Development of a Method for the Determination of Naphthalene and Phenanthrene in Workplace Air Using Diffusive Sampling and Thermal Desorption GC-MS Analysis

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Received 30 August 2010; in final form 5 May 2011

Diffusive sampling methods have been validated for the determination of naphthalene and phenanthrene in workplace air. The diffusive sampler tested was the Perkin Elmer ATD tube, and the analysis was performed with thermal desorption, gas chromatography, and mass spectrometric detection. The sampling methods were validated in controlled test atmospheres, mainly according to the protocol proposed in the European standard EN 838. For the determination of naphthalene, the diffusive sampling rate was 0.41 ml min$^{-1}$ with a coefficient of variation (CV) of 19%. The mean sampling rate for phenanthrene was 0.49 ml min$^{-1}$ with a CV of 21%. Field tests confirmed the naphthalene results but could not be used to confirm the phenanthrene results. The method is not recommended for phenanthrene sampling unless the method has been tested in the specific environment and the results confirm the laboratory tests.

Keywords: diffusive monitoring; passive sampling; polycyclic aromatic hydrocarbons

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are aromatic compounds with two or more fused benzene rings. PAH compounds can exist in the gaseous phase, in the particulate phase, or in both, depending upon their vapor pressures and environmental conditions. Naphthalene and phenanthrene, with two and three rings, respectively, are present almost entirely in the gaseous phase. Compounds with five or six rings exist almost entirely in particulate form (Kuusimäki et al., 2003; Rappaport et al., 2004).

Occupational measurements are important not only for hazard identification and evaluation in order to prevent illness due to chemical exposure in the work environment but also for epidemiology and toxicology studies. For the determination of PAHs in air in occupational settings, including, naphthalene and phenanthrene, pumped sampling with a combination of filter and adsorbent has been used (Petry et al., 1996; NIOSH Manual of analytical methods 4th ed., 1998; Strunk et al., 2002; Kuusimäki et al., 2003; Preuss et al., 2005). The filter captures the particulate phase and the adsorbent after the filter captures the gaseous phase as well as compounds evaporated from the particles captured on the filter. Pumped sampling entails not only the use of sampling pumps and flow measurement devices but also skilled people to handle the equipment. The equipment can affect the work performance and is not always accepted by the worker. Diffusive sampling methods are often preferred since
the methods are user-friendly and more acceptable to the wearer than pumped sampling methods. The easy handling of many diffusive sampling devices enables them to be handled and used by the workers themselves for self-assessment (Levin, 2002). Diffusive sampling is restricted to gases and vapors and cannot be used for sampling aerosols, which makes it impossible to use for the particle-bound PAHs. Nevertheless, naphthalene and phenanthrene are suitable for diffusive sampling since they are present almost entirely in the gaseous form. A sampling rate for naphthalene with the Perkin Elmer ATD diffusive sampler has been reported, but no information on how the testing was performed, or testing parameters, was reported (Brown, 1998). The purpose of this work was to evaluate a method for diffusive sampling of naphthalene and phenanthrene in workplace air. The diffusive sampler tested was the Perkin Elmer ATD tube (Brown et al., 1981; MDHS 80, 1995), a system with thermal desorption and gas chromatographic (GC) analysis. Together with mass spectrometric detection, low detection limits are achieved. The diffusive sampler was evaluated for the determination of naphthalene and phenanthrene under controlled conditions in test atmospheres.

MATERIALS AND METHODS

Chemicals, standard solutions, and calibration standards

Chemicals used were methanol (analytical grade; Merck), naphthalene (Merck), phenanthrene (Sigma–Aldrich), and toluene (analytical grade; Merck).

Stock solutions were prepared by weighing naphthalene or phenanthrene and dissolving in toluene (for naphthalene) or methanol (for phenanthrene). The solution was treated ultrasonically for 15 min to dissolve small particles of the phenanthrene. Standard solutions were prepared in methanol and were injected into the diffusive sampler with a 1-μl syringe. The sampler was maintained at 100°C to vaporize the injected volume. Helium was passed through the sampler at 60 ml min⁻¹ during injection. This process was carried out for 3 min for each standard. The equipment for preparation of standard tubes is shown in Fig. 1.

