

An Affordable and Easily Accessible Approach for Acrylonitrile Monomer Purification through a Simple Column Technique

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Abstract

This manuscript presents a dataset detailing a method for purifying monomers. Purification plays a crucial role in every chemical process, as it leads to an improvement in product quality through the removal of impurities. The primary method for monomer purification, like acrylonitrile (AN), is the distillation technique. However, this technique is unsafe and hard to set up or handle. A straightforward, risk-free, low-cost method like the column technique resolves these issues. A simple column technique demonstrated the successful execution of purifying AN. Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) analyses confirmed that AN was successfully purified, with purity reaching 99.8%. FTIR spectra revealed changes in the position and intensity of the stretching vibration peaks after purification. Also, the functional groups of the inhibitor monomethyl ether of hydroquinone (MeHQ) were undetected after purification. Furthermore, after purification, NMR spectra revealed the absence of aromatic protons and carbons associated with MeHQ. In conclusion, the column technique is a successful and inexpensive way to purify AN monomers. This makes it useful for a wide range of applications, especially in polymerization reactions where MeHQ needs to be removed to prevent self-polymerization during the initiation process.

Keywords

Liquid Monomers, Acrylonitrile, Purification, Inhibitor, Simple Column

1. Introduction

The end products of organic reactions are rarely pure. The starting material or the reactions' byproducts frequently contaminate them. The technique used for purification is highly dependent on the nature of the compound and the types of byproducts that may be present. Besides, removing impurities improves the product's quality and standard, whether organic compounds are acquired from nature or synthesized in laboratories [1]. Eliminating impurities or byproducts is termed purification, and the purified material should undergo quantitative and qualitative testing. Popular purification techniques include filtration, crystallization, fractional crystallization, sublimation, distillation (fractional, under reduced pressure, steam, or azeotropic), differential extraction, and chromatography [2] [3] [4] [5].

Researchers are increasingly interested in altering polymers into added-value products, especially in energy storage and conversion. Copolymerization, grafting, and crosslinking are all ways to change some properties of the host polymer, and they all need monomers as one of the reactants [3] [6]. As is well known, stabilizers are added to liquid monomers like styrene, acrylonitrile, vinyl chloride-d3, methyl acrylate, acryloyl chloride, 2-chloroethyl vinyl ether, etc., in the form of 4-tert-butylcatechol (TBC), 35 - 45 ppm monomethyl ether hydroquinone (MeHQ), and 400 ppm phenothiazine (PTZ) to prevent the monomers from self-polymerizing or being started by light, heat, or air. Thus, inhibitors are needed to process, transport, and store unsaturated monomers like acrylates, vinyl chloride, butadiene, and styrene. However, it should usually be removed before polymerization. Otherwise, it will react too early with the free radical initiator, reducing its efficiency and concentration [7].

Acrylonitrile (AN) and acrylic acid (AA) are examples of liquid monomers that can be purified by distillation at a constant temperature of 69.5°C and 80°C - 130°C, respectively [8] [9]. However, the distillation method has some disadvantages, such as being unsafe, cumbersome, and time-consuming. In addition, the distilled monomer would likely be exposed to moisture if not used immediately after distillation [10]. Column chromatography is a modern method for separating, isolating, identifying, and purifying small amounts of organic compounds. This method is based on the fact that the parts of a mixture move at different rates through a porous medium (the stationary phase) when a solvent or gas (the mobile phase) is present. This project is about finding a fast, safe, cheap, and easy-to-use way to purify AN monomer. A simple column is used to solve these problems. This study looked into the performance of a simple column on AN purification attributed to the advantages of this technology, as described in **Figure 1**. The authors' main goal is to conduct a study to investigate and assess the performance of the simple column technology for acrylonitrile monomer purification. This study selected AN as a monomer because it has unique properties like high filmability, transparency, optical clarity, adhesive characteristics [11], and good grafting efficiency compared to vinyl monomers

