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Characterization and Evaluation of Technical Grade Solvents and Comparison to their Purified Counterparts

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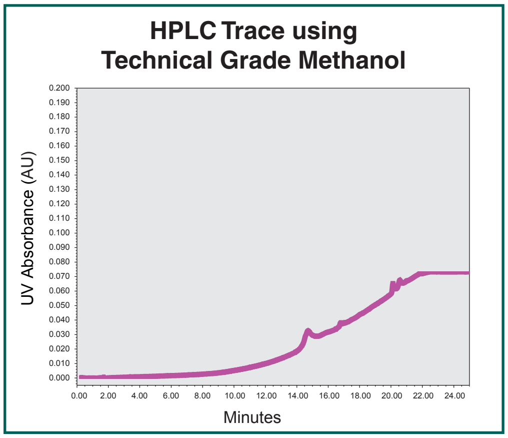
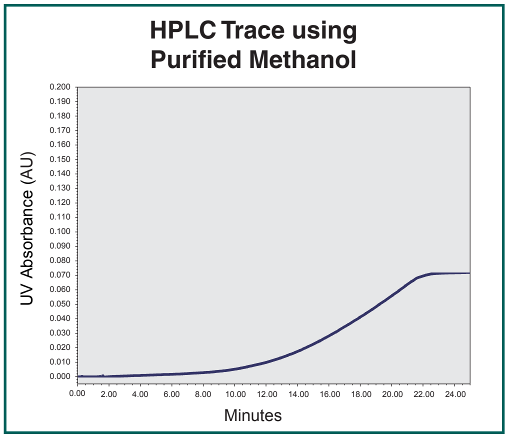
Abstract:

Technical grade solvents and their purified counterparts are separately useful for many different applications. One important application for the common solvents acetonitrile, methanol and acetone is in organic synthesis. Another important application for acetonitrile and methanol is as a diluent or mobile phase in chemical analysis, ie: UV-VIS spectroscopy, HPLC and LC-MS. We have observed and identified a number of impurities in these solvents that may interfere with synthesis and/or accurate analytical testing. For instance, a common contaminant in acetonitrile is acrylonitrile. Trace aldehydes and ketones can be found in methanol. Diacetone alcohol is commonly found in acetone. We have characterized impurity levels in commonly used solvents and will show the variability present in technical grade and purified solvents, using GC, GC-MS and LC-MS. Results on the impurities and their probable effect on synthesis and analytical testing will be presented.

METHANOL

HPLC Comparison of Methanol Grades





HPLC Method

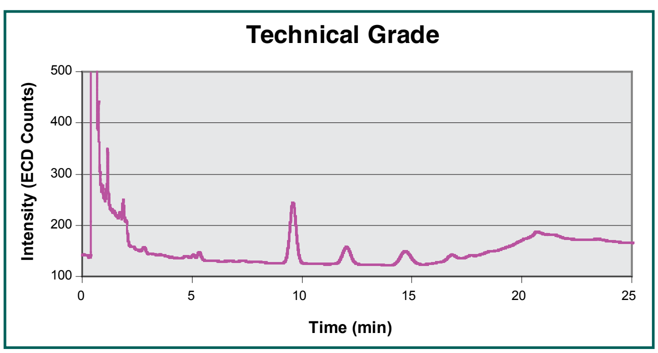
Time (min)	% Water	% Methanol
0	95	5
20	0	100
25	0	100
30	95	5
35	95	5

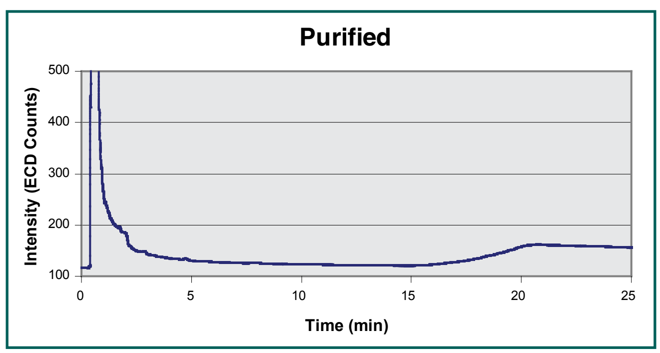
Method/Instrument parameters:
Column: B&J HLD Octyl OC5 (C8)
Column (15 X 0.46cm, 5um #9511)
Flow Rate: 1.5mL/min
Water used: Honeywell B&J Brand Water, #365-4
UV absorbance at 220 nm

Methanol has applications in purge and trap and headspace analysis of various samples, including in environmental and drug sample analyses. It is also important in HPLC and GC applications.

