

# Thermal Management in Supercritical Fluid Chromatography

In supercritical fluid chromatography, very high degrees of accuracy are required for temperature control. On the fluid supply end of the system, cooling is critical. On the separation end, heating is important. This paper discusses temperature control in the HP G1205A supercritical fluid chromatograph.

by **Connie Nathan and Barbara A. Hackbarth**

Supercritical fluid chromatography (SFC) is a technique that has gained acceptance in the analytical chemistry marketplace as a complement to gas chromatography (GC) and liquid chromatography (LC). In the development of the HP G1205A supercritical fluid chromatograph (Fig. 1), leveraging of major components from HP GC and LC products was a primary goal. As a result of this goal, thermal management in the system was a challenge because the components were not intended to operate in the temperature range required for SFC. For example, the LC pumping module was designed to pump fluids at room temperature, while for SFC fluids optimal delivery is at 5°C or lower.

Modifications were made to the components to integrate them into one product. Some components were optimized for SFC. This helped to improve the chromatographic technique by incorporating new ways to manage and control temperature. This paper examines the design modifications made to components to meet the thermal requirements for SFC while leveraging current HP analytical product components.

## SFC System

An SFC unit consists of four major systems: fluid delivery (pumps), separation, detection, and data collection. A brief description of chromatography accompanies this article to provide the reader with an overview of the technology (see page 39).

The HP G1205A SFC project goal of using, wherever possible, components from already proven HP GC and LC instrumentation resulted in reuse of the HP 5890 GC oven, the HP 1050 LC pumping module, a variety of both GC and LC detectors, and the HP ChemStation instrument control software. The major components of the HP G1205A SFC system will now be described in further detail.

**Pumping Module.** The HP G1205A SFC system is available as a single-pump system using CO<sub>2</sub> (or other fluids) for its supercritical mobile fluid or as a dual-pump system that allows modifiers to be added to the CO<sub>2</sub>. Both pumps consist of reciprocating dual pistons in series, allowing for continuous, reliable, and unattended pumping. This eliminates the inconvenience of refilling syringe pumps and allows for control of the flow and changing of the composition. The pumps have feedback control algorithms that dynamically compensate for



**Fig. 1.** HP G1205A supercritical fluid chromatography system.

optimum fluid compressibility and minimize the pressure ripple of the reciprocating pistons.

The HP G1205A modifier pump design parallels the HP 1050 LC pump closely since both are intended to pump incompressible liquids. This is not the case with the supercritical fluid pump, which required more extensive modifications. To pump compressible fluids like CO<sub>2</sub> efficiently, the

## What is SFC?

Chromatography is a process in which a chemical mixture, carried by a mobile phase, is separated into components as a result of differential distribution of the solutes as they flow over a stationary phase. The distribution is the result of differing physical and/or chemical interactions of the components with the stationary phase. On a very basic level, chromatography instrumentation consists of (1) a delivery system to transport the sample within a mobile phase, (2) a stationary phase (the column) where the separation process occurs, (3) a detection system that identifies or distinguishes between the eluted compounds, and (4) a data collection device to record the results (see Fig. 1).

The choice of which chromatographic method to use depends on the compounds being analyzed. In gas chromatography (GC), the mobile phase that carries the sample injected into the system is a gas. GC is generally a method for volatile and low molecular weight compounds. High-performance liquid chromatography (HPLC) is primarily used for analysis of nonvolatile and higher molecular weight compounds. A combination of desirable characteristics from both of these methods can be obtained by using a supercritical fluid as the mobile phase. A supercritical fluid is a substance above its critical point on the temperature/pressure phase diagram (see Fig. 2). Above the critical point, the fluid is neither a gas nor a liquid, but possesses properties of both.

