A High Sensitive, Precise Programable Mass Spectrometer†

FUSAFUMI NAKAO* AND TERUMASA YAMAMOTO*

(Received 15 March 1974)

A programable quadrupole mass spectrometer has been developed to make continuous observation of the gaseous pollutant materials and respiratory gases, and to make continuous monitoring of the gaseous species present in the high vacuum atmosphere. The equipment has a multi-channel high speed programable scanner which consists of high speed IC switching circuits and accurate mass selector controls. A detailed description of the circuit and its function are given. A maximum scan speed is 1 msec per amu in the case of 100 channels. The equipment has a reproducibility of better than 99.6 % and a detection limit of 10 ppm for SO₂ of the pollutant gases in the chimney flue.

1. Introduction

Continuous and simultaneous analysis of several components of a mixture is often necessary in the handling of the gaseous materials present in the vacuum evaporators, outgassing or thermal decomposition studies and the kinetics of reactions at low pressures. Continuous monitoring of the respiratory gases or of the gaseous pollutant materials has become increasingly important. The technique most frequently used to facilitate those is mass spectrometry, but the useful information must be found out from a confusing array of spectral data. The significant data in those mass spectrometric analyses will normally be obtained by monitoring only a few mass peaks. In order to observe the transient phenomena of interest components, it is necessary therefore either to repeat the experiment several times with the mass spectrometer set on each mass peak of interest or to have some means for recording the behavior of all mass peaks simultaneously during a single experiment.

A programable mass spectrometer makes possible the selection of those mass peaks of interest while disregarding the balance of the spectrum. With conventional magnetic deflection type mass spectrometers a quasi-continuous observation of several mass peaks has been made by changing the magnetic field in a predetermined manner. This method is somewhat limited since it is not very easy to change the magnetic field in a high speed scanning mode due to the large transient effect of the magnet coil current.

We therefore have selected a quadrupole mass spectrometer (hereafter QMS) for this task because it offers some distinct advantages. A simple method for continuous observation of a few mass peaks with QMS has been proposed by Arthur and LePore. They have done continuous observation of thermal decomposite species under high vacuum conditions. We have developed a new multi-channel high speed programable scanner of a different circuit from theirs. The multi-channel programable scanner consists of accurate mass

† Partially presented at the Sixth International Vacuum Congress held at Kyoto on March, 1974.
* Central Research Laboratory, Matsushita Electric Industrial Co. Ltd., 1006 Kadoma, Osaka 571, Japan
selector controls for determination of the peak top of desired mass number and a high speed IC switching circuit for automatic repetitive scanning. Here we describe a detailed circuit diagram, show results of an application to continuous observation of several gas components in the outgassing process of the high vacuum system. We also demonstrate an accuracy and a reproducibility of the repetitive observation of pollutant gases in a chimney flue by using a continuous gas inlet system, and thus discuss the capability of our programable mass spectrometer.

2. Description of Method

Mass selection by QMS is accomplished by varying the amplitude of the rf and dc voltages applied to the quadrupole rods while the ratio of the voltages is held constant. For each mass number, in other words, there is one specific set of these voltages to generate a field in which only the ions of that specific mass have stable trajectories. In fact, when QMS operates in the single peak monitoring mode, the sweep function is disconnected from an internal sweep generator and placed under control of the specific dc voltages that correspond to the specific mass number to be monitored. Therefore, if operator selects beforehand only the mass peak needed to analyze for the desired components, the behavior of each mass peak can continuously be observed by switching the specific dc voltages in rapid succession.

2.1 Block Diagram

The circuit diagram, which we report here, is an extension of the single peak monitoring mode by QMS. A block diagram of the circuit is shown in Fig. 1.

In the automatic mode, when the command ramp voltage coming from the sweep generator attains to some threshold level, the comparator \((C_n)\) output may consist of an abrupt departure from the quiescent level but is otherwise independent of the command ramp voltage. After being differentiated the comparator output, a square pulse is shaped by the monostable multivibrator \((MM_n)\). The square pulse is subjected to the differential \((D_n)\) again. The flip-flop circuits \((FF_n)\) from \(FF_1\) to \(FF_5\) are triggered by the negative triggering pulse from the preceding channel, and are triggered again by the positive triggering pulse from the self-channel after a given time interval; thus any number of channel units may be linked in series. The output voltage from the flip-flop is applied to the buffer amplifier \((B_n)\). Because the buffer amplifier provides the adjustable mass selector control, any voltage level for detection of the peak top of desired mass

![Fig. 1. Block diagram of the five-channel programable scanner.](image-url)
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number can easily be obtained. The output dc voltages from the buffer amplifier are applied to the rf and dc generator circuitly. Then the programable scanner makes the mass spectrometer jump rapidly from the first of the mass peaks to the second mass peak, to the third mass peak, and repeats this pattern automatically. We call the set of circuits \( C_n, D_{n1}, MM_n, D_{n2}, FF_n, \) and \( B_n \) as the \( n \)-th channel.

