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Fast mass programming controller for a supersonic gas chromatography mass spectrometer

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Abstract

In a gas chromatograph mass spectrometer employing a quadrupole mass filter, molecules are ionized and transferred to a mass analyzer, where their mass to charge ratios ($m/z$) are measured. After the ionization step, the ions pass through a series of ion lenses that focus and guide them into the mass analyzer. The voltages on these lenses can be optimized for each specific $m/z$ value (as the rest of the system is also optimized) to increase the number of ions reaching the mass analyzer. In certain cases, this dynamic mass-dependent optimization of the lenses can increase the signal by a factor of 2 or more. To implement this dynamic optimization, a digital circuit was developed, based on a digital signal controller and high-voltage (HV) amplifiers, that is able to optimize eight independent HV channels ranging between $\pm 150$ V at a rate of 100 $\mu$s.

Keywords: GC/MS, mass programming, supersonic molecular beam

(Some figures in this article are in colour only in the electronic version)

1. Introduction

One of the important instruments in the field of analytical chemistry is the mass spectrometer (MS) \cite{1, 2}. In an MS, the analyte molecules are ionized and then transferred to a mass analyzer, where their mass to charge ($m/z$) ratios are measured. One type of mass analyzer is the quadrupole mass filter \cite{3, 4}, which has a scan-like operating procedure: the voltages on its rods (including an RF voltage), if kept constant, allow only a small range of $m/z$ values to pass and reach the ion detector, while all the other ions collide with the rods and neutralize. By varying the rod voltages quickly and repeatedly, a scan over a range of the desired $m/z$ values is performed.

Before the analyte molecules reach the quadrupole, they must first be ionized. In most cases, when the MS is coupled with a gas chromatograph (GC) \cite{5} (and in some cases with a liquid chromatograph (LC) \cite{6}), the electron ionization (EI) ion source is used. After the ionization step, the ions pass through a series of ion lenses that focus and guide them into the mass analyzer. The voltages on these lenses can be optimized for each specific $m/z$ value to increase the number of ions reaching the quadrupole. It can be beneficial, in terms of sensitivity, for the voltages on these ion lenses to be synchronized with the quadrupole voltages scan, so that all the ion manipulating elements are perfectly tuned to the same specific $m/z$ value at any given time. In certain cases, this dynamic mass-dependent optimization of the lenses can increase the signal by a factor of 2 or more.

This paper describes an implementation of such optimization and the synchronization between the ion lenses and the quadrupole. The system is composed of an Agilent 5975 GC/MS \cite{7} system with an Aviv analytical supersonic molecular beam (SMB) interface \cite{8, 9} that includes an independent EI ion source \cite{10, 11} whose ion-lens voltages are governed by the dedicated and separate electronics board devised during this work. A scheme of the ion source, through which the molecules fly, become ions and are maneuvered into the mass analyzer, can be seen in figure 1.

To implement a dynamic mass-dependent optimization controller, a digital circuit based on a DSP and high-voltage...
Figure 1. A scheme of the ion source, through which the molecules fly, become ions and are maneuvered into the mass analyzer. The elements whose names are colored red are the elements that are dynamically programmed by the controller.

Figure 2. Electronic circuit block diagram. The circuit is composed of four blocks: DSC, DAC, HV AMP and BUFFERS.

(HV) amplifiers was developed. A fast algorithm was used in order to calculate the optimized voltages in real time (using interpolation), utilizing only a small amount of memory. The controller can optimize up to eight independent HV channels ranging between ±150 V at a rate of 100 μs, and can work in two operation modes: static and dynamic.

2. Electronic circuit

Figure 2 is a block diagram of the electronic circuit that is composed of four blocks: DSC, DAC, HV AMP and BUFFERS. The description of the DSP and DAC blocks is depicted in figure 3. The heart of this block is an advanced, Texas Instruments TMS320F28335 150 MHz DSC [12]. This controller, in addition to 512 KB of flash memory for programming and 68 KB of SRAM for data, has 16 channels of fast ADC, floating point unit (FPU) and a wide range of peripheral units (UART, SPI, TIMERS, I2C, PWM, etc). As one can see, the circuit includes, in addition to the processor, several supported standard hardware items (dark block): Clock, JTAG, Boot, RS-232, USB and diagnostic LED. All the above digital components and the following analog ones are combined into a tailor-made printed circuit board, designed for this system. The remainder of the connections are for the external DAC and internal ADC. The 16 bits serial input DAC is an Analog Devices AD5360 [13] with 16 input channels and an output voltage of ±10 V. The DAC communicates with the controller by the SPI bus and a few more digital I/O pins. The internal ADC is unipolar, and accepts voltages that are scaled beforehand to the range of 0–3 V.

