



Uncertainty Analysis of Flow Measurement of the VOCs Sampler

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Abstract

In this paper, the flow measurement uncertainty of the VOCs sampler is analyzed in detail which is widely applied in environmental monitoring, medical and health care, factories, and mining enterprises. Based on the detection of the soap film flow-meter standard device and the mass flow-meter standard device, the mathematical and physical uncertainty model of the VOCs sampler is derived and obtained. The flow measurement uncertainty is evaluated and analyzed respectively based on the mathematical and physical uncertainty models of two standard devices. The relative expansion uncertainty of the soap film flow-meter standard device and the mass flow-meter standard device for detecting VOCs sampler is calculated to be 0.9% and 1.4% respectively. There is a difference in the relative expanded uncertainty of the two standard devices for detecting VOCs samplers, which is mainly due to the difference in the standard uncertainty introduced in the standard device and the repeatability test. In particular, the above process and result analysis are effective for the VOCs sampler with the high-precision electronic flow-meter as the standard conditions.

1 Introduction

The volatile organic compounds (VOCs) sampler is widely applied in ecological environment monitoring, healthcare, factories and mining enterprises, colleges, scientific research, labor protection, and other institutions. It uses solid adsorbents to enrich VOCs such as polycyclic aromatic hydrocarbons, polychlorinated biphenyls, aniline, dioxins, and so on in the air. The sampling flow range of the sampler is (10~200) ml/min, which is composed of a flow measurement and control system, air pump, sampling pipeline, adsorption device, ambient atmospheric pressure measurement system, ambient temperature, and humidity measurement system. According to the HJ 644-2013 “Ambient air - Determination of volatile organic compounds - Sorbent adsorption and thermal desorption/gas chromatography mass spectrometry method” and the HJ 734-2014 “Stationary source emission - Determination of volatile organic compounds-Sorbent adsorption and thermal

desorption gas chromatography mass spectrometry method”, the commonly used operating flow points are 20 ml/min, 40 ml/min, 50 ml/min, 100 ml/min and 200 ml/min.

With the increasingly strict country monitoring of ambient air and the requirements of relevant industries for the detection of VOCs in ambient air becoming more accurate and efficient, it is crucial to analyze the measurement uncertainty of the VOCs sampler. At present, the scholar Jiang Yijia^[1] has studied the composition and application of the sampler used to determine volatile organic compounds in indoor air. Sun Siyu^[2-5] has studied the research progress of VOCs collection technology in the air of workplaces, but there is a lack of analysis and research on the uncertainty of the VOCs sampler flow measurement. Take Wang Wei^[6-11] and others' research on the uncertainty evaluation of atmospheric sampling flow measurement and JJF (Yu) 058-2021 “Volatile organic compounds(VOCs) sampler calibration specification” as a



reference, the gas flow standard device based on the principle of soap film flow-meter and mass flow-meter is used as the main standard to detect the VOCs sampler in the market commonly used, to analyze the flow measurement uncertainty of the VOCs sampler.

2 Mathematical physical model

At present, there are two kinds of commonly used flow standard devices for VOCs sampler. One is the gas flow standard device based on the principle of soap film flow-meter, and the other is based on the mass flow-meter. The mathematical and physical models and the uncertainty sources of the VOCs sampler flow measurement are different with different standard devices.

2.1 The soap film flow-meter standard device detects VOCs sampler

The flow relative indication error of the VOCs sampler is analyzed by the propagation rate of measurement uncertainty. The relative indication error model of a single measurement is shown as formula (1).

$$\Delta Q_{rel} = \frac{Q_N}{\frac{V}{t} \times 60 \times \frac{T_S}{P_S} \times \frac{P}{T}} - 1 \quad (1)$$

which, ΔQ_{rel} is the flow relative indication error of single measurement of VOCs sampler; Q_N is the flow indication of VOCs sampler under standard conditions, mL/min; V is the volume of soap film pipe section, mL; P is the ambient atmospheric pressure, pa; t is the timing time of the stopwatch, s; T is the detected ambient temperature, K; T_S is the temperature under standard state, 293.15K; P_S is the atmospheric pressure under standard state, 101.325kPa.

