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ON THE RELIABILITY OF IMPEDANCE AND ADMITTANCE DATA MEASURED WITH LIMITED BANDWIDTH AT AN OBJECT THAT VARIES WITH TIME, THE DROPPING MERCURY ELECTRODE, ALSO COMPLICATED BY SHIELDING EFFECTS, IN PARTICULAR

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ABSTRACT

The consequences of the presence of a sluggish tuned amplifier in an a.c. bridge used for measurements at a dropping mercury electrode are discussed. Also a digital simulation is made of the response of a network analyser with limited bandwidth. In order to explain the experimental results the drop size dependence of the shielding of the mercury drop is treated in a semi-quantitative way. These consequences appear to be minor under circumstances that apply to the way double layer capacitances are usually measured but in the study of electrode kinetics errors are likely to be introduced.

INTRODUCTION

In electrochemistry measuring the impedance of a cell that is time dependent, is not uncommon. The origin of this time dependency can be manifold, e.g. concentration changes, progressive adsorption, recrystallization at the electrode surface, change in porosity, varying d.c. bias and varying surface area.

The most pronounced example of the latter case, we believe, is the dropping mercury electrode. We will therefore confine this discussion to this electrode, though the results also will apply to other objects the impedance of which is changing.

Impedance measurements at dropping mercury electrodes have been performed in order to study the double layer capacitance and the kinetics of heterogeneous redox reactions and coupled processes at this electrode. In both fields ultimate accuracy of the measurements has been aimed at lest no systematic error in the measurement would introduce artefacts into the result of an analysis of the impedance data. This is also the reason why the dropping mercury electrode became so popular: it is a most attractive way to produce a clean surface reproducibly.

The opinion that the rate of change of the impedance should be low compared to the frequency at which this impedance is measured is general. However, we have not been able to find quantitative study of this problem in literature.

Until recently all impedance measurements on electrochemical cells were performed with a.c. bridges. The imbalance of the bridge is detected mostly on an oscilloscope. In order to achieve a high sensitivity and a high rejection of noise and overtones the imbalance of the bridge in later work (see e.g. ref. 1) was preamplified by a tuned amplifier with a narrow bandwidth. Such amplifiers suffer from slow response and might degrade the measurements significantly in the case of a changing object. We therefore decided to perform a series of measurements at a dropping mercury electrode with the intent to show the gravity of the errors due to sluggishness of a tuned amplifier.

With the dropping mercury electrode as the object, also shielding of the electrode by the glass capillary will occur. Its dependence on drop size will be discussed.

The results will also qualitatively apply to modern directly indicating instruments like lock-in amplifiers and network analysers because also these instruments will have a finite bandwidth, and to Fast Fourier Transform techniques due to the finite magnitude of the time window [2].

THEORY

Formulae exist (see e.g. ref. 3) for the value of the imbalance of an a.c. bridge. Also the time dependency of the impedance of a dropping mercury electrode in the absence of a redox couple can be taken to be:

$$Z' = R_{\mathrm{hom}} + (\rho/4\pi)(4\pi\sigma/3mt)^{1/3} \tag{1}$$

$$Z'' = (1/4\pi\omega C_{\mathrm{d}})(4\pi\sigma/3mt)^{2/3} \tag{2}$$

where R_{hom} is the resistance of the homogeneous part of the cell and the mercury in the capillary, ρ is the specific resistance of the electrolyte, m the rate of flow of the mercury (g s^{-1}), here supposed to be constant, and σ the density of mercury. It will be clear that $(4\pi\sigma/3mt)^{-1/3}$ stands for the drop radius r. Substitution of this time dependent cell impedance $Z = Z' - \mathrm{j}\, Z''$ into the expression for the imbalance of the bridge allows the lag in the output of the tuned amplifier to be calculated if the characteristics describing the behaviour of the amplifier towards a time dependent amplitude of the input signal are known. Ultimately the degree of miscompensation of the bridge could be calculated as a function of all variables involved.

Here we do not wish to perform such a calculation because it would both be complex and of limited value as a consequence of the presence of the output transformer in the bridge, the input impedance of which neither can be neglected nor be supposed to be infinite.

Therefore in the case of the a.c. bridge it is more useful to demonstrate the magnitude of the effect by experiment.

