[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

The Hydroxyanthraquinones as Analytical Reagents. The Colorimetric Determination of Zirconium or Hafnium

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The use of the hydroxyanthraquinones in analytical chemistry has grown steadily since Atack[1] discovered that aluminum could be detected with alizarin red S,[2] the sodium salt of alizarin sulfonic acid. Their value as colorimetric reagents for precise quantitative work, however, has not been appreciated widely partly because the compounds (lakes) which these dyes form with all or nearly all metallic cations[3] are sparingly soluble, and partly because the dyes themselves are so intensely colored that the quantitative estimation by simple visual comparison of a small amount of lake in the presence of excess dye is practically impossible. In working with zirconium and hafnium, we have minimized the first difficulty by maintaining the lakes at great dilution in 95% ethyl alcohol. Color interference, the second difficulty, does not exist when a spectrophotometer[4] is used. This investigation is an attempt to establish the hydroxyanthraquinones as colorimetric reagents upon a systematic quantitative basis through accurate measurements of the light absorbed by these dyes and their lakes.

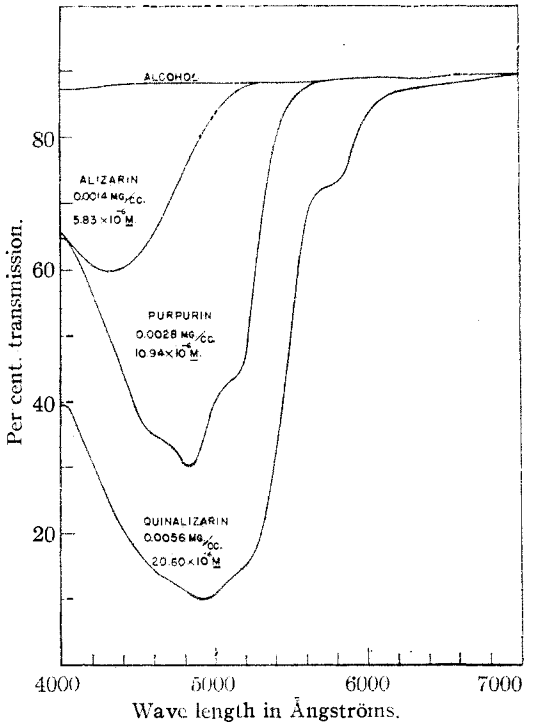

Fig. 1.—Transmission curves for each of the three hydroxyanthraquinones in dilute alcoholic solution.

The lakes formed by alizarin with most metallic cations, including aluminum, do not persist when an excess of a strong acid is added. The extraordinary stability of the alizarin–zirconium lake under these conditions was discovered by deBoer[5] as he attempted to use Atack's reaction to detect aluminum in the presence of zirconium. His work afforded us a welcome point of departure in the development of the colorimetric methods given below, with which it is possible to determine even a few micrograms of zirconium or hafnium with reasonable accuracy.

The absorption of visible light by acid alcoholic solutions of alizarin (1,2-dihydroxyanthraquinone), purpurin (1,2,4-trihydroxyanthraquinone) and quinalizarin (1,2,5,8-tetrahydroxyanthraquinone) is shown in Fig. 1. Each of these curves belongs to a family that was obtained to establish the molar extinction coefficients of the dyes, to be subsequently reported. Occasionally small decreases in transmission were observed near 6000 Å. with concentrated dye solutions; these were probably due to slight impurities not present in the stock solutions and introduced haphazardly in preparing the specimens for the transmission measurements; because of their infrequent, random occurrence, they were not investigated further.

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[1] Atack, *J. Soc. Chem. Ind.*, **34**, 936 (1915).

[2] *Cf.* Feigl, "Qualitative Analyse mit Hilfe von Tüpfelreaktionen," Akademische Verlagsgesellschaft, Leipzig, 1938, for an excellent discussion of and reference to the use of the hydroxyanthraquinones in analytical chemistry.

[3] *Cf.* Beilstein, "Handbuch der organischen Chemie," 4th Ed., Erstes Ergänzungswerk, Vol. VIII, Verlag von Julius Springer, 1931, pp. 711, *et seq.*

[4] Michaelson and Liebhafsky, *Gen. Elec. Rev.*, **39**, 445 (1936), give a description of the General Electric Company recording photoelectric spectrophotometer, which plots accurately the absorption spectrum of a solution for the visible range as a function of wave length in two and one-half minutes.

[5] (a) DeBoer, *Chem. Weekbl.*, **21**, 404 (1924). The work was extended to include the detection of hafnium and fluorine with alizarin and other hydroxyanthraquinones by (b) deBoer, *Rec. trav. chim.*, **44**, 1071 (1925); (c) deBoer and Basart, *Z. anorg. Chem.*, **152**, 203 (1926), who give a method for the titration of fluoride in which the zirconium-alizarin lake serves as indicator. The zirconium-purpurin lake is utilized similarly by (d) Kolthoff and Stansby, *Ind. Eng. Chem., Anal. Ed.*, **6**, 118 (1934).

General Experimental Details.—All transmission measurements were made with the General Electric Company recording photoelectric spectrophotometer.[4] The alcoholic solutions (or suspensions) were usually contained in a cylindrical quartz cell (inside length, 5.15 cm., inside diameter, 2.40 cm.) with nearly plane ends, which was always inserted into the instrument in the same way.

