TABLE I

YIELDS AND PHYSICAL CONSTANTS OF CARBINOLS

Acetylene	Carbonyl cpd.	Yield, %	B. p., °C.	Press., mm.	$n^{20}D$	d^{20}_4	*MR* obsd.	*MR* calcd.
Acetylene	Acetone	23	60	120	1.4207	0.8618	24.74	24.81
Acetylene	Acetone	55[a]						
Acetylene	Me Et ketone	60	78	150	1.4310	.8688	29.24	29.43
Acetylene	Me Et ketone	72[a]						
Acetylene	Me *n*-Pr ketone	50	58	26	1.4338	.8620	33.88	34.05
Acetylene	Me *n*-Am ketone	40	88	26	1.4396	.8547	43.20	43.28
Acetylene	Cyclohexanone	55	74	14	1.4820	.9873	36.35	36.47
Acetylene	Acetophenone	7[b]	101	14	1.5370	1.0314	44.26	44.30
Acetylene	Benzophenone	50	M. p. 49°					
Acetylene	Benzaldehyde	45	114	12	1.5508	1.0655	39.56	39.68
1-Hexyne	Me Et ketone	55	96	18	1.4487	0.8555	48.33	47.90
1-Hexyne	Acetaldehyde	21	88	40	1.4347	.8577	38.37	38.66
1-Hexyne	Me *n*-Pr ketone	65	106	20	1.4490	.8539	52.92	52.52
1-Heptyne	Me *n*-Pr ketone	65	120	19	1.4508	.8561	57.32	57.14

[a] Acetylene gas was passed through the mixture during the entire reaction. Mr. Froning has obtained 60% yields of dimethylethynylcarbinol and 15% yields of the glycol by this method, on 5-mole runs. See J. F. Froning, Master's Dissertation, University of Notre Dame, 1938. [b] Other workers have obtained poor yields from acetophenone. See Carothers and Coffman, THIS JOURNAL, 54, 4071 (1932).

Summary

1. A general method has been described for the preparation of acetylenic carbinols from the sodium salt of acetylene or a monoalkylacetylene, and an aldehyde or ketone, in liquid ammonia solution.

2. Several new acetylenic carbinols have been prepared and characterized.

3. The preparation of the chloride from methylethylethynylcarbinol has been described.

NOTRE DAME, INDIANA RECEIVED AUGUST 3, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY AND PHARMACOLOGY, SCHOOL OF MEDICINE AND DENTISTRY, THE UNIVERSITY OF ROCHESTER]

Relation of Refractive Index to Density in Dental Hard Tissues[1]

BY RICHARD S. MANLY[2]

In certain biological mixtures and in many mineral series, the refractive index has become valuable because it is linearly related to the density. Since in previous work[3] a number of density fractions of pure enamel and dentine had been prepared, the mean refractive indices were determined to discover any similar relations in these tissues.

The reported values for the refractive indices of enamel are in good agreement. Von Ebner[4] and Hoppe[5] report a figure of 1.627 for the ordinary ray and the former, 1.6234 for the extraordinary ray. Taylor and Sheard[6] and Eisenberg[7] noted that the refractive index of enamel prisms ranges between 1.612 and 1.625. Wishart in 1933 (personal communication) examined a few specimens of enamel and found the refractive index to be less than 1.625, usually near 1.618, but appearing to vary somewhat from that number. For two samples of normal dentine Taylor and Sheard[6] found a refractive index of 1.577 ± 0.003. No values for the refractive index of cementum have been reported.

Experimental

A "mean refractive index" was estimated by the following interpolation procedure. A few milligrams of the 60-mesh enamel or dentine powder was stirred into a drop of liquid of known refractive index and placed on a constant temperature stage under a microscope. A "sodium" filter (Eastman Kodak Co. filters nos. 64 and 73) was used over the light source. Determination of the mean refractive index, *i. e.*, the refractive index at which half the particles were higher and half lower than the liquid, was made by interpolation from the counts obtained with 3 or 4 different liquids.

(1) This work was supported in part by the Rockefeller Foundation and in part by the Carnegie Corporation of New York.

(2) From a thesis submitted to the Division of Graduates Studies of the University of Rochester in partial fulfilment of the degree of Doctor of Philosophy, June, 1938.

(3) Manly, Hodge and Ange, *J. Dent. Research*, in press.

(4) Von Ebner, *Deut. Monatsh. Zahnhlk.*, **41**, 65 (1903).

(5) Hoppe, *Virchow's Arch. path. Anat.*, **24**, 13 (1892).