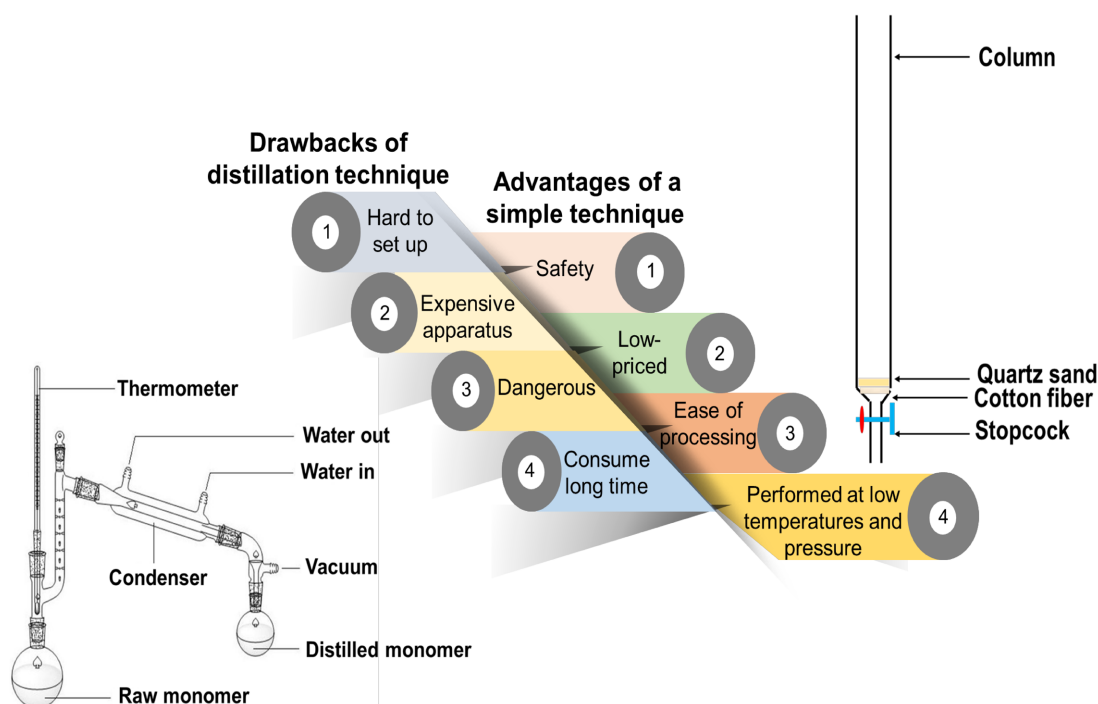


Figure 1. A schematic diagram of a simple column's advantages versus the distillation technique's drawbacks.

[6] [12]. To our knowledge, there has been no publication of this study. This work's long-term viability depends on a simple, low-cost approach for purifying monomers. In addition, this technique will increase the use of purified monomers in many processes, particularly polymerization reactions.

2. Experimental Procedure

2.1. Materials

Acrylonitrile (C_3H_3N , $\geq 99\%$ *w/v*, contains 35 - 45 ppm MeHQ as an inhibitor), acrylic acid ($C_3H_4O_2$, 99% *w/v*, contains 200 ppm MeHQ as an inhibitor), basic aluminum oxide (Al_2O_3 , 99.9% *w/w*), and potassium carbonate (K_2CO_3 , 98% *w/w*) were purchased from Sigma-Aldrich (Zwijndrecht, Netherlands; St. Louis, Germany; and St. Louis, MO, USA, respectively). The chemical structures of AN, AA, and MeHQ are displayed in **Figure 2**.

2.2. Monomers Purification

The monomers were purified similarly to what was described in the MRG Lab-Notes [10], but with a few minor changes. The monomer purification was carried out in two stages: 1) column preparation and 2) purification.

2.3. Preparation of Columns

After thoroughly cleaning the work area within a fume hood, the column diameters were selected based on the quantity of monomers to be processed (approximately 100 mL). This led to the choice of columns with a diameter of roughly 4 cm. The cotton fibers were inserted into the stopcock at the base of the columns

