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**Characterization of Pollutant Emissions from Paint and Varnish:
Temperature and Relative Humidity Variations**

Lisa De Bellis

A Thesis

in

The Department

of

The Centre for Building Studies

Presented in Partial Fulfillment of the Requirements
for the Degree of Masters of Applied Science at
Concordia University
Montreal, Quebec, Canada

December 1995

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ISBN 0-612-10839-2

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ABSTRACT

Characterization of Pollutant Emissions from Paint and Varnish: Temperature and Relative Humidity Variations

Lisa De Bellis

High concentrations of volatile organic compounds (VOCs) and other pollutants found in indoor air contribute to poor indoor air quality. Sick Building Syndrome (SBS) has become a recognized and well documented problem. Indoor building materials, furnishings, and finishes are the predominant sources of these VOCs due to their large surface areas exposed to air. Building material emissions can depend on surrounding conditions such as: temperature, relative humidity, and air velocity.

The objectives of this study were to conduct a comprehensive review of earlier work and to evaluate the impact of temperature and relative humidity on building material emissions via small chamber testing. Two materials, paint and varnish, were chosen for this study because of their extensive use in all buildings.

The results indicate that temperature and relative humidity have a significant impact on the rate of material emissions. However, the trends established for Total VOC (TVOC) cannot be generalized to represent the emissions from individual compounds. Further, the impact of temperature and relative humidity was shown to differ significantly for the two materials tested.

Two bake-out investigations were also carried out. The results indicate that the VOC emissions did diminish immediately following the bake-outs. However, higher reductions in VOCs over the same study period occurred in a mechanically ventilated house as compared to a naturally ventilated house that underwent a bake-out.

Acknowledgements

A debt of gratitude is extended to my supervisor, Dr. Fariborz Haghghat, for his guidance and steadfast encouragement during the completion of the work contained herein; and to Mrs. Ying Zhang for her often sought help and advice.

A very special thanks to Mr. Hans Obermeir for his skilled craftsmanship which helped build the facilities required for the testing; to Mrs. Dorina Banu for being so generous with her time and knowledge when it came to chemistry; and to Mr. Jacques Payer for his often sought services.

My acknowledgements to Dr. M. Kanabus-Kaminska at the National Research Council, National Fire Laboratory, for her contribution to the calibration of the Gas Chromatograph; and to the National Sciences and Engineering Research Council for their financial support.

My most heart-felt thanks to my husband, Fernando, for his understanding and patience at my long absences from home and for his continuous encouragement; and to my parents and family for their ever-present support and confidence.

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CHAPTER I

INTRODUCTION

1.1 Indoor Air Quality Problems

The root of poor Indoor Air Quality (IAQ) lies predominantly with the high concentrations of Volatile Organic Compounds (VOCs) and other pollutants in the indoor air, which cause uncomfortable odours and sensations to the buildings' occupants. Sick Building Syndrome (SBS) and Building Related Illness (BRI) have become recognized and well documented problems.¹ Approximately 65% of buildings operate under SBS conditions [2].

SBS and BRI were terms never heard of twenty years ago. If one were to consider the reasons why they are so widely known today, one may look at the evolution which occurred in the indoor environment and the trend in modern construction toward more airtight buildings. The sources of VOCs vary but can be, for the most part, accounted for by building materials, office equipment, human beings and their environment, and outdoor air. However, it has become common knowledge that indoor building materials, furnishings, and finishes are the predominant sources due to their large surface areas

¹ The first phase of a pilot study on IAQ, conducted by NATO (North Atlantic Treaty Organization) and its subcommittee CCMS, Committee on the Challenges of Modern Society, has recently come to an end. The purposes of this study were to discuss and identify regulatory, research and technical issues related to IAQ. In its final report, SBS and BRI are given the following definitions. BRI refers to an illness where symptoms are identified and an airborne agent and its source are determined. Symptoms are usually specific and serious; lung and respiratory diseases may develop. Examples are Legionnaires' Disease, Humidifier Fever, and Hypersensitivity Pneumonitis [1]. SBS refers to a series of non-specific complaints that occur in high prevalence among occupants of certain buildings, but which cannot be linked to a specific agent in a building. Symptoms usually develop while being in the building and subside or disappear shortly after leaving the building. SBS symptoms include irritation of the eyes, nose, throat; dry skin; mental fatigue; headache; runny nose; chest tightness; and odour complaints [1].

exposed to air [3]. Modern offices are filled with pollutant emitting materials:

- › Furniture, including desks and bookshelves, are made from engineered wood products. Engineered wood, products such as particle-board and medium density fibreboard, are made with wood shavings or chips that are mixed with a resin (2%) and processed under intense heat and pressure. It is the resin, usually a phenol-formaldehyde or urea-formaldehyde blend, that is off-gassed [4,5].
- › Carpets are widely used as floor coverings. Carpets, their under-pads and adhesives, form a complex, composite source of emissions. Long time identified as strong indoor air pollutants, the carpet industry, in both Canada and the United States, have worked hard to meet strict criteria. This is illustrated by the USA Carpet Industry's willingness to participate in the "Carpet Policy Dialogues" with the Environmental Protection Agency (EPA), where they agreed to develop an emissions test method for their products [6,7]. Especially cut back are the emissions of the very odorous 4-phenylcyclohexene (4-PC), found predominantly in the carpet backing, and a high source of complaint [8,9]. According to Healthy Materials [10], 4-PC levels have dropped by approximately 70% in newly manufactured carpets. In Canada, the Carpet and Rug Institute (CRI), has established voluntary guidelines for carpet manufacturers. These are presented as maximum allowable emission factors for [8,10]:

Total VOC (TVOC)	500 micrograms/m ² h;
Styrene	400 micrograms/m ² h;
4-PC	100 micrograms/m ² h; and
Formaldehyde	50 micrograms/m ² h.

Apart from VOC emissions, carpets are also sources of IAQ complaints due to their inherent ability to store dust and allergens [8].

- › Chairs are upholstered with chemically treated synthetic fabrics for increased durability. Standing partitions have become commonplace, providing a semi-private atmosphere. However, these are usually made of particle-board covered in, once again, a chemically treated synthetic fabric.
- › Personal computers, photocopier and facsimile machines can also be found at or near every work station [2,11].

Worst still, with this bombardment of pollutant sources, ventilation requirements have been reduced or, at best, have remained constant. Thus, SBS and BRI have found their way into, among other places, office buildings, newspapers, television documentaries

and, most recently, court rooms, leading to billions of dollars lost in productivity [2].

It has been suggested to increase ventilation requirements in order to reduce the concentrations of pollutants in an environment. However, it is recognized that, while increasing energy costs, this method does not guarantee 100% removal of the pollutants. Even assuming that the ventilated air reaches all material surfaces, it can only serve to remove emissions on the surface. Increased ventilation (outdoor air) will not increase the rate of emission [12]. After installation, material emissions are high; over time, however, the emission rate decreases and emissions become low but relatively continuous [13,14].

Another means of reducing indoor VOC concentrations in newly built or renovated buildings is the bake-out. The results of the study conducted here will provide a better understanding of the theory behind this procedure. The bake-out is a relatively new concept in the indoor air quality field. To date, several researchers have conducted bake-outs, with inconclusive results; rendering the procedure controversial, as will be shown in detail in later chapters.

1.2 Remediation of the Problems

A better, and well approved means of combatting emissions from materials is to target the source. In short, a long term, futuristic approach and strategy is to control emissions by careful planning, developing, manufacturing, and use of low emitting materials [15,16]. While the solution to the problem is stated this simply, applying it has been delayed by the lack of available and trustworthy data on material emissions, including the lack of consensus on experimental techniques; lack of clear, predictable

relationships between material emissions exposure and health effects; and the obvious difficulties and expense required to identify and measure the vast number of compounds emitted by all building materials [2,16]. As a consequence, much research and enterprising activities have been concentrated in this area.

There are two basic methods of evaluating material emissions. These are [17]:

- (1) Sensory tests, which use human response to exposed levels of VOCs, and
- (2) Small or large scale environmental chamber tests to identify and quantify emissions.

The sensory testing procedure has mixed reviews amongst researchers. While the method is relatively simple, quick and inexpensive to implement, research has shown that there is a poor correlation between some sensory results and actual building conditions, including ventilation rate, chemical measurements, and occupant complaints/dissatisfaction [18, 19].

Environmental chamber tests combined with gas chromatography best identify the type of contaminants emitted from a particular material sample and their corresponding concentrations. These tests can be used to screen products for particular emissions, rank products according to a given criterion (for example, the concentration of a particular compound), or provide data which can help design a model for predicting IAQ in real buildings [20].

As a consequence, the most commonly used test method has been the small environmental chamber. Test chambers with a volume of up to 5 cubic metres are

classified as small environmental chambers. Chambers with volumes in excess of 5 m³ are considered to be large [20].

Small chamber tests can provide the necessary tool in forming and developing models which can simulate true life conditions at much less expense [21]. Field tests are expensive to execute, especially if we consider the broadness of the material emission field. To perform a sufficient number of field tests to enlighten researchers of the mechanisms of each and every material's emission is impossible.

As emission testing is increasingly growing as a preventative measure in combating IAQ problems, standardizing the procedure is required for reliable product comparisons. If and when chamber data can be used to model material emissions, under a wide range of environmental factors, and predict indoor concentrations, then chamber tests and models will become invaluable tools for selecting indoor materials for healthy indoor environment design [22]. In the past, IAQ and health considerations were not weighed in the selection of building materials. Selection criteria was usually influenced by maintenance, cost, life expectancy, aesthetics, and functional performance/physical properties (acoustics, structure, etc.) [1,23].

The American Society of Testing and Materials (ASTM) has developed a guideline (ASTM D5116-90) for small chamber testing in the hopes of standardizing the procedure. In addition, the European Concerted Action "Indoor Air Quality and its Impact on Man" has adopted this same document, with some modifications, as a guideline in their area of the world [24].

We must keep in mind that there are some limitations to small chamber tests. They

are only capable of testing samples of whole materials. Therefore, assemblies, such as furniture, cannot be tested in a small chamber. Small chambers may only provide part of the emissions profile of a compound. Concentrations determined from small chamber tests cannot be used as a substitute for the emissions in a life size building [20].

While ASTM D5116 serves as a guideline to testing material emissions, there are several questions which must still be addressed. Under in situ conditions, environmental parameters may vary. Under normal or typical indoor air conditions, temperature can be recorded anywhere between 20 to 25 °C. Locally, however, some materials can be subjected to even higher temperatures if they are very near central/electric heaters or experiencing solar heat gains through windows [3]. Building material emissions can depend on surrounding conditions such as: temperature, air velocity, moisture in the air and material, surface treatments, and the pollution absorbed by the materials [25].

In addition, the types of pollutants may vary with the time of year because of varying temperatures and relative humidity [12]. As an example, high heat and relative humidity increase the rate of formaldehyde emission, such that higher concentrations can be recorded during the summer months [11]. A second example was reported in the Netherlands where water barriers consisting of oligomeric or polymeric alkylalkoxy-silane resins are used. It has been reported that these resins diffuse through the walls and evaporate at the wall surface. With higher temperatures, these processes increase. Wind pressure and high solar radiation can also contribute to an increase in diffusion rate. During the winter months, these resins are released indoors because of the high temperature differences occurring between the indoor and outdoor air [2].

Also, the process of conditioning and distributing the outdoor air causes some materials to be exposed to even higher temperatures, air velocities, and relative humidities than the room air. These materials include the thermal and acoustical duct materials commonly used to line the interior of air handling units, reheat coils, variable air volume units, mixing and diffuser boxes, and duct systems. Resin adhesives are used to bind insulation materials to steel ducts and other HVAC (Heating, Ventilation, Air Conditioning) components.

Another problem occurs, if ventilation rates are decreased while temperature increases, as usually occurs during off peak hours in a building; sorption of VOCs by materials is greatly increased [11,26]. This is especially of importance when one considers a newly built or recently renovated building. High concentrations of emissions will be released as the interior finishes of the building are completed. Activities such as painting, carpet installation, or caulking, can be under way simultaneously in different rooms or on different floors. During this pre-occupancy period, the ventilation requirements are not specified. Often times, to save on energy the HVAC system is not turned on, or quite possibly its complete installation has not been achieved. Consequently, if insufficient time is allotted before occupancy of the building takes place, the occupants will be exposed to very high amounts of VOCs. ASHRAE (American Society of Heating, Refrigerating, and Air Conditioning Engineers) Standard 62-1989, Ventilation for Acceptable Indoor Air Quality, does not consider the pre-occupancy stage.² The problems above also apply

2

Standard 62-1989 specifies ventilation rates based on two procedures. The first procedure, known as the IAQ Procedure, is to provide a maximum acceptable concentration of a VOC to which a person may be exposed without suffering any ill side effects. The Ventilation Rate Procedure, the second means of providing VOC concentration limits, is achieved by indirectly specifying ventilation rates and the degree of fresh air required within a space for human comfort. This would help flush out any unwanted pollutants in the indoor air [27]. This standard is under revision and according to Indoor Air Bulletin [28], proposed changes will include a more explicit treatment of sources and design guidelines for transient occupancy. This revised edition, originally slated for release in 1995, will be delayed due to an extensive reviewing process, which has met opposition from special interest groups (e.g. the tobacco industry) [29]

when renovations are taking place in a partly occupied building. If careful provisions are not made for the HVAC zoning/scheduling, complaints may be generated by the high emissions being transported to occupied zones.

In order to design suitable emission procedures, knowing how these different factors affect material emissions at different stage's of a product's life is required [30]. If consensus on testing procedures is reached, chamber emissions data can become a powerful tool in developing models which can simulate and predict material emissions under many environmental states in true life cases, thus, improving material selection at the design stage [31]. This mandate is exceptionally vast in scope. For the purposes of this thesis, only a small portion of this field could be realistically explored.

1.3 Main Objectives of This Work

The objectives of this study are:

- 1) to conduct a comprehensive review of earlier work,
- 2) to evaluate the impact of temperature on building material emissions, and
- 3) to evaluate the impact of relative humidity on building material emissions.

Two materials were chosen for this study. It was decided that these should be paint and varnish because of their extensive use in all buildings. As they are obvious emitters of VOCs, especially soon after application, they are often the cause of complaints. Volatile organic compounds (acting as drying agents, mildewcides, and fungicides [32]) commonly found in paints and varnishes include aliphatic hydrocarbons (octane, undecane, decane), aromatic hydrocarbons (toluene, xylene, ethylbenzene), alcohols (n-propanol), and some

ketones and aldehydes [3,33,34].

1.4 Contributions of This Research

This work is of significance to the indoor air quality field for several reasons. Its main contributions include:

- (1) Knowing how environmental variables effect emissions of a given product can help predict in situ emissions. This is especially of importance during the pre-occupancy period of a newly built or renovated building.
- (2) The Concentration vs Time data is needed to help develop models for predicting Indoor Air Quality in buildings.
- (3) The results from this research can help to better understand the mechanisms behind the building bake-out procedure.

CHAPTER II

LITERATURE REVIEW

2.1 Limitations/Lack of Consensus

The ASTM D5116 standard recognizes five critical parameters. These are temperature, relative humidity, air exchange rate, product loading, and time (age) [20]. These factors have also been noted in many other reports by other researchers [22,23,33]. Further, other researchers have suggested that chamber wall effects causing adsorption/desorption at their surfaces need to be determined [33,35]. Products themselves may vary due to variations in the manufacturing processes and natural aging [23]. Tucker [22] stipulates that, in addition to those factors named above, the total content of vaporizable constituents in the material and their distribution at the material surface and its interior also have an influence. The ASTM guideline does not address all these parameters. Its mandate is simply "to provide assistance by describing equipment and techniques suitable for determining organic emissions from indoor materials" [20]. It does not discredit other means of emissions testing. As a result, much testing taken place in recent years, since 1990, has used varied and considerably different approaches. Further, at a recent (April 1994) ASTM meeting held in Montreal, the subcommittee D-22 responsible for the guideline D5116 stated that this guideline, due for revision in November 1995, is in very much need of it [36].

2.2 Research Related to Temperature and Relative Humidity

From a literature review conducted to date, most chamber tests have been

conducted under static environmental conditions [37]. A summary of these efforts, with the environmental settings used is shown in Table 1.

As can be seen from the information provided in Table 1, the environmental conditions do not vary significantly between the tests summarized.

In the case of Bremer's research [40], where three temperatures were used, the emission variations with temperature were not reported in the paper. The authors' state that the influence of temperature was closely examined and that the emitted substances were temperature dependent. However, the data presented does not reveal a systematic comparison of the effect of the different temperatures on the emissions from a PVC flooring. Rather, they show results for three different PVC (poly-vinyl chloride) floorings, each tested at a different temperature.

In the experiment conducted by Colombo et al [47], several levels of relative humidity were used, depending on the material sample, for preliminary testing of the influence of relative humidity on the material adsorptivity. The authors concluded no apparent influence of relative humidity. Contrary to this, other researchers have found that temperature and relative humidity do cause variations in material emissions.

In research conducted in Sweden by Berglund [11], it was determined that material emissions vary inversely with relative humidity. Thus as relative humidity is increased, emissions from materials, such as furnishings, carpeting and wall coverings are decreased. These were based on sensory test results.

Sollinger et al [59] conducted experiments on ten types of textile floor coverings using two chambers: a 33 L glass chamber and a 1000 L stainless steel chamber. Both

Table 1: Summary of Small Chamber Test Conditions and Procedures Conducted to Date

Researchers	Conditions							Objective/Purpose of Experiment
	Temperature (°C)	Relative Humidity (%)	Volume and Material of Chamber	Product Loading m ² /m ³	Air Change Rate (ach)	Sampling Procedures		
R.C. Fortmann et al [13]	23	50	52.7 L stainless steel	1.45	1.0	emissions measured during first 24 hours following application; paint applied with brush on one side of glass plate (828 cm ²) alkyd paints: samples taken at 1, 4, 8, 24 hours sample volumes of 0.1 - 10 mL latex paints: extracted with methylene chloride; purified air used	comparison of 7 methods for analyzing paint emissions, one of which was small chamber	
M.S. Black et al [38]	23 ± 1	50 ± 5	0.05 m ³ stainless steel	0.41 ± 0.02	1.0 ± 0.05	96 hour exposure time	emissions from softback and hardback carpets	
M. De Bortoli et al [39]	23	45	0.28 m ³ n/m ¹	1	0.5	VOCs sampled by drawing 1 L of air through Tenax cartridge; desorbed 20 minutes at 250 °C; GC program 0 - 280 °C, 4 °C/min	analyze emission of formaldehyde, vinyl chloride, VOCs and plasticizers from different wall coating materials	
J. Bremer et al [40]	23, 30, 40	45	100 L cylindrical stainless steel	0.4	1.0	emissions tested over several weeks, during which time samples stay in climatic chamber	tested PVC flooring	
R. Gehrig et al [41]	23	45	1 m ³ stainless steel	0.17	1.0	purified air; velocity = 0.3 m/s vertical; air samples taken at exhaust; drew 125 - 3000 mL of air through adsorption tubes	analyze wall paint emissions as a function of time and effect of material on which applied	
H. Gustafsson & B. Jonsson [42]	23 ± 2	50 ± 5	FLEC ²	n/m	171	synthetic air used; 24 hour sampling period; air flow = 100 mL/min; tested 4 weeks and 26 weeks after sample preparation	tested VOC emissions from different floor coverings	

¹ n/m: no mention of information in the report/paper

² FLEC stands for Field and Laboratory Emission Cell; it is circular in shape with an internal diameter of 150 mm and made of stainless steel [42].

