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Direct Analysis of Liquid Components in Glycerol Hydrogenolysis to Propanediols System*
甘油氢解产物的测定方法研究

HUANG Kai[1]，LONG Si-yu[1]，LIAO Dan-kui[2]，HUANG Ri-bo[1]
黄　慨[1]，**龙思宇**[1]，**廖丹葵**[2]，**黄日波**[1]

(1. State Key Laboratory of Non-food Biomass Enzyme Technology，National Engineering Research Center for Non-food Biorefinery，Guangxi Biomass Industrialization Engineering Institute，Guangxi Key Laboratory of Biorefinery，Guangxi Academy of Sciences，Nanning，Guangxi，530007，China；2. Guangxi University，Nanning，Guangxi，530004，China)
(1. **广西科学院，非粮生物质酶解国家重点实验室，国家非粮生物质能源工程技术研究中心，广西生物质产业化工程院，广西生物炼制重点实验室，广西南宁**　530007；2. **广西大学，广西南宁**　530004)

Astract：**【Objective】**This study focused on directly and rapidly quantitative analysis of liquid products of glycerol hydrogenolysis to propanediols(1，3-PDO；1，2-PDO) without derivatization by using gas chromatography.**【Methodes】**The test method of gas chromatography direct analysis was established by using the ZB-5HT column in gas chromatography，methanol as solvent，and n-butyl acetate as the internal standard.**【Results】**Experimental results showed that linear correlation coefficients (R) were 0.9993～0.9995 with the components concentration in the range of 0～27 mg·mL^{-1}，and the standard errors (SE) were 0.0040～0.0112. Parallel determination experiments were carried in six real products of hydrogenation，and the maximum relative deviation (MRD) was in the range of 0.06～0.09.**【Conclusion】**The average recovery rate was 99.19%～100.42%，which could meet the requirements of analyzing the liquid products of glycerol hydrogenation.

Key words：gas chromatography，internal standard，hydrogenolysis，glycerol，propanediol

摘要：**【目的】研究快速直接测定未经衍生化处理甘油氢解产物**(1，3-**丙二醇**；1，2-**丙二醇**)**的方法。【方法】以甲醇为溶剂，醋酸正丁酯为内标物建立气相色谱分析测试方法，并采用** ZB-5HT **气相色谱柱。【结果】当样品组成浓度在** 0～27 mg·mL^{-1}**范围内，内标法校正实验工作曲线的线性相关系数** R **达到** 0.9993～0.9995，**标准残差**(SE)**为** 0.0040～0.0112。**对** 6 **个实验真实样品进行平行定量测定，结果表明最大相对偏差为** 0.06～0.09，**平均回收率为** 99.19%～100.42%。**【结论】该方法可以满足直接测定甘油氢解液相产物的要求。**

关键词：**气相色谱　内标法　氢解　甘油　丙二醇**
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0　Introduction

【Research significance】Hydrogenation of glycerol for preparing 1，3-PDO is a good way to receive

