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Sampling and analysis of nanoparticles with cold fibre SPME device

Abstract

A new approach is described to capture nano-size aerosols on internally-cooled micro tubing of the solid-phase microextraction (SPME) device followed by convenient introduction of the collected analytes into analytical instrument. Particles were generated using an aerosol formation by homogeneous nucleation of an organic vapor, and subsequent growth to nano-size particles by coagulation of decanedioic acid, bis[2-ethylhexyl] ester (DEHS). The approach was validated by using carbon dioxide-cooled micro tubing to collect the nanosize DEHS particles followed by analyses on GC-flame ionization detector (FID). Particle size ranged from 150 to 590 nm. Temperature difference between the SPME device and DEHS particles mixture created a temperature gradient and resulted in thermophoretic effect that was determining the extraction rate. SPME device was cooled to as low as -75°C , while the DEHS remained close to room temperature. Several aspects of nanoparticle sampling were tested to demonstrate the principle of the sampling approach. These included the effects of thermal gradient, sample flow rate, sampling time, CO₂ delivery mode (constant coolant delivery vs. constant temperature), and particle size. Results were normalized to measure particulate concentrations using direct sampling with PTFE filters. Nanoparticle extractions of DEHS mass were proportional to sampling time. Normalized mass of DEHS extracted increased with increase in temperature gradient and with increase of the cross flow velocity. Preliminary results indicate that the variation of heat transfer boundary layer caused by the variation in the cross flow velocity produce self-compensating effect at constant coolant delivery, indicating that this approach could be used for field determinations including the time-weighted average sampling of nanoparticles. Thus, it may be possible to develop simple device based on this concept for field applications.

Keywords

SPME, nanoparticles, thermophoresis, sampling, DEHS

Disciplines

Bioresource and Agricultural Engineering | Environmental Monitoring | Environmental Sciences | Process Control and Systems

Comments

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Short Communication

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**SAMPLING AND ANALYSIS OF NANOPARTICLES WITH COLD FIBRE SPME
DEVICE**

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List of nonstandard abbreviations:

DEHS = decanedioic acid, bis[2-ethylhexyl] ester

FID = flame ionization detector

SPME = solid-phase microextraction

TWA = time-weighted average

Keywords: SPME, nanoparticles, thermophoresis, sampling, DEHS

24 **ABSTRACT.** A new approach is described to capture nano-size aerosols on internally-cooled
25 SPME fiber device followed by convenient introduction of collected analytes into analytical
26 instrument. Particles were generated using a simple setup based on aerosol formation by
27 homogeneous nucleation of an organic vapor, and subsequent growth to nano-size particles by
28 coagulation of decanedioic acid, bis[2-ethylhexyl] ester (DEHS). The approach was validated by
29 using carbon dioxide-cooled SPME device to collect the nanosize DEHS particles followed by
30 analyses on GC-FID. Particle size ranged from 150 to 590 nm. Temperature difference between
31 the SPME device and DEHS particles mixture resulted in thermophoretic effect that was
32 determining the extraction rate. SPME device was cooled to as low as -75 °C, while the DEHS
33 remained close to room temperature. Several aspects of nanoparticle sampling were tested to
34 demonstrate the principle of the sampling approach. These included the effects of thermal
35 gradient, sample flow rate, sampling time, CO₂ delivery mode (constant coolant delivery vs.
36 constant temperature), and particle size. Results were normalized to measure particulate
37 concentrations using direct sampling with PTFE filters. Nanoparticle extractions of DEHS mass
38 were proportional to sampling time. Normalized mass of DEHS extracted increased with
39 increase in temperature gradient and with increase of the cross flow velocity. Preliminary results
40 indicate that the variation of heat transfer boundary layer caused by the variation in the cross
41 flow velocity produce self-compensating effect at constant coolant delivery, indicating that this
42 approach could be used for field analysis including the time-weighted average sampling of
43 nanoparticles. Thus, it may be possible to develop simple device based on this concept for field
44 applications.

