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The Application of SW-846 Method 8261 to New SAM Analytes. Part Two: Method Performance for Water

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Introduction

Method 8261 provides analysis of problematic matrices and introduces novel quality tools, including the determination of method performance by analyte in each analysis. This method uses analyte chemical properties, boiling point, and relative volatilities to measure method performance as functions of those chemical properties. Boiling point values for compounds are readily available in the literature but relative volatility values are unique to Method 8261.¹ An overview of method 8261 chemistry is available on these web pages:

<http://www.epa.gov/nerlesd1/chemistry/vacuum/training/pdf/theory-rev5.pdf>.²

This study was performed to provide initial data demonstrating the viability of Method 8261 in determining analytes that are listed in SAM³ that had not been studied for Method 8261 analyses.

Experimental

Vacuum Distiller: A Cincinnati Analytical Instruments vacuum distiller (Model VDC1012) performed the distillations in the study. The operating conditions are presented in Table 1. Vacuum distillation times were varied, and the flush time was extended so that the vacuum distillation cycle time matched the GC/MS cycle time.

<i>Stage</i>	Time (min)
Vacuum distillation	7.5
Transfer	2.5
Bake-out	2.5
<i>Temperature</i>	°C
Condenser heat	95
Condenser cool	-10
Cryotrap desorb	120
Cryotrap trapping	-160
Cryotrap bake-out	200

Transfer line	200
Vacuum distiller lines	95
Multiport valve	200
Autosampler lines	95
<i>Decontamination</i>	
Cycles	16
Pressurization time (min)	0.1
Evacuation time (min)	1.4

GC/MS Apparatus. The vacuum distiller is interfaced to a GC/MS so that the vacuum distillate is transferred directly to the GC/MS for analysis after a distillation. In this study, the GC/MS was a Thermo DSQ mass spectrometer and Trace GC. The GC capillary column was a 30 m x 0.25 mm i.d., 1.5 μ m film VOCOL column (Supelco, Bellefonte, PA). The GC operating conditions were 2.5 min at -20 °C, 40 °C/min ramp to 60 °C, 5 °C/min ramp to 120 °C and held at 120 °C for 1 min, 20 °C/min ramp to 220 °C and held for 12 min resulting in a GC run time of 34 min. The injection was split 60:1 with a constant flow rate of 1.4 ml/min. The mass spectrometer scanned between 35 and 300 amu at 1 scan/sec.

Study Approach: Standards containing the study analytes were prepared at varying levels to identify the limit of quantitation as well as identify any potential interference. Triplicate analyses of 5 mL water and 25 mL water samples, spiked with low-level amounts of analytes were used to document method performance. Data processing that is unique to Method 8261 was performed by the software available on the web.⁴

Standards: The preparation of standards was found to be critical in calibration and evaluating method performance. Both ethylene oxide and propylene oxide standards degraded rapidly when mixed with the other analytes and therefore they were studied separately from the other analytes. 1, 4-dithiane was not readily soluble in methanol; and a solution more dilute than desired was therefore required.

Results and Discussion

The calibration data in this document was also used in a presentation “Creating the Calibration Curve and Generating Method 8261 Quantitation Reports through SMCReporter V4.0” (<http://www.epa.gov/nerlesd1/chemistry/vacuum/methods/software.htm#calibration>).⁵ The calibration curve can be downloaded (and data that was used to generate it) along with the presentation. The internal standards, surrogates, and analytes used in this study are identified in Table 2. The calibration ranges demonstrated in this study for each analyte are presented in Table 3.

