MEASUREMENT OF REFRACTIVE INDICES OF AIR, NITROGEN, OXYGEN, CARBON DIOXIDE AND WATER VAPOUR AT 3 360 Mc/S

By W. JASINSKI, Ph.D.(Eng.), B.Sc.(Eng.), Associate Member, and J. A. BERRY, B.Sc.

SUMMARY

A sensitive and accurate method for the measurement of the refractive indices of gases at 3 360 Mc/s is described and critically examined to assess the systematic errors. The method is based on the measurement of the change of the resonant frequency of a cavity resonator when evacuated and when filled with a gas. A frequency modulation technique is used in conjunction with an oscillograph display. The standard deviation in the measurement of changes of the resonant frequency of the high-Q-factor cavity employed, was 77 c/s; this made possible the determination of $(n - 1)$, where n is the refractive index, to four significant figures. This accuracy was achieved with the aid of a crystal-controlled frequency standard.

The results obtained for $(n - 1) \times 10^6$ at 0° C, 760 mm Hg are as follows:

Dry carbon-dioxide-free air	$288 \cdot 2_6 \pm 0 \cdot 2$
Nitrogen	$294 \cdot 4_7 \pm 0 \cdot 2$
Oxygen	$266 \cdot 1_7 \pm 0 \cdot 2$
Carbon dioxide	$494 \cdot 5_9 \pm 0 \cdot 35$
Water vapour (at 20° C and 10 mm Hg)	$61 \cdot 3_1 \pm 0 \cdot 1$

The permanent electric moment of the water molecule was calculated to be $(1 \cdot 845 \pm 0 \cdot 001) \times 10^{-18}$ e.s.u.

The method of measurement is equally suitable for other microwave frequencies.

(1) INTRODUCTION

In recent years a number of measurements of the refractive indices of gases at microwave frequencies have been published (see Table 1). The measurements of Birnbaum et al.,[1] Gabriel[2] and Essen[3] at approximately 9 000 Mc/s, and those of Essen and Froome[4] at 24 000 Mc/s, claim errors in the range of 0·2 to 1·4 parts in 10^6 in $(\epsilon - 1)$, where ϵ is the dielectric constant. The detailed examination of the results presented in Table 1 shows they do not always agree within the experimental errors quoted. The result of Birnbaum et al. for air was recalculated by Smith and Weintraub.[5] This gave a reduced error and good agreement with Essen and Froome, although it is not clear by what procedure the reduced error was derived.

Further, at the time when the present measurements commenced, only one set of measurements—that of Essen and Froome—claimed an accuracy of the order of $0 \cdot 2 \times 10^{-6}$ in $(\epsilon - 1)$ for oxygen and nitrogen as distinct from air.

Under these circumstances it was considered fruitful to undertake further measurements, this time at 3 000 Mc/s. On theoretical grounds there should be no change in the refractive index of air and its constituents at all frequencies up to at least 30 000 Mc/s.

The method of measurement of the refractive index of a gas at microwave frequencies is essentially an extension of the method used at low frequencies for the measurement of the dielectric constant. The gas condenser of the low-frequency lumped tuned circuit is replaced at microwave frequencies by the gas cavity. In both cases the introduction of the gas results in a change of the resonant frequency; it is this detuning which

is measured. The use of a cavity resonator gives the advantage of a much higher Q-factor and consequently of considerably greater accuracy in the resonant frequency setting. However, in the cavity resonator the gas fills not only the region of stored electric energy, as in the case of a gas condenser of the lumped tuned circuit, but it also fills the region of stored magnetic energy. In consequence the change of the resonant frequency of a cavity resonator, which results from the introduction of a gas, depends not only on the dielectric constant but also on the magnetic permeability of a gas; hence, in evaluating one of these quantities the other one must be assumed. Of the constituents of air only oxygen shows a strong paramagnetic effect, and the permeability of the other gases may be assumed equal to unity (in the C.G.S. system of units).

The method of measurement makes use of the following relation between the refractive index n, the resonant frequency of the cavity when evacuated, f_v, and the resonant frequency of the cavity when filled with a gas, f_g (the cavity dimensions are assumed fixed):

$$n = \frac{f_v}{f_g} \qquad \ldots \ldots \quad (1)$$

The above equation follows from the fact that in both instances of resonance the wavelength of the energizing radiation in the medium filling the cavity must remain constant. This holds strictly for lossless gases; at the frequency of measurement air and its constituent gases may be assumed not to exhibit absorption.

Microwave measurements of the refractive index fall broadly in two classes: either the change of the resonant frequency is measured or the frequency is kept constant and the cavity is brought into resonance by a measured change in its dimensions. The latter method was employed by Phillips[6] and others, who used a simple resonator of adjustable length. The refractive index was deduced from the ratio of the lengths of standing waves when the resonator was first evacuated and then filled with a gas. In this method the energizing frequency must be stable but it need not be known. The measurement is essentially one of length.

For the purpose of discussing the methods in which the change of frequency is measured it is convenient to rewrite eqn. (1) in the form

$$n - 1 = \frac{f_v - f_g}{f_g} \qquad \ldots \ldots \quad (2)$$

As $(n - 1)$ for gases is usually less than 10^{-3} it is easily seen that $(n - 1)$ is more sensitive to $(f_v - f_g)$ than to the absolute value of the frequency. This brings out the advantage of a high-Q-factor cavity resonator.

