

ASSESSMENT OF THE UNCERTAINTY OF MEASUREMENT RESULTS OF HEXACHLOROBUTADIENE IN INDOOR AIR

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ABSTRACT

Within the frame of the development of a method for the measurement of concentration levels from 0.003 to 10 parts per billion by volume of hexachlorobutadiene in indoor air an assessment has been performed of the uncertainty of the measurement results. This assessment - fully based on the principles of the ISO Guide to the Expression of Uncertainty in Measurement (ISO-GUM) - has shown that – even for the measurement of such extremely low concentrations – uncertainty levels of < 25% (95% confidence) are achievable.

INDEX TERMS

Air monitoring, measurement uncertainty, hexachlorobutadiene, thermal desorption, GC-MS.

INTRODUCTION

ICI Regional and Industrial Businesses has recently conducted a large survey of the indoor air quality of houses near historical chemical waste deposit sites. The primary aim of the survey was to assess the health risk due to exposure of inhabitants to hexachlorobutadiene (HCBd). Based on toxicological considerations a limit value for concentrations of HCBd of 0.6 parts-per-billion by volume (ppbv) was set by the UK Department of Health Committee on Toxicity (COT). For measurement of HCBd around this limit value a method was developed for quantitation at concentration levels from 0.003 to 10 parts per billion by volume. The method was based on 24-hour sampling on to a sample tube containing Tenax TA and analysis by thermal desorption and gas chromatography with mass-spectrometric detection (TD/GC-MS/SIM).

For valid comparisons with the limit value the uncertainty of the measurement results has been assessed according to the principles of the ISO Guide to the Expression of Uncertainty in Measurement, the 'GUM' (ISO, 1995). As the described approach is generic it may also be applied to indoor air measurement problems based on separate sampling and analysis other than the present case.

METHODS

Uncertainty assessment according to GUM

Briefly, the approach to the assessment of measurement uncertainty according to GUM consists of the following steps [ISO, 1995]:

- identification of all factors contributing to the measurement uncertainty using equations describing the measurement process
- quantification of contributions of these factors either by experiment (the so-called 'type A' approach) or from existing knowledge (the so-called 'type B' approach)

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- combination of the contributions according to specified rules
- expansion of the combined uncertainty to reflect a certain level of confidence (usually 95 %).

Equations describing the measurement problem

A general equation for the measurement of a compound in indoor air by pumped sampling expressed in dimensionless units (e.g., parts per billion by volume, ppbv) is given by

$$C = \frac{m_{sam} - m_{bl}}{V_{sam}} \cdot \frac{V_m}{M} \quad (1)$$

in which

C = concentration of HCBd in units of ppbv

m_{sam} = mass of HCBd in sample (usually in nanogrammes)

m_{bl} = mass of HCBd in sample blank (usually in nanogrammes)

V_{sam} = volume of air sample at actual mean pressure and temperature conditions (usually in litres)

V_m = molar volume of air at actual mean pressure and temperature conditions (in litres per mol)

M = molar mass of HCBd (in grams per mol).

Assessment of the uncertainty of measurement results of HCBd in indoor air therefore requires the assessment of the uncertainties of m_{sam} , m_{bl} , V_{sam} , V_m and M .

Note: if the concentration is expressed in units of mass-per-volume, the molar volume of air and the molar mass of the compound can be excluded from further considerations.

Sampled volume of air

An equation used for the determination of V_{sam} based on the general practice of measuring the sample flow rate before and after sampling [ISO, 2001] reads

$$V_{sam} = \frac{(\phi_{start} + \phi_{end})}{2} \cdot t \quad (2)$$

in which

ϕ_{start} = sample flow rate at the beginning of the sampling period (usually in millilitres per minute)

ϕ_{end} = sample flow rate at the end of the sampling period

t = sampling time (in minutes).

Hence, the uncertainty in the volume of air sampled is built up of contributions from

- the measurements of the flow rates before and after sampling
- the measurement of the sampling time.

In addition possible variations of the flow rate during sampling may contribute to the uncertainty.

Sample flow measurement

The uncertainty in the measurement of flow rates before and after sampling is calculated from

- the uncertainty in the readings of the flow meter used which can be derived from calibration certificates, assuming the calibration is fully traceable to primary standards of flow
- the uncertainty of the mean of the flow rate measurement results.

Sampling time

The sampling time t was measured to within ± 0.5 min. For a sampling time of 24 hours the relative uncertainty due to the measurement of t is ± 0.02 %.

Variations in flow rate during sampling

The uncertainty in the flow rate during sampling was estimated from a large series of flow measurements before and after sampling.

Molar volume of air

For the conversion of concentrations from mass-per-volume to volume-per-volume units V_m may be described as a function of air pressure and temperature as

$$V_m = V_{m,0} \cdot \frac{P_0}{P} \cdot \frac{T}{T_0} \quad (3)$$

in which

P = actual air pressure

T = actual air temperature

and subscripts 0 refer to conditions of standard temperature and pressure.

The uncertainty in V_m is assessed from the contributions of the uncertainties of the values of the actual temperature and pressure during sampling.

Molecular mass of HCBD

When using data on molecular masses of atoms with sufficient significant figures (usually 5) the relative uncertainty in the calculated molecular mass of HCBD is ± 0.01 %.

Mass of HCBD in sample

The mass of HCBD in the air samples may be expressed as

$$m_{sam} = \frac{m_{anal}}{se \cdot stab \cdot rec} \quad (4)$$

in which

se = sampling efficiency

$stab$ = sample stability

rec = recovery of HCBD on desorption

m_{anal} = uncorrected analytical mass of HCBD in the analytical sample.