Table 1 (cont'd): Summary of Small Chamber Test Conditions and Procedures Conducted to Date

Researchers	Conditions							Objective/Purpose of Experiment
	Temperature (°C)	Relative Humidity (%)	Volume and Material of Chamber	Product Loading m ² /m ³	Air Change Rate (ach)	Sampling Procedures		
S. Kirchner et al [6]	23	45	stainless steel, glass, and teflon chambers	n/m	1.0	purified air used	tested VOC emissions from different floor coverings	
A. Nieslochowski & E. Kazimierzak [43]	23 ± 2	n/m	0.2 m ³ ; stainless steel	1	1.0	general BRI (Building Research Institute) control method; 2 hour sampling time	tested VOC emissions from floor and wall coverings, insulations, paint, glue, furnishings	
B. Berglund et al [44]	22	-	1.9 m ³ ; stainless steel	2.2	0.5	ventilated with air that is filtered with carbon; 15 Litres of air samples absorbed on porous polystyrene filters using a flow rate of 1 L/min	to evaluate whether it is possible to re-establish concentrations of VOCs of a room in a small test chamber by transferring samples of predominating building materials from the room to the chamber	
T. Tirkkonen et al [45]	23	45	1 m ³ ; stain-ss steel	0.41	0.5	paint allowed to dry for 2 weeks before measuring; samples conditioned in chamber for 2 days before testing; paint applied to gypsum board; sample volume 10 Litres; sampling time 30 minutes	VOC emissions from wall coverings, insulation materials, flooring	
Environment Institute of the Joint Research Centre in Ispra, Italy and the Hygiene Institute of Aarhus University, Denmark inter-laboratory research [46]	23	45	two 450 l, glass chambers	0.4 (particle board); 1.4 (gypsum board); 0.2 (plywood)	0.25	three building assemblies were tested: particleboard with glued on carpet, gypsum board with wallpaper pasted on both sides, and a plywood sandwich with one layer stained and painted with a polyurethane lacquer.	compared the number of compounds emitted and their magnitude for the three building assemblies	

Table 1 (cont'd): Summary of Small Chamber Test Conditions and Procedures Conducted to Date

Researchers	Conditions						
	Temperature (°C)	Relative Humidity (%)	Volume and Material of Chamber	Product Loading m^2/m^3	Air Change Rate (ach)	Sampling Procedures	Objective/Purpose of Experiment
A. Colombo et al [47,48]	23 ± 0.5 °C	< 10 to 70 ± 5%	2 glass chambers each 0.45 m ³ ; 1 stainless steel, 0.28 m ³	1.1 for dynamic tests; 1.8 for static testing	0 to 1	sample of carpet, blown vinyl wall coating, and gypsum board	tested the adsorptivity of common building materials to VOCs, such as n-dodecane, n-decane, 1-4-dichlorobenzene.
B. Jensen et al [49]	n/m	50	FLEC	n/m	n/m however, flow rate specified as 100 ml/min	12 linoleum products; compared emissions after 24 hours in FLEC and after one month's storage in a well ventilated room	purpose was to identify emission characteristics of linoleum products; and to establish a link between emitted VOCs and odour perception
Colombo et al [50]	23 ± 0.5	45 ≤ 1 (3 products) 50 ≤ 1 (2 products)	n/m	n/m	0.507	test equipment equipped with devices capable of controlling temperature, relative humidity, ad air flow rate.	studied the VOC emissions from five household products by chamber testing and compared these results with those obtained from headspace analysis
ORTECH Corporation [51]	23	50	55 L	various loadings depending on material	0.5	a dynamic chamber test procedure was followed; chamber under positive 0.05 inch water pressure; 37 material samples tested representing both conventional and recycled (Build Green) building materials; examples are carpet, carpet under-cushion, insulation, cabinetry, counter tops, and drywall.	compared the emissions from the conventional building materials with those of the Build Green materials

Table 1 (cont'd): Summary of Small Chamber Test Conditions and Procedures Conducted to Date

Researchers	Conditions							Objective/Purpose of Experiment
	Temperature (°C)	Relative Humidity (%)	Volume and Material of Chamber	Product Loading m^2/m^3	Air Change Rate (ach)	Sampling Procedures		
J.T. Makohon and D.A. Figley [52]	23 ± 1	50 ± 5	n/m	various loadings depending on material	0.3 ± 0.0015	37 materials were tested for VOC emissions; 20 materials were tested for formaldehyde emissions	developed an environmental chamber test procedure; used these to test materials to establish a data bank for selection of lower emitting materials, and to provide data for IAQ computer simulation	
EPA [53,54]	37 ± 3 (source chamber) 24 ± 2 (exposure chamber)	50	Four 10 gallon (38 L) glass aquariums	n/m	n/m	samples of in situ carpet were used; samples were heated to 35 to 70 °C	EPA wished to replicate testing conditions achieved by Anderson Laboratories when exposure to carpet emissions killed laboratory mice	
P. Tappler et al [55]	23 ± 0.2	45 ± 3	1 m ³ stainless steel	1	0.5 ± 0.1	ventilated with clean filtered air; after each test temperature was raised to 110 °C to eliminate traces of absorbed substances	to compare the emissions from 12 textile floor coverings	
K. V. Vejrup and P. Wolkoff [56]	22	50	FLEC	n/m	507	air velocity was 1 cm/sec; samples tested over 1 week duration	compared emissions from 10 cleaning agents	
J.F. van der Wal et al [57]	21 ± 1	35 ± 5	1 m ³ stainless steel	1	1		to develop a quick evaluation technique for dynamic sorption effects of indoor composite materials	
G. Iwashita and K. Kimura [58]	22	40 ± 6	4 aluminum boxes each .3 * .45 * .3 m	n/m	41.2	different air velocities were used (0.05, 0.5, 1.0, 2.0 m/sec); samples of chipboard, carpet, rubber, and straw mat were used; used trained panel of 12 judges to evaluate air out of the box chambers	to evaluate influence of air velocity on perceived air quality	

were equipped to vary temperature from room to 60 °C in the glass chamber, and 70 °C in the stainless steel chamber. Relative humidity and air change per hour could be varied within a wide range. The experiments were conducted under static and dynamic conditions. The purpose of the static experiments was to identify emitted compounds and to determine their dependence on temperature and relative humidity. In their study, it was found that temperature variations did not have a significant effect on the concentrations of volatile compounds, but showed a stronger effect on less volatile compounds. For example, the concentration of styrene did not change with increasing temperature but the less volatile compound, benzothiazole, was strongly influenced by temperature variations. The relative humidity was noted to have little effect on all compounds with the exception of aniline. The report does not record the ranges of temperature or relative humidity used. Tucker [22] notes the same varied effect of relative humidity and attributes that only products which contain highly polar compounds require testing for relative humidity effects.

ASHRAE research subcommittee TC2.1 recently completed a draft report [60] on the effects of temperature and relative humidity on perceived air quality. Their experimental set-up included an 800 L stainless steel chamber equipped with a temperature and relative humidity controller and a computer controlled distribution and dilution system which transported the emissions to the subjects in a random manner. The subjects were located in a conditioned chamber ($T = 23$ °C; $rh = 45\%$; ventilation of 6 cfm per person). Ten building materials were tested, including nylon carpet, painted sheetrock, vinyl tile, plywood, and particle-board. Each material was placed in the 800

L chamber which was ventilated at 6 L/minute. Five temperatures and relative humidities were evaluated; the ranges of which were 19.1 to 26.2 °C and 29 to 69.5%, respectively. As the report was preliminary in nature, data could not be cited or quoted. However, the results, in general, can be summarized as follows:

- (1) Emissions (chemically and perceived) from all materials increased as the temperature increased;
- (2) The effects of the humidity variations cannot be generalized into a common trend for all the materials tested. For the most part, emissions increased as the humidity increased, though the reverse occurred for some materials (e.g vinyl tile). This was true for both chemical and perceived results.

In the research conducted by Gehrig et al [41], it was concluded that the characterization of emissions from building materials in real rooms is very difficult. Many parameters influence the VOC concentrations, including furnishings, fluctuating temperatures, relative humidity, air changes, indoor activities, and sink effects.

The European Collaborative Action, called "Indoor Air Quality and its Impact on Man", published a report on an inter-laboratory comparison of small chamber measurements [61]. The importance of this experiment was based on the upcoming preparation of databases on material emissions, providing an even further reason to standardize small chamber tests. In this report, the effects of temperature, air exchange rate, and compound volatility on material emissions were measured. Most tests were carried out under controlled environmental conditions, namely 23 °C, 45% relative

humidity and 1.0 air change per hour. In the case of temperature, tests were carried out at two laboratories and results showed that with an increase in temperature from 23 to 60 °C, the emission rate, both by concentration or weight loss for n-dodecane, increased. This was after the removal of the source; which, it was concluded, indicates the possibility of sink effects.

The US Environmental Protection Agency (EPA) have performed tests to characterize the emissions from a variety of sources of indoor air contaminants and to identify the effects of various factors on the emission rates. These factors included temperature, relative humidity, air changes per hour, and chamber loading. The testing facility included two 166 L stainless steel environmental chambers. Environmental parameters were controlled within the following limits: temperature ± 0.1 °C; relative humidity ≤ 2 %; airflow ≤ 0.7 % of reading. All materials were first analyzed using headspace testing to identify the chemical compounds emitted. The results of the effects of air change rate and temperature on moth crystal emissions was reported. Two temperatures, 23 and 50 °C; two relative humidities, 20 and 50 %; and several air changes per hour, from 0.25 to 2.0 ach were tested. The results show that for para - dichlorobenzene (main component in moth crystals) an increase in temperature caused increased emissions; as did increased air change rates. The author states that the air change was especially of importance in its effect on wet materials. Emissions decreased sharply during the first hours of application, and was especially aided by a higher air exchange rate. The effects of relative humidity during these tests, were not reported [21,23,35,62].

Sheldon et al [63] noted that conditions such as temperature, relative humidity, amount of material tested, and curing time affect chamber test results. While these can vary among different tests in one chamber, when comparisons are made between studies by different researchers, results vary enormously.

Gebefugi and Korte [64] studied the chemical accumulation on different textile materials, such as cotton, acrylic, and lambs wool, placed in a small chamber (50 x 50 x 50 cm) when the walls of the chamber were coated with such products as Pentachlorophenol (PCP), Lindane, Fumemcyclox, and Dichlofluenuid. The textile samples were then analyzed by capillary gas chromatography with electron capture and flame ionisation detectors within 72 hours of their exposure. The samples were tested at three different temperatures, 18, 23, and 28 °C without ventilation. The results show that adsorption increased with a temperature increase. These reported results were for tests conducted using Fumemcyclox. The group also noted that higher relative humidities caused higher adsorption by the textile samples, although no results were published.

Emission data related to formaldehyde have been extensively researched. The Housing and Urban Development Agency (HUD) in the United States have developed standards for formaldehyde use in pressed wood products. These standards were based on chamber tests and the use of an equation, which relates formaldehyde concentrations at 25 °C, 50 % relative humidity to those recorded in chamber tests at various temperatures and relative humidities. In this way, the predicted formaldehyde concentrations increase with increasing temperature and relative humidity. Other models have been developed which relate formaldehyde concentrations to more factors, such as air change

rate and product loading. One such model, developed by Matthews et al, predicts increasing concentration with increasing air changes per hour and with decreasing product loading [33].

Indoor Air Quality Update holds that increased humidity levels increase off-gassing and desorption of gases from some building materials [9,65]. Researchers in West Germany have studied emissions from carpets under headspace analysis in a 100 ml flask. With an increase in temperature from 24 to 50 °C, emissions increased by 500 %. This shows how susceptible carpet emissions are to temperature, although the researchers hold that this significant increase in emission rate could not be due to vapour pressure differences alone [9].

Levin [66] reports on the results obtained while evaluating building products and materials during the design of a large office building situated in California. The project involved reviewing materials/products to identify those most likely to emit contaminants; screening these materials using literature and manufacturer's data; testing selected material to determine chemical content, emission rate, or change in composition due to environmental exposure, and to make recommendations to the building owner and architect for material selection, modification, and handling to reduce indoor air contamination. When testing the materials, the bulk testing, environmental chamber and headspace air sampling methods were used. The effect of temperature variations on emissions using headspace and chamber testing was evaluated, however, the author reports that the number of temperature tests and the use of the results are limited. Two temperatures were used, 23 °C and 37 °C. The chamber was made of sheet metal, 1.7 m³

in volume with controlled airflow and temperature. Air change within the chamber was typically 12 per hour. Humidity was not controlled during testing, though, it was recorded to be between 50 - 55% for most test runs. The author did not present the results for the temperature effect tests because insufficient data was obtained to inspire enough confidence in the results obtained and in the testing facilities used.

While chamber testing was not used in the study conducted by van der Wal et al [67], interesting results were discovered from the experiment on thermal insulation. Results show that at elevated temperatures, 50 °C, odours from wet insulation (insulation which may be exposed to environmental moisture) were significantly greater than when dry. Also the increased presence of aliphatic and aromatic aldehydes was noted under the same conditions. Quantities were almost one hundred times greater. The researchers concluded that the binder material of the mineral wool decomposed faster under wet and elevated temperatures.

Shriever and Marutzky [68] studied VOC emissions from varnished parquetry floors. They compared measurements and results obtained from three sources, in two real-life rooms and in chamber testing. The authors did not control the temperature in the real-life rooms, but recorded them to range from 19 to 25 °C in one room and 20 to 30 °C in the other, and hold that this variation would have some effect on the VOC's reported, although this is not quantified in any way. The chamber tests were conducted in a 1 m³ chamber to evaluate formaldehyde emissions. The test was conducted at 23 °C, 45 % relative humidity, and 0.5 ach.

Pickrell et al [69] studied formaldehyde emissions from different products to

evaluate the influence of chamber loading, relative humidity, temperature, and multiple products. Samples of a particle-board, plywood, insulation material and carpet were tested. A 0.45 m³ dynamic chamber was used. Temperature was varied to maintain at 25 or 35 °C. The relative humidity was maintained at either 40 or 90 %. Results show that the change in temperature or relative humidity did not have a significant effect on formaldehyde emissions for the particle-board or plywood. The authors explain that these results are contradictory to other researchers but explain that their product loading was higher than that normally used by other researchers.

2.3 Other Findings

Fortmann et al [13] compared seven different methods for analyzing the emissions from architectural coatings, where paint was predominantly used. One of these methods was the small chamber. The research concluded that additional development in the area of evaluating methods of VOC emissions was required.

Plehn [34] evaluated the solvent emissions from 25 low polluting paints and varnishes. The objectives of his study were threefold: (1) to determine the solvent composition of samples via headspace analyses; (2) to measure solvent emissions via chamber tests; and (3) to measure the emissions in a real-life situation. The chamber tests were conducted in a 17 m³ chamber. The walls of the chamber were covered by aluminum foil to avoid adsorption/desorption effects. The air change through the chamber was 0.8 ach. The product loading was 100 g of paint for every 1 m² of aluminum foil used. The author found that the paints labelled as low-polluting had significantly lower

emissions than the regular paints.

NASA (National Aeronautics and Space Administration) in the United States has one of the most extensive databases, with over 5000 entries (in 1989), collected on material emissions [23,70]. These products are strongly related to the spacecraft industry, including those used in construction and operation, as well as those that may be carried by personnel [63]. The testing method used by NASA involved a small chamber of, at least, 2 Litres in volume, commonly 4 Litres was used. The chamber was heated to a temperature of 120 °F for a 72 hour duration. The material was then analyzed, that is, air samples within the chamber were taken and analyzed at room temperature [62,70]. Ozkaynak et al [70] report that the emission testing used by NASA is somewhat conservative for several reasons including the high temperature of 120 °F used, the reduced pressure of 12 psia used, and that all material samples used were freshly prepared.

One study by Baechler et al [63], compared some of the results recorded in the NASA database to other results obtained when similar products were tested by other researchers in small chambers or field tests. The investigation concluded that the emission rates recorded in different studies were significantly different. The authors recognized some shortcomings involved in such a comparison. These included: differences in experimental facilities; NASA used a temperature of 120 °F while others used room temperature; NASA did not consider relative humidity; comparisons with field measurements is made difficult because of the dynamics of the temperature and relative humidity in a true life building.

De Bortoli et al [71] report on a second inter-laboratory comparison, conducted by the European Collaborative Action, involving the comparison of the emissions from paint in small chamber tests conducted in 18 laboratories from 10 countries. The paint was a waterborne styrene/acrylic paint, applied onto stainless steel plates with a nominal wet thickness of 200 micrometers. All labs met the following test conditions: chamber loading of $0.5 \text{ m}^2/\text{m}^3$, temperature of $23 \text{ }^\circ\text{C}$, relative humidity at 45 %, one air change per hour, and an air speed of 10 cm/s. Chamber volumes varied between 35 cm^3 to 1.47 m^3 . The results showed that there were considerable variations in the results from the different labs. It was concluded by the authors that these differences can be attributed for the most part to the paint sample thickness/uniformity and to the GC/MS analysis. For the latter, the labs were permitted to use their preferred methods.

