Variability and repeatability of olfactometric results of 
\( n \)-butanol, pig odour and a synthetic gas mixture

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Abstract For the purposes of a research project for the Flemish authorities, olfactometric measurements were carried out at six closed pig farms and six fattener farms. The results of these olfactometric measurements were compared with the olfactometric results of \( n \)-butanol samples and samples of a synthetic gas mixture of ethanethiol, methylacetate and 2-propanol in nitrogen, both analysed on the same days as the air samples from the pig farms. The results of the \( n \)-butanol tests for all panellists showed that nobody was qualified according to the CEN criteria, and that, consequently, these criteria are rather stringent. Comparing the variability of the results for the three different odours showed that the mean and standard deviation of the mean variance were not significantly different for the three odour types, which means that the repeatability of the panellist results was equal for the examined odour types. The principle of traceability was checked by comparing the variance of the \( n \)-butanol, pig odour and synthetic mixture ratio. For the complete dataset, the principle of traceability could not be proven for \( n \)-butanol. For the restricted dataset, the principle of traceability was more valid for \( n \)-butanol than for the mixture, but differences were small. Finally, normalization was looked for with regard to olfactometric measurements of air samples from pig farms based either on \( n \)-butanol or on the synthetic mixture. Both models had low determination coefficients, but the model based on the synthetic mixture gave better results than the one based on \( n \)-butanol.

Keywords Mixture; \( n \)-butanol; normalization; olfactometry; repeatability; traceability; variability

Introduction

After a long period of standardization and inter-laboratory comparisons (Heeres and Harssema, 1996; Van Harreveld et al., 1999), finally, the quality requirements of the European standard on olfactometry prEN 17325 (CEN, 2000) have led to a distinctly measurable and stable improvement of the reliability of odour concentration measurements. An important fact in this standard is the use of \( n \)-butanol as reference material to serve as the basis for quality control, including regular performance evaluation of panellists.

The use of a reference material for qualification of panellists is based on the principle of traceability, which means that if the sensitivity of a panellist/panel to the reference odour (\( n \)-butanol) is high/low, that their relative performance should be the same with environmental odours. Dollnick et al. (1988) describe the results of olfactometric analyses of four different odorants (\( \text{H}_2\text{S}, \text{n-butanol, propionic acid and isomyl alcohol} \) carried out by 20 laboratories with various olfactometers. The ratio of 16 and 84 percentiles for all odorants under consideration was in the same order (between 10 and 30). From these results, Dollnick et al. (1988) concluded that an odorant-independent sensitivity hierarchy exists between panels, or that traceability could be assumed.

Van Harreveld and Heeres (1995) found that the standard deviation for the parameter \( \Delta Z \), which is the ratio between each individual threshold estimate and the group threshold, was not significantly different for environmental odorants and for \( n \)-butanol. From these results, it could be assumed that the behaviour of panel members judging environmental odorants is predicted by their behaviour for \( n \)-butanol. Qu et al. (2001) confirmed the
principle of traceability, and developed a normalization model in order to rescale a measurement of an environmental odour by a non-qualified panel to the one by a panel whose n-butanol threshold is 40 ppbv. They stated that the model should be valid for all odours, but that further investigations are needed to confirm this inference.

Although n-butanol is defined as a reference material in the CEN standard, many experts agree upon the fact that one or more single substances are only an intermediate solution towards the aim of applying a reference odour mixture for panel selection. Laska and Hudson (1991) and Van Harreveld and Heeres (1997) suggested that in order to reduce variability and increase testing efficiency, odour mixtures rather than single substances should be used.

Mannebeck and Mannebeck (2001) performed some experiments with coffee flavour, but this odour cannot be regarded as a manageable reference odour mixture, because sample preparation is inconvenient and the odour concentration and character is stable only for a short period after preparation.