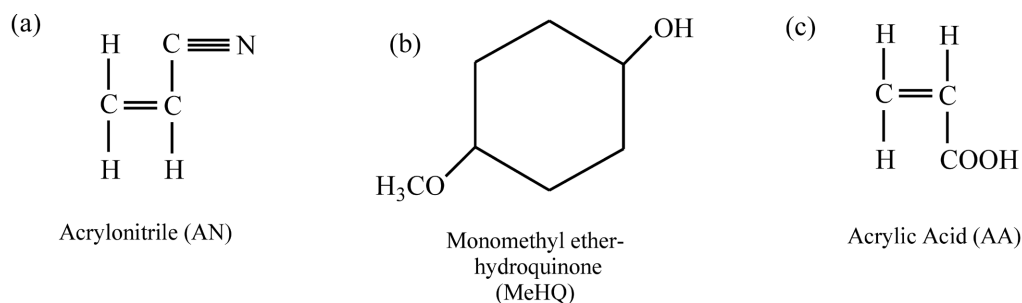


Figure 2. The chemical structures of (a) AN, (b) AA, and (c) MeHQ.

to act as effective filters. Subsequently, quartz sand was carefully poured over the cotton, ensuring that the sand level extended beyond the conical portion of the columns, reaching approximately 1.5 cm, to facilitate sample loading. Following this step, Al_2O_3 was meticulously added to the columns without inhaling the powder. This aluminum oxide layer was about 8 cm above the sand and acted as the stationary phase, removing impurities and MeHQ inhibitors from the samples by absorbing them. Lastly, oven-dried K_2CO_3 was added to the columns to a depth of about 3 cm to act as a barrier and stop the purified monomers from collecting when the impurified monomers in the columns got close to their top.

2.4. Purification Process

The requisite monomers were left at room temperature (RT) for two hours to prevent further water absorption via condensation. Subsequently, the monomers were meticulously introduced into the columns using glass funnels until the columns reached full capacity. Following this, the stopcocks were unsealed to enable a gentle, pressure-free flow of monomers through the columns, thereby preventing cloudiness. However, the AA monomer moved slowly through the column because the $-\text{COOH}$ group of the AA reacted with the K_2CO_3 , causing the column to bubble. In contrast, the AN monomer effortlessly descended to the column's base. A small quantity of AN monomer was then collected in a clean vial to examine for Al_2O_3 contamination, revealing the AN monomer's clarity. Subsequently, the purification continued, maintaining a continuous stream of AN monomer to prevent column desiccation. Purified AN monomer was collected in a securely sealed container once it became evident that impurities and inhibitors retained at the Al_2O_3 layer were not progressing further down the column (into the sand). Collection ceased when the impure monomer reached the upper portion of the K_2CO_3 . Subsequently, the columns underwent thorough rinsing with multiple passes of acetone. For more testing, the purified AN was kept in a cold place with dry nitrogen to stop it from polymerizing at RT. A depiction of the experimental setup for the monomer purification procedure is illustrated in **Figure 3**.

2.5. Characterizations

2.5.1. Determining the Percentage Purity of the Purified AN

The purified monomer's purity was calculated according to the mass of the purified chemical divided by the mass of the sample times 100 percent as follows:

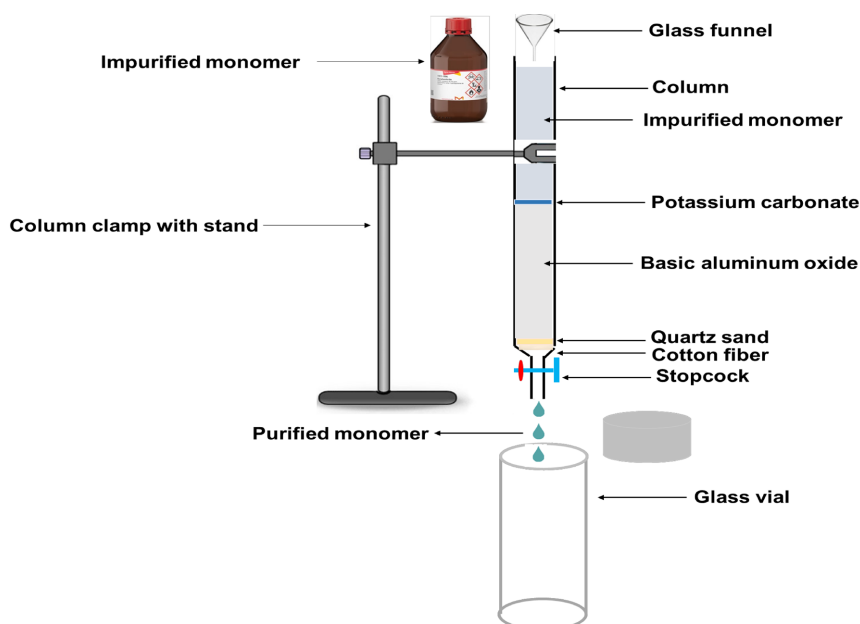


Figure 3. Experimental setup of monomer purification procedure.

