Comparison of various detection limit estimates for volatile sulphur compounds by gas chromatography with pulsed flame photometric detection

Lionel J.J. Catalan a,*, Victor Liang a, Charles Q. Jia b

a Department of Chemical Engineering, Lakehead University, Thunder Bay, Ont., Canada
b Department of Chemical Engineering and Applied Chemistry, University of Toronto, Ont., Canada

Received 12 July 2006; received in revised form 14 September 2006; accepted 19 September 2006
Available online 27 October 2006

Abstract

This paper addresses the variations that presently exist regarding the definition, determination, and reporting of detection limits for volatile sulphur compounds by gas chromatography with pulsed flame photometric detection (GC-PFPD). Gas standards containing hydrogen sulphide (H2S), carbonyl sulphide (COS), sulphur dioxide (SO2), methyl mercaptan (CH3SH), dimethyl sulphide (DMS), carbon disulphide (CS2), and dimethyl disulphide (DMDS) in concentrations varying from 0.36 ppb (v/v) up to 1.5 ppm (v/v) in nitrogen were prepared with permeation tubes and introduced in the gas chromatograph using a 0.25-ml gas sampling loop. After measuring the PFPD response versus concentration, the method detection limit (MDL), the Hubaux–Vos detection limit (xD), the absolute instrument sensitivity (AIS), and the sulphur detectivity (Ds) were determined for each sulphur compound. The results show that the MDL determined by the US Environmental Protection Agency procedure consistently underestimates the minimum concentrations of volatile sulphur compounds that can be practically distinguished from the background noise with the PFPD. The Hubaux–Vos detection limits and the AIS values are several times higher than the MDL, and provide more conservative estimates of the lowest concentrations that can be reliably detected. Sulphur detectivities are well correlated with AIS values but only poorly correlated with MDL values. The AIS is recommended as a reliable and cost-effective measure of detection limit for volatile sulphur compounds by GC-PFPD, since the AIS is easier and faster to determine than the MDL and the Hubaux–Vos detection limit. In addition, this study confirmed that the PFPD response is nearly quadratic with respect to concentration for all volatile sulphur compounds.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Pulsed flame photometric detector; PFPD; Gas chromatography; Detection limit; Volatile sulphur compounds; Sulphur

1. Introduction

Quantitative analysis of volatile sulphur compounds (VSCs) is most commonly carried out by gas chromatography (GC) due to its excellent separation performance and the availability of several detection methods that are both sensitive and selective to sulphur compounds. These include flame photometric detection (FPD), pulse flame photometric detection (PFPD), sulphur chemiluminescence detection (SCD), and atomic emission detection (AED) [1–7]. PFPD provides improved detection sensitivity and much higher selectivity for sulphur compared to FPD [8,9]. Although less sensitive than SCD and AED [7], PFPD is more economical. For very low concentrations (e.g., less than 20 ppbv), PFPD has been successfully used in conjunction with a preconcentration step, such as cryogenic trapping [10,11], sorption on porous polymers and molecular sieves [12–14], or solid-phase microextraction [15].

The PFPD system differs from the FPD system in that the flow of combustible gases (hydrogen and air) to the PFPD system is too low to sustain a continuous flame. After the combustible gases are ignited by a heated ignitor coil at the top of the detector, the flame propagates downwards through a quartz combustor tube and extinguishes once the combustible gases are depleted. The next ignition occurs after fresh combustible gases flowing upward from the base of the detector have flushed the combustion products from the combustor and reached the ignitor.

* Corresponding author. Tel.: +1 807 343 8573; fax: +1 807 343 8928.
E-mail address: Lionel.Catalan@lakeheadu.ca (L.J.J. Catalan).

0021-9673/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2006.09.056
at the top. The pulsing rate of the PFPD system is controlled by the flow rate of combustible gases, and can range from 1 to 10 Hz. The capillary column effluent containing the sulphur compounds to be analyzed is introduced with the combustible gases at the bottom of the detector. During flame propagation, compound molecules are broken down into simpler molecules or atoms that further react to form excited radicals such as $S_2^*$, $OH^*$, and $CH^*$. The relaxation of these radicals produces light (chemiluminescence), which is detected by a photomultiplier after passing through a light guide (quartz rod) perpendicular to the axis of the combustor. PFPD achieves a much better selectivity to sulphur than FPD by separating the sulphur emission ($S_2^*$) from the background emission of combustion products ($OH^*$, $CH^*$, and $C_2^*$) over time. For example, the emission from $CH^*$ and $OH^*$ occurs within 2–4 ms after ignition, whereas the $S_2^*$ emission is delayed and peaks 5–6 ms after the end of the $CH^*$ and $OH^*$ emission. The PFPD signal is integrated over the time period corresponding to the sulphur emission, leaving out most of the background emission. Because the sulphur emission is mainly the result of $S_2^*$ relaxation, the PFPD signal is expected to be proportional to the square of the amount of sulphur eluted. Moreover, since sulphur compound molecules are broken down in the pulsed flame, the PFPD response is considered independent of molecular structure, and depends only on the number of sulphur atoms in the molecule [8,9,16]. For example, a gas standard containing equal molar concentrations of $H_2S$ and $CS_2$ is expected to generate a PFPD response (e.g., chromatographic peak height or area) four times larger for $CS_2$ than for $H_2S$.