The advantage of SFC is that the high density of a supercritical fluid gives it the solvent properties of a liquid, while it still exhibits the faster physical flow properties of a gas. In chromatographic terms, supercritical fluids allow the high efficiency and detection options associated with gas chromatography to be combined with the high selectivity and the wider sample polarity range of high-performance liquid chromatography. Applications that are unique to SFC include analysis of compounds that are either too polar, too high in molecular weight, or too thermally labile for GC methods and are undetectable with HPLC detectors. Another benefit of SFC over LC is the reduction of toxic solvent use and the expense associated with solvent disposal. This aspect has become increasingly important as environmental awareness becomes a larger issue.

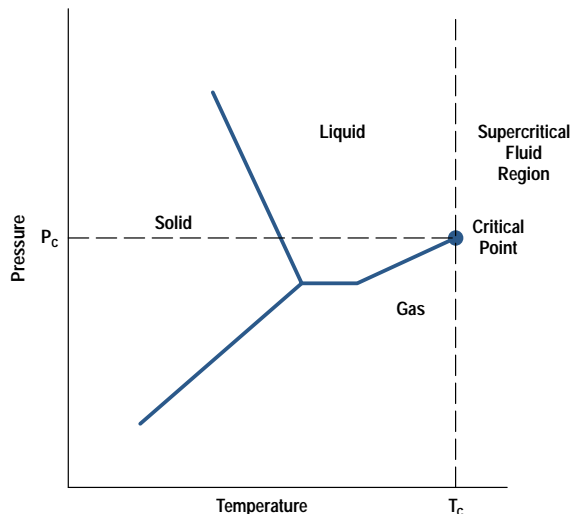


Fig. 2. Phase diagram with critical point and supercritical region.

Hewlett-Packard developed and manufactured its first SFC instrument in 1982. For the past decade, SFC has primarily been used in R&D laboratories. The market has now expanded to include routine analysis for process and quality control as SFC is continuing to gain acceptance as a complementary technique to GC and LC.

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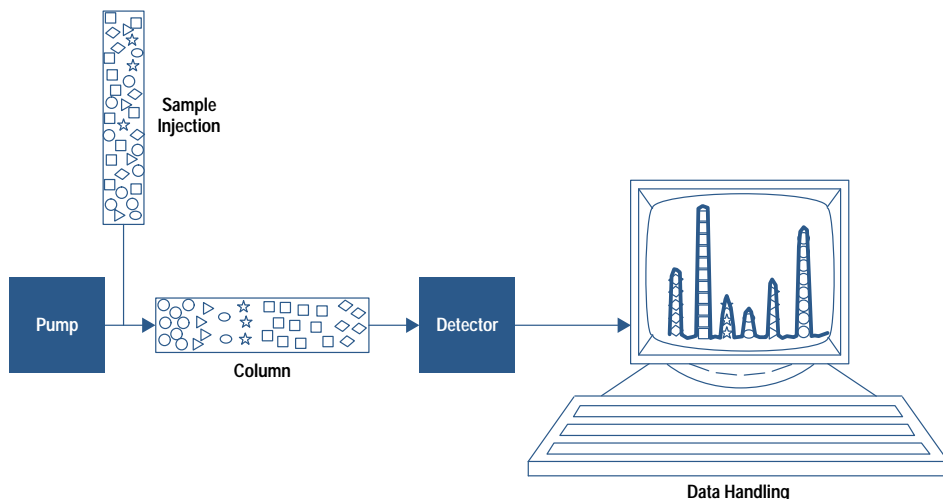


Fig. 1. Basic components of a chromatographic system.

supercritical fluid pump head must be cooled to lower temperatures. Peltier cooling was selected for its clean, self-contained, quiet, and reliable operation. Additionally, the Peltier elements provide precise temperature control, minimizing pump flow noise and allowing more accurate compressibility compensation.

**Separation Phase.** The column is where the actual separation of components occurs. The unique interactions of the compounds with a given stationary phase at certain conditions

results in different elution times from the column. The HP G1205A system can be used with capillary, narrow bore, or packed columns. Viscosity of a supercritical fluid is at least one order of magnitude higher than the viscosity in the gaseous state, but is one to two orders of magnitude less than in the liquid state. This translates into a pressure drop across the column that is ten times greater with HPLC than it is with SFC. The lower viscosity of SFC allows longer columns, which yield better separation of closely related compounds.

