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A MASS-SPECTRUM-DIGITIZER FOR THE ATLAS TYPE CH-4 MASS-SPECTROMETER

by

M.J. MOL

1966

Joint Nuclear Research Center
Ispra Establishment - Italy

Chemistry Department
Analytical and Inorganic Chemistry

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CONTENTS

SUMMARY

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1. INTRODUCTION

With the ATLAS type CH-4 mass-spectrometer spectra are obtained by varying the magnetic deflection field, and by simultaneously recording the intensities of the ion-beams that are focussed on the collector slit in a sequence corresponding to the mass-numbers of the ions. The recording system, consisting of an electrometer amplifier and a potentiometric strip-chart-recorder, is connected to the ion collector in such a way that positive ions striking the collector cause a negative amplifier output.
Therefore, the spectrum of positive ions consists of a series of negative peaks, and if the spectrometer has been adjusted for quantitative analytical work the amplitudes of these peaks are directly proportional to the intensities of the associated ion-beams.

Before any computing technique for quantitative interpretation of the spectra can be applied, the amplitudes of the individual peaks have to be measured on the record and the corresponding mass-numbers have to be found by experience or by comparison with known spectra. This time consuming operation can be eliminated by using a digital spectrum recorder, that automatically detects the presence of each peak and prints the peak amplitude together with a mass-number reference value in digital form.

Three such instruments are commercially available, i.e. the C.E.C. type 34-201, the model MSD-2 from Non Linear Systems Inc., and the "Digitoprint" made by ATLAS.

The C.E.C. type 34-201 is specially designed for operation with the C.E.C. type 21-103C mass-spectrometer. Its mass-number digitizer, based on electric field scanning, and its limited input signal range are incompatible with our CH-4 mass spectrometer. Furthermore, the peak detection circuit is not sensitive enough for the scan-rates normally used with the CH-4.

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The N.L.S. model MSD-2 is also designed for the C.E.C. type 21.103C spectrometer and therefore, its mass-reference reading system is also based on electric field scanning. Since the input signal range is too small, and no automatic high-speed attenuator is included, this instrument is also not useful for our purpose.

ATLAS makes the "Digitoprint" especially for the CH-4 mass-spectrometer. However, since no provisions for a mass-reference reading are included, its application is illusory. In addition, the "Digitoprint" requires manual attenuator switching to cover the entire output range of the spectrometer with a sufficient accuracy. The peak detection sensitivity is so low, that peaks with an amplitude up to 10 mV. are not detected. The measuring principle of the "Digitoprint" requires an interruption of the scanning during each peak measurement, which introduces a timing error depending on the number of peaks in the spectrum.

Since the commercial digitizers are not suitable, a Mass-Spectrum-Digitizer (MSD) has been constructed, that is fully compatible with the output signals and scanning mechanism of the CH-4. It operates without influencing the scan-rate or any other parameter of the spectrometer, thereby keeping the analytical conditions essentially constant. The sensitive peak detection circuit and the high reading accuracy of the MSD enable its application for all analytical purposes, without any deterioration of performance compared to the analog recording system.

2. THE MASS-SPECTROMETER

The basic properties of a mass-spectrum are determined by the operating principle of the spectrometer. The instrument parameters that have a specific influence on the spectrum, like the mass resolution, the collector slit size, the scanning mechanism and the electrometer amplifier, have to be considered to define the signal conditions at the output of the spectrometer that are essential for the operation of the MSD.

2.1. The scanning of spectra

The CH-4 mass-spectrometer is a single focussing instrument with a 60 degrees magnetic analyzer having a 200 mm radius of curvature. An ion-beam focussed on the collector enters and leaves the deflecting field perpendicular to the field boundaries. For this analyzer geometry a beam of ions with mass-number M has a first order angular focussing on the ion collector slit, if

$$M = k.\frac{H^2}{E} \quad \left[\frac{m}{e}\right] \qquad (1)$$

where H = magnetic field-strength in Gauss,
E = ion accelerator potential in Volts,
M = mass-number (mass to charge ratio of ions in atomic units)
$k \approx 0.02$ for the units used.

For the value of M satisfying eq. (1), the mass-dispersion in the collector plane is given as

$$\Delta D = \frac{200}{M} . \Delta M \quad [\mathrm{mm}] \qquad (2) \qquad , \text{ if } \Delta M \ll M$$

If B_c is the width of an ion-beam near the collector, and is defined as the cross section of the beam in which 98 % of the ions are concentrated,

$$B_c = S_s + 200. \frac{\Delta E}{E} + A \quad [\mathrm{mm}] \qquad (3) .$$

Where S_s = width of the source exit slit in mm.
ΔE = energy spread of the ions in eV.
A = aberration of the mass-spectrometer.

The resolving power of the spectrometer is given as

$$R_p = \frac{200}{S_c + B_c} \quad \left[\frac{M}{\Delta M}\right] \qquad (4) ,$$

where S_c = width of the collector slit in mm.

To scan a spectrum the current through the coils of the analyzer magnet is varied exponentially with time. If the nonlinearity and hysteresis of the magnet core are neglected, the magnetic fieldstrength becomes also an exponential time function. So

$$H_{(t)} = H_o \cdot \exp.\left(\frac{t}{T}\right) \qquad [\text{Gauss}] \qquad (5),$$

where H_o = magnetic fieldstrength in Gauss at t = 0.
T = time constant of the scan-circuit.

Combining eq.(1) and (5), and substituting $a = \frac{2}{T.\ln 2}$,
gives the mass-number as a function of time as

$$M_{(t)} = M_o. \exp.\left(a.t.\ln 2 \right) \qquad \left[\frac{m}{e}\right] \qquad (6).$$

Where M_o = mass-number in focus at t = o.
a = scan rate in octaves/second

From the mass dispersion in eq. (2) the scan-velocity with which the ion-beams pass across the collector slit can be calculated, and is $v = \left(\frac{\Delta D}{\Delta t}\right)_{\Delta t \to 0} = \frac{200}{M_{(t)}} .d \frac{M_{(t)}}{dt}$ or

$$v = 200.a.\ln 2 \qquad [\text{mm/second}] \qquad (7)$$

The fact that the scan-velocity remains constant throughout the spectrum is a significant property of the scanning system used. A switch in the scan-circuit of the spectrometer enables the selection of different scan-rates as required for the individual applications. The scan-rates and corresponding scan-velocities, normally used for spectrum recording, are listed in table I.

Each ion-beam passing the collector slit causes an ion-current peak in the collector circuit. Since the resolution of the CH-4 mass-spectrometer is not sufficient to separate doublets or triplets at a single mass-number, the maximum peak-repetition rate during the scanning of a spectrum is

$$P_{max.} = a.\ M_{max.}\ .\ \ln 2 \quad [\text{peaks/sec.}] \quad (8)$$

Where a = scan-rate in octaves/sec.

$M_{max.}$ = highest mass-number at which a peak is present in the spectrum.

Peaks due to double or triple charged ions occur only in the lower half, resp. lower third, of the mass-spectrum and therefore, the value of $P_{max.}$ given by eq. (8) is not exceeded. In fig.1 $P_{max.}$ has been plotted as a function of $M_{max.}$ for several of the available scan-rates.

The duration and shape of an ion current peak depend on the scan velocity, the width of the ion-beam and the width of the collector slit. If T_b is the duration of a peak measured between the points of 1 % amplitude,

$$T_b = \frac{S_c+B_c}{v} \quad [\text{sec.}] \quad (9^a) \quad \text{or}$$

$$T_b = \frac{1}{R_p.a.\ \ln 2} \quad [\text{sec.}] \quad (9^b) \quad .$$

The condition $B_c < S_c$, which must be satisfied in order to obtain peak amplitudes proportional to the ion-beam itensities, results in peaks with a flat top, as illustrated in fig. 2. The top duration, measured between the points of 99 % amplitude, is

$$T_t = \frac{S_c - B_c}{v} \quad [\text{sec.}] \quad (10) \quad (\text{if } B_c < S_c),$$

whereas the duration of each peak slope is

$$T_s = \frac{B_c}{v} \quad [\text{sec.}] \quad (11)$$

The factor $F_p = \dfrac{S_c - B_c}{S_c + B_c} = \dfrac{T_t}{T_b}$ is significant for the peak shape.

If T_m is the time interval during which the peak amplitude is within 0.1 % of its maximum, the factor $F_m = \frac{T_m}{T_b}$ indicates during what fraction of the total peak duration the amplitude can be established with an accuracy of 0,1%.

Optimum focussing cannot be obtained over the entire mass range of the spectrometer. Especially at lower masses the aberration increases, causing an increase in B_c, which in turn results in an increase in T_b, a decrease in R_p and T_t, and an appreciable reduction in F_p.

With the available slit combinations two standard operating conditions of the spectrometer can be selected.

For the "LOW-RESOLUTION" setting a 0.3 mm source slit and a 0.9 mm collector slit are used. Optimum focussing at M = 40 gives a resolving power $R_p = 140$, and peak shape factors $F_p = 0.31$ and $F_m = 0.23$. Below M = 18, the defocussing causes a noticable decrease in R_p, with an associated increase in T_b and a reduction in T_t and T_m.

The HIGH-RESOLUTION setting, that is accompanied by a lower instrument sensitivity, is obtained by using a 0.1 mm source slit, a 0.3 mm collector slit, and by optimum focussing for M = 132. The measured effective collector slit-width S_c is 0.42 mm and the beam width B_c is 0.22 mm. Thus, $R_p = 330$, and $F_p = 0.31$, whereas F_m is found to be 0.24. With this slit arrangement the defocussing becomes important below M = 50. In the region of M = 40 the aberration is so large, that $B_c \approx S_c$ and R_p drops to 240, which results in a nearly triangular peak shape. At lower masses R_p becomes even smaller, and B_c exceeds S_c. In that case, both the peak amplitude and the peak shape are a function of the ion distribution in the beam, as is illustrated in fig. 2.

The peak durations at different scan-rates for $R_p = 140$ and for $R_p = 330$ are listed in table I.
Under normal conditions of sample introduction and ion source operation the intensity of the individual ion-beams does not exceed 2.10^{-9} A.

2.2. The mass-spectrometer output signals

2.2.1. The ion-current signal

The DC feedback electrometer amplifier incorporated in the mass-spectrometer and connected to the ion collector has an open loop gain of over 3000. For routine analytical purposes a 3.10^{10} Ohms feedback resistor is connected between the input and output of the amplifier, resulting in a linearity deviation of less than 0.03 % over an output range of -100 V to +10 V, corresponding to an input current range of $-3.3 \cdot 10^{-10}$ A. to $+3.3 \cdot 10^{-9}$ A.

The specified zero drift at the output is 2 mV./hour maximum, but under normal operating conditions the drift remains below 0.4 mV./hour.
The 3.10^{10} Ohms feedback resistor causes an input timeconstant of approximately 6.5 mSec., corresponding to an amplifier bandwidth of 25 cps.
With zero input to the amplifier the following output signals are present:

- The thermal noise generated in the feedback resistor. For the given resistor value and amplifier bandwidth the noise voltage is in the order of 0.15 mV_{rms}.
- A 50 cps. and 100 cps. ripple varying in amplitude between 3 mV_{ptp} and 10 mV_{ptp}. This ripple is due to inductive and capacitive pick-up in the amplifier circuit.