The standard zirconium solution, containing 1 mg. of zirconium per cc., was prepared by dissolving C. P. $ZrOCl_2 \cdot 8H_2O$ in strong hydrochloric acid at room temperature and diluting until the acid concentration was about 2 *N*; the strength of this solution, determined by igniting and weighing the precipitate obtained from a known volume with ammonium hydroxide, showed this salt to be over 99% pure. The standard hafnium solution was prepared by dissolving a known weight of hafnium dioxide (Deutsche Auer Gesellschaft, Berlin) in mixed concentrated hydrofluoric and nitric acids, fuming three times with sulfuric acid, diluting, repeatedly precipitating the hydroxide with ammonium hydroxide until the washings from the precipitate gave no test for sulfate, and finally dissolving this hafnium hydroxide in strong hydrochloric acid and diluting the resulting solution until the acid concentration was about 3 *N*. The hafnium content of this solution was determined by igniting the precipitated hydroxide. A large excess of acid is necessary to make certain that no hydrolysis beyond MO^{++} occurs; such hydrolysis interferes with the colorimetric methods given below.

The dyes, of good quality, were not purified further. They were dissolved by warming them in contact with 95% ethyl alcohol; the resulting solutions were cooled, filtered, and diluted with additional solvent. Solutions thus prepared precipitated the solute even after weeks or months of standing in the laboratory; this annoying behavior, which is in accord with Hüttig's[6] observations on aqueous solutions of alizarin, is probably due to the formation of unstable colloidal suspensions during the heating. (That the tendency to form suspensions of this sort is even more pronounced with the lakes formed by these dyes will appear subsequently.) The stable solutions finally employed contained: alizarin, 1.250 mg./cc.; purpurin, 0.754 mg./cc., quinalizarin, 0.328 mg./cc. Presumably solutions of these concentrations would have been stable initially.

The Colorimetric Method.—The following detailed instructions gradually evolved as zirconium determinations were carried out over a period of several months. Reasonably close adherence to them is advisable if precise results are desired.

The lakes are formed in clean glass-stoppered graduated cylinders that have been rinsed with alcohol. The proper volume (satisfactory volumes of our solutions: alizarin, 0.5 cc.; purpurin, 1 cc.; quinalizarin, 1.5 cc.) of the stable dye solution is added to a small amount (up to, say, 120 micrograms—the maximum amount permissible varies with the dye employed) of the zirconyl ion contained in 1 cc. or less of about 2 *N* hydrochloric acid solution. Strong ammonium hydroxide is now added drop by drop until the color change of the dye reveals that the solution is slightly alkaline. The mixture is then allowed to stand for two minutes, neutralized with 1 *N* hydrochloric acid, and 0.1 cc. of 7 *N* hydrochloric acid finally added. When this mixture has been diluted with alcohol to the proper volume (in our case 27 cc.), its absorption from 4000 to 8000 Å. is measured on the spectrophotometer.

The rate at which the lake forms when no ammonium hydroxide is used decreases as the acidity increases; the addition of ammonium hydroxide eliminates this difficulty. When, in subsequent work, the lakes were formed differently, the differences are described.

Analytical Results.—The transmission curves obtained for a series of zirconium–alizarin determinations are given in Fig. 2, those for a zirconium–purpurin series in Fig. 3. The curves for the zirconium–quinalizarin families resemble those of Fig. 3 closely enough so that it is unnecessary to reproduce them. The absorption due to the dye alone occurs mainly at the shorter wave lengths as the curve for the first colored solution in each series shows; at wave lengths beyond 5600 Å. (alizarin) or 5800 Å. (purpurin) this absorption is so small that the transmission of the dye solution can be taken as I_0 in evaluating the results according to Beer's law

$$\log_{10} \frac{I_0}{I} = \epsilon_2 \, l \, (L) = k\epsilon_2 \, l \, (ZrO^{++}) \qquad (1)$$

I is the light transmitted at a longer wave length by the sample containing dye and lake; ϵ_2 is the molar absorption coefficient of the lake; *l* is the length of the cell in cm.; (ZrO^{++}) is the "concentration" (moles/liter) of this ion calculated from the micrograms of zirconium added to 27 cc.; *k* is a proportionality constant introduced because the combining ratio of zirconium to dye is unknown; (*L*) is the "concentration" (moles/liter) of the lake in the final solution. The data of Figs. 2 and 3 evaluated in this way for several wave lengths are shown in Figs. 4 and 5; a quinalizarin series is evaluated in Fig. 6; the product $k\epsilon_2$ is given in parentheses for each line beside the corresponding wave length. Examination of these figures reveals that: (1) alizarin gives precise results over the entire range of abscissa explored; (2) quinalizarin is the most sensitive reagent (largest value of $k\epsilon_2$), purpurin being intermediate; (3) as increasing amounts of the zirconium–purpurin lake are formed, *I* becomes too small, leading to positive deviations from Beer's law, which *increase* with the wave length; (4) under the same conditions, *I* for the quinalizarin lakes becomes too large, leading to negative deviations that tend to *decrease* with the wave length. The positive deviations will be discussed below; the negative in a subsequent article. We have found it convenient to use the following

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[6] Hüttig, *Z. physik. Chem.*, **87**, 129 (1914).

