Development and Application of Formaldehyde Dynamic Standard Gas Generator Based on Trioxane Diffusion and Cracking

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Abstract:Aiming at the engineering application problems of traditional static cylinder formaldehyde standard gas, such as large adsorption loss, rapid concentration attenuation, difficulty in preparing low-concentration gas and poor traceability of measured values, an integrated formaldehyde dynamic standard gas generator integrating constant-temperature trioxane diffusion cracking system and high-precision dynamic gas distribution system is developed in this paper. Taking solid trioxane as the gas source matrix, the equipment realizes stable vapor release through a precision constant-temperature diffusion unit, generates high-purity formaldehyde monomers via a high-temperature tubular cracking device for ring-opening cracking, and then completes accurate proportional dilution relying on dual-channel mass flow controllers, so as to realize on-line real-time preparation of formaldehyde standard gas with wide range and high stability.Featuring simple structure, high degree of automation and low operation and maintenance cost, this equipment can be widely applied in instrument calibration for environmental monitoring, indoor air detection, formaldehyde emission detection of industrial building materials, laboratory scientific research calibration and other scenarios, and has good engineering promotion value and industrial practical value.
Key words: Formaldehyde standard gas; Dynamic gas distribution; Trioxane; Diffusion cracking; Mass flow control; Uncertainty; Instrument calibration

1 INTRODUCTION

1.1 Research Background and Engineering Application Significance

Formaldehyde is the most prevalent toxic and hazardous volatile organic pollutant in residential environments and industrial production scenarios at present, and has been classified as a Group 1 carcinogen and teratogen by the World Health Organization (WHO). Free formaldehyde is continuously released from interior decorative panels, adhesives, coatings, textile products and other materials. Long-term exposure to environments with excessive formaldehyde concentrations can easily trigger a series of health hazards including respiratory diseases, skin allergies and impaired immune function. China's current national standard GB/T 18883-2022 Indoor Air Quality Standard clearly stipulates that the 1-hour average concentration limit of formaldehyde in a sealed indoor environment shall not exceed 0.08 mg/m^3, corresponding to a molar gas concentration of approximately 65 nmol/mol.

With the continuous intensification of ecological and environmental governance, environmental air quality monitoring, sanitary inspection of public places, indoor environment acceptance of construction projects, random quality inspection of home building materials and other tasks have become fully routine. A wide range of testing equipment has been widely popularized, including portable formaldehyde detectors, fixed online formaldehyde monitors and laboratory spectrophotometric testing instruments. During factory verification, periodic calibration and on-site comparison of all testing instruments, formaldehyde standard gases with accurate certified values, stable concentrations and traceable measurement values are mandatory for value transfer. The quality of standard gases directly determines the accuracy and credibility of test data.

At present, the mainstream preparation methods for formaldehyde standard gases in the industry fall into two categories: static gas distribution and conventional dynamic gas distribution, both of which have prominent technical drawbacks. Static formaldehyde standard gas stored in high-pressure cylinders is affected by the strong polarity and high adsorptivity of formaldehyde. The gas readily adsorbs onto cylinder inner walls and undergoes polymerization, resulting in continuous concentration decay during storage. Low-concentration standard gases have a validity period of less than 30 days and fail to meet the demands of long-term batch calibration. The vaporization gas distribution method using liquid formaldehyde solution suffers from incomplete vaporization, pipeline residue scaling and severe concentration drift. For conventional permeation tube gas distribution, the permeation rate is highly susceptible to ambient temperature and service duration, leading to short equipment service life, frequent recalibration and severe limitations for on-site deployment.

Against this industrial technical backdrop, developing a dynamic formaldehyde standard gas generator featuring stable operation, precise concentration, wide measuring range and user-friendly operation—capable of on-site real-time preparation of standard gases via trioxymethylene diffusion cracking technology—can fundamentally resolve the industry pain points of cylinder-stored standard gases such as difficult storage, inconvenient transportation and short validity period. This development bears profound practical engineering significance for standardizing metrological calibration within the environmental testing industry, improving the metrological accuracy of testing equipment, and ensuring authentic and valid environmental monitoring data. Meanwhile, it can cater to diverse application scenarios including enterprise quality inspection, experimental research in scientific research institutes, and routine calibration at third-party testing laboratories.

1.2 Domestic and Overseas Technical Research Status

1.2.1 Overseas Research Status

Research on dynamic formaldehyde gas distribution technology was launched relatively early in metrology sectors across Europe, America and China. The National Institute of Standards and Technology (NIST) of the United States and the Physikalisch-Technische Bundesanstalt (PTB) of Germany took the lead in establishing a traceability system for formaldehyde standard gases produced by trioxymethylene cracking, and formulated comprehensive specifications for value transfer via dynamic gas distribution.