In the manual mode, the input of the flip-flop is connected to the negative dc voltages through a protection resistor. The output voltage from the flip-flop is similarly applied to the buffer amplifier. A characteristic voltage corresponding to the specific mass number is then routed from the buffer amplifier. This dc voltage is also applied to the rf and dc generator circuit.

2.2 Circuit Function

An example of logical states at several points in the block diagram is shown in Fig. 2. A, B1, D1, E1, F1, G1 etc. correspond to the positions designated by the same symbols in the block diagram shown in Fig. 1.

The command ramp voltage, \( A \), increases monotonically from 0 to 10 volts according to the scan speed determined by the sweep generator. The comparator \( (C_n) \) is placed at the input stage of each channel, and the command ramp voltage and the reference voltage having an opposite polarity to that of the command ramp voltage are applied to the comparator input through the input resistors. An operating point of the comparator is determined by the ratio of input resistors as given by the form

\[ E_t = -E_{ref} \frac{R_{com}}{R_{ref}} \]

where \( E_t \) is the threshold value of the comparator, \( E_{ref} \) is the reference voltage, \( R_{com} \) is the input resistor of the command ramp voltage side, \( R_{ref} \) is the input resistor of the reference voltage side.

When the command ramp voltage attains to the threshold value, the comparator output in the channel one changes abruptly from logical state 1 to logical state 0 but is otherwise independent of the command ramp voltage. The logical state at B1 retains the quiescent state at logical 0, until the command ramp voltage returns to the original level. Accordingly, the comparator can be operated with the same time interval provided that the input resistor is adequately determined.

The abrupt change of the comparator output is differentiated by the first stage differential circuit, \( (D_{n1}) \), and only the negative triggering pulse triggers the monostable multivibrator, \( (MM_n) \). The negative square pulse of 10 \( \mu \text{sec} \) length is shaped by the monostable multivibrator. The output of this monostable multivibrator, D1, stays at logical 0 for a time interval. We call the square pulse as a timing pulse. The time interval of the timing pulse is determined by the ratio of the input resistors at the

Fig. 2. Change of logical states at the several points of the programable scanner.
comparator and scan speed of the sweep generator, while the pulse length of the timing pulse is always kept at 10 μsec. Again, the timing pulse is differentiated by the second stage differential circuit, \( D_n2 \), and the positive and negative triggering pulses, \( E_1 \), are obtained. The positive triggering pulse is utilized as a trigger of the flip-flop in the channel one and the negative triggering pulse is used as a trigger of the flip-flop in the channel two. The logical state of the output of the flip-flop, \( F_1 \), is shown in Fig. 2 together with the triggering pulses.

The hold time of the flip-flop is determined by the time interval of the timing pulse. The circuits in the channel two operate similarly except that the flip-flop is triggered by the negative triggering pulse from the preceding channel. Similarly, the flip-flop \( FF_3 \) to \( FF_5 \) are triggered successively. After a scan cycle has been completed, the flip-flop in channel one is reset to "on-state" by the negative triggering pulse obtained from the second stage differential circuit in channel five and a new cycle is initiated.

The output from the flip-flop circuit is applied to a non-inverting input of the buffer amplifier, \( B_1 \). Because the buffer amplifier consists of a voltage feedback amplifier and a set-point potentiometer, it also acts as the mass selector controls. The voltage resolution obtained by this circuit is less than 1 mV in the wide range from 0 to 10 volts. It is therefore very easy to adjust the voltages corresponding to the peak top of the specific mass number. The output from the buffer amplifier is routed via a protection diode and is applied to the modulator driver amplifier which is placed in the feedback loop of the rf and dc generator. The under trace in Fig. 2 depicts the resulting output signals of the five-channel programmable scanner.

