ABSTRACT

GARY W. THOMAS. Evaluation of a First Order Autoregressive Model for the Determination of Physiological Damping Under Field Conditions. (Under the Direction of Stephen M. Rappaport, PhD)

The first order autoregressive (AR1) model proposed by Rappaport and Spear (1988) to determine physiological damping for solvent exposures over short time intervals was evaluated under field conditions. Two sets of data were collected for ethyl acetate, methylene chloride and perchloroethylene, respectively. Evaluation of the correlograms for each data set indicates that an AR(1) process may not be appropriate. The observed transmittance factors (inverse of damping) ranged from 0.47 to 0.64. The significance or causality of this observation is not presently known.

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ACKNOWLEDGEMENTS

Praise God for His strength and wisdom. I have made my request known unto the Lord and He has granted me peace and kept me in Christ Jesus (Phil 4:4-7).

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INTRODUCTION

The assessment of chronic effects from occupational exposures to organic solvents is at best tenuous. Much research has been conducted on absorption, metabolism, retention and elimination of various solvents, but little has been done on providing the industrial hygienist with the means to assess transient exposure to solvents which are not acutely toxic. Rappaport and Spear (1988) employed a first order autoregressive (AR1) model to quantitate physiological damping over brief periods in terms of the solvents elimination rate, time interval of exposure and the air exchange rate. Physiological damping is the reduction of variability of the levels of a contaminant inside the body relative to the variability of airborne exposure (Rappaport, Spear and Selvin, 1988). Damping occurs as the body burden increases (accumulation at the receptor site) over some time interval in proportion to the half-time ($T_{1/2}$) of the solvent (Rappaport, 1991); hence, the greater the value of $T_{1/2}$ then the greater will be both the body burden and the damping. Damping is therefore an indicator of the potential risk of biological damage by a toxicant during brief but intense exposures (Rappaport, 1991). The purpose of this study is to evaluate physiological damping over short time scales

(hours) under field conditions.

The AR(1) model has its theoretical basis in the concepts initially proposed by Roach (Roach, 1966; Roach, 1977). Assuming a single compartment model with first order kinetics and purely random exposures, Roach proposed that, as the solvent accumulates within the body, the variance of body burden over time decreases. The transmittance of exposure variability is expressed as the ratio of the coefficients of variation of body burden (CV_x) to that of the ambient air concentration (CV_c). This ratio, referred to as the "transmission factor" ($1/A_t$) indicates the proportion of ambient variation that is transmitted to the body burden. Physiological damping is the inverse of transmittance. This implies that a solvent with a high CV_x/CV_c or $1/A_t$ would produce little damping while a solvent with a low $1/A_t$ would be significantly damped. Roach derived the following theoretical expression for determining $1/A_t$ in terms of the solvent's first-order elimination rate constant ($k\ hr^{-1}$) and the interval between exposures (Δt hr):

$$1/A_t = \frac{CV_x}{CV_c} = \sqrt{\frac{1 - e^{-k\Delta t}}{1 + e^{-k\Delta t}}} \qquad (1)$$

From Equation (1) we note that $1/A_t$ varies directly with the solvent's elimination constant (or inversely if compared to the biological $T_{1/2}$). As k decreases (indicating slower elimination), 1/At decreases proportionally. This is

reasonable since a solvent with a slow elimination rate will accumulate to a greater extent in the body than will one that is metabolized or eliminated faster. If Δt is decreased, $1/A_t$ decreases as well indicating less transmittance of the ambient concentration variability to the body.

Ambient concentrations within the work environment are seldom constant. They tend to vary in time due to changes in the strength of the pollutant, the amount of ventilation and mobility of the worker (Roach, 1977; Francis, et al., 1989.). If a set of sequential ambient air samples are collected within a workshift, it is often observed that the current air concentration is influenced by the previous concentrations (Petreas, 1990). For a stationary stochastic process, the correlation between two subsequent values depend only on the time interval between them which is referred to as the lag (Spear, Selvin and Francis, 1986). The measure of correlation between samples in a series is referred to as the autocorrelation coefficient at lag h and is determined by the following equation (Chatfield, 1984):

$$r(h) = \frac{\sum_{t=1}^{n-h} (X_t - \bar{X}) * (X_{t+h} - \bar{X})}{\sum_{t=1}^{n} (X_t - \bar{X})^2} \qquad (2)$$

A series (e.g. h = 1, 2, 3, . . .) of autocorrelation coefficients r(h), at successive lags, can be determined for

a time series. These coefficients can then be graphically plotted in a correlogram (r(h) versus h). Values of r(h) for an AR(1) process will exponentially decay.

An AR(1) model assumes a stationary process (mean and variance do not change with time) where the present air concentration depends on a proportion of the previous concentration plus some random value (Chatfield, 1984; Rappaport and Spear, 1988). Mathematically, this is expressed by

$$C_t = wC_{t-1} + Z_t \qquad (3)$$

where w represents the proportion of the previous exposure carried over to the current concentration. The rate of decay for the AR(1) process is inversely proportional to the weight factor (w) (Rappaport and Spear, 1988).

By assuming instantaneous mixing of the solvent in the breathing zone, the air exchange rate (b) can be related to the first lag autocorrelation coefficient, that is,

$$r(h) = w^h = e^{-bh\Delta t} \qquad (4)$$

where h is equal to one. The air exchange rate can have a dramatic impact on the ambient concentration. The amount of solvent available for inhalation and subsequent absorption by the body will affect the body burden and therefore the transmission factor. Using this information, Rappaport and Spear (1988) incorporated the effect of the air exchange rate into equation (1) and derived the following

relationship,

$$1/A_t = \sqrt{\frac{(1-e^{-k\Delta t})\,(1+e^{-(k+b)\Delta t})}{(1+e^{-k\Delta t})\,(1-e^{-(k+b)\Delta t})}} \qquad (5)$$

Unlike Equation (1), this equation takes into consideration the effect of the air exchange rate on ambient concentrations in the breathing zone. The slower the air exchange in the breathing zone, the higher the autocorrelation of the time series of exposures, and hence the higher $1/A_t$. If the air exchange rate increases significantly, the term $e^{-(k+b)\Delta t}$ goes to zero and Equation (5) reverts back to Equation (1) (Rappaport and Spear, 1988).

Solvent metabolism

The generalized distribution of inhaled ethyl acetate, methylene chloride or perchloroethylene solvent vapors within the body can be expressed by partition coefficients. Partition coefficients for blood/air ($\lambda_{b/a}$), water and oil for these solvents are presented in Table 1. Solvents that are hydrophilic will have $\lambda_{b/a}$'s greater than 200 while those that are hydrophobic will have very small $\lambda_{b/a}$'s (Brown, et al., 1987). Additionally, high $\lambda_{b/a}$'s imply that alveolar concentrations are expected to be low (Astrand, 1975). These coefficients represents the relative degree of solubility for each solvent in the blood or fat component of the body. For example, ethyl acetate has a $\lambda_{b/a}$ of 222 which means that it is approximately 22 times more soluble

in the blood than methylene chloride or perchloroethylene, $\lambda_{b/a}$'s are 9.7 and 13.1 respectively. This implies that ethyl acetate, when inhaled, is absorbed more quickly than the other two solvents. The $\lambda_{b/a}$ has a pronounced influence on the blood concentration of a solvent in relation to the exposure (Kelman, 1982). The oil/air partition coefficient is an indicator of the relative fat solubility of the solvent. Perchloroethylene has an oil partition coefficient (Table 1) that is 5 to 10 times higher than the other two solvents; hence, perchloroethylene is more soluble in fat. Fat soluble solvents are absorbed and eliminated slower than solvents that are not soluble in fat.

Upon being absorbed, ethyl acetate is rapidly removed from the body by hydrolysis to acetic acid and ethanol (Fernandez and Droz, 1974). Studies conducted by Schrikker (Schrikker, de Vries and Luijenkijk, 1985) showed that ethyl acetate could not be detected in the breath a few minutes following exposure. Since this solvent has a $\lambda_{b/a}$ of 222, it quickly dissolves in the blood and is thus available for enzymatic degradation. Methylene chloride, in comparison, has a lower $\lambda_{b/a}$ of 9.7 and as a result less is absorbed to be metabolized (Astrand, Ovrum and Carlsson, 1975). Only 9% of the absorbed portion of this solvent is retained in the body and subsequently metabolized into carbon monoxide (Perbellini, et. al., 1977). Perchloroethylene, like methylene chloride, has a low $\lambda_{b/a}$ of 13.1 and thus dissolves

poorly in blood. Only 1-3% of the inhaled solvent is metabolized into trichloroacetic acid or trichloroethanol (Monster, et. al., 1983), the remainder is exhaled unchanged.

METHODOLOGY

Study design

The intent of this study was to serially collect ambient air and alveolar air samples to evaluate the AR(1) model proposed by Rappaport and Spear (1988). Observed transmittance factors of the solvents being studied were compared to the theoretical values determined by Equation (5).

Serial samples of ambient, filtered and alveolar air for each respective solvent being studied were collected from a single subject while in a work environment. Sample collection was not initiated until the subject had been in the work environment 30 to 45 minutes. This delay was intended to allow the subject's body to equilibrate with ambient solvent concentrations. Ambient temperatures ranged from 75 to 85°F for each set of data collected.

The study involved collecting two sets of serial samples for ethyl acetate, methylene chloride and perchloroethylene within a work environment. Each solvent was an organic solvent that possessed different chemical, physical and pharmacokinetic properties (Table 1). Sample collection for all six sets of data was performed on five different days. One set of data for ethyl acetate and

methylene chloride were collected concurrently. All other data sets were collected on separate days.

Data for methylene chloride and ethyl acetate were collected during the paint stripping and cleaning of small jet aircraft. This process involved cleaning areas of the aircraft with ethyl acetate that were sensitive to methylene chloride, covering and taping these areas, applying a gel solution composed of 50% methylene chloride to the uncovered regions, waiting approximately 15 minutes, removing the methylene chloride gel and finally cleaning/washing with ethyl acetate to remove residual deposits of paint, hardened gel or film. The stripping/cleaning process took two days to perform. Day one involved the initial cleaning with ethyl acetate and the subsequent stripping with methylene chloride. On day two, final touch up cleaning and washing with ethyl acetate was accomplished. Both solvents were manually applied to the surface of the aircraft. The subject sat approximately 10 feet from each of these operations for a period of 5 hours. The first sets of data for methylene chloride and ethyl acetate were collected concurrently because paint stripping on the aircraft had not been completed the day before; therefore, some areas of the aircraft were being stripped and others were being cleaned at the same time. The second set of data for these solvents were collected in the same hangar but on different days.

Samples for perchloroethylene were collected on

different days at two different dry-cleaning facilities. The first dry cleaning plant was a training facility that provided hands-on-instruction to its students on the operation and maintenance of dry cleaning equipment. The second facility was a small commercial dry cleaning plant. The subject was exposed to perchloroethylene for 7 hours in the first plant and for 5 hours in the second plant.

Subject

The subject was a male, 38 years old, 170 cm tall and weighing 75 kgs (18% fat, determined by a standard table based on waist and neck measurements and weight). Incidental exposure to ethyl acetate, methylene chloride and perchloroethylene was not significant in the month preceding the study. The subject was healthy and volunteered with informed consent to participate in this study.

Instrumentation

Analysis of the ambient, filtered and alveolar air was performed with a portable gas chromatograph (Photovac Instruments, Ontario, Canada, model 10S50) that had been modified internally to reduce residual carryover (Rappaport, et al., 1991). The device was equipped with a photoionization detector that operated at 11eV. The instrument had a 1 meter pre-column and a 10 meter analytical column. Both columns were DB-5 with a 0.53 mm

inner diameter and a 1.2-μm film thickness (Alltech Associates, Deerfield, Illinois). The analytical column was housed in an isothermal oven that was operated at 40°C for ethyl acetate and methylene chloride, and at 50°C for perchloroethylene. The flowrate for the carrier gas was set at 2 ml/min for ethyl acetate and methylene chloride, and at 15 ml/min for perchloroethylene.

Two three-way values were connected in series with the inlet of the instrument. Manual operation of these values allowed flexibility in selecting the type of sample to be analyzed (ambient, filtered or alveolar). The instrument had an internal pump that pulled the selected sample into a 1-ml loop. To ensure that the alveolar sample was primarily air from the alveolar region of the lung, a stainless steel Haldane-Priestly tube (Haldane and Priestly, 1905) 0.95 cm in diameter and 120 cm in length was used. One end of the tube was connected to an aluminum fitting that accepted a disposable mouthpiece (Cardboard #1021-250, Vacuumed, Inc., Ventura, California) and the other end was open to the ambient air. The top three way value was connected to the tube approximately midway between the mouth piece and exit port (Petreas, 1990). Toward the end of exhalation, when the subject felt the pressure of exhalation drop, the GC was activated to sample the last part of exhaled air.

The serial sequence of ambient, filtered and end-exhaled air was followed for all analysis. In a previous

study conducted by Petreas (1990), the instrument demonstrated a significant amount of memory of the sampled ambient air. Petreas identified the Teflon tubing used in the inlet and transfer lines as the cause of this problem. These lines were subsequently replaced with stainless steel. Ambient air, which was filtered through 1.2 grams of 20/40 mesh activated coconut carbon, was measured as part of the experimental sequence so that the amount of residual carry-over from one sample to the next could be determined. Air concentrations were adjusted accordingly for any residual solvent that was detected.

The instrument was calibrated in the laboratory with standards prepared in Tedlar bags (SKC West). Standards were prepared by injecting microliters of the solvent into a bag with a known amount of clean air. Concentrations within the Tedlar bag were determined by the following equation (Fiserova-Bergenova, 1983),

$$C(ppm) = \frac{(V_l)\,(\rho)\,(V_m)\,(10^{-3})}{(MW)\,(V_t)} \qquad (6)$$

where ρ (g/cm^3) is the solvent's density, V_l (μl) the amount of solvent injected, V_t (l) the volume of clear air contained inside the Tedlar bag, V_m (l/mole) the volume of one mole of the solvent, and MW (g/mole) the molecular weight of the solvent. Calibration checks were performed in the field with standards prepared in Tedlar bags on the same day of data collection.

Instrument precision for analysis was determined to be between 2-5% as a coefficient of variation (3 determinations with 10 measurements per determination). The lowest detectable concentration was 220 ppb for ethyl acetate, 949 ppb for methylene chloride and 22 ppb for perchloroethylene.