$$\% \text{ Purity} = \frac{m_1}{m_2} \times 100$$

where m_1 and m_2 are the mass of the purified monomer in the sample and the total mass of the impurified sample, respectively, the purity (99.8%) was estimated from the volume of monomer taken for purification (about 100 mL), the volume of the purified monomer (99.8 mL), and the density of acrylonitrile (0.81 g/cm³).

2.5.2. Fourier Transform Infrared (FTIR) Spectroscopy

Perkin-Elmer 2000 Frontiers Fourier-transform infrared (FTIR) (Waltham, MA, USA) was used to determine the chemical functional groups in the impurified and purified AN samples. The samples were analyzed using a spectral area ranging from 650 to 4000 cm⁻¹, a scan resolution of 2 cm⁻¹, and an accumulation of 32 scans at RT.

2.5.3. Nuclear Magnetic Resonance (NMR)

Fourier transform nuclear magnetic resonance (FT-NMR) at Bruker/Advance III HD 400 MHz (Bruker, Rheinstetten, Germany) with a standard-bore H-X probe and direct-polarization (DP) and cross-polarization (CP) models were used to do one-dimensional (1D) ¹H-NMR and ¹³C-NMR. About 0.037 mL of AN samples were dissolved in 0.6 mL of deuterated chloroform (CDCl₃) to study the proton and carbon environments of both purified and impurified AN at RT.

3. Results

3.1. FTIR Analysis

FTIR analysis was employed to elucidate the structural characteristics of AN af-

ter purification. The examination also facilitated the identification of alterations in distinctive bands associated with functional groups, contributing to a comprehensive understanding of structural modifications induced by the purification process through a simple column. The impact of purification on the FTIR spectrum of purified AN, in contrast to impurified AN, is depicted in **Figure 4**. Both spectra exhibited prominent peaks at 2230, 1736, 1614, and 967 cm^{-1} , corresponding to the $-\text{C}\equiv\text{N}$, $-\text{C}=\text{C}$ stretching vibration, $-\text{C}=\text{N}$ stretch resonance, and $-\text{C}-\text{H}$ wagging motion vibration of butadiene, respectively—considered as the principal functional groups in the AN structure [6] [13] [14]. Nevertheless, discernible variations in peak intensities were observed in the purified AN, attributed to the successful elimination of impurities during the purification process.

Notably, the impurified AN spectrum manifested $-\text{C}-\text{H}$ stretching peaks for sp^2 carbon above 3000 cm^{-1} , indicative of CH stretch in the aromatic ring. Additionally, overtone absorption between 2000 and 1667 cm^{-1} , attributed to para-substituted 4-methoxyphenol in MeHQ [15], was identified in the impurified AN but not in the purified AN. Furthermore, alterations in absorption bands associated with $-\text{CH}_2$ scissoring ($\delta_s -\text{CH}_2$), $-\text{CH}_2$ rocking ($\rho -\text{CH}_2$), $-\text{C}-\text{C}$ stretch, and $-\text{C}-\text{H}$ stretch within the range of 1450 to 650 cm^{-1} —characteristic of the alkene structure—were changed after purification. These findings collectively suggest the successful removal of MeHQ, characterized by an aromatic ring with di-substituted benzene, as illustrated in **Figure 2(b)**, following the purification of AN through a simple column.

