Analysis of Exempt Paint Solvents by Gas Chromatography Using Solid-Phase Microextraction

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Acetone, methyl acetate, and parachlorobenzotrifluoride (PCBTF or Oxsol® 100) have been exempted as VOC solvents by the U.S. Environmental Protection Agency. In measuring coating VOC content, separate methods for determining exempt solvents are required. One such method utilizes solid-phase microextraction (SPME) to sample the headspace of solvent-based coatings to which the surrogates acetone-d6, methyl acetate-d3, and/or metachlorobenzotrifluoride have been added. The sampled exempt coating solvents are thermally desorbed and analyzed using gas chromatography with flame ionization or mass spectral detection. The SPME headspace method has also been used to analyze MEK, butyl acetate, tert-butyl acetate, toluene, and xylene in solventborne coatings, and alcohols in waterborne systems. This paper presents the results obtained for acetone and toluene in a large number of aerosol paints. Additionally, the results from a round-robin study for acetone, methyl acetate, and parachlorobenzotrifluoride in commercial solvent-based coatings are reported.

INTRODUCTION

Acetone, methyl acetate, and parachlorobenzotrifluoride (PCBTF) have been exempted as volatile organic compound (VOC) coatings solvents and are not included in the measurement of coating VOC content. A separate method for the determination of exempt solvents must therefore be carried out when VOC is determined by EPA Method 24[1] (ASTM Practice D 3960[2]). As of December 4, 1997, the EPA has received petitions requesting VOC exempt status for tert-butyl acetate,[3] dimethyl succinate and dimethyl glutarate,[4] 1-bromopropane,[5] and other solvents normally not used in coatings. As each new solvent is approved and finds use in coatings, the VOC determination becomes ever more complex since each of the exempt solvents requires a unique method of measurement. Gas chromatography appears to be the only method currently available for carrying out the determination of individual solvents.

It has been shown that the speciated and total VOC content of waterborne paints may be determined by direct injection into a gas chromatograph.[6] The results obtained were generally good, and the method used is particularly effective for analyzing low VOC content coatings. Direct gas chromatography of whole paints has also been used to study both solventborne[7] and waterborne coatings to obtain information on hazardous air pollutants (HAPs) using EPA Method 311.[8] The results obtained in an ASTM interlaboratory study of EPA Method 311 indicated that the precision was generally poor.[9] The direct quantitative gas chromatographic analysis of volatile solvents in coatings is often difficult due to the relatively complex nature of most coatings matrixes. The non-volatile components present in many coatings often make it difficult to obtain homogeneous solutions/dispersions with diluting solvents. When coatings solutions/dispersions are injected onto a gas chromatographic column, decomposition of the non-volatile components may occur in a heated injection port generally maintained above 240°C, giving unwanted chromatographic signals and possibly resulting in fouling of expensive analytical systems and columns. Analytical precision is often compromised and time is often wasted in restoring analysis capabilities.

For solventborne systems we have developed a unique distillation method for quantitatively separating volatile components from non-volatile components.[10] The method is a modification of ASTM Method D 3272, "Vacuum Distillation of Solvents from Solvent-Reducible Paints for Analysis."[11] In the modification, a one- or two-gram sample of the coating is mixed with 5 mL of dioctyl phthalate (di-2-ethylhexyl phthalate) and two grams of tetradecane. The mixture is then vacuum distilled, and the distillate is trapped in liquid nitrogen. The non-volatile dioctyl phthalate serves as a dispersion medium for the coating, and the tetradecane serves as a chase solvent for the coating volatiles during the distillation. Since most coatings contain volatiles with boiling points below that of tetradecane, distillation of a portion of the tetradecane allows quantitative transfer of the coatings volatiles to the liquid nitrogen trap. In addition, the temperature during vacuum distillation is not allowed to exceed 110°C thus minimizing potential non-volatile decomposition and approximating the same temperature used during determination of the coating volatile content by ASTM Method D 2369.[12] The distillate is gas chromatographed on both a 100 m × 0.25 mm polydimethylsiloxane and 60 m × 0.25 mm Carbowax™ capillary column and quantitatively speciated after determination of relative response factors for each analyte present in the sample. After determination of total volatile content by ASTM D 2369, absolute amounts of each analyte may be determined. Alternatively, an internal standard can easily be incorporated prior to the vacuum distillation and then used to determine absolute amounts of each analyte. This method has been used to analyze the liquid coating portion of more than 40 diverse solventborne aerosol paints.[13]

