THE FLAME IONIZATION DETECTOR

A SIMPLE ELECTROMETER FOR LINEAR, LOGARITHMIC AND INTEGRAL RESPONSES

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INTRODUCTION

This paper discusses a relatively simple and inexpensive electrometer circuit for use with the flame ionization detector, providing wide-range linear, logarithmic or integral responses.

At the high sensitivity end of the linear range, the responses are adequate for most practical purposes, and at the low sensitivity end macro concentrations can be handled. Provision is made so that sensitivity can be varied during a run over the whole range without moving the baseline. The logarithmic mode automatically provides for stepless sensitivity changes across the available range so that no peaks go off-scale, while small traces still show up: this is a feature very useful for preliminary scouting work. The integral mode provides a simple coulometric device peculiarly adapted to the flame detector, and requires little additional expense.

The construction of the circuit is fairly straightforward, and practical hints are given, based on long experience of battery-operated high impedance DC electrometers. While no criticism of highly sensitive mains-operated AC stabilized electrometers is intended (apart from expense and sometimes temperamental behaviour), their sensitivity is largely wasted on the flame detector, which generates relatively large currents, so large indeed that the drift problem with simple DC circuits can be eliminated for practical purposes by operating at very low gain. For the special requirements of the logarithmic circuit, which requires a voltage swing of about 0.5 V at the input, the low gain is an advantage. It is possible that some of the more complicated circuits would be overloaded with such a voltage. In any case, the installation of the logarithmic or integrating circuits would require internal modifications to commercial electrometers and would need expert advice.

In the discussion, a good deal of attention is given to input circuit background compensation, since this is not only convenient for normal linear response but essential for integration, and we are not aware of any published analysis of the theory of compensation in the input circuit.

DISCUSSION

Background compensator

Compensation for background current in the input circuit is advantageous for two reasons. Firstly, it allows the sensitivity to be varied over the whole available range without shifting the baseline, and secondly it avoids overloading the electrometer with useless input voltage from high backgrounds.

In its simplest form, the compensator consists of a very high resistance in series with a variable voltage source, connected across the detector between collector and ground. The polarity is such that ion current is drawn from the collector and returned to the jet electrode, by-passing the range resistor. The variable voltage is adjusted until the background ion current is exactly neutralized and there is then no current through the range resistor in the absence of a signal, and hence no voltage across it. A different range resistor can thus be inserted without shifting the baseline. In this simple form, the compensator has been described by DESTY, GOLDUP AND WHYMAN[1].

This compensator causes a reduction in the response when a signal appears, because the signal current divides between the compensator and range resistors in inverse proportion to their resistances: thus, if the compensator resistance is $10^{12}\ \Omega$ and the range resistance $10^{10}\ \Omega$, then 1 % of the signal response is lost. The errors are thus easily calculable, and in many cases negligible.

If the background current is high, as from column bleeding, then the compensator voltage required may become inconveniently large if the high value compensator resistance is retained. The alternative is to reduce the compensator resistance to allow for the greater compensation required. Generally, this procedure is convenient since high sensitivity is in any case impracticable at high background because of drift. The principle can be extended to cope with very high background currents, the available sensitivity being restricted then to low levels, in the ranges in which thermal conductivity detectors are usually employed, where linear response is still obtainable from the flame detector if electrode geometry and voltage are adequate[2].

The compensator can be modified so that there is no error arising from division of signal current. This is done by feeding back from the output a voltage equal to the input signal voltage and subtracting this feedback from the compensator voltage. The net voltage across the compensator resistor is thus unaffected by the signal, and the current drawn through it remains equal to the background current only. The feedback is most conveniently and reliably derived from a re-transmitting slidewire on the recorder. For simple linear operation, this refinement is not essential since the error introduced by the compensator is easily calculable. The situation is different for integration at high sensitivity (*vide infra*) because the error is cumulative with time and not easily calculable, although large signal currents can still be handled without substantial error.

