ENVIRONMENTAL MONITORING OF WORKERS EXPOSED TO PERCHLOROETHYLENE IN DRYCLEANING ESTABLISHMENTS

A thesis submitted in partial satisfaction of the requirements for the degree of Master of Science in Environmental and Occupational Health

by

Foster Johnston

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The Thesis of Foster Johnston is approved:

California State University, Northridge
To my wife, Monica, and my parents, whose encouragement and support helped make this thesis possible.

Special thanks to Dr. Brad Garber, Dr. Dennis Kelly, and the International Fabricare Institute for their advice and assistance during this study.
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ABSTRACT

ENVIRONMENTAL MONITORING OF WORKERS EXPOSED TO PERCHLOROETHYLENE IN DRYCLEANING ESTABLISHMENTS

by

Foster Johnston

Master of Science in Environmental and Occupational Health

A study was conducted in drycleaning establishments to determine employee exposure to perchloroethylene. It was determined that employees performing the transfer cycle had the greatest risk of overexposure. Results showed that employee exposure was below the standard of 100 ppm calculated as an 8-hour-time-weighted average. However, the maximum concentrations of perchloroethylene that occurred during the transfer cycles were well above the maximum allowable peak concentration of 300 ppm. These high concentrations that occurred during the transfer process could have a deleterious effect on the body, especially the liver. Commonly used control measures were evaluated and found to be inadequate. Better ventilation or the use of drycleaning machines with no transfer cycle would help eliminate or lower employee exposure to perchloroethylene.
Literature Review

Perchloroethylene, \( \text{C}_1\text{C} \equiv \text{C}_2\text{Cl}_2 \), is a clear, colorless, non-corrosive, highly volatile chlorinated hydrocarbon solvent. It has a high molecular ratio of chlorine to carbon making it non-flammable and nonexplosive (Considine, 1974). Perchloroethylene is insoluble in water, but is freely miscible with alcohol or ether. Due to its chemical stability, nonflammability, volatility, and poor solubility in water, perchloroethylene is a very versatile solvent and one of the most widely used chlorinated hydrocarbon solvents in American industry.

While perchloroethylene is not highly reactive, slow thermal decomposition can occur if it comes into contact with open flames, welding arcs, or other high temperature sources (Andersson, 1975). Rinzema (1971) reported that when perchloroethylene is in the air near arc welding, phosgene gas may be liberated due to decomposition of the solvent. He also stated that the hydrogen chloride and chlorine gas, which are simultaneously formed, may not always provide an adequate warning against the presence of phosgene.

The normal route of entry into the human body by perchloroethylene is by inhalation. Bolanowska (1972) found that retention of perchloroethylene vapor in the respiratory tract was ap-
approximately 62%. Perchloroethylene excretion in exhaled air was 25% of the inhaled dose. When expected excretion of perchloroethylene in exhaled air after daily exposure, is calculated by graphic summation of the individual daily curves, the results indicate there should be little accumulation of perchloroethylene in the body. This contradicts the study by Ikeda (1973), who found the biological half-life (T 1/2) of the urinary metabolites of perchloroethylene to be approximately 144 hours. This suggests that perchloroethylene accumulates in the body.

The other routes of entry into the body by perchloroethylene are by ingestion and skin absorption. The former route rarely occurs in the occupational setting while the latter is of minor importance due to poor absorption through the skin (Stewart, 1964). On prolonged contact with the skin, perchloroethylene causes a severe burn (Ling, 1971). This commonly occurs when the solvent is trapped between the workers' clothing and his skin.

One of the predominate effects of overexposure to perchloroethylene is depression of the central nervous system (Stewart, 1961), (Lackore, 1970) and (Stewart, 1970). The signs and symptoms of central nervous system depression may be manifested in a variety of different ways such as lightheadedness, dizziness, fatigue, confusion, alcohol-like intoxication, malaise, headache, nausea, and vomiting (Rowe, 1952), (Stewart, 1961), (Stewart, 1969) and (Medek, 1973). If overexposure persists for long periods of time, a loss of consciousness can occur eventually leading to death (Gobbato, 1968). The narcosis that is produced by the
absorption of perchloroethylene is of a general nature, common to central nervous system depressants, and cannot be distinguished from that caused by absorption of other chlorinated hydrocarbons.

Another common effect of overexposure to perchloroethylene is damage to the liver (Kylin, 1963), (Kylin, 1965) and (Zavon, 1967). This seems to be a chronic effect and is especially dangerous to persons who consume large quantities of alcohol.

Coler (1953) did a study concerned with the exposure of workers to perchloroethylene in a single, small industry's degreasing operation. He suggested that the chronic exposure of personnel to perchloroethylene in concentrations above the maximal allowable concentration may produce an adverse effect on the liver. Three employees studied showed alterations in the sulfobromophthalein sodium test. Two of these also showed alteration in the serum protein pattern, and one showed a 3+ reaction to the cephalin-cholesterol flocculation test. The latter employee was known to have cirrhosis of the liver. Coler believed the question of the toxicity of perchloroethylene to the liver should be more thoroughly investigated, rather than disregarded on the basis that perchloroethylene is a perfectly harmless solvent. The fact that three workers out of seven, showed definite or suggestive signs of liver damage cannot be overlooked in this connection. Coler also thought that a survey of drycleaning establishments might be of substantial importance.

Meckler (1966) reported a case of a 47-year-old woman who had worked in a drycleaning establishment for 2 1/2 months and was
exposed to unknown amounts of perchloroethylene. She was hospitalized with an acute stage of hepatitis attributed to the inhalation of perchloroethylene vapors. Her laboratory values returned to normal within two months, but she still had an enlarged liver six months after discharge. The author noted the widespread use of perchloroethylene as a drycleaning solvent and the frequent elicitation of symptoms that are the early manifestations of toxicity.

In the occupational environment, perchloroethylene is used as a solvent in drycleaning, as a degreasing solvent for liquid and vapor cleaning of metals, in the manufacture of blended safety solvents, and as a chemical intermediate. It is also used in the pharmaceutical industry for extraction purposes and in the manufacture of fluorochemicals. The majority of perchloroethylene is used by drycleaners as the principal solvent for the cleaning of soiled clothing.

