Waters Lab Highlights

An Internal Communication of Applications and Techniques

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Use of Waters™ Solvent Delivery Systems in Supercritical Fluid Applications

Recently several customers have asked if it is possible to use Waters solvent delivery systems to pump mobile phases for supercritical fluid chromatography and extraction. As we shall see, the answer, based on reports published by Greibrokk and coworkers,[1,2] is a qualified yes. These investigators have modified an M6000A and an M590 for use with carbon dioxide.* Carbon dioxide is the mobile phase used in the overwhelming majority of supercritical fluid applications. In a closed system at room temperature (21°C) carbon dioxide is a liquid having a vapor pressure of 853 psi (58.8 Bar). The carbon dioxide is thus delivered to the inlet side of a pump as a highly volatile liquid, and as such poses the same challanges to the solvent delivery system as do other volatile substances (such as dichloromethane), only to a greater degree. (Carbon dioxide becomes a supercritical fluid only when heated above its critical temperature, 31°C.)

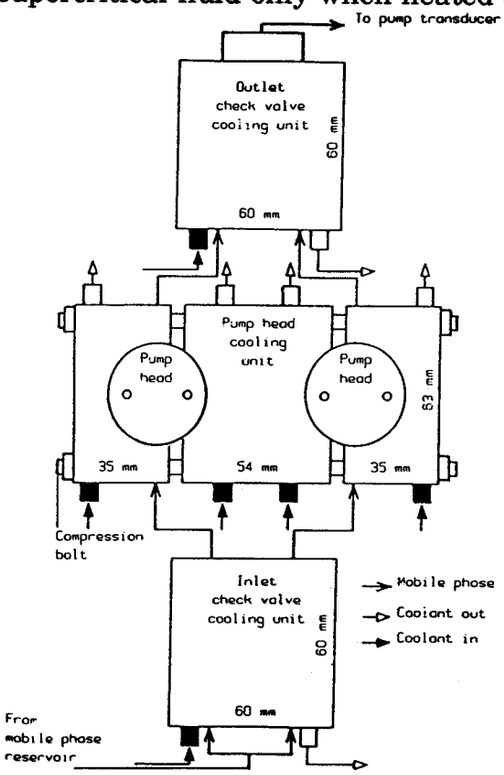

Figure 1: Dimensions and flow diagram of pump head and check valve cooling units.

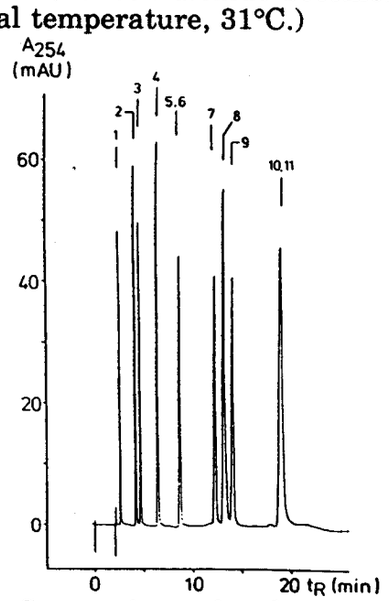

Figure 2: Separation of toluene (1), naphthalene, (2), biphenyl (3), Fluorene (4), phenanthrene (5), anthracene (6), Fluoranthene (7), benzo [a] fluorene (8), pyrene (9), and triphenylene + chrysene (10,11). The flow of liquid CO2 was increased from 0.2 to 0.4 mL/min over a 5 min. period. The pressure on the pump was measured to 125-180 bar. Detector was at 254nm. Column temperature was 37°C. Injector temperature was 32°C.

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In order to successfully pump liquid carbon dioxide, several issues must be addressed. These issues are cavitation in the pump heads during the fill stroke, materials compatability, and pulsation. Cavitation can be controlled by reducing the vapor pressure of the liquid carbon dioxide. This is accomplished by chilling the pump heads and check valves by means of a circulating coolant. Greibrokk and coworkers[2] constructed a bolt-on cooling manifold for the round pump heads of the 590.** This arrangement is illustrated in Figure 1. The rectangular pump heads of the M6000A were cooled by means of coolant channels drilled directly into the heads.

In addition to the provision for chilling the pump heads, extra sets of inlet and outlet check valves (non-Waters) were added,[1] and a 2 micron inline filter was placed in the mobile phase supply line. Stainless steel tubing must be used for the supply lines.

The performance of the modified 590 and 6000A pumps was quite satisfactory. In more than three years of operation, no measureable leaks were observed at the plunger seals.[2] There were some problems associated with absorption of carbon dioxide by the O-rings in the added (non-Waters) check valves, however. In constant flow mode, both models produced baseline noise on a UV detector less than 10^{-4} absorbance units in amplitude.[1] More significant noise was seen with a flame ionization detector, which is sensitive to mass flow through the detector.[2] In constant pressure mode (desirable in supercritical fluid applications), the 590 reportedly produced greater noise than when in constant flow mode. From the published reports, it appears that the modified Waters pumps described above are best suited for supercritical fluid chromatography with packed columns (1 - 2mm I.D.) and UV detection (Fig. 2), and for supercritical fluid extraction, where small pulsations do not interfere.

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* Waters Solvent Delivery Systems are designed and intended for use with ordinary "sub-critical" liquids. Successful use for any other purpose cannot be guaranteed by Waters, and the user is liable for the proper implementation of any component modifications. The warranty status for Waters pumping systems, however, is compromised only in respect to the modified component(s). The warranty status on all other pump component(s) is not affected by adaption for supercritical fluid applications. Waters does not provide parts or installation service for any of the modifications described in this Lab Highlight.

** The same arrangement may be used on other Waters pumps with round heads (510, 600 series). The solvent proportioning valve should be bypassed on 600 series gradient models, however.

References

1 T. Greibrokk, A. L. Blilie, E. J. Johansen, and E. Lundanes, *Anal. Chem.* **56**, (1984) 2681-4.

2 T. Greibrokk, J. Doehl, A. Farbrot, and B. Iversen, *J. Chrom.*, **371**, (1986) 145-152.

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