Uncertainty Assessment of Carbon Monoxide in Exhaust Gas Based on Fixed Potential Electrolysis

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Abstract: In order to ensure the accuracy and reliability of the test results, the carbon monoxide content in the waste gas of fixed pollution sources was used on the field data. By explaining the steps and principles of the field operation, Establishing a mathematical model for the uncertainty of the carbon monoxide content in the exhaust gas, the main sources of the uncertainty components are analyzed, and the uncertainty assessment of class A and class B is passed. The results show that the main sources of uncertainty components include repetitive measurement, instrument value error and CO standard gas, which are 4.15%, 0.982% and 1.15% respectively; the extended uncertainty is ± 10 mg/m^3 (k=2). The results show that under the condition of ensuring the stability of the process emission, increasing the number of field measurement is the key to reduce the uncertainty, which is conducive to improving the quality level of the fixed source waste gas monitoring data.

Keywords: Carbon Monoxide; A Uncertainty; B Uncertainty; Potential Method

1. Introduction

According to the relevant rules of the Assessment and representation of measurement Uncertainty, there is a quantitative description of the measurement results, so that people can understand their reliability, and the measurement results and the specified reference values in a certain period range, introducing the "uncertainty" definition [1]. Uncertainty is used to characterize the parameter [2] that reasonably assigns the measured value dispersion, related to the measured results. In the daily testing laboratory, according to the requirements of the testing methods, the requirements of the user, etc., to determine whether the width of the error limit, the uncertainty of the evaluation. Hereby, we assess the uncertainty of monitoring the waste gas of the fixed pollution source and measuring the carbon monoxide in the waste gas by the fixed potential electrolysis method.

2. Materials and Methods

2.1 Method Basis

According to the requirements of *Stationary source emission — Determination of carbon monoxide — Fixed potential by electrolysis method (*HJ973-2018), Measure the measurement uncertainty of carbon monoxide in the exhaust gas of fixed pollution sources.

2.2 Method and Principle

Samples are drawn into a sensor mainly composed of electrolytic cell, electrolyte and electrode (sensitive electrode, reference electrode and counterelectrode). Carbon monoxide spreads to the surface of the sensitive electrode through the permeable membrane, and the oxidation reaction occurs on the sensitive electrode.

$$CO + 2H_2O \rightarrow CO_3{}^{2-} + 4H^+ + 2e$$

From this Generates a limiting diffusion current (i) arises. Under the specified working conditions, the electron transfer number (Z), the Faraday constant (F), The gas diffusion area (S), diffusion coefficient (D) and diffusion layer thickness (δ) are constant [3], and the size of the limiting diffusion current (i) is proportional to the carbon monoxide

$$i = \frac{Z \bullet F \bullet S \bullet D}{\delta} \times c \quad (1)$$

2.3 Instruments and Reagents

(1)Laoshan application of 3012H smoke and gas tester
(2)Carbon monoxide standard gas (certified standard gas, uncertainty 2%)
(3)Zero gas (nitrogen of 99.99% purity or clean air not interfering with the assay)
(4)Standard gas cylinder (with adjustable pressure reducing valve, adjustable rotor flow meter and guide pipe)

2.4 Sampling and Determination

According to the requirements of *Stationary source emission — Determination of carbon monoxide — Fixed potential by electrolysis method (*HJ973-2018). After the calibration and calibration of the instrument, connect the instrument with the pipeline sampling gun, meet the working conditions of the instrument, and then start the self-test calibration and zero in the ambient air, the instrument enters the test function. Under stable condition, put the sampling gun into the sampling hole and plug the cotton cloth to keep it from leaking. When the instrument test shows that the concentration change is stable, save the measured data by minutes, and take the average value of the measured data for 5 minutes ~15 minutes as one measurement value. Record (print) the test data; after the reading, place the sampling gun in ambient air, clean the sensor, turn off the instrument and cut off the power supply. The CO in the boiler flue gas is measured continuously for 4 consecutive periods according to GB/T16157, HJ 397 and other relevant monitoring specifications, and take the average value as the final measurement result [4].

2.5 The Mathematical Model

According to the requirements of *Stationary source emission — Determination of carbon monoxide — Fixed potential by electrolysis method (*HJ973-2018),Deof CO in fixed source exhaust. The concentration of CO in the boiler flue gas can be directly measured by the flue gas analyzer, and the mathematical model formula (2) is as follows:

$$Cs = X + \Delta X \quad (2)$$

In the formula Cs: instrument shows CO mass concentration in flue gas, mg/m^3; X: CO mass concentration in boiler flue gas, mg/m^3; ΔX: instrument value error.

