SYNTHESIS AND CHARACTERIZATION OF METHYL AMINO POLYSTYRENE AS RESIN MATERIAL OF CHROMATOGRAPHY

by Hadi.kuncoro82@gmail.com 1

Submission date: 20-Sep-2021 03:13AM (UTC-0500)
Submission ID: 1652791942
File name: 204-Article_Text-397-1-10-20190118.pdf (520.52K)
Word count: 2390
Character count: 13286

Journal of
Tropical Pharmacy
And Chemistry

SYNTHESIS AND CHARACTERIZATION OF METHYL AMINO POLYSTYRENE AS RESIN MATERIAL OF CHROMATOGRAPHY

Herman[1,2,3,*], Anni Anggraeni[1,3], Abdul Mutalib[1,3], and Husein H. Bahti[1,3]

[1]Chemical Analysis and Separation Laboratory, Departement of Chemistry,
Faculty of Mathematics and Natural Sciences, Universitas Padjadjaran,
Jl. Raya Bandung-Sumedang Km 21, Jatinangor, West Java, 45363 Indonesia
[2]Departement of Pharmaceutical Chemistry,
Pharmaceutical Research & Development Laboratory of FARMAKA TROPIS
Pharmacy Faculty, Universitas Mulawarman, Samarinda,
East Kalimantan, 75119 Indonesia
[3]Biomolecular Laboratory, Departement of Chemistry,
Faculty of Mathematics and Natural Sciences, Universitas Padjadjaran,
Jl. Singaperbangsa, Bandung, West Java, 40132 Indonesia
*Corresponding author: herman@farmasi.unmul.ac.id

ABSTRACT

Ion-exchange chromatography has been widely used in various separation process and purification. Commercial ion-exchange resin mostly uses polystyrene as base. This study reviewed the synthesis of cation-exchange resin with polystyrene as starting material. Polystyrene must be activated in order to make one of aromatic carbon chains being able to be binding with acetamide n-hidroxymethyl electrophilic. Polystyrene activation was conducted through two stages, i.e. (1) the formation of amidomethyl polystyrene (AMDP), and followed with (2) hydrolysis of acyl group. The activation of polystyrene generated white methylamino polystyrene (MAP) resin, of which its characterization used spectrophotometry UV, Fourier Transform-Infrared (FTIR), and density of MAP resin confirmed by pycnometer. The results showed that the characterization of FTIR and spectrophotometer UV for AMP exhibited the forming of primary amino group and disappearance of spectrum band of C=O group at 3374.52 cm^{-1} with λ_{max} 230 nm, the average of density of AMP resin sample was 1.7158 g/mL.

Keywords: Cation-Exchange Resin, Methylamino Polystyrene

Submitted on: 5 December 2018 Accepted on: 30 December 2018

DOI: https://doi.org/10.25026/jtpc.v4i4.204

INTRODUCTION

Ion-exchange chromatography is an easy separation method and highly used to separate and determine organic and inorganic ions in a mixture, so that it has been widely used either in laboratory or

industry. In general, starting material which is used for fabrication of ion-exchange resin is polymer, either natural or synthetic polymer [1]. The use of polystyrene as resin has been developed for increasing the efficiency of peptide synthesis as polymer with very good mechanic stability which is from polystyrene divinylbenzene [2].

The separation and purification can be conducted with ion-exchange chromatography method, because theoretically it has a high separation power. Ion-exchange chromatography method requires a big quantity of resin. While resin has high price, so it may be one of constrains in the financial sector. The expensive price of resin is caused by the comparable with complexity of its fabrication. Therefore, a renewable innovation is needed through home-made resin.

Fathy [3,4] reported that resin or ion-exchange polymer was a small un-dissolved matrix, generally white or yellowish white, fabricated from organic polymer substrate. Ion-exchange resin was well-known as chelating resin. Typical characteristic of resin is as ionic component which is able to separate selectively in separation process or purification.

