Microtrap modulated flame ionization detector for on-line monitoring of methane

Chongdee Thammakhet [a], Panote Thavarungkul [b], Roman Brukh [c],
Somenath Mitra [c], Proespichaya Kanatharana [a],*

[a] *Analytical and Environmental/Trace Analysis Research Unit, Department of Chemistry, Faculty of Science, Prince of Songkla University,
Hat Yai, Songkhla 90112, Thailand*
[b] *Biophysics Research Unit: Biosensors and Biocurrents, Department of Physics, Faculty of Science, Prince of Songkla University,
Hat Yai, Songkhla 90112, Thailand*
[c] *Department of Chemistry and Environmental Science, New Jersey Institute of Technology, Newark, NJ 07102, USA*

Abstract

A microtrap for on-line analysis of trace methane was developed. Silicosteel tubing, 15 cm long, 1.02 mm i.d. and 1.59 mm o.d. was packed with Carbosphere 80/100 mesh and placed between the standard gas source and the flame ionization detector (FID) to be used as a preconcentrator and an injector. The sample stream was passed continuously through the microtrap that was heated at a fixed interval by an electric pulse. To achieve the highest adsorption and desorption efficiency, parameters affecting the response of the system were optimized, and adsorption temperature in the range of 25 to $-50\,^\circ$C was studied. The response from the microtrap as compared to that from direct-flame ionization detector was enhanced by as much as 260 times. The on-line microtrap system showed good linearity ($r^2 > 0.99$), low detection limit (28.3 ppbv) and good long term stability (relative standard deviation, RSD of less than 5.0%). Therefore, this simple device is suitable for on-line analysis of trace methane and similar small molecules in the environment as in high purity gases.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Methane; Microtrap; Carbosphere; High purity gases

1. Introduction

Methane, due to its abundance, can occur even in high purity gases which are crucial for research and development applications and this contamination can have a negative impact on the process [1]. Therefore, measurements and control of the impurities play an important role in high purity gases research applications.

To determine methane concentration, samples are generally collected before injected into a gas chromatograph [2]. A small injection volume is preferred but this will limit the sensitivity of the detector and a preconcentration step is generally needed. Even when the sensitivity is increased by a precon-centration step, there is always the delay between sampling and analysis [3–5]. This is clearly not acceptable for continuous, on-line monitoring, but also adds error to the measurement process. One approach is using an on-line cryogenic trap to focus the sample in a narrow band at the head of the column. The trap rapid cooling and re-heating, ensuring the reproducibility and optimum peak shape. However, if the source has a lot of water, it freezes and plugs the sorbent trap [6]. It is also quite complicated to apply, therefore, a microtrap was introduced as an alternative.

A microtrap is a small capillary tubing packed with a small amount of adsorbent. Sample containing the analytes continuously flow into the microtrap, and the organics are trapped by the sorbent while the gas flows through. The retained organics are rapidly desorbed by resistive heating with pulse of electric current which make an injection for GC separation.

The main advantage of microtrap as an injection device over a sample valve is, it also serves as a sample preconcentrator, which allows the larger sample volume to be analyzed for trace components [7–10].

In this paper, the development of an on-line microtrap that is interfaced directly to the flame ionization detector (FID) for the determination of methane is reported.

2. Experiment

2.1. Instrumentation

Fig. 1a shows the schematic diagram of the on-line system used for methane monitoring. All experiments were carried out by a gas chromatograph equipped with a conventional FID and the results were integrated by CR-4A Integrator (GC-14A and CR-4A Integrator, Shimadzu, Japan). Methane standard concentration of 11.6 part per million by volume (ppmv) (TIG, Thailand) was used to study the characteristics of the microtrap packed with a suitable adsorbent.

2.2. Microtrap

By considering the suitability of pore size and surface area, Carbosphere 80/100 mesh (Alltech, IL, USA) was selected as the adsorbent. It was packed in a 15 cm long, 1.02 mm i.d., and 1.59 mm o.d., silicosteel welded/drawn 304 grade stainless steel tubing (Restek Co., Bellefonte, PA, USA). The microtrap was placed in-line of the stream of the standard gas and in front of the detector to act as a trap/concentrator as well

as an injector (Fig. 1a). The microtrap was rapidly heated by applying a current pulse from a lab-built heating system and a temperature as high as 250–300 °C was reached within a few milliseconds. This was to desorb and to inject the analyte into the FID. The effect of heating was similar to using an injection port in term of retention time, peak height, band duration and terminal band length [7]. A microprocessor-based timer was used to control the interval between the adsorption and desorption times and the duration for which the current was applied.