The word drycleaning is misleading since there is nothing really "dry" about drycleaning. However, the solvent, which dissolves and lifts away the soils that make the clothes dirty, normally contains less than one percent water and thus the "dry" reference.

Drycleaning originated in Paris over a hundred years ago when Jolly Belin tipped over a table lamp and the spilled oil removed spots from the table cloth (Keil, 1975). Camphene, a fuel used for lamps was originally used as the solvent. Later, benzene and gasoline were employed, but abandoned because of
their high flammability (Keil, 1975).

In 1934, perchloroethylene replaced carbon tetrachloride as the principal solvent used in the drycleaning industry (Considine, 1974). Its excellent solubility and nonflammability are two reasons perchloroethylene is in such wide use as a drycleaning solvent. However, in 1934 it was chosen because perchloroethylene was considered much less toxic than carbon tetrachloride (Coler, 1953).

In a drycleaning store using perchloroethylene, the first operation in the actual cleaning of the garments is the wash cycle. During this cycle, the solvent passes through a rotating cylinder containing the clothes and the removal of dirt, grease, and oil is accomplished. A continual recirculation of the solvent occurs during which time the perchloroethylene passes through a diatomite or cartridge filter for clarification.

Upon completion of the wash cycle, an extraction or centrifuging process follows. This is necessary to remove as much solvent as possible from the clothes before drying. In all perchloroethylene plants, the wash and extraction cycles transpire in the same machine.

The final operation in the cleaning of the clothes is the drying cycle during which the solvent remaining after the extraction cycle is removed. In a few perchloroethylene plants, the washing, extraction, and drying of clothes can be accomplished in one machine called a "hot" unit. However, in the majority of the plants a separate machine, called a recovery tumbler, is
utilized for the drying cycle. Throughout the course of the drying cycle, air is heated within a rotating cylinder and is then passed through the clothes. The solvent-laden air leaving the clothes is passed over a water-cooled condenser for recovery of the solvent. This same air is reheated, producing a continual recirculation of the air within the recovery tumbler. After an appropriate period of drying, fresh air is brought into the recovery tumbler where it is quickly exhausted, providing deodorization of the clothing.

When a drycleaning store utilizes a separate washer/extractor and recovery tumbler, it becomes necessary for an employee to manually transfer the clothing from the washer to the recovery tumbler. The process, in which the clothing is removed from the washer/extractor and placed in the recovery tumbler, is known as the transfer cycle. This is the process which, without proper ventilation, can expose an employee to the greatest danger. This is due to the fact that, under normal operating conditions, this process produces the highest and most hazardous concentrations of perchloroethylene in the employee's breathing zone (International Fabricare Institute, 1975). The transfer cycle can last as long as two minutes with approximately three transfer cycles per hour. If, however, a drycleaning store has more than one washer/extractor and dryer, this would mean more transfer cycles and therefore, more employee exposure to the vapors of perchloroethylene.

In a study by the International Fabricare Institute (1975), concentrations of perchloroethylene in the employee breathing
zone, during the transfer cycle, were measured using a direct reading instrument. Peak exposures in about 91% of the perchloroethylene plants with a transfer cycle were found to be 1000 ppm or more. Of the total number of drycleaning establishments in the United States, 74% nationally and 89% in California are perchloroethylene plants. Approximately 84% of the perchloroethylene plants nationally utilize a transfer cycle.

**Occupational Standards**

Identical occupational standards for perchloroethylene have been promulgated by both the Federal Occupational Safety and Health Administration (OSHA) and the California Occupational Safety and Health Administration. The standards are designed to protect the health and safety of workers for an 8-hour day, 40-hour week over a working lifetime. Compliance with the standards should prevent adverse effects of perchloroethylene on the health of workers.

A summary of the OSHA regulations for perchloroethylene vapor concentrations are as follows (Federal Register, 1974):

0-100 PPM: Acceptable concentration range. Time-weighted average (TWA) must be below 100 ppm.

101-200 PPM: Excursions may occur in this range providing the TWA concentration remains below 100 ppm.

201-300 PPM: Concentrations in this range may not exist for a duration of more than 5 minutes in any three hours during an eight-hour workday.
Above 300 PPM: Concentrations in this range are not permitted unless a personal vapor respirator is worn.

Statement of the Problem

The majority of the drycleaning establishments in the United States using perchloroethylene, utilize a transfer cycle during the drycleaning process. This cycle requires an employee to manually transfer solvent-laden clothing from the washer/extractor to the recovery tumbler. At the present time, very little research has been done to determine the concentration of perchloroethylene in the employee's breathing zone during the transfer cycle.

The purpose of this study is to: 1) measure the concentration of perchloroethylene in the employee's breathing zone during the transfer cycle, and 2) determine if OSHA standards for permissible airborne exposure are being exceeded.

This study was designed to answer the following questions:

1. Does employee exposure to perchloroethylene in drycleaning establishments exceed the OSHA standard of 100 ppm for an 8-hour time-weighted average?
2. Does employee exposure to perchloroethylene during the transfer cycle exceed the OSHA standard of 300 ppm as an acceptable maximum peak above the ceiling concentration?
Chapter 2

METHODOLOGY

Environmental monitoring of perchloroethylene, in five dry-cleaning establishments, was performed on five days between 7/9/76 and 7/19/76 in the Southern California area. All the drycleaning stores used perchloroethylene as the cleaning solvent and had at least one washer/extractor and recovery tumbler in operation.

The owners of the drycleaning establishments were contacted in advance to gain permission to perform this study in their store. A letter of introduction, in Appendix A, was made available as an explanation of the purpose of the study and the confidentiality of the sources of all data.

