ISSN:2790-1688 DOI: 10.56028/aetr.3.1.30

Determination of Quinoline in Textiles by Gas Chromatography － Mass Spectrometry

Kejie Fu[1], Qingqing Ren[1*], Qibei Bao[2], Sumei Lian[3], and Jun Liu [4,5]

[1] Technology Center, Ningbo Customs District, Ningbo, P. R. China

[2] NingBo College of Health Sciences, Ningbo, P. R. China

[3] Shijiazhuang Customs District, Shijiazhuang, P. R. China

[4] Technology Center, Chengdu Customs District, Chengdu, P. R. China

[5] Urumqi Customs, Urumqi Xinjiang, P.R China

*Corresponding author e-mail: ren860703@163.com

Abstract. A method for the determination of quinoline in textiles by gas chromatography-mass spectrometry(GC－MS) was developed. The experimental conditions for extraction were optimized. The textile samples were ultrasonically extracted with toluene as organic solvent. The extraction solution was filtered with 0.45 μ m polytetrachloroethylene filter membrane, and the filtrate was subjected to GC-MS. Under the optimal conditions, the linear correlation coefficient of this method was 0.9998, with a low detection limit of 0.1 mg/kg in the concentration range of 0.1-1.0 mg • L-1. Recoveries ranged from 82. 9% to 92.0 % with RSDs ranged from 1.4% to 3.8%.

Keywords: textiles; quinoline; toluene; gas chromatography - mass spectrometry(GC- MS)

1. Introduction

Quinoline(CAS:91-22-5), also known as benzopyridine, is a class of compounds involved in the manufacture of dyes[1,2], belongs to aromatic compounds and is an important raw material for organic synthesis. Quinoline derivative is a kind of important alkaloids, which have important physiological activities and are widely used in medicine, pesticides and fine chemicals[3-5]. In the dyeing and finishing industry, quinoline is the manufacture of dyes[6-9], mainly used to prepare cyanine blue pigment and photosensitive pigment. With quinoline and quinoline derivatives, C.I. Acid Yellow 3, C.I. direct yellow 22, C.I. solvent yellow 33 and Palanil yellow 3G can be synthesized. In addition, Disperse yellow 54 and disperse yellow 64, which are used for dyeing polyester fiber， are also mainly synthesized with quinoline as raw material[10].

Quinoline is considered to be possible carcinogenic to humans[11-13] and toxic for the aquatic environment[14-16]. The European Chemical Agency (ECHA) also has classified quinoline as a CMR (carcinogenic, mutagenic or toxic to reproduction) substance, and quinoline was discussed under the theme of "CMR substances in textiles". In 2018, the Oeko-Tex standard 100 required the detection of quinoline in textile products. In 2019, the Oeko-Tex standard 100 further specified that its limit value was 50 mg • kg-1. More importantly, the European Commission issued a new regulation (EU) 2018/1513, which stipulated the list of restricted substances related to clothing and related accessories, textiles and footwear products directly contacting the skin, which were classified as CMR categories 1A and 1B in Annex XVII of EU REACH Regulation (EU) No. 1907/2006. Quinoline was one of them. In Annex XVII of REACH regulation, the limit value of quinoline was also clearly required to be less than 50 mg • kg-1, and this limit requirement has been implemented since November 1, 2020. However, there is no detection standard for quinoline residues in textiles at home and abroad.

Analytical methods for quinoline in textile products would be of great significance toward promoting the ecological development of the global textile industry and the protection of human health. Many researchers used GC or HPLC or GC-MS to detect quinoline in chemicals[17], cigarette smoke[18], dyeing and finishing auxiliaries[19] or electrosynthesis reaction solution[20].

ISSN:2790-1688 DOI: 10.56028/aetr.3.1.30
Besides, the available pretreatment method for detecting quinoline in the above substances is simpler than that of textiles, because of higher extraction rate of dyes dissolved in solvents and better extraction effect. However, when determining quinoline in textiles, the proper pretreatment conditions and extraction method are needed to be further studied. In this study, quinoline residues in textiles was extracted using optimized pretreatment method and analyzed by GC-MS.

2. Experimental

2.1 Materials and instruments

Cotton fabric complying with ISO 105-F02:2009 Textiles – Tests for colour fastness – Part F02: Specification for cotton and viscose adjacent fabrics. Wool fabric complying with ISO 105-F01:2001 Textiles –Tests for colour fastness – Part F01: Specification for wool adjacent fabric. Polyamide fabric complying with ISO 105-F03:2001 Textiles-Tests for colour fastness–Part F03: Specification for polyamide adjacent fabric. Polyester fabric complying with ISO 105-F04:2001 Textiles –Tests for colour fastness – Part F04:Specification for polyester adjacent fabric. These were obtained from Shanghai textile industry institute of technical supervision.