Selectivity refers to the selective physicochemical interactions between the sample components and the column. In SFC, the selectivity of compounds is adjusted by changing temperature, mobile phase density, and/or composition of added modifiers. These control parameters are a combination of those available in either a pure GC or a pure LC application. The column is installed in a temperature-controlled environment, the GC oven.

**Detection.** SFC not only supports both capillary and packed columns but also a variety of GC and LC detector options. Detectors are devices that sense the presence of the different compounds eluting from the column and convert this information into an electrical signal. Selection of which detector to use depends on several factors including the type of information needed from the analysis, the sensing level required, and the complexity of the compounds.

GC detectors that are available in SFC are the flame ionization detector, the nitrogen phosphorus detector, and the electron capture detector. The electron capture detector is a halogen-sensitive detector primarily used in pesticide analysis. The flame ionization detector is a universal detector for a wide variety of organic compounds. The nitrogen phosphorus detector is a selective detector for compounds containing nitrogen and phosphorus, and is also used for pesticide and clinical applications. A new dimension to detection capability is made possible with the use of modifiers with the electron capture and nitrogen phosphorus detectors. The flame ionization detector and the nitrogen phosphorus detector required design changes for SFC use.

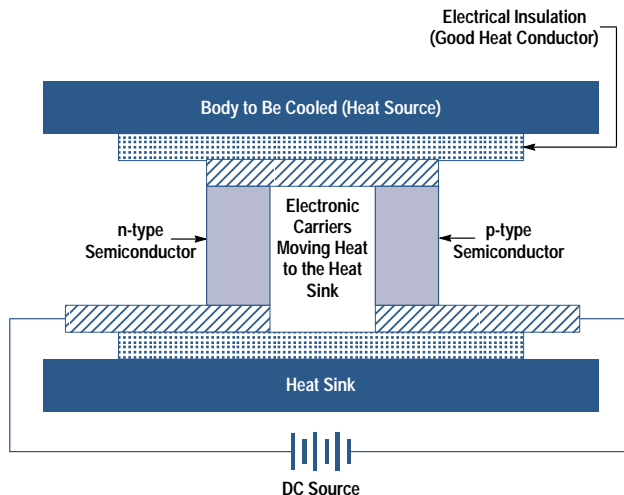
LC detectors available in SFC include the multiple wavelength detector, the variable wavelength detector, and the diode array detector. These cover application needs for high sensitivity and selectivity.

**Data Acquisition System.** The data acquisition system sorts and executes the many different signals, functions, and commands. For example, the first thing the instrument needs to know is how it is configured (one pump, two pumps, which detectors, injection method, etc.). Commands are given to operate the system at particular conditions (fluid flow rate, pressure, temperature, etc.). Electronic signals from the detectors are collected and converted to useful chromatographic information. Analytical results are stored and later presented in a meaningful report format determined by the user. The software platform for the HP G1205A SFC was leveraged from existing ChemStation platforms. Working through Microsoft® Windows as the operating control system, it can multitask with other applications and network with other data systems.

The remainder of this article focuses on the thermal design of the SFC pump and one of the detectors.

### SFC Pump

The pump module is an LC pump optimized to operate with supercritical fluids at low temperatures and high pressures. Supercritical fluids such as CO<sub>2</sub> are pumped through the system at rates as high as 5 milliliters per minute and pressures as high as 400 bars. The initial approach was to use cryogenic CO<sub>2</sub> to cool the pump surface. The proposed design was a channel of metal tubing with cryogenic CO<sub>2</sub> flowing through it. Using a network of channels, the cryogenic CO<sub>2</sub> is evenly



**Fig. 2.** Thermoelectric (Peltier) cooler.

distributed through the pump and provides an efficient method of cooling. The design could be further optimized by using materials with high thermal conductivity for the pump head to improve the efficiency and enhance the cooling.