The quantitative analysis of sulphur compounds at trace levels (ppb levels or less), especially for some reduced sulphur compounds such as hydrogen sulphide, is complicated by their high reactivity, which can result in severe losses during sampling and analysis. The materials that come in contact with the samples must be inert toward sulphur compounds to minimize these losses [17].

The detection limit is generally defined as “the lowest concentration of an analyte that the analytical process can reliably detect” [18]. A more precise definition is “the concentration of analyte that gives a signal significantly different from the blank or background signal” [19]. The US Environmental Protection Agency (EPA) provides a statistical definition of the method detection limit as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero [20]. In practice, various procedures are in use to determine the detection limit of PFPD-based analytical systems, which makes results difficult to compare. For example, the method detection limit measured by the EPA procedure [20] is reported in units of concentration such as parts per billion (ppb), whereas the inventors of the PFPD system and various instrument manufacturers report the detection limit in units of pg/s [8,9,16].

### 2. Theory

In this section, the most common procedures for determining the detection limits of PFPD-based analytical systems are reviewed.

#### 2.1. Method detection limit

The EPA procedure for determining the method detection limit (MDL) requires analyzing a minimum of seven replicate samples with a sufficiently low concentration (less than 10 times the expected MDL). Each replicate must be processed through the entire analytical method. The MDL is calculated as follows:

$$\text{MDL} = t_{n-1, \alpha=0.01} \times s$$

where $n$ is the number of replicate analyses, $s$ is the standard deviation of the replicate analyses, and $t$ is the student’s $t$ value for $n - 1$ degrees of freedom at 99% confidence level. The EPA procedure assumes that the measured concentrations are normally distributed (i.e., their frequency distribution is represented by a Gaussian curve) and that the standard deviation of the distribution is constant at low concentrations (at least in a range of concentrations extending from zero to the concentration used to determine the MDL). When the assumptions of normal distribution and constant standard deviation at low concentration are valid, the MDL is the minimum concentration that can be differentiated from the background noise with a 99% confidence level (Fig. 1).

The assumption of uniformity of variance can be tested by analyzing a second set of replicate samples having a different concentration from the first set (but still less than 10 times the MDL). The standard deviation of the second set of analyses is calculated, and a statistical $F$-test is carried out to test the hypothesis of equal variance in the two data sets. This involves calculating the ratio $s^2_A / s^2_B$, where $s_A$ and $s_B$ refer to the standard deviations of the two sets of replicate analyses, with $s_A > s_B$ to ensure that the ratio is greater than one. The ratio of variances is then compared to the critical $F$-value, $F_{crit}$, which is a function of the number of replicates in each data set ($n_A$ and $n_B$, respectively) and of the confidence level specified by the EPA procedure $(1 - \alpha = 0.90)$. If $s^2_A / s^2_B$ is less than $F_{crit}$, then the hypothesis of equal variances cannot be rejected with a 90% confidence level, and the two sample variances are pooled as follows:

$$s^2_{pooled} = \frac{(n_A - 1)s^2_A + (n_B - 1)s^2_B}{n_A + n_B - 2}$$

Fig. 1. Frequency distribution of measured concentrations for a low concentration gas standard (right) and expected distribution for blank replicate measurements (left). Note that the standard deviations are assumed to be the same for both distributions. Only 1% of the blank measurements will exceed the MDL.
A new MDL is then calculated using the pooled standard deviation:
\[
\text{MDL} = t(\alpha_p + \alpha_b - 2, \alpha = 0.01) \times S_{\text{pooled}} \tag{3}
\]

