MR 546

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DATE: 1952

TITLE: A comparison of the dielectric behavior of pure water and human blood at microwave frequencies.

SOURCE: Brit J Appl Phys 3:249-255

MAIN SUBJECT HEADING:

AN	(HU)	AT	IH	M
ANALYTICS	HUMAN EFFECTS	ANIMAL TOXICITY	WORKPLACE PRACTICES-ENGINEERING CONTROLS	MISCELLANEOUS

SECONDARY SUBJECT HEADINGS: (AN) HU AT IH M

Physical/Chemical Properties

Review

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Uses

Reactions

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Methods of Analysis

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A comparison of the dielectric behaviour of pure water and human blood at microwave frequencies

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MR 546

[*Paper received* 21 *February*, 1952]

Methods used to measure the complex dielectric constant of water and blood at frequencies from $1{\cdot}7 \times 10^9$ to $2{\cdot}4 \times 10^{10}$ c/s are described. The results obtained for water at temperatures between 0 and 60° C are given and analysed with relation to the Debye and the Cole–Cole dispersion equations. The possibility that the dispersion in water is characterized by a narrow spectrum of relaxation times is briefly discussed. The complex dielectric constant of whole human blood has been measured at temperatures between 15 and 35° C. The dispersion observed is attributed entirely to water relaxation. It is shown to fit the Debye dispersion equations if the effects of a frequency-independent ionic conductivity are allowed for. Comparison of the results for blood with those for water leads to approximate estimates of the erythrocyte intracellular ionic conductivity and haemoglobin hydration.

As part of the initial stage in investigations of the propagation of hyper-high-frequency radio energy in human tissues, a study has been made of the dielectric properties of pure water and blood in the frequency range $1{\cdot}7 \times 10^9$ to $2{\cdot}4 \times 10^{10}$ c/s. It was anticipated that the electrical behaviour of these liquids would be similar at such high frequencies, and that a comparison would yield information regarding the electrical properties of the intracellular contents of human erythrocytes in their normal environment.

The anomalous dielectric dispersion of water at microwave frequencies has been widely investigated in the past. The serious lack of agreement between the results of various early workers has been attributed to several causes, notable among these being the use of sources producing damped waves. The advent of stable continuous wave sources of microwaves and improved techniques of measurement has enabled more reliable measurements to be made in recent years. However, at the time of the commencement of the present work serious discrepancies between the results of the most recent workers were apparent. The work of Connor and Smyth,[1] Abadie,[2] and Saxton and Lane[3] showed lack of agreement regarding the relaxation time when the results were analysed in terms of Debye's dispersion equations:

$$\epsilon' = \frac{\epsilon^* - \epsilon_\infty}{1 + (\omega\tau)^2} + \epsilon_\infty$$

$$\epsilon'' = \frac{\epsilon^* - \epsilon_\infty}{1 + (\omega\tau)^2}\omega\tau$$

where $\epsilon = \epsilon' - j\epsilon''$ is the dielectric constant at frequency $\omega/2\pi$,

ϵ^* and ϵ_∞ are the low and high frequency values of ϵ' on either side of a dispersion frequency region (ϵ^* is not necessarily the static constant)

τ is a generalized relaxation time.

While the present work was in progress Collie, Hasted and Ritson[4] published the results of a comprehensive investigation of the dielectric properties of water at microwave frequencies. They pointed out the discrepancies between previous workers' results and claimed that their own satisfied the Debye equations (with a single relaxation time) within the experimental error (approximately ± 2% in both ϵ' and ϵ''). At the same time, the results of workers in America came to general notice (Montgomery[5]) and large differences between these results and those of Collie and others were apparent. Whereas the latter indicated a single relaxation time for water, the American results showed a wide relaxation time spectrum to be present. Thus the present work was continued with an object additional to the primary one in that a full investigation of the dielectric behaviour of water in its dispersion region might confirm one or other of the above conclusions.

In the case of whole human blood little reliable work in any range of frequency in the radio frequency spectrum was known to the author. Work on the blood of various animals has been reported[6, 7, 8, 9] and the observed dispersion discussed in terms of an extension of Wagner's theory for inhomogeneous dielectrics.[10, 11] The only work at frequencies higher than about 10^9 c/s is that on whole human blood by England and Sharples[12] and England.[13] Their method of measurement of the dielectric constant of blood in the frequency range 3×10^9 to $2{\cdot}4 \times 10^{10}$ c/s was not well suited to the measurement of a material of such high dielectric constant and loss. The present investigation was intended to obtain results of higher accuracy than was achieved by these workers, and to use similar specimens at all frequencies.