Methanol, n-hexane and toluene(chromatographically pure)

were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All other chemicals were of analytical grade and obtained from China National Pharmaceutical Group Corporation (Shanghai, China).

Analysis was performed using an Agilent 7890 gas chromatograph with mass selective detector system (5975C, Agilent Technologies Co., Ltd., USA) and a DB-5MS capillary chromatograph column (30 m, 0.25 mm ID, 0.5 μm film thickness; J&W Scientific, USA). A KS-500E II ultrasonic extractor (Kesheng Ultrasonic Equipment Co., Ltd., China) was used for sample preparation.

2.2 Preparation of Standard Solutions

Standard stock solution containing 1000 mg ·L-1 quinoline was prepared with toluene as solvent, which had a shelf life of three months and was stored at 0-4℃. The standard solution was diluted stepwise with toluene to prepare different concentrations as needed.

2.3 Sample Preparation

A total amount of 1.0 g (cut in 5 mm ×5mm, accurate to 1 mg)was placed in a centrifuge tube, 15 ml of toluene was added to the sample before extraction. Each sample was subjected to ultrasonic extraction at 40℃ for 30 min. After extraction, the organic phase was passed through a 0.45 μm filter membrane to obtain a solution for qualitative and quantitative determination by GC-MS.

2.4 GC-MS analysis

A DB-5MS capillary column (30 m×0.25 mm×0.5 μm) was used for GC-MS. The sample inlet temperature was set at 250℃, the sample injection volume was 1.0 μl, and the split ratio was splitless. Helium was used as the carrier gas at a flow rate of 1.0 mL/min. The oven temperature program was as follows: 90℃ for 2 min, increased to 260℃ at a rate of 20 ℃ /min, held at 260 ℃ for 3 min. Mass spectrometry was performed using a quadrupole temperature of 230℃, ion source temperature of 150℃, electron impact ion source (EI, 70 eV), interface temperature of 250℃, mass scan range of 30-200 amu, and solvent delay time of 2.0 min, SIM qualitative analysis.

ISSN:2790-1688 DOI: 10.56028/aetr.3.1.30

3. Results and discussion

3.1 Selection of sample

Quinoline in textiles mainly comes from the dyes used. Considering the application range of different dyes with quinoline, positive samples of cotton, polyester, acrylic, polyamide and wool were selected as the research objects.

3.2 Selection of extraction method

The commonly used extraction methods include ultrasonic assisted extraction, Soxhlet extraction, oscillating extraction, microwave extraction and accelerated solvent extraction. Among which Soxhlet extraction has high efficiency, but takes more time and larger reagent consumption. The accelerated solvent extraction equipment is expensive and has low utilization. Considering the general applicability and operation convenience, ultrasonic method was selected as the extraction method.

3.3 Selection of extraction solvent

According to the physical and chemical properties of quinoline, methanol, dichloromethane, n-hexane, ethyl acetate and toluene were selected as alternative extraction solvents, normalized the results based on the recovery rates with ethyl acetate as solvent. The results demonstrated that under the same extraction conditions, the extraction rate with toluene as the extraction solvent was the best (see Table 1). Thus, toluene was selected as the solvent for quinoline extraction.

Table 1 Effect of different solvents on quinoline extraction

Solvent	**Extraction rate of different materials (%)**				
	Cotton	*Polyester*	*Acrylic*	*Polyamide*	*Wool*
Methanol	88.26	82.33	81.03	92.52	87.56
Dichloromethane	100.64	97.49	95.06	104.87	100.18
n-hexane	101.57	95.06	100.26	102.10	98.80
Ethyl acetate	100.00	100.00	100.00	100.00	100.00
Toluene	103.77	101.19	103.65	110.82	104.25

3.4 Selection of ultrasonic extraction conditions

3.4.1 Selection of ultrasonic extraction temperature

Using toluene as the solvent, set different ultrasonic extraction temperatures including room temperature (about 25℃), 40℃, 50℃, 60℃ and 70℃, and conducted ultrasonic extraction for 30min with a frequency of 40KHz, the effect of extraction temperature was studied. Normalized the results based on the ultrasonic extraction effect at 40℃. The results demonstrated that the influence of water bath temperature on ultrasonic extraction was not significant, but with the increase of extraction temperature, the extraction rate decreased slightly (see Table 2), because the increase of extraction temperature might accelerate the volatilization of quinoline. All five materials obtained highest extraction rate at 40℃. Thus, the extraction temperature was selected as 40℃ for quinoline extraction.

