ISSN 1027-5495. Functional Materials, 26, No.2 (2019), p. 381-383.
doi:https://doi.org/10.15407/fm26.02.381

A novel gas chromatography analysis nethod of acryloyl chloride

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Received April 25, 2019

A novel method for the determination of acryloyl chloride in industrial products by aniline derivatization and gas chromatography is described. In this method, ethyl acetate was used as solvent but not toluene or benzene. The precision and recovery of this method were 0.474 % – 1.64 % and 95.3 – 98.2 %, respectively and up to the analysis standard. And the method had achieved non-irritation and non-corrosive.
Keywords: gas chromatography, acryloyl chloride, derivatization.

Описан новый метод определения акрилоилхлорида в промышленных продуктах путем дериватизации анилина и газовой хроматографии. В этом методе в качестве растворителя использовали этилацетат, вместо толуола или бензола. Точность и степень извлечения для этого метода составляли 0,474 % – 1,64 % и 95,3 – 98,2 %, соответственно, что даже выше, чем при выполнении стандартного анализа. Этот метод также исключает процессы коррозии и появления раздражающих веществ.

Новий метод аналізу акрилоілхлориду за допомогою газової хроматографії. *Ціхуей Шень, Сіньчень Сюй, Ян Люй, Мяо Лі, Янь Лю.*
Описано новий метод визначення акрилоілхлориду у промислових продуктах шляхом дериватизації аніліну і газової хроматографії. У цьому методі в якості розчинника використано етилацетат, замість толуолу або бензолу. Точність і ступінь вилучення для цього методу становить 0,474 % – 1,64 % і 95,3 – 98,2 %, відповідно, що навіть вище, ніж при встандартному аналізі. Цей метод також виключає процеси корозії і появи речовин, що подразнюють.

1. Introduction

Acryloyl chloride was an important chemical raw material [1, 8]. It was easy to decompose with water or hot and had strong irritation and corrosiveness [2], so it was difficult to accurately determine the content of acryloyl chloride through a simple and rapid method. In this work, we reported a new method for analysis the content of acryloyl chloride. In this method, derivatization was used to avoid the corrosiveness of acryloyl chloride, and the sampling quantity was increased and interior standard was used in order to reduce the error. The experimental results showed that the measurement accuracy and precision were favorable.

2. Experimental

1.1. Materials

Aniline (99.5 %) and ethyl acetate (99.5 %) were obtained from Sinopharm Chemical Reagent Co. Ltd.. acryloyl chloride (96 %) and dibutyl phthalate (99.5 %) were obtained from Shanghai Aladdin biochemical polytron technologies Inc. All the reagents were used without further purification.

1.2. Analysis procedure

2 mL aniline solution (10 % V/V in ethyl acetate) and 2 mL dibutyl phthalate solution (60 g/L in ethyl acetate) were

added into a centrifuge tube. Then, 1.0 mL acryloyl chloride (50 g/L in ethyl acetate) was added. The tube was mixed and centrifuged for 5 min at 10000 rpm. Then, 1 μL clear supernatant was applied for gas chromatography (GC) analysis.

1.3. Gas chromatography analysis

Gas chromatography measurements were performed on gas chromatograph Fuli-9720 equipped with flame ionization detection (FID) and OV-17 filled column (2 mm×3 m). The temperatures of detector and injection were maintained at 250°, the temperature of oven was maintained at 200°. The carrier gas was nitrogen and the flow of nitrogen, hydrogen and air were 30, 30, 500 mL/min.

3. Results and discussion

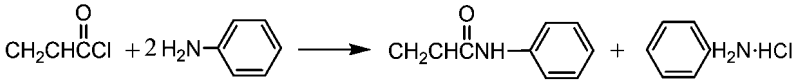
Derivatization was a common method for the substance which was not suitable for direct GC analysis [4, 5]. Because of the reaction of acryloyl chloride and aniline was very rapid and thorough, the strong irritation and corrosiveness of acryloyl chloride could be solved by derivatization with aniline [3] according to reaction equation 1. Usually, the derivatization was carried out in the benzene [7] because of the difference in solubility of products, and the aniline hydrochloride produced by this reaction was easy to remove due to the poor solubility, meanwhile, achieved the purpose of removing strong corrosive chlorine. Due to the toxic of benzene [6], a "friendly" solvent which could dissolve other substances and the internal standard substance except aniline hydrochloride was needed to replace it. So we selected ethyl acetate as a solvent in this method. Before performing the analysis, the standard working curve was drawn first. According to the analysis procedure, 0.1, 0.3, 0.5, 0.7, 1.0 mL acryloyl chloride solution were added into centrifuge tubes and the volume of the mixing was fixed to 5 mL with ethyl acetate respectively (corresponding to the acryloyl chloride concentration of 1, 3, 5, 7, 10 mg/mL). Each sample of different concentration was measured in parallel nine times (Table 1). The working curve was obtained by linear regression of the peak area ratio (acrylonitrile chloride to dibutyl phthalate) to the corresponding acryloyl chloride concentration (Fig. 1). The regression equation was $y = 0.0782x$ and the correlation coefficient (R^2) was 0.9995.

