RELEASE OF ETHANOL TO THE ATMOSPHERE DURING USE OF CONSUMER CLEANING PRODUCTS

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ABSTRACT

Liquid laundry and dishwashing detergents contain volatile organic compounds, including ethanol. Because of the role of such compounds in urban, photochemical air pollution, these detergents are a potential target of regulations aimed at improving air quality. However, the fate of ethanol in liquid detergents is not known. The objective of this study was to measure the release of ethanol to the atmosphere during simulated household use of liquid detergents. Three experimental runs, plus a blank, were conducted in a 20-m^3 environmental chamber for each of four conditions: "typical" dishwashing (DT), "high-release" dishwashing (DH), "typical" laundry (LT), and "high-release" laundry (LH). Measurements of airborne ethanol concentration as a function of time were interpreted by means of a single-chamber model to determine the emission of ethanol to the atmosphere for each run. Average amounts of ethanol transferred to the atmosphere per use (and the fraction of ethanol used so liberated) were 32 mg (0.038) for DT, 100 mg (0.049) for DH, 18 mg (0.002) for LT, and 110 mg (0.011) for LH. Thus, a large fraction of the ethanol added to wash solutions with liquid detergents is discharged to the sewer rather than transferred to the atmosphere during use.

INTRODUCTION

Despite considerable effort throughout the past two decades, many urban areas in the United States remain out of compliance with federal air quality standards. Of the pollutants that are regulated, ozone is most frequently found at concentrations that exceed federal standards. Ozone is formed in the atmosphere by photochemical reactions involving nitrogen oxides and hydrocarbons. To control urban ozone concentrations, emissions of hydrocarbons and/or of nitrogen oxides must be reduced.

Early efforts to control ozone focused on reducing emissions from sectors of human activity that were the largest contributors to hydrocarbon and nitrogen oxide emissions. These sectors included internal combustion engines for transportation, heavy industrial processes, electric utilities, and refining and delivery of petroleum products. As the most cost-effective control

measures for these sectors are now in place, attention has recently been directed to smaller, and often less obvious sources of hydrocarbon emissions.

Ethanol is a volatile organic compound (VOC) that can serve as a precursor of ozone. Potential emissions of ethanol into the atmosphere are large. For example, a byproduct of the action of yeast cultures in bread dough is the production of ethanol. Recently, a ruling was issued in the San Francisco Bay Area that will require the installation of control devices in five large bakeries to reduce ethanol emissions by an estimated total of a metric ton per day. During the research described in this report, it was discovered that bread liberates substantial amounts of ethanol even after baking (see Appendix).

Ethanol also is used as a solvent in liquid laundry and dishwashing detergents, constituting as much as 10% of the mass of these products. Because of a large usage rate of these products in areas that are currently out of compliance with ozone standards, these detergents are a potential target for regulations to reduce the emissions of ethanol and other VOCs into the atmosphere.

A key issue in the deliberations concerning whether or not to regulate these products is the fate of ethanol and other volatile compounds that are present in the detergents. Among the possible fates are release to the atmosphere during product use, release to the atmosphere from sewers and sewage treatment plants, and biodegradation (to carbon dioxide and water in the case of ethanol) in sewers and sewage treatment plants. Clearly, VOCs in detergents have a potential for urban air pollution impact only to the extent that they are emitted to the atmosphere rather than being biodegraded to carbon dioxide and water.

The goal of the research presented in this report was to measure the release of ethanol to the atmosphere during ordinary use of liquid laundry detergents and liquid hand dishwashing detergents. The experiments were conducted in a laboratory under controlled, simulated use conditions. The results are reported in terms of (1) mass of ethanol released to the atmosphere per use and (2) the fraction of ethanol added to the wash solution that escapes to the atmosphere during use. The results demonstrate that a large majority of the ethanol in these products is discharged with the wastewater, rather than being released to the atmosphere during use.

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EXPERIMENTAL PROTOCOLS

All experiments were conducted in a 20-m^3 environmental chamber at Lawrence Berkeley Laboratory. The interior surfaces of the chamber are stainless steel. Three oscillating fans were operated continuously to insure thorough mixing of the chamber air. To avoid enhancing the transfer of ethanol from water to air, these fans were placed and oriented to avoid producing a noticeable draft at the washing site. Air exchange to the chamber was controlled with a filtered ventilation system and measured with a turbine flow meter. Air-exchange rate was also determined by means of monitoring the decay of tracer gas concentration, sulfur hexafluoride, as described in a subsequent section.

For both dishwashing and laundry detergent experiments, three runs were executed under each of two sets of conditions. Target characteristics for these conditions are given in Table 1 for the dishwashing detergent and in Table 2 for the liquid laundry detergent. These characteristics were specified by the research sponsor based on studies of consumer habits. The "typical" characteristics were selected to represent the most prevalent use habits; "high release" characteristics were selected to increase the potential for ethanol release while remaining within the range of consumer habits. For each set of conditions an additional "blank" run was conducted. The protocol and measurement procedures in the blank runs were identical to those of the experimental runs except that no detergent was used for the blanks.

Each run is designated by a three-character code. The first letter denotes dishwashing (D) or laundry (L). The second letter denotes typical conditions (T) or high-release conditions (H). The third character denotes either a blank run (B) or the number (1-3) of the detergent run.

The detergents used in the experiments were prepared by the Procter and Gamble Company for the purpose of this study. Information on the constitution of these detergents is given in Table 3. These samples contain formula components at levels that are representative of commercially available products. The ethanol content of the detergents was verified by gas-chromatography measurements in our laboratory.

Dishwashing

In each run, an assortment of plates, cups and glasses was washed by hand in a plastic basin, using a cotton cloth. The dishes were rinsed in a separate basin.

The basic sequence of events was as follows:

1) Calibrate instruments.

2) Monitor background concentration of ethanol in chamber (20-30 min.).

3) Enter chamber, inject sulfur hexafluoride tracer gas.

4) Begin to fill wash basin, add detergent aliquot, then continue filling wash basin.

5) (High-release conditions only) Soak dishes for one hour.

6) Begin washing. Continue washing until 10 minutes has elapsed from the addition of the detergent (typical conditions) or from the beginning of washing (high-release conditions).

7) Collect sample of wash water.

8) Drain wash basin, then drain rinse basin.

9) Exit chamber.

10) Continue monitoring chamber air for approximately 100 minutes.

11) Recalibrate instruments.

The chamber was exited after the basin was filled and re-entered for the wash period. The opening and closing of the chamber door during the run had no appreciable effect on species concentrations in the chamber, based on inspection of the tracer-gas data. The concentration traces show no signs of abrupt discontinuities associated with either entering or exiting the chamber.

For the runs conducted under typical conditions, a solid stream of water was used for the rinse. For the runs conducted under high-release conditions, a spray was used. In both cases the water was turned on and off for each rinsed dish. Water was supplied to the chamber from a circulating water bath with an adjustable thermostat and a pump capable of delivering approximately 4 L min^{-1}. The water was removed from the basins with a large peristaltic pump.

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Both basins and the wash rag were removed from the chamber at the end of the wash. The dishes were left in the chamber.

Laundry

The laundry experiments were carried out in the same chamber as the dishwashing experiments using the same ventilation system and mixing fans.

A used General Electric washing machine was purchased and installed in the chamber. Water was supplied to the washer through access ports using garden hose. The machine was drained into a plastic utility tub, which was emptied to a drain outside of the chamber by means of a peristaltic pump. A single assortment of clothing and towels was used for each experiment. The bundle weighed 3.1 kg dry and contained both natural and artificial fibers. For each run, the machine was set for normal wash and spin speed and for high water level. The wash cycle for each run was set for 9 minutes.

The sequence of events for all runs was the same:

1) Calibrate instruments.

2) Monitor background concentration of ethanol in chamber (20-30 min.).

3) Enter chamber, and inject sulfur hexafluoride tracer gas.

4) Start fill cycle, then add detergent aliquot.

5) Add clothing bundle.

6) After the wash cycle and before the first spin cycle, collect a wash water sample.

7) Exit chamber at completion of the final spin. Leave clothing in the machine with the lid down.

8) Continuing monitoring for approximately 100 minutes.

9) Recalibrate instruments.

MEASUREMENT TECHNIQUES

Ethanol in Air

Airborne ethanol concentrations were measured with a Miran 1A variable path length infrared spectrophotometer. The wavelength was initially set to 9.5 μm; then the absorption was maximized by adjusting the cell path length and the wavelength setting. Maximum absorption was observed at a wavelength of 9.45 μm and a path length, according to the instrument's dial, of 21.3 m. Chamber air was drawn from the chamber and through the infrared analyzer by means of a metal bellows pump. All sampling lines were made of Teflon. The analog output of the spectrophotometer was measured either manually by means of a Keithley voltage meter equipped with a digital display or automatically by means of a Keithley data acquisition system.

The infrared analyzer was calibrated for ethanol response using gas standards created in 2-L glass bulbs equipped with septa. A closed loop of known volume was made by connecting the inlet and outlet of the pump to the inlet and the outlet of the analyzer. Aliquots containing a known amount of ethanol were withdrawn from the bulb with a gas-tight syringe and injected into the infrared analyzer through a septum in the pump. Standard concentrations were adjusted so that the amount of ethanol in a 1 cm^3 aliquot would yield a volume fraction (moles of ethanol per mole of air) of either 0.25 parts per million (ppm) or 0.5 ppm in the analyzer. Sequential injections of such aliquots provided a stepwise increase in concentration. Calibration data consisted of a set of measured voltages, each corresponding to a certain level of light absorption, versus prescribed ethanol volume fractions in the analyzer air. The response of the instrument was observed to be linear over the range of interest for these experiments (see Figure 1.)

The baseline voltage of the analyzer was observed to drift significantly with time. This baseline drift was monitored during the experiments to permit subsequent correction of the experimental data. At the beginning of each run, the zero offset voltage of the analyzer was adjusted while dry, compressed air, free of ethanol, was passed through the analyzer. At intervals

during the course of the run, the same source of air was used to purge the ethanol from the analyzer and the output voltage of the instrument was recorded.

To verify that the infrared analyzer response was due to ethanol and not some other species, air samples from a blank and an experimental high-release laundry run were loaded onto sorbent tubes and analyzed by gas chromatography-mass spectroscopy (GC-MS) after the method of Hodgson and Girman (1989). The ethanol was concentrated by sampling from the air space above the surface of the wash water, with the lid of the machine sealed with duct tape to reduce the air exchange rate. A mass-flow controller was used to accurately measure the volume of the sampled air. The analyses clearly showed that, as expected, ethanol was the dominant species released to the air in the experimental run. Ethanol was not detected in the blank sample.

Water Vapor

Water vapor is an effective absorber of infrared radiation. In each run in this experiment, the water vapor content of the chamber air increased during the washing activities. Thus, to accurately determine ethanol release to the chamber air, it is necessary to make a correction for the effect of water vapor on analyzer response. To this end, an EG&G Model 911 Dew-All cold mirror hygrometer was placed immediately downstream of the infrared analyzer. The hygrometer response was either recorded manually from the digital readout of the instrument, or automatically, by sampling its analog output voltage with a Keithley data acquisition system.

The infrared analyzer was calibrated for water vapor response using the arrangement shown in Figure 2. Air was humidified to a specified level by blending an adjustable flow rate of dry air with a second portion that was passed through a bubbler filled with water at a controlled temperature. The mixture was then supplied to the infrared analyzer and the hygrometer. After steady readings for each instrument were obtained, the dew point determined by the hygrometer and the corresponding output voltage of the infrared analyzer were recorded. The blend of dry and wet air was changed to obtain another humidity value. By taking measurements at three or four different points a calibration curve could be constructed. The dew point readings were converted

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to partial pressures of water to give an absolute measurement of the amount of water vapor present in the air. The response of the infrared analyzer was linear with changes in water vapor content of the air, as shown in Figure 3.