In this study, olfactometric analyses were done for three types of odour: odour samples from pig farms, n-butanol and a three-component synthetic gas mixture of ethanethiol, methylacetate and 2-propanol in nitrogen. First, the results of the n-butanol tests for the panellists will be looked at in the light of qualification according to the CEN criteria. A second objective is to see whether the variation between the two odour concentrations determined in the two rounds of one olfactometric analysis, is different for three odour types (pig odour, n-butanol and the synthetic gas mixture). Finally, the principle of traceability is examined, and a normalization model for olfactometric measurements of air samples from pig farms, based either on n-butanol or on the synthetic mixture, will be looked for. The measurements of the pig odour samples and n-butanol ran from August 2002 until March 2003. As the measurements with the synthetic mixture only started in February 2003, the measurements of the three odour types for this short period will be treated separately in order to make a proper comparison.

**Methods**

**Air samples**

Within the framework of a project for the Flemish Authorities where odour emissions from pig farms must be determined, odorous air samples for olfactometric analysis were taken at six closed pig farms and six fattener farms in Flanders. Here, the results from August 2002 until March 2003 will be used. At the closed pig farms, samples were taken for four different animal categories (weaned piglets, fatteners, dry sows and farrowing sows), while, at fattener farms, only one animal category is present. For the samples, 60 L Nalophane™ bags were used.

Next to the air samples from the pig farms, two other kinds of samples were also presented to the panel assessors. A first one was n-butanol as this is indicated as a reference material in the European standard for olfactometry (CEN, 2000). Until 13/03/2003 a first gas cylinder was used with an n-butanol concentration of 60.2 ppm ± 2%, from 14/03/2003 onwards a second gas cylinder with an n-butanol concentration of 57.4 ppm ± 2% was used. A third type of sample was a synthetic gas mixture of ethanethiol, methylacetate and 2-propanol in nitrogen (hereafter called “mixture”). The concentration in the steel gas cylinder was 0.10 ppm ± 0.03 ppm ethanethiol, 600 ± 30 ppm methylacetate and 1,000 ± 50 ppm 2-propanol. The use of these concentrations was based on the human olfactory thresholds for these components mentioned by Devos *et al.* (1990).

**Olfactometric analysis**

Olfactometric analyses were carried out according to the European standard prEN 13725 (CEN, 2000) using a forced-choice olfactometer type Olfactomat-n1 (PRA, Amsterdam)
and a panel of three to five human assessors. Students aged between 18 and 25 years were used as assessors.

For the determination of the odour concentration of an air sample, according to the CEN the sample is presented to the panel members in at least two rounds. To make terminology easier, all the rounds of n-butanol performed on one day, in this article count as one n-butanol sample. Normally, two rounds a day were done for n-butanol, but occasionally it was more.

**Results and discussion**

**Selection of panel members**

The CEN standard prEN13725 give strict requirements for selecting qualified panellists in terms of sensitivity and stability. On the basis of the results of 10 rounds for n-butanol (further called “n-butanol tests”) on three separate days, panellists should then be accepted or excluded. Here, in total, 45 panellists participated in the experiments. Each day, pig odour samples were analysed, also at least two n-butanol tests were done. For only eight of the 45 panellists, at least 10 n-butanol tests were available and none of these eight panellists complied with both the two criteria mentioned in the CEN. For seven of the eight panellists, the geometric mean of the individual threshold estimate expressed in concentration units of the reference gas was lower than 20 ppb. For the other panellist, this value was 24.6 ppb. According to the CEN, it should be between 20 and 80 ppb. For three of these eight panellists, the standard deviation of the 10 n-butanol tests was lower than 2.3 ppb, as required by the CEN. These results show that the selection criteria of the CEN are rather stringent, which is a confirmation of the findings of Clanton *et al.* (1999).

Clanton *et al.* (1999) performed olfactometric experiments with air from a pig farm, at three different strengths. The population mean was used as the reference value to compare the 16 panellists. Comparing the individual mean to the population mean, six of the 16 panellists were outside the range of 0.5 and two times the reference value (population mean) for the low-strength sample, and five and two panellists were outside the range for the medium- and high-strength samples respectively. According to the authors, these results may indicate that the European standard requirement for n-butanol tests for the geometric mean to be between 0.5 and two times the reference value may be too restrictive and could result in the elimination of too many potential panellists.