2.2. Hubaux–Vos detection limit \((x_D)\)

The Hubaux–Vos procedure for calculating detection limits relies on calibration data plotted as response versus true concentration [21]. It is recommended that the calibration data include at least four concentration levels with a minimum of four replicate samples at any level and a total of at least 20 samples processed separately through the entire method sequence [22]. The Hubaux–Vos procedure assumes that the response variance is constant throughout the range of concentrations used in the calibration and that the measured responses are normally distributed around their expectation at each true concentration level. Decision and detection limits are obtained graphically from the plot of the regression line with lower and upper prediction limit lines corresponding to confidence levels of \(\alpha\%\) and \(\beta\%\), respectively (see Fig. 5 for an example of the Hubaux–Vos graphical procedure applied to calibration data for \(\text{H}_2\text{S}\)). Usually, both \(\alpha\) and \(\beta\) are set equal to 0.5\% for a total confidence level of 99\%. The decision limit, \(y_c\), is defined as the point where the upper prediction limit line crosses the \(y\)-axis. Any response higher than \(y_c\) has only a negligible risk (i.e., less than \(\alpha\)) to be caused by a sample with zero concentration (blank sample). Therefore, \(y_c\) is the minimum response required to decide that the analyte is present in the sample with a confidence level greater than \((100 - \alpha)\%\). The detection limit, \(x_D\), is obtained by drawing a line parallel to the \(x\)-axis from \(y_c\) until reaching the lower confidence limit line and then proceeding vertically to the \(x\)-axis. The probability that a sample with concentration higher than \(x_D\) will produce a response lower than \(y_c\) (i.e., the probability of finding that the analyte is absent when it is actually present) is less than \(\beta\%\).

2.3. Absolute instrument sensitivity

The absolute instrument sensitivity (AIS) is calculated from the background noise and corresponds to the concentration at which a signal should be measurable [23]. A signal-to-noise ratio yielding a compound specific value of sulphur detectivity, and this terminology will be used in the following to differentiate \(D_s\) from the MDL and the Hubaux–Vos detection limit \((x_D)\), which are both reported in units of concentration. If the gas standard contains several sulphur compounds, Eq. (6) can be used successively with each chromatographic peak, thus yielding a compound specific value of sulphur detectivity.

3. Materials and methods

Gas standards containing \(\text{H}_2\text{S}\), \(\text{CO}_2\), \(\text{SO}_2\), \(\text{CH}_3\text{SH}\), DMS, CS\(_2\), and DMDS at concentrations in the ppb (v/v) (ppbv) range were generated by Dynacal permeation tubes provided by VICI Metronics, Poulsbo, WA, USA. Fig. 2 shows a schematic of the gas standards generator set-up that was used for all runs. The
permeation tubes were held in a glass U-tube immersed in a water bath. The temperature of the water bath was controlled at 30.0 °C to ensure constant permeation rates. Permeation rates (Table 1) were determined by measuring the change in weight of the permeation tubes over a period of 21 weeks. Measured permeation rates generally fall within the range specified by the manufacturer. Pure nitrogen gas flows through the U-tube holder at a rate set by the mass flow controller MFC-1. The purest nitrogen source is obtained from the gas withdrawal valve of a low pressure liquid nitrogen tank. Nitrogen supplied by ultra-high-purity nitrogen cylinders was found to be contaminated by small concentrations of COS that interfered with the determination of this compound. The gas exiting the U-tube holder is mixed with a dilution flow of pure nitrogen at the tee junction T-1. The dilution flow rate is controlled by the second mass flow controller MFC-2. Analyte concentrations at the outlet of the calibration set-up are inversely proportional to the total nitrogen flow rate (MFC-1 + MFC-2), which ranged from 20 to 6000 ml/min. The tested range of concentrations for each sulphur compound is shown in the last column of Table 1. Because permeation rates take several hours to equilibrate after a change in nitrogen flow rate through the U-tube holder, analyte concentrations are typically varied by adjusting the dilution flow rate while maintaining a constant flow rate through the U-tube holder. All gas lines downstream of the U-tube holder are made of PTFE, and fittings are treated with Sulfinert coating (Restek, Bellefonte, PA, USA) to minimize surface interactions with sulphur compounds. When the total calibration gas flow rate exceeds the gas flow rate through the gas chromatograph, the excess gas is vented at the tee junction T-2.