DESCRIPTION AND PRINCIPLE OF THE EXPERIMENTAL METHODS

The essential feature of the methods used was that the measured quantities were largely, or completely, independent of an air-liquid reflexion coefficient. With high dielectric constant materials the measurement of such a coefficient to an accuracy sufficient to obtain ± 1% accuracy in ϵ' is very difficult. Thus methods were employed where the liquid propagation constant, $\alpha + j\beta$, was measured directly, as far as possible, to an accuracy commensurate with limits of error of approximately ± 1% in ϵ' and ± 2% in ϵ''.

The derivation of the relationships between $\epsilon' - j\epsilon''$ and the propagation constants for materials contained in coaxial lines or wave-guides and carrying travelling or standing waves is well known[14] and it suffices only to state them:

$$\epsilon' = \left[\beta^2 - \alpha^2 + \left(\frac{2\pi}{\lambda_c}\right)^2\right]\left(\frac{\lambda}{2\pi}\right)^2$$

$$\epsilon'' = 2\alpha\beta\left(\frac{\lambda}{2\pi}\right)^2$$

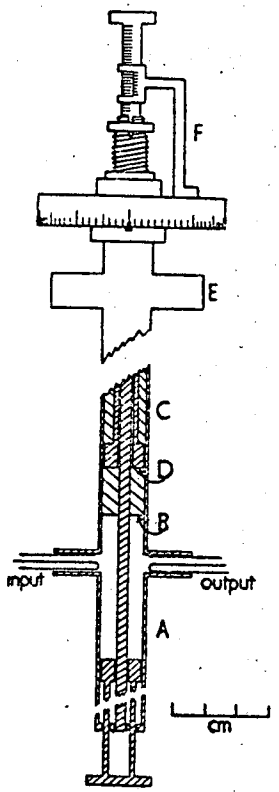
where λ = free space wavelength and λ_c = cut-off wavelength.

For coaxial lines $\lambda_c = \infty$ for the principal wave, and in

(NWL)

the wave-guide it is dependent on the guide geometry and order of mode. Where λ and λ_c are known to high accuracy it follows that, when $\beta^2 \gg \alpha^2$, to obtain the required accuracy in $\epsilon' - j\epsilon''$ it is necessary to measure β to within $\pm 0{\cdot}5\%$ and α to within $\pm 1{\cdot}5\%$.

(*a*) *Methods used at frequencies lower than* 5×10^9 *c/s.* To enable a wide frequency range to be covered in one apparatus a coaxial line method was employed. This was the coaxial version of the twin-wire method used by Knerr[15] and Cooper[16], and is similar to a method described by Abadie. A diagrammatic section of the apparatus is shown in Fig. 1. The theory of the method has been given by Knerr



A, resonant air section; *B*, thin mica window; *C*, liquid filled section; *D*, plunger, movement of which is measured by micrometer or scale and vernier, *F*; *E*, liquid reservoir. (Not shown are the joint in the line at *B*, and the water jacket which extends from above *E* to below *B*.)

Fig. 1. Diagrammatic section of coaxial line apparatus used at frequencies lower than 5×10^9 c/s

and Cooper. Briefly, the method consists of varying the signal output of the air-filled section (previously tuned to resonance) by movement of the reflecting plunger in the liquid-filled section. Maxima and minima of the signal output occur and are related to the position of the plunger. The maxima and minima recur for successive movements of the plunger through $\pi/2\beta$, and their relative amplitudes are related to α. The accuracy of the method depends upon:

(i) the stability of the signal generator output power and of the signal detection apparatus;
(ii) the accuracy of measurement of frequency, plunger movement and temperature.

The klystron oscillators used were operated from well-stabilized power supplies derived from automatically regulated alternators. Their outputs were very stable. Similarly, the signal measuring apparatus, consisting of a microwave mixer and intermediate frequency amplifier, was operated on independent supplies and gave very stable amplification. The relationship between the second detector current (read on a 6 in, 1 mA full-scale meter) and the relative signal input to the mixer was established by use of inputs from an accurate cut-off attenuator. Frequencies near 3×10^9 c/s were measured to an accuracy of $\pm 0{\cdot}05\%$ by means of a cavity wavemeter, while other frequencies were measured to $\pm 0{\cdot}1\%$ by the use of a line wavemeter. The plunger movement was normally between 1 and 4 cm, corresponding to a number of half wavelengths in the liquid equal to, or greater than, three. It was measured by a micrometer providing length readings accurate to $\pm 0{\cdot}01$ mm. Temperature was controlled by a large water jacket surrounding the apparatus. During a set of observations at any one temperature it remained constant to within $\pm 0{\cdot}1°$ C except at the higher temperatures employed. The final accuracy of measurement of β was estimated to be $\pm 0{\cdot}4\%$, and of α to be $\pm 2\%$ for water at temperatures near room temperature. Thus the final accuracy achieved for water was approximately $\pm 1\%$ in ϵ' ($\beta^2 \gg \alpha^2$) and $\pm 2{\cdot}5\%$ in ϵ'', with somewhat greater limits of error at temperatures lower than 10° C and higher than 30° C.

