



## Project Summary

# Laboratory and Field Evaluations of Methodology for Measuring Emissions of Chlorinated Solvents from Stationary Sources

Anna C. Carver, William G. DeWees, and Easter A. Coppedge

**An evaluation of the use of EPA Method 18 for sampling and analysis of chlorinated solvents was needed to support possible future regulations by the U. S. Environmental Protection Agency. The solvents specifically addressed are: carbon tetrachloride (CCl<sub>4</sub>), chloroform (CHCl<sub>3</sub>), perchloroethylene (PERC), and trichloroethylene (TCE). Laboratory and field studies were performed to evaluate sampling and analytical procedures for measuring these solvents from stationary sources. Conclusions and recommendations are made regarding the application of Method 18 to organic solvent sampling and analysis.**

*This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, 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

Several chlorinated solvents are being evaluated by the U. S. Environmental Protection Agency (EPA) for possible future regulations for emissions from stationary sources. Entropy Environmentalists, Inc. (Entropy) was

commissioned by the Quality Assurance Division (QAD) of EPA's Atmospheric Research and Exposure Assessment Laboratory (AREAL) to evaluate methods for sampling and analysis of some of the high priority solvents. Those solvents included in the evaluation were carbon tetrachloride (CCl<sub>4</sub>), chloroform (CHCl<sub>3</sub>), perchloroethylene (PERC), and trichloroethylene (TCE). The work was conducted in two phases: (1) a field evaluation of sampling and analytical techniques for measuring emissions of PERC, and (2) laboratory and field evaluations of the collection of all four solvents under high temperature/high moisture conditions.

The use of EPA Method 18<sup>1</sup> was previously evaluated as a sampling and analysis method for PERC emissions in a laboratory study sponsored by the EPA.<sup>2</sup> Since perchloroethylene is widely employed as a solvent in the chemical degreasing industry, a degreasing facility was selected for field evaluation of the candidate method. Gaseous samples collected in Tedlar bags were analyzed directly using a gas chromatograph equipped with a flame ionization detector (GC/FID). Emission samples were also adsorbed onto activated charcoal in sorbent tubes and likewise analyzed by GC/FID after desorption with an appropriate solvent.

Laboratory evaluation of EPA Method 18 techniques modified to include an in-

line gas conditioning system for high temperature/high moisture sample collection involved (1) the identification of adsorption media that will effectively collect organic solvents under these conditions and (2) the effectiveness of the gas conditioning system in permitting sample collection in Tedlar bags. A field evaluation of the sorbents chosen and the gas conditioning system developed was conducted at a gas-fired boiler where the exhaust gas stream was spiked with the chlorinated solvents. Samples collected both in Tedlar bags and on the adsorption tubes were analyzed using GC/FID.

### Experimental Procedures

All samples were analyzed using a Hewlett-Packard 5890A series gas chromatograph with dual flame ionization detectors. One injection port was equipped for liquid injections while the other was equipped with a manually operated gas sampling valve. Column selection and operating procedures were based on those followed in previous evaluations.<sup>3</sup> For all analyses, the hydrogen and air pressures supplied to the dual FID's were maintained at 22 and 20 psi, respectively. These values were selected by optimizing the FID response according to manufacturer's suggestions. For the GC/FID analysis, calibration standards were prepared, in bags with nitrogen or in the appropriate desorbing solution, using measured amounts of each solvent. These were injected into the GC to obtain a linear calibration curve in the range of the samples to be analyzed.

Dual quadruplicate-train sampling runs were conducted at the inlet and outlet to a carbon bed adsorber at the degreasing facility according to EPA Method 18. Gaseous samples were collected simultaneously in four Tedlar bags and four charcoal adsorption tubes. Double-seamed Tedlar bags were fabricated for the collection of gaseous samples as specified, and each bag was leak-checked before and after use in the field. Adsorption tubes were packed with charcoal and checked for migration of PERC from the primary to the backup portion. The sampling flow rate for collection of the Tedlar bag samples was maintained using adjustable needle valves at a rate of 55 - 60 cm<sup>3</sup>/min, while the charcoal tube samples were collected at a flow rate of 0.08 L/min, also using critical orifices. The gaseous Tedlar bag samples were injected directly into the GC/FID and quantified according to Method 18. The adsorbed charcoal tube

samples were desorbed using a fixed volume of methylene chloride to allow GC/FID analysis using liquid injection of the resulting solutions.