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作者简介：**黄　慨**(1977-)，**男，博士，主要从事生物质基化学品，生物质基材料和生物质废弃物综合利用研究。**
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the polymer intermediates, and 1,3-PDO is main material in the manufacture of polytrimethylene terephthalate(PTT)[1]. Glycerol is one of the top 12 building block chemicals which can be derived from plant sources[2]. With the rapid development of biodiesel production, large quantities of glycerol are available as a byproduct. As a result, glycerol could be the ideal renewable feedstock to produce 1,3-PDO. **【Achieved research progress】**Some researchers have reported the conversion of glycerol into 1,3-PDO through bio-catalytic, homogeneous or heterogeneous processes[3~6]. But most of them had found that the direct quantity analysis of the liquid product of glycerol hydrogenlysis was very complicated. In Yohei[7] research, the liquid phase and the gas phase products were analyzed by a gas chromatograph (GL Science GC-353) equipped with FID. The capillary column TC-WAX (diameter: 0.25 mm, length 20 m) was used as the separation column. And the column temperature was 220℃. 1,2-PDO, 1,3-PDO n-PrOH and iso-PrOH were quantitatively analyzed but without glycerol. A prep-LC (Preparative Liquid Chromatography, Waters) system was used by Cho[8] in the chromatographic purification step. The Prep-LC system consists of a pump (Waters Delta Prep 4000), a chromatographic column (SUS 304), a UV detector (Waters 409E), and a data processing unit. The column (2 cmi. d. 180 cm length) was packed with silica resin (Merck, 0.040~0.063 mm) and eluted with a sufficient amount of ethyl acetate/methanol at 98/2 (V/V) in order to stabilize the packed bed. Tomohisa[9] analyzed the products using gas chromatograph (GC-353; GL Sciences Inc.) equipped with flame ionization detector (FID). ATC-WAX capillary column (diameter 0.25 mm, length 20 m) was used for separation and it's temperature was 220℃. The products detected included 1,3-PDO, 1,2-PDO, n-propanol (n-PrOH), and iso-propanol (iso-PrOH), and ethylene glycol (EG), ethanol, methanol and methane were degradation products. But the glycerol had not been detected directly in their work. Long[10] identified both the liquid and vapor products by GC (6890N, Agilent, USA) with a coupled mass spectrometer (MS, 5973, Agilent, USA) and a capillary Chromatographic column J &W DB-WAX. 1,3-PDO, 1,2-PDO and ethanol were detected but not glycerol. Vasiliadou[11] analyzed and indentified liquid samples by GC (Varian 3300, FID, DB-Wax 30 m ×0.53 mm × 1.0 μm) and identified by GC-MS (DB-Wax 30 m ×0.53 mm ×1.0 μm). N-butanol was used as solvent for the GC analysis. The multiple point internal standard method was used for the quantification of conversion and selectivity determination. Gas analysis was performed in Varian 3700 (TCD, Porapak Q, MS-5A). The liquid products detected mainly included 1,2-propanediol, 1,3-propanediol, ethylene glycol, hydroxyacetone (acetol), 1-propanol, 2-propanol, ethanol and methanol. Qin[12] analyzed the liquid products using a SP-6800A GC (Shandong Ruihong Chromatogram Analysis Co., Ltd, China) equipped with a flame ionization detector (FID) and a capillary column (Alltech ECTM-1 capillary column, 30 m×0.53 mm× 1.2 μm). The quantitative analysis was based on internal standard method using n-butanol and 1,4-butanediol as double internal standard. Leifeng[13] analyzed the sample of liquid phase products after it was esterified by acetic anhydride, using an Agilent 7890 equipped with a flame ionization detector (FID) and a HP-5 capillary column. Nakagawa[14] analyzed both liquid and gas phase products using GC (Shimadzu GC-2014) equipped with FID and GC-MS (Shimadzu QP5050). Silvia[15] analysed 1,3-PDO, acetol and n-PrOH using an Aminex HPX-87C (Bio-Rad) column. HPLC was maintained at 180℃, with a mobile phase of ultrapure filtered water flowing at 0.6 mL $\cdot$ min^{-1}. Ethanol, methanol, glycerol, ethylenglycol and 1,2-PDO were analysed using an Aminex HPX-87H (Bio-Rad) column. Yasushi[16] analyzed products using two kinds of gas chromatographs (Shimadzu GC-2014 and GC-17A) equipped with FID. A TC-WAX capillary column (diameter 0.25 mm, 30 m) or a Rtx-1-PONA capillary column (diameter 0.25 mm, 100 m) was used for the separation. PDO, PrOH even ethanol, ethane and methane were detected directly but glycerol was only calculated in the end. **【Current entrypoint】**The main problem of direct analysis is that the no-reaction glycerol will interfere with gas chromatography analysis. So

many researchers would like to indirectly quantitatively analyze the sample and they have to derivate glycerol into short carbon chain carboxylic glyceride firstly. These kinds of indirectly methods are likely to cause the losses in the derivation process. Rapid and direct analysis method is very important in the industry or research for monitoring each component in the liquid product of glycerol hydrogenation to propanediol. As the goal of industrial production (used as polymer intermediate of PTT), propanediol was dominated in the first stage of glycerol hydrogenation which can be divided into three stages. The other two stages are further hydrogenolysis into propyl alcohol and even propane, respectively, and these is unfavorable for producing propanediol. Therefore, it is urgent for many researchers to look for a direct and effective analysis method. **【Critical problem solved】**In our study, rapid and direct analysis of the liquid product of glycerol hydrogenation were carried out without any derivatization only using methanol as solvent, n-butyl acetate as internal standard, by Agilent Company's 7890A Gas Chromatography. This is quick, sensitive and accurate method. It could be applied in the industry or research for monitoring each component in the liquid product of glycerol hygrogenation to propanediol. Thus the depth of glycerol hydrogenation would be effectively controlled by the operator.

