following ions interfere because of the formation of precipitates due either to the acids present or to columbate ions: barium, plumbous, strontium, zirconyl, ferrocyanide, silicate, and iodide. Table I lists the interfering ions and their effect.

SUMMARY

A high concentration of sulfuric acid and the addition of phosphoric acid are important for the development of percolumbic acid exhibiting maximum absorbancy in the ultraviolet region. The effect of 51 diversions was determined. Ferric, molybdate, titanic, chlorate, chloride, nitrate, nitrite, fluoride, vanadate, and tungstate ions are the chief sources of error. The ultraviolet spectrophotometric method that was developed is more sensitive than the conventional colorimetric method for determining columbium as percolumbic acid.

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Spectrophotometric Determination of Rhodium with Hypochlorite

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This study was undertaken to investigate the possible application, for spectrophotometric determination of rhodium, of the blue color formed by treatment of rhodium(III) with sodium hypochlorite. Below pH 3.5, very little color developed; above pH 10, a dark blue-green precipitate formed. Within the pH range 4.7 to 7.2, maximum constant blue color was produced. At room temperature about 1 hour was required for maximum color development; the resulting color was stable for an hour, after which slow fading occurred. The color could be restored by addition of more hypochlorite. Heating accelerated both the developing rate and the fading rate. The system has a transmittancy minimum at 665 mμ, and conforms to Beer's law. Palladium, platinum, gold, iron, chromium, and nickel ions can be tolerated in relatively large amounts, and ruthenium, osmium, iridium, cobalt, manganese, and copper in moderate quantities relative to rhodium. Salts of iridium and cobalt catalyze the decomposition of the hypochlorite. Of the common anions, only iodide and iodate interfere. When transmittancy measurements are made at 665 mμ in 1-cm. cells, the optimum range is about 5 to 20 p.p.m. of rhodium; in this range maximum photometric accuracy corresponds to about 0.6% relative error.

THE determination of rhodium by precipitation either as hydrous oxide or as sulfide, followed by ignition in hydrogen or by reduction of its compounds with active metals or with titanium(III) salts (*6*, p. 274 *et seq.*; *8*) is tedious and subject to many possible sources of error. Rhodium has been determined gravimetrically with thiobarbituric acid (*4*). Many organic nitrogen compounds form colored precipitates with rhodium(III), some of which have been used for microscopic identification (*10*). The red color produced by treating rhodium(III) with tin(II) chloride in hydrochloric acid solution (*7*) has been used as a test for rhodium (*9*, *11*), and also for its estimation (*3*).

Demarçay (*5*) reported that rhodium solutions treated with sodium hypochlorite gave a yellow precipitate, soluble in acetic acid, and that the solution slowly changed to orange yellow, followed by the formation of a gray precipitate and a sky-blue solution. Alvarez (*1*) observed that when chlorine was passed into a solution of a rhodium salt in sodium hydroxide the liquid became yellowish-red, then deep red, followed by formation of a green precipitate, which finally dissolved forming a blue solution. It was the purpose of the present investigation to study the formation of the blue reaction product with a view to its application as a spectrophotometric method for the determination of rhodium.

REAGENTS

Rhodium metal powder was obtained from A. D. Mackay, Inc. Spectrographic examination of the sample detected no osmium nor ruthenium, and only trace quantities of palladium, platinum, iridium, gold, copper, and silver (amounts far below the tolerance limits in the determination of rhodium with hypochlorite). Sodium hypochlorite was used in the form of Chlorox bleaching solution. All other chemicals were analytical reagent grade.

APPARATUS

A Beckman Model DU spectrophotometer, operated at high constant sensitivity, was used for the transmittancy measurements. The slit width for measurements at 665 mμ was 0.08 mm. The matched Corex cells had a 1.000-cm. light path.

EXPERIMENTAL

Preparation of Standard Sample. Weighed samples of rhodium metal powder were placed in a small porcelain boat and mixed with finely ground and previously ignited sodium chloride; 1

gram of sodium chloride was used for each 0.1 gram of rhodium. The mixture was heated in a combustion furnace at 750° C., while chlorine was passed through the combustion tube at a rate of about 500 ml. per minute. Although conversion was not quantitative in 5 hours (*6*, p. 274), by the end of 2 hours about 98% of the rhodium was converted to the soluble chloro-compound. The melt was dissolved in water containing 5 ml. of hydrochloric acid in 250 ml., and insoluble material filtered off. After the filter paper was burned off, the residue was again treated with sodium chloride and chlorine. By this procedure the conversion of the rhodium was complete. The combined solutions, which were a light raspberry-red color, were diluted to known volume.