Table 1. The GC analytical results of working curve

Concentration (mg/mL)	The peak area ratio	RSD(%)
0.977	0.07233	1.74
2.93	0.2394	2.03
4.89	0.3786	1.54
6.84	0.5431	2.33
9.77	0.7576	1.55

The precision of this analysis method was evaluated by repeated analysis of three samples at same concentration for nine times respectively. Table 2 showed the relative standard deviation (RSD) which was investigated at different concentration. The values of RSD were in the range 0.474 % – 1.64 %. The corresponding RSD value increased when the concentration of acrylonyl chloride reduced, but the RSD value only was 4.79 % even if the concentration was 0.016 mg/mL. Furthermore, the recovery of this method was 95.3 – 98.2 %.

The real sample was detected according to the analysis process, and the result was used to calculate the content of acryloyl chloride in the sample. Fig. 2 had shown the chromatogram of real sample which were derived from the prepared process of acryloyl chloride. The content of acryloyl chloride cal-



Formula 1. The reaction equation of the derivatization of acryloyl chloride with aniline.

Table 2. The precision of the acrylonyl chloride GC analysis method

Concentration (mg/mL)	RSD[a]	RSD[b]
9.72	0.141 %, 0.634 %, 0.379 %	0.474 %
5.65	0.340 %, 0.817 %, 0.698 %	0.658 %
0.92	1.20 %, 1.69 %, 0.941 %	1.64 %

[a] The RSD values of the each sample. [b] The RSD values of the samples at the same concentration.

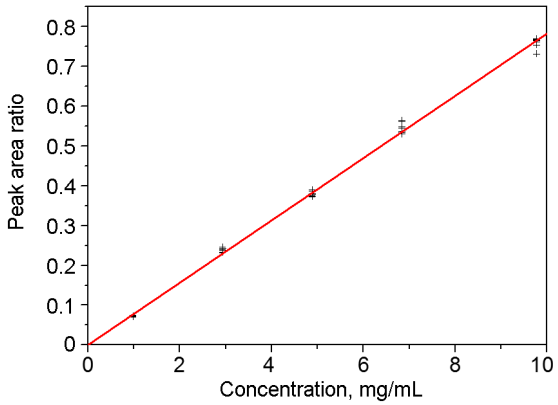


Fig. 1. The working curve of the peak area ratio (acrylonyl chloride to dibutyl phthalate) to the concentration of acryloyl chloride.

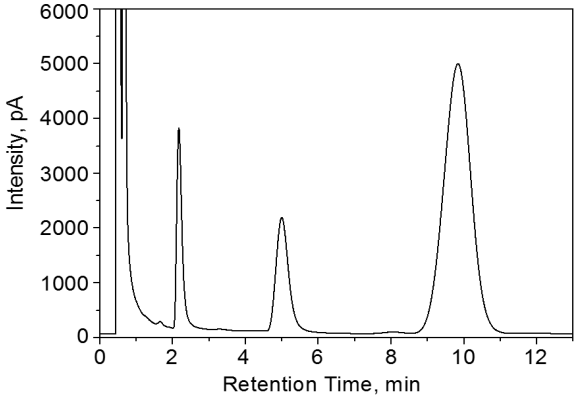


Fig. 2. Chromatogram of real sample (retention time 2.21 min: derivatization of acryloyl chloride, 4.96 min: raw material, 9.96 min: dibutyl phthalate).

culated according to the working curve in the sample was 20.1 %, respectively.

4. Conclusions

Through the derivative with aniline, the content of acryloyl chloride was analysis by GC. The precision and recovery of this method were 0.474 % – 1.64 % and 95.3 % – 98.2 %, respectively and up to the analysis standard. A GC detection method of acryloyl chloride without irritation and corrosive was achieved by used ethyl acetate as solvent.

Acknowledgements. This work was financially supported by the National Sciences Foundation of China (21805107).

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