1 Materials and methods

1.1 Reagents and instruments

n-Propyl alcohol (n-PrOH), iso-propyl alcohol (iso-PrOH), methanol and glycerol are HPLC grade reagents purchased from Shanghai Aladdin Reagent Company. 1,3-Propanediol and 1,2-propanediol (analysis standard purity over 99.7%) were purchased from Shanghai Aladdin Reagent Company, and n-butyl acetate (n-BuAce) served as internal standard (GC standard purity over 99.7% purchased from Shanghai Aladdin Reagent Company). Agilent Company's 7890A Gas Chromatography, Agilent Company's Capillary column HP-5 30 m×0.25 mm×0.25 μm and Phenomenex Company's Capillary Column (Zebron™ ZB-5HT 30 m×0.32 mm×0.25 μm, Zebron™ ZB-WAXplus 30 m×0.25 mm×0.25 μm) were used with FID as detector.

1.2 Simulation and real samples of products of hydrogenation

According to the literature data[13], simulation liquid products in different ratio were prepared as shown in Table 1 in order to determine the correction factor between internal standard and each composition in the mixture system.

1.3 Experiment hydrogenation of glycerol

Appropriate amount of catalyst (fresh Ni-Cu based catalyst or Pt based Catalyst, prepared in this work) was placed into the autoclaves. After the reactor being sealed, air inside was replaced with hydrogen (purity 99.99%) three times and the pressure was increased to 1 MPa at last. Autoclaves were then heated to 120℃ for the reduction pretreatment. The temperature was monitored using a thermocouple inserted in the autoclave. After 1 h, an aqueous solution of glycerol was purged into the autoclaves with stirring. The pressure was increased to 6 MPa and then the vale was sealed with being heated to 200℃. The reaction of hydrogenation lasted for 2 h. After that, the reactors were cooled down and the gases were collected in a gas bag. The autoclave contents were transformed to vials, and the catalysts were separated by centrifugation and filtration.

Table 1 Ratio of each composition in the simulation of liquid samples

Component	Concentration ($mg \cdot mL^{-1}$)	Ratio between composition with n-BuAce(W/W)						
		1#	2#	3#	4#	5#	6#	7#
1,3-PDO	50.695±0.005	0.120	0.240	0.600	1.199	2.398	5.996	11.992
1,2-PDO	49.675±0.005	0.118	0.235	0.588	1.175	2.350	5.875	11.750
Glycerol	54.235±0.005	0.128	0.257	0.641	1.283	2.566	6.415	12.829
n-PrOH	39.500±0.005	0.093	0.187	0.467	0.934	1.869	4.672	9.344
iso-PrOH	38.380±0.005	0.091	0.182	0.454	0.908	1.816	4.539	9.079
n-BuAce	42.275±0.005	—	—	—	—	—	—	—

1.4 Gas chromatography analysis

Quantitative analysis is based on internal standard method. All of the liquid products were identified by GC(7890A, Agilent, USA) with Phenomenex Company's Capillary Column (ZebronTM ZB-5HT 30 m×0.32 mm×0.25 μm). Methanol was used as solvent, and n-butyl acetate as internal standard. Sample quantity was 0.5 μL, vaporization at 598 K; split ratio is 50 : 1. Flame ionization was set up 350℃ and hydrogen velocity holding at 40 mL·min^{-1} with the air velocity of 400 mL·min^{-1}. Oven profile was initial from 60℃, and rose up to 60℃ with 8℃·min^{-1}, 100℃ to 290℃ with 40℃·min^{-1}, 290℃ to 300℃ with 10℃·min^{-1} and held for 6 min in the end. Sample carrier gas was nitrogen. Column flow rate was programmed in gradient velocity from 1.5 mL·min^{-1} to 3.5 mL·min^{-1}.

1.5 Quality control and quality assurance

Sample preparations and analytical procedures were performed according to quality assurance and quality control measures. Limits of detection were estimated by testing seven groups of simulated mixture samples (formulated by chromatographic grade standrad). Thestandard concentration ranged 1,3-PDO 0.25～25.34 mg·mL^{-1}, 1,2-PDO 0.25～24.83 mg·mL^{-1}, glycerol 0.28～27.11 mg·mL^{-1}, n-PrOH 0.20～19.75 mg·mL^{-1} and iso-PrOH 0.20～19.19 mg·mL^{-1}.

