



Project Summary

Evaluation of EPA Method 603 (Modified)

S. V. Lucas, T. F. Cole, A. Riggan, and W. M. Cooke

EPA Method 603 was modified and evaluated with newly established chromatographic conditions for the determination of acrolein, acrylonitrile, and acetonitrile. The recommended chromatographic column and conditions specified in the original method were found to be unsuitable when acetonitrile was included as a method parameter. Porapak QS was found to perform well as a gas chromatography (GC) packing for the three method parameters, and method validation using reagent water, Publicly Owned Treatment Works (POTW) outfall water, and industrial wastewater was successfully performed. Recoveries and precisions were determined at two spiking levels in each of the three matrices. Seven replicates were analyzed for each of the six spike-level/matrix sets. For acetonitrile, recoveries for the six sets ranged from 86 to 111 percent (average, 99 percent), with precisions ranging from 3 to 17 percent relative standard deviation (RSD), (average, 11 percent RSD). The corresponding values for acrylonitrile were recoveries ranging from 84 to 104 percent (average, 97 percent) and precisions ranging from 3 to 8 percent RSD (average, 4 percent RSD). Acrolein was unstable in the industrial wastewater, even though the water was buffered at pH 4.5 before spiking. For the other two matrices, the acrolein recovery ranged from 80 to 104 percent (average, 94 percent) and the precisions ranged from 1 to 4 percent RSD (average, 3 percent RSD). The loss of acrolein due to apparent chemical or biological degradation in the industrial wastewater underscores the current lack of understanding of the chemical factors that control the stability of

acrolein in aqueous systems. All of the data sets were quantified using both an internal standard method and an external standard method, and both methods of quantification provided essentially identical accuracy and precision results.

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This Project Summary was developed by EPA's Environmental Monitoring and Support Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The Environmental Protection Agency's (EPA's) Environmental Monitoring and Support Laboratory (EMSL), Cincinnati, Ohio, has primary responsibility for developing and evaluating monitoring methods for organic pollutants in industrial wastewaters. Method 603, developed by EPA, for wastewater monitoring involves the use of a heated purge-and-trap technique and gas chromatographic (GC) analysis for the determination of acrolein and acrylonitrile.

This method validation study was undertaken in response to the experience of various laboratories which suggested that Method 603 was not a reliable analysis method. For example, a previous single laboratory method validation study performed for EPA by another contracting

laboratory produced no useful data. In addition, several investigators have queried EPA regarding difficulties with the reproducibility of the gas chromatography and problems encountered from acetone interference. Thus, development and use of improved chromatographic conditions was a critical first step in this work.

In an effort to increase the usefulness and scope of Method 603, Battelle Columbus Laboratories was contracted to conduct research to: (1) recommend modifications to Method 603 for improving the GC analysis; (2) evaluate the feasibility of including acetonitrile as a method parameter; and (3) validate the method, as modified, using three matrices (reagent water, POTW wastewater and a relevant industrial wastewater) and two spiking levels ([a "low" level near the method detection limit (MDL) and a "high" level at least 10-fold higher than the "low" level]).

Analytical Method Evaluation

GC Column Evaluations

Since acetonitrile was to be included in the parameter list of Method 603, the identification of a suitable GC column for the separation of all three compounds, acetonitrile, acrolein, and acrylonitrile, was a necessary first step. The separation of methylene chloride and acetone from the method parameters was also a consideration in selecting the column to be used for validation.

Both of the columns specified in the 1982 revision of Method 603 were determined to be unacceptable. Chromosorb 101 resulted in exact coelution of acrolein and acetonitrile and partial resolution of acetone from acrylonitrile but otherwise it performs adequately for acrolein and acrylonitrile in the absence of acetonitrile. Durapak CW400/Porasil C resulted in coelution of acetone and acrolein and such severe peak tailing that low level injections (100 ng) did not provide usable data. Other column packings were tried, and the results obtained were as follows: (1) 1 percent SP-1000/Carbopack B (moderate tailing and acrolein-acetone coelution); (2) 0.1 percent CW400/Carbopack C (inadequate retention and severe peak tailing); and (3) Chromosorb 104 (high temperature of elution, unacceptable isothermal elution time for acetonitrile and moderate tailing). The column packing used in this work (Porapak QS) was the only one tested that provided good GC peak shape at low levels and baseline separation between the method

analytes as well as two potential interferences of interest to EPA (acetone, which elutes between acrolein and acrylonitrile, and methylene chloride, which elutes between methanol and acetonitrile).

Purge-and-Trap Conditions

The purge-and-trap conditions for this validation effort included an 85°C purge with helium at 20 mL/minute flow rate for 15 minutes, a 1.5 minute desorption at 180°C, and a 210°C trap bake for 10 minutes. These conditions were recommended by EMSL staff, and were compared to the original Method 603 conditions. In summary, the conditions gave improved peak heights for acetonitrile and acrolein and better reproducibility, due, apparently, to the more rapid delivery of trapped analytes to the GC column and the resulting production of narrower and taller GC peaks. Actual recoveries, however, were about the same for the two conditions. The trap bake temperature of 210°C was employed, since it is generally desirable that the trap bake temperature be higher than the desorption temperature. The low (100°C) desorption temperature specified in the 1982 version of Method 603 was required by the initial GC column temperature of 45°C and the sensitivity of Durapak CW400/Porasil C to the presence of liquid water on the column, which would be caused by rapid trap heating to 180°C. For the Porapak QS column packing, problems caused by liquid water are of no concern, since the initial column temperature is 110°C. Moreover, macroreticular phases are generally not susceptible to water damage.