(6) Taylor and Sheard, *Proc. Soc. Exptl. Biol. Med.*, **26**, 257 (1928); *J. Biol. Chem.*, **81**, 479 (1929).

(7) Eisenberg, *Am. Dental Surg.*, **50**, 225 (1930).

The counting method employed was the Becke line test.[8,9] One hundred particles were counted for each sample in various liquids. For refractive index standards, mixtures of α-chloronaphthalene (n^{25}D 1.63) and liquid petrolatum (n^{25}D 1.475) were prepared whose indices ranged from 1.530 to 1.630 in steps of 0.005. Calibration was made at 25 ± 0.1° with an Abbe refractometer.

Discussion

In enamel a proportionality exists between the mean density and refractive index as shown in Fig. 1. The equation is $d = 7.69\,n - 9.494 \pm 0.001$. The probable error of n is ±0.001, which is within the variations due to birefringence.[10] Inasmuch as mineral apatites usually have refractive indices of about 1.634, the upper limit of enamel is of interest: only 0.09% of the original enamel exhibited a refractive index greater than 1.6293.

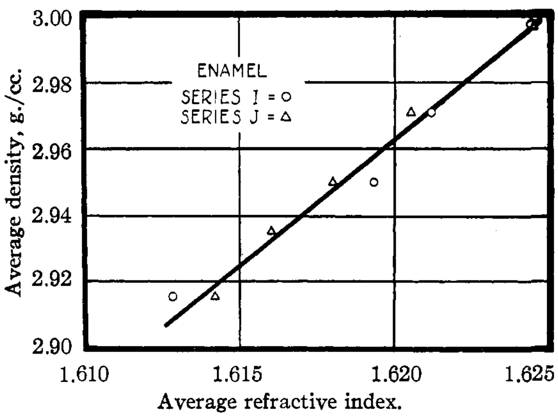

Fig. 1.—Enamel refractive index is proportional to the density.

In dentine the relation between refractive index and density is shown by the straight line in Fig. 2. The slope, 8.6, is somewhat steeper than that of enamel and the line lies 0.45 g. per cc. below the enamel curve when the latter is extrapolated to a density of 2.7. This fact suggested that the dentinal tubules were filled with air during the density and refractive index determinations. From the usual equation relating refractive index and density of a mixture[11] the volume per cent. of air, apatite, and protein in one dentine fraction (n, 1.5495; d, 2.135) was calculated. Values for density and refractive index of air, apatite and protein were taken from the literature. The calculated air space of 9 volume per cent. compares favorably with Feiler's estimation[12] of 12 to 24% tubule space. The calculated inorganic percentage was 75.0, in fair agreement with the value 78.4%, found by analysis.

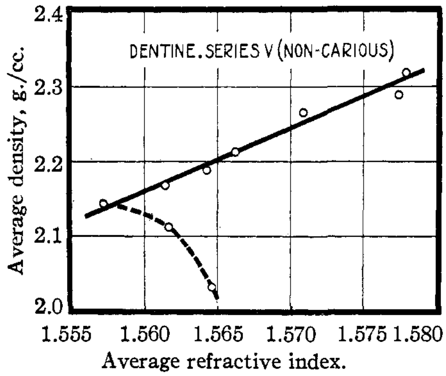

Fig. 2.—Refractive index–density relations for dentine. The two points on the dotted line are cementum.

Pulverized secondary cementum was found to have a refractive index range of 1.560 to 1.570. The two points on the dotted line of Fig. 2 are cementum, since they fall within this range and have the correct density[3] for cementum.

On vacuum drying for seven hours at 110°, an average decrease of 0.0018 was found in refractive index on six fractions of enamel. With dentine the decrease was much greater, 0.02–0.03, and the linear relationship with the original, oven-dry density was abolished. Cementum, on the other hand, behaved like enamel since the refractive index of the *oven-dry* material was decreased by only 0.001 on vacuum drying while the refractive index of *air-dry* cementum actually increased with the same treatment. As a tentative explanation for these differences in behavior, it may be assumed that neither capillary formation nor shrinkage is possible in the highly consolidated enamel, the former occurs chiefly in dentine and the latter in cementum.