Analysis

A gas chromatograph (HP 6890), mass selective detector (HP 5973), and an automatic thermal desorption system (ATD 400 Perkin Elmer) were used for the analyses. Thermal desorption of the samples was accomplished by heating the tubes to 220°C while flushing with helium for 5 min at 12.9 p.s.i. to a cold trap at −30°C. The cold trap temperature was then increased to 250°C immediately to inject the sample into the GC system. The GC column was a DB-5MS, 31.4 m, inner diameter (ID) 250 μm with a stationary phase coating of 0.25 μm. GC oven temperature programming comprised an initial temperature of 150°C for 2 min followed by 20°C increments to 240°C which was maintained for 6 min. The total runtime was 12.5 min. The mass detector was set to total ion scan mode. For the preparation of standards with liquid spiking, a conventional gas chromatographic injection port was used (ISO 16017-2, 2003). Nitrogen with a flow of 100 ml min⁻¹ was used as purge gas. The first part of the tube (25 mm) was heated to 100°C. Loaded standard sorbent tubes were prepared by injecting 1 μl of an appropriate standard solution and keeping in the injection unit for 2 min.

Generation of naphthalene and phenanthrene

Standard atmospheres of naphthalene or phenanthrene were dynamically generated according to Fig. 2. A naphthalene or phenanthrene solution was slowly injected into an air stream by means of a motor-driven microinjection pump (Carnegie Medicine CMA/100, Stockholm, Sweden). Different gas-tight syringes were used for the injection, depending on concentration and sampling time. The needle was connected to a fused silica capillary, which was inserted into a nebulizer (Meinhard nebulizer TR-30-A7; J.E. Meinhard Associates). The air flow rate through the nebulizer was 11 min⁻¹. The aerosol from the nebulizer was mixed with heated air (41 min⁻¹, 41–49°C for naphthalene and 44–52°C for phenanthrene) in an evaporation chamber with a volume of ~1 l. The air mixture was further diluted with humidified air and transported to an exposure chamber made of Teflon, 900 × 80 × 60 mm. The total air flow through the

Fig. 1. Equipment for preparation of standards in ATD tubes.

Fig. 2. Equipment for air generation of naphthalene and phenanthrene.
exposure chamber was 40 l min\(^{-1}\), giving a flow rate of 0.3 m s\(^{-1}\) in the chamber. The air was controlled with respect to relative humidity by passing clean air through one to four gas-dispersion bottles. The temperature in the exposure chamber was 22°C. The generation equipment and exposure chamber have been previously reported (Levin et al., 1986; Lindahl et al., 1996). For the diffusive samplers, a number of sampling ports on top of the exposure chamber were used, through which the tubes were inserted so that the orifices of the samplers were in the middle of a cross-section of the exposure chamber. The samplers were equipped with diffusive caps during exposure.

**Diffusive sampling**

Perkin Elmer ATD diffusive tube samplers (length 90 mm, 6.3 mm outer diameter [OD], 5.0 mm ID) were used. Approximately, 60 mm of the adsorbent Tenax TA was packed into ATD stainless-steel tubes, 90 mm × 6.3 mm OD × 5.0 mm ID. The distance between adsorbent and orifice of the sampler was 14 mm. The tubes with Tenax TA were conditioned for 1 h at 310°C with 100 ml min\(^{-1}\) nitrogen gas flow (Markes Sample tube conditioning/dry purge model TC-20). The tubes were sealed with Swagelok fittings with PTFE inserts (Swagelok Co., Solon, OH, USA). Tubes were equipped with Perkin Elmer diffusion caps during sampling.

**Reference method**

As reference method, pumped sampling with Perkin Elmer ATD tubes (Perkin Elmer Inc., Wellesley, MA, USA) with Tenax TA was used, i.e. the same sampler as for the diffusive sampler. The sampling rate was varied between 30 and 50 μl min\(^{-1}\). Pumped sampling was performed twice, in the beginning and at the end of each experiment. For a diffusive sampler, exposure time of 1 h, pumped sampling was carried out once for the first 15 min and once for the last 15 min by using three samplers each time. In case of 8-h diffusive sampler sampling time, the sampling times for the pumped samplers were 1 h for the lower concentrations and 15 min for the higher concentrations.