2 Results and discussion

2.1 Correction factors of each component with internal standard

Simulation samples were injected into the gas chromatography, and were parallelly injected three times. The experimental data was statistics calculated to obtain average relative peak area ratio (PAR) and actually concentration ratio (ACR) between each simulation sample and internal standard, as shown in Figures 1～3.

There is a relationship between PAR and ACR as follows:

$$ACR = f' \times PAR。\quad (1)$$

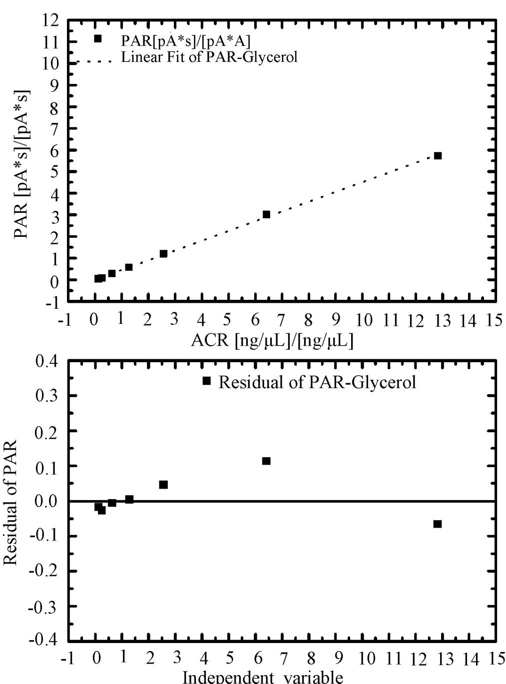

Figure 1 Linear fitting of glycerol for relative correction factor

The relative correction factor (RCF, f'), correlation coefficient (R) and standard error (SE) could be statically calculated in Table 2.

Table 2 Statistical parameter (RCF, R, SE) of each component

Component	RCF	R	SE
1,3-PDO	1.3481	0.9993	0.0073
1,2-PDO	1.3163	0.9995	0.0067
Glycerol	2.2173	0.9995	0.0040
n-PrOH	0.8963	0.9993	0.0112
iso-PrOH	1.0622	0.9993	0.0092

Quantitative calculation equation is shown as follow:

$$w_i = f'_i \times \frac{A_{Sam_i}}{A_{Sta}} \cdot \frac{m_{Sta}}{m_{Sam}} \times 100\%。\quad (2)$$

w_i is the mass percentage of component I; A_{Sam} and A_{Sta} refer to the PAR of simulation sample and internal standard; m_{Sam} and m_{Sta} refer to the accurate mass of simulation sample and internal standard.

In order to confirm the accuracy of the determination method further, proof experiment as following was carried out. The samples of glycerol hydrogenation were analyzed by using this method.