Prior to the second field evaluation, seven commercially available sorbents (Bio-Rad's Bio Beads<sup>®</sup> SM-2 and SM-4; Supelco's Amberlite XAD-8<sup>®</sup> Carbotrap<sup>®</sup> and Carboxen; Water's C<sub>18</sub>-Octadecyl<sup>®</sup> and Union Carbide's TRI-X-100R) were evaluated for collecting the solvents of interest under simulated high temperature/high moisture conditions. All sorbents were pretreated according to manufacturer's instructions. Two-gram quantities of each were packed into sampling tubes and subjected to retention and breakthrough (time at which sorbent is no longer retaining one or more of the solvents) tests. Sorbent tubes were challenged with a mixture of CCl<sub>4</sub>, CHCl<sub>3</sub>, PERC, and TCE each at 100 ppm from a Tedlar bag at an approximate flow of 1.0 L/min, for a 1-hour period, using a diaphragm pump. The gas exiting the tubes was introduced directly into the GC/FID.

High temperature/high moisture stack gas containing the chlorinated solvents was simulated by drawing the same mixture at the same flow for the same time period through a heated impinger containing 400 ml of water. This gas was then drawn through the candidate in-line gas conditioning system condenser for cooling and a primary sorbent tube, followed by a knockout jar for condensate collection and a second (backup) sorbent tube. The pressure differential of the system was monitored, as was the gas flow rate. The resulting sample was introduced directly into the GC/FID.

The two sorbents with acceptable retention and breakthrough characteristics under the simulated high temperature/high moisture conditions, were examined for efficiency of solvent removal for analysis (desorption efficiency). The desorption efficiency was determined for three different desorbing solutions: acetonitrile, methanol, and methylene chloride. Multiple tubes of each sorbent were charged with 1.0 µl each of the chlorinated solvents and set aside for 1 h. Using a separate tube for each sorbent/desorbing solution combination, they were desorbed with 4 ml of the appropriate solution which was then analyzed by GC/FID. The percent desorption efficiency for each solvent from each sorbent was calculated based on the known charge of that solvent.

To apply Tedlar bag sampling to a high temperature/high moisture source, an in-line gas conditioning system was

designed. The system consisted of a condenser to cool the gas stream, followed by a knockout jar to collect the moisture, and then the Tedlar bag. In a laboratory check of this system design, condensate collected in the knockout jars was analyzed. High temperature/high moisture stack gas containing the solvents was simulated as previously described and drawn through the sampling system at approximately 1.0 L/min for 1 h. Aliquots of the condensate collected were passed through a C<sub>18</sub> cartridge, eluted with methanol, and injected into the GC/FID, or placed into 4 ml of methylene chloride and injected into the GC/FID.

An emission spiking system was developed to introduce known quantities of the solvents into a stack with relatively clean emissions. A mixture of the solvents equivalent to the desired stack gas concentrations was passed through a pressurized atomizer to create a fine mist that would be vaporized in the high temperature emissions. A Speedaire<sup>®</sup> paint sprayer was modified to include a deVilbiss nebulizing nozzle. The system pressure was used to regulate the flow. A Teflon flow meter was placed in-line for fine adjustment of the flow rate.

A preliminary test run was conducted to determine any need for modification in the sampling system. Then field evaluation testing using the refined protocols was conducted according to EPA Method 18 with modification of the sampling systems to include in-line conditioning for the high temperature/high moisture gas stream. Each of five sampling runs was conducted over a 1-h time period. The spiking system was started 5 minutes before sampling began, and sampling continued 5 minutes after all of the solvent mixture had been introduced into the stack. The sampling probe, which was constructed of Teflon tubing, was inserted into a port with the inlet at the center of the stack approximately 18 feet downstream of the point of injection of the solvents. A diaphragm pump was used to pull the sample gas into a heated sampling manifold constructed of stainless steel piping. Twenty sampling lines were attached to the manifold, allowing generation of up to 20 simultaneous samples during a single sampling run (see Figure 1 for a detailed schematic of an eight-train setup). Eight of the sample lines were equipped for Tedlar bag sampling, while the other twelve were equipped for sorbent tube sampling. A sampling rate less than that specified by Method 18 was used for 12 of the 16 bag