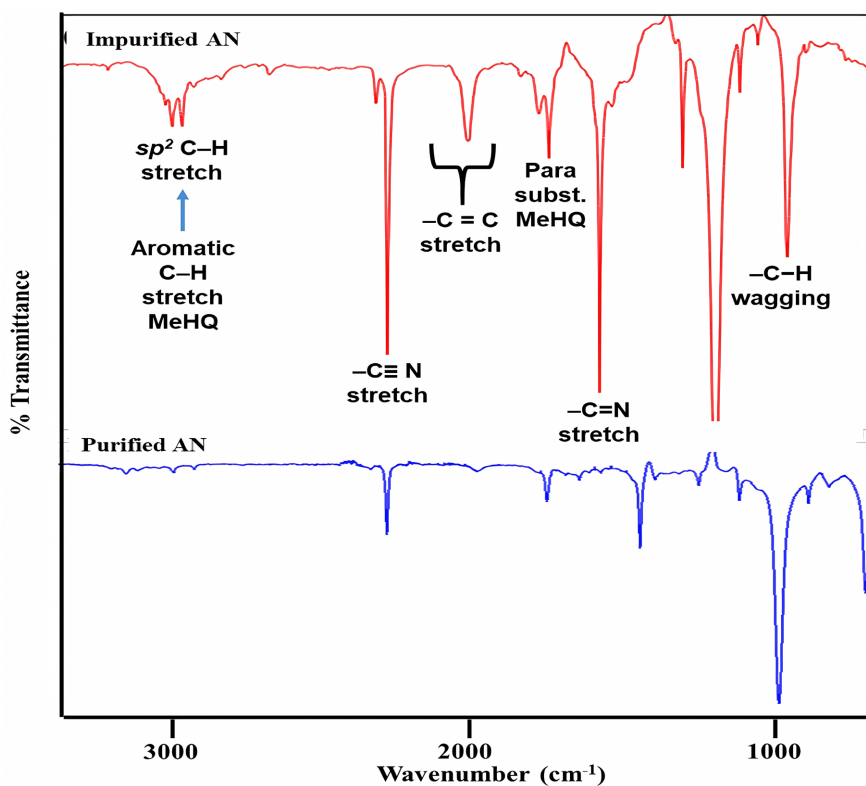
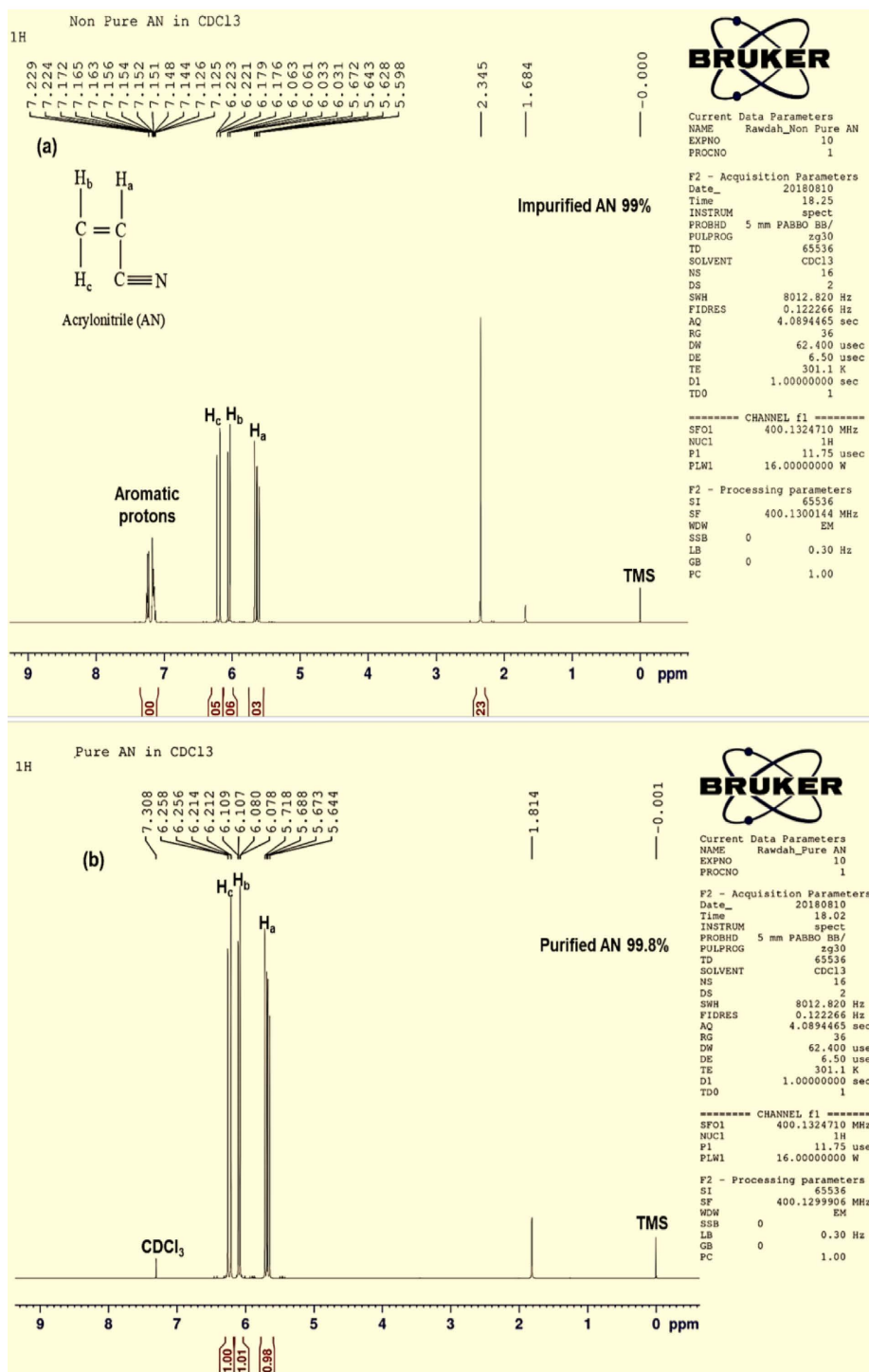