Independent of input variables Q_N 、 V 、 t 、 T 、 P , so the correlation coefficient $r(x_i, x_j) = 0$. The relative synthetic standard uncertainty of ΔQ_{rel} is calculated by the formula (2).

$$u_r(\Delta Q_{rel}) = u_c(\Delta Q_{rel}) / |\Delta Q_{rel}| = \sqrt{\sum_{i=1}^N \left(\frac{\partial f}{\partial x_i} \right)^2} u_r^2(x_i) \\ = \sqrt{[u_r(Q_N)/Q_N]^2 + [-1u_r(V)/V]^2 + [u_r(t)/t]^2 + [u_r(T)/T]^2 + [-1u_r(P)/P]^2} \\ = \sqrt{[u_r(Q_N)]^2 + [-u_r(V)]^2 + [u_r(t)]^2 + [u_r(T)]^2 + [-u_r(P)]^2} \quad (2)$$

which, $u_r(P)$ is the relative standard uncertainty introduced by pressure gauge; $u_r(T)$ is the relative standard uncertainty introduced by thermometer; $u_r(t)$ is the relative standard uncertainty introduced by the stopwatch; $u_r(V)$ is the relative standard uncertainty

introduced by volume inaccuracy of soap film pipe section; $u_r(Q_N)$ is the relative standard uncertainty introduced by VOCs sampler and pipeline connection section.

2.2 The mass flow-meter standard device detects VOCs sampler

The flow relative error of the VOCs sampler is analyzed according to the measurement uncertainty propagation rate and the relative indication error model of a single measurement is shown as formula (3).

$$\Delta Q_{rel} = \frac{Q_N}{Q_R \times \frac{T_S}{P_S} \times \frac{P}{T}} - 1 \quad (3)$$

which, Q_R is the mass flow-meter standard device operating condition flow without temperature and pressure correction, mL/min.

Independent of input variables Q_N 、 Q_R 、 T 、 P , and $r(x_i, x_j) = 0$. Therefore, the relative synthetic standard uncertainty of ΔQ_{rel} is calculated by (4).

$$u_r(\Delta Q_{rel}) = \sqrt{[u_r(Q_N)]^2 + [-u_r(Q_R)]^2 + [u_r(T)]^2 + [-u_r(P)]^2} \quad (4)$$

which, $u_r(Q_R)$ is the relative standard uncertainty introduced by the flow rate of the standard device under working conditions.

The relative indication error must be measured three times according to the provisions of the calibration specification for the VOCs sampler.

$$\overline{\Delta Q_{rel}} = \Delta Q_{rel} + \delta \Delta Q_{rel} \quad (5)$$

which, $\overline{\Delta Q_{rel}}$ is the average value of relative indication error for multiple flow measurements of the VOCs sampler; $\delta \Delta Q_{rel}$ is the correction value of relative indication error obtained from each repeated measurement.

The relative synthetic standard uncertainty of $\overline{\Delta Q_{rel}}$ is calculated by the formula (6).

$$u_r(\overline{\Delta Q_{rel}}) = \sqrt{[u_r(\Delta Q_{rel})]^2 + [u_r(\delta \Delta Q_{rel})]^2} \quad (6)$$

which, the relative standard uncertainty $u_r(\delta \Delta Q_{rel})$ is adopt type A evaluation of uncertainty with formula (7) (8) (9) considering the influence of repeatability measurement.

$$u_r(\delta \Delta Q_{rel}) = \frac{s(\Delta Q_{rel})}{\sqrt{n}}, \quad n = 3 \quad (7)$$

$$s(\Delta Q_{rel}) = s(\delta \Delta Q_{rel}) = \sqrt{\frac{\sum_{i=1}^n (\Delta Q_{rel,i} - \overline{\Delta Q_{rel}})^2}{n-1}}, \quad n = 10 \quad (8)$$



$$\overline{\Delta Q_{\text{rel}}} = \left(\sum_{i=1}^n \Delta Q_{\text{rel}i} \right) / n, \quad n=10 \quad (9)$$

which, $s(\Delta Q_{\text{rel}})$ is the standard deviation of a single measurement experiment.

3 The evaluation process of flow measurement uncertainty

3.1 The soap film flowmeter standard device detects VOCs sampler

3.1.1 The relative standard uncertainty $u_r(Q_N)$ introduced by the VOCs sampler and the pipeline connection section

The flow measurement of the VOCs sampler adopts a high-precision electronic flowmeter, which is converted into the flow under standard conditions by the equation of state during detection. In addition, the relative standard uncertainty of the flow-meter of the VOCs sampler is introduced by the minimum resolution, the artificial error of the flow setting value, and the inaccurate electronic automatic correspondence, which are all concentrated in the type A uncertainty caused by the measurement repeatability, so no longer considered. The connection section between the VOCs sampler and the soap film flow-meter is connected by transparent, heat-insulating, corrosion-resistant rubber pipes and checked for air tightness, its relative uncertainty component is not considered here. Therefore, the relative standard uncertainty value introduced by the VOCs sampler and the pipeline connection section is zero.

