I. Spectroscopic Methods

The Primary Standard of Wave-Length

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THE first international action regarding a primary standard of wave-length occurred in 1907 when the International Union for Co-operation in Solar Research (I.U.C.S.R.) adopted the following resolution:[1] "The wave-length of the red ray of light from cadmium produced by a tube with electrodes is 6438.4696 angstroms in dry air at 15°C on the hydrogen thermometer, at a pressure of 760 mm of mercury, the value of g being 980.67 (45°). This number will be the definition of the unit of wave-length." This value was taken from the intercomparison of wave-length and meter by Benoit, Fabry, and Perot in 1906. It agrees closely with the first value of this relation obtained by Michelson and Benoit in 1893. In the past 15 years five more such inter-comparisons have been made and the mean of all seven after correction and adjustment to uniform conditions is 6438.4693A, the average deviation being ±0.0012A, or one part in five million.[2] The uncertainty in this value arises mainly from the difficulty of comparing a wave-length with a ruled-line standard.

The value (6438.4696A) adopted as a primary standard of wave-length in 1907 by the I.U.C.S.R. was taken over in 1922 by its successor, the International Astronomical Union[3] (I.A.U.) and in 1927 it was provisionally adopted by the International Committee on Weights and Measures (I.C.W.M.).[4] Since this value was derived from the H-type of cadmium vapor lamp designed by Michelson, both the I.A.U. and the I.C.W.M. have considered it important to specify construction details and operating conditions of the light source in order that the standard may be accurately reproduced. Specifications for the production of this primary standard were adopted by the I.A.U.[5] in 1925 and by the I.C.W.M.[4] in 1927. They differed in some details, and a discussion of the divergences resulted in the adoption in 1935 by the I.C.W.M.[6] of the following:

"Specifications for the cadmium lamp of Michelson type. In order to emit under favorable conditions the primary ray of luminous wave-lengths $\lambda = 6438.4696$A, the cadmium lamp of Michelson type, carrying internal electrodes and excited by electric current, continuous or alternating industrial frequency, must be maintained at a temperature near 300°C (in any case not exceeding 320°) and contain air under a pressure between 0.7 mm and 1 mm of mercury at that temperature. If it possesses a capillary tube or more generally a constriction designed to increase its brightness any lateral dimension of this constriction must not be less than 2 mm. The intensity of the exciting current shall not exceed a value of 7 ma per square millimeter of the narrowest section of the region observed."

This specification was adopted by the I.A.U.[7] in 1938.

From time to time objections have been raised against the use of the cadmium lamp of Michelson, and even against the red line itself. For example, the discharge tube which must be maintained at 300°C (to 320°C) in a furnace is not an ideal or convenient source to operate. The relatively high temperature widens the line and radiation from the furnace disturbs the interferometer. The capillary discharge viewed end-on does not permit the illumination of long slits or of large interferometer plates with high intensity. Fear has been expressed that the high voltage may produce a Stark effect widening or displacement.

Furthermore, cadmium has been criticized as a source of the primary standard because its lines are afflicted with hyperfine structure, its red line has low visual intensity, and under certain conditions it may show self reversal.

In defense of the red line of cadmium it may be said that it exhibits no Stark effect, it is not easily reversed, and to this day its hyperfine structure has resisted the best efforts at resolution.

At various times it has been suggested that the red line of Cd be replaced by neon or krypton lines as a primary standard, and the I.A.U.[8]

actually adopted 8-figure values of such lines with the assurance that they are equivalent to the primary standard within 1 part in 50 million. However, the neon lines have isotopic satellites that cause the mean wave-length to vary with order of interference, and many of the krypton lines show hyperfine structure due to nuclear spin. Among the noble gases argon would appear to be best suited as a source of standards because it consists mainly of one even isotope (99.6 percent mass number 40).

During the past decade some remarkable developments have been made in commercial lamps containing metal vapors, and a number of experiments have been performed to determine if commercial cadmium lamps could be substituted for the Michelson tube as a source of the primary standard. Thus, in 1933 Sears and Barrell[9] compared the wave-lengths of the red radiation from an Osram cadmium lamp and the Michelson lamp by alternately observing the fringes with Fabry-Perot interferometers with path differences of 19.4 to 241.1 mm. Non-linear temperature changes in the interferometer with time limited the precision, but it was concluded that the wave-lengths did not differ more than 1 part in 16 million.