A method was needed to validate the results obtained by vacuum distillation/gas chromatography and since a large

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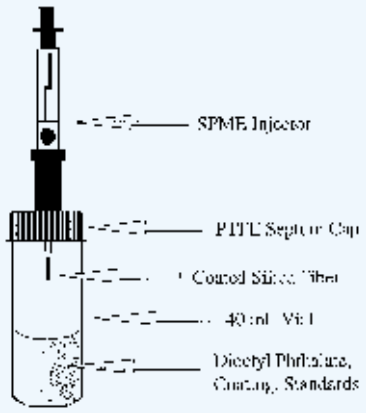

Figure 1—Solid-phase microextraction of coatings.

number of the samples contained acetone and/or toluene, these analytes were determined separately by solid-phase micro-extraction (SPME). The SPME method was found to be simple to use and gave very precise results. We have extended the SPME method for the analysis of other common solvents found in coatings, including parachlorobenzotrifluoride (PCBTF or Oxsol® 100), xylene, methyl ethyl ketone, butyl acetate, tetiary butyl acetate, methanol, ethanol, and 2-propanol. A round-robin SPME study was conducted for the solvents acetone, methyl acetate, and PCBTF since these have been exempted as VOCs by the U.S. Environmental Protection Agency. In the round-robin study, both flame ionization detection (SPME/GC/FID) and mass spectral detection (SPME/GC/MS) were used to measure analyte concentrations.

SPME was initially developed by Janusz Pawliszyn[14-16] at the University of Waterloo, Ontario, Canada and involves the extraction of analytes from a liquid headspace or from an aqueous solution onto a coated fiber. The SPME fiber consists of a section of fused silca, coated with an appropriate adsorbent, which is attached to a modified GC syringe. In using this method for determining paint solvents, a sample of paint is weighed into a septum-capped vial containing a dispersion medium of dicoctyl phthalate (solventborne paint) or salt solution (waterborne paint). Depending on the analyte of interest, an appropriate surrogate is weighed into the vial and the mixture is agitated and allowed to equilibrate. The headspace above the solution is sampled with an SPME fiber and then desorbed in a heated GC inlet onto a capillary column. A fiber coated with a 65 µm film of Carbowax-divinyl-benzene was used for all analytes studied. A diagram for the experimental extraction setup is shown in *Figure* 1.

One of the most significant characteristics of the headspace SPME method is that the amount of each analyte extracted by the fiber is not proportional to the amount of that analyte present in the headspace. An equilibrium is established between the amount of analyte in the headspace and the amount of analyte adsorbed on the fiber. Larger molecules are adsorbed more strongly to the fiber resulting in preferential adsorption to the fiber. This effect is illustrated in *Figure* 2 for equal masses of acetone, methyl ethyl ketone, methyl propyl ketone, methyl isobutyl ketone, and methyl amyl ketone dispersed in dioctyl phthalate. The headspace of this ketone mixture was sampled using both a gas-tight syringe and an SPME syringe and injected/desorbed onto a gas chromatograph. The resulting relative peak areas, as the molecular weight increases, were 100:32:11:5:1 when sampled by gas-tight syringe and 100:104:118:101:82 when sampled by SPME. The same effect was observed for a mixture of methyl acetate, ethyl acetate, and butyl acetate. Gas-tight syringe sampling gave an area ratio of 100:49:8 and SPME sampling gave an area ratio of 100:112:190. When sampling the headspace of a paint, high boiling solvents, even when present in very low concentration in the headspace, are preferentially absorbed onto an SPME fiber relative to a much higher headspace concentration of a low molecular weight material.