Compound	Type ^a	Relative volatility	Boiling point
Diethyl ether- <i>d</i> ₁₀	Istd-RV III&IV	32.5	35
Acetone- ¹³ C	Istd-RV IV&V&VI	600	57
Methylenechloride- <i>d</i> ₂	Surrogate	11.1	40
Nitromethane- ¹³ C	Surrogate	510	101
hexafluorobenzene	Istd-RV I&FP	0.86	81.5
Tetrahydrofuran- <i>d</i> ₈	Istd-RV IV&V	355	66
Ethylacetate- ¹³ C	Surrogate	150	77
Pentafluorobenzene	Istd-BP I	1.51	85
Benzene- <i>d</i> ₆	Surrogate	3.92	79
1,2-Dichloroethane- <i>d</i> ₄	Istd-RV FP	20	84
Fluorobenzene	Istd-RV I&FP	3.5	85
1,4-Difluorobenzene	Istd-RV I&II	3.83	88.5
1,2-Dichloropropane- <i>d</i> ₆	Surrogate	11	95
1,4-Dioxane- <i>d</i> ₈	Istd-RV V&VI	5800	101
Toluene- <i>d</i> ₈	Istd-BP I	4.28	111
Pyridine- <i>d</i> ₅	Surrogate	15000	115
1,1,2-Trichloroethane- <i>d</i> ₃	Surrogate	26.6	112
1,2-Dibromoethane- <i>d</i> ₄	Istd-RV III&IV	26	131
Chlorobenzene- <i>d</i> ₅	Istd-RV II&II	6.27	131
<i>o</i> -Xylene- <i>d</i> ₁₀	Istd-RV II&II	6.14	143
4-Bromofluorobenzene	Surrogate	8.05	152
Bromobenzene- <i>d</i> ₅	Istd-BP I&II	7.93	155
1,2-Dichlorobenzene- <i>d</i> ₄	Istd-BP II	8.03	181
Decafluorobiphenyl	Surrogate	3.03	206
Nitrobenzene- <i>d</i> ₅	Surrogate	87.5	210
Acetophenone- <i>d</i> ₅	Surrogate	161	202
1,2,4-Trichlorobenzene- <i>d</i> ₃	Istd-BP II&III	7.88	213
Naphthalene- <i>d</i> ₈	Istd-BP III	18	217
1-Methylnaphthalene- <i>d</i> ₁₀	Istd-BP III	67	241
2-Chloroethanol- <i>d</i> ₄	Istd-RV VI	13800	129
Ethylene oxide	Analyte	75	10.5
Propylene oxide	Analyte	106	34.2
1, 4-Dithiane	Analyte	610	200
Allyl alcohol	Analyte	6077	96
1, 4-Thioxane	Analyte	2560	147
2-Chloroethanol	Analyte	13800	128

^a Type reflects the compound's purpose. RV reflects a relative-volatility internal standard followed by what range of values it belongs (grouping). BP is a boiling-point internal standard followed by its grouping. See references 1 and 2 for further explanation.

A unique attribute of Method 8261 is that calibration is in units of mass, and not concentration. Because of Method 8261's use of internal standards to mitigate the effects from matrices (*e.g.*, water), the method is not as dependent on sample size or matrix as other methods. Therefore the

low mass in the calibration curve is used as the limit of quantitation. Therefore, for method 8261 the limit of quantitation (LOQ) is determined as the low standard divided by the sample size.

Therefore, we can look at the low calibration point in the calibration curve and determine the LOQ simply by dividing by the sample size desired. For instance, the low standard value of 15 ng divided by 5 mL results in a LOQ of 3 ng/mL.

Table 3. Calibration and Analyte Sensitivity

Volatile Organic Compounds	High Standard	Low Standard	Calibration		LOQ 5 mL	LOQ 25 mL
	(ng) ^a	(ng) ^b	Cts/ng	(%dev)	(µg/L)	(µg/L)
ethylene oxide	250	15	3539	22	3	0.6
propylene oxide	250	5	1073	21	1	0.2
1, 4-dithiane	250	15	4520	19	3	0.6
allyl alcohol	4270	85	588	12	17	3.
1, 4-thioxane	250	5	2707	13	3	0.6
2-chloroethanol	51000	10200	48	23	2000	400

^a Five standard runs generated the curve. The high standard is listed and the other four standards were 0.6, 0.2, 0.06, and 0.02 as much as the high standard.

^b Lowest viable standard is listed.

The chromatography for the study compounds is displayed in Figures 1-6. In each figure the upper chromatogram is for all ions from 41 to 300 m/z. The lower chromatogram displayed is for the quantitation ion of the compound (e.g., ethylene oxide with its quantitation ion, 44 m/z, displayed in Fig 1).