— Slow fluctuations with a maximum amplitude of 0,3 mV_{ptp} and covering a frequency spectrum of a few cps.

— A damped oscillation with a frequency of approximately 100 cps. occurs after each mechanical excitation of the analyzer cabinet. These oscillations are caused by a microphonic effect in the preamplifier flanged to the collector side of the analyzer.

With the electrometer amplifier connected to the ion collector each ion-beam passing the collector slit supplies a positive current peak to the amplifier input,resulting in a negative peak at the amplifier output. With maximum ion-beam intensities of 2.10^{-9}A. the maximum output swing of the amplifier is -60 Volts.

The limited bandwidth of the amplifier causes a noticable peak form distortion for peak durations less than 1 second. An input current peak that has the shape of a trapezium, with F_m = 0.2 and a duration T_b = 250 mSec, produces a peak at the amplifier output with a reduced top duration, as illustrated in fig. 3.

2.2.2. The mass-number reference signal.

With the usual 3 KV. accelerating potential, a magnetic deflection field of 3900 Gauss is required to focus ions with M = 100 on the collector. This fieldstrength is obtained with a current of 100 mA. through the magnet coils. A voltage proportional to the magnet current at 0.45 V/mA. is readily available from the magnet current regulator and is therefore used as mass-number reference signal.

3. THE MASS-SPECTRUM DIGITIZER (MSD)

3.1. General

3.1.1. Design considerations

If the MSD is operated in combination with the mass-spectrometer under the same conditions as for analog recording, the accuracy of the peak amplitude reading and the peak detection sensitivity must be high enough to obtain a performance at least equal to that of the analog recorder. Therefore, the relative accuracy of the digital peak amplitude reading must be $\pm$ 0.2 % $\pm$ 0.1 mV, over the range of 0 to -100 V.
This accuracy can only be obtained by using four decades, the last in steps of 0.1 mV., with additional switching of the decimal point.

The peak detection circuit must be able to distinguish peaks from drift, noise and transients in the spectrometer output. Its sensitivity must be sufficient to detect peaks of 1 mV., with durations between several tenth of a second to a few seconds, with a high reliability.
For each scan-rate the slope duration of a peak is equal to, or larger than, the value of T_s given by eq. (11) for optimum focussing. Therefore, a peak detection logic can be used that responds only to a changing input signal, if the rate of change exceeds a threshold value during a period of time exceeding a preset time limit.

To enable the identification of each mass up to M = 100, the mass-number reference reading must be reproducable within 0.2 %.

The construction of the MSD is based on these requirements and on the charcteristics of the input signals described in section 2.2.

3.1.2. Principle of operation.

The MSD is connected to the electrometer amplifier and magnet-current regulator in the mass spectrometer as shown in fig. 4. The electrometer output passes through a filter and automatic attenuator to the input of a digital voltmeter (DVM). Its digital reading, and the information in which direction the input signal changes, are applied to a control-unit. If the DVM input changes continuously in the negative direction , a peak-detection logic in the control-unit switches to the "ON" state, and remains in that state until the DVM input starts changing in the positive direction. As long as the peak-detection logic is "ON", each new digital reading is transferred into a storage register. However, with the logic in the "OFF" state, data transfer is inhibited. As a result, the most negative reading, being the peak amplitude, is retained in the storage register. Immediately after the peak-detection logic returns to the "OFF" state, the input of the DVM is switched over from the electrometer output to the mass-number reference signal from the magnet current regulator. The digital reading of this signal is stored in a second storage register. With the storage into this second register completed, the control-unit resets itself to its initial state and starts the print-out of the peak amplitude and mass-number reference value.

The complete system consists of four sub-units, the digital-voltmeter (DVM), the control-unit, the digital printer and the power supplies, interconnected in the control-unit.

3.2. The digital voltmeter (DVM).

In the MSD the analog to digital conversion is performed by a modified digital voltmeter, the type DM-2020 manufactured by "Digital Measurements Ltd". This instrument uses, the successive approximation method to obtain a digital reading with a maximum of 19999 at a rate of 50 measurements/second, synchronized with the power line frequency. Only one of the available sensitivity ranges, the 1.9999 Volts range, is utilized in the MSD. In that range the input impedance is 10.000 Megohms, and the relative accuracy is 0.01 % $\pm$ 1 unit in the least significant decade.
The digital reading and its polarity are visually displayed on the front panel and are also available as a binary-coded-decimal (BCD) output signal in the 8-4-2-1 code.

A simplified block diagram of the instrument is shown in fig.5.

The DVM starts each measurement with a 10 mSec. sampling period during which the input signal is applied to input A of the balance amplifier through the chopper A. The amplifier output is connected to input B via the chopper B, and the capacitor connected to input B is thus charged to a voltage equal to input A.
After the end of the sampling period chopper B isolates the B input from the amplifier output and chopper A transfers the A input from the input signal to the output of a digital potentiometer. The balance amplifier now amplifies the difference between the stored input signal and the digital potentiometer output.

The arms of the digital potentiometer are switched to a reference voltage by means of solid state switches controlled by bistables. During conversion these digit-bistables are operated sequentially by a commutating ring, starting with the most significant digit. Each digit-bistable remains set if the voltage step is accepted by a logic controlled by the balance amplifier output. If the step is rejected a logic opens a gate and the bistable is reset before the next one is set. By sequential switching of all bistables the digital potentiometer is balanced against the stored input voltage.

Whether a conversion takes place after sampling, depends on the state of a read-bistable. If the read-bistable is in the "ON" state, a reset-trigger-pulse, generated 1.5 mSec. after the end of the sampling period, switches a reset-bistable, causing all digit-bistables to be reset. Thereafter, a start pulse switches a clock-bistable, which unlocks the clock-generator. The clock-generator switches the commutating ring and conversion takes place as described. Approximately 6.5 mSec. after the reset-bistable has been switched to "ON" the last element in the commutating ring switches, which causes the read-bistable to be switched "OFF" and to clamp both the reset-bistable and the clock-bistable in their "OFF" positions. The digital reading obtained is held until the reset-bistable is switched "ON" again.

If, at the moment the reset-trigger-pulse is generated the read-bistable is in the "OFF" state, the reset and clock-bistables remain clamped "OFF" and the reset-trigger has no effect. In that case no conversion takes place and the digital potentiometer setting remains unchanged.

The state of the read-bistable is controlled by a trip-circuit that can be switched for different modes of operation. Two of these are utilized in the MSD.

In the "maximum mode" the trip-circuit is connected to the output of the balance amplifier. If the amplifier output exceeds an adjustable positive threshold value at the moment the reset-trigger-pulse is applied, the trip-circuit switches the read-bistable to "ON". As a result, the read-bistable and the reset-bistable are switched simultaneously, starting the conversion cycle.

However, if the balance amplifier output is less than the threshold value the read-bistable remains "OFF", which prevents a new conversion and holds the previous reading. When the reset-trigger-pulse occurs, the choppers A and B are in the read position and the balance amplifier amplifies the difference between the stored input voltage E_i and the output of the digital potentiometer E_d. Therefore the condition for a new conversion is:

$$E_i \geqslant E_d + h \qquad (12)$$

Where h = positive threshold voltage.

Consequently, the DVM reading follows only changes in the positive direction and holds the reading of the maximum input.

In the "minimum mode" the same circuitry is used as for the maximum mode, with the exception that the read-bistable is only switched "ON" if the balance amplifier output is less than a preset negative value, which gives the conversion condition:

$$E_i \leqslant E_d - h \qquad (13)$$

Consequently, the DVM follows only negative going signals and the minimum reading is retained.

For operation in the MSD the positive threshold "h" of the DVM is set to its minimum value, corresponding to one unit in the least significant digit.

In both operating modes the read-bistable can also be set by applying a 9 Volts positive step to an external-trip line, to start a conversion independent of the trip-logic.

The reset-bistable not only supplies the reset pulse to the digit-bistables, but also controls a display-inhibit circuit that prevents visual display and de-energizes the output code lines during a conversion. A "conversion-complete" signal (CPLS), generated by the display-inhibit circuit, is available at the DVM output.

For operation in the MSD some modifications of the DVM circuitry are necessary.

Although the input filter incorporated in the DVM is switched off, to obtain the necessary fast reponse, a small memory effect was observed. After applying a large voltage step, corresponding to a reading of 9999, the first reading was 9993, increasing to the final value 9999 during subsequent readings. This effect could be reduced by removing the 500 pF capacitor parallel to the input chopper contacts. The application of said voltage step now results in a reading of 9999 within three subsequent measurements.

A mode switching relay has been fitted, that enables the switching from the minimum-mode to the maximum-mode by energizing the relay from the control-unit.

The reset-trigger generator and the output of the read-bistable have been wired to the DVM output plug.

Since the reset-trigger (RST), the read-bistable signal (RDS) and the conversion-complete signal (CPLS) are used for peak-detection in the control-unit, their amplitudes and waveforms, shown in fig. 6, are essential for the operation of the MSD.

The RST drops to -12.3 V. during each sampling period and steps to 0 V. after the DVM switches from sampling to reading. The RST does not depend on the operating mode of the DVM and remains the same for "conversion" or "no-conversion".

The RDS from the read-bistable is at -1.7 V. during each sampling period (read-bistable "OFF"), and remains at that level, if the conditions for a new conversion are not satisfied and the previous reading must be retained. However, if the conditions for a new conversion are given, the read-bistable is set at the moment the RST is applied, which causes the RDS to step from -1.7 to +6.2 V. simultaneously with the positive step of the RST.

The CPLS is generated by the display-inhibit circuit and is normally at -12.4 V. During a conversion the CPLS is clamped to 0 V. and the de-energizes the output code lines.

3.3. The control-unit.

The control-unit contains the peak-detection circuitry and the registers for the storage of the digital readings. It commands the storage and the print-out of the data and controls the signal applied to the DVM.
The unit can be divided in three sub-assemblies i.e., the input circuit, the control-logic, and the storage registers.

3.3.1. The input circuit.

The output of the electrometer amplifier in the mass-spectrometer is connected to the input circuit in the control-unit, shown in fig. 7. The signal passes first through a passive lowpass filter. A filter switch enables the selection of three filter characteristics depending on the amount of noise rejection required and on the tolerable bandwidth reduction.

In position 1, a single section RC low-pass filter with a 3 mSec. time constant is used.

In position 2, a double T selective rejection network tuned to 100 cps. is added, which gives a 60 dB rejection at 100 cps and increases the time constant to 10 mSec.

In position 3, the 100 cps. rejection is retained and a second double T filter, tuned to 50 cps., is added. With the resulting composite filter the attenuation at 50 and 100 cps. exceeds 60 dB, whereas the time constant becomes 27 mSec.

Since the DVM uses a sampling rate of 50 cps, synchronized with the line frequency, a 50 or 100 cps. ripple at the DVM input has no effect on the digital reading, as long as the phase and amplitude of the ripple remain constant. Unfortunately the ripple at the electrometer output is not of constant amplitude, so filtering is necessary to prevent reading errors of the MSD. The 100 cps. filter also rejects the interfering microphonic signal.

Because of the accuracy requirements, signal overshoots must be kept below 0.1 %. For that reason sharp cut-off filters cannot be used. The combination of double T filters with a single section RC network gives the necessary filtering, without increasing the time constant too much, and without introducing undesirable overshoots. The frequency response in each of the filter positions is shown in fig. 8.