Monitoring Procedures

Personal sampling. As described in Appendix B, the 8-hour time-weighted average exposure was measured using a charcoal tube and a Sipin Personal Sampler Pump (Anatole J. Sipin Company, Model SP-2). The pump was carried in a shirt pocket or on a belt. Only those persons who performed the transfer cycle were sampled. A measured quantity of air was drawn by the pump through the activated charcoal tube (Anatole J. Sipin Company, Lot No. 101), which was in close proximity to the employee's breathing zone. Employees were sampled for the entire period they were in the plant. The sampling duration varied according to the number of loads of clothing the drycleaner
had on that particular day. Immediately after sampling, the charcoal tube was sealed with the supplied plastic caps. Another charcoal tube was handled in the same manner as the sample tube, except that no air was drawn through this tube. This tube was labeled as a blank. The charcoal tubes were taken to the laboratory for analysis.

Calibration of the personal pumps was done by determining the cc per stroke factor \( K_v \). This was done by drawing air through a representative charcoal tube preceded by a soap bubble flow meter. This factor, \( K_v \), was checked prior to and after sampling each drycleaning store.

**Air sampling.** The maximum concentration of perchloroethylene vapor was measured by means of a GasTech Halide Detector (GasTech Inc., Model 1322). This is a portable, direct-reading AC-operated instrument equipped with three sensitivity ranges. The principle of operation is based on the change in the light intensity of an electric arc in air, which brightens when halogenated compounds are present. The increase in brightness of the arc in the ultraviolet region is directly proportional to the halogen concentration present in the sample. The detector was attached to a Linear Instruments Integrating Chart Recorder (Linear Instruments Corp., Model 252A).

The detector was calibrated using procedures similar to those described in Appendix C. However, instead of a 5 gallon glass bottle, a 12 gallon Pyrex container was used. Spectroquality
tetrachloroethylene (Matheson, Cole & Bell, TX 170) was the solvent used in the calibration procedure. Calibration curves, as shown in Figures 1 & 2, were prepared and used to check the halide detector prior to and after sampling each drycleaning store.

Air sampling was done with a ten foot, flexible, Teflon probe attached to the halide detector. The probe was placed in the employee's breathing zone during the entire transfer cycle.

Ventilation measurement. The exhaust ventilation, that is activated whenever the washer/extractor door is opened, was measured by means of an Alnor Thermo-Anemometer (Alnor Instrument Company, Type 8500). The instrument probe was placed at different locations in front of the doorway of the washer/extractor. The average of these measurements was used as the final indicator of air flow by the system.

Analytical Procedures

Gas chromatography. The procedures used to analyze the charcoal tubes were very similar to those described in Appendix D. A Perkin-Elmer Gas Chromatograph (Perkin-Elmer Corp., Model 3920B) was utilized to determine the amount of perchloroethylene in the charcoal tubes. A flame ionization detector was used with the following air and gas rates:

Nitrogen - 25cc/minute
Hydrogen detector - 20 psi
Air detector - 55 psi
PPM OF PERCHLOROETHYLENE - Figure 1
Calibration Chart for GasTech Halide Detector - Range 1 - 7/8/76 & 7/14/76
Figure 2
Calibration Chart for GasTech Halide Detector - Range 3 - 7/8/76 & 7/14/76
Temperatures:

Oven - 230°C
Injector - 240°C
Detector interface - 230°C

Column Conditions:
Chromosorb 102, 80/100 mesh, 12' long
The attenuation was 256 x 10

The gas chromatograph was attached to a Linear Instruments Integrating Chart Recorder (Linear Instruments Corp., Model 252A).

Integrator Conditions:
Recorder - 1mv
Chart speed - 40cm/hour
Integrator - 3000 counts/minute
Chapter 3

RESULTS

Time-Weighted Average Concentrations

The gas chromatographic analysis of the charcoal tubes for perchloroethylene showed no employees at any of the five drycleaning establishments were exposed to greater than the 100 ppm standard calculated as an 8-hour time-weighted average. The concentrations ranged from 0 - 41 ppm and are presented in Table I. This summary lists the five drycleaning establishments and the time-weighted average concentrations.

Analysis of the charcoal tube for Drycleaning Store No. 3 showed the sample value obtained for the backup section to be approximately 31% of that found on the front section. According to the National Institute of Occupational Safety and Health (NIOSH), this indicates that the possibility of sample loss exists. If this is true of the sample for Drycleaning Store No. 3, then the time-weighted average concentration is at least 41 ppm. The problem arises from the uncertainty of how high the time-weighted average concentration really is. Migration of the compound throughout the charcoal tube can occur, during sample storage, until equilibrium is reached with 33% of the sample on the backup section. However, the possibility of this occurring is unlikely since all charcoal tubes were frozen during storage.
Table I
Time-Weighted Average Concentrations

<table>
<thead>
<tr>
<th>Drycleaning Store No.</th>
<th>Time-Weighted Average Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>41</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>8</td>
</tr>
</tbody>
</table>
Ambient Air Concentrations

The maximum concentrations during the transfer cycles showed a large variation between the drycleaning establishments. These concentrations ranged from 350 - 6000+ ppm and are presented in Table II. This summary lists the five drycleaning establishments, the transfer cycles, and the maximum concentrations that occurred during that cycle. The number of transfer cycles was dependent on the number of loads of clothing that the drycleaners had on that particular day. Drycleaning Store No. 3 was the only establishment that did the cleaning throughout the entire day. It was felt that, in this case, measurement of eight transfer cycles was representative of the maximum concentrations that would occur for that entire day.

The results also showed a large variation within the drycleaning establishments. These concentrations are presented in Table III. This summary lists the five drycleaning establishments and the maximum concentration range. Also listed is the mean concentration for each store. The maximum concentrations with a "plus" sign attached indicates an off-scale reading from the halide detector. These numbers were not used in figuring the mean concentrations.