Pérard[10] investigated a similar lamp, but with a 3-mm constriction, and found the wave-length of the cadmium red line 0.0002A greater than that given by the Michelson lamp although the sharpness of the former was superior at 1 ampere. A current of 2 amperes in this lamp produced self-reversal in the line and a change in wave-length of +0.0005A.

C. V. Jackson[11] in 1936 made a similar comparison of Osram and Michelson lamps with interference paths 10 to 100 mm and concluded that the red lines did not differ more than 0.0001A if the current in the former did not exceed 1.1 ampere. With 2 amperes the wave-length increased 0.0002A.

In 1938 Williams and Gogate[12] compared the red radiation from Osram and Schüler lamps but omitted the Michelson lamp on account of its low intensity. They outlined a method of simultaneous observation of the same wave-length from 2 different sources by polarizing the two beams at right angles, projecting both sets of fringes on the slit and separating them on the photographic plate by mounting a double image prism in the spectrograph. Instead of using this method they made alternate exposures to the two sources, shifted the plate laterally between exposures, and examined coincidence of the fringes. In spite of elaborate care the optical path of the interferometer always increased during exposure, which made it necessary to abandon the coincidence method and substitute measurements of the fractional part of the order. If we assume that the path difference increased uniformly with time in selected spectrograms, the greatest difference recorded was less than 1 part in 100 million.

There is still another method of comparing the same wave-length from 2 different light sources; namely, compare each with a third source. Thus, if the adopted values of neon and krypton lines obtained from comparisons with the Michelson lamp are accepted, any other Cd source can be measured in terms of neon or krypton lines. For measurements of the red line of Cd the red neon lines are preferred because these lie above and below and close to Cd red so that corrections for dispersion of phase change and for non-standard air are negligible.

We have adopted this method to compare the wave-length of the red line emitted by a Cd vapor lamp made by the Lamp Division of the Westinghouse Electric & Manufacturing Company. The lamp is operated on a 220-volt a.c. circuit with series resistance to regulate the current between 2 and 5 amperes. The potential drop in the lamp is 25 to 15 volts. The tube has a large bore (1 cm) so that the neon (or any other) source can be imaged inside the Cd lamp and both observed simultaneously in the same interferometer and spectrograph. Simultaneous observation eliminates all external differential effects on the wave-lengths to be compared, and should be mandatory for all interferometer comparisons of wave-lengths.

The mean of 10 determinations based on neon lines and 50-mm etalons gave the wave-length of the red line of cadmium as 6438.4699A (±0.00002) when the cadmium vapor lamp was operated with a current of 2.5 amperes (60 watts). When the current in the cadmium lamp was increased to 5 amperes (80 watts) the intensity of the red line was ten times greater but its observed wave-length was then 6438.4703A ($\pm$0.00006A).

There is no doubt that metal vapor lamps containing a considerable amount of argon will exhibit a pressure effect. It is customary to put from 5 to 10 mm Hg pressure of argon in such lamps and if the operating temperature rises to 300°C the gas pressure will double. This will be 10 to 20 times greater than the specified gas pressure in a Michelson lamp and commercial lamps containing relatively large amounts of argon will therefore not reproduce the primary standard exactly.

TABLE I. Principal isotopes of some elements.

Element	Mass number	Percent	Spin
Ne	20	90	0
	22	9.7	0
A	40	99.6	0
Kr	84	56.9	0
	86	16.7	0
	83	11.8	9/2
	82	11.8	0
Cd	114	28	0
	112	24.2	0
	111	13	1/2
	110	12.8	0
	113	12.3	1/2
	116	7.3	0
Hg	202	29.4	0
	200	23.1	0
	199	17	1/2
	201	13.7	3/2
	198	10	0
	204	6.7	0

In view of new developments in light sources and modern information concerning the structure of atomic spectra, it seems appropriate to open a discussion of the features or characteristics that should be required of the primary standard of wave-length.

In general, the light source should be simple and convenient to operate, and the radiation should be as monochromatic and reproducible as possible, and possess satisfactory intensity. On this basis the Michelson lamp may be criticized because it requires an auxiliary furnace for its operation, the effective temperature is high enough to add undesirable Doppler-Fizeau width to the lines, the intensity is relatively low, and it is not the "extended source" needed for illuminating large areas. The commercial cadmium lamps now available are free from all these objections but their wave-lengths are definitely a function of the power input or temperature. This increase of wave-length with intensity is probably a pressure effect and can therefore be controlled by specifying the total effective pressure in operating the lamp. In any case there is no practical reason for increasing the wave-length more than 1 part in 20,000,000, which is only $\frac{1}{4}$ of the average deviation from the mean of all meter-cadmium wave intercomparisons.