The input filter is followed by a three position precision attenuator with range factors x1, x10 and x100, operated by the three reed relays K_3 to K_5, energized from the control-logic. The switching time of the relays is 1 mSec.

The attenuator resistors have been specially selected from a series of wirewound resistors of 0.1 % tolerance, in order to obtain an attenuator accuracy of 0.1 %.
To prevent errors when switching the input filter, the filter switch connects dummy resistors in series with the input when a filter section is disconnected.

To enable the setting of a convenient read-out value for the mass-number reference, the mass-number reference signal is connected to a continuously variable voltage divider. By energizing the reed relay K_1 and de-energizing K_2, the input of the DVM is transferred from the precision attenuator to the mass-number reference signal. Both relays have a switching time of 1 mSec. and are operated by the control-logic.

3.3.2. The control-logic.

For the description of the operating principle, reference is made to the simplified circuit diagram in fig. 9.
The RST, RDS and CPLS from the DVM are the main inputs to the control-logic.

The RST is applied to a buffer amplifier, followed by a delayed pulse generator. The output of this generator is the RST-delayed pulse, that goes from -12V. to 0 V. during 0.1 mSec., with a 1 mSec. delay in respect to the positive step of the RST.

The RDS is also connected to an amplifier. If the RDS is at -1.7 V. the amplifier output is at -12 V. However, with the RDS at + 6.2 V the amplifier output is 0 V.

The negative step of the CPLS at the end of a conversion triggers a 0.3 mSec. monostable. When the monostable switches back to its stable state it starts a pulse generator, that produces the CPL-delayed pulse, going from -8 V. to 0 V. during 40 uSec.

Each switching of the mode-bistable energizes or de-energizes the mode switching relay in the DVM through the relay driver and switch S_1. This causes the DVM to change from the minimum to the maximum-mode or vice versa.

If, at the end of a sampling period of the DVM, no conversion takes place, the RDS remains at -1.7 V and the RDS amplifier keeps the junction C_1-C_2 at -12 V through R_1. The RST-delayed pulse clamps the junction to 0 V through diode D_1 during 0.1 mSec., which produces a positive pulse that switches the mode-bistable. Thus, if in a certain mode of operation no conversions take place, the mode-bistable switches the DVM immediately into the other operating mode. Consequently, a constant input signal to the DVM, perfectly balanced by the digital potentiometer, causes mode switching after each sampling period.

If, the condition for a new conversion is given, the RDS steps from -1.7 V. to +6.2 V. at the moment the RST goes to 0 V. As a result, the RDS amplifier drives the junction C_1-C_2 to 0 V. through R_1, which prevents switching of the mode-bistable by the RST-delayed pulse. Therefore, the DVM remains in either maximum or minimum-mode, as long as new conversions are made.

With the DVM in minimum-mode and switch S_1 in the position shown, the mode-bistable output connected to R_2 is at -12 V. If the DVM input changes in the negative direction, a conversion takes place, leaving the mode bistable unchanged and keeping the junction R_2-C_3 at -12 V. After completion of the conversion the CPLS starts the 0.3 mSec. monostable, which clamps the junction to 0 V. through diode D_3.

This clamping action not only produces an input pulse to the 3 bit binary counter, formed by the bistables C-1 to C-3, but also switches the accept-bistable "ON". When the accept-bistable switches "ON", it triggers a 0.75 Sec. monostable, that resets the binary counter to zero when it returns to the stable state.

If the DVM is in the maximum-mode and a conversion takes place, the junction R_3-C_5 is kept at -12 V. Upon clamping by the 0.3 mSec. monostable through diode D_4, the reject-bistable is set to "ON". This resets the 0.75 Sec. monostable through diode D_9 and simultaneously resets the binary counter through D_{10}-C_{12}-Q_2.

Both the accept and reject-bistables are reset to "OFF" by the RST-delayed pulse.

The binary counter receives an input pulse for each conversion in the minimum-mode. Resetting to zero occurs each time a conversion is started in the maximum-mode, but ultimately 0.75 Sec. after the first count. Therefore, the counter reading represents how many conversions have been made in the minimum-mode, without any conversion in maximum-mode. The binary output of the counter is converted into decimal form with a small diode matrix. The six output lines of the matrix, representing the numbers 2 to 7, are normally at -12 V., but each line switches to 0 V. as soon as its corresponding counter reading is obtained. By means of the switch S_2, one of the matrix outputs can be selected to hold the base of transistor Q_3 negative until the selected count number is reached. At that moment, the base of Q_3 steps to 0 V. and its emitter supplies a positive set pulse to the peak-bistable through diode D_{19}.

Switching of the peak-bistable to the "ON" state is significant for the presence of a peak. The fact, that it requires a number of n (n = 2...7) conversions in the minimum-mode within a period of 0.75 Sec., and without any conversion in the maximum-mode, defines the conditions for peak acceptance as follows:

1. The DVM input voltage must change continously in the negative direction with an average rate of change exceeding 1.4 n.c. mV./Sec.

2. The duration of the continuous change must exceed 0.02 n Sec. and be long enough to result in an input change of at least n.c mV.
   The factor "c" indicates the voltage difference for a single unit change in the least significant digit of the DVM, expressed in mV.

The peak-bistable is switched "OFF" by setting the reject-bistable "ON". Consequently, resetting of the peak-bistable occurs as soon as the input signal starts changing in the positive direction, and marks the point at which the most negative input voltage has passed.

Hitherto, the description was based on the detection of negative going peaks, as required for normal operation of the MSD in combination with the mass-spectrometer. However, in some cases, e.g. when an electron multiplier is used, the recording of positive going peaks is required. To measure positive going peaks with the MSD, the peak-detection logic can be inverted by changing the position of switch S_1. This inverts the accept and reject action in respect to the maximum and minimum-mode of the DVM.

With the peak-bistable "ON", diode D_{21} does not conduct and each CPL-delayed pulse applied to the base of transistor Q_7 is transmitted to Q_8 to form the transfer pulse nr. 1. This transfer pulse nr. 1 is fed to the storage register nr.1 and commands the transfer of the output reading of the DVM into the register. As long as the peak-bistable is "ON", each subsequent CPLS causes data transfer, and the storage register therefore follows the DVM reading.

With the peak-bistable "OFF", diode D_{21} clamps the collector of Q_7 to 0 V., to inhibit further transfer into register nr.1.

The return of the peak-bistable to its "OFF" state triggers the mass-bistable "ON", which in turn causes three different but simultaneous switching operations.

Firstly, the reed relay K_1 in the input circuit is energized and relay K_2 is de-energized, to switch the DVM input to the mass-number reference signal as described in sec. 3.3.1.

Secondly, the emitter of transistor Q_4 is driven positive, which holds the mode-bistable in the maximum-mode through diode D_2, and makes the base of transistor Q_1 positive through diode D_{11} to unlock the 300 cps. multivibrator. The multivibrator output is connected to the external trip connection of the DVM and sets the read-bistable during each sampling cycle, to override the trip-logic of the DVM.

Thirdly, a 62 mSec. monostable is started, that prevents resetting of the mass-bistable by the CPL-delayed pulse, until the 62 mSec. interval has elapsed.

Consequently, the mass-bistable remains "ON" for 80 mSec., allowing four subsequent readings of the mass-number reference signal. Four measurements are necessary to eliminate the memory effect in the DVM input circuit.

When the mass-bistable returns to the "OFF" state, the relays K_1 and K_2 switch the DVM input back to the electrometer signal. Transistor Q_1 is driven back into saturation to lock the 300 cps. multivibrator, and the holding of the mode-bistable is released. Furthermore, a transfer pulse nr. 2 is generated and applied to the storage register nr. 2, to command the storage of the last mass-number reference reading.

The transfer pulse nr. 2 also triggers a 150 mSec. monostable, that supplies the 150 mSec. print-command signal to the digital printer. Upon receipt of the print-command, the printer starts the print-out of the peak amplitude and mass-number reference readings held in the two storage registers. With the generation of the print-command signal the operating cycle of the control-logic has been completed.

If, at the end of a conversion the DVM reading exceeds 9999, the 10^4 code line drops to -10 V. This not only causes the junction C_{29}-C_{30} to go negative, but also drives transistor Q_{15} into saturation, holding the junction C_{28}- C_{31} at 0 V. The CPL-delayed pulse, applied through emitter follower Q_9 and diode D_{27}, clamps the junction C_{29} - C_{30} to 0 V, which produces a positive step that switches the A_1-bistable "ON". In case the A_1-bistable was already in the "ON" state, the positive step sets the A_2-bistable through diode D_{30}. When the A_1-bistable goes "ON", relay K_4 becomes energized and K_3 is de-energized, which changes the input attenuator from x 1 to x 10. Switching the A_2-bistable "ON" causes the attenuator to change from x 10 to x 100, by energizing K_5 and releasing K_4.

If after a conversion the DVM reading drops below 00800, the 10^4, 8.10^3, 4.10^3, 2.10^3, 10^3 and 8.10^2 code lines remain all at 0 V. As a result, the junction C_{29}-C_{30} remains at 0 V., but the junction C_{28}-C_{31} goes to -12 V, since transistor Q_{15} does not conduct. Clamping by the CPL-delayed pulse through diode D_{26} supplies a positive step to the reset input of the A_2-bistable. If the A_2-bistable was already "OFF", the positive step is also applied to the reset input of the A_1-bistable through diode D_{28}. Therefore, a DVM reading less than 00800 causes the attenuator to step back from x 100 to x 10, or from x 10 to x 1.

A BCD signal, representing the position of the automatic attenuator, is applied to storage register nr. 1, and stored simultaneously with the peak amplitude reading.

If the mass-bistable is "ON," D_{25} holds the base of Q_9 at -12 V, to inhibit range change. This has the advantage, that during the 80 mSec. interval for the mass-number reference reading the attenuator remains properly set for the electrometer signal.

Since each switching of the attenuator causes the input signal to step in a direction opposite to its actual change, the trip logic in the DVM must be py-bassed to prevent mode switching and erratic peak detection. For that reason, the outputs of the attenuator-bistables are connected to the set input of a trigger-bistable through differentiating networks. After each range change the trigger-bistable is set and unlocks the 300 cps. multivibrator through D_{13}-D_{12} and Q_1. The RST-delayed pulse resets the trigger-bistable, which locks the 300 cps. generator again.

3.3.3. The storage registers

The storage registers are used as memory elements for the attenuator position and for the digital readings from the DVM. Furthermore, the registers invert the digital signal levels in order to be compatible with the printer. Each storage register contains a series of bistables, one for each data bit to be stored.

The storage register nr. 1. has a 19 bit capacity for the storage of 4 amplitude digits of 4 bits each, one attenuator digit of 2 bits, and one polarity bit.

The storage register nr. 2 has a 17 bit capacity, to store 4 digits of 4 bits each, and one digit of one bit.

The operating principle of the registers can be seen from fig. 10.

