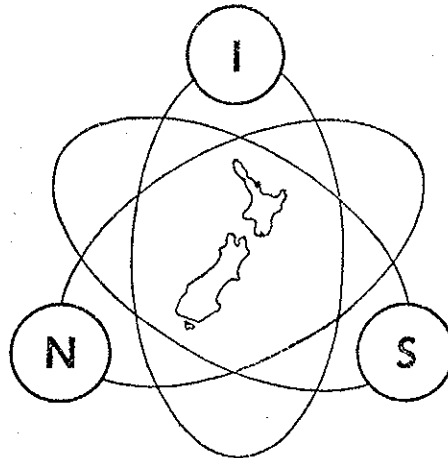


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# AUTOMATIC ATMOSPHERIC CO<sub>2</sub> MONITORING EQUIPMENT

By  
D. C. LOWE



May 1972

**INSTITUTE OF NUCLEAR SCIENCES**

Department of Scientific and Industrial Research

LOWER HUTT, NEW ZEALAND

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AUTOMATIC ATMOSPHERIC CO<sub>2</sub> MONITORING  
EQUIPMENT

D.C. Lowe

Contribution No. 551

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two stage pressure regulators and  $\frac{1}{8}$ " O.D. stainless steel tubing (see fig. 2).

The types of reference gases used are -

- 1) WORKING TANK (WT) with a CO<sub>2</sub> concentration about the same as that of atmospheric air, i.e., 320 ppm of CO<sub>2</sub>.
- 2) HIGH SPAN (HS) with a CO<sub>2</sub> concentration about 10 ppm above that of atmospheric air, i.e., 330 ppm of CO<sub>2</sub>.
- 3) SECONDARY STANDARD (SEC) with a CO<sub>2</sub> concentration about 10 ppm below that of atmospheric air, i.e., 310 ppm of CO<sub>2</sub>.
- 4) PRIMARY STANDARD (PRI) with a CO<sub>2</sub> concentration of about 310 ppm of CO<sub>2</sub>.

The reference gases used in New Zealand have their CO<sub>2</sub> concentrations determined in a standards laboratory at Scripps (P.R. Guenther, Scripps Internal Report). They are shipped out to New Zealand at a pressure of 2100 p.s.i. used on the equipment down to 400 p.s.i. and shipped back to Scripps for a final analysis in the standards laboratory.

Working tanks are used in New Zealand at the rate of one a month. Each time a working tank at 400 p.s.i. is exchanged for a new one, comparisons of the old and new working tank are made with the primary standard in a series of calibration cycles (see section 3.4).

All comparisons of the reference gases as well as the Scripps analyses are used to determine a final concentration "index" for the reference gases. Concentration drift with time of the reference gases may also be taken into account.

The final concentration figures for reference gases are used to determine the concentrations of the atmospheric CO<sub>2</sub> measurements made while each reference gas was in use.

#### 3.4 Gas sampling system

Use of the infra-red gas analyser to measure atmospheric CO<sub>2</sub> concentrations requires continual comparisons of the air against reference gas mixtures. This is done by using 24 V.D.C. gas solenoid valves to control the flow of air or reference gases through the analyser (see fig. 2). The flow rate of air or gases is regulated by manual metering valves and a flow meter on the exhaust side of the analyser. The flow rate of each of the reference gases and of air is set at 0.8 l/m by the position of the metering valves.

the earth's surface, however, is predominantly infrared and atmospheric carbon dioxide partially absorbs this in the absorption band at 13-17 micron. The subsequent raising of the atmospheric temperature is known as the "Greenhouse Effect".

Callender (1938, 1940, 1949) suggested that a rise in atmospheric carbon dioxide could account for the observed slight increase in the temperature of the northern hemisphere during the period 1890 — 1940. Calculations made by Plass (1955), using the known infrared absorption bands of carbon dioxide, showed that a 10% increase in atmospheric carbon dioxide would increase the earth's mean temperature by  $0.35^{\circ}\text{C}$ . Moller (1963) showed that Plass' calculations were valid only for a dry atmosphere and that the overlapping of the carbon dioxide and water absorption bands in the 15 micron region essentially diminished any temperature changes.

Since the heat capacity of the oceans and atmosphere is very large, rapid changes in temperature and climate are impossible. However, over several hundreds of years (still short when compared with geological time scales) even a minute temperature change could significantly alter the earth's present climatic conditions probably causing substantial melting of the polar ice caps with a subsequent rise in sea level. A comparison of the  $200^{\circ}$ - $300^{\circ}\text{C}$  surface temperatures of Venus with the earth's surface temperatures shows the importance of the greenhouse effect in a carbon dioxide laden atmosphere.

The importance of the greenhouse effect on the temperature of the earth's atmosphere has not been established, however. Before any conclusions can be made the true rate of increase of atmospheric carbon dioxide in the earth's atmosphere must be found.

A series of accurate measurements of atmospheric  $\text{CO}_2$  concentrations were begun in the International Geophysical Year at Mauna Loa Observatory, Hawaii. These measurements have continued to the present date and the increase and seasonal variations of atmospheric  $\text{CO}_2$  at this site have been well documented (Pales and Keeling, 1965).

Similar measurements have not been made in the mid-latitudes of the Southern Hemisphere, however. The southern Pacific Ocean in the "roaring forties" wind belt is believed to be a major sink for atmospheric  $\text{CO}_2$ . Also, as most of the industrial and natural sources of atmospheric  $\text{CO}_2$  are in the Northern Hemisphere, atmospheric  $\text{CO}_2$  concentration gradients exist between the hemispheres. This makes it difficult to determine the rate

of increase of  $\text{CO}_2$  in the atmosphere as a whole.

Measurements of atmospheric  $\text{CO}_2$  in New Zealand in conjunction with atmospheric  $\text{CO}_2$  measurements at other latitudes will assist in determining the rate of increase of  $\text{CO}_2$  in the atmosphere. New Zealand atmospheric  $\text{CO}_2$  measurements will also provide a basis for determining solutions to the boundary value problem for meridional carbon dioxide exchange

$$\nabla_K^2 q + Q = \frac{\partial q}{\partial t}$$

where  $q$  is the concentration of atmospheric  $\text{CO}_2$

$Q$  represents sources and sinks of  $\text{CO}_2$ .

In 1969 continuous atmospheric  $\text{CO}_2$  measurements were begun at Makara, New Zealand, as a joint undertaking by the New Zealand Institute of Nuclear Sciences and Scripps Institution of Oceanography, California.

This report contains a description of the techniques and equipment used in the automatic atmospheric  $\text{CO}_2$  monitoring equipment at Makara.

## 2. SUMMARY OF NEW ZEALAND ATMOSPHERIC $\text{CO}_2$ EQUIPMENT

As long-term measurements of atmospheric  $\text{CO}_2$  in remote locations are required, automatic equipment having a large data storage capacity and requiring little maintenance is needed.

The most convenient  $\text{CO}_2$  analysis equipment has been found to be an analyser of the non-dispersive infra red type. This type of analyser lends itself readily to automatic calibration and sampling and requires only a small amount of maintenance to keep it 100% operational.

Data logging is performed using an incremental magnetic tape recorder with a potentiometric chart recorder as a back-up system. Digital techniques are used to prepare the data for magnetic tape recording. This allows large amounts of data to be stored with high precision. The data is quickly retrieved from the magnetic tapes and worked up using a computer. In the system used at Makara a  $\frac{1}{2}$ " 1,200-ft long magnetic tape is capable of storing two weeks of wind speed, wind direction, and atmospheric  $\text{CO}_2$  concentration data.

### 3. INSTRUMENTATION AND TECHNIQUES

#### 3.1 Introduction

A block diagram of the automatic CO<sub>2</sub> monitoring equipment is shown in figure 1.