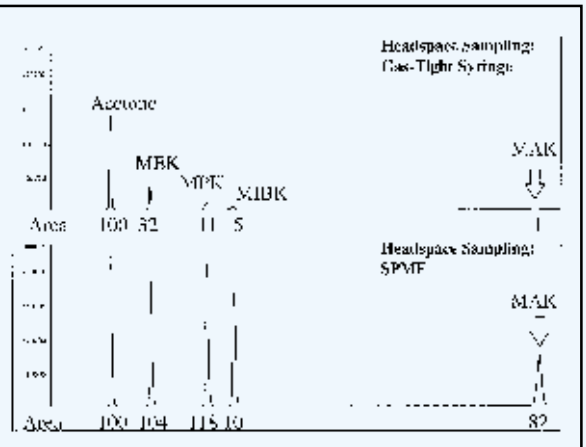

Figure 2—Gas chromatogram of a mixture of equal masses of ketones.

The analytes and corresponding surrogates studied, as well as their boiling points, are shown in *Table* 1. In all cases, except parachlorobenzotri-fluoride, butyl acetate, and tert-butyl acetate, the surrogate was a deuterated analog of the analyte. Surrogates were chosen based on the following criteria:

(1) The boiling point is nearly the same as the corresponding analyte;
(2) The structure is similar to that of the corresponding analyte;
(3) GC peak separation from the corresponding analyte occurs; and
(4) It is not a component of the paint sample being analyzed.

EXPERIMENTAL

The following is a detailed procedure for the analysis of acetone, methyl acetate, and parachlorobenzotrifluoride (PCBTF) in solventborne coatings using either SPME/GC/flame ionization detection or SPME/GC/mass spectral detection. The same procedure may be used for other analytes in solventborne paints by incorporating the appropriate internal standard as indicated in *Table* 1.

Apparatus and Reagents:

1.1—Manual SPME holder fitted with a Carbowax/Divinylbenzene (CW/DVB) fiber assembly, 65 µm film thickness, partially crosslinked (Supelco) was used.

1.2—Gas Chromatograph, FID Detection: Any capillary gas chromatograph equipped with a flame ionization detector may be used. Temperature programming capability is desirable, but isothermal operations may be utilized.

1.2.1—FID Instrument Conditions:
Detector—Flame ionization
Column—60 m × 0.25 mm DB Wax (J&W Scientific Co.) or equivalent, 0.5 µm film thickness.
Carrier Gas—Helium
Flow Rate—1.0 mL per min (20 cm per sec)
Split Ratio—200 to 1
Fiber Desorption Time—5 to 6 sec
Temperatures, °C
Inlet—260°
Detector—270°
Initial—35° for 12 min
Rate 1—30° per min to 100°, hold 10 min
Rate 2—30° per min to 240°, hold 2 min

1.2.2.—A 0.75 mm inlet liner should be placed in the injection port.

1.2.3.—Integrator—Any electronic integrator that can accurately quantify a gas chromatographic peak area is an acceptable integrator.

1.3—Gas Chromatograph, Mass Selective (MS) Detection: Any capillary gas chromatograph equipped with a mass selective detector may be used. The detector must be capable of measuring in the selected ion monitoring (SIM) mode at dwell times of 100 milliseconds or less.

1.3.1—MS Instrument Conditions:

Detector—Electron ionization or mass selective
Detection Mode—SIM of ions m/e 58, 64, 74, 77, and 180
Dwell Time—100 milliseconds or less
Solvent Delay—0.0 min
Column—25 m × 0.20 mm HP-5 (Hewlett Packard Co.) or equivalent, 0.11 µm film thickness
Carrier Gas—Helium
Flow Rate—1.0 mL per min (20 cm per sec)
Split Ratio—200 to 1
Fiber Desorption Time—5 to 6 sec
Temperature, °C
Inlet—260°
Detector—280°
Initial—40° for 2 min
Rate 1—10° per min to 90°, hold 1 min
Rate 2—40° per min to 240°, hold 1 min

1.3.2—A 0.75 mm inlet liner should be placed in the injection port.

1.3.3—The instrument should have a software data system to allow extraction and integration of the SIM ions.