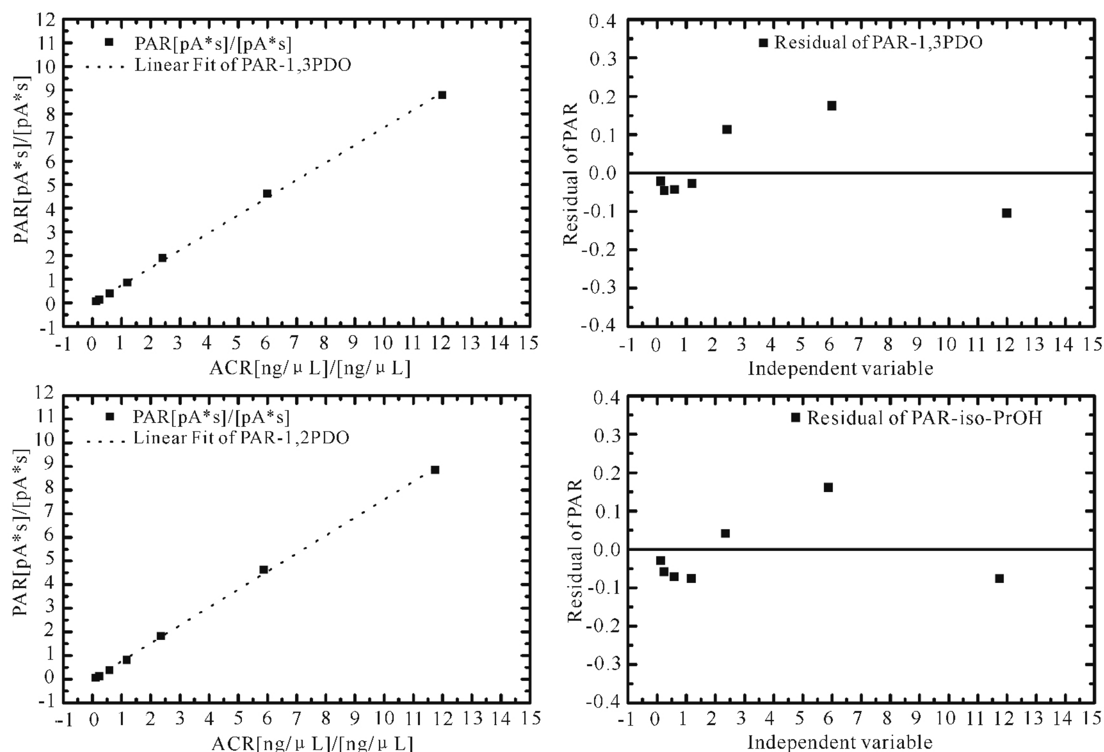

Figure 2 Linear fitting of PDOs for relative correction factor

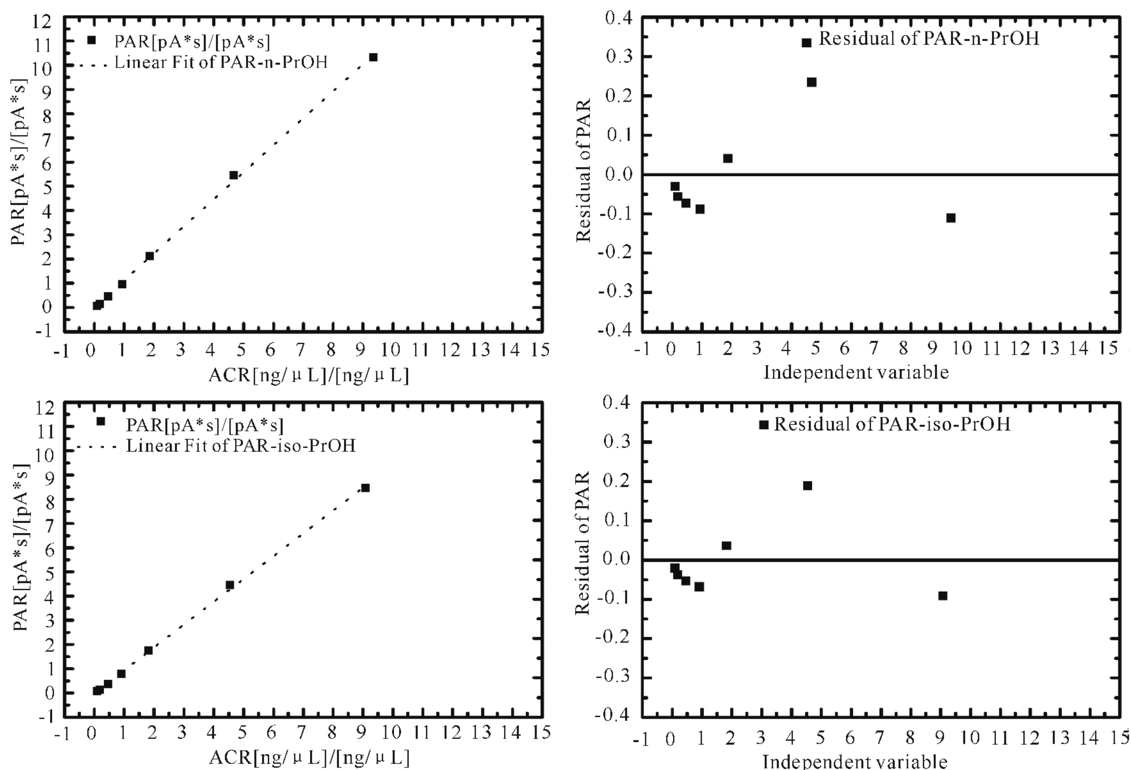

Figure 3 Linear fitting of PrOHs for relative correction factor

2.2 Sample analysis of glycerol hydrogenation and recovery determination

Six samples were prepared by using the method in the above mention. First of all, w_i of each component was determined by using internal standard method. And then, ten copies were divided from hydrogenation sample six (r6), and accurate mass of 1,3-PDO, 1,2-PDO, glycerol, n-PrOH, iso-PrOH and the internal standard (50 μL, 40.275 mg · mL^{-1}) was singly added into each copy with parallel twice. Finally, quantitative analysis was carried out by GC 7890A, and the results were shown

in table 3. It is found that the maximum relative deviation (MRD) value is lower than 0.1%, thus the accuracy of this internal standard determination method can be guaranteed.