The air whose CO<sub>2</sub> concentration is to be measured is pumped from the sample mast inlet via the air line to the gas sampling system. Reference gas mixtures of CO<sub>2</sub> and N<sub>2</sub> are also coupled to the gas sampling system. The flow of a reference gas or air from the gas sampling system into the infra-red analyser is controlled by the operation of a programmable diode matrix panel and a stepping switch. Selection of appropriate diode plugs on the matrix panel enables any desired sequence of gases to flow from the gas sampling system to the analyser. Before entering the analyser the gas or air stream is passed through a water vapour freeze out trap maintained at -40°C by a portable freon freezer plant.

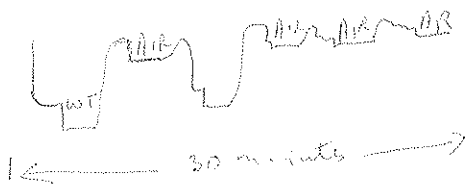
The output of the analyser is connected to a 5 mv. potentiometric chart recorder and to a voltage to frequency converter. The output of the converter is applied to an up-down counter in the digital interface where it is integrated over any desired time interval and stored. The digital interface then commands the tape recorder to record the stored data with a channel identifying code and time. Wind speed and direction data is also recorded on magnetic tape.

#### 3.2 Air sampling

The CO<sub>2</sub> equipment air sampling intake is attached with a recording cup anemometer and wind direction vane, to the top of a 15 metre high radiomast. A polyethylene air line with an inside diameter of 6 mm is used to transfer air from the sample mast to the equipment. The air line is protected against the sun's rays and against chafing by an outer sheath of heavy, opaque, plastic hose. Air is pumped through the air line at 0.8 l/m by a Neptune model 4K neoprene diaphragm pump and directed into the analyser or vented as required by the operation of the gas sampling system (see figure 2).

#### 3.3 Reference gases

Routine use and calibration of the analyser is performed with a series of reference gas mixtures of CO<sub>2</sub> and N<sub>2</sub>. The mixtures are stored in steel gas cylinders at 150 atmospheres and coupled to the gas sampling system via



The selection of reference gases and air from the gas sampling system is controlled in a series of 1/2-hour cycles by the diode matrix panel and stepping switch. Two kinds of cycles may be initiated automatically.

- 1) A normal or air measurement cycle;
- 2) a reference gas or calibration cycle.

1) Air measurement cycle. In this mode the diode matrix panel is set up so that the gas sampling system solenoid valves perform the following sequence of operations in each 30-minute cycle.

Minute of cycle	Gas Sampling System Operation	Analyser
↑ A ↓	1 - 3 Solenoid S <sub>2</sub> energised and WT flows at 0.8 l/m through analyser measurement cell	Measurement cell flushed with WT gas
↑ ↓	2 - 5 S <sub>2</sub> de-energised and WT flow stops	Measurement cell is now filled with WT gas at atmospheric pressure. Readings of analyser output are taken for 2 minutes
↑ B ↓	5 - 8 Solenoid S <sub>1</sub> energised and AIR flows at 0.8 l/m through the analyser measurement cell	Measurement cell flushed with AIR
↑ ↓	8 - 10 S <sub>1</sub> de-energised and AIR flow stops	Measurement cell is now filled with AIR at atmospheric pressure. Readings of analyser output taken for 2 mins.
↑ C ↓	10 - 13 13 - 15	A above is repeated
↑ D ↓	15 - 18 18 - 20	B above is repeated
↑ E ↓	20 - 23 23 - 25	B above is repeated
↑ F ↓	25 - 28 29 - 30	B above is repeated. The cycle resets at minute 30 and all the above operations are repeated cycle by cycle until a calibration cycle occurs.



2) Calibration cycle. In this mode the diode matrix panel is set up so that the gas sampling system solenoid valves perform the following sequence of operations.

	Minute of cycle	Gas Sampling System Operation	Analyser
A	1 - 3	Solenoid S <sub>2</sub> is energised and WT gas flows at 0.8 l/m through the analyser measurement cell	Measurement cell flushed with WT gas
	3 - 5	Solenoid S <sub>2</sub> de-energised and WT gas flow stops	Measurement cell is now filled with WT gas at atmospheric pressure. Readings of the analyser output are taken for 2 minutes
B	5 - 8	Solenoid S <sub>3</sub> is energised and SEC gas flows at 0.8 l/m through the analyser measurement cell	Measurement cell flushed with SEC gas
	8 - 10	Solenoid S <sub>3</sub> is de-energised and SEC gas flow stops	Measurement cell is now filled with SEC gas at atmospheric pressure. Readings of the analyser output are taken for 2 minutes
C	10 - 13	A above is repeated	
	13 - 15		
D	15 - 18	Solenoid S <sub>4</sub> is energised and HS gas flows at 0.8 l/m through the analyser measurement cell	Measurement cell is flushed with HS gas
	18 - 20	Solenoid S <sub>4</sub> is de-energised and HS gas flow stops	Measurement cell is now filled with HS gas at atmospheric pressure. Readings of the analyser output are taken for 2 minutes
E	20 - 23	B above is repeated	
	23 - 25		
F	25 - 28	D above is repeated	
	28 - 30		

The initiation of the air measurement and the calibration cycles is completely automatic. Air measurement cycles are run continuously except for twice daily calibration cycles which are run from 1000 - 1030 and 2000 - 2030. Calibration cycles are initiated either manually by the closing of a switch on the diode matrix panel, or automatically by the 1000 hour and 2000 hour pulses from the digital clock in the interface.

### 3.5 Diode matrix panel and stepping switch

The matrix panel consists of 10 rows and 30 columns of sockets, the tip connections of which are joined along each row and the base connections of which are joined along each column (see fig. 3). The column leads are connected sequentially to the peripheral contacts of a stepping switch. The armature of the stepping switch is driven by one-minute pulses from the digital clock and advances by one column per pulse. A reset line is provided on the 30th column to automatically return the stepping switch to the first column. As the stepping switch rotates each of the columns has +24 V.D.C. applied to it for one minute. The resetting of the stepping switch is synchronised with the digital clock to provide the  $\frac{1}{2}$ -hour cycles for the gas sampling system.

The rows of the matrix are coupled to the gas solenoid valves and the tape recorder enable. The insertion of a diode plug into a socket enables the solenoid in that row to be energised when the stepping switch applies 24 V.D.C. to the appropriate column. By inserting the appropriate diode plugs the air measurement and calibration cycles described in section 3.4 are programmed onto the diode matrix panel. This enables the stepping switch to energise and de-energise the gas solenoid valves in the desired sequence.

### 3.6 Infra-red gas analyser

The instrument used to measure atmospheric CO<sub>2</sub> concentrations is a non-dispersive infra-red gas analyser model URAS 1 Hartmann and Braun Instruments Limited, West Germany.

The analyser consists of two gold plated cylindrical gas sample cells through which mechanically chopped infra-red radiation from a pair of nernst filaments is passed. Emergent radiation from the cell is detected by a pneumatic infra-red detector of the Golay type (Potter and Eisenmann, 1962). As CO<sub>2</sub> strongly absorbs radiation in several infra-red bands the intensity of the emergent radiation is a function of the CO<sub>2</sub> concentration of the gases contained in the sample cells. The A.C. output of the

detector is applied to the first stage of a high gain amplifier incorporating a twin T feedback network tuned to the analyser chopper frequency. After being rectified and filtered the amplifier output is connected to a 5 mV potentiometric chart recorder and to a voltage to frequency converter used to digitise the analyser signals. The output of the analyser's amplifier is proportional to the difference in the CO<sub>2</sub> concentrations of the gases contained in the two cells. One of the cells was filled with a N<sub>2</sub>, CO<sub>2</sub> gas mixture containing about 300 ppm by volume of CO<sub>2</sub> and sealed. The analyser is used by alternately flushing working tank reference gas and air through the other cell (analyser measurement cell). This enables the air CO<sub>2</sub> concentration to be continually measured with respect to a known reference CO<sub>2</sub> concentration level (working tank reference gas lineout level).