samples collected. To validate the use of this reduced flow rate, one set of four bag samples was collected at the higher rate. The actual flow rates for the small bag samples were maintained (using critical orifices) between 0.038 and 0.040 L/min, while the higher flow rates were 0.440 to 0.470 L/min. The flow rates through the primary and backup sorbent tubes ranged between 0.230 and 0.240 L/min, also maintained by critical orifices. The resulting Tedlar bag samples were analyzed within 4 hours of sampling, and the sorbent tube samples were analyzed within 5 days of sampling.

## Results and Discussion

The optimum operating conditions identified for analysis of PERC samples collected in Tedlar bags during the first

field evaluation utilized a packed chromatography column containing 20% SP-2100/0.1% Carbowax 1500 on 100/120 mesh Supelcoport, operated isothermally at 120°C. PERC solutions obtained from the desorption of the charcoal tubes using methylene chloride were analyzed using an OV-101 column and the following temperature programming: 70°C (3 minutes)-ramp of 30°C/min (1 minute) - 100°C (3 minutes). For the PERC bag samples, the estimated limit of detection was 1.6 ppm, and the estimated quantifiable limit was 4.8 ppm. No upper detection limit was apparent below the level at which room temperature nitrogen is saturated with perchloroethylene. For liquid injections of 4.0 µl, dissolved PERC in amounts as low as 0.003 µl per 4 ml desorbing solution

resulted in discernable detector response, while concentrations above 160 µl per 4 ml of desorbing solution saturated the detector. Migration of PERC from the primary to the backup portion of the charcoal tubes was found to be insignificant at charge levels from 1.3 to 36.0 µL

All bag samples from the first evaluation were initially analyzed on site. The average coefficient of variation observed for the bag samples from the controlled emissions of PERC was 9.8%. A pooled standard deviation of 14 ppm was calculated for charcoal tube samples collected from the controlled emissions. The average coefficient of variation for these samples was 4.6%.