Table 3 Results of quantitative analysis

Sample	r1(%)	r2(%)	r3(%)	r4(%)	r5(%)	r6(%)	MRD
1,3-PDO	42.62	10.58	19.65	44.46	38.52	32.32	0.09
1,2-PDO	2.93	1.00	1.76	3.27	2.84	2.49	0.08
Glycerol	13.86	83.52	57.70	12.44	7.10	3.12	0.06
n-PrOH	33.02	3.35	17.87	31.86	41.52	51.55	0.07
iso-PrOH	7.58	1.55	3.01	7.97	10.02	10.52	0.08

The recovery determination experiments of each component were analyzed, and the results were shown in table 4.

From the results shown in Table 3 and Table 4, it confirms that the direct quantitative analysis of liquid product of glycerol hydrogenation achieves a high requirements, high accuracy and good reproducibility. Otherwise, the recovery rate of glycerol decreases following with the increase of its added amount. Therefore, glycerol concentration level will affect the quantitative accuracy. But it is ensured that the better catalytic effect of glycerol hydrogenation (ie the higher conversion of glycerol) will receive higher quantitative accuracy. This is consistent with the research requirement of glycerol hydrogenation reaction system. The comparisons between chromatograms are shown in Fig. 4.

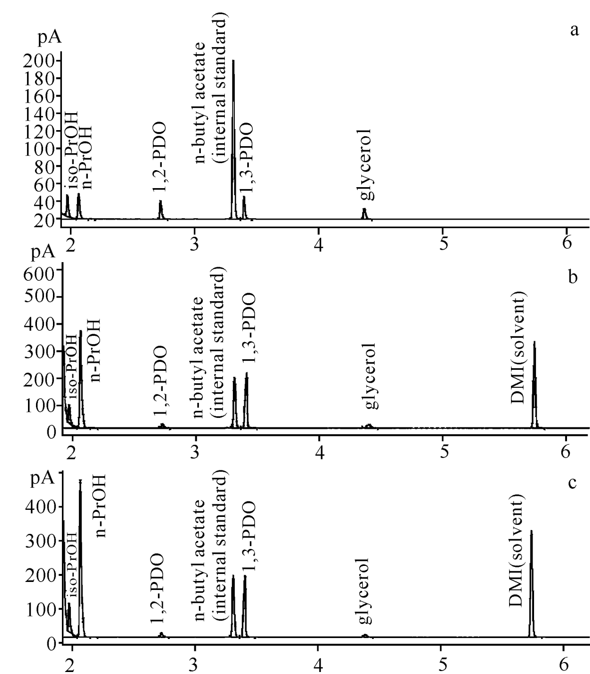

Figure 4 GC chromatograms of simulation sample 2# (a), fixed bed reactor hydrogenation sample r5(b) and high pressure autoclave hydrogenation sample r6(c)

3 Conclusion

Rapid and direct determination method for analyzing the liquid product of glycerol hydrogenation system is established in our study. The results show that the level of glycerol concentration will affect the quantitative accuracy of the glycerol. But in the range of 0～27 mg·mL^{-1}, it meets the requirement of analysis. With great advantages of simple operation, rapid analysis and good accuracy, this direct determination method can be appllied in the mixture with components at higher boiling point, and the highest detection temperature would reach the range of 280～380℃.

Table 4 Results of recovery determination

Sample	Add1(mg)	Recovery1(%)	Add2(mg)	Recovery2(%)	Average(%)
1,3-PDO	1.01±0.01	100.12	3.05±0.01	100.32	100.22±0.10
1,2-PDO	0.51±0.01	100.26	1.06±0.01	100.23	100.24±0.02
Glycerol	0.55±0.01	99.39	1.11±0.01	99.00	99.19±0.20
n-PrOH	4.50±0.01	100.29	9.05±0.01	100.53	100.41±0.12
iso-PrOH	1.02±0.01	100.40	2.03±0.01	100.43	100.42±0.02

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