Two methods have been used for the measurement of the frequency shift $(f_v - f_g)$, one employing frequency modulation and the other, used by Essen and Froome, a continuous-wave technique. The latter authors employed an Invar cavity tunable over a narrow frequency range in the vicinity of 24 000 Mc/s by means of a calibrated coaxial plunger. The cavity was placed

in one arm of a waveguide bridge in order to increase the precision of resonant frequency setting. A stabilized frequency oscillator was used to energize the cavity first evacuated and then filled with a gas. The frequency shift $(f_v - f_g)$ was measured by adjusting the oscillator frequency to coincide with a harmonic of a 100-kc/s calibration oscillator nearest to the resonant frequency of the cavity, and then adjusting the plunger to bring the cavity exactly to resonance. The accuracy with which this frequency shift was measured was the setting accuracy of the tuning plunger—namely 1 kc/s. It will be appreciated that this method combines frequency measurement with length measurement.

A method employing frequency modulation was developed by Birnbaum et al., at a frequency of about 9 000 Mc/s. Two cavity resonators were used; one was the gas cavity, and the other, equipped with a calibrated plunger tuning-control, was used as a frequency reference standard. The saw-tooth time-base of an oscillograph was used to modulate the frequency of a klystron oscillator which energized both cavities. The resonance curves of the two cavities were displayed simultaneously on one oscillograph trace by means of an electronic switch. Thus if the two resonant frequencies were different the two resonance curves separated. With the gas cavity evacuated the reference cavity was tuned so that both cavities resonated at the same frequency. When gas was admitted to the gas cavity the two curves separated. Their separation was measured by mixing the modulated frequency with a fixed-frequency signal of about 9 000 Mc/s. The resulting difference frequency was fed into a calibrated selective amplifier of $0 \cdot 6$ to 10-Mc/s tuning range, the output of which was used to brighten the trace. Two bright spots appeared on the trace and were brought to coincide with the peaks of the resonance curves by adjusting the fixed-frequency oscillator and the pass frequency of the selective amplifier. When so adjusted the pass frequency was equal to half the difference of the resonant frequencies of the two cavities.

The ultimate accuracy of this method depends upon (a) the precision with which the frequency of the evacuated cavity can be equalized with that of the reference-frequency cavity, (b) the precision with which the spots can be placed on the peaks of the separated resonance curves when the test cavity is filled with gas, and (c) the precision with which the pass frequency of the selective amplifier is known. The operations (a) and (b) could be performed with an error of 2 kc/s, which alone would give an accuracy in refractive-index determination of about 8 parts in 10^7.

(2) EXPERIMENTAL ARRANGEMENT

The measurements described in the paper were carried out using the frequency-modulation technique. Fig. 1 is a block diagram of the experimental arrangement employed for the measurement of the cavity resonant-frequency changes.

A cathode-ray-oscillograph time-base saw-tooth generator supplies a modulation voltage to the reflector of a klystron oscillator (CV67) operating in the nominal wavelength range $8 \cdot 9$–$9 \cdot 3$ cm. The saw-tooth voltage applied to the reflector is adjusted in amplitude by means of a potentiometer to give a frequency variation of about 500 kc/s for an accelerating voltage of about 1 200 volts. The frequency-modulated output from the klystron is fed, via 20-db well-matched resistive attenuators, to two cavity resonators. One, the "gas cavity," is cylindrical with a square axial cross-section of $11 \cdot 8$ cm side, and is made of silver-plated brass; it resonates in the H_{011} mode at roughly 3 360 Mc/s with a measured Q-factor of about 46 000. To displace its unwanted E_{111} mode there is a deep groove cut between the upper end-plate and the cylindrical wall. The gas cavity is placed under a glass dome where a vacuum of a few
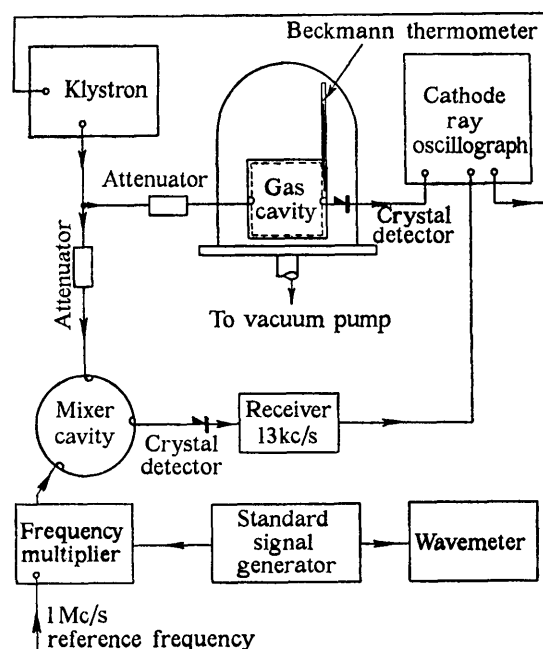

Fig. 1.—Block diagram of the experimental arrangement.

microns of Hg can be established. The gas-cavity magnetic field is detected by means of a silicon crystal diode in an untuned housing, and then amplified by the cathode-ray-oscillograph internal amplifier. By this means the cavity resonance curve is displayed on the cathode-ray-tube screen. The second, a tunable and re-entrant cavity, has a Q-factor of about 1 000; together with a coupled silicon crystal detector it serves as a frequency mixer. The klystron output and the output of a frequency multiplier are fed separately into this mixer.