1.4—Required reagents include: Acetone -d6, 99.9% isotopic purity; methyl acetate -d3, 99.9% isotopic purity; parachlorobenzotrifluoride (PCBTF), technical grade, 99+% was obtained from the Occidental Chemical Corporation and has the trade name Oxsol® 100; metachlorobenzotrifluoride (MCBTF), 97%.

Preparation of Standards:

2.1—Place 6 mL dioctyl phthalate into a 22 or 40 mL vial and seal with a septum cap.

2.2—Using dedicated 250 µL syringes, weigh approximately 100 mg each of parachlorobenzotrifluoride and metachlorobenzotrifluoride to 0.1 mg into the vial. Excess solvent should be wiped from the syringe needle prior to piercing the septum. Any solvent adhering to the outside of the septum cap after making the transfer should be wiped off with tissue. Weigh the amounts of PCBTF and MCBTF to 0.1 mg. Repeat the procedure by adding approximately 150 mg each of acetone, acetone-d6, methyl acetate and methyl acetate-d3 and weigh each component to 0.1 mg.

Table 1—Analytes and Corresponding Surrogates

Analyte, b.p. °C	Surrogate, b.p. °C
Acetone, 56.0	Acetone-d6, 55.5
Methyl ethyl ketone, 80	2-Butanone-1,1,1,3,3-d5
Parachlorobenzotrifluoride, 136-138	3-Chlorobenzotrifluoride, 137-138
Methyl acetate, 57.5	Methyl-d0 acetate-d3, 57.0
tert-Butyl acetate, 98	Methyl trimethylacetate, 101
Butyl acetate, 124-126	Methyl valerate, 128
Toluene, 110.6	Toluene-d8, 110
Xylene, 137-144	Ethylbenzene-d10, 134.6
	p-Xylene-d10, 135
	o-Xylene-d10, 142
Methanol, 64.7	Methanol-d3, 65.4
Ethanol, 78	Ethanol-d5, 78
2-Propanol, 82.4	2-Propanol-d7, 82

2.3—Manually shake the vial for 15 sec to mix the content and then let the vial stand at room temperature for 30 min.

2.4—Remove the cap and wipe the septum to remove solvent from the inner surface and reseal immediately, or replace the septum with a new one.

2.5—Sample the headspace with the SPME fiber for 60 sec.

2.6—Desorb the SPME fiber for 5 to 6 sec in the injection port of the gas chromatograph using either the conditions described in 1.2 or 1.3.

2.7—Clean the fiber by placing it in the GC injection port for 15 sec after the analytes of interest have passed through the capillary column.

2.8—If using the GC/FID procedure, measure the peak areas of the three analytes and three standards by integration. Curve fitting software (GRAMS/32, Galactic Industries) for measuring peak areas is advantageous in some instances.

2.9—If using the GC/MS procedure, measure the peak areas for the extracted ions as follows: analyte, m/e, retention time in minutes; acetone, 58, 1.26; acetone-d6, 64, 1.26; methyl acetate, 74, 1.34; methyl acetate-d3, 77, 1.34; MCBTF, 180, 4.84; PCBTF, 180, 4.90.

2.10—Calculate response factors (RF) for acetone, methyl acetate, and PCBTF according to the equation given in section 3.4. The numerical values should agree within 1% of each other.

Paint Analysis:

3.1—Weigh 0.5 to 1.0 g of well mixed paint into a septum-capped vial containing 6 mL of dioctyl phthalate using a disposable 1 mL syringe. The paint should drop directly into the dicoctyl phthalate. Carry out the same procedures as described in 2.3 to 2.7.

3.2—Determine which, if any, of the three exempt solvents are present in the paint sample and if interfering peaks are present at the retention times corresponding to the retention times of the internal standards.

3.3—Weigh to 0.1 mg, 0.5 to 1.0 g of paint sample and 100 mg of each of the internal standards, corresponding to the analytes found in 3.2, into a septum-capped vial containing 6 mL dioctyl phthalate. Carry out the same procedure as described in 2.3 to 2.9.