A difference has been observed in the refractive index behavior of the inorganic salts of enamel and dentine. When ashed by glycol procedure[13] the refractive index of the inorganic material of dentine was 1.591–1.605, of enamel, 1.614. Heating the dentine ash or the unashed dentine for five hours at 900° raised the refractive index to 1.641–1.644, showing an essential change in structure. Enamel became opaque after five hours at

(8) Becke, *Tschermak's mineralog. petrog. Mitt.*, **13**, 385 (1892).
(9) Larsen, U. S. Geol. Survey, Bull., Cir., Professional Papers, Water Supply Papers, No. 679, 1921.
(10) Keil, *Z. Zellforsch.*, **25**, 204 (1936).
(11) F. H. Getman, "Outlines of Theoretical Chemistry," 4th ed., John Wiley and Sons, Inc., New York, N. Y., 1928, p. 131.
(12) Feiler, *Deut. Monatsh. Zahnhlk.*, **41**, 65 (1923).
(13) LeFevre and Manly, *J. Am. Dental Assoc.*, **25**, 233 (1938).

900°, making refractive index determinations impossible.

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Summary

1. The mean refractive indices of powdered enamel and dentine samples, with differing and known density limits, were determined by the Becke line procedure.

2. The refractive indices of dried enamel lie between 1.612 and 1.630 and are proportional to the density.

3. The refractive indices of dried dentine lie between 1.555 and 1.580 and are roughly proportional to the density when the fractions are dried under the same conditions for both determinations. Vacuum drying brought about a marked lowering of refractive index.

4. Secondary cementum exhibited a refractive index of 1.560–1.570 which was little affected by vacuum drying.

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The Crystal Structure of Ammonium Cadmium Chloride, NH_4CdCl_3

BY HENRI BRASSEUR[1] AND LINUS PAULING

In crystalline cadmium chloride, $CdCl_2$, there are octahedral groups $CdCl_6$ condensed into layers, each chlorine atom being adjacent to three cadmium atoms.[2] Tetrahedral coördination is shown by cadmium[3] with cyanide groups in $K_2Cd(CN)_4$, and with sulfur, selenium and tellurium atoms in the sphalerite and wurtzite type crystals CdS, CdSe and CdTe, and might well occur with chlorine also. There are accordingly two types of reasonable structures for complexes with the composition $(CdCl_3)_x$, the first involving octahedra with shared corners, as for example in the cubic crystal $KMgF_3$, and the second involving rings or chains of tetrahedra, as in the metasilicates. We have determined completely the structure of the orthorhombic crystal NH_4CdCl_3, and have found it to be based on octahedral coördination about the cadmium atoms, the $CdCl_6$ octahedra being polymerized into infinite double rutile strings which extend parallel to the c-axis of the crystal.

Experimental Methods and Results

The crystals of NH_4CdCl_3 used in this investigation were obtained by evaporation of an aqueous solution containing equimolar amounts of NH_4Cl and $CdCl_2$. The transparent white needles used for the x-ray photographs were about 0.1 sq. mm. in cross section and 3 to 10 mm. in length. In addition to single crystals many twins were obtained; the nature of the twinning was not studied.

Crystallographic study[4] has shown the crystals to be orthorhombic, with axial ratios 0.6059:1:0.7992 and density 2.93. X-ray photographs prepared with 15° oscillation about the directions [100], [010], and [001], with use of CuKα radiation filtered through nickel, gave the following dimensions for the unit cell

$$a_0 = 8.96 \pm 0.02 \text{ Å}.$$
$$b_0 = 14.87 \pm 0.03 \text{ Å}.$$
$$c_0 = 3.97 \pm 0.01 \text{ Å}.$$

These lead to the axial ratios 0.603:1:0.267, in good agreement with the crystallographic values, after dividing the crystallographic c-axis by three. All indices used in this paper refer to the X-ray axes a_0, b_0, c_0 given above.

The observed reflections show the lattice to be simple. The absence of prism reflections $\{h0l\}$ with h odd and $\{0kl\}$ with $k + l$ odd provides strong evidence that the space group is $D_{2h}^{16}-Pnam$ or its subgroup $C_{2v}^{9}-Pna$. In the absence of any observed deviation from holohedral habit of the crystals, we have assumed the space group to be D_{2h}^{16}; this assumption is given later justification by the derivation of a satisfactory atomic arrangement based on the holohedral space group.

The Atomic Arrangement

The sets of equivalent positions provided by $D_{2h}^{16}-Pnam$ are

(1) Fellow of the Belgian-American Educational Foundation.

(2) L. Pauling, *Proc. Natl. Acad. Sci.*, **15**, 709 (1929); L. Pauling and J. L. Hoard, *Z. Krist.*, **74**, 546 (1930).

(3) R. G. Dickinson, THIS JOURNAL, **44**, 774 (1922).

(4) H. Traube, *Z. Krist.*, **29**, 602 (1898); A. Johnsen, *N. Jahrb. Mineral.*, **2**, 115 (1903).