Ion-exchange resin is a stationary phase that is used at column of ion chromatography. Ion chromatography offers an easy separation method and trusted for separating and determining organic and inorganic ions in a mixture [5]. Separation obstacle in ion-exchange chromatography at opened column is requiring the big amount of resin with high price, so that many scientists have been doing research regarding the fabrication of ion-exchange resin using polymer as starting material, either organic or inorganic polymer.

Resin fabrication in this study was conducted through two stages, i.e. (1) the formation of amidomethyl polystyrene (AMDP), and followed with (2) hydrolysis of acyl group from AMDP to be MAP. The consideration why polystyrene was chosen as matrix was because polystyrene was polymer which has good electricity, high heat stability, thermoplastic solid, and eco-friendly.

MATERIALS AND METHOD

Materials

Chemicals used in this study were purchased from Sigma Aldrich and Merck such as: boric acid, chloride acid, ammonia, nitric acid, trifluoroacetic acid, n-hidroxymethyl acetamide, dichloroethane, dimethylformamide (DMF), ethylene glycol, hydrogen peroxide, potassium bromide, methanol, methylene chloride, sodium hydroxide, polystyrene of DVB 1%, and tetrahydrofuran.

Polystyrene Activation to be Resin of Methyl Amine Polystyrene

Fabrication of Acetamidomethyl Polystyrene

1.0 gram of divinylbenzene (DVB) polystyrene 1% was dissolved with 10 mL dichloroethane (DCE). Then, the mixture was added with 0.5 mL (10 drops) n-hydroxymethyl acetamide and 2.5 mL trifluoroacetic acid (TFA) successively, afterwards refluxed about 22 hours. The reflux result was cooled at 26°C and centrifuged. Precipitation was washed gradually with tetrahydrofuran (THF), DMF: aquadest (3:1), DMC, and methanol. The precipitation was vacuumed by using desiccator and freeze dryer until gained the white precipitation of AMDP.

Hydrolysis of Acyl group

The AMDP precipitation was added with 5 mL ethylene glycol and stirred at 26 °C. While stirring, the mixture was added

with 5 mL HCl 35% successively and refluxed at 110°C for 22 hours. The result was cooled at 26°C and centrifuged to get a yellow solution. The yellow solution was washed successively with THF: NaOH 1N (3:1), THF: aquadest (3:1), THF, and methanol. The gained white filtrate was vacuumed by using desiccator and freeze dryer, so being gained MAP.

Characterization using FTIR

Approximately 1 mg of the AMDP precipitation was added with dry potassium bromide sufficiently. The mentioned solid was crushed using mortar so gaining pellet. The pellet was analyzed by using spectrophotometry FTIR. Same procedure was employed for MAP characterization.

Characterization using Spectrophotometer UV

The analysis using spectrophotometry UV was conducted by dissolving polystyrene into ethylene glycol solvent with concentration 10 ppm then analyzed using spectrophotometer UV. Same procedure was employed for MAP characterization in DMF solvent with concentration 10 ppm.

Determination of Density of MAP Resin

Pycnometer was washed, dried, and weighed until gaining constant result of the weighing in an empty state. Then, the pycnometer was filled with distilled water, and weighed again. Temperature of distilled water was measured. The pycnometer was dried again, then entered by resin, and weighed. After that, the pycnometer was filled by distilled water until densely, and weighed again. Temperature of distilled water was measured.

RESULTS AND DISCUSSION

Polystyrene activated can generate methyl amino polystyrene. MAP resin is a white resin with soft texture that is hard to dissolve in among organic, inorganic, or acidic solvent. This is because MAP is a polymeric resin which has many double bonds and big molecular weight that causes difficult to dissolve (shown in Figure 1).

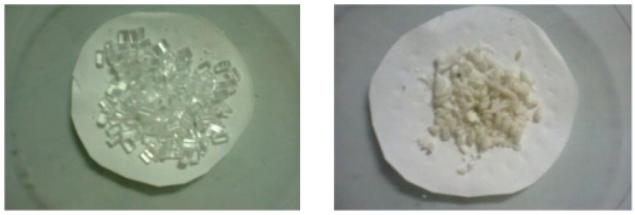
The first step for activating polystyrene was attaching amidomethyl group to benzene from polystyrene through reflux process at 65°C so that gaining AMDP compound in the form of a white precipitation that played a role as precursor. The formed precipitation of AMDP was caused by electrophilic aromatic substitution reaction taking place (depicted in Figure 2).