At a frequency of 3×10^9 c/s a second method was also used for measurements on water. A cylindrical water-filled wave-guide (H_{11} mode) was provided with a movable pick-up loop. The signal output was fed to an air-filled wave-guide section, into which was also fed a constant phase output from a cut-off attenuator (see Fig. 2). The attenuation in the water-filled guide was measured directly, and β was obtained from

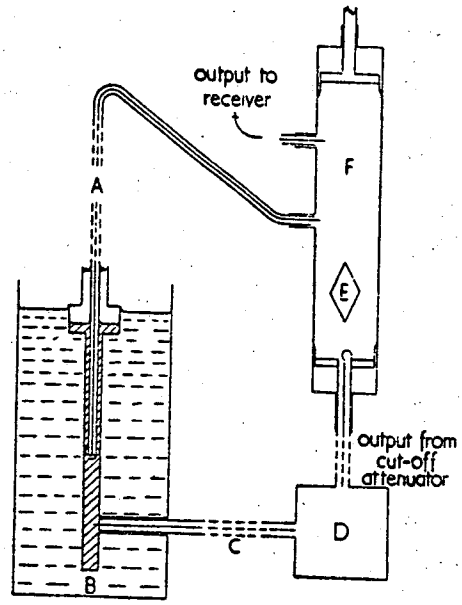


Fig. 2. Diagram of wave-guide apparatus used at 3×10^9 c/s

A, rack and pinion with scale and vernier; *B*, water jacket; *C*, lossy cable; *D*, signal generator; *E*, attenuator; *F*, rectangular guide, 3 × 1 in.

the movements of the pick-up loop providing successive minima in the combined output of the air-filled guide. The accuracy of measurement of both α and β was considered to be $\pm 1\%$, giving limits for ϵ' and ϵ'' of $\pm 2\%$.

(*b*) *Method used at approximately* 10^{10} *c/s and* $2{\cdot}4 \times 10^{10}$ *c/s.* Buchanan[17] has described a null method of measurement at these frequencies, and the measurements on water and butyl were made using his apparatus at 10^{10} c/s, and, at the higher frequency, on similar apparatus set up by Haggis[18] for work on protein solutions.

Briefly, the principle of the method is that on which the cylindrical wave-guide method used at 3×10^9 c/s was based

and which followed a suggestion by Buchanan. At the higher frequencies, rectangular wave-guide cells were used, the outputs from this and from a cut-off attenuator being fed to the arms of a hybrid tee and thence to a mixer and intermediate frequency amplifier. Movements required in the signal pick-up mechanisms of the liquid cell and attenuator to obtain successive nulls in the output of the hybrid tee are directly related to β and α for the H_{01} mode. An important feature of the method is that the measurements are largely independent of oscillator output instability, an annoying property of valves working at these frequencies. The best accuracy attainable for water near room temperature was $\pm 1\%$ for both ϵ' and ϵ''.

EXPERIMENTAL RESULTS

(*a*) *Water.* Results at four frequencies were obtained and are listed in Table 1. They have all been interpolated from

Table 1. *Experimental values of $\epsilon' - j\epsilon''$ for pure water*

Temp. (°C)	Frequency (c/s) 3·00 × 10⁹		4·63 × 10⁹		9·39 × 10⁹		2·377 × 10¹⁰	
0	(80·2	−j24·0)	(71·4	−j33·4)	(43·4	−j41·1)	(14·5	−j26·5)
5	80·0	20·3)	73·1	28·7	49·6	39·2	18·0	29·7
10	79·4	17·5	74·3	25·2	54·4	37·1	22·0	32·5
15	77·7	13·0	74·0	18·8	61·5	31·6	31·0	35·7
20	75·3	$9·9_0$	73·1	14·6	64·8	25·6	38·5	35·6
25	72·6	$7·5_5$	70·7	12·0	65·5	20·9	43·0	34·0
30	69·7	$5·9_5$	68·5	$9·4_0$	64·6	17·0	(46·3	30·8)
35	66·4	$4·6_0$	66·3	$7·4_0$	—		—	

graphs of a large number of observations made at different temperatures and at each frequency. Those for 3×10^9 c/s are the means from the two methods used at this frequency, the agreement obtained between these being well within the calculated limits of error.

(*b*) *Whole human blood.* The specimens were selected from normal males so that the red cell concentrations were within the limits $4·8$ to $5·0 \times 10^6$ per mm³. The corresponding total cell volume was 43%. 1·9 mg heparin was added to each 10 ml of whole blood to prevent coagulation. This substance does not ionize, and, in such low concentration, it was considered unlikely to affect the electrical properties of the specimens. The measurements were carried out in the apparatus used for water. A fortunate result of the use of a plunger or signal pick-ups moving in the liquid cells was that the blood was kept well stirred by this means alone. Measurements were made at a frequency lower than 3×10^9 c/s (the lowest used for water) to give more accurate information on the ionic contribution to dielectric loss. The full results, interpolated from experimental curves through a large number of individual observations at each frequency, are listed in Table 2.