Chamber studies

Chamber studies were performed on each of the solvents to determine the elimination rates of the solvent from the subject. The chamber was 3 meters long, 2.9 meters wide and 2.6 meters high (approx. 23 cubic meters). A predetermined amount of a single solvent was evaporated into the chamber to obtain a desired air concentration. The solvent was naturally evaporated and then mixed with a fan to distribute the vapors. The ambient air was periodically monitored during the uptake of the solvent. If the solvent's ambient concentration fell below 10% of the desired chamber concentration, additional solvent was evaporated. Since the intent of the chamber study was to determine decay constants and not uptake constants, it was not considered critical to maintain a constant chamber concentration. The decay curves of these studies are presented in Figures 1 to 3. Several of the chamber studies had to be repeated when it was determined that either the concentration of the solvent or length of the exposure was not sufficiently high or long enough to provide a suitable number of data points for

analysis.

In order to obtain a sufficient number of points for ethyl acetate, the exposure in the chamber had to be at 226 ppm for 2.5 hours. Exposure to methylene chloride was at a concentration of 102 ppm for 1.5 hours. For perchloroethylene, exposure for 1.5 hours at 50 ppm was sufficient.

RESULTS

End tidal or alveolar air was collected for GC analysis by normal exhalation into a Haldane-Priestly tube. Forced exhalation or breath holding prior to exhalation were avoided since some studies (Rahn, 1949; Guillemin and Guberan, 1982) had indicated that alveolar concentrations may be artificially elevated. Alveolar air was used as a surrogate for body burden (Petreas, 1990) instead of venous blood. It was assumed that a gaseous equilibrium existed across the alveolar membrane such that alveolar concentrations were proportional to mixed venous blood concentrations (Kelman, 1981). When one considers that approximately 15 breaths are taken each minute, it can be reasoned that the residence time of a solvent within the alveolar region of the lung, during a single breath, would be greater than 0.75 seconds. If this value was indeed exceeded, there was ample time to establish an equilibrium between alveolar and mixed venous blood concentrations (Opdam and Smolders, 1986). Since mixed venous blood had been used in the past by many researchers to evaluate body burden to various chemicals, it was not unreasonable to use alveolar air as a surrogate for body burden.

Half-time

Assuming first order kinetics, the $T_{1/2}$ value(s) were determined for each of the solvents by the method of residuals or "feathering" (Shargel and Yu, 1985), results are shown in Table 2. These constants represent the kinetics of the distribution and elimination phases of the solvent. The first compartment represents those tissues (lung, vessel rich and muscle) in which elimination and distribution occur rapidly while the second compartment represents the remaining tissue groups. The first compartment does not anatomically distinguish between the lung, vessel rich or muscle tissue groups.

Ethyl acetate had the shortest first compartment $T_{1/2}$ of 4.5 minutes compared to reported values for this solvent ranging from 1.6 to 8.9 minutes (Fernandez and Droz, 1974; Nomiyama and Nomiyama, 1974). Methylene chloride had a first compartment $T_{1/2}$ of 29 minutes which was reasonably close to the reported value of 40 minutes (Divincenzo, Yanno and Astill, 1971; Baselt, 1982). The $T_{1/2}$ for perchloroethylene, 34 minutes, appears to be significantly different from the 104 and 114 minute values found in literature (Stewart, et. al., 1961; Petreas, 1990).

Alveolar retention

The alveolar retention for each solvent was determined by,

$$\%Alveolar\ retention = \left(1 - \frac{C_{exh}}{C_{amb}}\right) x\ 100 \qquad (6)$$

where C_{exh} represents the concentration measured in the alveolar air of the test subject and C_{amb} is the ambient concentration (Nomiyama and Nomiyama, 1974) Observed alveolar retention values were averaged for both data sets for each perspective solvent. The observed alveolar retention of ethyl acetate was measured at 92% which agreed well with the Nomiyama and Nomiyama (1974) reported value of 99.8%. Methylene chloride's retention was determined to be 64%. This value is within the 30-70% range of values that have been reported (Astrand, Ovrum and Carlsson, 1975; Perbellini, et. al., 1977; Baselt, 1982; Fiserova-Bergerova, 1983). The alveolar retention of perchloroethylene was determined to be 58%. Reported retention values for this solvent ranged from 52 to 80% (Guberan and Fernandez, 1974; Fiserova-Bergerova, 1983; Monster, et. al, 1983; Gordon, et. al., 1988).

Ambient and alveolar air values

Six sets of data (Appendix A) were collected at three industrial sites. With the exception of the first data set for ethyl acetate and methylene chloride (collected concurrently), all sets of data were collected independently. A single subject was used to collect all sets of data. All of the industrial sites were naturally

ventilated. The test subject was located approximately 5 to 15 feet from each of the solvent using operations. Figures 4 to 9 graphically represent the ambient concentrations and alveolar air data points collected for each of the solvents of this study. The observed statistical parameters (mean, standard deviation and coefficient of variation) and $1/A_t$ values for all data are presented in Table 3.

Assuming that instantaneous mixing of the solvent occurs in the ambient air and that each ambient concentration is related by an AR(1) process (Rappaport and Spear, 1988), the air exchange rates (AER's) were calculated by using Equation (4). Resultant AER's range from 6 to 37 air exchanges per hour and are presented in Table 2. The AER's for the first set of data for ethyl acetate and methylene chloride are of particular interest. These solvents were collected concurrently in a large aircraft hangar that was naturally ventilated; however, the AER's are markedly different (6 for ethyl acetate and 37 for methylene chloride). This should not occur since the samples were collected in the same environment and at the same time.

Observed transmission factors were calculated for each set of data by taking the ratio of the coefficients of variation of alveolar to ambient air. Using Equation (1), the theoretical $1/A_t$ was determined for each of set of data. Observed and theoretical $1/A_t$ values are given in Table 2.

DISCUSSION

Alveolar retention values and first compartment $T_{1/2}$ for each of the three solvents agree with those reported in literature. This implies that sample collection and analysis obtained in this study is consistent with other studies.

In Table 2, it can be seen that there is a marked difference between the theoretical and observed $1/A_t$ values. Though the solvents have varied physical and pharmacokinetic attributes and are metabolized differently, all $1/A_t$ (observed) values fall in a range from 0.47 to 0.64. Additionally, the $1/A_t$ values determined by Petreas (1990) for styrene and perchloroethylene are also within this range.

The marked differences between observed values and responses in contrast to those predicted by the model warrants further investigation. This may be accomplished by evaluating the graphical representation or correlogram of the lag values for each set of solvent data. An AR(1) process should exhibit an exponential decay in its lag values calculated from Equation (2) (Chatfield, 1980). Correlograms for each set of data are presented in Figures 10 through 15. Since there are no shifts or trends apparent

in these figures, it is reasonable to assume that the exposure time series are stationary processes. Each type of ARIMA model has its own autocorrelation function (McDowall, et al., 1980). The general shape of all of the correlograms indicate that the data do not appear to fit an autoregressive or difference model (no exponential decay or parabolic increase of values). To determine if the data is first order, it is necessary to establish which r(h) values are statistically significant from zero. Each estimate r(h) value is compared to a 95% confidence interval given as $\pm$ 2 times the standard error (SE). The standard error is determined by the following equation:

$$SE = \sqrt{\frac{(1 + 2 \sum(r(h))^2}{N}} \qquad (8)$$

Only the first lag value of ethyl acetate data set #1 appears to be statistically different from zero ($\alpha = 0.05$). Chatfield (1984) states that approximately 1 out of 20 lag values that appear to be "significant" are a result of random chance; therefore, unless there is a reasonable effect to explain the "apparent significance," the coefficient is considered to be zero. When all r(h) values are considered to be equalled to zero, the observed data may be regarded as "white noise" or a series of random values that fluctuate around some mean value (McDowall, et al., 1980).

In relation to the AR(1) model, the AER can become so

great that w of Equation (3) approaches zero. This effectively forces the current ambient concentrations to be depended only on the random quantity, Z_t. This effectively makes the times series appears as "white noise." It is more appropriate to view the data as a series of independent effects of very brief duration (Chatfield, 1984).

The difference in the AER's for the first set of data on ethyl acetate and methylene chloride (collected concurrently) can not be attributed to any difference in the collection of these solvents. Since the AER's should be nearly identical, this suggest that the significant r(1) for ethyl acetate may be a chance occurrence. The other conceivable alternative is that a process other than an AR(1) process is involved.

In the cases where r(1) is not significant, it is assumed that b of Equation (4) approaches infinity. This forces the $e^{-(k+b)t}$ term in Equation (5) to zero, and Equation (5) reverts back to Equation (1). The $1/A_t$ values in Table 2 have been adjusted to reflect this assumption.

No conclusions can be drawn from Table 2 concerning the effect of autocorrelation on $1/A_t$ since none of the r(1) values are significant. It is noted that when the $1/A_t$'s of different solvents with the same Δt's (lags) are compared that $T_{1/2}$ and $1/A_t$ vary directly. This is not consistent with the model's prediction that they vary inversely.

Based on the marked differences of the $1/A_t$, the lack

of statistical significance of the r(1) values and the violation of the relation between $T_{1/2}$ and $1/A_t$, it appears that the AR(1) model is not appropriate for determining $1/A_t$ values.

The phenomena that all observed $1/A_t$'s lie within a narrow range despite the differences in chemical and pharmacokinetic attributes of these solvents and autocorrelation is not clearly understood. It is assumed that the body is constantly attempting to maintain an equilibrium and to reach steady state with its environment. Steady state is defined as the point where body burden increase is equal to body burden elimination (Rappaport, 1985). As gaseous or vaporous constituents in the ambient air vary in concentration, absorption and elimination by the lung takes places to maintain an equilibrium across the alveolar membrane. The time it takes a solvent to reach steady state within a compartment (VRG, MG, FG, e.g.) is approximately 3.3 times the solvent's $T_{1/2}$ for that compartment (Brugnone, 1985). Thus, in reference to the first compartment, it will take 14.7 minutes for ethyl acetate, 95 minutes for methylene chloride and 111 minutes for perchloroethylene to reach steady state conditions within this compartment; however, this is assuming a constant ambient concentration and first order elimination kinetics. If the ambient concentration is randomly fluctuating, time to steady state may be prolonged or

exaggerated to the point that it would exceed the workshift. If this is the case, the observed $1/A_t$'s measured during this study reflect non-steady state conditions. The mean and variance of body burden are thus changing in regards to time; therefore, body burden is not stationary. If these six sets of data are assumed to be typical representatives of worker exposure with solvent half-times near those in this study, it can be reasoned that an AR(1) model may not be generally applicable to work environments where solvent ambient concentrations frequently fluctuate.

Since ethyl acetate is rapidly metabolized by the body, the method of elimination appears to be concentration dependent (Fernandez and Droz, 1974); however, first order kinetics can be assumed if blood concentrations are very small compared to the Michaelis-Menten constant. Methylene chloride and perchloroethylene on the other hand do follow first order elimination kinetics. The effect that Michaelis-Menten kinetics would have on the $1/A_t$ is not known; however, varying ambient concentration levels do not appear to have any effect on the metabolism of a solvent (Baelum, et al., 1987). The relationship between exposure and alveolar air concentrations is unclear in regards to varying ambient concentrations (Raymer, et al., 1990).

The observed $1/A_t$ values may be attributed to the body burden being in a non-steady state condition. Additional studies should be conducted to determine if the body

burden's steady state or non-steady state condition influences the correlation of observed $1/A_t$ values to those predicted by the AR(1) model.

CONCLUSIONS

The evaluation of the model proposed by Rappaport and Spear (1988) indicates that an AR(1) process is not necessarily appropriate. Review of the corresponding correlograms for each solvent's data set does not reveal the expected exponential decay of r(h). All r(h) values were tested against $\pm$ 2SE (95% confidence level) to determine if they were significantly different from zero. Only r(1) of ethyl acetate's first data set was considered significantly different from zero. Since 1 out of 20 lag values may appear significant, it reasonable to assume, in relation to the other data sets, that the observed process was similar to "white noise," or that the value of b was so great that w of Equation (3) approached zero so that the series appeared to be "purely random." Additionally, (observed) $1/A_t$ did not vary inversely with $T_{1/2}$ for a given lag as predicted by the model.

All observed $1/A_t$ values occurred from 0.47 to 0.64. The cause of this is not clear and warrants further investigation; however, it may be attributed to the body burden not being in steady state.