For the second field test, optimization of instrument operating conditions for

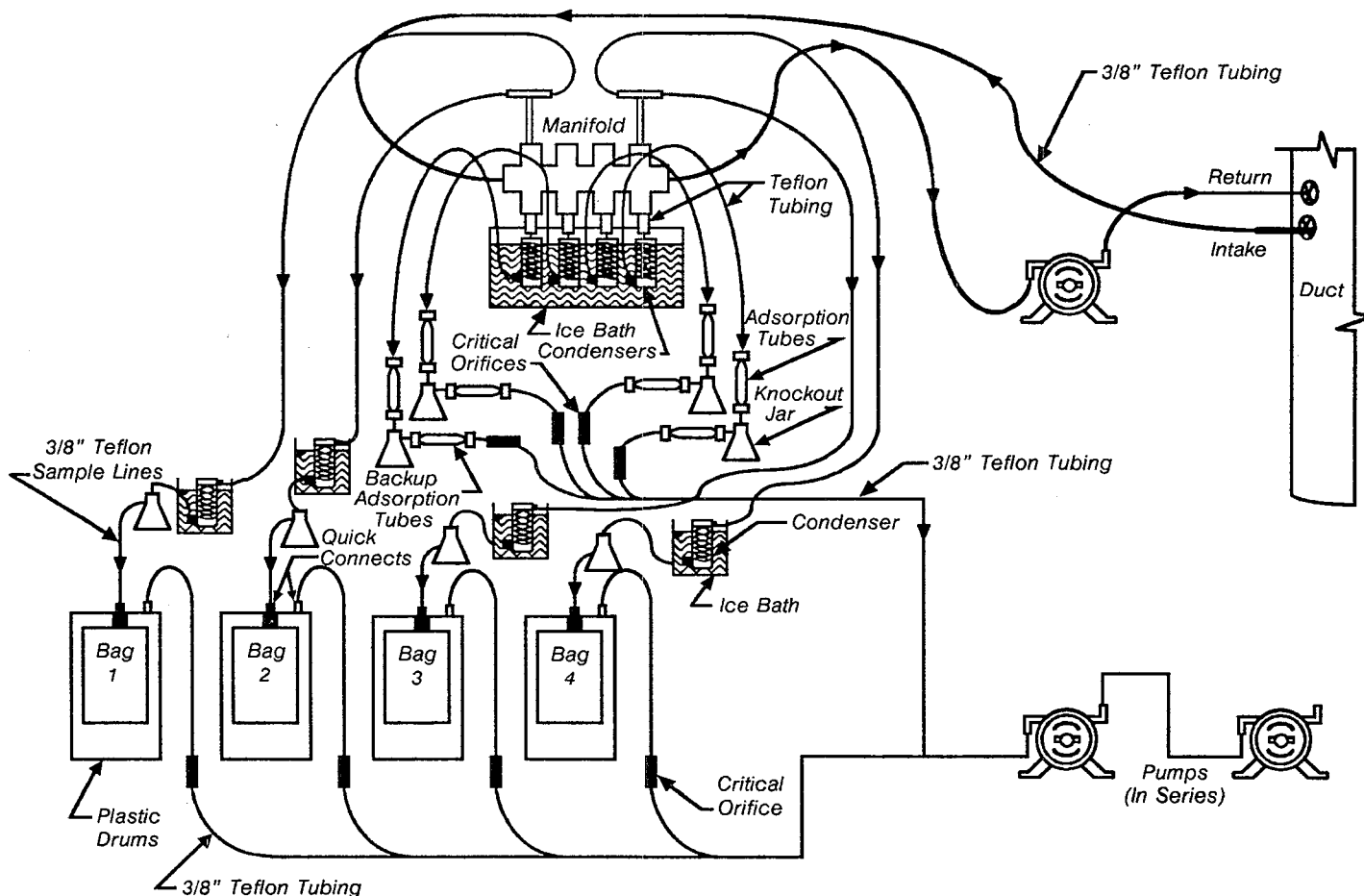


Figure 1. Detailed schematic of multiple bag/sorbent tube sampling train system.

analysis of bag and desorbed sorbent tube samples resulted in analysis of both types using a packed chromatography column of 1% SP-1000 on 60/80 Carboxen-B Supelcoport, operated isothermally at 200°C. The carrier gas flow was maintained at 20 mL/min for both the liquid and the gaseous sample injections.

Of the seven sorbents examined for chlorinated solvent collection under high temperature/high moisture conditions, two were selected for use in the field evaluation test. Supelco's Carboxen-564, a hydrophobic carbon molecular sieve which is designed to replace charcoal for the collection of airborne contaminants, demonstrated excellent collection efficiency for all the solvents. After 158 minutes of sampling the solvent mixture through the Carboxen sorbent tube at a flow rate of 0.460 L/min with 65% moisture and a stack gas temperature of 173°F, there was no evidence of breakthrough. Union Carbide's TRI-X-100, which is an inorganic highly hydrophobic silica oxide generally used for waste removal in industrial adsorption, also showed acceptable collection efficiency. Under similar sampling conditions with 46% moisture, an average stack gas temperature of 155°F, and a sample flow rate of 0.590 L/min, it showed 20% breakthrough of CCl<sub>4</sub>, while the other three solvents were retained. The other five sorbents did not retain the solvents under similar conditions.

The desorption efficiencies of the Carboxen and TRI-X-100 sorbents were evaluated. Although each of the chlorinated solvents could be analytically separated from each of the desorbing solutions, methylene chloride proved to be the most efficient in removing the solvents from both sorbents, with the lowest recovery being 82%. Methylene chloride was, therefore, chosen for desorption of the sorbent tubes for the remaining GC analyses.

GC analysis of the condensate collected by the in-line gas conditioning system for Tedlar bag sampling confirmed that the solvents were not being collected; none were detected.

