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## Introduction

The aim of this project is to evaluate a solid phase microextraction (SPME) method using a cooled extraction phase to achieve higher sensitivity for compounds with a large range of volatility and polarity when compared to the SPME commercial fibers.

In order to effectively exploit the headspace SPME, high temperature usually need to be used to accelerate the mass transfer. Thus releasing more analytes from the sample matrix to the headspace. However, since the absorption is an exothermic process, an increase in temperature decreased the distribution coefficients of analytes between the coating and the sample matrix resulting in lower extracted amount under equilibrium. Therefore, cold fiber SPME was developed to address this limitation by heating up the sample while simultaneously cooling the extraction phase. In this cooling/heating environment, the coating/sample matrix distribution coefficient of analytes increases dramatically according to the following equation [1].

$$K_T = K_0 \frac{T_2}{T_1} \exp \left[ \frac{C_p}{R} \left( \frac{\Delta T}{T_1} + \ln \frac{T_2}{T_1} \right) \right]$$

Where,  $K_0$  is the coating/headspace distribution coefficient of analyte when the coating and headspace temperature are both at  $T_1$ . The cold fiber device was coupled with GERSTEL autosampler to achieve completely automation [2]. A septumless head injector was utilized to accommodate the large external needle. Fourteen compounds within a large range of volatility and polarity were chosen as target compounds for fully evaluate the capacities of this device.

## Experimental set-up

**Instrument:** Gas chromatograph (GC) and mass spectrometer (MS) was used for separation and analysis. A GERSTEL multipurpose sampler (MPS 2) was coupled to achieve the automation.

### Experimental design:

- Fabrication of the fully automated cold fiber device.
- Evaluation of the reproducibility of the cold fiber SPME.
- Comparison of the extraction efficiency of cold fiber to the PDMS coating.
- Comparison of the extraction efficiency of cold fiber to the commercial DVB/CAR/PDMS coating.
- Comparison the linear range of calibration curve and limit of detection of cold fiber to other fibers

## Results and discussion

### • Fabrication of the fully automatic cold fiber device.

The cold fiber device was built on a 100 uL syringe barrel. The liquid CO<sub>2</sub> tubing was inserted inside the plunger tubing.