If a transfer pulse is applied to one of the storage registers, the bistables in that register will switch to, or remain in, the position giving 0 V. to their output lines, if the associated input lines are at -12 V. However, if an input line is at 0 V., the corresponding bistable switches to, or remains in, the position that puts -12 V. at its output line. The proper switching action is obtained by means of the networks R_1-C_1-D_1-D_2-R_2, and C_2-R_3-D_3. These networks apply the transfer pulse to either the set input or the reset input of the bistables, depending on the state of the input lines. The digital signal levels at the register input are those used by the DVM, with digital "0" = 0 V., and digital "1" = -12 V. The output levels are those required by the printer with digital "0" = -12 V., and digital "1" = 0 V.

3.4. The digital printer

The printer used is a BECKMAN model 1453 with a column capacity of 12 digits per line and a maximum printing rate of 3 lines/second.

The printing format is

xxxxx y zzzz

where xxxxx = mass-number reference,
y = attenuator position,
zzzz = peak amplitude reading.

The color control line of the printer is connected to the storage register bit that holds the polarity signal. As a result, negative readings are printed black and positive readings red.

To avoid erratic settings of the printing mechanism, the output signals of the storage registers are not allowed to change for a period of 150 mSec. after the beginning of the print-command. For normal applications in combination with the mass-spectrometer this condition is automatically satisfied, since the scan-rate is limited by the reponse of the electrometer amplifier and the input filter of the MSD. For special applications, a simple wire bridge in the control-logic is sufficient to install a clamping circuit, that inhibits transfer into the storage register nr. 1, as long as the 150 mSec. print-command pulse is applied to the printer.

3.5. The power supplies

Two transistorized stabilized power supplies deliver the +12 V. and -12V. required for the operation of the control-unit. Both supplies have a regulation of 0.1 %, and an output resistance of 0.05 Ohms. The current taken from the +12 V. supply is 50 mA, whereas the -12 V. supply delivers 0.6 A. A small -90 V. supply is required to operate the neon bulbs used as front panel indicators in the control-unit. The total current drain from that supply is less than 15 mA.

4. PERFORMANCE OF THE MSD

4.1. The MSD as an individual instrument

If the MSD is connected to a signal source with an output noise of less than 10 $uV._{ptp}$, the following performance specifications apply:

Detection logic	:	switchable for positive or negative going peaks
Peak acceptance conditions	:	rate of change on the slope 0.14.n mV/sec peak amplitude 0.1.n mV. slope duration 0.02.n Sec. (With n selectable from 2 to 7.)
Full scale reading	:	range x1 ± 0.9999 V. range x10 ± 9.999 V. range x100 ± 99.99 V.
Polarity selection	:	automatic and indicated by the printing color.
Range changing	:	automatic and completed within 20 mSec.
Relative accuracy of reading	:	0.1 % or ± 1 unit in the least significant digit, if the peak remains at its maximum value for at least 20 mSec.
Maximum peak-repetition rate	:	3 peaks/Second.

To satisfy the condition for the stated accuracy, the peak duration must exceed a certain value, depending on the peak shape and on the input filter used. For an ideal trapezium shaped peak with $F_m = 0.2$ the minimum peak durations are:

	Without range change	Including range change
Filter position 1 :	180 mSec.	250 mSec.
Filter position 2 :	330 mSec.	430 mSec.
Filter position 3 :	750 mSec.	820 mSec.

The digital reading of the mass-number reference signal is reproducable to within 0.01 % $\pm$ 1 unit in the least significant decade.

4.2. The MSD in combination with the CH-4 mass-spectrometer

If the MSD is connected to the mass-spectrometer, a deterioration in peak detection sensitivity and accuracy of the amplitude measurement occurs, due to the output noise of the electrometer amplifier. Furthermore, the timing of the control-unit and the hysteresis of the magnet core introduce an error in the mass reference reading.

4.2.1. The peak detection and amplitude measurement

If the noise, after filtering in the MSD input circuit, and not including the ripple synchronous with the line frequency, is E_n mV_{ptp}, its value depends on the filter switch position.
With the MSD input filter in position 1, E_n is approximately 0.6 mV_{ptp}.
However, in position 2, E_n is 0.5 mV_{ptp}, whereas the residual ripple contains only a 50 cps component.
With the filter switched to position 3, E_n is reduced to 0.25 mV_{ptp}, and the ripple is not any more detectable.

Because of the noise signal E_n, the relative accuracy of the digital peak amplitude reading is reduced to 0.1 % $\pm E_n \pm 1$ unit in the least significant decade.

To prevent the acceptance of noise by the peak detection-logic, the count number "n" in that logic must exceed $10.E_n$. As a result, the minimum peak that can be detected is mainly determined by the noise level.

The influence of the 50 and 100 cps. ripple depends on the changes in ripple amplitude and on the phase relation between the ripple and the switching of the input chopper in the DVM. Therefore, no typical figures can be given.

The minimum duration of the ion current peaks, that is required to obtain the specified accuracy, is higher than for the MSD alone, due to the time constant of the electrometer amplifier. Since the peak shape is not constant throughout the spectrum, the maximum usable scan-rate must be found experimentally for each spectrometer setting.

4.2.2. The mass-number reference reading

For each peak, the mass-number reference reading M_r is proportional to the magnet current at the moment the peak passes through its maximum amplitude. Due to the hysteresis and nonlinearity of the magnet core, the fieldstrength is not a completely linear function of M_r. Therefore, the mass-number M varies only approximately with the square of M_r.
However, if each spectrum is scanned by following a standard procedure, the deviations from the square function remain constant and can be compensated for by using a calibration table, that relates each mass-number reference reading M_r to the true mass-number M.

For ease of interpretation, the mass-number reference signal is set to give a reading of $M_r = 19999$ at $M = 400$.

Apart from the hysteresis effect, the measurement of M_r is subject to three errors:

The error due to the inaccuracy of the MSD reading, as specified in sec. 4.1. This error contributes to a maximum deviation of $\pm$ 0.08 mass units, up to $M = 400$.

The fact, that the mass-number reference reading occurs 80 mSec. after the detection of the peak maximum, results in a too high reading with $\Delta M = 0.08 \cdot a.M. \ln 2$, or an error of $8.a.\ln 2$ % in mass-number. Thus, at a scan-rate of $12.8 \cdot 10^{-3}$ octaves/Sec., the error at $M = 400$ is 0.28 mass unit. Since this is a systematical error, it can be eliminated by a calibration for each scan-rate.

If a peak has a perfectly flat top, the peak detection-logic starts the mass-number reference reading at the end of the top. In practice however, the noise superimposed on the peak may start the reading at any point of the flat top. Under the worst condition, the point of maximum detection may vary over the entire interval T_m, and, if $F_m = 0.24$, $M = 0.24 \frac{M}{R_p}$. Therefore, the maximum error is $\pm \frac{12}{R_p}$ %. This error is not reproducable and cannot be calibrated for.

4.3. Experimental results

For both standard settings of the spectrometer, the performance of the MSD was tested by recording a series of spectra simultaneously with the MSD and with the potentiometric recorder, and by comparing the digital data with the analog records.

4.3.1. Low resolution setting of the spectrometer (R_p = 140 at M =40).

With the input filter of the MSD in position 3 and the peak detection logic set for "n" = 5, several spectra of normal-butane were recorded at a scan-rate of 6.4 .10^{-3} octaves/sec. The amplitude of the base-peak at M = 43 was 3 Volts. With each peak exceeding 0.8 mV. detected, the MSD printed 41 peaks per spectrum, including those from the instrument background and from double charged ions and metastable ions.

Three of the relative spectra are shown in table II, with peaks less than 0.1 % of the base-peak omitted.

Under the same conditions spectra of Xenon were recorded, also at a scan-rate of 6.4 .10^{-3} octaves/Sec. The base-peak at M = 132 reached an amplitude of 2 Volts. For one of the scans, the relative spectra were calculated from the analog record and from the digital print. These relative spectra are shown in table III, compared to the theoretical spectrum, calculated from the standard isotope ratios of Xenon.

In order to find the influence of the peak duration on the amplitude reading, peaks at M = 27 and M = 57, having a slightly different peak shape, were measured at different scan rates. During this test the input filter switch in the MSD was in position 3. As can be seen from the results listed in table IV, the reading error increases at higher scan-rates, but the effect is less for the MSD than for the potentiometric recorder.

The low-resolution setting of the spectrometer is only used to record spectra that cover a mass range up to M = 130. For these applications, proper identification of all peaks in the spectra is possible if the mass-numbers of the peaks can be established with a reproducability of $\pm$ 0.3 %. This reproducability can be obtained with a scanning procedure that is suitable for routine work. A simple calibration table is sufficient to find the mass-numbers from the printed mass-number reference reading.

4.3.2. High-resolution setting of the spectrometer (R_p = 330 at M = 132)

With the MSD input filter switched to position 2, and the peak detection logic set for "n" = 5, spectra of normal-butane were recorded at scan-rates of 3.2×10^{-3} and 6.4×10^{-3} octaves/second. The amplitude of the base-peak at M=43 was 1.6 Volts. For each of the two scan-rates, one of the relative spectra obtained is shown in table V. The discrepancy between the two spectra at lower masses is due to the fact, that a considerable reduction in top duration of the peaks occurs below M = 50, as described in sec. 2.1.

> Note: The normal-butane spectra in table V are not fully identical to those in table II, since they were obtained with a different ion-source and with slightly different ion-source operating conditions.

With the same settings of the MSD, seven Xenon spectra were recorded at scan-rates of 3.2×10^{-3}, 6.4×10^{-3} and 12.8×10^{-3} octaves/second. Due to the slow response of the recorder, no reasonable analog record could be made at scan-rate 12.8×10^{-3}. The MSD reading also shows a considerable amount of clipping at this scan-rate, but since the peaks at higher masses are of nearly equal shape, the clipping has not much effect on the relative spectrum of Xenon, as can be seen from table VI.

Peaks at M = 27, M =43, M = 57 and M = 132, having different peak shapes, were recorded at various scan-rates. As shown in table VII, the peaks at lower masses, that have have a rather short top duration or even a nearly triangular shape require a low scan-rate if errors due to peak clipping have to be prevented. However, from the results of the test it is clear, that this restriction is also valid, and even more important, for the potentiometric recorder.

With the high-resolution setting, spectra are frequently recorded up to M = 350. For the correct identification of each peak the mass-number must be found with a reproducability of 0.1 % or better. Repetitive measurements with different spectra have proved, that this reproducability can only be obtained by precisely following a scanning procedure that requires the returning to zero of the magnet current after each scan, and a slow resetting to a fixed scan-start position. However, this procedure has been found impractical for routine operation of the spectrometer.

Since the disturbing mass-number errors are due to the hysteresis of the magnet, they can be eliminated if a mass-number reference signal truly proportional to the magnetic field-strength is used. This can be accomplished, by means of a Gaussmeter, equiped with a Hall element that can be installed in the magnet gap of the spectrometer. If the Gaussmeter gives an output signal proportional to the fieldstrength with a reproducability of 0.03 %, the reliable identification of each peak up to M = 400 becomes possible, without the need for a reproducable scanning procedure. A Gaussmeter suitable for this purpose will be installed in the CH-4 spectrometer in the near future.

5. CONCLUSIONS

The Mass-Spectrum Digitizer was originally designed to operate with the CH-4 mass-spectrometer over a limited mass-range up to M = 100, as required for the routine analysis of gaseous and volatile liquid samples.

During seven months of operation the MSD has proved to be very suitable for such applications, and to have a better linearity and reproducability than the potentiometric recorder used before.