Bjorseth and Malvik [72] have investigated the number of components in water based paints which have been identified to cause allergic or irritating effects. Three latex and one acrylate paints were tested. The authors used a 100 L stainless steel chamber equipped with small internal fans. The test conditions were $23 \pm 1 \text{ }^\circ\text{C}$; $50 \pm 5 \text{ \% rh}$; 0.5 ach ; and $1.2 \text{ m}^2/\text{m}^3$ product loading. The paints were applied to aluminum substrates. The results showed that the concentrations and, in some cases, the presence of the problem components decreased considerably in the more recent water-based paints as compared to water-based paints which have been on the market for a longer time.

Jorgensen et al [73] studied the influence of wall material on the emissions from paint. The substrates tested were aluminum, gypsum board, and gypsum board with wall coverings. In addition, two different paints were tested, both of which were water-based.

One was an acrylate paint, while the other was referred to as a "natural" paint. The paints were applied to the substrate and left at ambient temperature for 1 hour. Following this the samples were placed inside a glass test chamber for 23 hours. The chamber was conditioned at 23 °C, 35 % rh, 1.0 ach, and 0.15 m/s air velocity. The emissions were then tested using the FLEC. After the initial 24 hour conditioning period, the FLEC was placed onto the painted area and samples were taken. The sampling conditions were 23 ± 0.5 °C, 48 ± 3 % rh, and 507 ± 2 ach. Results showed that the emissions from the aluminum substrate were initially higher than for the other tested materials, but with time (over 30 days) the emissions were lower. Results also showed that the "natural" paint emission profile was considerably different from conventional emission decays.

2.4 Conclusions

In spite of the extensive research conducted and presented above, questions regarding emissions test data still remain unanswered. In a recent forum, held during the 2nd International Conference on Indoor Air Quality, Ventilation, and Energy Conservation (Montreal, May 1995), the following challenges are presently facing researchers in the area:

- Develop standards now?
- Commit to basic research to understand fundamental properties?
- Use emissions tests to validate fundamental principles?
- Address serious lack of health effects data?
- Address issues of material durability; life expectancy; maintenance; cleaning requirements?

The present study assists in understanding the fundamental properties involved in material emissions testing, contributing in part to overcoming these remaining challenges. Much of the research presented above have provided contradictory results. Further, no one, with the possible exception of the EPA, has undertaken a systematic study of the effects of temperature and relative humidity on building material emissions. J. White [74] expresses that "herein lies the future".

CHAPTER III

THEORETICAL REVIEW

Material emissions are the result of several mass transport processes. The interaction of these processes commonly occurs, but their effects on material emissions are somewhat complex. However, we can consider the emissions to stem from two main categories.

3.1 Diffusion within the Material

Diffusion of a compound through a material can be the result of a concentration, pressure, temperature or density gradient [75]. Diffusion is described by Fick's Second Law [75,76,77]:

$$\frac{\delta C_A}{\delta t} = D(\nabla^2 C_A) \quad (1)$$

where $\frac{\partial C_A}{\partial t}$ = rate of change in concentration of compound A with respect to time, (mg/m³ * h),

D = diffusion factor (m²/h), and

∇^2 = represents the Laplacian operator of C_A through the x, y, and z directions.

Each compound has its own diffusion factor, dependant upon its molecular weight, molecular volume, temperature, and the characteristics of the material within which the diffusion is occurring [75,78]. For a given sample, such as paint, the overall diffusion factor is very difficult to determine.

3.2 Surface Emissions

The surface emissions occur between the material and the overlying air as a consequence of several mechanisms, including evaporation and convection. As long as a concentration gradient exists between the two phases, surface emissions will occur. This phenomenon can be expressed as [75,78]:

$$E_A = k_A(C_s - C_a) \quad (2)$$

where E_A = surface emission rate of compound A ($\text{mg}/\text{m}^2 \cdot \text{h}$)

k_A = mass transfer coefficient (m/hr)

C_s = concentration of compound A at the surface of the material (mg/m^3), and

C_a = concentration of compound A in the overlying air (mg/m^3).

In liquids, the evaporation of a compound is a dominating process, and therefore, the vapour pressures of the compound and overlying air can be shown to be proportional to their concentrations in Equation (2) [78]. The mass transfer coefficient is dependant upon the environment in which these processes are taking place, including the surface velocity and turbulence, surface characteristics, and the properties of the overlying air [75,78]

Tichenor et al [79] report that Hansen (1974) determined that diffusion was not a controlling process in water-based paints. Rather, evaporation (surface emissions) controlled the emissions of volatiles even after a long elapse of time. However, Clausen

[80] reports a finding by Sullivan (1975) that established that after the sample has dried, the emissions may be controlled by either evaporation (surface emissions) or diffusion depending on the volatile organic compounds involved.

Adsorption/desorption processes also need to be considered. In a real room, materials may adsorb compounds emitted by other materials, releasing them at a later time. This complicates the investigation of material emissions in real rooms. However, in the chamber tests, the only materials present are the sample and stainless steel. As stainless steel is inert, its adsorption effects can be considered negligible. Therefore, the sample itself is the only source of adsorption, which can occur if the air exchange through the chamber is not high enough to eliminate these compounds.

3.3 Determining Emission Rates

Based on the equations above, theoretical and empirical models have been developed to predict mass transfer processes in material emissions. Two predominant empirical mass transfer models are in use.

3.3.1 First Order Decay Model

The simplest and most commonly used model for thin film sources is the first order decay, expressed as [20,22]:

$$E = E_0 e^{-kt} \quad (3)$$

where E = VOC emission rate ($\text{mg}/\text{m}^2 \text{ h}$) at time t

- E_0 = VOC emission rate ($\text{mg}/\text{m}^2 \text{ h}$) at time $t = 0$, and
 k = emission rate decay constant (h^{-1}).

This model can also be expressed in terms of concentration (C) in lieu of the emission rate, as E can be shown to be proportional to C.

3.3.2 Double Exponential Model

It has been shown that the first order decay model does not apply to many emission profiles measured experimentally [79]. As a result, Colombo et al [81] developed a double exponential decay model, given by:

$$c(t) = A[1 - e^{-Bt}] - C[1 - e^{-Dt}] \quad (4)$$

- where $c(t)$ = concentration at time t (mg/m^3),
 t = time (h),
 A, C = linear coefficients (mg/m^3), and
 B, D = rate coefficients (h^{-1}).

The authors have successfully applied this model to concentration versus time data obtained for a variety of materials.

3.3.3 Direct Calculation

As the work presented here is experimental in nature, the emission rates of the

samples tested will be determined by direct calculation. In a correspondence with Dr. Z. Guo [82], the direct calculation of the emission rates from the chamber concentration data can be determined by the following equation:

$$E(t) = \frac{\left(\frac{\Delta C}{\Delta t} + NC\right)}{L} \quad (5)$$

where $E(t)$ = emission rate at time t ($\text{mg}/\text{m}^2 * \text{h}$)

$\frac{\Delta C}{\Delta t}$ = concentration increment at time, t ($\text{mg}/\text{m}^3 * \text{h}$)

N = air exchange rate (h^{-1})

C = chamber concentration at time t (mg/m^3), and

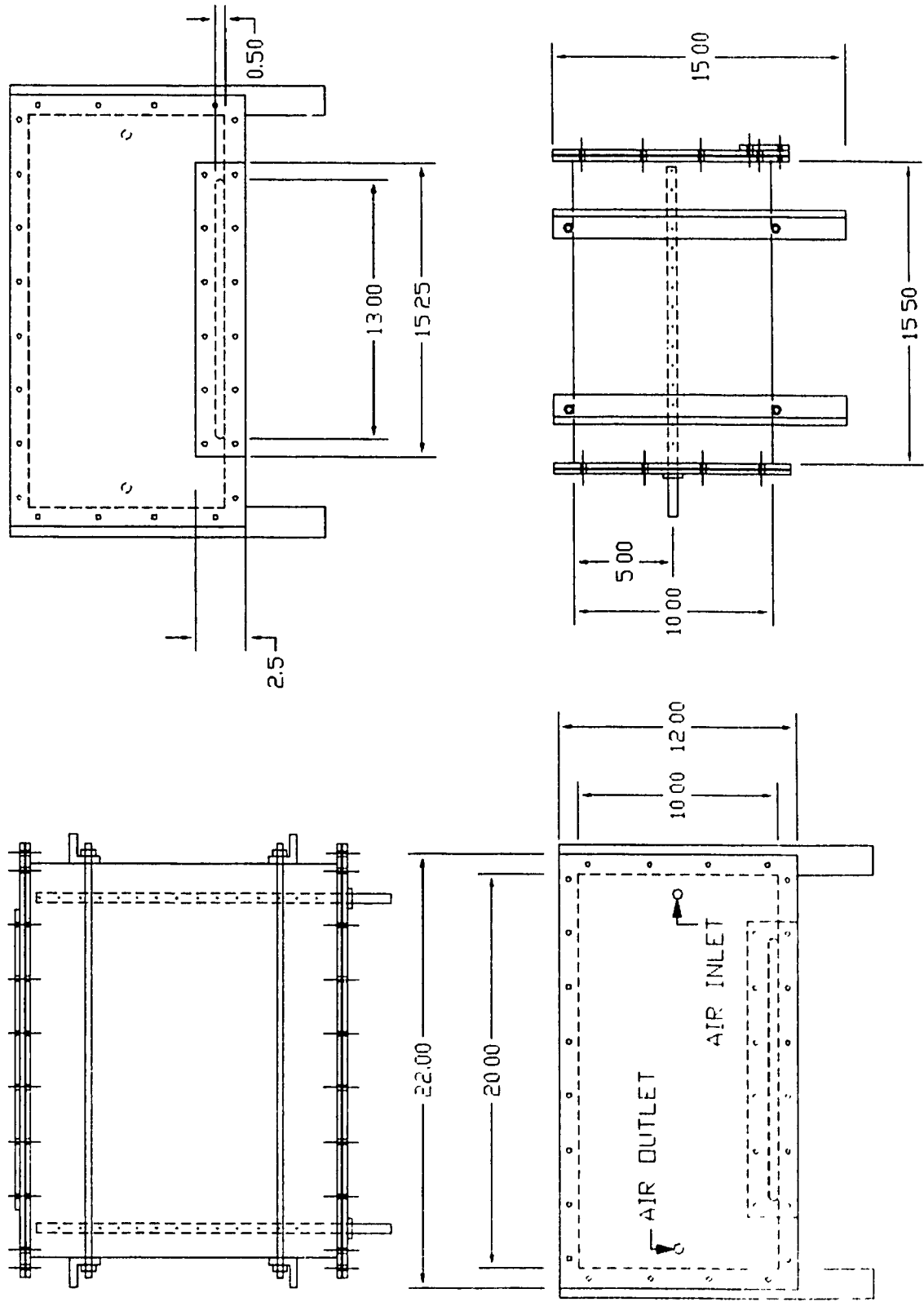
L = chamber loading factor (m^{-1}).

CHAPTER IV

EXPERIMENTAL SET-UP AND METHODOLOGY

4.1 Chamber Description

The small environmental chamber built for this work, shown in Figure 1, was based on the standard chamber used by the EPA; it is also in accordance with the ASTM guideline D-5116-90. The chamber is constructed of stainless steel with electropolished interior surfaces to ensure against adsorption/desorption effects. The chamber is 52.44 L in volume. Inlet and outlet ports, located at the transverse centre of the chamber, are made of teflon tubes. The ports extend into the full depth of the chamber and are perforated to allow for better air distribution. The back and front faces of the chamber are openable by removing the nuts and bolts around the perimeter. A self-adhesive gasket surrounds the inside perimeter of these surfaces to prevent air leakage. The gasket is made of 100% pure polytetrafluorethylene (PFTE) which, the manufacturer ensures, is suitable for many critical applications. The original (EPA) chamber design was slightly modified when initial experiments revealed an unwelcome problem. After equilibrium conditions were achieved, say the temperature was 35 °C and the relative humidity was 2 %, the sample was ready to be inserted. This could only be achieved by removing the entire back plate of the chamber. This disrupted the equilibrium conditions significantly. As a consequence, a slot (15.25" * 0.25") with cover (2.5" * 15.5" * 0.25") was machined at the base of the back face to allow for the easy and quick insertion of the sample during testing. This reduced the disturbance considerably. Again, a gasket (as described above) surrounds the



INCH SCALE 1:8

Figure 1: Schematic Views of Environmental Chamber

inside surface of the slot's cover to guard against leakage.

4.2 Air Supply

The air supply for all tests is provided by bottled air of a pure medical breathing grade. As such, the air is purely dry, 0% relative humidity, with no contaminants.

It was decided that an air exchange of 1.2 ach will be used for all tests. This corresponds to an air flow rate of 1 000 mL/min through the chamber. This flow rate was measured and controlled by a rotameter. The rotameter was calibrated with a bubble meter. The air flow rate out of the chamber was also measured to determine the leakiness of the chamber. This air flow rate was measured using an electronic mass flow meter. The mass flow meter was calibrated in the same manner as the rotameter. In general, the exit flow rate was at most 5% lower than the in-going flow. This is acceptable considering the pressure differences that the air must go through as it expands into the chamber and subsequently contracts through the exit port.

4.3 Temperature Control

A schematic representation of the entire testing facility for temperature is shown in Figure 2. Temperature control is achieved by placing this facility inside a temperature controlled chamber. This chamber, one of a twin, is equipped with a temperature controlled heating/cooling system whose range is between 10 - 40 °C. The chamber is 2.29 m * 2.27 m * 2.26 m. The desired temperature in the twin chamber is set and reached within minutes. However, the environmental chamber and its air supply are

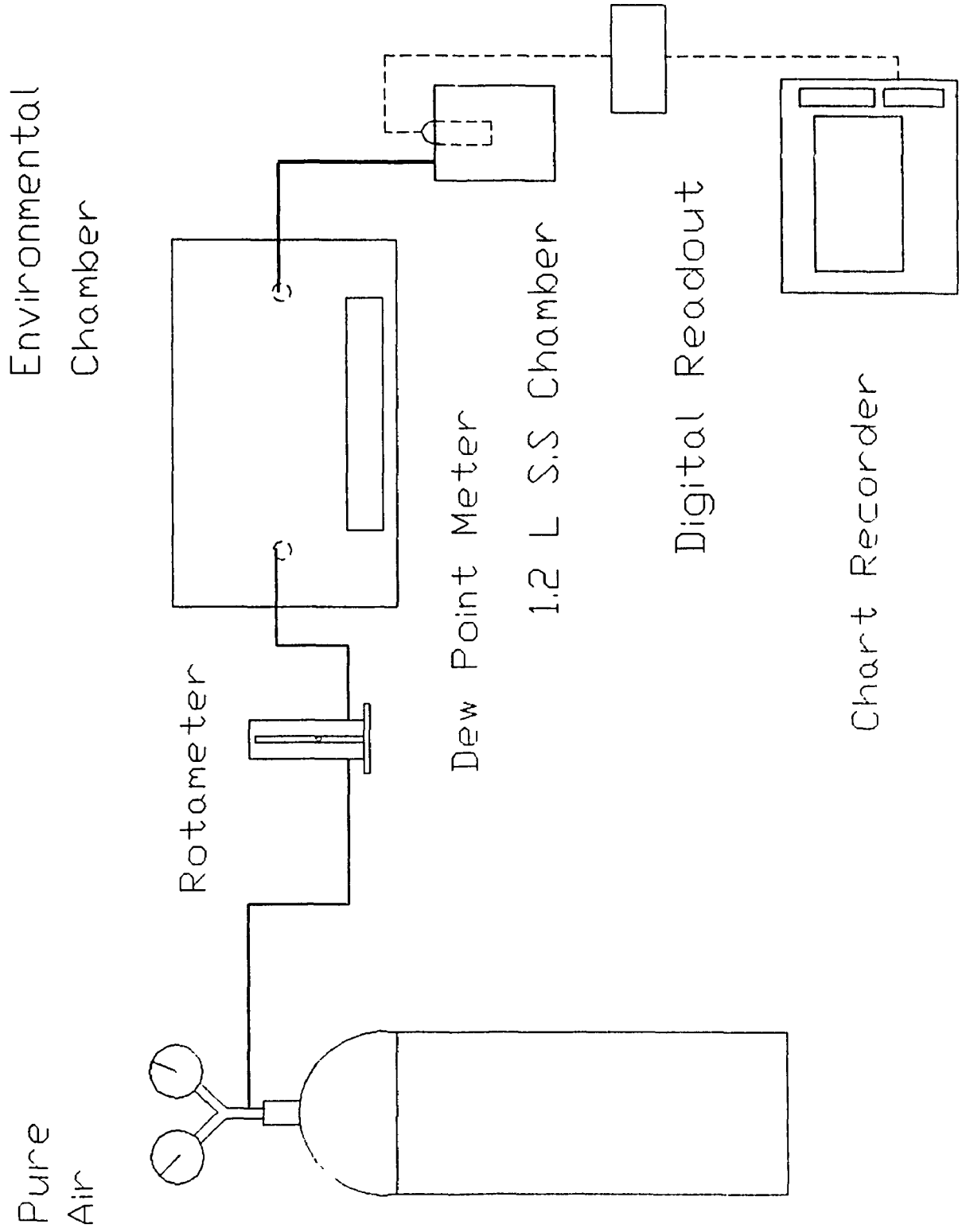


Figure 2: Schematic Drawing of the Temperature Test Set-Up

allowed to reach steady state before a sample is inserted and the test begins. Steady state is ensured by recording the air temperature and relative humidity in the environmental chamber using a chart recorder. The sensor used for this is a Protimeter Dewpoint Meter (DP 989M). The meter determines the relative humidity by measuring the dew point temperature. This is achieved through opto-electronic detection of the dew formed on an electrically cooled gold mirror. The temperature of the mirror is continuously monitored such that when dew is formed the new temperature is stored. This probe also carries a transducer for measuring ambient temperature. The meter can record within 1 to 100% relative humidity and -40 to 60 °C ambient temperature. The sensor is located in a 1.2 L stainless steel chamber connected to the exit port using Tygon tubing. It was not possible to place this sensor in the chamber itself as the head is 2 inches in diameter. This would have required machining a large hole in the chamber which would possibly lead to damaging the electropolished interior surface as well as compromising the airtightness of the chamber. If one of these mishaps occurred, the damage would be irreparable. Rather than take this chance, a 1.2 L stainless steel beaker was acquired and a plexiglass cover was machined to hold the sensor.