Figure 4. FTIR spectra of (a) impurified and (b) purified AN.

3.2. NMR Analysis

Proton and carbon nuclear magnetic resonance (^1H -NMR and ^{13}C -NMR, respectively) were also carried out to affirm the successful purification of the AN by simple column by studying the protons and carbon environment of the purified AN compared to the impurified sample. **Figure 5(a)** depicts three sets of protons



at δ 5.7 ppm, δ 6.1 ppm, and δ 6.2 ppm, denoting a doublet of H_a, H_b, and H_c in impurified AN. Besides, multiple peaks were detected at δ 7 - 8 ppm that belong to the aromatic protons of the inhibitor of MeHQ.

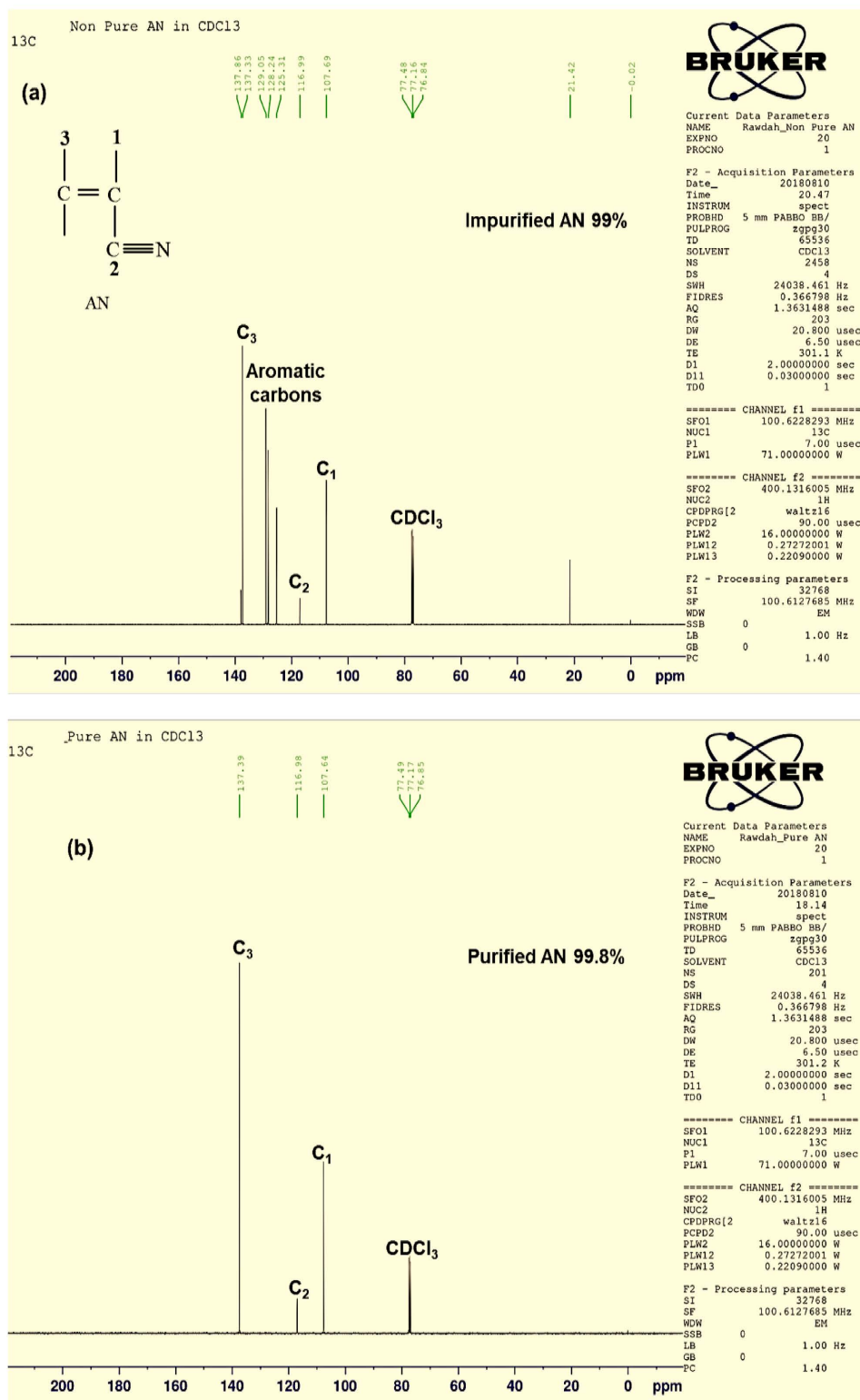


Figure 6. ¹³C-NMR spectra of (a) impurified and (b) purified AN.

As reported by Jacobsen [16], the benzene ring provides a general shift of $\delta 7 - 8$ ppm in the proton spectrum since the ring has a strong electron-donating group, such as the methoxy group ($-\text{OCH}_3$), which allows the aromatic ring to be electron-rich relative to benzene, with aromatic protons shielded and shifted upfield from the generic value of $\delta 7.28$ ppm. This result agreed with FTIR, which showed C-H stretching peaks for the sp^2 carbon at values greater than 3000 cm^{-1} , corresponding to the $-\text{CH}$ stretch in the aromatic ring. A strong peak was also observed at $\delta 2.5$ ppm that may be related to $-\text{OCH}_3$ of MeHQ, as shown in **Figure 2(b)**. However, no peaks of the aromatic protons, or $-\text{OCH}_3$, were detected in **Figure 5(b)**. It should be noted, within **Figure 5(a)**, that the unassigned peaks spanning the chemical shift range of $\delta 1 - 3$ ppm, which lacked explicit identification, are attributed to impurities present in the sample. After the purification process, the absence of these peaks in the spectrum indicates their successful removal from the specimen.