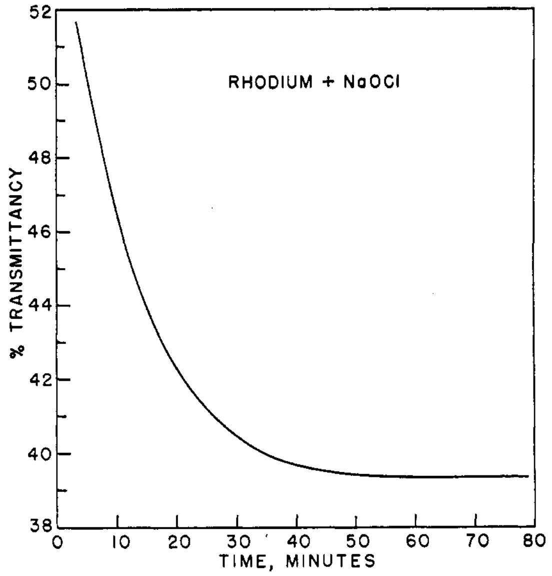

Figure 1. Development of Color

Development of Color. When treated with sodium hypochlorite, solutions of rhodium(III) chloride developed a blue color, provided the pH of the solution was neither too low nor too high. The color is very similar to that of ammoniacal solutions of copper(II) and to solutions of cobalt(II) chloride in ethyl alcohol or in concentrated hydrochloric acid. At room temperature (about 25° C.) the color developed slowly and reached maximum intensity in about 50 minutes (see Figure 1). The color was then stable for at least an hour, after which it began to fade slowly. When the reaction mixture was heated, the color intensity increased more rapidly for a short time, but the rate of fading was accelerated. Solutions that had faded by aging could be restored to full color intensity, for the amount of rhodium represented, by the addition of more hypochlorite.

Based upon the above facts, and upon the results of a study of the effects of pH (see below), the following standardized procedure was adopted: Ten milliliters of acetate buffer solution (50 ml. of glacial acetic acid and 200 grams of sodium acetate per liter) were mixed with 50 ml. of 5% sodium hypochlorite solution. An appropriate aliquot of the stock standard solution, to give the final concentration of rhodium desired, was added to the mixture and the solution was made up to 100 ml. After standing at room temperature for 1 hour, the transmittancy was measured, using as a blank a similar solution of reagents. If the rhodium solution was mixed with the acetate buffer and allowed to stand for some time before the addition of hypochlorite, the color was less intense than when the hypochlorite was added immediately; the difference in color intensity was roughly proportional to the time elapsed before the addition of the hypochlorite. When the reactants were mixed in rapid succession, good reproducibility of color was attained, regardless of the order of addition of reactants. The transmittancy of replicate samples was consistently reproducible to 0.2% (absolute).

Spectral curves for several rhodium concentrations are shown in Figure 2, which covers the wave-length range from 800 to 400 mμ. Below 400 mμ the transmittancy continues to decrease slightly, reaching a minimum at about 375 mμ, after which it increases rapidly to about 100% at about 340 mμ. The transmittancy minimum at 665 mμ was used for subsequent measurements. The color system conforms to Beer's law over the concentration range investigated (up to 40 p.p.m.).

Effect of Reagent Concentration. When varying amounts of hypochlorite reagent were used with fixed amounts of rhodium and buffer, the transmittancy decreased rapidly with increasing amounts of hypochlorite, up to about 40 ml. of hypochlorite solution per 100 ml. of final solution; the transmittancy was then constant with increasing amounts of hypochlorite (Figure 3). To provide a safe margin for routine work, 50 ml. of hypochlorite were used in the procedure finally adopted.

Effect of pH. It was apparent from the outset that the pH of the final solution had a marked effect on the color development. In order to establish optimum conditions of pH, samples of the acidic rhodium(III) solution were treated with varying small amounts of dilute sodium hydroxide and the color was developed with hypochlorite. The pH of the final solution was measured with a Beckman pH meter. Figure 4 shows the relation between transmittancy and the pH of the solution, for a constant amount of rhodium (8 p.p.m. in the final solution). Constant minimum transmittancy was obtained when the pH of the solution was within the limits of 4.7 to 7.2.