The HP supercritical fluid extractor (SFE), introduced in 1990, used a similar approach. The SFE uses a supercritical fluid to extract the sample and prepare it for analysis. The SFE pump, like the SFC pump, must be cooled. Cryogenic CO<sub>2</sub> through a single stainless steel tube is used to cool the surface of the LC pump head. Although this design met the functional objective, it required an additional source of CO<sub>2</sub>. Supercritical fluid grade CO<sub>2</sub> is not used for cryogenic purposes because it is more expensive and a purer form of fluid.

To make the product more compact and self-contained, a thermoelectric (Peltier) device was investigated. Thermoelectric cooling provides one of the simplest means of refrigerating electronic equipment without using compressors or liquid refrigerants. A thermoelectric device is a heat pump that operates electronically. The device is made from two semiconductors, usually bismuth telluride, that either have an excess (n type) or deficiency (p type) of electrons. Current passes through the dissimilar conductors creating a temperature differential across the device. Heat energy is transferred from the cold side (body to be cooled) to the hot side (heat sink) and dissipated. This is known as the Peltier effect. Fig. 2 is a schematic diagram of a thermoelectric device. Table I provides a comparison of a thermoelectric heat pump with other types of refrigerant cooling systems.

In applying thermoelectric technology successfully, three design issues to be considered are:

- The operating environment
- How to dissipate the heat efficiently
- Estimated amount of heat the device needs to remove.

To maintain a 5°C operating temperature, the final design (see Fig. 3) includes several thermoelectric devices sandwiched between an aluminum heat sink and a copper cold plate.

Preliminary results showed that the thermoelectric device could maintain a temperature of 4°C at the pump head surface. If the heat sink reaches the temperature of the hot side

**Table I**  
**Refrigerant Cooling Comparison**

	Thermoelectric	Cryogenic Fluids
Source	No liquid coolant	Requires liquid coolant source
Temperature Operating Range	Can accommodate temperature extremes (-100°C to +100°C)	Provides cooling only
Operation	Electronically controlled	Moving components or valves to control fluid flow
Physical Attributes	Modular and compact	Bulky with extra hardware (valves, tanks, etc.)

of the Peltier device, then the heat sink alone cannot effectively dissipate the heat. A boxer fan at the rear of the pump cools the heat sink. The interfaces between the Peltier cooler, the heat sink, and the cold side of the pump head are secured with screws and epoxy to minimize thermal losses and provide a good thermal circuit.

Further efforts to optimize the design included the selection of materials with high thermal conductivity. A nickel heat exchanger with porous sintered nickel is incorporated in the design to cool the CO<sub>2</sub> conductively before it enters the system. The temperature of the CO<sub>2</sub> as it enters the pump is near room temperature. The heat exchanger is in thermal contact with the cold plate. The cold temperature is conducted into the heat exchanger to lower the fluid temperature to 5°C.

The thermoelectric device combined with conductive and convective cooling techniques allows the pump module to be self-contained and modular. This approach requires no external source for cryogenic cooling.

### Flame Ionization Detector

As described above, the separation and detection module includes a choice of columns and detectors. The flame ionization detector is thermally optimized for SFC. It is mounted to the top of the GC oven, which controls the temperature of the column that contains the sample. The flame ionization