ISSN:2790-1688 DOI: 10.56028/aetr.3.1.30

Table 2 Effect of ultrasonic extraction temperature on quinoline extraction

Ultrasonic extraction temperature	Extraction rate of different materials (%)				
	Cotton	*Polyester*	*Acrylic*	*Polyamide*	*Wool*
Room temperature	98.72	95.99	102.23	94.74	99.21
40℃	100.00	100.00	100.00	100.00	100.00
50℃	98.58	97.87	98.65	95.38	96.98
60℃	98.78	93.11	95.85	99.90	97.20
70℃	97.29	94.81	95.53	98.90	96.67

3.4.2 Selection of ultrasonic extraction time

Using toluene as the solvent, set ultrasonic extraction temperature at 40℃ with a frequency of 40KHz, and conducted ultrasonic extraction for 20min, 30min, 40min, 50min and 60min, the effect of extraction time was studied. The results demonstrated that cotton, polyester and polyamide obtained the best extraction effect after extraction for 30min while polyamide obtained the best extraction effect after extraction for 20min (see Table 3). The effect of extraction time on wool was not obvious, and the extraction rate was high. Considering the extraction effect on five samples, the extraction time was selected as 30 minutes.

Table 3 Effect of ultrasonic extraction time on quinoline extraction

Ultrasonic extraction time	Extraction rate of different materials (%)				
	Cotton	*Polyester*	*Acrylic*	*Polyamide*	*Wool*
20 min	99.63	96.90	104.89	86.55	101.22
30 min	100.00	100.00	100.00	100.00	100.00
40 min	100.09	94.30	92.19	95.39	105.48
50 min	92.05	86.40	96.21	94.30	102.43
60 min	99.54	93.34	100.86	89.55	98.54

3.5 Selection of chromatographic condition

3.5.1 Selection of inlet temperature

The inlet temperature shall not only ensure the complete gasification of the liquid to be measured, but also ensure that the target substance will not decompose. The boiling point of quinoline is about 240℃, therefore, the inlet temperature was set at 240℃-290℃ to study the effect of different inlet temperature on the quinoline detection results. The results demonstrated the maximum response value was obtained when the inlet temperature was 250 ℃(see Figure 1).

3.5.2 Selection of initial temperature of chromatographic column

The effect of initial temperature of gas chromatography column on quinoline detection results was analyzed from the peak time and response value. The results demonstrated that with the increase of the initial temperature, the peak time of the target got earlier and earlier, and the response value increased first and then decreased. When the initial temperature was 70℃, the peak time was appropriate and the response value was the highest(see Figure 2). However, the peak shape of the peak at 70℃ was wide, which affected the integration accuracy and thus the quantitative accuracy. Considering peak time and response value, the initial temperature of chromatographic column was selected as 90℃, at which the peak time was about 5.6min, and the peak shape was narrow and sharp.

3.5.3 Selection of heating rate of chromatographic column

The effect of heating rate of gas chromatography column on quinoline detection results was analyzed from the peak time and response value. The results demonstrated that in the range of

ISSN:2790-1688 DOI: 10.56028/aetr.3.1.30
heating rate of 10 ℃ -30 ℃ /min, with the increase of heating rate, the peak time of the target substance got earlier and earlier and the response value of quinoline increased first and then tended to slow down. When the heating rate was 20 ℃ / min, the peak time was appropriate and the response value was high(see Figure 3). Considering peak time and response value, the heating rate was selected as 20℃/ min.

3.5.4 Selection of termination temperature of chromatographic column

The selection of termination temperature needs to take into account the components with the highest boiling point and the maximum temperature of the stationary phase. The results demonstrated that the response value of quinoline increased first and then decreased with the increase of the termination temperature. When the termination temperature was 240 ℃ and 260 ℃, the response value of quinoline was the highest and the second(see Figure 4). Considering that the boiling point of quinoline was about 240℃, the selection of 260℃might be conducive to the outflow of quinoline residual energy in the capillary column and the improvement of the column state. Thus, the termination temperature was selected as 260 ℃.