Sampling efficiency

The sample volume (28.8 L nominally; ICI, 2001) was kept well below the experimentally established breakthrough volume (>140 L; ICI, 2001); hence, the sampling efficiency was 100% and did not contribute to the uncertainty in m_{sam} .

Stability

The sample stability has been experimentally established for storage at room temperature over a 4-week period. As a test of (in)stability both t-test as well as regression analysis were used. The uncertainty due to stability was expressed as the pooled standard uncertainty of stability measurements performed under repeatability conditions.

Recovery

The recovery of HCBD and its uncertainty were obtained from replicate measurements on certified reference materials (CRM) supplied by NMI. The uncertainty in the mean recovery for each level was calculated from contributions of

- the uncertainty in the concentration of the CRM
- the standard deviation of the mean recovery.

In addition significant systematic deviations of the recovery from 1 were included in the uncertainty assessment since no correction was applied [ICI, 2001].

Uncorrected analytical mass of compound

The uncertainty in the uncorrected analytical mass of a compound is determined by

- the uncertainty in the concentrations of the calibration standards used
- the lack-of-fit of the calibration function
- drift of the detector response between calibrations.

In addition, the uncertainty may be influenced by a lack of selectivity of the method. In practice this contribution was negligible due to the use of highly selective detection (MS-SIM).

Concentrations of calibration standards

Calibration standards were produced by spiking blank sample tubes with known volumes of solutions of HCBD of known concentration and subsequent purging of the excess solvent.

The uncertainty is built up of contributions from

- uncertainties in purities of the base compounds
- uncertainties in the procedure for the preparation of the standard solutions
- uncertainties in spike volumes used.

Lack-of-fit of calibration function

The uncertainty due to lack-of-fit of the calibration function was calculated for the relevant concentration range from residuals of a series of calibration functions obtained by least-squares linear regression.

Drift in detector response

The uncertainty due to response drift was estimated from data on the relative differences in responses between subsequent calibrations.

Mass of compound in sample blank

The sample blank level of a compound was determined by replicate analysis of sample blanks and was found to be below the level of detection of the method (0.04 ng; ICI, 2001).

Combination and expansion of uncertainties

Uncertainties were expressed as standard uncertainties and combined according to the rules of GUM. For calculation of the expanded uncertainty a coverage factor of 2 – reflecting a 95 % confidence level – was used. In summary, the equation used to derive the expanded uncertainty reads as follows:

$$U_c = 2 \cdot u_c = \sqrt{\sum_i u_i^2} \quad (5)$$

in which

U_c = expanded uncertainty

u_c is combined standard uncertainty

u_i = individual standard uncertainty contribution.

Independent verification of the uncertainty assessment

In the course of the method validation 20 replicate samples were taken in an indoor environment [ICI, 2001]. The standard deviation in the mean of the results obtained was considered to be a measure of the combined uncertainty caused by all random sources in sampling and analysis.

RESULTS AND DISCUSSION

Uncertainty contributions

The uncertainty contributions calculated are given in Table 1 for a level of HCBD corresponding to its limit value: 187 ng per sample for a nominal sample volume of 28.8 L at standard temperature and pressure (20 °C and 101.3 kPa).

Table 1. Uncertainty contributions

<i>Source of Uncertainty</i>	<i>Relative uncertainty (%)</i>
Sample volume	
• Calibration of flow meter - bias	1.5
• Calibration of flow meter - precision	0.5
• Sample flow before	0.7
• Sample flow after	0.7
• Difference between sample flow before and after	4
• Sample time	0.02
Conversion of concentration to ppbv	
Air temperature	1.1
Air pressure	3
Sampling efficiency	0
Sample stability	
Measurements of sample stability	2.0
Systematic deviation from 1	0
Recovery	
Certified value of CRM	4
Measurements of CRM	0.9
Systematic deviation of recovery from 1	8
Analytical measurement of mass of HCBD	
Analytical calibration standards (random part)	4
Lack-of-fit of calibration function	1.0
Response drift	3
Blank level	0.006

The above data show that the major source of uncertainty was the recovery of HCBD from the certified reference material. In principle significant biases for thermal desorption are atypical since desorption conditions can be optimized to give complete desorption. Alternative – more plausible - sources may be hitherto undetected systematic errors in the preparation of the calibration standards.

Combined and expanded uncertainty

By combination of the above relative standard uncertainties according to equation (5) a combined relative uncertainty for the measurement of HCBD at the level of 0.6 ppbv of $\pm 12\%$ was obtained. The expanded relative uncertainty (at the 95 % confidence levels) was $\pm 23\%$.

Independent verification

The relative standard deviation of the mean of the results of the 20 replicate ‘field’ measurements (0.22 ppbv) was found to be $\pm 5.1\%$. The uncertainty calculated from the random parts of the sources described above was $\pm 5.2\%$ showing the correctness of the GUM-based assessment.

CONCLUSIONS

Based on the ‘GUM-approach’ the expanded relative uncertainty of measurement results of HCBD in indoor air at the limit value of 0.6 ppbv using pumped sampling on Tenax TA and analysis by thermal desorption/GS-MS with selected ion monitoring has been evaluated to be $\pm 23\%$. The major source of uncertainty is believed to be the preparation of calibration standards by liquid spiking of clean Tenax TA sample tubes leading to systematic error in the concentration of HCBD. All other sources of uncertainty have been minimized by careful application of various elements of quality assurance/quality control, such as method validation, the use of a selective and sensitive analytical technique, traceable calibration, use of control standards and samples and the use of certified reference materials [Crump, 2002].

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