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Determination of methane-D4 and ethane-D6 in ethylene-D4 by gas chromatography

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Abstract: *Deuterated ethylene-D4 is a special molecule formed by replacing the hydrogen atom-^1H on the molecule with deuterium atom-D. It has more stable properties and can significantly improve the chemical stability of the corresponding site. The special properties of ethylene-D4 make it have important applications in fields such as healthcare, military manufacturing, aerospace, and aviation. With the continuous development of science and technology, the application of ethylene-D4 is becoming more and more extensive, and the quality requirements for ethylene-D4 products are also increasing. Deuterated methane-D4and deuterated ethane-D6 are the main deuterated impurities in ethylene-D4 products, and their concentration seriously affects the quality of ethylene-D4 products. Therefore, it is necessary to study a detection method to meet the requirements. A method was developed for the determination of methane-D4 and ethane-D6 impurities in ethylene-D4 products by gas chromatograph, using gas valve injection and alumina (deactivated by sodium sulfate) capillary column. Through the selection of chromatographic column, the optimization of shitter ratio and column flow instrument conditions, the peak order of the compound is changed to avoid the interference of the principal component on the impurity detection. The qualitative and quantitative analysis is carried out under the hydrogen flame ionization detector. By using the external standard method, record the peak areas of each component and directly calculate the content of the compound. Methane-D4 and ethane-D6 compounds have good linearity in the range of 0.0020 % ~1.00 %, and the correlation coefficient (R^2) is greater than 0.995. The method detection limits of the two components were 0.0003% and 0.0002%, and the recoveries were 97.1% ~106.1% and 97.3% ~104.7%, precision range between 1.95%~ 3.73% and 1.65%~2.98%. The established method was applied for actual sample detection, the three components of deuterated ethylene, deuterated methane, and deuterated ethane were completely separated. All types of components have good peak shapes and high responses, and the air component in the sample does not interfere with the target component. The method established by the research has the characteristics of simple operation, low detection limit, high accuracy, and good reproducibility, which meets the detection requirements of methane-D4 and ethane-D6 in ethylene-D4 products.*

Keywords: *gas chromatography; ethylene-D4; methane-D4; ethane-D6; determination*

1. Introduction

Ethylene-D4 (C_2D_4) is a special molecule formed by replacing the hydrogen atom (1H) on the molecule with the deuterium atom (D) [1]. Its physical and chemical properties are similar to those of ethene. However, the zero-point energy of carbon-deuterium bond is 0.047eV lower than that of C-H bond in olefin, and the property is more stable, which can significantly improve the chemical stability of the corresponding site [2]. This makes it have better application performance under certain specific conditions [3]. C_2D_4 is an isotope gas with special functions and wide application value, which is widely used as a monomer in the synthesis of high-performance polymers, as well as in the preparation of polymer materials such as polycarbonate, polyurethane and polyester. In addition, the special properties of C_2D_4 can also be used as an intermediate for laser target materials. It has critical applications in medical and health, military manufacturing, aerospace and other fields [4]. With the continuous development of science and technology, the application of C_2D_4 is more and more extensive, and the quality requirements of C_2D_4 products are also increasing. Methane-D4 (CD_4) and ethane-D6 (C_2D_6) are the main deuterated impurity components of C_2D_4 products, and their concentrations seriously affect the quality of C_2D_4 products.

Deuterated compounds are commonly detected by gas chromatographic mass spectrometer (GCMS), liquid chromatographic mass spectrometer (LCMS), nuclear magnetic resonance

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spectrometer (NMR), Raman spectrometer (CARS), etc. [5]. Resonance enhanced Raman spectroscopy (CARS) has the potential to analyze deuterated compounds because of its unique working principle. CARS is mainly based on the inelastic scattering of light. Through incident laser photons, the molecular vibration of Raman activity in the material is triggered to produce a specific optical signal, which can reflect the structure and characteristics of the molecule, thus displaying the unique "Raman fingerprint" of the compound. In the detection of deuterated compounds, the CARS method can achieve the qualitative and quantitative analysis of molecules to a certain extent. When used in deuterated drug research, the location of deuterated atoms and the strength of deuterated chemical bonds can be identified by the characteristic peaks in Raman Atlas. However, CARS technology is sensitive to experimental conditions (such as optical parameters and environmental factors), especially the system is vulnerable to optical interference, such as laser frequency drift, sample light scattering effect strength change and other limitations[3]. So that its practical application frequency is lower, and it is more in the basic science research stage at present.