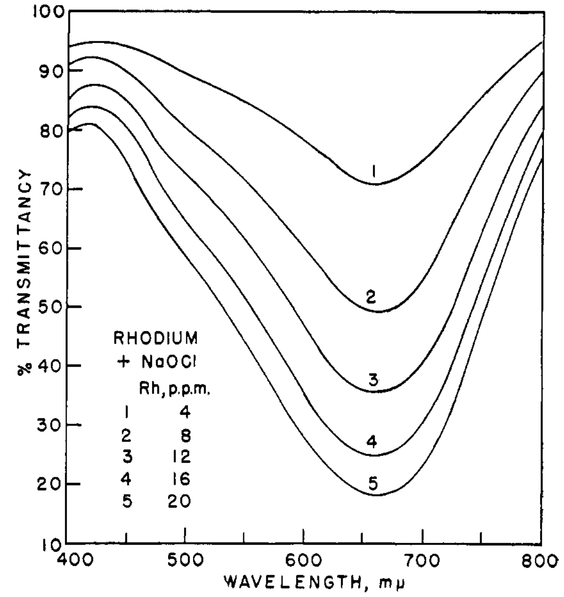

Figure 2. Spectral Curves for Rhodium

Because the rhodium(III) chloride stock solution contained hydrochloric acid, and the hypochlorite solution was alkaline, the use of a buffer was indicated, to ensure in each sample a constant pH within the above range. Citrate, benzoate, phosphate, and acetate buffers were tried; only the phosphate and the acetate buffers were suitable. Citrate buffers accentuated the fading of the color; benzoate buffers lacked the capacity and range desired. The use of the acetate buffers was adopted for the standardized procedure described above. In the series measurements for constructing the standard curve, the final solutions had a pH of 6.2.

Effect of Diverse Ions. In order to form a preliminary estimate of possible interference by various ions, especially the ions of the other platinum metals, observations were made on solutions of various ions treated with acetate buffer and hypochlorite reagent. Varying amounts of the ion under investigation were then added to a constant amount of rhodium, the color was devepoled by the standardized procedure, and the transmittancy was measured at 665 mμ. The tolerance of the rhodium system for the contaminating ion was taken as the amount of that substance

Table I. Effect of Diverse Ions

(All solutions contained 8 p.p.m. of rhodium)

Interfering Substance	Visual Color, Interfering Substance + Reagents	Visual Color,[a] Rh + Interfering Substance + Reagents	Amount Tolerated, P.P.M.
Palladium(II)	Red	Red-amber	200
Platinum(IV)	Yellow[b]	Green	50
Ruthenium(III)	Red-yellow[b]	Blue	10
Osmium(IV)	Black colloid	Blue-black, opaque	6
Iridium(IV)	Yellow then violet	Blue	3
Gold(III)	Yellow[b]	Blue-green	15
Iron(III)	Red-brown ppt.	Blue[c]	70[c]
Cobalt(II)	Olive-green	Blue	5
Nickel(II)	Black ppt.	Blue[c]	20[c]
Manganese(II)	Black ppt.	Blue[c]	5[c]
Chromium(III) or (VI)	Yellow	Green	15
Copper(II)	Blue-green	Blue	5
Iodide, Iodate	Colorless	Blue	1

[a] Color at tolerance concentration of interfering substance.
[b] Same color as solution of test ion.
[c] Observations made after filtration.

which gave a transmittancy not more than 0.4% (absolute) different from that of the rhodium alone. The results of the interference tests are shown in Table I. Chloride, bromide, bromate, perchlorate, nitrate, sulfate, and phosphate gave no interference up to at least 100 p.p.m.; hence higher concentrations were not tried.

The visual color of the developed solutions containing rhodium and a contaminating ion were, in some cases, markedly different from the color when rhodium alone was present, without influencing appreciably the transmittancy at 665 mμ. For example, a solution containing 8 p.p.m. of rhodium and relatively large amounts of palladium was a dark red-amber color, but the transmittancy at 665 mμ was very little influenced by the palladium. In the cases of iridium and of cobalt compounds, either alone or in the presence of rhodium, catalytic decomposition of the hypochlorite to form oxygen was very pronounced. This catalytic action is being investigated further.