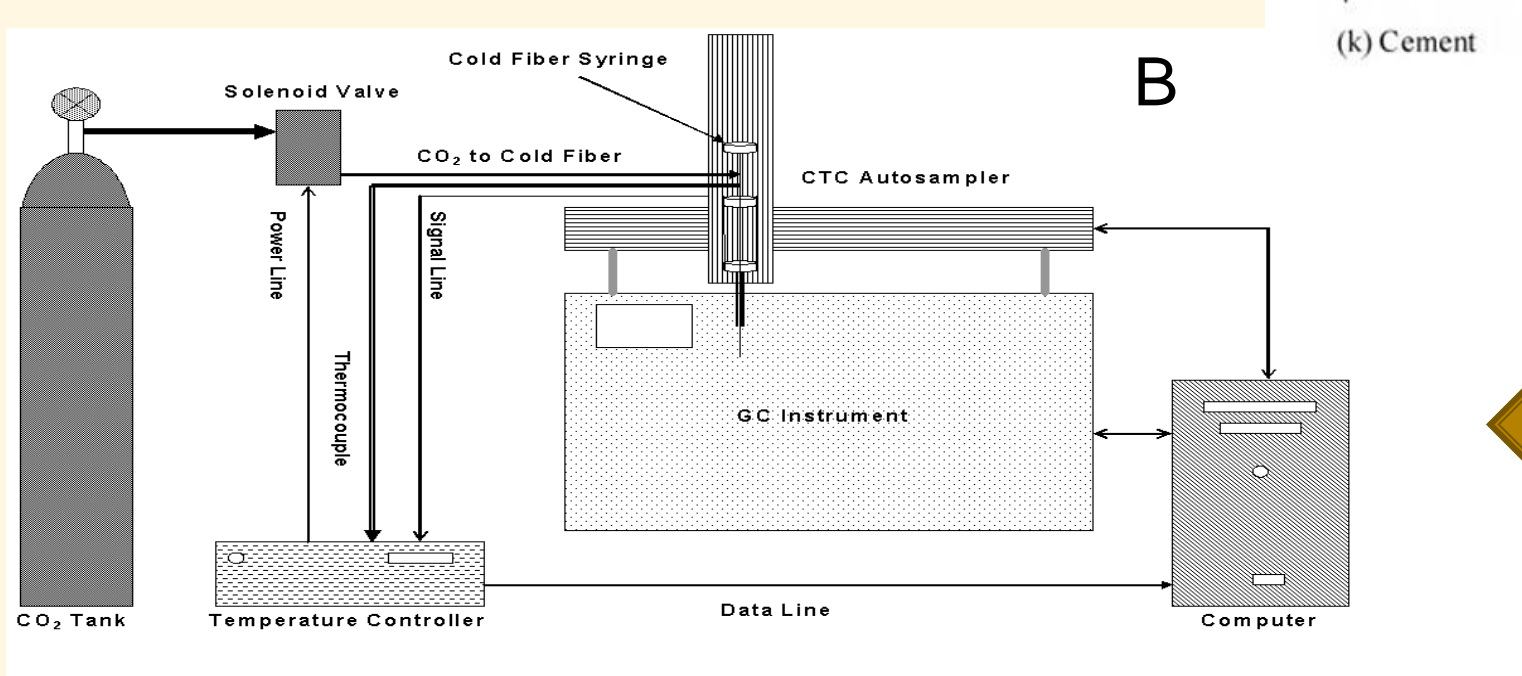
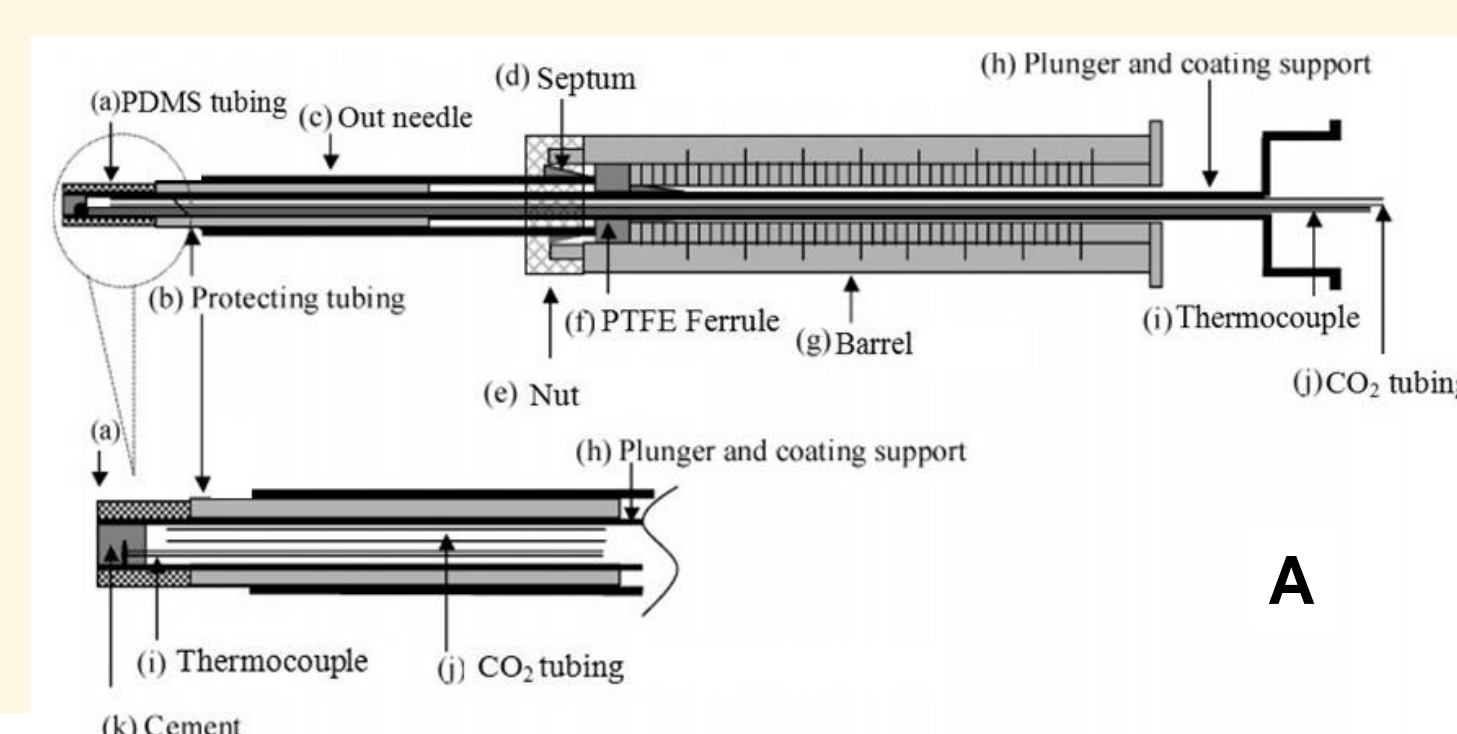