Due to a change in the analytical program, the CH-4 is now frequently used for the analysis of higher molecular substances, which requires the recording of spectra up to M = 350. The MSD can also be used for these applications without deterioration of performance, if the mass-number reference signal is obtained from a Gaussmeter.

Although specially designed for the CH-4, the MSD could also be used in combination with other mass-spectrometers. However, the performance of such a combination depends on the characteristics of the spectrometer output signals, especially on the output noise of the ion-current amplifier. Furthermore, a spectrometer with electric field scanning would require an additional computing servo, that produces a mass-number reference signal inversely proportional to the fieldstrength.

The spectral information printed by the MSD is only accessible by visual examination of the print. For automatic calculations with a digital computer, the digital data from the MSD have to be stored and edited for computer entry. Therefore, an extra digital output is provided for the connection of an additional data processing system.

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SCAN SWITCH POSITION	SCAN-RATE 10^{-3} OCT/sec.	SCAN VELOCITY mm/sec.	PEAK DURATION Tb	
			LOW RESOLUTION Rp = 140	HIGH RESOLUTION Rp = 330
5	1.1	0.15	9.4 sec.	4.0 sec.
6	1.6	0.22	6.5 sec.	2.75 sec.
7	2.2	0.31	4.7 sec.	2.0 sec.
8	3.2	0.44	3.2 sec.	1.4 sec.
9	4.45	0.62	2.3 sec.	1.0 sec.
10	6.4	0.89	1.6 sec.	0.7 sec.
11	8.9	1.24	1.16 sec.	0.5 sec.
12	12.8	1.78	0.8 sec.	0.35 sec.
13	17.8	2.48	0.6 sec.	0.25 sec.
14	43	6.0	0.24 sec.	0.1 sec.

TABLE I

TABLE II

RELATIVE SPECTRA OF NORMAL-BUTANE. SCAN-RATE $6.4 \cdot 10^{-3}$.
Rp = 140 at M = 40

MASS-nr. m/e	POTENTIOMETRIC-RECORDER run 1	run 2	run 3	MASS-SPECTRUM-DIGITIZER run 1	run 2	run 3
14	0.24	0.23	0.24	0.24	0.25	0.25
15	1.50	1.49	1.49	1.48	1.50	1.50
25	0.22	0.23	0.23	0.23	0.24	0.24
25.5	0.30	0.31	0.31	0.31	0.32	0.32
26	3.64	3.62	3.64	3.62	3.63	3.63
27	26.33	26.18	26.14	25.94	25.97	25.95
28	27.53	27.31	27.42	27.13	27.12	27.13
29	37.10	36.80	36.86	36.87	36.87	36.86
30	0.81	0.82	0.82	0.82	0.83	0.83
MS 30.4	0.12	0.13	0.13	0.13	0.14	0.15
MS 31.9	0.15	0.16	0.12	0.17	0.18	0.18
37	0.69	0.69	0.69	0.69	0.70	0.71
38	1.41	1.41	1.41	1.40	1.41	1.41
39	9.90	9.84	9.80	9.83	9.86	9.85
40	1.40	1.36	1.40	1.39	1.40	1.40
41	27.93	27.77	27.78	27.53	27.55	27.54
42	12.90	12.82	12.81	12.82	12.84	12.83
43	100.00	100.00	100.00	100.00	100.00	100.00ref
44	3.52	3.50	3.53	3.51	3.52	3.54
49	0.34	0.35	0.35	0.35	0.36	0.36
50	1.20	1.21	1.21	1.20	1.21	1.21
51	0.99	0.98	0.99	0.99	0.99	0.99
52	0.23	0.24	0.24	0.24	0.25	0.25
53	0.75	0.75	0.75	0.76	0.77	0.76
54	0.18	0.19	0.19	0.19	0.19	0.20
55	0.98	0.99	0.99	0.98	0.99	1.00
56	0.76	0.77	0.76	0.77	0.78	0.76
57	2.67	2.66	2.67	2.64	2.65	2.65
58	13.30	13.20	13.20	13.17	13.20	13.21
59	0.89	0.56	0.56	0.56	0.58	0.58

TABLE III

RELATIVE SPECTRA OF XENON FROM M=126 TO M=136.

SCAN-RATE : $6,4 \cdot 10^{-3}$. Rp=140 at M = 40

MASS-nr. (m/e)	POTENTIOMETRIC RECORDER	MSD	THEORATICAL
126	0.32	0.35	0.33
128	7.09	7.13	7.13
129	98.11	98.11	98.32
130	15.18	15.15	15.17
131	78.42	78.86	78.77
132	100.00	100.00	100.00
134	38.96	38.82	38.82
136	32.96	33.00	32.99

SCAN-RATE 10^{-3} OCT/sec.	M = 27 NORMAL BUTANE					M=57 NORMAL BUTANE				
	Tb sec.	Tt sec.	Tm sec.	READING ERROR IN % ANALOG RECORDER	MSD	Tb sec.	Tt sec.	Tm sec.	READING ERROR IN % ANALOG RECORDER	MSD
<1	>10	>3	>2	—	—	>10	>3	>2	—	—
1.6	6.5	2.0	≈ 1.2	-0.25	<0.1	6.5	2.0	≈ 1.5	<0.2	<0.1
3.2	3.2	1.0	≈ 0.6	-0.4	<0.1	3.2	1.0	≈ 0.75	<0.2	<0.1
6.4	1.6	0.5	≈ 0.3	-0.5	<0.1	1.6	0.5	≈ 0.37	<0.2	<0.1
12.8	0.8	0.25	≈ 0.15	-1.1	-0.15	0.8	0.25	≈ 0.18	-0.6	-0.4
43	0.24	0.075	≈ 0.043	-8.2	-6.5	0.24	0.075	≈ 0.055	-8.8	-0.8

READING ERROR AT DIFFERENT SCAN-RATES FOR M=27 AND M=57.

LOW RESOLUTION Rp = 140 at M = 40 MSD INPUT FILTER IN POS. 3.

PEAK SHAPE FOR M=27 : Fp = 0.31 Fm$\approx$0.18

PEAK SHAPE FOR M=57 : Fp = 0.31 Fm$\approx$0.23

TABLE IV

TABLE V

RELATIVE SPECTRA OF NORMAL-BUTANE AT TWO SCAN-RATES.
HIGH RESOLUTION SETTING. Rp = 330 at M = 132

MASS-nr. m/e	SCAN-RATE $3.2 \cdot 10^{-3}$		SCAN-RATE $6.4 \cdot 10^{-3}$	
	RECORDER	MSD	RECORDER	MSD
14	0.17	0.18	0.16	0.17
15	1.11	1.13	1.23	1.12
25	0.20	0.22	0.19	0.21
25.5	0.30	0.32	0.28	0.30
26	3.40	3.41	3.39	3.40
27	26.00	26.10	26.00	25.93
28	27.20	27.30	27.03	27.08
29	37.97	37.83	37.76	37.62
30	0.84	0.87	0.84	0.85
37	0.64	0.65	0.64	0.65
38	1.33	1.34	1.30	1.33
39	9.50	9.52	9.53	9.53
40	1.29	1.33	1.28	1.32
41	29.90	30.06	29.88	30.02
42	12.82	12.78	12.80	12.73
43	100.00	100.00	100.00	100.00
44	3.36	3.38	3.36	3.37
49	0.33	0.35	0.33	0.35
50	1.23	1.23	1.21	1.23
51	1.00	1.01	0.99	1.00
52	0.23	0.25	0.22	0.24
53	0.77	0.78	0.76	0.76
54	0.16	0.19	0.17	0.19
55	1.56	1.00	1.00	0.98
56	1.33	0.77	0.99	0.78
57	2.51	2.52	2.52	2.52
58	10.45	10.43	10.44	10.42
59	0.45	0.46	0.44	0.46

MASS-nr. m/e	MASS-SPECTRUM-DIGITIZER							RECORDER				
	SCAN-RATE $3.2 \cdot 10^{-3}$			SCAN-RATE $6.4 \cdot 10^{-3}$		SCAN-RATE $12.8 \cdot 10^{-3}$		SCAN-RATE $3.2 \cdot 10^{-3}$			SCAN-RATE $6.4 \cdot 10^{-3}$	
	RUN 1	RUN 2	RUN 3	RUN 4	RUN 5	RUN 6	RUN 7	RUN 1	RUN 2	RUN 3	RUN 4	RUN 5
124	0.38	0.36	0.38	0.37	0.35	0.36	0.35	0.34	0.34	0.34	0.34	0.32
126	0.33	0.34	0.35	0.34	0.34	0.33	0.34	0.31	0.31	0.33	0.30	0.31
128	7.12	7.12	7.11	7.13	7.12	7.11	7.13	7.06	7.06	7.08	7.21	7.22
129	98.12	98.03	98.03	98.19	98.11	98.14	98.23	97.99	97.74	97.98	98.47	97.96
130	15.12	15.12	15.12	15.11	15.12	15.10	15.12	15.43	15.15	15.16	15.26	15.28
131	78.76	78.71	78.76	78.81	78.76	78.73	78.67	78.39	78.39	78.59	79.93	79.85
132	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
134	38.82	38.79	38.80	39.01	39.06	38.81	38.79	38.69	38.61	38.79	39.03	39.03
136	32.99	32.97	32.98	33.07	32.98	32.97	32.99	32.91	32.91	32.91	33.08	33.08

XENON SPECTRA AT DIFFERENT SCAN-RATES.

HIGH RESOLUTION SETTING. $R_p = 330$ at $M = 132$
MSD INPUT FILTER IN POSITION 2

TABLE VI

SCAN-RATE 10^{-3} OCT/sec	RECORDER ERROR %				M.S.D. ERROR %			
	M = 27	M = 43	M = 57	M = 132	M = 27	M = 43	M = 57	M = 132
< 1	—	—	—	—	—	—	—	—
1.6	0.15	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
3.2	1.25	0.4	0.4	<0.1	1.0	0.3	0.3	<0.1
6.4	3.6	1.4	1.2	0.5	3.0	0.9	0.9	0.3
12.8	9.5	5.8	5.4	3.8	8.0	3.6	3.4	2.9

READING ERROR FOR DIFFERENT PEAKS AT VARIOUS SCAN-RATES.