In interpreting data from the experimental runs, measurements from the infrared analyzer were corrected for response to water vapor, based on the dew point hygrometer readings. The ethanol concentrations were then determined by applying the calibration curves to the residual absorption voltage. This procedure is appropriate if the response of the infrared analyzer to a mixture of water vapor and ethanol is the sum of its responses to the water vapor and ethanol separately. To test whether the instrument response could be so described, an experiment was conducted in which the infrared analyzer was calibrated against ethanol concentration at several varying values of humidity. This test showed, as illustrated in Figure 4, that the response of the infrared analyzer to a mixture of water vapor and ethanol could be treated as a linear superposition of the responses to the gases individually.

Tracer Gas Concentration

During these experiments, the air-exchange rate of the chamber was determined by two independent methods. In one method, the rate at which air was supplied to the chamber was measured by means of detecting the rate of rotation of the calibrated fan. The air-exchange rate was then obtained by dividing the air flow rate by the measured chamber volume. The second method was the tracer-gas decay method (ASHRAE, 1985), with sulfur hexafluoride serving as the tracer gas.

Sulfur hexafluoride (SF_6) measurements were made using a Baseline Industries gas chromatograph (GC) equipped with a Valco Instrument Company electron capture detector (ECD). A peristaltic pump provided a continuous flow of chamber air to the GC sampling loop. A timer-controlled valve was switched, once per minute, to direct the contents of the sampling loop onto the GC column. The ECD signal was monitored with a chart recorder. Peak heights, which

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corresponded to minute-by-minute samples of the SF_6 concentration in air, were measured manually.

The GC was calibrated against standard compressed-gas mixtures of SF_6 in air, obtained from Scott Speciality Gases and transferred to gas-tight bags from which the GC sampled. A third standard was created by diluting one of the primary standards with SF_6-free air in a 250 mL gas-tight syringe. To assure constant pressures in the sampling loop, the calibration gas samples were delivered to the GC sampling loop with the peristaltic pump used for sampling the chamber air.

Ethanol in Wash Water

Samples of wash water were collected in EPA sampling vials, sealed with Parafilm and refrigerated prior to analysis. Ethanol content was measured using a Varian 3700 gas chromatograph with a J&W DBWax capillary column and a flame ionization detector. Undiluted aliquots of the wash water samples were injected directly onto the column through a heated glass-lined injector. The GC signal was integrated with a Nelson Analytical Model 2600 Chromatography Software system.

The GC was calibrated using a dilution standard of pure ethanol in deionized water. The average of replicate injections of different volumes of the standard were used to construct an ethanol response curve.

Column temperatures of 45-50 °C provided good resolution of the ethanol peak with short retention times. Water accumulation in the column tended to retard the eluted ethanol peak over time. By increasing the column temperature to above 100 °C after every third or fourth run, this potential problem was avoided. When wash water samples were analyzed, the column temperature was increased to 180 °C after every third or fourth run to remove the high boiling point compounds present in the detergent along with the excess water.

Temperature Measurements

Air temperatures in the chamber were measured either with a pair of thermocouples monitored automatically by a Keithley data acquisition system or manually with a YSI Series 700

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thermistor connected to a Digitec Model 5831 electronic thermometer. The thermocouples were calibrated using a mercury thermometer traceable to the National Bureau of Standards. The probes were suspended from the ceiling of the chamber.

Wash water temperatures in the dish detergent experiments were measured with a submersible YSI Series 700 thermistor placed directly in the wash basin. The thermistor was connected to the same Digitec thermometer used for the air temperature measurements. The inlet and rinse water temperatures were taken to be the same as the temperature of the water bath that fed them.

Wash and rinse water temperatures in the laundry detergent experiments were measured with the same submersible thermistor lowered into the machine through a hole in its lid. The probe was removed from the machine during spin cycles to avoid damage. The inlet temperature was measured by holding a probe in the stream of water entering the machine.

DATA ANALYSIS

The mass of ethanol liberated to the atmosphere from use of the detergents was determined from the profiles of ethanol and SF_6 concentrations versus time. The chamber was represented as a well-mixed chemical reactor (Shair and Heitner, 1974), with the species treated as being chemically inert. Prior to the beginning of the experiment, an aliquot of SF_6 was released in the chamber air and mixed to a uniform concentration. For subsequent times, the time rate of change of ethanol and SF_6 concentrations in the chamber are described by the following equations, based on a material balance:

$$\alpha \frac{dC_e}{dt} = \varepsilon_e - \alpha\, C_e \frac{Q}{V} \tag{1}$$

$$\frac{dC_s}{dt} = -\, C_s \frac{Q}{V} \tag{2}$$

where C_e and C_s are the ethanol and sulfur hexafluoride concentrations (more properly: mole fractions) in parts per million (ppm), Q is the flow rate of fresh air through the chamber (m^3 min^{-1}), V is the chamber volume (20 m^3), t is time, and ε_e is the rate of release of ethanol from the washing activity into the room (g min^{-1}). The coefficient α is needed to convert from a gas concentration in ppm to an emission rate in g min^{-1}. Its value is given by

$$\alpha = 10^{-6} \frac{PV}{RT} MW_e \qquad (3)$$

where P is the barometric pressure (atm), R is the gas constant (82.06×10^{-6} atm m^3 mol^{-1} K^{-1}), T is the air temperature (K), and MW_e is the molecular weight of ethanol (46 g mol^{-1}).

The experiments were conducted under conditions in which the parameters Q, T, and P are approximately constant. Under such conditions, equation (2) can be integrated to yield

$$\ln [C_s(t)] = \ln [C_s(0)] - \frac{Q}{V} t \qquad (4)$$

Where ln[ ] represents the natural logarithm of the parameter in brackets. Measurements of the natural logarithm of the SF_6 concentration were plotted as a function of time for each experimental run (Figure 5). From equation (4), it can be seen that the slope of the resulting line yields the air flow rate through the chamber (Q) normalized by the chamber volume (V).

The total emission of ethanol (E, units: g) from the washing activity to the atmosphere is defined as the integral of the emission rate over time:

$$E = \int_0^\tau \varepsilon_e(t) \, dt \qquad (5)$$

where τ is the duration of the experimental run. The relationship between the total emission of ethanol and the ethanol concentration profile is obtained by integrating equation (1), with the result

$$E = \alpha \left[\left\{ \frac{Q}{V} \int_0^\tau C_e(t) \, dt \right\} + \left\{ C_e(\tau) - C_e(0) \right\} \right] \qquad (6)$$

or

$$E = \alpha \left[\frac{Q}{V} \overline{C_e} \, \tau + C_e(\tau) \right] \qquad (7)$$

where $\overline{C_e}$ represents the time-weighted average concentration of ethanol for the duration of the experimental run, and $C_e(\tau)$ represents the concentration of ethanol remaining in the chamber air at the end of the run. In obtaining equation (7) from equation (6), it is assumed that the ethanol concentration is zero at the beginning of the run.

The average ethanol concentration, $\overline{C_e}$, was determined by summing, over the entire run, the product of the measured concentration and the time interval about which it was centered, then dividing the sum by the period of the run. The final ethanol concentration, $C_e(\tau)$, was determined from the measured air-exchange rate, Q/V, and measured peak ethanol concentration, C_p, according to the expression

$$C_e(\tau) = C_p \exp[- \frac{Q}{V} (\tau - t_p)] \qquad (8)$$

The term in equation (7) involving $C_e(\tau)$ is generally much smaller than the term involving $\overline{C_e}$, so any inaccuracy in determining $C_e(\tau)$ has a diminished effect on the accuracy of determining E.

The other parameters on the right-hand side of equation (7) were determined for each run in this manner. The volume of the chamber, V, was taken to be 20 m^3, based on measurement of its dimensions. The barometric pressure, P, was measured during each run at the chamber site. The time-weighted average air temperature measured in the chamber was used for T. Values of T and P for each run are given in Table 4. The air-exchange rate (Q/V) was obtained as the slope of the linear regression of ln[SF$_6$ concentration] vs. time. Values of Q/V for each run are presented in

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Table 5. Where a range of values in given, the mean of the upper and lower limit was used in the analysis. The tracer gas decay results are seen to be in excellent agreement with the volume-normalized flow rate measurements. The duration of the experiment, τ, was defined to be the time from the addition of detergent to the wash solution to the termination of sampling.

The recorded data from the infrared analyzer were in the form of voltage as a function of time. The ethanol concentration as a function of time ($C_e(t)$) was determined by applying several conversions or corrections to the voltage readings. First, all of the readings were corrected for drift in analyzer response to dry gas, free of ethanol. A piecewise linear function that passed through each of the observations was used for interpolation. A correction for response to water vapor was then applied to each of the voltage readings during the experimental run. This correction was determined from pre-run and post-run calibrations of the infrared analyzer response to water vapor (see Figure 3 for an example). Linear interpolations in time were applied to determine the slope and intercept of the water-vapor response function appropriate for each sampling point. The water vapor content at each instant was determined from the dew-point hygrometer reading. The residual voltage from the infrared analyzer was taken to be a response to ethanol. The concentration was determined from this residual voltage by applying data from the pre-run and post-run calibrations of the analyzer to ethanol (see Figure 1 for an example). Again, linear interpolations in time were applied to determine the slope and intercept of the analyzer response to ethanol appropriate for each residual voltage. Finally, the ethanol concentrations in each run were all adjusted for baseline offset by adding to the reading a constant (positive or negative) concentration as necessary to make the mean ethanol concentration zero during the 20-30 minute background concentration period. This final correction is based on the assumption that the ethanol concentration is zero prior to an experimental run.

The quantitative model described by equation (7) for relating the emission rate to the concentration data is valid only if ethanol released in the chamber does not react significantly, either homogeneously or on surfaces. The hypothesis that this model is appropriate was tested by comparing the rates of decay of ethanol and SF_6 concentrations after the completion of washing

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activities for each of the high-release runs. The ethanol concentration-decay profiles are depicted along with those for SF_6 in Figures 5b and 5d. The mean rate of decay of ethanol concentrations for the six runs (1.19 ± 0.18 h^{-1}) was the same as the mean rate of decay of SF_6 concentrations (1.21 ± 0.07 h^{-1}). This is strong evidence demonstrating that gas-phase ethanol can be considered to be chemically inert for the purposes of this study.

RESULTS AND DISCUSSION

Table 4 summarizes the results of temperature, humidity, and barometric pressure measurements for each experimental run. For the water temperatures, wherever a range of values is given, the first number corresponds to the beginning of the appropriate period and the last number corresponds to the end. For each experimental condition, except LH (high-release laundry), the inlet water temperature was set to be within the upper half of the specified range. For LH, the maximum water temperature that was available in the laboratory was used. During washing activity, the water temperature tended to cool. No effort was made to maintain the temperature within the target range.

For air temperature and dew point, the range of values reported in Table 4 correspond to the minimum and maximum measured values during each run. Both parameters tended to increase during the use of warm or hot water, then decrease after the wash period was completed. These parameters are within a range considered reasonable for indoor environments.

The measured air-exchange rate for each run is reported in Table 5. The values are within the range observed for residential buildings (Nazaroff et al., 1987).

Figure 6 shows the ethanol concentration profiles for each run. In each frame of this figure, the vertical axis represents the ethanol concentration in the chamber. The horizontal axis represents time, referenced to an arbitrary initial point. The traces begin with the period of background check of the chamber. The time at which the washing activity begins is given by the first number in the "Time" column of Table 6. It corresponds to the initial rapid rise in ethanol concentration observed in each of the traces from non-"blank" runs.

From the data presented in Figure 6, the time-weighted average ethanol concentration, $\overline{C_e}$, and the final ethanol concentration, $C_e(\tau)$, were computed. These parameters are presented in Table 6, along with other data needed to compute, from equation (7), the emission, E, of ethanol to the atmosphere.

The blank runs show a tendency to yield a negative average ethanol concentration. This tendency is probably an artifact of the correction of the infrared analyzer for water vapor content. The impact of this tendency on the interpretation of the results is not large.

Among the non-blank runs, three of the traces—all for typical conditions—possess unusual features. For DT2, the ethanol concentration apparently jumps suddenly by about 0.25 ppm at t=125 minutes and remains high for about 40 minutes before returning to a value that follows the previous trend. Although this behavior coincides with the sampling line falling suddenly from its normal position, the reason for the perturbation remains unknown. In interpreting the data from this run, the experimental period was terminated at t=110 minutes, before the perturbation.