Figure 1. (A) The schematic diagram of the internally cooled SPME device and (B) when the device was mounted on the the autosampler.

### • The reproducibility of different fibers

Table 1. The comparison of fibers' reproducibility of peak area and the maximum shift of retention time

Compounds	Cold fiber		DVB/CAR/PDMS		CF no cooling		commercial PDMS		CF empty vial**	
	PA* RSD% (n=10)	RT* shift (min)	RSD% RT	shift (min)	RSD% shift (min)	shift (min)	RSD% shift (min)	shift (min)	RSD% shift (min)	shift (min)
2-hexanone	11.78	0.49	6.16	0.02	14.42	0.04	16.38	0.03	6.90	0.03
Ethyl butanoate	8.38	0.39	4.77	0.02	9.10	0.03	7.44	0.01	12.00	0.02
Heptanone	7.60	0.28	5.95	0.02	9.75	0.02	10.71	0.01	11.50	0.01
Heptanal	9.55	0.27	5.05	0.02	7.59	0.01	6.11	0.01	10.40	0.01
1-heptanol	6.77	0.10	9.40	0.02	12.56	0.01	ND	0.00	9.90	0.02
Octanal	11.49	0.12	7.02	0.01	8.62	0.01	8.67	0.01	13.50	0.01
2-nonanone	8.96	0.05	8.13	0.01	9.63	0.00	7.08	0.00	9.70	0.01
Ethyl heptanoate	8.58	0.05	6.12	0.01	7.01	0.00	6.46	0.00	9.40	0.01
Nonanal	14.06	0.05	6.90	0.01	8.31	0.00	6.06	0.00	10.00	0.01
Nonanol	11.20	0.02	11.41	0.01	14.37	0.00	6.51	0.00	9.20	0.01
2-tridecanone	6.12	0.01	2.93	0.00	7.43	0.00	4.94	0.00	8.60	0.00
Heptadecane	27.87	0.01	19.69	0.00	29.15	0.00	12.53	0.00	7.60	0.00
2-heptadecanone	18.32	0.01	22.51	0.00	14.59	0.00	13.32	0.00	8.80	0.00
Ethyl hexadecanoate	32.56	0.00	31.77	0.00	23.80	0.00	24.81	0.00	8.90	0.00