4.4 Relative Humidity Control

The schematic representation of the testing facility for humidity is shown in Figure 3. It is similar to the temperature set-up, with the exception of the inlet conditions. Before entering the chamber, the dry air from the cylinder is split into two paths. One portion enters directly into a mixing chamber, while the other portion flows through a plugged

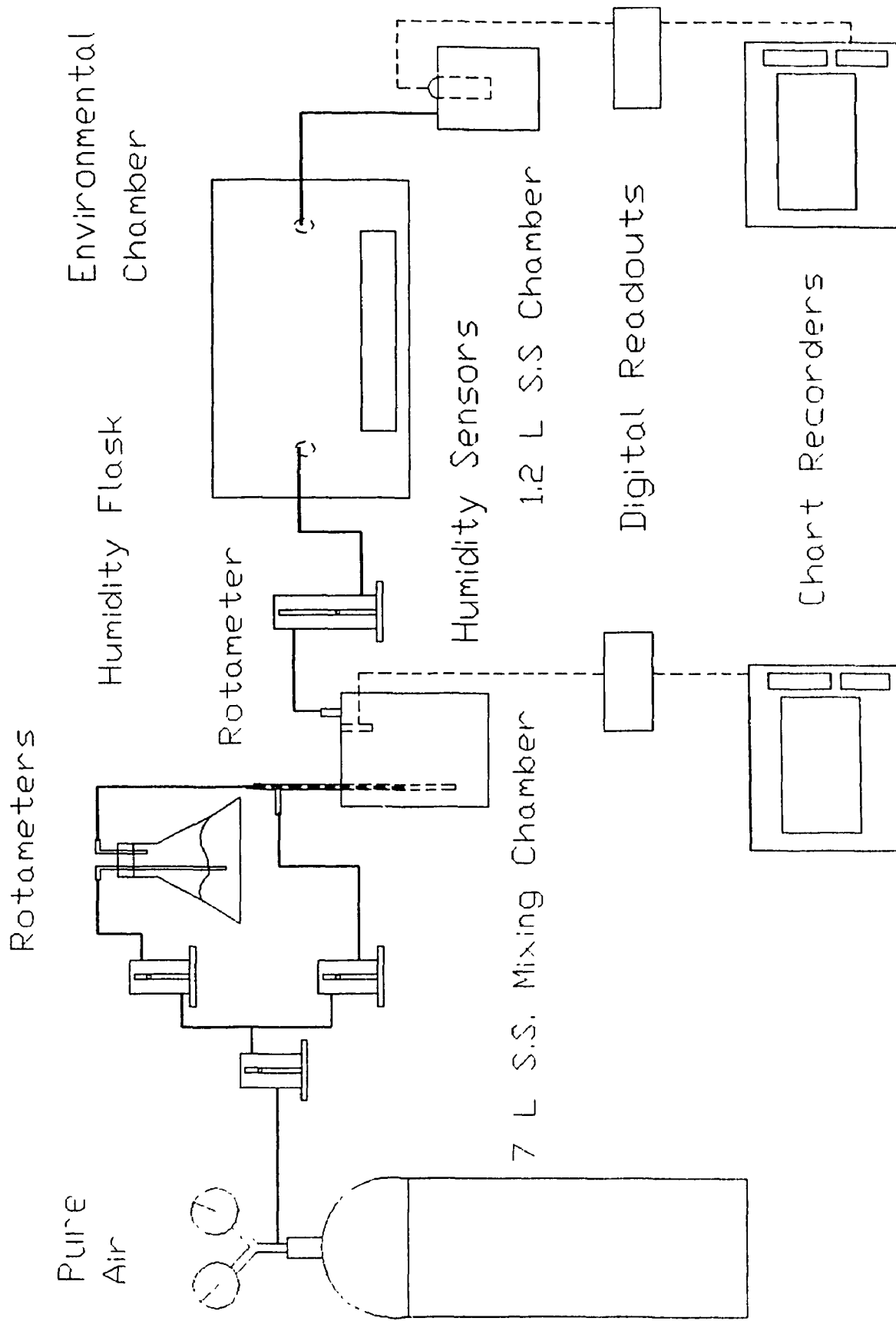


Figure 3: Schematic Drawing of the Relative Humidity Test Set-Up

flask filled with distilled water, picking up moisture before entering the mixing chamber. The flask contains two glass straws. The inlet straw carries in-coming air into the depths of the water; while the shorter outlet straw carries the moist air into the mixing chamber. The mixing chamber is a 7 Litre stainless steel flask, with a plexiglass cover. Its inlet port consists of two stainless steel pipes, one inside the other, allowing the dry and moist air streams to begin mixing before they actually enter the mixing chamber. A humidity sensor inside the mixing chamber records the relative humidity of the mixture. This sensor is a capacitative type, where the humidity level is proportional to its capacitance. The sensor is accurate to $\pm 2\%$ rh from 0 to 90 % and $\pm 3\%$ rh for 90 - 100 %. The desired inlet humidity level is achieved by adjusting the portions of air which enter each path. This is achieved by adjusting the flow through the rotameter connected to each path. From the mixing chamber, the air mixture, at the desired humidity, flows through another rotameter to achieve the flow rate required for 1.2 ach. When the system reaches equilibrium, the inlet and outlet levels of relative humidity recorded by the two humidity sensors are within 1% of one another. This is very acceptable considering the manufacturers' specified accuracy.

4.5 Sample Description

The paint used for this experimental work was a water-based gloss acrylic. It is suitable for both interior and exterior applications. The manufacturer's label boasts that the paint is fast drying with low odour. However, health and safety advice on the label also suggests that when applying the paint, always ensure good ventilation. At 21 °C, the

paint should be dry to the touch within 1 hour and ready for a second coat within 12 hours.

The varnish selected is a polyurethane plastic finish varnish for interior or exterior use. It has a drying time of within 8 hours.

4.6 Test of Air Mixing in the Experimental Chamber

The tracer gas decay technique was used to test the air mixing in the environmental chamber. Air entrainment, a result of poor air mixing, can effect the transport of the contaminants emitted by the sample, thus yielding questionable results. The tracer gas used was sulphur hexafluoride (SF_6). A known amount of SF_6 tracer gas (50 μL) was injected through the Tygon tubing located in the in-stream air. Fifteen minutes elapsed before samples were taken at 10 minute intervals for a total duration of 1 hour. Samples were taken at two locations. One point corresponds to the Tygon tubing carrying out-going air. The samples were taken by inserting a syringe into the tubing and drawing out 50 mL of air. The other point was chosen in air at a position just above the surface of the sampling area. One bolt from the slot door was removed, exposing the threaded hole. A straw, 21 cm long, was inserted to a depth of 15 cm. The exposed end of the straw was taped to prevent air leakage. Samples at this location were taken by inserting a syringe through the taped end, and drawing air in through the other end of the straw. Again 50 mL samples of air were drawn. At each time interval, the 50 mL air samples drawn through the syringe were injected into labelled vacutainers, similar to those used to preserve blood samples. The concentrations of SF_6 in the air samples were

analyzed using the Varian 3400 Gas Chromatograph. The air exchange rate based on these SF₆ concentrations at known times was determined by using a computer program written in Matlab by Dr. J. Rao [83]. The results obtained indicated that the air in the chamber can be confidently considered as well mixed.

4.7 Sample and Chamber Preparation

Product loading is defined as the ratio of material surface area to the volume of the chamber it is occupying. It has been shown that the product loading effects the emission rate determined through small chamber tests. As such, the product loading should remain constant for all tests if it is to be eliminated as a variable in the changes in recorded or measured emissions. As shown in Chapter 2, Table 1, many researchers have tested at different values of product loading. Therefore, it was decided to choose a value for the product loading which would be typical or indicative of a real life situation. As such, a room was hypothetically chosen, 5 m * 5 m * 3 m in size; say, a good sized office. It was assumed that the four walls in the room were painted and the floor varnished. Typically, panels are used at the ceiling. Thus, the surface area within the room that is covered with paint is 60 m², and that covered by varnish is 25 m². The volume of the room can be calculated to be 75 m³. Therefore, the product loading of paint in this room is 60/75, or 0.8 m²/m³. This value was then used as a target product loading for the testing described here. With a chamber volume of 52.44 L, corresponding to 0.05244 m³, a painted surface area of approximately 0.0420 m² is needed. This relates to an area of approximately 20.5 cm * 20.5 cm. For simplicity, a square of 20 cm * 20

cm was used. Though the painted area is set, it does not necessarily ensure that the amount of paint used per test would be the same. Thus, it was necessary to determine the weight of the paint used. To do this, the substrate with a 20 cm * 20 cm outline pencilled on it, was weighed. The paint was then applied with a brush as uniformly as possible to cover the 20 cm * 20 cm area. The substrate and paint were then weighed again. It was determined that 10.2 grams of paint were needed to uniformly paint the area. All subsequent tests were then conducted with a 10.2 g sample of paint. In a similar manner, the product loading for varnish was calculated to be 25/75 or 0.33 m²/m³. This corresponds to an area of 0.0173 m² within the chamber. Based on this, a sample area of 13 cm * 13 cm was chosen. When the varnish was applied uniformly over this area, it was determined that 2.0 grams were needed. Thus all varnish tests were conducted using a 2.0 g sample weight.

A stainless steel substrate was chosen as it is an inert material, and would not contribute to the emissions profile. However, the stainless steel plates (cut into 30 cm * 30 cm squares for leeway) could only be used for one application. Cleaning the substrate would be a lengthy process, as well as, requiring a highly volatile solvent, such as paint thinner or turpentine. As numerous tests would be conducted, many steel plates would be needed, amounting to an expensive and meagre use of steel. Thus, it was decided to use a polyethylene wrap, containing no plasticizers, as a protective cover over the steel. The wrap is the same as that used to cover food. The wrap was tested for emissions and yielded nothing. In this manner, the sample was applied to the steel substrate, covered with a small square piece of wrap. At the end of each test, the wrap with the dried sample

was easily discarded. The steel substrate was then washed with an alkaline detergent and allowed to dry before the next test.

Initially and following all tests, the interior surfaces of the environmental chamber were washed with an alkaline detergent (as recommended by ASTM Guideline D-5116-90), and allowed to dry. Subsequently, pure fresh air was allowed to flow through the chamber for a minimum of 12 hours prior to the following test. As a further precautionary measure, before a new test was started, a sample of the air in the chamber was taken and analyzed by Gas Chromatography to ensure the background air was clean.

The paint sample was applied using a 2" polyester bristled paint brush. After each application of the acrylic paint, the brush was immediately washed with soap and hot water and allowed to dry before its next use. When samples of varnish were applied, it was necessary to clean the brush with a paint thinner or turpentine. As these are very volatile solvents, it was unclear what effect they may have on the subsequent varnish sample applied. Consequently, it was decided to use a newly bought, clean paint brush for each varnish application.

4.8 Air Sampling and Analysis

Air samples from the chamber are taken at varying time intervals, depending on the environmental test conditions. At a minimum, a sample was taken at the following time intervals immediately following the insertion of the sample into the chamber: 15 minutes, 1, 2, 3, 4, 8, 12, 24, and every subsequent 24 hours until the emissions curve has reached steady state. The air samples were drawn from the exit port using a calibrated

pump. The connection to the exit chamber is disconnected during sampling time in order to connect the sorbent tube necessary to trap the air, see Figure 4. The pump is calibrated to 100 mL/min \pm 2 mL/min, and each sampling period lasted twenty minutes for the paint samples and ten minutes for the varnish samples; thereby drawing an air sample volume of 2 Litres and 1 Litre, respectively, from the chamber. Other sample volumes, such as 500 mL and 1000 mL for paint and 250 mL and 500 mL for varnish, were also verified. For both the paint and varnish samples, the results at different volumes were not significantly different. It was decided that a larger volume would ensure a better representation of the air in the chamber. Volumes greater than these were not attempted for fear of exceeding the capacity of the sorbent tube.

The sampling tubes are multi-sorbent, consisting of glass beads/ 150 mg 20/35 mesh Tenax -TA/ Amborsorb/ Charcoal. Each tube is made from Pyrex and is 20 cm long with an outer diameter of 6 mm. The different layers serve to trap a broad range of high and low molecular weight compounds. This particular blend retains volatile compounds as well as compounds with high boiling points; while simultaneously allowing carrier gases, air, and water vapour to pass. Immediately after analysis, each tube is cleaned and conditioned. This is achieved using the Envirochem Model 785 single unit trap/tube conditioner. The conditioning process involves a five minute period where nitrogen gas is allowed to flow (rate of 45 mL/min) through the tube; followed by a heating period of 45-60 minutes at 300 °C during which time the nitrogen is always flowing; and a final cooling off stage where the heating element has been turned off and the nitrogen gas flows through the tube until it is sufficiently cooled to atmospheric temperature (usually

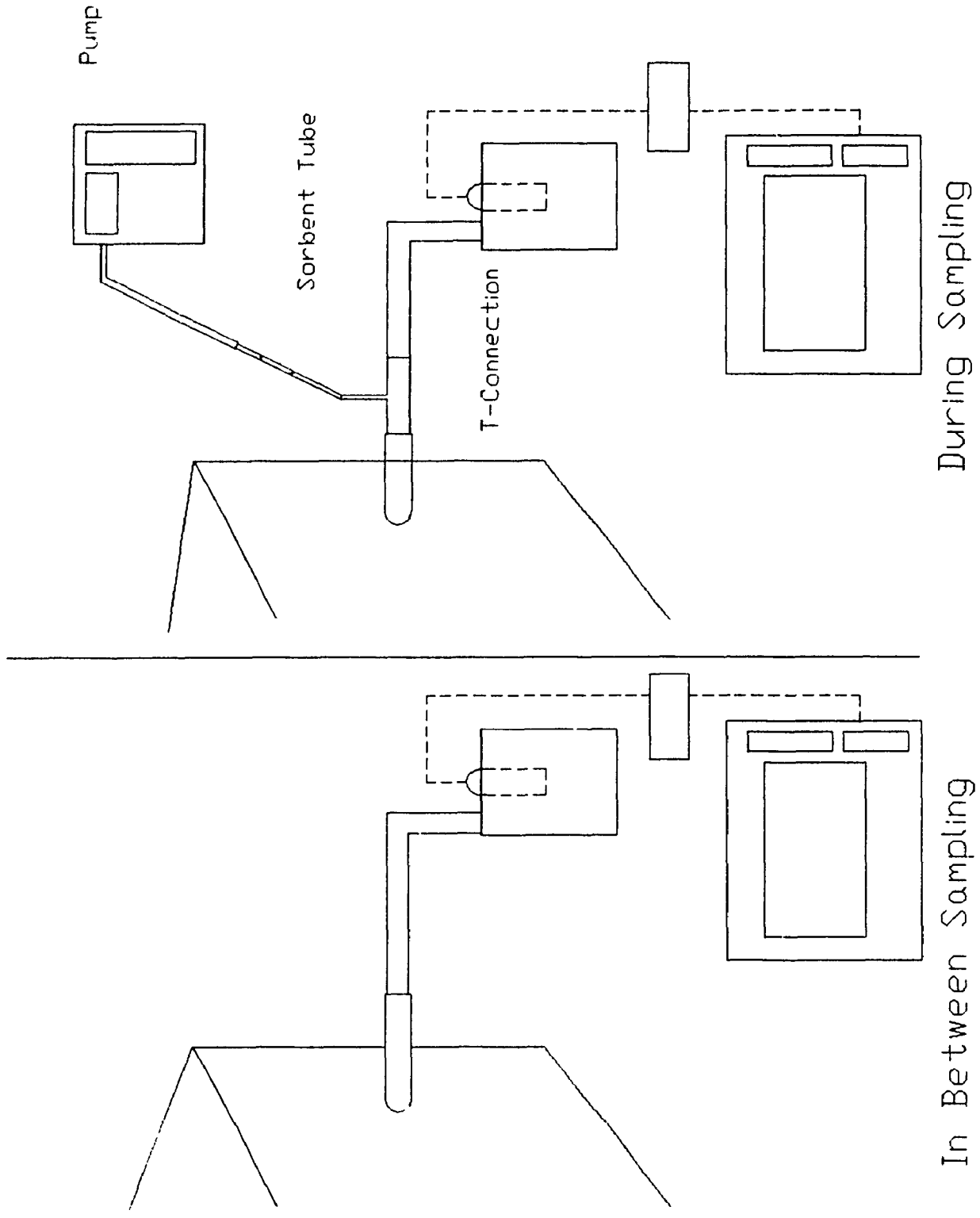


Figure 4: Exit Connection In Between and During Sampling

5 - 10 minutes).

The samples are analyzed using the Hewlett Packard 5890 Series II gas chromatograph (shown in Figure 5).

The samples are introduced into the gas chromatograph through the trap desorber (Figure 5). The trap desorber is a Tekmar 6000 AERO Trap Desorber. The trap desorber desorbs volatile organic compounds from the multi-sorbent tube and concentrates them for delivery into the gas chromatograph. This is done in five steps: (1) the tube is loaded into the front panel of the desorber; (2) the cryogenic trap is cooled with liquid nitrogen to a temperature of $-165\text{ }^{\circ}\text{C}$; (3) sample or sweep gas flows through the multi-sorbent tube and carries away water vapour and oxygen; (4) the multi-sorbent tube is then heated to release the volatiles which are carried away by carrier gas and deposited into the internal trap; (5) the internal trap is heated to desorb the volatiles which are sent to the GC by a back flush of carrier gas.

As the sample is introduced into the GC, it is mixed with the carrier gas, Helium. This stream of gas enters a split inlet where it is separated at a 1:50 ratio. The one part enters the column, while the 50 part is vented out. A split inlet is required when samples are very volatile, as in the case of the VOCs being tested [84]. The GC contains a capillary column, 50 m long with an internal diameter of 0.32 mm. The capillary type column is an open tube lined with a thin film of liquid [85]. In our case, the tube is made of fused silica with a polymer lining composed of a cross link of 5% diphenyl and 95% dimethyl polysiloxane, 1.05 μm thick. The manufacturer's information boasts that this lining is widely used due to its high efficiency, inertness, and low bleed (the cross-linking



Figure 5: Photograph of GC (right) and Trap Desorber (left)

immobilizes the film) [86]. As the sample passes through the column, the individual compounds will adhere onto the column surface thereby separating. The longer the column is the more efficient the separation will be [86]. From the column, the gas stream enters the GC detector, where each component is identified individually in chronological order, establishing their retention times.