3.1.2 The relative standard uncertainty $u_r(V)$ introduced by volume error of the soap film tube
The maximum permissible error of the soap film tube obtained from the measurement standard examination certificate is $\pm 0.5\%$. It is uniformly distributed and $u_r(V) = 0.29\%$ is obtained by the formula (10).

$$u(x) = \frac{a}{k} \quad (10)$$

which, a is the half-width of the range of measured possible values; k is the inclusion factor.

3.1.3 The relative standard uncertainty $u_r(t)$ introduced by the stopwatch

The indication error at the checkpoints of 10s, 600, and 1200s is 0s by referring to the verification certificate of the stopwatch. The detection sampling time of the VOCs sampler is 600s in this paper. It is estimated to be uniformly distributed and $u_1(t) = 0$ s is obtained by the formula (10).

The error of the stopwatch is due to manual control, the average reaction time of normal people is taken as 0.3s^[12]. It is estimated to be uniformly distributed and $u_2(t) = 0.173$ s is obtained by the formula (10).

The resolution of the stopwatch is 0.01s and uniform distribution, $u_3(t) = 0.006$ s is obtained by formula (10).

But the standard uncertainty introduced by the resolution of the stopwatch is reflected in the standard uncertainty introduced by the repeatability, so $u_3(t) = 0$ s. So $u_r(t) = 0.029\%$ is calculated by the formula (11).

$$u_r(t) = \frac{u(t)}{t} = \frac{\sqrt{u_1^2(t) + u_2^2(t) + u_3^2(t)}}{t} \quad (11)$$

3.1.4 The relative standard uncertainty $u_r(P)$ introduced by the empty box pressure gauge

Refer to the verification certificate of the empty box pressure gauge, and the errors at the pressure verification points of 1012 hPa, 1010 hPa, and 990 hPa are 0.2 hPa, 0.3 hPa, and 0 hPa respectively. Take the maximum permissible error ± 2 hPa of the empty box pressure gauge for evaluation. It is uniformly distributed and $u_1(P) = 1.155$ hPa is calculated by the formula (10).

The standard uncertainty is introduced by the resolution of the empty box pressure gauge, and the resolution is 1hPa. It is uniformly distributed and $u_2(P) = 0.577$ hPa is obtained by formula (10).

Taking the average atmospheric pressure of Chongqing as 983.20 hPa. It is uniformly distributed and $u_r(P) = 0.13\%$ is calculated by the formula (12).

$$u_r(P) = \frac{u(P)}{P} = \frac{\sqrt{u_1^2(P) + u_2^2(P)}}{P} \quad (12)$$

3.1.5 The relative standard uncertainty $u_r(T)$ introduced by the standard mercury thermometer

The temperature error between the temperature measured before the standard used standard mercury thermometer and the temperature of the VOCs sampler measured is $\pm 0.15^\circ\text{C}$. The laboratory temperature is 20°C , it is uniformly distributed and $u_1(T) = 0.087$ K is calculated by the formula (10).

Standard uncertainty is introduced by the resolution of the standard mercury thermometer. The resolution is 0.1°C , with uniform distribution, $u_2(T) = 0.058$ K. $u_r(T) = 0.04\%$ is obtained by formula (13).

$$u_r(T) = \frac{u(T)}{T} = \frac{\sqrt{u_1^2(T) + u_2^2(T)}}{T} \quad (13)$$



3.1.6 The relative expanded uncertainty $U_r(\overline{\Delta Q_{rel}})$

Because of the influence of various factors, measurement values are not necessarily the same. The standard uncertainty introduced by repeatability must be considered. 10 sets of repeatability tests are conducted according to 50% of the upper flow limit of the VOCs sampler. The results are shown in Table 1.

Table 1: Repeatability test of gas passing through soap film tube

No.	1	2	3	4	5
Time/s	610.3	603.5	602.8	608.9	609.7
No.	6	7	8	9	10
Time/s	608.4	604.6	609.5	606.8	604.9

The relative synthetic standard uncertainty of $\overline{\Delta Q_{rel}}$ is calculated as $u_r(\overline{\Delta Q_{rel}}) = 0.42\%$ by formula (2) (6) (7) (8) (9).

