

Fast Mass Programming and PWM Controllers for Super Sonic GC-MS Using DSP

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ABSTRACT

In a Gas Chromatograph Mass Spectrometer (GC-MS) 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 amount 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. In addition, any GC-MS interface requires that the molecules vaporized and separated by the Gas Chromatograph (GC) will be transferred into the Mass Spectrometer (MS) at high temperature in order to avoid condensation. Any GC-MS and especially those with a supersonic molecular beams interface can benefit from the ability to change the temperature of this transfer-line between the GC and MS. To implement this dynamic optimization a digital circuit was developed, based on a digital signal controller and high voltage amplifiers that is able to optimize 8 independent high voltage channels ranging between ± 150 V at a rate of $100 \mu\text{s}$. In addition, 4 independent channels of high resolution PWM unit within the above mentioned controller was utilized in order to control the temperature.

1. INTRODUCTION

One of the important instruments in the field of analytical chemistry is the Mass Spectrometer [1,2]. In an MS, the analyte molecules are ionized and are 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 [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 [5] (and in some cases with a Liquid Chromatograph (LC)[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 amount 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 comprised of an Agilent 5975 GC-MS [7] system with an Aviv Analytical Supersonic Molecular Beam (SMB) interface [8,9] that includes an independent EI ion source [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 maneuvered into the mass analyzer, can be seen in figure 1.

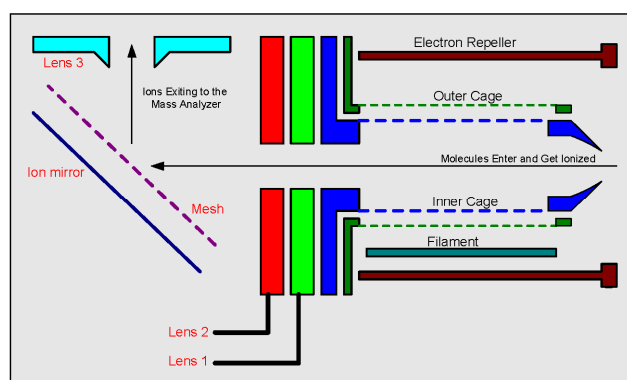


Figure 1: A scheme of the ion source.

To implement a dynamic mass-dependent optimization controller, a digital circuit based on a TI DSP and high voltage amplifiers was developed. A fast algorithm was used in order to calculate the optimized voltages in real time, utilizing only a small amount of memory. The controller can optimize up to 8 independent high voltage channels ranging between ± 150 V at a rate of $100 \mu\text{s}$, and can work in two operation modes: static and dynamic.

Another real-time control implemented using the same

hardware is a Pulsed-Width Modulator (PWM) for the heating of the transfer-line between the GC and the MS. In the GC, the injected solution is vaporized and its different compounds are separated from one another using an analytical column. Most of the column, through which the compounds travel, resides within the GC oven that control its temperature, but at the end of the separating process the column and the different compounds within it leave the oven and are transferred into the MS. The tube connecting the GC with the MS, called a "transfer line", must be heated so that the compounds within the column remain in the gas phase and retain their separation from one another.

It is desirable that the transfer line temperature could be programmed so that it will reach its maximum temperature only at the end of an analysis to reduce the undesired effect of a process called "column bleeding" (in which the inner coating of the column is released into the gas stream due to the elevated temperature). This heating method also keeps the transfer line portion of the column passivated (long time column bleed can induce column active sites) and helps in the analysis of relatively volatile thermally labile compounds. In the Aviv Analytical system described above, the transfer-line heater serves another important purpose - it also heats a supersonic expansion nozzle through which the molecules exit on their way to the MS. The nozzle's temperature affects several key aspects of the analysis process such as the nozzle flow rate and the SMB cooling efficiency, and should therefore be considered in the method development step.

A simplified sketch of the Aviv Analytical Cold-EI GC-MS can be seen in figure 2, in which the transfer-line and supersonic nozzle, being heated using the PWM control, are clearly seen. The transfer line is heated (normally between 150°C to 350°C) by an electric cartridge heater of 48 VDC / 200 Watts, while the temperature is measured by a K type thermocouple.