Eight outputs of the DAC are connected to the HV amplifiers to produce the voltage to the electrostatic lenses of the system. The HV amplifiers are based on a Cirrus-Logic PA240 operational amplifier [14]. The PA240 is a 350 V power operational amplifier that exhibits a very low quiescent current of 2.2 mA, a unity gain bandwidth of 3 MHz and a slew rate of 30 V μs⁻¹, suitable for the task of fast mass programming. The circuit of this inverting amplifier is shown in figure 4. The gain is determined by the ratio R1/R2; in the described circuit, the gain is 12, producing an output voltage in the range of ±120 V from the ±10 V outputted by the DAC. The diodes D1 and D2 protect the input from overvoltage and the resistor R1 protects the output via a current limit (10 mA). The supplied voltage ±HV can be produced by a dc to dc converter. In the
described application, voltages of $\pm 125$ V were used for all channels.

The last block—BUFFERS—is a scale buffer for the ADC. As mentioned above, the ADC accepts voltage in the range of 0–3 V; thus, the sensing voltage must be scaled to this range. A circuit of the buffers is shown in figure 5. The circuit is designed for unipolar signals while the attenuation $G$ is $R_A/(R_A + R_B)$. In the system described here, the attenuation is $1/20$ to allow input voltages in the range of 0–50 V. There are two sensing inputs: one for monitoring the MS voltage and the other for future purpose.

The power pins of all analog devices must bypass by 0.1 $\mu$F and 10 $\mu$F capacitors. All the auxiliary power supplied can be produced from one main power supply by low-cost dc to dc converters.

Figure 3. Details of DSP and DAC blocks. The heart of this block is a TMS320F28335 DSC. The DAC communicates with the controller by the SPI bus.

Figure 4. The circuit of the HV amplifier—the gain $G$ is $R_1/R_2 = 12$. 
3. Architecture and embedded software design

The real-time mechanism of the software is based on a hardware timer (TIMER0) that produces an interrupt with the highest priority every 100 $\mu$s. This clock is the trigger for both the sampling process and the mass programming control process.

The input voltage is one of Agilent’s original ion source voltages that is not used for other purposes due to the incorporation of the new dedicated fly-through ion source. This voltage can be made to scan (a native capability) with the rest of the system between $-0.2$ and 42.7 V with a step size of 0.168 V, consisting of 256 values (8 bits). The system discussed here can suffice with less resolution and for simplicity reasons it uses only positive voltages between 0 and 40 V representing $m/z$ values between 0 and 1000 Th (Thomson units).

Since there are eight independent channels (lenses), $8 \times 256 \times 2$ bytes of random access memory were needed to store the full conversion tables used for their voltage programming. (If the input voltage resolution is 12 bits, then the memory size is $8 \times 4096 \times 2$ bytes.) In order to minimize memory consumption and work only with the controller internal RAM, a small lookup table was used, utilizing a small amount of memory, and interpolation was used to calculate the programming voltage in real time. Eight predetermined mass values and eight programming voltage values were used for each lens. All of the mid-point voltages between the predetermined mass values are linearly interpolated with 16 bits resolution.

Figure 6 represents the relevant flowchart of the control routine. Every 100 $\mu$s the spectrometer voltage (SV) is monitored. Then, the routine finds the range (index $k$) of the measured SV in the mass table $MV[k]$. After that, the routine makes eight loops (index $j$), one for each lens, calculating the interpolate voltage (IV) from the mass voltage (MV), lens voltage (LV) and index $k$. Finally, if the corresponding lens is enabled, the interpolated voltage is sent to the lens by the DAC.

The transmission time of 24 bits to the serial DAC, by the 10 MHz SPI bus, is about 2.5 $\mu$s, so the time for eight channels is about 20 $\mu$s. One can see that the overhead of that routine is about 20% of the 100 $\mu$s clock. Under this condition, there is enough time for other tasks the system performs.

Code Composer Studio (CCS) 3.3 environment [12] and ANSI C language were used for the writing of the embedded program (assembly or C++ were also optional).

4. User interface and communication software

The controller is designed to work with an advanced Supersonic Molecular Beams GC/MS system [15]; therefore, the computer interface for programming and monitoring is required.

