

PURIFICATION OF ACETONITRILE
AND
TESTS FOR IMPURITIES

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PURIFICATION OF ACETONITRILE AND TESTS FOR IMPURITIES

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Nitriles can be prepared by a large variety of methods^{1, 2}. It became known only recently that in the United States acetonitrile is currently obtained in large quantities as a by-product in the preparation of acrylonitrile. Little information can be obtained at present from manufacturers (at least in the United States) about the impurities present in their products. Technical data reports are available from Eastman Kodak Co. for n- and isobutyronitrile, but not for acetonitrile. However, the major impurities present in acetonitrile from several sources could be identified by polarographic and other techniques, described below.

EFFECT OF IMPURITIES IN ACETONITRILE

Acetonitrile is a relatively inert solvent, being a weaker base and a much weaker acid than water. Consequently many possible impurities are sufficiently reactive to modify its properties significantly, even when present in extremely low concentrations. Ammonia and acetic acid are of special concern, since these compounds can be formed by hydrolysis of acetonitrile (fortunately only under relatively severe conditions). The presence of either of these substances will be highly objectionable in certain studies, particularly those involving unbuffered solutions of weak acids or bases. For example, ammonia at concentrations as low as 10^{-5} M seriously interferes in studies concerned with the ionization of weak acids in acetonitrile³, and the same is true of acetic acid in measurements involving weak bases⁴. Furthermore, one of the most insidious complications caused by the presence of acidic or basic impurities in any solvent is the uncertainty introduced into the evaluation of the solvent correction which must be applied to the conductance of acids and bases⁴.

The presence of water in acetonitrile is less disastrous, but nevertheless quite low concentrations of this persistent impurity can cause significant errors in certain (not all) measurements. Three particularly striking examples are given below.

(i) The dissociation constant of the protonated form of the Hammett indicator 4-chloro-2-nitro-N-methylaniline increases by a factor of 6.5 when 1.7×10^{-2} M (3.1×10^{-2} % by volume) water is added⁵. This large effect is caused mainly by the pronounced increase in the solvation

energy of the proton which occurs when the relatively strong base, water, converts the species CH_3CNH^+ into H_2OH^+ (and higher hydrates):



It should be noted⁶ that distillation of acetonitrile from anhydrous calcium sulphate (a desiccant frequently used for this purpose) typically leaves approximately 2×10^{-2} M water in the product. Hence a much more effective drying agent is required.

(ii) The half-wave potential of the solvated proton (as 1×10^{-3} M perchloric acid) at the dropping mercury electrode becomes 0.15 V more negative on adding 1×10^{-2} M water⁷. This pronounced shift is due, in part, to the direct effect of the increase in solvation energy of the proton on its reduction potential, and in part to an increase in the hydrogen over-potential on mercury.

(iii) The conductivity of n-butylamine is doubled by adding 8×10^{-2} M water⁴. Actually, the total effect of water is much greater than that indicated by the increase in conductivity, since relatively stable BH^+OH^- ion pairs are formed. Here the relatively strong acid properties of water are involved, resulting in extensive hydration (hydrogen bonding) of the amine, as shown by infrared measurements.

For the sake of maintaining a proper perspective, it should be pointed out that the three examples given above represent extreme cases. Usually the effect of water is much less.

PURIFICATION OF ACETONITRILE

The traditional method for the purification of acetonitrile generally involves preliminary shaking with a cold, saturated aqueous solution of potassium hydroxide, intended to remove acetic acid, followed by repeated distillation from phosphorus pentoxide until the residue is no longer coloured (orange or black). There can be little doubt that the pretreatment with potassium hydroxide does more harm than good, since undesirable base-catalyzed hydrolysis may occur and it is difficult to remove subsequently the large amount of water introduced. Either alumina^{3, 6} or calcium hydride⁶ effectively removes acetic acid without causing undesirable side effects.

Repeated distillation of acetonitrile from phosphorus pentoxide has the disadvantage that it usually causes extensive polymerization of the solvent. Formation of the polymer (an orange gel) not only decreases the yield, but often also causes bumping and therefore less efficient fractionation. Formation of this gel does not occur in every distillation, and is an unpredictable event. In extreme cases the overall yield from 4 to 6 distillations (as recommended by Walden⁸ and many subsequent authors) may be as low as 20 per cent.

In view of these disadvantages of the conventional methods, several alternative procedures have been investigated in this laboratory, using acetonitrile from a variety of sources. Two procedures which give superior

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results were developed, and are described below. In addition, polarographic and other tests are given for common impurities. Full details appear elsewhere⁶.