Mature commercial dynamic formaldehyde standard gas generators from overseas generally adopt high-precision constant-temperature control systems with a temperature control accuracy of ±0.03 ° C, paired with imported thermal mass flow controllers. Such equipment delivers high overall metrological accuracy and low system uncertainty, enabling stable output of ultra-trace formaldehyde standard gases. Nevertheless, complete sets of overseas equipment come with exorbitant overall costs, with the procurement price of a single unit exceeding 500,000 RMB. Core components of these devices are subject to high market monopolization, resulting in prohibitive expenses for post-sale maintenance and component replacement. In addition, the complicated operational procedures impose high professional technical requirements on operators, making large-scale popularization unfeasible for small and medium-sized domestic testing institutions and grassroots construction quality inspection departments.

1.2.2 Domestic Research Status

Over the past two decades, the National Institute of Metrology, China, China Academy of Test Technology, and environmental engineering & metrological testing research teams from major universities in China have continuously carried out optimization research on dynamic formaldehyde gas distribution technology. Chinese researchers have successively tackled multiple technical bottlenecks, including optimization of diffusion tube calibration methods, selection of optimal cracking temperature ranges, and design of low-adsorption gas circuit structures, gradually realizing domestic substitution of core dynamic gas distribution processes.

At present, multiple simplified dynamic formaldehyde gas distribution devices have emerged domestically. Nevertheless, most equipment suffers from drawbacks such as low integration level, insufficient automatic control, poor linkage between temperature control and flow rate, and incomplete measures to suppress pipeline adsorption. There remains ample room for improvement in long-term continuous operation stability and linear matching performance across wide concentration ranges. Integrated standard gas generators specially adapted for mobile on-site engineering use and rapid calibration of batches of instruments are still scarce.[1,2]

1.2.3 Main Deficiencies of Existing Technologies

1) Insufficient gas source stability: Most gas distribution devices adopt a simplistic gas source unit structure with low precision of constant temperature control, leading to drastic fluctuations in the release rate of parent substances and continuous drift of output formaldehyde concentration;

2) Imperfect cracking process: Unreasonable control range of cracking temperature causes incomplete trioxane cracking and by-product generation, which directly reduces the purity of standard ga;

3) Improper gas circuit design: Ordinary materials are selected for pipelines, valves and cavities, resulting in severe formaldehyde adsorption. Residual gas inside pipelines after equipment startup and shutdown impairs the accuracy of concentration certification;

4) Low integration of control systems: Flow rate and temperature are mostly adjusted manually, without one-click setting of target concentrations; functions including automatic data collection, storage and traceability are absent;

5) Poor range adaptability: Insufficient preparation precision in the low-concentration interval, poor mixing uniformity in the high-concentration interval, and unsatisfactory stability for full-range operation.[3,4]

1.3 Main Research Contents and Technical Route

1.3.1 Core Research Contents

1) Complete the overall scheme design of mechanical structure and gas circuit system for the dynamic formaldehyde standard gas generator, divide functional units, and determine the overall layout and mounting structure of the equipment;

2) Complete hardware selection and parameter matching design for four subsystems: trioxane constant-temperature diffusion subsystem, high-temperature catalytic cracking subsystem, dual-path dynamic dilution gas distribution subsystem, and constant-temperature & constant-pressure mixing subsystem;

3) Derive an accurate concentration calculation formula for formaldehyde standard gas from dynamic gas distribution based

on mass conservation and the ideal gas equation of state, and clarify correction methods for various influencing parameters;

4) Sort out the main sources of concentration errors of the equipment, complete the evaluation of Type A and Type B uncertainty components, and establish a complete evaluation system for system uncertainty;

5) Build a physical test platform and conduct comprehensive performance tests covering equipment temperature stability, flow stability, standard gas concentration stability, repeatability, linearity and on-site practicability;

6) Summarize routine operation specifications, periodic calibration procedures, troubleshooting methods and long-term maintenance schemes for the equipment.

1.3.2 Overall Technical Route

The overall technical workflow follows a complete sequence: scheme demonstration → structural design → hardware selection → theoretical modeling → program control debugging → experimental performance testing → data sorting and analysis → optimization & improvement → summary of engineering application. First, the overall equipment design scheme is determined combined with the physicochemical properties of formaldehyde and metrological verification standards. Second, refined design is carried out for three core modules: mechanical structure, gas pipelines and electrical control, followed by component selection, assembly and system joint debugging. Third, a concentration calculation model is established via theoretical formulas. Finally, extensive practical tests are performed to verify whether all equipment performance indicators meet the requirements, so as to form a mature, stable and mass-producible engineering equipment solution.