With a phase-sensitive alternating current measuring instrument, however, the problem is more surveyable and a digital simulation can be made (see Appendix). In Figs. 1 and 2 the result of such a calculation is shown pertaining to a real cell for which both amplitude (Fig. 1) and phase angle (Fig. 2) of the admittance have been calculated both as true and measured quantities.

Figures 1 and 2 were obtained starting with eqns. (1) and (2) with R_{hom} =

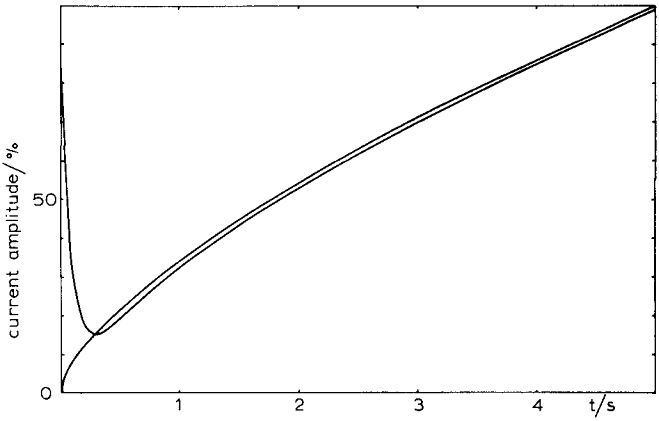

Fig. 1. The amplitude vs. time calculated and simulated respectively for a dropping mercury electrode in a base electrolyte. Explanation: see text.

10 Ω, ρ = 10 Ω cm, m = 1 mg s^{-1}, ω = 1200 rad s^{-1}, c_d = 20 μF cm^{-2} and a drop time of 5 s.

Evidently both the measured amplitude and the measured phase angle lag the true ones to an appreciable extent. The calculations were made for an alternating current measuring device with a time constant of 87 ms which is the time constant of the HP 3570 A network analyser in use in this laboratory.

It clearly can be seen that the absolute error in the amplitude at the end of drop life slowly goes down to a virtually constant value, which means that the relative error in the measured value of C_d goes down only with $t^{-2/3}$ and is still 1.3% at the end of drop life.

Also in the presence of a redox system the calculation will be feasible, inserting a more complex expression for the cell impedance. In this paper we will confine to a cell with an equivalent circuit consisting of a simple R_s—C_s series combination with time dependent R_s and C_s.

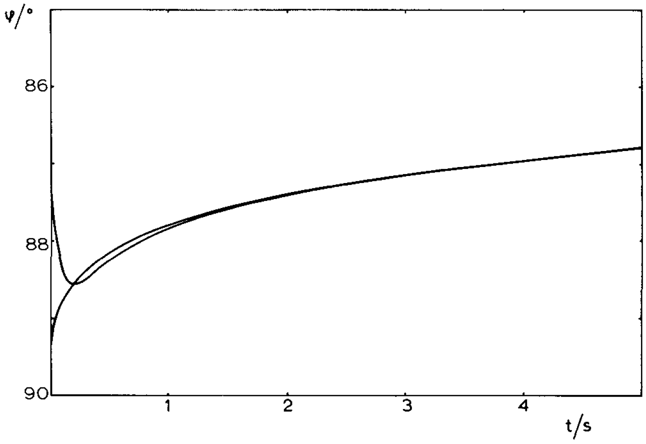

Fig. 2. The phase angle vs. time. Further as Fig. 1.