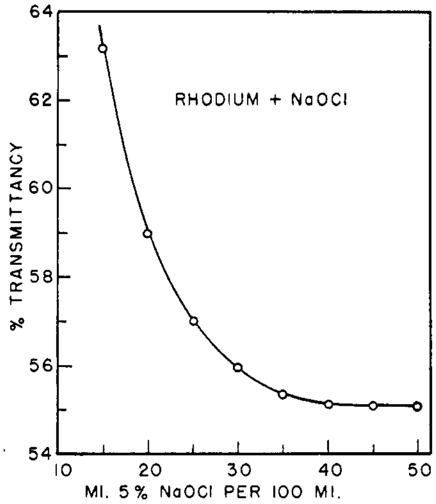

Figure 3. Effect of Reagent Concentration

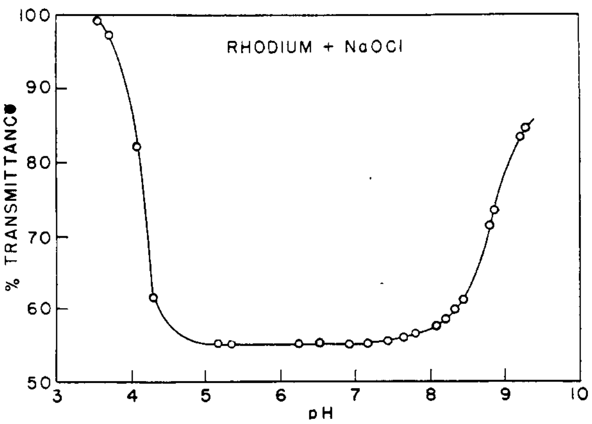

Figure 4. Effect of pH

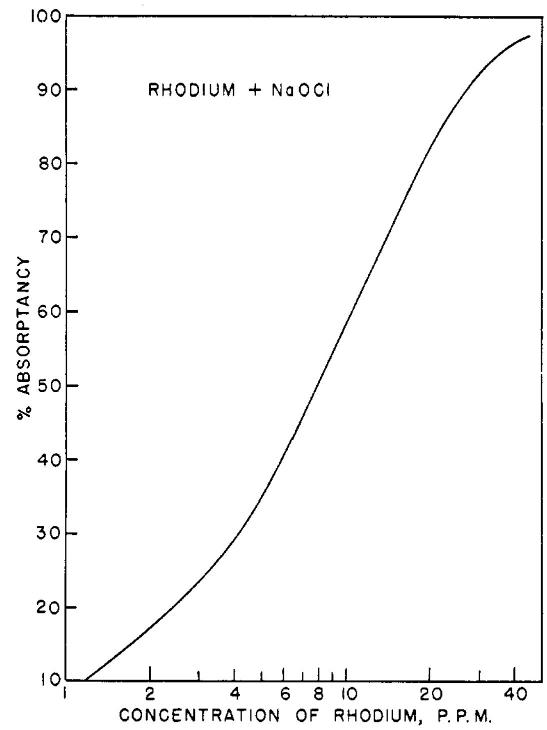

Figure 5. Range and Accuracy

Range and Accuracy. In Figure 5, standard series data are plotted as per cent absorptancy (100 − % transmittancy) against logarithm of concentration (*2*). The concentration range for best accuracy, for the conditions and technique used, is about 5 to 20 p.p.m.; in this range the relative analysis error is 2.8% per 1% absolute error in transmittancy. For a precision of 0.2% absolute transmittancy, the relative error is therefore about 0.6% in the concentration range given above. Relative errors of photometric origin will not exceed 1% in the concentration range 3 to 25 p.p.m.

DISCUSSION

At no time during this investigation did the authors observe the series of color changes recorded by Demarçay (*5*), to which reference was made above. By the procedure described the change was always from the pale raspberry-red color of the rhodium(III) chloride solution to an immediate, although faint, blue color, which increased in intensity as the mixture was allowed to stand, finally giving a deep blue solution. A yellow to red solution was not observed; in samples at a pH greater than 10, a blue or blue-green precipitate formed.