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46

47 INTRODUCTION

48 Collection of particles of nanometer size for the purpose of both characterizing and determining
49 the concentration is a very difficult task. Typical particle collection devices, such as impactors,
50 electrostatic precipitators and filters, are active sampling devices in the sense that a known
51 quantity of air needs to be drawn through the instruments. In many cases their collection
52 efficiency for particles significantly smaller than 100 nm is poor. [1, 2, 3]. Thermophoresis is a
53 physical phenomenon occurring as the drift of the dispersed particles against the thermal gradient
54 towards the cooler surface [4, 5]. The drift is caused by the difference in kinetic energy transfer
55 during collision of particles with gas molecules in a medium with temperature gradient. In the
56 ultrafine particle range, the thermophoretic velocity is independent of the particle size. When
57 sedimentation forces and diffusion can be neglected, the nanoparticle collection efficiency on a
58 cooled surface is independent of particle size. Thermophoresis has been demonstrated to be very
59 effective in the collection of nanoparticles in air [6].

60

61 In this communication, we present and discuss the initial results showing a new approach to
62 thermophoretic collection of nanoparticles using a cold fibre in the SPME device. This was
63 followed by a convenient interface to analytical instruments, and therefore, convenient
64 introduction to analytical instrument for characterization of the matrix of the particle and/or the
65 chemical species adsorbed on its surface. Simplicity of sampling, even in on-site applications,
66 automation, and storage has been already demonstrated using uncooled SPME devices [7]. We
67 have showed convenience in characterization of large particulate matter using the fibre format
68 after the impact collection [8, 9]. Recently, two new designs of cooled fibre SPME have been
69 implemented [10, 11], which make the proposed approach practical even for on-site applications.

70

71 **THEORY**

72 For a low Reynolds number flow around a cooled cylinder, we assume two major mass transfer
73 mechanisms: diffusion and thermophoresis. The mass flux is determined by two boundary layers:

74

75 The thermal boundary layer:

$$76 \quad \delta_t = \frac{d_f}{Nu} = 0.4d_f \quad (\text{for } Re=10) \quad (1)$$

77 and the concentration boundary layer:

78

$$\delta_c = (APe)^{-1/3}$$

$$79 \quad A \approx \frac{1}{4}$$

$$Pe = Re Sc$$

$$Sc = \frac{\nu}{D}$$

80 D is the particle diffusion constant ($D= 5 \cdot 10^{-4}$ cm²/s for a 10 nm particle), and ν is the gas81 viscosity = 0.2 cm²/s. For $Re = 10$, we have $\delta_c = 0.1 d_f$.82 The mass flux onto the fiber surface is given by $j = v_{dep} c$, where c is the aerosol concentration83 outside the boundary layer and v_{dep} is the so-called “deposition velocity”.

84 For diffusional deposition: $v_{dep}^{diff} = \frac{D}{\delta_c}$

85 For thermophoretic deposition: $v_{dep}^{therm} = \alpha \frac{\Delta T}{\delta_t}$

86 where $\beta = 2.8 \cdot 10^{-4}$ (δ_t in cm, ΔT in K). From this we get the ratio of the thermophoretic and
 87 diffusional mass flux:

$$88 \quad \Gamma = \frac{v_{dep}^{th}}{v_{dep}^{diff}} = \frac{\beta \Delta T \delta_c}{D \delta_t} \quad (2)$$

89 This number takes a value of 3 for 10 nm particles and increases for larger particles since the
 90 particle diffusion constant decreases.

91

92 The discussion above indicates that the thermophoretic deposition is the controlling mass transfer
 93 mechanism even for a relatively small temperature difference between the fiber surface and the
 94 surrounding gas. For a 1 cm fiber, a fiber diameter of 300 μm , and a mass concentration of
 95 particles in the air of 1 mg/m^3 , the mass transfer rate is:

$$96 \quad R = 5 \cdot 10^{-2} \frac{\text{ng}}{\text{s}} \quad (3)$$

97 The above discussion indicates that the collection rate of the particles is proportional to its
 98 concentration and can be calculated from the amount of the particle collected at defined
 99 convection conditions.