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TABLE 1

SOLVENT ATTRIBUTES

	ETHYL ACETATE	METHYLENE CHLORIDE	PERCHLORO-ETHYLENE
PHYSICAL CHARACTERISTICS[1]			
Formula:	$CH_3COOCH_2CH_3$	CH_2Cl_2	$CCl_2 = CCl_2$
Molecular weight:	88.12	84.94	165.85
Boiling point: (°C)	77.1	40.1	121.2
Melting point: (°C)	83.6	96.7	-23.4
Density:	0.9003	1.325	1.623
Vapor pressure: (mm of Hg)	100	440	20
Solubility:	Water Alcohol	Slight water Alcohol Ether	Slight water Alcohol Ether
PHARMACOKINETIC CHARACTERISTICS			
Partition coefficient: (blood/air)	222[2]	9.7	13.1
Partition coefficient: (water)	145	7.2	0.4
Partition coefficient: (oil)	479	152	1920
Half-time:	1.8-8.9[3]	40[4]	104[5]
% Retention:	99.8	30-70	52-80

[1]Clayton and Clayton, 1981
[2]Sato and Nakajima, 1987
[3]Fernandez and Droz, 1974; Nomiyama and Nomiyama, 1974
[4]Divincenzo, et al., 1971; Baselt, 1982
[5]Stewart, et al., 1961

TABLE 2

SUMMARY OF AIR MEASUREMENT RESULTS

	Ethyl Acetate		Methylene Chloride		Perchloro-ethylene	
Data set #	I	II	I	II	I	II
1st Compartment Half-time (mins):	4.5		29		34	
% Retention:	91	93	64	64	61	54
Autocorrelation Coefficient[1]:	0.52*	-0.09	0.02	0.13	0.07	0.15
AER (per hr):	6	37	36	22	20	20
Lag (min)[2]:	6.4	6.2	6.5	5.5	8.1	5.6
Obs. $1/A_t$:	0.47	0.50	0.62	0.64	0.60	0.57
Exp. $1/A_t$[3]:	0.68	0.67	0.28	0.26	0.29	0.24

* significant at $\alpha = 0.05$

[1]Value represents the first lag autocorrelation coefficient of the ambient air measurements

[2]This value represents the average time between measurements

[3]Included in the table for comparison

TABLE 3

STATISTICAL SUMMARY OF DATA

	Ambient			Alveolar			
	Mean	Std.	CV	Mean	Std.	CV	$1/A_t$
Ethyl Acetate:							
Data Set #1	11.96	15.41	1.29	0.60	0.37	0.62	0.47
Data Set #2	8.65	8.86	1.02	0.46	0.23	0.50	0.50
Methylene chloride:							
Data Set #1	19.64	17.80	0.91	5.09	2.86	0.56	0.62
Data Set #2	17.92	16.71	0.93	4.90	2.96	0.60	0.64
Perchloroethylene:							
Data Set #1	0.55	0.52	0.95	0.15	0.09	0.60	0.60
Data Set #2	6.13	5.82	0.95	2.35	1.27	0.54	0.57