2.3. Breakthrough characteristics

To determine breakthrough in a microtrap, the method using the variation in microtrap response as a function of injection interval [4] was implemented. The capacity, in term of breakthrough, was studied by passing a stream of standard methane gas (11.6 ppmv) through the microtrap. Methane molecules were adsorbed while the background stream served as a carrier gas. The system was first investigated at room temperature (25 °C). Desorption voltage and time were varied in the range of 10–50 V and 1–4 s. The optimum desorption voltage and time were then used to determine the breakthrough by varying the adsorption time until stable response peaks were obtained.

2.4. Enhancement of microtrap capacity

The most important factor for trace quantity analysis is enhancement. A higher enhancement (or enrichment) factor can be obtained by decreasing the microtrap temperature. The microtrap was placed inside an insulating foam box, surrounded by dry ice. The temperatures were varied from 25 °C (room temperature) to −50 °C by varying the amount of dry ice. At each adsorption temperature, the optimized desorption voltage and time were investigated to obtain the maximum desorbed analyte from the microtrap. The adsorption time at each temperature was then varied to determine the breakthrough time. The responses were used to calculate enhancement.

2.5. Performance of the microtrap

To study the linear response of the on-line microtrap system, a series of standard gas concentrations, 11.6, 5.8, 3.9, 1.1 and 0.2 ppmv, was prepared by dynamic dilution method [11] using nitrogen gas (99.99% TIG, Thailand) as the dilutor. Each concentrations of methane were continuously passed through the microtrap. The injections were made at 6 min interval using a pulse time of 3.5 s at 40 V for five replications at −50 °C. The signals were used to plot the standard curve.

High purity nitrogen gas (99.99%) was used as blank. It was continuously applied through the microtrap. The desorptions, i.e., injections were done every 6 min and the obtained data were used to calculate the limit of detection based on IUPAC method [12].
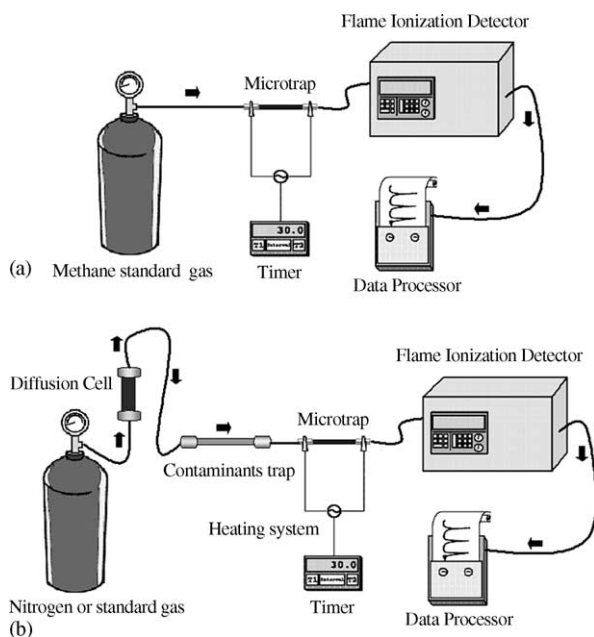

Fig. 1. Schematic diagram showing the analysis system. (a) microtrap interfaced to flame ionization detector for on-line determination of methane. (b) Diffusion cell was used to introduce organic in the N_2 stream to test the ability of the contaminants trap to remove the organic.

2.6. Contaminants trap

A contaminants trap was placed in front of the micro-trap to remove the contaminants that might interfere with the on-line trace methane analysis system (Fig. 1b). A suitable adsorbent was evaluated. These included activated charcoal (Palm Shell), coated Carbopack B, and Carbopack C, selected by considering their surface area, and pore size. Each of these adsorbents was packed in a stainless steel tube (1/4″ o.d. × 4 mm i.d. × 16 cm).

