



## Project Summary

# Field Tests of Chloroform Collection/Analysis Methods

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The Clean Air Act Amendments of 1990 call for the regulation of numerous toxic chemical species emitted from stationary sources. One of the toxic species is chloroform, an organic compound emitted from paper mills employing the chlorine/chlorine dioxide bleaching process. Two candidate methods were selected and field tested for the collection and analysis of chloroform. Collection efficiencies of a Tedlar bag/glass lung method and a charcoal adsorbent tube method were compared. Samples from each method were collected from the hypochlorite tower vent (300 ppm chloroform source) of a paper mill bleach plant in South Carolina. The two methods were compared using the statistical procedures listed in EPA Method 301, *Field Validation of Emission Concentrations from Stationary Sources*. Based upon the comparison, the charcoal tube method was selected; revision and further testing of that method was performed at a second paper mill bleach plant in North Carolina.

Results from a number of laboratory studies of the methods, as well as from the presurvey and field sampling, are presented and discussed. Both methods demonstrated acceptable precision. The bias and precision of the revised charcoal tube method were found to be acceptable per EPA Method 301 specifications. The revised charcoal tube method is recommended for use in the collection and measurement of chloroform emissions from stationary sources.

*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

The Clean Air Act Amendments of 1990 call for regulation of toxic chemical species emitted from stationary sources. One of the toxic species is chloroform, an organic compound emitted from paper mills that employ the chlorine/chlorine dioxide bleaching process. The objective of this work was to conduct laboratory and field studies to select a method for the collection and analysis of chloroform and validate the method according to EPA Method 301, *Field Validation of Emission Concentrations from Stationary Sources*.

A review of source-level methods for chloroform yielded two candidates for consideration. The first method (based on work by the National Council of the Paper Industry for Air and Stream Improvement, NCASI) uses activated charcoal to adsorb chloroform, a 9:1 solution of hexane:methanol for desorption, and gas chromatography with electron-capture detection (GC/ECD) for quantification. The second method employs a collapsed Tedlar plastic bag mounted inside a rigid container and connected to the exterior via a quick-connect fitting. As the container's interior is evacuated, the bag expands and draws in a sample. Analysis is by gas



chromatography with flame ionization detection (GC/FID). Both these methods were studied in the laboratory prior to and following the first field evaluation.

The first field evaluation of the methods took place at a paper mill hypochlorite tower vent where the chloroform concentration was about 300 ppm. Results showed that both methods met the EPA Method 301 precision criterion but only the charcoal tube method met the sampling bias criterion. Studies of the Tedlar bag method were discontinued. Prior to the second stage of field evaluation, improvements were made in the sampling, spiking, and analysis procedures for the charcoal tube method. The method was then tested at another paper mill at a chlorine scrubber vent where the chloroform concentration was about 220 ppm. In these tests the revised charcoal tube method met all validation criteria specified by EPA Method 301.

## Experimental Approach

### Laboratory Evaluations

Laboratory studies were conducted to test the effects of sodium thiosulfate crystals on chloroform concentration, optimize spiking and recovery procedures, and assess sample stability. GC/FID with a packed column (1% SP-1000 on Carbowax B 60/80, 1/8 in. x 8 ft. SS) was used in studies of the Tedlar bag method; GC/ECD with a capillary column (DB-624, 30-m, 0.53-mm diameter) was used in studies of the charcoal tube method. The GC/FID was calibrated with standards prepared using a pressure dilution technique in which liquid chloroform is diluted with nitrogen in a Summa stainless steel canister to produce known concentrations. The FID response was linear ( $r^2 = 0.99992$ ) over the range of 0 to 597 ppm. The GC/ECD was calibrated with standards prepared by diluting liquid chloroform in hexane:methanol desorbing solution. The ECD response was linear ( $r^2 = 0.998$ ) over the range of 0 to 10,500 ng/mL.

To test the effect of a chlorine-scrubbing material (sodium thiosulfate crystals) on chloroform, a Teflon U-tube containing either dry or wet crystals was assembled and 242 ppm chloroform in nitrogen was passed through the tube at 400 cm<sup>3</sup>/min. The gas entering and exiting the tube was analyzed by GC/FID to determine changes.