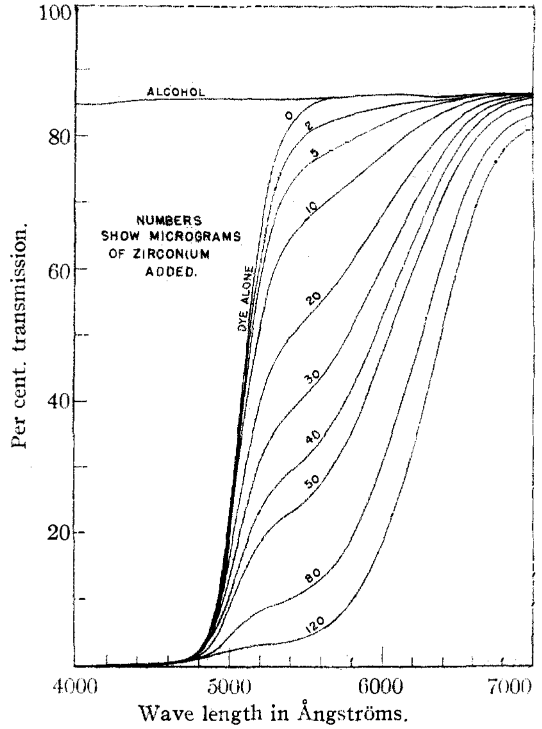

Fig. 2.—Standard transmission curves for the estimation of zirconium with alizarin.

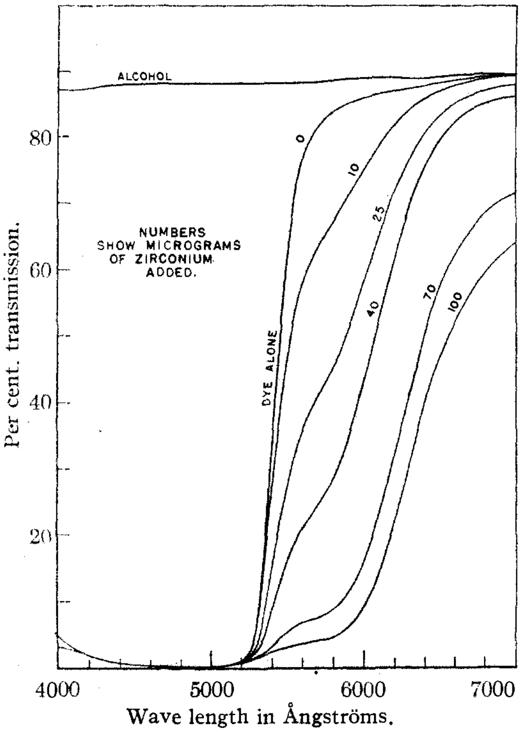

Fig. 3.—Standard transmission curves for the estimation of zirconium with purpurin.

wave lengths (at which absorption by the dye is negligible) in analytical work: alizarin, 5600 Å.; purpurin, 5800 Å.; quinalizarin, 6200 Å.

Effect of Added Substances.—Since the problem of removing interference by most other metallic cations often can be solved by increasing the acid concentration until interfering lakes will not form, the effect of added acid on lake formation was investigated. As 12 *N* hydrochloric or perchloric acid was added before dilution with alcohol to the lake formed from 50 micrograms of zirconium, a minimum in the transmission for 5600 Å. was observed with 0.05 cc. of excess acid. The other transmissions corresponded to the following decreases in micrograms of zirconium: 4.2 (no excess acid); 4.2 (0.5 cc. excess); 11.6 (1 cc. excess). The large transmission at 7000 Å. increased continuously with added excess of acid and the change expressed in micrograms of zirconium was much more pronounced at this wave length.

Sulfate and fluoride ions unite with zirconyl ion to form complex ions so stable that lake formation in the presence of sulfuric or hydrofluoric acid is decreased or prevented.[7] Preliminary experiments indicate that our colorimetric method is adapted to estimating small amounts of either of these interfering anions. Sulfate ion has been studied more thoroughly, and with the following results. When the alizarin lake is formed in the usual manner, and sulfuric acid is added before dilution, the color due to the lake disappears at a measurable rate which increases with greater amounts of added acid. When the acid is added after dilution, the change is similar but less rapid; the transmissions in such experiments increased markedly at first, more slowly afterward: when 0.05 cc. of 12 *N* acid was added to the final (27 cc.) volume, the transmissions at 5600 Å. for different times were 55.1% (one-half hour); 68.6% (fifteen hours); 70.4% (twenty-three hours); 71.2% (forty-seven hours). (The transmission without added sulfuric acid was 13.6% at 5600 Å. and increased only a few per cent. in forty-eight hours.) When the sulfuric acid is present initially, much less lake is formed; if ammonium hydroxide is used, lake formation is less than when the sulfuric acid is not neutralized;

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(7) Feigl (ref. 3, p. 254) mentions that fluorides, sulfates, phosphates, organic hydroxy acids, molybdates and tungstates interfere with or modify the formation of the zirconium-alizarin lake. The literature on complex zirconium ions containing fluoride and sulfate is extensive; *cf.* (a) Venable, "Zirconium and its Compounds," Chemical Catalog Co., New York, 1922; (b) Ruer and Levin, *Z. anorg. Chem.*, **46**, 449 (1905); (c) Chauvenet, *Ann. chim.*, [9] **13**, 59 (1920).