In fairness to AC stabilized electrometers, it should be said that the simple forms of the compensator are probably always adequate with them since their dynamic input resistance is reduced by a large factor, due to high negative feedback, so that the effective ratio of the compensator resistance to the range resistance is much larger than that calculated from the static resistances.

Linear circuit and basic design (Fig. 1)

The linear ranges are conventional and arranged in decades in the input, with a single step output attenuator. The bias on the cathode is set to correspond with the low end of the straightest portion of the characteristic curve, and for the designed maximum positive input voltage swing of 0.5 V (with output attenuator at X1) the linearity of response across the chart does not err by more than about 0.5 %. Using

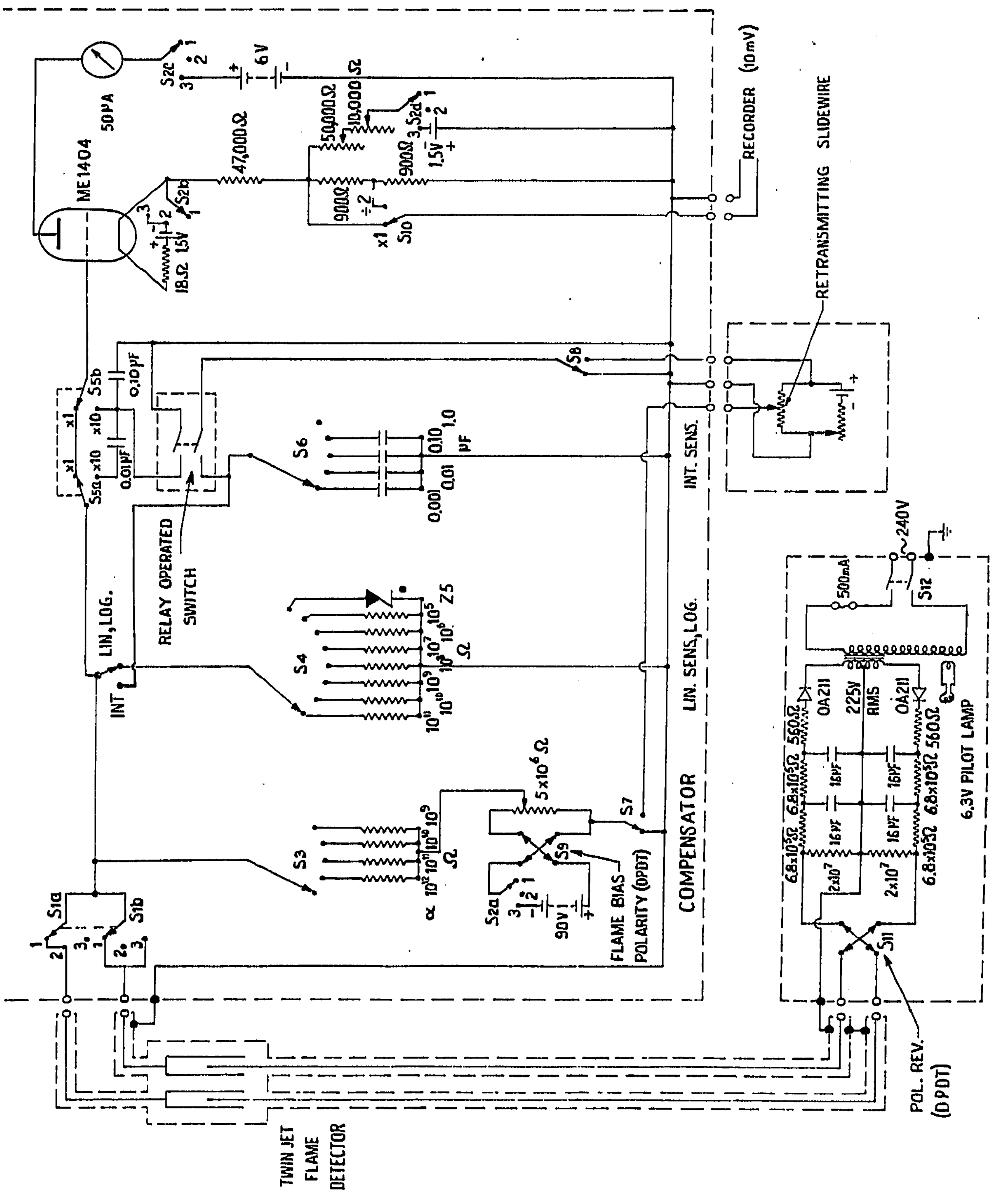

Fig. 1. Electrometer and power supply for twin jet flame detector.