Ventilation Measurements

Results from the exhaust ventilation measurements revealed a major inadequacy in all the washer/extractors. The results are presented in Table IV. This summary lists the five drycleaning
establishments and the average air velocity in feet per minute.
### Table II
Maximum Concentrations of Perchloroethylene During Transfer Cycles

<table>
<thead>
<tr>
<th>Drycleaning Store No.</th>
<th>Transfer Cycle No.</th>
<th>Maximum Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>4300</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3800</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>4500+</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>4325</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>600</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>350</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>485</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>5925</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>800</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>4750</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>3140</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>6000+</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>2340</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>1325</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>2700</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>425</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>450</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>600</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>325</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>2825</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>450</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>2250</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1350</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>900</td>
</tr>
</tbody>
</table>
Table III
Maximum Concentrations of Perchloroethylene During Transfer Cycles

<table>
<thead>
<tr>
<th>Drycleaning Store No.</th>
<th>Concentration Range (ppm)</th>
<th>Average Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3800 - 4500+</td>
<td>4142</td>
</tr>
<tr>
<td>2</td>
<td>350 - 600</td>
<td>478</td>
</tr>
<tr>
<td>3</td>
<td>800 - 6000+</td>
<td>2940</td>
</tr>
<tr>
<td>4</td>
<td>325 - 600</td>
<td>450</td>
</tr>
<tr>
<td>5</td>
<td>450 - 2825</td>
<td>1555</td>
</tr>
</tbody>
</table>
Table IV
Exhaust Ventilation Measurements on the Washer/Extractors

<table>
<thead>
<tr>
<th>Drycleaning Store No.</th>
<th>Average Air Velocity (feet per minute)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>65</td>
</tr>
<tr>
<td>2</td>
<td>70</td>
</tr>
<tr>
<td>3</td>
<td>85</td>
</tr>
<tr>
<td>4</td>
<td>75</td>
</tr>
<tr>
<td>5</td>
<td>70</td>
</tr>
</tbody>
</table>
Temperature Readings

The temperatures within the transfer areas showed some variation between the drycleaning establishments. However, there appears to be no correlation between the temperatures and the maximum concentrations produced during the transfer cycles. The temperatures are presented in Table V.
Table V
Temperatures in the Transfer Areas

<table>
<thead>
<tr>
<th>Drycleaning Store No.</th>
<th>Temperature (°F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>85</td>
</tr>
<tr>
<td>2</td>
<td>78</td>
</tr>
<tr>
<td>3</td>
<td>82</td>
</tr>
<tr>
<td>4</td>
<td>91</td>
</tr>
<tr>
<td>5</td>
<td>76</td>
</tr>
</tbody>
</table>
Chapter 4

DISCUSSION

At the outset of this study, very little was known about employee exposure to perchloroethylene in drycleaning establishments. It was determined that the employee at the greatest risk was the one who would be performing the transfer operation.

The results of this study indicate that the time-weighted average concentration is well within the limits set by OSHA. This is due to the short duration of exposure to perchloroethylene. The majority of the employee's time is spent in a relatively perchloroethylene-free atmosphere which tends to keep the TWA low. This time also allows the person to recover from any of the effects of narcosis that might have been produced during the transfer cycle.

Another factor which reduces this exposure is the number of transfer cycles. This is dependent on the amount of clothes that must be cleaned on a particular day. This becomes an important factor to this study since the summer time is the slowest season for a drycleaning establishment. During the winter, it is common for drycleaners to be cleaning clothes for the entire day, instead of the three to four hours, that is typical, during the summer months.

The most important finding of this study is the extremely high concentrations of perchloroethylene which occur during the transfer cycles. The high concentrations that are experienced
during this short period of time could produce a serious health effect. The critical site of injury would be the liver. Here again, the slowness of the summer months means less transfer cycles per day than during the winter. A future study might determine whether a significant difference in employee exposure exists during the winter as opposed to the summer months.

The peak concentration during the transfer cycle is dependent on factors such as: 1) duration of the transfer cycle; 2) type of clothing being cleaned; 3) amount of clothing being cleaned; 4) distance between the washer/extractor and recovery tumbler; and 5) the general ventilation of the store and particularly the transfer area.

The majority of the measurements, at each store, were reasonably consistent from one transfer cycle to the next. A large variation occurred at Drycleaning Store No. 3 due to a variation in time spent performing the transfer cycles. The low concentration during Transfer Cycle No. 2, as shown in Table II, was due to a light load of clothing and a quick transfer cycle. This is also true of Transfer Cycle No. 2 for Drycleaning Store No. 5.

The instrumentation proved to be reliable and operated without any major malfunctions occurring. The zero on the GasTech Halide Detector tended to drift slightly during its operation. The detector also had to be calibrated twice during this study. The only major problem in the study was breakthrough occurring with the charcoal tube for Drycleaning Store No. 3. This dry-cleaning establishment had some of the highest concentrations
during the transfer cycles. This appears to have caused the charcoal to become quickly saturated and breakthrough occurred. This possibly resulted in a loss of solvent, creating a source of error in this study. Studies in the future should take this into consideration whenever extremely high concentrations of solvent are present during personal sampling.
Chapter 5

CONCLUSIONS

Based on the results from the charcoal tubes, it can be concluded that employee exposure is below the OSHA standard of 100 ppm for an 8-hour time-weighted average. If the concentrations were to exceed 100 ppm, it would indicate a health hazard might exist. However, below this level the drycleaning workers are probably safe from the standpoint of the 8-hour dose. Since the peak concentrations were so high, however, serious health effects might still occur. The measurements of the transfer cycles with the GasTech Halide Detector showed the maximum concentrations to be consistently above the OSHA standard of 300 ppm.

While drycleaning establishments will differ somewhat in their overall operations, a few conclusions can be made concerning the majority of the stores. First, an employee is exposed to high concentrations of perchloroethylene during the transfer cycle but the majority of the time will be spent in a relatively solvent-free atmosphere. This is assuming that there is no leakage of perchloroethylene from the washer/extractor or recovery tumbler.

Second, the time spent performing the transfer cycle is the most important factor in determining how high the concentrations of perchloroethylene will become. Operations in which sorting and separating of the clothes is done, while being loaded into the recovery tumbler, can lead to concentrations as high as 5000 to 6000 ppm.
Third, the exhaust ventilation, that is a part of all washer/extractors, does not provide an adequate air flow during the transfer cycle. The purpose of the exhaust ventilation is to pull back into the washer any vapors that are produced while removing the clothing during the transfer cycle. According to this study's results, the air velocities in all five stores are approximately one-half the amount necessary to accomplish this.