HIGH RESOLUTION. Rp = 330 at M = 132

FOR M = 27 PEAK SHAPE : Fp = 0.07 Fm < 0.02

FOR M = 43 PEAK SHAPE : Fp = 0.12

FOR M = 57 PEAK SHAPE : Fp = 0.2 Fm = 0.12

FOR M = 132 PEAK SHAPE : Fp = 0.31 Fm = 0.28

TABLE VII

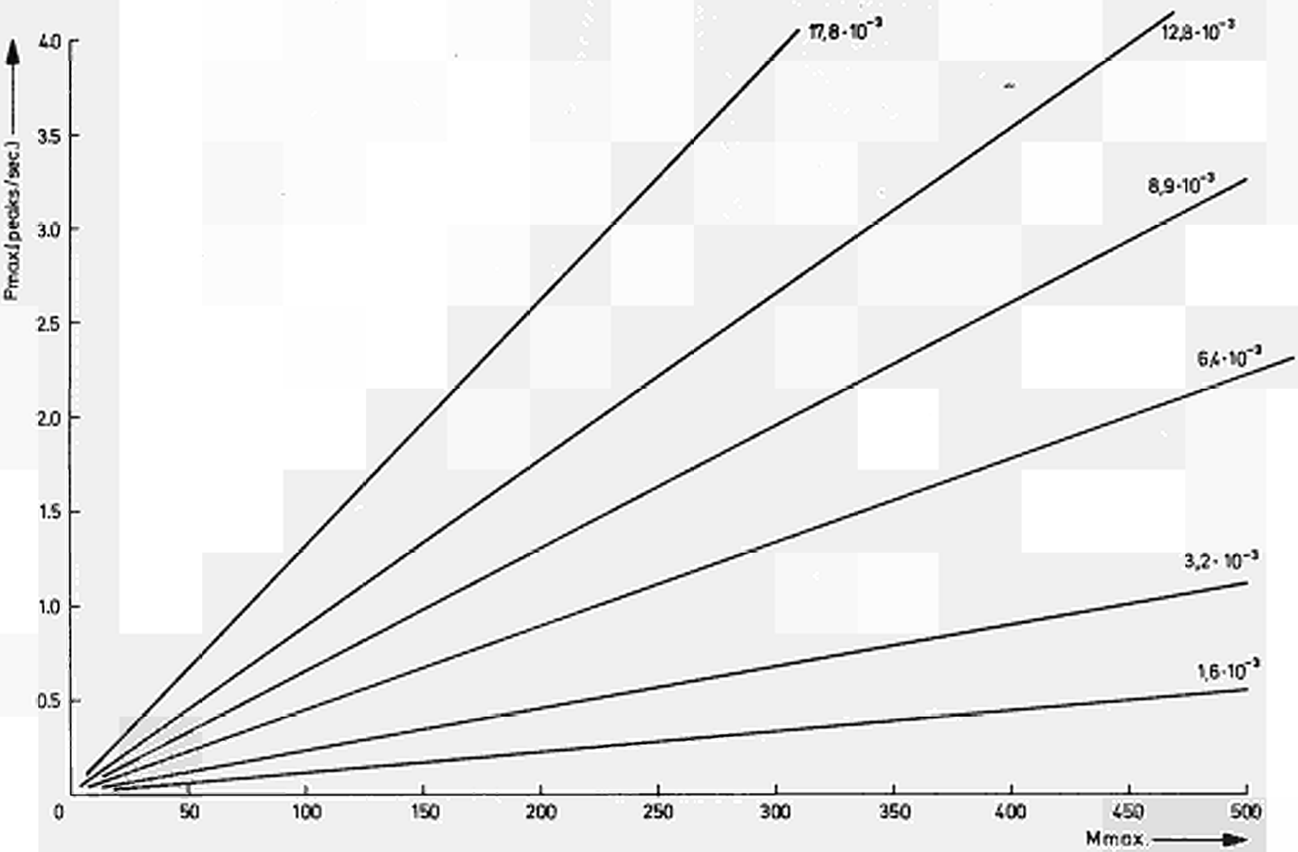

Fig. 1 MAXIMUM PEAK REPETITION RATE AS A FUNCTION OF Mmax FOR DIFFERENT SCAN-RATES.

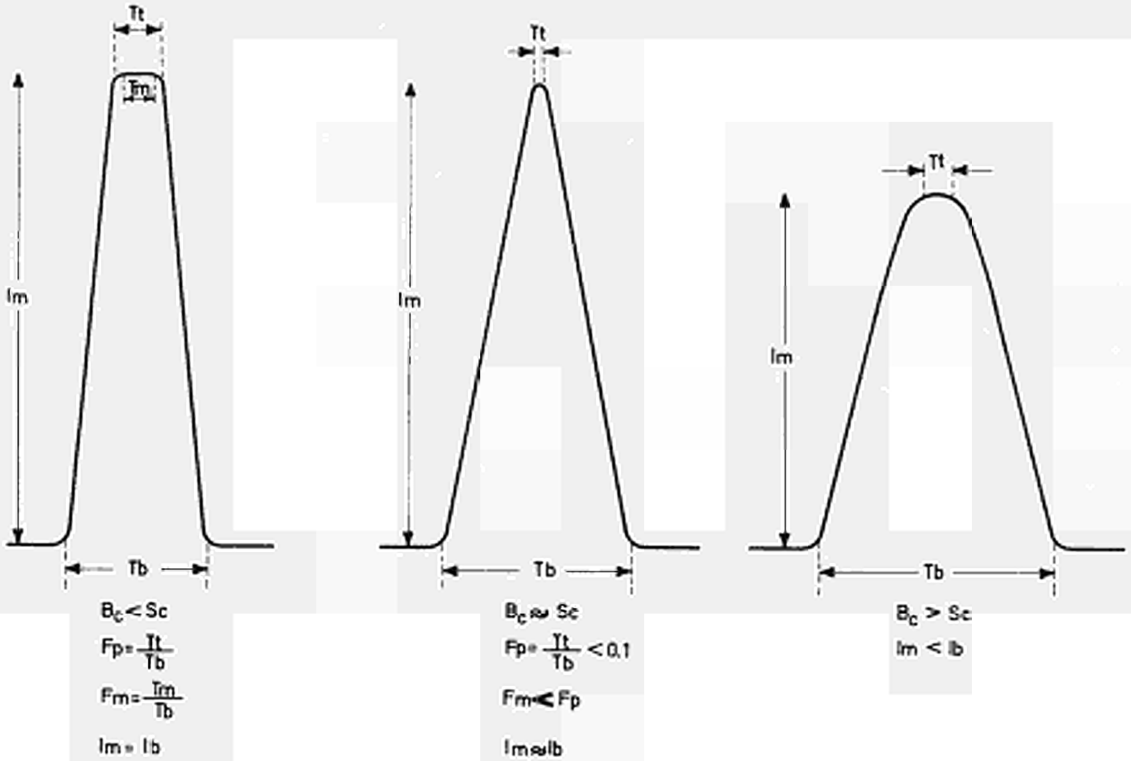

Fig. 2 PEAK SHAPE AND PEAK AMPLITUDE FOR CONSTANT SLIT WIDTH Sc, CONSTANT BEAM INTENSITY Ib, AND VARYING BEAMWIDTH Bf.

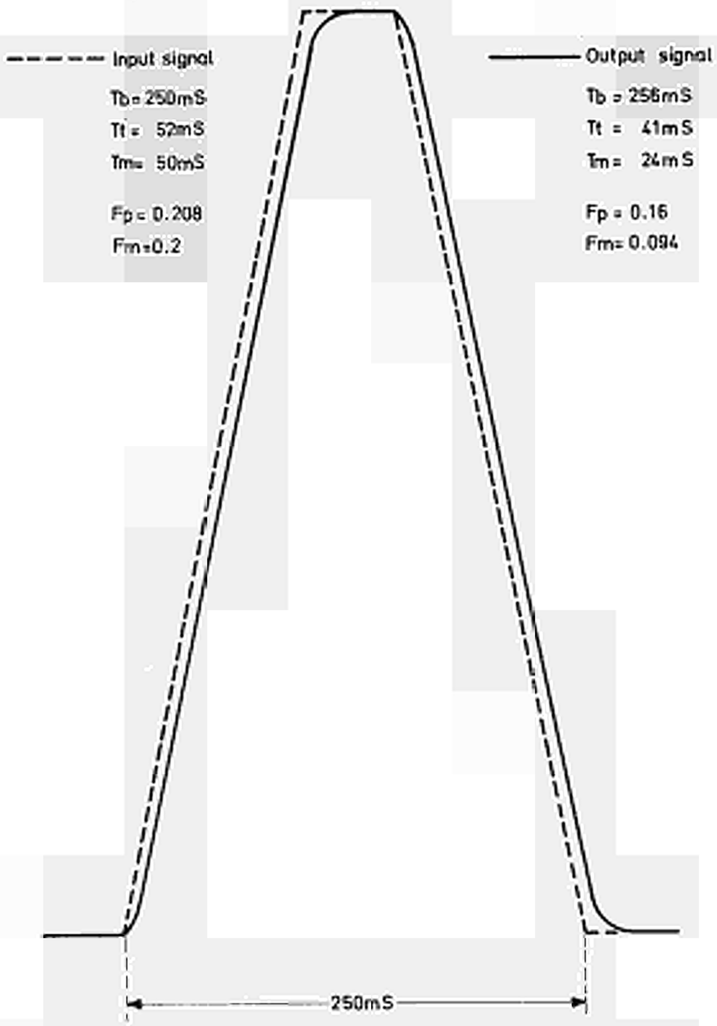

Fig.3 EXAMPLE OF PEAK SHAPE DISTORTION AT HIGHER SCAN-RATES FOR AN AMPLIFIER TIME CONSTANT OF 6.5mS.

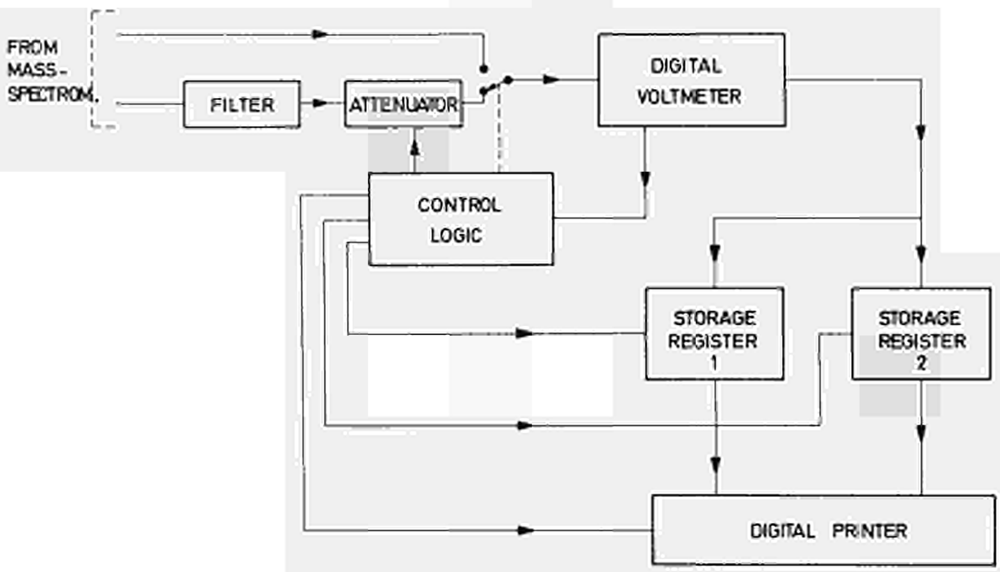

Fig. 4 BLOCK DIAGRAM - MASS SPECTRUM DIGITIZER.

