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Note

Rapid determination of acrylonitrile in water and acetonitrile by high-performance liquid chromatography

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Acrylonitrile is widely used in the polymer and chemical industries, and can be found both as a synthetic reagent and a by-product. Evidence has been presented for its toxicity, carcinogenicity and teratogenicity. In light of these potential hazards, the Food and Drug Administration (FDA), Occupational Safety and Health Administration (OSHA) and the Environmental Protection Agency (EPA) have issued regulations concerning this substance.

A wide range of analytical methods have been published for acrylonitrile determinations in aqueous solutions, from spectrophotometric[1] to polarographic[2] to titrimetric[3]. The majority, however, rely on gas chromatography[4], particularly with nitrogen–phosphorus detectors[5–7] in the assay step and either with or without preconcentration of the sample. Although recoveries from spiked samples have been shown to be quite high ever after complicated sample preparation steps[8], the labor-intensive nature of these methods limits the number of samples which can be conveniently analyzed. To data, no single method offers both high sensitivity and last throughput.

The method described here makes use of the increasingly ubiquitous high-performance liquid chromatography (HPLC) to determine acrylonitrile in aqueous samples down to a detection limit of 5 ppb* without sample preparation. The only HPLC method in the literature[9] makes use of a refractive index detector, and the limits of detection are accordingly high. The described method offers both the speed of methods requiring no sample preparation and the high sensitivity obtained with preconcentration. In addition to aqueous samples, data are given for analyses of several lots of commercially available acetonitrile.

EXPERIMENTAL

Apparatus

Separations were performed on a system composed of a Model 660 solvent programmer (Waters Assoc., Milford, MA, U.S.A.), in conjunction with two Model M6000A pumps (Waters), a WISP Model 710B auto injector (Waters) and a Model SF 770 variable-wavelength detector used at 195 nm (Schoeffel Instrument Division,

* Throughout this article, the American billion (10^9) is meant.

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Westwood, NJ, U.S.A.). Chromatograms were recorded on a Data Module Integrator (Waters) interfaced with the auto injector. C_{18} columns (Waters; and Bio-Rad Labs., Richmond, CA, U.S.A.) were used as received.

Reagents

Reagent-grade potassium phosphate, monobasic, and potassium hydroxide were used to prepare the mobile phase. Organic solvents used in the column wash cycle were either distilled-in-glass (Burdick & Jackson Labs., Muskegon, MI, U.S.A.) or HPLC grade (Fisher Scientific, Pittsburgh, PA; and J. T. Baker, Phillipsburg, NJ, U.S.A.).

Procedure

The mobile phase consisted of 0.025 *M* KH_2PO_4 in distilled water adjusted to a pH of 5.5 with 0.1 *M* potassium hydroxide solution. Sufficient buffer was prepared for both chromatography and dilution of the acrylonitrile standards. Wash solution was prepared by mixing acetonitrile, methanol and distilled water in a 50:25:25 (v/v/v) ratio. A 300-μl volume of standards and samples was injected onto the column and eluted. After a 7-min elution phase, the column was washed for 8 min with the wash solution and allowed to equilibrate for 10 min with the mobile phase before injection of the next standard or sample. Both elution and wash cycles were performed with a solvent flow of 2 ml/min. Water and acetonitrile samples were injected without pre-treatment, aside from dilutions where applicable; standards were prepared on a v/v basis at a concentration of 96 ppb. Using a detector range of 0.02 a.u.f.s., samples were quantitated by peak height measurement and external standard calculation. Linearity studies used appropriate detector ranges to ensure that all peaks remained on scale.

Caution: Because of the hazardous nature of acrylonitrile, appropriate safety precautions are necessary during preparation of the standard solutions.

RESULTS

Typical chromatograms of a water sample spiked with 10 ppb acrylonitrile and an acetonitrile sample are shown in Fig. 1. Water samples from fourteen locations revealed no interferences with the acrylonitrile peak. Variations between chromatograms were most often seen in the solvent front.