The commercial cadmium vapor lamps with large bore viewed side-on are guaranteed to emit the red line without self-reversal and they permit the illumination of long slits or large interferometers with satisfactory intensity. Above all, these new Cd lamps for the first time make possible efficient, simultaneous observation of two or more light sources by imaging those to be compared with Cd directly inside the latter itself, thus obviating all the difficulties and uncertainties connected with alternate exposures to different light sources.

Finally, we may review the desirable characteristics of a primary standard of wave-length from the standpoint of spectral structure and general properties of atomic radiation. In order to insure high homogeneity and exact reproducibility in a wave-length standard, it is necessary to avoid or minimize the Doppler-Fizeau effect, hyperfine structure, self-reversal, and excessive pressure.

At low pressures and potential gradients the widths of spectral lines are accounted for by the Doppler-Fizeau effect, and (in λ units) are proportional to $\lambda(T/M)^{\frac{1}{2}}$, where λ represents wave-length, T absolute temperature, and M molecular weight. The sharpness or fineness of a line may be defined[14] by the maximum order of interference, $N=1.22\times10^6(M/T)^{\frac{1}{2}}$, obtainable with it. Heavy atoms at low temperatures will emit the sharpest lines. For the standard cadmium lamp $N=1.22\times10^6(112/593)^{\frac{1}{2}}=530{,}000$, but this can be increased somewhat by operating at a lower temperature with a cooled hollow cathode or Schüler lamp. With water-cooled mercury lamps $N=1.22\times10^6(200/290)^{\frac{1}{2}}=1{,}000{,}000$. The limiting orders of interference for spectral lines of the noble gases in ordinary Geissler tubes are about 320,000 for neon, 450,000 for argon, and 600,000 for krypton. Under the conventional operating conditions cadmium lines from the Michelson lamp are little sharper than argon lines but mercury lines are twice as sharp. Of course, everyone knows that the reason a line characteristic of ordinary mercury is not used as a standard is because mercury lines are notorious for hyperfine structure.

Hyperfine structure of spectral lines originates in the isotopic constitution of certain chemical elements. The isotopes with odd mass numbers possess nuclear spins which produce hyperfine multiplets, while those of even mass numbers give slightly different wave-lengths. The most abundant isotopes of elements under discussion as sources of a primary standard of wave-length are shown in Table I.

TABLE II. Analogous lines of Cd and Hg.

Combination	Cd (I.P. = 72539 cm^{-1}) Levels cm^{-1}	Wave-length A	Hg (I.P. = 84178 cm^{-1}) Levels cm^{-1}	Wave-length A
$^1P_1-{}^1D_2$	43692–59220	6438	54066–71330	5791
$^3P_2-{}^3S_1$	31827–51484	5086	44040–62348	5461

About $\frac{1}{4}$ of all cadmium atoms have odd mass numbers with spin $\frac{1}{2}(\frac{1}{2}h\pi)$, and the hyperfine structure of cadmium lines has been thoroughly investigated. It is noteworthy that all reliable attempts to resolve or detect structure in the red line (6438.4696A) have failed.[15] Even the investigations with atomic beams of cadmium have only indicated a slight isotopic widening[16] and possible asymmetry[17] in the red line.

Nearly $\frac{1}{3}$ of the ordinary mercury atoms have nuclear spins, and these in addition to shifts from even isotopes account for the complex structure of ordinary mercury lines. If a single even isotope, say 202, which constitutes nearly 30 percent of ordinary mercury, could be isolated it would solve the problem of the primary standard to the satisfaction of all. This appears to be too difficult, but the same end may be attained in another way. In 1940, Alvarez and Wiens[18] transmuted, by bombardment with neutrons, sufficient gold into Hg (198) to produce a light source emitting mercury lines free from any trace of hyperfine structure. The National Bureau of Standards and the University of California are now cooperating in a project to prepare a permanent spectral tube containing Hg (198). If this experiment succeeds it is probable that the mercury line with wave-length 5461A will eventually displace Cd 6438A as the primary standard of wave-length. This green line of mercury is at the visibility maximum, and its intrinsic intensity is much greater than that of the red line of cadmium.

The relative intensities, reversibilities, and pressure susceptibilities of analogous lines in the spectra of cadmium and mercury may be compared by referring to spectral terms or atomic energy levels shown in Table II.