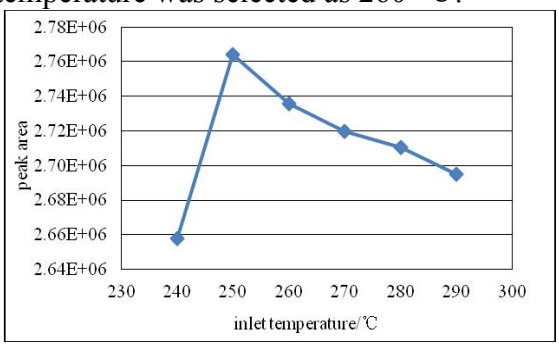

Figure 1 Effect of different inlet temperature on quinoline detection results

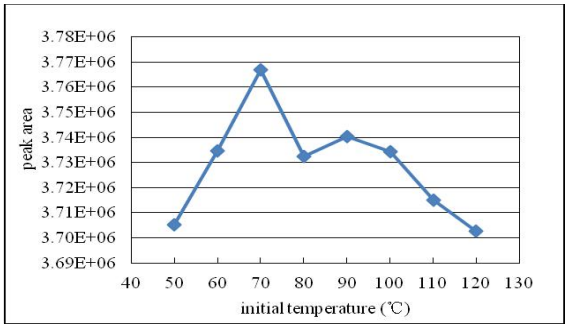

Figure 2 Effect of different initial temperature on quinoline detection results

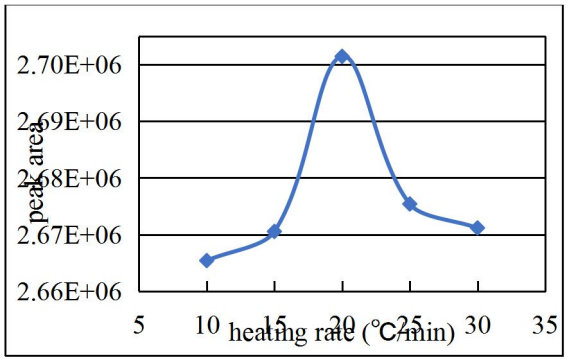

Figure 3 Effect of different heating rate on quinoline detection results

ISSN:2790-1688 DOI: 10.56028/aetr.3.1.30

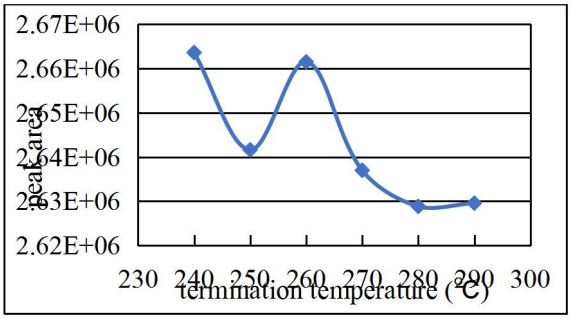

Figure 4 Effect of termination temperature on quinoline detection results

3.6 Qualitative and Quantitative Analysis of quinoline by GC-MS

The qualitative and quantitative analyses of quinoline were carried out according to the GC-MS analysis conditions described above. Under these conditions, the chromatographic peak of quinoline in the sample could be separated very well. The peak time of quinoline was found at 6.596 minutes. A sharp peak, efficient column separation, and high accuracy could be attained. Figure 5 and Figure 6 showed the results for the full-scan quinoline total ion chromatography and the mass spectrum. The characteristic ion peaks of quinoline were m/z 129, 102, 123, and 51. The abundance ratio was 129:102:123:51 = 10:3:2:1. Therefore, SIM m/z129 was adopted for qualitative analysis and external standard method for quantitative analysis, which could render higher precision.