For runs LT1 and LT2, the measured ethanol concentration drops substantially below zero at the end of each run. The data from these runs were interpreted to yield both minimum and maximum estimates of the total emission of ethanol (see Table 6). For the minimum estimate, the apparent zero from the monitor was considered to be the baseline and the experimental run was assumed to end when the measured concentration fell below zero. For the maximum estimate, the mean value for the level-concentration period at the end of the run was assumed to represent zero ethanol, and the concentrations were determined with respect to this baseline (horizontal dashed lines in Figure 6c). The mean of the minimum and maximum estimates for each of these runs is reported in Table 7.

The emission of ethanol to the atmosphere from washing activities is summarized in Table 7 and Figure 7. The first column in Table 7 identifies the experimental run. The second column reports the mass of ethanol added to the wash water, based on the mass or volume of detergent added and the mass fraction of ethanol in the detergent as reported in Table 3. The third column reports the mass of ethanol discharged to the sewer with the wash water as it is drained. These

data are based on measurements of the volume of water discharged and gas-chromatographic analysis for ethanol content of water samples collected while the water was draining. The fourth column gives the ratio of the numbers in the third and second columns, thereby representing the measured fractional discharge of ethanol to the sewer. These data, which are entirely independent of the measured concentration of ethanol in air, indicate that 90% or more of the ethanol added to the wash water is discharged to the sewer.

The fifth column in Table 7 gives the mass of volatilized ethanol from washing activities during each run, transcribed from the final column of Table 6. The mean value for the four conditions considered ranges from 18 mg for a typical laundry load to 110 mg for a laundry load under high-release conditions. For dishwashing, a single episode under typical conditions liberates, on average, 32 mg of ethanol to the atmosphere, whereas under high-release conditions, 100 mg is released. The sixth column of Table 7 gives the fractional release of ethanol to the atmosphere, i.e., the ratio of the mass of volatilized ethanol to the mass of ethanol added to the wash solution. The data in this column and in the previous column are not corrected for the results of the blank runs. The final column in Table 7 represents the sum of the data in columns four and six, i.e. the fraction of ethanol added to the wash water that is accounted for by measurements of ethanol released to the atmosphere and ethanol discharged to the sewer. Thus, this column gives an overall indication of the precision and accuracy of the experiment. Considering the twelve runs independently, the mean total recovery (± one standard deviation) is 0.96±0.06, compared with a value of 1.00±0.00 for a perfect experiment.

Figure 7 depicts the fraction of ethanol released to the atmosphere for the four conditions. Four points are shown for each case: (1) the minimum, (2) the mean, and (3) the maximum value corresponding to the sixth column in Table 7; and (4) the maximum value from Table 7 with a correction applied for the blank run. The scatter in the points is a reflection of both experimental uncertainty and variation in the release rate due to details of the runs that were uncontrolled. One source of measurement uncertainty results from the low ethanol concentrations in the chamber air.

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The ethanol concentration during the experimental runs often was comparable in magnitude with the detection limit of the infrared analyzer (0.1 ppm), particularly for typical use conditions.

The results show consistently and clearly that a very small fraction of the ethanol contained in liquid laundry detergents is liberated to the atmosphere during a washing machine cycle. For a typical load, only 0.2% on average and a maximum (blank adjusted) of 0.4% is released. For high-release conditions, an average of 1.1% and a maximum (blank adjusted) of 1.4% of the ethanol added to the wash water is liberated. For dishwashing, the liberated fraction is higher, but still small. For activities corresponding to washing a single load of dishes, under typical conditions, 3.8% on average and a maximum (not blank adjusted) of 4.9% is released. For high-release conditions, 4.9% on average and a maximum (blank adjusted) of 6.6% is volatilized.

The differences in fractional release of ethanol from one set of washing conditions to another appears to be a result of two primary factors: (1) temperature and (2) degree of agitation of the wash solution. The effect of agitation can clearly be seen in the high-release dishwashing runs. The traces each show two sharp rises in ethanol concentration. The first occurs when detergent and water are first added to the wash basin. The second occurs after the soaking period when active washing begins. The effect of temperature is evident from the large increase in ethanol release in the laundry runs for high-release conditions compared with typical conditions. The only differences between these two conditions are the temperatures of the wash and rinse water. Smaller differences in fractional release are observed between high-release and typical conditions for the dishwashing runs, probably because of the long soak period under high-release conditions, during which the wash water cools substantially.

It remains to determine what happens to ethanol from detergents once the used wash water is discharged to the sewer. Although it is possible that a significant fraction is transferred to the atmosphere, it seems unlikely that this fraction is high because of the relatively low temperatures in sewer lines and wastewater treatment plants, and because of the competing effect of biodegradation. If the largest release of ethanol from detergents to the atmosphere occurs during

use, then the impact of ethanol-containing detergents on urban air quality is only a small fraction of that which would result from complete volatilization.

APPENDIX

At the outset of this project, we planned to conduct the experiments *in situ* in a private apartment. Preliminary runs were carried out on location in the same fashion as the chamber runs described in the body of the report, but attempts to measure the ethanol release were severely hampered by background interference. All obvious sources of ethanol (i.e., cleaning products, detergent, empty beer cans, etc.) were removed from the premises, but the background signal persisted and we eventually decided to move to the laboratory where conditions could be more rigorously controlled. A serendipitous discovery during these initial trials suggested that bread is a significant source of ethanol in indoor air. Subsequent experiments confirmed this initial finding.

To estimate the amount of ethanol in bread, the following experiment was conducted. A one-gallon paint can was fitted with inlet and outlet ports mounted to its lid. Dry air from a compressed-air cylinder was supplied to the inlet of the paint can, and the outlet port was connected to the infrared analyzer. With the dry air flowing, the output voltage of the infrared analyzer was adjusted to zero in the same manner as for the chamber experiments. The infrared analyzer was calibrated in the manner described in the body of this report, using injections of pure ethanol instead of gas standards because of the high concentrations involved. The paint can was then opened briefly, a piece of bread of known mass was placed in it, and then the can was resealed. The gas stream passing through the paint can was then sampled for a period of a few hours. From exposure to the dry air, gases—including water vapor and ethanol—were released from the bread to the air stream. Because the system was closed, all the ethanol released by the bread was detected by the infrared analyzer. During the sampling periods, the response of the analyzer rapidly rose to a high peak value, then gradually decayed to the original baseline. The increase in water vapor content of the air stream due to drying of the bread could account for only a small fraction of the infrared analyzer's response. The remainder of the response is attributed to

TABLE 1. Prescribed use conditions for determining release of ethanol from liquid hand dishwashing detergents [a]

Parameter	Use Conditions [b]	
	Typical	High-release
Wash water temperature (°C)	43-46	52-57
Soak duration, with detergent (min)	0	60
Wash duration (min)	10	10
Detergent usage (mL)	15	37.5
Rinse method	running water	spray
Rinse water temperature (°C)	38-43	52-57

[a] Personal communication, M. J. Irwin, Procter and Gamble Company, 1989.
[b] Other specified conditions: Wash solution volume: 7.6 L; Agitation method: hand wash with cloth or sponge; Items to wash: mixed cups/glasses/plates.

TABLE 2. Prescribed use conditions for determining release of ethanol from liquid laundry detergents [a]

Parameter	Use Conditions [b]	
	Typical	High-release
Wash water temperature (°C)	32-38	52-57
Rinse water temperature (°C)	18-24	32-38

[a] Personal communication, M. J. Irwin, Procter and Gamble Company, 1989.
[b] Other specified conditions: Product usage: 110 mL; Washer type: General Electric (any age) or Kenmore/Whirlpool (more than three years old); Wash cycle selection: normal; Wash Water Fill Volume Selection: medium (for "large capacity" washer) or full (for "normal capacity" washer); Laundry bundle: 2.7-3.2 kg of mixed fibers; Washer drainage: stationary tub; Order of addition: detergent first, laundry second, and water third.

TABLE 3. Composition (mass fraction) of liquid detergents [a]

Compound	Detergent	
	Laundry	Dishwashing
Solvents		
Ethanol	0.085	0.054
Monoethanol amine	0.02	0
1,2-Propanediol	0.04	0
Surfactants		
anionic, nonionic, cationic	0.25-0.30	0.30-0.35
Builders		
soaps, citrates	0.10-0.15	0
Stabilizers		
hydrotropes, formates, etc.	0.01-0.04	0.01-0.04
Other		
Water	0.35-0.40	0.55-0.60
minor ingredients (each)	trace	trace

[a] Personal communication, M. J. Irwin, Procter and Gamble Company, 1989.

TABLE 4. Measured water and air temperatures, dew point and barometric pressure during experiments [a]

Run	Temperatures (°C)				Dew point (°C)	Baro. Press. (atm.)
	Inlet water	Wash water	Rinse water	Air		
Dishwashing: Typical (DT)						
DTB[b]	46.1-43.9	46.1-40.5	46.1-43.9	23.3-25.4 (24.7)	8.9-14.1	0.976
DT1	44.5-42.0	44.5-39.5	44.5-42.0	21.6-23.5 (22.9)	8.4-13.6	0.979
DT2	44.6-42.8	44.6-40.5	44.6-42.8	23.6-26.3 (25.1)	10.7-15.0	0.979
DT3	44.6-42.2	44.6-40.5	44.6-42.2	22.8-25.6 (24.5)	12.8-17.5	0.976
Dishwashing: High-release (DH)						
DHB[b]	55.1	50.0-35.8 (41.7)	55.1	22.4-25.4 (24.7)	10.4-18.4	0.972
DH1	55.1	45.4-37.4 (38.5)	55.1	21.3-25.6 (24.1)	8.9-17.9	0.974
DH2	55.0	49.5-38.2 (41.3)	55.0	22.4-26.5 (25.2)	8.6-18.2	0.976
DH3	55.0	47.6-37.7 (42.0)	55.0	24.5-26.6 (26.2)	9.2-19.1	0.975
Laundry: Typical (LT)						
LTB[b]	36.1	33.4-33.4 (33.4)	22.1-23.3	21.5-23.7 (23.3)	10.8-13.9	0.972
LT1	36.2	32.9-32.9 (32.9)	22.5-22.7	20.8-23.4 (23.0)	10.5-13.3	0.974
LT2	36.1	32.9-32.9 (32.9)	23.1-23.2	20.7-23.5 (23.0)	10.1-12.4	0.975
LT3	35.6	31.9-32.0 (32.0)	22.2-22.3	19.6-22.2 (21.9)	10.0-12.6	0.972
Laundry: High-release (LH)						
LHB[b]	>50	>50-46	40	19.9-26.7 (25.2)	8.7-17.4	0.976
LH1	50.8	50.0-46.8 (47.6)	35.5-35.5	22.8-28.6 (27.2)	11.7-20.7	0.972
LH2	51.5	47.6-47.1 (47.3)	35.6-35.6	22.6-26.1 (24.5)	13.6-20.7	0.972
LH3	52.0	50.3-49.7 (50.0)	37.2-37.0	23.3-26.3 (25.7)	14.8-20.7	0.974

[a] Range of values given (with time-weighted mean in parantheses) whenever substantial variability occurred during experiment. Summary of experimental conditions: Dishwashing: Typical (10 min. wash, stream rinse, 15 mL detergent); Dishwashing: High-release (60 min. soak, 10 min. wash, spray rinse, 37.5 mL detergent); Laundry: Typical (warm wash, cold rinse, approx. 110 mL detergent, 9 minute wash, normal spin); Laundry: High-release (hot wash, warm rinse, approx. 110 mL detergent, 9 minute wash, normal spin); see also Tables 1 and 2.
[b] Blank run (no detergent used).