the output attenuator (voltage swing 1 V) the non-linearity does not exceed 1 %. Linearity is assisted by the cathode resistance, which biases the cathode (and does not affect the dynamic resistances of the range resistors). It is important to connect the filament battery and associated current-limiting resistance as shown, for positive-going signals (*i.e.* for positive jet, negative collector); the whole filament and cathode circuit would need rearranging for negative-going signals.

The output load resistances shown are calculated for a 10 mV recorder. They may be changed appropriately for other sensitivities within reason, without interfering appreciably with the bias. Where a variety of recorder sensitivities may be used from time to time, it is convenient to arrange plug-in change-over sets of matched resistors. The coarse recorder-balancing potentiometer may be placed inside the cabinet.

The microammeter is very useful for fault-finding, and occasionally for following the progress of very large off-scale peaks: sometimes it is possible to detect the existence of several peaks. The normal base current is about 28 μA. The ganged switch S2 (two decks, three pole, three position) switches the filament on before the anode, in line with generally recommended procedures with electrometer tubes, to reduce circuit drift: the middle position also serves for stand-by, and the associated gangs switch the other batteries on and off.

The filament source is a 1.5 V heavy duty dry cell, which will last at least a year with normal daily operation. It is important to insulate this cell from the electrometer case, since leakage through the cardboard shell by-passes the cathode resistor and causes serious noise. Insulation is simply and reliably provided by wrapping in polythene. Current sources except the flame high tension are placed within the cabinet and wedged to prevent movement.

The valve is a Mullard ME 1404 sub-miniature electrometer triode, mounted vertically to reduce filament sag, and upside down for convenience in wiring. The gain of the circuit is about $^1/_{50}$, wired as shown for a 10 mV recorder, with the output attenuator X1. The low gain reduces circuit drift to negligible amounts and is compensated for by using higher value input resistors: the main disadvantage is that on the highest sensitivity ($10^{11}\ \Omega$ input) the time constant is appreciable (about 5 sec), but in any case at this sensitivity some damping is required for flame noise.

All the high impedance circuitry must be well insulated. Ceramic decks are used on the wafer switches. Wiring is done with heavy gauge rigid tinned wire without spaghetti. Including all auxiliary circuit switches, the insulation resistance should be about $5 \cdot 10^{12}\ \Omega$, with desiccation. Desiccation is not essential, at around 50% r.h., except for the highest sensitivities.

All ground leads should be brought to a common point within the cabinet, before connection to frame: this avoids transient pick-up which can arise if any portion of the cabinet forms part of the circuit.

The flame high tension should be at least 320 V, and is provided in the circuit shown by a simple two-polarity source using half-wave rectification, unstabilised but heavily smoothed. Batteries can of course be used instead. Twin jets are shown for use with a reference column when desired: when so used the reference jet is made negative. This arrangement is preferable to symmetrical balanced circuits because the background currents mutually cancel and do not tend to saturate the input. In theory opposed twin jets dispense with the need for a compensator, balance being obtainable by regulating the gas rates.

The circuit is designed for use with jets insulated from ground. We use 23 gauge hypodermic tube with glass press-shrunk insulators. For moderately high temperatures sealing with Araldite is feasible. Some designers go to considerable lengths to keep the jets at ground potential, but we are inclined to think that this practice leads to as many difficulties as it avoids.

We do not recommend placing ignition or temperature measuring devices in the vicinity of the jet tip since they distort the field and lead to non-linear response at high loadings.