In both cases the singlet $p-d$ transition requires considerably greater excitation energy than the triplet $p-s$ transition, and the intensity ratio is of the order of 1 to 10.

Only the lines involving the ground state (or low excited states) of the atom are readily reversed, whereas pressure effects are greatest for lines involving highly excited states approaching the ionization limit. Consequently in selecting a primary standard least susceptible to reversal and pressure it is necessary to avoid both low and high atomic energy states. Obviously the only way to accomplish this is to choose transitions from the middle of the atomic energy diagram. Such compromises are represented by the Cd and Hg lines in Table II. The singlet $p-d$ transitions may be slightly more sensitive to pressure than the triplet $p-s$, whereas the latter may be somewhat easier to reverse because the final states are metastable and lower. Except for hyperfine structure, these lines meet the theoretical requirements for a primary standard about as well as any that can be found. The fact that Michelson[19] selected the best of these more than half a century ago, without quantum theoretical considerations to guide him, is proof of the incomparable skill and thoroughness with which he conducted his search for an acceptable primary standard of length.

BIBLIOGRAPHY

(1) Trans. I.U.C.S.R. **2**, 20 (1907).
(2) J. E. Sears, Sci. Prog. **31**, 209 (1936).
(3) Trans. I.A.U. **1**, 35 (1922).

(4) Procès-Verbaux Comité Int. Poids et Mésures [2] **12,** 67 (1927).
(5) Trans. I.A.U. **2,** 47, 232 (1925).
(6) Procès-Verbaux Comité Int. Poids et Mésures [2] **17,** 91 (1935).
(7) Trans. I.A.U. **6,** 79 (1939).
(8) Trans. I.A.U. **5,** 86 (1936).
(9) J. E. Sears and H. Barrell, Proc. Roy. Soc. **A139,** 202 (1933).
(10) A. Pérard, Comptes rendus **198,** 727 (1934).
(11) C. V. Jackson, Proc. Roy. Soc. **A155,** 407 (1936).
(12) W. E. Williams and D. V. Gogate, Proc. Roy. Soc. **A167,** 509 (1938).
(13) W. F. Meggers and C. J. Humphreys, unpublished.
(14) H. Buisson and Ch. Fabry, J. de Phys. [5] **2,** 442 (1912).
(15) H. Westmeyer, Zeits. f. Physik **94,** 590 (1935).
(16) R. Minkowski and H. Bruck, Zeits. f. Physik **95,** 284 (1935).
(17) K. W. Meissner, J. Opt. Soc. Am. **32,** 196 (1942).
(18) W. Alvarez and J. Wiens, Phys. Rev. **58,** 1005 (1940).
(19) A. A. Michelson, Phil. Mag. [5] **34,** 280 (1892).

DISCUSSION

S. Mrozowski, *University of Chicago:* Although at first I was very enthusiastic about the use of the line 5461A emitted by the single isotope 198 of mercury for the primary standard of wave-length, I gradually became more and more pessimistic as I tried to develop a source of light which would show as little absorption of gas as possible. In the original arrangements of Wiens and Alvarez for Hg^{198} and of Segré and myself for investigations of some other substances obtained by bombardment in the cyclotron, the gas obtained in the discharge tube disappears by absorption in a few minutes. Following a suggestion by Professor Dempster I developed here in Chicago a hollow cathode tube of a total volume of 1 cm^3, which, filled with helium at 1 mm, has been operated for more than 36 hours at 60 ma before the gas disappeared by absorption. Mercury vapor probably would be absorbed much sooner, perhaps in the course of some 4–6 hours. Even such a source is far from being satisfactory for the determination of the wave-length of a primary standard and for the subsequent comparison with secondary standards. I would therefore suggest using for the primary standard one of the lines of lead, since the even isotopes of this element can be obtained in a relatively pure state (uranium or thorium lead) and in a not too small quantity. As a source, a hollow cathode discharge tube should be satisfactory.

G. S. Monk, *University of Chicago:* Professor Meissner suggested the use of an atomic beam source for the primary standard. Several questioned the practicability of this on account of its complexity and cost.

Later in the day the writer demonstrated a new type of cadmium source. This consisted of a capsule of glass or quartz of about 5- to 10-cc volume with a very small amount of cadmium distilled into it. The capsule is energized by a high frequency high voltage oscillator, and is started by preheating with a Bunsen burner or hand torch. Preliminary measurements show that the wave-length is the same as that obtained with a Michelson tube. The line width depends upon the amount of cadmium vapor in the tube, and this must be carefully controlled.