Finally, these unusually high perchloroethylene concentrations, which seem to be inherent in the transfer cycle, pose a possible health hazard to an employee. This could result in the type of chronic liver damage that has been referred to by Coler (1953) and Meckler (1966).
Chapter 6

RECOMMENDATIONS

1. Use a "hot" unit to completely eliminate exposure to high concentrations of perchloroethylene during the transfer cycle.

2. Improve the exhaust ventilation on washer/extractors so that air flow is approximately 150 feet per minute.

3. Improve the general ventilation within the transfer area.

4. Perform epidemiological studies to determine if there is an increased prevalence of liver damage among persons who perform the transfer cycle.

5. Evaluate employee exposure to perchloroethylene in drycleaning establishments during the winter season.
Chapter 7

SUMMARY

An environmental study of five drycleaning stores was conducted between 7/9/76 and 7/19/76 in the Southern California area. The purpose of the study was to, 1) measure the concentrations of perchloroethylene in the employee's breathing zone during the transfer cycle, and 2) determine if OSHA standards for permissible airborne exposure were being exceeded.

Personal sampling was performed using charcoal tubes and Sipin Personal Sampler Pumps. A GasTech Halide Detector was used to measure peak concentrations of perchloroethylene during the transfer cycle. A thermo-anemometer was used for air flow measurements of the exhaust ventilation on the washer/extractors.

The results showed that the exposure to perchloroethylene was within the limits of 100 ppm for an 8-hour time-weighted average. The peak concentrations, measured during the transfer cycles, were extremely high at times and consistently exceeded the 300 ppm standard. Evaluation of the control measures showed them to be inadequate in all five drycleaning establishments.

This study also found that the summer months are the slowest time for a drycleaning establishment. This results in fewer loads of clothing to be cleaned per day. Any future studies should measure employee exposure during the winter months to determine if a difference exists.
REFERENCES


Federal Register, June 27, 1974, 39(125), Washington, D.C.


International Fabricare Institute: Experimental Study on Solvent Discharge From Drycleaning Establishments to the Environment (Field Study of Selected California Drycleaning Plants). Silver Springs, Maryland, 1975.


Appendix A

Letter of Introduction
March 12, 1975

Dear Sir:

This letter will introduce Mr. Foster Johnston who is a graduate student in our Occupational Health Program. For his thesis, Mr. Johnston is studying potential employee exposure to perchloroethylene vapors in dry cleaning establishments. The faculty at California State University, Northridge would deeply appreciate any help you are able to offer Mr. Johnston in his studies. All data provided or measurements taken will be maintained in strict confidentiality.

Again, many thanks for your help.

Sincerely,

Dennis L. Kelly, Ph.D.
Associate Professor and Coordinator, Environmental and Occupational Health

DLK:bjh
Appendix B

Sipin Personal Sampler Pump
Instructions for Use with Charcoal Tubes
SIPIN PERSONAL SAMPLER PUMP - MODELS SP-1 AND SP-2

Instructions for Use with Charcoal Tubes

The pocket-size, Personal Sampler Pumps, Models SP-1 (flow range 40 to 200 cc/min) and SP-2 (flow range 20 to 100 cc/min) are expressly designed for use with Charcoal Tubes and other sorbent tubes, for the collection of vapors and gases.

1. Carrying the Pump

The personal sampler pump is provided with a spring clip to permit carrying in a pocket (e.g. shirt pocket), or on a belt. A charcoal tube holder to retain and protect the charcoal tube, is supplied with the pump. The charcoal tube holder is provided with a clip to permit its attachment to a shirt collar or lapel, so that the sample will be taken from the breathing zone. A filter tube assembly, to connect the pump and charcoal tube holder, is also supplied. At one end, the filter tube assembly contains a filter plug to prevent any bits of glass or other particles from entering the pump. A strain relief spring is provided at the other end of the filter tube assembly, to prevent any obstruction of air flow due to kinking. The filter tube assembly has sufficient length so that it can be cut to fit any individual.

Secure the pump in the selected carrying location by means of the clip. Connect the filter end of the filter tube assembly to the outlet fitting of the charcoal tube holder. Cut the other end of the filter tube assembly to the proper length for connection to the pump. Allow sufficient slack (about 3 inches) so as not to apply strain on the filter tube assembly due to body motion. Slip the cut end of the filter tube securely over the pump inlet fitting, and then slide the strain relief spring over the fitting and tube. Simultaneous clockwise rotation of the strain relief spring will facilitate installation.

2. Charcoal Tube Application

When using a NIOSH standard charcoal tube, both ends of the charcoal tube should be broken, so as to provide openings at least 2 millimeters in diameter (roughly one-half the internal diameter of the glass tube itself).

After openings have been made, insert the charcoal tube through the O-ring seal located in the outlet of the charcoal tube holder. The arrow on the charcoal tube must point toward the O-ring (in the direction of air flow). Make sure that the O-ring bears against the cylindrical surface of the charcoal tube. The resistance to insertion will decrease as the charcoal tube seats into the O-ring. After the charcoal tube is in place, assemble the protective cap of the charcoal tube holder. The cap contains an inlet screen to prevent foreign matter from entering the charcoal tube.

The charcoal tube holder should be attached so that the charcoal tube is carried in approximately a vertical position during sampling.
After sampling, the charcoal tube should be removed from the holder and immediately sealed with the plastic caps supplied with each charcoal tube.

3. **Sampling**

(a) Set the desired flow rate by positioning the mark on the flow control knob at the appropriate scale value on the dial. This is determined from a table on the calibration sheet provided with the sampler pump.

For more precise setting of the flow rate, connect a voltmeter (with an input impedance of 20,000 ohms/volt or greater) to the flow control, to provide the required voltage. This voltage equals the desired flow rate (cc/min) divided by a factor, $K_f$ (cc/min/volt), plus a constant, $a$, the values of which are provided on the calibration sheet.