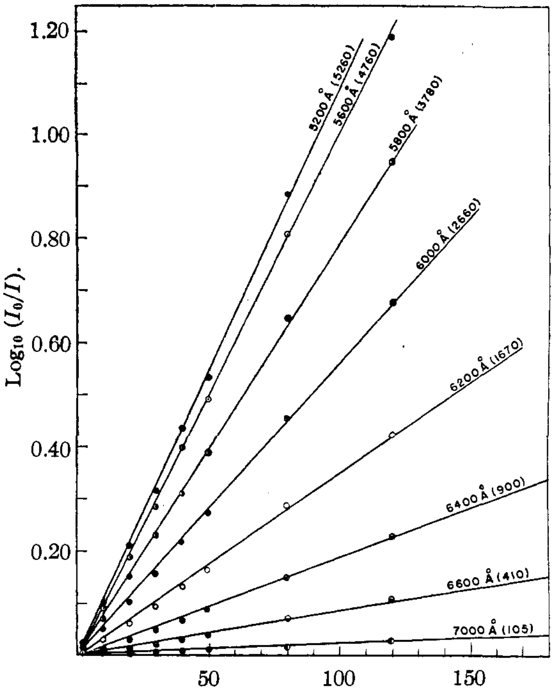

Fig. 4.—Beer's law curves for Fig. 2.

in the 0.05 cc. sulfuric acid experiment soon after mixing, the transmissions at 5600 Å. were 64.8% in the former case and 61.0% in the latter. (It is strange that these transmissions should be smaller than the limiting value, near 70% observed above.) Since the presence of 30 mg. of sulfuric acid increases the transmission due to the zirconium lake from 14 to 65%, it is obvious (since the transmission values are accurate to 0.1 or 0.2%) that this colorimetric method could be used for a rapid estimation of sulfate as well as for studying the formation of zirconyl-sulfate complex ions. A parallel investigation for fluoride ion ought to present no serious difficulty.

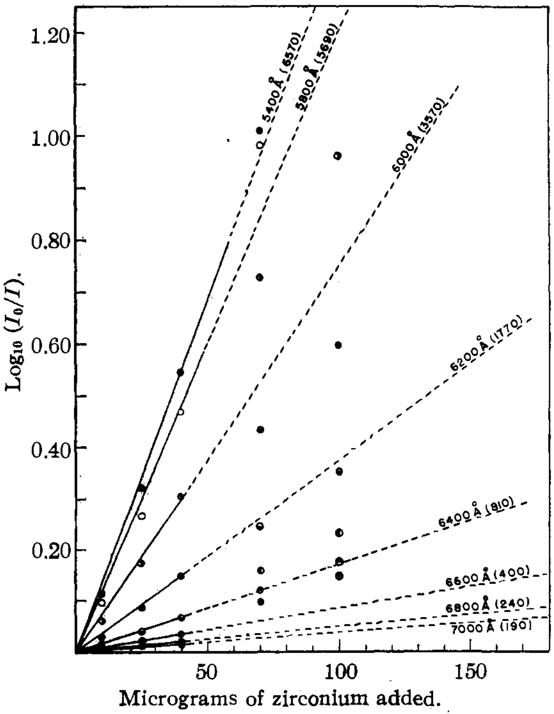

Fig. 5.—Beer's law curves for Fig. 3.

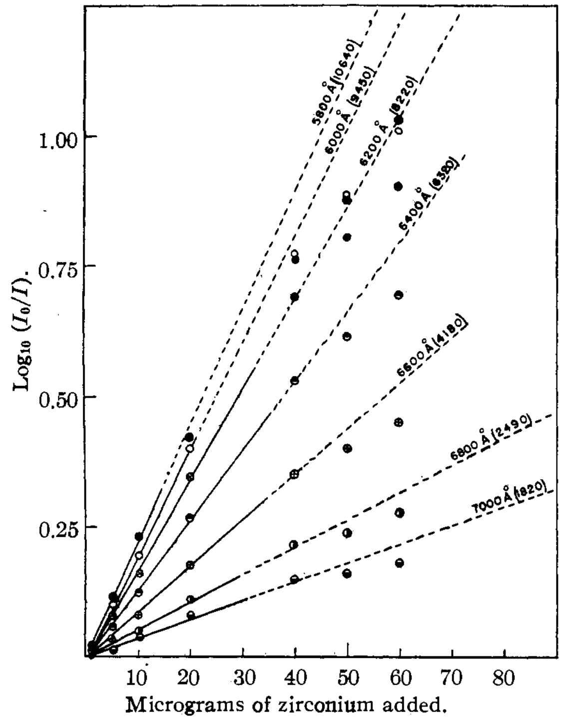

Fig. 6.—Beer's law curves for zirconium–quinalizarin experiments like the alizarin experiments of Fig. 2.

The interference of representative metallic cations not in the same periodic table group with zirconium was studied by adding 1 mg. of these ions to 10 micrograms of zirconium and then forming the lakes in the usual manner, that is, using 0.1 cc. of 7 *N* hydrochloric acid in excess. Under these conditions, the amount of zirconium cannot be determined accurately from data like those in Fig. 4; but the discrepancy in most cases will not exceed 50%, and may be positive or negative. Fe^{III}, Cr^{III} and Co^{II} decrease the transmission most markedly, without changing greatly the shape of the curve; W^{VI} and Mo^{VI} give curves much steeper than those for zirconium in the 5600 Å. region; many cations (Cd^{++}, Cu^{++}, Pb^{++}, Al^{+++}), when added in the presence of hydrochloric acid, increase the transmission, indicating that here, as with sulfate and fluoride, lake formation is decreased. In order to discover whether this decrease persists when chloride ion (which readily forms complexes) is absent, the experiments described in Fig. 7 were performed.