Gas standards are introduced in the gas chromatograph (Varian CP 3800, Palo Alto, CA, USA) via a 0.25-ml sampling loop. The temperature of the loop is maintained at 150 °C with a valve oven. The temperature program for the column oven is as follows: initial temperature of 35 °C, ramping at a rate of 20 °C/min to 165 °C, and holding at 165 °C for 4.5 min. All sample lines are treated with Silcosteel coating (Restek) to prevent adsorption of active sulphur compounds. Both Silcosteel and Sulfinert are silicon-based coatings applied by chemical vapour deposition at high temperature (400 °C) to metal surfaces. The Sulfinert treatment includes secondary and tertiary coatings to reduce the effect of pinholes and porosity created during the coating process. The chromatographic separation is done by a Varian CP-SIL 5CB capillary column having dimensions of 50 m x 0.32 mm I.D., and 5-μm film thickness. A Varian PFPD system is used to selectively detect sulphur compounds. The detector is operated at 200 °C with the following combustible gas flow rates: H2 = 14 ml/min, Air1 = 17 ml/min, and Air2 = 13 ml/min. Other PFPD parameters are as follows: photomultiplier tube voltage = 600 V, gate delay = 6.0 ms, gate width = 20.0 ms, trigger level = 200 mV, and gain factor = 20. The flow rate of the carrier gas (helium) measured at the outlet of the PFPD detector is 2.3 ml/min. The air–hydrogen needle valve that controls the ratio of wall flow to combustor flow in the PFPD system is set so that the detector is operating close to tick-tock mode (but not in tick tick mode). This is done by monitoring the time dependence of the PFPD signal with an oscilloscope. When no sulphur compound flows through the detector, the oscilloscope shows two light spikes separated by a few milliseconds. The first spike (triggering spike) is due to the flame hitting the upper combustor lips. The second spike, which is caused by the pulsed flame passing by the light collection window at the centre of the combustor, is present on every pulse outside of tick tock mode [8]. The time separation between the two light spikes is a measure of the pulsed flame velocity that depends on the combustible gas composition. The air–hydrogen needle valve is adjusted so that the time separation between the maximum of the two spikes is always 2.0 ms to ensure consistency in combustible gas composition over time. The PFPD pulse rate is stable at 3.8 Hz.

4. Results

4.1. PFPD response versus concentration

Fig. 3 shows the complete analytical data set as integrated detector response (peak area) versus concentrations on a volume basis (ppbv). Note that this unit of concentration is equivalent to ppb on a molar basis. Only concentrations for which an analyte peak could be identified are plotted in Fig. 3. For example, H2S concentrations below 25 ppbv did not produce a recognizable peak and are therefore not shown. As expected, molecules containing two sulphur atoms (DMDS and CS2) yield the highest response for a given concentration. Intermediate responses are

---

Table 1

Table 1 shows the permeation rates and tested range of concentrations at 30.0 °C for several sulphur compounds. The detector response (peak area) versus concentrations on a volume basis (ppbv). Note that this unit of concentration is equivalent to ppb on a molar basis. Only concentrations for which an analyte peak could be identified are plotted in Fig. 3. For example, H2S concentrations below 25 ppbv did not produce a recognizable peak and are therefore not shown. As expected, molecules containing two sulphur atoms (DMDS and CS2) yield the highest response for a given concentration. Intermediate responses are
obtained for COS, SO$_2$, CH$_3$SH, and DMS. The lowest response is provided by H$_2$S. The fact that the response for H$_2$S is consistently lower than for other molecules containing a single sulphur atom shows that although the PFPD response may be independent of molecular structure, the response of the overall analytical system is compound specific. The low response for H$_2$S may be attributable to relatively higher losses of this compound in the analytical system. These results demonstrate the importance of determining individual calibration curves for individual sulphur compounds when using the PFPD system. The apparent departure from equimolar response for PFPD and the relatively low response obtained for H$_2$S are consistent with results from previous studies [4,6].

The calibration curves are well fitted by straight lines on a logarithmic plot, which indicates that peak area and concentration are related by the following equation:

$$\log(A_p) = m \log C + a$$  \hspace{1cm} (7)

where $A_p$ is the chromatographic peak area (counts), $C$ is the analyte concentration (ppbv), $m$ is the slope factor, and $a$ is the intercept. The numerical values and standard errors of the parameters $m$ and $a$ for each sulphur compound, obtained by regression analysis, are given in Table 2. Slope factors are generally very close to 2.0, indicating a nearly quadratic response of the PFPD system, consistent with results reported by others [6,9]. DMDS and DMS exhibit the largest deviations from the quadratic response with slope factors of 1.76 ± 0.03 and 1.82 ± 0.03, respectively. Substantially larger deviations from the quadratic response for DMDS and DMS were previously reported at concentrations larger than 400 and 2000 ppbv, respectively [4]. However, these concentrations are above the range of concentrations tested in the present study.

Fig. 4 shows chromatographic peak height versus concentration for several sulphur compounds.