The frequency multiplier, driven by a 1-Mc/s crystal oscillator, produces a signal of 3 360 Mc/s. The last stage of the frequency multiplier is modulated by a strong signal from a signal generator working at frequencies of the order of a few hundred kilocycles per second. Thus the output of the frequency multiplier consists of the carrier frequency and of the two sideband frequencies; all three frequencies are fed into the mixer. The rectified output of the mixer is fed into a sensitive heterodyne receiver tuned to 13 kc/s. The measured frequency drift of the 1-Mc/s crystal oscillator was about 5 parts in 10^9 during five months, and the hourly scatter was about $\pm 0 \cdot 5$ part in 10^9. The signal generator is of standard grade, and its exact frequency is measured by a frequency meter combining very high stability with good frequency discrimination. (The guaranteed stability is one part in 10^7, and the meter reads direct in cycles per second.)

When the klystron frequency sweeps the range the receiver output consists of three pairs of sharp voltage pulses. There is one pair for each of the three frequencies present in the output of the frequency multiplier, and the spacing of the members of each pair is twice the frequency to which the receiver is tuned, i.e. 26 kc/s. The three pairs of voltage pulses are displayed on the double-beam cathode-ray-oscillograph (see Fig. 2). The signal generator frequency is adjusted until the peak of the resonance curve lies in the middle of one pair of the displayed sideband pulses. When so adjusted the appropriate sideband frequency of the frequency multiplier is equal to the resonant frequency of the cavity, provided that the resonance curve is symmetrical. In fact the method is used to find the difference of two resonant frequencies. This difference does not depend on asymmetry of the resonance curve displayed but would be affected by any change in asymmetry over the range of variation
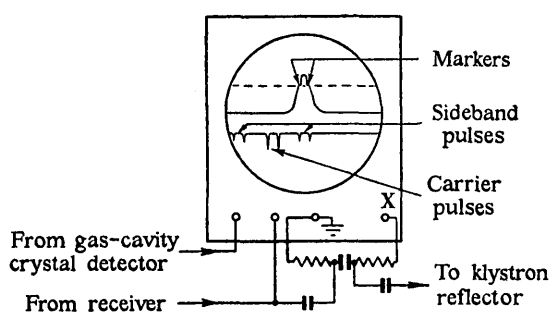
Fig. 2.—Display unit.

of frequency. This, however, is certainly negligible, as the resonant frequency shift $(f_v - f_g)$ is small compared to the absolute value of the resonant frequency.

To increase the accuracy of the symmetrical adjustment of the two sideband pulses with respect to the peak of the cavity resonance curve, a special network is connected to the cathode-ray-oscillograph terminals, as shown in Fig. 2. Its purpose is to superimpose the voltage pulses from the receiver, suitably attenuated, on the saw-tooth voltage supplied by the cathode-ray-oscillograph time-base generator from the terminal marked X. Hence the two voltage pulses change abruptly the linearity of the klystron frequency variation in the corresponding two short time-intervals and cause appearance of two sharp kinks on the otherwise smooth cavity-resonance curve. By altering the receiver gain and bandwidth, the two kinks can be adjusted to present sharp well-defined horizontal plateaux which, from now on, will be referred to as markers. For the exact determination of the cavity-resonant frequency the signal-generator frequency is adjusted to place the two markers on one horizontal line of the cathode-ray-oscillograph graticule, i.e. symmetrically about the peak of the resonance curve, as shown in Fig. 2. The signal-generator frequency is then accurately measured and added or subtracted from the known carrier frequency.

A measure of the sensitivity of the above method is given by the fact that a vertical separation of $0 \cdot 1$ in between the two markers corresponds roughly to 1 200 c/s; a signal-generator frequency change of about 100 c/s (effected by using the generator "zero control") is quite sufficient for the two markers to depart appreciably from the horizontal position, one sliding up and the other down the cavity-resonance curve.

While the two markers are horizontally adjusted, the gas-cavity temperature is accurately determined. For this purpose the mercury reservoir of the Beckmann thermometer is permanently placed in a blind hole drilled in the cavity wall. To maintain good thermal contact between the thermometer and the cavity wall the hole is filled with a low-pressure vacuum oil. To prevent the sticking of the mercury column in the capillary tube, an electric vibrator is employed to shake the thermometer just before a reading is taken.

(3) EXPERIMENTAL PROCEDURE

The experimental procedure employed was reduced to the measurement of the resonant frequency of the cavity filled with the gas and the simultaneous measurement of the temperature and the gas pressure. Certain further additional data were required, however, to evaluate the refractive index from the above measurements. The resonant frequency of the evacuated gas-cavity was accurately determined at several temperatures from which the frequency/temperature coefficient of the gas cavity was established so that the cavity resonant frequency at vacuum could be inferred from its temperature. A correction was also calculated to allow for the slight change in

the resonant frequency which results from the hydrostatic expansion of the cavity walls due to the evacuation of the glass dome. Further the zero of the Beckmann thermometer was calibrated in terms of the centigrade scale and a correction experimentally determined for the expansion of its mercury reservoir which had to be applied to measurements of temperature when the glass dome was evacuated.