Sneath (2001) tested 142 people, using n-butanol. On basis of the criteria mentioned in the CEN, about 43% of the people had to be rejected because they were not sensitive enough, and 12% because they were too sensitive to n-butanol. Of those who had a qualifying sensitivity, about two-thirds had a threshold above the accepted reference value of 40 ppb. For the panel members tested here, only seven of the 45 people had a threshold value for n-butanol above 40 ppb, which is opposite to the results of Sneath (2001).

**Results of n-butanol and pig odour samples**

*Repeatability of panellist results for n-butanol and pig odour samples.* For the determination of the odour concentration of an air sample, according to the CEN, the sample is presented to the panel members in at least two rounds. The odour concentration of the sample is then calculated as the geometric mean of these two rounds. In order to see whether the variation between the two rounds is different for n-butanol than for the pig odour samples, for each sample the variance of the odour concentrations of the two rounds was calculated. By performing these calculations, something can be said about the repeatability of the panellist results concerning n-butanol and pig odour. For each panel member, the mean of all the variances of all the samples was determined ($VAR_{\text{mean}}$). With the statistical software package SPSS for each panellist, an independent samples $t$-test was carried out to deter-
mine whether the mean variance for \( n \)-butanol was significantly different from the mean variance for the pig odour samples. The results of these calculations for each panel member with more than two \( n \)-butanol samples, are given in Table 1.

From Table 1, it can be seen that for 14 of the 26 considered panel members, the mean variance for the \( n \)-butanol samples was higher than the mean variance for the pig odour samples; for 12 panel members this was lower. However, for only one person (panel number 22) was the difference between the mean variance for \( n \)-butanol and the mean variance for pig odour found to be significant (significance level of independent samples \( t \)-test < 0.05). The mean and standard deviation of the parameter \( \text{VAR}_{\text{mean, but}} \) are higher than the mean and standard deviation of the parameter \( \text{VAR}_{\text{mean, pig}} \). A paired sample \( t \)-test showed, however, that this difference was not significant (significance level of 0.347), which means that panellists showed the same variability in determination of odour concentrations for \( n \)-butanol and pig odour samples.

The fact that the standard deviation for \( \text{VAR}_{\text{mean, pig}} \) is lower than for \( \text{VAR}_{\text{mean, but}} \) is in line with the results mentioned by Van Harreveld and Heeres (1997) where a lower spread of the results was also found for a complex environmental odour than for \( n \)-butanol. Also, Laska and Hudson (1991) found a trend towards lower variability with increasing stimulus complexity when investigating threshold determinations for unmixed odorants and three-, six- and 12-component mixtures.

### Normalization of olfactometric results

Based on the property of traceability among panellists/panels, Qu et al. (2001) developed a normalization model to transfer a measurement of an unknown odour by a non-qualified

<table>
<thead>
<tr>
<th>Number of panellists</th>
<th>Number of ( n )-butanol samples</th>
<th>Number of pig odour samples</th>
<th>( \text{VAR}_{\text{mean, but}} )</th>
<th>( \text{VAR}_{\text{mean, pig}} )</th>
<th>Significance level</th>
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<td>0.324</td>
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<td>36</td>
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<td>0.024</td>
<td>0.626</td>
</tr>
<tr>
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<td>0.220</td>
<td>0.662</td>
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<tr>
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<td>3</td>
<td>15</td>
<td>0.222</td>
<td>0.200</td>
<td>0.904</td>
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<tr>
<td>44</td>
<td>10</td>
<td>43</td>
<td>0.309</td>
<td>0.092</td>
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</tbody>
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Mean: 0.142
Standard deviation: 0.119
panel to the one by a panel whose \( n \)-butanol threshold is 40 ppbv. The following equation was found between the \( n \)-butanol ratio and the environmental odour ratio:

\[
\ln (Y_{\text{env}}) = 0.6484 \times \ln(Y_{\text{nbut}}) \quad \text{with } R^2 = 0.58
\]

with \( Y_{\text{env}} = \frac{X_{\text{env}}^*}{\mu_{\text{env}}} \) (environmental odour ratio)