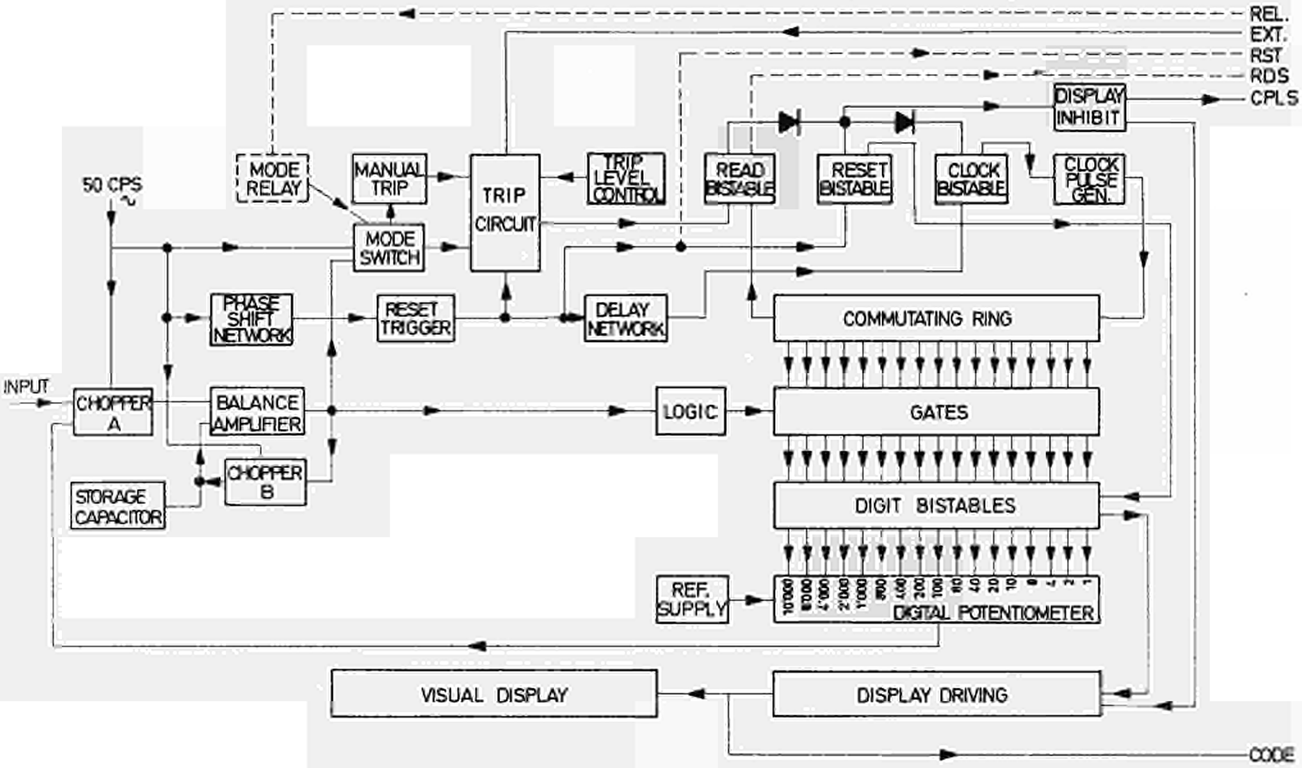

Fig. 5 SIMPLIFIED BLOCK DIAGRAM OF THE DIGITAL VOLTMETER.

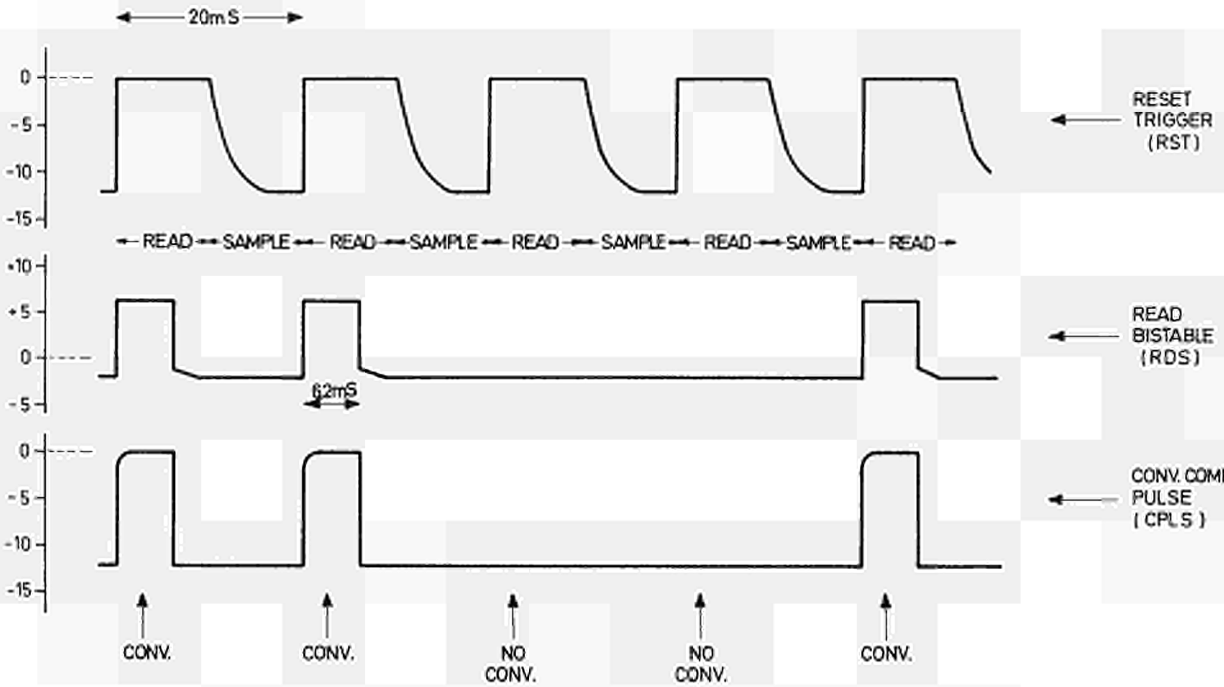

Fig. 6 TIMING OF CONTROL SIGNALS IN DIGITAL VOLTMETER.

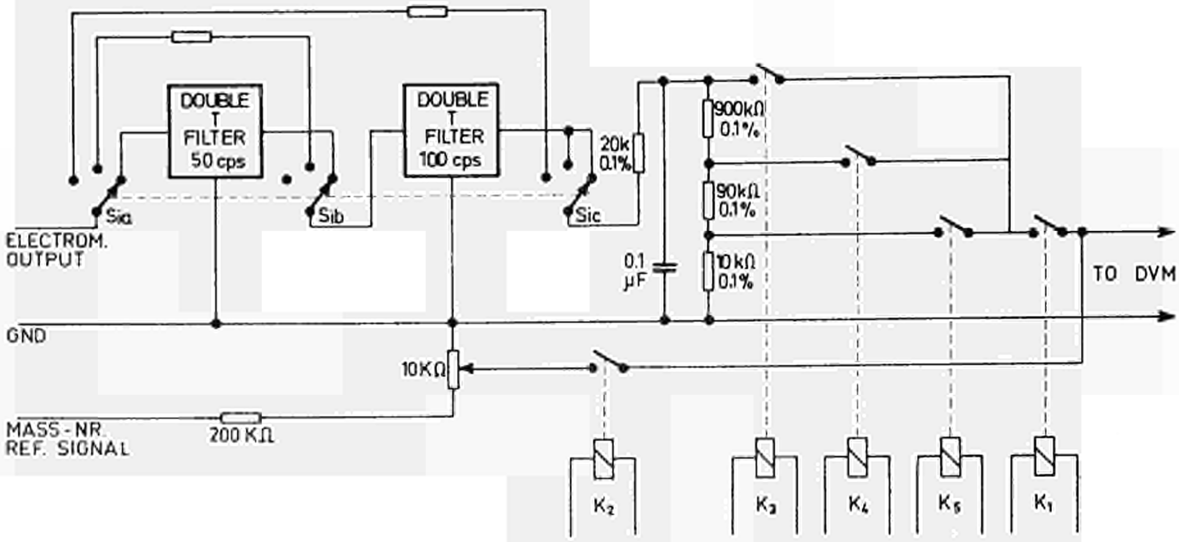

Fig. 7 CONTROL-UNIT INPUT CIRCUIT.