Logarithmic response

In our experience of service work in a fairly large chemical firm, the need was often felt for some kind of logarithmic response when doing qualitative work involving all sorts of samples in which trace impurities might be important, and in which perhaps even the major components and their relative amounts were unknown or doubtful. With the normal linear presentation, often either several runs at various sensitivities and sample sizes are required, or considerable agility and close attention must be exercised in range changing during the run. At fixed sensitivities some peaks are likely to be off-scale and the peak maximum position indeterminate, while on the other hand small traces may be missed because no tests are made with large injections at high sensitivity. With range changing, although the compensation of the steady background is a big help, the tails of large peaks are inevitably blown up on switching to higher sensitivity, and the record is correspondingly messy. Automatic attenuation has its virtues but again the record is not very easy to read and the apparatus is an additional expense.

A logarithmic response covering five or six decades would provide for most sensitivity requirements and give an unbroken trace.

Early attempts to obtain logarithmic response were based on the known principle that in a triode taking positive grid current the logarithm of grid current may be proportional, or roughly proportional, to plate current. These attempts were reasonably successful using a Mullard ME 1404 operated, as indicated by the makers, for log response. However, it was not found easy to get a good log/linear effect, and the sensitivity in the vicinity of the baseline was governed by the magnitude of the background current, all of which flowed through the grid. Circuit modifications were required which made switching from the linear to the logarithmic mode rather complicated.

We have now found that the resistance *versus* current characteristic of a silicon diode in the forward direction gives the required log/linear relationship over many decades (nine or more if desired) if the diode is placed in the position of a normal range resistor, while the resistance near 0 V can in selected cases be high enough for reasonably high sensitivity, *e.g.* equivalent to a linear resistance of $10^{10}\ \Omega$. Used with the compensator circuitry already described, no modifications to the normal circuit are required (except an additional position on the linear range switch) provided the voltage swing at the electrometer input for full scale on the recorder is of the order of 0.5 V. The measured slope of the diode characteristic is about 78.5 mV for each decade in current flow, so that 0.5 V will allow for over six decades. In other words, 1 % of full scale near the maximum on the recorder represents about a million times more sample concentration at the flame than the same deflection near the minimum.

Three diodes were examined experimentally to determine the slope (all nearly parallel, 78.5 mV per decade) but the resistances at a given current differed considerably. Since the highest possible resistance is desirable at the low current end, to give high sensitivity while still in the log/linear region, it is necessary to select the particular diode to be used. Of the three examined, two were zeners and one was an ordinary diode. The forward bias voltage required on each to reach the log/linear region was about 120 mV and at this voltage the measured currents corresponded to resistances as follows:

Phillips OA 200: $1.2 \cdot 10^8\ \Omega$.
Intermetall Z5: $10^{10}\ \Omega$.
Intermetall Z10: $4 \cdot 10^9\ \Omega$.

Thus, the Z5 zener was the best, and this was used since it gave quite adequate sensitivity for practical purposes. At lower forward bias, the sensitivity is higher but not quite log/linear, and near 0 V, the capacitance effect of the diode itself makes response very sluggish. It seems very probable that higher resistances and/or lower capacitances could be found among the many silicon diodes available, if one was prepared to examine a number of classes and a number within each class. A quick selection without the need for a very sensitive electrometer could be made by measuring the current at a fixed voltage above about 0.5 V. Thus, the Z5 passed 4.2 μA at 0.55 V, and the other two gave larger currents than this at the same voltage. Manufacturers' data sheets do not usually give adequate information at low currents, and the variability within a class appears to be high. Subsequent tests over a number of diodes showed that about one in eight Intermetall zeners were suitable, while none could be found among ordinary diodes.