**Laboratory experiments**

The laboratory validation of the diffusive sampler was conducted in the exposure chamber described above where variable naphthalene or phenanthrene atmospheres and humidity were produced. The samples were analyzed the same day as the experiment was conducted except for the storage tests where the samples were stored 14 days after exposure before they were analyzed. The sampling times varied between 1 and 8 h. The relative humidity varied between 20 and 80%. For the back diffusion tests, the samplers where exposed to naphthalene or phenanthrene atmosphere for 1 h followed by exposure to clean air for 7 h. The detection limit was defined as three times the noise level determined with a method proposed by Burkart (Burkart, 1986).

**Field study**

Diffusive sampling was compared with pumped sampling in connection with another study of PAH exposure at a coke oven situated in the north of Sweden. For the pumped sampling, 13-mm glass fiber filter (Type AE, 0.3 μm; SKC Inc., Eighty Four, PA, USA) in a Swinnex cassette, followed by a XAD-2® tube (226-30; SKC Inc.) were used. The pumps were either Aircheck 2000 or Airlite (SKC Inc.). The flow was 1 l min\(^{-1}\). The XAD tubes were analyzed with liquid chromatography (HPLC) (Waters 2695) and a Waters 474 Fluorescence detector according to a previously described method (Levin et al., 1995). The comparison was performed as paired stationary sampling at different locations on the coke oven. The temperature was ~5°C. The sampling times varied between 280 and 340 min, with the same sampling times for both methods. The concentrations found with the ATD method were compared with the gaseous naphthalene concentrations sampled with the XAD-2® tubes.

**Statistical analysis**

For the statistical evaluation, MODDE ver 8 2008 (Umetrics AB, Umeå, Sweden) was used. Multiregression analysis was performed to test the influence of the tested variables on the sampling rate of naphthalene or phenanthrene. \(m\) is the coefficient of each independent variable \(x\) in the equation \(y = m_1x_1 + \ldots + m_mx_m + b\), where \(y\) is the sampling rate and \(b\) is the \(y\)-intercept (average sampling rate). The variables were centered and scaled from −1 to 1 to give the same influence within the experimental domain independent of the absolute values.

**RESULTS AND DISCUSSION**

The sampling methods were validated mainly according to the protocol proposed in the European standard EN 838 (CEN European committee for standardization, 1995). This protocol describes an experimental design for determining sampling rate and effects on sampling rate of various factors, such as pollutant concentration, exposure time, humidity, and air velocity. No tests on air velocity was performed in this study as previous studies have shown the sampler used
in this study is largely unaffected by both low and high air velocities (Brown et al., 1981; Ballach et al., 1999).

Sampling rate was determined by exposing diffusive samplers to known concentrations of naphthalene or phenanthrene in air. Samplers were exposed to different air concentrations, humidity, and sampling time. Pump sampling was used as a reference method to determine the actual air concentration inside the chamber. The measured naphthalene concentrations were within ±20% of the theoretically calculated values and with a mean value of 107% of the theoretical value. For the tests with phenanthrene, the pumped reference values varied from 62 to 97% of the theoretical values with a mean value of 77%. The pumped reference values were used for all calculations for both naphthalene and phenanthrene.

The range of concentrations of phenanthrene is rather narrow because of problems with deposition and/or condensation on the walls inside the evaporation chamber during experiments with higher concentrations. A low vapor pressure of 0.000014 kPa and too slow evaporation causes this problem with the available generation equipment. The vapor pressure of naphthalene is 0.0072 kPa and none of these problems was seen for naphthalene.

The results from the laboratory experiments to study effects of sampling time, concentration, and relative humidity on sampling rate for the determination of naphthalene are shown in Table 1. The mean sampling rate was 0.41 ml min\(^{-1}\) with a coefficient of variation (CV) of 19%. A multiple regression analysis showed no significant effect of sampling time and relative humidity, as can be seen in Table 2. For the tested parameter concentration, a significant effect could be seen resulting in a variation of the sampling rate with ±9% within the experimental domain. Detection limits for both naphthalene and phenanthrene were ~0.1 ng corresponding to 0.0005 mg m\(^{-3}\) for an 8-h sampling period.