\( Y_{\text{nbut}} = \frac{X_{\text{nbut}}^*}{\mu_{\text{nbut}}} \) (\( n \)-butanol ratio)

From the above equation, the normalization model can be obtained:

\[
\bar{\mu}_{\text{env}} = x_p^* \left( \frac{X_{\text{nbut}}^*}{\mu_{\text{nbut}}} \right)^{-0.6484}
\]

Since only the ratio of odour concentrations was involved in data processing, Qu et al. (2001) stated that the normalization model should be valid for all odours, but that confirmation of this inference is, however, necessary.

In order to confirm the results of Qu et al. (2001) a similar normalization model was looked for with the dataset here of olfactometric analyses using 45 panel members. On one day, different pig odour samples were analysed, together with one \( n \)-butanol sample. The environmental odour ratio of one pig odour sample, together with the \( n \)-butanol ratio for that day, forms one case. In total, the dataset consisted of 505 cases.

To verify whether traceability could be assumed, the variance of the \( n \)-butanol ratio was compared with the variance of the pig odour ratio with an \( F \)-test for normal variances. For this test, the normality of both groups is required. As the parameters \( Y_{\text{env}} \) and \( Y_{\text{nbut}} \) were not normally distributed, the test was carried out on the parameters \( \ln(Y_{\text{env}}) \) and \( \ln(Y_{\text{nbut}}) \). The test statistic \( F_0 \) is calculated as the ratio of the variances of the two groups. The decision rule is given below:

- If \( F_0 < F_{\alpha/2, f_1, f_2} \) or \( F_0 > F_{1-\alpha/2, f_1, f_2} \) → reject \( H_0 \) (or \( \text{var} \, 1 \neq \text{var} \, 2 \))
- If \( F_{\alpha/2, f_1, f_2} < F_0 < F_{1-\alpha/2, f_1, f_2} \) → conclude \( H_0 \) (or \( \text{var} \, 1 = \text{var} \, 2 \))

The results of these tests (Table 2) showed that the variances of \( \ln(Y_{\text{env}}) \) and \( \ln(Y_{\text{nbut}}) \) were significantly different and, as a consequence, the principle of traceability was not confirmed here. These results are in contradiction with the results of Van Harreveld and Heeres (1995) who found that the standard deviation for the parameter \( \Delta Z \), which was the ratio between each individual threshold estimate and the group threshold, was not significantly different for environmental odorants and for \( n \)-butanol.

Although traceability was not confirmed, a normalization model was looked for. Regression between the parameters \( \ln(Y_{\text{env}}) \) and \( \ln(Y_{\text{nbut}}) \) gave the following result:

\[
\ln(Y_{\text{env}}) = 0.0038 + 0.249 \ln(Y_{\text{nbut}}) \quad \text{with } R^2 = 0.119
\]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Variance</th>
<th>( F_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \ln(Y_{\text{env}}) )</td>
<td>0.2904</td>
<td>0.5206</td>
</tr>
<tr>
<td>( \ln(Y_{\text{nbut}}) )</td>
<td>0.5579</td>
<td></td>
</tr>
<tr>
<td>( F_{0.975,504,504} )</td>
<td>1.1910</td>
<td></td>
</tr>
<tr>
<td>( F_{0.025,504,504} )</td>
<td>0.8396</td>
<td></td>
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</tbody>
</table>
In the scatter plot of the data, outliers were observed. Therefore, standardized residuals of the above regression were calculated with SPSS, and those with a value higher than two were omitted from the dataset. In this way, 11 cases were excluded from the dataset. Since the constant in the above regression was not significantly different from zero, the regression was also forced through zero. The regression results after these adaptations, together with a scatter plot of the data, are given in Figure 1.