The AMD precipitation that has acyl group must be eliminated to remove acyl group because if this was not conducted, it would have been able to cause the derivative of carboxylic acid easy to encounter nucleophilic substitution. When the reflux was on going at 110°C, the formation of AMP occurred through hydrolysis reaction of amide so that acetyl group was replaced by other groups which were basic such as amine shown in Figure 3. Elimination of acyl group to AMDP resulted the white MAP resin.

Characterization using Fourier Transform-InfraRed

Analysis by using FTIR to the result of AMDP indicated spectrums shown in Figure 4.

Of the interpretation result, the data showed that the formation of AMDP in this study was formed due to being resulted the specific spectrum at wavelength number absorption 3418.88 cm^{-1} (1 band) which was secondary amide group (-NH-) that was bound on benzene from polystyrene, and at wavelength number 1716.68 cm^{-1} which was characteristic of the present of carbonyl group (C=O).



(a) (b)

Figure 1. (a) Polystyrene resin before synthesis.
(b) The synthesis result of MAP resin.

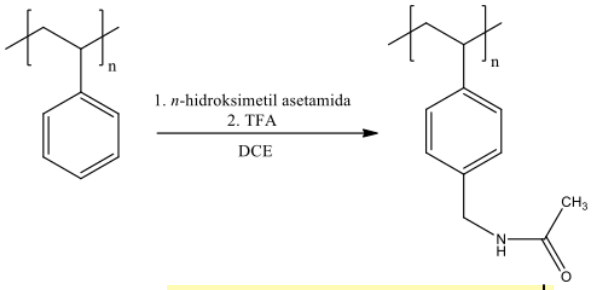


Figure 2. The formation reaction of AMP [2].

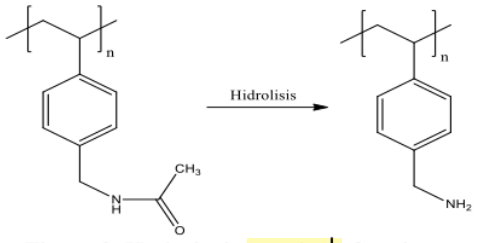


Figure 3. Hydrolysis reaction of acyl group [2].

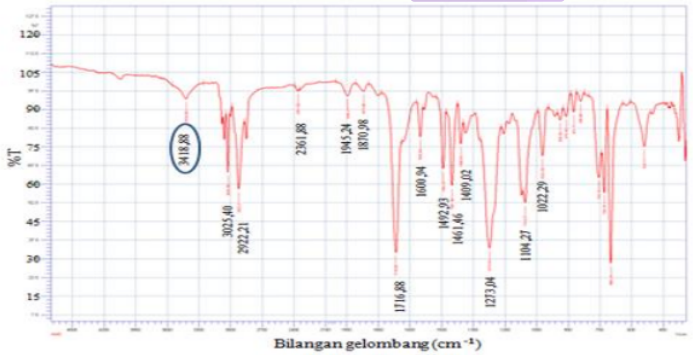


Figure 4. Spectrum of FTIR characterization for AMDP.

Table 1. Interpretation data of FTIR result for AMDP.

ν (cm^{-1})	Band	Intensity	Allegation
3418,88	Sharp	medium	stretching N-H (amida 2°)
3025,40	Sharp	Strong	stretching C-H (-CH_2-)
2922,21	Sharp	Strong	stretching C-H (siklik)
1716,68	Sharp	Strong	stretching C=O (C-karbonil)

Characterization of MAP using FTIR

The synthesis result of MAP resulted was next characterized by using FTIR. In this case, FTIR characterization of the synthesis result of MAP was compared to the FTIR spectrums of MAP in Zhang research [6] so that being able to compare typical spectrum on MAP. The FTIR characterization for MAP in Zhang [6] showed that there was amino group binding benzene from polystyrene at wavelength number 3439.67 cm^{-1} (2 bands) shown in Figure 5.