The resonance frequency shift is very sensitive to variations of temperature. A change of $0 \cdot 01°$ C corresponds to a change in resonant frequency equivalent to 2 parts in 10^7 in the refractive index. Hence particular attention must be paid to the measurement of change of the temperature (though not of the absolute value) which occurs during the measurements.

Each determination of the cavity resonant frequency consisted of a set of at least ten individual measurements of the signal-generator frequency together with the corresponding Beckmann-thermometer readings after accurate resetting of the markers to lie exactly on one horizontal line. During the course of a set of measurements, which usually lasted some 15 min, the cavity temperature should not vary by more than a few thousandths of a degree centigrade for the final results to be consistent; otherwise the thermal lag of the thermometer would cause an appreciable error. The subsequent calculations were based on the average temperature and the measured signal-generator frequency. Precautions had to be taken, therefore, to maintain the necessary stability of the cavity temperature, and for this reason the measurements were rather time consuming; the measurements on water vapour were carried out in a thermally lagged room.

In all the measurements with the exception of those on water vapour, the gas pressure was the prevailing atmospheric pressure. This was read from a Fortin barometer, the readings of which were reduced to millimetres of mercury at 0°C. The measurements on water vapour were carried out in the pressure range 3–20 mm Hg. These pressures were measured by means of a differential oil manometer which took the form of a U-tube, one limb of which was open to an evacuated enclosure and the other was open to the water vapour in the dome. The density of the Apiezon oil used was accurately determined with the appropriate corrections for the temperature and the air buoyancy.

To get consistent results in the refractive index the cavity had to be flushed several times with the gas to be measured, to clear the adsorbed traces of the previous gas.

After the introduction of a gas some time had to be allowed for the pressure to attain a constant value; this was particularly noticeable with water vapour at pressures near the saturation value, where the delay involved was at least one hour. The time required for the pressure to settle was also sufficient for the temperature to reach a steady value provided the apparatus was in thermal equilibrium before the gas was introduced.

As already mentioned, it is essential to ensure that any asymmetry of the resonance curve should always remain the same. Some of the asymmetry observed was found to be due to mains-frequency hum. It thus became necessary to control the mean frequency of the klystron so that the peak of the resonance curve always coincided with the peak of the hum waveform displayed for the purpose on the second trace of the oscillograph. This was done by adjusting the mean potential of the klystron reflector. Thus the asymmetry due to hum was both reduced and rendered constant.

When all the above-mentioned precautions were observed, the measured values of $(n - 1)$ reduced to s.t.p. became repeatable to within one part in 10^7 of the average. To this maximum scatter, observed in four or five consecutive measurements, the estimated systematic error has to be added to obtain the overall accuracy.

(4) THE DRYING TRAINS

The importance of using dry gases in the measurements is easily seen by quoting the fact that an error of one part in 10^7 in the refractive index of "dry" air results from the presence of about 2×10^{-2} mm Hg of water vapour.

To remove any traces of moisture in the commercial-quality gases available, two types of drying train were made and their effectivenesses were compared by the measurement of refractive index of air. The first train comprised the following reagents in suitable glass containers: calcium chloride, concentrated sulphuric acid followed by anhydrous sodium carbonate (to remove any acid spray from the passing gas), and phosphorus pentoxide. The second train consisted of two towers each one foot high, one containing calcium chloride, to remove the main water content, and the other containing phosphorous pentoxide which was continually shaken to prevent the formation of gas conduits. With an air flow of two litres per minute the two trains gave the same measured refractive index within the experimental error. Still smaller rate of air flow did not affect the result, and it was therefore concluded that the residual water vapour content could be neglected.

To remove carbon dioxide, air was in addition passed through a tube 6 ft long containing soda lime.

(5) EXTRAPOLATION EQUATIONS

The values of $(n_{tp} - 1)$ for dry air (free of CO_2), nitrogen, oxygen and carbon dioxide, obtained at the prevailing temperature, t, and pressure, p, were reduced to s.t.p. using the ideal gas law with the van der Waals pressure correction. Therefore the extrapolation formula for the above gases took the form

$$(n_{0,760} - 1) = (n_{tp} - 1) \frac{760_i}{p_i} \frac{273 \cdot 16 + t}{273 \cdot 16} \quad . \quad . \quad (3)$$

where 760_i is the internal gas pressure at s.t.p. and p_i is the corrected measured pressure given by the expression

$$p_i = p \left[1 + \frac{p}{RT} \left(\frac{a}{RT} - b \right) \right] \quad . \quad . \quad . \quad (4)$$

where a and b are the van der Waals constant.

It has been found that the above extrapolation formula gives results almost identical, over the usual temperature and pressure range, with the extrapolation formula developed by Barrell and Sears[7] for dry air and used by Essen and Froome. In the case of extrapolation from $20°$ C and the pressure of 760 ± 20 mm Hg to s.t.p., the two formulae agree to within 3 parts in 10^8. For $40°$C and the same pressure range the agreement is within 4 parts in 10^8. It is evident that these differences are negligible in comparison with the experimental error. As it is not certain whether or not the Barrell and Sears formula applies for oxygen and nitrogen the van der Waals equation was used throughout. It is probably immaterial which formula is used.