Comparison of Methanol Grades by GC with Electron Capture Detector

- The ECD detector is selective for electronegative compounds, such as halogens, organometallic compounds, nitriles and nitro compounds.
- The contamination peaks in the technical grade methanol detected by ECD range from 0.1-54pg (based on heptachlor epoxide as the standard). While the contamination peaks in the purified methanol are less than 0.3pg (based on heptachlor epoxide as the standard).
- Note the solvent front interference and many large contamination peaks in technical grade methanol are absent in the purified methanol.





Method: 200mL of methanol was concentrated (400x) and exchanged into hexane. The data was obtained on an Agilent 6890N GC with an ECD detector and a Restek Rtx-5 30 meter column. Sample injection = 5 microliters. The initial oven temperature was held at 200°C for 15 minutes then increased by 10°C/min until 250°C, then held for 10 minutes.

Common Impurities in Technical Grade Methanol

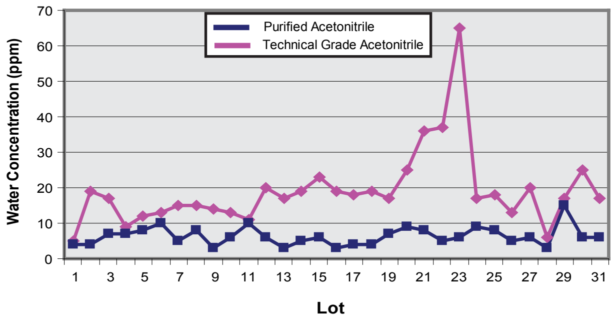
Some impurities that are commonly present in technical grade methanol are: 2-butanone (MEK), 3-pentanone, N, N-dimethyl acetamide and 2,3-butanedione. These are detectable by GC-MS in the technical grade material, indicating that their concentration is at least 1ppm. However, these impurities are not detected by GC-MS in purified methanol.

ACETONITRILE

Lot-to-Lot Variablility in Acetonitrile Grades

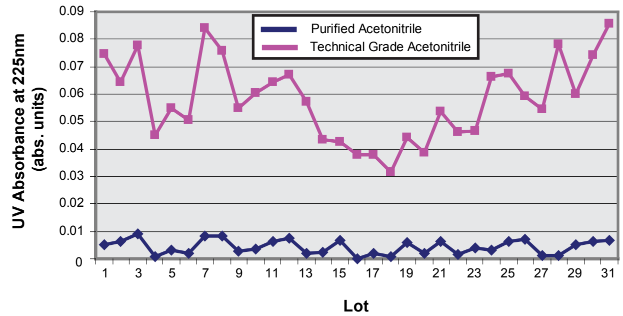
The following graphs show the variability which is normally seen in different lots of technical grade acetonitrile as well as the decrease in variability of purified acetonitrile. Data from 31 consecutive lots of technical grade acetonitrile and 31 consecutive lots of purified acetonitrile were collected and graphed.

Lot-to-Lot Variability in Water Concentration in Technical Grade and Purified Acetonitrile



Lot-to-Lot Variability in Water Concentration. The water concentration was measured by Karl-Fisher Titration.

Lot-to-Lot Variability in UV Absorbance of Technical Grade and Purified Acetonitrile

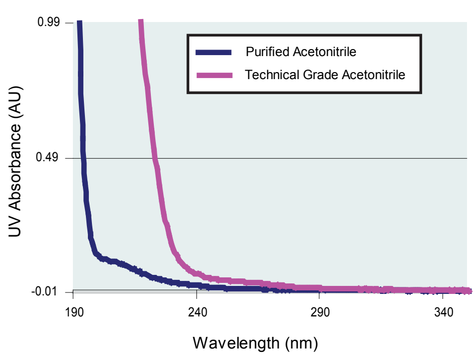


Lot-to-Lot Variability in UV Absorbance at 225nm. UV Absorbance was determined with a Varian Cary 400 Scan UV-Visible Spectrophotometer utilizing a path length of 1 cm.

