



Project Summary

Single Laboratory Validation of EPA Method 8030—Acrolein, Acrylonitrile, and Acetonitrile

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EPA Method 8030 was modified and evaluated with revised chromatographic conditions for the determination of acrolein, acrylonitrile, and acetonitrile in groundwater, solid, and organic liquid matrices. Method validation studies were conducted on each of the four sample preparation techniques included in Method 8030, namely (1) heated purge-and-trap (HP&T); (2) polyethylene glycol (PEG) extraction followed by HP&T; (3) direct liquid injection (DLI); and (4) manual heated headspace (HHS). Each method validation involved the determination of the method detection limit (MDL) and seven replicate analyses of one or two matrices, each analyzed unspiked and spiked at two concentration levels. Groundwater was analyzed by the HP&T method; a solid waste was analyzed by the PEG/HP&T technique and by the HHS method; and a liquid organic waste was analyzed by DLI and by HHS methods.

The HP&T method gave good recovery (85 to 96 percent) and precision for the three method analytes in groundwater. The PEG/HP&T method gave good recovery (76 to 96 percent) for acetonitrile and acrylonitrile in the solid waste but poor recovery for acrolein (10 percent), which apparently decomposed in that matrix. Problems encountered with the carryover of PEG indicated that additional modifications of this method are needed. The DLI technique gave good results for the determination of all three analytes (86 to 111 percent recovery) in the organic liquid waste; however, late eluting material may present serious problems in some cases. The HHS method gave distinctly less

accurate and less precise results than the PEG/purge-and-trap method for the determination of acetonitrile and acrylonitrile in the solid waste sample. Acrolein was not recovered at all by the method due, apparently, to decomposition during the one-hour equilibration at 90°C. The HHS method gave extremely erratic results for the analysis of the organic liquid waste and was, therefore, considered completely unsatisfactory for such samples.

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 objective of this program was to perform single-laboratory validation of U.S. EPA Method 8030, which covers the gas chromatographic (GC) determination of acrolein, acrylonitrile, and acetonitrile in groundwater, liquid wastes, and solid wastes.

Method 8030 provides four sample preparation options: (1) heated purge-and-trap (HP&T) using EPA Method 5030; (2) polyethylene glycol extraction followed by HP&T (PEG/HP&T) using EPA Method 5030; (3) DLI onto the GC column (DLI); and (4) heated headspace sampling (HHS) using EPA Method 5020.

This method validation study was undertaken in response to a variety of prior experience which suggested that Method 603, on which Method 8030 is

based, was not a reliable method. A previous single laboratory method validation study performed for EPA 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.

Analytical Methods Evaluation

Gas Chromatography (GC)

Investigations were conducted to identify a GC column which would effectively provide analysis capability for the three method analytes. Both of the columns specified in the 1982 revision of EPA Method 603, on which EPA Method 8030 is based, were found to be unacceptable. 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. Chromosorb 101 resulted in exact coelution of acrolein and acetonitrile and partial resolution of acetone from acrylonitrile; but otherwise, this column performs adequately for acrolein and acrylonitrile in the absence of acetonitrile. Other column packings were tried and the following results were obtained: 1 percent SP-1000/Carbopack B gave moderate tailing and acrolein-acetone coelution; 0.2 percent CW 1500/Carbopack C resulted in inadequate retention and severe peak tailing; and Chromosorb 104 provided high temperature of elution, unacceptable isothermal elution time for acetonitrile and moderate tailing. The Porapak QS column packing used in this work was the only one tested which provided 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. This packing also provided good GC peak shape at low concentrations.