Table 2. *Experimental values of $\epsilon' - j\epsilon''$ for whole human blood (cell concentration $4·9 \times 10^6$ per mm³)*

Temp. (°C)	Frequency (c/s) 1·77 × 10⁹		2·99 × 10⁹		9·39 × 10⁹		2·377 × 10¹⁰	
0	(59·2	−j17·8)	(59·9	−j19·9)	(42·4	−j26·7)		
5	56·8	17·8	57·5	17·1	45·5	23·0	(25·0	−j24·8)
10	56·2	18·1	56·0	15·9	47·8	19·7	30·2	26·0

The results are considered to be within $\pm 2\%$ for ϵ' and 5% for ϵ'' of the true values for male blood containing average cells in concentration $4·9 \times 10^6$ per mm³ (43% of total volume).

ANALYSIS OF THE RESULTS AND COMPARISON WITH PREVIOUS WORK

(*a*) *Water.*

Analysis. The results for water were analysed in relation to both the Debye dispersion equations and the empirical form of these due to Cole and Cole.[19] These authors show that many materials behave in their dispersion regions according to the equation:

$$\epsilon - \epsilon_\infty = \frac{\epsilon^* - \epsilon_\infty}{1 + (j\omega\tau)^{1-\alpha}}$$

where α is a parameter depending on the width of a spectrum of relaxation times characterizing the dispersion. For a single relaxation time α is zero and the equation then becomes identical with the corresponding Debye equation.

The outcome of the analysis can be summarized as follows:

(i) The best average fit of the experimental results to values calculated from the Debye equations was obtained if ϵ^* was taken as the static dielectric constant as given by Lattey and others,[20] ϵ_∞ was 5·0, and the single values of τ shown in Fig. 3 were used. Only half the experimental values agreed with calculated ones within the experimental error.

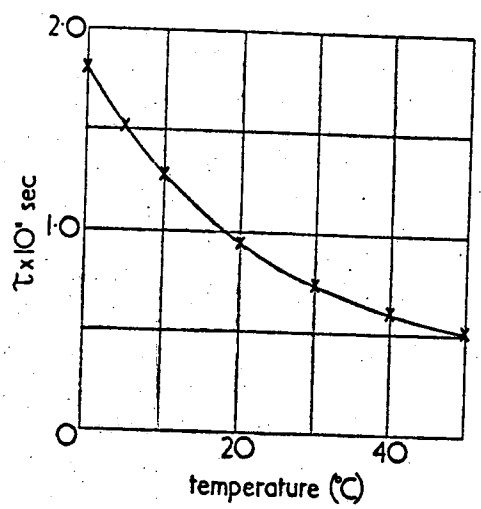


Fig. 3. Variation of relaxation time with temperature for pure water

(ii) Slightly better overall agreement was obtained between the experimental results and values calculated from the Cole and Cole equation if $\epsilon_\infty = 4·0$ (the far infra-red value[21, 22]), $\alpha = 0·02$ at all temperatures, and τ had values approximately 2% lower than those of Fig. 3. In this case two-thirds of the experimental results agreed with calculated ones within experimental limits of error.

(iii) In both the above cases ϵ_∞ was assumed independent of temperature. Improved agreement was obtained when ϵ_∞ was allowed to vary with temperature, but the results are not sufficiently accurate to warrant any conclusions regarding any systematic dependence of ϵ_∞ on temperature. Similarly, in (ii), agreement was improved when α was allowed to vary with temperature.

It must be concluded that the accuracy of the present results is not sufficiently high to be able to state that the anomalous dispersion of water is definitely characterized by a single relaxation time and a temperature-independent ϵ_∞. The possible existence of a narrow relaxation time spectrum

cannot be ruled out. The latter possibility is attractive in that the far infra-red results can be linked with those in the microwave region without introducing an additional dispersion process at frequencies between the two regions.

Comparison with previous work. Good agreement exists between the present results and those of Collie and others. The relaxation times shown in Fig. 3 are within 2% of these workers' values. Whereas Collie and others found $\epsilon_\infty = 5{\cdot}5$ gave the best average fit to the Debye equations, the present work provides a lower estimate of 5·0. It should be noted that their experimental results can also be fitted reasonably well to the Cole and Cole equation with $\alpha > 0$. The results referred to by Montgomery are approximately consistent with the Cole and Cole equation with $\epsilon_\infty = 15$ and $\alpha = 0{\cdot}19$ and differ markedly from the present results and those of Collie and others. The large discrepancies may be due to the use by the American workers of techniques unsuited to dielectric measurements on water. Saxton analysed the results of Saxton and Lane and found water to obey the Debye equations with $\epsilon_\infty = 5{\cdot}5$. Later work (private communication) by Saxton and Lane suggests 4·9 as the value of ϵ_∞ to use in the Debye equations to obtain best agreement between theory and experiment.