- Low water content is very important in applications such as automated DNA/RNA synthesis and organic synthesis since the water may compete with the reactants in the reaction pathway.
- UV absorbance background is critical for HPLC acetonitrile for two reasons: First, most organic impurities contribute to UV absorption. Second, the most commonly used detection mode in HPLC instruments is the UV detector, which means the lower the UV absorbance of acetonitrile, the lower the chromatographic baseline background, and hence the higher the sensitivity and the lower the detection limit.

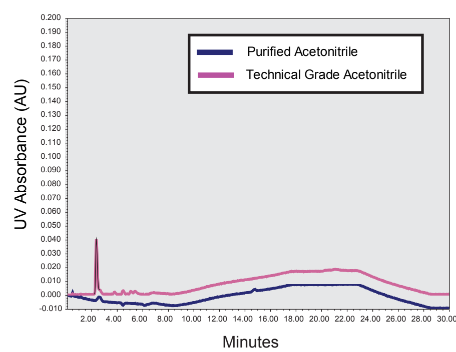
Spectral Comparison of Acetonitrile Grades

UV Comparison of Acetonitrile Grades



This graph shows a comparison of the typical absorbance of a technical grade acetonitrile sample and that of its purified counterpart. This data was obtained with a Varian Cary 400 Scan UV-Visible Spectrophotometer utilizing a path length of 5 cm. The higher absorbance between 240 and 195 nm is indicative of contaminants in the technical grade acetonitrile.

HPLC Comparison of Acetonitrile



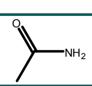
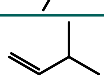
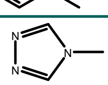
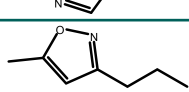
HPLC Chromatograms at 200 nm for technical grade and purified acetonitrile.

HPLC Method

Time (min)	% Water	% Acetonitrile
0	70	30
5	70	30
15	30	70
20	30	70
25	70	30
30	70	30

Method/Instrument parameters:
Column: B&J OD5 (C18) (#9575) (25 X 4.6cm, 5mm)
Flow Rate: 1.0 mL/min
Water used: Honeywell B&J Brand Water, #365-4

Common Impurities in Technical Grade Acetonitrile

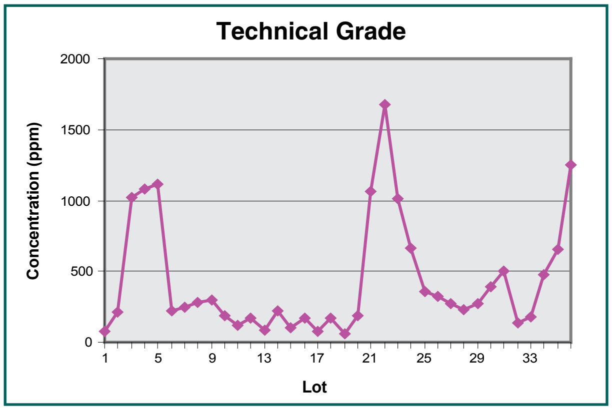
Impurities Detected by GCMS*		Approximate Concentration in Technical Grade	Approximate Concentration in Purified Grade
	Acetamide	5-20ppm	Not Detected
	3-Methyl-1-Butene	2-10ppm	Not Detected
	4-Methyl-4H-1,2,4-Triazole	2-10ppm	Not Detected
	5-Methyl-3-Propyl-Isoxazole	Not detected-5ppm	Not Detected

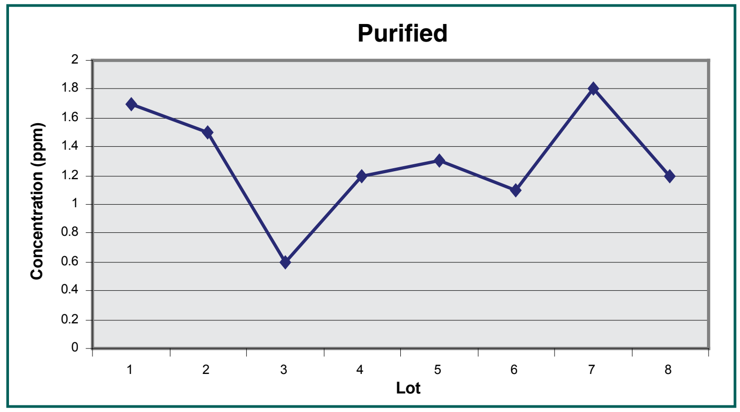
Data was collected on a Shimadzu QP2010 GCMS using A Restek Rtx-1 105m X 0.32mm column. The temperature program started at 60°C and progressed to 260°C at 5°C/min.