Take the inclusion factor $k = 2$ and confidence probability $P = 95\%$, and the relative expanded uncertainty $U_r(\overline{\Delta Q_{rel}}) = 0.9\%$ is calculated by the formula (14).

$$U_r(\overline{\Delta Q_{rel}}) = k \cdot u_r(\overline{\Delta Q_{rel}}) \quad (14)$$

3.2 The mass flow meter standard device detecting VOCs sampler

3.2.1 The relative standard uncertainty $u_r(Q_N)$ introduced by the VOCs sampler and the pipeline connection section

The evaluation process refers to 2.1.1, the relative standard uncertainty introduced by the VOC sampler and pipeline connection section is zero.

3.2.2 The relative standard uncertainty $u_r(Q_R)$ introduced by the flow part of the standard device

According to the user manual, the maximum permissible error value of the flow-meter of the standard device is $\pm 1.0\%$. The detected flow point is 100ml/min and it is estimated to be uniformly distributed, and $u_1(Q_R) = 0.5774\text{mL}/\text{min}$ is obtained by formula (10).

The standard uncertainty is introduced by the flow resolution of the standard device, and the resolution is 0.1ml/min. It is uniformly distributed and

$u_2(Q_R) = 0.029\text{mL}/\text{min}$ is obtained by formula (10). But the standard uncertainty introduced by resolution is reflected in the standard uncertainty introduced by repeatability, so $u_2(Q_R) = 0\text{mL}/\text{min}$. And $u_r(Q_R) = 0.58\%$ is obtained by formula (15).

$$u_r(Q_R) = \frac{u(Q_R)}{Q_R} = \frac{\sqrt{u_1^2(Q_R) + u_2^2(Q_R)}}{Q_R} \quad (15)$$

3.2.3 The relative standard uncertainty $u_r(P)$ introduced by atmospheric pressure part of standard device

The indication error of the atmospheric pressure gauge is ± 5 hPa. It is uniformly distributed and $u_1(P) = 2.887\text{hPa}$ is obtained by formula (10).

The standard uncertainty introduced by the resolution is 0.2 hPa of the atmospheric pressure gauge. It is uniformly distributed and $u_2(P) = 0.058\text{hPa}$ is obtained by formula (10).

The average atmospheric pressure in Chongqing is 983.20hPa, which is uniformly distributed. And $u_r(P) = 0.30\%$ is obtained by formula (13).

3.2.4 The relative standard uncertainty $u_r(T)$ introduced by the temperature sensor part of the standard device

The temperature error between the temperature measured before the standard used standard mercury thermometer and the temperature of the VOCs sampler measured is $\pm 0.2^\circ\text{C}$. The temperature in the constant temperature and humidity laboratory is 20°C , it is uniformly distributed, and $u_1(T) = 0.116\text{K}$ is calculated by the formula (10).

The standard uncertainty introduced by the resolution which is 0.1°C of the temperature sensor is uniformly distributed and $u_2(T) = 0.029\text{K}$ is calculated by the formula (10). $u_r(T) = 0.04\%$ is calculated by the formula (13).

3.2.5 The relative expanded uncertainty $U_r(\overline{\Delta Q_{rel}})$

Each measurement value is not necessarily the same, and the standard uncertainty introduced by repeatability needs to be considered. 10 sets of repeatability tests are conducted according to 50% of the upper flow limit of the VOCs sampler. The results are shown in Table 2.

Table 2: Flow repeatability test of gas passing standard device

No.	1	2	3	4	5
Flow/ $\text{mL} \cdot \text{min}^{-1}$	98.5	99.4	99.2	99.5	99.1
No.	6	7	8	9	10
Flow/ $\text{mL} \cdot \text{min}^{-1}$	98.9	99.5	99.7	98.6	99.2

The relative synthetic standard uncertainty of $\overline{\Delta Q_{rel}}$ is



calculated as $u_r(\overline{\Delta Q_{rel}}) = 0.70\%$ by formula (4) (6) (7) (8) (9).

Taking the coverage factor $k = 2$ and confidence probability $P = 95\%$, the relative expanded uncertainty $U_r(\overline{\Delta Q_{rel}}) = 1.4\%$ is obtained by formula (14).

4 Conclusion

In this paper, the relative expanded uncertainty of the VOCs sampler detected by the soap film flow-meter standard device and the mass flow-meter standard device is 0.9% and 1.4% respectively. There is a difference in the relative expanded uncertainty of the two standard devices for detecting VOCs samplers, which is mainly due to the difference in the standard uncertainty introduced in the standard device and the repeatability test. In particular, the above process and result analysis are effective for the VOCs sampler with the high-precision electronic flow-meter in the standard condition. The VOCs sampler with a high-precision electronic flow-meter sampling set as a working condition must be converted into standard condition before the above uncertainty analysis and evaluation.

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