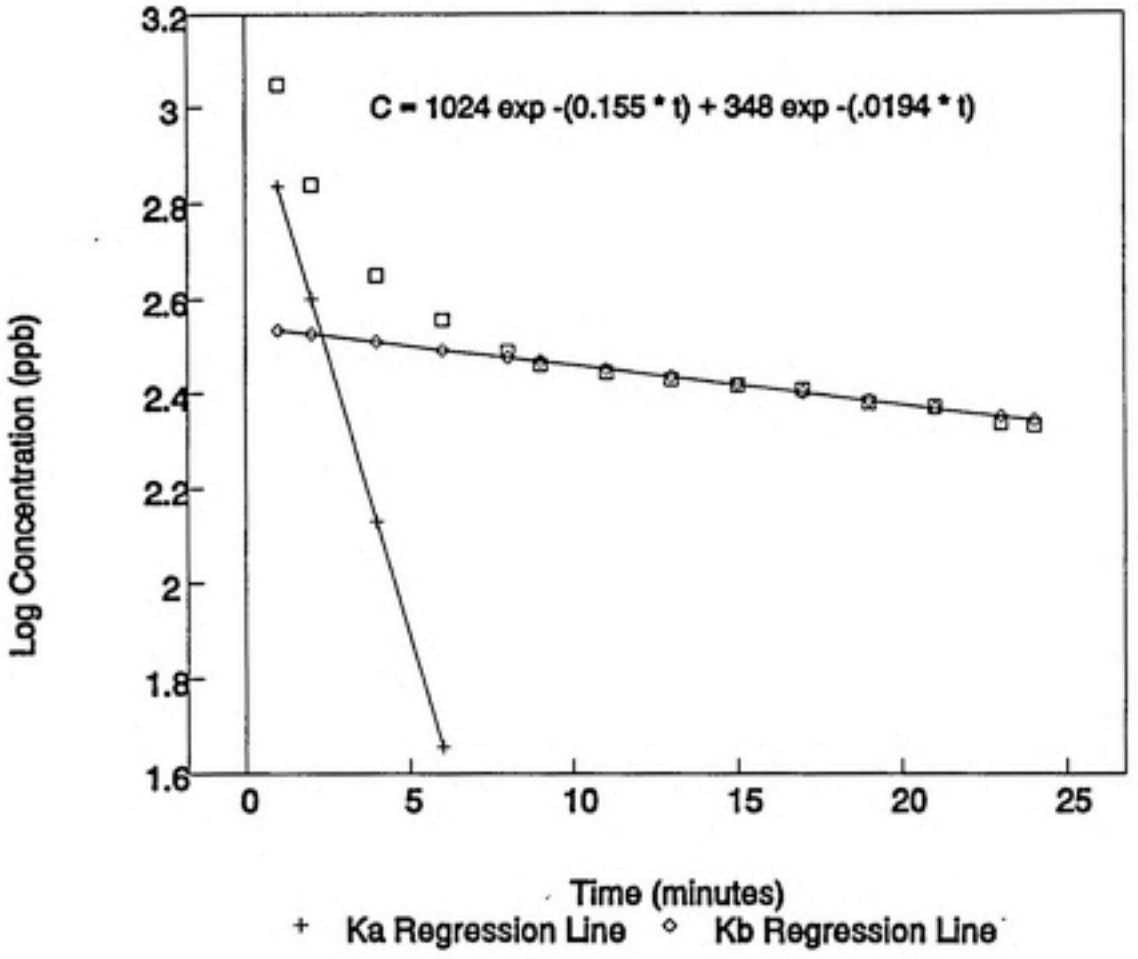


Figure 1 - Ethyl Acetate Decay Curve

Ka is first compartment and Kb is second compartment

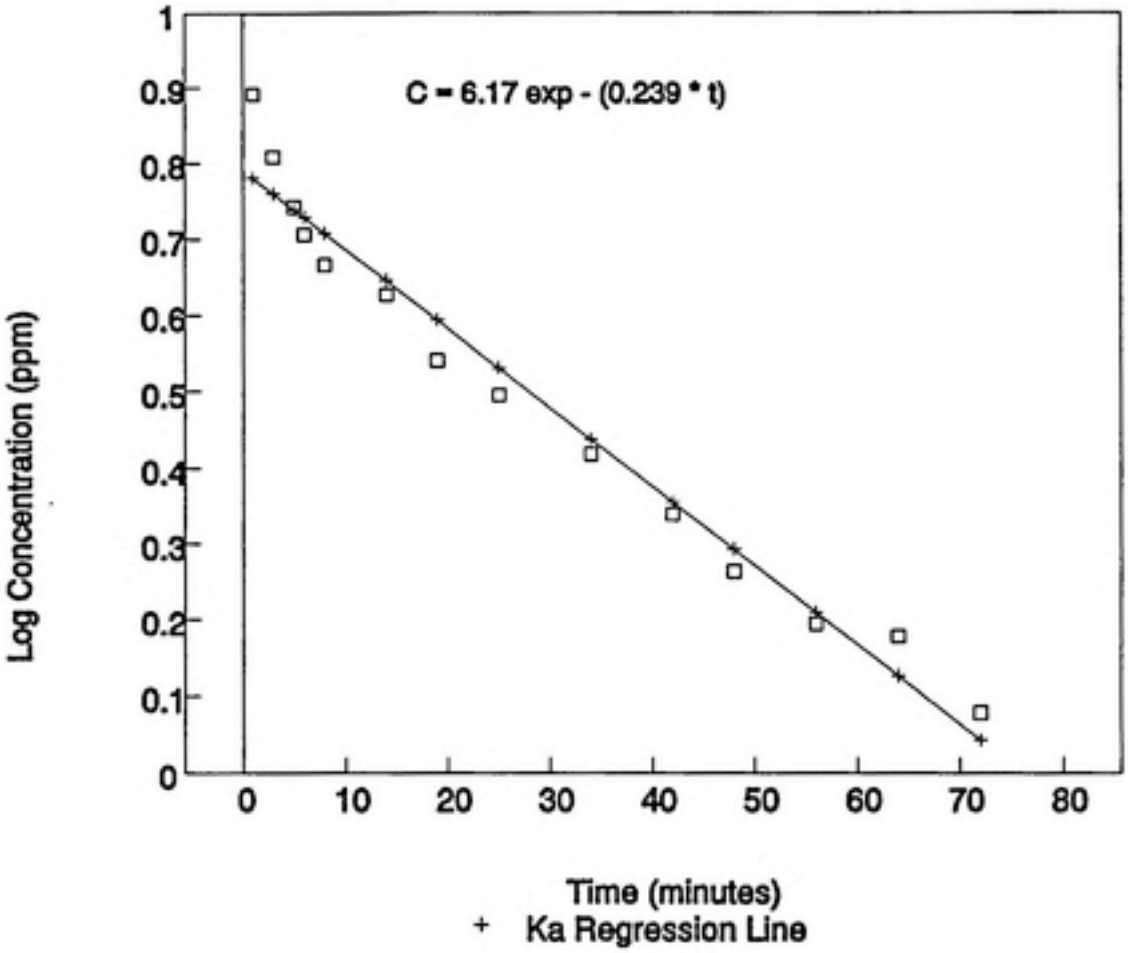


Figure 2 - Methylene Chloride Decay Curve

Ka is first compartment and Kb is second compartment

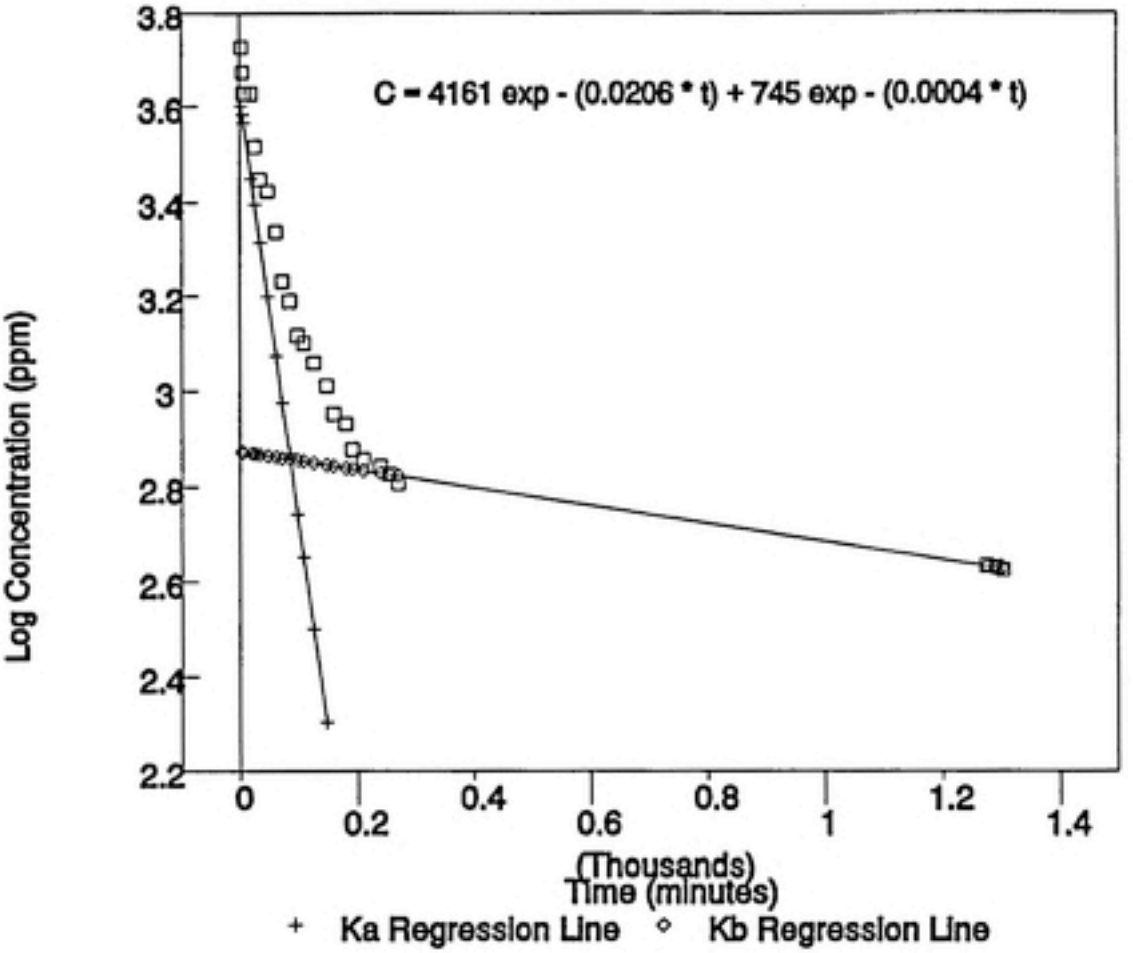


Figure 3 - Perchloroethylene Decay Curve

Ka is first compartment

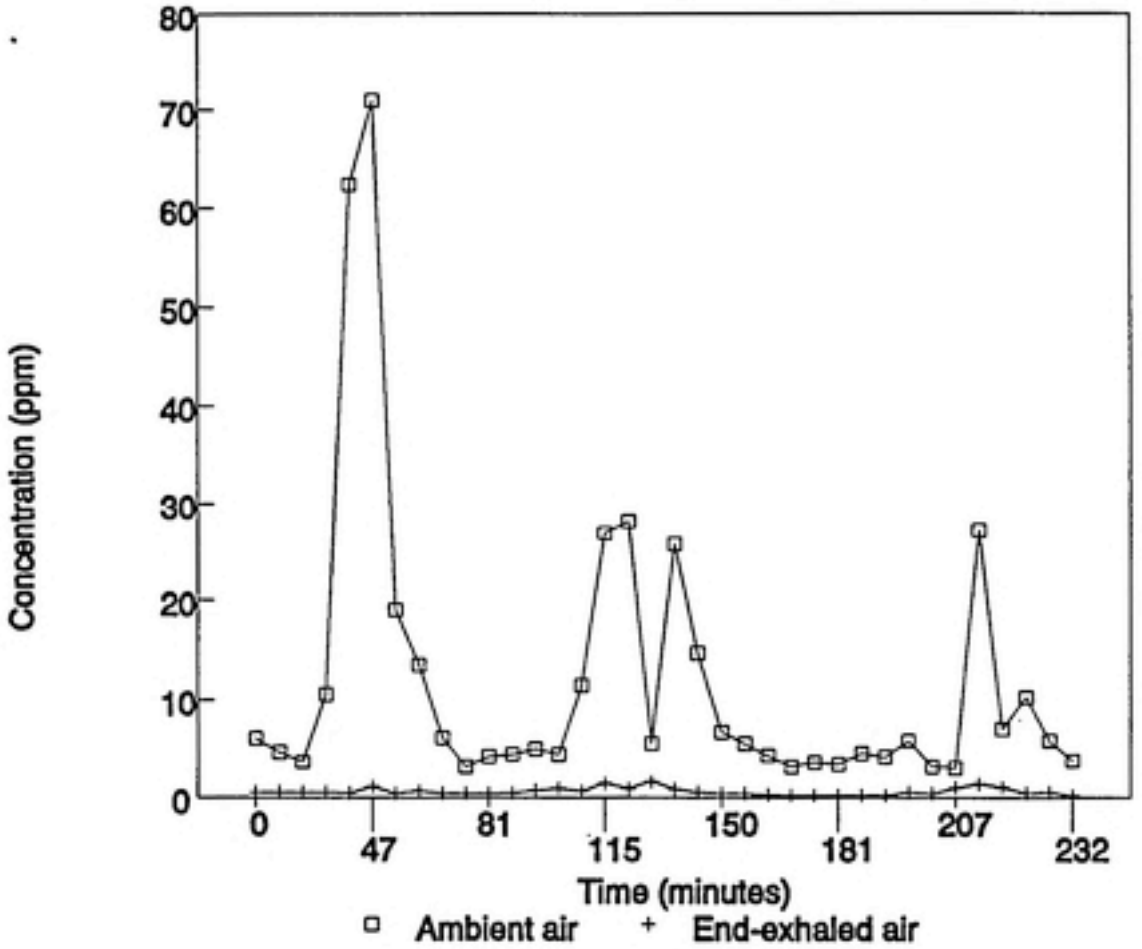


Figure 4 - Ethyl Acetate Data Set #1
Breath and Ambient Air Concentrations

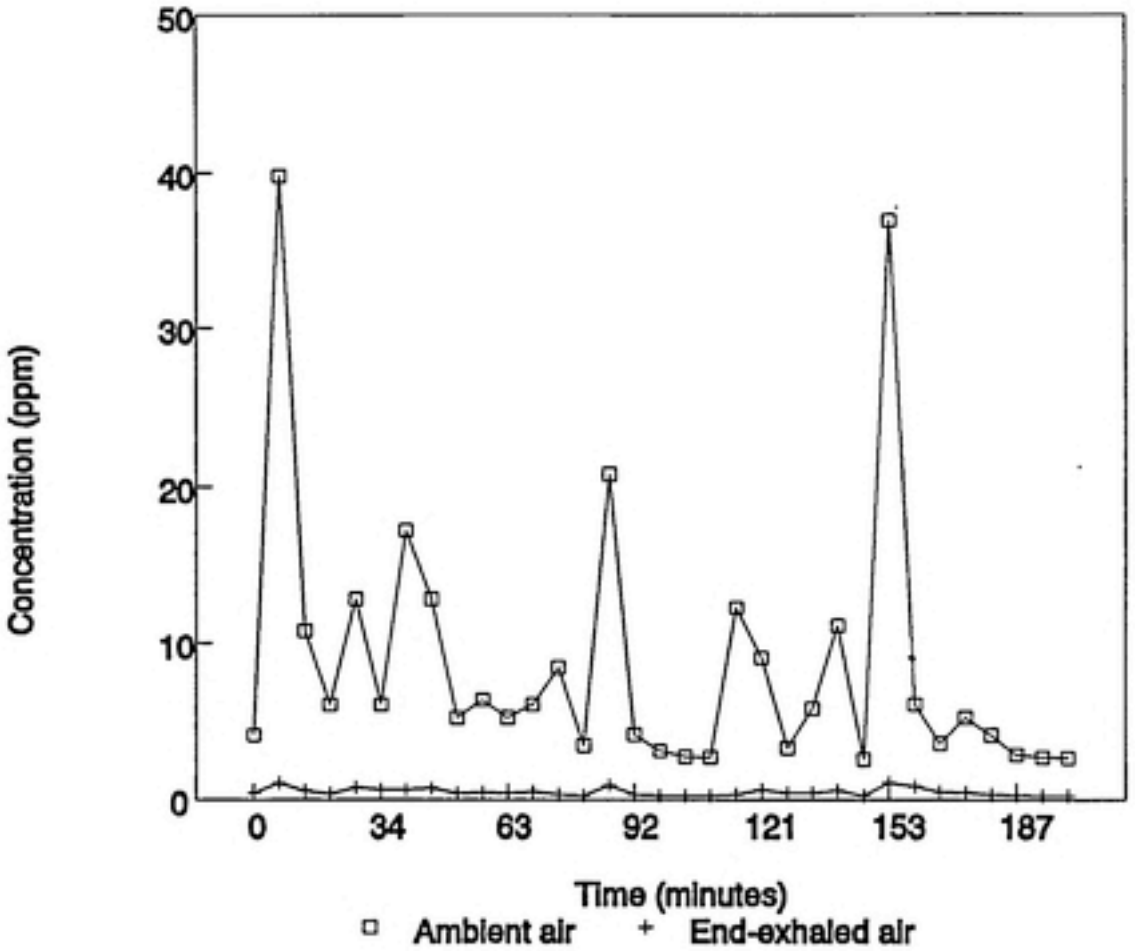


Figure 5 - Ethyl Acetate Data Set #2
Breath and Ambient Air Concentrations

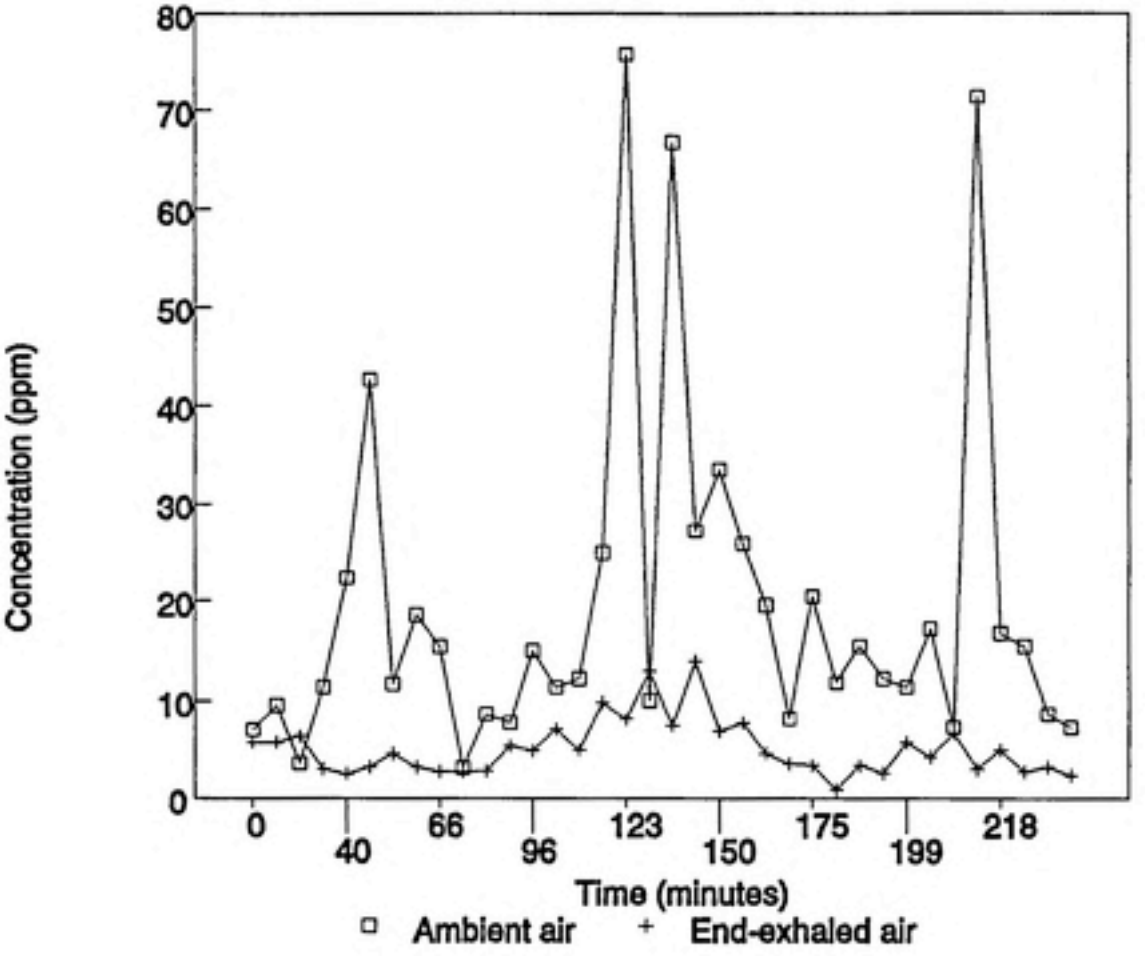


Figure 6 - Methylene Chloride Data Set #1
Breath and Ambient Air Concentrations

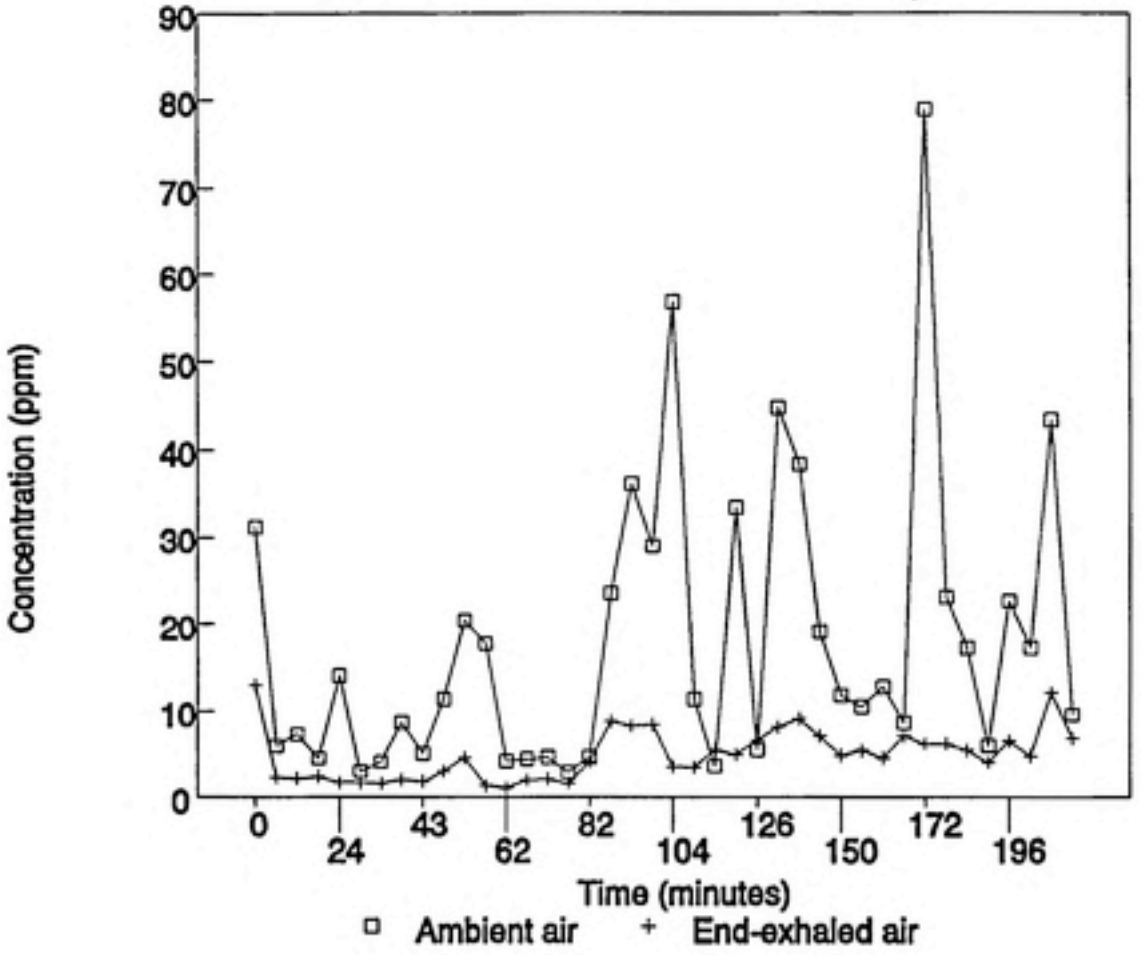


Figure 7 - Methylene Chloride Data Set #2
Breath and Ambient Air Concentrations

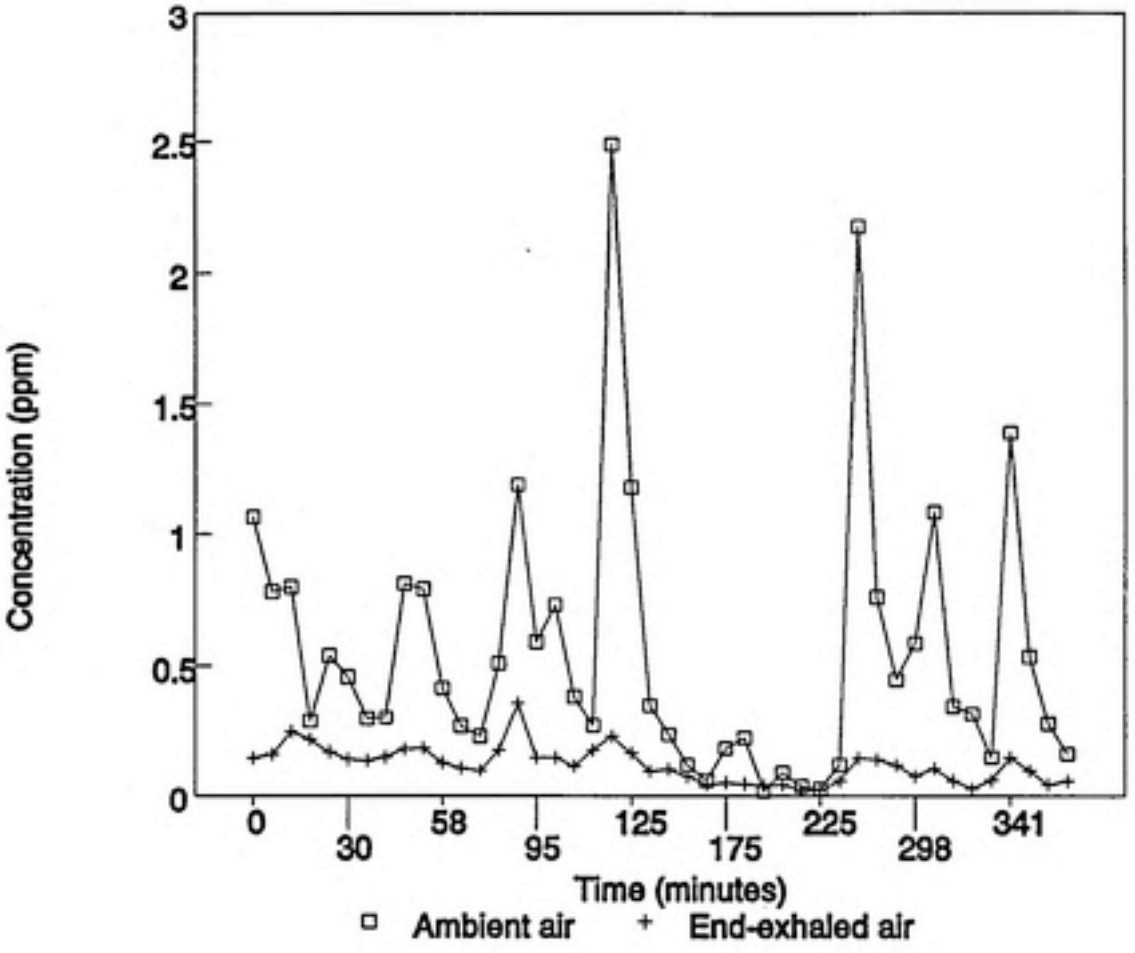


Figure 8 - Perchloroethylene Data Set #1
Breath and Ambient Air Concentrations

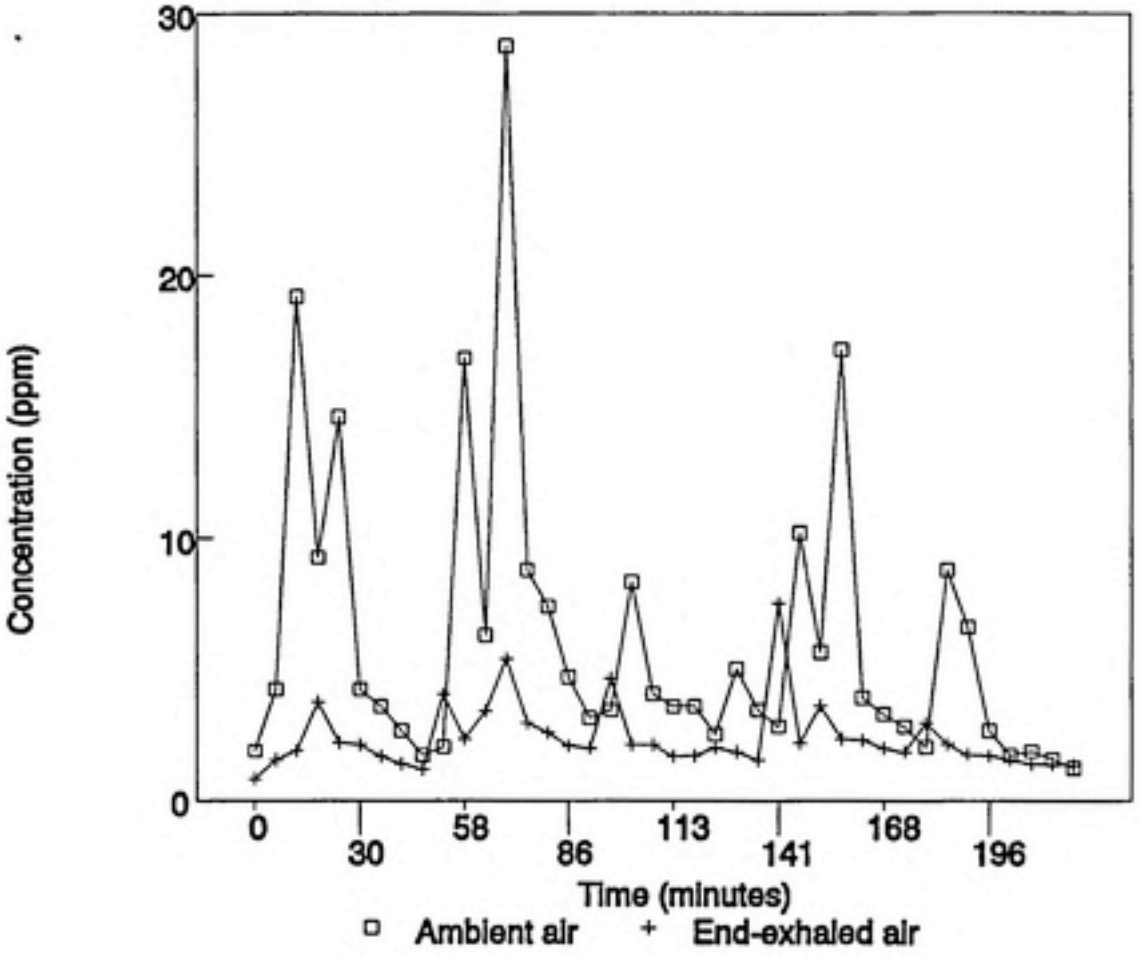


Figure 9 - Perchloroethylene Data Set #2
Breath and Ambient Air Concentrations

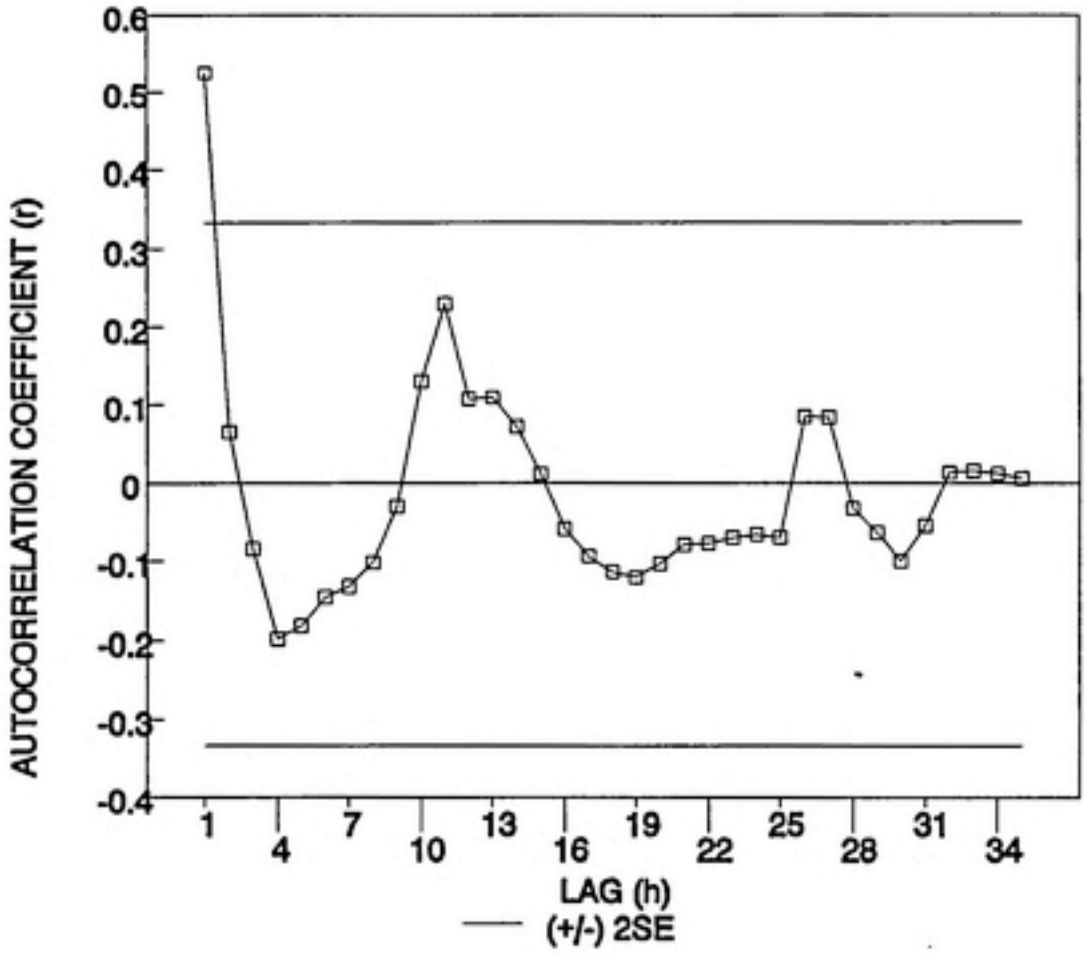


Figure 10 - Correlogram for Ethyl Acetate
Data Set #1

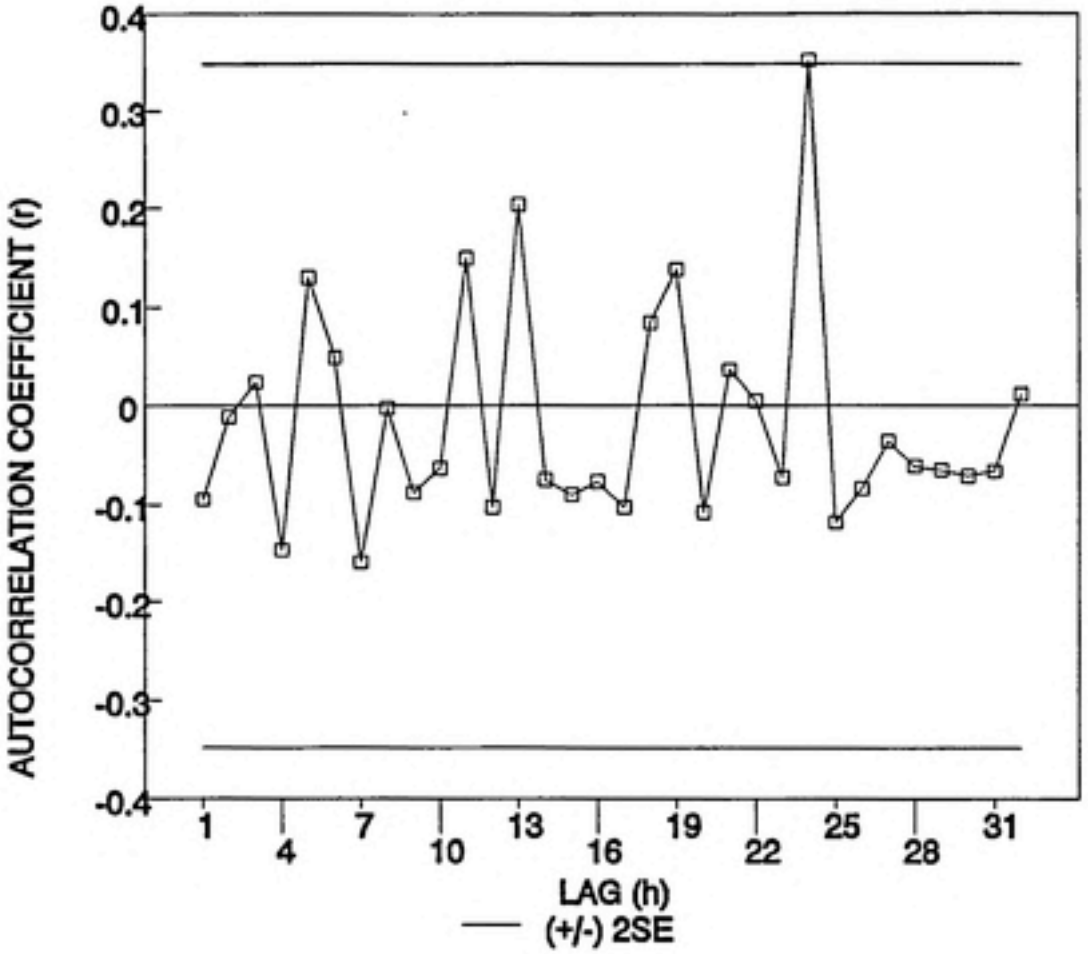


Figure 11 - Correlogram for Ethyl Acetate
Data Set #2

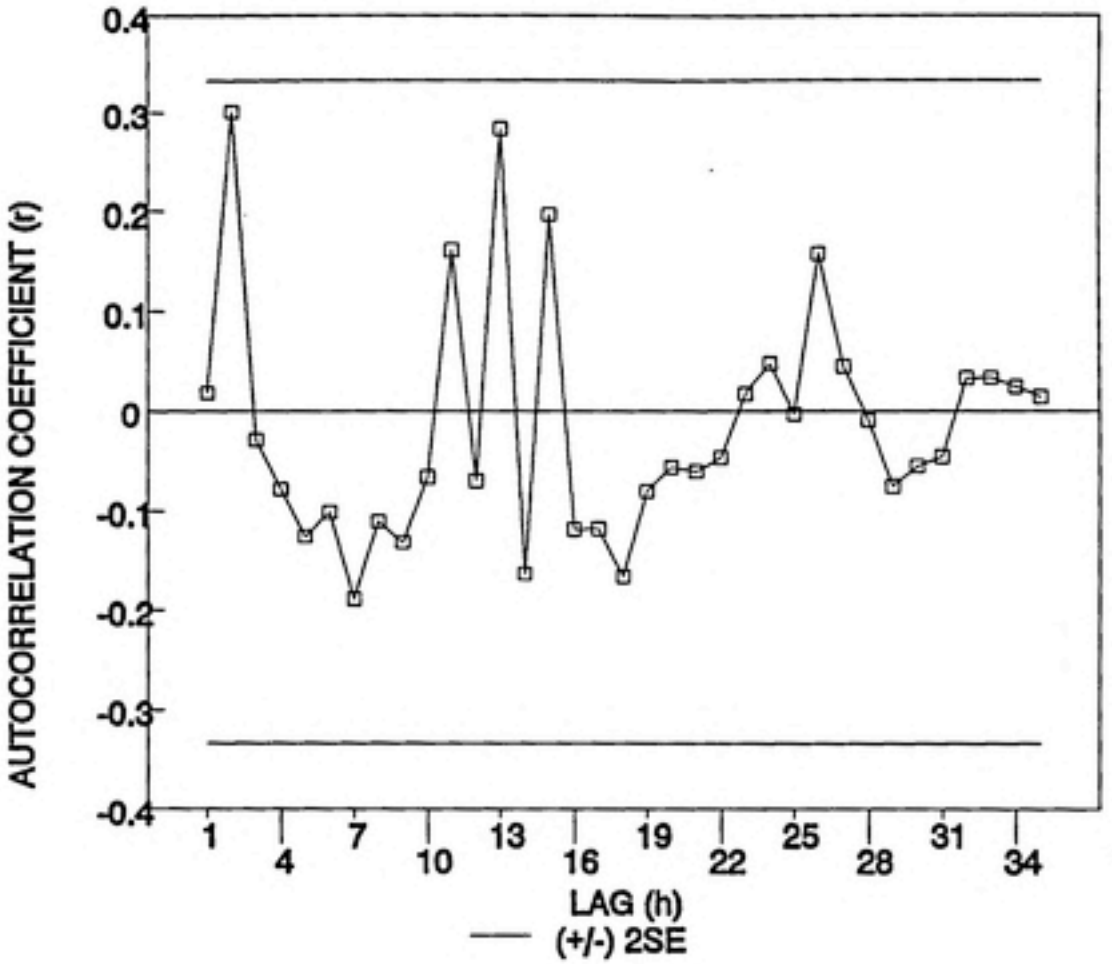


Figure 12 - Correlogram for Methylene Chloride
Data Set #1

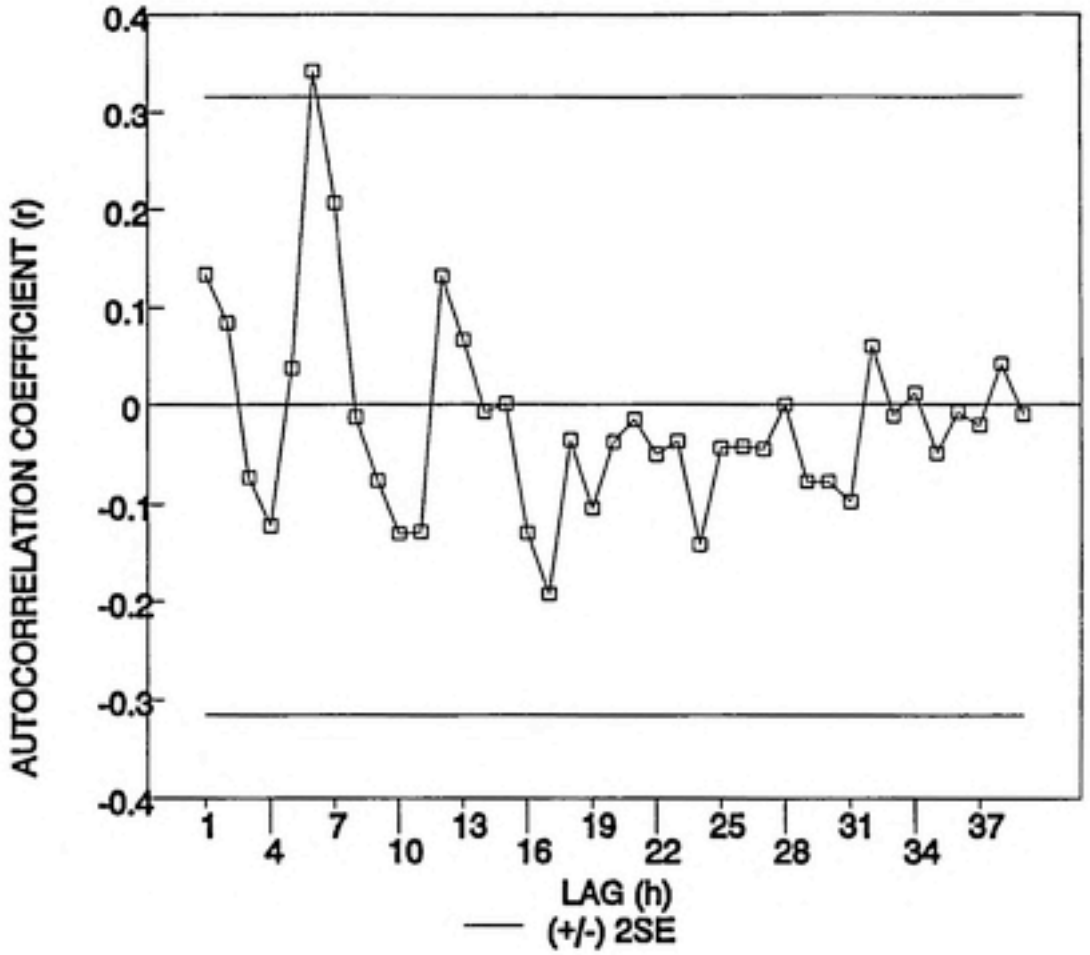


Figure 13 - Correlogram for Methylene Chloride