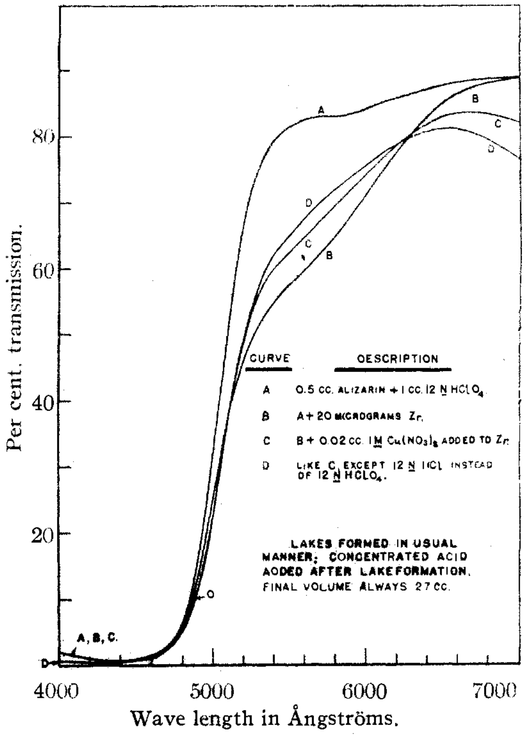

Fig. 7.—Interference of cupric ion with the determination of zirconium.

The curves show that lake formation is decreased even with perchloric acid, although to a smaller extent than with hydrochloric. (It was proved in experiments not given that the absorption near 7000 Å. persists when no dye is used; *i. e.*, it is the absorption due to the blue, solvated cupric ion.) The simplest explanation for the decreasing lake formation encountered when cations like Cu^{++} are added assumes that complex ions (*e. g.*, $CuCl_4^{=}$) derived from them unite with the zirconyl ion. If this explanation is correct, it is surprising to discover that a similar union can occur when perchlorate is the principal anion present: if ZrO^{++} can involve perchlorate in complex ion formation, it probably can react similarly with any other anion.

Experiments have shown that positive errors encountered with ions like Fe^{+++} can be reduced by increasing the amount of excess hydrochloric acid added; under these conditions, of course, the absorption due to the zirconium lake is also decreased.

To summarize: When present in hundred-fold excess, many cations interfere with the colorimetric estimation of zirconium because they either form lakes themselves or because they involve the zirconyl ion in complex formation. The former interference can be mitigated at the expense of sensitivity by increasing the excess of added acid; the latter, by working with perchlorates; either type of error can be compensated obtaining data like those in Fig. 4 with the interfering ion present; the shape of the spectrophotometric curves often reveals whether interference is occurring. There is no reason to believe that these cations will influence appreciably the colorimetric determination of a comparable amount of zirconium.

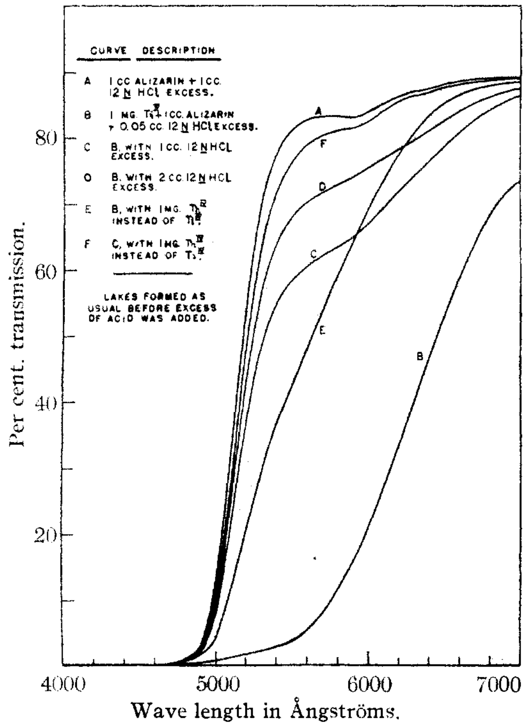

Fig. 8.—Interference of $Ti^{(IV)}$ and $Th^{(IV)}$ with the determination of zirconium.

Other Elements of Group IV.—Figure 8 shows the transmission curves obtained when varying excesses of concentrated hydrochloric acid were added to alizarin lakes formed in the usual manner with hydrochloric acid solutions containing Ti^{IV} and Th^{IV}. The curve from the thorium experiment with 1 cc. of excess acid is not greatly different from the curve for the dye alone; in other words, under our conditions interference by thorium is less serious than interference by titanium. Also, the absorption spectrum of the thorium lake differs markedly from those of the titanium and zirconium lakes, which resemble each other. This difference probably can be traced to the much smaller tendency of thorium to hydrolyze.

Although the close chemical similarity of hafnium to zirconium militates against the existence of any marked difference in their reactions with the hydroxyanthraquinones, there was some hope of finding a difference detectable by the spectrophotometer. Curves analogous to those of Fig. 2 were obtained for each of the three lakes, but they are not reproduced because each is qualitatively identical with the curve for the corresponding zirconium lake. The Beer's law data for the hafnium–alizarin family are given in Fig. 9. Comparison of these $k\epsilon_2$ values with those of Fig. 4 shows the latter to be, on the average, 1.30 times larger; in other words, a gram atom of zirconium combined as the alizarin lake behaves toward the spectrophotometer like 1.3 gram atoms of hafnium similarly combined. It follows that 1 g. of zirconium is spectrophotometrically equivalent to 2.55 g. of hafnium, and that the two elements can be determined in a known weight of sample provided other metallic cations can be removed if they are present. Experiments on hafnium lake formation with varying excesses of perchloric or sulfuric acid gave results similar to those obtained with zirconium.