To prevent interference to the CO<sub>2</sub> analysis caused by the overlapping of water vapour and CO<sub>2</sub> infra-red spectral bands, water vapour is frozen out of the analyser gas stream. This is done with a stainless steel cold trap maintained at -40°C by a portable freon freezer plant. This leaves the analyser air stream with a residual water vapour concentration of 200 ppm V. As the dry reference gases are also passed through the water vapour freezer trap their residual water vapour concentration becomes the same as that of the analyser air stream. This enables the analyser to compare the air and reference gases on the basis of their CO<sub>2</sub> concentrations alone. Comparisons of reference gas measurements always produce results consistent to better than 0.1 ppm by volume of CO<sub>2</sub> when compared with the concentrations assigned to the reference gases by laboratory analysis at Scripps.

### 3.7 Freezers and cold traps

The stainless steel cold traps used on the equipment are maintained at -40°C by portable freon freezer plants. Two freezers with cold traps are used and operated on a week-on week-off basis. After a week in service, freezer number 1 is removed from the system and replaced with freezer number 2. (Quickfit 1/4" Swagelok fittings are used to facilitate replacement and removal.) After removal from the system, a cap on the bottom of cold trap number 1 is removed thus allowing accumulated ice to thaw and fall from the trap.

After freezer number 2 has been in service for a week, the cap on freezer cold trap number 1 is replaced, the freezers are exchanged and the above process is repeated with freezer number 2.

After two months of routine service, compressed air is used to remove dust from the freezers' heat exchangers.

### 3.8 Digital interface and incremental magnetic tape recorder

3.8-1 Capabilities. The digital data logging system used provides simultaneous data logging facilities for five independent data inputs. The data is recorded as a six digit decimal number along with identifying channel numbers, a polarity sign and the time at which the data was taken. The time for which any particular data input is sampled can be selected manually. The final six digit number (N) recorded on the tape after the specified sample time (T) is complete, is the time integral of the data input signal (g(t)), taken over the specified time interval,

$$\text{i.e., } N = \int_0^T g(t) dt$$

Provision is also made for recording the date on which data is taken and this is recorded automatically every minute in the form of a day number (e.g., 1 February = DAY 032).

3.8-2 Component parts and mode of operation. Figure 4 shows the basic component parts (in block form) and sequence of operations of the data logger.

Voltage to frequency converters: These are used to convert the analogue voltage signals from the data inputs to a series of 5 V pulses compatible with the digital logic of the interface. The frequency of the pulses is directly proportional to the voltage signal from the data input.

The converter used on the analyser output is a Newport Laboratories C1580.

The voltage to frequency converters used on the wind equipment are voltage controlled as table multivibrators - one for the east-west component of the wind velocity and one for the north-south component of the wind velocity (see fig. 5).

Six digit up-down counters: One of these is provided for each data input (channel). On the receipt of a command from the interface the counter is set to zero and allowed to count the pulses from its voltage to frequency converter (see fig. 6). The count is stopped as soon as the required sample time is reached and the total count is recorded on magnetic tape.

Digital clock: This provides the timing signals for all the operations in the interface as well as the time and day number for each recording (figs 7 and 8).

Unit selecting commutator (U.S.C.): This is an electronic stepping switch which steps around each of the data inputs in turn (fig. 9). If a data input has data ready to record (i.e., the required sample time has been completed) the stepper switch stops and enables a data line containing the six data digits the time and channel identifying codes to be recorded. After recording is complete, the stepper switch continues stepping around the data inputs. When it finds another data input with data waiting to be recorded the above process is repeated.

Character selecting commutator (C.S.C.): This is also an electronic stepping switch and is shown in fig. 10 with the tape recorder control circuitry (digital interface). When the U.S.C. finds data ready to be recorded the C.S.C. begins from character number zero to remove the data character by character from the interface registers. When the C.S.C. selects a character it is directed onto a common data bus leading to the tape recorder and recorded. This process is repeated until all the characters (16) making up a data line are recorded. After the last character (end of line character) has been recorded the C.S.C. resets to zero and waits until the U.S.C. picks another "ready" data channel. As soon as this occurs, the C.S.C. starts up again and records another 16 character data line.

In this manner all the data is recorded on the tape in the form of data lines containing six data digits, time, channel identification and polarity numbers.

Magnetic tape recorder: The recorder used is a Kennedy Incremental magnetic tape recorder model 1600. The tape recorder is used to record standard NRZI incremental characters at the rate of 250 a second, and 200 to the inch.

The four lower tracks on the tape are used to record the characters in 8421 BCD form. The next two tracks, A and B, are used to record special symbols, e.g., polarity sign + or - and end of line character. The seventh track is a parity channel and is maintained even.

3.B-3 Magnetic tape format. The data is recorded in the form of data lines each containing 16 characters. Each character is a single

binary coded decimal number which always corresponds to the same function in every data line recorded. A list of the characters and their functions is shown in table 1. The order shown is the same as the character order of the data line.

The data is automatically split into records containing 16 data lines each by inserting an inter-record gap between records.

To indicate the end of interruption of an experiment, the data can be split into files by manually inserting a file gap.

The hierarchy is as follows:

1 B.C.D. decimal data digit = 1 character; 16 characters = 1 data line; 16 data lines = 1 record; any number of records = a file.

### 3.9 Data manipulations

3.9-1 Magnetic Tape processing. Two main programs (CARB and HAIR) are used to process the carbon dioxide and wind data from the magnetic tapes.

CARB is used first to reduce the magnetic tape data into:-

- i) Hourly averages and standard deviations of counter differences between the analyser air and WT levels;
- ii) two High Span/Working Tank and two Secondary/Working Tank counter differences per calibration cycle (with standard deviations);
- iii) four averages per hour of wind speed and direction.

The reduced data is printed out on an ASR33 Teletype and punched in ASCII code on paper tape.

The second program, HAIR, uses the differences output by the CARB program to compute actual concentrations of atmospheric CO<sub>2</sub>. This is done by computing an average counter scale factor (C.S.F.) in units of  $\frac{\text{ppm}}{\text{count}}$  for two consecutive calibration cycles. This is obtained from the observed High Span/Working Tank counter differences and the analysed High Span and Working Tank CO<sub>2</sub> concentrations.

When the C.S.F. has been computed the hourly average atmospheric CO<sub>2</sub> indices for data taken between the two calibration cycles are computed using:-

$$\text{H.A. CO}_2 \text{ (ppm)} = \text{WT (ppm)} + \text{C.S.F.} \left( \frac{\text{ppm}}{\text{count}} \right) \times \text{HS/WT DIFF (COUNTS)}$$

The final output is -

- i) A series of hourly averages of CO<sub>2</sub> concentration indices with time and day number;
- ii) the average wind speeds and directions from CARB.

3.9-2 Chart processing. In the event of a failure in the digital data logging system atmospheric CO<sub>2</sub> data may also be retrieved from the strip chart.

The computation process is essentially the same as that used with the magnetic tapes with the exception that differences are measured in terms of cms of chart paper, rather than counts. Differences between the air and working tank levels and the calibration cycle differences are entered onto daily log sheets. The air/working tank differences are averaged into hourly differences and these are used to calculate the hourly average atmospheric CO<sub>2</sub> concentrations.

#### ACKNOWLEDGEMENTS

The idea of continuous atmospheric CO<sub>2</sub> measurements by non-dispersive infra-red techniques originated from Dr C.D. Keeling, Scripps Institution of Oceanography, California.

The design of the digital equipment described in this report was by A.E. Bainbridge. The construction of the equipment was undertaken by W.H. Price and R.T. Williams also of Scripps Institution of Oceanography, California.

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Nos 1-11, 1952-1966.



Table 1: Data line characters and respective functions.