4.2. EPA Method detection limit

Table 3 summarizes the MDL calculations for all sulphur compounds except COS. The MDL for COS could not be evaluated because its permeation rate was too high to achieve a concentration lower than 10 times its expected detection limit. The uniformity of variance was tested for H$_2$S, DMS, and DMDS by carrying out replicate analyses at two different concentrations less than 10 times the MDL. The results show that the hypothesis of equal variances could not be rejected with a 90% confidence level ($s^2_A/s^2_B < F_{crit}$), and therefore the two sample variances were pooled to calculate the MDL for H$_2$S, DMS, and DMDS with Eq. (3). For the other sulphur compounds (SO$_2$, CH$_3$SH, and CS$_2$), the MDL was calculated with Eq. (1) using the standard deviation from one set of replicate samples. MDL values range from 1.47 ppbv for CS$_2$ to 12.4 ppbv for SO$_2$. The MDL for compounds containing two sulphur atoms (CS$_2$ and DMDS) are on average 4.8 times lower than for compounds containing a single sulphur atom (H$_2$S, SO$_2$, CH$_3$SH, and DMS). This is consistent with the quadratic response of the PFPD detector, which generates a response four times larger when the number of sulphur atoms is doubled.

The last line of Table 3 reports MDL values in mass units (pg). The relationship between mass-based and concentration-based MDL values is as follows:

$$\text{MDL (pg)} = \frac{10^3 \rho V M_w}{RT} \text{MDL (ppbv)}$$  \hspace{1cm} (9)

Table 2: Calibration parameters $m$, $a$, $n$, and $b$ for several sulphur compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>H$_2$S</th>
<th>COS</th>
<th>SO$_2$</th>
<th>CH$_3$SH</th>
<th>DMS</th>
<th>CS$_2$</th>
<th>DMDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m$</td>
<td>1.89 ± 0.04</td>
<td>1.89 ± 0.02</td>
<td>1.96 ± 0.02</td>
<td>1.95 ± 0.02</td>
<td>1.82 ± 0.03</td>
<td>1.92 ± 0.01</td>
<td>1.76 ± 0.03</td>
</tr>
<tr>
<td>$a$</td>
<td>−0.88 ± 0.07</td>
<td>−0.41 ± 0.05</td>
<td>−0.71 ± 0.04</td>
<td>−0.67 ± 0.03</td>
<td>−0.36 ± 0.05</td>
<td>0.112 ± 0.020</td>
<td>0.45 ± 0.04</td>
</tr>
<tr>
<td>$n$</td>
<td>1.99 ± 0.02</td>
<td>1.94 ± 0.02</td>
<td>2.09 ± 0.02</td>
<td>1.99 ± 0.01</td>
<td>1.91 ± 0.03</td>
<td>1.94 ± 0.02</td>
<td>1.86 ± 0.03</td>
</tr>
<tr>
<td>$b$</td>
<td>−4.55 ± 0.05</td>
<td>−3.94 ± 0.05</td>
<td>−4.45 ± 0.05</td>
<td>−4.08 ± 0.03</td>
<td>−3.82 ± 0.06</td>
<td>−3.16 ± 0.03</td>
<td>−2.99 ± 0.04</td>
</tr>
</tbody>
</table>

Notes: The parameters $m$ and $a$ are the slope factor and intercept, respectively, in the calibration equation for chromatographic peak area: $\log(A_p) = m \log C + a$. The parameters $n$ and $b$ are the slope factor and intercept, respectively, in the calibration equation for chromatographic peak height: $\log(H_p) = n \log C + b$.  

Fig. 4. Dependence of chromatographic peak height on concentration for several sulphur compounds.
Table 3
Calculated USEPA method detection limits (MDL)

<table>
<thead>
<tr>
<th>Compound</th>
<th>H2S</th>
<th>SO2</th>
<th>CH3SH</th>
<th>DMS</th>
<th>CS2</th>
<th>DMDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (ppbv)</td>
<td>38.5</td>
<td>57.8</td>
<td>27.1</td>
<td>31.5</td>
<td>24.0</td>
<td>35.9</td>
</tr>
<tr>
<td>Number of analyses</td>
<td>8</td>
<td>10</td>
<td>7</td>
<td>7</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>Degrees of freedom (ν)</td>
<td>7</td>
<td>9</td>
<td>6</td>
<td>6</td>
<td>7</td>
<td>9</td>
</tr>
<tr>
<td>Standard deviation (σ)</td>
<td>4.54</td>
<td>3.06</td>
<td>3.96</td>
<td>3.07</td>
<td>3.07</td>
<td>2.93</td>
</tr>
<tr>
<td>t(ν, α=0.01)</td>
<td>3.00</td>
<td>2.82</td>
<td>3.14</td>
<td>3.14</td>
<td>3.00</td>
<td>2.82</td>
</tr>
<tr>
<td>MDL (ppbv)</td>
<td>13.6</td>
<td>8.6</td>
<td>12.4</td>
<td>9.6a</td>
<td>13.2</td>
<td>8.3</td>
</tr>
<tr>
<td>s2A/s2B</td>
<td>2.19</td>
<td>2.24</td>
<td>1.19</td>
<td>2.51</td>
<td>2.51</td>
<td>2.55</td>
</tr>
<tr>
<td>Fcrit (νA−1, νB−1, α=0.1)</td>
<td>2.51</td>
<td>3.64</td>
<td>1.06</td>
<td>2.58</td>
<td>2.58</td>
<td>2.602</td>
</tr>
<tr>
<td>MDL (pg)</td>
<td>9.8b</td>
<td>4.2b</td>
<td>3.3a</td>
<td>9.4b</td>
<td>4.2b</td>
<td>2.8b</td>
</tr>
<tr>
<td>MDL (pg)</td>
<td>2.4b</td>
<td>5.7a</td>
<td>1.47a</td>
<td>0.81a</td>
<td>0.81a</td>
<td>1.9b</td>
</tr>
</tbody>
</table>

