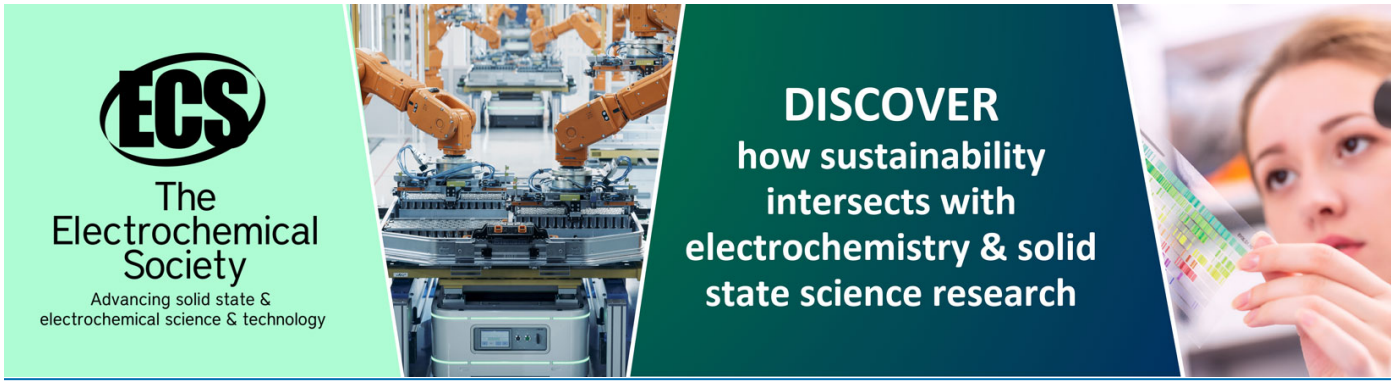
Headspace-Gas Chromatography Method for Determination of Formaldehyde Content in Wastewater



Headspace-Gas Chromatography Method for Determination of Formaldehyde Content in Wastewater

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Abstract: Through the use of headspace-gas chromatography, the sensitivity and detection limit of formaldehyde content in wastewater obtained by the standard curve method and the standard addition method are compared in order to obtain the best detection method. The results show that the calibration curve correlation of the standard insertion method for testing the formaldehyde content in wastewater is 0.9991, the detection limit of the method is 0.18 mg/L, and the lower limit of determination is 0.69 mg/L. Excellent standard curve method; this method is used for samples with low, medium and high concentrations. The range of standard recovery rate calculated is 85.1%~112.9%, the relative standard deviation in the laboratory is 2.7%~ 6.3%, which is also better than the standard curve method and meets the test requirements. This method is easy to operate, high sensitivity, and low detection limit for the determination of formaldehyde in wastewater, which meets the requirements of analysis and testing.

1. INTRODUCTION

Formaldehyde is harmful to human health, long-term exposure can cause cancer and teratogenicity. The minimum discharge standard of formaldehyde in the "Integrated Wastewater Discharge Standard" is 1.0mg/L.

Formaldehyde Content test when water has made the use of gas chromatography, as Yao Yao et al[1] found by solid phase microextraction-gas chromatography feasible for determination of trace formaldehyde in water; Gu Xiao-chun[2]that uses purge and trap-The gas chromatography method for the determination of formaldehyde in surface water is simple, with high enrichment efficiency and low detection limit, which meets the requirements of analysis and testing; Wang Ru et al[3] believe that the purge and trap-gas chromatography method is suitable for the analysis of formaldehyde and acetaldehyde in surface water .

The headspace-gas chromatography method is also feasible for the measurement of formaldehyde content in water. Zhang Yan-jun[4] uses the headspace-gas chromatography method to determine the formaldehyde content in surface water and believes that this method is suitable for the determination of formaldehyde content in surface water. Different from surface water, wastewater contains a large number of interfering substances. In the process of surface water testing, a better accuracy and precision test method can be obtained. It may not be applicable when testing wastewater. For example, Lu Guibin[5]uses purge and trap. Set-gas chromatograph, the recovery rate of formaldehyde content in

wastewater obtained by the standard curve method is only 78.0%.Therefore, it is necessary to study a test method suitable for the content of formaldehyde in wastewater.

2. MATERIAL ANG METHOD

2.1 Instruments and reagents

American Agilent 7890A gas chromatograph, hydrogen flame ionization detector (FID), EW-2HS headspace sampler, NHA-300 nitrogen-hydrogen air integrated machine, DB-WAX chromatographic column. Formaldehyde standard solution (BW3450): developed by the Chinese Academy of Metrology, diluted with ultrapure water to 96mg/L formaldehyde standard intermediate solution.

2.2testing method

Sampling: According to HJ 494-2009 "Water Quality Sampling Technical Guidelines".

Calibration curve: Measure 9mL of ultrapure water / water sample and add it to a headspace bottle containing 3g of sodium chloride (dry to constant weight), shake gently, and add 0mL, 0.05mL, 0.1mL with a pipette, respectively, 0.2mL, 0.4mL, 0.6mL, 0.8mL, 1mL formaldehyde standard intermediate solution, dilute to 10mL, and seal it.

Precision and recovery rate experiment: Take a water sample and divide it into 8 evenly for precision experiment; take another water sample and add a fixed concentration of formaldehyde standard intermediate solution to calculate the recovery rate.

Headspace sampling conditions: sample 10ml, equilibrium temperature 60℃, equilibrium time 20min.Chromatographic conditions: column temperature 160℃, injection port temperature 180℃, FID detector temperature 220℃.