The result from the storage test, 0.46 ml min\(^{-1}\) (CV 4%, N = 4), was not statistically different (T-test, 5% level) from the mean result shown in Table 1 or from the back diffusion test with no zero exposure (Table 1). For the back diffusion tests, no statistical difference (T-test, 5% level) in sampling rates could be seen between the samplers exposed to clean air for 7 h after naphthalene exposure and the samplers with only naphthalene exposure (Table 2).

The laboratory experiments to study effects of sampling time, concentration, and relative humidity on sampling rate for the determination of phenanthrene are presented in Table 3. The mean sampling rate was 0.49 ml min\(^{-1}\) with a CV of 21%. No statistical effect on sampling rate from the parameters concentration, sampling time, or relative humidity could be seen in the multiple regression analysis shown in Table 4. The back diffusion test showed no statistical difference (T-test, 5% level) in sampling rates between the samplers exposed to clean air for 7 h after phenanthrene exposure and the samplers with only phenanthrene exposure (Table 3).

| Table 1. Sampling rate for the diffusive sampler at various naphthalene concentrations, relative humidities (RHs), and sampling times. CV - coefficient of variation, N-number of determinations |
|-----------------|-----------------|-----------------|-----------------|
| Concentration (mg m\(^{-3}\)) | Time (min) | RH (%) | Sampling rate (ml min\(^{-1}\)) | CV (%) | N   |
| 0.01 | 120 | 20 | 0.44 | 10 | 3  |
| 0.01 | 120 | 80 | 0.38 | 22 | 4  |
| 0.01 | 480 | 80 | 0.36 | 19 | 5  |
| 0.05 | 240 | 50 | 0.43 | 9 | 5  |
| 0.15 | 120 | 20 | 0.46 | 6 | 4  |
| 0.15 | 120 | 80 | 0.49 | 13 | 4  |
| 0.15 | 480 | 20 | 0.45 | 10 | 6  |
| 0.15 | 480 | 80 | 0.42 | 13 | 4  |
| 0.46 | 239 | 50 | 0.45 | 7 | 6  |
| 1.39 | 242 | 50 | 0.42 | 8 | 6  |
| 4.63 | 120 | 20 | 0.37 | 3 | 6  |
| 5.00 | 132 | 80 | 0.36 | 6 | 6  |
| 5.02 | 480 | 20 | 0.38 | 14 | 6  |
| 5.02 | 480 | 80 | 0.37 | 15 | 6  |
| 1.00 | 120 | 50 | 0.41 | 6 | 4 a |
| 1.00 | 120 | 50 | 0.42 | 7 | 4 b |
| 1.08 | 120 | 50 | 0.46 | 4 | 4 c |
| Mean | 0.41 | 14 | 71 d |

* a, Back diffusion test, no zero exposure.
  b, Back diffusion test, after 6 h of exposure to clean air.
  c, Storage test, analysis 14 days after exposure.
  d, Results from the storage and back diffusion tests are not included.

| Table 2. Multiregression analysis of the influence of tested variables on the sampling rate of naphthalene. P value, probability to obtain the displayed value for the parameter if the true value was zero |
|-----------------|-----------------|-----------------|-----------------|
| Variable | Parameter estimate (mL/min) | Standard error | P | Parameter significance at 95% confidence level |
| Intercept | 0.40 | 0.009 |
| Concentration | -0.036 | 0.010 | 0.001 | S |
| Sampling time | -0.004 | 0.009 | 0.665 | NS |
| RH | -0.011 | 0.009 | 0.197 | NS |

S, significant; NS, not significant.

a, Sampling rate.
b, RH, relative humidity.
The theory of diffusive sampling is based on Fick’s first law of diffusion, which with the assumption that the concentration on the surface of the collector, i.e. the adsorbent layer, is zero, results in the following equation (Rose and Perkins, 1982)

\[
\frac{m}{t} = \frac{DA}{L} C = SC,
\]

where \( m \) = mass transported, \( t \) = time, \( D \) = diffusion coefficient, \( A \) = cross sectional area of diffusion path, \( L \) = length of diffusion path, \( C \) = ambient concentration of contaminant, \( S \) = DA/L = sampling rate for the contaminant.

