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STUDY OF COMPUTER CONTROL DYNAMIC VOLUMETRIC METHODS AND PREPARATION OF WATER CALLIBRATION GASES

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Abstract – A new type apparatus of dynamic volumetric calibration system was designed and made in correspond with ISO 6145. The main parameters of dynamic volumetric method can be monitored, recorded and calculated by a personal computer. The calibration gases of water in nitrogen with ranges of 10^{-7}~10^{-6} mol/mol were prepared in the form of diffusion tubes by dynamic volumetric method. Test in comparison with a standard dew point apparatus expressed that the water diffusion tubes are reliable and accurate, and the uncertainties of the calibration gases of water in nitrogen are in the ranges of 3%~4%.

Key word: Dynamic Computer Water diffusion tube.

1. INTRODUCTION

The calibration gases were used widely in many fields. As the development and increasing of variety environmental monitoring and investigation. The market requirement amounts of volatile, corrosive and adsorptive calibration gases in the ranges of 10^{-8} ~ 10^{-5} were increased quickly. However, for the kinds of these calibration gases prepared by gravimetric method could not meet the requirement stability and accuracy, and also difficult to guarantee the traceabilities of these kinds of calibration gases. ISO 6145 expressed that the calibration gases prepared by dynamic volumetric methods can be used to purge sampling lines and instrumentation, and minimize adsorption effects that are prevalent with these substances [1]. In 1978, The first apparatus of diffusion tube calibration gases prepared by dynamic volumetric methods were designed and made by US Instrument Analysis Company [2]. In 1980, the dynamic volumetric methods diffusion was recommended by ISO. Afterwards, there are lot of researches about the dynamic volumetric methods diffusion in the past teen years [3~6]. But the computer control dynamic volumetric methods have been not studied yet. This paper designs a new type apparatus of dynamic volumetric calibration system to be controlled by a personal computer and gives the merits of the computer control dynamic volumetric methods. With the apparatus designed, the water diffusion tube calibration gases in the ranges of 10^{-7} ~ 10^{-6} were prepared and verified by a standard dew point apparatus. The test results expressed that the water diffusion tubes are reliable and accurate, and the uncertainties of the diffusion tube calibration gases of water in nitrogen are in the ranges of 3%～4%.

2. DYNAMIC METHOD AND APPARATUS DESIGNING

2.1 Principle of Dynamic method

By selection of appropriate combinations of diffusion cell design, flow rates and temperatures and with the use of pure liquid phase from which to derive the components in the vapour phase, and a dilutent gas, the volume fraction of the component of interest can be varied within a range of 10^{-6} ~ 10^{-9}. As different minor components can influence the design characteristics of a diffusion cell including the material of construction and its dimensions, the user should refer to the relevant manufacturers for technical advise on the maximum flow achievable. The minor component of the calibration gas mixture is placed in its liquid state in a suitable diffusion cell and its vapour diffuses along a uniform tube. A stream of dilutent gas at known flow rate passes across the further end of the tube where it mixes with the component flow producing the calibration gas mixture. Varied concentrations can be achieved by changes in flow rate of the dilutent gas.

2.2 Apparatus designing

The basic system for the computer control dynamic volumetric method is shown in Fig. 1.

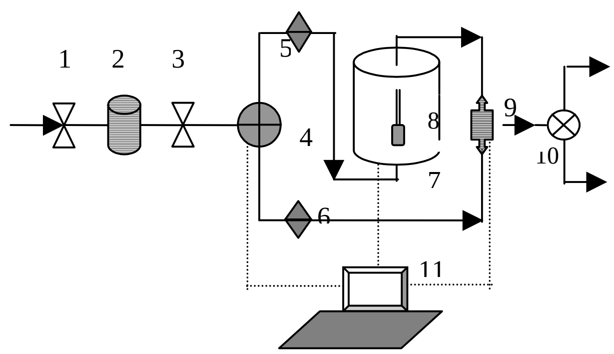

Fig. 1. Schematic Diagram of Dynamic Volumetric Method

Where, (1) and (3) pressure maintaining valve; (2) drying and purifying installation; (4) mass flow meter; (5) and (6) flowrator;

(7) air thermostatic bath; (8) diffusion tube; (9) mixing chamber with temperature and pressure sensor; (10) three-port valve; (11) personal computer

The photocopy of the dynamic volumetric method system and the water diffusion tubes are displayed in Fig. 2 and Fig. 3 respectively.