2.3Calculation

Calculated according to HJ 168-2010 "Technical Guidelines for the Development and Revision of Environmental Monitoring and Analysis Methods Standards", and statistical analysis using Origin Lab software.

3. RRSULTS AND DISSCUTION

3.1Two different test methods

Prepare a calibration curve with water samples and ultrapure water as the diluted solution, add 0mg/L ~ 10mg/L formaldehyde to qualitatively determine the retention time and quantify the peak area. Calculate the formaldehyde content in the water sample. The test results are shown in Fig. 1 :

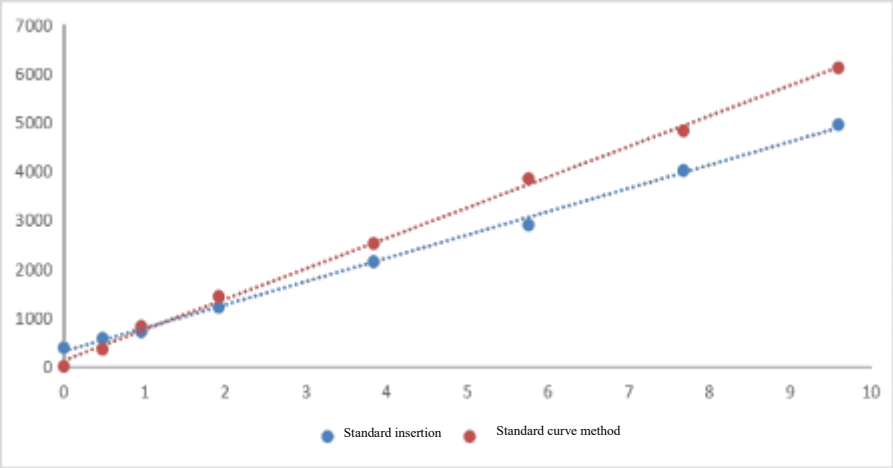

Fig. 1 Linear fitting results of two standard curves

It can be seen from Fig. 1 that the slope of the standard curve method is smaller and the intercept is small, and its response value is positively correlated with the content of the analyte; the response value of the standard interpolation method is slightly higher than that of the standard curve method at low concentrations, which may be related to water Formaldehyde itself is related to the base substance in the sample.

3.2Detection limit of standard addition method

Dilute the water sample to a suitable concentration according to the sample analysis procedure, repeat the test 8 times, and calculate the standard deviation of the parallel determination and the detection limit of the method. The results are shown in Table 1 : It can be seen that during the test of formaldehyde content, the correlation coefficient of the calibration curve can meet the standard requirements, and the detection limit of the standard interpolation method is slightly lower than that of the standard curve method, and the sensitivity is higher.

Table 1 Regression equations and detection limit results obtained by different methods

testing method	Curve equation	relativity	Standard deviation S	Method detection limit MDL	Lower limit of determination
Standard insertion	y = 625.38x+123.32	0.9991	0.06	0.18	0.69
Standard curve method	y = 476.93x+306.71	0.9990	0.08	0.24	0.90

3.3 Two different standard addition methods test accuracy and precision

Test 8 parts of water spiked samples, water samples spiked by a low base concentration 0.48mg / L, a concentration of 3.84mg / L and a high concentration
7.68mg/L test, obtained accuracy and precision levels from different calibration curves, the results show (Table 2): The formaldehyde content obtained by the two standard methods in testing the formaldehyde content of the water sample is 0.64mg/L respectively, 0.71mg/L, the difference is not big; in the sample addition test, the recovery rate of the standard insertion method performed well, ranging from 85.1% to 112.9%, and the relative standard deviation range from 2.7%~6.3% ; the recovery rate of the standard curve method is 63.5%~141.3%, and the relative standard deviation range is 2.2%~4.6%.This may be related to the interfering substances in the water sample matrix.

Table 2 Accuracy and precision statistics of different concentrations

testing method	Water sample formaldehyde base mg/L	Sample spike amount mg/L	Standard recovery rate %	relative standard deviation %
Standard insertion	0.64	0.48	90.0 ~ 108.0	6.3
		3.84	105.6 ~ 112.9	2.7
		7.68	85.1 ~ 96.6	4.5
Standard curve method	0.71	0.48	63.5 ~ 87.1	2.2
		3.84	131.6 ~ 141.3	2.9
		7.68	108.2 ~ 123.3	4.6

4. CONCLUSION

When the composition of the headspace gas is different from theoriginal composition, the impact on the quantitative analysis is very serious, and the quantitative analysis error is large. The standard

addition method is a widely used test method to check the accuracy of the instrument. This method can check whether there are interfering substances in the sample.

The calibration curve obtained by the two test methods in the testing process of this laboratory has excellent linearity and correlation, which can meet the needs of normal quantification; the standard interpolation method calibration curve and the standard curve method intersect near the low concentration, and the high concentration When the corresponding value is lower, this may be related to the matrix sample containing formaldehyde and volatile substances.

Repeat the test of the blank sample 8 times, the detection limit and the limit of quantification of the standard insertion method are better than the standard curve method; through the addition test of low, medium and high concentrations of water samples, the laboratory standard obtained by the standard insertion method The deviation and recovery rate of standard addition are also better than the standard curve method, indicating that the test method is feasible.

This paper compares the accuracy and precision of the standard curve method and the standard insertion method. The result is that the standard insertion method has better accuracy and precision than the standard curve method, higher sensitivity and easier It is more applicable to detect accurate sample content.

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