The analysis of samples collected during the preliminary sampling yielded an average relative standard deviation of (RSD) 14.1% and an average accuracy of

±9.6% for the solvents collected on TRI-X-100. The average RSD for the solvents collected on the Carboxen-564 was 10.0%, with an average accuracy of ±8.8%. For the Tedlar bag sample analysis, the precision, in terms of the average RSD, was 6.1%, with an average accuracy of ±9.8%. All adsorption tubes were desorbed with 4 ml of methylene chloride. One problem noted with the sampling system during the preliminary test run was that the sample conditioning devices connected to the end of the manifold farthest from the stack gas flow were not collecting as much condensate as the others. As a result, the sorbent tubes were not equally exposed to the high moisture conditions and system modification was necessary to ensure that the gas sampled by all the trains was equivalent. Therefore, the manifold was wrapped with a heating coil to prevent loss of heat at the end of the manifold. It was also discovered that some of the critical orifices were clogging, which was most likely caused by fine particles of the sorbent exiting the tubes. This was remedied by including filters in-line behind the tubes.

The refined sampling system was used to collect the organic solvents spiked in the high temperature/high moisture gas-fired boiler emissions. The overall average RSD for the small bag samples was 13.5%, and the overall average RSD for the large bag samples was 23%, with an average accuracy of -14.0% and +8.7%, respectively. For the sorbent tube analysis, over 90% of each solvent was collected on the primary Carboxen tube, while as much as 50% of each solvent was found on the backup TRI-X-100 tube when the sorbent was exposed to high moisture conditions. A pooled standard deviation was calculated for both the TRI-X-100 tubes and the Carboxen tubes. The pooled standard deviations for TRI-X-100 tubes were: 4.28% for CCl<sub>4</sub>, 12.95% for CHCl<sub>3</sub>, 3.13% for PERC, and 3.06% for TCE. The pooled standard deviations for the Carboxen tubes were: 6.09% for CCl<sub>4</sub>, 5.92% for CHCl<sub>3</sub>, 5.50% for PERC, and 3.18% for TCE. The overall average standard deviation for solvent collection on TRI-X-100 was 5.85%, while the overall average standard deviation for the Carboxen samples was 5.17% using a

combination of the primary and backup tube values. The average accuracies calculated for the Carboxen and the TRI-X-100 tubes were +8.8% and +9.8%, respectively.

## Conclusion

Method 18 sampling procedures and gas chromatography using flame ionization detection were found to be acceptable for the measurement of PERC at degreasing facilities.