Meanwhile, the result of FTIR characterization for MAP in this study showed spectrums like in Figure 6.

Of the characterization results, the typical spectrums of MAP were found at wavelength number absorption 3374.52 cm^{-1} (2 bands) which indicated that the primary amine (1°) bound on polystyrene, and disappearance of band at wavelength 1716,68 cm^{-1} indicated that there was no C=O group on the MAP compound.

Characterization of polystyrene using spectrophotometer UV

Analysis by using spectrophotometer to polystyrene that has not been activated indicated the curve shown in Figure 7.

The characterization result of polystyrene generated the highest peak at maximum wavelength 221 nm with absorbance 0.321 that is a consequence of electron transition process from orbital $\pi \rightarrow \pi^*$ due to C-H double bond on aromatic.

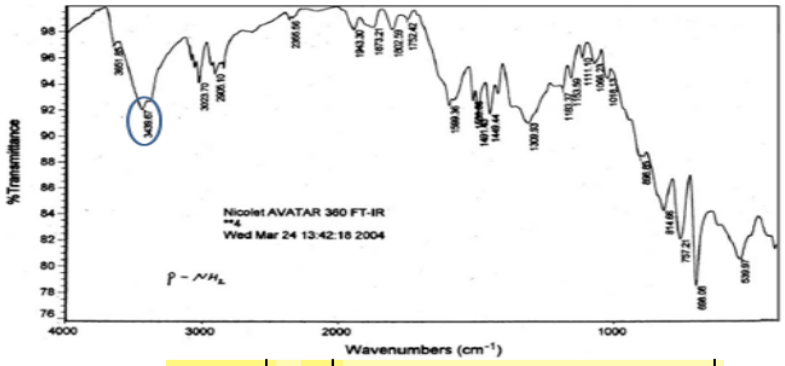


Figure 5. Spectrum of the FTIR characterization for MAP [6].

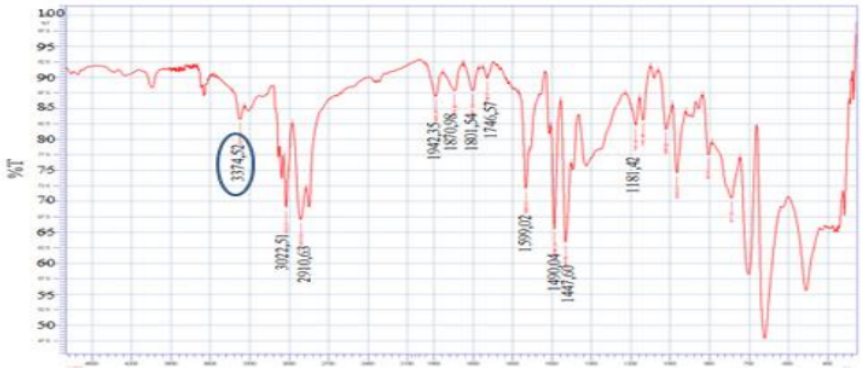


Figure 6. Spectrum of FTIR characterization for the result of MAP synthesis.

Table 2. Interpretation data of FTIR result for MAP.

ν (cm^{-1})	Band	Intensity	Allegation
3374,52	Sharp	medium	Stretching N-H (-NH_2-) 1°
3022,51	Sharp	Strong	Stretching C-H (-CH_2-)
2910,63	Sharp	Strong	Stretching C-H (-CH-)
1599,02	Sharp	Strong	Bending N-H (2°)
1024,22	Sharp	medium	Stretching C-N (Amina)

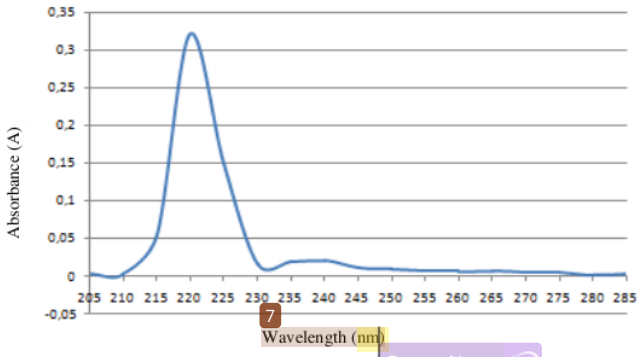


Figure 7. The characterization of spectrophotometer UV for polystyrene.

