Application of dynamic temperature gradients and profiles for capillary LC through the application of a new thermoelectric array based column heater

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Having a defined and well regulated control of temperature during chromatographic separations is of critical importance for every separation method. Capillary columns exhibit rapid thermal equilibration and precise application and control of longitudinal temperature gradients along the capillary column could provide interesting insights into band broadening processes within the column itself. By using thermoelectric modules in a platform column heater, simultaneous heating and cooling is possible. By creating an array of such modules with distinct thermally isolated zones, the generation of both static and dynamic temperature gradients and profiles along the length of the column can be created. The advantages and applications of such a system are numerous; increased separation efficiency, peak selectivity, temperature based trap and release, intermediate cooling or heating, flow through reaction control and thermal polymerisation to name but a few applications.

Thermoelectric modules, in this case Peltier modules, are used extensively in the electronics industry, usually for cooling components that are prone to overheating. The processor inside your PC is one example of a component that probably has a Peltier element attached to it. The operational principles behind thermoelectric modules is beyond the scope of this article, but suffice to say that they operate as a heat pump, drawing heat from one side of the device and emitting it on the other.

Construction

Work was undertaken to construct a thermoelectric array of ten modules, which would use a simple heat exchanger to dissipate heat during cooling operations. The heat exchanger flows air through a series of fins attached to the bottom surface of each thermoelectric module – during cooling operations, this side of the modules will be the hot side, and so by dissipating this heat it allows the upper surface to cool. Each module is wired so that both heating and cooling can take place simultaneously along the array. A thermistor mounted on the surface of each module measures the temperature of that module, while the power output to each one may be varied individually through a basic control board. The capillary column is attached to the array using commercially available thermal paste which ensures good thermal conductivity between the array and the column. Since the thermal paste is not an adhesive it also allows for the easy removal of the column. Figure 1 shows a typical arrangement of a capillary column

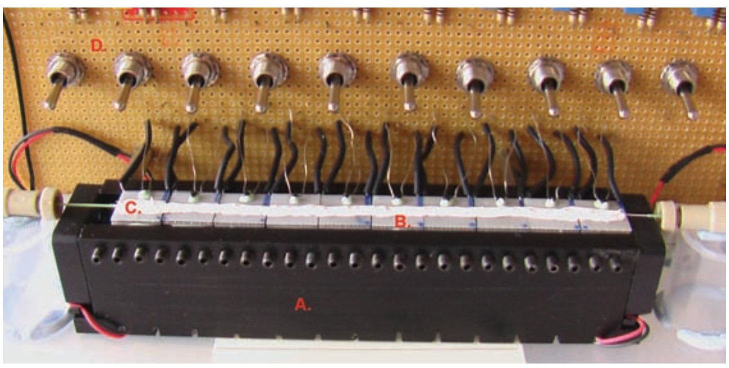

Figure 1. Array of thermoelectric modules with capillary column attached, showing; A. Heat Exchanger, B. Peltier Array, C. Capillary Column, D. Control Board

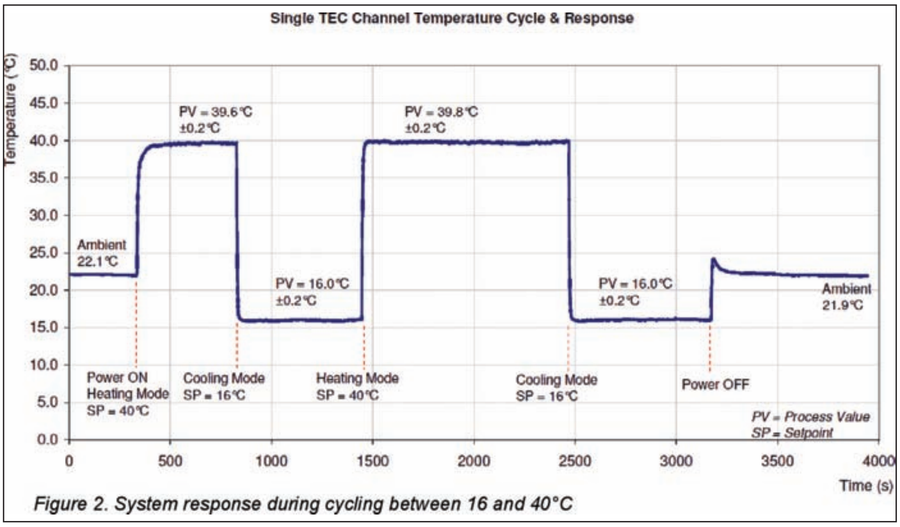

Figure 2. System response during cycling between 16 and 40°C

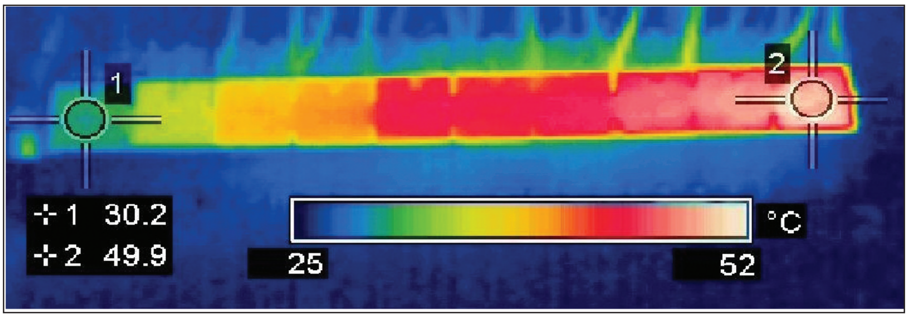

Figure 3. Thermal image of assembled array and capillary showing heating mode gradient from 50°C to 30°C