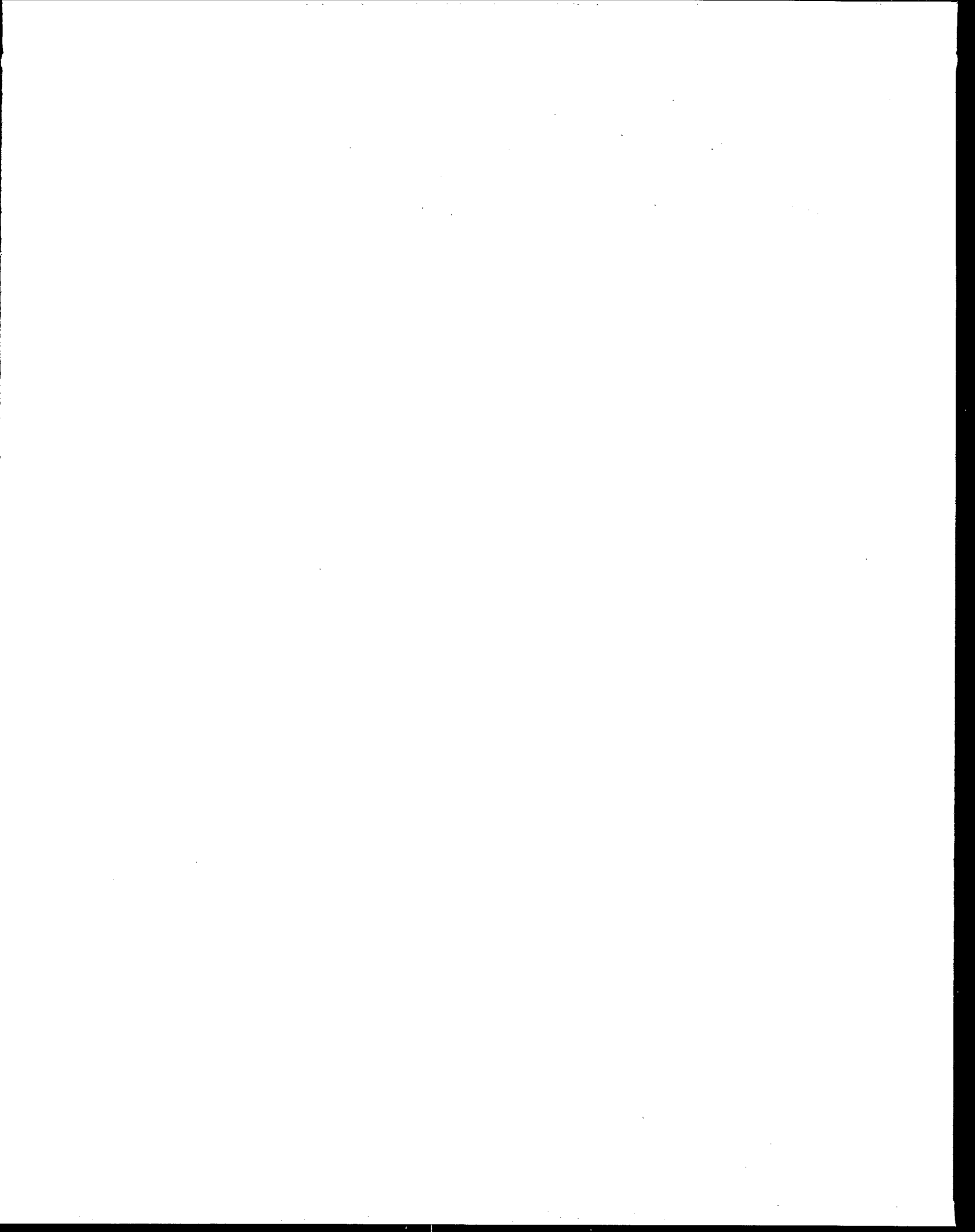
Method 18 procedures modified for sample collection under high temperature/high moisture conditions were found to be acceptable for sampling and analysis of emissions of CCl<sub>4</sub>, CHCl<sub>3</sub>, PERC, and TCE.

The Supelco sorbent, Carboxen-564, is effective for sample collection of CCl<sub>4</sub>, CHCl<sub>3</sub>, PERC, and TCE emissions in high temperature and high moisture environments. TRI-X-100 appears to be effective for the collection of these solvents under high temperature conditions; however, its collection efficiency is decreased in the presence of high moisture.

An in-line gas conditioning system employing a condenser for cooling the sample gas stream and a knock-out jar for eliminating moisture collection is appropriate for Tedlar bag sampling of the above solvents under high temperature and high moisture conditions.

## References

1. "Method 18: Measurement of Gaseous Organic Compound Emissions by Gas Chromatography," 40 Code of Federal Regulations 60, July 1, 1987.
2. Knoll, J. E., M. A. Smith, and M. R. Midgett, "Evaluation of Emission Test Methods for Halogenated Hydrocarbons" - Vol. 1, CCl<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>, Cl<sub>2</sub>Cl<sub>4</sub>, Publication No. EPA-600/4-79-02, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina.
3. "Method 18: Measurement of Gaseous Organic Compound Emissions by Gas Chromatography," Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III, Publication No. EPA-600/4-77-027b, August 1977.



*A.C. Carver and W.G. DeWees are with Entropy Environmentalists, Research Triangle Park, NC; E. A. Coppedge (also the Project Officer) is with the Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC. 27711.*

*The complete report, entitled "Laboratory and Field Evaluations of Methodology for Measuring Emissions of Chlorinated Solvents from Stationary Sources," (Order No. PB90-155 565/AS; Cost: \$17.00, subject to change) will be available only from:*

*National Technical Information Service  
5285 Port Royal Road  
Springfield, VA 22161  
Telephone: 703-487-4650*

*The EPA Project Officer can be contacted at:  
Atmospheric Research and Exposure Assessment Laboratory  
U.S. Environmental Protection Agency  
Research Triangle Park, NC 27711*

United States  
Environmental Protection  
Agency

Center for Environmental Research  
Information  
Cincinnati OH 45268

---

Official Business  
Penalty for Private Use \$300

EPA/600/S3-90/009

• •

• •