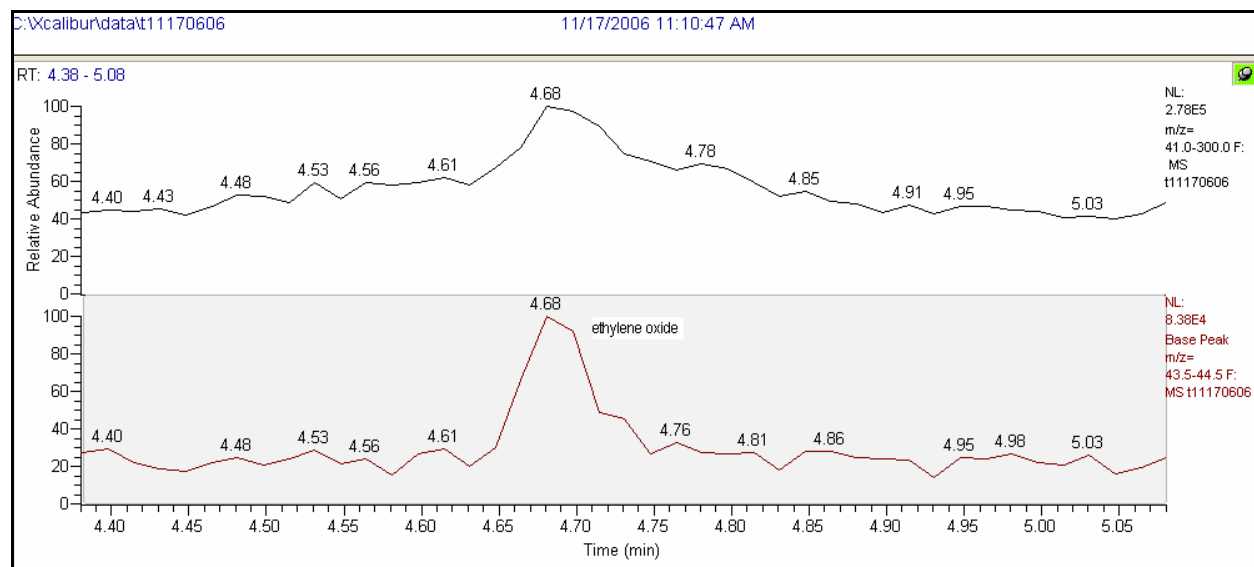


Figure 1 Chromatogram of 50 ng ethylene oxide

Figure 1 shows the response of ethylene oxide. The analyte is well resolved. However, its quantitation ion of 44 is prone to background interference making the detection of very low levels of the compound difficult to integrate.

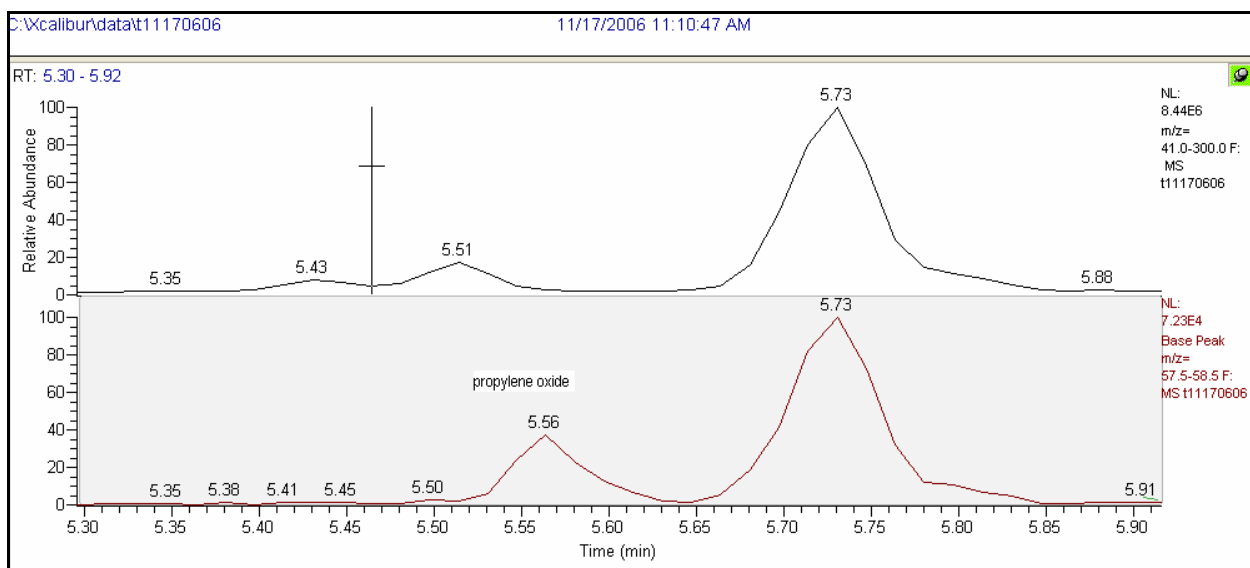


Figure 2 Chromatogram of 50 ng propylene oxide

Figure 2 shows the chromatography of propylene oxide. The resolution is quite good but the compound elutes very near acetone which could be a potential for interference.