Character and C.S.C. number	Function
0	Minutes (tens)
1	Minutes (units)
2	Seconds (tens)
3	Seconds (units)
4	Space
5	Channel number
6	Sub-channel number
7	Space
8	Polarity sign ( $\pm$ )
9	) Most significant digit } Six data digits from } channel picked by } U.S.C. } Least significant } digit
10	
11	
12	
13	) End of line character
14	
15	

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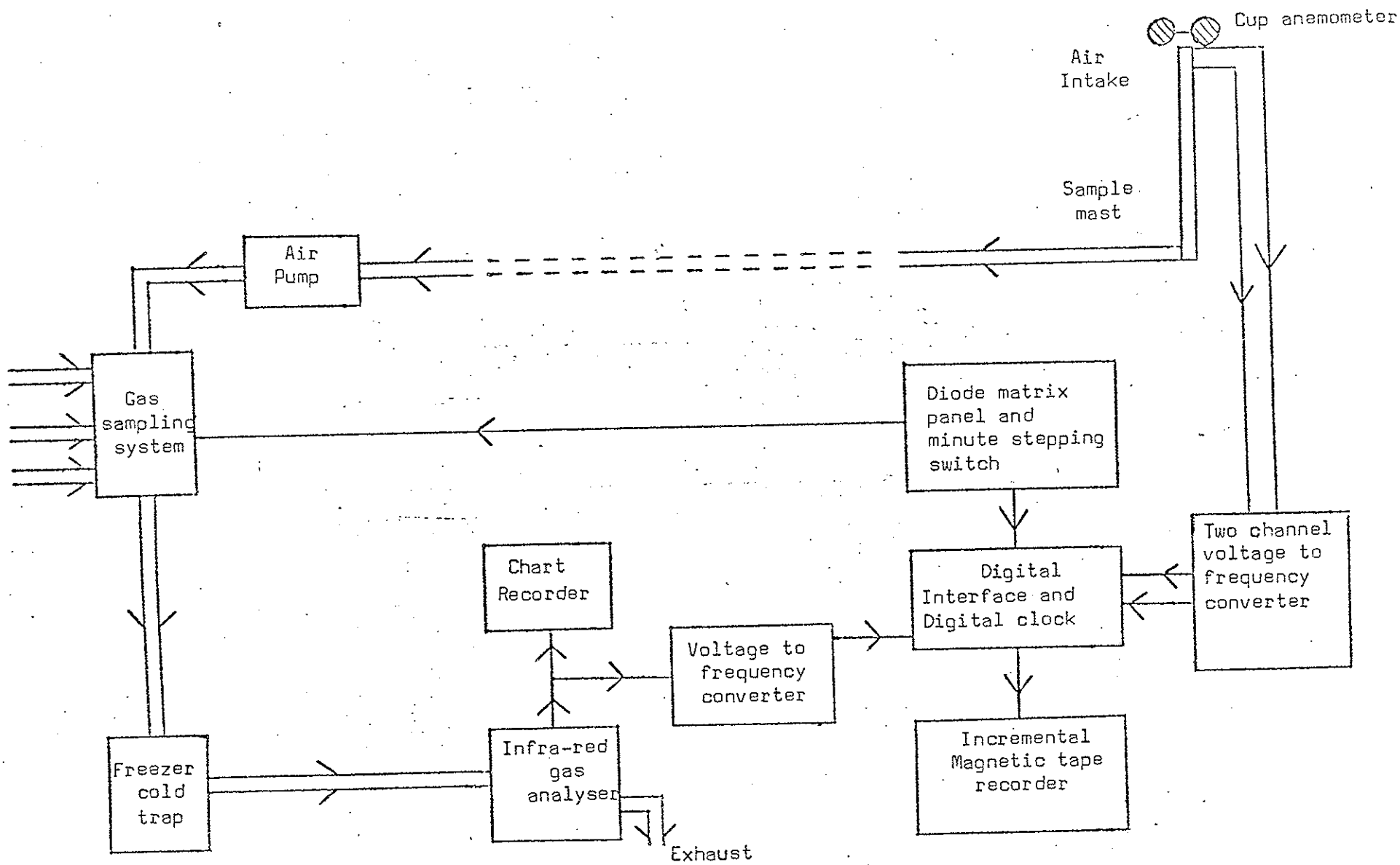


Figure 1. Block diagram of automatic CO<sub>2</sub> monitoring equipment.

