CHEMICAL ENGINEERING TRANSACTIONS
VOL. 62, 2017
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet
Guest Editors: Fei Song, Haibo Wang, Fang He

ISBN 978-88-95608- 60-0; **ISSN** 2283-9216
DOI: 10.3303/CET1762074

Application of GC-MS in Determinating the Trace Impurities of Benazolin

Qiong He

Changzhou Vocational Institute of Engineering, School of Pharmaceutical and Environmental Engineering, Changzhou 213164, China
heqiong@126.com

This paper establishes the method of gas chromatography-mass spectrometry (GC-MS) for determination of the trace impurities in Benazolin. Firstly, with this method major components of Benazolin have been separated from its impurities and quantitative analysis has been conducted of the major components in Benazolin, the result of which shows a good linear relationship. Then with the mass spectrometry, main components and impurities of the herbicide have been ionized for determiantion of the impurity chemical structure via combination of the m/z data with the preparation process of Benazolin. Excellent experimental results obtained will be of guiding significance for the qualitative and quantitative analysis of Benazolin in the future.

1. Introduction

Benazolin is a kind of benzothiazole herbicide that can prevent and kill off various kinds of weeds in the fields of cereals, rape as well as soybean and owns wide application. Benazolin 15% is mainly used as postemergence herbicide for broadleaf weeds in the fields of rape or other upland crops. It is not only useful in preventing a variety of broadleaf weeds, but also, more importantly, much safer for the latest and succeeding crops. In addition, it is an excellent variety compared to the existing domestic herbicide in rape field.
In recent years, export of pesticides and the registration of new varieties have required complete analysis of their components (qualitative and quantitative analysis of impurities in the substance). Therefore, it is urgent to find a rapid and accurate analysis method with low cost.
For organic compounds, the commonly used methods of qualitative and quantitative analysis mainly include such methods of mutual coupling as UV, fluorescence, gas chromatography, liquid chromatography, mass spectrometry, etc..
GC-MS technology is the method of determinating the molecular weight by separating compounds with GC and then smashing them into fragments with the mass spectrometry (Cai and Lin, 2005). The gas chromatography is a major scientific and technological achievement in the 1950s. As a new separation and analysis technology, it has been widely used in the industry, agriculture, national defense, construction and scientific research (Liao ang Guo, 2015). It can be divided into gas-solid and gas-liquid chromatography and refers to the chromatography using gas as the mobile phase. As the substance passes fast in the gas phase, its component can instantaneously reach balance between the mobile and the stationary phases. In addition, there are many substances that can be used as the stationary phase, so this method is a separation and analysis one with high analysis speed and separation efficiency. In recent years, with the use of highly sensitive selective detector, it has been of high sensitivity with wide applications. In the petroleum chemical industry, it can be utilized for analysis of most raw materials and products (Wang and Wang, 2016); In the power sector, it can be used to check the latent fault of the transformer; In terms of environmental protection, it can be used to monitor the status of the air and water in city; In the agriculture, it can work for detecting pesticide residues in crops; In the commercial sector, it owns the function of testing and identifying the food quality; In medicine science, it can be used to study the human physiological functions; In terms of space flight and the aviation it can be used to automatically monitor the sealed gas storehouse on the spacecraft, etc (Li et al., 2016).

Please cite this article as: Qiong He, 2017, Application of gc-ms in determinating the trace impurities of benazolin, Chemical Engineering Transactions, 62, 439-444 DOI:10.3303/CET1762074