a MDL based on the standard deviation from one set of replicate samples.
b MDL based on the pooled standard deviation from two sets of replicate samples.

Table 4
Comparison of mass-based MDL values between the present study and Kim [4] for H2S, CH3SH, DMS, and DMDS

<table>
<thead>
<tr>
<th>Compound</th>
<th>H2S</th>
<th>CH3SH</th>
<th>DMS</th>
<th>DMDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDL (pg), present study</td>
<td>2.4</td>
<td>3.3</td>
<td>4.2</td>
<td>1.9</td>
</tr>
<tr>
<td>MDL (pg), Kim [4]</td>
<td>1.7</td>
<td>1.8</td>
<td>2.6</td>
<td>0.9</td>
</tr>
<tr>
<td>Difference (%)</td>
<td>29</td>
<td>45</td>
<td>53</td>
<td>0.9</td>
</tr>
</tbody>
</table>

where P is the gas sampling loop pressure (101325 Pa), V is the gas sampling loop volume (0.250 × 10−6 m3), T is the gas sampling loop temperature (423 K), R is the universal gas constant (8.314 J/mol K), and Mw is the analyte molecular weight (for example, Mw = 34.08 g/mol for H2S). Mass-based MDL values range from 0.81 pg for CS2 to 5.7 pg for SO2.

Table 4 compares mass-based MDL values found in the present study with those determined in an earlier study [4] using a GC-PFPD system with a larger sampling loop size (0.5 ml). Although the range of MDL is similar in both studies (a few pg), the MDL values for individual compounds (H2S, CH3SH, DMS, and DMDS) are between 29 and 53% higher in the present study. These differences appear to contradict previous findings that decreasing the loop size (or injection volume) increases the GC-PFPD sensitivity [6]. However, other differences in the analytical system (PFPD model, carrier gas flow rate, air and hydrogen flow rates to the detector, column type and size, etc.) may also have contributed to the differences in mass-based MDL values.

4.3. Hubaux–Vos detection limit

The Hubaux–Vos procedure is only applicable to linear calibration curves. Since the PFPD response was found to be nearly quadratic for all the sulphur compounds, the square root of the peak area was plotted versus concentration, thus yielding a linear calibration curve. The lower and upper prediction limit lines corresponding to a total confidence level of 99% (α = β = 0.5%) were used to determine the decision limit yC and the detection limit xD for each sulphur compound. Fig. 5 shows an example of this determination for H2S, and the results for all sulphur compounds are summarized in Table 5. Linear regression calculations were carried out with the NCSS statistical software (Kaysville, UT, USA).

The Hubaux–Vos detection limits range from 7.2 ppbv for DMDS to 28.8 ppbv for SO2. Compounds containing two sulphur atoms (CS2 and DMDS) have significantly lower xD than compounds containing a single sulphur atom. Decision limits

Table 5
Detection limits calculated with the Hubaux–Vos procedure

<table>
<thead>
<tr>
<th>Compound</th>
<th>H2S</th>
<th>COS</th>
<th>SO2</th>
<th>CH3SH</th>
<th>DMS</th>
<th>CS2</th>
<th>DMDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decision limit, yC (area counts1/2)</td>
<td>4.18</td>
<td>6.42</td>
<td>6.35</td>
<td>4.73</td>
<td>5.89</td>
<td>5.24</td>
<td>6.18</td>
</tr>
<tr>
<td>Detection limit, xD (ppbv)</td>
<td>27.5</td>
<td>22.2</td>
<td>28.8</td>
<td>22.6</td>
<td>18.4</td>
<td>11.5</td>
<td>7.2</td>
</tr>
<tr>
<td>Detection limit, xD (pg)</td>
<td>6.8</td>
<td>9.6</td>
<td>13.3</td>
<td>7.8</td>
<td>8.2</td>
<td>6.3</td>
<td>4.9</td>
</tr>
</tbody>
</table>
Fig. 6. Calculated sulphur detectivity as a function of gas standard concentration for (a) H$_2$S, (b) SO$_2$, (c) CH$_3$SH, (d) DMS, (e) COS, (f) CS$_2$, and (g) DMDS.
Table 6