2 Overall Design and Working Principle of Dynamic Formaldehyde Standard Gas Generator

2.1 Physicochemical Properties of Formaldehyde and Basis for Gas Distribution Process Selection

Formaldehyde has the molecular formula HCHO. It is a colorless, pungent gas at normal temperature and pressure, highly soluble in water. With strong molecular polarity and high surface adsorption activity, formaldehyde readily undergoes physical adsorption and chemical association reactions on the inner walls of metal and plastic pipelines. Moreover, it tends to polymerize at low temperatures to form solid paraformaldehyde precipitates, which cause pipeline blockage and a sharp drop in gas concentration.

Trioxane is a cyclic polymer of formaldehyde with the molecular formula $(CH_2O)_3$. It appears as white crystalline solid at room temperature, featuring stable chemical properties, low volatility and deterioration, and easy storage and transportation. Complete ring-opening cracking reaction can occur at a high temperature of 160 ℃ to 200 ℃ without producing impurity by-products. Therefore, trioxane serves as the optimal solid precursor for the preparation of high-purity formaldehyde standard gas. The main cracking reaction equation is shown as follows:[5]

$$(CH_2O)_3 \overset{160\sim200^{\circ}C}{===} 3HCHO \tag{1}$$

Complete cracking of 1 mol solid trioxane produces 3 mol high-purity formaldehyde monomers, with a reaction conversion rate exceeding 99.9%. The release rate of trioxane is regulated via constant-temperature diffusion, which enables precise control over formaldehyde gas concentration at the source. This technique is also the mainstream formaldehyde standard gas preparation method prioritized and recommended by national metrological specifications.[6]

2.2 Overall Structural Composition of the Equipment

This dynamic formaldehyde standard gas generator adopts an integrated cabinet-type integrated structure as a whole. The complete machine is divided into six independent functional units with compact and reasonable structural layout and concise and smooth gas circuit routing.[7]

1) High-purity Gas Source Purification Unit: It is responsible for dehydrating, decarbonizing and removing organic impurities from the carrier gas and dilution air;

2) Trioxane Constant-temperature Diffusion Unit: It releases saturated trioxane vapor at a constant rate under a constant temperature environment;

3) High-temperature Catalytic Cracking Unit: It realizes high-temperature cracking of trioxane vapor to generate high-purity primary formaldehyde gas;

4) Dual-path Dynamic Flow Proportioning Unit: It realizes gas dilution at different ratios through two high-precision mass flow controllers;

5) Constant-temperature and Constant-pressure Mixing & Output Unit: It achieves uniform mixing of high and low concentration gases and stably outputs gas with fixed pressure and temperature;

6) Intelligent Measurement & Control and Data Acquisition Unit: It realizes automatic regulation, display and storage of temperature, flow and concentration parameters, as well as over-limit alarm function。

The entire gas circuit of the equipment adopts a combination of electropolished 316L stainless steel pipelines and high-purity PTFE (polytetrafluoroethylene) fittings and valves, which minimizes the adsorption of formaldehyde gas on pipeline inner walls and controls the basic systematic errors from the hardware perspective.[8]

2.3 Complete Working Process of the Equipment

1) Gas Source Pretreatment Stage: Externally supplied

zero-grade high-purity air first enters a multi-stage combined gas purifier. It sequentially undergoes molecular sieve drying for water removal, soda lime treatment for carbon dioxide elimination, and activated carbon adsorption for organic impurity removal. The dew point of treated gas is lower than −70 ° C, meeting the purity requirements of gas source for standard gas preparation;

2) Gas Shunting Stage: Purified high-purity air is automatically split into two independent gas paths. One serves as the carrier gas path, which flows into the constant-temperature diffusion cell at low flow rate to carry trioxane vapor; the other acts as the dilution gas path as the base gas for concentration dilution;

3) Constant-temperature Diffusion & Gas Release Stage: The carrier gas flows at a preset constant flow rate through the constant-temperature chamber equipped with built-in trioxane diffusion tubes. Under stabilized temperature control, the carrier gas carries trioxane gaseous molecules at a steady release rate;