The spiking procedure and equipment used in the first field test was studied in the laboratory. Cylinder gas containing 242 ppm chloroform in nitrogen was passed through a manifold from which the Tedlar bag method train sampled at about 350 cm<sup>3</sup>/min. While the sampling train was in

operation, a 100 cm<sup>3</sup> volume syringe was used to slowly introduce spiking gas (4490 ppm chloroform in N<sub>2</sub>) through a septum in a stainless steel tee mounted in the sampling line just upstream of the scrubber. The concentrations of spiked and unspiked samples were then compared.

For the second field test, two types of dynamic, flow-controlled spiking systems were calibrated and tested in the laboratory. The first system employed a precision needle valve to control flow from a gas cylinder. It was used for the laboratory spike recovery study and for spiking during the collection of presurvey samples. The second system employed mass flow controllers and was used for spiking charcoal tubes during the second field test.

For the charcoal tube spiking recovery study, the sampling train was set up as it was in the field except that the sodium thiosulfate tube was omitted. A heated manifold and humidifier system supplied "source gas" as dry or humidified house nitrogen at 58 °C. The sample was pulled into a jumbo-size charcoal tube (1800 mg in the front section; 200 mg in the back section) at a flow rate of 286 cm<sup>3</sup>/min; chloroform from a 4376 ppm cylinder was added through a Teflon tee in the sampling line at a flow rate of 26 cm<sup>3</sup>/min. Sampling continued for 20 min, and spiking occurred continuously during the first 18 min. Six samples were taken and four extraction procedures were tried to determine which produced the best recovery.

Sample stability of chloroform in Tedlar bags was studied for laboratory-generated samples and actual source samples by analysis of bag contents several times during an 18-day period. The stability of chloroform adsorbed onto activated charcoal was not evaluated.

### Field Testing and Methods Validation

Field testing was conducted at two different sites. The primary objective of the tests at the first location (Site A) was to obtain and compare estimates of the precision and accuracy of the Tedlar bag and charcoal tube methods under field conditions. The objective of studies at the second location (Site B) was to obtain precision and accuracy estimates of a revised version of the charcoal tube method and check their acceptability per EPA Method 301 criteria. A pre-survey visit was made to each site to determine the suitability of the site for testing and to collect several samples for analysis so that the chloroform spike level for the validation study could be set.

In accordance with the validation process of Method 301, the field test of the

method consisted of four sampling trains run in parallel for six runs (24 samples total). The four probes were bound together, inserted into a single port, and placed perpendicularly to the flow of gas in the center of the vent. During each run, two of the four trains were spiked with chloroform. The precision of the method was estimated using the standard deviation of the difference between the spiked or unspiked pairs; the accuracy of the method was estimated as the sampling bias; and the bias difference between two methods was calculated by use of the t-statistic.

### Field Site A: Hypochlorite Tower Vent

The sample collection site was a small port in the 19.25-in. diameter stainless steel vent of a hypochlorite tower of a bleach plant. The vent gas temperature was 57 °C. Four unheated, 0.25-in.-OD Teflon tube probes were inserted through a thick rubber sheet that was taped across the vent port. The probe inlets extended to the center of the vent pipe and were separated from each other by about 3 inches. A schematic of the sampling systems as used at Site A is shown in Figure 1. On the first day of sampling, eight sets of quadruplicate samples were taken using the charcoal tube method. Two runs were discarded due to insufficient flow or leaks. On the second day, seven sets of samples were taken using the Tedlar bag method. One run was discarded due to a leak.

### Field Site B: Chlorine Scrubber Vent

The sample collection site was a port in a 30-in.-diameter fiberglass vent from a bleach plant chlorine scrubber. The vent gas temperature was approximately 61 °C. Four heated stainless steel probes, each containing a 3/8-in. OD liner of Teflon or glass tubing were bound together and inserted into a single port of the vent and positioned so that the inlets were in the approximate center of the vent. A schematic of the sampling system used at Site B is shown in Figure 2. A revised version of the charcoal tube method was used at Site B. Significant revisions in the method were: use of a heated probe, replacement of the stainless steel spike injection tee with Teflon, use of a mass flow controlled dynamic spiking system rather than a gas syringe, thermostating the sodium thiosulfate scrubber tube to ~28 °C rather than 0 °C, and analysis by automated, rather than manual, injection to the GC/ECD. On the first day of sampling, five sets of quadruplicate samples were taken.