TABLE 1

Experimental impedance values in 1 *M* KCl at −1038 mV vs. SCE

Data between brackets measured with low Q

t/s	Drop surface/ cm^2	2000 Hz		1000 Hz		520 Hz		230 Hz		170 Hz	
		R_s/Ω	C_s/nF	R_s/Ω	C_s/nF	R_s/Ω	C_s/nF	R_s/Ω	C_s/nF	R_s/Ω	C_s/nF
1.04	0.01756	54.4	283.5	58.0	281	74	278	145	280	180	272
		(54.7)	(284.5)	(58)	(283)	(74)	(283)	(140)	(282)	(235)	(282)
1.25	0.01997	52.2	319.5	55.5	319.5	69	318	155	314.5	220	316
		(51.0)	(320)	(55)	(321)	(67.5)	(318.5)	(140)	(320)	(185)	(324)
1.56	0.02333	49.3	378	51.0	377.5	54.5	375.5	48	369	53	367
		(49.3)	(379)	(49.5)	(377.2)	(51)	(377)	(52)	(376)	(56)	(374)
2.08	0.02830	48.2	459.5	50.6	456	56	455.5	80	454	80	454
		(48.4)	(459.5)	(50.0)	(456)	(55)	(458)	(75)	(461)	(85)	(459)
3.20	0.03828	45.8	626.5	46.8	627.0	48.1	625	60	623	69	620.5
		(45.8)	(626.7)	(46.6)	(627)	(48.8)	(626.6)	(60)	(626.5)	(70)	(626)
4.17	0.04570	44.4	752.0	44.4	752.0	45.5	753.5	45	746	46	744.5
		(44.4)	(752.0)	(44.4)	(753)	(44.6)	(753)	(47)	(750)	(46)	(744)
4.86	0.05022	44.4	832	45.4	835.5	48.7	836	58	836	66	835
		(44.4)	(833.8)	(45.3)	(836)	(47.9)	(837.5)	(58)	(840)	(66)	(841)

EXPERIMENTAL

The experiments were performed in 1 *M* KCl with an a.c. bridge with potentiostatic electrode potential control that will be published separately. In order to minimize shielding a sharp polarographic capillary with an orifice of 0.030 cm outer and 0.013 cm inner diameter was applied. Its natural drop time at the d.c. potential (—1038 mV) and the mercury column height (50.0 cm) used was 4.86 s. The cell was carefully cleaned and steamed out before the experiment. Bidistilled mercury was used and the solutions were prepared from p.a. KCl and freshly bidistilled water. The tank nitrogen was freed from oxygen with a BTS catalyst. The cell was thermostated at 25° C.

As the tuned amplifier a Brookdeal Model 464 a.c. null detector was chosen because of the possibility easily to switch from small bandwidth ("high *Q*") to a larger bandwidth ("low *Q*") or flat, which means a slow, medium and fast response of the amplifying system.

In the case of the flat detector there is no noise discrimination and the balancing of the bridge is rather difficult even with this type of bridge. Therefore the amplitude of the a.c. signal across the bridge was chosen rather high, 22 mV r.m.s. In order to minimize the occurrence of overtones the d.c. potential was chosen at —1038 mV, where the value of the double layer capacitance does not vary much with potential in this solution.

The cell impedance was at first measured at predetermined times after drop fall by means of a digital timer that was started at the instant of drop fall by means of the H.F. drop fall detector published earlier [4] and at a number of frequencies. Though all data obtained in that way clearly showed the influence of the slow response of the tuned amplifier the results were found to be affected by varying flow rate of the mercury due to back pressure [5].

Therefore we will confine to report results obtained in a different way viz. at

TABLE 2

Double layer capacitances ($C/\mu F\ cm^{-2}$) calculated from Table 1

Data between brackets measured with low *Q*

t/s	2000 Hz	1000 Hz	520 Hz	230 Hz	170 Hz
1.04	16.14	16.00	15.83	15.95	15.49
	(16.20)	(16.12)	(16.12)	(16.06)	(16.06)
1.25	16.00	16.00	15.92	15.75	15.82
	(16.02)	(16.07)	(15.95)	(16.02)	(16.22)
1.56	16.20	16.18	16.06	15.82	15.73
	(16.25)	(16.17)	(16.16)	(16.12)	(16.03)
2.08	16.24	16.11	16.10	16.04	16.04
	(16.24)	(16.11)	(16.18)	(16.29)	(16.22)
3.20	16.37	16.40	16.33	16.27	16.21
	(16.37)	(16.38)	(16.37)	(16.37)	(16.35)
4.17	16.45	16.46	16.49	16.32	16.29
	(16.45)	(16.48)	(16.48)	(16.41)	(16.28)
4.86	16.57	16.64	16.65	16.65	16.63
	(16.60)	(16.65)	(16.68)	(16.73)	(16.75)

TABLE 3

Time constants of preamplifier Brookdeal model 464

Frequency/Hz	Time constant/ms)	
	High Q	Low Q
170	63	18
320	37	10
520	20	6
1000	12	5
2000	7	2.5

a dropping mercury electrode that was knocked off by a magnetic hammer at a well determined instant. In that way the area of the drop can independently be obtained by calculation from drop weight. The cell impedance was measured at 1.04, 1.25, 1.56, 2.08, 3.12, 4.17 and 4.86 s after drop birth and at 2000, 1000, 520, 230 and 170 Hz.