Mass spectrometry is a method of determinating the analytes via the mass-to-charge ratio. Samples to be analyzed need first ionized, and based on the different motor behavior of various ions in an electric field or a magnetic field, the mass spectrometry graph can be obtained by separating ions according to the mass-to-charge ratio (m/z). Then on the basis of the mass spectrometry and related information of the sample, one can obtain its qualitative and quantitative analytical results. Combined together, these two methods can be conducted separately at the same time (Yan et al., 2017; Li et al., 2016).
In previous literature, there has been description of the liquid chromatography, the liquid chromatography combined with the mass spectrometry as well as the gas chromatography in analysis of Benazolin, while there has no research on the component analysis of Benazolin with the gas chromatography-mass spectrometry. In this study, the GC-MS technology, being of low cost, simple operation, good repeatability and high precision compared with the method of liquid chromatography (Li and Geng, 2016), has been used for separating the major components of Benazolin from its impurities and for conducting qualitative and quantitative analysis of those components with satisfactory results obtained (Tarasov and Zheleznov, 2016).

2. Experiment

2.1 Instruments

All instruments used in this experiment are listed in Table 1.

Table 1: Instructions

Instruct	Model	Manufactor
GC-MS	QP 2010 Ultra	SHIMADZU (China) Co., Ltd.
Automatic sampler	AOC-20i	SHIMADZU (China) Co., Ltd.
Electronic balance	AY120	SHIMADZU (China) Co., Ltd.
Vortex Mixers	HQ-60	North positive Biotechnology Development Co
Nitrogen purge apparatus	HGC-12A	Tianjin Heng Ao technology development company
Electric constant heat drying oven	ON-450	ASONE Corporation
Constant temperature water tank	B-490	BUCHI company
Centrifuge	LD5-2A	Beijing medical centrifuge factory
Micro injector	10 μL	SHIMADZU (China) Co., Ltd.

2.2 Reagents and solutions

Benzenedicarboxylic acid dibutyl ester (AR, excluding the interference analysis of impurities); Benazolin (CP, Standard substance). All reagents were purchased from the Sigma company.
Ethanol (AR; Sinopharm Chemical Reagent Co., Ltd.); Ultra pure water (25 °C; resistivity: 18.2 MΩ•cm; Milli-Q Reference ultra water purification system).

2.3 Experimental conditions

Table 2 shows the conditions of the gas chromatography and mass spectrometer detector. Under such conditions, the retention time were 4.2 min and 2.7 min respectively for Benazolin and the internal standard solution.

Table 2: Experimetal Conditions

Instruct	Condition	
GC	Carrier gas	Helium
	Injection temperature	250°C
	Column temperature	50°C maintains 1 min, 10°C/min, programmed to 230°C and remains 10 min
	Interface temperature	280°C
	Carrier gas velocity	1 mL/min
	Sample size	1 μL
	Sampling method	split-flow (Diversion ratio 10:1)
MS	Ion source	EI
	Electron bombardment voltage	70 eV
	Scanning range	30-450 amu
	Ion source temperature	230°C
	Quadrupole temperature	150°C

2.4 Sample determination

Preparation of the internal standard solution: Take 2g (accurate to 0.0002g) din-butyl phthalate into a 100ml bottle, then dissolve it with absolute alcohol and dilute water until it reached the calibration, then shake it up.
Preparation of the standard sample solution: Take 0.04g (accurate to 0.0002g) standard sample into a 10ml bottle, then add 2ml internal standard solution and shake it up.
Preparation of the sample solution: Take 0.04g (accurate to 0.0002g) Benazolin into a 10 ml volumetric flask, then add 2 ml internal standard solution and shake it up.
Instrument debugging: When the instrument got stable, inject continuously several needles of standard sample solution, then calculate the repeatibility of the relative response value for each needle. When the relative response values of two adjacent needles change within less than 1.5%, determinate the amount of sample in the sequence of standard sample solution, sample solution, sample solution and standard sample solution.
Statistic analysis: Use the SHIMADZU GC-MS Postrun analysis software to measure the percentage of the peak area and give equal weight to the peak area of the experimental components, then conduct the intuitive variance analysis of multiple factor s.
Linear analysis: Take a certain standard sample, then add 2ml internal standard solution and shake it up; Use the instrument for determination once it was stable. Then the curve of the linear equation was plotted with good linearity with mass ratio (Mi/Ms) as the abscissa and peak area ratio (Ai/As) as the ordinate.
Recovery test: add a certain amount of sample into a sub standard sample with known content, then test its concentration to obtain the recovery rate of the sample by deducting the designated value of the sub standard sample.