(b) Record the initial pump counter reading before turning the pump on, and the final counter reading, after turning the pump off.

(c) To calculate the volume sampled:

1. Final counter reading - initial counter reading = no. of strokes.
2. No. of strokes x cc per stroke = total cc sampled.

(The factor, $K_v$, for cc per stroke varies with each pump and is provided on the calibration sheet.)

4. **Recharging the Pump**

The charger is designed so that extended charging periods will not damage the charger or pump. The pump should be charged for 16 hours to bring the batteries up to full capacity. A charging light is built into the charger. The light will not operate unless the pump battery is charging properly. CAUTION: Make sure the charging plug is completely inserted into the pump jack. The lamp may light brightly as the plug is inserted into the pump charging jack. If it does not dim within 20 seconds, discontinue charging.

5. **Calibration of the Pump**

The pump may be calibrated simply by checking the cc per stroke factor. This may be done by drawing air through a charcoal tube preceded by a soap bubble flow meter.

$$\frac{\text{Total cc's sampled}}{\text{No. of strokes required}} = \text{factor (}K_v\text{)}$$

The factor has been initially determined by calibration, and it is provided with each pump.
PRERECAUTIONS

1. Do not use the pump without a filter in the inlet line.

2. The pump has sufficient battery capacity for eight hours of operation per day. However, the pump batteries should be recharged after each day of use, even if the full eight-hour sampling capacity has not been used.

3. The pump is designed for use with charcoal tubes having a resistance of 2.5 (or less) inches of water pressure drop at a flow rate of 200 cc per minute. Do not abuse the pump by using it with collection devices which have greater resistances.

4. Be certain that the ends of the charcoal tube are broken so that openings at least 2 mm in diameter are achieved. Smaller openings may act as limiting orifices and cause the volume measurement to be inaccurate. The charcoal tube end may be broken by inserting it into a small hole and snapping off the end. The eyelet in the spring clip of the charcoal tube holder can be used for this purpose. A uniform break can be obtained by scoring the end of the charcoal tube with a fine-tooth triangular file about 1/8" from the neck-down point.

5. Care should be taken to avoid handling sharp broken ends of the charcoal tube when inserting or withdrawing it from the charcoal tube holder. A 1/4" I.D. plastic tube that can be used as a charcoal tube insertion tool is provided as an aid. To insert the charcoal tube, first place it half-way into the plastic tool, and then, holding the charcoal tube by squeezing the plastic tool, insert the charcoal tube into the O-ring. To remove the charcoal tube, place the plastic tool over the end of the charcoal tube until it bottoms in the charcoal tube holder, and, again squeezing the tool, extract the charcoal tube.

6. If the pump is to be used in excessively dusty or dirty areas, precautions should be taken to seal the apertures in the pump case. One method that has been used, is to place the pump in a plastic bag and to seal the bag (e.g. with a rubber band). If this is done, some small holes should be made in the bag for ventilation.

7. If the pump is carried in the pocket of a shirt made of very thin or smooth fabric, a secondary means of securing the pump against dislodgment, in addition to the spring clip, may be desirable. A safety pin attached to the shirt through the hole in the spring clip, or a guard chain terminated in a safety pin, or alligator clip can be used for this purpose.
SIFIN PERSONAL SAMPLER PUMP - MODELS SP-1P AND SP-2P

Instructions for Use with Charcoal Tubes and Gas Sampling Bags

The pocket-size, Personal Sampler Pumps, Models SP-1P (flow range 40 to 200 cc/min) and SP-2P (flow range 20 to 100 cc/min) are expressly designed for use with Charcoal Tubes and other sorbent tubes as well as for use with Gas Sampling Bags for the collection of vapors and gases.

1. Use with Charcoal Tubes

For use with charcoal tubes, attach the inlet (straight fitting on the top of the pump case) to the filter tube assembly, which connects the inlet to the charcoal tube holder. Leave the short filter in place over the outlet (elbow fitting on the side of the pump case), as supplied with the pump.

In all other respects follow the instructions for use with charcoal tubes of the Models SP-1 and SP-2 pumps.

2. Use with Gas Sampling Bags

For use with gas sampling bags, remove the short filter from the outlet and place over the inlet fitting. Connect the outlet to the gas sampling bag. (The connection will depend on the type of gas sampling bag.)

Sifin Models SP-1P and SP-2P pressure and suction sampler pumps supply air or gas at constant low flow rates to permit collection of a time weighted average sample over a reasonably long period of time with a reasonably small gas sampling bag.
Appendix C

GasTech Halide Detector
Calibration Method
IX. CALIBRATING SAMPLE PREPARATION

With a modest amount of care the Halide Detector can be calibrated by the user in his own lab. Most labs use one of three techniques in obtaining varying concentrations of halogenated vapors to develop data for calibration curves. These are: 1. Syringe Pump, 2. Mylar or Teflon bag samples and 3. Glass containers. The use of a syringe pump is the more expensive method and there are difficulties in using this method with low volatility liquid samples. Once set up this is probably the most accurate and consistent calibration method, particularly when gaseous samples are used. However, the setup cost is prohibitive except where frequent calibrations are to be run. Plastic bags of Mylar, Teflon and in some cases polyethylene can be used to mix samples. In preparing samples in those bags the primary drawbacks are that they frequently develop leaks and the volume of the inflated bag is difficult to determine and repeat accurately. They are however relatively inexpensive, easy to store and can be taken into the field for on-the-spot reference. Glass containers have two primary drawbacks: they are heavy and difficult to handle, and they are susceptible to breakage. To their advantage they have stable volumes, are inert to most sample materials and have a low surface area to volume ratio. For those users who wish to calibrate only occasionally, for a few toxic halogenated vapors, we most frequently recommend the use of glass bottles and one or two syringes.