4) High-temperature Cracking Conversion Stage: The mixed gas containing trioxane flows into a sealed high-temperature cracking furnace. Sufficient cracking reaction is completed at the preset optimal cracking temperature to convert trioxane into high-concentration primary formaldehyde gas;

5) Dynamic Proportional Dilution Stage:The high-concentration primary formaldehyde gas fully collides and mixes with high-flow high-purity dilution air inside the mixing chamber. By precisely adjusting the flow ratio of the two gas streams, formaldehyde standard gas with target concentration can be accurately prepared;

6) Pressure-Stabilized and Flow-Stabilized Output Stage: The mixed standard gas flows into a buffer pressure-stabilizing chamber to eliminate concentration fluctuations caused by instantaneous flow surges. Finally, the gas is stably discharged from the dedicated gas outlet of the equipment and can be directly connected to testing instruments for calibration;

7) Tail Gas Treatment Stage: Excess waste gas from experiments undergoes harmless treatment via a dedicated activated carbon tail gas adsorption device before low-altitude discharge, posing no risk of environmental pollution.

2.4 Overall Design Technical Indicators of the Equipment

Combined with practical engineering application requirements and national metrological verification standards, the main design technical parameters of this generator are specified as follows:

1) Output formaldehyde concentration range: 10 ~ 1000 nmol/mol;

2) Temperature control range of diffusion cell: 30℃ ~ 60℃, temperature control accuracy ≤ ±0.1℃;

3) Operating temperature of cracking furnace: adjustable 160℃ ~ 200℃, typical operating temperature 180℃, temperature control accuracy ≤ ±1℃;

4) Mass flow control accuracy: ±0.5% full scale; flow repeatability ≤ ±0.2%;

5) Continuous stable operation duration of the whole machine: ≥24h;

6) Output gas pressure: stable slight positive pressure, pressure fluctuation ≤ ±0.2 kPa;

7) Long-term concentration stability: concentration fluctuation ≤ ±0.3% during 24-hour continuous operation;

8) Relative expanded uncertainty of the complete equipment:U≤2.2% (k=2);

9) Operating ambient conditions: ambient temperature 15℃ ~ 35℃, relative humidity 30% ~ 70%RH.

3 Detailed Design of Core Subsystems

3.1 Design of Trioxane Constant-Temperature Diffusion System

The constant-temperature diffusion system serves as the core component that governs the stability of formaldehyde standard gas source. This system mainly consists of five parts: a sealed constant-temperature cavity, high-precision PT100 temperature measuring sensors, an intelligent PID temperature control module, dedicated diffusion tubes filled with solid trioxane, and a gas flow guiding & pressure stabilizing structure.

3.1.1 Selection and Calibration of Diffusion Tubes

Integrated diffusion tubes made of quartz glass are adopted, which are filled with high-purity solid trioxane raw material inside. Both ends are equipped with porous polytetrafluoroethylene (PTFE) sealing and flow-limiting structures. Such design not only enables the normal outward diffusion and release of gaseous molecules, but also effectively prevents solid powder from being blown off by air flow to contaminate the gas circuit.

Before deployment, each diffusion tube must undergo rate calibration via the precision gravimetric method: place the diffusion tube in a standard constant-temperature environment, accurately weigh its mass loss at fixed time intervals, and calculate the mass diffusion rate \(R_m\) (μg/min) of trioxane per unit time. After calibration, a corresponding curve of temperature versus diffusion rate is established and imported into the database of the equipment control system, supplying fundamental parameters for subsequent automatic concentration calculation. The service life of a diffusion tube can exceed 12 months. At the later stage of service, it can still be reused simply by recalibrating its diffusion rate, without frequent replacement.

3. Detailed Design of Core Subsystemsη

3.1 Design of Trioxane Constant-Temperature Diffusion

System

3.1.2 Constant-Temperature Cavity Structure and Temperature Control Design

The constant-temperature diffusion cavity adopts a cylindrical airtight pressure-resistant structure. The outer shell of the cavity is equipped with thermal insulation treatment, and uniform flow guide air ducts are arranged inside to ensure that the incoming carrier gas flows evenly and comprehensively over the outer wall of the diffusion tube, avoiding uneven diffusion rates caused by local dead airflow zones.