3. Exploration

3.1 Gas chromatogram of benazolin

Under the conditions above, the major component of Benazolin can be separated better from its main impurities with the gas chromatogram as shown in Figure 1.

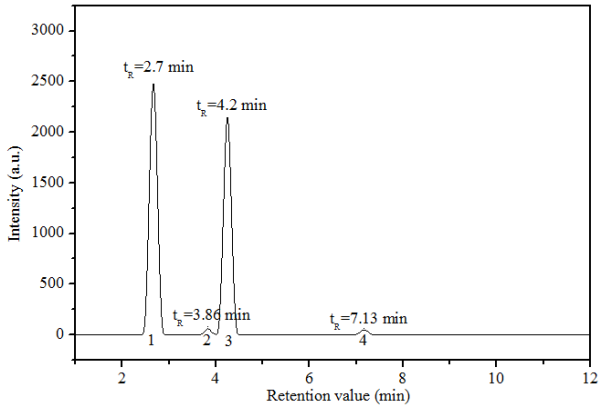

Figure 1: Gas Chromatogram of Benazolin

As shown in Figure 1, there are four peaks in the gas chromatogram of Benazolin. The peak marked as 1 is the standard sample added into the solution, besides, there are three kinds of compounds in Benazolin with a retention value of 3.86 min, 4.2 min and 7.13 min respectively. Here the compound with a retention value of 4.2 is the main component of Benazolin while impurities are the substances with the retention value of 3.86 min or 7.13 min.
As shown above, there are two kinds of impurities in Benazolin and a further exploration is needed.

3.2 Linear analysis

In order to obtain the purity of Benazolin, a linear analysis was conducted of the reference material and the curve of the linear equation was drawn as shown in Figure 2 with the mass ratio (M_i/M_s) as the abscissa, and the peak area ratio (Ai/As) as the ordinate.
As shown in Figure 2, a linear correlation coefficient of 0.99983 can be obtained with the gas chromatogram detector when the mass ratio falls between 0.65 and 1.5, indicate that the gas chromatogram technology can be used for the quantitative analysis of Benazolin.

The table 3 shows the recovery rate of Benazolin determinated with the gas chromatogram at different concentrations, proving that the gas chromatogram can be used to conduct the quantitative analysis of Benazolin with an excellent performance.

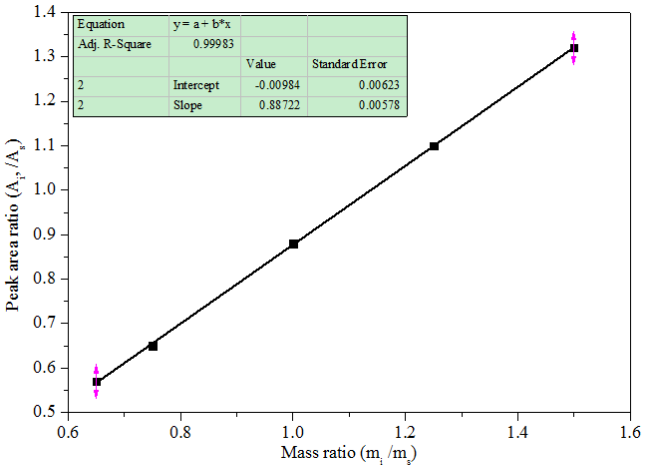

Figure 2: Linear Analysis of Gas Chromatogram

Table 3: Experimental Conditions

Concentrations (g/L)	1	2	4	6	8
Recover Rate (%)	99.93	100.03	100.10	99.91	100.07

3.3 Mass spectrometric analysis

Though with the gas chromatogram one can get to know there are two impurities as shown in Figure 1, their molecular formulas are uncertain while the m/z test can only be realized after separation through combination of the mass spectrometric with the gas chromatogram. Figure 3 shows the mass spectrometric graph of the two impurities after separation.