Method Validation

Validation consisted of the analysis of seven replicates at two spiking levels for each of three matrices: reagent water, Columbus POTW secondary effluent, and industrial wastewater from the outfall of a manufacturing plant producing two of the analytes. The water samples were buffered before spiking at pH 4.5 ± 0.2 by the addition of sodium citrate to approximately 0.1 mM and pH adjustment using a glass electrode pH meter. Spiked samples were allowed to equilibrate overnight at ice temperature before analysis on the following day.

A summary of the results for the method validation using reagent water, Columbus POTW effluent, and the industrial wastewater are presented in Tables 1, 2, and 3, respectively. All quantifications were

performed using both external standard calibration and internal standard (IS) calibration with 1-chloropropane, but only the external standard results are presented in the tables. In general, no significant differences were observed in the results for the two methods of quantification. Acceptable recoveries and precisions were obtained for all method parameters at both spiking levels in the reagent water and Columbus POTW effluents. For the industrial wastewater, acrolein apparently decomposed or was biodegraded despite pH adjustment to a value of 4.5 prior to spiking, and the recoveries for this matrix were less than 12 percent for all replicates analyzed.

With the results for reagent water spiked at the lower level, MDLs of 2.7, 0.7, and 0.5 were calculated for acetonitrile, acrolein, and acrylonitrile, respectively.

Summary and Conclusions

The validation data collected in this research support the usefulness of Method 603 for the analysis of acetonitrile, acrolein, and acrylonitrile using the newly established chromatographic conditions. The following conclusions can be drawn:

- Both of the previously recommended GC columns are unsuitable for the separations needed if acetonitrile is to be included as a method parameter. A Porapak QS column provides the required separation of all three analytes.
- The method appears to be precise and accurate for acetonitrile determination even though the purging efficiency of acetonitrile is only about 50 percent.
- No apparent advantage is gained by the use of an internal standard calibration procedure. However, the quality assurance feature of an internal standard may have merit in some cases.
- Factors that affect acrolein stability in aqueous samples are still not well understood.

Table 1. Method Validation Results for Reagent Water Using Modified Method 603

Method Parameter	Low Level Spike Results						High Level Spike Results					
	Background Level, µg/L	Level Spiked, µg/L	Average Recovery, µg/L	SD ¹	RSD, ² %	Average Percent Recovery	Background Level, µg/L	Level Spiked, µg/L	Average Recovery, µg/L	SD	RSD, %	Average Percent Recovery
Acetonitrile	0.9	10.0	9.5	0.8	9	86	1.3	100.0	112	12	11	111
Acrolein	0.0	5.0	5.2	0.2	4	104	0.2	50.0	51.6	0.7	1.4	103
Acrylonitrile	1.1	5.0	5.3	0.1	3	84	1.0	50.0	52.4	1.5	3	103

¹Standard Deviation.²Percent Relative Standard Deviation.**Table 2. Method Validation Results for Columbus POTW Secondary Effluent Using Modified Method 603**

Method Parameter	Low Level Spike Results						High Level Spike Results					
	Background Level, µg/L	Level Spiked, µg/L	Average Recovery, µg/L	SD ¹	RSD, ² %	Average Percent Recovery	Background Level, µg/L	Level Spiked, µg/L	Average Recovery, µg/L	SD	RSD, %	Average Percent Recovery
Acetonitrile	0.3	10.0	10.4	1.5	14	101	0.3	100	98	9	9	98
Acrolein	0.2	5.0	4.2	0.2	4	80	0.2	50	61	1.1	1.8	121
Acrylonitrile	0.9	20.0	21.0	0.8	4	100	0.9	100	107	1.6	1.5	106

¹Standard Deviation.²Percent Relative Standard Deviation.**Table 3. Method Validation Results for Industrial Wastewater Using Modified Method 603**

Method Parameter	Low Level Spike Results						High Level Spike Results					
	Background Level, µg/L	Level Spiked, µg/L	Average Recovery, µg/L	SD ¹	RSD, ² %	Average Percent Recovery	Background Level, µg/L	Level Spiked, µg/L	Average Recovery, µg/L	SD	RSD, %	Average Percent Recovery
Acetonitrile	1.2	10.0	11.0	0.3	3	98	0.3	100.0	99	17	17	99
Acrolein	0.3	5.0	0.4	0.1	25	2	0.6	100.0	9.9	1.1	11	9
Acrylonitrile	2.1	10.0	11.2	0.8	8	91	0.8	100.0	105	3.2	3	104

¹Standard Deviation.²Percent Relative Standard Deviation.

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James E. Longbottom is the EPA Project Officer (see below).

The complete report, entitled "Evaluation of EPA Method 603 (Modified)," (Order No. PB 85-146 629/AS; Cost: \$11.50, subject to change) will be available only from:

*National Technical Information Service
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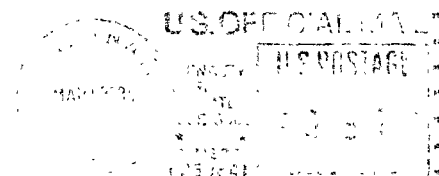
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