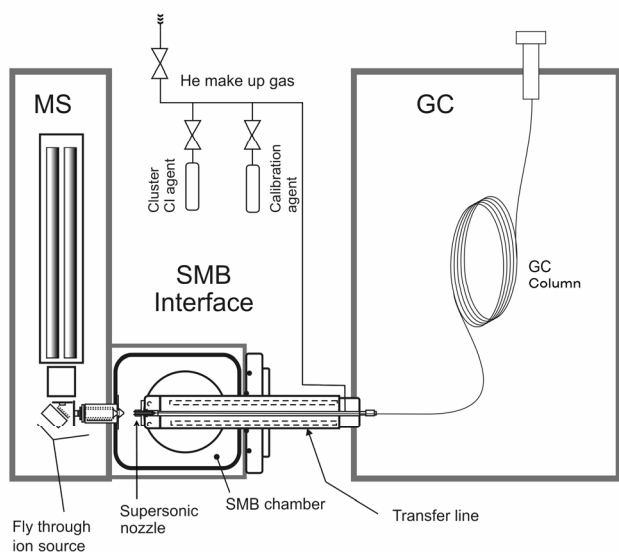


Figure 2: sketch of the Aviv Analytical Cold-EI GC-MS.

2. ELECTRONIC CIRCUIT

Figure 3 is a block diagram of the electronic circuit that is composed of seven blocks: DSC, DAC, HV AMP, DRIVER, IGBT, BUFFER and TC AMP. The heart of this block is a Texas Instruments [12] TMS320F28335 150 Mhz DSC. This controller, in addition to the 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 and more). All the above digital components and the following analog ones are combined into a tailor-made printed circuit board (PCB), designed for this system. The 16 bits serial input DAC, is an Analog Devices [13] AD5360 with 16 input channels and an output voltage of ± 10 volt. The DAC communicates with the controller by 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 volt.

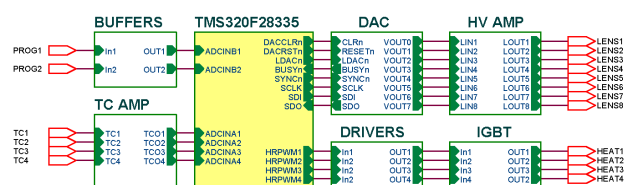


Figure 3: Electronic circuit block diagram.

Eight outputs of the DAC are connected to the high voltage (HV) amplifiers to produce the voltage to the electrostatic lenses of the system. The HV amplifiers are based on a Cirrus-Logic [14] PA240 operational amplifier. The PA240 is a 350 V power operational amplifier that exhibits a very low 2.2 mA of quiescent current, a unity gain bandwidth of 3 MHz and slew rate of 30 V/ μ s, suitable for the task of fast mass programming. The gain of the amplifier is 12, producing an output voltage in the range of ± 120 V from the ± 10 V outputted by the DAC.

The block – BUFFERS - is a scale buffer for ADC. As above mentioned, the ADC accepts voltage in the range of 0-3 volt, thus, the sensing voltage must be scaled to this range. In the system described here the attenuation is 1/20 to allow input voltages in the range of 0-50 volt. There are 2 sensing inputs, one for monitoring the mass spectrometer voltage and the other for future purpose.

To implement the temperature controller we used 4 HRPWM channel of the DSC in order to regulate the current of the heater. Figure 4 shows an electronic circuit of the PWM gate driver and IGBT switch (one channel of four). The circuit includes opto-coupler, to isolate the DSP from power devices, the smart gate driver TD350 and IGBT for switching. TD350 is an advanced gate driver for IGBT, while the control and protection functions are included and allow the design of high reliability. An innovative active Miller clamp function avoids the need for a negative gate

drive in most applications. The TD350 includes a two-level turn-off feature with adjustable level and delay. This function protects against excessive overvoltage at turn-off in case of overcurrent or short-circuits conditions.

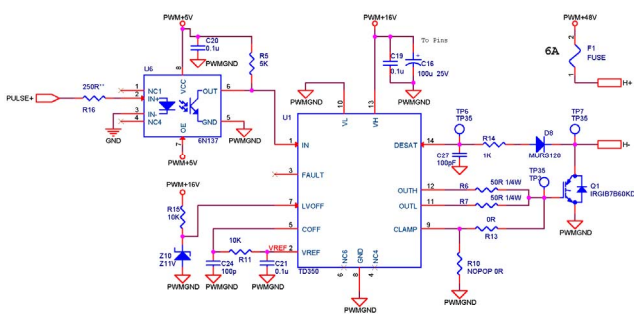


Figure 4: Electronic circuit of gate driver and IGBT.

The TC AMP block consists of the AD595. This amplifier is a complete instrumentation amplifier and thermocouple cold junction compensator on a monolithic chip. It combines an ice point reference with a pre calibrated amplifier to produce a high level (10mV/°C) output directly from a thermocouple signal. This gain after scaling allows us to measure temperature in the range of 0 °C - 500 °C.

3. 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 μs. This clock is the trigger for the sampling process, the mass programming control process and PWM PID loop.

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 -0.2V and 42.7V with a step-size of 0.168V, consisting of 256 values (8bit) (The lenses high voltages output such as the DAC are with a resolution of 16 bits). The system discussed here can suffice with less resolution and for simplicity reasons uses only positive voltages between 0 - 40V representing m/z values between 0-1000 Th.