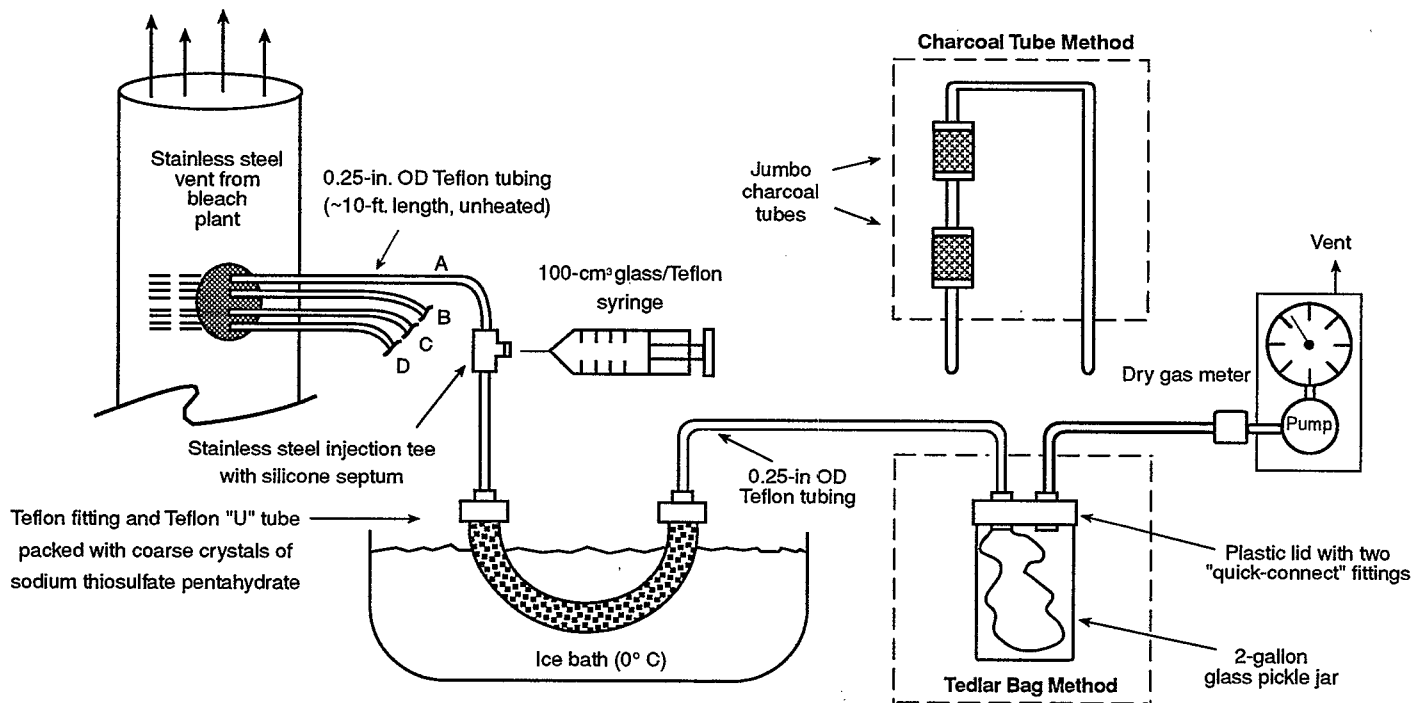


Figure 1. Diagram of initial sampling system for chloroform emissions.

Two additional sets were taken the next day. However, data from these two sets could not be used due to excess water flooding into the charcoal tube, limiting its collection efficiency.

## Results

### Laboratory Evaluations

#### Effects of Sodium Thiosulfate on Chloroform Concentrations

Under dry or moist and room or ice-bath temperature conditions, the recovery of 242 ppm chloroform, passed over sodium thiosulfate crystals at 400 cm<sup>3</sup>/min, was always better than 95 percent. It is concluded that the crystals did not affect chloroform concentration appreciably.

#### Spiking and Recovery Studies

The average recovery of chloroform from five different spiked Tedlar bags was 95 ± 3 percent. The average recovery of six spikes onto charcoal tubes was 90 ± 1 percent. The charcoal tube recoveries were essentially the same whether the desorbing solution volume was 15 or 20 mL and whether the amount of methanol in hexane was 1 or 2 percent. No

chloroform was found on the backup section of the tube or on a second tube placed downstream as a precaution against breakthrough.