In the field measurement process of the air, Introducing air dilutions or participating in the combustion, the monitoring results are expressed by the reasonable reference oxygen content of formula (3) into the CO emission concentration of flue gas:

$$C_f = C_S \times (21 - O_{2,b}) / (21 - O_{2,\ a}) \quad (3)$$

Formula C_f the converted CO mass concentration of flue gas, mg/m^3; $O_{2,b}$ *Boiler Air Pollutant Emission Standard* GB13271-2014 stipulates that the base oxygen content of coal (formed biomass) is 9%; $O_{2,a}$ the average oxygen content measured in flue gas%.

According to the detection method and mathematical model, the uncertainty component is analyzed, according to the uncertainty propagation law, according to the formula (4) synthesis standard uncertainty

$$U_{rel}(C) = \sqrt{U_{rel}^2(Cs) + U_{rel}^2(O_2) + U_{rel}^2(R)} \quad (4)$$

$$U_{rel}(Cs) = \sqrt{U_{rel}^2(X) + U_{rel}^2(\Delta X)}$$

In the above formula

$U_{rel}(C)$ —The relative standard uncertainty of CO in flue gas

$U_{rel}(C_S)$ —The relative standard uncertainty of flue gas CO measurement;

$U_{rel}(O_2)$ —The relative standard uncertainty introduced by measuring the excess air coefficient;

$U_{rel}(X)$ —Relative standard uncertainty introduced by the repeatability measurement;

$U_{rel}(\Delta X)$ —Relative standard uncertainty introduced by the instrument display value;

$U_{rel}(R)$ —Relative standard uncertainty of the CO standard gas.

2.6 Analysis of Uncertainty Component Sources

In order to clearly and intuitively understand the source of each uncertainty component [4], it is expressed in the form of analysis diagram, as detailed in Figure 1.

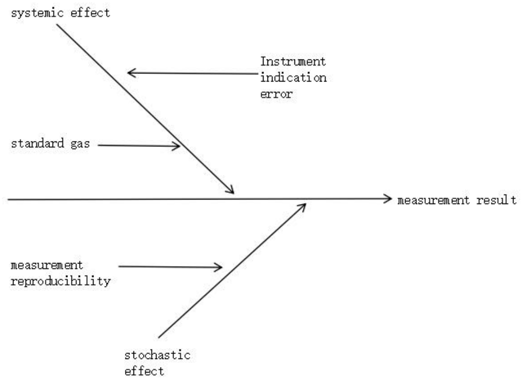

Figure 1. Analysis of Uncertainty Components

3. Results and Discussion

3.1 Uncertainty Introduced by the Instrument for Measuring Flue Gas CO

3.1.1 Assessment of standard uncertainty due to random effects

In the field measurement process, ensure the stability of the waste gas treatment process[5], the field repeated measurement for 5 minutes, the average data as a measurement value, the continuous measurement of carbon monoxide measurement mean 125,103,110,110 mg/m^3, the total mean is 112mg/m^3, converted CO results of 224,185,197,197mg / m^3, the final monitoring results reported the mean of 200.6mg/m^3 ,the statistical results are shown in Table 1.

Using class A evaluation method, the standard deviation of the mean value[6] is calculated according to formula (5), that is, the standard uncertainty.

Table 1. Data Sheet of Carbon Monoxide Monitoring Results

min	Period 1	Period 2	Period 3	Period 4
1	125	105	109	111
2	125	100	110	110
3	124	102	110	108
4	126	103	111	112
5	123	105	112	108
average value	125	103	110	110
Conversion concentration	224	185	197	197

$$U(X)=S_R/\sqrt{4}=\sqrt{\frac{\sum_{i=1}^{n}\left[X_i-\overline{X}\right]^2}{4(n-1)}}=8.03mg/m^3 \quad (5)$$

$$U_{rel}(X)=\frac{U(X)}{\overline{X}}=\frac{8.03}{200.6}=4.15\%$$

3.1.2 Standard uncertainty caused by system effects

The measurement uncertainty caused by the system effect of the measuring instrument is mainly based on the CO calibration result index given in the soot instrument 3012H calibration certificate (certificate number J2016215460), and [7] by class B method. The value error of CO and oxygen given in the calibration certificate is-1.7% within the measurement range, considering the uniform distribution, taking the inclusion factor k $=\sqrt{3}$. The standard uncertainty introduced by the instrument presentation value error is:

$$U_{rel}(\Delta X)=\frac{a}{k}=\frac{1.7\%}{\sqrt{3}}=0.982\%,$$

$$U(\Delta X)=0.982\%\times 200.6mg/\mathrm{m}^3=1.97mg/\mathrm{m}^3$$

Therefore, the uncertainty of flue gas CO measurement

$$U_{rel}(Cs)=\sqrt{U_{rel}{}^2(X)+U_{rel}{}^2(\Delta X)}/\overline{X}=\sqrt{4.15^2+0.982^2}/200.6\text{=2.12\%}$$

3.2 Uncertainty Component of Excess Air (Oxygen Content)

Class B method is used for evaluation. In the verification certificate of 3012H soot (gas) tester, the maximum allowable error of measuring oxygen content is ± 1.0%. Since the excess air in the flue gas is calculated from the oxygen content, the relative standard uncertainty introduced by the oxygen content is calculated

$$U_{rel}(O_2)=\frac{1\%}{k}=\frac{1\%}{\sqrt{3}}=0.577\%$$

3.3 Relative Standard Uncertainty of the CO Standard Gas

The CO standard gas is the standard substance provided by Foshan Gas Chemical Co., LTD.

According to the certificate of standard gas (GBW (E) 060163), the relative uncertainty of CO standard gas concentration is 2%. According to the normal distribution (at 95% confidence level, including factor k=2), the calculation results of the uncertainty introduced by carbon monoxide standard gas are[8]

$$U_{rel}(R)=\frac{2\%}{\sqrt{3}}=1.15\%$$

3.4 Synthesis uncertainty of each component

For the calculated statistics of each uncertainty component mentioned above, see Table 2.

Table 2. List of uncertainty components

uncertainty component product	Source of uncertainty	Relative standard uncertainty (%)
$U_{rel}(C_S)$	The relative standard uncertainty of the instrument measuring flue gas CO introduction	2.12
$U_{rel}(O_2)$	Relative standard uncertainty introduced by the excess air coefficient	0.577
$U_{rel}(X)$	Relative standard uncertainty introduced by repeatability measurements	4.15
$U_{rel}(\Delta X)$	Relative standard uncertainty introduced by the instrument value error	0.982
$U_{rel}(R)$	Relative standard uncertainty of the CO standard gas	1.15

The synthetic relative standard uncertainty is

$$U_{rel}(C)=\sqrt{U_{rel}^2(Cs)+U_{rel}^2(O_2)+U_{rel}^2(R)}=\sqrt{2.12^2+0.577^2+1.15^2}=2.48\%$$

The synthesis standard uncertainty is

$$U_c(C)=U_{rel}(C)=2.48\%\times 200.6mg/m^3=4.97mg/m^3$$

4. The Extended Uncertainty, U

Extended uncertainty is the amount to determines the measurement result interval, and most of the distribution of measured values is expected to be included in this interval. Actually the extended uncertainty (U) is a measurement uncertainty expressed by a multiple (k) of the synthetic standard uncertainty (Uc). Therefore, taking the inclusion factor k=2 (about 95% confidence probability), the extended uncertainty is:

$$U=kU_c(C)=2\times 4.97mg/m^3\approx 10mg/m^3$$

By calculating an extension uncertainty of 10 mg/m^3 , in order to characterize the accuracy of the measurement result relative to the difference between the measured result and its uncertainty, usually expressed as the ratio of the extended uncertainty divided by the measured result, thus obtaining a relative expansion uncertainty of 4.97%. Therefore, the smaller the control of the relative extension uncertainty, the smaller the difference between the measurement result and its uncertainty, which can improve the precision of the measurement.

5. Conclusion

The average value of the carbon monoxide concentration in the exhaust gas is 201, and the extended uncertainty is 10 mg/m^3 (k=2), and the result is expressed as (201±10) mg/m^3 , k=2.

According to the statistical analysis of the above uncertainty components, the relative standard uncertainty introduced by the repetitive measurement is the main factor affecting the measurement results. Therefore, we can reduce the components of the uncertainty by increasing the measurement times, improve the quality of the fixed source exhaust carbon monoxide monitoring data, and ensure the accuracy and reliability of the on-site monitoring data.

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