Using this equation, theoretical sampling rates for naphthalene and phenanthrene were calculated according to Table 5. The diffusive coefficients in Table 5 are theoretically calculated and both random and systematic deviations from true values may occur. For both naphthalene and phenanthrene, the measured sampling rates are within ±25% of the theoretical values and thus fulfill the requirements in the European standard EN 838 (CEN European committee for standardization, 1995). The determined sampling rate for naphthalene differs by ~15% from a previously reported value of 0.480 ml min⁻¹ (Brown, 1998). The agreement of these comparisons confirms the validity of the determined sampling rate for naphthalene.

The naphthalene ISO/Cal value in Table 5 is in agreement with corresponding values for toluene, styrene, ethyl benzene, and trimethyl benzene which show lower sampling rates than the theoretically predicted values. But the corresponding phenanthrene value is higher as the determined sampling rate is higher than the theoretically determined value. The reason for this may be that phenanthrene has much higher boiling point (340°C) than the other components and can be described as semi-volatile (Simpson and Wright, 2008). For semi-volatile compounds adsorption on the sampler walls can occur. This will shorten the mean diffusion path length and the uptake rate will be higher (Simpson and Wright, 2008).

To confirm the laboratory experiments, diffusive sampling of naphthalene and phenanthrene with the ATD method was compared with pumped sampling at a coke plant. The results from the comparison, performed as paired stationary sampling of vapor phase naphthalene at different locations close to the coke oven, shown in Fig. 3, confirms the results from the laboratory study. The 17% difference between the two methods is acceptable as there is not only a comparison between two different sampling methods but also two different analysis methods, GC-MS and HPLC with fluorescence detection. The field test with phenanthrene is a little more problematic and cannot be used to confirm the laboratory tests. There are few data points and no consistency in the results. This may be due to the problems associated with semi-volatile compounds that have previously been reported (Simpson and Wright, 2008) but may also be due to problems in measuring vapor in a mixed aerosol/vapor environment. The low temperature during sampling, 5°C, may have increased the problems with phenanthrene.

### Table 3. Sampling rate of the diffusive sampler at various phenanthrene concentrations, relative humidities (RHs), and sampling times. N, number of determinations

<table>
<thead>
<tr>
<th>Concentration (mg m⁻³)</th>
<th>Time (min)</th>
<th>RH (%)</th>
<th>Sampling rate (ml min⁻¹)</th>
<th>CV (%)</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03</td>
<td>60</td>
<td>20</td>
<td>0.51</td>
<td>11</td>
<td>6</td>
</tr>
<tr>
<td>0.06</td>
<td>60</td>
<td>20</td>
<td>0.50</td>
<td>7</td>
<td>5</td>
</tr>
<tr>
<td>0.03</td>
<td>60</td>
<td>80</td>
<td>0.49</td>
<td>20</td>
<td>6</td>
</tr>
<tr>
<td>0.07</td>
<td>60</td>
<td>80</td>
<td>0.50</td>
<td>7</td>
<td>5</td>
</tr>
<tr>
<td>0.006</td>
<td>480</td>
<td>20</td>
<td>0.67</td>
<td>15</td>
<td>6</td>
</tr>
<tr>
<td>0.09</td>
<td>480</td>
<td>20</td>
<td>0.43</td>
<td>13</td>
<td>5</td>
</tr>
<tr>
<td>0.009</td>
<td>480</td>
<td>80</td>
<td>0.38</td>
<td>14</td>
<td>6</td>
</tr>
<tr>
<td>0.08</td>
<td>480</td>
<td>80</td>
<td>0.47</td>
<td>9</td>
<td>5</td>
</tr>
<tr>
<td>0.10</td>
<td>60</td>
<td>20</td>
<td>0.43</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>Mean</td>
<td>0.49</td>
<td>21%</td>
<td>44</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*aBack diffusion test, after 6 h of exposure to clean air.

*bResults from the storage and back diffusion tests are not included.