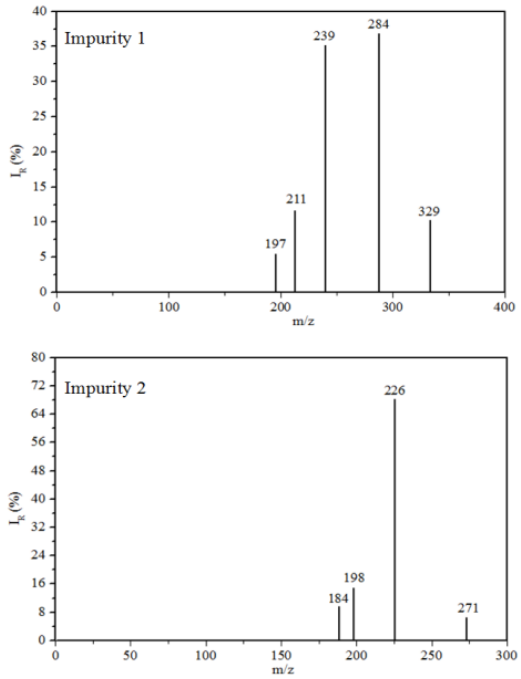

Figure 3: Mass Spectrometric of Two Kinds of Impurities

As shown in Figure 3, the two impurities own a molecular weights of 329 and 271 respectively.

In order to analyze the impurities in Benazolin, after consideration Benazolin was prepared via hydrolysis with the ethyl chloroacetate of the 2-chlorophenylthiourea after its cyclization reaction.
In combination with the molecular weight of the impurity, impurity 1 is the product of Benazolin after reaction and hydrolysis with ethyl chloroacetate of the 2-chlorophenylthiourea, as illustrated as below:

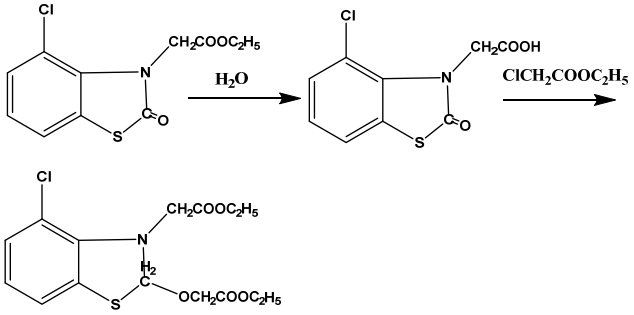

Figure 4: The Source of Impurity 1

Impurity 2 is the product of the reaction as below:

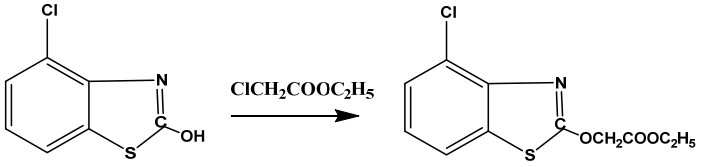

Figure 5: The Source of Impurity 2

3.4 Determination of the impurity structure

In order to prove the correctness of the presumed impurity structure, the impurity products shown above were synthesized and tested with the GC technology. And the retention value in Figure 6 has been compared with that in Figure 1. And the property of the compound can indicate whether it is synthetics of the impurities.