Purge-and-Trap Conditions

In the initial work on this program, some experiments were performed to compare method performance using the trap desorption conditions recommended by EPA Method 5030 with modified conditions recommended by EPA's Environmental Monitoring and Support Laboratory in Cincinnati, OH (EMSL). Standards containing 30 µg/L of each analyte

were analyzed in triplicate using the desorption conditions specified by EPA Method 5030 and those recommended by EMSL. The modified desorption conditions, 180°C for 1.5 min, used in the validation analyses resulted in recoveries reduced 4 to 8 percent compared to those obtained with the EPA Method 5030 conditions of 100°C for 2.0 min. However, significantly better relative standard deviation (RSD) values of 1.1, 1.2, and 1.2 percent for the 180°C/1.5 min conditions were obtained compared to 9.3, 8.0, and 1.8 percent for the 100°C/2.0 min conditions for acetonitrile, acrolein, and acrylonitrile, respectively. In summary, the 180°C/1.5 min desorption conditions gave improved peak heights for acetonitrile and acrolein resulting in better reproducibility, which is probably due to the more rapid delivery of trapped analytes to the GC column. The small difference in recovery may not be significant since these values are less than the observed standard deviations for the 100°C/2.0 min 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 EPA Method 5030 was required by the initial GC column temperature of 45°C and the sensitivity of the primary column (Durapak CW400/Porasil C) to the presence of liquid water on the column which would be introduced by rapid trap heating to 180°C. While the Porapak QS column packing is generally not susceptible to problems caused by liquid water, this potential problem is avoided since the initial column temperature (110°C) prevents condensation of water vapor.

Linear Dynamic Range of the Detector

The linear dynamic range (LDR) of the gas chromatographic system was evaluated for acetonitrile, acrolein and acrylonitrile using septum GC injections of aqueous calibration standards ranging in concentration from 0.5 to 500 µg/mL. The regression line analysis results showed excellent linearity of the GC system and FID detector over the three orders of magnitude range tested for the three method analytes.

Method Validation

Method validation was conducted for EPA Method 5030 using four different sample introduction techniques: (1) EPA Method 5030, a heated purge-and-trap

method (HP&T) was evaluated with an 85°C purge for aqueous samples; (2) a HP&T method with a polyethylene glycol (PEG) extraction for solid samples; (3) a direct liquid injection (DLI) procedure for the analysis of liquid wastes; and (4) EPA Method 5020, a heated headspace method (HHS) for direct injection of an aliquot of headspace of a sample equilibrated at 90°C. A validation data set for a particular technique consisted of a determination of the background levels of analyte in the matrix and analysis of samples spiked at two levels with seven replicates at each level. Table 1 indicates the scope of this method validation study by showing the seven replicate data sets which were produced. The results of the MDL determinations and the individual validation experiments for groundwater, a solid sediment waste sample, and a liquid waste sample using HP&T, PEG/HP&T, DLI, and HHS at both low and high spiking levels are summarized in Table 2. These results are discussed individually below by sample matrix type and analysis technique.

HP&T Groundwater Analysis Results

Groundwater was obtained from the well of a Battelle staff member who lives in rural Union County, Ohio. The well depth was approximately 30 ft, and the raw groundwater was broadly classified as very hard with high levels of carbonate and iron. The RSD's for all compounds spiked at the low level of 5 to 10 µg/L in the groundwater were less than six percent with average recoveries ranging from 90 to 95 percent. As for nearly all sample sets analyzed, the RSD's for acetonitrile are significantly higher than those for acrolein and acrylonitrile. The reason for the lower precision for acetonitrile in all determinations appears to be due to the relatively low purging efficiency of this compound, estimated to be 40 to 50 percent. The RSD's for all compounds spiked at the high level of 75 to 150 µg/L in groundwater were less than seven percent with average recoveries ranging from 85 to 91 percent.

PEG/HP&T Sediment Analysis Results

Sediment from a waste stream settling basin at a chemical plant producing two of the three method parameters was provided to Battelle by the chemical plant personnel. The results for low level sediment spikes ranging from 5 to 15 mg/kg indicated that acrolein apparently decom-

posed in the solid waste sample after storage overnight at 4°C and the average recovery for this compound was only 10 percent. Average recoveries for acetonitrile spiked at 15 mg/kg and acrylonitrile spiked at 5 mg/kg were 97 and 76 percent, respectively, with RSD's of less than 10 percent in both cases. As determined for the low-level spike samples, acrolein was lost due to apparent decomposition in the high-level spike samples also, while the average recoveries for acetonitrile and acrylonitrile, both spiked at the 100 mg/kg level, were 96 and 84 percent, respectively.