Compared to CARS, nuclear magnetic resonance spectroscopy (NMR) is another very mature and reliable tool for analyzing deuterated compounds. It works on the basis of the magnetic moment generated by the spin of the atomic nucleus [6]. Under the external magnetic field, the orientation of the magnetic moment of the nucleus will change, thus absorbing electromagnetic waves and forming specific nuclear magnetic resonance signals. Deuterated compounds exhibit unique chemical shift and spin coupling patterns in NMR detection, which makes NMR an important means of qualitative analysis of deuteration rate, and can accurately identify the structure composition and deuteration location of samples by analyzing their spectra. Although NMR has a high ability to identify deuteration of molecular structures, its sensitivity is generally low, and there are significant limitations to the precise quantification of specific deuterated chemical species. Therefore, NMR is more suitable for high-precision qualitative studies, and is rarely directly applied to quantitative analysis [7].

GCMS and LCMS conduct qualitative analysis of analytes by detecting the relationship between ion mass charge ratio and relative strength, and quantitative analysis by ion strength [3]. However, LCMS is difficult to detect volatile gas samples [8]. GCMS is used to detect gas, the air component is easy to interfere with the determination of methane-D4 and other compounds. In summary, although many advanced analytical instruments can be used for the study of deuterium compounds, they cannot be applied in the actual industrial detection process.

Gas valve sampling - gas chromatography was used in this study. The retention time was determined using standard gases for qualitative purposes. The contents of CD_4 and C_2D_6 components in C_2D_4 products were directly calculated by using the external standard method of the peak area of each component. The proposed method has the advantages of simple operation, low detection limit, high accuracy and good reproducibility. It also provides a new idea for the determination of other deuterated compounds.

2. Test Section

2.1 Instruments and Reagents

To complete the determination and analysis of the component contents of CD_4 and C_2D_6 in the C_2D_4 sample in this study, the main instruments and reagents used in the test system were shown as follows:(1) 7890B Gas Chromatograph (Agilent) was selected, this type of gas chromatograph has high sensitivity, high stability, fast response and excellent performance for the separation and analysis of complex gas samples, which provides a reliable guarantee for the accurate detection of complex deuterated compounds. (2) Model 4600A Gas diluter (Beijing BCT Technology LTD) was selected, this diluter provides a stable, controlled dilution of the gas, ensuring that the concentration of the sample entering the gas chromatograph is precisely adjustable, further improving the accuracy and stability of the test results. (3) Max 40psig Suma jar (Beijing BCT Technology LTD) was selected, this type of Suma tank is passivated on the inside, excellent gas retention performance to avoid sample contamination or component degradation, which ensure the integrity and reliability of standard samples. (4) methane-D4 (CD_4, Peric Technology Co., Ltd, Chemical purity＞99%), ethane-D6 (C_2D_6, Peric Technology Co., Ltd, Chemical purity＞99%).

2.2 Standard Gas Preparation

In order to ensure the accuracy of the experimental data and the reliable construction of the standard

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curve, high precision gas distribution equipment was used in the preparation of the standard gas. And the experiment uses high-purity nitrogen (purity 99.999%) as the dilution gas and the Suma tank as the container. This measure can significantly reduce the possible adsorption or reaction loss of gas components.

CD_4 and C_2D_6 gases are mixed through the gas distribution device to prepare working standard gases of about 0.0020%, 0.0050%, 0.010%, 0.020%, 0.030% and 0.050% to draw a low concentration standard curve, and 0.050%, 0.20%, 0.40%, 0.60%, 0.80%, 1.00% of the working standard gas to draw the high concentration standard curve. Throughout the preparation process, all working standard gases are carried out in accordance with the principle of "use now mix" to ensure maximum stability of the gas sample and repeatability of each experimental operation.

2.3 Chromatographic condition

Inlet temperature: 220 ℃; hydrogen flame ion detector (FID); detector temperature: 240℃; oven temperature program: the initial temperature was 35 ° C for 2 min, the heating rate rose to 70 ℃ at 10 ℃/min and held for 3 min; carrier gas: nitrogen (99.999%); constant flow mode, column flow rate: 2.0 $ml \cdot min^{-1}$.

3. Results and Discussion

3.1 Optimization of chromatographic separation conditions

The purpose of optimization of separation conditions is to achieve the required separation results in the shortest analysis time. In C_2D_4 product impurities, CD_4 and C_2D_6 molecules are small, and the structure is similar, and the components are not easy to separate during the detection process. The chromatographic column, shunt ratio and column flow rate were selected and optimized through the test of standard gas.

