Because the concentrations are already defined in mole per cent units, the mole % D in the water may be expressed as:

$$\text{Mole \% D in water} = [D_2O(l)] + \tfrac{1}{2}\,[HDO(l)] \qquad (14)$$

Substitute Equations 11 and 13 into 14:

$$\text{Mole \% D in water} = \frac{K_3K_6K_2K_5\,100\,[D_2] + K_7K_2K_5\,50\,[HD]}{K_7K_2K_5[HD] + K_3K_6K_2K_5[D_2] + K_6K_7[H_2]} \qquad (15)$$

Equation 15 is the equation for water isotopic composition in terms of the equilibrated gas composition and the equilibria constants involved in the reaction.

Insert the values for the constants into Equation 15 (all these values are correct at 25° C.):

$K_2 = 3.62$
$K_3 = 3.11$
$K_5 = P_{H_2O}$
$K_6 = P_{HDO}$
$K_7 = P_{D_2O}$

and using the relationship $\frac{P_{D_2O}}{P_{HDO}} = \left(\frac{P_{D_2O}}{P_{H_2O}}\right)^{1/2} = 1.067$

$$\text{Mole \% D in water} = \frac{1055[D_2] + 159.0\,[HD]}{3.179[HD] + 10.55[D_2] + 0.8231\,[H_2]} \qquad (16)$$

Equation 16 may be used to calculate the isotopic composition of the water from the experimentally determined composition of the equilibrated gas. The equation holds good for the reaction at 25° C. for any composition of water. The gas molecule concentrations may, of course, be expressed in any consistent set of units; mole per cent of each gas species is probably the most convenient set of units to use. This equation could be simplified to eliminate one of the three types of gas molecules, from the calculation, yet it has been found advisable to keep it as given above.

EXPERIMENTAL

A series of water standards of known isotopic composition was prepared by weight dilution methods, using normal distilled water and nearly pure deuterium oxide as the ingredients. For each analysis about 5 ml. of the water specimen, a few milligrams of platinum oxide catalyst, and an atmosphere of equilibrating gas were introduced into a small flask, about 30 ml. in volume. The flask and its contents were allowed to stand for about 1 hour, during which time the equilibration reaction proceeded to equilibrium. Analyses were performed on two separate portions of each water standard, using tank hydrogen and tank deuterium, respectively, as the equilibrating gases. In this manner it was possible to approach the state of equilibrium from both directions for each water specimen. After the reaction had proceeded to equilibrium, the gas was analyzed on a mass spectrometer of the Nier type (*9*). In several cases the gas was reanalyzed after standing for a considerably longer period of time with the water specimen and catalyst to provide a check on whether or not the reaction had been at equilibrium the first time. Corrections were applied to all gas analyses to eliminate error from dilution or concentration of the water by the gas during the reaction.

The results of the analyses are given in Table I.

Table I. Water Analyses

Calcd. Mole % D	Exptl. Mole % D
49.4	48.4
24.9	26.1
78.9	77.3
57.5	55.6
37.7	36.0

LITERATURE CITED

(1) Clemo, G. R., and Swan, G. A., *J. Chem. Soc.*, **1942**, 370.
(2) Crist, R. H., Murphy, G. M., and Urey, H. C., *J. Chem. Phys.*, 2, 112 (1934).
(3) Farkas, A., "Light and Heavy Hydrogen," pp. 134–6, London, Cambridge University Press, 1935.
(4) Farkas, A., *Trans. Faraday Soc.*, **32**, 413 (1936).
(5) *J. Applied Phys.*, **13**, 526–69 (1942).
(6) Kistiakowsky, G. B., and Tichenor, R. I., *J. Am. Chem. Soc.*, **64**, 2302 (1942).
(7) LaMer, V. K., Eichelberger, W. C., and Urey, H. C., *Ibid.*, **56**, 248 (1934).
(8) Lewis, G. N., and MacDonald, R. T., *Ibid.*, **55**, 4730 (1933).
(9) Nier, A. O. C., *Rev. Sci. Instruments*, **11**, 212 (1940).
(10) Smyth, H. D., "Atomic Energy for Military Purposes," U. S. War Department, 1945.
(11) Topley, B., and Wynne-Jones, W. P. K., *Nature*, **134**, 574 (1934).
(12) Urey, H. C., Brickwedde, F. G., and Murphy, G. M., *Phys. Rev.*, **39**, 164, 864 (1932); **40**, 1 (1932).

RECEIVED September 10, 1947. Based on work performed under Contract No. W-31-109-eng-38 for the Atomic Energy Project at the Argonne National Laboratory, and the information contained therein will appear in Division III of the National Nuclear Energy Series (Manhattan Project Technical Section). Although this work was completed in 1945, the results were not released for publication until August 29, 1947. At that time, the intermediate numerical data involved in the analyses were not available to the authors.