The linearity of peak response with concentration and the precision for a spiked sample were examined by two analysts using different instruments and C_{18} columns. These results are given in Tables I and II. Based on these data, the detection limit of the method was estimated as 5 ppb.

Water sampled from fourteen sources was assayed by an external standard method; samples were injected without further preparation. Six samples of commercially available acetonitrile were also assayed after a 1 ml/100 ml dilution in mobile phase. Without this dilution, acetonitrile was found to pull acrylonitrile off the column, precluding quantitation. The results of these determinations are given in Tables III and IV.

To test for interferences, aqueous solutions containing 50 ppb acrylonitrile and 1 ppm of eight possible contaminants were prepared. Acetonitrile, methacrylonitrile,

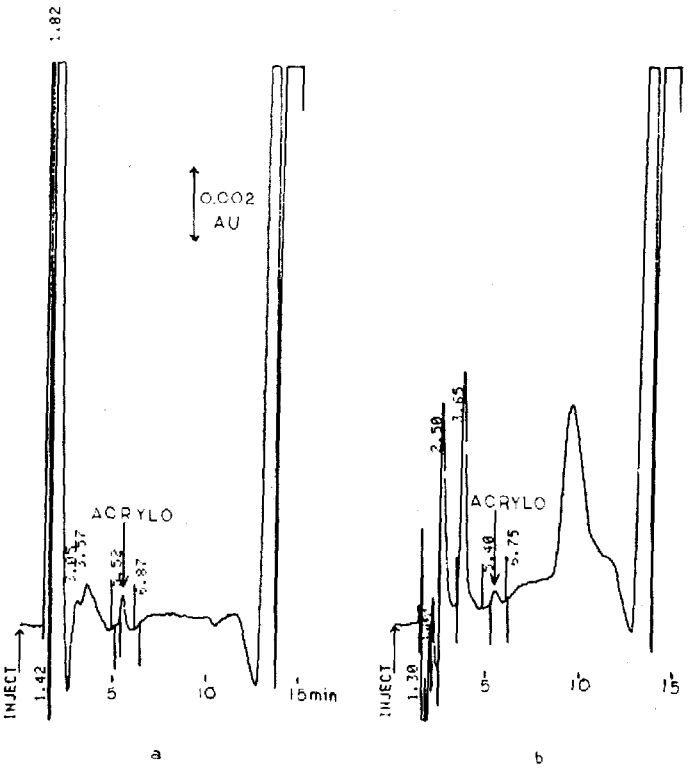

Fig. 1. HPLC chromatograms of samples containing acrylonitrile: (a) tap-water sample spiked with 10 ppb; (b) acetonitrile, reagent grade, after 1:100 dilution. Conditions as given in the Experimental section.

proprionitrile, *o*-toluidine, aniline, 2,5-dimethylpyrazine, pyridine and cyclohexanone were thus eliminated as potential interferences. Acrylamide was tested more stringently, and the method was found acceptable for simultaneous determination of acrylamide and acrylonitrile.

Water samples were kept refrigerated prior to analysis, and were assayed within 24 h after sampling. Samples assayed by two analysts over a time span greater than 1 day were found to contain various amounts of acrylonitrile, with older samples containing less than fresh samples. To avoid the possibility of degradation during storage, immediate analysis is recommended.