(*b*) *Whole blood.* It has been shown by Danzer and by Schwan that the dispersion of the dielectric constant of animal blood at frequencies lower than 10^8 c/s can be explained approximately in terms of an extension of the theory for inhomogeneous dielectrics due to Wagner.[23] The effects of dispersion due to inhomogeneity are, however, negligibly small at frequencies higher than 10^9 c/s.[8] ϵ' remains constant over a small range in the region of this frequency. The present results show dispersion at frequencies higher than this and it is reasonable to conclude that this is due to the large water content and not inhomogeneity.

Therefore, the results were analysed in relation to the Debye equations, in which an additional term was included to allow for ionic conductivity, σ. It is assumed that σ is independent of frequency at hyper-high frequencies. It was found that all the experimental results agreed with values calculated from the modified Debye equations, within the experimental limits of error, if, in these, ϵ_∞ was taken as 4·5 and the values of the other constants used were as in Table 3.

Table 3. *Whole blood—constants derived from analysis of experimental results*

Temp. (° C)	ϵ^*	τ (sec)	σ (Ω^{-1} cm^{-1})
15	62·0	$1{\cdot}19 \times 10^{-11}$	0·010
25	58·0	$0{\cdot}90 \times 10^{-11}$	0·012
35	56·0	$0{\cdot}70 \times 10^{-11}$	0·014

Comparison of the values of $\epsilon' - j\epsilon''$ at 35° C in Table 2 can be made with the results of England and Sharples, and England, for a temperature of 37° C. Allowing for the wider range of cell concentrations and higher temperature of their specimens, reasonable agreement exists between the two sets of results.

DISCUSSION OF THE DIELECTRIC PROPERTIES OF BLOOD

For the purposes of this discussion the effect of cells other than erythrocytes present in blood will be neglected, since the erythrocytes far outnumber the other cells.

(*a*) *Dispersion at radio frequencies.* The phenomena observed can be discussed in terms of Wagner's extension of Maxwell's theory for inhomogeneous dielectrics possessing ionic conductivity. Maxwell considered the case of a heterogeneous medium consisting of strata of materials with different dielectric constants and ionic conductivities and showed that dispersion would result. Wagner extended the theory to cover the case of spheres, and bodies of other shapes, suspended in a medium of different dielectric properties. This Maxwell-Wagner theory is well established and has been discussed by many authors (see, for instance, Jackson[24] and Hartshorn[25]). Briefly, the theory proposes that dielectric dispersion occurs in such a heterogeneous medium as a result of restricted movement of ions at the boundaries of the constituents. For example, if a constant potential difference is set up in such a medium, ionic accumulations occur at the boundaries of the constituents. These lead to polarization electromotive forces being set up in opposition to the applied potential difference, and then to a simple, or complex, exponential decay of current depending on the number of different types of boundary present. This is a relaxation process and can be described by dispersion equations similar in form to those of Debye for dipole relaxation.

Danzer applied the theory to the type of inhomogeneity represented by blood and derived equations which can be written

$$\epsilon' = \frac{\epsilon_s - \epsilon^*}{1 + \omega^2 T^2} + \epsilon^*$$

$$\sigma = \sigma_s + \frac{(\epsilon_s - \epsilon^*)}{(1 + \omega^2 T^2)} \frac{\omega^2 T}{4\pi}$$

where ϵ_s is the dielectric constant at zero frequency,
ϵ^* is the value of ϵ' between the dispersion regions due to inhomogeneity and water relaxation,
σ_s is the conductivity at zero frequency,
σ is the conductivity at a frequency, $\omega/2\pi$,
T is a time constant (relaxation time), related to the radius and thickness of the cell membrane and its dielectric constant, and to the conductivity of its contents.

Schwan has used Danzer's equations to discuss the dispersion of blood observed at frequencies well below those of microwaves. He shows that the published results on animal blood are approximately consistent with the theory if ϵ_s is about 5 000 and T between 10^{-7} and 10^{-8} sec. Confirmation that blood has such a high dielectric constant at low frequency is provided by the results of Iwase who obtained $\epsilon' = 3\,15$ at 30 kc/s for rabbits' blood at 14·5° C. Rajewsky and Schwan have more recently obtained results on sheep's blood at wavelengths between 36·5 and 185 cm, showing agreement between the experimental results and those calculated from Danzer's equations.

The present results have provided the values of ϵ^* and σ. No measurements were made of ϵ_s for the specimens used in the investigation, but σ_s was measured at 1 000 c/s in a cell designed to minimize the effects of polarization. Using the values thus obtained for σ_s, and those for σ from Table 3, the time constants, T, for human blood have been calculated on the assumption that $\epsilon_s - \epsilon^* = 5\,000$. Table 4 lists the results.