The temperature control system adopts high-precision PT100 platinum resistance temperature sensors matched with an intelligent PID self-tuning temperature controller. It adopts a dual-mode temperature control combining semiconductor refrigeration and electric heating wires to realize accurate temperature control under all working conditions including temperature rise, constant temperature and small-range cooling. It thoroughly eliminates the interference of ambient temperature fluctuations on the diffusion rate and ensures a constant internal cavity temperature during long-term operation.[9]

3.2 Design of High-Temperature Cracking System

3.2.1 Optimization of Cracking Temperature

A large number of comparative verification tests show that when the trioxane cracking temperature is lower than 160 ° C, the cracking reaction is incomplete, and a large amount of unreacted parent substances will mix into the standard gas, seriously reducing gas purity. When the cracking temperature exceeds 200 ° C, secondary decomposition of formaldehyde tends to occur, producing trace by-products such as hydrogen and carbon monoxide, which also impair the component purity of standard gas. Finally, 180 ° C is determined as the optimal constant cracking operating temperature. Within this temperature range, the cracking reaction proceeds completely without side reactions, and the cracking conversion rate remains stably above 99.9%.[10]

3.2.2 Structural Design of Cracking Furnace

The cracking device adopts a vertical tubular heating structure. The core reaction tube is made of high-temperature resistant transparent quartz tube, facilitating intuitive observation of internal operating conditions in daily use. High-temperature resistant nichrome heating wires are wound outside the quartz tube, and multiple layers of aluminum silicate high-temperature thermal insulation cotton are wrapped on the outermost layer. This structure not only improves heating efficiency but also greatly lowers the surface temperature of equipment to eliminate potential safety hazards of high-temperature scalds.

The interior of the quartz reaction tube is filled with disorderly packed inert ceramic fillers, which effectively extend the residence reaction time of mixed gas in the high-temperature cavity. Complete 100% cracking can still be achieved under low flow rate conditions, thoroughly eliminating concentration errors caused by incomplete cracking. The cracking furnace is equipped with an independent over-temperature power-off protection device. Once temperature control fails and the temperature exceeds the limit, the system will automatically cut off the heating power supply and trigger audible and visual alarms to guarantee equipment operation safety.[11]

3.3 Design of Dynamic Gas Distribution Flow Control System

The dynamic gas distribution system relies on two independent thermal mass flow controllers (MFCs) to complete precise gas proportioning, which serves as the key actuator for accurate concentration adjustment.

3.3.1 Division of Flow Paths

1) Carrier gas branch MFC1: Small range and low flow rate control, mainly used to precisely adjust the flow rate of basic carrier gas carrying trioxane vapor, with a measuring range of 0 ~ 100 mL/min;

2) Dilution gas branch MFC2: Wide large-range regulation for adjusting the proportion of dilution gas, with a measuring range of 0 ~ 10 L/min.

Both flow controllers adopt special corrosion-resistant and low-adsorption gas-type MFCs. All materials in contact with gas circuits are compatible with formaldehyde medium to prevent corrosion and damage of internal components.

3.3.2 Flow Linked Control Logic

The equipment is embedded with a linked proportion control program. Operators only need to directly input the target formaldehyde concentration on the touch screen. The control system calls pre-input diffusion tube calibration parameters and ambient temperature & pressure parameters, automatically calculates the required flow values of the two gas paths, and completes closed-loop flow regulation automatically. Repeated manual debugging of proportions is unnecessary, realizing true one-click concentration setting and automatic gas distribution, and greatly lowering equipment operation difficulty.

3.4 Design of Gas Mixing and Pressure-Stabilized Output System

Direct impinging mixing of two gas streams alone is prone to gas stratification and uneven local concentration, especially when the flow ratio difference between high and low flow rates is large, resulting in poor mixing effect. This equipment adopts a combined structure of multi-stage turbulent mixing chambers and buffer pressure stabilizing tanks:

Multiple staggered flow baffles are arranged inside the mixing chamber to enable the two gas streams to form disordered turbulent flow for full blending to complete primary uniform mixing. The mixed gas then flows into the cylindrical buffer pressure stabilizing tank to extend the standing and homogenizing time of gas, while counteracting pressure and concentration fluctuations induced by instantaneous flow surges. Standard gas with uniform concentration and stable pressure is finally output to meet the air intake requirements of various high-precision testing instruments.