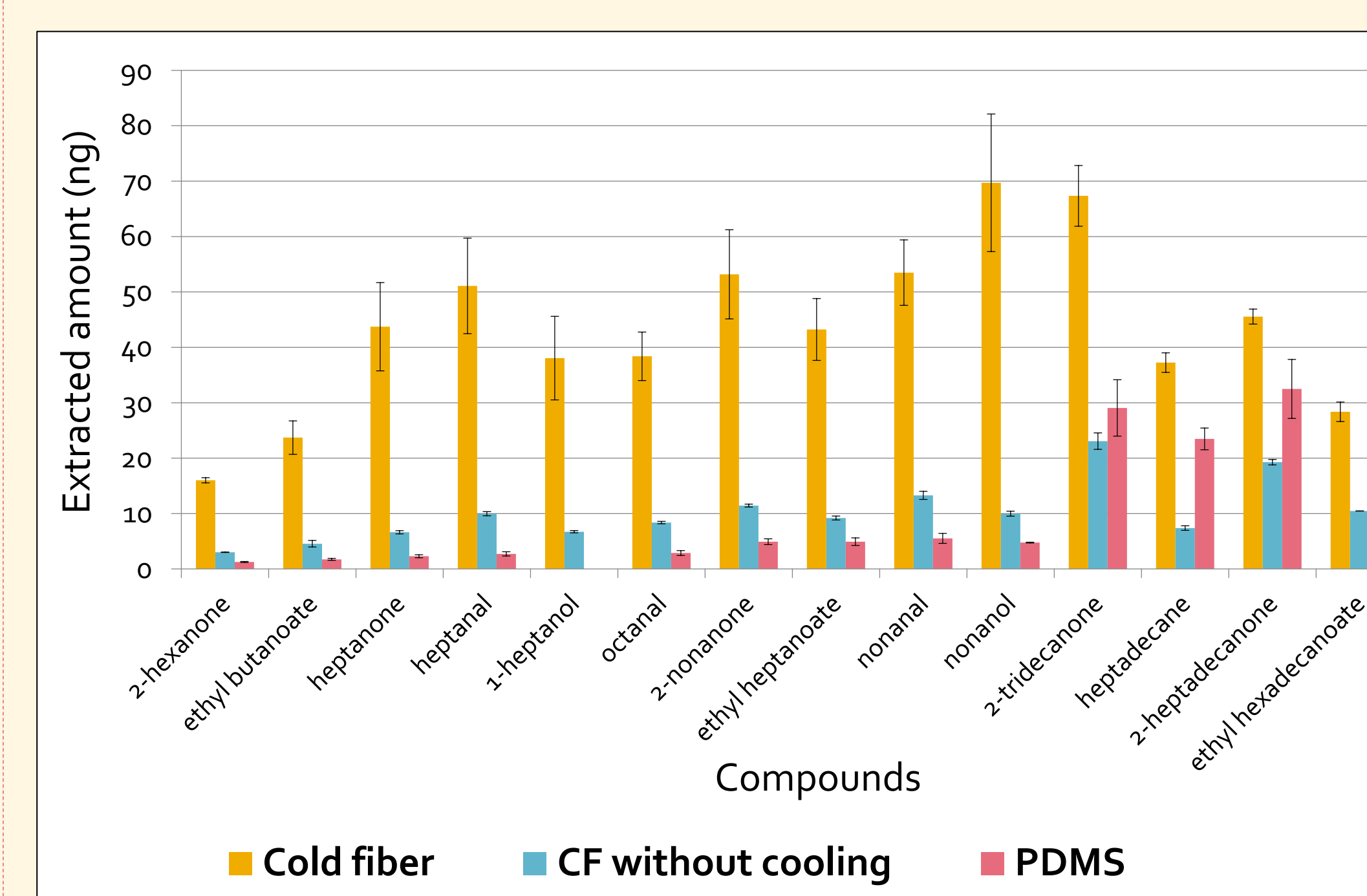
\* PA and RT represents for peak area and retention time respectively.

\*\* Empty vial means the standard were spiked directly to the empty vial without aqueous.

### Discussion:

- The peak area reproducibility of the automated cold fiber is comparable to the commercial fibers.
- The larger retention time shift of cold fiber especially for the volatile compound is caused by the introducing of the water during injection.

### • The comparison of cold fiber extraction efficiency other PDMS fibers.



Extraction time: 40 min  
Extraction temperature:  
Cold fiber: 90 °C for sample matrix and 35 °C for coating.  
Cold fiber without cooling and commercial PDMS: 70 °C for sample matrix and coating.