Determination of Major Constituents of Cedar Oil Vapor in Cedar Chests

F. W. HAYWARD AND R. B. SEYMOUR
Industrial Research Institute, University of Chattanooga, Chattanooga, Tenn.

A procedure is given for rapid colorimetric determination of cedrene and cedrol in the air of cedar chests. The method is based on a red-violet color formation resulting from the reaction of cedrene with vanillin in the presence of hydrochloric acid. The cedrol is dehydrated in situ by phosphoric acid and determined as cedrene.

CEDAR chests are made from the heartwood of the eastern red cedar (*Juniperus virginiana*). The aroma in these chests is due to the volatile oil which is present in cedar wood to the extent of about 2%. Rabak (*3*) found the principal constituents of this oil to be sesquiterpenes, a hydrocarbon, cedrene ($C_{15}H_{24}$), and an alcohol, cedrol ($C_{15}H_{26}O$). In this investigation a method has been developed for the determination of these volatile constitutents in cedar chests.

Semmler (*6*), Ruzicka (*5*), and Treibs (*7*) determined in principle the structural formulas of these compounds. Cedrol was found to have a tertiary alcohol group and could be dehydrated with formic acid to produce cedrene, which had a double bond. Rosenthaler (*4*) discovered that turpentine reacted with vanillin in hydrochloric acid to give a green coloration. Bogatskiĭ (*1*) applied this reaction to a quantitative colorimetric method for turpentine and found that compounds containing active double bonds such as pinene and dipentene also reacted with this reagent.

EXPERIMENTAL

Preliminary experiments showed that cedrene in ethanol reacted with vanillin in hydrochloric acid to produce a red-violet color, whereas cedrol did not react under these conditions. It was found that 1% vanillin in hydrochloric acid formed a pink color which masked the violet coloration caused by cedrene, but that 0.1% vanillin was satisfactory. To produce a stable color it was necessary to use a volume of vanillin-hydrochloric acid reagent equal to that of alcoholic cedrene. Cedrol in ethanol was easily dehydrated by phosphoric acid to cedrene, which was then determined colorimetrically. Thus by using two aliquots of an ethanol solution of the unknown, it was possible to determine the total of cedrene plus cedrol as well as cedrene alone. The cedrol content was then found by difference.

REAGENTS

Ethanol, 95%. Ortho phosphoric acid, 85%.

Vanillin hydrochloric acid reagent, 0.1 gram of vanillin placed in a 100-ml. volumetric flask and made up to volume with concentrated hydrochloric acid. This reagent was most satisfactory when freshly prepared.

Standard solutions of cedrene in 95% ethanol were prepared, containing 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, and 1.0 mg. of cedrene per ml.