The experiments consisted of two parts. First was to test the trapping efficiency of the contaminants trap. It was placed between the standard hexane gas (from diffusion cell) and the microtrap packed with coated Carbopack B (Fig. 1b). This microrap was used to monitor hexane that could not be adsorbed by the contaminants trap. The second part was to test the effect of contaminants trap on the response of methane. The diffusion cell was removed and standard methane gas was flowed through the contaminants trap before passing through the microtrap packed with Carbosphere. The signals obtained with and without the contaminants trap were compared.

3. Results and discussion

3.1. Breakthrough characteristics of the microtrap

Breakthrough is an important parameter since it can indicate the capacity of the microtrap in term of the volume or the time that the microtrap can retain the analytes without loosing them. The adsorption time of the microtrap was varied from 0.5 to 4 min, and then desorbed by applying the current to the microtrap at optimum conditions, 15 V, 2.5 s, at room temperature (25 °C). The response increased with adsorption time (Fig. 2) up to 2.0 min, and then became constant and this was the breakthrough time. Two minutes was then used as the optimum adsorption time for each analysis cycle.
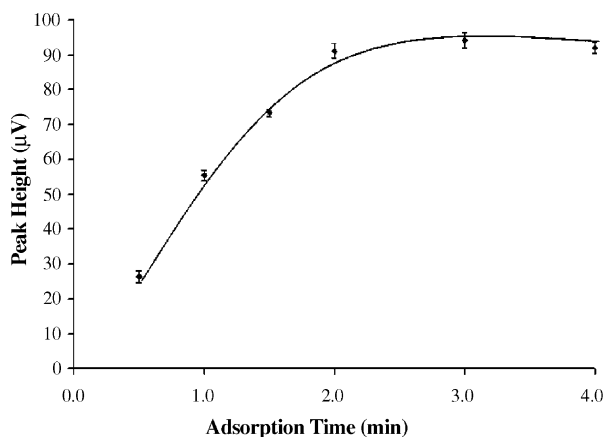
Fig. 2. Response at different adsorption times used to determine break-through time of the microtrap at room temperature (25 °C). The microtrap was heated at desorption voltage of 15 V for 2.5 s.

Optimum conditions at room temperature provided chromatograms with an average peak height of 90 μV for 11.6 ppmv of methane. With this response, the on-line system could not be used to detect trace methane in high purity gas which are in the range of 0.1–5.0 ppmv [13]. Therefore, the sensitivity of the on-line microtrap must be increased.

3.2. Relationship between breakthrough volume and temperature

Adsorption is an exothermic phenomenon and the logarithm of the breakthrough volume (BTV) is inversely proportional to the temperature [14,15]. To increase the response and the breakthrough, the adsorption temperature was decreased. Table 1 shows optimum desorption conditions that provide the highest desorption efficiency. For all temperatures the thermal desorption could be done by heating the microtrap for a few seconds and the analytes were carried to the detector as a plug resulting in very sharp peaks (Fig. 3).

The results confirmed the Van't Hoff-type relationship [14,15], that is, the lower the adsorption temperature the higher the breakthrough volume (Fig. 4). This is because when the temperature decreased, the average time molecules resided on a surface increased. Therefore, more methane can accumulate on the surface of the adsorbent which caused the increase of the breakthrough of the microtrap. The linear relationship is $\log(BTV) = 0.42 \times 10^3 (1/T) + 0.65$, and this can be used to calculate the breakthrough volume of methane on Carbosphere. The slope of the curve is, $-8.1 \, kJ \, mol^{-1}$, the adsorption enthalpy (ΔH_{ad}) [14]. Since the maximum observed enthalpies reported for physical adsorption was $-21 \, kJ \, mol^{-1}$ while the enthalpies for chemisorption were in the region of $-200 \, kJ \, mol^{-1}$ [15]. The result indicates that, methane was adsorbed on the Carbosphere by physisorption.