100

101 **EXPERIMENTAL**

102

103 **Nanoparticle generation and sampling system**

104 Particles were generated using a simple setup based on aerosol formation by homogeneous
 105 nucleation of an organic vapor and subsequent growth to nano-size particles by coagulation [12].
 106 Decanedioic acid, bis[2-ethylhexyl] ester (DEHS) (CAS = 122-62-3) was used to generate

107 particles. A high purity (from Sigma-Aldrich) DEHS was first heated to 195 °C in a heating
108 vessel at the base of the particle generator to an equilibrium. This was followed by controlled
109 release and immediate adiabatic cooling inside a 6- L coagulation chamber at room temperature.
110 The DEHS is characterized by very low vapor pressure, and thus, a controlled nucleation to
111 particle phase proceeds. The growth of DEHS particles by coagulation is well-controlled and
112 reproducible [12], between approx. 100 nm to 600 nm and particle concentrations from $\sim 10^7/\text{cm}^3$
113 to $5.2 \times 10^5/\text{cm}^3$, respectively. Typical growth times range from approx. 30 s for 100 nm particles
114 to 60 min for 590 nm particles, respectively. Gas-phase concentrations of DEHS are typically 4
115 orders of magnitude lower than particle concentrations in temperatures close to room
116 temperatures used in this research.

117
118 The coagulation chamber was gently flushed with controlled flow of dry nitrogen. The nitrogen
119 flow was controlled by various critical orifice devices under vacuum. The effluent from
120 coagulation chamber was directed to a 125- mL flow-through air sampling bulb (from Sigma-
121 Aldrich) equipped with a sampling port. The sampling port was fitted with a half-hole
122 Thermogreen septum for insertion of SPME devices and collection of nanoparticles at controlled
123 airflow conditions. Sampling with SPME by a flow-through bulb was simultaneous with
124 conventional extraction on a teflon-coated glass fibre filter (27 mm diameter, Emfab filters,
125 thickness 178 μm , weight: 5.0 mg/cm^2 , Pallflex Products Corporation, Putnam, CT).

126
127 Schematic of the particle generator device and the experimental setup is shown in Figure 1.

128

129 **SPME device.**

130 The cold fibre SPME device design used was described recently by Chen and Pawliszyn [10].
131 The device used liquid CO₂ delivered via a small capillary to the tip of the SPME. The tip was
132 also equipped with a thermocouple mounted on the inside the SPME tip and serving as feedback
133 for temperature setpoint and the liquid CO₂ valve actuation. No polymeric phases were used, i.e.,
134 a bare SPME device consisting of a stainless steel hollow rod with O.D. = 0.7 mm was exposed
135 at constant length of 20 mm for all experiments.

136

137 **Effects of CO₂ delivery rate**

138 Two modes of SPME device operation were used: (a) with constant temperature setting, and (b)
139 with constant liquid CO₂ delivery rate controlled with a valve. The constant temperature setting
140 mode (a) was used to generate ΔT from 0 to 70 °C between the ambient gas with nanoparticles
141 and the SPME device. In this mode, the feedback control thermocouple signal was used to
142 actuate the liquid CO₂ valve in frequent and regular on-off operation. This resulted in variable
143 temperature of the SPME sampling device (approx. ± 5 °C). The constant liquid CO₂ delivery
144 (mode (b)) was generated by setting the control valve in constant position. This mode resulted in
145 constant cooling, and therefore, the effects of convection/boundary layer and cooling could be
146 compared.

147

148 **Effects of SPME sampling time**

149 Effects of sampling time with cold SPME device were tested by exposing the cold fibre SPME
150 device from 30 s to 5 min with all other variables set constant. Mean particle size $d_p = 300$ nm,
151 setpoint $\Delta T = 40$ °C, and cross flow velocity $u = 1.6$ cm/s.

152

153 Effects of particle size

154 Effects of particle size were tested by exposing cold SPME device to different particle sizes
155 ranging from $d_p = 150$ nm to 590 nm. All other variables were kept constant, i.e., SPME
156 sampling time at 30 s, $\Delta T = 40$ °C, and the cross flow velocity $u = 50$ cm/s.