#### Sample Stability

The stability of chloroform samples in Tedlar bags was determined. Samples were stored at room temperature and protected from light. Recovery of laboratory-supplied chloroform (250 ppm) was 96 percent six days after filling the bag. For field samples that measured 334 and 540 ppm two days after collection, recoveries 18 days later were 91 and 90 percent, respectively. To achieve better than 90 percent recovery, analysis of chloroform collected in Tedlar bags should occur within 10 days after collection. Although no stability studies of chloroform adsorbed onto charcoal or desorbed into solvent were performed in this study, previous studies indicate that ice-cooled charcoal tubes should be extracted and promptly analyzed within two weeks after sample collection (2). Analysis of the Tedlar bag or charcoal tube field samples in this study occurred within two to seven days after collection.

### Field Testing and Methods Evaluations

#### Field Site A: Hypochlorite Tower Vent

The presurvey results from Site A were similar for both the Tedlar bag and charcoal tube methods. Source chloroform concentrations were approximately 230 ppm by either method. No breakthrough of chloroform onto the backup section of the charcoal sorbent tube occurred. Isothermal and temperature-programmed GC analysis revealed no peaks other than chloroform in the region of interest.

The charcoal tube and Teflon bag methods showed very good precision (less than 5 percent RSD for spiked samples) during field validation testing where the vent's chloroform concentration was about 300 ppm. The average recovery of the spike was 82 ± 13 percent for the charcoal tube method and 74 ± 10 percent for the Tedlar bag method. A statistical analysis per Method 301 showed the bias of -43 ppm was acceptable for the charcoal tube method but the Tedlar bag method's bias of -59 ppm was unacceptable. As noted in the Experimental Approach section, the

charcoal tube method was revised to improve its performance before use at field site B and plans to further develop the Tedlar bag method were discontinued.

### Field Site B: Chlorine Scrubber Vent

A revised charcoal tube method was used for testing at Site B. The presurvey sample results indicated chloroform concentrations of about 120 ppm at the vent. Temperature-programmed GC/ECD analysis showed no peaks near that of chloroform. In the field validation study at the same vent, this time at about 220 ppm chloroform, the paired trains of the method showed precision to be within 5 percent

RSD. The average recovery of the spiked samples was  $95 \pm 7$  percent. The bias of -8 ppm was much improved and well within the acceptable limits of Method 301.

### Quality Assurance

A cylinder containing chloroform at 334 ppm in dry nitrogen was used to provide performance audit samples at field test Sites A and B. The audit gas was sampled from a glass manifold using the charcoal tube or Tedlar bag sampling train operating just as it would have been used in sampling from a vent. At site A, two charcoal tube samples showed an average recovery of 90 percent of the designated audit value. The Tedlar bag method's re-

covery was 84 percent based on a single sample. At Site B the charcoal tube method's average recovery of audit gas for four samples was  $90 \pm 0.7$  percent.

### Conclusions and Recommendations

The data from site A field tests indicated that the charcoal tube method performed better than the Tedlar bag method. All further studies were made with the charcoal tube method. A number of revisions to the sample collection and spiking procedure for the charcoal tube method were made, based on the results of the first field study. These revisions included: heating the sample probe; replacing the