The Lakes as Suspensions.—The general behavior of the lakes formed in this colorimetric work proves that they form suspensions, not true solutions. No matter what dye is used, the lakes eventually will settle out provided excess dye is present; the settling occurs more rapidly with purpurin and quinalizarin; the purpurin lakes are the most turbid initially, while those of alizarin seem at first to be in solution; the quinalizarin lakes form the most voluminous precipitate. The alizarin and purpurin lakes are red, with the latter darker; the quinalizarin lakes are purple. Having once settled out, the lakes can be re-dispersed easily by shaking; the transmission curve of the re-dispersed lake is very little different from that of the lake freshly prepared.

Crude sedimentation experiments[8] gave 1 micron as the order of magnitude of the average particle diameter in these lakes. Microscopic examination revealed that the diameters ranged, say, from 0.5 to 5 microns; the larger particles appeared to be clusters of smaller ones. It appears, therefore, that we are dealing with particles, near 1 micron in diameter, suspended in an alcoholic dye solution, from which they precipitate as coagulation occurs.

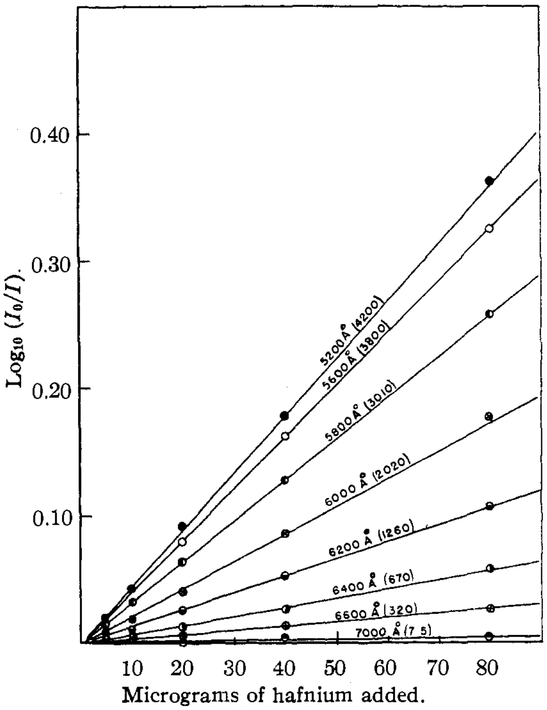

Fig. 9.—Beer's law curves for hafnium–alizarin experiments like the zirconium experiments of Fig. 2.

The rates at which these particles form and dissociate are of interest. Variation, by addition of alcohol, of the volume in which the zirconium–alizarin lake was formed gave the following transmissions for 5600 Å.: 10.0% (usual volume, *ca.* 0.5 cc.); 16.7% (10 cc.); 19.6% (25 cc.). Eight hours later these transmissions were: 10.0, 14.9 and 17.4%; obviously, lake formation, complete in the first experiment, was proceeding very slowly in the other two. To test the reverse reaction, 0.2 mg. of zirconium was converted to the lake with 1 cc. of dye solution and diluted to 50 cc. with alcohol. Aliquot parts of the resulting suspension were diluted 5 and 25 times; the following transmissions were measured at 5600 Å. (the transmission of alcohol was taken as I_0):

Relative dilution	1	5	25
Log (I_0/I) after 1 hr.	1.01	0.179	0.028
Log (I_0/I) after 24 hrs.	0.94	.181	.013

With no change whatever occurring, the values of log (I_0/I) should be inversely proportional to the relative dilution; this is nearly true, not only im-

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(8) *Cf.* Freundlich, "Kapillarchemie," Vol. 1, Akademische Verlagsgesellschaft, Leipzig, 1930, p. 491.

mediately after preparation but also after one day's standing. (An increase in transmission from 83.6 to only 84.3 caused the large change in log (I_0/I) for the most dilute experiment.) Since no appreciable dissociation of the lake was observed in these experiments, more extreme conditions were sought. A zirconium–quinalizarin lake was centrifuged out of the dye solution and redispersed in alcohol: no quinalizarin absorption was detected in this suspension even after several days of standing, after violent shaking (the lake precipitated from alcohol also), or after boiling for five minutes on the steam-bath; the transmission curve of the lake was virtually unaltered by this treatment. The conclusion from these experiments is either that an infinitesimal concentration of the dye or zirconium prevents the dissociation of the lake, or (what is much more probable) that this reaction is very slow. The latter explanation is more easily reconciled with the observation, already mentioned, that sulfuric acid will react with a small amount of lake even when the total volume is 27 cc.

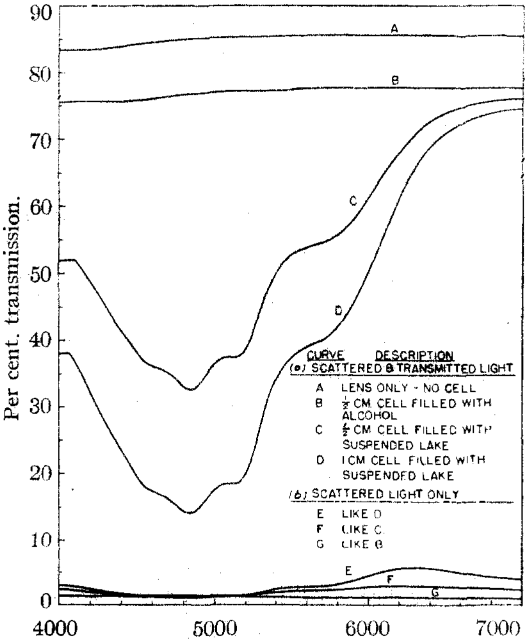

Fig. 10.—Direct measurement of light scattered by a suspended zirconium–purpurin lake.