DLI Liquid Organic Waste Results

The nonaqueous liquid organic waste used in this validation was a black, ink-like, low-viscosity mixture of chlorinated hydrocarbons with a density of 1.25 gm/mL. The principal constituents previously identified by EPA Method 624 were dichloroethane, trichloroethane, and tetrachloroethane isomers. Numerous other halogenated C₂- and C₃-compounds were also present.

Recoveries for the low-level spike liquid waste ranged from 86 percent for aceto-

nitrile to 111 percent for acrylonitrile for 2.5 to 12 mg/L spike levels and all relative standard deviations were less than 4 percent. For the high-level spike liquid waste samples at the 125 mg/L spike level, recoveries ranged from 98 percent for acrylonitrile to 109 percent for acetonitrile, with relative standard deviations of 11 to 12 percent in all cases.

HHS Sediment Analysis Results

The sediment sample used in the PEG/HP&T validation was also used for the HHS method validation work using EPA Method 5020. As described above for the PEG/HP&T analyses, acrolein was not stable in this matrix, and no analysis results were tabulated for this analyte.

Results for the low-level spike samples yielded percent recoveries and percent RSD's of 46 ± 48 and 51 ± 32 for the 10 and 100 mg/kg levels of acetonitrile and acrylonitrile, respectively. The corresponding values for the high-level spike samples were 120 ± 65 and 76 ± 20, for the 100 and 500 mg/kg levels of acetonitrile and acrylonitrile, respectively. The high percent RSD values (20 to 80 percent) observed for the solid waste data sets can be attributed to variability in the manual headspace sampling and injection procedure. When sampling headspace in equilibrium at 90°C with a wet sample, a significant but variable amount of liquid, estimated to be 50 to 200 µL, condenses in the 5-mL sampling syringe which is at room temperature. Upon injection of the sample, a variable amount of this condensate, which is enriched in the spiked analytes, is delivered to the GC column.

Table 1. Scope of the Method Validation Experiments Performed

Method (Matrix)	Seven Replicate Data Set Obtained (X)			
	MDL ^(a)	Nonspike	Low Spike ^(b)	High Spike ^(b)
5030, HP&T (groundwater)	(c)	(d)	X	X
5030, PEG/HP&T (solid waste)	X	(d)	X	X
DLI (liquid waste)	X	X	X	X
5020, HHS (liquid waste)	X	X	X	X
(solid waste)		X	X	X

^(a)The matrix for method detection limit (MDL) was reagent water for all but DLI for which the matrix was toluene.

^(b)Low spike levels were chosen to be at or near the MDL level when possible, high spike levels were generally 10-fold higher.

^(c)The groundwater low spike data were used to compute MDL.

^(d)Three to six replicates of unspiked samples were analyzed with both the low and high spike data sets; no separate seven replicate experiment was performed.

Table 2. Summary of Method Validation Results

Method ^(a) (Matrix)	Acetonitrile			Acrolein			Acrylonitrile		
	MDL ^(b)	Percent Recovery ± Percent RSD ^(c)		MDL ^(b)	Percent Recovery ± Percent RSD ^(c)		MDL ^(b)	Percent Recovery ± Percent RSD ^(d)	
		Low Spike	High Spike		Low Spike	High Spike		Low Spike	High Spike
5030, HP&T (groundwater)	3 µg/L	95 ± 5	92 ± 6	0.7 µg/L	90 ± 2	95 ± 6	0.5 µg/L	94 ± 2	86 ± 2
5030, PEG/HP&T (solid waste)	1 mg/kg ^(d)	98 ± 10	95 ± 13	0.7 mg/kg ^(d)	10 ± 8	8 ± 7	0.3 mg/kg ^(d)	76 ± 5	83 ± 6
DLI (liquid waste)	0.8 mg/L	86 ± 2	109 ± 11	0.6 mg/L	94 ± 3	101 ± 12	0.5 mg/L	111 ± 2	98 ± 12
5020, HHS (solid waste)	1 mg/kg	46 ± 48	120 ± 65	0.3 mg/kg	(e)	(e)	0.4 mg/kg	32 ± 51	76 ± 20
(liquid waste)		-20 ± 1900	700 ± 100		(e)	(e)		70 ± 2100	250 ± 1300

^(a)HP&T: heat purge-and-trap; PEG: polyethylene glycol; DLI: direct liquid injection; HHS: heated headspace sampling.