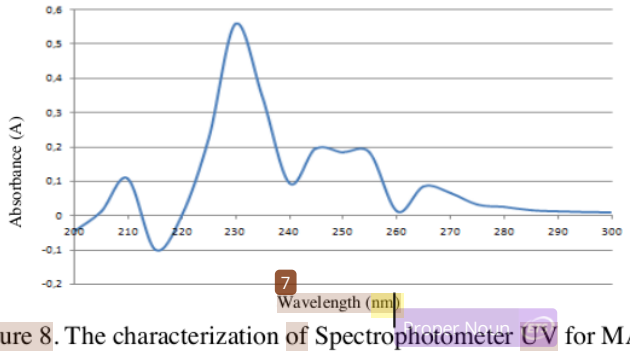


Figure 8. The characterization of Spectrophotometer UV for MAP.

Table 3. The data of determination of MAP resin density

The determination of resin density			
	Experiment 1	Experiment 2	mean
The empty pycnometer	16.1515 g	16.1516 g	16.1516 g
Pycnometer + water	24.0450 g	24.346 g	24.1955 g
Pycnometer + resin	16.9852 g	16.9853 g	16.9853 g
Pycnometer + resin + water	24.5449 g	24.5448 g	24.5449 g
The average of density: 1.7158 g/mL			

The characterization of MAP using spectrophotometer UV

Analysis by using spectrophotometer UV to polystyrene that has been activated to be AMP showed curve shown in Figure 8.

The characterization result of MAP generated the highest peak at maximum wavelength 230 nm with absorbance 0.560 that is a consequence of electron transition process from orbital $n \rightarrow \sigma^*$ due to quiet electron on nitrogen heteroatom from N-H bond (-NH_2). Transition $n \rightarrow \sigma^*$ occurred required the small energy. If the analysis result between polystyrene that has not been activated compared to polystyrene that has been activated, i.e. MAP, so MAP has resulted the presence of shift of wavelength that was not big enough. This was because of the formation of new bond to the benzene ring from polystyrene, i.e. methyl-amino bond.

Density of MAP resin

The determination of MAP resin density shown in Table 3.

Table 3 showed that MAP resin of DVB1 polystyrene has density 1.7158 g/mL. Meanwhile, water (in same temperature) has the density 0.9968 g/mL. MAP resin has higher density than water. Based on Haddad [5], the developing resin should have higher density than water.

CONCLUSION

Polystyrene could be activated being methyl amino polystyrene so forming a white MAP resin and being characterized using Fourier Transform-InfraRed (FTIR) and Spectrophotometer UV in which it indicated the formation of amino group at 3374.52 cm^{-1} with λ_{max} 230 nm which was N-H bond (-NH_2). The average density of the sample of MAP resin was 1.7158 g/mL.

REFERENCES

[1] Anggraeni, A., E. Aghnia M., Sofyatin, T., Hendrati, D., Bahti, H. H. 2017. Preparation of Phosphonated Cation Exchanger Resins and The Exchange Efficiency of Rare Earth Elements, *Jurnal Sains dan Terapan Kimia*, Volume 11, No. 2 (Juli 2017), 45-51

[2] Lee, Y. S., S. J., Ryoo & T. K., Lee. 2008. Aminomethyl Polystyrene Resin and Preparation Process for the Same. *United States Patent US 7,442,745B2*.

[3] Fathy, M., T. A. Moghny., M. A. Mousa., A. H. A. A. El-Bellihi., & A. E. Awadallah. 2015. Sulfonated Ion Exchange Polystyrene composite Resin For Calcium Hardness Removal. *International Journal of Emerging Technology and Advanced Engineering, Volume 5, Issue 11, November 2015*.