Scattering of Light.—Particles approximately 1 micron in average diameter will scatter visible light of all wave lengths. Since this diameter does not greatly exceed the average wave length of visible light, the scattering is intermediate between scattering according to Rayleigh's law (amount of scattered light proportional to $1/\lambda^4$) and scattering by white fog (amount of scattered light independent of wave length).[9] It would not be surprising, therefore, to find that the amount of light scattered by the suspended lakes decreased slightly with the wave length.

Two methods of utilizing the spectrophotometer for measuring scattered light were employed. (1) A lens was inserted in the path of the transmission beam so that this beam, normally almost an ellipse (1″ × $^{13}/_{16}$″ or 2.54 × 2.06 cm.) at the entrance to the integrating sphere, converged to an approximate rectangle ($^1/_{16}$″ × $^3/_{16}$″ or 1.58 × 4.75 mm.) at that point. A removable piece of black tape just large enough to block out the beam could be placed on the cell to permit separate measurement of the scattered, and of the scattered plus transmitted light (Fig. 10). (2) Transmission measurements were made with a 1-cm. cell in two positions: against the integrating sphere ("near" position) and 5.5 cm. removed ("far" position). The proportion of scattered light entering the sphere obviously would be much less in the second position (Fig. 11). Glass cells were used for this work; reference to a description of the instrument[4] will aid in showing how the measurements were carried out.

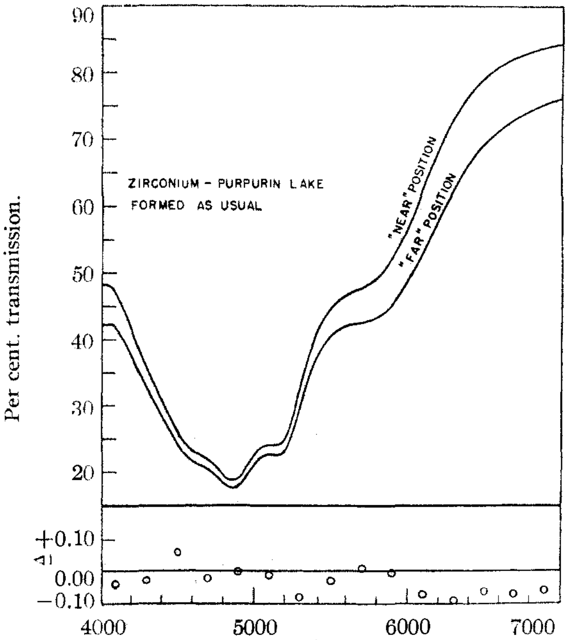

Fig. 11.—Indirect measurement of light scattered by a suspended zirconium–purpurin lake.

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[9] Langmuir and Westendorp, *Physics*, **1**, 273 (1931).

In connection with Fig. 11, assume (1) that a narrow transmitted beam I^t decreases in intensity from I_0^t to I_1^t as it passes through a 1-cm. cell; (2) that the scattering and the spatial distribution of scattered light are independent of wave length; (3) that the scattered light I_1^s entering the sphere results from a narrow beam I_m^s, whose intensity is proportional to that of the transmitted beam, from which it deviates at a point[10] m, where the intensity, the "mean" intensity, of the latter is I_m^t. I_m^s will travel through the cell along a path a, which is greater than l-m, and will have decreased in intensity to I_1^s when it reaches l. In the "near" position, the light entering the sphere will be $I_1^t + I_1^s$; in the "far" position, the entering light will be assumed equal to I_1^t, although it will be slightly greater since this position is not at infinite distance from the sphere. Under these simplified conditions, if second-order effects are neglected, it can be shown that

$$-\mathrm{d}\log\left(\frac{I_1^s}{I_1^t}\right)\Big/\mathrm{d}\lambda = [(m + a) - l]\mathrm{d}\epsilon/\mathrm{d}\lambda \quad (2)$$

This treatment is so approximate that $[(m + a) - l]$ will be taken as unity, thus anticipating the results to some extent. Then

$$\Delta = \mathrm{d}\log\left(\frac{I_1^s}{I_1^t}\right)\Big/\mathrm{d}\lambda + \mathrm{d}\epsilon/\mathrm{d}\lambda = 0 \quad (2a)$$

For Fig. 11, I_1^s/I_1^t at every wave length was calculated as the difference of the two transmission curves divided by the transmission, I_1^t, for the "far" position; ϵ was deduced according to Beer's law from I_0^t, the transmission of alcohol, and I_1^t; the results obtained by applying Eq. 2 to the curves in Fig. 11 are given in the lower part of the figure. (An increase of 0.1% in I_1^t at 4800 Å. produces, other things equal, a decrease of 0.15% in the absolute value of I_1^s, and a decrease at 4700 Å. in Δ from -0.02 to -0.06. This extreme example illustrated the precision required of the spectrophotometer for these measurements.) At the longer wave lengths, Δ is consistently negative, which means, since ϵ is decreasing continuously in this region, that I^s is not increasing rapidly enough. Beyond 5800 Å., log I_1^s/I_1^t actually decreases; only in this region do both quotients in Eq. 2 have the same sign. The simplest explanation of this behavior is that here the second assumption made above is no longer valid—probably because the wave length is large enough relative to the diameter of the particles to decrease their scattering power. Similar calculations have not been carried out for Fig. 10 because the scattering background (near 1% at all wave lengths as shown by the Curve G) is so large that I_1^s cannot be estimated for all wave lengths. Qualitatively Figs. 10 and 11 are in agreement; the decrease in I_1^s is particularly noticeable in the former.