In *Figure 1* are presented the polarographic waves of several samples of

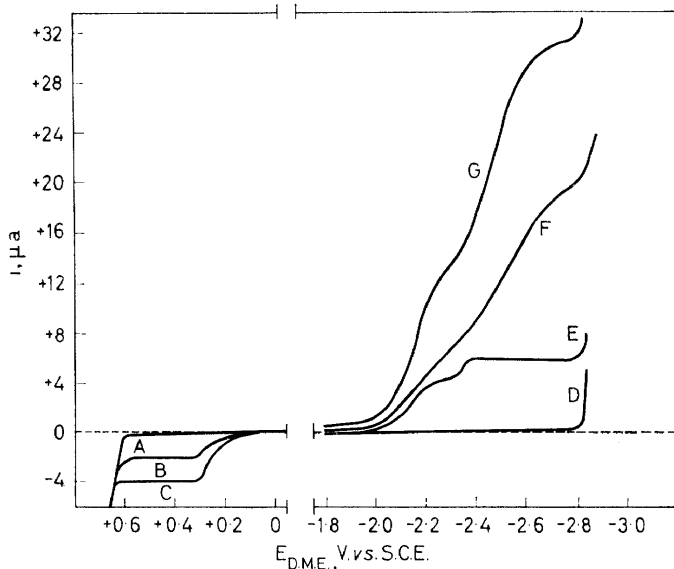
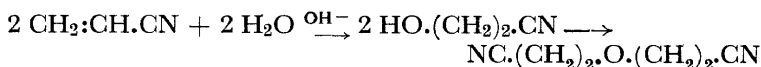


Figure 1. Polarographic waves of common impurities in acetonitrile. (Solvent: Eastman practical grade acetonitrile; supporting electrolyte: 0.05 M tetraethylammonium perchlorate)
AD: acetonitrile purified by procedure II
AE: acetonitrile purified by procedure I, or by distillation from either phosphorus pentoxide or anhydrous calcium sulphate
AG: 1×10^{-2} M acetic acid added to solvent from calcium sulphate distillation
BF: unpurified acetonitrile
CE: 1×10^{-3} M ammonia added to solvent from calcium sulphate distillation.

acetonitrile and of added acetic acid and ammonia. The two incompletely resolved cathodic waves of curve *AE* were shown to be caused by unsaturated nitriles, such as acrylonitrile (*Figure 2*), and not by acetic acid, as previously assumed.

RECOMMENDED PURIFICATION PROCEDURES

For the majority of uses of acetonitrile, Procedure I is recommended. In those few instances where the presence of traces of unsaturated nitriles (less than 1×10^{-3} M) would be objectionable, for example with reagents such as mercaptans and halogens, Procedure II can be followed, which incorporates a cyanoethylation reaction to convert unsaturated nitriles into high-boiling products:



However, Procedure II generally introduces traces of ammonia, as might be expected, and therefore must not be used for experiments in which am-

monia interferes. As alternatives to Procedure II, the last step of Procedure I may be repeated under the highest possible reflux ratio, or the chlorination procedure of Keefer and Andrews⁹ may be useful for certain work.

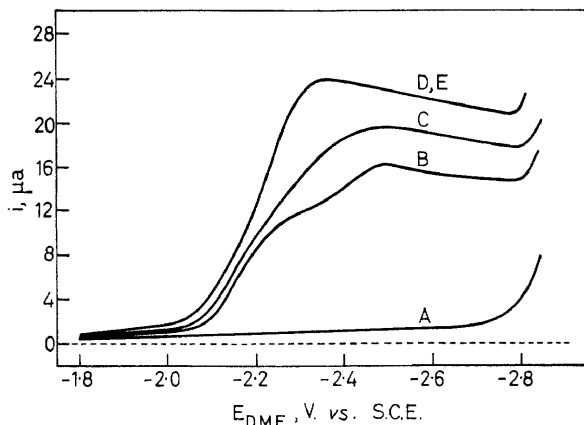


Figure 2. Polarographic waves of acrylonitrile in acetonitrile. (Solvent: Fisher Spectrograde; supporting electrolyte: 0.1 M tetraethylammonium perchlorate)

A: residual current curve
 B: 3×10^{-3} M acrylonitrile added
 C, D, E: 0.17, 0.51 and 0.85 M water added to B.

Recently, Forcier and Olver¹⁰ have found that sodium hydride is more effective than potassium hydroxide in removing unsaturated nitriles. O'Donnell, Ayres and Mann¹¹ have removed traces of aromatic hydrocarbons with potassium permanganate, and apparently obtained high purity acetonitrile by distilling first from benzoyl chloride and then from potassium permanganate. We have not yet tested these procedures, but advise workers to do so if the presence of trace amounts of unsaturated compounds must be avoided.

In the recommended Procedures I and II, one distillation from phosphorus pentoxide is retained to remove possible basic impurities. Calcium hydride is used to remove acidic impurities, including remaining traces of water.