157

158 Chemical Analyses

159 All chemical analyses were performed on a 5890 HP gas chromatograph equipped with a FID
160 detector and a 30 m DB-5 column (Hewlett Packard, Palo Alto, CA). The system was operated
161 in splitless mode. GC injector was modified with a septumless cap (Gerstel GmbH, Mullheim,
162 Germany). After each sampling experiment, the cold SPME device was disconnected from CO₂
163 delivery line, transferred to the injection port for subsequent desorption, separations and analyses.
164 The mass of extracted DEHS was estimated using calibration curved developed with standard
165 solutions of DEHS in hexane. The SPME device remained in the injector for the entire GC run.
166 No carryover of DEHS was observed between subsequent runs. The GC oven program was set
167 to initial temperature of 150 °C for 3 min, ramping at 10 °C/min to 300 °C where it stayed for 3
168 min. Data were analyzed using ChemStation software.

169

170 Particle concentrations were determined using the same analytical approach. The extracted
171 filters were desorbed for a second time to ensure completeness of the desorption. No carryover
172 was observed. Used PTFE filters with DEHS collected (Figure 1) were extracted in 1 mL of
173 hexane and the resulting mixtures were injected for analysis into the GC-FID.

174

175 **RESULTS AND DISCUSSION**

176 Nanoparticle generator system (Figure 1) was a batch reactor, i.e., each batch of nanoparticles
177 was potentially different. Also, the concentration of particles inside the sampling bulb was
178 affected by the N₂ flow rate. Thus, a teflon-coated glass fibre filter was used for each batch of
179 nanoparticles to determine actual PM concentration for each experiment. For this reason, all
180 results are presented as the ratio of DEHS concentration and measured PM concentration using
181 filters to adjust for the variation in particle concentration. In this approach, we assumed that the
182 PTFE filter perfectly traps all particles. This was not an appropriate assumption for particles
183 smaller than 500 nm as we determined during the experiment.

184

185 **Effect of the fibre temperature**

186 As expected, the amount of collected particles was proportional to the ratio of SPME-collected
187 particles and DEHS concentration determined using filter. To ensure that the correct temperature
188 difference was used, the surface temperature of the fibre and the temperature of the particle
189 mixture was used. The results showed, as expected, that the collected amounts of particles
190 increased with the temperature difference increase. For example, with a temperature difference
191 of 25 °C, the rate of collection was 2.2 ng/min/(mg/m³), and for 31 °C, it was 5.6 ng/min/
192 (mg/m³). The typical RSD of the measurement was about 30 %, primarily because of variation
193 and uncertainty of accurately measuring and estimating the fibre surface temperature along the
194 20 mm length used for collections of particles

195

196 **Effects of SPME sampling time**

197 Effects of sampling time with cold SPME device were tested by exposing cold SPME device
198 from 30 s to 5 min with all other variables set constant, i.e., mean particle size $d_p = 300$ nm,
199 setpoint $\Delta T = 40$ °C, and gas-phase velocity $u = 1.6$ cm/sec. The measured surface temperature
200 vs. sample temperature difference was about 25 °C. Mass extracted and the ratio of mass
201 extracted to the measured PM concentration increased with time. For example, normalized
202 amount extracted by the cold fibre was 4.2 ng after 2 min and 15 ng after 5 min.

203

204 **Effects of particle size**

205 In theory, no effect due to particle size should be observed. This has been verified
206 experimentally for other cold surfaces. However, in our experiment, it is apparent that the ratio
207 of mass of DEHS extracted to the measured PM concentrations was affected by PM size, i.e., the
208 larger the particle, the lower the thermophoretic effect (Figure 2). The theoretical flux of
209 particles reported in Figure 2 was estimated using Equation 3. We suspected that the reason for
210 this observation was breakthrough of particles through the sampling PTFE filter media. We
211 tested this postulate by fitting two filters in series, one after another, and monitored the relative
212 collections of the particulates on the second filter compared to the first one. We observed that
213 the breakthrough effect was larger for smaller particles and almost nonexistent for relatively
214 large particles (590 nm) where the measured and theoretical mass collection rates were very
215 similar (Figure 2). This apparent breakthrough affected the results for the measured PM
216 concentrations smaller than 500 nm. This result clearly demonstrates a critical need to develop
217 non-discriminating methods of nanoparticle collection, such as the one proposed in this paper to
218 replace the filter approach to capture small particles.