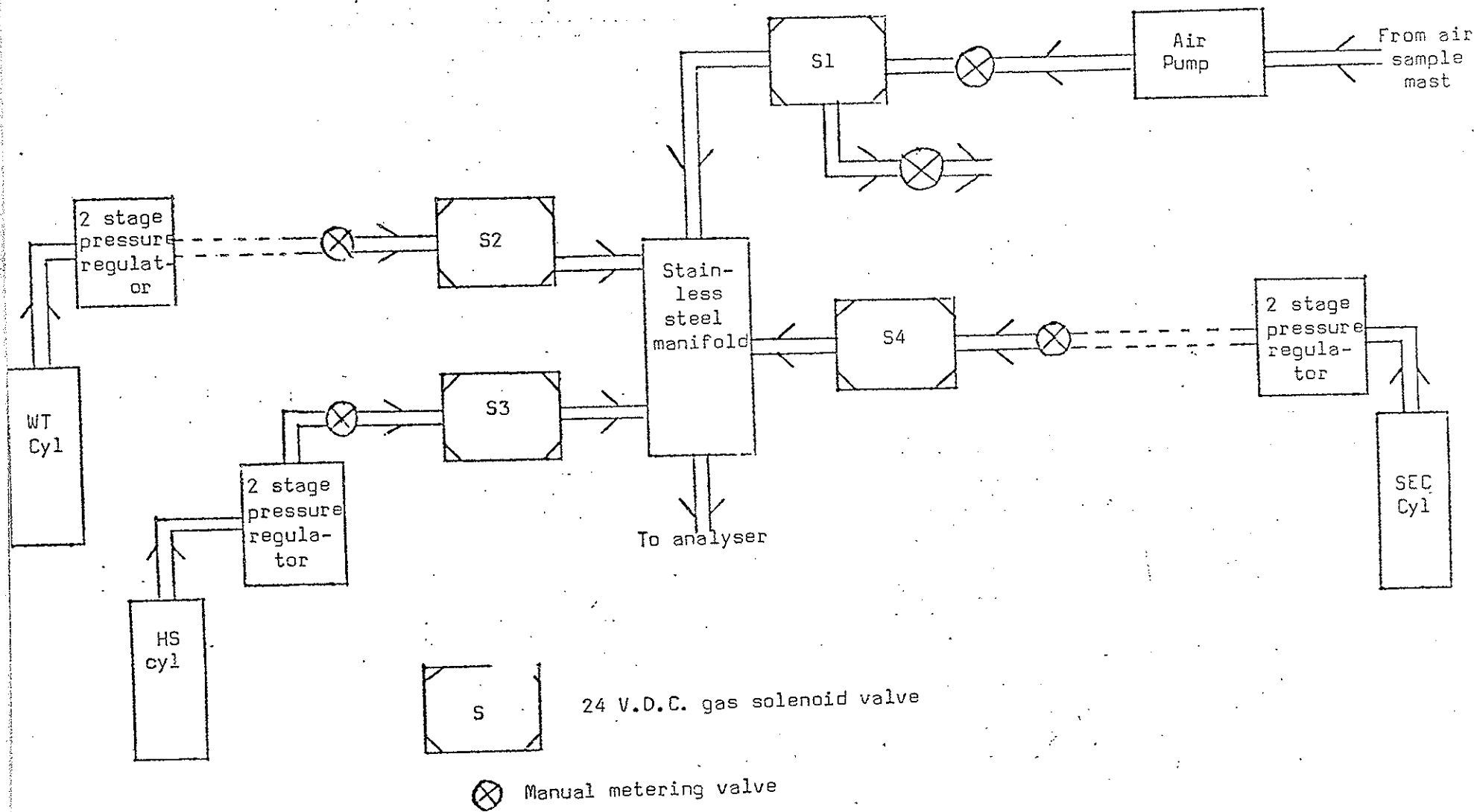
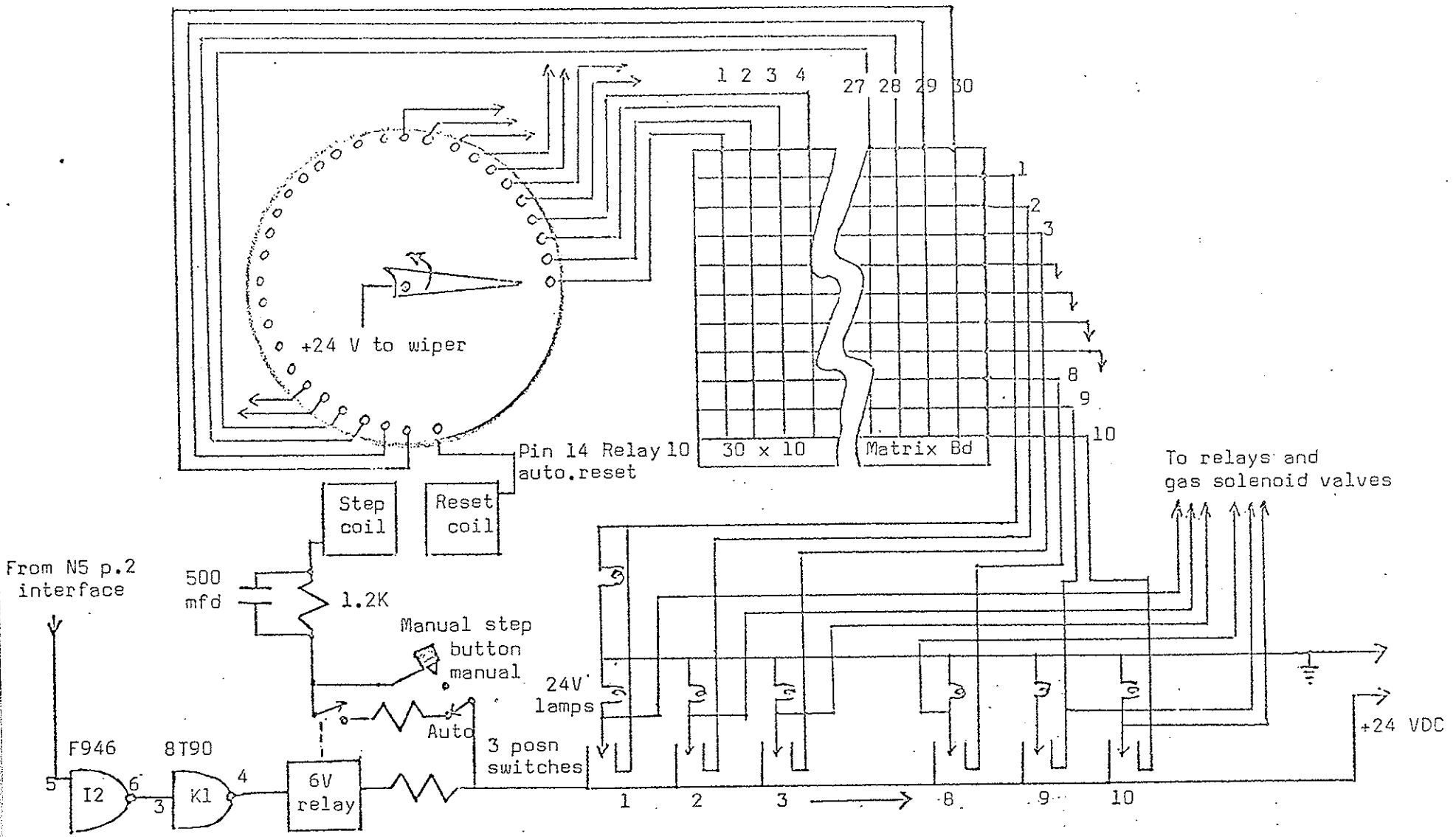


Figure 2. Gas sampling system.

Figure 3. Diode matrix panel and minute stepping switch.