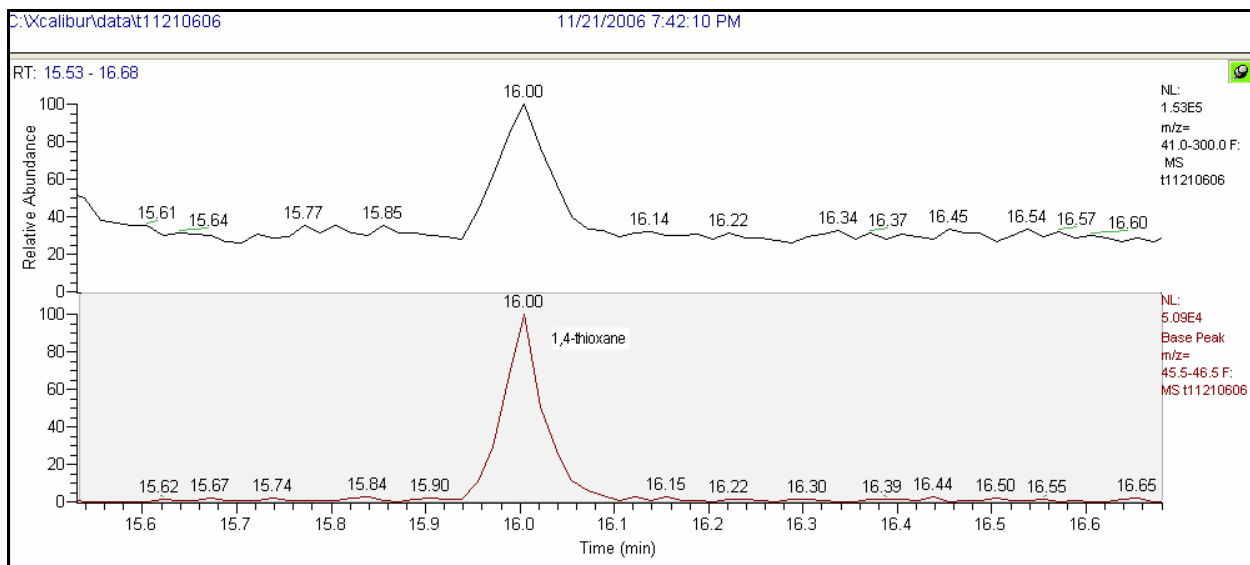


Figure 3 Chromatogram of 50 ng 1,4-thioxane

Figures 3 and 4 show chromatography for 1,4-thioxane and 1,4-dithiane. These compounds have good resolution and are free from background interferences.

