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PURIFICATION OF ACETONITRILE WITH IMPROVEMENT IN QUALITY, YIELD AND REDUCTION OF INDUSTRIAL WASTE

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ABSTRACT

Efforts were made to improve the purity and yield of acetonitrile with reduced waste, which is basically by-product, but a good solvent. The effect of amount of potassium permanganate, sodium carbonate and phosphorous pentoxide was observed and these were optimized to get better sample of acetonitrile (HPLC grade). It was supported by absence of any peak in the retention time of 35-40 min as evident from gradient analysis. This purification process may save a lot of money.

KEYWORDS : Acetonitrile, Purification, Better Quality, Yield

Acetonitrile is the by-product of acrylonitrile, which is the major raw material in the manufacture of plastic as acrylic fibers, ABS resins, etc. In the laboratory, it is used as a medium polarity solvent that is miscible with water and a wide range of organic solvents but not with saturated hydrocarbons. It has convenient liquid range and a high dielectric constant of 38.8 with a dipole moment of 3.92D (Steiner and Gordy, 1966). Acetonitrile dissolves a wide range of organic and non-polar compounds and is useful as a mobile phase in HPLC and LC-MS. The N-C-C-C skeleton is linear with a short C-N distance of 1.16 Å. Most of the acetonitrile manufacturers produce acrylonitrile as a major product and acetonitrile as by-product. As it is a by-product, the quality is not maintained by the manufacturer. However, during the last 10 to 15 years, the demand for acetonitrile has increased considerably due to its use in HPLC analysis across the world. This has necessitated controlling the quality and purity of the by-product acetonitrile. Since the quality of acetonitrile has to be improved from technical grade, new and varied methods of purification were looked up. Acetonitrile procedure is produced with the better quality, maximum yield and low impurities on changing the purification procedure..

Acetonitrile, a colorless liquid, is the simplest organic nitrile (Hydrogen cyanide is a simpler nitrile but here, the cyanide anion is not classed as organics (DiBiase et al., 2003). It is used as a polar solvent (organic solvent) in organic synthesis and in the purification of butadiene. Acetonitrile (HPLC gradient grade) manufactured by industries exhibited certain impurities. Though, the acetonitrile batches manufactured pass the specifications of UV spectroscopy but they fail to pass the gradient analysis test having peaks at retention time of 35-45 min in the base line. These peaks interfere with the HPLC analysis of certain drugs and intermediates manufactured by different pharma companies. Hence, they require smooth and straight base line in the gradient graph. This project was taken up to improve the quality of acetonitrile (HPLC gradient grade) so as to meet the requirement of pharma companies for HPLC analysis of drugs and to ensure that gradient graph is smooth and straight between retention time 0 to 45 min. as per the requirement of pharma companies (Comwall, 2011).

MATERIALS AND METHODS

Acetonitrile, (2012) (Raw material received as technical grade) is double distilled to produce acetonitrile HPLC grade. This is produced in two 7000 Litre capacity stainless steel 316 dedicated distillation assemblies. Both distillation vessels are provided with stainless steel 316 stirrers and stainless steel 316 packed columns of 400 mm dia. and 12 m height. They are packed with stainless steel 316 pot rings packing material for efficient separation. These vessels are provided with stainless steel 316 limpet coils for circulation of hot oil and cold water. The column is provided with water condenser for vapour cooling, water condenser for product cooling and reflux divider for reflux and distillation. The column in both the vessels is not directly installed on vessels but through 'S' bend of almost 6 feet. This avoids the residue from the distillate directly

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going into the column. Column tapping arrangement is provided for sample tapping during distillation at various levels. The first distillation vessel (V1) is provided with 7000 Litre capacity stainless steel 316 receiver (R1) placed horizontally on the platform. The first distillation of acetonitrile with potassium permanganate and sodium carbonate was carried out in this vessel and the entire distillate is received in receiver (R1). From receiver R1, the first distillate is transferred by gravity to second distillation vessel (V2). In this vessel, acetonitrile from first distillate is treated with phosphorous pentoxide and distilled. The distillate is collected in two 7000 Litre capacity vertical receivers (R2). These are provided with bottom outlet and valve. These receivers are under nitrogen pressure. Except for charging acetonitrile (technical form, that is raw material) received in 30 x 200 Litre drums is transferred to distillation vessel (V1) by vacuum, charging of reactants in vessel is also through vacuum and rest all the operations were done without manual handling. Since both the distillation assemblies are dedicated for acetonitrile distillation, the chances of cross contamination are minimal.