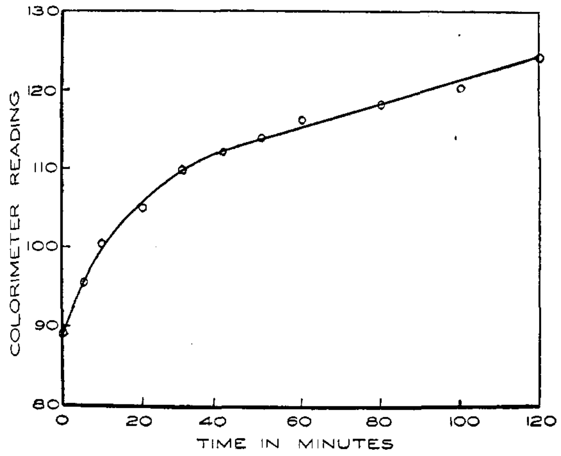

Figure 1. Color Stability

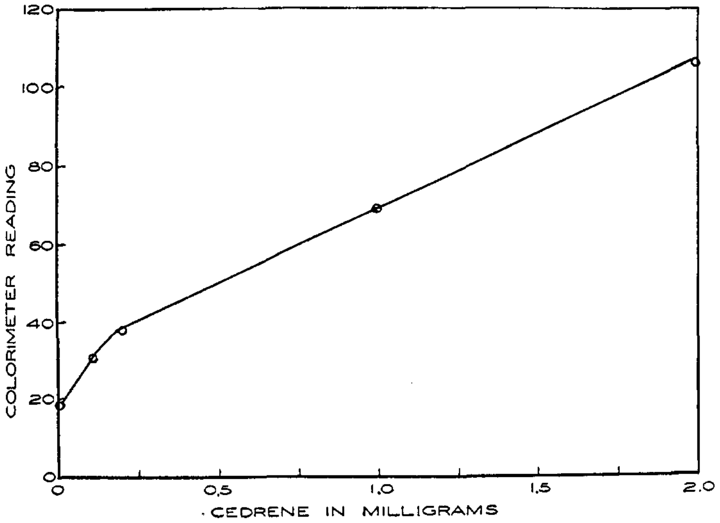

Figure 2. Determination of Cedrene

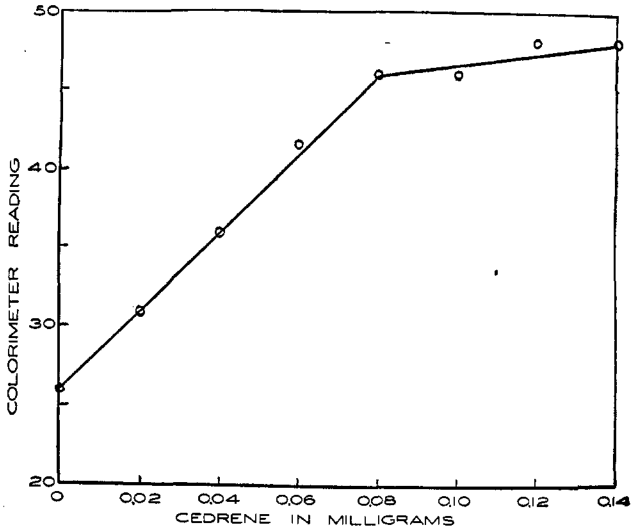

Figure 3. Cedrene at Low Concentrations

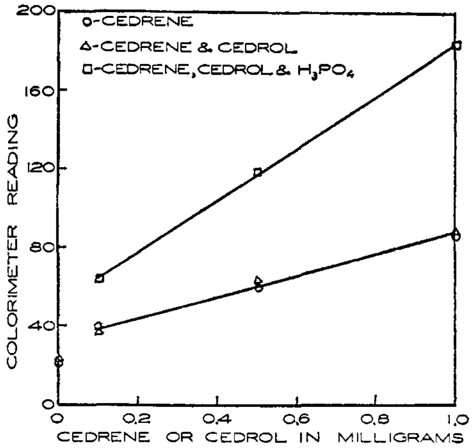

Figure 4. Cedrene-Cedrol Mixtures

APPARATUS

A Klett-Summerson photoelectric colorimeter equipped with green filter. Colorimeter tubes, graduated at 5 and 10 ml. Pipets of assorted sizes, 1 to 5 ml.

Gas sampling tube, large size, 2 to 4 liters. Gas absorption tube, microadaptation of Nichols (*2*) air lift pump gas absorber built in 18 × 150 mm. side-arm test tube.

PROCEDURE

Sampling. The lock is removed from the chest being tested and a rubber stopper containing a glass tube is inserted in the lock hole. Inside the chest is attached a rubber tube of such length that the air sample is obtained from the middle of the chest. The outlet of the absorber is connected to the top of a large water-filled gas sampling tube used to draw the air sample through the absorber. The volume of water removed from this tube is equal to the volume of air in the sample.

In practice the chest under test is closed and the outer rubber tube is clamped. After sufficient time for the chest to reach equilibrium has elapsed, 10 ml. of ethanol are placed in the absorption tube and 1 liter of air is drawn through slowly. Aliquots of this solution are used for analysis.

Analysis. Aliquots of standard and unknown solutions in alcohol are pipetted into colorimetric tubes and 1 ml. of phosphoric acid is added to the samples in which it is desired to determine the total of cedrene plus cedrol. These samples are shaken to ensure mixing and allowed to stand for 30 minutes to complete the dehydration of cedrol.

All samples are then diluted to the 5-ml. mark with ethanol and 5 ml. of the vanillin–hydrochloric acid reagent are added. Uniformity of the solutions is assured by inverting the tubes five times and allowing them to stand at least 30 minutes before color intensities are read.

Color intensities are determined with a Klett-Summerson photoelectric colorimeter equipped with a green filter. A tube of ethanol is used for the zero setting of the instrument and a blank is run along with the samples using alcohol alone.

RESULTS

To ascertain the stability of the color formed, the color intensity of a sample was determined at frequent intervals over a period of 2 hours (Figure 1). The rapid initial increase in intensity is due to the course of the reaction of cedrene with vanillin. The slower linear increase with time after the first 30 minutes is believed to be due to the concentration of color caused by contraction of the solution on cooling. Later work showed that no appreciable fading occurred after 16 hours.

That the change of color intensity with cedrene concentration was essentially linear in the range of 0.1 to 2.0 mg. of cedrene per determination is demonstrated by the data plotted in Figure 2. A similar linearity but a different slope was observed over the range of 0 to 0.1 mg. of cedrene (Figure 3). As little as 0.01 mg. of cedrene or cedrol was detectable. Experiments showed that the determination of cedrene was unaffected by the presence of cedrol, as shown by coincidence of the two curves in Figure 4. The total of cedrene plus cedrol was determined by the use of phosphoric acid. This is clearly shown by the increased slope of the curve in Figure 4 when phosphoric was used.