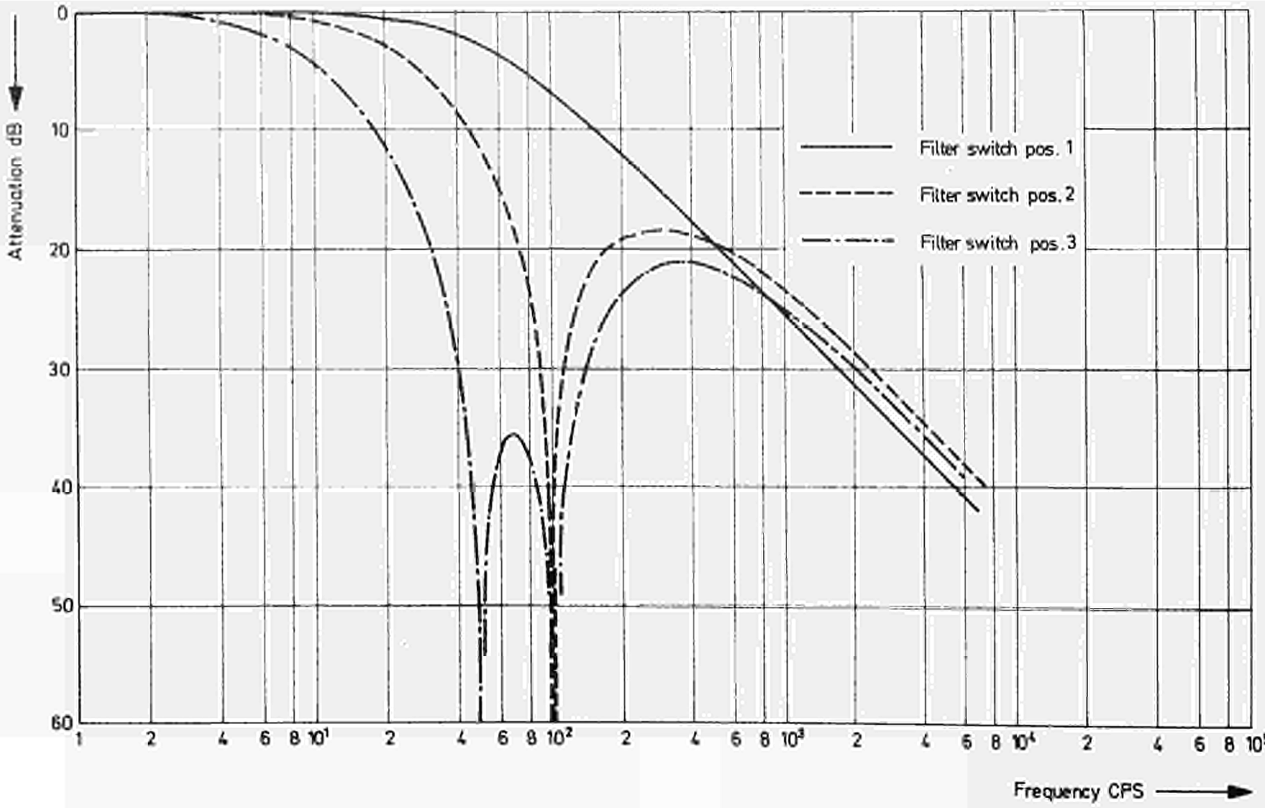

Fig. 8 FREQUENCY RESPONSE OF THE INPUT FILTER

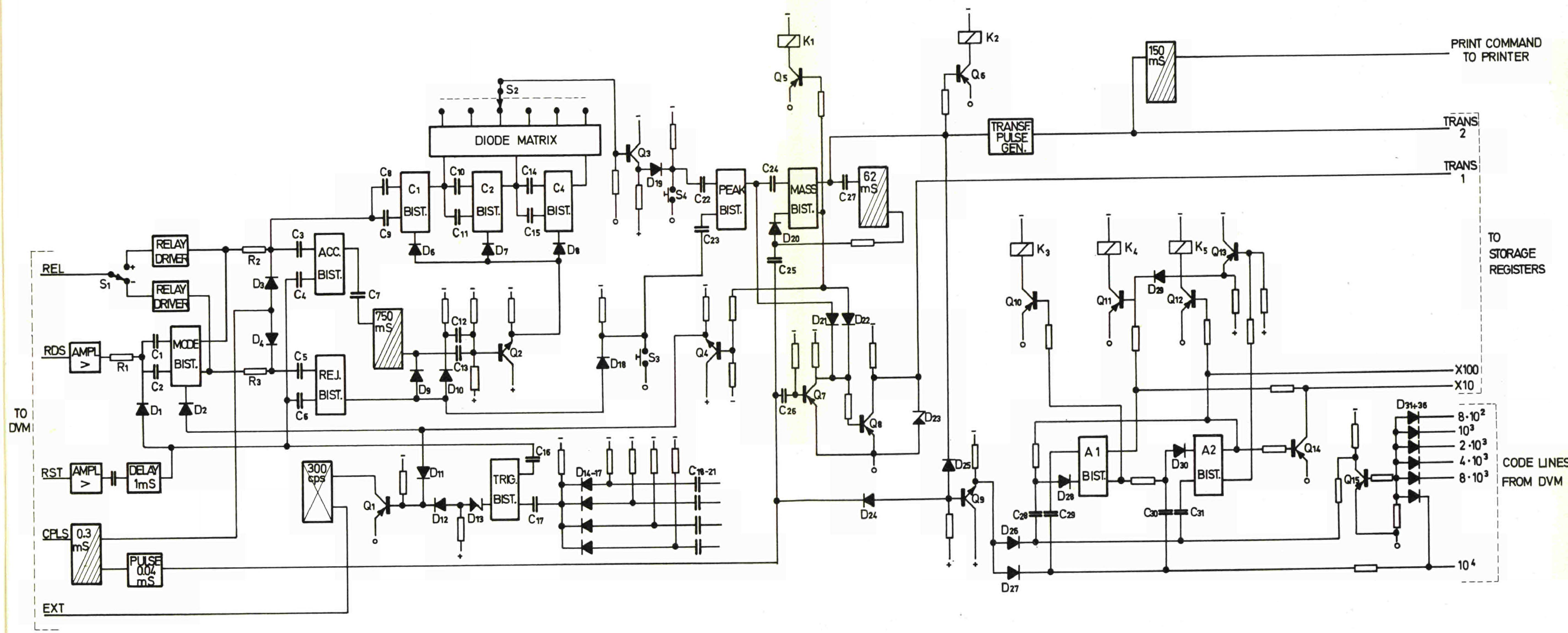

Fig. 9 SIMPLIFIED CIRCUIT DIAGRAM OF THE CONTROL-LOGIC

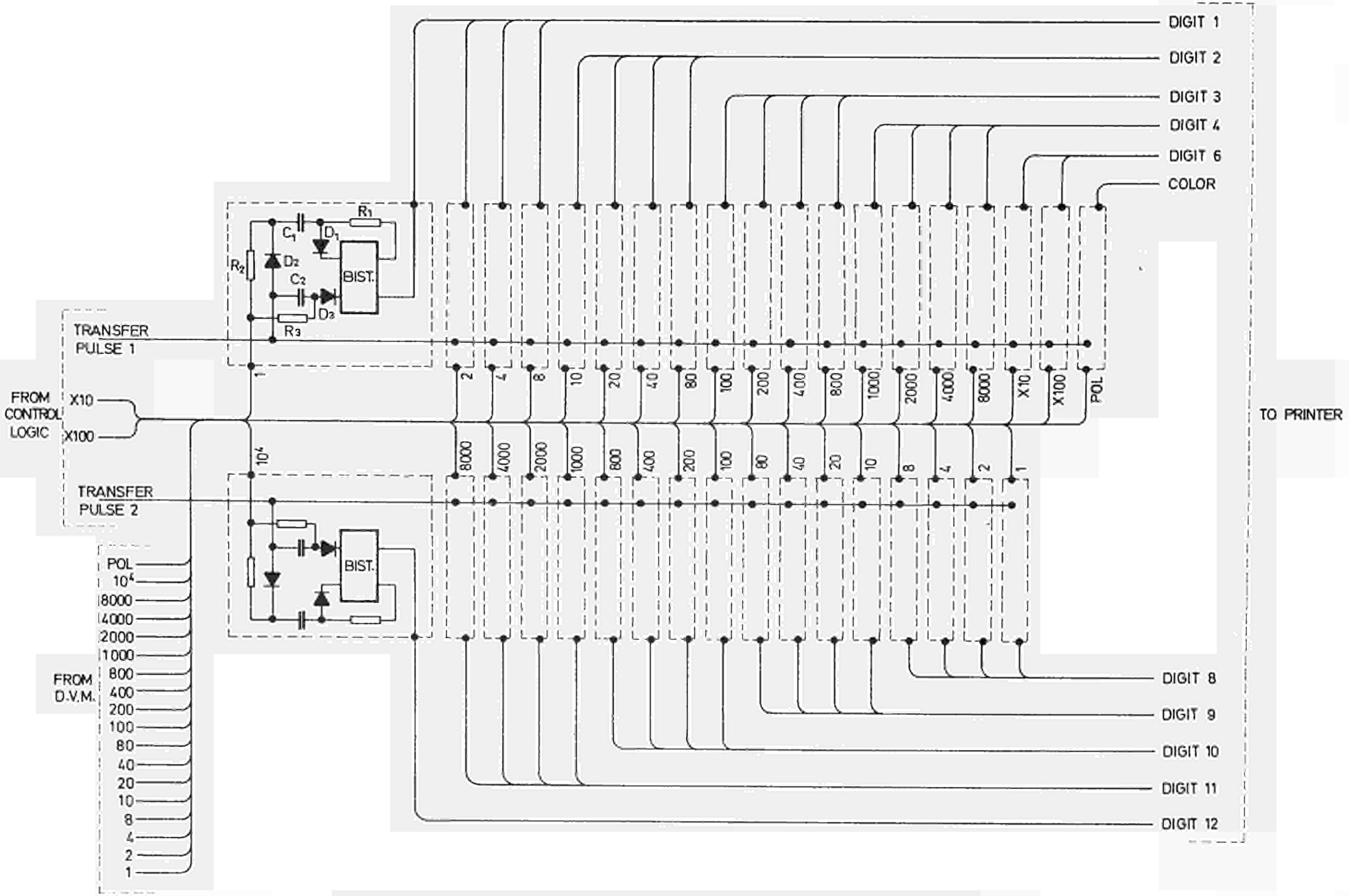

Fig. 10 SIMPLIFIED CIRCUIT DIAGRAM OF THE STORAGE REGISTERS.

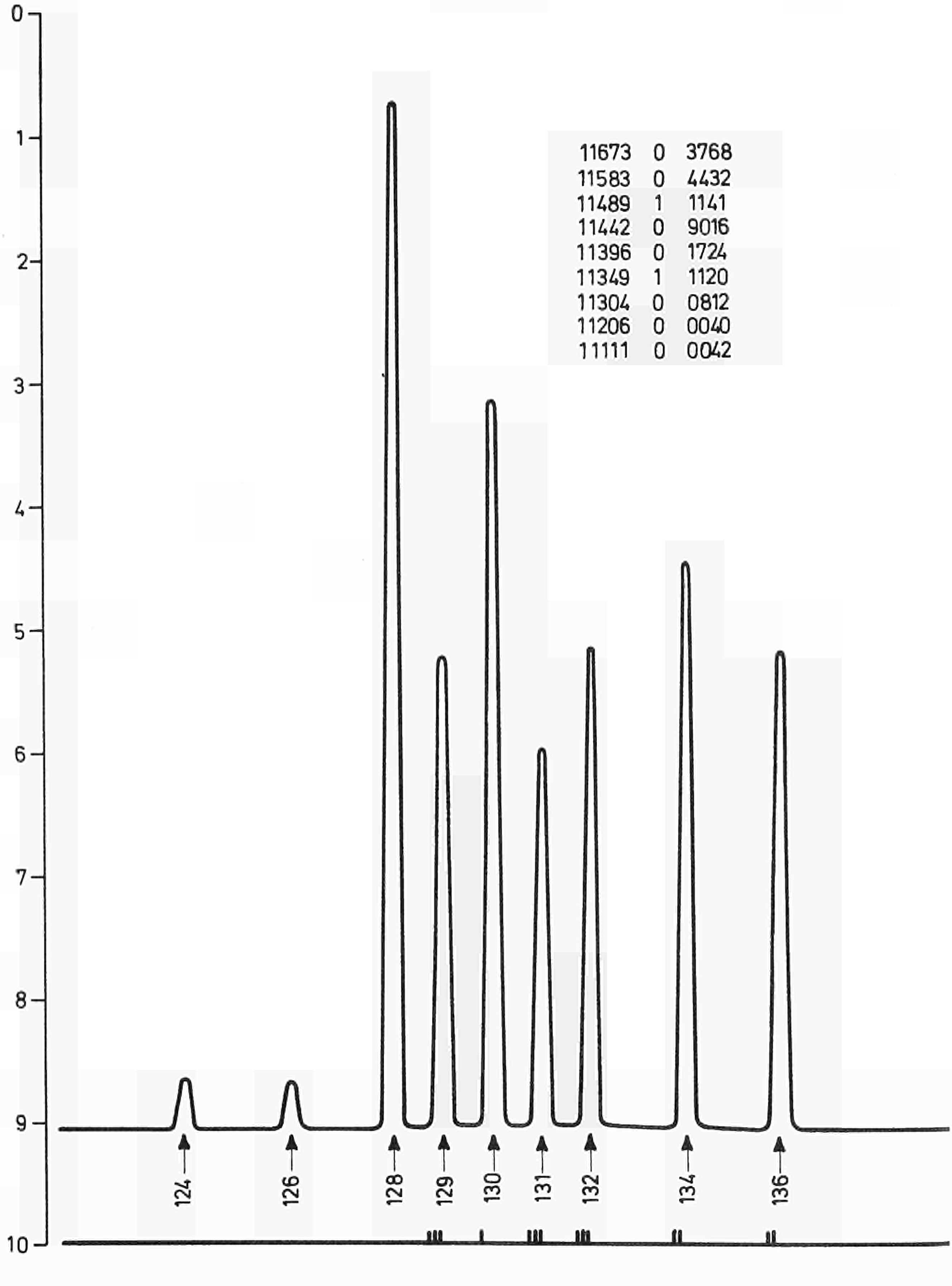

FIG.11 DIGITAL AND ANALOG RECORD OF A SPECTRUM.
(XENON MASS 124 TO 136, SCAN-RATE 3.2.10^{-3} OCT/SEC)

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To disseminate knowledge is to disseminate prosperity — I mean general prosperity and not individual riches — and with prosperity disappears the greater part of the evil which is our heritage from darker times.

Alfred Nobel

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