Data Set #2

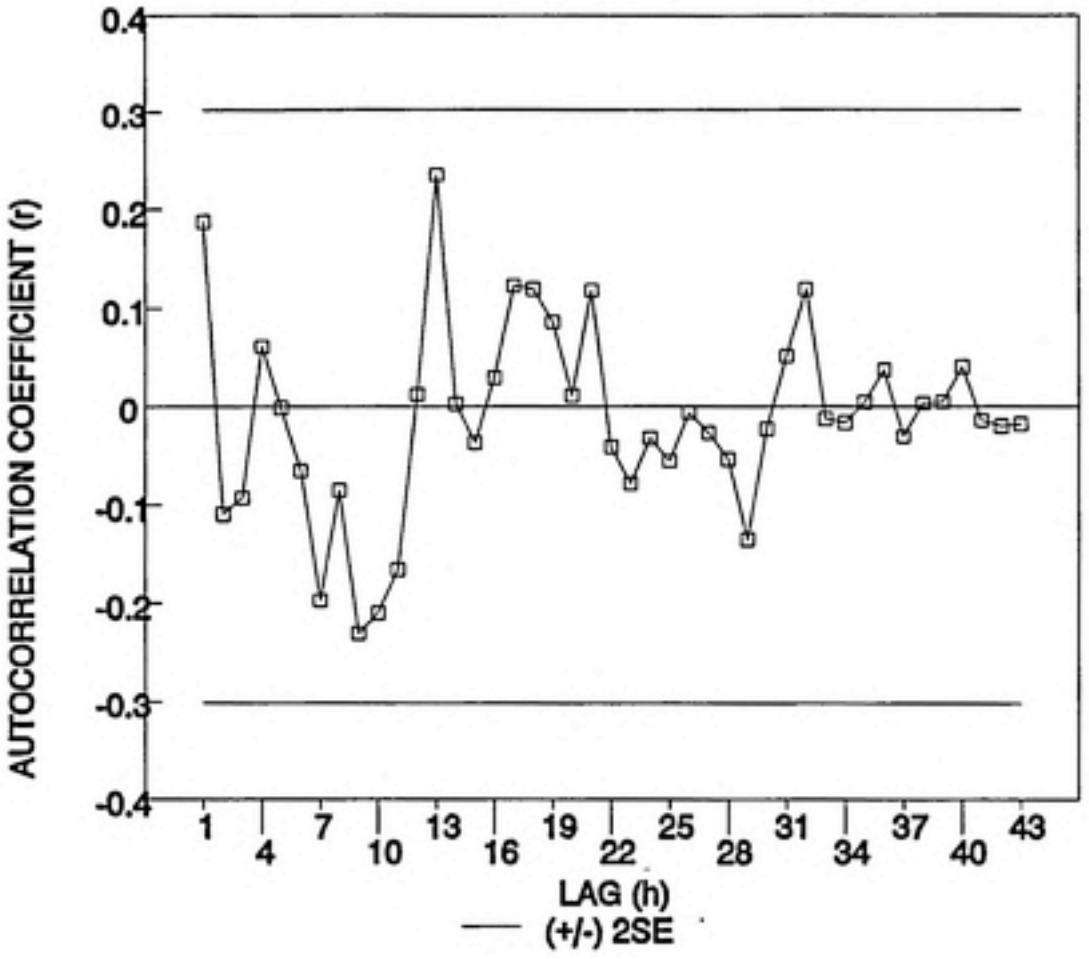


Figure 14 - Correlogram for Perchloroethylene
Data Set #1

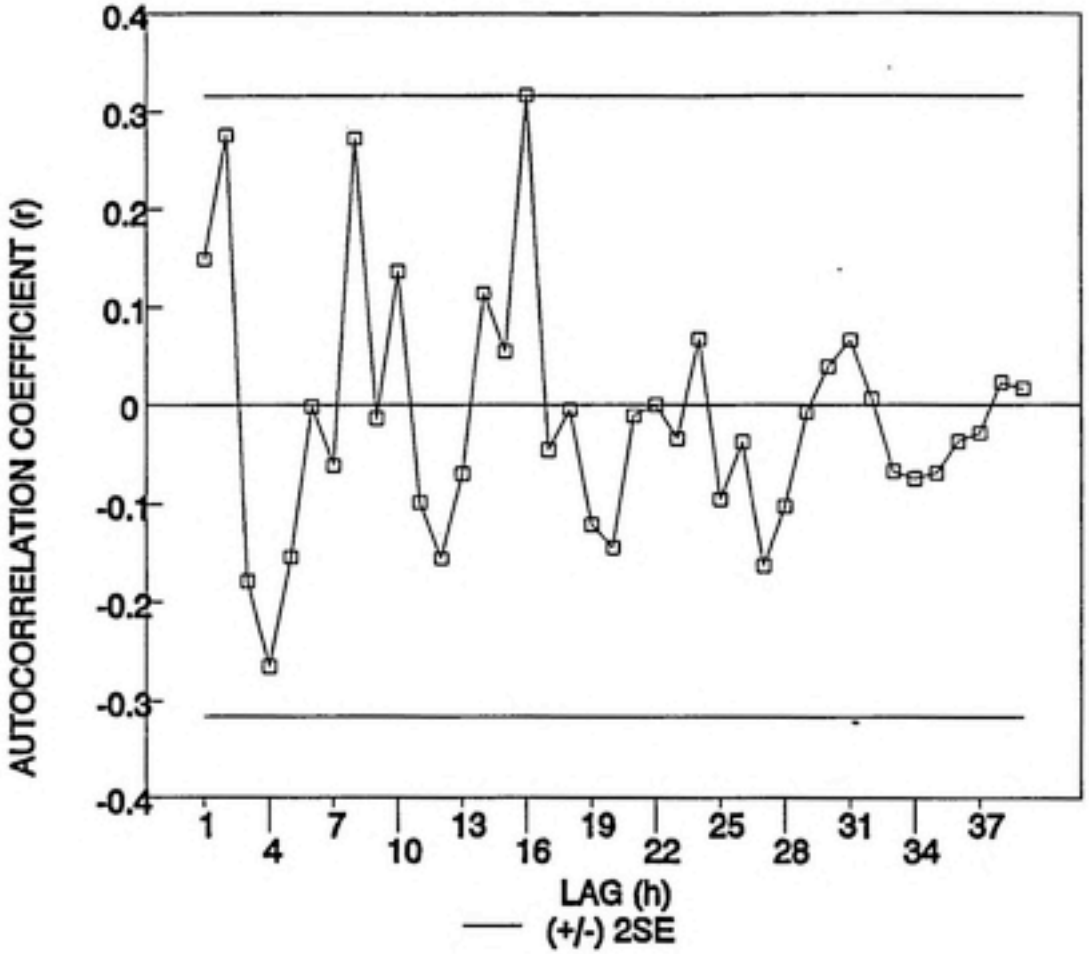


Figure 15 - Correlogram for Perchloroethylene

Data Set #2

APPENDICES

APPENDIX A-1

ETHYL ACETATE DATA SET #1

Ethyl Acetate measured in ambient and end-exhaled air during exposure at a shop in an aircraft rework facility involving stripping and cleaning a small jet aircraft. Time measurements commenced at the collection of the first ambient air sample.

Task: Cleaning aircraft prior to taping
Time between samples: 6.444 min

AMBIENT		END-EXHALED		AMBIENT		END-EXHALED	
TIME (min)	CONC (ppm)	TIME (min)	CONC (ppm)	TIME (min)	CONC (ppm)	TIME (min)	CONC (ppm)
0	6.078	4	0.504	19	5.785	201	0.506
11	4.609	15	0.502	202	3.103	205	0.417
26	3.643	31	0.538	207	3.034	209	0.988
34	10.477	38	0.540	211	27.194	214	1.371
40	62.388	45	0.484	217	6.958	219	1.037
47	70.893	51	1.120	222	10.184	226	0.457
52	18.982	58	0.444	228	5.785	230	0.517
60	13.410	64	0.632	232	3.781	234	0.220
66	6.078	70	0.402				
75	3.145	79	0.381				
81	4.178	85	0.412				
87	4.388	94	0.465				
96	4.975	101	0.734				
103	4.364	107	0.951				
109	11.357	113	0.636				
115	26.901	120	1.455				
123	28.074	127	0.909				
129	5.491	134	1.622				
136	25.728	138	0.858				
142	14.583	147	0.563				
150	6.664	154	0.379				
156	5.491	161	0.364				
163	4.290	167	0.239				
169	3.109	173	0.215				
175	3.599	179	0.215				
181	3.412	185	0.215				
186	4.497	191	0.215				
191	4.098	196	0.215				

APPENDIX A-2