3.1.1 Column Selection

The fixed liquid determines the polarity of the column, which is generally divided into non-polarity, weak polarity, medium grade and strong polarity. According to the principle of similar dissolution, the more similar the polarity, the stronger the adsorption of the fixed liquid to the substance, the longer the retention time.

Capillary chromatographic columns can be divided into: 1) Wall Coated Open Tubular Column (WCOT): The inner wall is pretreated, and then the fixing solution is applied to the inner wall of the capillary; 2) Carrier Coated Tubular Column (SCOT): In order to increase the coating amount of fixed liquid inside the open column, a layer of very fine porous particles is coated on the wall of the tube, the porous layer is coated with fixed liquid with thick film suitable for trace analysis. 3) Porous Layer Open Tubular Column (PLOT): A layer of porous adsorbent solid particles is coated on the tube wall, and the fixing solution is not coated.

In this study, PLOT gas chromatographic column is used. The porous layer capillary chromatographic column can reduce the phase ratio, and its fixed liquid film is thin, which is conducive to improving the mass transfer resistance and column efficiency, and is often used for the determination of volatile compounds. Hydrocarbon separation from C_1-C_{10} can be achieved above 35 ° C without cryogenic technology or low temperature cooling of column temperature chamber.

Two kinds of porous layer open tube chromatographic columns were selected experimentally. The HP-PLOT-Q (30m x 0.53mm x 40.0μm) column has a fixed term of polystyrene divinylbenzene, and the polarity is between Porapak-Q and Porapak-N. Specially developed for the separation of non-polar and polar target compounds. It has good separation effect for small molecule isomers such as C_1-C_3. However, because the peak position of C_2D_4 is in front of C_2D_6, the determination of C2D6 will be affected because the peak shape of C_2D_4 is too wide or trailing. Another HP-PLOT Al_2O_3S (25m x 0.53mm x 15.0μm) column is the weakest alumina stationary phase column, deactivated by sodium sulfate, especially suitable for C_1-C_8 hydrocarbon isomer analysis. The peak time of C_2D_6 in this column is before C_2D_4, so the integral quantification of C_2D_6 is not affected due to the wide peak type of C_2D_4. The improvement is shown in Figure 1.

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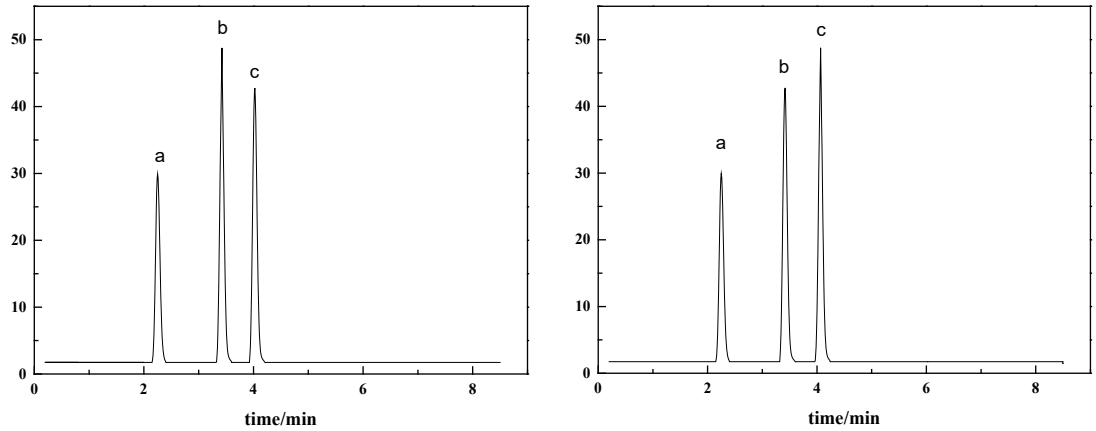

a——CD_4; b——C_2D_4; c——C_2D_6;
(I)CD_4, C_2D_6 and C_2D_4 chromatogram were determined by HP-PLOT-Q column

a——CD_4; b——C_2D_6; c——C_2D_4;
(II)CD_4, C_2D_6, and C_2D_4 chromatographs were determined by HP-PLOT Al_2O_3S

Fig.1 Standard sample chromatogram of CD_4, C_2D_6 and C_2D_4 on different columns

3.1.2 Shunt Ratio and Column Flow

Because the concentration of the components to be measured is low in the actual detection process, if the shitter ratio is too large, the actual sample volume of the injected gas chromatograph will be greatly reduced, resulting in a low response value of the instrument, so that some low-concentration group signals cannot be effectively detected and quantified. On the contrary, due to the high content of C_2D_4 in the sample, if the shard ratio is too small, the chromatographic peak of C_2D_4 will be wider, and the peak time will be moved forward, thus affecting the qualitative and quantitative determination of the components to be measured. In addition, there will be phenomena beyond the linear range of the instrument, affecting the accuracy of the data.