Water vapour is a polar gas, and its dielectric constant therefore obeys Debye's equation:

$$\epsilon - 1 = p \left(\frac{A}{T} + \frac{B}{T^2} \right) \quad . \quad . \quad . \quad . \quad (5)$$

where A represents the contribution of the electronic and atomic polarizations, and B that of the permanent electric moment; p stands for the measured vapour pressure, and T for the absolute temperature.

All the measurements on water vapour were made at temperatures close to $20°$ C, and therefore the two constants A and B could not be determined. The value of A was taken as $(1 \cdot 904 \pm 0 \cdot 154) \times 10^{-4}$. This is the value given by Birnbaum

and Chatterjee[8] and is a weighted average of results obtained by those authors and by three other investigators.

The above value of the constant A agrees well with the one derived by summation of the contribution due to the electronic polarization (found by extrapolating to infinite wavelength the optical dispersion formula for water vapour as established by Barrell and Sears), and that due to the atomic polarization as calculated by Greenfield and Brown,[9] the sum being equal to $1 \cdot 896 \times 10^{-4}$. However, the value given by Birnbaum and Chatterjee was used by the present authors, since it was derived more directly from experimental results.

On the basis of Debye's equation the value of B was computed for each value of temperature and pressure from the measured values of $(n_{tp} - 1)$ and the assumed value of A. The average value for the constant B was found to be $0 \cdot 9980 \pm 0 \cdot 0015$; this value is based only on the measurements made at pressures near 10 mm Hg, for at the lower and higher pressures the accuracy of the pressure determination was insufficient.

Using the above values of the constants A and B, the following extrapolation formulae are obtained:

$$\epsilon - 1 = \frac{p}{273 \cdot 16 + t} \left(1 \cdot 904 \times 10^{-4} + \frac{0 \cdot 9980}{273 \cdot 16 + t} \right) \quad (6)$$

and

$$n - 1 = \frac{95 \cdot 2p}{273 \cdot 16 + t} \left(1 + \frac{5\,240}{273 \cdot 16 + t} \right) \quad . \quad . \quad (7)$$

It may be noted that any error in the value of the constant A is largely compensated by the different value of the constant B that is obtained as a result; such an error will not therefore affect appreciably the accuracy of the above formulae.

It can be shown[10] that

$$B = \frac{4\pi\mu^2}{3k^2} \frac{1 \cdot 01325 \times 10^6}{760} \quad . \quad . \quad . \quad (8)$$

where μ is the dipole moment and k is the Boltzmann constant. Taking B equal to $0 \cdot 9980$, the following value of the dipole moment of the water molecule is obtained:

$$\mu = (1 \cdot 845_4 \pm 0 \cdot 0014) \times 10^{-18} \text{ c.g.s. unit}$$

(6) RESULTS

The results obtained for $(n - 1)$, together with the calculated results for $(\epsilon - 1)$, both reduced to s.t.p., are shown in Table 1. For comparison the results of other recent measurements are also shown. For air and oxygen $(\mu - 1) \times 10^6$ (where μ is the magnetic permeability) was taken as $0 \cdot 38$ and $1 \cdot 9$ respectively.

The measurements on water vapour were made at a temperature close to $20°$ C and at pressures varying from about 3 mm Hg to about 20 mm Hg, which correspond to the relative humidity range from about 15 to 96%. Each measurement was extrapolated to $20°$ C and 10 mm Hg using Debye's equation; this value corresponds roughly to 50% relative humidity. These extrapolated values are plotted in Fig. 3.

It was rather difficult to measure the water-vapour pressure at low and high limits of the range, and accordingly the result given in Table 2 is based on the reduced values of measurements taken in the pressure range $9 \cdot 8$–$11 \cdot 5$ mm Hg.

However, from the results obtained for the whole pressure range, it may be concluded that the dielectric constant of water vapour obeys the simple Debye equation up to 96% relative humidity within the limits of the experimental error.

Table 2 shows the summary of the results obtained for $(n - 1)$ and for the dipole-moment strength of water vapour at $20°$ C and 10 mm Hg.

Table 1

DRY CO_2-FREE AIR AT 0°C AND 760 MM HG

$(n-1) \times 10^6$	$(\epsilon-1) \times 10^6$	Frequency	Author	Year
		Mc/s		
	$570 \pm 0\cdot7$	$0\cdot11$	Lovering and Wilt-shire[11]	1951
	$567\cdot0 \pm 1\cdot0$	1	Hector and Woern-ley[12]	1946
	569 ± 4	3 000	Hughes and Arm-strong[13]	1952
	$606 \pm 2\cdot3$	3 036	Phillips[6]	1950
$288\cdot2_6 \pm 0\cdot2$	$576\cdot2_2 \pm 0\cdot4$	3 360	Jasinski and Berry	1953
	572	9 000	Crain[14]	1948
	$577\cdot0 \pm 1\cdot0$	9 000	Lyons et al.[15]	1948
	$575\cdot3 \pm 1\cdot4$*	9 000	Birnbaum et al.[1]	1951
	$575\cdot7 \pm 0\cdot3_6$†			
$288\cdot10 \pm 0\cdot1$		9 200	Essen[3]	1953
$287\cdot8 \pm 0\cdot1$	$575\cdot4 \pm 0\cdot2$	9 423	Gabriel[2]	1952
	$575\cdot4 \pm 2\cdot1$	9 470	Zieman[16]	1952
$288\cdot15 \pm 0\cdot1$	$576\cdot0 \pm 0\cdot2$	24 000	Essen and Froome[4]	1951

* The value given by Birnbaum et al. was $575\cdot4 \pm 1\cdot4$. The present authors adjusted this figure to exclude the CO_2 content.
† This figure for Birnbaum et al. is that quoted by Smith and Weintraub and corrected by the authors to exclude CO_2.