The results for the normalization model mentioned in Figure 1, do not really confirm the normalization model of Qu et al. (2001). The regression coefficient is only half of the one found by Qu et al. (2001), and the determination coefficient \( R^2 \) is also very poor, which shows again that the principle of traceability was not valid here.

**Results of mixture**

*Repeatability of panellist results for n-butanol, pig odour samples and mixture.* From 27/02/2003 olfactometric analyses were also done using a synthetic mixture of ethanethiol, methylacetate and 2-propanol in nitrogen. The measurements with pig odour samples and \( n \)-butanol continued during this period. Also in order to make a proper comparison, for \( n \)-butanol and the pig odour, only the results from 27/02/03 onwards were used here. In total, the results of 14 panel members were available. For each panellist, the mean variance (\( \text{VAR}_{\text{mean}} \)) for all the samples of that restricted period was calculated for the three types of odour. The results are given in Table 3.

From Table 3, the following conclusions can be drawn:
- for nine panel members, the mean variance of the synthetic mixture is higher than the mean variance of \( n \)-butanol
- for another nine panel members, the mean variance of the synthetic mixture is higher than the mean variance of the pig odour samples
- for only three panel members, both the synthetic mixtures as well as the pig odour samples (both mixtures of odour components) had a lower mean variance than the \( n \)-butanol samples.

In order to check whether the population means of the parameters \( \text{VAR}_{\text{mean, mix}} \), \( \text{VAR}_{\text{mean, but}} \) and \( \text{VAR}_{\text{mean, pig}} \) were significantly different, a one-way ANOVA was carried out with SPSS. The significance level was 0.094 (>0.05), which means that the mean vari-
ance for the three odour types is not significantly different and that the repeatability of pan-
ellist results is the same for the three odour types.

From Table 3 it also follows that the standard deviation of the mean variance has the
lowest value for the pig odour and the highest value for the synthetic mixture. Also here, the
higher standard deviation for $\text{VAR}_{\text{mean,pig}}$ but than for $\text{VAR}_{\text{mean,but}}$ agrees with the results of
Van Harreveld and Heeres (1997) and Laska and Hudson (1991). Based on the results of
these authors, a lower standard deviation for the mean variance of the synthetic mixture
was, however, expected here.

Mannebeck and Mannebeck (2001) compared mean values and standard deviations of
olfactometric analyses of three individual substances ($n$-butanol, hydrogen sulphide and
tetrahydrothiophen) as well as a natural odour mixture (coffee flavour). They also did not
find a lower spread of results for the odour mixture (coffee flavour) than for $n$-butanol. Of
the four odours that were tested, the lowest standard deviation was found for $n$-butanol. In
the current study, the lowest standard deviation was found for the mean variance on the pig
odour samples.

### Normalization of olfactometric results

In this paragraph, normalization for olfactometric measurements of pig odour samples based either on $n$-butanol or on the synthetic mixture will be looked for. On one day, different pig odour samples were analysed, together with one $n$-butanol sample and one synthetic mixture sample. The environmental odour ratio of one pig odour sample, together with the $n$-butanol ratio and the synthetic mixture ratio ($Y_{\text{mix}}$) for that day forms one case. In total, for the restricted period, 126 of such cases were available.

To verify the principle of traceability, $F$-tests for normal variances were again carried out. An overview of the results is given in Table 4.

From the results in Table 4, it can be concluded that the variances of $\ln(Y_{\text{env}})$ and $\ln(Y_{\text{mix}})$ were significantly different, with the other variances being equal. It has to be mentioned, however, that for the comparison of the variances of $\ln(Y_{\text{env}})$ and $\ln(Y_{\text{but}})$ and the variances of $\ln(Y_{\text{env}})$ and $\ln(Y_{\text{mix}})$, the test statistic is a border case to reject or conclude the hypothesis of equality of variances. These results show that the principle of traceability is more valid for $n$-butanol than for the synthetic mixture, but, however, differences are very small.