[4] Fathy, M., M. A. Mousa., T. A. Moghny., A. Hameed., E. Bellihi., & A. E. Awadallah. 2016. Novel Synthesis of Chloromethyl Functionalized Waste Polystyrene or Amorphous Carbon Thin Film Composite Resin. *Int. J. Sci.: 14(3), 2016, 1243-1250. ISSN 0972-768 X*.

[5] Haddad, P. R. & P. E .Jackson. 1994. *Ion Chromatography: Principles and Applications*. Elsevier. New York.

[6] Zhang, Q., Shouxin, W., & Ziqiang, Lei. 2006. Heterogeneous Baeyer-Villiger Oxidation of Ketones using Hydrogen Peroxide as Oxidant Catalyzed by Aminomethyl Polystyrene resin Supported Tin Complex. *Q. Zhang et al. L Reactive & Functional Polymers 66 (2006) 1278-1283*.

SYNTHESIS AND CHARACTERIZATION OF METHYL AMINO POLYSTYRENE AS RESIN MATERIAL OF CHROMATOGRAPHY

ORIGINALITY REPORT

23%	21%	5%	7%
SIMILARITY INDEX	INTERNET SOURCES	PUBLICATIONS	STUDENT PAPERS

PRIMARY SOURCES

1	garuda.ristekbrin.go.id Internet Source	13%
2	Submitted to Surabaya University Student Paper	5%
3	Submitted to Franklin & Marshall College Student Paper	1%
4	Islamudin Ahmad, Adisya Miftah Syakfanaya, Azminah Azminah, Fadlina Chany Saputri, Abdul Mun'im. "Optimization of betaine-sorbitol natural deep eutectic solvent-based ultrasound-assisted extraction and pancreatic lipase inhibitory activity of chlorogenic acid and caffeine content from robusta green coffee beans", Heliyon, 2021 Publication	1%
5	scidoc.org Internet Source	1%
6	doaj.org Internet Source	1%

7	T. S. CHENG, T. YUAN, Y. C. CHAO, C. C. LU, D. C. WU. "Premixed Methane-Air Flame Spectra Measurements Using UV Raman Scattering", Combustion Science and Technology, 1998 Publication	1 %
8	www.ijetae.com Internet Source	<1 %
9	www.science.gov Internet Source	<1 %
10	Zanyar Movasaghi, Shazza Rehman, Dr. Ihtesham ur Rehman. "Fourier Transform Infrared (FTIR) Spectroscopy of Biological Tissues", Applied Spectroscopy Reviews, 2008 Publication	<1 %

Exclude quotes	On	Exclude matches	Off
Exclude bibliography	On		

SYNTHESIS AND CHARACTERIZATION OF METHYL AMINO POLYSTYRENE AS RESIN MATERIAL OF CHROMATOGRAPHY

Article Error You may need to use an article before this word.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Article Error You may need to use an article before this word.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Article Error You may need to use an article before this word.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Article Error You may need to use an article before this word.

Article Error You may need to use an article before this word.

Proper Noun If this word is a proper noun, you need to capitalize it.

Article Error You may need to use an article before this word.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Article Error You may need to use an article before this word.

Article Error You may need to use an article before this word.

Missing "," You may need to place a comma after this word.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Article Error You may need to use an article before this word.

Article Error You may need to use an article before this word.

Article Error You may need to use an article before this word. Consider using the article **a**.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Article Error You may need to use an article before this word. Consider using the article **the**.

P/V You have used the passive voice in this sentence. Depending upon what you wish to emphasize in the sentence, you may want to revise it using the active voice.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Article Error You may need to use an article before this word.

Article Error You may need to use an article before this word.

Article Error You may need to use an article before this word.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Article Error You may need to use an article before this word. Consider using the article **the**.

Prep. You may be using the wrong preposition.

Article Error You may need to use an article before this word.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Article Error You may need to use an article before this word.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Article Error You may need to use an article before this word. Consider using the article **the**.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Article Error You may need to use an article before this word. Consider using the article **a**.

