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ENVIRONMENTAL PROTECTION STANDARD OF THE PEOPLE'S REPUBLIC OF CHINA

HJ 57-2017

Replacing HJ 57-2000

Stationary source emission - Determination of sulfur dioxide - Fixed potential by electrolysis method

固定污染源废气 二氧化硫的测定

定电位电解法

Issued on: November 28, 2017

Implemented on: January 01, 2018

Issued by: Ministry of Environmental Protection

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Stationary source emission - Determination of sulfur dioxide - Fixed potential by electrolysis method

1 Scope

This standard specifies the fixed potential electrolysis method for the determination of sulfur dioxide in stationary source emission.

This standard applies to the determination of sulfur dioxide in stationary source emission.

The detection limit of this standard is 3 mg/m³. The lower limit of determination is 12 mg/m³.

2 Normative references

The contents of this standard refer to the following documents or their terms. For undated references, the valid version applies to this standard.

GB/T 16157 The determination of particulates and sampling methods of gaseous pollutants emitted from exhaust gas of stationary source

HJ 75 Specifications for continuous emissions monitoring of SO₂, NO_x, and particulate matter in the flue gas emitted from stationary sources

HJ 76 Specifications and test procedures for continuous emission monitoring system for SO₂, NO_x and particulate matter in flue gas emitted from stationary

HJ/T 46 Technical conditions of detector of sulfur dioxide concentration for constant potential electrolysis method

HJ/T 373 Technical specifications of quality assurance and quality control for monitoring of stationary pollution source (on trial)

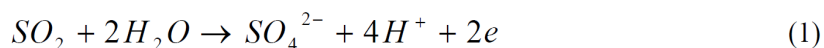
HJ/T 397 Technical specifications for emission monitoring of stationary source

3 Terms and definitions

3.1

4 Principle of method

The sample is taken into a sensor consisting mainly of an electrolytic cell, an electrolyte, electrodes (sensitive electrode, reference electrode, counter electrode). Sulfur dioxide diffuses through the permeable membrane to the surface of the sensitive electrode; an oxidation reaction occurs on the sensitive electrode:



This results in an ultimate diffusion current (i). Under the specified working conditions, the number of electron transfer (Z), Faraday constant (F), gas diffusion area (S), diffusion coefficient (D), thickness of diffusion layer (δ) are constant; the magnitude of the ultimate diffusion current (i) is proportional to the sulfur dioxide's concentration (c), so it may use the ultimate diffusion current (i) to determine the sulfur dioxide's concentration (c).

$$i = \frac{Z \cdot F \cdot S \cdot D}{\delta} \times c \quad (2)$$

5 Interference and elimination

5.1 The particulate matter, moisture and sulfur trioxide in the gas to be tested are easy to condense on the surface of the sensor's permeable membrane and cause damage to the sensor, which affects the determination; it shall be filtered by a dust filter device, a dehumidifier, a mist filter, etc. to eliminate the influence.

5.2 Ammonia, hydrogen sulfide, hydrogen chloride, hydrogen fluoride, nitrogen dioxide, etc. will cause some interference to the determination of samples. It may use phosphoric acid absorption, lead acetate adsorption, gas filter filtration and other measures to reduce interference.

5.3 Carbon monoxide's interference is significant, so the concentration of carbon monoxide must be determined simultaneously when measuring the sample. When the concentration of carbon monoxide does not exceed 50 $\mu\text{mol/mol}$, the sample can be determined by this standard. When the concentration of carbon monoxide exceeds 50 $\mu\text{mol/mol}$, the interference test of carbon dioxide shall be carried out before the initial use of the sulfur dioxide analyzer (see Appendix A). Within the range of the highest concentration of sulfur dioxide and the highest concentration of carbon monoxide as determined by the interference test, the sample can be determined by this standard.

It is equipped with adjustable pressure reducing valve, adjustable rotor flowmeter, air duct.

7.3 Gas bag

Used to calibrate the analyzer by air bag method. The volume is 4 L ~ 8 L; the lining material shall be selected from the aluminum-plastic composite film, polytetrafluoroethylene film and other inert materials that have little influence on the measured components.

7.4 Emission parameter tester

An instrument capable of testing parameters such as moisture content, flue gas's temperature, flue gas's pressure, flue gas's flow rate, flow rate.

7.5 Carbon monoxide measuring device

A device or apparatus capable of measuring the concentration of carbon monoxide in an emission.

8 Sampling and determination

8.1 Determination of sampling points and sampling frequency

According to GB/T 16157, HJ/T 397, HJ/T 373, HJ 75 and HJ 76 and related requirements, determine the sampling position, sampling point, sampling frequency.

8.2 Inspection of tester's air tightness

According to the instruction manual of the instrument, connect the analyzer, sampling tube, air duct, etc. correctly. After reaching to the working conditions of the instruments, check the airtightness according to GB/T 16157 or HJ/T 46. If the inspection fails, it shall find the leakage and repair it, until the inspection is qualified.

8.3 Calibration of analyzer

8.3.1 Zero calibration

Lead zero gas into the analyzer to calibrate the instrument's zero point.

8.3.2 Calibration of range

Lead the sulfur dioxide standard gas into the analyzer for measurement. If the calibration error meets the requirements of 7.1.2 a), the analyzer is available; otherwise, it requires calibration. The calibration method is as follows:

again to calculate the calibration error and system bias. If the calibration error and system bias meet the requirements of 7.1.2 a) and b), the determination result of the sample is valid; otherwise, the determination result of the sample is invalid.

Note: It may use the inspection of the calibration error of the whole system including the sampling tube, the air guiding tube and the dehumidification device to substitute the inspection of the calibration error of the analyzer and the system bias [the evaluation follows the requirements 7.1.2 a)].