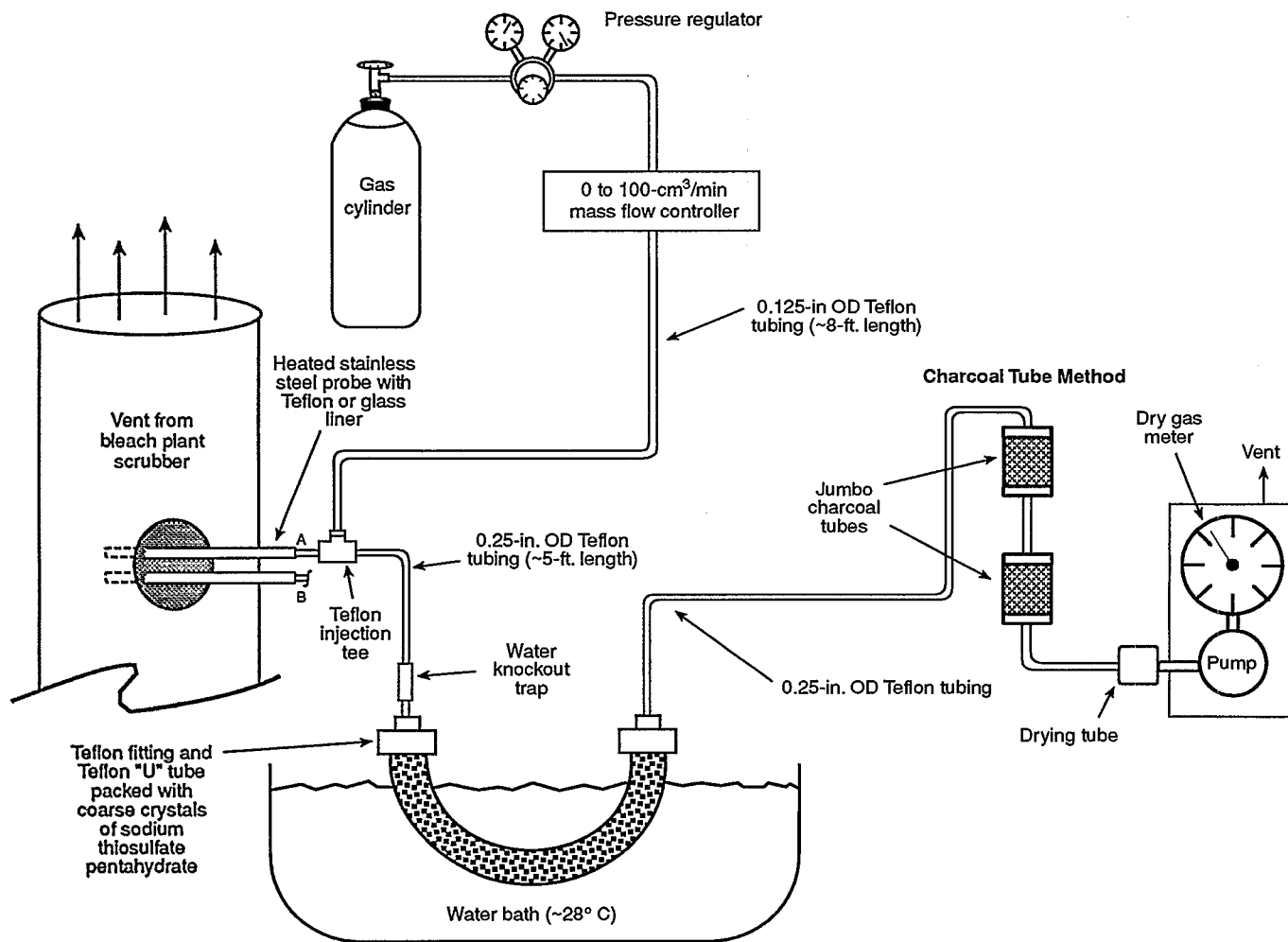


Figure 2. Diagram of revised sampling system for chloroform emissions.

stainless steel spiking tee with a Teflon tee; using mass-flow-controlled dynamic spiking rather than syringe injection spiking; thermostating the sodium thiosulfate scrubber tube at approximately 28 °C instead of ice water temperature; and analyzing the extracts of the charcoal tubes with an automated gas chromatograph sample injection system. A validation study of the revised charcoal tube method was conducted at the bleach plant scrubber of a paper mill identified as site B. Results of the latter study were much improved over those of the former study and met the requirements of EPA Method 301.