TABLE 5. Measured air-exchange rates in experimental chamber[a]

Run	Volumetric air flow rate per chamber volume (h^{-1})	Air-exchange by tracer-gas decay (h^{-1})
Dishwashing: Typical (DT)		
DTB[b]	2.0	2.3
DT1	2.0	2.1
DT2	2.0	2.1
DT3	2.0	2.3
Dishwashing: High-release (DH)		
DHB[b]	2.0	2.1-2.2
DH1	1.3	1.1-1.3
DH2	1.3	1.1-1.2
DH3	1.3	1.0-1.2
Laundry: Typical (LT)		
LTB[b]	1.3	1.2
LT1	1.3	1.3
LT2	1.3	1.2
LT3	1.3	1.3
Laundry: High-release (LH)		
LHB[b]	1.3	1.3
LH1	1.3	1.3
LH2	1.3	1.3
LH3	1.3	1.2

[a] See Tables 1, 2, and 4 for experimental conditions. Chamber volume = 20 m^3.
[b] Blank run (no detergent used).

TABLE 6. Data used for determining ethanol release to the atmosphere from use of detergents [a]

Run	Time (min)	τ (min)	Q (m³/min)	$\overline{C}_e$ (ppm)	C_p (ppm)	t_p (min)	$C_e(\tau)$ (ppm)	P (atm)	T (K)	E (g)
Dishwashing: Typical (DT)										
DTB[b]	26-134	108	0.77	0.017	—	—	—	0.976	298	0.003
DT1	36-137	101	0.70	0.243	0.71	16	0.036	0.979	296	0.033
DT2	34-110	76	0.70	0.204	0.58	12.5	0.063	0.978	298	0.022
DT3	38-190	152	0.77	0.192	0.64	14.8	0.007	0.976	298	0.042
Dishwashing: High-release (DH)										
DHB[b]	119-300	181	0.72	-0.095	—	—	—	0.972	298	-0.023
DH1	188-300	172	0.40	0.824	1.87	83	0.315	0.974	297	0.116
DH2	125-341	216	0.38	0.530	1.92	74	0.129	0.977	298	0.085
DH3	280-502	222	0.37	0.693	2.23	74	0.144	0.975	299	0.109
Laundry: Typical (LT)										
LTB[b]	122-281	159	0.40	-0.080	—	—	—	0.972	296	-0.009
LT1(min)	112-210	98	0.43	0.241	0.53	29	0.120	0.974	296	0.023
LT1(max)	112-290	178	0.43	0.287	0.75	29	0.030	0.974	296	0.042
LT2(min)	105-175	70	0.40	0.132	0.28	29	0.123	0.975	296	0.011
LT2(max)	105-267	162	0.40	0.094	0.35	29	0.025	0.975	296	0.012
LT3	112-276	164	0.43	0.066	0.27	26	0.014	0.973	295	0.009
Laundry: High-release (LH)										
LHB[b]	116-272	156	0.43	-0.065	—	—	—	0.976	298	-0.008
LH1	95-256	161	0.43	0.973	2.21	31	0.135	0.972	300	0.127
LH2	105-275	170	0.43	0.670	1.55	32	0.080	0.973	298	0.093
LH3	153-325	172	0.40	0.922	2.33	5	0.083	0.974	299	0.119

[a] See Tables 1, 2, and 4 for experimental conditions. Definition of column headings: Time (min)—start and end time for experimental run (referenced to an arbitrary starting time); τ (min)—duration of experimental run; Q (m³/min)—flow rate of air out of chamber; $\overline{C}_e$ (ppm)—time-weighted average concentration of ethanol during experimental run; C_p (ppm)—peak concentration of ethanol during run; t_p (min)—elapsed time during run at which peak ethanol concentration was recorded; $C_e(\tau)$ (ppm)—ethanol concentration at end of run (based on peak concentration and measured air exchange rate); P (atm)—barometric pressure; T (K)—mean air temperature in chamber during run; E (g)—total ethanol emission to atmosphere during experimental run.
[b] Blank run (no detergent used).

TABLE 7. Summary of ethanol release to the atmosphere from use of detergents [a]

Run	Ethanol added to wash solution (g) [b]	Ethanol discharged to sewer (g)	Fractional discharge of ethanol to sewer	Ethanol released to atmosphere (g)	Fractional release of ethanol to atmosphere	Fractional recovery of ethanol
Dishwashing: Typical (DT)						
DTB[c]	0	0	—	0.003	—	—
DT1	0.86±0.01	0.77	0.90	0.033	0.038	0.94
DT2	0.86±0.01	0.80	0.93	0.022	0.026	0.96
DT3	0.86±0.01	0.75	0.87	0.042	0.049	0.92
Mean	**0.86±0.01**	**0.77±0.03**	**0.90±0.03**	**0.032±0.010**	**0.038±0.012**	**0.94±0.02**
Dishwashing: High-release (DH)						
DHB[c]	0	0	—	-0.023	—	—
DH1	2.11±0.01	2.12	1.00	0.116	0.055	1.06
DH2	2.11±0.01	2.15	1.02	0.085	0.040	1.06
DH3	2.11±0.01	2.10	1.00	0.109	0.052	1.05
Mean	**2.11±0.01**	**2.12±0.03**	**1.01±0.01**	**0.103±0.016**	**0.049±0.008**	**1.06±0.01**
Laundry: Typical (LT)						
LTB[c]	0	0	—	-0.009	—	—
LT1	9.66	8.74	0.90	0.032	0.003	0.90
LT2	9.56	8.58	0.90	0.012	0.001	0.90
LT3	9.73	9.05	0.93	0.009	0.001	0.93
Mean	**9.65±0.09**	**8.79±0.24**	**0.91±0.02**	**0.018±0.013**	**0.002±0.001**	**0.91±0.02**
Laundry: High-release (LH)						
LHB[c]	0	0	—	-0.008	—	—
LH1	9.95	8.74	0.88	0.127	0.013	0.89
LH2	9.79	9.36	0.96	0.093	0.009	0.97
LH3	9.67	9.05	0.94	0.119	0.012	0.95
Mean	**9.80±0.14**	**9.05±0.31**	**0.93±0.04**	**0.113±0.018**	**0.011±0.002**	**0.94±0.04**

[a] See Tables 1, 2, and 4 for experimental conditions. Lines labelled "mean" give average±one standard deviation for the three sample runs without correction for blank runs.

[b] Uncertainty for dishwashing runs determined as the standard deviation of the mass of three aliquots of detergent delivered in the same manner as in the experimental runs.

