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OCCUPATIONAL EXPOSURE TO

# NITRILES



U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE  
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Center for Disease Control  
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#### IV. ENVIRONMENTAL DATA, SAMPLING, AND ANALYTICAL METHODS

##### Environmental Data

Data on workplace air concentrations for the various nitriles are limited. Air monitoring data for adiponitrile and acetonitrile were obtained during plant visits [4]. For adiponitrile monitoring, 43 samples (8-hour TWA's) for two field operators showed no detectable exposure (lower detection limit of 0.02 ppm). Of 12 stationary samples, 10 showed no detectable adiponitrile, whereas 1 sample indicated 0.25 ppm and another near a temporary high exposure source indicated 7.5 ppm. In a second plant, all samples for adiponitrile indicated TWA concentrations below 1 ppm. In a third plant using acetonitrile in a closed system, a single full-shift TWA concentration of 9.46 ppm was obtained. Several plants also monitor for the presence of hydrogen cyanide or total cyanide [4].

##### Sampling

Few papers discuss methods of collecting samples of nitriles in workplace air. Marich and Borskii [90] discussed a method of collecting succinonitrile by drawing 2 liters of air, during 10-15 minutes, through a porous plate absorber containing 2 ml of a nitrating mixture. Colorimetric determination of succinonitrile in the resulting solution was then performed. A syringe-type air sampler has been used to collect acetonitrile at a flowrate of 300 cc/minute [91]. This sampling procedure was used in conjunction with the potassium permanganate method of analysis.

Kondo et al [92] experimentally sampled for acetone cyanohydrin and acetonitrile and other organic cyanides in air using a glass and Teflon apparatus consisting of: (1) a charcoal Celite column for cleaning the air sample, (2) absorbent cotton soaked with a known quantity of an organic cyano compound, (3) a drying tube, (4) collecting tubes with an absorbing solution of deionized water, and (5) a pump. A flowrate of 500 ml/minute was used, and 100% recovery was found for acetone cyanohydrin and acetonitrile when up to 20 liters of air were drawn. Recovery sharply declined with air samples of over 20 liters. Experimentation with flowrates of from 345 ml/minute to 10 liters/minute, with a fixed sample volume of 10 liters, yielded total recovery of nearly 100% in all cases.

Charcoal tube sampling was found to be in use at various plants in the United States [4] for collection of acetonitrile, adiponitrile, and propionitrile. Methylene chloride or chloroform was used as a desorption solution for adiponitrile, and carbon disulfide plus 2% acetone was used for desorbing propionitrile. In a NIOSH health hazard evaluation and technical assistance report [93], acetonitrile was sampled with charcoal

tubes and desorbed with toluene. The NIOSH Manual of Analytical Methods [94] recommends sampling with charcoal tubes for acetonitrile and for tetramethylsuccinonitrile; acetonitrile is desorbed with benzene, and tetramethylsuccinonitrile is desorbed with carbon disulfide. A 10-liter air sample is obtained at a rate of 0.2 liter/minute or less. For sampling, the tubes are placed in a vertical position, and after sampling, the tubes are sealed at each end and submitted to a laboratory for analysis. This charcoal tube method has undergone a thorough laboratory evaluation by NIOSH, and the sampling method has been rated as "B," or "acceptable." A similar charcoal tube sampling method has been recommended for tetramethylsuccinonitrile [94]. A calibrated personal sampling pump with a flowrate that can be accurately determined at  $\pm 5\%$  for 1.0 liter/minute is required, and a sample of 50 liters is recommended. A larger air sample than that required for estimation of acetonitrile is necessary to detect tetramethylsuccinonitrile in the range 1.80-8.20 mg/cu m (0.3-1.5 ppm).

A solid sorption tube containing sodium hydroxide flakes, developed for collection of concentrations of airborne hydrogen cyanide [95], is being considered by industry for collection of total cyanide in atmospheres where both hydrogen cyanide and a cyanohydrin are present (J Mair, personal communication, July 1978). Collection of acetone cyanohydrin in dilute sodium hydroxide has been attempted experimentally [96]. Complete dissociation of acetone cyanohydrin occurred during collection of air containing this compound at 0.8 liter/minute in absorption vessels containing 5 ml of 0.05 normal sodium hydroxide. Hydrogen cyanide was analyzed by colorimetric determination. Since acetone cyanohydrin is more stable in some acidic media [4], collection in an impinger containing an acid-absorbing solution may be necessary if the cyanohydrin is to be analyzed separately from hydrogen cyanide.

Because succinonitrile, malononitrile, and tetramethylsuccinonitrile exist as solids at room temperature (Table XII-2), sampling for particulates would be an appropriate additional method of nitrile collection. However, no such sampling data have been identified.

NIOSH recommends that tetramethylsuccinonitrile be sampled with charcoal tubes and desorbed with carbon disulfide. Because benzene has been shown to be quite toxic [97], it is recommended that toluene be substituted for it as a desorbing solution for acetonitrile following collection by charcoal tube. The use of charcoal tubes is preferable to alternate methods because the tubes are relatively simple to prepare, ship, and store; personal sampling is easily achieved; and sampling tubes and pumps are commercially available. Sampling with charcoal tubes may suffice for the collection of other mononitriles and dinitriles, but sorbent capacity for these compounds and effectiveness of desorbing solvents need to be determined. The recommended methods of sampling for acetonitrile and tetramethylsuccinonitrile are described in Appendix I. There are, at the

present time, no recommended sampling methods for n-butyronitrile, isobutyronitrile, propionitrile, adiponitrile, malononitrile, succinonitrile, acetone cyanohydrin, and glycolonitrile.