3.3. Enhancement

The enhancement at various sampling temperatures is the ratio of the response from the on-line microtrap system to the direct-FID. When the temperature decreased, the enhancement increased (Fig. 5). At −50 °C the enhancement factor reached 260, i.e., the response increased tremendously from

Table 1
Optimum desorption conditions and optimum adsorption time (breakthrough time) at various adsorption temperature

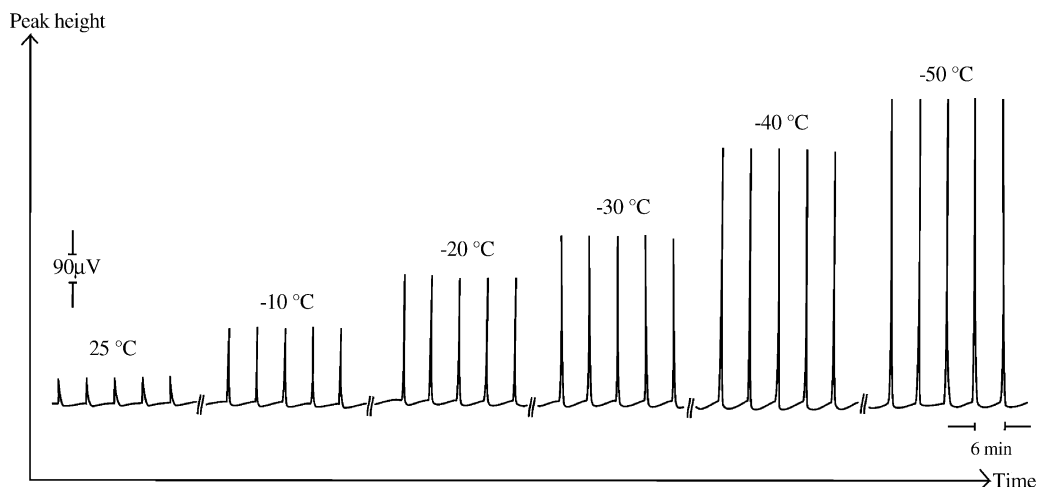| Adsorption temperature (°C)	Desorption conditions		Optimum adsorption time or breakthrough time (min)
	Voltage (V)	Duration of pulse (s)	
25	15	2.5	2.0
−10	20	1.5	3.0
−20	30	2.5	4.0
−30	35	2.5	4.0
−40	40	2.5	5.0
−50	40	3.5	6.0

Fig. 3. Chromatograms of the on-line monitoring microtrap at various temperatures.

3.99 μV obtained from direct-FID to 1040 μV using a microtrap and this makes it very suitable for trace methane analysis.

Due to the limitation of the lab-built cooling box, the lowest temperature that can be obtained was $-50\,°$C. However, at this temperature, the signal for 11.6 ppmv of methane had already increased from 90 μV at room temperature to 1040 μV and this should be high enough to detect trace methane contaminated in high purity gases which are in the range of 0.1–5.0 ppmv [13] and this is confirmed in 3.4.

3.4. Performance of the on-line microtrap

The linear relationship between the peak height and the concentration of methane standard gas was investigated between 0.2 and 11.6 ppmv. A linear calibration curve from the microtrap was obtained as peak height (μV) = 99.9 concentration (ppmv) + 11.7 ($r^2 = 0.995$). That is, a very good linearity was obtained and this system can certainly be applied for quantitative analysis of methane.

The limit of detection was also studied to ensure that this system is sensitive enough to determine the concentration of

methane in high purity gas and it was found to be 28 ppbv. This is much better than the 300 ppbv determined without preconcentration reported by Kamiński et al. [16]. Therefore, this proposed system is more suitable to be used as an on-line device to be placed in line of the production processes for the continuous monitoring of the pure and research purity gases where the concentration of methane must not be higher than 0.1 ppmv [13].

3.5. The contaminants trap

To further increase the selectivity of a microtrap, a contaminant trap can be applied to the system to remove other compounds, except methane, before reaching the microtrap. The results from three different contaminants traps are shown in Fig. 6, indicating that all of the studied adsorbents could adsorb the impurity/contaminant (hexane was used as the representative of the impurity at 500 ppmv) with efficiencies of higher than 99%. So, the effect of contaminant trap on methane signal and the lifetime of the trap were used as the parameters for adsorbents selection. Fig. 6 shows that activated charcoal had a much greater lifetime (>9000 min) com-
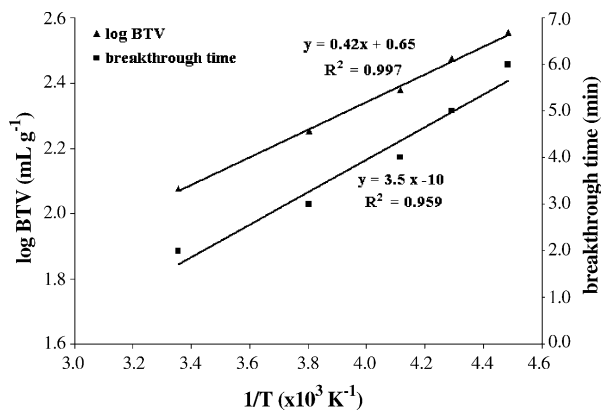