Since there are 8 independent channels (lenses), 8x256x2 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-bit, then the memory size is 8x4096x2 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. 8 predetermined mass values and 8 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 5 represents the relevant flowchart of the mass programming control routine. Every 100 μs the spectrometer voltage is monitored. Then the routine finds the range (index k) of the measured spectrometer voltage (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) by 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 DAC.

The transmission time of 24 bits to the serial DAC, by 10 MHz SPI bus, is about 2.5 μs, so the time for 8 channels is about 20 μs. One can see that the overhead of that routine is about 20% of the 100 μs clock. In this condition there is enough time for other tasks the system performs.

In addition, the thermocouples voltage is monitored every 100 μs. The temperature is averaged continuously and the PID loop is calculated using FPU command¹⁸.

Code Composer Studio13 3.3 (CCS) environment and ANSI C language were used for the writing of the embedded program (assembly or C++ were also optional).

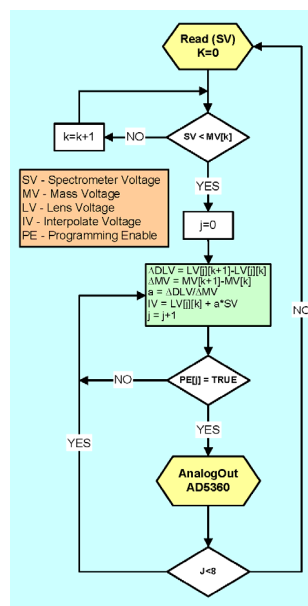


Figure 5: The flowchart of the mass program routine.

4. GRAPHICAL USER INTERFACE

The controller is designed to work with an advanced Supersonic Molecular Beams GC/MS system [15]; therefore, computer interface for programming and monitoring is required. To test the system, a test application was written using the National Instrument [16] Lab Windows CVI environment which has full compatibility with ANSI C. Figure 6 shows the mass programming and PWM graphical user interface (GUI). As seen, the GUI includes the mass programming voltages table, the mass voltages values, the operation modes of the lenses (static or

dynamic) and the lenses' static values.

In addition, the GUI includes all operating parameters for the PWM: the operating mode (set temperature target or fixed duty-cycle), the target duty-cycle or temperature, the read back measured values, the PID coefficients, the maximum allowed temperature and the maximum allowed duty-cycle. This GUI include four lines as there are four separate independent PWM channels even though only one is normally used in the Aviv Analytical 5975 Cold-EI GC-MS system.

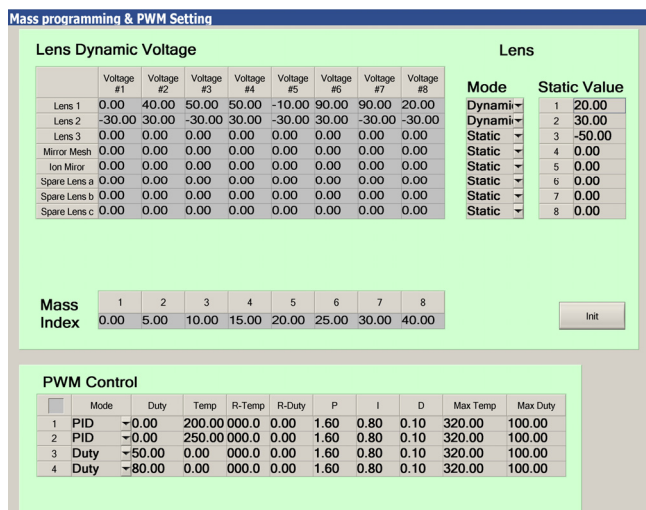


Figure 6: Graphical User Interface.

5. RESULTS

In order to characterize and demonstrate the performance of the controller, several tests were conducted using the mention above testing application [17]. Figure 7 represents the operation of mass programming in real time.

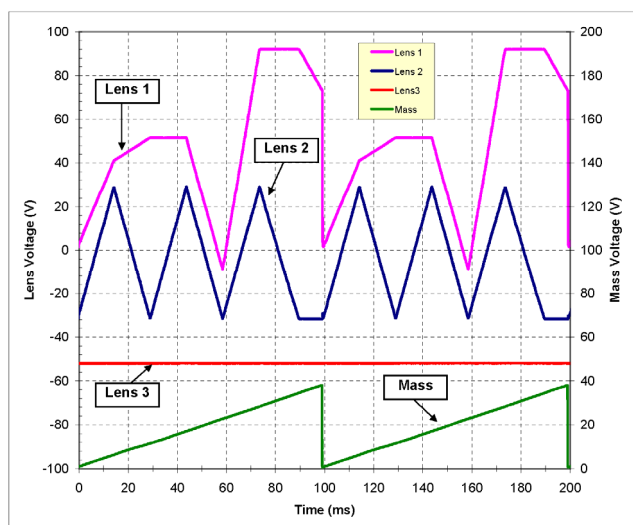


Figure 7: The operation of mass programming in real time.