NITROGEN AT 0°C AND 760 MM HG

$(n-1) \times 10^6$	$(\epsilon-1) \times 10^6$	Frequency	Author	Year
		Mc/s		
	$578 \pm 0\cdot7$	$0\cdot11$	Lovering and Wilt-shire[11]	1951
	$579 \pm 1\cdot0$	1	Hector and Woern-ley[12]	1946
$294\cdot4_7 \pm 0\cdot2$	$589\cdot0_2 \pm 0\cdot4$	3 360	Jasinski and Berry	1953
	587 ± 2	9 000	Lyons et al.[15]	1948
	$586\cdot9 \pm 2\cdot9$	9 000	Birnbaum et al.[1]	1951
$294\cdot1 \pm 0\cdot1$		9 200	Essen[3]	1953
	$587\cdot0 \pm 2$	9 470	Zieman[16]	1952
$294\cdot1 \pm 0\cdot1$	$588\cdot3 \pm 0\cdot2$	24 000	Essen and Froome[4]	1951

OXYGEN AT 0°C AND 760 MM HG

$(n-1) \times 10^6$	$(\epsilon-1) \times 10^6$	Frequency	Author	Year
		Mc/s		
	$528 \pm 0\cdot7$	$0\cdot11$	Lovering and Wilt-shire[11]	1951
	$523 \pm 1\cdot0$	1	Hector and Woern-ley[12]	1946
	$532\cdot5 \pm 1\cdot3$	1	Jelatis[17]	1948
$266\cdot1_7 \pm 0\cdot2$	$530\cdot5_1 \pm 0\cdot4$	3 360	Jasinski and Berry	1953
	$532\cdot0 \pm 2\cdot0$	9 000	Lyons et al.[15]	1948
	$530\cdot0 \pm 1\cdot9$	9 000	Birnbaum et al.[1]	1951
$266\cdot2 \pm 0\cdot2$		9 200	Essen[3]	1953
	$532\cdot0 \pm 2\cdot1$	9 470	Zieman[16]	1952
$266\cdot4 \pm 0\cdot2$	$531\cdot0 \pm 0\cdot4$	24 000	Essen and Froome[4]	1951

CARBON DIOXIDE AT 0°C AND 760 MM HG

$(n-1) \times 10^6$	$(\epsilon-1) \times 10^6$	Frequency	Author	Year
		Mc/s		
	$987 \pm 0\cdot7$	$0\cdot11$	Lovering and Wilt-shire[11]	1951
	$987\cdot5 \pm 2\cdot0$	1	Hector and Woern-ley[12]	1946
$494\cdot5_9 \pm 0\cdot35$	$989\cdot4_2 \pm 0\cdot7$	3 360	Jasinski and Berry	1953
	$988 \pm 2\cdot0$	9 000	Lyons et al.[15]	1948
	$985\cdot5 \pm 3\cdot0$	9 000	Birnbaum et al.[1]	1951
	$987\cdot5 \pm 4\cdot1$	9 470	Zieman[16]	1952
$494 \pm 1\cdot0$	$988 \pm 2\cdot0$	24 000	Essen and Froome[4]	1951

Table 2

$(n-1)$ AND DIPOLE-MOMENT STRENGTH OF WATER VAPOUR AT 20°C AND 10 MM HG

$(n-1) \times 10^6$	Dipole moment $\times 10^8$ e.s.u.	Frequency	Author	Year
		Mc/s		
$61\cdot3 \pm 0\cdot4$	$1\cdot831 \pm 0\cdot006$	$0\cdot5$	Stranathan[18]	1935
$62\cdot7$	$1\cdot842 \pm 0\cdot008$	1	Sänger[19]	1930
$62\cdot4$		3 000	Phillips[6]	1950
$61\cdot3_1 \pm 0\cdot1$	$1\cdot845_4 \pm 0\cdot001_4$	3 360	Jasinski and Berry	1953
$60\cdot7 \pm 0\cdot2$	$1\cdot832 \pm 0\cdot002$	9 200	Essen[3]	1953
	$1\cdot846 \pm 0\cdot005$	9 280	Birnbaum and Chatterjee[8]	1952
$60\cdot7 \pm 0\cdot1$		24 000	Essen and Froome[4]	1951

In the measurement of the dielectric constant of water vapour at low radio-frequencies it was found that this did not obey Debye's law.[18] This was ascribed to the polarization of the film of water adsorbed on the insulators used in the construction of the gas condensers. This effect became more pronounced as the vapour pressure approached the saturation value. Birnbaum and Chatterjee[8] in their experiments with microwave resonators did not find any departure from Debye's formula up to 90% relative humidity. This was considered to be due to the very weak electric field which exists at the boundaries of a cavity in the H_{011} mode. The present authors found similar results up to 96% relative humidity.