In order to study the problem of gradient analysis, the raw materials viz. acetonitrile (Technical grade) supplied by various manufacturers were analyzed by GC-MS and LC-MS to find out impurity profile. Acetonitrile technical grade supplied by four major manufacturers contains two major impurities viz. Diisopropyl ether (about 0.03%) and propanenitrile (about 0.01%). The UV-transmission test that is UV cut off wavelength between 210 nm to 220 nm is not more than 1 absorbance for all the samples (Malmberg and Maryott, 1956). Acetonitrile technical grade is satisfactory and meets the requirement. Purity of all of them is about 99.8% and it is much better than, what was available about six years back.

Since the acetonitrile (Technical grade raw material) received does not contain much impurities except diisopropyl ether and propanenitrile, it is assumed that during processing, some additional impurities are formed and get carried into distillate. In order to prove this, number of experiments were carried out in the laboratory with different composition of reactants such as potassium permanganate, sodium carbonate (anhydrous) and phosphorous pentoxide.

RESULTS AND DISCUSSION

The existing process uses 0.5% potassium permanganate, 0.25% sodium carbonate (anhydrous) and 0.5% phosphorous pentoxide. The output of the distilled products from all the raw materials received from four manufacturers is shown in the Table 1. In order to know, how potassium permanganate affects the quality?, some laboratory scale experiments were carried out on 500 mL acetonitrile using 0.16%, 0.125% and 0.08 % potassium permanganate. The results were quite encouraging. The distillate passed the UV-transmission test satisfactorily and meets the requirement for samples of all the manufacturers. The purity of all of them was about 99.8%. There is

Table 1: Initial Purification Process of Acetonitrile (Raw Material Received From Different Manufacturers) Resulted in Below Gradient Analysis And % UV Transmission

Manufacturer (Supplier of raw material)	Gradient analysis	Transmission							
		Wavelength (nm)	191	195	200	210	220	230	240
		Minimum % transmission	35	80	90	95	97	98	99
Supplier-1	Peaks observed at 35-45 min	% Transmission observed	47.7	87.2	98.2	98.8	99.8	100.2	100.2
Supplier-2	Peaks observed at 35-45 min		45.2	82.7	94.8	97.3	98.9	99.5	99.7
Supplier-3	Peaks observed at 35-45 min		46.6	84	95.8	96.9	98.4	99.6	99.8
Supplier-4	Peaks observed at 35-45 min		44.7	83.2	98.4	99.1	99.3	100	100

Table 2: Second Stage Improvement in Purification Process of Acetonitrile (Raw Material) Received from Different Manufacturers Resulted in Below Gradient Analysis and % UV Transmission

Manufacturer (Supplier of raw material)	Gradient analysis	Transmission							
		Wavelength (nm)	191	195	200	210	220	230	240
		Minimum % transmission	35	80	90	95	97	98	99
Supplier -1	Base line showed mi nimal peaks at the 30 to 45 min	% Transmission observed	46.5	83.3	94.7	94.2	96.5	99.2	99.9
Supplier -2	Base line showed mi nim al peaks at the 30 to 45 min		45.7	85.7	96.7	97.8	98.9	99.6	99.9
Supplier -3	Base line showed minimal peaks at the 30 to 45 min		45.9	83.0	95.6	96.9	98.4	99.3	99.6
Supplier -4	Base line showed mi nimal peaks at the 30 to 45 min		45.8	85.5	98.2	98.5	99.3	99.6	99.6