Fig. 2. The dynamic volumetric method apparatus

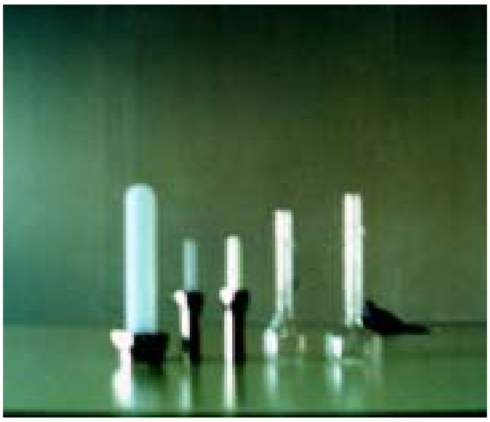

Fig. 3. The designed water diffusion tubes

The apparatus was designing and making according to the ISO 6145-8 (Gas Analysis, Preparation of calibration gas mixtures - Dynamic volumetric methods). The personal computer was introduced into the system and the control operation software was compiled by application the Lab Windows / CVI of The US National Instruments. Communications between the main controllers such as temperature, pressure and flow etc. and the personal computer were realised. The main parameters can be displayed and recorded and calculated by the computer. And the instantaneous possible variation of the principal parameters of the technique as well as any possible drift of these parameters during the calibration procedure can be plotted and calculated by the computer immediately. This will increase the accuracy of the reading and getting parameters and improve the practical of the dynamic volumetric method.

2.3 *The apparatus performance parameters*

The main performance *parameters* are listed in table 1.

TABLE 1. The apparatus performance parameters

Air thermostatic bath Temp.	Flow	Pressure	Mixing cell Temp.
±0.05^{0}C	±1 ml/min	±200 Pa	±0.02^{0}C
Rel. Stand. Uncertainty, %	Rel. Stand. Uncertainty, %	Rel. Stand. Uncertainty, %	Rel. Stand. Uncertainty, %
0.1	0.7	0.7	0.1

2.4 Sources of uncertainty

By take into consider all kinds of the factors that could effect the uncertainty of the dynamic method. The relative standard uncertainty of the calibration gases prepared by the apparatus can be combined by equation (1):

$$\mu_c = \frac{\mu_c[C(x)]}{C(x)} = \sqrt{\mu_T^{\,2} + \mu_p^{\,2} + \mu_Q^{\,2} + \mu_R^{\,2} + \mu_x^{\,2} + \mu_W^{\,2}} \qquad (1)$$

Where, μ_c is the relative standard uncertainty of the dynamic method; μ_T is the temperature determination relative uncertainty; μ_p is the pressure determination relative uncertainty; μ_Q is the gas flow determination relative uncertainty; μ_R is the diffusion rate determination relative uncertainty; μ_x is the purities of the component of interest determination relative uncertainty; μ_w is the weight measurement relative uncertainty. The total uncertainty of the apparatus is about within the range of 2% and 5% with 95% confidence interval and a coverage factor is 2.

3. STUDY OF WATER CALIBRATION GASES

3.1Method

*W*hen high volumes of a calibration gas mixture are needed or adsorption problems are critical, it is essential that the mixture is obtained continuously through a interest source in the stationary state and in a dilution gas flow. Knowledge of the interest dilution gas rate is also required. Thus, the fundamental problem for the dynamic gas mixture production is the appropriate choice of the generation source. As the preparation of a calibration gas mixture from volatile adsorption liquids was a problem, it was decided to use the diffusion method to solve it. The gas diffusion phenomenon is represented by the empirical rate diffusion equation [4]:

$$R = 2.21\times10^6 \times \frac{DMPA}{TL}\log(\frac{P}{P-p}) \qquad (2)$$

Where, R=diffusion rate (μg/min); D=diffusion coefficient (cm^2/s); M=molecular mass of the compound investigated (g/mol); P=pressure in the diffusion cell (kPa); p=partial pressure of the diffusion vapour at temperature T (kPa); T=absolute temperature of diffusion tube (K); A=cross-sectional area of the diffusion tube (cm^2); and L=diffusion path length (cm).

The non-ideal behaviour of equation (2) has already been verified, therefore, it can not be applied directly to predict the diffusion rate of real system. But the theoretical estimate of the diffusion rates provided useful indications to assess if the volatility of compounds investigated was sufficiently high to make the gravimetric method reliable and not time-consuming, and give the useful information to the designing of an alternatives diffusion tube.

