

# Uncertainty Evaluation of Toluene Determination in Room Air by Thermal Desorption–Gas Chromatography

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**Abstract.** The method of uncertainty evaluation of determination of toluene in room air has been established. Gas chromatography with thermal desorption was used for determining of toluene. The main factors which can affect on the analytical results were identified. The measurement repeatability, standard solution preparation process, calibration curve fitting, sampling process and the instrument are the main sources of toluene uncertainty. The Uncertainty of calibration curve fitting has been identified as the greatest effect on the analytical results.

## Introduction

Toluene is a common organic solvent with high toxicity. Determination of the toluene in the air by thermal desorption–gas chromatography has been proved as sensitive and reliable [1]. Many factors, such as sampling process, preparation of standard solution, calibration curve fitting, instrument measurement, repeatability of analysis results, will affect the confidence and accuracy of the analytical results. Uncertainty evaluation should be used for controlling of the determination [2, 3].

## Measurement process

Sampling tube with Filled Poly-2,6 diphenyl phenyl ether (Tenax), was used for concentration of toluene in ambient air and indoor air under the normal temperature. Sampling tube will be heated after connected into the thermal desorption instrument, and desorption toluene can be determined by gas chromatography with flame ionization detector (FID).

## Mathematical model

The concentration of toluene can be identified as:

The sampling volume,  $V_t$ , converted into standard condition sampling volume  $V_0$

$$V_0 = V_t \times \frac{T_0}{273+t} \times \frac{P}{P_0} \quad (1)$$

The concentration of toluene in air can be calculated:

$$C_i = \frac{m - m_0}{V_0} \quad (2)$$

Then

$$C_i = \frac{m - m_0}{V_i \times \frac{T_0 \times P}{(273 + t) \times P_0}} \quad (3)$$

Which:

$C_i$ : concentration of toluene in air, mg/ m<sup>3</sup>

$m$ : the mass of toluene in sampling tube, mg

$m_0$ : the mass of toluene in blank sampling tube, mg

$P_0$ : atmospheric pressure under standard conditions, 101.3kPa.

$P$ : sampling point pressure, kPa

$T$ : sampling point temperature, °C

$T_0$ : the absolute temperature under standard conditions, 273K

$V_i$ : volume of sampling, m<sup>3</sup>

### Sources of uncertainty

The main sources of measurement uncertainties were from sub-uncertainties of sample preparation, calibration solution preparation, calibration curve fitting and instrument measurements, etc.

### Uncertainty of repeatability of analysis results

Table 1 Uncertainty of repeatability of analysis results

toluene	Result (mg/m <sup>3</sup> )										mean value (mg/m <sup>3</sup> )	standard deviation
	1	2	3	4	5	6	7	8	9	10		
	0.046	0.048	0.048	0.049	0.047	0.048	0.049	0.046	0.048	0.047	0.048	0.0011

From Table 1, the uncertainty of repeatability of analysis results can be calculated:

$$U_{\text{repeatability}} = \frac{s}{\sqrt{n}} = \frac{0.0011}{\sqrt{10}} = 3.48 \times 10^{-4} \text{ mg / m}^3 \quad (4)$$

Relative standard uncertainty:

$$U_{\text{rel(repeatability)}} = \frac{u_{\text{repeatability}}}{\bar{c}} = \frac{3.48 \times 10^{-4}}{0.048} = 0.0072 \quad (5)$$

### Uncertainty of calibration curve fitting

The concentration of toluene was calculated by using calibration curve with the area of the peak of toluene. Chromatographic pure toluene was diluted to give the standard solutions which concentrations of 5、10、20、50、100μg/ mL, respectively. The standard solution were detected by gas chromatography, regression equation of toluene,  $A = 16.538c + 348.91$ , was fitted with the peak area and concentration, slope is 16.538, intercept is 348.91, correlation coefficient  $r = 0.9955$ .

The standard deviation of calibration curve can be calculated:

$$u(y) = S_{y/x} = \sqrt{\frac{\sum_{i=1}^n \sum_{j=1}^m (y_{ij} - y_i)^2}{m \bullet n - 2}} \quad (6)$$

Which:

$y_{ij}$ : response of instrument measurement on sample

$y_i$ : response which calculated by calibration curve

$n$ : number of different concentration of standard solution for detection

$m$ : the number of repeated measurements of each sample

$$u(y) = 50.48 \text{ A}$$

Uncertainty of calibration curve:

$$u_{(curve)} = \frac{S_{(y/x)}}{b} \sqrt{\frac{1}{n} + \frac{1}{N} + \frac{(\bar{x}_{sample} - \bar{x})^2}{\sum (x_i - \bar{x})^2}} \quad (7)$$

$$u_{(curve)} = \frac{50.48}{16.54} \sqrt{\frac{1}{2} + \frac{1}{5} + \frac{(50.15 - 37)^2}{152}} = 4.14 \mu\text{g} \cdot \text{mL}^{-1}$$

Which:

$n$ : the number of repeated measurements of each sample

$b$ : slope of calibration curve

$N$ : number of different concentration of standard solution for detection, involve the repeat times of analysis

$\bar{x}_i$ : mean value of concentrations calculated by calibration curve

$\bar{x}_{sample}$ : mean value of concentrations of standard solution.