As the programmed signals to be applied to the modulator driver amplifier necessarily start from the first mass number, so the circuit is initiated by a rescan switch. The scan time is determined by a capacitor and a variable resistor in the scanning circuit. The scan time in the case of five channel units can be chosen in the range from 20 msec to 200 sec per amu. The data obtained is represented as a bar graph which has the same time interval.

In manual operation, a manual-automatic switch is placed in the manual position. An inverting input of the comparator of the command ramp voltage side is disconnected from the internal sweep generator and is connected to the ground. A manual channel selection is made in such a way that the flip-flop is switched by the manual channel selection switch to a stabilized dc power supply of \(-15\) volts through the protection resistor; thus the flip-flop output retains some quiescent level. Only the dc voltages that correspond to the specific mass number are therefore routed from the buffer amplifier and are applied to the modulator driver amplifier. The manual channel selection is made by switching the dc voltages to the input of the flip-flop. A detailed logical circuit is shown in Fig. 3.

The circuits mentioned above were assembled on a printed board in the dimensions of \(130 \times 130\) mm\(^2\). The construction figure of the printed board integrates the five channel units on one printed board, and the photographic is shown in Fig. 4. Figure 5 shows the front panel of the programmable mass spectrometer. All the electronics needed to control the mass spectrometer operation, the high speed programmable scanner and mass selector controls were mounted on an electronic chassis together with an oscilloscope for the observation of rapid phenomena, a digital mass meter for tuning the desired mass number and push button switches for the
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Fig. 3. Logical circuit of the five-channel programable scanner.

Fig. 4. The photograph of the high speed five-channel programable scanner, which is assembled on the printed board in the dimensions of 130×130 mm².

Fig. 5. Front view of the programable mass spectrometer. All the electronics, the oscilloscope, and the digital mass meter are assembled in the electronic chassis.

manipulations. The programable mass spectrometer not only enables the program analysis of desired masses, but also has the function of ordinary mass spectrometer.

3. Experimental
An analyzer head of the mass spectrometer used is an EAI 150A for residual gas analysis. The analyzer head has rods ~130 mm long by ~6 mm diameter and a two-filament ionizer.
The entrance and exit apertures of the filter were 3 mm in diameter. The box and grid type secondary electron multiplier was mounted behind the filter exit aperture. The ion currents
were measured with a high speed response electrometer. The data was recorded on the oscilloscope and a two-channel strip chart recorder. The vacuum system was diffusion pumped, with a liquid nitrogen trap, a metal bellows valve, and an ionization gauge. The test gases were introduced through the continuous gas inlet system for all the experiments.

To tune the desired mass number for each channel, the equipment described above was operated in the manual mode. Mass peaks are selected by tuning the mass selector controls to the desired mass number for each channel, either by visually observing the spectrum on the oscilloscope, or by using the digital mass meter. For fine tuning, the fine control is adjusted for the maximum peak amplitude in the manual mode of operation. Mass peaks to be monitored can be determined in any portion of the mass spectrum, in any sequence, and without restrictions as to proximity to one another. Because the programable scanner and mass selector controls are driven with a highly regulated and stabilized power supply, it will display exactly the maximum amplitude of a mass peak, provided that operator has carefully selected the mass peak before the operation is started.

In order to confirm the operation of the programable mass spectrometer, krypton was continuously introduced into the ion source with the continuous gas inlet system. Five masses with major peaks as $M/e=80$, 82, 83, 84, and 86 were programmed, and were automatically and repetitiously scanned every 90 seconds. The output was recorded on the strip chart recorder. The relative isotope abundance ratio of krypton obtained by this method is shown in Table 1. For a series of some ten scans, a relative accuracy of the order of 0.2 percent was obtained, although the correction to the relative isotope abundance ratio was quite not made. If the gas pressure introduced is adequately adjusted, the relative abundance ratio of the isotope can directly be measured as shown in Fig. 6. The mass numbers in Fig. 6 are rearranged as $M/e=80$, 82, 84, 83, and 86 with the programable scanner, because the ratio of $M/e=82$ and 83 is almost the same.

Figure 7 shows one example of measurement

Table 1. Relative isotope abundance ratio of krypton measured with the program mode. No any correction was made on the measured values.