Table 3: Third Stage Improvement in Purification Process of Acetonitrile Raw Material Received from Different Manufacturers resulted in Below Gradient analysis and % UV Transmission

Manufacturer (Supplier of raw material)	Gradient analysis	Transmission							
		Wavelenth (nm)	191	195	200	210	220	230	240
		Minimum % transmission	35	80	90	95	97	98	99
Supplier-1	No base line drift and no peaks observed at 35-45 min	% Transmission observed	44.4	83.9	95.7	96.4	97.7	99	99
Supplier-2	No base line drift and no peaks observed at 35-45 min		46.3	84.9	96.8	98	99	99.7	100
Supplier-3	No base line drift and no peaks observed at 35-45 min		45.5	84	95.7	96.5	97.6	98.9	99.4
Supplier-4	No base line drift and no peaks observed at 35-45 min		45.5	85.3	97.7	97.8	98.5	99.1	99.4

considerable improvement in the base line showing very minimal peaks in the retention time of 30 to 45 min. of gradient analysis.

Following four plant batches from different manufacturers supplying raw material acetonitrile (Technical grade 6000 Liter input) were carried out as per old process involving 0.5% potassium permanganate, 0.25% sodium carbonate anhydrous and 0.5% phosphorous pentoxide, where it shows peaks and spikes between retention time of 30 to 45 min. (Table 1).

Based on laboratory scale experiments, following four plant batches from different manufacturers supplying raw material, acetonitrile (Technical grade) of 6000 Liter input was carried out using reduced quantity of 0.16% potassium permanganate, 0.08% sodium carbonate anhydrous and 0.16% phosporous pentoxide. There is considerable improvement in the base line showing very minimal peaks in the retention time of 30 to 45 mins. (Table 2).

In order to still improve the base line further, the laboratory scale experiments were carried out with still further reduction of reactants. The batches were run with optimum quantity of reactants viz. potassium permanganate 0.08%; sodium carbonate anhydrous. 0.04% and phosphorous pentoxide 0.16%. These batches were analyzed as per specifications and the gradient analysis The graphs exhibit the base line straight without any peaks or spikes between 0 min. to 45 min. retention time.

Based on the above pilot plant study, the batch using 5 Kg potassium permangnate, 2.5 Kg sodium carbonate (anhydrous) and 10 Kg phosphorous pentoxide per batch of 6000 liter acetonitrile (Technical grade, raw material) were run in the manufacturing plant. Potassium permanganate 0.08%; sodium carbonate (anhydrous) 0.04% and phosphorous. pentoxide 0.16%). These batches were analyzed as per specifications and the gradient analysis. The graphs exhibited the base line straight without any peaks or spikes between 0 min. to 45 min retention time (Table 3 and gradient graph 3).

Benefits

The reduction of the catalyst potassium permanganate 0.08 %; sodium carbonate (anhydrous). 0.04% and phosphorous. pentoxide 0.16 % resulted in gradient analysis graphs with very minor to negligible peaks or spikes that were observed between 0 to 45 min. The base line was found to be almost straight as required by many pharma companies. No polymeric or rubber like residue was observed, since quantity of phosphorous pentoxide was reduced from 30 Kg to 10 Kg per batch in final distillate. Cleaning time of distillation assemblies has reduced considerably since quantity of potassium permanganate and phosphorous pentoxide was reduced from 30 Kg to 5 Kg and 30 Kg to 10 Kg, respectively. Frequency of cleaning of 1 and 0.2 micron line filters on packing line was reduced considerably due to reduction in phosphorous pentoxide. The yield of acetonitrile HPLC gradient grade per batch of 6000 Litre input has increased from 5450 Liters to 5500 Liters. Increase of 50 L was observed, which works out to almost 0.8% higher yield. Thus, raw materials inputs have reduced the cost per batch by Rs. 7710. Considering about 120 batches produced in an year, present work has a saving of Rs. 9,25,200 per annum. Considering 50 Litre yield increase per batch, the saving based on yield works out to approximately. Rs 9.0 Lakhs per annum. Thus, total savings per annum works out to be Rs. 18 Lakhs.

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