In order to enable the reader to make his own (re)calculations the raw data are given in Table 1. The double layer data reported in Table 2 are calculated from Table 1 by $C_d = C_s$/surface area.

Because the time constant of the tuned amplifier increases at lower frequency (Table 3) and because the rate of change of the cell impedance is large at small drop size the effect we wish to show will be minimal at 2000 Hz and 4.86 s and maximal at 170 Hz and 1.04 s.

In Table 2 this expectation can be seen to be met. In between parentheses also the corresponding values obtained with the tuned amplifier in the "low Q" mode are given. Data obtained in the "flat" mode were identical to the latter though much more uncertain.

Flash light pictures of the mercury drop were taken during drop growth with the flash light actuated by a timer started by the drop fall detector.

DISCUSSION

At first sight Table 2 demonstrates the effect quite well. Also the "best" value of the double layer capacitance at long drop time and high frequency agrees well with the value of 16.50 μF cm^{-2} reported by Grahame and Parsons [6]. The double layer values found are only independent of bandwidth at the left hand size of the zigzag line in Table 2.

A more close inspection of Table 2, however, reveals that there is a (identical) time dependency at the values of the double layer capacitance at high frequencies both in the "high Q" and the "low Q" mode.

This must mean that this time dependency does not originate from slow response of the amplifier and that the decrease of the C_d values at short times at 2000 and 1000 Hz must have a different origin. Shielding of a part of the surface area of the mercury drop by the capillary that is comparatively important at small drop size could explain the effect. The maximal effect, however, one could imagine is the complete blocking by an area equal to the outer cross section of the capillary, i.e. 7×10^{-4} cm^2. Recalculation of the data with the surface area diminished by 7×10^{-4} cm^2 led to the conclusion that though the drop time dependence of C_d decreases after this overestimation of the shielding it has not disappeared. This leads to the conclusion that a drop-size dependent shielding is present, the shielding decreasing with increasing drop size. It will be clear that in this paper shielding is defined as the area of the electrode surface apparently prevented from contributing to the electrode admittance by the glass capillary (cm^2).

As a semiquantitative measure of the shielding occurring at a dropping mercury electrode we take the reciprocal value of the distance y between a point at the circumference of the glass capillary and the point on the drop surface vertically underneath, as indicated in Fig. 3.

In the case of a purely spherical mercury drop from simple geometrical construction the value of $1/y$ can be determined as a function of drop radius r, taking the inner and outer diameters of the capillary equal to the values pertaining to the capillary used in the experimental part, 0.013 and 0.030 cm, respectively.

Values of $1/y$ obtained from spherical drops and values obtained from pictures of real drops together have been plotted in Fig. 4. Evidently the "absolute" value of the shielding behaves completely differently in these two cases due to deformation of the drop under the influence of gravity.

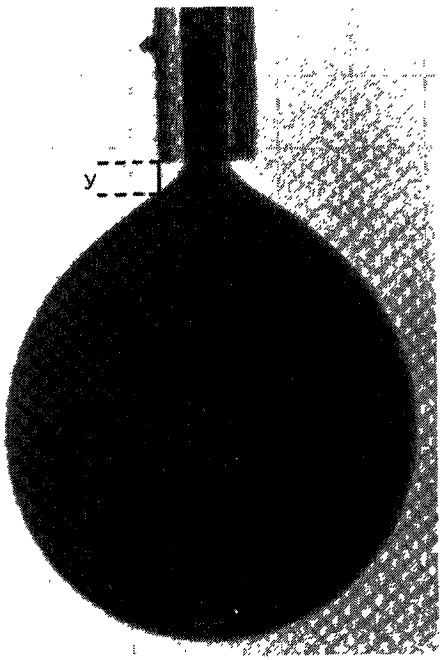

Fig. 3. y as a measure of the shielding.