In order to investigate the behaviour of $(n-1)$ and the cavity Q-factor in the presence of adsorbed water vapour it was decided to introduce an insulator into a region of strong electric field. To ensure a large surface area the insulator was made in the form of a cylindrical polythene cup placed coaxially in the resonator. The cup was $3\cdot75$ cm high, $2\cdot5$ cm outside diameter and the thickness was approximately $0\cdot1$ cm. The Q-factor of the cavity was measured by placing the markers at the half-power points of the resonance curve. This involved an adjustment of the receiver frequency (previously fixed at 13 kc/s). It also involved the assumption that the resonance curve was sym-
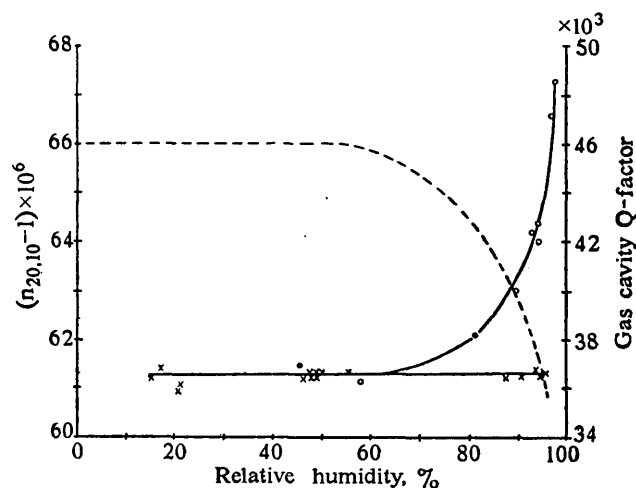

Fig. 3.—Relations between $(n-1) \times 10^6$ for water vapour, reduced to 20° C and 10 mm Hg, and the relative humidity.

—x— $\frac{x}{x \ x}$ Measured with empty cavity.

—o— $\frac{}{o \ o}$ Measured with the dielectric inside the cavity.

- - - - - - - - Cavity Q-factor with the dielectric.

metrical. Thus the Q-factor was taken as equal to $f_r/2f_R$, where f_r is the resonant frequency of the cavity and f_R is the frequency to which the receiver is tuned. The accuracy of this measurement is considered to be about 5%.

It is found (Fig. 3) that the value of $(n - 1)$, reduced to 20° C and 10 mm Hg, remained constant up to about 60% relative humidity. After that it rose in an exponential manner, while the Q-factor of the cavity similarly decreased. Both these effects can be explained by the presence of water, which gives rise to additional polarization and to conduction currents.

(7) ACCURACY

In the method described, the smallest measurable resonant-frequency change of the gas cavity is determined by the precision in the horizontal alignment of the two markers. This was accurately determined under constant experimental conditions; the standard deviation in the frequency measured amounted to 77 c/s, corresponding to an uncertainty of 2 parts in 10^8 in the determination of the refractive index; this represents the sensitivity of this experimental method described and the ultimate limit of accuracy.

In the experiments described in the paper the number of measurements taken is insufficient for significant statistical treatment. Accordingly the random error limits were taken as being equal to the maximum deviation of the measured values; this amounted to about 1 part in 10^7 for all the gases measured except carbon dioxide.

For dry air, nitrogen and oxygen the total systematic error in the refractive index is the sum of the following constituent errors:

(a) Temperature calibration of the Beckmann thermometer was within $\pm 0\cdot 02°$ C; that uncertainty gives rise to a systematic error not greater than 2 parts in 10^8.

(b) Systematic error due to uncertainty of Fortin barometer calibration is considered to be not greater than 2 parts in 10^8.

(c) Systematic error due to the uncertainty of the value of the bulk modulus of brass used in the calculation of the hydrostatic expansion correction; this is considered to be not more than 3 parts in 10^8.

(d) Systematic error due to the uncertainty in the determination of the temperature coefficient of the resonant frequency of the cavity is not more than $1\cdot 5$ parts in 10^8.

(e) The uncertainty associated with a possible error of $0\cdot 002°$ C in the experimental determination of the Beckmann thermometer temperature for the difference between the atmospheric pressure and the vacuum; this gives rise to a systematic error of 5 parts in 10^8.

The total systematic error for air, nitrogen and oxygen is thus estimated to be not more than $13\cdot 5$ parts in 10^8. For carbon dioxide the sources of error cited under (a) and (b) are nearly twice as great, so for this gas the total systematic error does not exceed 17 parts in 10^8. The total systematic error for the dielectric constant is double the above figures.

In the measurements of the refractive index of water vapour the systematic errors are less, for the maximum pressure was about 20 mm Hg, and the temperature was much more stable than with the previous gases, since the measurements were made in a thermally lagged room. The total systematic error for water vapour is considered not to exceed 2 parts in 10^8.

The variation in the loading of the cavity over the used frequency range is considered to be too small to affect the accuracy of the results. Similarly the effect of the receiver delay can be neglected, as the rate of frequency change was constant.

In the Tables the errors for the results obtained combine the statistical error with the total systematic error as estimated above. The assessment of the total probable error is definitely on the pessimistic side, for it is unlikely that all the systematic errors are of the same sign.

The gases used for the measurements were of commercial quality. Nitrogen was stated to be of 99·9% purity, containing approximately 20 volumes per million of water vapour, less than 10 volumes per million of oxygen and up to 20 volumes per million of carbon dioxide. Oxygen was stated to be of at least 99·5% purity with approximately 10 volumes per million of carbon dioxide and about 200 volumes per million of water vapour. Carbon dioxide was stated to contain 1% of air and 0·01% of water vapour. Water vapour was generated by the evaporation of distilled water from a glass vessel; when not in use the outlet from the vessel was closed from the outside air by means of a high-vacuum tap.