To calibrate the recorder for logarithmic presentation on an arbitrary scale, it is first necessary to establish the pen movement corresponding to one decade. This can be done by applying sufficient current to the input through a resistance high enough to allow neglect of the diode resistance. For example, with the Z5 two pen positions are established using a 10^9 resistor with two voltages, 30 and 300, in the ratio of $^1/_{10}$. The difference between the pen positions then gives the length of one decade to within an approximation error of 1 %. This gives the initial basis for laying off the logarithmic scale. However, since it is desirable to have the low end starting with zero for zero signal, and as this cannot be done on a true logarithmic scale, the initially plotted log scale is further modified. If the initial plot is numbered 1, 10, 100, etc. on the main index lines, subtraction of unity from all values gives a new scale with the index lines now labelled, 0, 9, 99, etc. (It will be seen that the function has been changed from log x to log $(x + 1)$. When $x = 0$, log x is minus infinity, but log $(x + 1)$ is zero.) The higher decades on this scale are practically identical with the original scale, and the infinity of decades between 0 and 1 on the original scale have been compressed into the space between 0 and 1 (originally 1 and 2) on the new scale.

To provide the necessary forward bias of 100–120 mV when using the flame detector it is only necessary to undercompensate for the baseline current. For example, with the circuit shown, having a gain of $^1/_{50}$, the compensator is adjusted until the pen is about 2 mV upscale from true input zero. The modified log scale is then moved along to place the zero over the pen position, and relative signal strengths can then be read off directly. The log presentation does not look very handsome at first sight, because the peak bases are very broad because of adsorption tails. This appearance, however, merely indicates the enormously greater sensitivity at the low end as compared with the other. There is no actual loss of resolution or of available information, indeed the clear indication of long adsorption tails is quite a striking demonstration of how persistent such effects can be.

We have not ourselves attempted to use the logarithmic presentation for accurate quantitative work but there is no reason why it should not be used for quite reasonable accuracy, and it could be used for example, for monitoring plant gas streams for impurity tolerances without elaborate automatic sensitivity switching. For the highest accuracy the diode should be thermostated, since for a given current the voltage developed is a rather complicated function of temperature.

Integrating circuit

A circuit for the integration of the output of ionization detectors has been published by VAN DER GRINTEN AND DIJKSTRA[3]. In this circuit the driving voltage for the detector is provided by a charged condenser, and the integral is obtained by measuring the decay in the voltage of the condenser as current is drawn from it.

A compensator is provided for background current, but this compensator is not applicable for ordinary linear response.

We have now devised an integrating circuit which makes use of the same compensator as for linear response, and which can be incorporated with the linear and logarithmic circuitry discussed above with comparatively little extra trouble.

In our integrator the range resistors are disconnected and replaced by a range of condensers. Signal current is then accumulated on an integrating condenser instead of being dissipated through a resistor. Since the instantaneous signal is essentially a current, the integrated signal is essentially coulombic, and the voltage developed is directly proportioned to coulombs accumulated. The maximum voltage is limited to that corresponding to full scale deflection on the recorder, the integration being then continued by automatically and momentarily shorting the condenser.

Normally, condenser integration is not feasible in simple DC systems because the back voltage affects the signal, and also when the signal decreases the charge leaks away through the source. In the special case of the flame ionization detector neither of these effects applies. In the first place the signal current is a saturation current, driven by a large excess voltage, and is not affected in the least by small back voltages; while in the second place the detector is effectively equivalent to a perfect diode and cannot leak back. Leakage does take place through the compensator resistor, and for good results at high sensitivities (*i.e.* when using small integrating condensers) the compensator feedback refinement is advisable. For low sensitivity work the leakage may be tolerable without feedback. At the lowest sensitivity the size of the condenser required becomes embarrassingly large (10 μF), and for convenience the circuit can be arranged to divide the voltage developed across a smaller condenser, by use of a supplementary condenser network, thus multiplying the effective value of the integrating condenser. In the circuit shown a nominal 10 to 1 multiplication is effected, extending the effective maximum capacity from 1 μF to approximately 10 μF. If the capacitor values are precisely as shown, *viz.* 1.0, 0.1 and 0.01 μF for the integrating condensers and division network, the actual multiplication factor would be 11.1. The condenser shorting mechanism not only shorts the integrating condenser, but when the multiplier is used a second contact is closed as a precaution to ensure that the grid is kept to reference potential, although in fact drift caused by grid current is negligible at this low sensitivity.

The condensers used must have a high quality dielectric (*e.g.* polystyrene) since lossy dielectrics retain charge on shorting.