Lens 1 and lens 2 are programmed to operate dynamically with a parameter that is shown in figure 6, while lens 3 is programmed to use a static voltage of -50V. The mass programmed input is given as a sweep voltage of 0V-40V 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 -50V as expected.

Finally we tested the mass programming controller and the temperature regulator with the entire system to characterize the influence of dynamic technique. A mixture of 5 compounds was injected to be analyzed by the GC/MS system, the mixture contained octafluoronaphthalene (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 8 (static voltages row in the table).

In the second experiment the lenses were fine tuned to produce different voltages at different masses using perfluorotributylamine (PFTBA) as the tuning compound with the ions at 69 Th (Thomson units = m/z), 219 Th and 502 Th. A list of the lenses and their mass dependent voltages can be seen in figure 8 (dynamic voltages rows in the table). Figure 8 also shows graphs of the mass dependent voltages and static voltages of each lens.

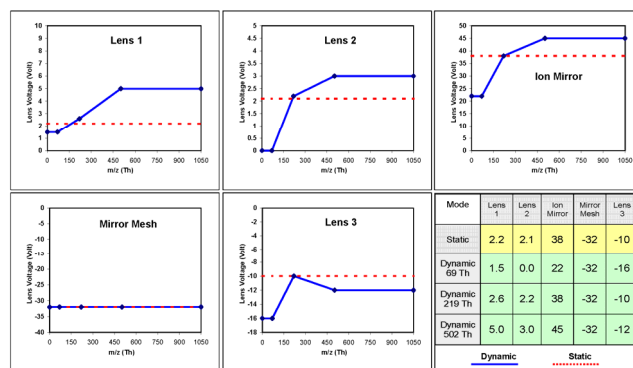


Figure 8: The dynamic mass programming values.

The results of both experiments can be seen together in figure 9, showing the measured Single Ion Monitoring (SIM) chromatograms of the ions with m/z values of 272.0 Th, 226.3 Th, 298.3 Th, 386.3 Th 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 seconds 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 that for hexadecane (C₁₆H₃₄) 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 who 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 (C₃₂H₆₆) 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.

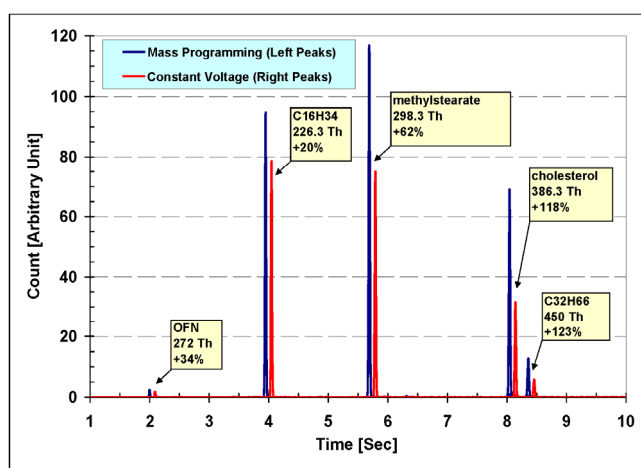


Figure 9: Comparison of dynamic and static method.

The PWM heater control was tested with the user selected PID constant values of $\alpha=1.6$, $\beta=0.8$ and $\gamma=0.1$. Figure 10 shows the behaviour of the system as it is lowered from 250°C to 200°C and then raised back to 250°C. The lower trace shows the PWM Duty Cycle and its convergence to the optimal value. This flexible transfer-line temperature enables smarter methods with enhanced results as discussed before.

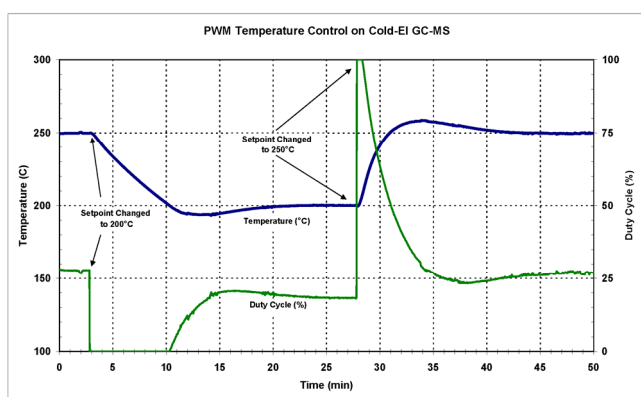


Figure 10: Temperature regulation using PWM technique.

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