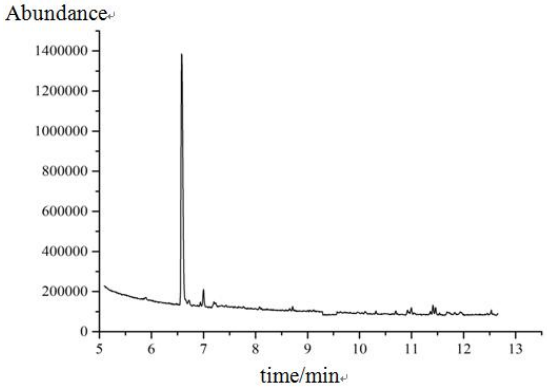

Figure 5 Total ion flow chromatogram of quinoline

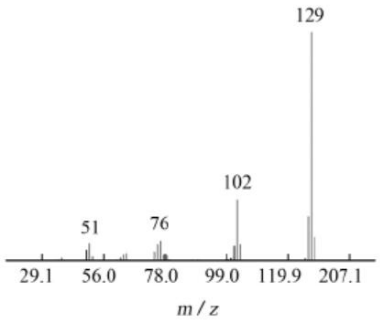

Figure 6 Mass spectra of quinoline

3.7 Standard curve, detection limit and lower limit of determination

Determine the standard solution series (0.01, 0.05, 0.15, 0.2, 0.25mg·L-1) of quinoline according to the working conditions of the instrument. Using mass concentration of quinoline as the abscissa and the corresponding peak area as the ordinate, a standard curve was constructed, giving a regression equation of y=761.3x-13.40 (y=peak area, x=concentration (mg·L-1) and a correlation

ISSN:2790-1688 DOI: 10.56028/aetr.3.1.30
coefficient (R2) of 0.9998, with a good linear relationship. The limit of detection (LOD) was 0.1 mg·kg-1, obtained from three times the baseline signal-to-noise ratio. The lower limit of the method was 0.3mg·kg-1, obtained from three times the detection limit.

3.8 Recoveries and precision

Polyester samples containing no quinoline were prepared for recovery test with concentration of 0.01, 0.05, 0.25mg·L-1. Each spiked sample was measured for 6 times in parallel. The relative standard deviation (RSD) of the recovery rate and measured value was calculated(see Table 4).

Table 4 Results of precision and recovery (n=6)

Spiked concentration ρ /(mg·L^{-1})	**Measured value ρ / (mg·L^{-1})**	**Recovery/%**	**RSD/%**
0.01	0.0829	82.9	2.4
0.05	0.0419	83.7	3.8
0.25	0.2300	92.0	1.4

3.9 Determination of actual samples

According to the test method, 22 samples randomly collected from the market were tested. and quinoline was detected in 5 samples, accounting for 23%. The mass fraction of quinoline is 2.7-27.8mg·kg-1, which met the requirement of STANDARD 100 by OEKO-TEX(below 50mg·kg-1).

Actual sample 1#, sample 2# and sample 3# were further subjected to recovery test. The addition amount was 1mg·kg-1 and 10 mg·kg-1 respectively. The recovery rates of quinoline were calculated(see Table 5). The results demonstrated that the recovery rates of quinoline in the actual samples was 86.0%-101%, indicating that the established method can accurately determine the content of quinoline in textile samples.

Table 5 Results of recovery of actual samples

Spiked concentration ρ /(mg·kg^{-1})	**Sample 1#**			**Sample 2#**			**Sample 3#**		
	Measured value ω/(mg·kg^{-1})	Total measured value ω/(mg·kg^{-1})	Recovery/%	Measured value ω/(mg·kg^{-1})	Total measured value ω/(mg·kg^{-1})	Recovery/%	Measured value ω/(mg·kg^{-1})	Total measured value ω/(mg·kg^{-1})	Recovery/%
1	22.35	23.32	97.0	34.81	35.67	86.0	27.84	28.75	91.0
10		31.89	95.4		44.65	98.4		37.92	101

4. Conclusions

A simple and effective analysis method, utilizing ultrasonic extraction technology combined with GC-MS, was developed to determine quinoline in textiles. Toluene was selected as the best extraction solvent. Ultrasonic extraction parameters and the best chromatographic separation conditions for quinoline were also determined. The linear correlation coefficient of this method was 0.9998, with a low detection limit of 0.1 mg kg-1. Recoveries ranged from 82.9 to 92.0 %, with RSDs 1.4-3.8%. The results applied to actual samples method showed that the method was accurate and can be applied to quinoline analysis in textiles to meet STANDARD 100 by OEKO-TEX or REACH regulations.

ISSN:2790-1688 DOI: 10.56028/aetr.3.1.30

Acknowledgment

This work was supported by the Basic Public Welfare Research Program of Zhejiang Province(LGF22H010014) and the Major Science and Technology Projects of Xinjiang Uygur Autonomous Region(2020A03002-2).

References

[1] Gao, Y.G., Niu, Z.Y. ，Luo, X.，Ye X.W.，Zhang Y.Y.，Lian, S.M.(2020) Determination of quinoline and isoquinoline in textiles by Gas Chromatography- Mass Spectrometry. Journal of Instrumental Analysis, vol. 39, pp. 283-286.