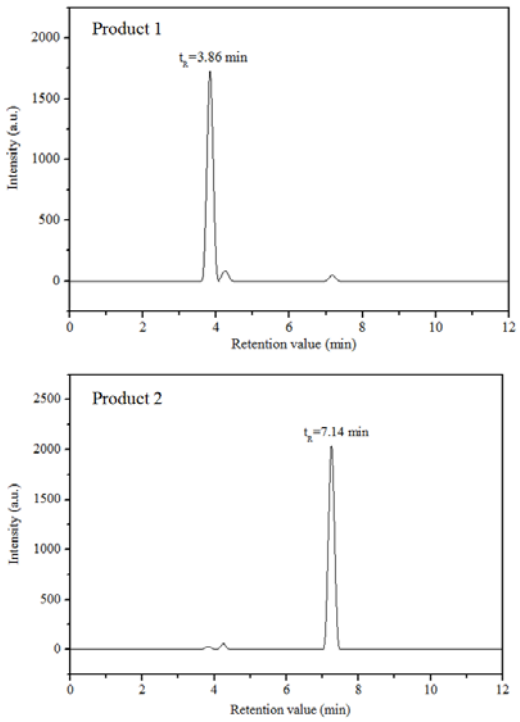

Figure 6: Gas Chromatogram of Two Products

Comparison of the retention value of the two products in Figure 6 with that in Figure 1 has reaffirmed the molecular formula of the impurities.

4. Conclusion

After a series of experiments, it is proved from the following four aspects that the gas chromatography-mass spectrometry can realize the analysis and detection of Benazolin:

1) The impurities can be separated from the main components of Benazolin with the gas chromatography;

2) The quantitative analysis can be conducted of the main components and impurities of Benazolin via the peak area. And the results show good linear relationship and high recovery rate;

3) The molecular weight and main groups of the impurities have been analyzed with the mass spectrometry, and the molecular structures of the impurities have been obtained via the synthesis of them.

4) The retention values of the synthesized impurities in Benazolin have been determinated with the gas chromatography, confirming the above results again.

Reference

Cai J.B., Lin P., 2005, Analysis of Essential Oil Components by GC/FTIR and GC/MS, Spectroscopy and Spectral Analysis, 25(10), 1599-1602, DOI: 10.3321/j.issn:1000-0593.2005.10.017.

Li J., Geng Y.Q., 2016, Analysis of polar components in mainstream smoke-absorbed simulated buccal cavity absorption solution using EG-SBSE extraction-gas chromatography-mass spectrometry, Acta Tabacaria Sinica, 22(3), 17-23, DOI: 10.16472/j.chinatobacco.2015.334.

Li L., Ping X.W., Yin X.H., 2016, Determinating the saturation magnetization of grain-oriented silicon steel sheets in MRI, IEEE International Workshop on Electromagnetics: Applications and Student Innovation Competition, 1-4, DOI: 10.1109/iWEM.2016.7505048.

Li Q., Qiao J., Cui Z., Huang D., Wang M., 2016, An analytical approach for determinating the shear strength parameters and its application in lijiahe hydro-power station, Geotechnical & Geological Engineering, 34(4), 1215-1221, DOI: 10.1007/s10706-016-0020-z.

LI Y.P., Chen N.N., Liu X.Q., 2017, Research on determinating condition for three organotion compound in seawater by HPLC-ICP/MS. Journal of Salt Science & Chemical Industry, 4-7, DOI: 10.1093/chromsci/42.4.217.

Liao Y.F., Guo Z.G., 2015, Analysis of Pyrolysis Mechanism of 5-Hydroxymethyl Furfural by Using PY-GC-MS and In-Situ FT-IR, Journal of South China University of Technology (Natural Science Edition), (6), 15-21, DOI: 10.3969/j.issn.1000-565X.2015.06.003.

Tarasov E.M., Zheleznov D.V., 2016, Development of an intelligent system of determinating the coordinates and the speed of the train.Transport & Telecommunication Journal, 17(2), 138-143, DOI: https://doi.org/10.1515/ttj-2016-0013.

Wang N.X., Wang X.Q., 2016, Study of By-product from Cyclohexane Oxidation by Multiple Mass Spectrometry Technologies, Journal of Chinese Mass Spectrometry Society, 37(1), 43-51, DOI: 10.7538/zpxb.youxian.2015.0052.