The chromatograph is equipped with both a flame ionisation detector (FID) and an electron capture detector (ECD). In an FID, hydrogen and air (ultra pure carrier grade) mix to produce a flame. When an organic compound is introduced to the flame, a large increase in ions occurs. Because of its polarity, ions will be attracted to the collector in the detection zone. This will produce a current proportional to the amount of the organic compound introduced, which in turn is translated into a peak on a chromatogram by the HP Chemstation Software interface. The FID is used for the analysis of all samples here because it responds well to all organic compounds with little response to carbon dioxide, carbon monoxide, water, nitrogen, oxygen, and inert gases; thereby eliminating air and carrier gases from the chromatograms. The FID is also very sensitive to hydrocarbons which are predominant components in the paint/varnish samples. This is contrary to the ECD which is not very sensitive to hydrocarbons, as well as ethers, esters, ketones, and aliphatic alcohols [87]. As some of these are expected components in our material samples, the ECD was not used. Each sample analyzed by the GC takes a total time of 56.5 minutes. The method set on the GC involves an initial oven temperature of 10 °C for a two minute duration. This is followed by a ramp step of 4 °C/minute up to 200 °C (total time of 47.5 minutes); this is then followed by a second ramp step of 25 °C/min

up to a temperature of 250 °C (total time of 2 minutes); this temperature is maintained for 5 minutes.

4.9 Gas Chromatograph Calibration

Prior to use, the chromatograph was calibrated using pure standards of known contaminants. These contaminants were from the alcohol, ketone, hydrocarbon, and aldehyde families, as well as a pre-mixed VOC standard. The full list of compounds is shown in Table 2. The standard compounds were diluted with methyl alcohol to obtain three different concentrations. Twenty microlitre samples from all the concentrations created were analyzed on the GC. This was done by drawing the liquid sample using a syringe and injecting it into a multi-sorbent tube. The tube, connected to a pump at 60 mL/min, was pumped for 3 to 5 minutes to trap the compounds within it. Each concentration was repeated two to three times to ensure consistency.

The calibration results are required for two reasons. First, they provide the retention times for the compounds calibrated. Secondly, they provide a means of relating peak area/height to concentration. This is done by establishing the response ratio. For example, Figure 6 shows the calibration curve obtained for toluene. The three points represent the responses from the three different concentrations of toluene analyzed. At each point, toluene's peak area is divided by the amount present in the original sample, in this case, either 1000, 2000, or 4000 nanograms, to obtain the response (rsp). The (amt, rsp) coordinates are plotted for each sample and a best fit line is drawn. The slope of this line is determined to establish the response ratio, expressed in equation form. For an

Table 2: List of Calibrated Compounds

Hydrocarbons	VOC Mix	2-heptanone
2-methylbutane	benzene	3-heptanone
n-pentane	bromobenzene	4-heptanone
2-methylpentane	n-butylbenzene	
n-hexane	ethylbenzene	Alcohols
2,4-dimethylpentane	p-isopropyltoluene	methanol
n-heptane	toluene	ethanol
toluene	styrene	1-propanol
n-octane	m-xylene	2-propanol
p-xylene	1,3,5-trimethylbenzene	1-butanol
n-propylbenzene	1,2,4-trimethylbenzene	2-butanol
n-decane	1,2,4-trichlorobenzene	
n-butylbenzene	naphthalene	Aldehydes
n-dodecane	1,2,3-trichlorobenzene	pentanal
n-tridecane		nonanal
n-tetradecane	Ketones	benzaldehyde
n-pentadecane	2-butanone	octanal
	2-pentanone	heptanal
	3-pentanone	hexanal
	2-hexanone	propanal

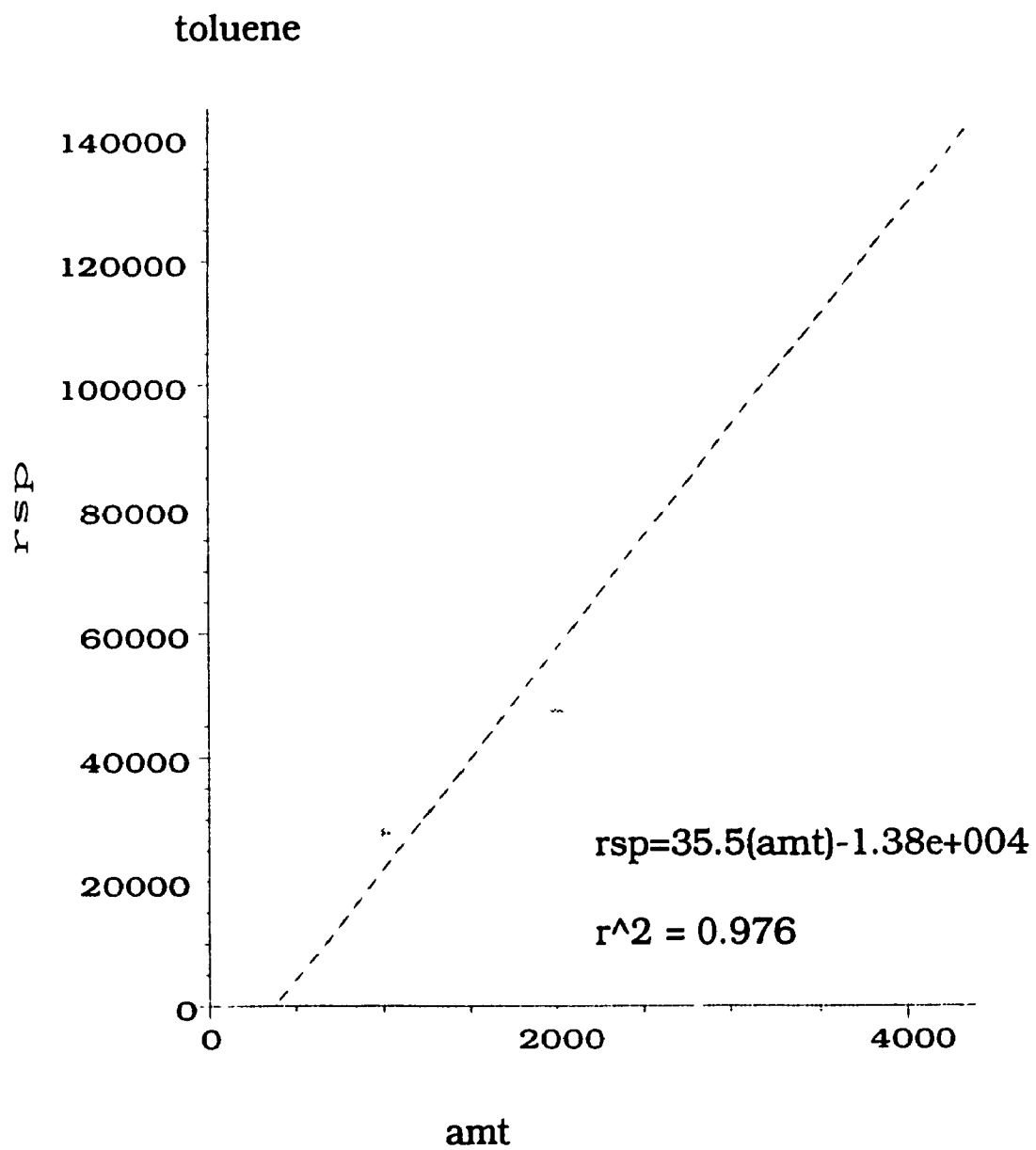


Figure 6: Calibration Curve for Toluene

unknown sample, the area of the peak is input into the equation (rsp) to obtain the corresponding concentration present in the sample.

4.10 Determining TVOC Values

The method used to determine Total Volatile Organic Compounds (TVOC) values present in our samples is a semi-quantitative method. Samples of the paint and varnish obtained from headspace analysis were sent to the National Research Council's (NRC) National Fire Laboratory for mass spectrum (MS) analysis. Like a finger print, the MS of a compound is unique. Therefore, it can be used to identify specific compounds present in the samples. However, there is still a degree of error in the method. The results obtained from the NRC provided values of percent likelihood of accuracy. For example, if a peak, identified as toluene, was accompanied by a 98%, then there is a 98% likelihood that it is indeed toluene. From this information, it was possible to confidently identify several compounds present in our samples; while others either remained unidentified or had very low percent accuracies. An example of a chromatogram obtained for a paint and varnish sample are shown in Figures 7 and 8, respectively. Each peak corresponds to a compound. From the GC analysis, it was possible to match several peaks with the retention times of the calibrated compounds. In some instances, these also matched compounds identified through the MS analysis. However in all, the majority of compounds remained unidentified. Though we cannot put a name to these peaks, they must still be included in the calculation of the TVOC. Thus, to do this, we are forced to use a semi-quantitative approach.

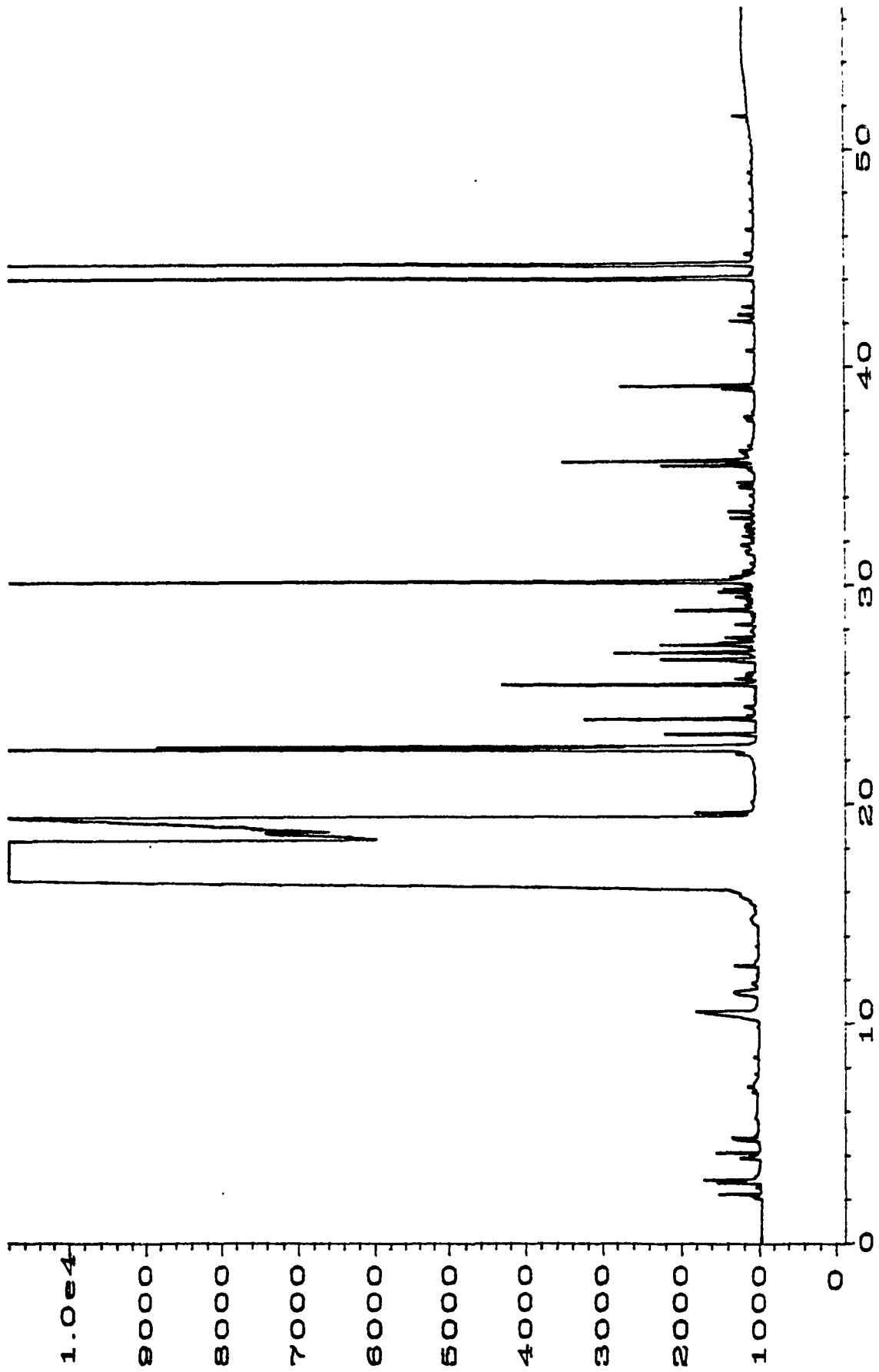


Figure 7: Sample Chromatogram for the Acrylic Paint (10 hours)

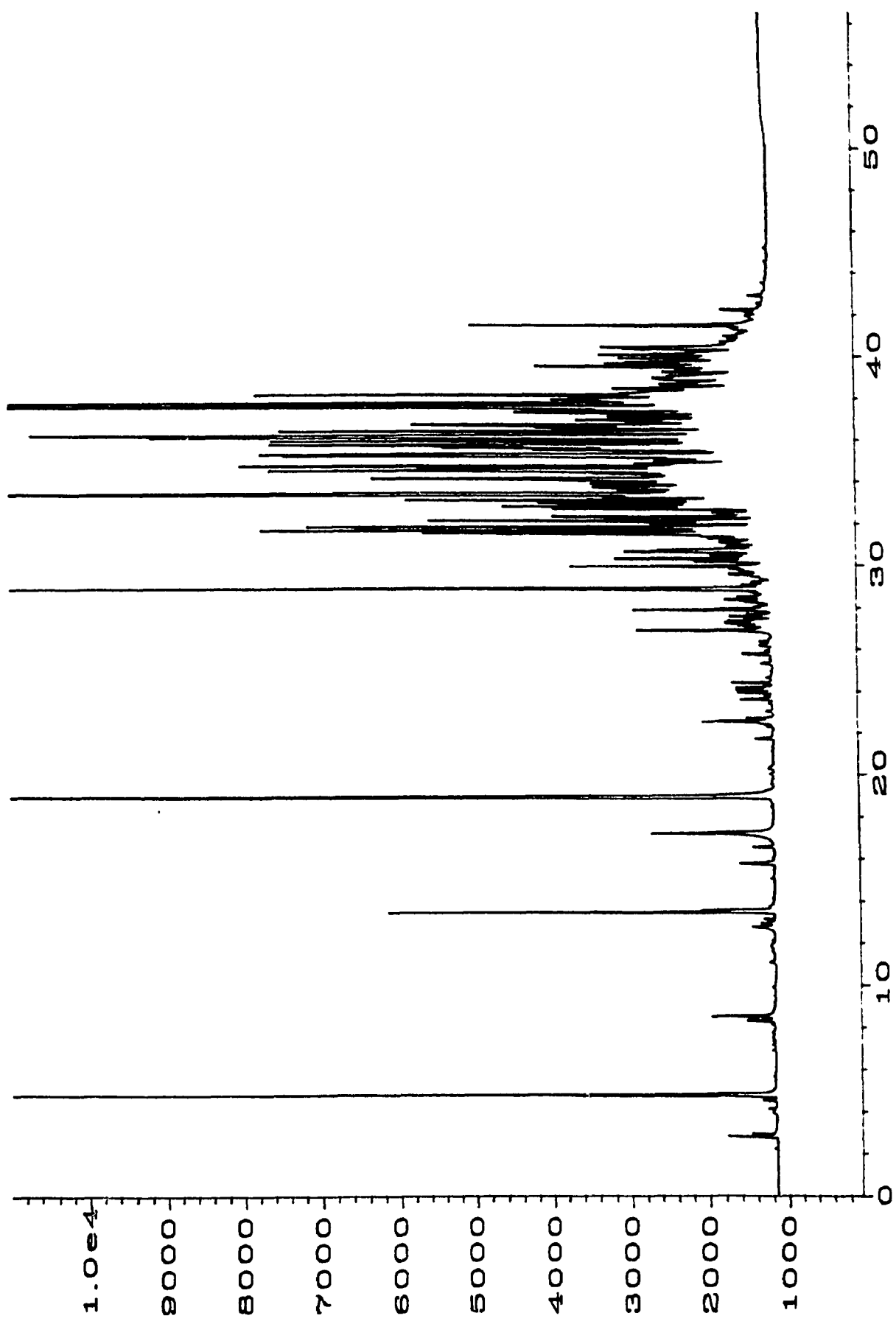


Figure 8: Sample Chromatogram for the Varnish (24 hours)

A reference response factor equation from a calibrated compound was chosen. In this way, the TVOC of a sample is determined by plugging the value, corresponding to the total area under its chromatogram, into the response factor equation to obtain a concentration. While this may not provide the most accurate value of the actual TVOC, it is the only means available of obtaining a ball-park figure for the TVOC value for comparison purposes. For this research, it was decided to use the reference response factor for toluene. The reasons are because toluene was confidently identified as a component in both the varnish and paint samples; its calibration curve has a very high coefficient of determination (r^2); and it has been found to be used by other, more experienced, researchers for the same purpose [88].

4.11 Repeatability

As shown earlier, emissions testing conducted at different laboratories have shown to yield controversial, or at best, varying results. However, as Fortmann [13] noted, there is high variability between duplicate tests performed even at the same facilities. He noted that the precision was acceptable for some compounds emitted but not for others.

The repeatability of the tests conducted here was verified by repeating randomly selected tests for at least a 24 hour duration. For these tests, the data from a point to point basis varied slightly, largest difference was approximately 30%, however, the overall pattern of the curve was similar. The repeatability was therefore deemed to be acceptable. Any variations are explained by the many variables involved, including the uniformity of the sample, the sensitivity of the analysis (GC) method, and natural aging of the sample.

CHAPTER V

TEMPERATURE EXPERIMENTS: RESULTS & DISCUSSION

5.1 Acrylic Paint Results and Discussion

The results obtained when subjecting samples of acrylic paint to various temperatures are summarized in Figures 9 through 19.

5.1.1 Temperature and Relative Humidity During Testing

For the duration of each test, the temperature and relative humidity were recorded at the chamber outlet. The temperature throughout the test duration remained fairly constant at the set-point value, with slight fluctuations of no more than ± 3 °C.

While the inlet relative humidity was fairly constant at approximately 5% or lower (pure dry air), the humidity at the exit of the chamber reached very high levels, 70 to 80 %, depending on the temperature. Within the first 12 hours, as the paint dried, these levels dropped significantly and were back to inlet conditions between 36 to 48 hours.