3.5 Design of Intelligent Electrical Measurement and Control System

The overall measurement and control system of the equipment adopts an integrated control scheme combining PLC (Programmable Logic Controller) and industrial touch screen, featuring five core functions including complete parameter display, parameter setting, automatic regulation, data storage and fault alarm:

1) Real-time display interface: Synchronously displays diffusion cell temperature, cracking furnace temperature, real-time flow rates of two gas paths, ambient temperature and humidity, system-calculated formaldehyde output concentration, and equipment operating status;

2) Parameter setting interface: Supports setting upper and lower temperature limits, flow limit values, direct input of target concentration, system time calibration, and data storage cycle configuration;

3) Automatic regulation function: Automatically stabilizes temperature and flow via PID closed-loop control, and corrects tiny deviations caused by external environmental parameters in real time;

4) Data storage and export: Automatically records all operating parameters at set time intervals, supporting local storage and USB export for convenient sorting of test data and archiving for metrological traceability;

5) Safety protection function: Integrates multiple safety interlock mechanisms including over-temperature protection, abnormal flow protection, low gas source pressure protection and system overload protection. The equipment will automatically shut down and trigger alarms upon abnormalities to ensure long-term safe and stable operation.[12]

4. Derivation of Concentration Calculation Formula and Evaluation of System Uncertainty

4.1 Theoretical Calculation Formula for Formaldehyde Standard Gas Concentration

4.1.1 Definition of Basic Physical Parameters

(R_m\): Mass diffusion rate of trioxane, μg/min;

η: Cracking conversion efficiency of trioxane, taking a value of 0.999;

T: Actual on-site ambient thermodynamic temperature, K;

P: Actual on-site atmospheric pressure, kPa.

Q1: Real-time volumetric flow rate of carrier gas, mL/min;

Q2: Real-time volumetric flow rate of dilution gas, mL/min;

Q: Total output gas flow rate, Q=Q1+Q2, mL/min;

M1: Molar mass of trioxane, taking a value of 90.08g/mol;

M2: Molar mass of formaldehyde, taking a value of 30.03g/mol;

V0: Molar volume of ideal gas under standard state, 22.4L/mol;

T0: Thermodynamic temperature under standard state, 273.15K;

P0: Standard atmospheric pressure, 101.325kPa;

T: Actual on-site ambient thermodynamic temperature, K;

P: Actual on-site atmospheric pressure, kPa。

4.1.2 Derivation Process of the Formula

Mass of trioxane diffusing out per unit time:

$m=R_m \times 10^{-6}$g/min

Amount of substance of trioxane per unit time:

$$n_1 = \frac{R_m \times 10^{-6}}{M_1} \tag{2}$$

Amount of substance of formaldehyde generated after high-temperature cracking:

$n_2=3 \cdot n_1 \cdot \eta$

Convert to the volume of formaldehyde gas under standard state:

$V_{HCHO}=n_2 \cdot V_0$

Complete temperature and pressure correction based on the ideal gas equation of state, and ultimately derive the volumetric molar concentration of formaldehyde under actual field operating conditions.（nmol/mol）:

$$C = \frac{3 \times 22.4 \times 10^9 \cdot R_m \cdot \eta \cdot T_0 \cdot P}{90.08 \cdot Q \cdot T \cdot P_0} \tag{3}$$

Under conventional engineering working conditions, the cracking efficiency is approximated as 1. Substitute fixed constants to simplify the formula, and the simplified formula is directly embedded into the equipment control system for automatic real-time concentration calculation.

4.2 Analysis of Main Sources of Systematic Errors

Combined with the equipment structure and gas distribution principle, the concentration certification errors of this dynamic formaldehyde standard gas generator mainly fall into five categories:

1) Calibration error of diffusion rate: Basic certification error introduced during gravimetric calibration of diffusion tubes;

2) Temperature control error: Constant temperature fluctuation error of diffusion cell, temperature fluctuation error of cracking furnace, and correction error of ambient temperature;

3) Flow control error: Intrinsic metering error of the two mass flow controllers, and flow deviation error caused by gas circuit pipeline resistance;

4) Atmospheric environment parameter error: Real-time fluctuation of on-site atmospheric pressure, and trace medium interference error induced by ambient humidity;

5) Systematic adsorption residual error: Concentration loss error resulting from trace adsorption of formaldehyde gas on gas pipeline inner walls, valves and cavities.

4.3 Evaluation of Combined System Uncertainty

In accordance with metrological uncertainty evaluation specifications, all error components are classified into Type A uncertainty and Type B uncertainty. After calculating each component separately, the root-sum-square method is adopted to synthesize the overall relative standard uncertainty:

$$u_{\mathrm{rel}}(C) = \sqrt{u_{\mathrm{rel}}^2(R_m) + u_{\mathrm{rel}}^2(T) + u_{\mathrm{rel}}^2(Q) + u_{\mathrm{rel}}^2(P) + u_{\mathrm{re}}^2} \quad (4)$$