To test the computer–user interface and the controller, a test application was written using the National Instrument [16] Lab Windows CVI environment which has full compatibility
5. Results

In order to characterize and demonstrate the performance of the controller, several tests were conducted using the testing application. Figure 8 represents the operation of mass programming in real time. Lens 1 and lens 2 are programmed to operate dynamically with a parameter that is shown in figure 7, while lens 3 is programmed to use a static voltage of −50 V. The mass programmed input is given as a sweep voltage of 0–40 V with a frequency of 10 Hz (its voltage is shown as the green line related to the right axis named ‘Mass Voltage’). One can see that lens 1 and lens 2 follow the interpolated values as determined by the table, while lens 3 keeps the voltage static on −50 V as expected.

Finally, we tested the mass programming controller with the entire system. A mixture of five compounds was injected to be analyzed by the GC/MS system; the mixture contained octafluoronapthalene (OFN), hexadecane, methylstearate, cholesterol and dotriacontane.

In the first experiment, used as control, the lenses were all given constant voltages (without mass programming) that were previously chosen to give the best general response. A list of the lenses and their static voltages can be seen in figure 9 (row of static voltages in the table).

In the second experiment, the lenses were fine tuned to produce different voltages at different masses (synchronized dynamic voltages) using perfluorotributylamine (PFTBA) as the tuning compound with the ions at 69 (Thomson
Figure 8. The operation of mass programming in real time. Lens 1 and lens 2 are programmed to operate dynamically, while lens 3 is programmed to use a static voltage of $-50 \text{ V}$. The mass programmed input is given as a sweep voltage of 0–40 V with a frequency of 10 Hz. The green line shows the mass programmed input and is related to the right axis named ‘Mass Voltage’.

Figure 9. The graphs show the dynamic mass programming values (solid blue lines) placed on five of the lenses compared with the static voltages (dashed red lines). A list of the lenses together with their static and dynamic mass-dependent voltages can be seen at the lower right side.
Figure 10. Two chromatograms showing two experiments: one with static voltages (right peaks) and another with dynamic voltages (left peaks). The static voltages chromatogram is shifted 6 s forward to facilitate the graphical comparison. The chromatograms are a depiction of the overall SIM signals of ions with m/z values of 272.0, 226.3, 298.3, 386.3 and 450.5 Th (corresponding to five different compounds). It is easy to see that dynamic voltage programming increases the intensities of all five peaks.

units \( \equiv m/z \), 219 and 502 Th. A list of the lenses and their mass-dependent voltages can be seen in figure 9 (row of dynamic voltages in the table). The figure also shows graphs of the mass-dependent voltages and static voltages of each lens.

The results of both experiments can be seen together in figure 10, showing the measured single-ion monitoring (SIM) chromatograms of the ions with m/z values of 272.0, 226.3, 298.3, 386.3 and 450.5 Th—the molecular ions of the five compounds introduced. The chromatogram measured in the first experiment (using static voltages) is shifted 6 s forward to facilitate the graphical comparison.

Looking at the figure, it is easy to see the benefits of using synchronized dynamic voltages: in a single experiment, running with constant conditions, dynamic voltages increased the signal for each and every ion scanned. The reason why for hexadecane \((\text{C}_{16}\text{H}_{34})\) the signal only shows a relatively small increase of \(~20\%\) when dynamic voltages are used is clear when the graphs in figure 9 are examined: the optimum static voltages used in the first experiment were mainly chosen to be those which maximize the signal of the ions at 219 Th, and therefore the effect of dynamic voltages on ions with masses in the vicinity of 219 Th will be small. The signal for the 450 Th ion \((\text{C}_{32}\text{H}_{66})\) for example increased by 123\%, which is a significant increase. It is obvious that dynamic voltages, if tuned correctly, can guarantee the optimal signal for each mass, making it valuable especially with higher masses where the noise is less frequent.

6. Conclusion

In conclusion, the design principles of a fast mass programming controller for MSs have been demonstrated. This design can be used by all systems that require a dynamic output voltage and can supply a synchronizing signal. Testing the controller in the GC/MS system showed extraordinary results, giving a SIM signal increase for all ions up to a factor of 2.2 for dotriacontane, compared with the previously used static voltages setting. These factors show the general potential of dynamic voltages, and since they depend on many system variables, different values may be recorded with different systems (with different components and different static and dynamic tune voltages) and even with the same system when methods change or components get dirty or damaged.

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