Table 4. *Whole blood—the time constant, T*

Temp. (° C)	σ_s (Ω^{-1} cm^{-1})	σ (Ω^{-1} cm^{-1})	T (sec)
15	0·0050	0·010	$8{\cdot}9 \times 10^{-8}$
25	0·0060	0·012	7·4
35	0·0072	0·014	6·5

Following Schwan, these values of T are approximately consistent with the following properties of spherical cells: internal conductivity 0·01 Ω^{-1} cm^{-1}, membrane dielectric

constant = 6, membrane thickness = 30 Å, and cell radius = 3×10^{-4} cm. The foregoing shows that the ionic contribution to dielectric loss observed at hyper-high frequencies is reasonably consistent with existing dispersion theories and approximate cell data. It will now be of value to compare the observed microwave ionic conductivity of whole blood with that of blood plasma, since this leads to information regarding the internal conductivity of the cells.

(*b*) *Intracellular conductivity.* The relationship between the specific conductivity of whole blood, blood plasma and cell contents given by Danzer can be written

$$\sigma = \sigma_1\left(1 + 3\rho\frac{\sigma_2 - \sigma_1}{\sigma_2 + 2\sigma_1}\right)$$

where σ, σ_1, and σ_2 are the conductivities of whole blood, blood plasma, and cell fluid respectively, and ρ is the volume concentration of cells.

This appears to be the approximation for spheres at low concentration to the relation derived by Fricke[26] for any suspension:

$$\frac{\sigma - \sigma_1}{\sigma + x\sigma_1} = \rho\frac{\sigma_2 - \sigma_1}{\sigma_2 + x\sigma_1}$$

where x is a numerical factor dependent on the shape of the suspended particles and on σ_2/σ_1. For spheres, $x = 2$, and, when σ nearly equals σ_1, the equation can be simplified to the form given by Danzer.

Applying Fricke's relation to blood at microwave frequencies it is necessary to assume that the cell membrane reactance is negligible at such frequencies, and that the relation holds for high concentrations. Fricke[27] has shown the theory to apply in the cases of the low-frequency conductivity of blood and of cream up to a concentration of 70% of cream in skimmed milk. He has also given the values of x for spheroids of various axial ratios and for the full range of variation of σ_2/σ_1.[26] It is established[28] that human erythrocytes behave electrically at low frequencies (according to Fricke's relation) as oblate spheroids of axial ratio 1 : 4. Table 5 shows the results of calculations made using Fricke's equation. Here, the ionic conductivities of

Table 5. *Whole blood—ionic conductivities of blood, plasma, and cell contents*

Temp. (° C)	σ (Ω^{-1} cm^{-1}) Blood	Plasma	Cells	x
15	0·010	0·0108	0·0090	1·90
25	0·012	0·0128	0·0100	1·92
35	0·014	0·0155	0·0122	1·88

the blood are taken from Table 3, and those for the plasma the ionic conductivities measured at low frequency (100 c/s) and assumed to be unchanged at hyper-high frequencies.

The ionic conductivity of the intracellular fluid is lower than that of the plasma, the ratio of the two being approximately that calculated from published data[29] for the ion concentration of normal human erythrocytes and plasma. There appears to be no previous dielectric work on human erythrocytes leading to an estimate of intracellular conductivity. Cole and Curtis[30] list the results of several workers on the conductivity of other animals. The present work indicates that the intracellular ionic conductivity of human erythrocytes is lower than that for erythrocytes of other animals.

The dispersion of the dielectric constant in the microwave region.

Relaxation time. It has been noted that the dispersion in this frequency region is characterized approximately by a single relaxation time. Comparison of the relaxation times of blood with those of water at the same temperature show the former to be nearly 10% longer. Thus the dispersion in blood can be attributed to water relaxation with times increased probably by hydrogen bond formation to active groups of other types of molecule. (A large increase in relaxation time has recently been reported when water associates with dioxan.)[31, 32]

(ii) *Interpretation of ϵ^* in terms of hydration.* Comparison can also be made between the values of ϵ^* for blood and water. In the case of blood it can safely be assumed that contributions to the polarization corresponding to ϵ^* from protein relaxation are negligibly small, since the relaxation times of proteins in aqueous solution lie in the region of 10^{-7} sec.[33] The polarization can then be attributed to the orientation polarization of water molecules and to the atomic and electronic polarizations of all the constituents of blood.

When the value of ϵ^* for blood is calculated using any existing dielectric theory for solutions, mixtures or suspensions, it is found that the experimental value is lower than the calculated one. Following previous workers, the explanation for this is that some water is bound in such a way to ions and proteins as not to contribute to orientation polarization. Estimates of hydration can thus be made from a comparison of dielectric constants, the estimate depending upon which dielectric theory is assumed to apply.