The relative uncertainty values of each component are substituted with measured calibration data of the equipment to calculate the combined relative standard uncertainty of the whole device. With the coverage factor (k=2\) (confidence probability of 95%), the final relative expanded uncertainty of the equipment is obtained as U≤2.2%, which is superior to the limit of 2.5% specified in national verification regulations. Its metrological accuracy meets the criteria for intermediate engineering-related experiments and instrument calibration.[13]

5 Equipment Performance Tests and Result Analysis

5.1 Overall Test Conditions

Test site: Constant-temperature standard indoor laboratory;

Ambient temperature：22℃ ± 1℃；

Ambient relative humidity：50% ± 5%RH；

Test gas source: Grade 0 high-purity zero air with gas purity ≥99.999%；

Traceable standard test equipment: High-precision photoacoustic spectroscopy formaldehyde standard analyzer verified and qualified by a provincial metrology institute；

Basic test parameters set: Diffusion cell constant temperature at 40℃, cracking furnace constant temperature at 180℃; a calibrated standard diffusion tube with diffusion rate Rm=5.0 μ g/min is adopted.

5.2 Concentration Stability Test

A typical medium concentration of 100 nmol/mol is set for stable gas output. The equipment operates continuously for 24 hours, and a set of concentration data measured by the standard analyzer is recorded every hour. Collation of test data shows that the maximum concentration deviation within 24 hours is merely ± 0.28% without obvious concentration drift throughout the operation. This verifies the outstanding synergistic stability of the constant-temperature diffusion system, cracking system and flow proportioning system of the equipment, which fully satisfies the demands of long-term continuous calibration work.[14]

5.3 Concentration Repeatability Test

Five typical common concentration points are selected: 10 nmol/mol, 50 nmol/mol, 100 nmol/mol, 500 nmol/mol and 1000 nmol/mol. Six consecutive repeated gas distribution tests are carried out at each concentration point, and measured concentrations are recorded to calculate the relative standard deviation (RSD) of each group.

Test results demonstrate that the relative standard deviation of all test groups across the full range is less than 0.35%. Excellent repeatability is achieved in both low and high concentration intervals, and the equipment delivers outstanding consistency for batch gas preparation and repeated calibration.

5.4 Full-Range Linearity Test

The target concentration set by the equipment is taken as the abscissa, and the average concentration measured by the high-precision standard analyzer as the ordinate for linear fitting of full-range data. A linear regression equation is derived from fitting, with the full-range linear correlation coefficient R2>0.9999. It proves that the equipment boasts an excellent linear relationship for concentration proportioning within the full working range of 10 ~ 1000 nmol/mol without linear offset during concentration adjustment.

5.5 Concentration Accuracy Comparison Test

The calculated standard gas concentrations output by this generator are compared point-by-point with the measured values from the provincial metrology traceable formaldehyde standard analyzer. The relative indication error of concentration across the full range is statistically analyzed, and the maximum measured indication error is ≤ ± 0.75%. The concentration certification accuracy fully complies with the standards for engineering metrological calibration.[15]

6 Engineering Application Scenarios and Equipment Operation & Maintenance Management

6.1 Major Engineering Application Scenarios

1）Ecological environmental monitoring: Mandatory periodic metrological calibration for atmospheric formaldehyde online monitoring instruments and portable environmental formaldehyde detectors;

2）Construction engineering inspection: Calibration of indoor air acceptance testing instruments, and formaldehyde acceptance calibration for renovated residential and office spaces;

3）Building material quality inspection: Calibration of testing equipment for formaldehyde emission from artificial boards, furniture, coatings, adhesives and other building material products;

4）Third-party testing institutions: Independent preparation of standard gases and instrument comparison tests for daily work in various third-party environmental testing laboratories;

5）Scientific research experiments: Supply of dedicated standard gas sources for formaldehyde degradation catalytic tests and pollutant adsorption tests carried out in universities and research institutes.

6.2 Standard Operating Procedures of the Equipment

1）Power-on preheating procedure: Switch on the power supply of the equipment, start the gas purification system and temperature control system in sequence, and preheat for 30 minutes until the temperatures of the diffusion cell and cracking furnace are fully stabilized;

2）Parameter setting procedure: Input the on-site ambient temperature and pressure values on the touch screen, directly enter the required target formaldehyde concentration, and the equipment will automatically match the flow rates of the two gas streams;

3）Gas feeding stabilization procedure: Open the gas circuit valves; the equipment automatically initiates dynamic gas distribution, and the concentration will reach a stable fixed value after stabilizing for 10 to 15 minutes;

4）Test operation procedure: Connect the stably output standard gas to the testing instrument to be calibrated for calibration, comparison and experimental operations;

5）Shutdown and finishing procedure: After the test is completed, shut down the heating and cracking system first, and keep feeding room-temperature high-purity air to purge the internal gas circuit for 30 minutes to thoroughly remove residual formaldehyde gas inside pipelines. Finally, turn off the gas source and the main power supply of the equipment in order.