3.4—Calculate analyte concentrations according to the following equations:

$$RF = \frac{AA * MI}{AI * MA} \quad \text{and} \quad \%Analyte = \frac{AA * MI * 100}{AI * RF * MC}$$

where RF = Response factor
AA = Area of analyte
MI = Mass of internal standard
AI = Area of internal standard
MA = Mass of analyte
MC = Mass of coating

3.5—Repeat the procedure given in section 3.3 using paint and internal standard amounts such that the relative peak areas of the analyte and its internal standard chromatographic peak areas are approximately the same size. A duplicate injection of the same sample should give relative peak areas which agree within one percent of each other.

RESULTS

Aerosol Coatings

In the course of a study of more than 40 diverse solventborne aerosol paints, the propellant from each was transferred to a gas sampling bag, and the remaining liquid coating was distilled under vacuum to separate the volatiles and non-volatiles. The volatile portion was gas chromatographed to give the speciated profile of the volatile compounds

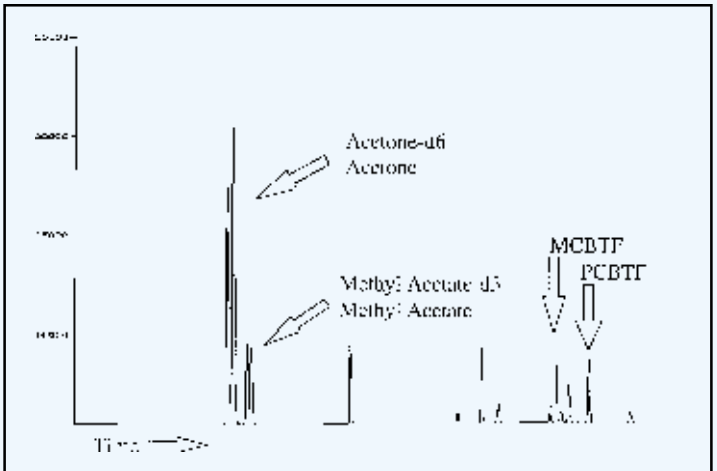

Figure 3—Gas chromatogram of nitrocellulose lacquer containing acetone, added methyl acetate and PCBTF, and internal standards.

for each coating. SPME/GC/FID was used to validate the results obtained for acetone and/or toluene in 23 of these aerosol coatings. A comparison of these two entirely different methods indicate that both methods gave very good results (*Table* 2). Of 18 samples which contained acetone, the average difference between the two methods was 0.52%. Of 10 samples which contained toluene, the average difference between the two methods was 1.16%. Based on these results, it was believed that the SPME/GC method could serve as a simple and clean method for quantifying exempt and other individual solvents in coatings.

Round-Robin Analysis of Coatings Containing Exempt Solvents

A round-robin was conducted involving five laboratories. The laboratories participating in the round-robin were experienced in both gas chromatography and SPME methodology. All of the laboratories used the SPME sampling technique. Three of the laboratories used FID to measure analyte amounts, and two of the laboratories used MS detection to measure analyte amounts.

Six commercial solventborne coatings were analyzed. Four of the coatings contained acetone and two of the same four coatings contained both acetone and parachlorobenzotrifluoride. Coatings containing methyl acetate were not yet available in the marketplace when this round-robin was carried out and were, therefore, prepared by adding known amounts of methyl acetate to different cellulose nitrate lacquers. Four of the six coatings were nitrocellulose lacquers obtained from two different manufacturers. Two of the six coatings were parts of a two-component pigmented primer which were analyzed as two separate coatings. A typical FID chromatogram of a nitrocellulose lacquer containing acetone, added methyl acetate, added PCBTF, and the appropriate internal standards is shown in *Figure* 3.

Precision data was calculated separately for the three laboratories using FID and the two laboratories using MS detection and also for the combination of FID and MS detection. Average values, repeatability standard deviations (Sr), reproducibility standard deviations (SR), repeatability at the 95% confidence limit (r), and reproducibility at the 95% confidence limit (R) are given for each coating and exempt solvent in *Tables* 3 and 4.