### Analytical Methods

Several methods have been used to measure the selected nitriles in air samples. The two major analytical methods are based on colorimetry and gas chromatography.

A general colorimetric method for determination is based on the decomposition of nitriles in alkaline solution with liberation of free ammonia [98]. The free ammonia is determined colorimetrically using Nessler's reagent. However, this method is nonspecific for nitriles, and ammonia, formaldehyde, and hydrogen sulfide interfere. Marich and Borskii [90] developed a colorimetric method for analyzing samples of succinonitrile, utilizing the pink-violet reaction products of succinonitrile nitro derivatives with alkali in a toluene-acetone medium followed by acidification of the solution. The method is sensitive to less than a microgram of succinonitrile in the final solution and provides a stable color for up to 30 minutes; however, nitro and halogenated aromatic hydrocarbons interfere with the determination.

Collection and determination of acetonitrile by the permanganate oxidation method has been used [91]. This method was developed for acrylonitrile and was adapted for acetonitrile analysis. A sample of approximately 800 cc of air is required, and reduction of permanganate ions by the nitrile yields quadrivalent manganese ions, indicated by a change in the color of the solution from pink to blue green. The color change is rapid for acetonitrile concentrations in excess of 25 ppm (42 mg/cu m). It is possible to estimate concentrations down to 25 ppm, and the reduction of permanganate by acetonitrile may be useful in obtaining on-the-spot estimates for the concentration of acetonitrile [91]. However, acrylonitrile, ethyl acrylate, methyl methacrylate, methyl vinylpyridine, and similar compounds interfere in the analysis.

Acetonitrile has been detected alone at 125 ppm with 20% error using laser absorption spectroscopy [99]. In a prepared gas mixture, the minimum detectable concentration was 400 ppm.

A spot test for malononitrile [100], using benzofurazan oxide in an alkaline medium, yields an intense violet color. The color develops to a maximum in 20-30 minutes and then slowly fades to red. The reagent is also useful for detecting malononitrile on thin-layer chromatography plates or determining it colorimetrically in solutions.

Another spot test for malononitrile involves the reaction of nitroprusside with the nitrile in alkali hydroxide solution to yield a

blood-red color [101]. Use of such a reaction may allow a determination of malononitrile in submicrogram quantities in solution.

Several gas chromatographic techniques [98,102-106] have been described for analysis of nitriles. These techniques allow for the separation and identification of nitriles from other nitriles and related substances. Adiponitrile has been collected and determined in the presence of impurities associated with its production from adipic acid [102] or acrylonitrile [105]. Traces of acetonitrile and other impurities have been determined in acrylonitrile by gas chromatography using a flame-ionization detector [106]. A similar procedure allowed separation and determination of acetonitrile and propionitrile in the presence of unsaturated nitriles [103].

The solutions obtained by Kondo et al [92] in experimental air sampling were injected directly into a gas chromatographic column. Using 10-liter air samples collected at 760 mmHg and 25 C, the authors found that the minimum detectable concentrations of acetone cyanohydrin and acetonitrile were 2.15 and 4.46 ppm, respectively. It was determined that several organic solvents with boiling points above 100 C and deionized water gave excellent separation of the organic cyanides from the solvent peaks. The packing agent PEG 6000 proved best for stability and sharpness of peaks. A mixture of acrylonitrile, propionitrile, butyronitrile, succinonitrile, and adiponitrile in an aqueous solution containing hydrochloric acid and potassium chloride was successfully analyzed by gas chromatography using a hot wire detector [104]. However, gas chromatographic methods do not provide for specific determination of nitriles, and substances with similar retention times may interfere. In the absence of interfering substances, nitriles may be separated and determined by comparison with appropriate standards.

The use of a gas chromatograph equipped with a flame-ionization detector is recommended for analysis of acetonitrile and tetramethylsuccinonitrile in the NIOSH Manual of Analytical Methods [94]. Method S165 for acetonitrile was validated over the range 31.4-140.2 mg/cu m with a coefficient of variation of 0.072. Method S155 for tetramethylsuccinonitrile was found to have a coefficient of variation of 0.075 when validated over the range 1.80-8.20 mg/cu m. The same method, with appropriate modifications, may be applied to the determination of concentrations of other airborne mononitriles and dinitriles because of the similar physical and chemical properties of compounds in each category (Table XII-2). The plants visited in preparation of this document used gas chromatography with a flame-ionization detector for analysis of samples of propionitrile and adiponitrile [4]. However, the application of this method to n-butyronitrile, isobutyronitrile, propionitrile, adiponitrile, malononitrile, and succinonitrile has not as yet been tested or validated by NIOSH. There are, at the present time, no recommended methods for analyzing acetone cyanohydrin and glycolonitrile.