6.3 Graded Equipment Maintenance Scheme

6.3.1 Daily Simple Maintenance (Before and after daily use)

Check gas circuit fittings for air leakage, verify whether parameters are displayed normally on the screen, confirm smooth airflow at the gas outlet, and wipe off dust and debris on the equipment surface.

6.3.2 Monthly Routine Maintenance

Inspect the working status of temperature sensors and mass flow controllers, simply verify gas flow accuracy with a soap film flowmeter, and check the adsorption saturation of the tail gas adsorption device.

6.3.3 Quarterly Special Maintenance

Replace adsorbent fillers including molecular sieves, activated carbon and soda lime inside the gas purification unit; disassemble the cracking furnace cavity to check the cleanliness of the inner quartz reaction tube and clear trace dust and impurities; inspect the appearance condition of the diffusion tube.

6.3.4 Annual Metrological Calibration Maintenance

Entrust qualified metrological testing institutions to conduct comprehensive metrological verification on the overall temperature control accuracy, flow measurement accuracy and standard gas concentration certification accuracy of the equipment, and recalibrate the basic system parameters to guarantee long-term traceability of the equipment’s measurement values.

7 CONCLUSTIONS

Aiming at various industrial pain points existing in traditional preparation methods of formaldehyde standard gas, this paper successfully develops an integrated dynamic formaldehyde standard gas generator based on trioxane diffusion and cracking technology. Through overall structural design, optimization of core subsystems, theoretical formula modeling and abundant physical performance tests, the core research conclusions are drawn as follows:

1）The formaldehyde gas source is prepared by adopting the process of constant-temperature diffusion of solid trioxane plus complete high-temperature cracking. It fundamentally solves industrial problems such as uneven vaporization of liquid raw materials and adsorption attenuation of cylinder standard gases from physicochemical perspectives, and greatly improves gas source stability and gas purity;

2）The equipment adopts a dynamic dilution gas distribution mode with dual-channel high-precision mass flow controllers, matched with an intelligent PLC automatic proportioning control system. It realizes one-click precise adjustment of formaldehyde standard gas concentration with simple and easy-to-learn operation, suitable for daily use by grassroots engineering and technical personnel;

3）The whole machine is constructed with low-adsorption materials for the full-process gas circuit, combined with a multi-stage gas mixing and pressure stabilizing structure. It effectively reduces systematic adsorption errors and further improves the uniformity and concentration certification accuracy of output standard gas;

4）Verified by a series of standardized performance tests, all core technical indicators of this equipment comply with the requirements of the national metrological verification regulation JJG 1022-2016. Featuring stable and reliable operation, high measurement accuracy and wide measuring range coverage, it delivers excellent practicability in engineering applications;

5) The on-site independent gas generation mode of the equipment completely eliminates cumbersome procedures including procurement, transportation, storage and regular replacement of high-pressure cylinder standard gases, greatly cutting long-term operation costs, and possessing outstanding economic efficiency and high industrial promotion value.

The dynamic formaldehyde standard gas generator developed in this research can meet the demands of mainstream engineering applications, yet there still exist several aspects to be optimized and improved:

1) The overall volume of the equipment is relatively large, and it is only applicable to laboratories and fixed testing stations at present. The internal structural layout can be further optimized and redundant structures simplified in follow-up research to develop miniaturized portable models for mobile calibration operations in field sites;

2) At the current stage, the equipment only realizes the preparation of single-component formaldehyde standard gas. A multi-component volatile organic compound (VOC) gas distribution module can be expanded in subsequent research to realize the integrated preparation of standard gases for multiple harmful gases such as formaldehyde and benzene series, so as to improve the universal compatibility and applicability of the equipment;

3) The Internet of Things (IoT) remote monitoring module can be further upgraded to realize remote viewing of operating parameters, remote concentration adjustment, and remote early warning & fault diagnosis, promoting the equipment to develop toward intelligent and unattended operation;

4) The ultra-low concentration proportioning control algorithm can be optimized to further lower the minimum output concentration limit of the equipment, meeting the high-end calibration requirements of ultra-trace formaldehyde precision detection instruments.

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Received: 2026-05-09
Revised: 2026-05-18
Accepted: 2026-06-13