Figure 3. Comparison of extraction efficiency of cold fiber, cold fiber without cooling and commercial PDMS fiber for 14 compounds under the optimized condition for each fiber.

### Discussion:

- The extraction efficiency of the automated cold fiber is much higher than that achieved by the cold fiber without cooling due to the effect of cooling increasing the distribution coefficient.
- The higher extraction efficiency of cold fiber without cooling compared to the commercial PDMS fiber for volatile compounds results from the high volume of extraction phase.
- For the semi-volatile compounds, the amount extracted by the cold fiber is not significantly higher than that obtained with the PDMS fiber. One reason is that the equilibrium time for cold fiber extraction is much longer than 40 min due to the low diffusion coefficient. Another reason may be caused by the condensation of water on the surface of the fiber during extraction. The hydrophobic property of semi-volatile compounds influences the diffusion process of those analytes on the coating surface.

### • The comparison of cold fiber extraction efficiency with other PDMS fibers.

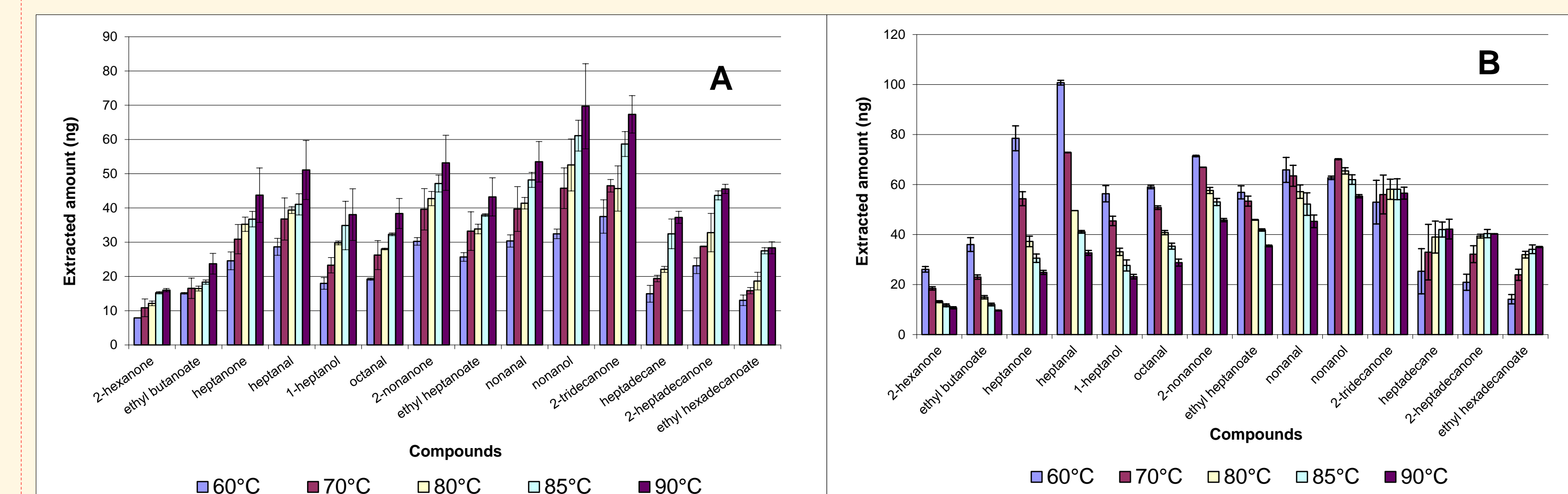


Figure 4. Extraction temperature profile of (A) cold fiber and (B) DVB/CAR/PDMS fiber for aqueous matrix sampling.

### Discussion:

- For cold fiber, the amount extracted for all compounds increased with an increase in the sample matrix temperature. This is due to the larger temperature gap created between the sample matrix and the coating.
- For the DVB/CAR/PDMS, the extraction amount is a compensation between the increase of Henry constant and decreased distribution coefficient.
- The major advantage of cold fiber is it can be used for high temperature sampling.