5.1.2 Effects of Air Exchange Rate

All tests were conducted at 1.2 air exchanges per hour. However, in reaching this value, other air exchange rates were tested. Figure 9 depicts the TVOC profiles at three different air changes. The effect of the different air changes is significant. At the highest air exchange (1.2 ach), the emissions peak earlier, at approximately 8 hours. It is for this reason, expediting the emissions, that 1.2 ach was chosen for all subsequent tests. At the

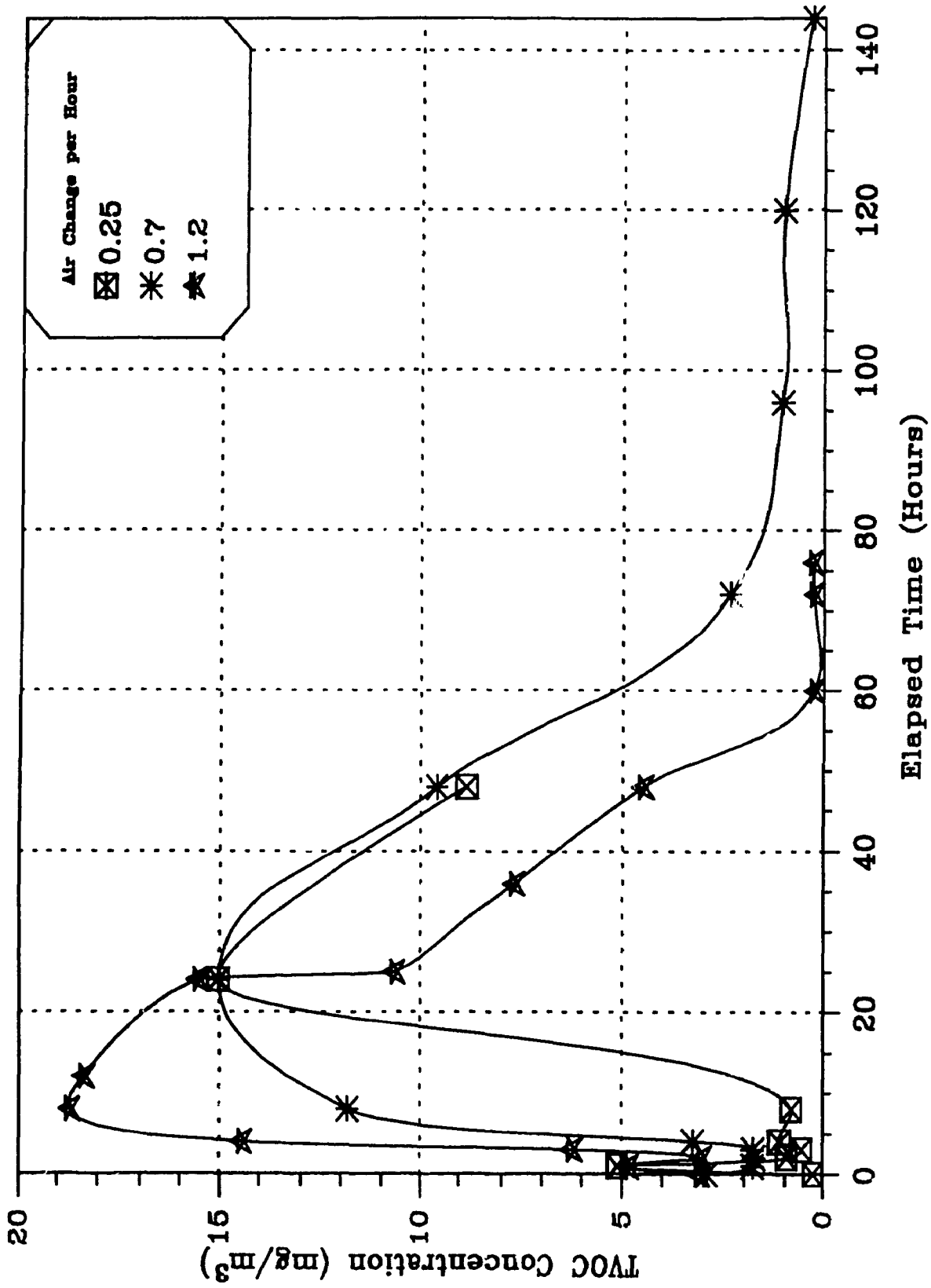


Figure 9: TVOC Concentration versus Time Profiles for Paint at 25 °C and Air Exchanges of 0.25, 0.7, and 1.2 ach

lower air exchanges, the peak only occurs after 20 hours, and the decline is at a much slower rate than for the 1.2 ach.

While the emission profiles for all tests are for 1.2 ach, it is important to remember this notable effect when considering emission profiles under real life conditions, with varying air exchanges.

5.1.3 TVOC Concentration Profile

Figure 10 illustrates the TVOC concentration profile for the paint samples versus time. In general, it can be said that with an increase in temperature, TVOC concentrations increased. However, certain differences or idiosyncrasies can be noted. At the earlier stages of each test fluctuations can be seen, the degree of which increase with temperature. At 35 °C, these fluctuations last the longest, approximately 16 hours, before the curve begins to decrease. The high levels of relative humidity recorded during this period must cause this strange phenomena. Though the air feeding into the system is very dry, the release of water vapour from the sample must impede the release of VOCs during this time. Vejrup and Wolkoff [56] noted similar effects when they tested cleaning agents. They attribute this to the water in the wet sample which prevents the more polar compounds from being released due to hydrogen bonding. As the recorded humidity drops to levels below 30% (12 to 24 hours), the curve begins to behave exponentially as expected. The peak concentrations measured at each temperature vary significantly. At 35, 25, and 15 °C, the highest TVOC concentrations obtained were 66, 19, and 10 mg/m³, respectively. The time of peak concentrations occurs later with dropping temperature. The

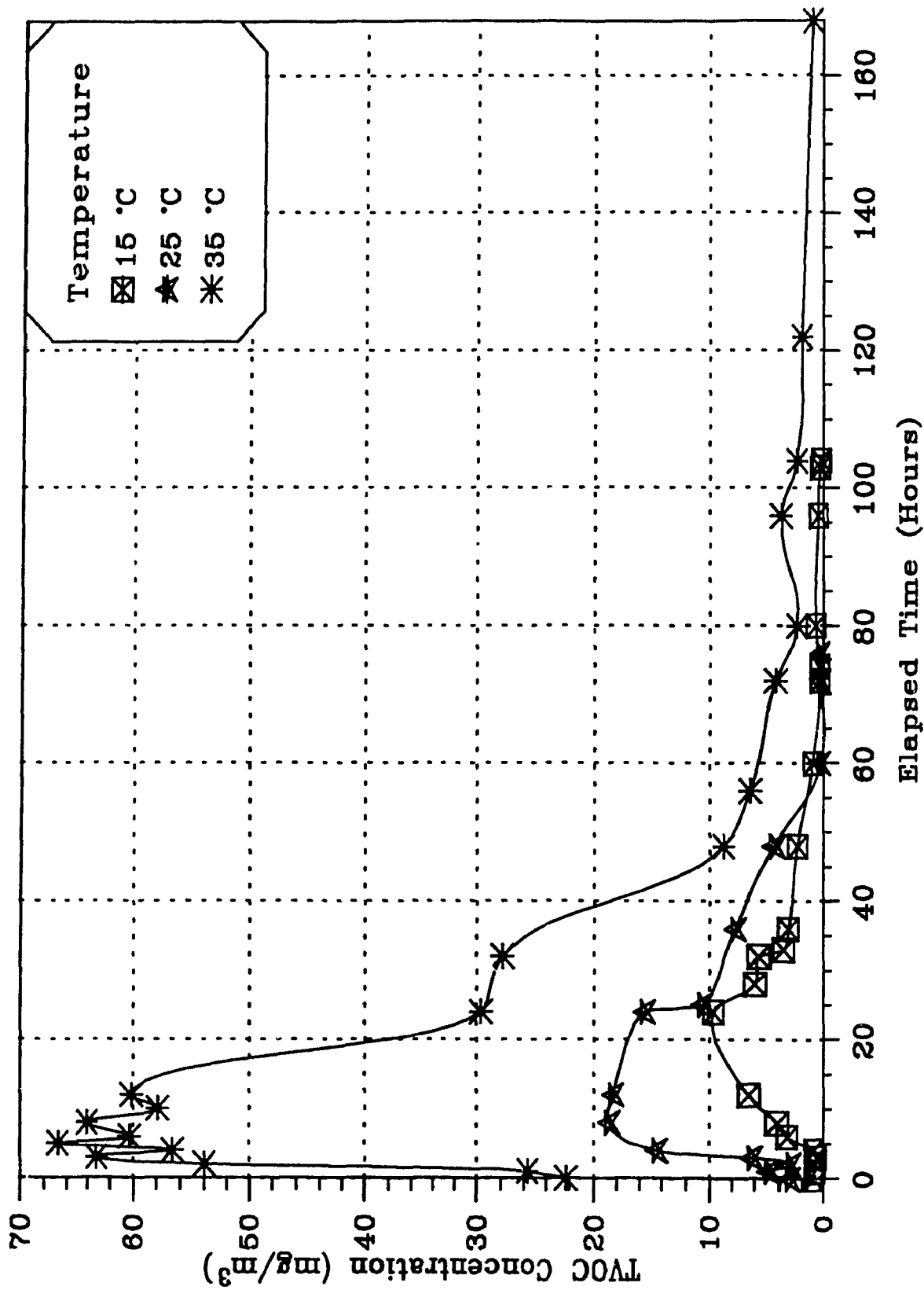


Figure 10: TVOC Concentration versus Time Profiles for Paint at 1.2 ach and Temperatures 15, 25, and 35 °C

TVOC concentrations released at 35 °C are significantly higher than those released during the 25 and 15 °C tests. It was expected that as temperature increases, the vapour pressures of the VOCs will increase, thereby encouraging their release. This is indeed the case at 35 °C. However, the jump from 15 to 25 °C, while still showing an increase, is not nearly as significant as the jump from 25 to 35 °C. The two profiles (15 and 25 °C) follow each other rather closely. The 25 °C curve has consistently higher values than the 15 °C curve, but depletion is reached at approximately the same time (22 hours).

5.1.4 Concentration Profiles for Individual Compounds

Figures 11 through 14 show the concentration versus time profiles for toluene, m,p-xylene, ethylbenzene, and hexanal, respectively. While the overall TVOC curve is generally shown to follow the expected trend, it was decided to investigate the effect of temperature on individual compounds. These individual compounds were positively identified as components in the acrylic paint tested. As can be seen from the different profiles, the effects of temperature on the compounds are difficult to predict and generalize. The toluene curves (Figure 11) for the early stages of the 25 and 35 °C tests are very erratic, but their patterns are somewhat similar. At 15 °C, the toluene has comparatively very low concentrations, as well as fairly constant, when compared to the higher temperatures. It would seem that toluene, being a very volatile compound, is significantly effected by temperatures at levels as low as room temperature. The profiles do not end at concentrations of zero because though concentrations of the compound were no longer detected, the response factor equation for toluene yields a minimum value. The

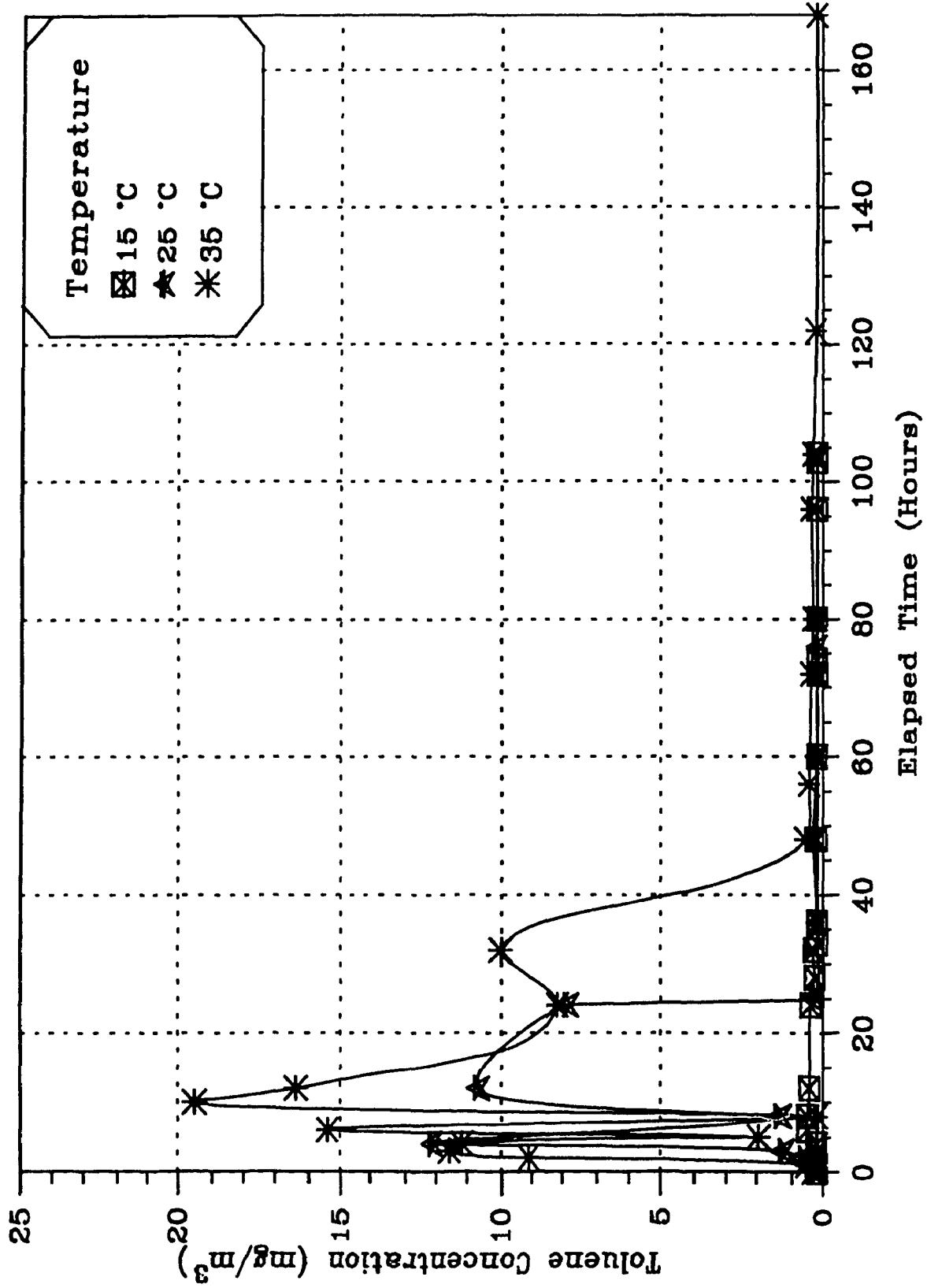


Figure 11: Toluene Concentration versus Time Profiles for Paint at 1.2 ach and Temperatures of 15, 25, and 35 °C

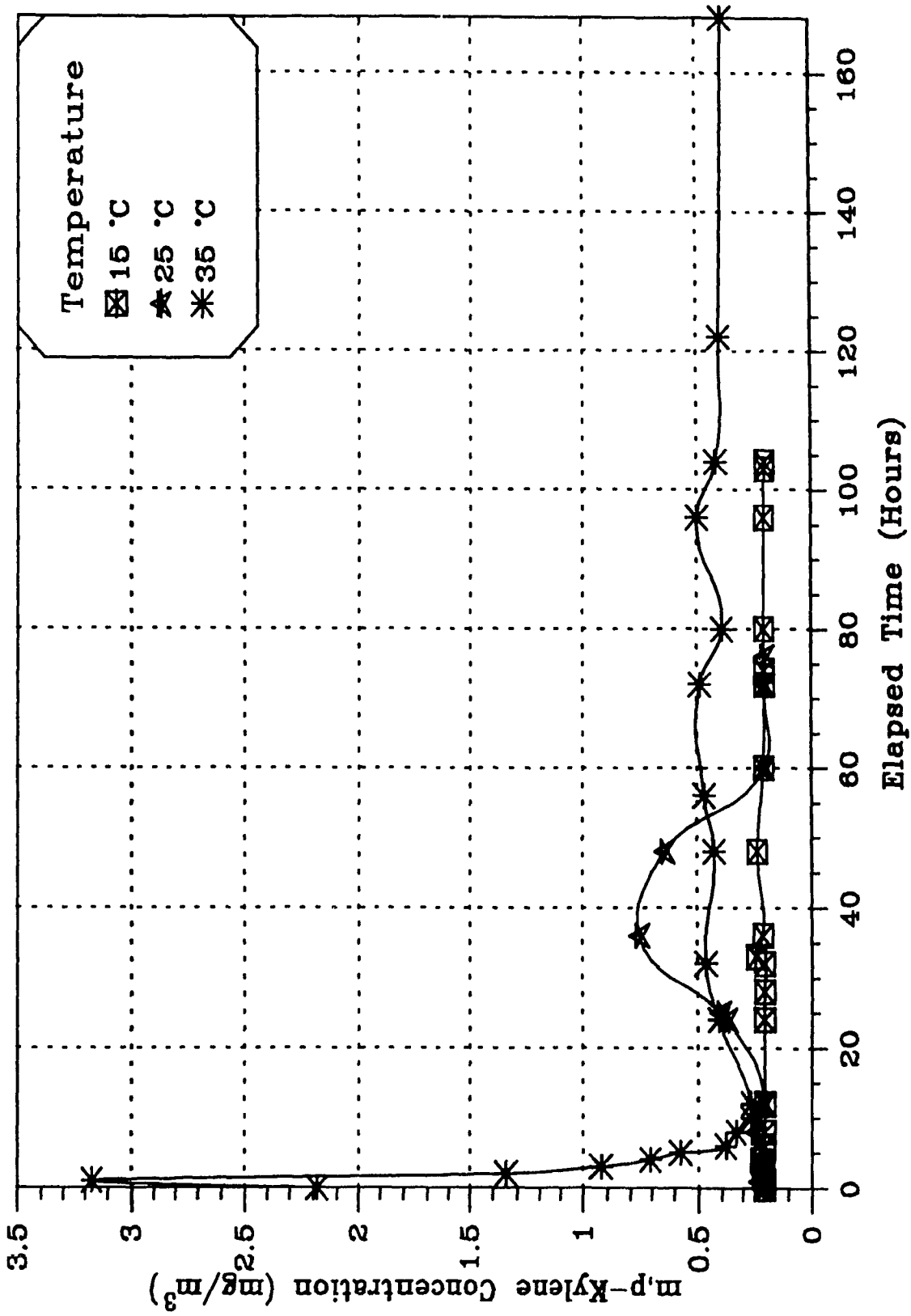


Figure 12: m,p-Xylene Concentration versus Time Profiles for Paint at 1.2 ach and Temperatures of 15, 25, and 35 °C