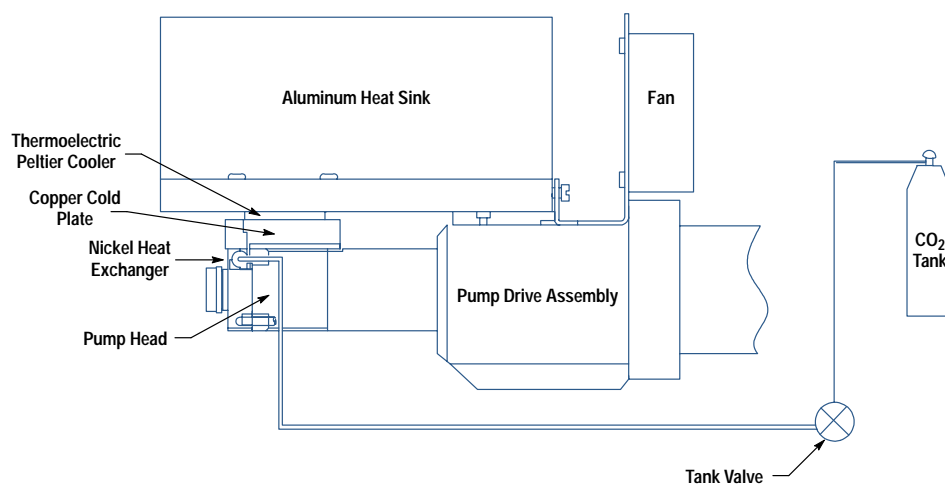
detector has two separate temperature-controlled heated zones. The base of the detector protrudes into the oven. The top of the detector, the collector, is a controlled zone exposed to room temperature. The oven and detector base both operate at temperatures up to 450°C with less than 0.5°C variations.

A flame ionization detector is a stainless steel block with a jet (a stainless tube) attached to it. Heat is applied by a rod heater. At the tip of the flame ionization detector jet, a flame is produced by the combustion of hydrogen and air. The sample elutes into the flame and ionizes. The detector generates a signal that represents the amount of carbon in the sample. Fig. 4 compares GC and SFC flame ionization detectors. The temperature of the zone just below the jet is critical. Slight changes in the temperature affect the reproducibility of the results.

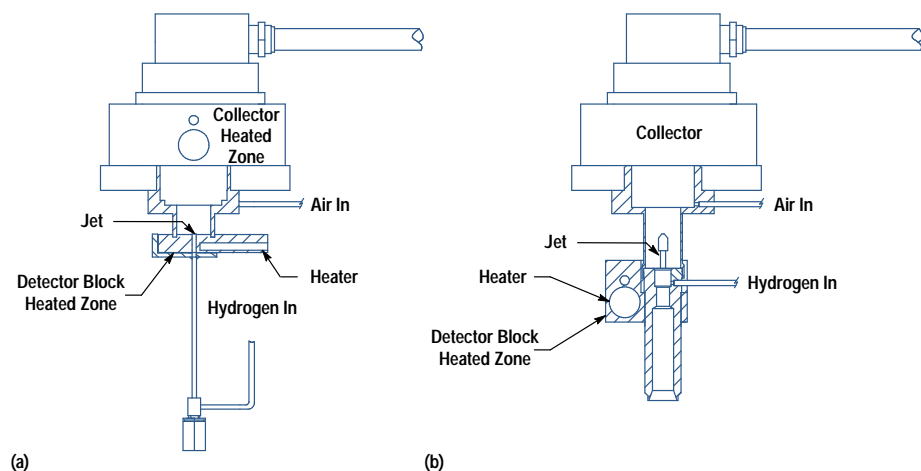
The GC flame ionization detector was evaluated for potential use with SFC. The GC detector has a long heated zone with a removable jet positioned above the zone as shown in Fig. 4. A temperature gradient exists between the heated block and the jet tip of the GC flame ionization detector because of the position of the heater and sensor and the location of the jet relative to the heater. When this GC design is used for SFC, spiking and flameout occur. Spiking is a fluctuation in the signal that shows up in a chromatogram. It is the result of the CO<sub>2</sub> icing. Flameout occurs if there is too much CO<sub>2</sub> flowing through the jet. A long heated zone also causes undesirable density drops in CO<sub>2</sub> that allow the sample to precipitate.

Customers familiar with flame ionization detectors expect the results to be clear and reproducible. The primary design consideration for optimization of the flame ionization detector for SFC was to solve the problems seen with the GC design, that is, to minimize density drops and eliminate spiking and flameout.