<table>
<thead>
<tr>
<th>Compound</th>
<th>H2S</th>
<th>COS</th>
<th>SO2</th>
<th>CH3SH</th>
<th>DMS</th>
<th>CS2</th>
<th>DMDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>AIS (ppbv)</td>
<td>39.5</td>
<td>21.1</td>
<td>29.5</td>
<td>22.8</td>
<td>19.1</td>
<td>8.4</td>
<td>7.5</td>
</tr>
<tr>
<td>AIS (pg)</td>
<td>9.7</td>
<td>9.1</td>
<td>13.6</td>
<td>7.9</td>
<td>8.6</td>
<td>4.6</td>
<td>5.1</td>
</tr>
</tbody>
</table>

The calculated absolute instrument sensitivity (AIS) for H2S and SO2 are significantly higher than for other sulphur compounds containing a single sulphur atom. The AIS for H2S and SO2 is nearly constant value at higher concentrations.

The concentation and molecular structure of the analyte used for the determination of sulphur detectivity is independent of the gas standard. Therefore, it assumes that the sulphur detectivity based on DMDS is stable at 1.5 pg/s for DMDS peaks, the detectivity initially worsens (i.e., Ds decreases) as the molecular weight increases: it is highest for H2S (2.6 pg S/s) and lowest for CS2 (0.64 pg S/s).

Fig. 7 shows that a statistically significant correlation exists between the calculated sulphur detectivity and the molecular weight of sulphur compounds. The sulphur detectivity values in the range 0.2–0.3 pg S/s with optimized analytical conditions provided by Varian (1 pg S/s) and previously reported values in the range 0.2–0.3 pg S/s with optimized analytical conditions [8,9]. It is worth noting that these low Ds values were determined with sulphur compounds (e.g., methylparathion) dissolved in liquid solutions, which are not as susceptible to analytical losses as the gas samples that were used in the present study. Hence, the higher detectivities determined in the present study may be attributable to losses of sulphur compounds in the gas sampling process.
analytical system in spite of the precautions taken to minimize them. If differences in calculated sulphur detectivities between compounds are related to losses in the analytical system, then the results suggest that these losses increase as the compound molecular weight decreases.

The concentration dependence of sulphur detectivity determined with COS, CS$_2$, and DMDS can be explained by variations in the chromatographic peak width at quarter height as a function of concentration. For example, Fig. 8 shows that the DMDS peak width sharply decreases as the DMDS concentration increases from 7 to 20 ppbv, and then remains nearly constant at higher concentrations. In accordance with Eq. (6), a decrease in peak width causes an increase in sulphur detectivity (Fig. 6g). By contrast, the width of the SO$_2$ peak is constant throughout the entire concentration range, thus explaining that the sulphur detectivity calculated with SO$_2$ is also constant (Fig. 6b). Similar relationships between chromatographic peak width and sulphur detectivity were obtained for the other sulphur compounds.

5. Discussion

Fig. 9 and Table 7 compare the values of the MDL, $x_D$, and AIS for several sulphur compounds. Although the MDL and the AIS are correlated ($r^2 = 0.69$, $p = 0.04$), MDL values are between 2.0 and 5.7 times lower than AIS values, depending on the sulphur compound. Hubaux–Vos detection limits ($x_D$) are better correlated with AIS values ($r^2 = 0.86$, $p = 0.003$), and the ratio of AIS to Hubaux–Vos detection limits only varies between 0.73 and 1.44. Moreover, the values of AIS and $x_D$ nearly coincide for COS, SO$_2$, CH$_3$SH, DMS, and DMDS. Hence, the results suggest that the MDL determined by the USEPA procedure significantly underestimates the minimum concentrations of volatile sulphur compounds that can be detected with the PFPD. To corroborate this finding, gas standards with very low concentrations of sulphur compounds were analyzed to estimate the lowest concentration that produces a chromatographic peak, which could be visually separated from the baseline noise on the chromatograms. This concentration, which is denoted lowest separable concentration (LSC), is compared to the AIS and the MDL values in Table 7. For each sulphur compound, the LSC is bounded by the lowest concentration at which a distinct peak could still be visually identified and the highest concentration at which the peak could not be visually separated from the noise. The analyses at concentrations just above and below the LSC were repeated to ensure reproducibility of the results (i.e., separation and non-separation of the chromatographic peak from noise, respectively). Note, however, that the LSC is not statistically derived. Table 7 shows that LSC values are consistently higher than MDL values and smaller than AIS and $x_D$ values. The ratio of LSC to MDL values ranges from 1.2 to 4.5. This confirms that the MDL underestimates the concentrations at which sulphur compound can be practically detected. By contrast, the AIS and Hubaux–Vos detection limits provide more conservative and consistent estimates of the lowest concentrations that can be reliably detected.

