

The Pulsed Electrolytic Hygrometer

The electrolytic hygrometer was first developed by Kiedel in 1959; since that time many different forms have been developed. They all depend on the adsorption of water vapour from a known flow of gas and the simultaneous electrolysis of the adsorbed water. The system normally used is an adsorbent film of phosphoric acid/phosphorus pentoxide with platinum wire electrodes embedded in the film. The Systech cell is illustrated - Fig 1.

Hygrometers are normally operated with a continuously applied DC voltage, in the case of the cell used in the Systech electrolytic hygrometers 50 volts DC. The current passing under an equilibrium condition is related to the rate of entry of water into the cell in the gas stream by the classical laws of electrolysis. If the gas flow is known and is within the design limits of the cell, all the water entering the cell is adsorbed and electrolysed and the water content of the gas entering the cell can be obtained by direct calculation. Experience with two hygrometers in series has shown that, provided that the cell linear velocity is not excessive so that diffusion to and adsorption on the cell was virtually complete on reaching the cell exit, the film on the first hygrometer is capable of taking high water loadings without breakthrough to the second.

The lower limits of detection of the electrolytic hygrometer are determined in practice by the relation between the electrolysis current and the non-electrolytic leakage current. In practice this is found to be of the order of 10 micro amps, so that even under high flow conditions the practical lower limit of measurement is 0.05 vpm.

It appeared possible to extend this range by using the hygrometer as a cumulative device operating for a period without electrolysis then electrolysing and integrating the current peak to give the quantity of water adsorbed during the accumulating period - Fig 2.

In order to understand fully the behaviour of a cell in this mode of operation it is necessary to define the terms electrolytic and non-electrolytic background. If a hygrometer used on continuous electrolysis on a gas of fixed water content is operated at several different flow rates it is found that the relationship between flow and current is:

$$i = K_1 F C + (e + B) \quad (1)$$

Where

i = current

K_1 = a constant derived from the Faraday Laws

F = mass flow

C = water content of gas

e = electrolytic background

B = non-electrolytic background

Fig 2. Typical integration peak

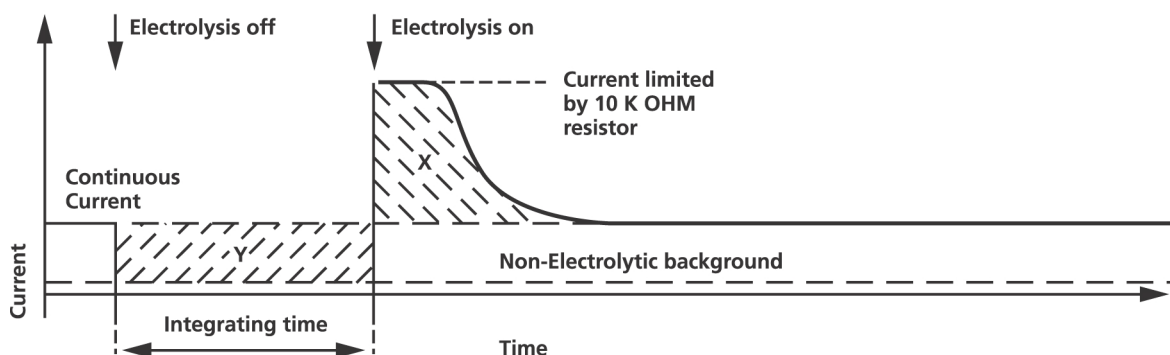
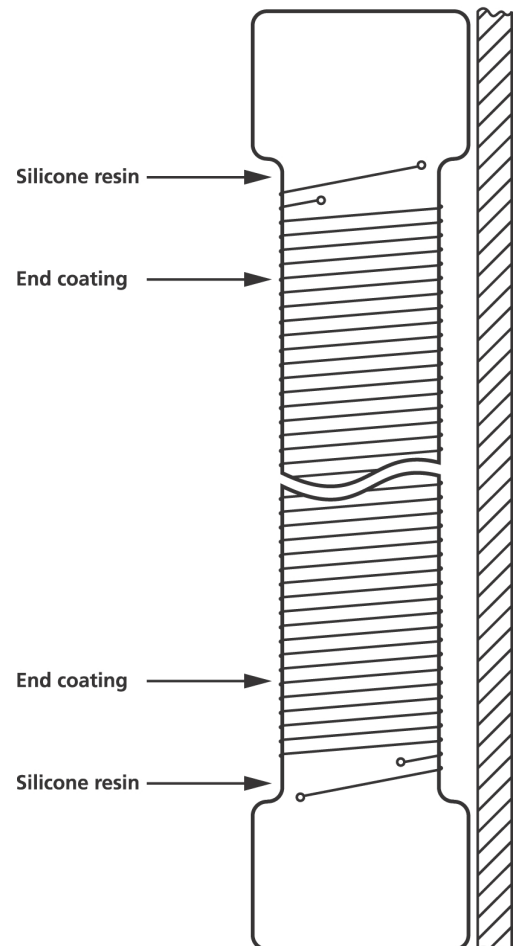