The shorting mechanism consists of a microswitch (closed by the pen carriage when it reaches full scale) which actuates a relay inside the electrometer cabinet. This indirect circuit is used to avoid high impedance lines to the recorder. The relay is an ordinary two contact normally-open type, but modified by removing the spring and relying on gravity (by tilting) to effect opening, and also modified by remounting the fixed contacts on high insulation material (Perspex). The coil is bridged by a 100 μF condenser to eliminate transients, which have already been minimised by the low power requirement.

When the relay closes the pen returns towards baseline, but signal is not lost since, except during the moment of shorting, the charge is still being accumulated. The pen recommences its upscale traverse at the reading corresponding to the charge accumulated during its downscale movement, and up to a point the pen speed does not affect the result. This point is reached when the rate of charge is so large that the pen cannot follow it, and the indication of this condition is failure of the pen to return more than halfway towards the baseline. If this happens a larger condenser is required. Chart speed is only significant with respect to readability. The total integral is measured from the baseline reference, not from the lower points of the trace (which incidentally give an envelope roughly indicative of the peak shape).

If the compensator feedback refinement is used, it is sufficient for ordinary purposes to adjust the feedback voltage until the full end to end voltage across the retransmitting slidewire, applied across the electrometer input, is just sufficient to drive the recorder full scale. This is done by closing switch 8, holding down the microswitch on the recorder, and adjusting the rheostat of the slidewire. The feedback provided—by setting the slidewire current on the more sensitive ranges—is virtually inoperative when using the condenser multiplier, as the feedback then also needs increasing tenfold. This of course could be done if thought worthwhile. For the most accurate and sensitive work a further fine adjustment can be made such that no detectable drift occurs with the pen at any position on the scale: this adjustment allows for constant ohmic leakage other than through the compensator and also for the constant component of grid current.

(Condenser integration on the above lines could be applied to any one-way current generating device substantially unaffected by small back voltage, *e.g.* photoemissive cells, ion chambers.)

A rough correlation between an integrator reading and sample size can be calculated by allowing 0.1 C per gram atom of carbon in oxidation states not higher than alcohols or ethers. Thus for example a 10 mV excursion on the recorder for the circuit shown (output X1, gain $^{1}/_{60}$) using the 1.0 μF condenser is equivalent to 0.5 V at the condenser or $5 \cdot 10^{-7}$ C, or $5 \cdot 10^{-6}$ gram atoms of carbon (as above defined), or 60 μg. With the equivalent of 10 μF the range thus extends up to milligrams, the maximum possible depending on the speed characteristics of the recorder and the rapidity of elution.

At the other end of the scale, with the 0.001 μF condenser and a reading of

1 % of full scale on the recorder, the smallest readable amount would be 0.0006 μg. For accuracy in absolute terms at high sensitivity the stray capacitance of the input, including the appreciable capacitance of the cable to the detector would need to be measured independently. The stray capacitance can be as much as 50 pF, and this could be used alone as the integration capacitance if the ultimate realisable sensitivity was required. The usefulness of extremely sensitive integration is perhaps limited more by chemical drift than by instrumental possibilities.