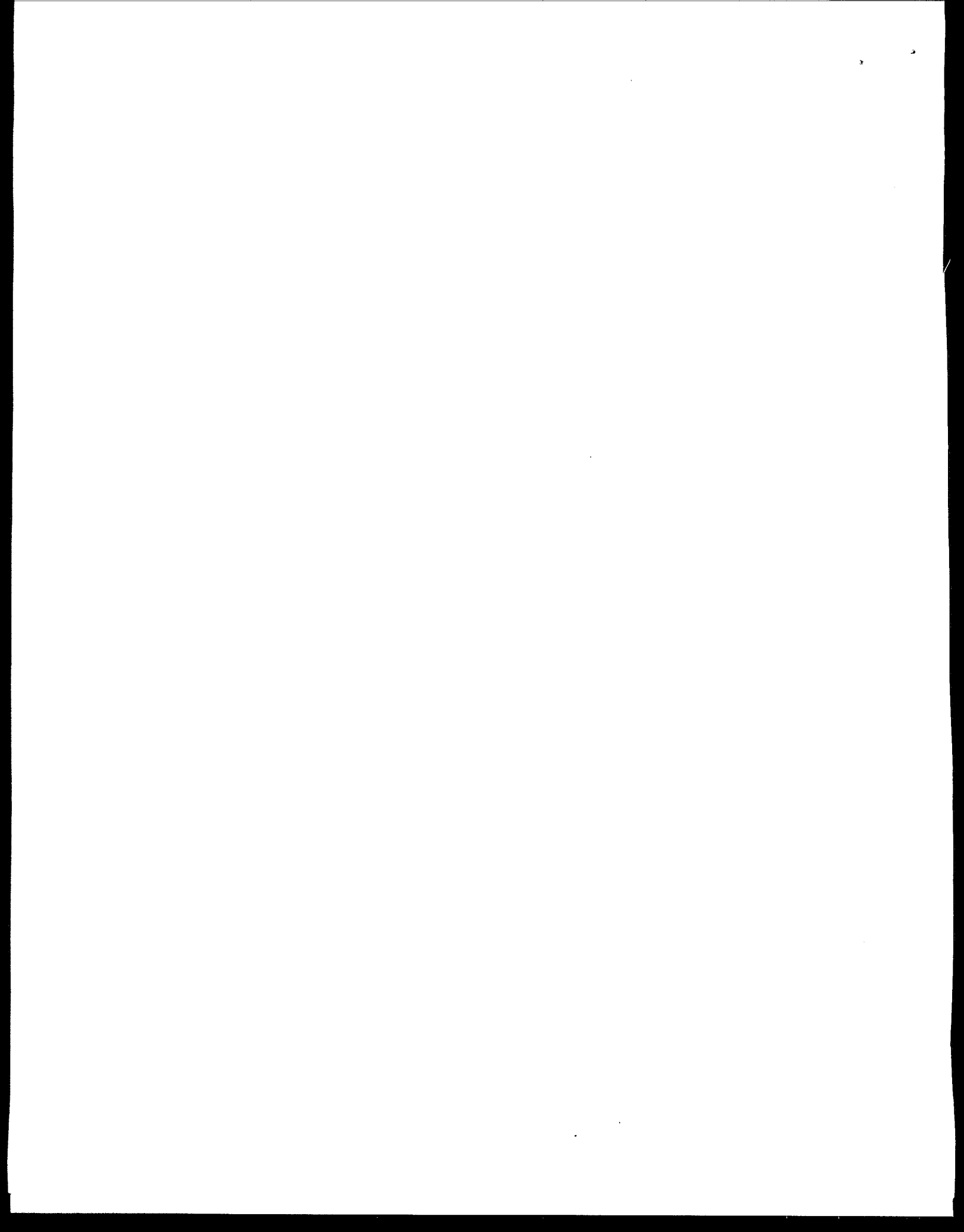
Conclusions concerning the performance of the methods are as follows. Studies under isothermal and temperature-programmed conditions showed that no interfering compounds were present in