Fig 1. Cell diagram showing winding and coating



Thus the total background can be derived from a graph of current against flow provided that an adequate time (at least 30 mins) is allowed to elapse between each flow change for the system to re-equilibrate.

The electrolytic background is assumed to be derived from desorption from the sampling pipe and recombination both representing flow independent sources of moisture. The non-electrolytic background is simply derived from resistive current paths in parallel with the cell coating better than 1 megohm.

An idealised representation of the current from a cell undergoing pulsed electrolysis is shown in Fig 3. Over a fixed period of time the mean rate of electrolysis must equal the rate of entry of water into the cell, that is the number of electrolytic coulombs passed in a fixed period in the pulsed mode must equal those which would have passed had the cell been electrolysing continuously. Area X must equal area Y in Fig 3.

If the electrolysis time = t
 The total cycle time = T
 The intermittent current = I
 Then
 $(I-B)t = (i-B)T$ (2)

$$(I-B)/(i-B) = (T/t)$$

or:

$$i = (t/T)(I - B) + B$$
 (3)

The ratio of pulsed to continuous current, that is, the amplification factor, is determined by the ratio T/t .

In normal practice it is convenient to work with a constant electrolysis time t , so that if I is plotted against T the intercept of the line in the current axis gives the value of B . Equating i from (1) and (3) then

$$I = (T/t)(K_1 FC + e) + B$$
 (4)

Initial experiments were made to determine the peak shape using a chart recorder with a chart speed of 10 cm/s. Fig 4 shows a typical electrolysis peak with a 2 s electrolysis period. The peak is virtually rectangular so that it was assumed that the value of I could be derived from a chart recorder with a response time of 1 s by taking it as the maximum value shown.