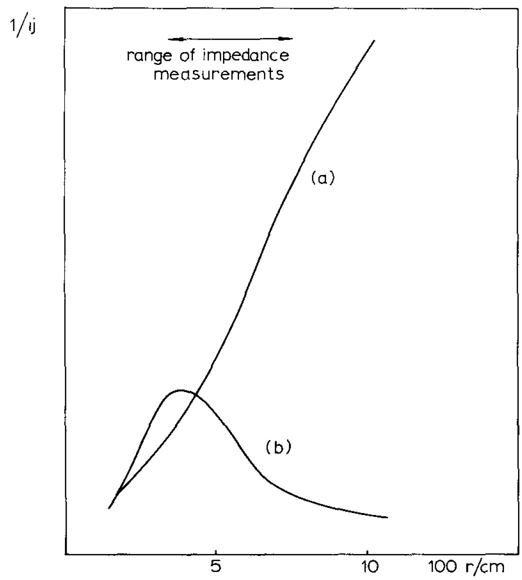

Fig. 4. $1/y$ as a function of drop radius. (a) For pure spheres. (b) From pictures of real drops.

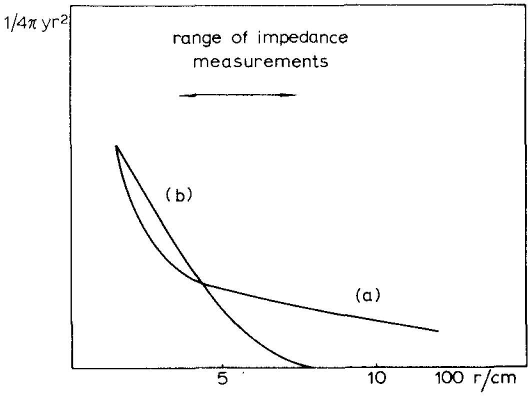

Fig. 5. $1/4\pi r^2 y$ as a function of drop radius. (a) For pure spheres. (b) From pictures of real drops.

Figure 5 shows the "relative" shielding, $1/4\ \pi r^2 y$ of the drop, both in the theoretical and the practical case. Evidently neck formation turns out to be most helpful in decreasing shielding. Fortunately the rather heavy deformation gives only a surprisingly small increase of the surface area, as has been reported before [7,8].

We found from enlarged pictures of our largest drop (t = 4.86 s) an increase of 0.6%, which leads to the conclusion that the double layer capacitance values in Table 2 for t = 4.86 s could be 0.1 μF cm^{-2} too high.

That the shielding is still present for this largest drop also is evident from the frequency dependence of the double layer capacitance measured with low Q. Extrapolation of these capacitance values to zero frequency in order to get rid of shielding, as was proposed by Grahame [9] leads to a significantly higher

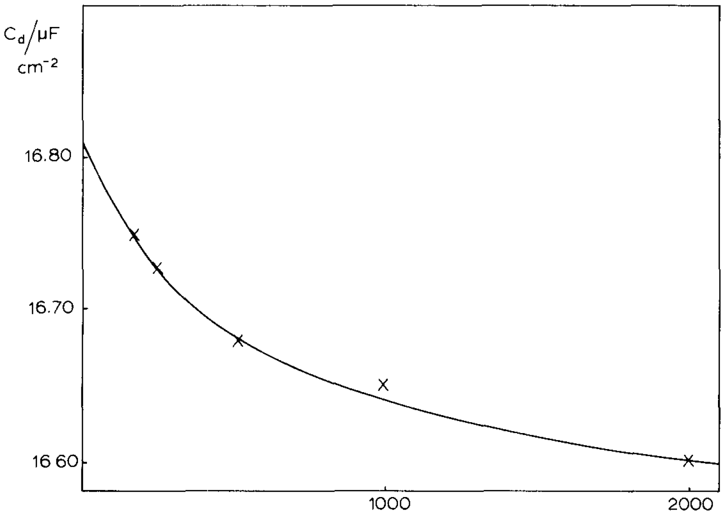

Fig. 6. The extrapolation of the experimental double layer capacitance measured at t = 4.86 s and with low Q to zero frequency.

value (Fig. 6) than the one reported in literature, 16.50 μF cm^{-2} [6].

Note however, that at the same drop time the results obtained at high Q are virtually frequency-independent, yielding a value 16.6 μF cm^{-2}.

Evidently at this drop time and with the amplifier used the two effects, shielding and slow response obscure each other. From the complete Table 2 it can be concluded that similar extrapolations at other drop times would all lead to different values at zero frequency. Therefore, somewhat cautiously we could infer that the value 16.8 is probably the "best" value, but not undisputably the "exact" value.