ETHYL ACETATE DATA SET #2

Ethyl Acetate measured in ambient and end-exhaled air during exposure at a shop in an aircraft rework facility involving stripping and cleaning a small jet aircraft. Time measurements commenced at the collection of the first ambient air sample.

Task: Cleaning aircraft after stripping
Time between samples: 6.242 min

AMBIENT		END-EXHALED		AMBIENT		END-EXHALED	
TIME (min)	CONC (ppm)	TIME (min)	CONC (ppm)	TIME (min)	CONC (ppm)	TIME (min)	CONC (ppm)
0	4.117	5	0.406	181	4.093	185	0.303
7	39.805	13	1.037	187	2.834	191	0.258
15	10.770	20	0.571	193	2.658	198	0.222
22	6.078	26	0.350	200	2.617	204	0.222
28	12.823	32	0.734				
34	6.078	38	0.645				
40	17.222	44	0.614				
46	12.823	50	0.683				
52	5.198	56	0.399				
58	6.371	62	0.432				
63	5.198	67	0.366				
69	6.078	73	0.445				
75	8.424	77	0.332				
81	3.427	85	0.227				
87	20.742	91	0.887				
92	4.130	96	0.308				
98	3.102	102	0.222				
104	2.705	108	0.222				
110	2.679	114	0.233				
116	12.237	119	0.300				
121	9.011	125	0.592				
127	3.281	131	0.394				
133	5.785	137	0.373				
139	11.064	143	0.520				
145	2.529	149	0.222				
153	36.872	161	1.037				
163	6.078	167	0.823				
169	3.554	173	0.446				
175	5.198	179	0.433				

APPENDIX A-3

METHYLENE CHLORIDE DATA SET #1

Methylene Chloride measured in ambient and end-exhaled air during exposure at a shop in an aircraft rework facility involving stripping and cleaning a small jet aircraft. Time measurements commenced at the collection of the first ambient air sample.