^(b)Matrices: HP&T, buffered reagent water and groundwater; PEG/HP&T, reagent PEG; DLI, toluene; HHS, buffered reagent water.

^(c)RSD = Relative Standard Deviation

^(d)Assuming a 1-gm sample extracted with 40 mL PEG and a 200-µL PEG extract aliquot analyzed.

^(e)Acrolein was not stable under HHS conditions.

HHS Organic Liquid Analysis Results

The organic liquid used in the evaluation of the DLI method was also used in the validation of the HHS method.

Results for the low-level spike liquid organic waste samples yielded percent recoveries and percent RSD's of -20 ± 1900 and 40 ± 2100 for the 10 and 100 mg/kg level of acetonitrile and acrylonitrile, respectively. The corresponding values for the high level spike are 700 ± 110 and 250 ± 1300 , respectively, as before. The extremely poor accuracy and reproducibility observed for these samples is due to the problem of sample condensation in the 5-mL syringe during headspace sampling which was described above for the solid waste samples. In all cases except the unspiked sample set, the two-standard-deviation confidence interval for the average amount found extends to negative values. The large degree of irreproducibility encountered for this matrix using the heated headspace approach does not allow even an order-of-magnitude confidence interval in a single replicate analysis protocol.

Comparison of MDLs and Validation Results

The PEG/HP&T, DLI, and HHS methods all have approximately the same MDL values for their respective clean matrices which were toluene for DLI and reagent water for the PEG/HP&T and HHS. As expected, the MDL values for direct HP&T are about 1000-fold lower. Solid waste was analyzed by both PEG/HP&T and HHS, and the PEG/HP&T approach is clearly superior in both accuracy and precision for the solid waste used. The liquid organic waste was analyzed by both DLI and HHS, and the former method is clearly the more acceptable one for the matrix used. Poor recovery of acrolein for the solid waste by PEG/HP&T compared

with that for groundwater using HP&T suggests that acrolein was either irreversibly adsorbed or decomposed during the 4°C overnight equilibration with the solid waste. In the case of the HHS method, the data clearly indicate that decomposition of acrolein during the 1-hr, 90°C equilibration is a major factor since the standard addition of acrolein, added just prior to the 90°C equilibration, is also nearly quantitatively lost.

Conclusions

The validation results contained in this report support the following conclusions regarding the performance of Method 8030 and associated sample introduction techniques for the determination of acetonitrile, acrolein, and acrylonitrile in groundwater, a solid waste, and an organic liquid waste:

- The previously recommended GC column (Chromosorb 101) is unsuitable for the separation of acetonitrile from acrolein and acrolein from acetone, a common interference.
- The HP&T analysis option (Method 5030) works very well for the determination of low parts-per-billion levels of the method analytes in groundwater.

- The PEG sample preparation method for solids (Method 5030) provides good precision and accuracy at the low parts-per-million level, but is subject to failure upon extended use due to apparent aerosolization of PEG which contaminates the purge-and-trap apparatus and leads to inconsistent results.
- The PEG cleanup procedure from Method 5030 is not sufficient to provide clean reagent to analyze the method analytes at low parts-per-million levels.
- Acrolein stability is not understood completely, and more work is necessary to develop sample preservation criteria for this analyte particularly in solid matrices.
- The DLI sample introduction technique is precise and accurate for the determination of method parameters at low parts-per-million levels.
- The manual heated headspace procedure does not provide acceptable results for analysis of the organic liquid waste sample and provides such a high level of imprecision for solid samples that it should be used only for approximation (i.e., a maximum of one significant figure).

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The complete report, entitled "Single Laboratory Validation of EPA Method 8030—Acrolein, Acrylonitrile, and Acetonitrile," (Order No. PB 85-165 827/AS; Cost: \$16.00, subject to change) will be available only from:

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