Another solution to the shielding problem could be to determine dC_s/dA at a drop size where shielding is independent from drop size, i.e. in the maximum in Fig. 4. Unfortunately accuracy is too low at these small drop times.

CONCLUSIONS

Although the effects discussed in the foregoing are difficult to separate, the following qualitative conclusions can be drawn.

(1) Even with a rather fast responding amplifier a.c. bridge measurements at a DME are subject to lagging, leading to differences in capacitance values (in general: interfacial admittance values) at different drop times. The differences are still significant in the range of usually applied drop times, 2—5 s.

(2) As expected this effect is more striking at low frequency, so that it seems not to mar seriously the determination of the double layer capacitance at the usually applied frequency of 1 kHz. However, if an attempt is made to remove the influence of shielding by extrapolation to zero frequency, the result is strongly dependent on the drop time chosen.

(3) Contrary to the study of the double layer, in the study of the kinetics of electrodes reactions it is of prime importance also to use impedance data obtained at low frequencies, because nearly always the frequency range of the measurements should be as large as possible. As an example where slow amplifier response most probably in part will have influenced the results we would like to make reference to the paper of Tessari et al. [10] who carefully performed precise impedance measurements down to 50 Hz with a General Radio 1232-A tuned amplifier in the bridge.

(4) The results reported may be considered as an example of the errors that can be made in bridge measurements with tuned amplifiers. It may be noted that we did not use a highly critically tuned amplifier. For instance with a Rohde and Schwartz type UBN amplifier, that can have a time constant as high as 20 ms even at 1 kHz, the effects would have been much more dramatic. We feel that this is not always recognised.

(5) It is also imaginable that the rate of impedance change is larger than in our case. Especially experiments where an electrode admittance is measured while the d.c. potential is swept through a faradaic region, should be scrutinized with suspicion as for instrumental artefacts.

(6) It does not seem possible to find a reliable correction procedure for the slow response in the case of bridge measurements. However, when using a directly indicating phase sensitive device, we expect that an exact correction procedure can be worked out by measuring the rate of change of the cell

response by taking two samples closely spaced in time. This idea is being elaborated in this laboratory.

APPENDIX

Simulation of observed admittance amplitude and phase angle for a directly indicating device

Denoting the observed amplitude by A_m and the true amplitude by A_t, the rate of change of A_m is given by

$$dA_m/dt = (1/Q)(A_t - A_m) \quad \text{(A1)}$$

This differential equation can be solved (most easily by Laplace transformation) if A_t is a linear function of t, e.g.

$$A_t = c + ht \quad \text{(A2)}$$

The solution is

$$A_m = A_t - hQ + [A_m(t = 0) - c + hQ] \exp(-t/Q) \quad \text{(A3)}$$

In the more complex case of a DME, A_t contains non-integer powers of t, e.g. $t^{2/3}$ and $t^{1/3}$ which makes the problem inaccessible for an analytical solution. Therefore we perform a "semi-digital simulation" in the following way. The graph representing A_t vs. t is divided into small segments corresponding to equal time intervals Δt (say $\Delta t = 0.001$ times the assumed drop time). The value of A_t is calculated at each interval and denoted by

$$A_{t,n} = A_t(t = n\Delta t) \quad \text{(A4)}$$

Each segment is supposed to be approximately linear, which can be expressed by

$$A_{t,n+1} - A_{t,n} = h\Delta t \quad \text{(A5)}$$

Consequently the corresponding value of A_m can be approximated by

$$A_{m,n+1} = A_{t,n+1} - hQ + [A_{m,n} - A_{t,n} + hQ] \exp(-t/Q) \quad \text{(A6)}$$

analogous to eqn. (A3), provided that h is repeatedly calculated from eqn. (A5).

In view of the periodic character of a DME, difference must be made between the so-called "first drop" and an arbitrary "sequent" drop. For a first drop $A_{m,0}$ will equal zero, while for a sequent drop $A_{m,0}$ must be taken equal to the value obtained at the end of drop life τ of the foregoing drop; approximately we have therefore $A_{m,0} \approx A_t(t = \tau)$.

The same reasonings apply to the phase response of the directly indicating device.

The calculations for Figs. 1 and 2 have been performed using a HP 9830 desk calculator. The program, in basic, is available on request.

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