In the USA the most easily obtained glass bottles of sufficient size are 5 gallon water bottles, as used for distilled or drinking water. These consistently contain 19.5 to 20 liters and if 20 l. is used in the calculations one would not expect to see errors greater than 2.5%. Measured volumes of gas or liquid are injected into the bottle, and allowed to vaporize and mix completely, after which the bottle is used as a reservoir from which samples of known concentration can be withdrawn. Sample times should be kept short since the sample volume withdrawn by the instrument amounts to 1.4% per minute or a 10% dilution error after about 7-1/2 min. of continuous sampling.

Concentrated samples used in preparing mixtures should be of good purity. In many cases the solvent used in the process being evaluated can be used to make up calibration samples. If the gases or liquids used are mixtures or are contaminated with water or other material, serious errors can be made in the calculations.

For gaseous samples the calculations are very simple if the sample syringe and the 20 l. bottle are at the same temperature and pressure. For each part per million of sample, introduce \[ \frac{0.02 \text{ cc of pure gas}}{1 \text{ million}} = \frac{20,000 \text{ cc}}{1,000,000} \]

100 ppm of a toxic gas mixture add 2.0 cc to the 20 l. bottle.
Since the recommended exposures to most substances of interest are based on a volume to volume ratio, it will make no difference whether the sample is methyl chloride, one of the Freons or other gases, the volume of material introduced is the same for a given ppm mixture.

When liquid samples are used to make up calibration mixtures, several additional steps are necessary. The calculations must include terms which tell us what volume of liquid is necessary to evaporate to form the desired parts per million volume to volume ratio in the mixture. The volume of liquid may be calculated from:

\[
\text{Volume of liquid, ml} = \frac{\text{Formula Weight} \times \text{Vol of Container}}{\text{Specific gravity}} \times \frac{\text{PPM}}{1,000,000} \times \frac{273}{\text{Temp, } ^\circ\text{K}} \times \frac{\text{Atmospheric Pressure, mm Hg}}{760}
\]

For a 100 ppm mixture prepared in a 20 liter bottle, at sea level and at 25°C, the formula reduces to the following:

\[
\text{Vol. of liquid, ml} = 0.0000818 \times \frac{\text{Formula Wt.}}{\text{sp. gr.}}
\]

As an example, consider 1,1,1, trichloroethane, one of the most popular degreasing agents. The Threshold Limit Value, as listed by the American Conference of Governmental Industrial Hygienists, is 350 ppm. The formula weight is 133.42 and the specific gravity is 1.325 at 26°C. To prepare a 350 ppm mixture, the volume would be calculated as:

\[
\frac{350 \times 0.0000818 \times 133.42}{100} \times \frac{1}{1.325} = 0.0288 \text{ ml}
\]

Syringes in the range of 50 microliter (.05 ml) are available from lab supply houses. Once liquid has been injected, allow plenty of time (20 to 30 minutes) for vaporization and mixing of the sample.
Appendix D

NIOSH Recommended Methods for Collection and Analysis
ORGANIC SOLVENTS IN AIR

Physical and Chemical Analysis Branch

Analytical Method

<table>
<thead>
<tr>
<th>Analyte:</th>
<th>Organic Solvents (See Table 1)</th>
<th>Method No:</th>
<th>P&amp;CAM 127</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix:</td>
<td>Air</td>
<td>Range:</td>
<td>For the specific compound, refer to Tables I&amp;II</td>
</tr>
<tr>
<td>Procedure:</td>
<td>Adsorption on charcoal desorption with carbon disulfide, GC</td>
<td>Precision:</td>
<td>10.5% RSD</td>
</tr>
<tr>
<td>Date Issued:</td>
<td>9/15/72</td>
<td>Classification:</td>
<td>See Table 1</td>
</tr>
<tr>
<td>Date Revised:</td>
<td>7/15/74</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, graduated test tube and desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

The lower limit in mg/sample for the specific compound at 16 x 1 attenuation on a gas chromatograph fitted with a 10:1 splitter is shown in Table 1. This value can be lowered by reducing the attenuation or by eliminating the 10:1 splitter.

3. Interferences

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped. Preliminary experiments indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more solvents are known or suspected to be present in the air, such information including their suspected identities, should be transmitted with the sample; since with differences in polarity, one may displace another from the charcoal.
3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Hence, retention time data on a single column, or even on a number of columns, cannot be considered as proof of chemical identity. For this reason it is important that a sample of the bulk solvent(s) be submitted at the same time so that identity(ies) can be established by other means.

3.4 If the possibility of interference exists, separation conditions (column packing, temperatures, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The mean relative standard deviation of the analytical method is 8% (Ref. 11.4).

4.2 The mean relative standard deviation of the analytical method plus field sampling using an approved personal sampling pump is 10% (Ref. 11.4). Part of the error associated with the method is related to uncertainties in the sample volume collected. If a more powerful vacuum pump with associated gas-volume integrating equipment is used, sampling precision can be improved.

4.3 The accuracy of the overall sampling and analytical method is 10% (NIOSH's unpublished data) when the personal sampling pump is calibrated with a charcoal tube in the line.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more solvents suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists. During sample storage the more volatile compounds will migrate throughout the tube until equilibrium is reached (33% of the sample on the backup section).
5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 An approved and calibrated personal-sampling pump for personal samples. For an area sample any vacuum pump whose flow can be determined accurately at 1 liter per minute or less.

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 fpm.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (20 ft x 1/8 in) with 10% FFAP stationary phase on 80/100 mesh, acid-washed DMCS Chromosorb W solid support. Other columns capable of performing the required separations may be used.

6.5 A mechanical or electronic integrator or a recorder and some method for determining peak area.

6.6 Glass stoppered micro tubes. The 2.5-ml graduated microcentrifuge tubes are recommended.

6.7 Hamilton syringes: 10 ul, and convenient sizes for making standards.

6.8 Pipets: 0.5 ml delivery pipets or 1.0 ml type graduated in 0.1 ml increments.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Spectroquality carbon disulfide (Matheson Coleman and Bell)
7.2 Sample of the specific compound under study, preferably chromatoquality grade.