<table>
<thead>
<tr>
<th>Compound</th>
<th>H$_2$S</th>
<th>COS</th>
<th>SO$_2$</th>
<th>CH$_3$SH</th>
<th>DMS</th>
<th>CS$_2$</th>
<th>DMDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDL (ppbv)</td>
<td>9.8</td>
<td>ND</td>
<td>12.4</td>
<td>9.6</td>
<td>9.4</td>
<td>1.47</td>
<td>2.8</td>
</tr>
<tr>
<td>$x_D$ (ppbv)</td>
<td>27.5</td>
<td>22.2</td>
<td>28.8</td>
<td>22.6</td>
<td>18.4</td>
<td>11.5</td>
<td>7.2</td>
</tr>
<tr>
<td>AIS (ppbv)</td>
<td>39.5</td>
<td>21.1</td>
<td>29.5</td>
<td>22.8</td>
<td>19.1</td>
<td>8.4</td>
<td>7.5</td>
</tr>
<tr>
<td>LSC (ppbv)</td>
<td>24.7–27.5</td>
<td>10.3–12.3</td>
<td>19.7–24.6</td>
<td>16.1–18.8</td>
<td>10.2–12.1</td>
<td>5.7–7.6</td>
<td>4.3–5.4</td>
</tr>
<tr>
<td>AIS/MDL</td>
<td>4.0</td>
<td>ND</td>
<td>2.4</td>
<td>2.4</td>
<td>2.0</td>
<td>5.7</td>
<td>2.7</td>
</tr>
<tr>
<td>AIS/$x_D$</td>
<td>1.44</td>
<td>0.95</td>
<td>1.02</td>
<td>1.01</td>
<td>1.04</td>
<td>0.73</td>
<td>1.04</td>
</tr>
<tr>
<td>LSC/MDL</td>
<td>2.7</td>
<td>ND</td>
<td>1.8</td>
<td>1.8</td>
<td>1.2</td>
<td>4.5</td>
<td>1.7</td>
</tr>
</tbody>
</table>
These findings have interesting practical consequences since the AIS can be readily determined from the rms noise, which is automatically calculated by the chromatography software, and from the calibration curve of chromatographic peak height versus concentration. By contrast, the determination of the MDL and the Hubaux–Vos detection limit are more complex and time consuming. The USEPA procedure for determining the MDL involves trial and error to select a concentration less than 10 times the MDL and the analysis of a minimum of seven replicate samples (or more samples if the assumption of uniform variance is to be tested). The Hubaux–Vos procedure requires the preparation and analysis of a minimum of 20 samples and the use of advanced statistical software. Hence, the AIS appears to be the most cost-effective measure of detection limit for the GC–PFPD method.

Fig. 10 shows that the sulphur detectivity $D_s$ is well correlated with the AIS ($r^2 = 0.71, p = 0.02$), which is not surprising since both quantities are based on signal-to-noise ratios. However, the sulphur detectivity is only poorly correlated with the MDL ($r^2 = 0.23, p = 0.34$).

6. Conclusions

The main conclusions of this study are as follows:

- The PFPD response (chromatographic peak area or height) is nearly quadratic with respect to concentration for all volatile sulphur compounds.
- MDLs calculated by the EPA procedure underestimate the concentrations at which sulphur compound can be practically detected.
- Hubaux–Vos detection limits are several times higher than the MDL values and are consistent with AISs.
- The AIS is recommended as a reliable, conservative, cost-effective, and relatively simple measure of the detection limit for volatile sulphur compounds by GC–PFPD.
- Sulphur detectivities decrease with the molecular weight of the compound used for their determination and are well correlated with the AIS.

Acknowledgement

This research was supported by the Environmental Consortium of the University of Toronto Pulp and Paper Centre.

References

[16] Pulsed flame photometric detector (PFPD) for CP-3800, Operator’s manual, 03-914657-00:4, Varian Analytical Instruments, Walnut Creek, CA, 2001.