Fig. 4. Relationship between the breakthrough volume (BTV) and breakthrough time of the microtrap and sampling temperature.
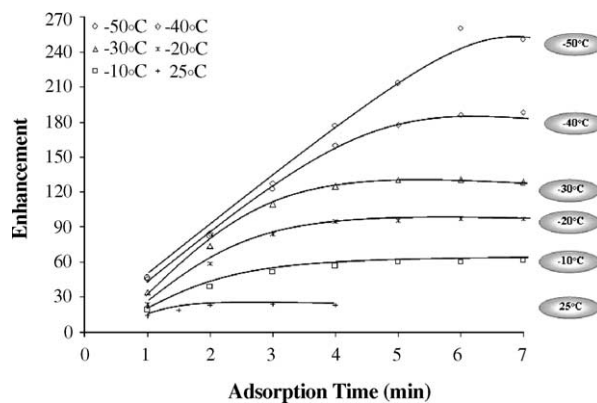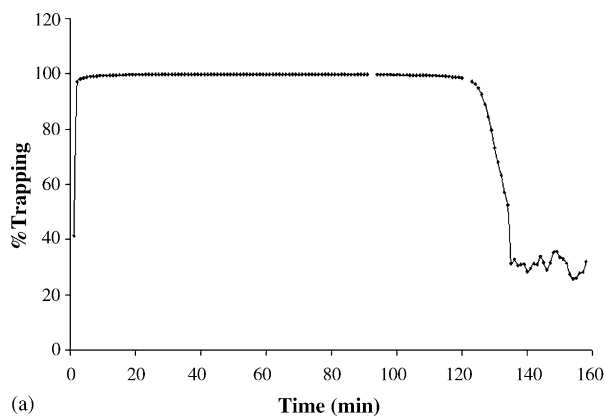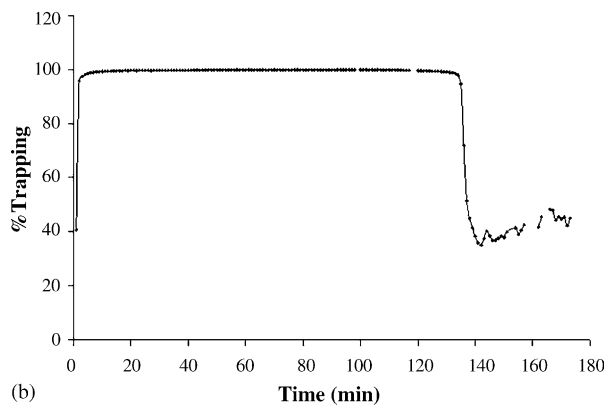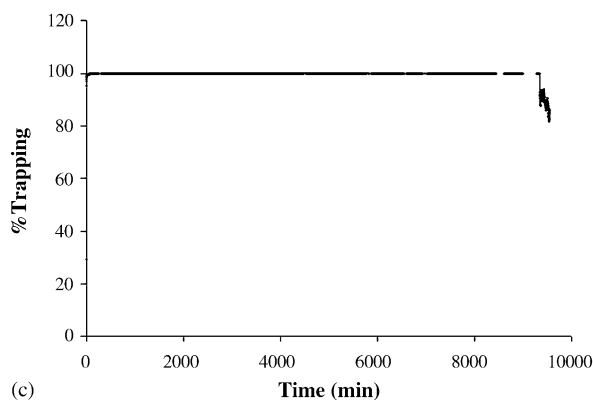

Fig. 5. Enhancement at various sampling temperature and adsorption time (injection interval).

Fig. 7. Effect of contaminants trap on methane signal.

with a rate of $5.0 \, \text{mL min}^{-1}$. Nearly 2000 injections were made by applying current through the wall of the microtrap every 2 min for 64 h. The average response was $89.2 \pm 3.8 \, \mu V$ (relative standard deviation, RSD <5%). Since $-50 \, ^\circ C$ was the optimum adsorption temperature, the stability of the on-line system at this temperature was also studied. It was tested for a work day period, which is 8 h. The injections were made every 6 min with desorption voltage and time of 40 V and 3.5 s, respectively. The average peak height was $1037 \pm 51 \, \mu V$ (RSD <5%).