Relative standard uncertainty:

$$u_{rel(curve)} = \frac{4.14}{50.15} = 0.083$$

### Uncertainty of preparation of standard solution

The concentration of certified reference material, toluene, is 1.00mg / mL, and the relative standard uncertainty is 3%. The uncertainty of purity of certified reference material should be:

$$U_{rel(purity)} = \frac{\sqrt{0.015^2}}{1.00} = 0.015$$

10μL syringe: The given allowed deviation of capacity is 3.8%, calculated with the uniform distribution, the relative uncertainty should be:

$$U_{rel(syringe)} = \frac{0.038}{\sqrt{3}} = 0.022$$

1.0 mL measuring pipet: According to instrument calibration certificate, the given allowed deviation of capacity is 0.015 mL, calculated with the uniform distribution, the relative uncertainty should be:

$$U_{rel(pipet)} = \frac{0.015}{\sqrt{3}} = 0.0090$$

10 mL volumetric flask: According to instrument calibration certificate, the given allowed deviation of capacity is 0.10 mL, calculated with the uniform distribution, the relative uncertainty should be:

$$U_{rel(flask)} = \frac{0.1}{10\sqrt{3}} = 0.00577$$

Uncertainty of preparation of standard solution:

$$U_{rel(solution)} = \sqrt{0.015^2 + 0.022^2 + 0.0090^2 + 0.0058^2} = 0.029$$

### Uncertainty of sampling

**Sampling process.** Pumping air 0.1L/ min for 10min, the temperature is 25°C, atmospheric pressure P = 101.2kPa. The standard condition sampling volume should be:

$$V_0 = V_t \times \frac{T_0}{273+t} \times \frac{P}{P_0} = 1 \times \frac{273 \times 101.2}{299 \times 101.3} = 0.915L$$

**Uncertainty of flowmeter.** According to instrument calibration certificate, the given error of indication of flowmeter is 5%, error of flow repeatability is 2%, error of flow stability is 5%. Assumed uniform distribution:

$$u_{(Rv)/R} = \sqrt{\left(\frac{0.05}{\sqrt{3}}\right)^2 + \left(\frac{0.02}{\sqrt{3}}\right)^2 + \left(\frac{0.05}{\sqrt{3}}\right)^2} = 0.042$$

**Uncertainty of thermometer.** According to instrument calibration certificate, the given uncertainty of thermometer is 0.3°C(coverage factor k=2), calculated with the uniform distribution, the relative uncertainty should be:

$$u(t) = \frac{0.3}{2} = 0.15 \text{ } ^\circ\text{C}, \quad \frac{u(t)}{T} = \frac{0.15}{25} = 0.0060$$

**Uncertainty of air pressure gauge.** According to instrument calibration certificate, the given error of indication of flowmeter is ±0.6 hPa, calculated with the uniform distribution, the relative uncertainty should be:

$$u(p) = \frac{0.6}{\sqrt{3}} = 0.346 \text{ hpa}, \quad \frac{u(p)}{P} = \frac{0.346}{1012} = 3.41 \times 10^{-4}$$

Uncertainty of sampling:

$$U_{rel(sampling)} = \left( [u(R_v) / R]^2 + [u(t) / T]^2 + [u(p) / P]^2 \right)^{1/2} \\ = (0.042^2 + 0.0060^2 + 0.000341^2)^{1/2} = 0.042$$

### Uncertainty of instruments

**Uncertainty of gas chromatography.** According to instrument calibration certificate, the given error of stability of oven temperature is 0.1%, error of repeatability is 0.9%, uncertainty of FID is 3.8% (coverage factor k=2), the relative uncertainty of FID should be  $\frac{0.038}{2} = 0.019$ . The uncertainty of GC should be:

$$U_{rel(GC)} = \left( \left( \frac{0.001}{\sqrt{3}} \right)^2 + \left( \frac{0.009}{\sqrt{3}} \right)^2 + 0.019^2 \right)^{1/2} = 0.020$$

**Uncertainty of thermo desorption.** According to instrument calibration certificate, the given uncertainty of thermo desorption is 2%, the relative uncertainty should be:

$$U_{rel(TD)} = \frac{0.02}{\sqrt{3}} = 0.012$$

Uncertainty of instruments:

$$U_{rel(instrument)} = (0.020^2 + 0.012^2)^{1/2} = 0.023$$

### The combined relative standard uncertainty

Relative standard uncertainty can be combined:

$$\begin{aligned} U_{rel}(C) &= \sqrt{u_{rel(repeatability)}^2 + u_{rel(curve)}^2 + u_{rel(solution)}^2 + u_{rel(sampling)}^2 + u_{rel(instrument)}^2} \\ &= \sqrt{0.0072^2 + 0.083^2 + 0.042^2 + 0.029^2 + 0.023^2} = 0.10 \end{aligned}$$

### The expanded uncertainty

Because of the measurement error is obeyed to normal distribution, confidence level  $p=95\%$ , coverage factor  $k=2$ , expanded uncertainty should be:

$$U_{rel} = k \times u_{rel}(C) = 2 \times 0.10 = 0.20$$

The concentration of toluene in air is  $0.052 \text{ mg/m}^3$ , the expanded uncertainty should be:

$$U = 0.052 \times 0.20 = 0.0104 \text{ mg/m}^3$$

### Expression of result

The determination of concentration of toluene in air by using GC, the result can be representing:

$$C_{toluene} = 0.052 \pm 0.0104 \text{ mg/m}^3, \text{ confidence probability is } 95\%$$

### Conclusion

The uncertainty of determination of toluene in room air mainly originates from the change of the calibration curve fitting. A reasonable and accurate calibration curve can be used to control the degree of uncertainty. The uncertainty evaluation of determination of toluene may be helpful for improving the confidence and accuracy of the test results, and reduce the uncertainty of the test results.

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