On the other hand, the choice of carrier gas flow rate also has a significant impact on the separation effect. If the column flow rate is too high, the residence time of the components in the column decreases, resulting in insufficient mass transfer time between the fixed phase and the mobile phase. This will reduce the efficiency of the separation column, widen the color peak, and lead to the phenomenon of overlapping peaks of some components, so that the complete separation of the components to be measured cannot be achieved. On the contrary, the low column flow rate will delay the retention time of the components in the column, which will only lead to a long detection cycle, and may also appear tail phenomenon, chromatographic peak symmetry and quantitative accuracy. Therefore, the column flow rate must be optimized to ensure the separation efficiency, so as to achieve good column efficiency and balanced peak shape. Based on the above, through a large number of tests and optimization, the optimal shunting ratio and flow rate determined in this study were 40:1 and 2.0 $ml \cdot min^{-1}$, respectively.

3.2 Linearity, Detection Limits, Precision and Accuracy

The linearity of the analytical method is used to characterize the relationship between the concentration or quantity of the substance to be measured and the response value. Its effect is that in a given concentration range, the detection result can be obtained directly or by mathematical formula through linear relationship. Detection limit is an important index to characterize the detection ability of a method. In addition, because it is difficult to achieve consistency between the sample solution and the standard solution matrix in the work, whether there is interference in the matrix can be determined by adding the standard recovery experiment. The recovery rate is measured by adding the standard material to the tested sample. The practicability and reliability of this method are ensured by verifying the linear range, detection limit, and recovery rate. The impurities of CD_4 and C_2D_6 in C_2D_4 were qualitatively and quantitatively analyzed according to the analytical conditions described in this study. The mass percentage (%) of the target object is taken as the horizontal coordinate, and the corresponding peak area intensity value is taken as the vertical coordinate. Methods The detection limit (MLD) was determined by gas chromatography of environmental samples. At the specified confidence level, the low-concentration sample determination was repeated n times ($n \geq 7$) according to the sample analysis procedure, and the standard deviation of the n parallel determination was calculated. The product of the standard deviation and the value of the T-distribution with 99% confidence and n-1

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degrees of freedom is the detection limit. The standard sample with 0.0010% concentration was prepared in a clean Suma tank for repeated determination for 7 times. Meanwhile, the accuracy and precision tests were conducted by preparing three simulated samples with different concentrations of 0.010%, 0.050% and 0.50% in a clean Suma tank for repeated determination for 6 times, and the relative standard deviation and standard recovery rate were calculated. Details of test results are shown in Table 1.

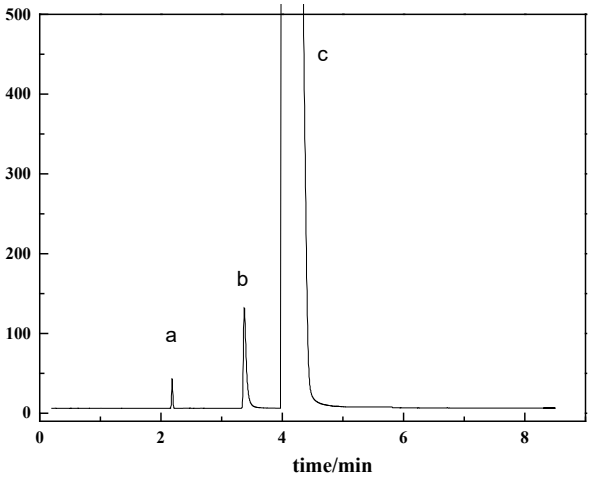
The results showed that CD_4 and C_2D_6 components in C_2D_4 had good linearity in the ranges of 0.0020%~0.050% and 0.050%~1.00%. The correlation coefficients (R^2) were ≥0.995. The detection limits of CD_4 and C_2D_6 components were 0.0003% and 0.0002%, respectively. The recoveries ranged from 97.1% to 106.1% and 97.3% to 104.7%, and the precision ranged from 1.95% to 3.73% and 1.65% to 2.98%, respectively. The method has good precision and accuracy.