Task: Stripping paint from aircraft
Time between samples: 6.528 min

AMBIENT		END-EXHALED	
TIME (min)	CONC (ppm)	TIME (min)	CONC (ppm)
0	7.049	4	4.527
11	9.568	15	4.527
26	3.602	31	4.976
34	11.400	38	2.670
40	22.300	45	2.349
47	42.600	51	2.798
54	11.700	58	3.759
60	18.572	64	2.798
66	15.422	70	2.477
75	3.143	79	2.477
81	8.673	85	2.541
87	7.773	94	4.271
96	14.972	101	3.951
103	11.373	107	5.488
109	12.273	113	4.015
115	24.872	120	7.346
123	75.718	127	6.193
129	10.023	134	9.525
136	66.718	140	5.745
142	27.122	147	10.165
150	33.421	154	5.360
156	25.772	161	5.937
163	19.472	167	3.759
169	8.223	173	3.054
175	20.372	179	2.926
181	11.823	185	1.260
187	15.422	192	2.926
194	12.273	197	2.413
199	11.373	202	4.527
203	17.222	206	3.502
208	7.323	210	5.232
212	71.218	215	2.670
218	16.772	221	4.015
223	15.422	227	2.477
229	8.673	231	2.798
233	7.323	235	2.221

APPENDIX A-4

METHYLENE CHLORIDE DATA SET #2

Methylene Chloride measured in ambient and end-exhaled air during exposure at a shop in an aircraft rework facility involving stripping and cleaning a small jet aircraft. Time measurements commenced at the collection of the first ambient air sample.

Task: Stripping paint from aircraft
Time between samples: 5.45 mins

AMBIENT		END-EXHALED		AMBIENT		END-EXHALED	
TIME (min)	CONC (ppm)	TIME (min)	CONC (ppm)	TIME (min)	CONC (ppm)	TIME (min)	CONC (ppm)
0	31.171	7	9.525	161	12.723	164	3.759
8	5.973	12	2.157	166	8.673	170	5.488
14	7.323	17	2.093	172	78.868	176	4.848
19	4.505	22	2.221	181	23.072	184	4.848
24	14.073	27	1.773	186	17.222	189	4.335
28	2.962	32	1.773	191	5.973	195	3.374
33	4.086	36	1.708	196	22.622	200	5.104
38	8.673	41	1.965	202	17.222	205	3.887
43	5.073	46	1.837	207	43.320	211	8.884
48	11.373	51	2.670	213	9.573	218	5.296
52	20.372	56	3.759				
58	17.672	61	1.516				
62	4.173	66	1.326				
67	4.402	70	1.965				
72	4.623	75	2.029				
77	2.867	80	1.708				
82	4.623	86	3.438				
87	23.522	91	6.642				
93	36.121	96	6.321				
98	28.921	102	6.385				
104	56.819	108	3.054				
109	11.373	113	2.990				
114	3.591	118	4.335				
119	33.421	124	4.015				
126	5.523	130	5.168				
131	44.670	135	6.193				
137	38.371	141	6.834				
143	19.022	148	5.488				
150	11.823	154	3.951				
155	10.473	159	4.335				

APPENDIX A-5

PERCHLOROETHYLENE DATA SET #1

Perchloroethylene measured in ambient and end-exhaled air during exposure at a dry cleaning training facility. Time measurements commenced at the collection of the first ambient air sample.

Task: Training on dry cleaning equipment
Time between samples: 8.140 mins

AMBIENT		END-EXHALED		AMBIENT		END-EXHALED	
TIME (min)	CONC (ppm)	TIME (min)	CONC (ppm)	TIME (min)	CONC (ppm)	TIME (min)	CONC (ppm)
0	1.066	4	0.250	281	2.175	285	0.207
6	0.779	10	0.232	287	0.758	291	0.176
12	0.795	17	0.309	292	0.448	296	0.142
18	0.293	22	0.280	298	0.586	302	0.101
24	0.540	28	0.221	304	1.082	308	0.145
30	0.458	34	0.191	310	0.347	314	0.082
36	0.301	40	0.179	315	0.319	319	0.053
41	0.306	45	0.191	323	0.151	327	0.060
47	0.806	51	0.228	341	1.388	345	0.224
53	0.789	56	0.227	348	0.534	351	0.136
58	0.417	62	0.166	353	0.280	357	0.069
64	0.273	68	0.139	360	0.163	364	0.060
69	0.233	75	0.123				
77	0.511	81	0.212				
82	1.191	86	0.397				
95	0.591	97	0.179				
101	0.731	106	0.200				
108	0.385	111	0.152				
113	0.273	117	0.210				
119	2.490	123	0.283				
125	1.180	128	0.203				
130	0.351	134	0.125				
136	0.238	140	0.104				
142	0.121	146	0.075				
148	0.061	152	0.045				
175	0.186	186	0.053				
190	0.226	194	0.047				
207	0.020	211	0.041				
214	0.091	218	0.043				
219	0.038	223	0.026				
225	0.027	229	0.022				
254	0.121	258	0.060				

APPENDIX A-6

PERCHLOROETHYLENE DATA SET #2

Perchloroethylene measured in ambient and end-exhaled air during exposure at a commercial dry cleaning facility. Time measurements commenced at the collection of the first ambient air sample.

Task: Operation of dry cleaning equipment
Time between samples: 5.600 min

AMBIENT		END-EXHALED		AMBIENT		END-EXHALED	
TIME (min)	CONC (ppm)	TIME (min)	CONC (ppm)	TIME (min)	CONC (ppm)	TIME (min)	CONC (ppm)
0	1.860	4	0.800	179	2.018	183	2.930
7	4.221	11	1.503	185	8.786	189	2.122
13	19.174	17	1.860	190	6.582	194	1.721
18	9.258	22	3.744	196	2.647	200	1.658
24	14.610	28	2.175	201	1.703	205	1.516
30	4.221	33	2.109	207	1.860	211	1.360
35	3.592	39	1.655	213	1.545	216	1.365
41	2.647	44	1.353	218	1.199	222	1.319
46	1.703	50	1.160				
52	2.018	56	4.038				
58	16.813	62	2.332				
63	6.267	67	3.410				
69	28.776	73	5.386				
75	8.786	78	2.920				
80	7.369	84	2.567				
86	4.693	89	2.052				
91	3.119	95	1.970				
97	3.434	100	4.648				
102	8.314	106	2.118				
108	4.064	111	2.119				
113	3.592	117	1.655				
119	3.592	123	1.657				
124	2.490	128	1.984				
130	5.008	134	1.807				
135	3.434	139	1.504				
141	2.805	144	7.493				
146	10.202	150	2.159				
152	5.638	156	3.597				
157	17.128	161	2.332				
163	3.906	167	2.269				
168	3.277	172	1.973				
174	2.805	178	1.823				

APPENDIX B

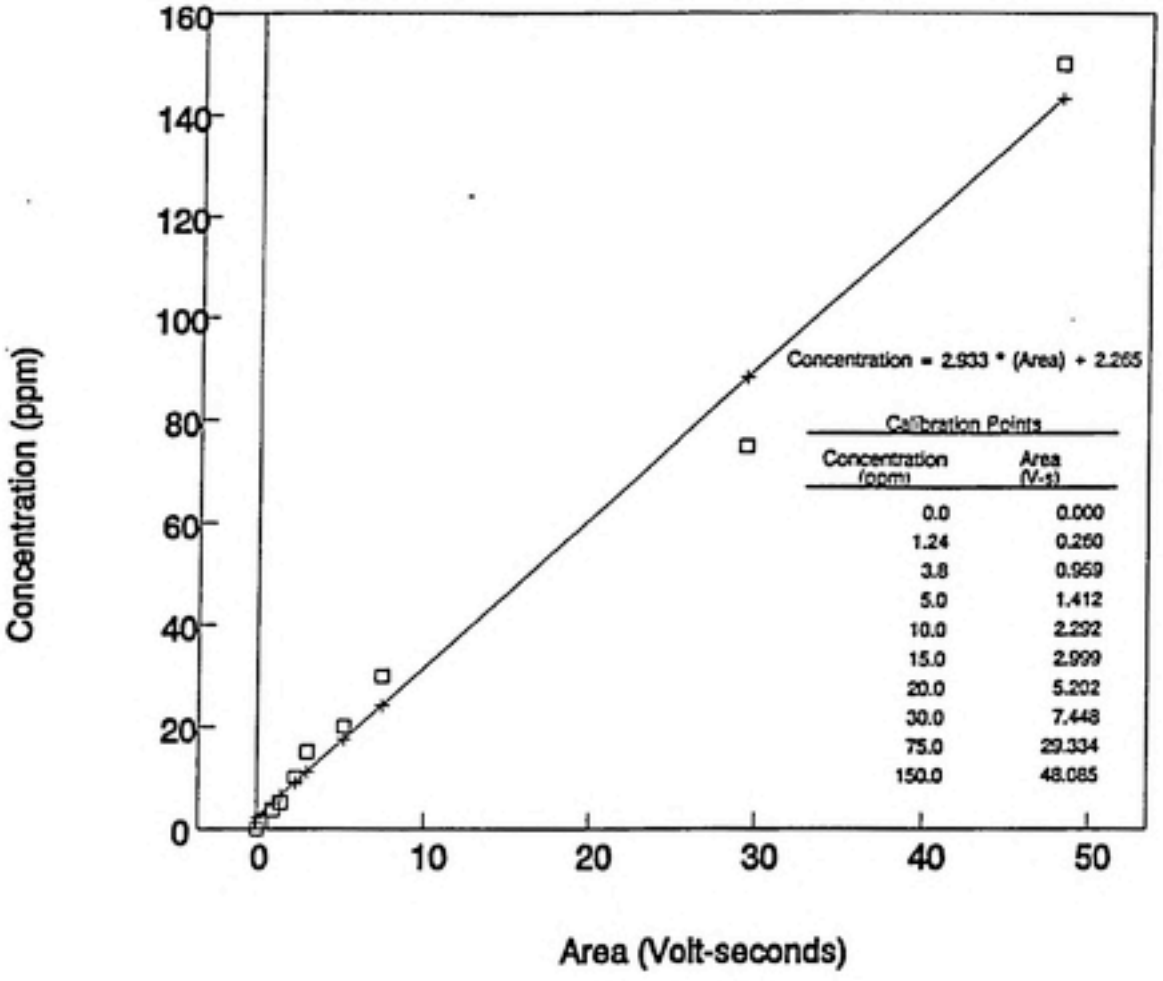
Decay Curve Constants

	1st compartment		2nd compartment		Microconstants (min^{-1})		
Compound	A	a	B	b	K	K_{12}	K_{21}
Ethyl Acetate	1180	0.5425	348	0.0194	0.076	0.347	0.139
Methylene Chloride	6.17	0.0239	****	******	0.023	*****	*****
Perchloro-ethylene	4162	0.0206	745	0.0004	0.003	0.015	0.003