This simplified analysis of scattering by the suspended lakes shows such scattering to be the cause of the positive deviations in Fig. 5; these deviations are greater at longer wave lengths because the ratio of scattered to absorbed light increases with the wave length. Scattering by the lakes (and hence their average particle size) decreases in the order purpurin, quinalizarin, alizarin; scattering by the dilute dye solutions is too small to be measured on the spectrophotometer. The increase in transmission at 7000 Å. observed when excess acid was used (see above) probably results from decrease in the amount of scattered light, indicating that the particle size is smaller with excess acid.

Applicability of the Methods.—Because lake formation by the hydroxyanthraquinones appears to occur with all metallic cations if the hydrogen ion concentration is properly adjusted, there is reason to believe that these dyes can be used for the accurate colorimetric estimation of, say, 10 micrograms of any isolated metallic cation. In other words, their value as *general* reagents for the estimation of any cation may well offset their failure to act as *specific* reagents in all cases. Perhaps the simplest way to carry out the estimation of any isolated metallic cation is by precipitating the lake in ammoniacal solution, washing it free of excess dye, and re-dispersing it in basic or acid alcohol for the transmission measurements. (Preliminary work on the estimation of small amounts of barium has shown the feasibility of this method.) When more than one metallic cation is present, specificity, to a limited degree at least, may be sought by adjusting the hydrogen ion concentration, or by adding ammonium salts to form complexes with the interfering cations.

The scope of the hydroxyanthraquinones as colorimetric reagents thus corresponds roughly with that of dithizone (diphenylthiocarbazone),

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(10) The point m should lie in the half of the cell nearest the integrating sphere for two reasons. (1) Scattered light originating in the other half of the cell must travel a longer path before reaching the sphere and hence will be more strongly absorbed. (2) Because of geometrical considerations, light from this half of the cell has a smaller chance of finding the opening in the sphere.

which Fischer[11] has so thoroughly investigated. Our experience indicates that dithizone is a good deal more sensitive than the hydroxyanthraquinones (thus ϵ_2 for copper dithizonate is about 35,000[11a]; ϵ_2 for the zirconium-quinalizarin lake is only 10,000); that the former reagent is much more difficult to prepare and to keep unchanged; that procedures involving it are likely to be more tedious, and that precise results are more difficult to obtain when it is used.

Summary

With the aid of a photoelectric recording spectrophotometer, precise colorimetric methods for the determination of zirconium or hafnium in small amounts have been developed. The methods involve lake formation with the hydroxyanthraquinone dyes.

Hafnium and zirconium, while qualitatively indistinguishable, can be estimated in a known weight of sample provided other cations can be removed if they are present.

The effect on lake formation of varying the acid concentration has been studied.

Interference by other cations is negligible unless these are present in larger excess.

The decrease in lake formation caused by complex formation between zirconyl and sulfate ions has been investigated. This decrease is pronounced enough to warrant the belief that the colorimetric methods could be used for the estimation of the various anions, particularly fluoride. that form complexes of this kind.

The scattering of light by the lakes, which are present as suspensions in the alcoholic dye solutions, has been briefly investigated and discussed.

A comparison of the hydroxyanthraquinones with dithizone, another colorimetric reagent that reacts with many cations, shows the latter to be several times more sensitive while the former are simpler to prepare and keep, and are capable of giving accurate results with the expenditure of less time and effort.

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[11] References to Fischer's valuable work are given by (a) Liebhafsky and Winslow, This Journal, **59**, 1966 (1937), who used the spectrophotometer to study dithizone as a colorimetric reagent.

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Artificial Radioactivity as a Test for Minute Traces of Elements

By G. T. Seaborg and J. J. Livingood

The high voltage and large current of the Berkeley cyclotron[1] have made it possible to obtain radioactive isotopes with activities of extremely high intensities, especially when deuterons are used as the bombarding particles. It is the purpose of this note to show how this circumstance has made it possible to identify extremely small amounts of impurities by means of their characteristic half-lives, after the substance containing the impurities has been bombarded with deuterons in the cyclotron. A quantitative estimation of the amount of the impurity can be made in those cases where the yield of the reaction involving the impurity has been previously determined. In the cases where this yield is not known an estimate can be made by means of a comparison with the known yield of some reaction of the same type. As an example the detection of extremely small amounts of gallium in iron is described. Other examples are given more briefly.

When a sample of iron was bombarded with deuterons it was found that two of the radioactivities produced could be ascribed to an extremely small amount of gallium impurity in the iron (~ six parts in one million, as will be shown later). This was established by the fact that the half-lives of the two activities, 22 min. and 14 hr. (electron emitters), were identical with the known half-lives of electron emitting Ga^{70} and Ga^{72}, respectively.[2,3] A chemical separation according to the methods of Noyes and Bray was performed upon a sample of bombarded iron to which a small amount of "carrier" gallium had been added after the bombardment. The 22 min. and 14 hr. periods appeared only in the gallium fraction.

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[1] Lawrence and Livingston, *Phys. Rev.*, **45**, 608 (1934); Lawrence and Cooksey, *ibid.*, **50**, 1131 (1936).

[2] Amaldi, D'Agostini, Fermi, Pontecorvo, Rasetti and Segre, *Proc. Roy. Soc.* (London), **A149**, 522 (1935).

[3] Sagane, *Phys. Rev.*, **53**, 212 (1937).