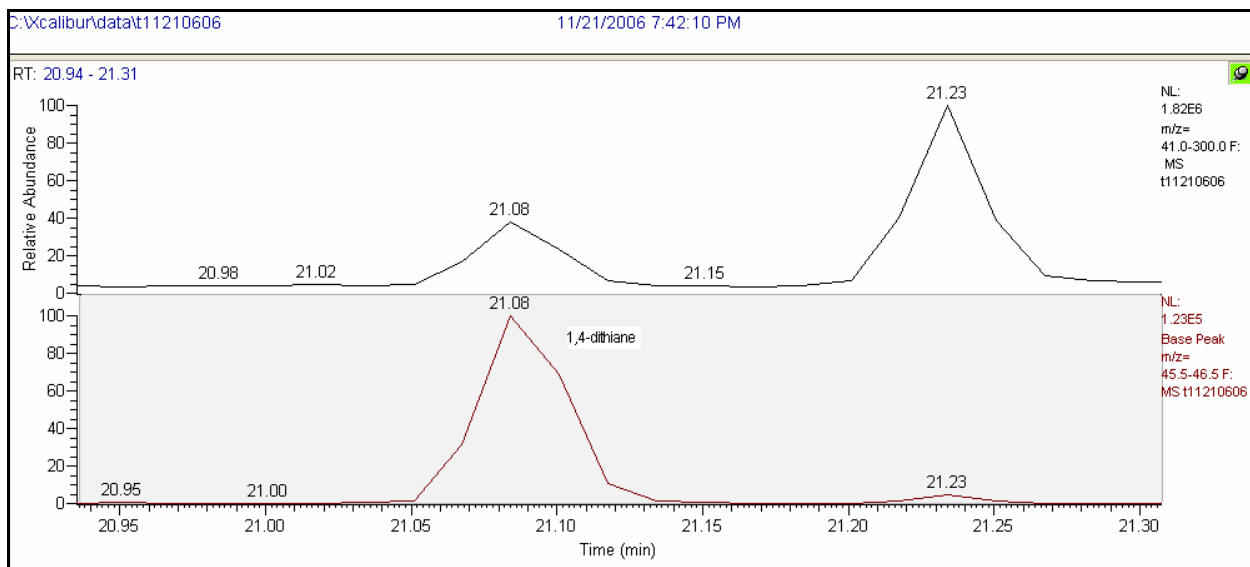


Figure 4 Chromatogram of 50 ng 1, 4-dithiane

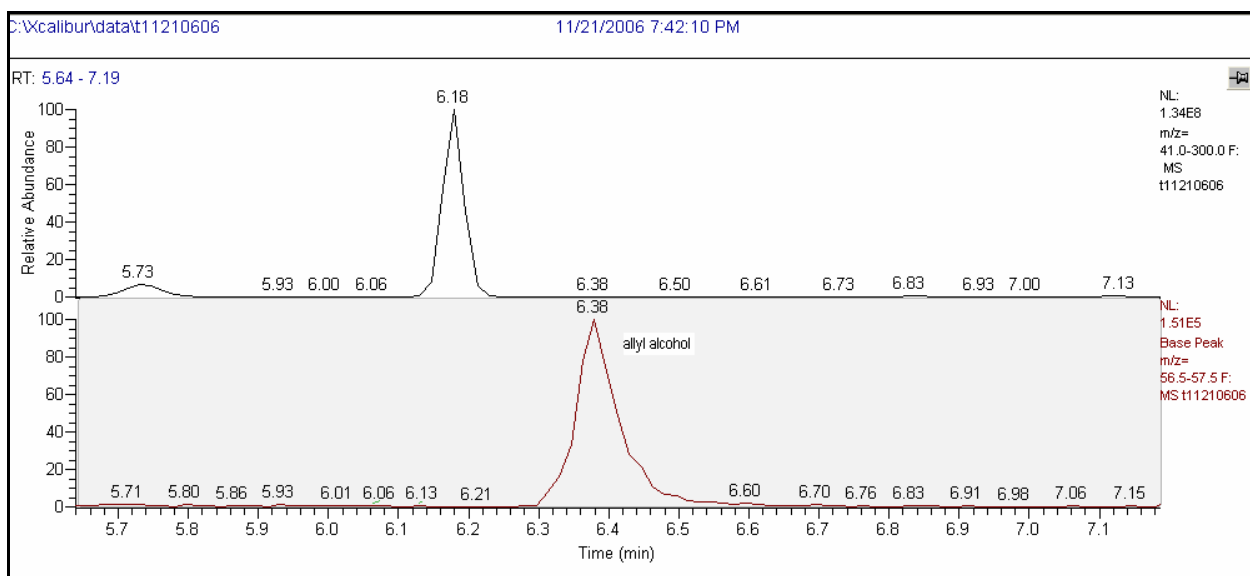


Figure 5 Chromatogram of 850 ng allyl alcohol

Figure 5 shows a chromatogram of allyl alcohol. The peak shape of this compound is not as sharp as the other analytes and the peak width is twice the other compounds at almost 20 seconds. While there appears to be little background interference, the compound would likely see interference in complex matrices.