7.3 Bureau of Mines Grade A helium.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, the ends of the tube should be broken to provide an opening at least one-half the internal diameter of the tube (2mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be vertical during sampling.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 The flow, time, and/or volume must be measured as accurately as possible. The sample should be taken at a flow rate of 1 \( \text{fpm} \) or less to attain the total sample volume required. The minimum and maximum sample volumes that should be collected for each solvent are shown in Table 1. The minimum volume quoted must be collected if the desired sensitivity is to be achieved.

8.3.6 The temperature and pressure of the atmosphere being sampled should be measured and recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.
8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly before they are shipped to minimize tube breakage during shipping.

8.3.10 Samples of the suspected solvent(s) should be submitted to the laboratory in containers furnished by NIOSH for such purpose. These liquid bulk samples should not be transported in the same container as the samples or blank tube. If possible, a bulk air sample (at least 50% air drawn through tube) should be shipped for qualitative identification purposes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a small stoppered test tube. The separating section of foam is removed and discarded; the second section is transferred to another test tube. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, one-half ml of carbon disulfide is pipetted into each test tube. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period. The use of graduated glass-stoppered, microcentrifuge tubes is recommended so that one can observe any apparent change in volume during the desorption process. Carbon disulfide is a very volatile solvent, so volume changes can occur during the desorption process depending on the surrounding temperature. The initial volume occupied by the charcoal plus the 0.5 ml CS₂ should be noted and corresponding volume adjustments should be made whenever necessary just before GC analysis.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 85 cc/min. (70 psig) helium carrier gas flow.
2. 65 cc/min. (24 psig) hydrogen gas flow to detector.
3. 500 cc/min. (50 psig) air flow to detector.
4. 200°C injector temperature.
5. 200°C manifold temperature (detector)
6. Isothermal oven or column temperature - refer to Table 1 for specific compounds.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blowback or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10 µl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back a short distance to minimize evaporation of the sample from the tip of the needle. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process for a given compound, provided the same batch of charcoal is used. The Physical and Chemical Analysis Branch of NIOSH has found that the desorption efficiencies for the compounds in Table 1 are between 81% and 100% and vary with each batch of charcoal.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 5cm, 4-mm I.D. glass tube, flame-sealed at one end (similar to commercially available culture tubes). This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped
with Parafilm. A known amount of the compound is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. The amount injected is usually equivalent to that present in a 10-liter sample at a concentration equal to the federal standard.

At least five tubes are prepared in this manner and allowed to stand for at least overnight to assure complete absorption of the specific compound onto the charcoal. These five tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.3.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of CS₂ with the same syringe used in the preparation of the sample. These are analyzed with the samples.

The desorption efficiency equals the difference between the average peak area of the samples and the peak area of the blank divided by the average peak area of the standards, or

\[
\text{desorption efficiency} = \frac{\text{Area sample} - \text{Area blank}}{\text{Area standard}}
\]

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml CS₂ because samples are desorbed in this amount of CS₂. To minimize error due to the volatility of carbon disulfide, one can inject 20 times the weight into 10 ml of CS₂. For example, to prepare a 0.3 mg/0.5 ml standard, one would inject 6.0 mg into exactly 10 ml of CS₂ in a glass-stoppered flask. The density of the specific compound is used to convert 6.0 mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5ml versus peak area.

NOTE: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.
10. Calculations

10.1 The weight, in mg, corresponding to each peak area is read from the standard curve for the particular compound. No volume corrections are needed, because the standard curve is based on mg/0.5 mL CS2 and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

\[ \text{Correct mg} = \text{mg}_s - \text{mg}_b \]

where:

\( \text{mg}_s = \text{mg found in front section of sample tube} \)
\( \text{mg}_b = \text{mg found in front section of blank tube} \)

A similar procedure is followed for the backup sections.

10.3 The corrected amounts present in the front and backup sections of the same sample tube are added to determine the total measured amount in the sample.

10.4 This total weight is divided by the determined desorption efficiency to obtain the total mg per sample.

10.5 The volume of air sampled is converted to standard conditions of 25°C and 760 mm Hg.

\[ V_s = V \times \frac{P}{760} \times \frac{298}{T+273} \]

where:

\( V_s = \text{volume of air in liters at 25°C and 760 mm Hg} \)
\( V = \text{volume of air in liters as measured} \)
\( P = \text{Barometric pressure in mm Hg} \)
\( T = \text{Temperature of air in degree centigrade} \)

10.6 The concentration of the organic solvent in the air sampled can be expressed in mg per m³, which is numerically equal to µg per liter of air

\[ \text{mg/m}^3 = \frac{\text{total mg (Section 10.4) x 1000 (µg/mg)}}{V_s} \]

10.7 Another method of expressing concentration is ppm, defined as µL of compounds per liter of air

\[ \text{ppm} = \frac{\text{µL of compound}}{V_s} \times \frac{24.45}{\text{MW}} \]

where:

24.45 = molar volume at 25°C and 760 mm Hg
MW = molecular weight of the compound (Table 1)
11. References


11.3 Federal Register, 37 (#202), 22139-22142 (October 18, 1972).

<table>
<thead>
<tr>
<th>Organic Solvent</th>
<th>Method Classification</th>
<th>Detection limit (mg/sample)</th>
<th>Sample Volume (l)</th>
<th>GC Column Temperature(°C)</th>
<th>Molecular Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
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<tr>
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</tr>
<tr>
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<td>0.5</td>
<td>13</td>
<td>150</td>
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</table>

(a) Minimum volume, in liters, required to measure 0.1 times the OSHA standard
(b) These are breakthrough volumes calculated with data derived from a potential plot (reference 11.2) for activated coconut charcoal. Concentrations of vapor in air at 5 times the OSHA standard (reference 11.3) or 500 ppm, whichever is lower, 25°C, and 760 torr were assumed. These values will be as much as 50% lower for atmospheres of high humidity. The effects of multiple contaminants have not been investigated, but it is suspected that less volatile compounds may displace more volatile compounds (See 3.1 and 3.2)