Article Error You may need to remove this article.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

P/V You have used the passive voice in this sentence. Depending upon what you wish to emphasize in the sentence, you may want to revise it using the active voice.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Article Error You may need to use an article before this word.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

P/V You have used the passive voice in this sentence. Depending upon what you wish to emphasize in the sentence, you may want to revise it using the active voice.

Article Error You may need to use an article before this word.

Wrong Article You may have used the wrong article or pronoun. Proofread the sentence to make sure that the article or pronoun agrees with the word it describes.

Article Error You may need to use an article before this word.

P/V You have used the passive voice in this sentence. Depending upon what you wish to emphasize in the sentence, you may want to revise it using the active voice.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

P/V You have used the passive voice in this sentence. Depending upon what you wish to emphasize in the sentence, you may want to revise it using the active voice.

Article Error You may need to use an article before this word. Consider using the article **the**.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Article Error You may need to use an article before this word.

P/V You have used the passive voice in this sentence. Depending upon what you wish to emphasize in the sentence, you may want to revise it using the active voice.

Article Error You may need to use an article before this word. Consider using the article **the**.

P/V You have used the passive voice in this sentence. Depending upon what you wish to emphasize in the sentence, you may want to revise it using the active voice.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Article Error You may need to use an article before this word.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Article Error You may need to use an article before this word. Consider using the article **the**.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Proofread This part of the sentence contains a grammatical error or misspelled word that makes your meaning unclear.

P/V You have used the passive voice in this sentence. Depending upon what you wish to emphasize in the sentence, you may want to revise it using the active voice.

Missing "," You may need to place a comma after this word.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Prep. You may be using the wrong preposition.

P/V You have used the passive voice in this sentence. Depending upon what you wish to emphasize in the sentence, you may want to revise it using the active voice.

Article Error You may need to use an article before this word.

Article Error You may need to use an article before this word. Consider using the article **the**.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Frag. This sentence may be a fragment or may have incorrect punctuation. Proofread the sentence to be sure that it has correct punctuation and that it has an independent clause with a complete subject and predicate.

Frag. This sentence may be a fragment or may have incorrect punctuation. Proofread the sentence to be sure that it has correct punctuation and that it has an independent clause with a complete subject and predicate.

Article Error You may need to use an article before this word.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

PAGE 5

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Article Error You may need to use an article before this word. Consider using the article **the**.

Article Error You may need to use an article before this word.

Article Error You may need to use an article before this word.

Article Error You may need to remove this article.

Article Error You may need to remove this article.

Verb This verb may be incorrect. Proofread the sentence to make sure you have used the correct form of the verb.

Proper Noun If this word is a proper noun, you need to capitalize it.

Article Error You may need to use an article before this word.

Missing "," You may need to place a comma after this word.

Article Error You may need to use an article before this word. Consider using the article **the**.

Article Error You may need to remove this article.

Frag. This sentence may be a fragment or may have incorrect punctuation. Proofread the sentence to be sure that it has correct punctuation and that it has an independent clause with a complete subject and predicate.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

PAGE 6

Proper Noun If this word is a proper noun, you need to capitalize it.

Frag. This sentence may be a fragment or may have incorrect punctuation. Proofread the sentence to be sure that it has correct punctuation and that it has an independent clause with a complete subject and predicate.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

PAGE 7

Proper Noun If this word is a proper noun, you need to capitalize it.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Article Error You may need to use an article before this word. Consider using the article **the**.

Article Error You may need to use an article before this word. Consider using the article **the**.

Article Error You may need to use an article before this word. Consider using the article **a**.

Proper Noun If this word is a proper noun, you need to capitalize it.

Article Error You may need to use an article before this word.

Article Error You may need to use an article before this word.

Confused You have used **quiet** in this sentence. You may need to use **quit** instead.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Article Error You may need to use an article before this word.

Article Error You may need to use an article before this word. Consider using the article **a**.

Proper Noun If this word is a proper noun, you need to capitalize it.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.

Sp. This word is misspelled. Use a dictionary or spellchecker when you proofread your work.