A shorter heated zone flame ionization detector was designed. The jet is an integral part of the heated zone (it is physically brazed to the zone) to ensure that there is no thermal break between the zone base and the jet. The heater and sensor are positioned close to the jet. The temperature gradient is minimized. The jet orifice size is optimized to prevent flameout at high CO<sub>2</sub> flow rates. A second heated zone is added to the SFC flame ionization detector to eliminate problems of spiking and condensation above the jet.



**Fig. 3.** Sketch of the SFC pump showing the major components and the thermoelectric (Peltier) device.



**Fig. 4.** Sketches of the SFC (a) and GC (b) flame ionization detectors. Note the difference in the heated block size and the location of the jet.

Condensation forms from the combustion of hydrogen and air when the detector block temperature is below 100°C. Table II is a comparison of the GC and SFC detectors.

**Table II**  
**Comparison of SFC and GC Flame Ionization Detectors**

	SFC Detector	GC Detector
Physical Size	6 mm thick, compact with jet permanently attached	25 mm thick with jet a separate part
Temperature Gradient	1°C from sensor to jet tip	17°C from sensor to jet tip
Problem Area	No spiking or flameout	Spiking and flame-out when used as an SFC detector
Collector	Heated collector zone	Collector not actively heated

The SFC flame ionization detector is insulated from the oven so that the heat from the oven has minimal effect on it. The SFC detector's minimum operating temperature is the oven temperature plus 10°C because of convection and conduction of heat from the oven.

To achieve temperature stability, the SFC flame ionization detector heated zone required changes in the temperature control parameters. The controller uses the Ziegler-Nichols algorithm<sup>1</sup> to obtain the proportional (P), integral (I), and derivative (D) terms in the control algorithm. This algorithm defines the PID constants such that the object reaches its desired steady-state temperature without large offsets or deviations. The PID controller is designed for larger masses such as the GC heated detector zones. Although it takes longer for larger masses to heat up, the oscillations are minimal and therefore it is easier to dampen the response and bring temperature under control. The SFC flame ionization detector is 1/4 the size of the GC design, so it heats up very quickly. Using the GC PID constants, large oscillations were seen because of poor temperature control. New initial values for the PID parameters for the SFC detector were derived using the Ziegler-Nichols tuning algorithm. A trial and error method was then applied to fine-tune the PID parameters to eliminate oscillations.

## Results

The major result was the introduction of an HP G1205A SFC system in May 1992 that meets its performance goals. It was a challenge to reuse existing components that were not designed with SFC in mind. In SFC, control of temperature in different regions of the system is critical to the success of the chemical analysis and the performance of the instrument. To make components perform under conditions for which they were not originally designed was a major success for the team. Another tangible result was the reduction of product cost by consolidation and reuse of components. The product is a compact modular design and maintains the integrity of the existing designs it leverages. The introduction of a thermoelectric Peltier-cooled pump head provides an advantage over designs that use a second source of CO<sub>2</sub> to cool the pump head. Other HP analytical products have incorporated the Peltier device. The SFC flame ionization detector, with its shortened zone, has improved the quality of the analytical results.

## Acknowledgments

The work described in this paper is the result of several years of development efforts by the R&D project team. Specifically, Hans Georg Haertl is responsible for successfully incorporating the Peltier device into LC pump design. Hans Georg was an engineer on loan to the site from the HP Waldbronn Division in Germany. The other members of the project team included Chris Toney (project manager), Elmer Axelson (software), Paul Dryden (firmware), Bill Wilson (chemist), Terry Berger (chemist), Mahmoud Abdel-Rahman (firmware and hardware), and Joe Wyan (hardware). Our success must also be shared by several other functional groups (manufacturing, marketing, purchasing, and administrative support) which were instrumental in the release of the product. Without the combined efforts of these individuals, the SFC would not have met its targeted release date.

## Reference

1. G.K. McMillan, *Tuning and Control Loop Performance*, Instrument Society of America, 1990, Chapter 1.

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