<table>
<thead>
<tr>
<th>$M/e$</th>
<th>Present work</th>
<th>Beynon*</th>
</tr>
</thead>
<tbody>
<tr>
<td>78</td>
<td>—</td>
<td>0.354±0.002</td>
</tr>
<tr>
<td>80</td>
<td>2.12±0.02</td>
<td>2.27±0.01</td>
</tr>
<tr>
<td>82</td>
<td>11.64±0.04</td>
<td>11.56±0.02</td>
</tr>
<tr>
<td>83</td>
<td>11.91±0.02</td>
<td>11.55±0.02</td>
</tr>
<tr>
<td>84</td>
<td>56.84±0.16</td>
<td>56.80±0.10</td>
</tr>
<tr>
<td>86</td>
<td>17.25±0.05</td>
<td>17.37±0.02</td>
</tr>
</tbody>
</table>

Fig. 6. Example of direct measurement results of the relative isotope abundance ratio of krypton. Mass numbers are programmed as $M/e=80$, 82, 84, 83, and 86 from left to right hand side.
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results of the behavior of the residual gases in the high vacuum system. Main residual gases such as hydrogen \( (M/e=2) \), methane \((16)\), water vapor \((18)\), carbon monoxide \((28)\) and carbon dioxide \((44)\) are programmed. The high vacuum system was baked out together with the mass spectrometer with a tape heater. Total and partial pressures of these residual gas components were increased with increasing temperatures. The behavior of residual gases

Fig. 7 (a). Continuous and simultaneous observation of the residual gas components in the high vacuum system. Residual gases showed were measured under the bake-out process just started.

Fig. 7 (b). Continuous and simultaneous observation of the residual gas components in the high vacuum system. Residual gases showed were measured under the baking process being stopped after two hours passed.
is very complicated and interesting, but by using the programable mass spectrometer the aspects of the behavior of these residual gas components and its magnitude can simultaneously be recorded on the strip chart recorder.

One example of measurement results of the pollutant gas components in a chimney flue is shown in Fig. 8. Gases to be analyzed were continuously introduced with the continuous gas inlet system. Four components such as carbon monoxide (28), nitrogen monoxide (30), carbon dioxide (44), sulfur dioxide (64), and a fragment of hydrocarbons (43) were programmed, and were repetitiously scanned every 90 seconds. The output was recorded on two channels of the strip chart recorder at two different sensitivities. In several tens of scans extending over several hours, no variations in peak heights could be detected. The stability of the equipment can also be demonstrated from the data, i.e. a reproducibility of better than 99.4 percent or a coefficient of variation of better than 0.6 percent is obtained from a series of some ten scans.

A detection limit is determined by the gain of the secondary electron multiplier, the electrometer amplifier, and gas pressures introduced but the detection limit obtained is about 10 ppm for SO2 of the pollutant gas components in the chimney flue without doing concentrations.

As was known from the results described above, it should be emphasized that the accuracy of measurements is limited by factors other than the equipment itself, for example, the accuracy of the recording system and the ability of reading the strip chart recording accurately. Finally, we show the capability of the programable scanner. For that reason, perfluorotributylamine (FC-43) was introduced as the test gas with major peaks as M/e=31, 69, 100, 131 and 219. The resulting data is shown in Fig. 9 together with the output signals from the buffer amplifier. The tested sample, FC-43, is of the liquid state but the reproducibility of the mass peaks introduced with a vapor phase was very excellent. The under trace in Fig. 9 shows the normal mass spectrum of perfluorotributylamine. Spectra showed were also obtained with the programable mass spectrometer which operates in the normal operation mode.
Fig. 9. One example of a wide range program. To confirm the ability of the programmable scanner, perfluorotributylamine (FC-43) was introduced into the ion source. Programmed masses were $M/e=31, 69, 100, 131$ and 219. The horizontal lines indicate the output signals from the buffer amplifier. The under trace shows the normal mass spectrum of perfluorotributylamine.

4. Summary
With the simple and inexpensive programmable mass spectrometer here described, a continuous and simultaneous observation of several gas components can easily be made, and a substantial increase of the efficiency in the mass spectrometric analysis has also been expected. Channel numbers of the programmable scanner will be able to extend up to one hundred channels. The equipment can easily be adapted to different instruments.
Acknowledgments

The authors are deeply indebted to Messrs. S. Nishimura and K. Iga of this Central Research Laboratory for their continual encouragement and interest for this work.

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