APPENDIX C-1

ETHYL ACETATE CALIBRATION CURVE

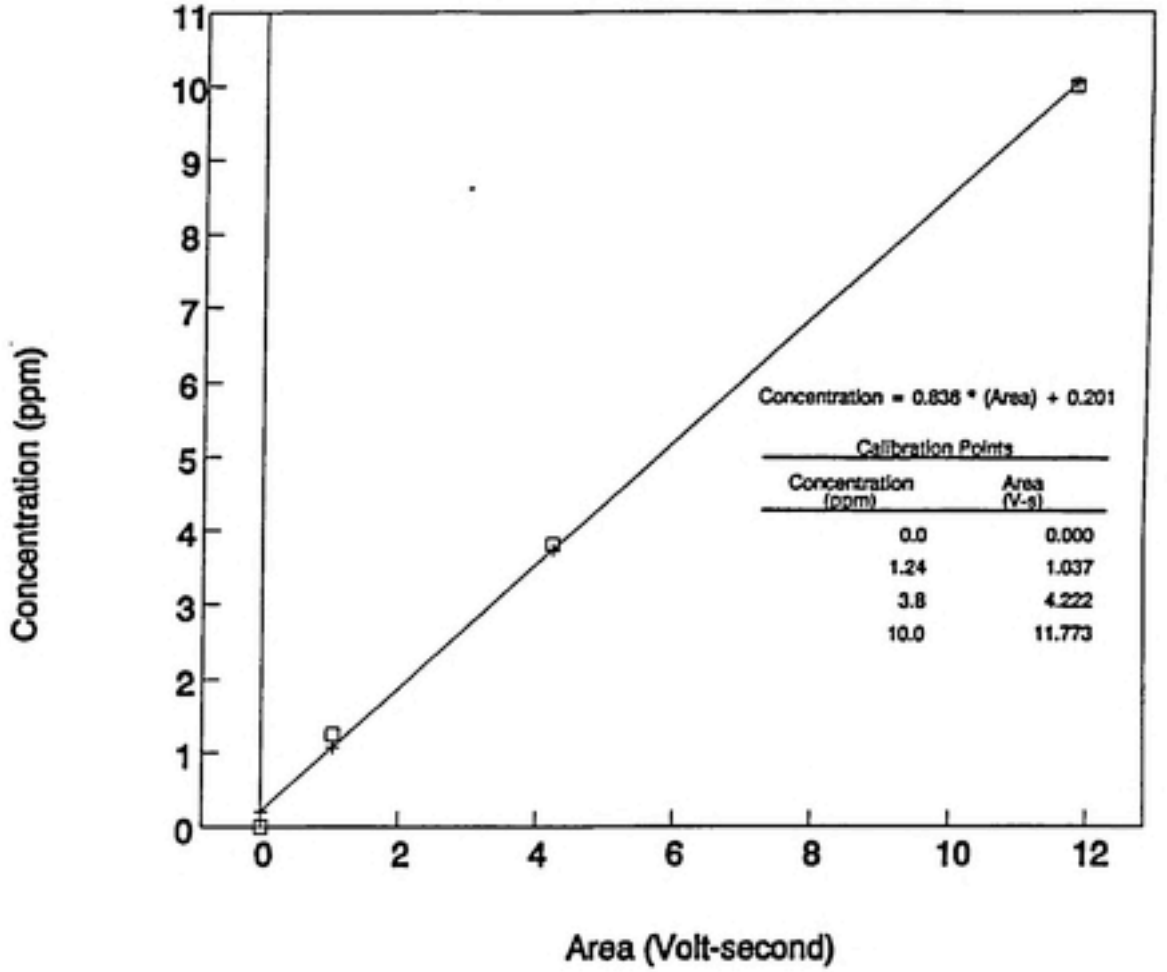
Gain = 5



APPENDIX C-2

ETHYL ACETATE CALIBRATION CURVE

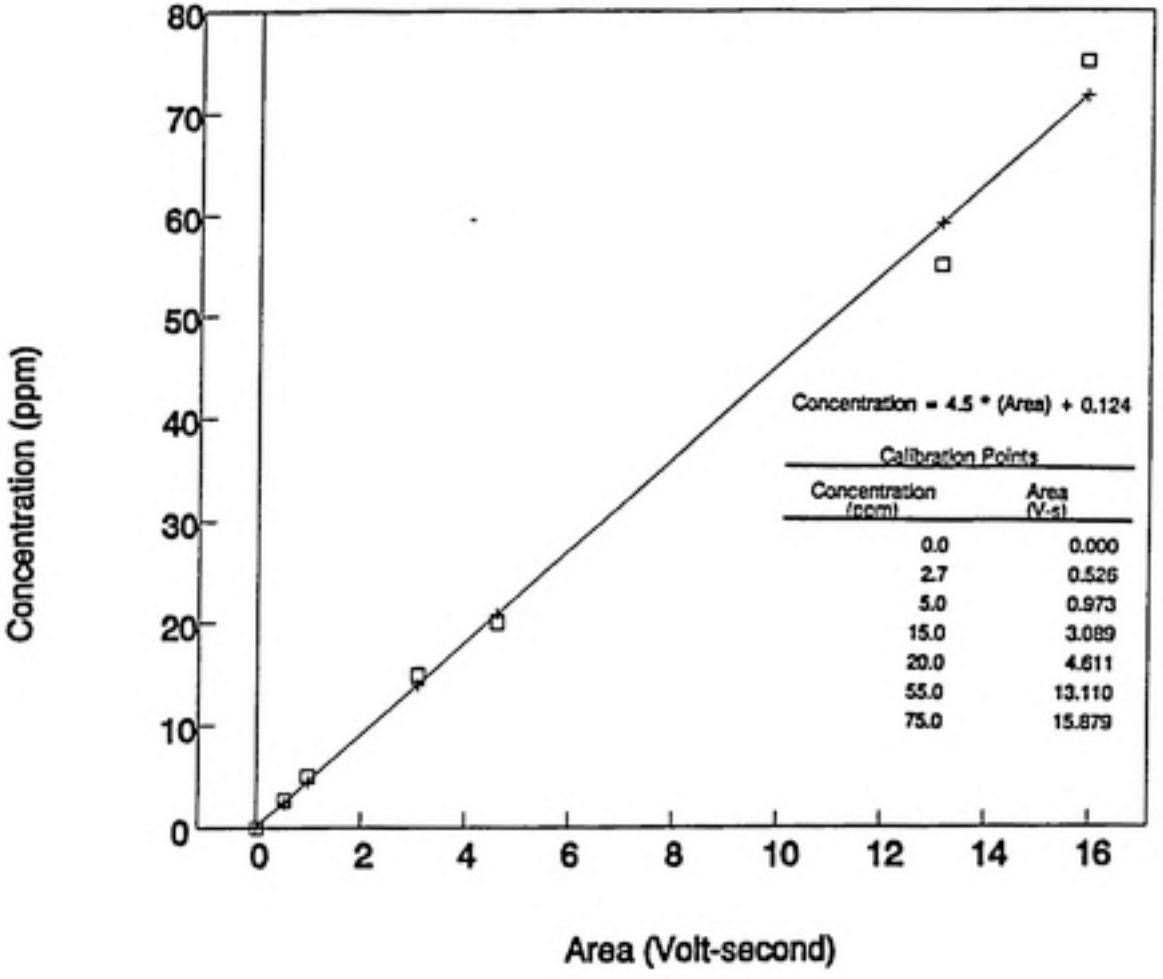
GAIN = 20



APPENDIX C-3

METHYLENE CHLORIDE CALIBRATION CURVE

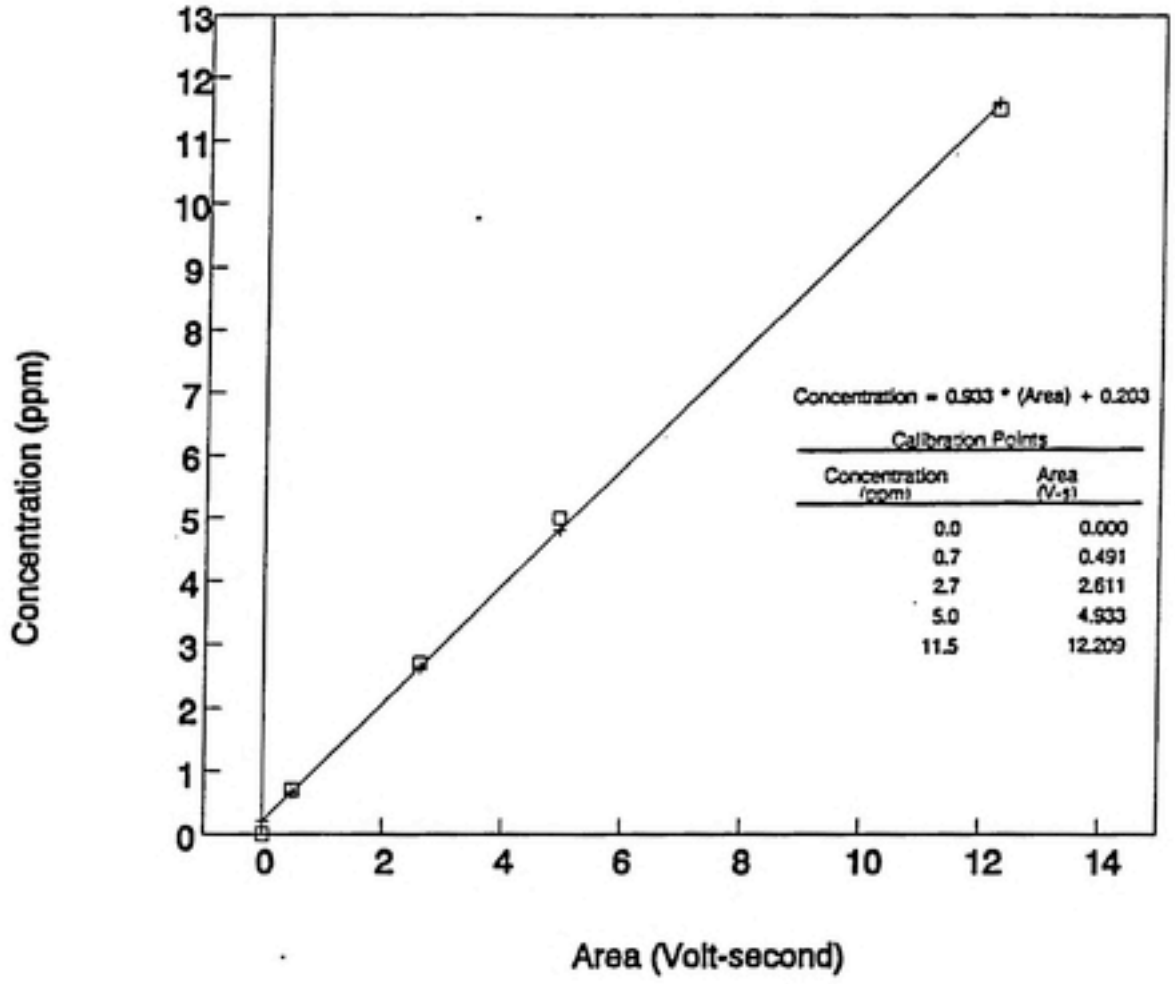
GAIN = 5



APPENDIX C-4

METHYLENE CHLORIDE CALIBRATION CURVE

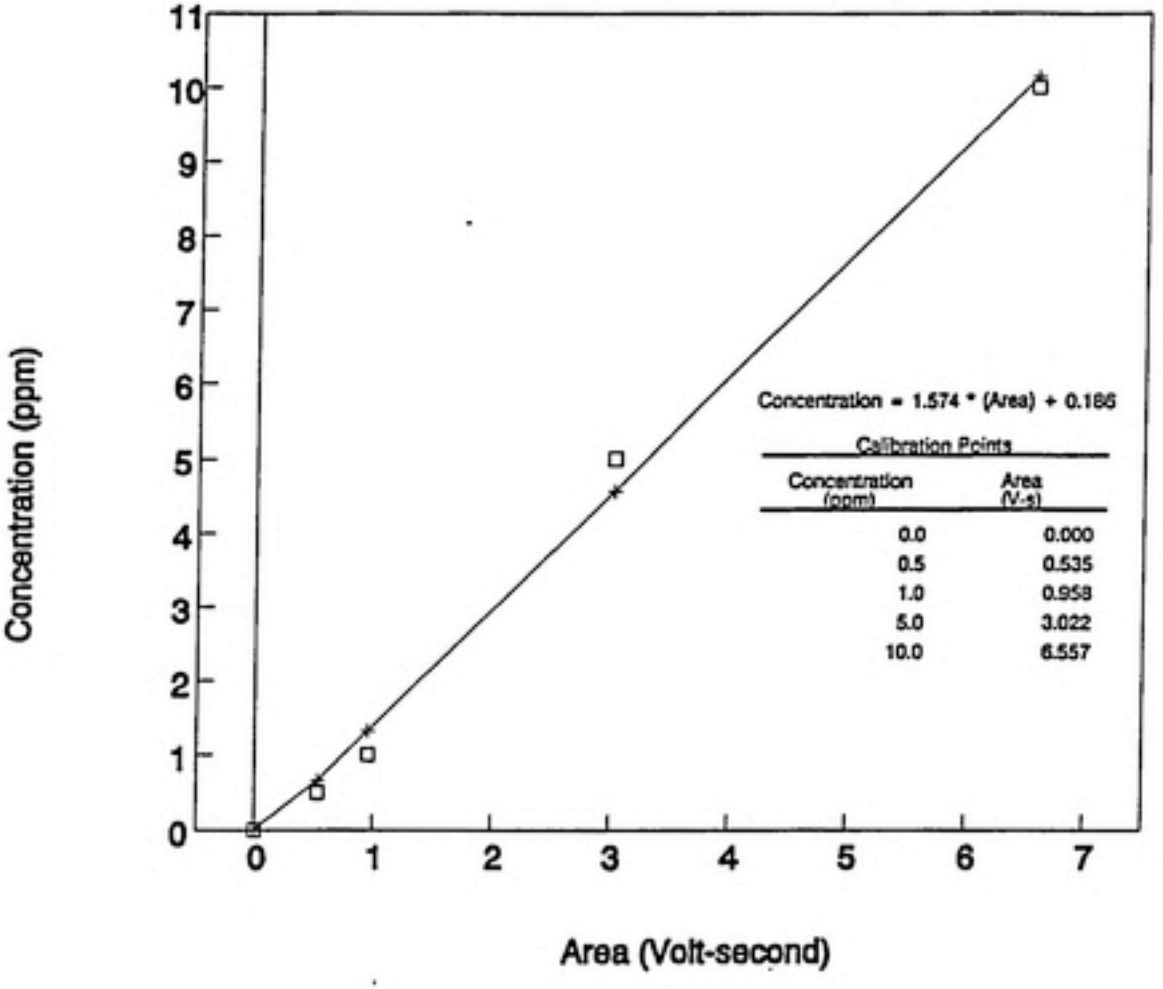
GAIN = 20



APPENDIX C-5

PERCHLOROETHYLENE CALIBRATION CURVE

GAIN = 2



APPENDIX D-1

AUTOCORRELATION COEFFICIENT PROGRAM
written by Gary W. Thomas

```
1 REM  PROGRAM WILL CALCULATE AUTOCORRELATION COEFFICIENTS
5 KEY OFF:SCREEN 0:COLOR 0,7,9
10 CLEAR:DIM X(50),R(50),D(50)
20 CLS:TOTAL = 0:R1=0:XT=0:XK=0:XT2=0
30 LOCATE 2,10:INPUT "Name of List - ";N$
40 LOCATE 4,10:INPUT "Enter the # of variables - ";T
50 FOR C = 1 TO T
55 LOCATE 6,10
60 PRINT "Variable";C;"is - ":LOCATE 6,26:INPUT " ";X(C)
65 LOCATE 6,26:PRINT "      "
70 TOTAL = TOTAL + X(C):MEAN = TOTAL/T
90 NEXT C
100 CLS:LOCATE 10,15
110 PRINT " Lag calculations in process - Please wait"
120 FOR C1 = 1 TO T
130 XT2=XT2+(X(C1)-MEAN)^2
140 NEXT C1
150 FOR L=1 TO (T-1)
160 FOR C = 1 TO (T-L)
170 B=C+L
180 XT= X(C)-MEAN:XK=X(B)-MEAN:R1=R1+(XT*XK)
190 NEXT C
200 R(L) = (R1*T)/(XT2*(T-1))
210 R1=0:XT=0:XK=0
220 NEXT L
235 CLS:LOCATE 8,25:PRINT"Computations are complete"
240 LOCATE 12,15:INPUT "Make sure printer is on and then
    push <return>";ANS$
250 LPRINT "     ";N$:LPRINT:LPRINT "           R";"
Lag value"
260 FOR L = 1 TO (T-1)
270 LPRINT "          ";L;"    ";R(L)
280 NEXT L
290 INPUT "Do you want to calculate 1/At";ANS$
300 IF ANS$="n" THEN 500 ELSE
310 PRINT "The lag factor, r(";1;") is ";R(1)
320 INPUT "Enter the first elimination rate ";K(1)
330 INPUT "Enter the second elimination rate ";K(2)
340 INPUT "Enter the time between samples ";T
350 B=LOG(R(1))/-T:REM Air exchange rate
360 LPRINT "The air exchange rate is ";B
370 FOR C= 1 TO 2
380 P1 = 1-EXP(-K(C)*T):P2=1+EXP(-K(C)*T)
390 P3 = 1+EXP(-(K(C)+B)*T):P4 = 1-EXP(-(K(C)+B)*T)
400 AT = SQR(P1*P3/(P2*P4))
410 LPRINT "1/At is = ";AT;" for the elimination rate
```

```
    k(";C;") of ";K(C)
420 NEXT C
430 INPUT "Do you wish to enter another data set (y/n)";ANS$
440 IF ANS$="y" THEN GOTO 10 ELSE END
500 KEY ON:COLOR 7,0,0:CLS:END
```

APPENDIX E

Photovac Model 10S50 Event Settings

Event	On	Off
Sample	0	10
Cal	0	10
3	10	250*
4	0	10
5	20	250*
6	0	0
7	0	0
8	0	0

* This setting represents the maximum time for analysis set by the programmer.

Note: Settings are determined by the programmer.

Gain Settings

	Ambient	Breath
Ethyl Acetate	5	20
Methylene Chloride	5	20
Perchloroethylene	2	2