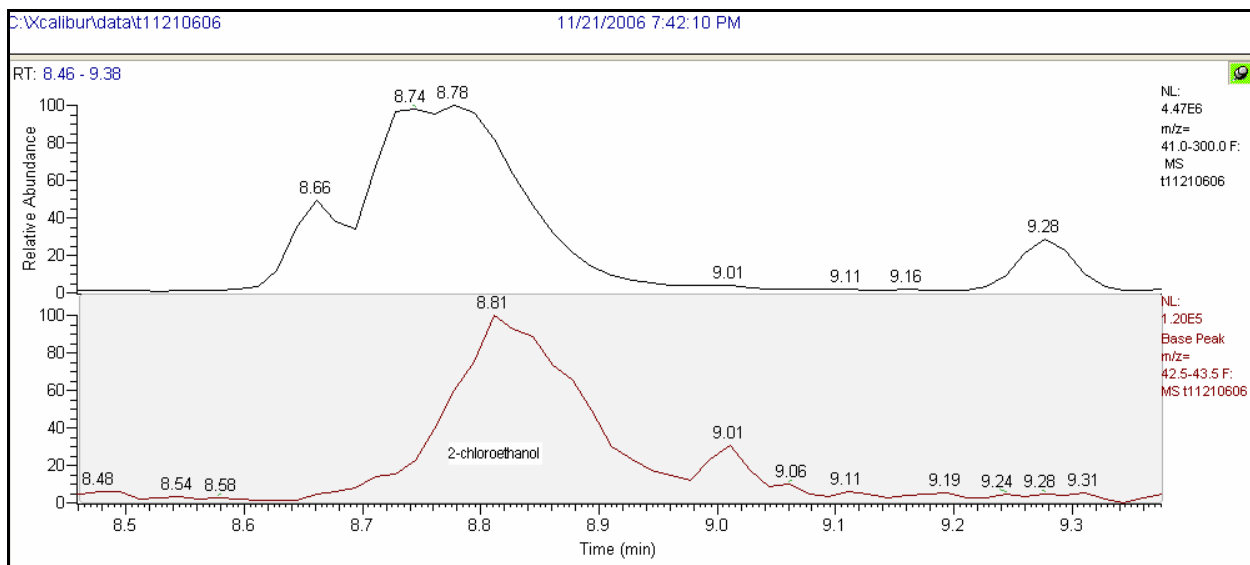


Figure 6 Chromatogram of 10000 ng 2-chloroethanol

Figure 6 shows the chromatogram of 2-chloroethanol. The chromatographic peak of this compound is quite broad, approaching 30 sec. The two compounds that appear to coelute with the analyte are the internal standards, fluorobenzene (8.66 retention time) and 1, 4-difluorobenzene (8.74 retention time). The internal standards do not interfere with the analyte's quantitation ion. However, considering the analyte's broad peak and that the quantitation ion is not intense or unique, the ability to quantify low-levels of this analyte would be difficult.

The next issue was testing the method performance by running triplicate analyses of 5 mL and 25 mL samples spiked with the analytes. The results are presented in Tables 3 and 4.

Some of the analytes were reactive (ethylene oxide and propylene oxide) and were not stable in solution with the other analytes. The standards and spiking solutions of compounds were prepared separately. Separate samples were spiked with only ethylene oxide and propylene oxide and internal standards. These analytes were found to be stable with the internal standards.

Table 3. Sample Performance for 5-mL Samples

Volatile Organic Compounds	Level 1 spike (ng/mL)	Recovery (%)	Relative Precision (%)	Level 2 spike (ng)	Recovery (%)	Relative Precision (%)
ethylene oxide	3.0	116	14	1	289	14
propylene oxide	3.0	121	21	1	138	40
1, 4-dithiane	3.0	40	36	0.6	56	26
allyl alcohol	17	82	13	10.	88	7
1, 4-thioxane	1.0	86	13	0.6	95	14
2-chloroethanol	612	173	38	122.	137	51

Table 4. Sample Performance for 25-mL Samples

Volatile Organic Compounds	spike (ng/mL)	Recovery (%)	Relative Precision (%)
Ethylene oxide	0.6	111	24
Propylene oxide	0.6	99	6
1, 4-dithiane	3.0	36	40
Allyl alcohol	3.4	74	22
1, 4-thioxane	0.2	88	28
2-chloroethanol	122.	137	51

Conclusion

It was demonstrated that the use of Method 8261 could detect and quantify the target analytes without modification of the distillation procedure.

References

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3. Standardized Analytical Methods for Use During Homeland Security Events Revision 2.0 Office of Research and Development, National Homeland Security, Research Center Sept. 29, 2005 <http://www.epa.gov/nhsrc/pubs/reportSAM092905.pdf>
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6. Hiatt, M.H., "Creating the Calibration Curve and Generating Method 8261 Quantitation Reports through SMCReporter V4.0" Presentation posted on the vacuum distillation web page May 2006.
(<http://www.epa.gov/nerlesd1/chemistry/vacuum/methods/software.htm#calibration>)