### Table 4. Multiregression analysis of the influence of tested variables on the sampling rate (Rₛ) of phenanthrene (ml min⁻¹). P value, probability to obtain the displayed value for the parameter if the true value was zero

<table>
<thead>
<tr>
<th>Variable</th>
<th>Parameter estimate (ml min⁻¹)</th>
<th>Standard error</th>
<th>Parameter significance at 95% confidence level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>0.495</td>
<td>0.013</td>
<td></td>
</tr>
<tr>
<td>Concentration</td>
<td>0.009</td>
<td>0.016</td>
<td>0.58 NS</td>
</tr>
<tr>
<td>Sampling time</td>
<td>0.016</td>
<td>0.014</td>
<td>0.23 NS</td>
</tr>
<tr>
<td>RH</td>
<td>0.022</td>
<td>0.016</td>
<td>0.17 NS</td>
</tr>
</tbody>
</table>

S, significant; NS, not significant.

*aSampling rate.

*bRH, relative humidity.

The standard deviations are rather high, but the minimum requirements in EN 482 (CEN European committee for standardization, 1994) can be considered to be fulfilled for naphthalene. Whether the method fulfills the minimum requirements for phenanthrene in EN 482 or not becomes a question of interpretation.

The standard deviations are rather high, but the minimum requirements in EN 482 (CEN European committee for standardization, 1994) can be considered to be fulfilled for naphthalene. Whether the method fulfills the minimum requirements for phenanthrene in EN 482 or not becomes a question of interpretation.
SUMMARY and CONCLUSIONS

ATD diffusive sampler has been tested for the determinations of naphthalene and phenanthrene in workplace air. The laboratory study showed no effect from the studied parameters concentration, sampling time, and relative humidity on sampling rate for phenanthrene, but a significant effect was seen from the parameter concentration on the sampling rate for naphthalene. This effect is small enough not to reduce the utility of the method. No negative effects from the back diffusion and storage tests could be seen. The field test confirms the naphthalene results from the laboratory tests. The study shows that the ATD diffusive sampler can be used for the determination of gaseous naphthalene in workplace air. For the determination of phenanthrene, the laboratory tests give acceptable results, but these could not be confirmed from the field test. Diffusive sampling of phenanthrene and other semi-volatile compounds should be more thoroughly studied including field tests in different environments to get a better understanding of the limitations of the methods. Diffusive sampling of phenanthrene is not recommended before the method has been tested in the specific environment and the results confirm the laboratory tests.

FUNDING

Swedish Council for Working Life and Social Research (06-030M).

REFERENCES


Table 5. Calculated sampling rates for ATD diffusive sampler. All sampling rates are in ml min$^{-1}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Diffusive coefficient$^a$ (cm$^2$ s$^{-1}/C_0$)</th>
<th>Sampling rate$^b$ (Cal)</th>
<th>Sampling rate$^c$ (EN ISO)</th>
<th>Sampling rate$^d$ (determined)</th>
<th>ISO/Cal$^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>0.0731</td>
<td>0.582</td>
<td>0.437</td>
<td>0.751</td>
<td>0.855</td>
</tr>
<tr>
<td>Styrene</td>
<td>0.0680</td>
<td>0.541</td>
<td>0.463</td>
<td>0.863</td>
<td>0.963</td>
</tr>
<tr>
<td>Ethyl benzene</td>
<td>0.0669</td>
<td>0.533</td>
<td>0.460</td>
<td>0.855</td>
<td>0.963</td>
</tr>
<tr>
<td>Trimethyl benzene</td>
<td>0.0626</td>
<td>0.499</td>
<td>0.480</td>
<td>0.855</td>
<td>0.963</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>0.0609</td>
<td>0.485</td>
<td>0.41</td>
<td>0.845</td>
<td>0.845$^f$</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>0.0510</td>
<td>0.406</td>
<td>0.49</td>
<td>1.21$^f$</td>
<td>1.21$^f$</td>
</tr>
</tbody>
</table>

$^a$Diffusion coefficient calculated according to Fuller, Schettler, and Giddings (FSG) (Fuller et al., 1966).
$^b$Sampling rate calculated from FSG diffusion coefficient and physical properties of the ATD sampler (diffusion length 14 mm and inner diameter 5 mm).
$^c$Sampling rates according to EN ISO 16017-2 (2003).
$^d$Determined mean sampling rates from Tables 1 and 3.
$^e$EN ISO 16017-2:2003 sampling rate (ISO) divided with calculated sampling rate (Cal).
$^f$Determined sampling rate divided with calculated sampling rate (Cal).