[2] Li, Z. J.(2010) Chem. Intermed., vol. 12, pp.: 22 - 26.

[3] Mukherjee S., Pal M.(2013) Quinolines: a new hope against inflammation. Drug Discov Today, vol. 18(7–8), pp:389–398.

[4] Vezmar M., Georges E. (2000) Reversal of MRP-mediated doxorubicin resistance with quinoline-based drugs. Biochem Pharmacol, vol.59(10), pp:1245–1252.

[5] Foley M., Tilley L.(1998) Quinoline antimalarials: mechanisms of action and resistance and prospects for new agents. Pharmacol Ther., vol.79(1), pp:55–87.

[6] P. Lam, C. Kan, M.C. Yuen, S. Cheung, R. Gambari, K. Lam, J.C. Tang, C. Chui(2012), Studies on quinoline type dyes and their characterisation studies on acrylicfabric, Color. Technol., vol. 128, pp: 192–198.

[7] Giovanna Luongo & Gunnar Thorsén & Conny Östman(2014), Quinolines in clothing textiles—a source of human exposure and wastewater pollution? Anal Bioanal Chem., vol 406, pp:2747–2756.

[8] A. Eisentraeger, C. Brinkmann, H. Hollert, A. Sagner, A. Tiehm, J. Neuwoehner(2008), Heterocyclic compounds: toxic effects using algae, daphnids, and theSalmonella/microsome test taking methodical quantitative aspects intoaccount, Environ. Toxicol. Chem., vol. 27, pp: 1590–1596.

[9] M. Nagao, T. Yahagi, Y. Seino, T. Sugimura, N. Ito(1977) Mutagenicities of quinolineand its derivatives, Mutat. Res. Fundam. Mol. Mech. Mutagen., vol. 42, pp: 335–341.

[10] Bao, Q.B., Mao, Y.J., Shen, B.Y., Qian. D.(2020), Determination of quinoline and its isomer isoquinoline residues in textiles by gas chromatography-mass spectrometry. Physical testing and Chemical analysis: part B: Chemical analysis, vol.56, pp:423-427.

[11] K.-T. Chung, S.E. Stevens, C.E. Cerniglia, (1992), The reduction of azo dyes by the intestinal microflora, Crit. Rev. Microbiol. vol.18, pp: 175–190.

[12] H.M. Pinheiro, E. Touraud, O. Thomas, (2004) , Aromatic amines from azo dye reduction: status review with emphasis on direct UV spectrophotometric detection in textile industry wastewaters, Dyes Pigm. vol. 61, pp: 121–139.

[13] T. Platzek, C. Lang, G. Grohmann, U.-S. Gi, W. Baltes(1999), Formation of acarcinogenic aromatic amine from an azo dye by human skin bacteria in vitro, Hum. Exp. Toxicol., vol. 18, pp: 552–559.

[14] NagaoMet al (1977)Mutagenicities of quinoline and its derivatives.Mutat Res., vol. 42, pp:335–341.

[15] Eisentraeger A et al(2008) Heterocyclic compounds: toxic effects using algae, daphnids, and the Salmonella/microsome test taking methodical quantitative aspects into account. Environ Toxicol Chem., vol.27(7), pp:1590–1596.

[16] Birkholz DA et al (1990) Aquatic toxicology of alkyl-quinolines. Water Res., vol. 24(1) , pp:67–73.

[17] Ba, D. B., Ma X.T.(1999), Analysis of β －Methylnaphthalene by gas chromatography. Liaoning Chem. Ind., vol.1999,28(5), pp: 304－305.

[18] Wu, Y. J.，Yu, W. F.，Qu, B. L.，Xu, X. F.，Zhuang, Q. H.(2011), Determination of Pyridine, Quinoline and Styrene in Mainstream Cigarette Smoke by Gas Chromatography Coupled with Mass Spectrometry. Fine Chem. Intermed.,vol. 41(4), pp: 70－72.

[19] GB/T 31531 － 2015. Determination of Quinoline in Dyestuffs and Textile Dyeing and Finishing Auxiliaries. National Standard of the People's Republic of China.

ISSN:2790-1688 DOI: 10.56028/aetr.3.1.30
[20] Zhao, J. H.，Li, Y. F.，Wang, J. S.，Wang, L. C.，Song, C. Y.(2013), Simultaneous determination of quinolinic acid and quinoline by high performance liquid chromatography. Zhengzhou Univ. : Eng. Sci., vol. 34(4), pp: 73－76.