When chlorine gas was passed into alkaline solutions of rhodium(III), many of the changes of color and of state reported by Alvarez (*1*) were confirmed, although the final mixture was purple and turbid, rather than a clear blue solution. It appears likely that many of the observed changes are dependent upon the pH changes accompanying the reaction of chlorine with the alkali present.

In the analytical method described herein, the production of

Table II. Spectral Characteristics of Rhodium-Hypochlorite Solutions at Various pH Values

pH	Visual Color	Transmittancy Minimum, mμ	Transmittancy Maximum, mμ
2	Lavender	565	460
6	Blue	665	480
8	Green	665	480
10	Yellow-orange	435	385, 640

maximum blue color, within the appropriate pH range, required an extremely high ratio of hypochlorite to rhodium. For a study of the system to deduce the composition of the complex by the method of continuous variation or by the method of mole ratios, the concentration of rhodium was increased and the concentration of hypochlorite was decreased to bring the ratio of reactants into a range suitable to these methods. It was then observed that for a given ratio of hypochlorite to rhodium, various colors appeared as the pH of the solution was varied. Starting with the acidic solution of rhodium and hypochlorite (in amounts to give a final solution 0.001 *M* in each reactant), slow addition of sodium hydroxide to increase the pH caused the appearance of different colors, as listed in Table II. The color changes were completely reversible upon decreasing the pH by slow addition of dilute hydrochloric acid.

The production of a green color at a pH intermediate between that at which the blue and the yellow-orange color appeared suggested that the visual green color might be a composite of a blue- and a yellow-colored species. The spectral curves for the different solutions had transmittancy minima and maxima shown in Table II. The absorption of the yellow-orange solution at 435 mμ is sharp and intense, but the spectral curve for the green solution shows no indication of increased absorption at this wave length. The yellow-orange variety appears to be a colloidal material. All the color systems are being investigated further.

ACKNOWLEDGMENT

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Spectrophotometric Studies on Raw Cane Sugars in Solution

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In a previous study of the color of refined sugars in solution it was found that the absorbancy index determined at 560 mμ, but not at other wave lengths, is equivalent to the color expressed in terms of brightness, purity, and dominant wave length. This work has been extended to 102 raw cane sugars from eleven countries. The transmittancy of 60 Brix solutions, filtered through Celite analytical filter aid, was measured throughout the visible spectrum. The plotted transmittancy curves were smooth, and similar to those of the refined sugars. The brightness, purity, and dominant wave length were computed from the transmittancies of the solutions, and a statistical analysis showed a correlation coefficient of 0.9992 between those three and the transmittancy determined under the same conditions at 560 mμ. Consequently, the corresponding absorbancy index at that wave length gives a measure of the color of the sugar within the limit of error of transmittancy measurements. Absorbancy indexes at any other wave length give erroneous color values. It is concluded that the color of raw cane sugars can be determined in the same manner as refined sugars, confirming the statement of Peters and Phelps.

A PREVIOUS study (*5*) on the color of 76 refined sugars in solution proved the correctness of the findings of Peters and Phelps (*4*) that the absorbancy index at wave length 560 mμ is equivalent, colorimetrically, to the integral absorption over the visible spectrum. In the present work the color of the sugar solution, as perceived by the eye, was computed in terms of the monochromatic analysis—i.e., brightness (luminance), excitation purity, and dominant wave length—by the selected ordinate method of Hardy (*2*) for illuminant C of the International Commission on Illumination, and the color thus expressed was compared statistically with the absorbancy index, *a*, at wave length 560 mμ, and with the transmittancy for the same wave length at 60 Brix and a thickness of 5 cm. It was shown that the absorbancy index of refined sugars at wave length 560 mμ is equivalent to the color within the limit of error of transmittancy measurements.

This study has been extended to 102 raw cane sugars, including 40 from Cuba, 10 each from Puerto Rico, Hawaii, the Philippines, and British West Indies, 8 from Louisiana, 5 from Peru, 4 from Australia, 2 each from the Dominican Republic and Florida, and 1 from Mauritius.

Solutions of approximately 60 Brix were prepared and filtered with Celite analytical filter aid, instead of with asbestos, for reasons explained in the previous paper. The transmittancies of the filtered solutions were measured with a Coleman Universal spectrophotometer at 13 points from 405 to 700 mμ, in cells of 2.46-