DISCUSSION

The linearity and precision of the HPLC method for acrylonitrile in aqueous samples are both excellent for the low levels examined. The method is fairly rugged, as can be seen by comparison of data from different analysts using different manufacturers' columns. (Since retention times can vary with columns obtained from different manufacturers, the mobile phase may have to be adjusted to compensate.) No major difficulties have been encountered in this laboratory with samples run over the space of more than 2 years on a dedicated column. As expected, the majority of tap-water and acetonitrile samples contained no measurable acrylonitrile; the two

TABLE I

LINEARITY OF PEAK HEIGHT RESPONSE OF ACRYLONITRILE

Concentration (ppb)	*Peak height (mm)*	
	Analyst 1 (Bio-Rad column)	*Analyst 2 (Waters column)*
300-μl injection		
0	0	0
32	7.8	17.5
64	16.1	36.7
96	24.1	55.8
128	32.0	75.4
160	45.0	92.5
Correlation coefficient	0.9999	0.9998
Slope (mm/ppb)	0.25	0.58
Intercept (mm)	−0.14	−0.49
50-μl injection		
0	0	0
320	23.5	32.5
640	52.7	70.0
960	81.8	105.0
1280	107.9	142.0
Correlation coefficient	0.9994	0.9998
Slope (mm/ppb)	0.086	0.111
Intercept (mm)	−1.64	−1.40

TABLE II

PRECISION OF ACRYLONITRILE DETERMINATION IN A SYNTHETIC SAMPLE AT 32 ppb

Replicate	*Assay (ppb)*	
	Analyst 1 (Bio-Rad column)	*Analyst 2 (Waters column)*
1	34.7	30.2
2	34.0	29.8
3	33.6	30.2
4	33.3	29.8
5	33.3	30.2
6	31.6	29.3
7	32.0	29.3
8	32.4	28.4
Mean (ppb)	33.1 ± 1.05	29.7 ± 0.63
Relative standard deviation (%)	3.2	2.1

TABLE III

ASSAY VALUES OF WATER SAMPLES

N.D. = Not detected.

Source	*Concentration acrylonitrile (ppb)*
Waukegan, IL —Tap	N.D.
North Chicago, IL —Tap	N.D.
Kenosha, WI —Well	N.D.
Lake Bluff, IL —Tap	N.D.
North Chicago, IL —Distilled	N.D.
North Side Milwaukee, WI —Tap	N.D.
Kenosha, WI —Lake Michigan Shore	N.D.
Nashotah, WI —Lake	N.D.
Near West Milwaukee, WI —Tap	N.D.
Nashotah, WI —Tap	N.D.
Lindenhurst, IL —Tap	N.D.

samples showing positive results were reagent grade and opened more than 6 months prior to the study. It should be noted that, in contrast to the detection limit of 5 ppb for water samples, the limit for acetonitrile samples is 500 ppb because of the 1:100 dilution.

One advantage of the mobile phase used is that the acrylonitrile peak is unresponsive to shifts in pH. Thus, acids and bases can be shifted away from the analyte peak by raising or lowering the pH without affecting the acrylonitrile peak itself.

Analyses are typically performed with an automatic injector, restricting analyst time to set-up and data calculations. Because no sample preparation is required (outside of dilutions of the acetonitrile samples, for example) hands-on time can be kept extremely low. Almost 60 samples can be run in a 24-h period with automation, rivalling the speed of other analyses and far surpassing them in the amount of analyst time freed for other assays. If greater throughput were needed, column switching technology could be used to alternate the washing and elution phases of the program cycle between two or three columns.

Although the samples considered here were relatively clean, the analysis of more complex matrices could easily be examined through comparison of spiked and blank samples to determine potential interferences. Simple clean-up steps such as filtration or passage through ion-exchange or other micro-scale columns could easily

TABLE IV

ASSAY VALUES OF ACETONITRILE SAMPLES

Source	*Concentration acrylonitrile (ppb)*
MCB reagent	770
Burdick & Jackson distilled-in-glass	N.D.
Fisher LC	N.D.
Baker LC	N.D.
Fisher reagent	24,000

be incorporated without the need for the sample concentration steps found in other methods. The lack of sample preparation also obviates the need for verification of extraction efficiencies, etc., since "recovery" can be determined simply by spiking a sample with acrylonitrile and comparing it with the unspiked sample. Very fast turn-around can be achieved if necessary by injecting samples on receipt, or samples can be kept in sealed vials and refrigerated until needed.

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