The results indicated that the system was very stable. It also showed that the adsorbed analytes were efficiently desorbed from the adsorbent without any memory effect.

4. Conclusions

The results demonstrated that the on-line microtrap can provide reliable data and good reproducibility. It can be operated over a very long period of time with good precision and without the degradation of the adsorbent. An enhancement of up to 260 times could be obtained when using a simple, cost effective cooling system. Therefore, this microtrap can certainly be applied to the gas production industries to check their production quality, not only for checking the methane contamination but also for determination of methane concentration required by the customers.

Fig. 6. Life time of the contaminants trap packed with various adsorbent; (a) coated Carbopack B, (b) Carbopack C, (c) activated Charcoal.

pared to coated Carbopack B and Carbopack C (120 min). However, it also trapped some methane on its active surface (Fig. 7). Therefore, either coated Carbopack B or Carbopack C would be a suitable adsorbent for contaminants trap since they showed very high removal efficiency and had no effect on methane signal.

3.6. Long term stability

Stability of this system was evaluated by continuously flowing 11.6 ppmv of methane standard at room temperature
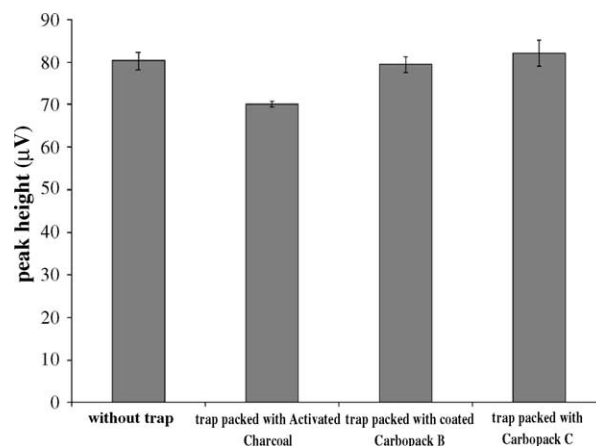
References

[1] Tigeroptics, Trace methane analyzer for inert, passive, toxic, and corrosive gases, 2003 http://www.tigeroptics.com/pdf/MTO-1000-CH4.pdf.

[2] S. Panda, Q. Bu, K.S. Yun, J.F. Parcher, J. Chromatogr. A 715 (1995) 279.

[3] S. Mitra, N. Zhu, X. Zhang, B. Kebbekus, J. Chromatog. A 736 (1998) 165.

[4] C. Feng, S. Mitra, J. Chromatog. A 805 (1998) 169.

[5] S. Mitra, C. Feng, L. Zhang, W. Ho, G. McAllister, J. Mass. Spectrom. 34 (1999) 478.

[6] H.J. Rafson, Odor and VOC Control Handbook, McGraw-Hill, New York, 1998.

[7] S. Mitra, C. Yun, J. Chromatogr. 648 (1993) 415.

[8] S. Mitra, Y.H. Xu, W. Chen, A. Lai, J. Chromatogr. A 727 (1996) 111.

[9] X. Guo, S. Mitra, Anal. Chem. 71 (1999) 4587.

[10] T.-Y. Chen, M.-J. Li, J.-L. Wang, J. Chromatogr. A 976 (2002) 39.

[11] R.L. Grob, Modern Practice of Gas Chromatography, second ed., Wiley, Toronto, 1985.

[12] G.L. Long, J.D. Winefordner, Anal. Chem. 55 (1983) 712A.

[13] Matheson Tri Gas, retrieved on January 4, 2004, http://www.matheson-trigas.com/mathportal/.

[14] V. Simon, M.-L. Riba, A. Waldhart, L. Torres, J. Chromatogr. A 704 (1995) 465.

[15] P.W. Atkin, Physical Chemistry, fifth ed., Oxford University Press, Oxford, 1994.

[16] M. Kamiński, R. Kartanowicz, D. Jastrzębski, M.M. Kamiński, J. Chromatogr. A 989 (2003) 277.