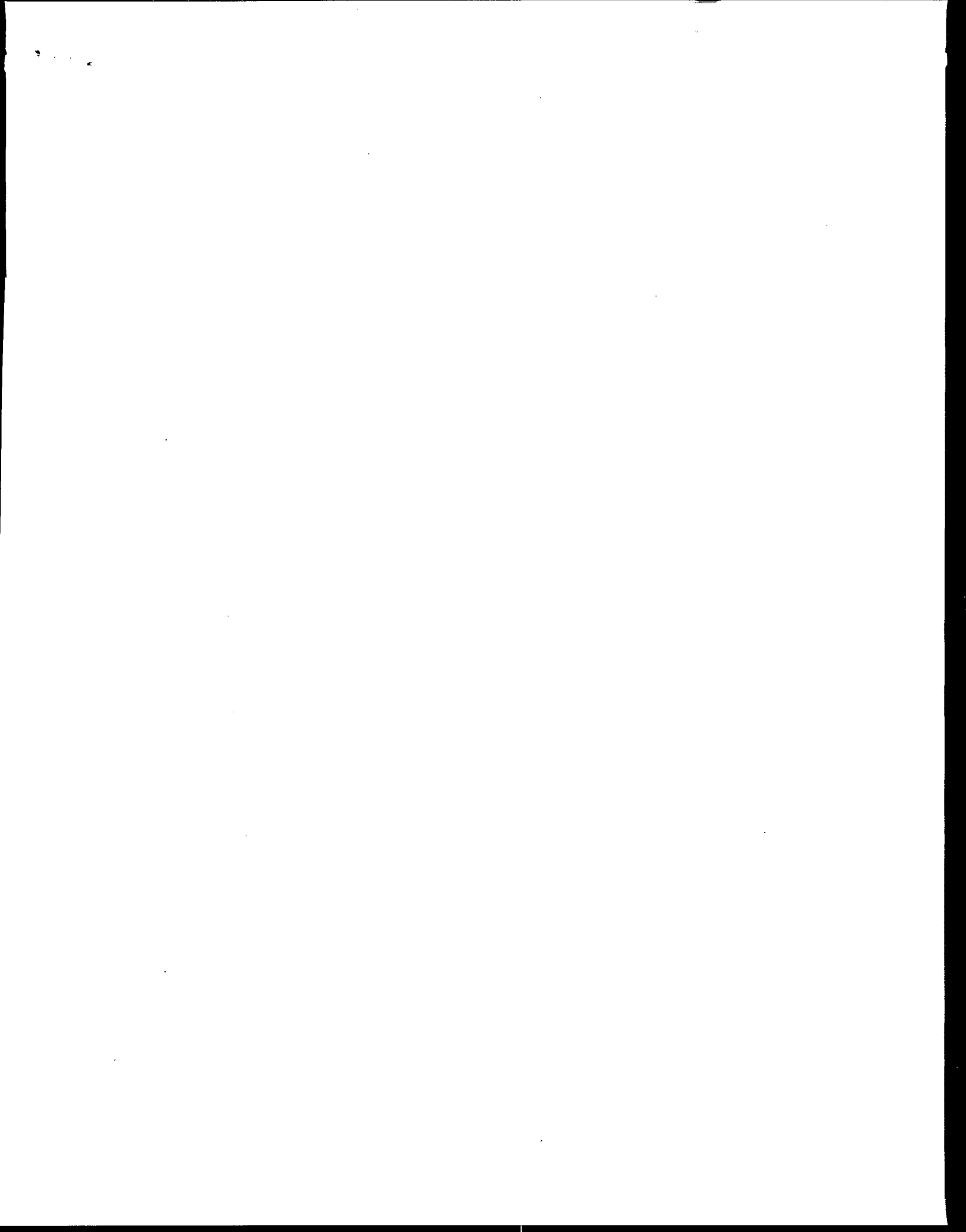
the chromatographic region where chloroform appears. The two methods, as initially evaluated at the Site A mill, were similarly precise (RSD of less than 5 percent for unspiked or spiked samples) and well within the acceptable limits specified by Method 301. Precision estimates for the charcoal tube method at Site B were also less than five percent. The sampling bias for the site A study results was unacceptable for the Tedlar bag method (-59 ppm) and marginally acceptable (-43 ppm) for the charcoal tube method. The sampling bias for the revised charcoal tube method as employed at Site B was acceptable (-8 ppm) and significantly improved over results from Site A. Average spike recovery at Site A was 74 percent for the Tedlar bag method and 82 percent for the initial charcoal tube method. Aver-

age spike recovery at Site B, using the revised charcoal tube technique, was 95 percent.

It is recommended that the charcoal adsorption tube method, as revised, be accepted for use in field sampling studies of chloroform. The precision of the method is quite good and the bias is reasonable. It is also recommended that a water knockout trap be placed between the probe and the sodium thiosulfate scrubber tube whenever water-saturated source gases are expected or encountered. This will prevent water droplets from reaching the charcoal sampling tube and compromising its collection efficiency.

Mention of trade names and commercial products does not constitute endorsement or recommendation for use.





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*Frank W. Wilshire is the EPA Project Officer (see below)*

*The complete report, entitled "Field Tests of Chloroform Collection/Analysis Methods," (Order No. PB94-176948/AS; Cost: \$17.50; subject to change) will be available only from:*

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