[c] Blank run (no detergent used).
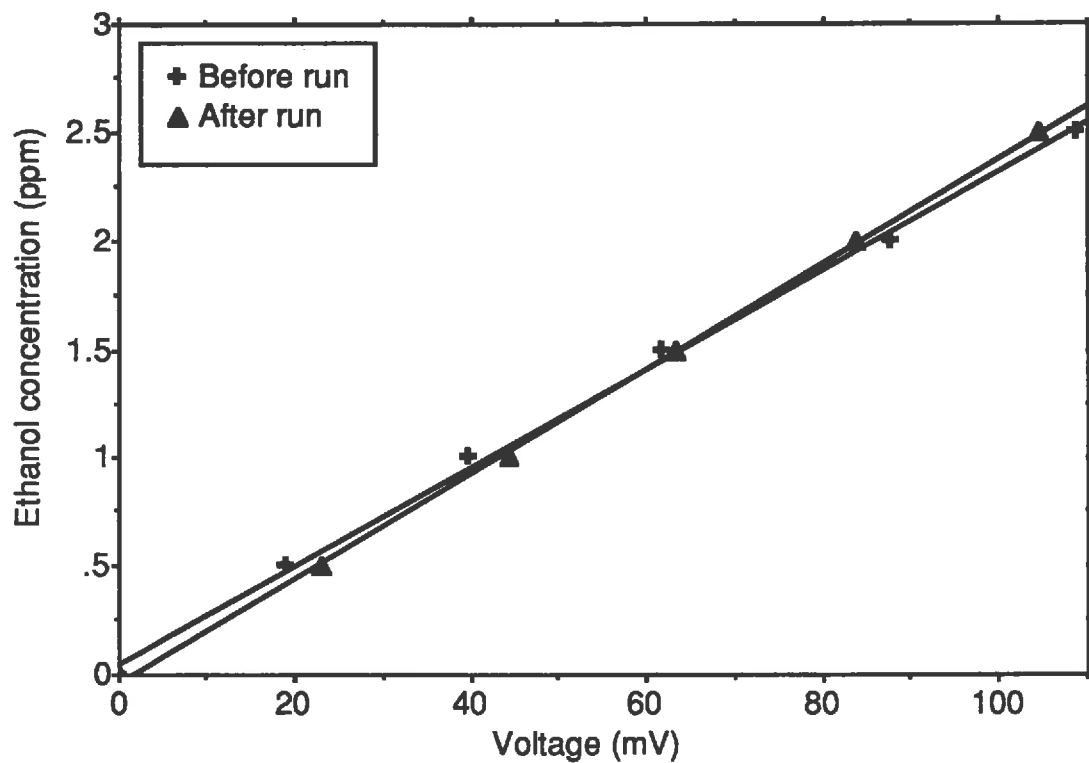
<u>Figure 1.</u> Sample ethanol calibration data for the infrared analyzer. Lines indicate the least-squares fit to the data. Voltage data have been adjusted so that zero ethanol concentration corresponds to zero mV.
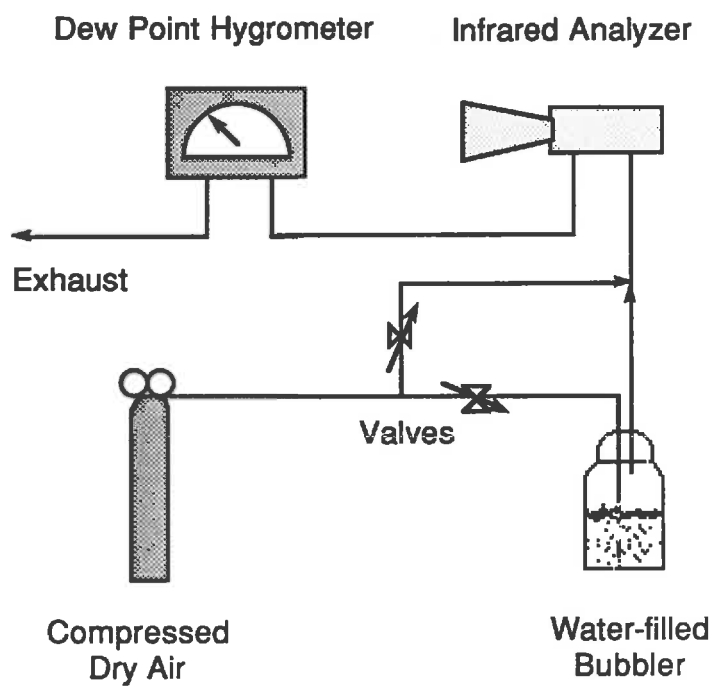
Figure 2. Schematic diagram of apparatus for calibrating the response of the infrared analyzer to water vapor.
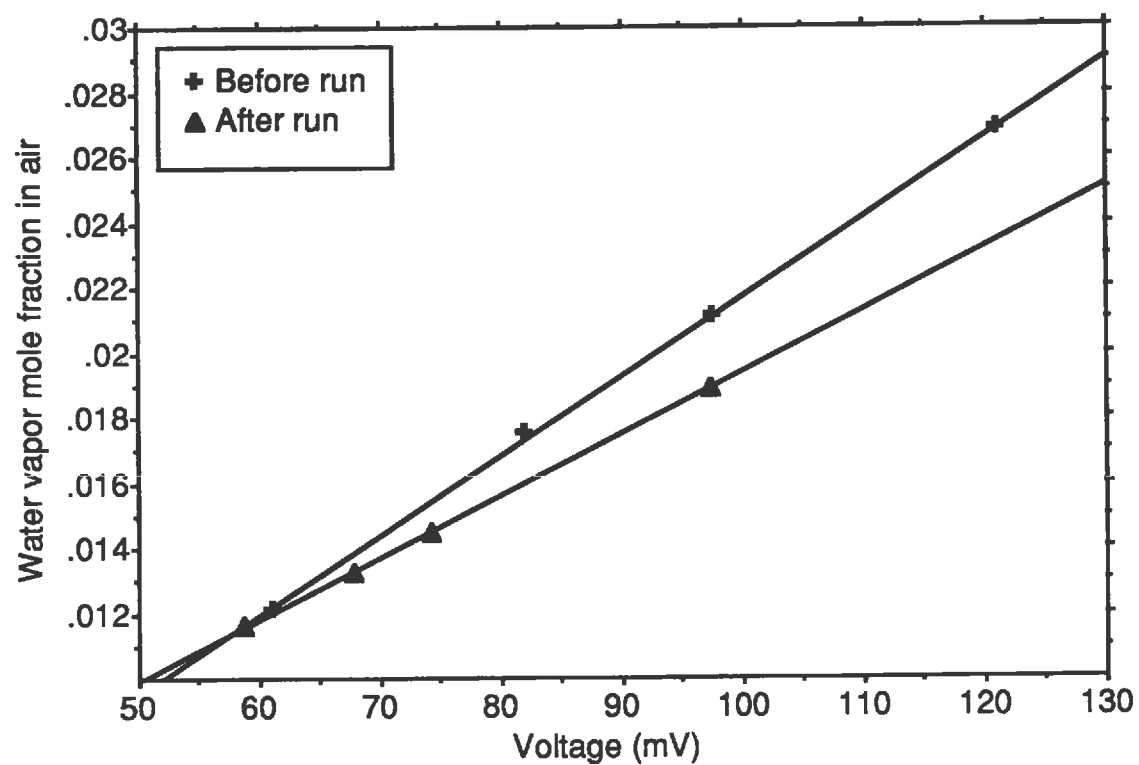
Figure 3 Sample water vapor calibration data for the infrared analyzer. Lines indicate the least-squares fit to the data.
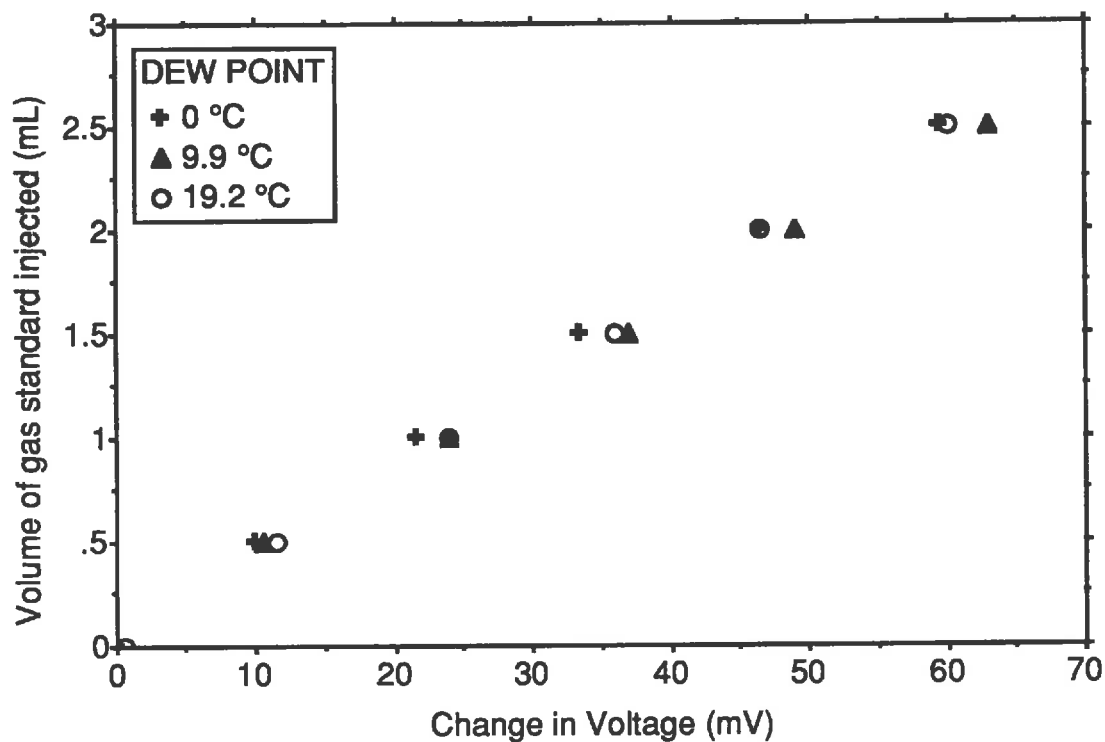
Figure 4 Infrared analyzer data showing the linear superposition of response to ethanol and water vapor. Each 0.5 mL aliquot of the standard yields a concentration of approximately 0.25 ppm in the analyzer cell. Voltage data have been adjusted so that zero ethanol concentration corresponds to zero mV.