Dielectric measurements at frequencies lower than in the microwave region have already been used to obtain hydration estimates. Errara[34] and Girard and Abadie[35] have worked with colloidal suspensions, gluten and other systems. Much of the work done on protein solutions has been summarized by Oncley. More recently, Hasted and others[36] showed that dielectric measurements at microwave frequencies could lead to hydration estimates in aqueous ionic solutions, and Haggis and others have extended the work to protein solutions.

In the present case of blood a hydration estimate for haemoglobin can be made. It is necessary to use a dielectric theory accounting for inhomogeneity since the dielectric constant of the cell contents differs from that of the plasma. The dielectric theories of Maxwell,[37] Wiener[38] and Fricke[39] all lead to the relation

$$\frac{\epsilon - \epsilon_1}{\epsilon + x\epsilon_1} = \rho\left(\frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + x\epsilon_1}\right)$$

identical in form to the conductivity equation. Hence ϵ, ϵ_1 and ϵ_2 refer to the suspension, suspending and suspended media respectively. x is Fricke's numerical factor, dependent on shape and ϵ_2/ϵ_1.

Table 6 gives the dielectric constants, ϵ^*, of blood plasma, whole blood and red cell contents.

Table 6. *Whole blood—the dielectric constant, ϵ^*, of blood, plasma and cell contents*

Temp. (° C)	ϵ^* Blood	Plasma	Cells
15	62·0	78·3	43·9
25	58·0	74·3	40·1
35	56·0	70·6	39·8

Those for plasma have been calculated from pure water values allowing for ionic and protein depression of the dielectric constant. The erythrocyte values have been obtained using the above equation with $\rho = 0{\cdot}43$ and $x = 1{\cdot}70$ (from Fricke, for oblate spheroid of axial ratio 1 : 4).

From the values of ϵ^* for red cell contents one can proceed

to derive the partial volume of the intracellular hydrated haemoglobin. It will be assumed that the erythrocyte contents represent an inhomogeneous dielectric and that the above relation applies. Using average cell data[40] and assuming a hydrated haemoglobin molecule is equivalent to an oblate spheroid of axial ratio = 1 : 2 and $x = 1{\cdot}72$, the partial volumes and hydration estimates shown in Table 7 have been obtained.

Table 7. *Human erythrocytes—partial volume and hydration of haemoglobin*

Temp. (° C)	Partial volume Hb. + water	Partial volume Hb.	Hydration (g water per g)
15	0·340	0·266	0·21
25	0·361	0·266	0·27
35	0·340	0·266	0·21

The further assumptions that have been made are: (*a*) the partial molar volume of haemoglobin = 0·75, (*b*) the hydrated haemoglobin molecules have a dielectric constant of 2·0 and are dispersed in a medium of dielectric constant equal to that of a saline solution of ionic conductivity as shown in Table 5, and (*c*) constituents other than water, haemoglobin and ions occupy 1·5% of the total volume and have a dielectric constant of 2·0.

Full consideration of all the limits of error involved shows that, as in all hydration estimates, the accuracy of the final estimate is very low. The best that can be claimed here is that the haemoglobin hydration for human erythrocytes is $0{\cdot}23 \pm 0{\cdot}16$ g water per g, assuming the inhomogeneous dielectric theory to apply. Agreement with the results of Haggis and others, who used aqueous solutions of haemoglobin, is reasonably good, though the hydration in a living cell may differ from that in a more dilute aqueous solution. It should be noted that if the hydration is calculated from simple volume proportions[41, 9] the estimate obtained is approximately double the above figure.

CONCLUSIONS AND SUMMARY

(*a*) *Water.* The present results show that the dispersion in water is such that ϵ' falls through the dispersion region from the static value to a value of 5·0 if a single relaxation time is assumed; but also that a fall to the infra-red value of 4·0 is equally possible if relaxation is characterized by a narrow spectrum of relaxation times. A decision between the two would only be possible if results of greater accuracy over a wider frequency range were obtainable. This would also enable any variations of ϵ_∞ with temperature to be detected.

(*b*) *Blood.*

(i) The dispersion at hyper-high frequencies is closely related to the "free" water content and to the ionic conductivity.

(ii) The dispersion effects of inhomogeneity, so great at lower frequencies, are negligibly small at hyper-high frequencies.

(iii) The values obtained for the dielectric constant and ionic conductivity at frequencies just lower than those where water dispersion becomes significant are consistent with Danzer's theory and with published results in the radio frequency region.

(iv) These values give reasonable estimates for the erythrocyte intracellular conductivity and haemoglobin hydration if Fricke's theory and data for inhomogeneous dielectrics is assumed to apply for high concentrations.

ACKNOWLEDGEMENTS

The author wishes to acknowledge the assistance he has received from his colleagues. In particular, thanks are due to Mr. T. J. Buchanan and Dr. G. H. Haggis for the use of apparatus set up by them, and for helpful discussions, and to Dr. J. W. Stewart for providing blood specimens.

The work formed part of a research programme leading to the Ph.D. degree of the University of London. It gives pleasure to thank Professor J. E. Roberts for his guidance and interest during the investigations.