(8) CONCLUSIONS

An accuracy of 2 parts in 10^7 in the value of $(n - 1)$ is claimed for the gases measured, with the exception of carbon dioxide, for which the accuracy is $3\cdot 5$ parts in 10^7. The experimental results agree with those of Essen and Froome,[4] Essen[3] and also with those of Lyons et al.,[15] and of Birnbaum et al.[1] The only exception is the result for water vapour, which agrees closely with that obtained by Stranathan.[18]

The technique used gives excellent sensitivity, a change of 2 parts in 10^8 being measurable. The technique depends fundamentally only on the measurement of a change of frequency. It is thus directly comparable with the method of Birnbaum et al. However, the following features of the technique employed are considered to be improvements on that used by Birnbaum et al.:

(a) The visual adjustment of the markers is carried out under optimum conditions, at a point where the slope of the resonance curve is very high; also the horizontal alignment of the two markers is made more precise because they move in opposite directions. It is estimated that the accuracy of alignment measured in cycles per second is improved in the present method by an order of magnitude above that of Birnbaum et al. (after account has been taken of the higher frequency used by Birnbaum et al.).

(b) Only one cavity is used in the measurements. The method used by Birnbaum et al. depends on two cavities remaining at precisely the same temperature.

(c) As a result of the high sensitivity the technique is capable of further refinement, e.g. by use of an Invar cavity resonator.

(d) The actual measurement of the frequency shift $(f_v - f_g)$ is made by means of a wavemeter which measures the frequency of the signal generator of high stability. In the method used by Birnbaum et al. the selective amplifier must be calibrated, which undoubtedly also involves the use of a signal generator and a wavemeter.

In comparison with the method of Essen and Froome[4] the present method possesses the advantage that it does not depend on the measurement of both a frequency shift and a displacement of the tuning plunger.

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DIGESTS OF INSTITUTION MONOGRAPHS
A NEW METHOD OF DETERMINING CORRELATION FUNCTIONS OF STATIONARY TIME SERIES

D. G. LAMPARD, M.Sc.

The importance of statistical methods and concepts for handling problems in a variety of fields is now firmly established.[1] A parameter which occurs frequently in the theoretical discussion of many of these problems is the correlation function of two stationary time series $x_1(t)$ and $x_2(t)$ which is usually defined (Reference 2, p. 5) as

$$\psi_{12}(\tau) = \lim_{T\to\infty} \frac{1}{2T}\int_{-T}^{+T} x_1(t)x_2(t+\tau)dt \quad . \quad . \quad . \quad (1)$$

$$= \overline{x_1(t)x_2(t+\tau)} \quad . \quad . \quad . \quad . \quad (2)$$

where the bar denotes time averaging in the sense specified in eqn. (1).

Because of the importance of this function it is natural that devices should be required, which, when presented with the time series $x_1(t)$ and $x_2(t)$, should carry out the operations implied by eqn. (1).

It is seen from eqns. (1) and (2) that the essential feature of this definition is the temporal delay τ between the $x_1(t)$ and $x_2(t+\tau)$. When the $x_1(t)$ and $x_2(t)$ are fluctuating voltages or currents the provision of this "pure" delay presents rather a problem. For very short delays (less than 100 microsec, say) simple artificial lines have been constructed to give the required delay without appreciable distortion of the waveform, while methods which have been used satisfactorily for longer delays include tape or film recording followed by playback with displaced recording heads, and pulse-sampling methods.

In the paper a method which is believed to be a new approach

to the problem of determining correlation functions will be presented. This method has the advantage that a "pure" delay is not required.

We suppose that any correlation* $\psi(\tau)$ can be expanded in a series of orthogonal functions (Reference 3, p. 22, and Reference 4, p. 49), thus

$$\psi(\tau) = \sum_{n=0}^{\infty} a_n\theta_n(\tau)[\omega(\tau)]^\gamma \quad . \quad . \quad . \quad (3)$$

where the $\theta_n(\tau)$ are polynomials which form an orthonormal set with respect to the weight function $\omega(\tau)$ in the range $0 \leqslant \tau < \infty$. Thus

$$\int_0^\infty \theta_n(\tau)\theta_m(\tau)\omega(\tau)d\tau = \left.\begin{array}{l} 0, m \neq n \\ 1, m = n \end{array}\right\} \quad . \quad . \quad (4)$$

The coefficients a_n in the series expansion shown in eqn. (3) can then be found in the usual way and are given by

$$a_n = \int_0^\infty \psi(\tau)\theta_n(\tau)[\omega(\tau)]^{1-\gamma}d\tau \quad . \quad . \quad (5)$$

Let us now consider the system of Fig. 1. We suppose that the linear network has an impulse response $h_n(t)$. Then it follows from the superposition theorem that the filter output $X_1(n; t)$ is given by

$$X_1(n; t) = \int_0^\infty x_1(t-u)h_n(u)du \quad . \quad . \quad . \quad (6)$$

Mr. Lampard was formerly at the Division of Electrotechnology of the Commonwealth Scientific and Industrial Research Organization, Australia, and is now at Corpus Christi College, Cambridge.

* The subscripts will be dropped when not necessary to the argument.