Table 2—Comparison of SPME and Distillation Results for Acetone and Toluene

	% Acetone				% Toluene			
Sample	SPME	Distillation	Error[a]	SPME/Dist[b]	SPME	Distillation	Error[a]	SPME/Dist[b]
27	28.53	27.12	–1.41	1.05	34.97	36.43	1.46	0.96
29	71.87	72.28	0.41	0.99	—	—	—	—
34	42.83	41.71	–1.12	1.03	40.49	42.17	1.68	0.96
35	51.55	52.39	0.84	0.98	—	—	—	—
36	11.18	9.47	–1.71	1.18	—	—	—	—
37	—	—	—	—	27.75	28.48	0.73	0.97
38	38.73	38.84	0.11	1.00	—	—	—	—
39	55.62	56.00	0.38	0.99	—	—	—	—
41	—	—	—	—	34.68	35.47	0.79	0.98
42	40.28	39.65	–0.63	1.02	—	—	—	—
43	—	—	—	—	11.57	11.96	0.39	0.97
44	—	—	—	—	13.43	13.82	0.40	0.97
45	40.68	40.40	–0.28	1.01	29.87	30.41	0.54	0.98
48	—	—	—	—	38.92	38.85	–0.08	1.00
49	50.06	49.19	–0.87	1.02	—	—	—	—
50	37.47	36.28	–1.19	1.03	—	—	—	—
51	54.24	53.23	–1.01	1.02	—	—	—	—
57	48.93	49.51	0.58	0.99	—	—	—	—
63	56.82	54.85	–1.97	1.04	—	—	—	—
64	40.36	39.27	–1.09	1.03	21.60	21.92	0.32	0.99
66	69.33	68.71	–0.62	1.01	—	—	—	—
67	54.66	56.70	2.04	0.96	—	—	—	—
87	13.47	13.62	0.15	0.99	67.06	70.66	3.60	0.95
Avg.	—	—	–0.52	1.02	—	—	1.16	0.97

(a) Difference between distillation and SPME result.
(b) Ratio of composition as determined by SPME, relative to distillation procedure. This should equal exactly 1.00 if the two methods produced identical results.

The results were analyzed for precision using ASTM Practice E 180-94.[17] For Laboratory *Precision (within-laboratory, between-days variability, formerly called repeatability)* the standard deviation of results (each of the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.42% absolute at 39 degrees of freedom for acetone, 0.35% absolute at 19 degrees of freedom for parachlorobenzotrifluoride, and 0.16% absolute at 19 degrees of freedom for methyl acetate. The 95% confidence limit for the difference between two such averages is 1.18% absolute for acetone, 0.97% absolute for parachlorobenzotrifluoride, and 0.46% absolute for methyl acetate.

The standard deviation for *Reproducibility (Multilaboratory)* of results (each the average of duplicates), has been estimated to be 0.69% absolute at 39 degrees of freedom for acetone, 0.53% absolute at 19 degrees of freedom for parachlorobenzotrifluoride, and 0.25% absolute at 19 degrees of freedom for methyl acetate. The 95% confidence limit for the difference between two such averages is 1.94% absolute for acetone, 1.47% absolute for parachlorobenzotrifluoride, and 0.70% absolute for methyl acetate.

SPME Analysis of Other Analytes

For tert-butyl acetate the surrogate methyl trimethylacetate (methyl pivalate) gave excellent results. The boiling points of these two solvents differ by only three degrees Celsius and they are structurally similar so they would be expected to adsorb onto the SPME fiber at about the same rate. Butyl acetate may be analyzed with methyl valerate as an internal standard. Methyl ethyl ketone may be analyzed with 2-butanone-1,1,1,3,3-d5 as an internal standard. Toluene, ethylbenzene, and the three isomeric xylenes may be analyzed using toluene-d8, ethylbenzene-d10, p-xylene-d10 or o-xylene-d10, respectively, as surrogates.