**Detection limit approximately 1ppm.*

Comparison of Diacetone Alcohol Levels in Acetone Grades

Most chromatographers find ketones, such as acetone, stable and easy to use. However, lower detection limits have created conditions in which solvent degradation effects are important. Ketones degrade over time through an acid or base catalyzed condensation. For acetone, the ketone reacts with its enol tautomer, to produce diacetone alcohol. This can undergo further reaction such as dehydration to produce mesityl oxide. High levels of diacetone alcohol may indicate material which has undergone degradation and may interfere with GC-FID and other sensitive instrumentation techniques.



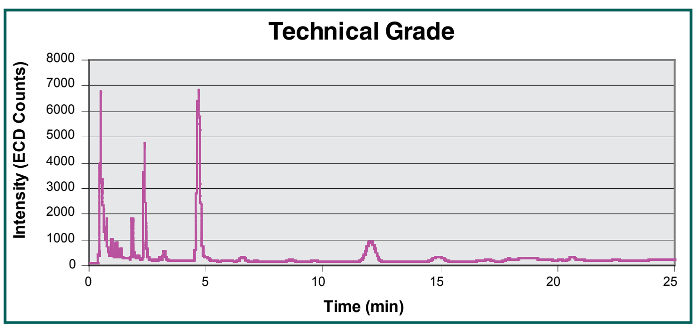


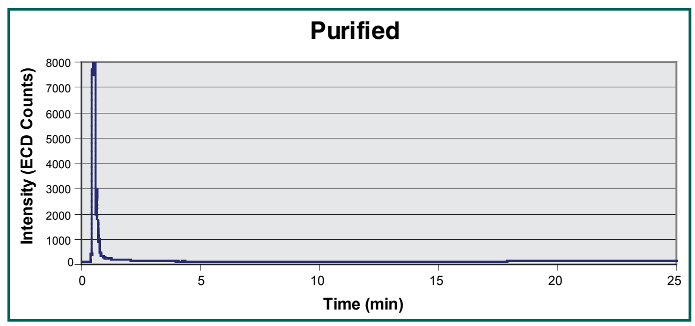
The first graph shows the large variability in the concentration of the impurity diacetone alcohol in technical grade acetone. The second graph highlights the effect that processing has on the concentration and variability of this same impurity.

An Agilent 6890N GC with a FID detector and a Restek Rtx-5 30 meter column was used for this experiment. Sample injection = 3 microliters. The initial oven temperature was held at 40°C for 5 minutes then increased by 10°C/min to 75°C, then held for 2 minutes.

Comparison of Acetone Grades by GC with Electron Capture Detector

High purity acetone is vital in environmental analysis for the quantitation of trace amounts of PCBs and pesticides. It is important in Solid Phase Extraction and Extraction by Soxhlet Extractor.





Method: 200mL of acetone was concentrated (400x) and exchanged with hexane. The data was obtained on an Agilent 6890N GC with an ECD detector and a 30 meter Restek Rtx-5 column. Sample injection = 5 microliters. The initial oven temperature was held at 200°C for 15 minutes then increased by 10°C/min until 250°C, then held for 10 minutes.

Common Impurities in Technical Grade Acetone

Some common impurities in technical grade acetone are: methanol, IPA, diacetone alcohol, benzene, 2-methylpropanal, and 2-butanone. The concentrations vary from lot-to-lot, but are detectable by GC-MS. These impurities are not detected by GC-MS in purified acetone.

The detection limit of diacetone alcohol by GC-MS is approximately 2ppm.

Conclusion:

We have shown that processing reduces the variability in technical grade solvents. The reduction in impurities in purified acetonitrile was shown by the decrease in the UV absorbance, the reduction in water concentration by Karl-Fisher and the reduction in the number and size of HPLC-UV peaks. The decrease in impurities in purified methanol was shown by HPLC-UV and GC-FID. The reduction in impurities in purified acetone was shown by GC-ECD (for halogenated compounds) and by GC-FID (for diacetone alcohol).

In conclusion, there are some applications for which technical grade solvents are appropriate, however, any process that requires consistently pure solvent should use purified solvent to insure that impurities and variability in impurities do not cause adverse affects, unwanted side-reactions or loss of sensitivity.

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