The water diffusion tube calibration gases was prepared in this job. Firstly, the dilution gas was purified by a series of purifier and dried by phosphorus pentoxide dryer. And the dilution gas dew point is about in the ranges of $-85\ ^0C \sim -86^0C$. The water used in this job is three times de-ionized water and the electric resistance is about 17.8 MΩ.cm. Then, the water calibration gases was produced by the dynamic apparatus and inspected and compared by a standard dew point control instrument. At last, the total uncertainty of the water calibration gases was estimated.

3.2 Experimental

The real diffusion rate of diffusion cell can be determined by periodic weighing and calculation of the mass release rate from the mass difference and the time interval between weighings.

The diffusion rates of water at different temperature were determined by using the diffusion tubes (gemetrically different) and a carrier gas (nitrogen) flow of 150 ml/min. The results were listed in table 2. The purity of the carrier gas nitrogen is 99.999%, which was dried by a series of dryer containing the power of phosphorous pentoxide (P_2O_5) before it got into the air thermostatic bath where the diffusion tube was laid.

TABLE 2. Diffusion rate of water at a carrier gas (N_2) of 150 ml/min

Temp. (±0.05 ^0C)	Diffusion tube 1 (A=5.3×10^{-2} cm^2; L=7.2 cm)	Diffusion tube 2 (A=2.3×10^{-2} cm^2; L=7.2 cm)
30.00	5.6 ± 0.2	3.1 ± 0.3
40.00	± 0.2	5.3 ± 0.2

With the diffusion rate of water diffusion tube we can calculate the content of water calibration gases prepared by the apparatus (dynamic calibration system) designed.

$$C_0 = \frac{P_0 V_0 T R}{T_0 P M Q} \times 10^3 \qquad (3)$$

Where C_0, P_0, V_0 and T_0 are the water calibration gases content (μmol/mol), standard air pressure (kPa), gas mole volume (dm^3) and absolute temperature of zero (K), respectively. P and T are the pressure (kPa) and temperature (K) of the mixing chamber, respectively. R, M and Q are the diffusion rate (μg/min), molecular mass (g/mol) and total flow of the carrier gas and dilution gas (ml/min), respectively.

In order to verify and test the water calibration gases prepared by the apparatus, the value of water calibration gases were determined by a standard Dew Point Control Instrument. Table 3 lists the experimental results.

TABLE 3. The experimental results of the water calibration gases determination by a standard dew point control instrument

Water calibration gases prepared by the apparatus, C_1, μmol/mol	Deter. by a standard dew point control instrument: Dew point, ^0C	Deter. by a standard dew point control instrument: Content, C_2, μmol/mol	Rel. Deviation %, $D_v = \frac{C_1 - C_2}{C_1} \times 100\%$
14.6	-57.4	15.1	3.4
12.1	-58.7	12.7	5.0
9.15	-61.0	9.32	1.9
8.13	-61.6	8.59	5.7
7.32	-62.4	7.69	5.1
		Average:	4.2

The combination of the uncertainty of diffusion tube calibration gases of water in nitrogen is listed in table 2.

TABLE 2. The combination of the uncertainties of water calibration gases in nitrogen

Types of Rel. Stand. Uncertainties %	Deter. of diffusion rate	Deter. of flow rate	Deter. of pressure	Deter. of water purity	Deter. of dilution gas	Deter. of temper atures	Total uncertai nty U_K, (K=2, 95%)
Water in nitrogen	1~1.6	0.6	0.5	0.05	0.5	0.1	3~4

4. CONCLUSIONS

A personal computer was introduced in the dynamic volumetric methods in this work. With the pressure sensor installed in the mixing chamber, we got the quantity results of the pressure variation and their effects to the total uncertainty of the dynamic calibration system. It will be useful to solve the problem of pressure variety and their effects to the diffusion rate. In this apparatus, we can read and calculate the main parameters immediately, thus, the dynamic characteristics could be realised and give the results more accurately and effectively.

The experimental expressed that the water diffusion tube calibration gases prepared by the apparatus designed in the ranges of 10^{-7} ~ 10^{-6} mol/mol are stability and valuable, and could be used as a standard gas generation source. The total uncertainty of the water calibration gases prepared by the apparatus is about within the range of 3% and 4% with 95% confidence interval and a coverage factor is 2.

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