11.3 The sample measurement result shall be between 20% and 100% of the calibration span of the instrument. Otherwise, it shall re-select the calibration span.

11.4 If the analyzer does not carry out the carbon monoxide's interference test or the carbon monoxide's interference test fails, the minute data of the sulfur dioxide concentration measured when the concentration of carbon monoxide in the exhaust gas exceeds 50 $\mu\text{mol/mol}$ shall be excluded as invalid data. If the analyzer has passed the carbon monoxide's interference test, the minutes data of the sulfur dioxide concentration as measured when the concentration of carbon monoxide in the emission exceeds the highest concentration of carbon monoxide determined by the interference test, as well as the minutes data of sulfur dioxide concentration exceeding the highest concentration of sulfur dioxide determined by the interference test shall be taken as invalid data and are rejected. For one measurement value, it shall obtain not less than 5 minutes data of valid sulfur dioxide concentrations.

11.5 After the analyzer is replaced with a sulfur dioxide sensor, it shall repeat the interference test.

11.6 At least one zero drift and span drift check shall be performed every month and shall comply with the requirements of 7.1.2 c) and d). Otherwise, the instrument shall be maintained or repaired in a timely manner.

11.7 The service life of the fixed potential electrolysis sensor is generally less than 2 years, which shall be replaced in time after expiration. When calibrating the sensor, if the dynamic range is found narrowed, the upper limit of the measurement cannot reach the full scale value, or when the calibration span of the instrument is rechecked, the calibration error exceeds the requirement of 7.1.2 a), it indicates that the sensor has failed and shall be replaced in time.

12 Precautions

12.1 The analyzer shall be operated under the conditions of its specified ambient temperature, ambient humidity, etc.

Appendix A

(Informative)

Carbon monoxide interference test - Dynamic aeration matrix test method

A.1 Reagents and materials

A.1.1 Sulfur dioxide standard gas

Commercially available certified standard gas, uncertainty $\leq 2\%$.

A.1.2 Nitrogen

Purity $\geq 99.99\%$.

A.1.3 Carbon monoxide standard gas

Commercially available certified standard gas, uncertainty $\leq 2\%$.

A.2 Instruments and equipment

A.2.1 Sulfur dioxide analyzer

Same as 7.1.

A.2.2 Carbon monoxide analyzer

Same as 7.5.

A.2.3 Dilution gas distribution device

It can dynamically distribute gas to standard gases such as sulfur dioxide, carbon monoxide, nitrogen. It has at least 3 input channels and 1 output channel. The mass flow meter controls the gas flow of each input and output channel, wherein the mass flow meter of the input channel shall not below 5 L/min, the mass flowmeter of the output channel shall be not less than 10 L/min, the accuracy shall be at or better than $\pm 2\%$.

A.3 Operation steps

A.3.1 Instrument preparation

A.3.1.1 Inspection of instrument's air tightness

Check the air tightness of the sulfur dioxide analyzer and the carbon monoxide analyzer, to ensure that the system is airtight.

A.3.1.2 Instrument calibration

Use the zero gas to calibrate the zero point of the sulfur dioxide analyzer and the carbon monoxide analyzer. Use the sulfur dioxide standard gas and carbon monoxide standard gas to respectively check or calibrate the instrument.

A.3.2 Carbon monoxide's interference test procedure

A.3.2.1 Determination of concentration level of sulfur dioxide in mixed gas

According to the range of the fixed potential electrolysis sensor used in the sulfur dioxide analyzer, respectively use the $(10 \pm 2)\%$, $(20 \pm 2)\%$, $(40 \pm 2)\%$, $(60 \pm 2)\%$, $(80 \pm 2)\%$, 95% ~ 100% of the range value as a concentration of sulfur dioxide in the mixed gas, to conduct carbon monoxide interference test.

A.3.2.2 Calculation of volume of mixed gas

Use the minimum concentration level of sulfur dioxide in the mixed gas determined by A.3.2.1 as a target, based on the standard gas concentration of sulfur dioxide and the standard gas concentration of carbon monoxide used, calculate the volume of mixed gas of sulfur dioxide, carbon monoxide, nitrogen and other standard gases.

A.3.2.3 Determination of initial value of sulfur dioxide concentration in mixed gas

According to the calculated mixed gas volume of standard gas, lead only the nitrogen gas and sulfur dioxide standard gas into the dilution gas distribution device; after the gas mixture is stabilized, use a sulfur dioxide meter to measure the sulfur dioxide concentration in the mixed gas, record it as the initial value of the sulfur dioxide concentration in the mixed gas ($C_{\text{SO}_2-t_0}$).

A.3.2.4 Determination of sulfur dioxide concentration under the interference of series carbon monoxide concentration

According to the calculated mixed gas volume of the standard gas, keep the mixed gas volume of sulfur dioxide standard gas unchanged. Gradually reduce the mixed gas volume of nitrogen gas. Gradually increase the mixed gas volume of carbon monoxide standard gas (but the sum of the mixed gas volume of nitrogen gas and carbon monoxide standard gas must be kept equal to mixed gas volume of nitrogen in A.3.2.3). Ensure that the concentration level of the sulfur dioxide in the mixed gas mixture is stable and unchanged, but the concentration of carbon monoxide can, in the range of 100 $\mu\text{mol/mol}$ to a higher concentration range, be increased gradually at a concentration difference of (200 ~ 2000) $\mu\text{mol/mol}$ [to form a series of carbon monoxide interference concentrations close to (100, 300, 500, 1000, 1500, 2000, 3000, 4000, 5000, 6000, 7000, 8000, 10000, 12000, 15000, 20000) $\mu\text{mol/mol}$]. At each

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