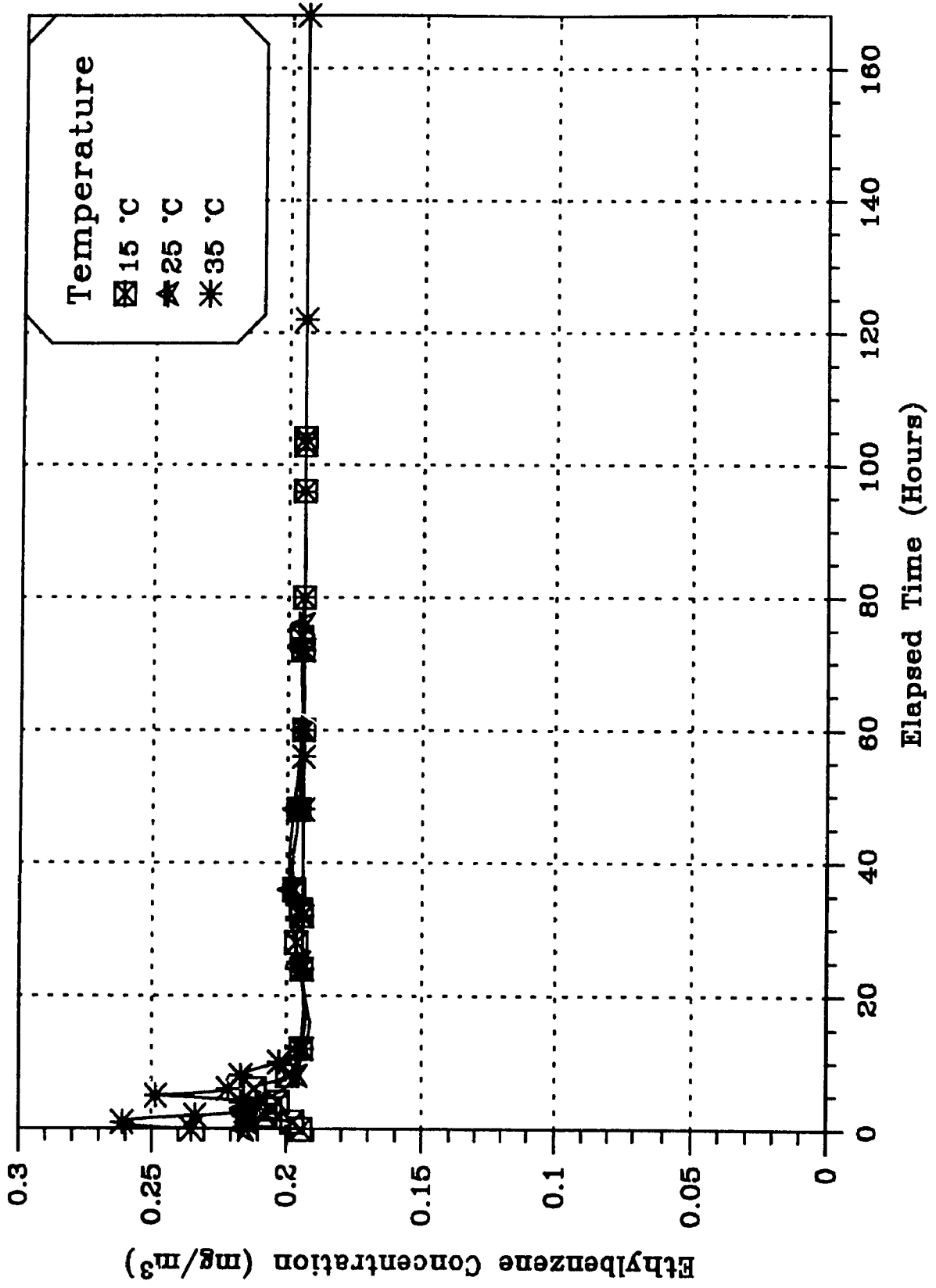


Figure 13: Ethylbenzene Concentration versus Time Profiles for Paint at 1.2 ach and Temperatures of 15, 25, and 35 °C

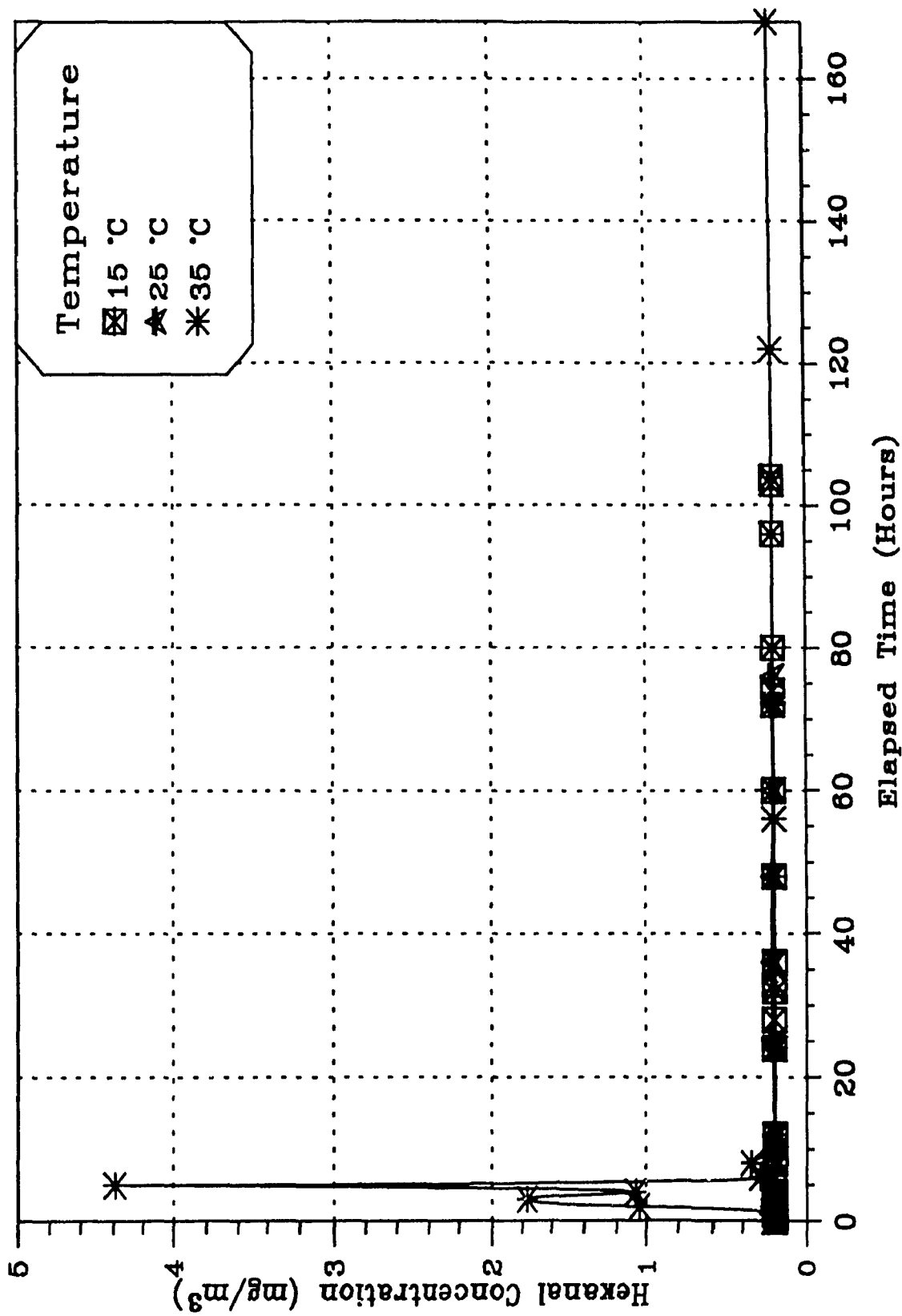


Figure 14: Hexanal Concentration versus Time Profiles for Paint at 1.2 ach and Temperatures of 15, 25, and 25 °C

same argument can be said about the concentrations of m,p-xylene, shown in Figure 12. Here however, the concentrations are not as erratic. At 35 °C, the peak is reached very early, and quickly (within 10 hours) descends to values similar to the other temperatures. The 25 °C curve, shows a peak value of the compound fairly late in the test. At approximately the same time, the 35 °C shows a slight increase in value before it becomes constant. This trend is not repeated for the 15 °C curve, which behaves very similarly to the toluene curve, that is, low and constant concentrations. Ethylbenzene, Figure 13, reaches peak values fairly early for all three temperatures, and goes on to constant concentrations in a consistent pattern after approximately 12 hours. Hexanal behaves in a similar way (Figure 14), except that peak values can only truly be identified for the 35 °C temperature. The other profiles are fairly low and constant, with the 35 °C curve joining them at about the 12 hour mark.

While the concentrations of the compounds at 35 °C may seem comparatively high, the peak values are well below limits specified by different regulatory agencies throughout the world, summarized in Table 3. However, it is important to note that some of these limiting values are meant for an industrial environment where higher levels are acceptable only because they are more likely to be expected. An extensive review of existing standards and guidelines in Canada was conducted [89], revealing that no regulations on VOCs, in buildings other than industrial, as yet exist.

5.1.5 Emission Rate Profiles

Figures 15 to 19 show the emission rate profiles, calculated using Equation (6),

Table 3: Comparative Table of Existing IAQ Guidelines [11,90]

VOC	ACGIH ³ TLV-TWA ⁸ (mg/h. ³)	OSHA ⁴ PEL ⁹ (mg/m ³)	NIOSH ⁵ REL ¹⁰ (mg/m ³)	WHO ⁶ TLV ¹¹ (mg/m ³)	MAK- Commission ⁷ MAK ¹² (mg/m ³)
benzene	32	3.1	0.32	30	16 (TRK) ¹³
toluene	377	375	375		380
ethylbenzene				433	440
m,p - xylenes	434	435		435	440
styrene				215	85
heptane	1 640	1 600	350	1600	2000
octane				1450	2350
nonane				1050	
iso - propyl benzene					245

³ ACGIH: American Conference of Governmental Industrial Hygienists⁴ OSHA: Occupational Safety and Health Administration (U.S.)⁵ NIOSH: National Institute of Occupational Safety and Health (U.S.)⁶ WHO: World Health Organization⁷ MAK-Commission: Federal Republic of Germany⁸ TLV-TWA: average concentration to which workers may be repeatedly exposed over a normal 8-hour day/40-hour week without adverse health effects⁹ PEL: permissible exposure limit¹⁰ REL: recommended exposure limit¹¹ TLV: threshold limit value¹² MAK: maximum workplace concentration¹³ TRK: No MAK values are set for confirmed human carcinogens, instead technical guidance concentrations are used.

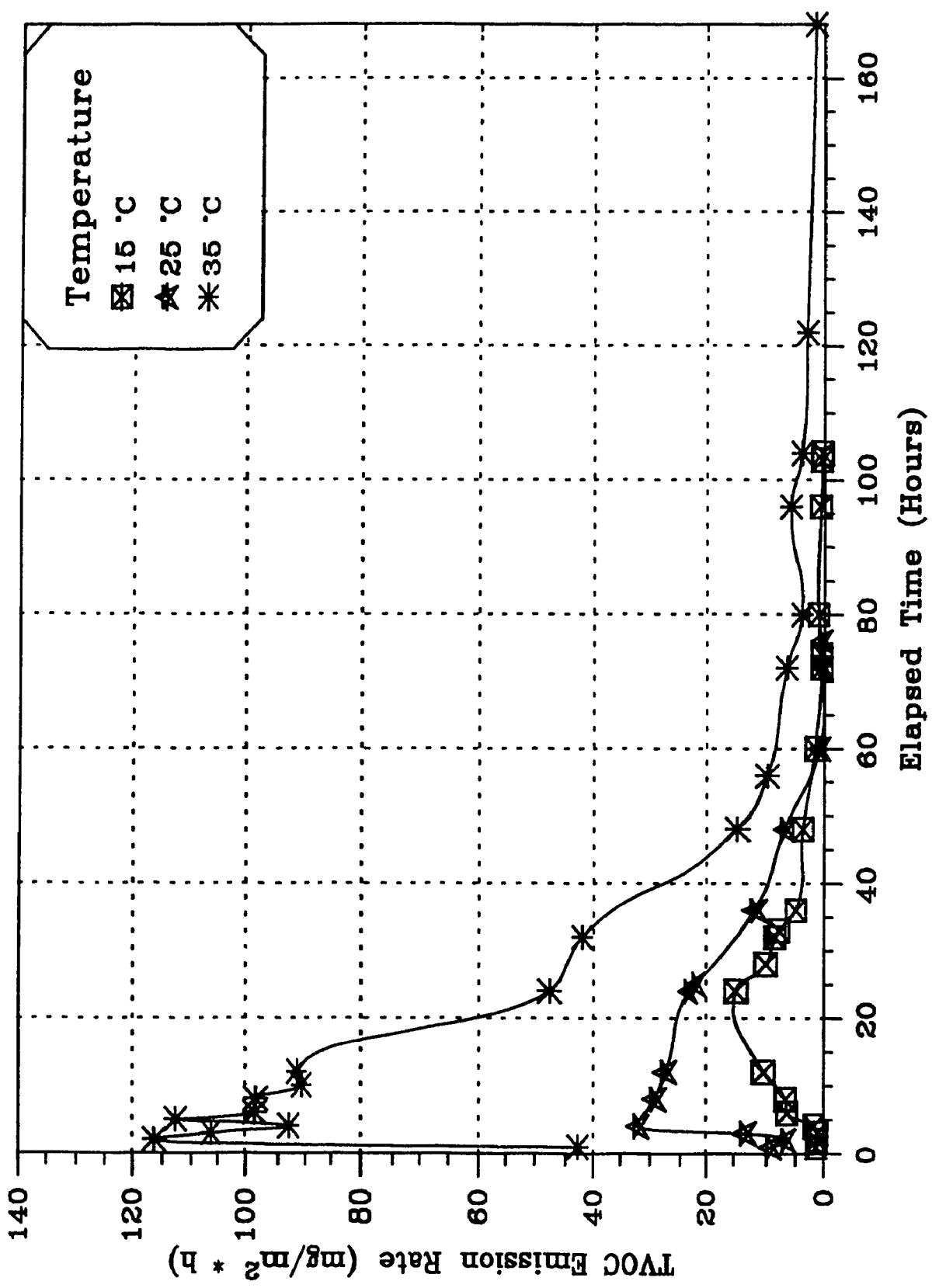


Figure 15: TVOC Emission Rate versus Time Profiles for Paint at 1.2 ach and Temperatures 15, 25, and 35 °C

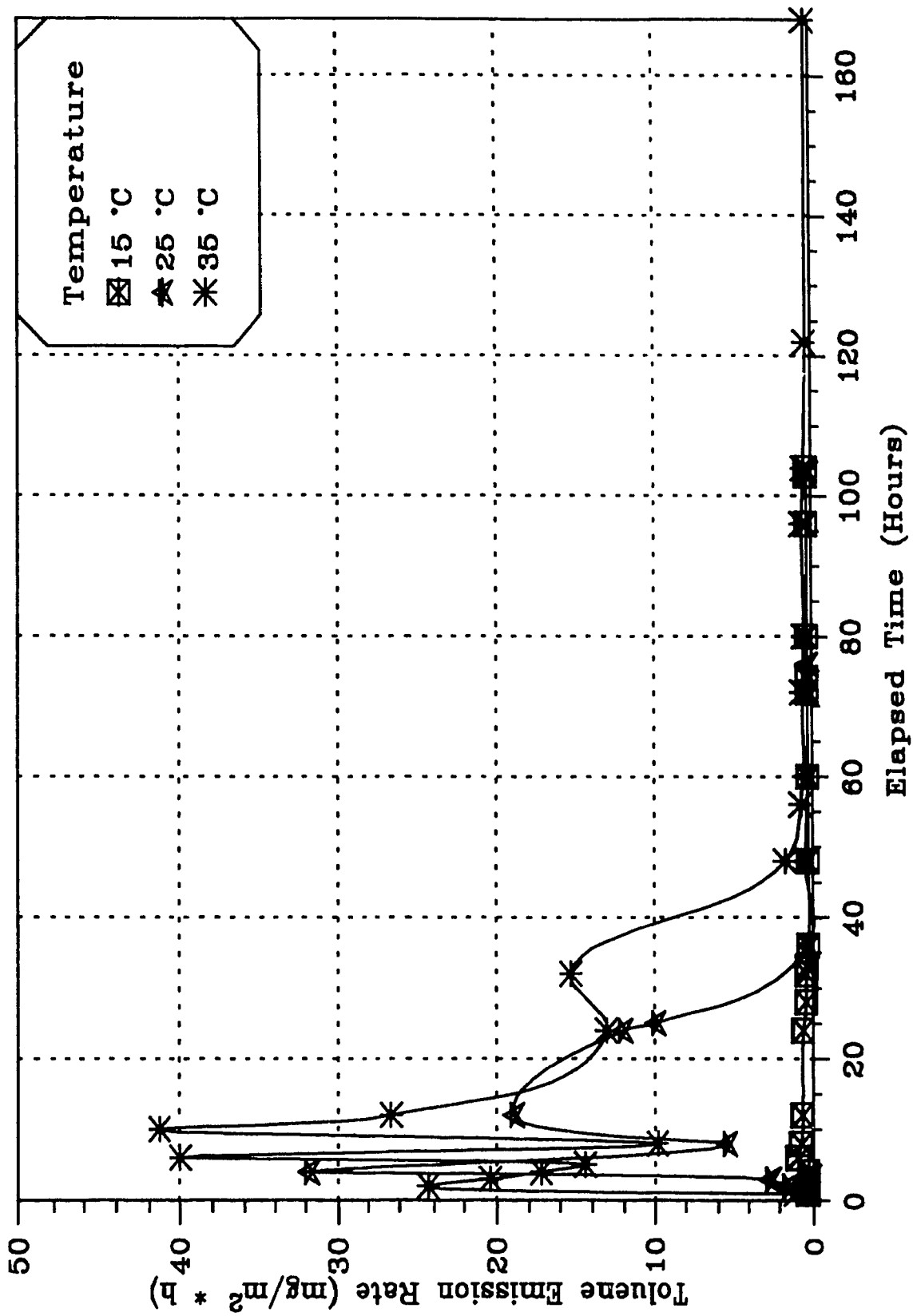


Figure 16: Toluene Emission Rate versus Time Profiles for Paint at 1.2 ach and Temperatures of 15, 25, and 35 °C