219

220

221 **Effects of CO₂ delivery rate**

222 Table 1 shows that the normalized mass of the extracted DEHS by the cold fibre SPME
223 increased with the increase of convection caused by increase in cross flow velocity and therefore
224 the decrease of the thermal and mass boundary layer thickness (see the Theory section). The
225 amount of particle collected on the cold fibre increased from 6.2 ng to 16 ng for 1 mg/m³ particle
226 concentration when the linear flow rate increased from 9.7 to 27 cm/s for $\Delta T = 25$ °C. Therefore,
227 practical application of this approach would require additional devices, such as fans to fix the
228 linear flow rate of the sample matrix at a calibrated flow rate. However, one would expect that
229 the fibre would be “heated” more efficiently by the higher gas flow rate because the thermal
230 diffusion layer is thinner at these conditions, which would require higher delivery of the coolant
231 to keep the same fibre temperature. Therefore, if coolant delivery is fixed, an increase in the
232 fibre surface temperature is expected as the gas flow rate increases, resulting in lower
233 temperature gradient and yet, similar sampling rate due to the reduction in boundary layer
234 thickness. This effect would create auto-compensating effect for particle sampling rate where
235 the effects of lower thermopheretic temperature gradient are off-set by the reduction of the
236 boundary layer around the fibre. Table 1 demonstrates that a reduction in variation of
237 accumulated amount is obtained experimentally. For example, no apparent change in particle
238 sampling rate wais observed (9.9 vs. 10.2 ng/min/(mg/m³)) under constant coolant delivery
239 conditions when the cross flow velocity increases by a factor of about 3 from 9.5 to 27 cm/s,
240 respectively. The change of particle sampling rate was also very small when the gas was 1.6
241 cm/s, considering that the RSD of the measurement was about 30 %. This effect makes the
242 proposed approach very attractive for use as a low-cost field sampling device, particularly for
243 time-weighted average applications (TWA). More fundamental work will follow to rationally

244 optimize the design and operating parameters of the cold SPME device for field sampling of
245 nanoparticles.

246

247 **CONCLUSIONS**

248 Chemical characterization of nano-size particles is very challenging due to a number of
249 uncertainties associated with sampling, sample preparation, characterization and determination.
250 Therefore, there is still a need for development of convenient tools for this important task due to
251 increased awareness and interest in fate of nanoparticles in environment. The initial results
252 indicate that the thermophoresis process, in combination with the cold fibre SPME device, could
253 address this need by facilitating convenient collection of nanoparticles that can be followed by
254 conventional chemical analysis. In particular, application of this approach for on-site monitoring
255 is appealing since it can be designed as a convenient portable sampling device using a small
256 carbon dioxide cylinder or the Peltier cooling system [11]. Preliminary results described in this
257 paper suggest that the effects of boundary layer associated with varying convection conditions
258 could be compensated for when constant cooling was used. This might result in a technique
259 requiring none or little calibration, not only for spot sampling, but for time weighted average
260 measurements as well. Growing interest in nanotechnology ensures that such measurement
261 would become important and might be conducted on regular basis. Potential applications of the
262 cold fibre SPME nanoparticle sampling approach include studying mass transfer processes
263 involving nanoparticles, on- site environmental monitoring, exhaust sampling, and
264 characterization of sorption properties of particles and particle-gas and particle-liquid
265 interactions. For example, for simple measurements of permeation of nanoparticles through
266 barriers, use of such membranes might be possible as it was recently demonstrated for permeation

267 of organic compounds [13]. Also, sampling using the described approach in liquid matrix might
268 be possible as well, which might lead to interesting applications including environmental
269 nanoparticles and bioparticles, such as virus concentration and subcellular components extraction.

270

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275

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- 295

296

297 **Figure Captions:**

298 **Figure 1.** Schematic of particle generator and experimental setup for collection of nanoparticles
299 with internally-cooled SPME device.

300 **Figure 2.** Comparison of the theoretical (red squares) vs. measured (blue diamonds) ratio of
301 mass of DEHS extracted to measured PM concentrations as a function of particle size.

302 Theoretical mass was estimated using Equation 3.

303