We have previously reported the SPME/GC analysis for 2-propanol.[6] Methanol and ethanol may be analyzed in the same manner using methanol-d3 and ethanol-d5 as surrogates. If these oxygenated solvents are present in a solventborne coating, dioctyl phthalate is used as the dispersion medium. If they are present in a waterborne coating, water is used as a dispersion medium. The addition of solid sodium chloride to the water dispersion medium increases the analyte concentration in the headspace and should be used when the analytes are present in low concentration.

Synthesis of Methyl Acetate-d3

The deuterated surrogate methyl acetate-d3 was synthesized from acetic acid-d3 and excess methanol-boron trifluoride complex. The pure ester was obtained by extracting with p-cymene, washing the extract with small quantities of water to remove excess methanol, and distillation to obtain the pure deuterated surrogate. In an alternate procedure, a mixture of two moles of acetic acid-d3 and one mole of methanol were stirred with Nafion® pellets and anhydrous magnesium sulfate for two weeks at room temperature. Filtration followed by two simple distillations gave isotopically pure methyl acetate-d3.

SUMMARY

We highly recommend the SPME/GC/FID or SPME/GC/MS method for the analysis of selected analytes in coatings. The method gives very good precision and is relatively simple to perform. A major advantage using SPME is that nonvolatile coating constituents are not introduced into the chromatographic system, which allows for continuous "clean" operation of the system. For the analysis of all the volatile components in a solventborne coating system, a distillation/GC method as described earlier is recommended. Since the modified vacuum distillation procedure is relatively simple to carry out, we recommend that it be

Table 3—Precision Data for Acetone

Material	Acetone			
Sample	A	B	C	D
Average % (FID)	28.4	46.9	29.0	89.3
Average % (MS)	27.1	47.3	28.6	88.7
Average % (FID + MS)	28.0	47.0	28.8	89.1
Sr (FID)	0.55	0.54	0.21	0.69
Sr (MS)	0.30	0.17	0.35	0.41
Sr (FID + MS)	0.45	0.39	0.27	0.58
SR (FID)	0.99	0.55	0.31	0.65
SR (MS)	0.29	0.57	0.55	0.49
SR (FID + MS)	1.05	0.58	0.49	0.66
r (FID)	1.54	1.52	0.59	1.94
r (MS)	0.83	0.46	0.99	1.14
r (MS + FID)	1.26	1.10	0.75	1.62
R (FID)	2.76	1.54	0.87	1.83
R (MS)	0.82	1.61	1.53	1.36
R (FID + MS)	2.93	1.61	1.38	1.83

Sr Repeatability standard deviation.
SR Reproducibility standard deviation.
r Repeatability, 95% confidence limit.
R Reproducibility, 95% confidence limit.

Table 4—Precision Data for Parachlorobenzotrifluoride and Methyl Acetate

Material	Parachlorobenzotrifluoride		Methyl Acetate	
Sample	A	B	E	F
Average % (FID)	16.8	10.6	21.0	12.0
Average % (MS)	16.1	11.1	21.0	12.1
Average % (FID + MS)	16.5	10.9	21.0	12.0
Sr (FID)	0.49	0.46	0.19	0.19
Sr (MS)	0.20	0.11	0.10	0.15
Sr (FID + MS)	0.38	0.32	0.15	0.17
SR (FID)	0.48	0.58	0.22	0.25
SR (MS)	0.28	0.22	0.34	0.19
SR (FID + MS)	0.55	0.51	0.28	0.22
r (FID)	1.38	1.28	0.53	0.54
r (MS)	0.56	0.30	0.29	0.41
r (MS + FID)	1.05	0.88	0.43	0.49
R (FID)	1.34	1.61	0.63	0.69
R (MS)	0.77	0.62	0.95	0.52
R (FID + MS)	1.53	1.42	0.78	0.63

Sr Repeatability standard deviation.
SR Reproducibility standard deviation.
r Repeatability, 95% confidence limit.
R Reproducibility, 95% confidence limit.

used for determination of hazardous air pollutants (HAPs). An internal standard can easily be incorporated prior to distillation, and the distillate may be chromatographed on any suitable capillary column without disrupting the integrity of the chromatographic system being used.

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