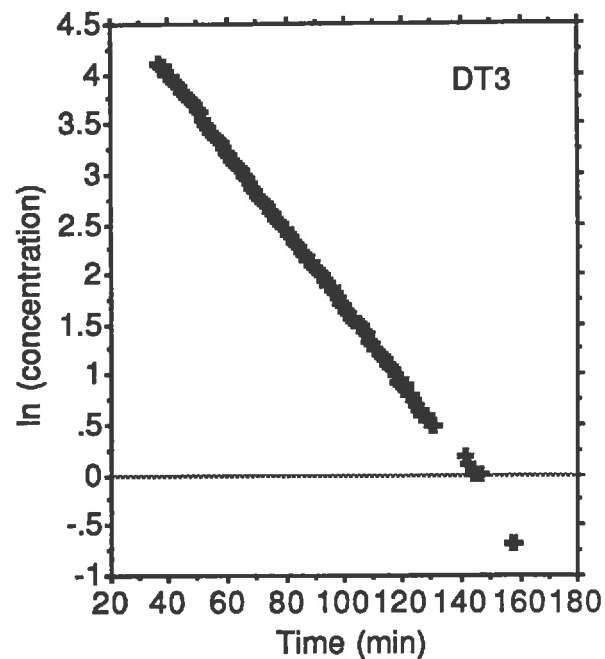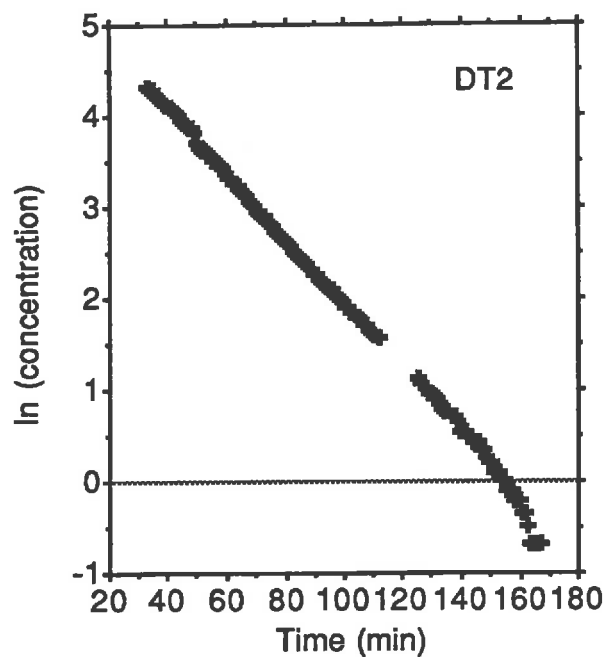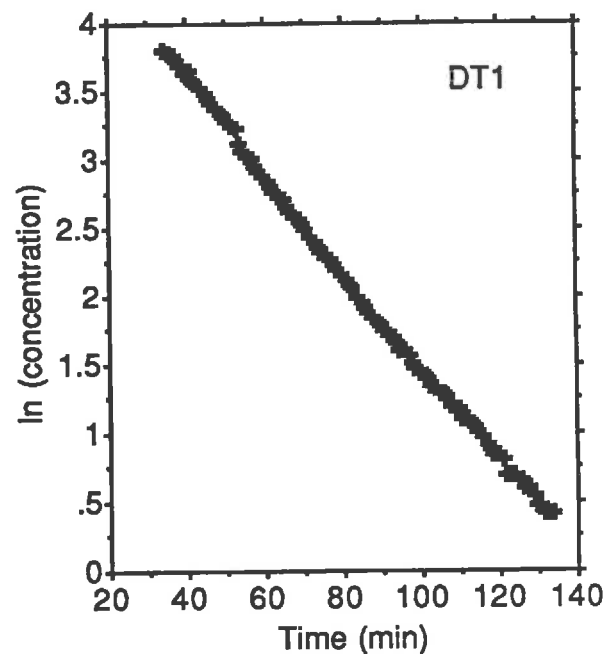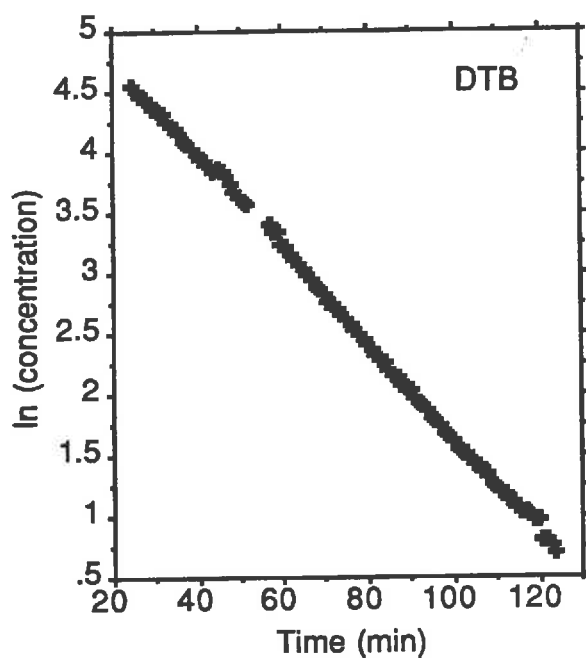
Figure 5a Sulfur hexafluoride concentration decay data for the dishwashing runs conducted under typical conditions. Concentration is in arbitrary units. The time scale is referenced to an arbitrary starting point.
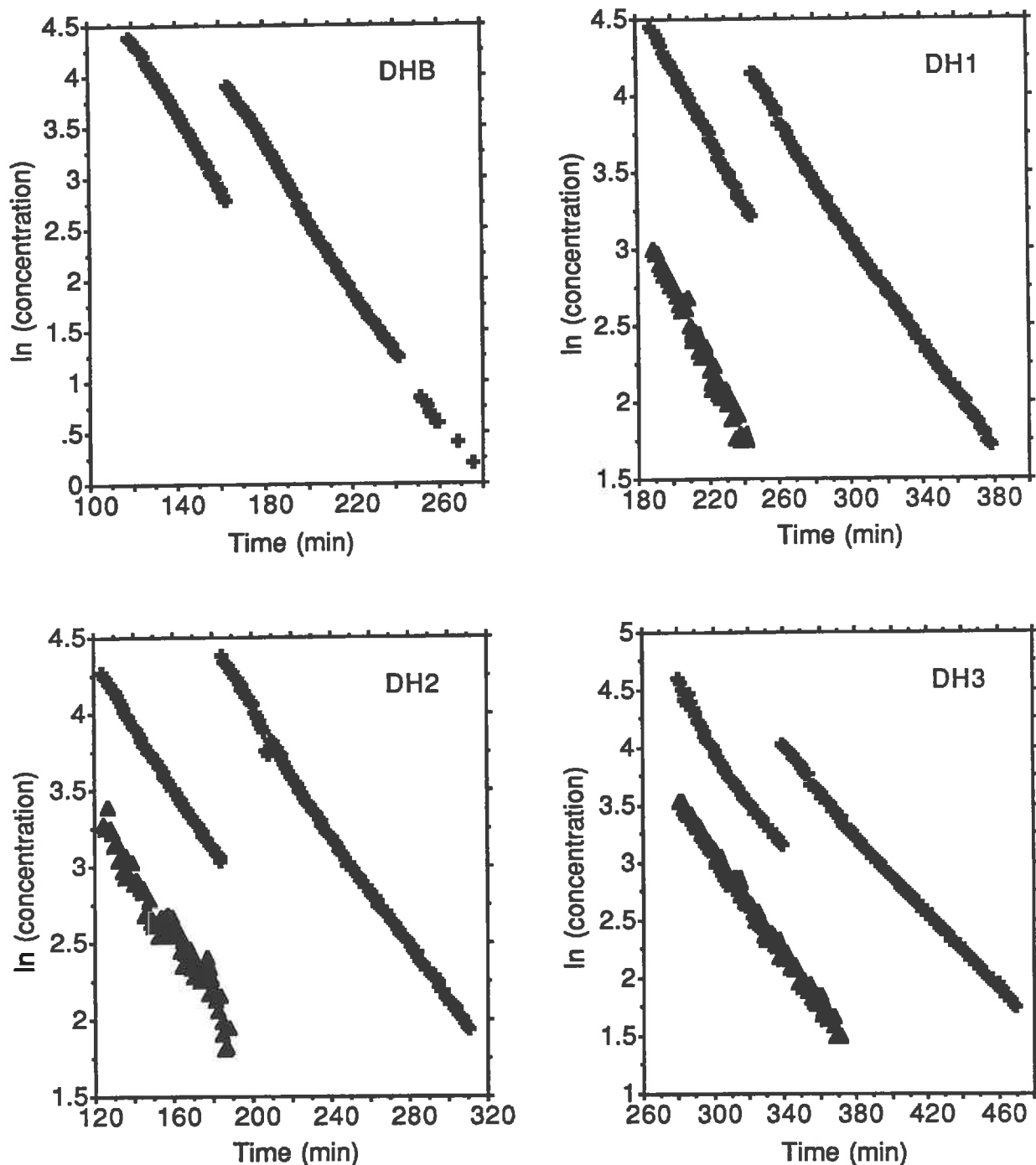
Figure 5b   Sulfur hexafluoride (upper trace, +) and ethanol (lower trace, ▲) concentration decay data for the dishwashing runs conducted under-high release conditions. The jump in SF6 concentration during the run is due to a booster injection of SF6 added at the end of the soak period. Concentration is in arbitrary units. The time scale is referenced to an arbitrary starting point.
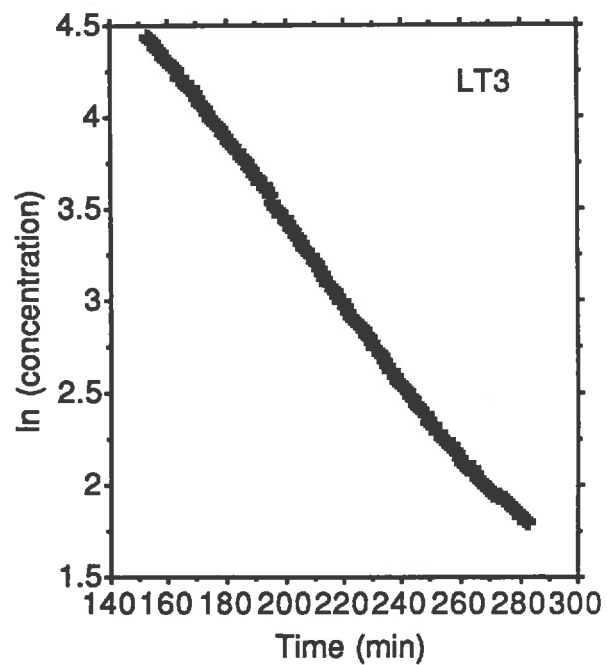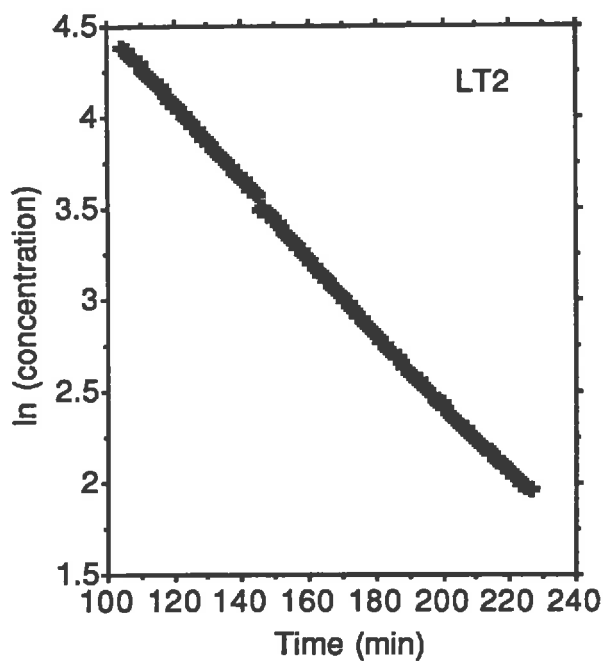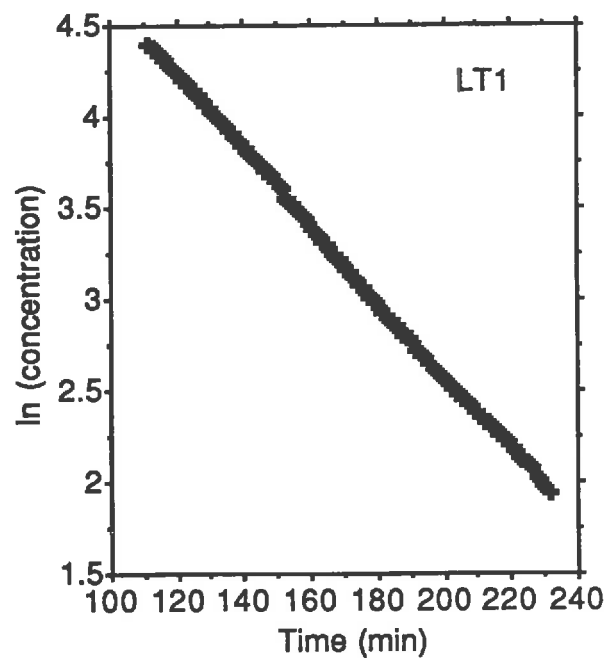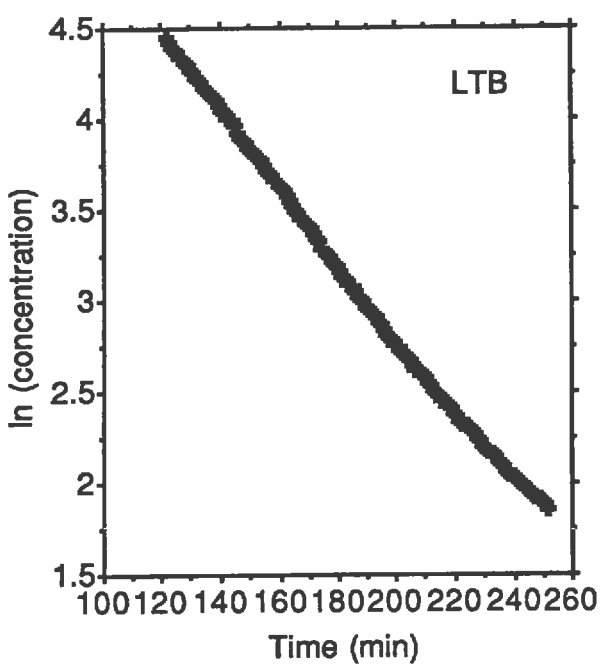