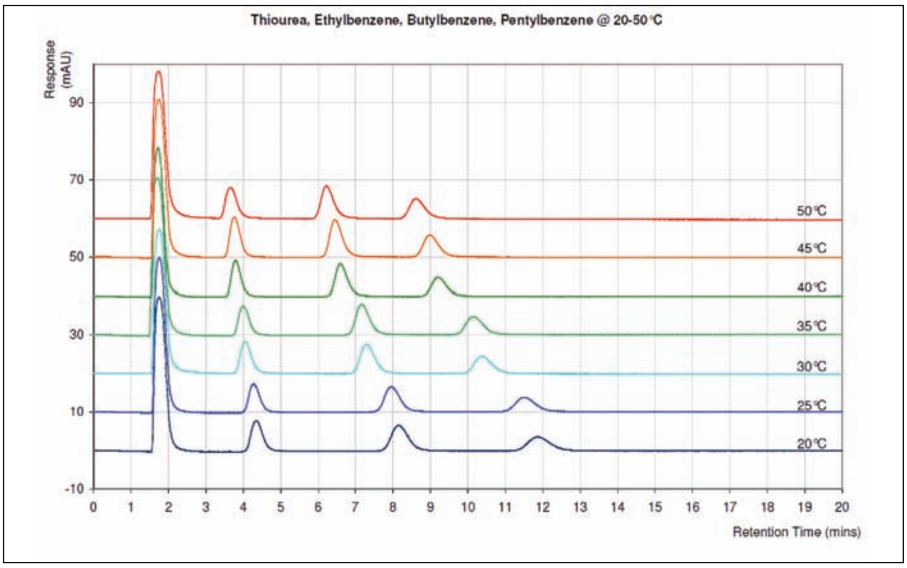

Figure 4. Retention times of alkylbenzenes at increasing temperatures

mounted on the array. Although the thermoelectric modules are capable of operating up to 230°C, the temperatures limits are set by the driver circuits for each of the modules and also by the efficiency of the heat exchanger. In order to protect the circuitry from overheating, the maximum and minimum operating temperatures were limited to 65°C and 15°C respectively. Working at these levels with the current heat exchanger the maximum current load for each channel is approximately 500 mA.

System Performance

The performance of the system was tested by measuring the individual response of each of the modules against time, and by also monitoring the thermal stability over time. System response during heating and cooling was found to be an impressive 6°Cs^{-1} during heating-to-cooling, or vice versa, and approximately 3°Cs^{-1} during power off to power on cycles. During stability testing it was found that deviation from steady state temperatures was in the region of ±0.2°C.

Figure 2 shows the system response while cycling between two set point temperatures of 16°C and 40°C. In addition to system response testing, the assembled system was monitored using a thermal imaging camera to detect any temperature variation between each of the heating zones and the attached capillary. Any variation would be an indication that the transfer of heat between the modules and capillary, or vice versa, was inefficient and that the capillary was at a different temperature than the module.

Figure 3 shows a thermal image of a capillary column attached to the device during a separation. The modules are set up to provide a temperature gradient of 20°C, starting from 50°C at the head of the column, down to 30°C at the end of the column. It can be seen from the image that the capillary column is not visible, confirming that there is an efficient thermal transfer between the column and the Peltier modules. By using the thermal imaging camera the temperature gradient along the column is highly visible and can be monitored in real-time. Although using thermal imaging to visualise thermal profiles and heat transfer was necessary during the construction and testing of the device, it is not used to monitor and control zone temperatures during normal operation.

Testing & Results

In order to test the effectiveness of the heating array, a mixture of alkylbenzenes (ethylbenzene, butylbenzene, and pentylbenzene) was separated on a lauryl methacrylate based monolithic capillary column. During initial trials, several separations were run at various isothermal set points and the retention factor (k) and number of theoretical plates were calculated for each temperature. Figure 4 shows the retention times of the different alkylbenzenes at increasing temperatures.

The effectiveness of the device as a simple column heater is demonstrated by the expected retention data shown in Figure 4, with column equilibration time between injections being a matter of just seconds, in both increased and decreased directions.

Current work is underway to further extend the temperature range of the prototype device and explore a range of novel applications of the new platform. However, this low cost and versatile capillary column heating/cooling platform certainly sets high performance standards for current commercially available column heaters to match.