Procedure I

Treat the acetonitrile by the following sequence of operations:

1. If a considerable amount of water is present (more than approx. 0.1 M), preliminary drying by shaking with silica gel or Molecular Sieves (e.g. Linde Type 3A) is advisable. This step often can be omitted.
2. Shake or stir (a magnetic stirrer is particularly effective) with sufficient calcium hydride to remove most of the remaining water, until hydrogen evolution ceases (relieve pressure). Decant.
3. Distil in an all-glass apparatus under a high reflux ratio from phosphorus pentoxide (not more than 5 g per litre, otherwise gel formation may be excessive). Protect the distillate from atmospheric moisture

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by means of a drying tube packed with anhydrous magnesium perchlorate. If extensive gel formation occurs, take care not to overheat the distillation flask. Discard the first 5 per cent of the distillate, and collect the next 80 to 85 per cent (if possible).

4. Reflux the distillate over calcium hydride (5 g per litre) for at least one hour, and then distil slowly under maximum reflux ratio (b.p. 81.6°C). Again collect the 5 to 90 per cent fraction. *Note:* Careful fractionation is required to reduce the acrylonitrile content.

Procedure II

1. Reflux the acetonitrile with a small amount of aqueous potassium hydroxide (1 ml of 1 per cent solution per litre) for at least one hour, longer if it proves necessary.
2. Distil fractionally. Collect the 10 to 90 per cent fraction.
3. Follow Procedure I, steps 2 through 4.

Alternative Procedure II (Forcier and Olver)

1. Reflux over sodium hydride (1 g per litre) for 10 min.
2. Distil rapidly.
3. Reflux over potassium bisulphate (2 g per litre) for 20 min, in order to remove amines produced in step 1.
4. Distil rapidly.
5. Follow Procedure I, step 4.

STORAGE AND HANDLING OF PURIFIED SOLVENT

It is probably advisable to protect acetonitrile from unnecessary exposure to light during storage. During storage and handling it should be carefully protected from moisture (it is fairly hygroscopic). It is convenient to dispense the solvent by means of a glass siphon fitted with a Teflon stopcock. Acetonitrile can be stored without any noticeable change in quality for at least several weeks. On prolonged standing traces of ammonia may be produced (for tests, see below) and the conductivity may increase slightly.

DETECTION AND DETERMINATION OF IMPORTANT IMPURITIES

1. Water

Carry out a Karl Fischer titration¹². The end point is not ideally stable, and experience is required to obtain reliable results. For water concentrations above *ca.* 1×10^{-2} M, titrate a blank of 20 ml of dry methanol in a 50 ml volumetric flask to a light brown end point, then add 5 ml of acetonitrile to the titrated solution and titrate as rapidly as possible until a light brown colour persists for 5 to 10 seconds. For lower water concentrations, use 25 ml of methanol as blank, and also 25 ml of acetonitrile, in a 100 ml flask. Limit of detection: *ca.* 1×10^{-3} M water. (*Note:* The "dead-stop" potentiometric method offers some advantage over visual detection of the end point in this case.)

If the recommended procedures are used, the water content should be below 1×10^{-3} M.

2. Acetic Acid

Acetic acid can be determined polarographically (*Figure 1*); limit of detection: *ca.* 1×10^{-4} M, less favourable if unsaturated nitriles are also present. However, acetonitrile obtained by the recommended procedures is absolutely free from acetic acid and other acidic impurities, since their reaction with calcium hydride is irreversible.

3. Ammonia

Ammonia can be determined polarographically (*Figure 1*); limit of detection: *ca.* 5×10^{-6} M. Lower concentrations can be determined from the increase in absorption of 1×10^{-4} M picric acid at $420 \mu\mu^3$. Limit of detection: *ca.* 1×10^{-6} M.

4. Unsaturated Nitriles

These compounds can be detected polarographically, particularly by observing that the diffusion current increases on adding a proton donor, such as water (*Figure 2*). For the determination of acrylonitrile, 0.5 M water should be added and the diffusion current measured at -2.5 V *vs.* aqueous S.C.E. Limit of detection: *ca.* 3×10^{-5} M.

5. Other Impurities

Other (usually less important) impurities may also be present in acetonitrile. Gas chromatographic analysis is useful for the detection of such compounds.

IMPORTANT PROPERTIES OF ACETONITRILE

Several of the properties listed below (especially boiling point, density, refractive index and conductivity) may be useful as criteria of purity in certain applications. (Data were taken from reference 13 except where indicated otherwise and refer to 25°C where applicable.)

Boiling point, 81.60°C ; freezing point, -45.72° ; vapour pressure, 89.0 mm; density, 0.7768 g per ml; viscosity, 0.344 c.poise¹⁴; refractive index (n_D), 1.34163; conductivity, as low as 4×10^{-8} (ref. 4), more generally near 1×10^{-7} ohm⁻¹ cm⁻¹; dipole moment, 3.37 d; dielectric constant, 36.0¹⁵; autoprotolysis constant, 3×10^{-29} (ref. 16).

PURIFICATION OF OTHER NITRILES

Procedure I is recommended for the purification of propio- and isobutyronitrile as well⁵, and should be applicable to all simple aliphatic nitriles. However, distillation of benzo- and phenylacetonitrile from calcium hydride appears to cause some decomposition of the solvent; in these cases vacuum distillation from phosphorus pentoxide is recommended⁵.

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