Figure 5c   Sulfur hexafluoride concentration decay data for the laundry runs conducted under typical conditions (LT). Concentration is in arbitrary units. The time scale is referenced to an arbitrary starting point.
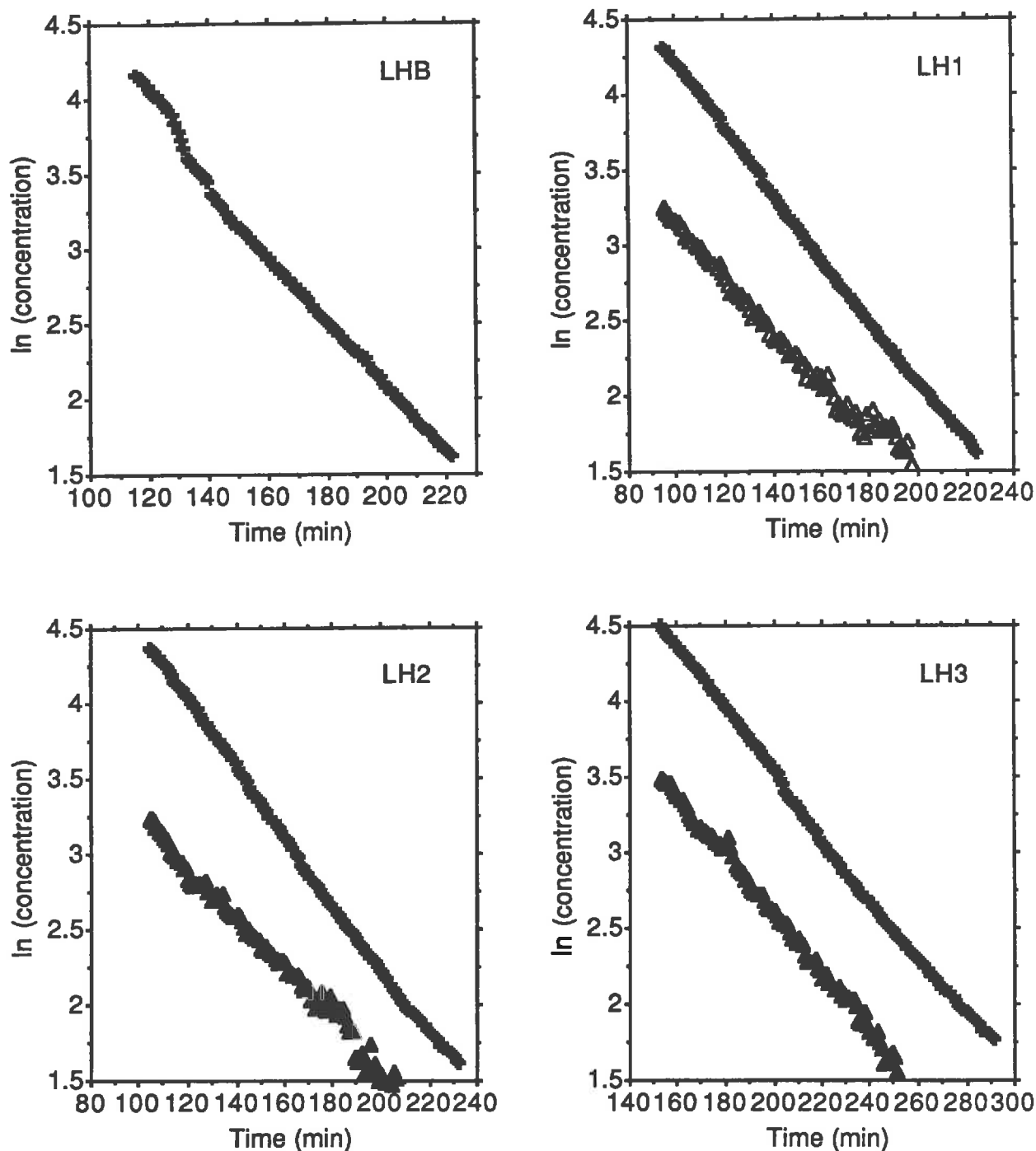
Figure 5d   Sulfur hexafluoride (upper trace, +) and ethanol (lower trace, ▲) concentration decay data for the laundry runs conducted under high-release conditions (LH).   Concentration is in arbitrary units.   The time scale is referenced to an arbitrary starting point.
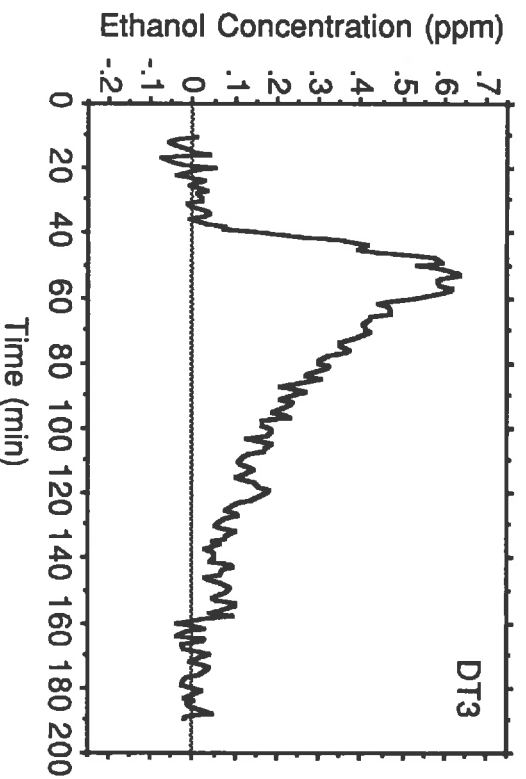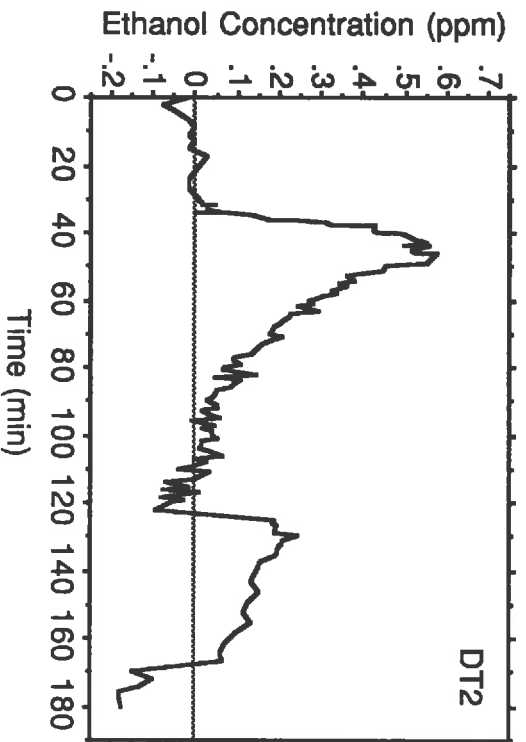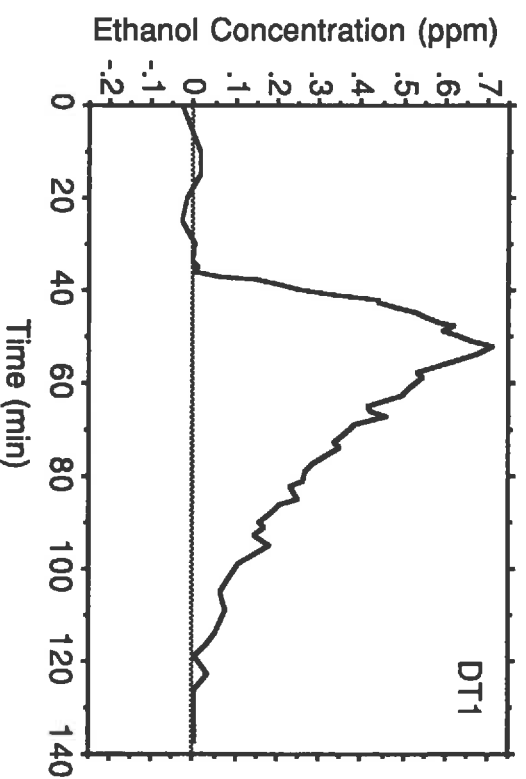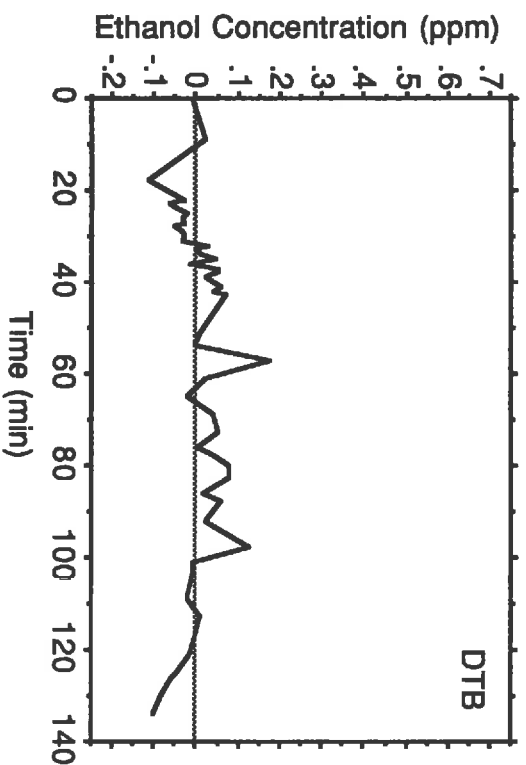
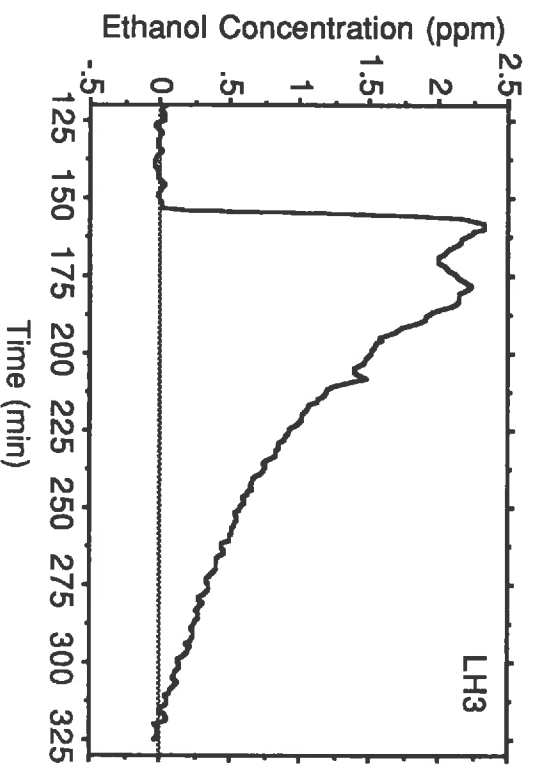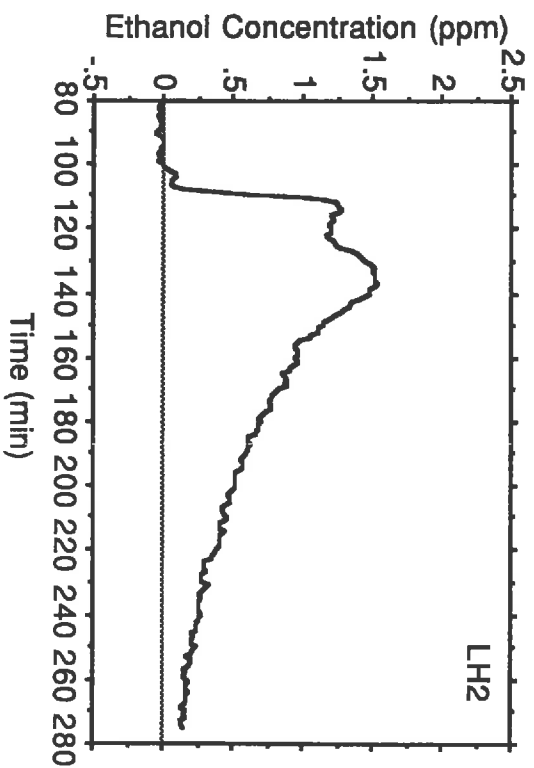Figure 6a   Ethanol concentration profiles for dishwashing runs conducted under typical conditions.