When the method was applied to the analysis of air from cedar chests, values of 0.05 to 0.6 mg. of cedrene or cedrol per liter of air were obtained. It is probable that such unsaturated minor constituents as cedrenene and cedrenol also react with vanillin-hydrochloric acid reagent and are thus calculated as cedrene.

ACKNOWLEDGMENT

The authors wish to express appreciation to the Chattanooga Medicine Company for supplying samples of cedrene and cedrol used in preparation of standards and to the Cavalier Corporation under whose sponsorship the investigation was carried out.

LITERATURE CITED

(1) Bogatskiĭ and Biber, *J. Chem. Ind. (Moscow)*, 5, 645 (1928).
(2) Nichols, *U. S. Pub. Health Repts.*, **53**, 538 (1938).
(3) Rabak, *Am. Perfumer Essent. Oil Rev.*, 23, 727 (1929).
(4) Rosenthaler, *Z. anal. Chem.*, 44, 292 (1905).
(5) Ruzicka and Van Melsen, *Liebigs Ann.*, **471**, 40 (1929).
(6) Semmler, *Ber.*, 40, 3521 (1907).
(7) Treibs, *Ibid.*, 68, 1041 (1935).

Received October 16, 1947. Presented at the Meeting-in-Miniature, Chattanooga Section of the American Chemical Society, Chattanooga, Tenn., October 11, 1947.

Determination of Alumina in Iron Ore

G. FREDERICK SMITH AND F. WM. CAGLE, JR., *University of Illinois, Urbana, Ill.*

A new procedure for the separation of alumina in iron ore, which is not dependent upon a carefully controlled pH for its efficiency, involves the formation of ferrous-bipyridine complex not precipitated by ammonium hydroxide or carbonate. By the process as described, aluminum in small amounts can be separated from large amounts of iron in one precipitation. A procedure is described for the recovery in high yield of the masking reagent bipyridine. The cost of reagent required per determination is at a minimum.

THE determination of alumina in an iron ore is rendered difficult by two factors: the chemical similarity of ferric oxide and alumina, and the fact that alumina almost always comprises less than 2% of the mixture (often much less).

The problem has been approached from many directions and attacked with great persistence and diligence (*5*). A recent survey of some of the schemes has resulted in the choice of the phenylhydrazine method of Hess and Campbell (*8*) as modified by Allen (*1*) and by Golowaty and Ssidorow (*6*). A purely physical method for the separation, which is capable of giving highly accurate results, is the removal of iron with a mercury cathode (*2*). The method was originally described for the determination of vanadium in steel but is as efficacious for aluminum (*3*).

The chemical methods that are used for the separation of alumina from iron ore require several steps and repeated precipitations for accurate work. The hydrochloric acid–ether method of Gooch and Havens (*7*) is useful if the iron is not in too great concentration, but would not be used for iron ores.

Ferrari (*4*) observed that the ferrous complex of 2,2′-bipyridine gave no precipitate with ammonium hydroxide and that alumina could be precipitated in the presence of 2,2′-bipyridine. His work was conducted on synthetic samples and was of only cursory nature. The samples employed by Ferrari did not contain the great preponderance of iron found in an iron ore.

The experiment was first tried on synthetic samples made up with known aluminum-iron ratios (Table I). Ammonium alum (Mallinckrodt's U.S.P.) was chosen as the source of aluminum because of its low aluminum content. Because this is a hydrated salt, it was analyzed before use and stored in a tight container after analysis. The source of iron was a sample of Mallinckrodt's reagent ferric alum. A blank on 6 grams gave an alumina precipitate of less than 0.1 mg. The analysis was conducted by ignition to the oxide and precipitation of hydrated alumina and ignition.

The 2,2′-bipyridine used was a commercial sample obtained from the G. Frederick Smith Chemical Company. To test for freedom from objectionable material, a 3-gram sample was

Table I. Analyses of Synthetic Samples

Method of Analysis	Al_2O_3 Found, %	
Ignition	11.40	Calculated for $NH_4Al(SO_4)_2.12H_2O$
	11.36	
Precipitation	11.25	Al_2O_3 = 11.24%
	11.25	

Table II. Separation of Aluminum from Iron in Sulfuric Acid Solution (Hydrochloric Acid Absent)

Sample No.	Al_2O_3 Taken *Mg.*	Al_2O_3/Mg.Fe_2O_3 *Mg.*	Al_2O_3 Found *Mg.*
1	131.4	1/1.27	131.9
2	25.5	1/7.42	25.4
3	25.5	1/39.2	29.6
4	12.1	1/82.6	15.7
5	14.3	1/70.0	14.3