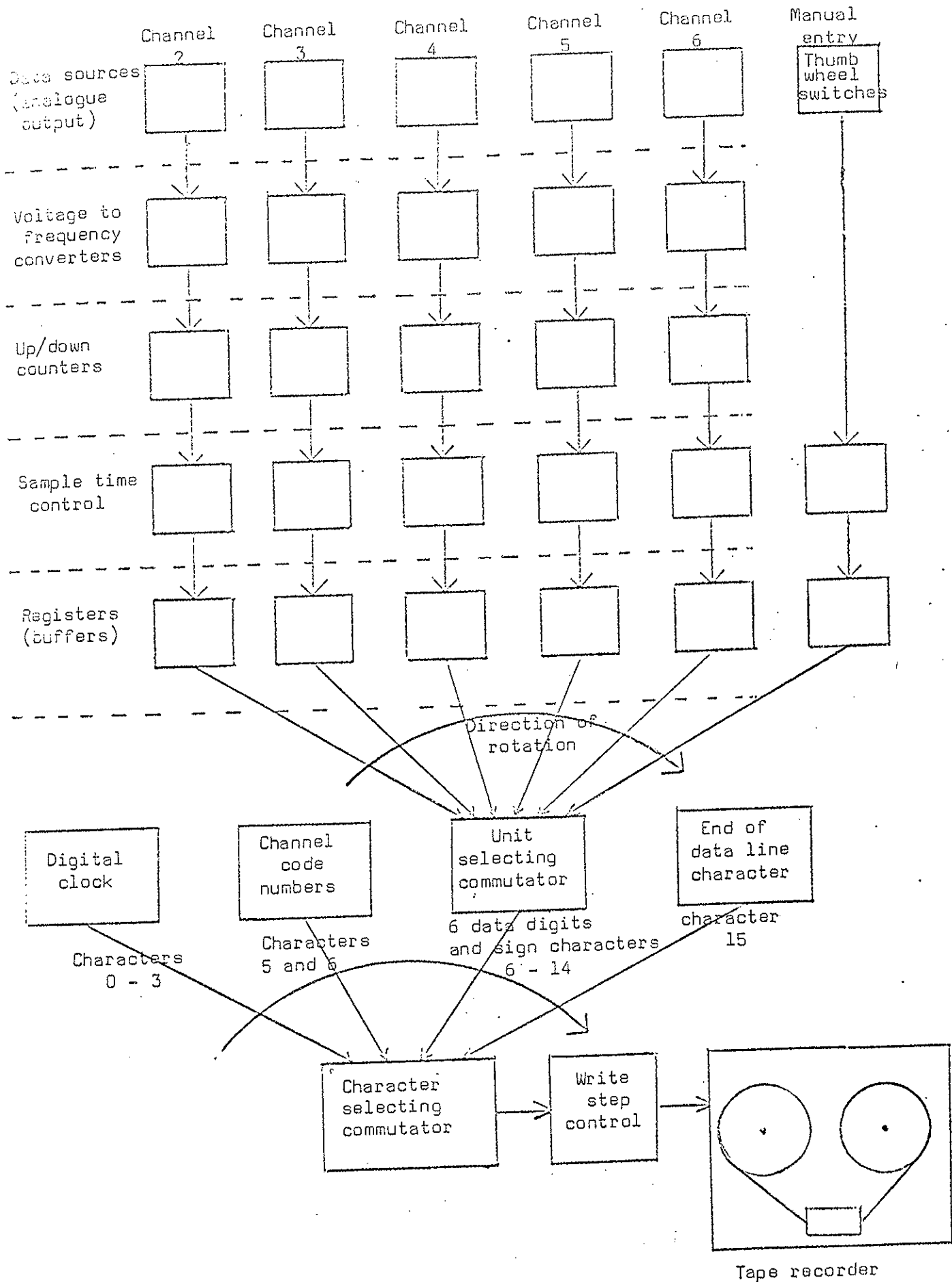
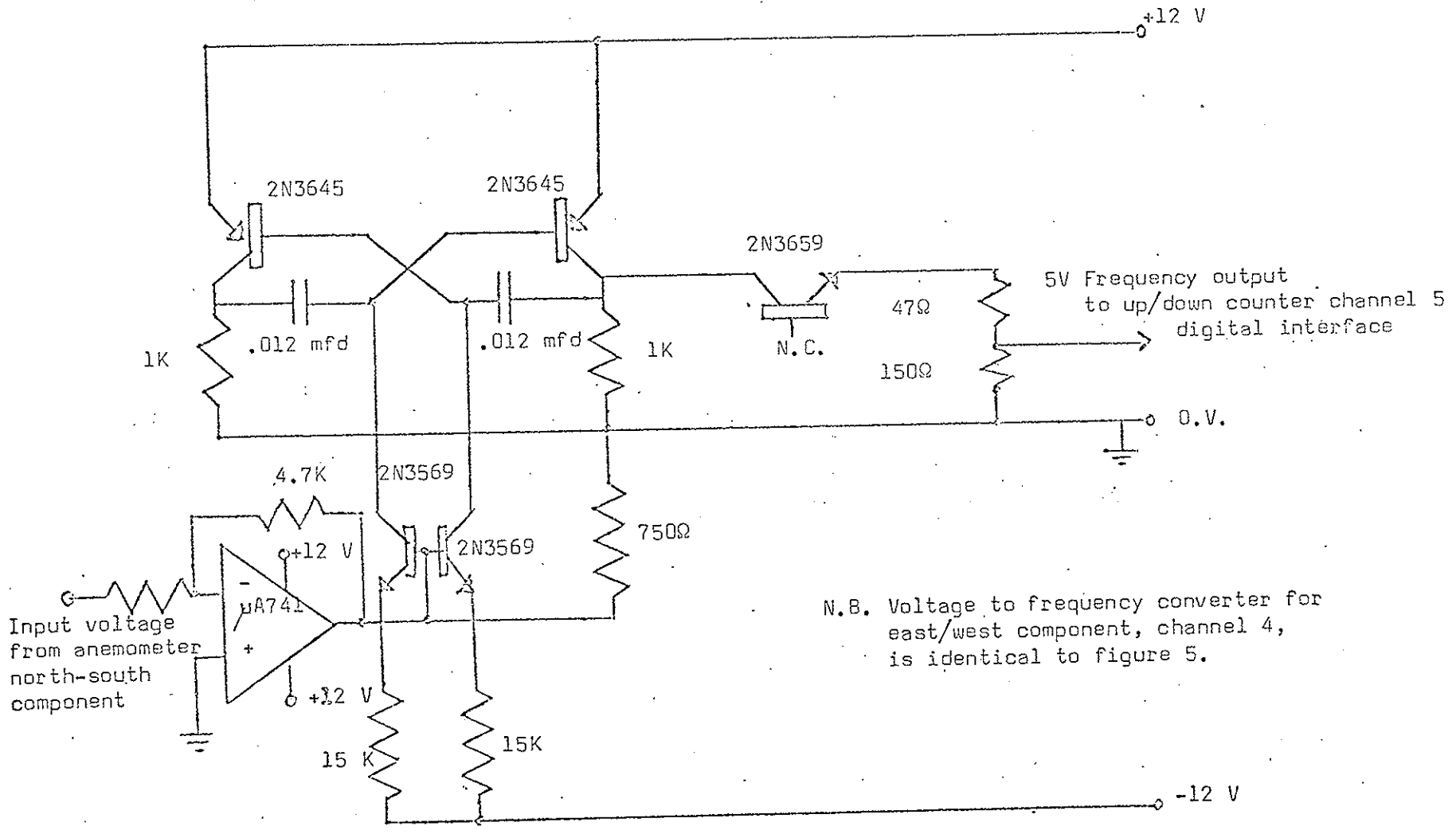


Figure 4. Block diagram of digital data logger.

Figure 5. Anemometer voltage to frequency converter - north-south wind component shown.



N.B. Voltage to frequency converter for east/west component, channel 4, is identical to figure 5.

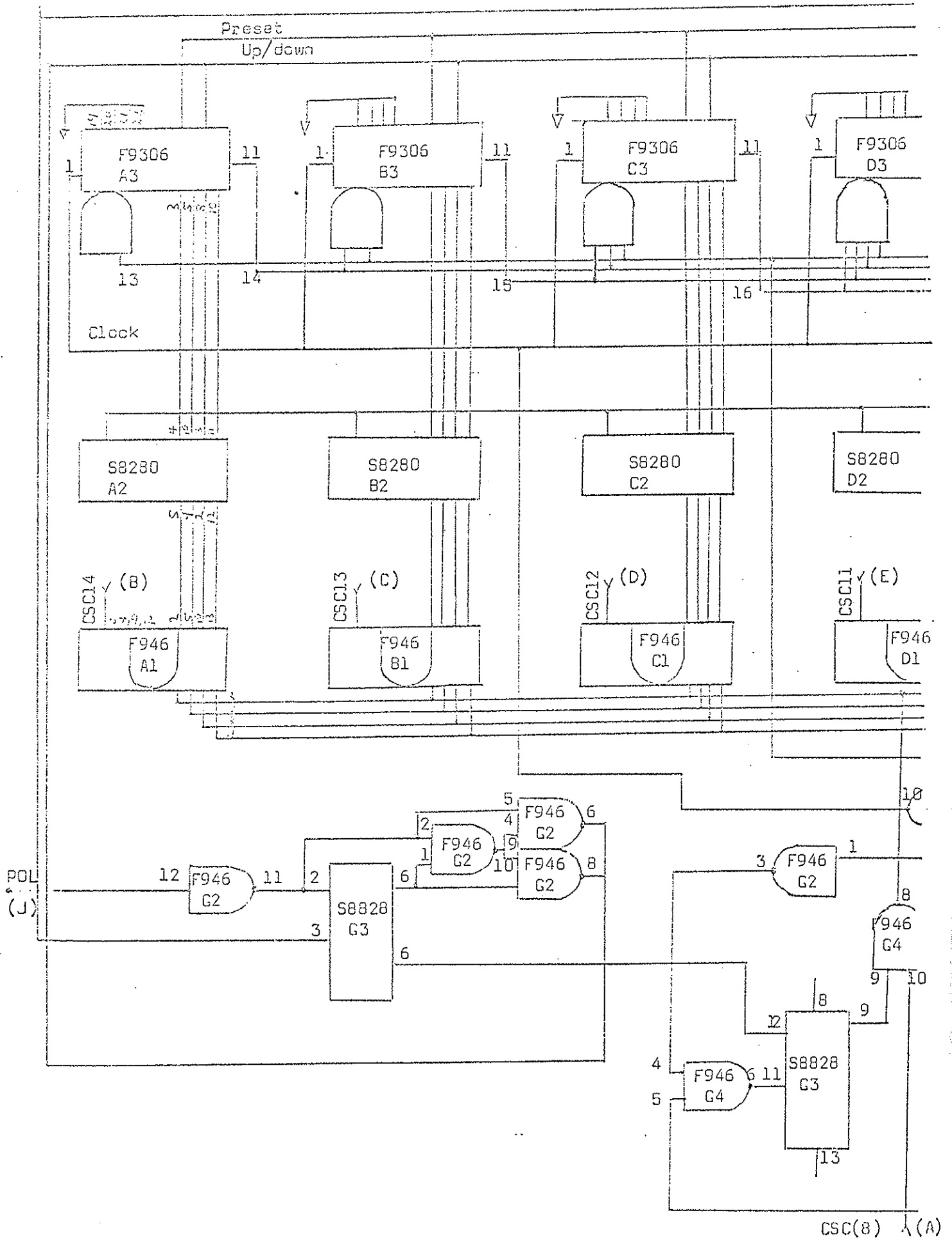


Figure 6A (facing fig. 6B).  
Digital up/down counter.