Tab.1 Linear equation, detection limits, accuracy and precision of CD_4 and C_2D_6

Index		Compound	
		CD_4	C_2D_6
High concentration standard curve		y=431.3x+5.511	y=702.5x+0.136
Correlation coefficient(r)		R^2=0.999	R^2=0.999
Low concentration standard curve		y=492.4x+0.190	y=613.7x+8.189
Correlation coefficient(r)		R^2=0.999	R^2=0.999
Detection limit(n=7)		0.003%	0.002%
Standard recovery	0.010	97.1%~106.1%	97.3%~104.7%
	0.050	98.5%~103.6%	98.5%~102.0%
	0.50	97.6%~104.0%	97.6%~104.4%
Relative standard deviation(n=6)	0.010	3.73 %	2.98%
	0.050	1.95 %	1.65%
	0.50	2.30 %	2.44%

3.3 Actual Sample Testing

According to the above method, several batches of C_2D_4 samples were analyzed in detail to verify the feasibility and effectiveness of the method in practical sample detection. In the experiment, the samples were tested by gas chromatography, and repeated experiments were combined to ensure the stability of the detection process and the reliability of the data. The chromatogram of the obtained sample is shown in Figure 2. It can be observed from the figure that the chromatographic peak shape of each target component is ideal, sharp symmetry of peak shape, no obvious tailing or broadening phenomenon. The results show that the method has good performance in sensitivity and separation degree. At the same time, it can also be seen from the figure that the common air impurity components in the sample do not interfere with the detection of the target components, which further verifies that the method has a strong anti-interference ability against the complex sample matrix.



a—CD_4; b—C_2D_6; c—C_2D_4;

Fig.2 Chromatogram of actual C_2D_4 sample

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The test data of several batches of deuterated ethylene samples were sorted out, and the relevant results were shown in Table 2. According to the experimental data, traces of by-product C_2D_6 were detected in the actual samples to varying degrees. The production of this by-product may be related to the trace polymerization or conjugation reactions that occur during the preparation, storage or transportation of the sample. A small amount of CD_4 was also detected in some batches of samples. It may be residual feedgas or by-products due to incomplete reactions during sample production. These results show that there are trace impurities in the actual samples. It is proved that this method has good applicability and stability in practical application. It provides effective technical support for the quality control of C_2D_4 samples and related scientific research.

Tab.2 Test results of actual sample

Compound / Sample number	CD_4	C_2D_6
1	0.14%	0.38%
2	0.02%	0.04%
3	0.09%	0.11%
4	＜0.003%	0.007%
5	＜0.003%	0.018%

4. Conclusion

In this paper, the trace impurities in C_2D_4 products were analyzed and determined by gas valve sampling combined with gas chromatograph. In the process of experiment, the key experimental conditions such as column type, shitter ratio and column flow rate were systematically optimized to ensure the separation degree, stability and sensitivity of the method. Based on the retention time of standard samples, the content of target components was qualitatively and quantitatively analyzed by external standard method, and an analytical method for the determination of CD_4 and C_2D_6 in C_2D_4 products was established. The results show that the method can effectively separate and accurately analyze the trace impurities CD_4 and C_2D_6 in C_2D_4 products. In the concentration range of 0.0020% ~ 1.00%, CD_4 and C_2D_6 showed a good linear relationship, and the correlation coefficient (r) of the linear regression equation was greater than 0.995. The detection limits of CD_4 and C_2D_6 were 0.003% and 0.002% respectively, which could meet the requirements of the detection of trace impurities in practical samples.

In order to verify the accuracy and repeatability of the method, the quantitative ability of the method was further evaluated by using relative standard variance and recovery rate. The recoveries of CD_4 and C_2D_6 ranged from 97.1% to 106.1%, indicating the accuracy of the method. The relative standard deviation of each component is less than 4.0%, which further proves the high repeatability of the method and the good consistency of the detection results under different concentration levels. Therefore, the actual sample analysis shows that the method can be applied to the daily quality detection and analysis of trace impurities in C_2D_4 products, which provides an efficient and reliable analysis means for the production process control and quality monitoring of products. It also provides a reference for the analysis and detection of trace impurities in similar systems.

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