The ^{13}C -NMR spectrum of impurified AN, as displayed in **Figure 6(a)**, exhibited three peaks at $\delta 107$ ppm, $\delta 117$ ppm, and $\delta 137$ ppm for C_1 , C_2 , and C_3 for AN. Peaks were also detected at $\delta 120 - 130$ ppm, thought to be for aromatic carbons [15]. However, no peaks of these aromatic carbons were noticed in **Figure 6(b)**, indicating the removal of the MeHQ from AN after purification. It should be pointed out that the peaks at $\delta 7.27$ ppm and $\delta 77$ in ^1H -NMR and ^{13}C -NMR ppm are associated with the CDCl_3 solvent residue.

4. Conclusion

A simple column technique was employed to purify the acrylonitrile monomer, and it exhibited excellent performance, resulting in a purity level of 99.8%. Analytical techniques such as FTIR and NMR confirmed the efficacy of this column-based purification process for acrylonitrile. These results affirm that the purification successfully eliminated impurities and inhibitors, particularly compared to a sample without purification. Notably, it should be noted that this purification technique is best suited for monomers lacking acidic functional groups. In summary, the significance of this purification method should not be underestimated, as it holds substantial potential benefits across various applications, particularly in the realm of polymerization reactions.

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Conflicts of Interest

No potential conflict of interest was reported by the authors.

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