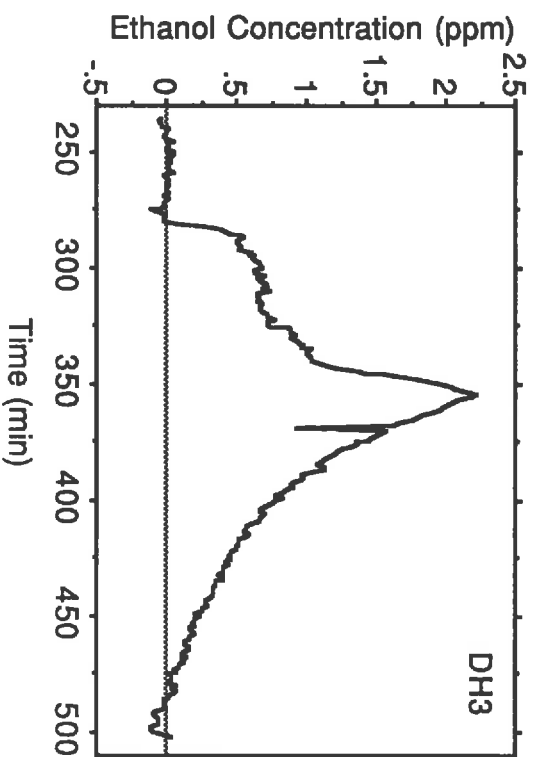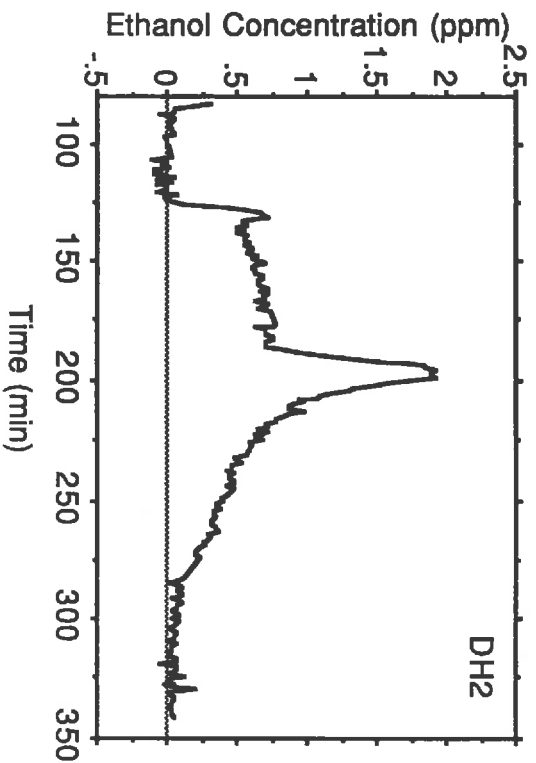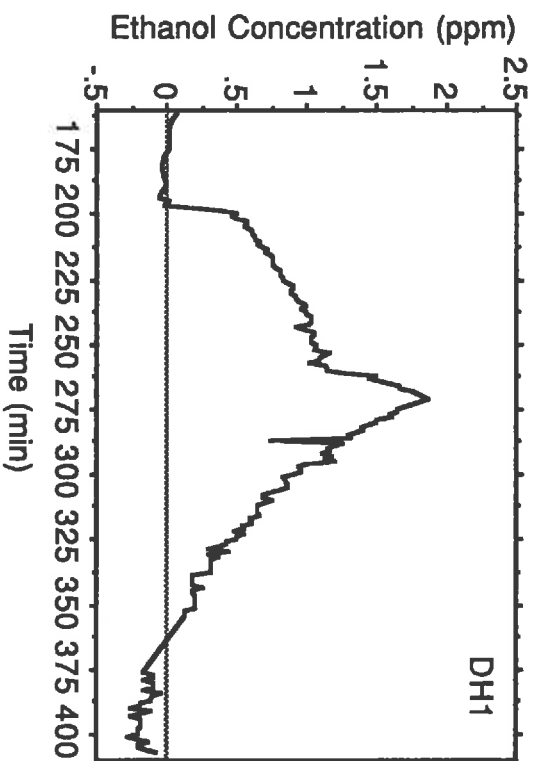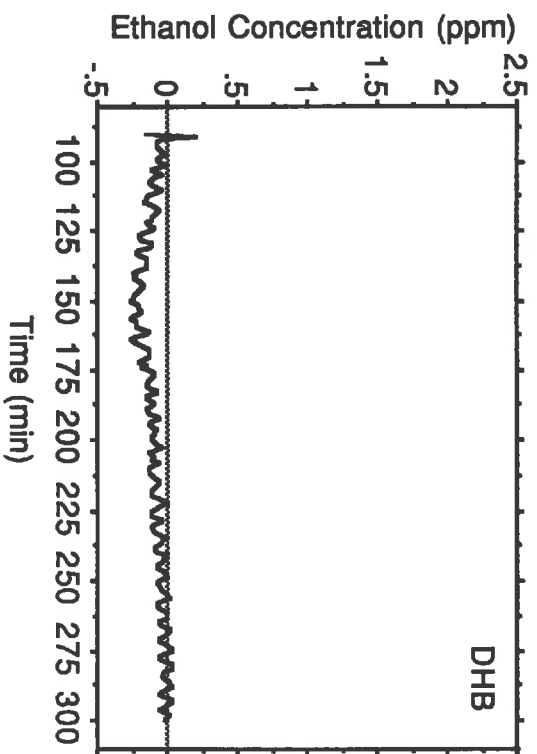
Figure 6b   Ethanol concentration profiles for dishwashing runs conducted under high-release conditions.
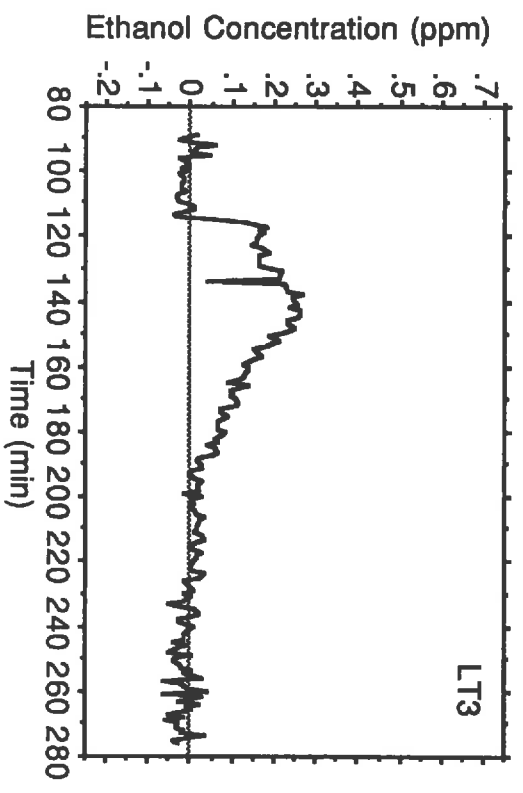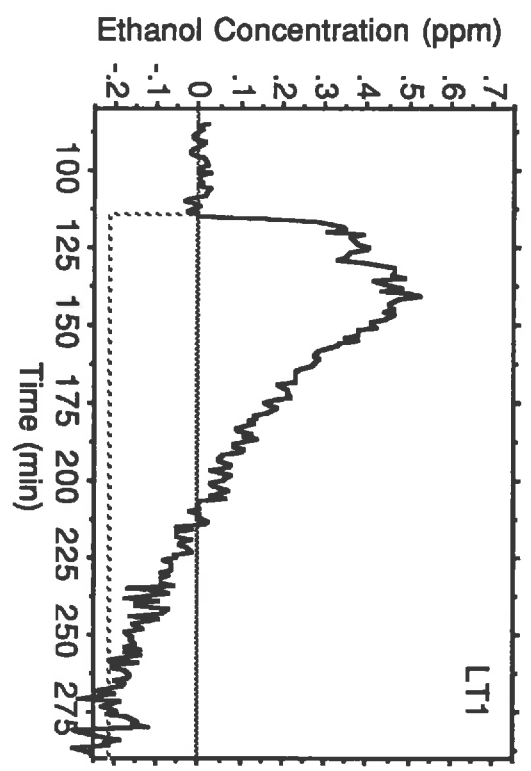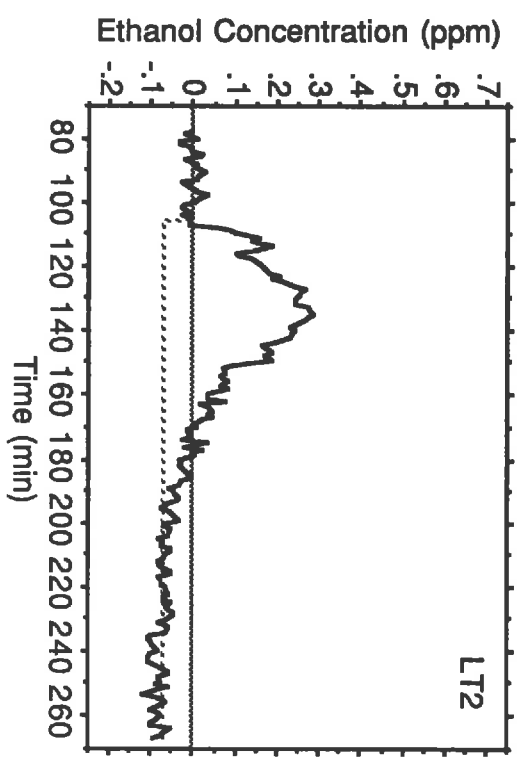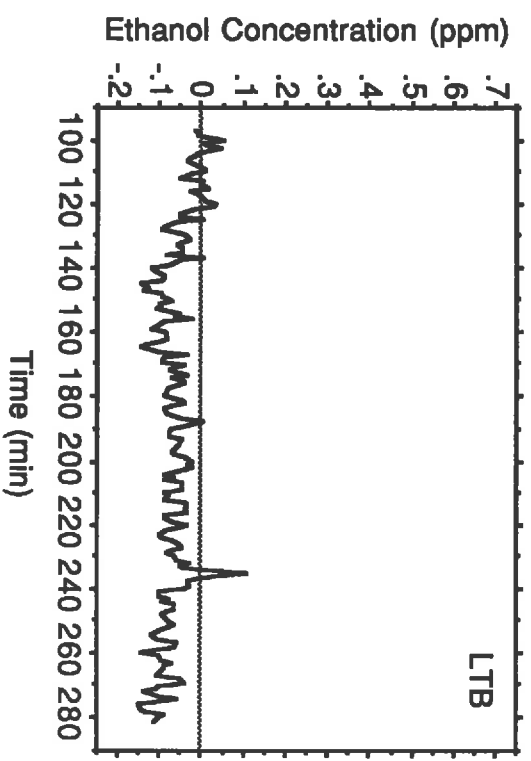
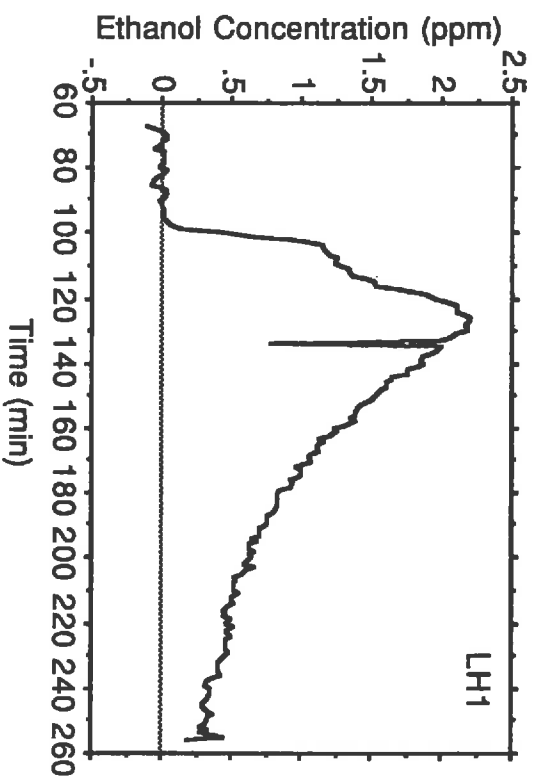Figure 6c   Ethanol concentration profiles for laundry runs conducted under typical conditions.
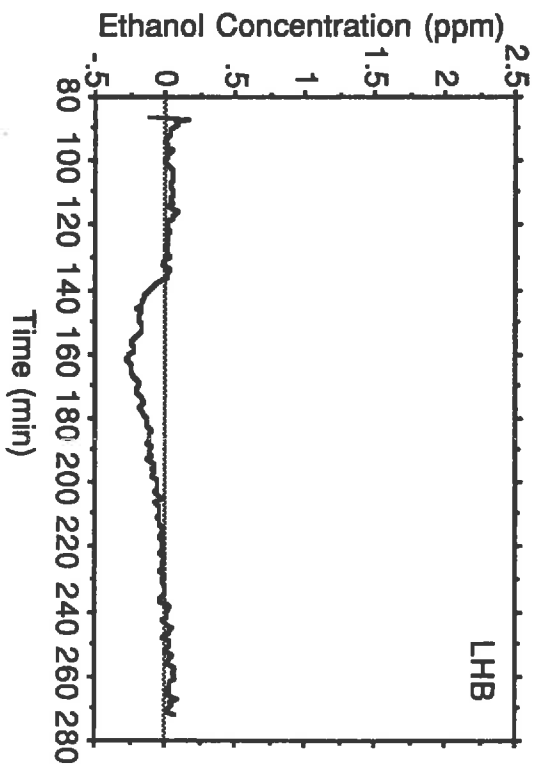
Figure 6d   Ethanol concentration profiles for laundry runs conducted under high-release conditions.
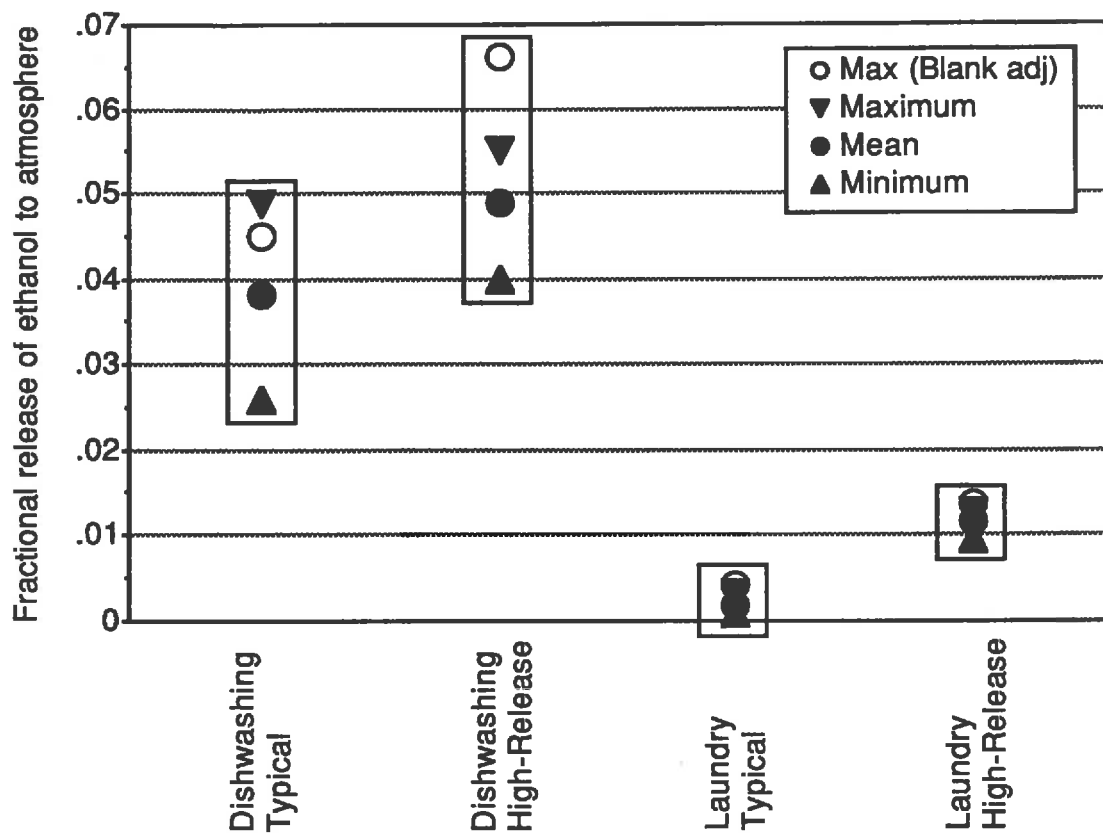
Figure 7   Summary of ethanol release data, showing the fraction of ethanol added to the wash solution that is released to the atmosphere prior to the wash solution being discharged to the sewer.