The results of the regression between the parameters $\ln(Y_{\text{env}})$ and $\ln(Y_{\text{but}})$ on the one

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**Table 3** Mean variance for mixture, $n$-butanol and pig odour samples for the restricted period

<table>
<thead>
<tr>
<th>Number of panellists</th>
<th>Number of mixture samples</th>
<th>Number of $n$-butanol samples</th>
<th>Number of pig odour samples</th>
<th>$\text{VAR}_{\text{mean,mix}}$</th>
<th>$\text{VAR}_{\text{mean,but}}$</th>
<th>$\text{VAR}_{\text{mean,pig}}$</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1</td>
<td>3</td>
<td>0.028</td>
<td>0.000</td>
<td>0.091</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0.044</td>
<td>0.000</td>
<td>0.035</td>
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hand, and ln(Y_{env}) and ln(Y_{mix}) on the other hand, are given below:

\[
\begin{align*}
\ln(Y_{\text{env}}) &= 0.0036 + 0.224 \ln(Y_{\text{nbut}}) \quad \text{with } R^2 = 0.071 \\
\ln(Y_{\text{env}}) &= -0.0085 + 0.309 \ln(Y_{\text{mix}}) \quad \text{with } R^2 = 0.137
\end{align*}
\]

As described above, for both regressions the standardized residuals with a value higher than two were removed from the dataset. For this reason, for the first regression, two cases were omitted, and, for the second regression four cases were omitted. The regressions were also forced through zero. These adaptations lead to the following results for the regressions:

\[
\begin{align*}
\ln(Y_{\text{env}}) &= 0.223 \ln(Y_{\text{nbut}}) \quad \text{with } R^2 = 0.077 \\
\ln(Y_{\text{env}}) &= 0.310 \ln(Y_{\text{mix}}) \quad \text{with } R^2 = 0.165
\end{align*}
\]

The two models mentioned above have a very poor determination coefficient. The model on the basis of the synthetic mixture (\(R^2 = 0.165\)), however, gives better results than that on basis of \(n\)-butanol (\(R^2 = 0.077\)), which was not expected from the \(F\)-tests, as there a better traceability was found for \(n\)-butanol than for the mixture.

### Conclusions

The results of the \(n\)-butanol tests for the different panellists showed that nobody was qualified according to the CEN criteria. Most of the panellists were too sensitive, 38 of the 45 panellists had a threshold value for \(n\)-butanol below 40 ppb. These results indicate that the CEN criteria for qualification of panellists are stringent and may lead to the exclusion of too many potential panellists.

A second objective was to see whether the variation between the two odour concentrations determined in the two rounds of one olfactometric analysis, was different for the three odour types (pig odour, \(n\)-butanol and a synthetic gas mixture of ethanethiol, methylacetate and 2-propanol). A higher mean and relative standard deviation of the mean variance were found for \(n\)-butanol than for the pig odour, which is in line with results from the literature. For the three odours, the highest mean and relative standard deviation was found for the synthetic mixture, and this result was not expected. Statistical tests showed, however, that the mean variance for the three odour types was not significantly different, which shows that the repeatability of the panellist results was equal for the three odour types.

Comparing the variance of the \(n\)-butanol, pig odour and synthetic mixture ratio confirmed the principle of traceability. For the complete dataset, the principle of traceability could not been proven for \(n\)-butanol. For the restricted dataset (which means that only qualified panellists were used), the principle was more valid for \(n\)-butanol than for the mixture but differences were, however, very small.
Finally, a normalization model for olfactometric measurements of air samples from pig farms based either on \( n \)-butanol or on the synthetic mixture were looked for. Both types of model had low determination coefficients, but the model, on the basis of the synthetic mixture, gave better results than the one on the basis of \( n \)-butanol.

The results from this work show that although many experts agree upon the fact that a reference odour mixture should be better for panel selection, it cannot be unambiguously proved here that a mixture give better results concerning variability and repeatability. Further research on this topic is, however, recommended.

References