Fig. 3 Diagram representing current flow during pulsed operation

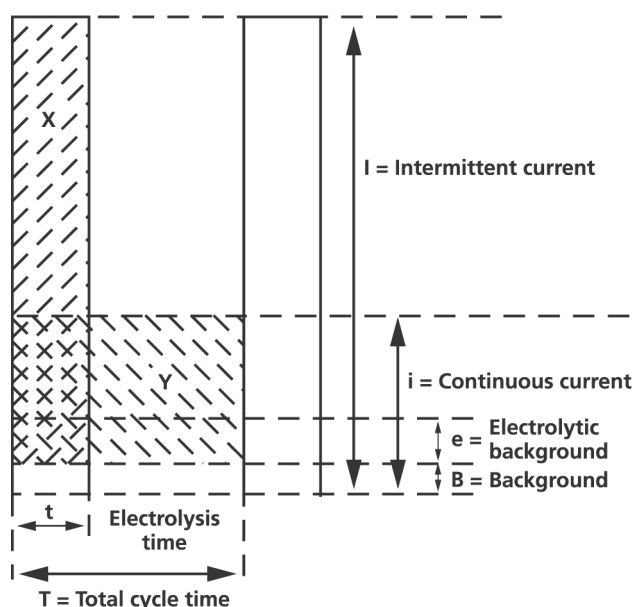


Fig 4. Fast chart recording of pulsed electrolysis peak

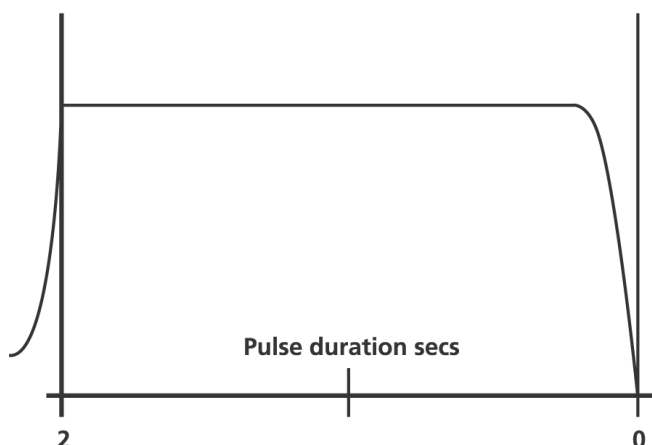


Fig 5 shows a typical trace on such a recorder using a fixed electrolysis time of 2 s which was kept constant for all the experiments. Typical results are shown in Fig 6 for gases of various water concentrations with varying cycle time. The low value of the non-electrolytic background current should be noted.

The development of pulsed electrolysis techniques has enabled the useful range of Systech hygrometers to be extended by a factor of 10 or more. The background i.e. current at cycle time equal to zero obtained from a graph of current against cycle time is always lower or equal to the background measured by flow variation and has been shown to be the background current due to insulation leakage.

One of the principal objections to the use of electrolytic hygrometer's as an instrument is its inherent fail to danger characteristics.

The viability of the instrument depends on the continued existence of an effective adsorption film of phosphoric acid. In very dry conditions loss of sensitivity by poisoning of the film with, for example, oil or other deposits would be undetectable using continuous DC electrolysis. Intermittent electrolysis using a variable pulse time offers a possible method of monitoring the continued efficiency of the hygrometer at low moisture levels.

Since the laboratory investigations the intermittent method of electrolysis has been used effectively to monitor operating levels of moisture in the range 0.01 to 0.1 vpm

Fig. 5 Typical pulsed electrolysis trace

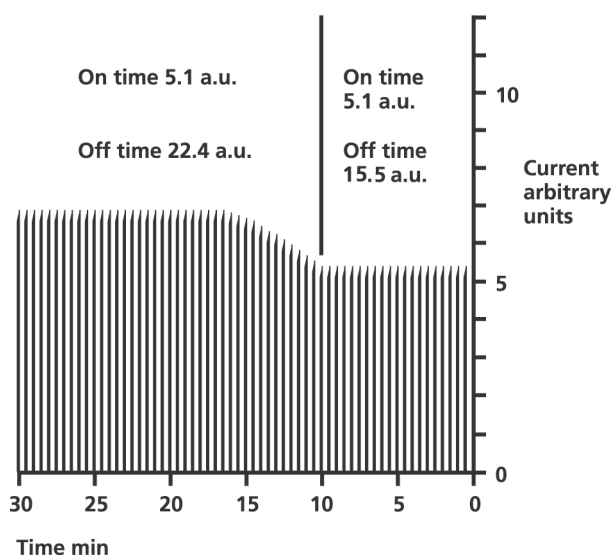
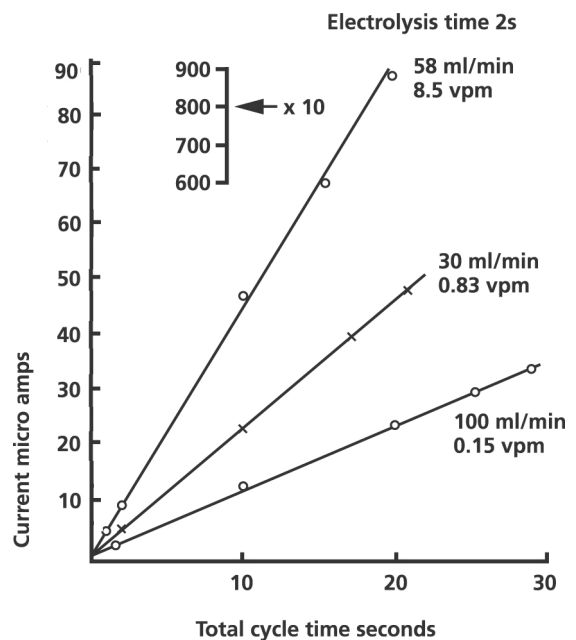


Fig. 6 Pulsed electrolysis typical results



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