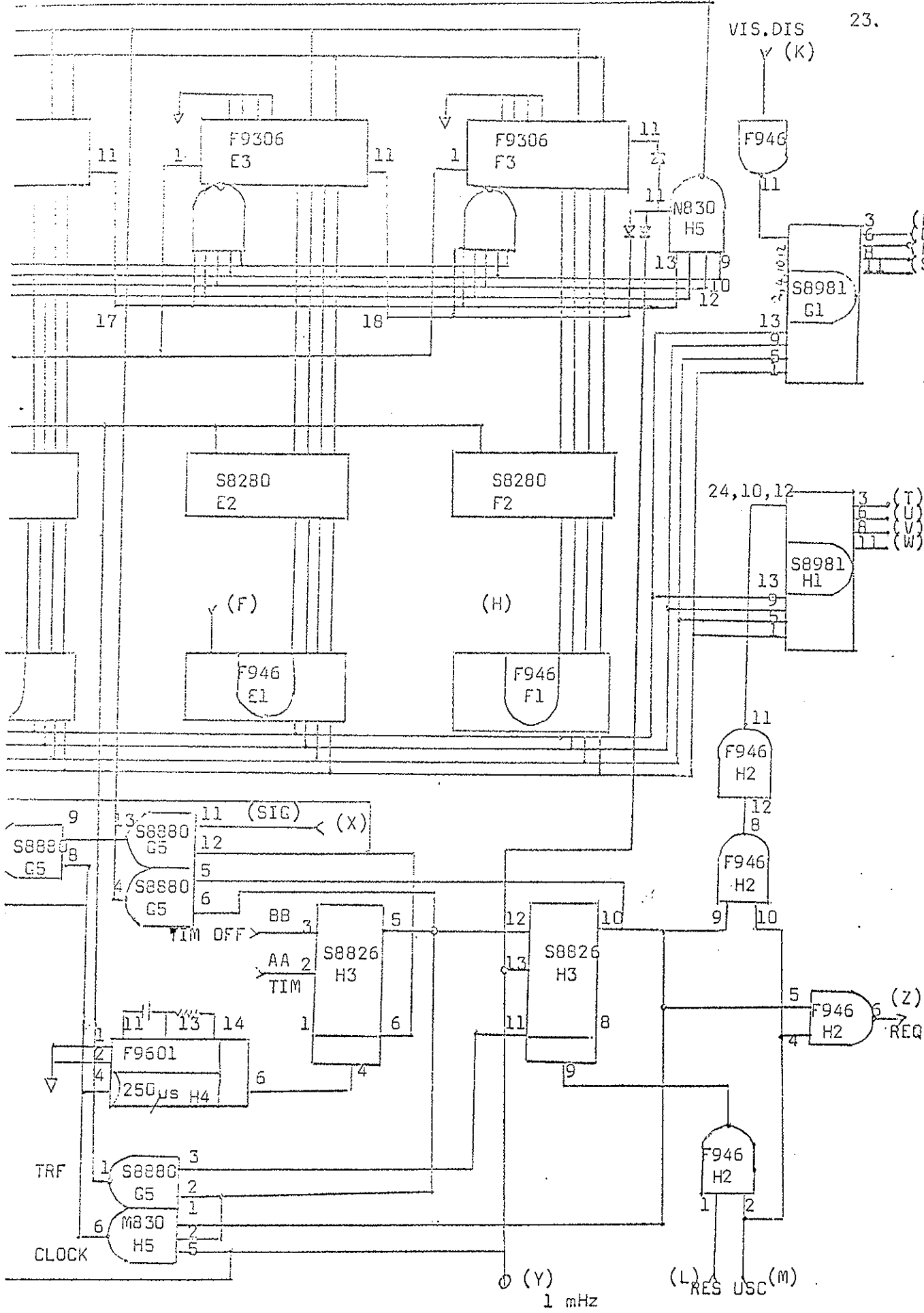


Figure 68. Digital up/down counter.

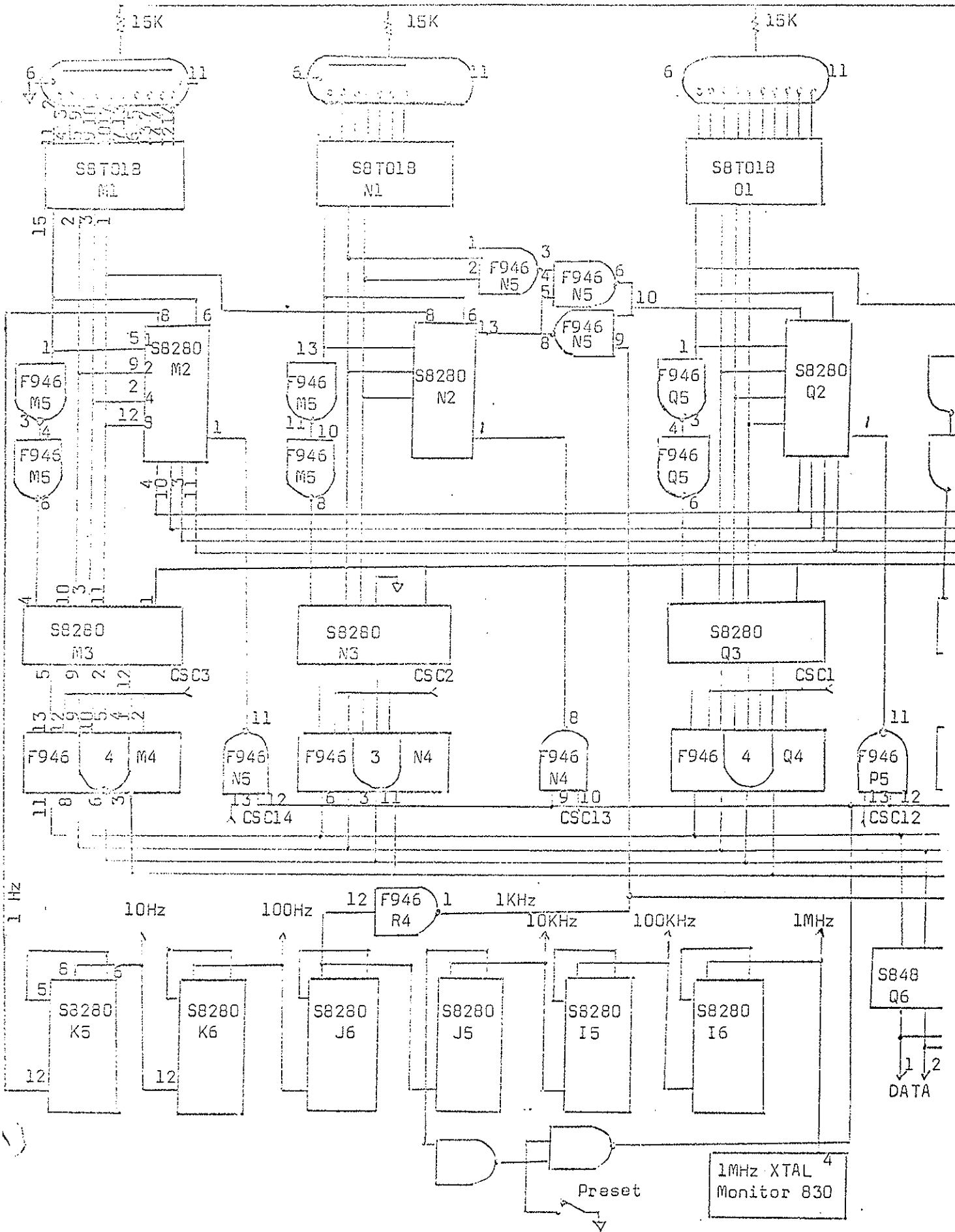


Figure 7A (Facing fig. 7B)  
Digital clock.