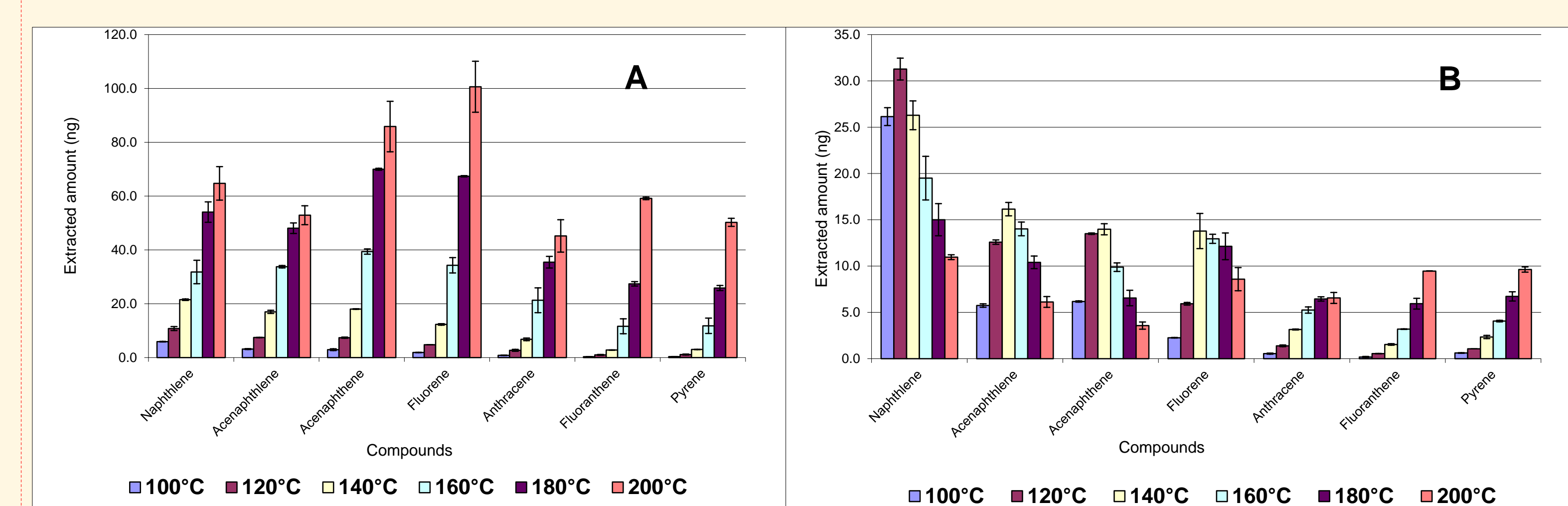


Figure 4. Extraction temperature profile of (A) cold fiber and (B) DVB/CAR/PDMS fiber for solid matrix sampling.

### Discussion:

- For higher extraction temperature extraction, the extraction efficiency of the cold fiber is much higher than the DVB/CAR/PDMS.

### • Comparison the linear range of calibration curve and limit of detection of cold fiber to other fibers

The linear range and LOD of cold fiber was compared to that obtained by commercial PDMS and DVB/CAR/PDMS fibers.

### Discussion:

- Calibration curve linear range of cold fiber is much larger than the DVB/CAR/PDMS.
- LOD for the cold fiber is lower than the commercial PDMS fiber.

## Conclusion

- The automated cold fiber SPME method can achieve higher sensitivity than other commercial fibers for solid sample sampling due to the cooling effect of the extraction phase.
- The cold fiber SPME is suitable for high temperature sampling exemplified by solid matrix sampling.

## Reference and acknowledgement

- [1] Z. Zhang, J. Pawliszyn, Anal.Chem 67 (1995) 34.
- [2] Y. Chen, J. Pawliszyn, Anal.Chem 78 (2006) 5222.

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