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The spectrophotometry of light sources

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[*Paper first received* 21 *February, and in final form* 24 *March*, 1952]

The calibration and use of simple, non-automatic equipment for spectrophotometry of light sources is described, with particular attention to precautions required for accuracy. The computation of chromaticity from the spectral energy distribution curves is illustrated, with results for a variety of lamps. These results show better agreement with visual colorimetry than in other recently published work. The change of chromaticity of fluorescent lamps with varied loading is analysed by the same methods, and the application to the study of phosphors briefly mentioned.

Spectrophotometry has been widely practised in the determination of transmittance and reflectance factors, and perhaps to a lesser degree in the study of light sources. Automatic instruments have been developed for this latter application.(1-3) The methods used, whether in automatic operation or otherwise, are well known in principle, and are surveyed in a National Bureau of Standards handbook,(4) but there is often a lack of experimental detail available to guide those interested in the technique. This paper shows how, with some precautions, simple apparatus may be used to give results which are not inferior in accuracy to those obtained by more elaborate methods, and which are valuable in problems concerning fluorescent lamps.

The curve of spectral energy distribution (s.e.d.) in the visible region, expressed as energy per unit wavelength interval against wavelength, is fundamental to considerations of colour and colour rendering. Examples of its use are: (i) the chromaticity or colour appearance of the light source can be calculated from this curve, while the agreement with a visual match on a reliable colorimeter is a crucial test of the accuracy of the experimental work; (ii) the curve is of considerable value in the investigation of solid inorganic phosphors, especially those in which preparative conditions are critical for the development of any desirable type of emission; (iii) the s.e.d. curve can be reduced to luminance coordinates instead of energy. From this, any division can be made into bands of specified wavelength intervals with a view to measuring the total luminance in each band. This method, probably not yet in its final form, provides a concise though approximate description of the colour rendering properties of the light source.

APPARATUS

A wavelength spectrometer by Adam Hilger Ltd., with glass prism ($n = 1{\cdot}74$) and wavelength drum was used as a monochromator with the entrance slit narrower than the exit slit, the latter normally at constant width (see below). The entrance slit received light directly from a fluorescent lamp mounted vertically and run at constant wattage or current as required. The whole of the emergent beam from the spectrometer was received on the cathode of a 1P22 photomultiplier cell by Radio Corporation of America mounted in a metal box provided with a tube fitting into the exit tube of the spectrometer. The sensitivity of this multiplier extends well into the red end of the spectrum: its very much higher sensitivity at the blue end is compensated by increasing absorption in the yellowish glass of the spectrometer prism. A stabilized a.c. supply and half-wave rectifier circuit provided the multiplier with about 1 kV during operation, while a potential divider ($\simeq 2$ MΩ total resistance) supplied about 100 V to each of the nine stages of amplification and about 50 V between the anode and the ninth dynode. The output was fed through a universal shunt (10 kΩ) to a d'Arsonval galvanometer (450 Ω) by the Cambridge Instrument Co. Ltd. with a sensitivity of about 1 300 mm/μA at 1 m, which was the scale distance used. For calibration of the apparatus by light of known s.e.d. a 1 kW tungsten projector lamp standardized for colour temperature was found convenient, with a magnesium oxide screen illuminated thereby fixed in front of the spectrometer slit.

PROCEDURE

After an initial period of running to stabilize the multiplier circuit and the fluorescent lamp, and to fatigue the photosurface, readings were taken of the galvanometer deflexion for each 50 or 100 Å interval on the wavelength drum, proceeding from red to blue. The total voltage on the multiplier was held constant at a value in the range 1 000–1 050 V by a variable 1 MΩ resistor in series, and the lamp loading controlled over the narrow range necessary by a variable resistor in series with the choke. Galvanometer deflexions were restricted to about 35 cm, above which a higher range on the universal shunt was introduced. This was chiefly required for the mercury line measurements which in the final form of the experiment were made after the readings through the spectrum of the phosphor bands. For each mercury line the maximum was found by trial adjustment of the drum, and two separate peaks recorded for the yellow doublet.

For calibration, numerous separate runs were made with the tungsten lamp at a colour temperature of 2 848° K (old temperature scale), firstly with an unstabilized a.c. supply with Variac control, which produced some unsteadiness in the resulting deflexions; secondly by a d.c. battery supply, with much improved stability. The observations agreed closely with the averaged a.c. ones. The smooth curve resulting from the mean of ten sets of d.c. observations was taken for the derivation of a table of factors F (F_λ = relative energy at λ of Planck radiator at 2 848° K/deflexion at λ), determined at each wavelength normally used, including those of the mercury lines, for application to all the readings taken for other light sources. The effects of variable exit waveband (in Å), uneven photocell sensitivity and certain instrument errors, were thus eliminated, while the error due to divergence of the standard