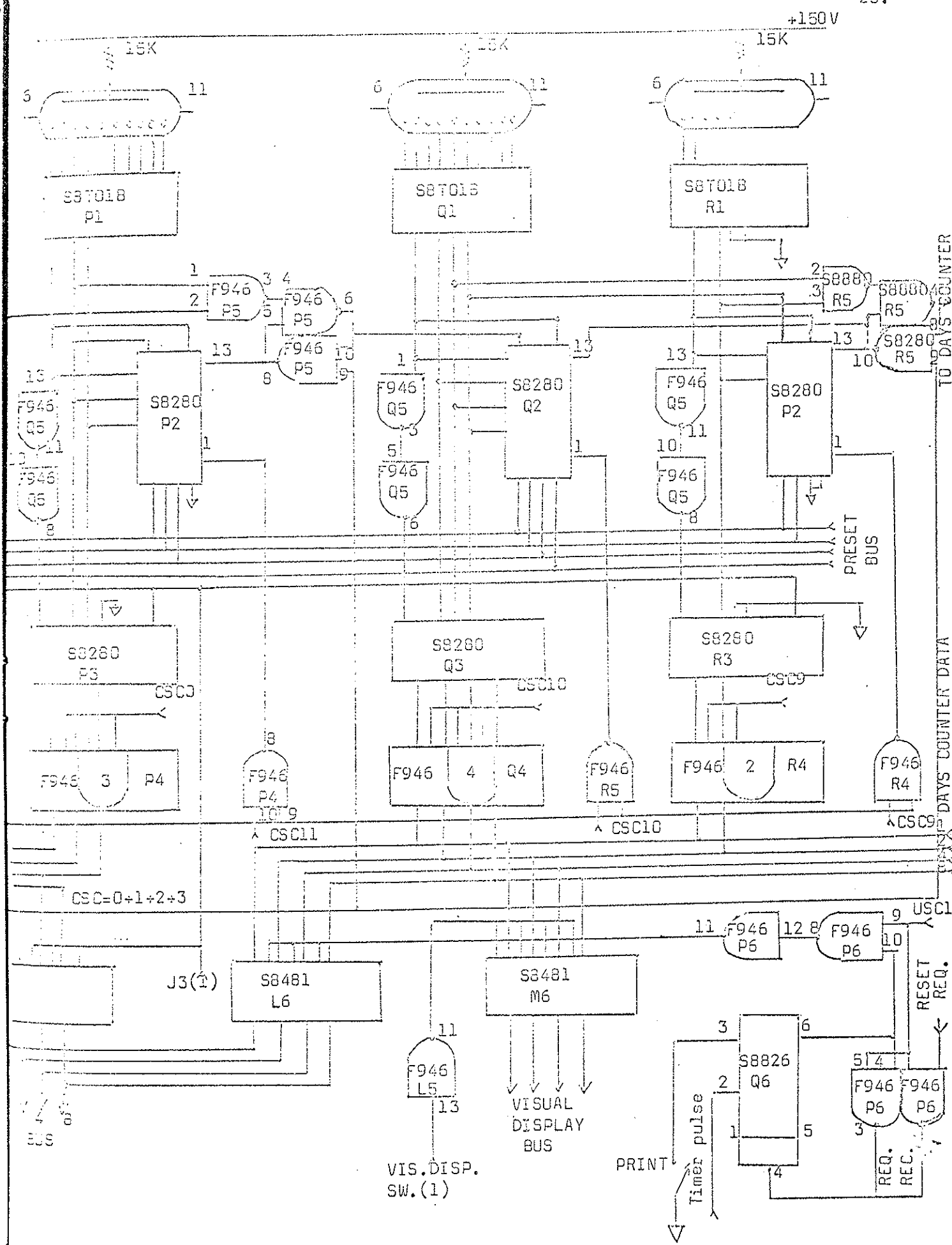


Figure 7B. Digital clock.

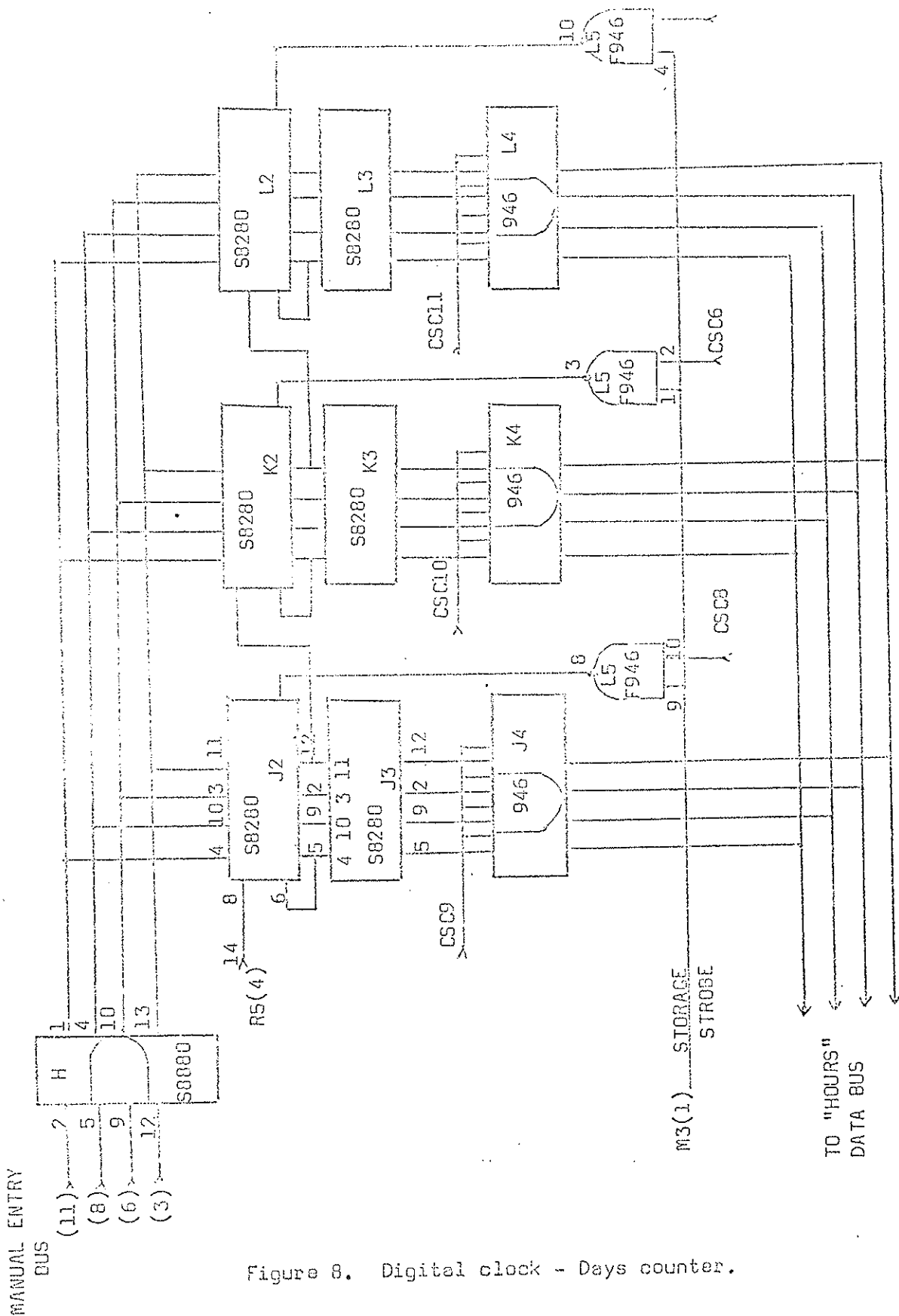


Figure 8. Digital clock - Days counter.