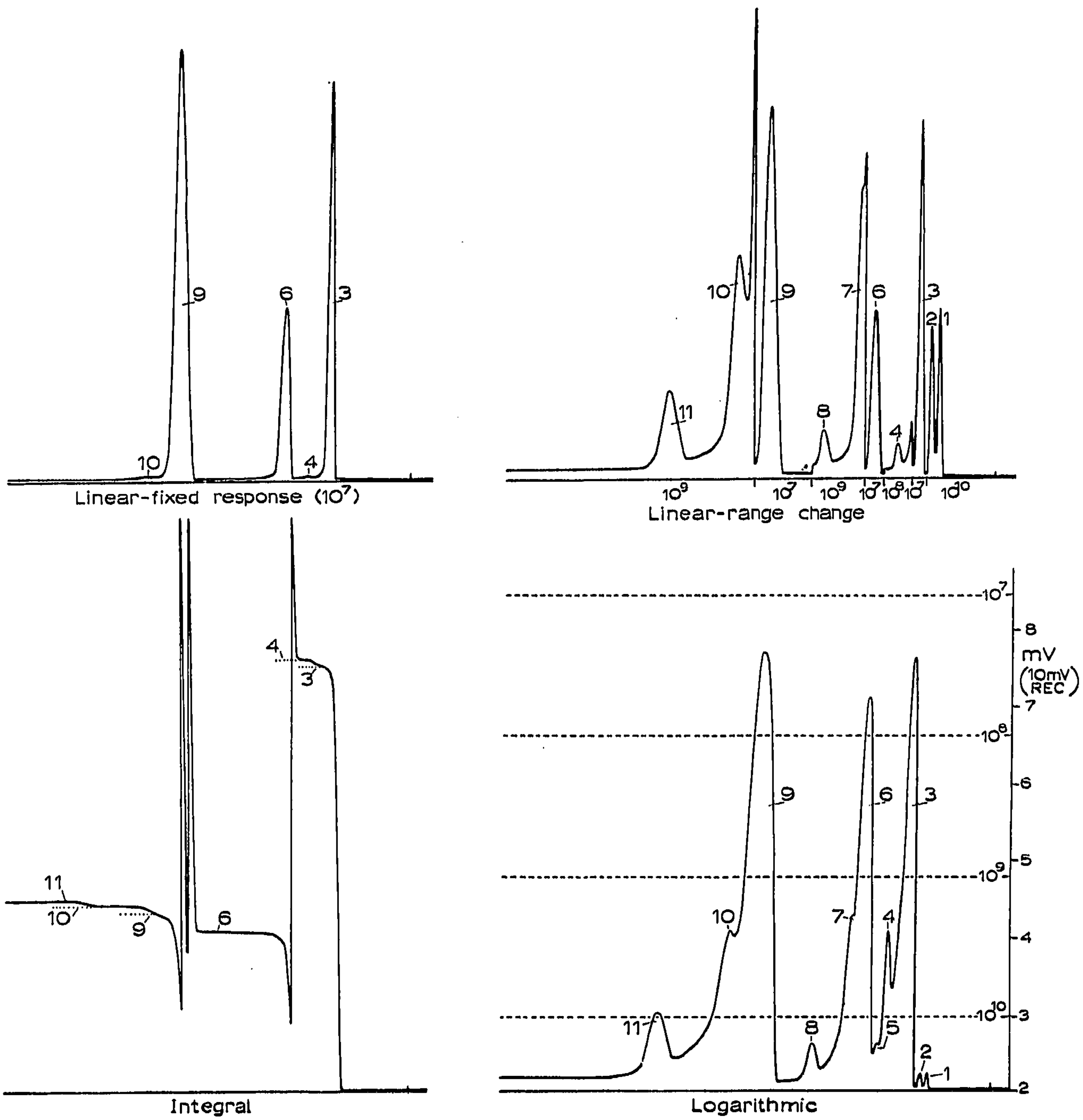

Fig. 2. Comparison of four types of presentation of the same signals. Vertical scale on log trace indicates linear resistors which must not be exceeded for on-scale linear traces of peaks up to the corresponding heights. Integrator set on 1.0 μF (without feedback).

Traces illustrative of the three functions of the circuit are shown in Fig. 2.

In conclusion we would like to suggest more use of the flame ionization detector at low sensitivities, where linearity can still be attained with adequate detector design, and where drift and noise problems are almost eliminated. There is still a large area of use for low sensitivity work because one is then not restricted to low volatility partition liquids. For these reasons we have designed the circuit to be operable under conditions permitting the use of volatile packings, and the injection of undiluted microlitre amounts of sample without splitting, assuming of course that an adequately designed detector is used in conjunction.

SUMMARY

A detailed description of a versatile DC electrometer for use with the flame ionization detector is given. The circuit provides for baseline compensation, and for logarithmic and integral responses, obtained by relatively simple electrical devices, all in the input circuit, as well as wide-range linear presentation in the usual way.

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