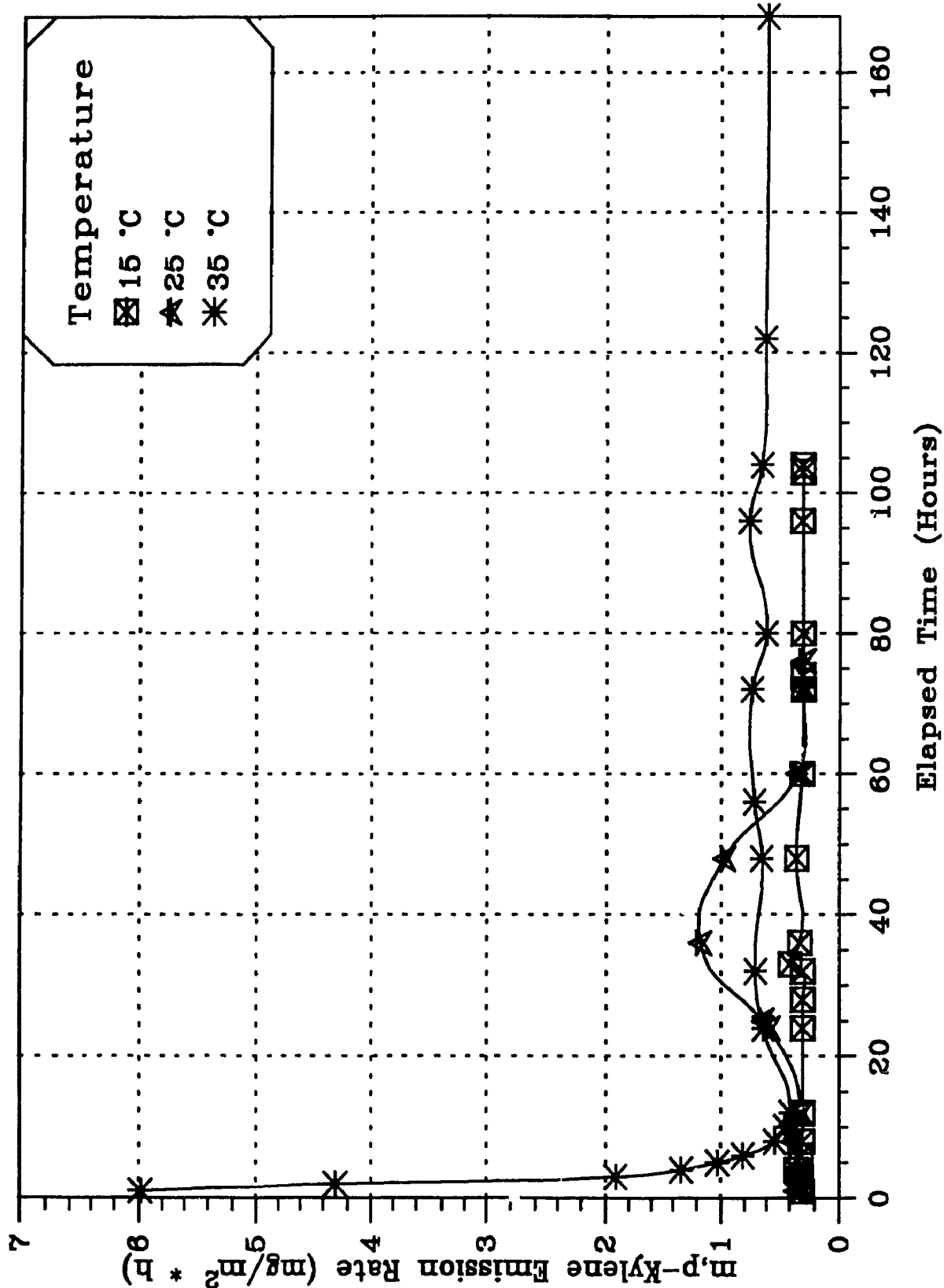


Figure 17: m,p-Xylene Emission Rate versus Time Profiles for Paint at 1.2 ach and Temperatures of 15, 25, and 35 °C

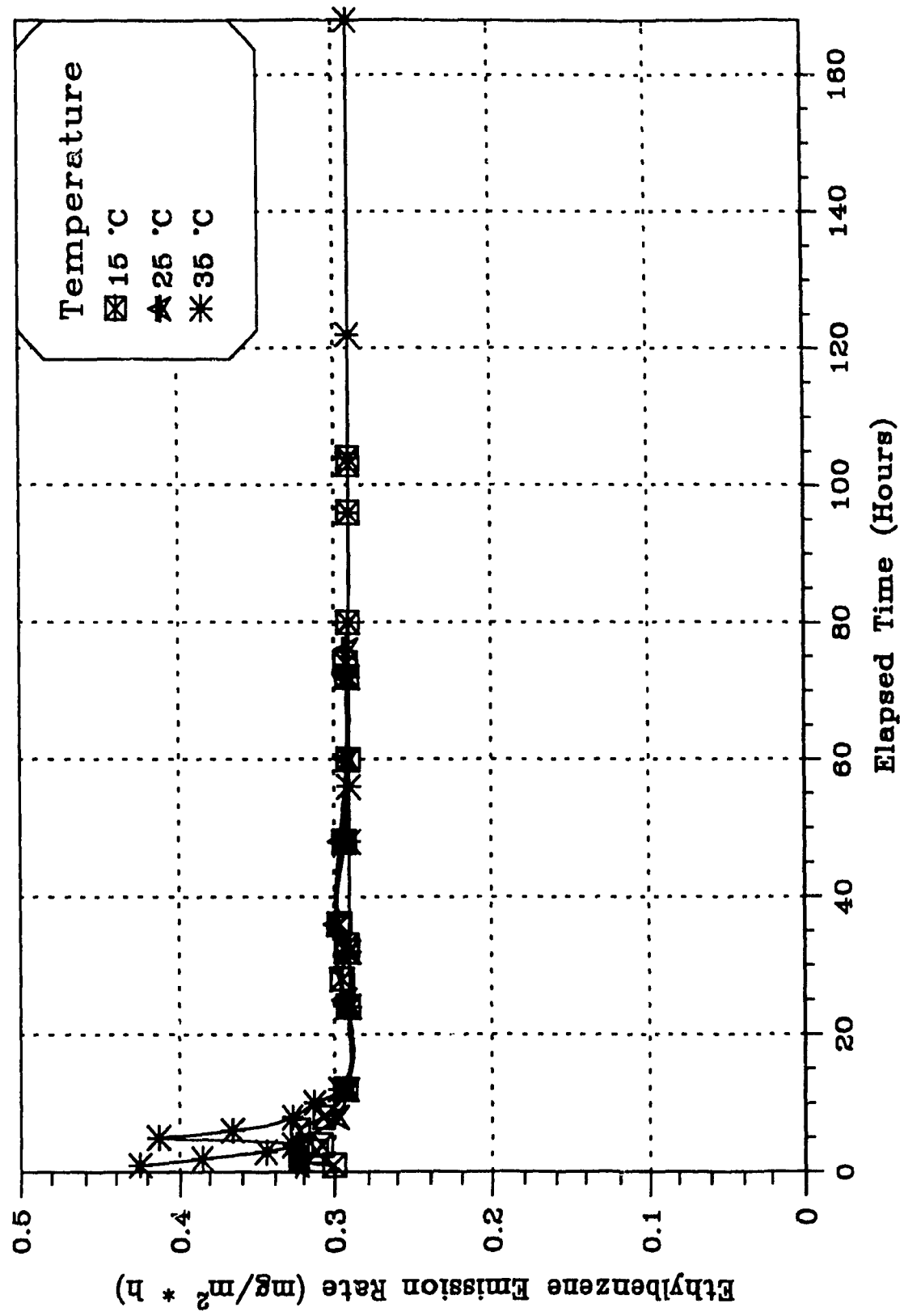


Figure 18: Ethylbenzene Emission Rate versus Time Profiles for Paint at 1.2 ach and Temperatures of 15, 25, and 35 °C

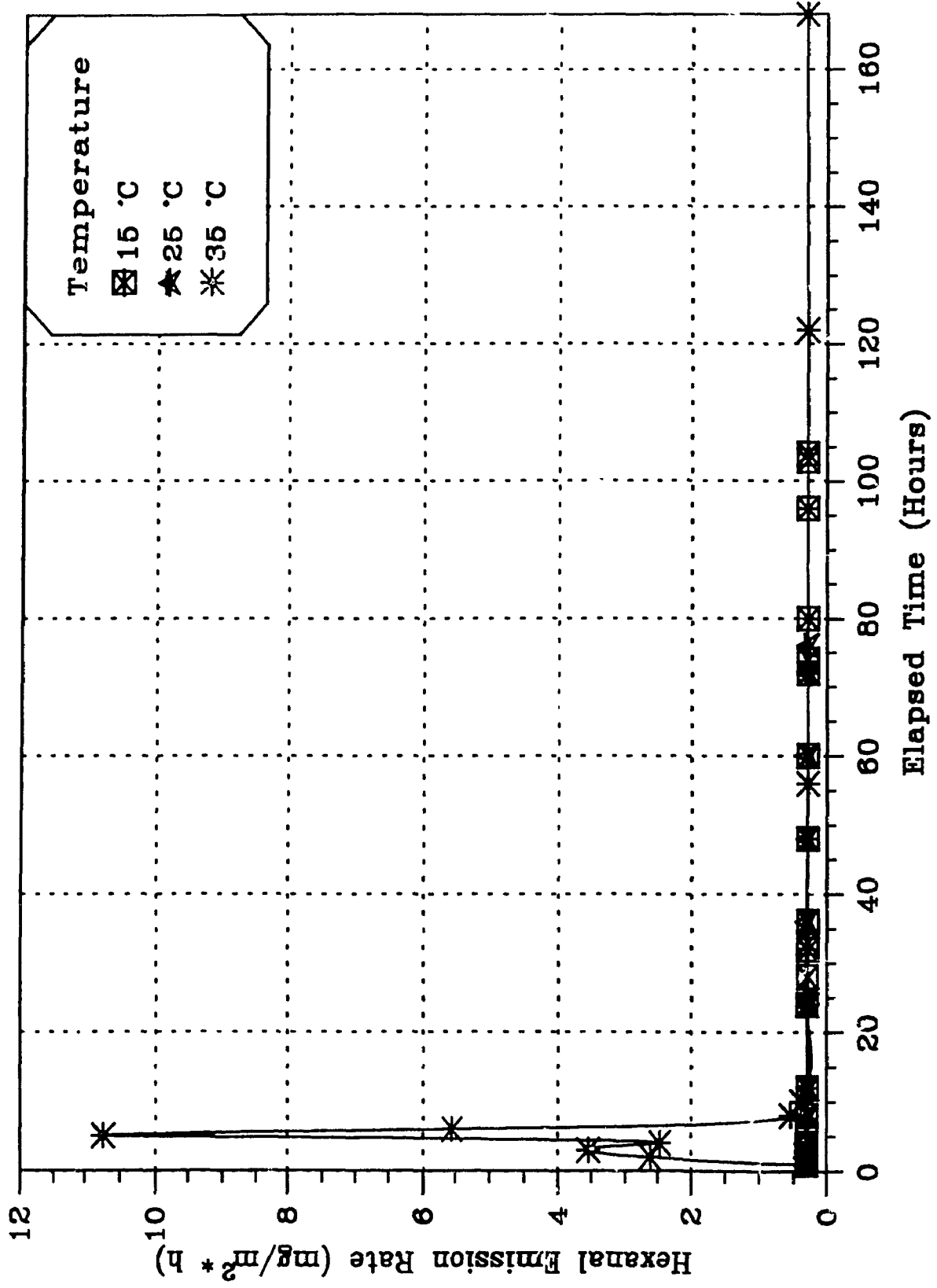


Figure 19: Hexanal Emission Rate versus Time Profiles for Paint at 1.2 ach and Temperatures of 15, 25, and 35 °C

for the TVOC and each individual compound discussed above. These profiles are very similar in shape to the concentration profiles. While it is predicted by most models that the emission rate curves follow an exponential decay, we see that most of the curves first follow an exponential increase at the early stages of each test, before following an exponential decay. From this, we can see that A. Colombo et al [81], are on the right track with their model as opposed to the First Order Decay Model used by many researchers. However, some of these researchers condition their samples, including paint, for a 24 hour period before testing for emissions. In this way, according to the profiles presented here, their emission rates would coincide with the exponential decay portion of the curves.

5.2 Varnish Results and Discussion

The results obtained when subjecting samples of varnish to various temperatures are summarized in Figures 20 through 29.

5.2.1 Temperature and Relative Humidity During Testing

As for the paint, the temperatures recorded during the tests remained at set-point values with variations of ± 2 °C. Again, the relative humidity jumped during the early, wet stages of the test. However, the highest relative humidity reached for the varnish samples was significantly lower than that released by the paint. This is, of course, explained by the fact that water is not used as a base in the varnish. With the exception of the 15 °C test which took 24 hours, the relative humidity reached original, and at times

even lower, levels within 12 hours of the test start.

5.2.2 TVOC Concentration Profile

The TVOC concentration profile for the varnish temperature tests is shown in Figure 20. Here we see that the varnish follows expected trends more closely than the paint. Not only do the concentrations increase with increasing temperatures, the depletion of TVOC occurs faster at the higher temperatures. This concept is the underlying theory behind the bake-out, discussed in detail later. The order of magnitude of the concentrations are significantly higher than those measured for the paint samples, showing indeed the benefits of using water-based products as opposed to solvent based. It is for this reason that the concentrations deplete very early, within the first 10 hours of the varnish tests. Solvents are extremely volatile and their sensitivity to temperature is more apparent.

5.2.3 Concentration Profiles for Individual Compounds

The individual compound concentration profiles for the varnish samples are depicted in Figures 21 to 24. Here, the chosen compounds, again confidently identified, include toluene, m,p-xylene, ethylbenzene, and 1,3,5-trimethylbenzene. The curves for these compounds can be generalized in that their concentrations reach peak values very early (0 - 2 hours) and are near depletion by the sixth hour. However, with the exception of 1,3,5-trimethylbenzene (Figure 24), the concentrations recorded for the 15 °C test are higher than the 25 °C, and in some instances the 35 °C, tests. This is not consistent with

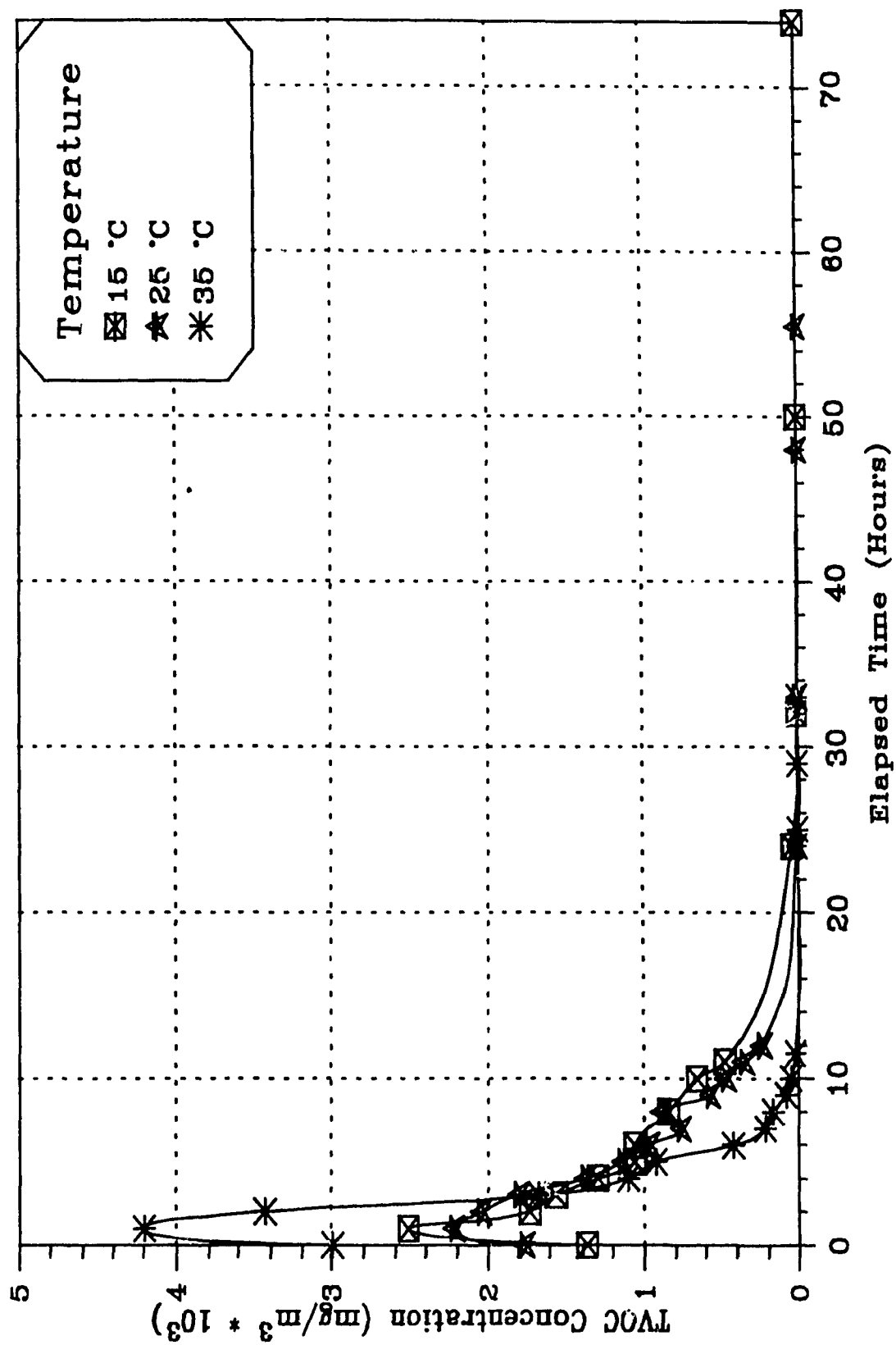


Figure 20: TVOC Concentration versus Time Profiles for Varnish at 1.2 ach and Temperatures 15, 25, and 35 °C

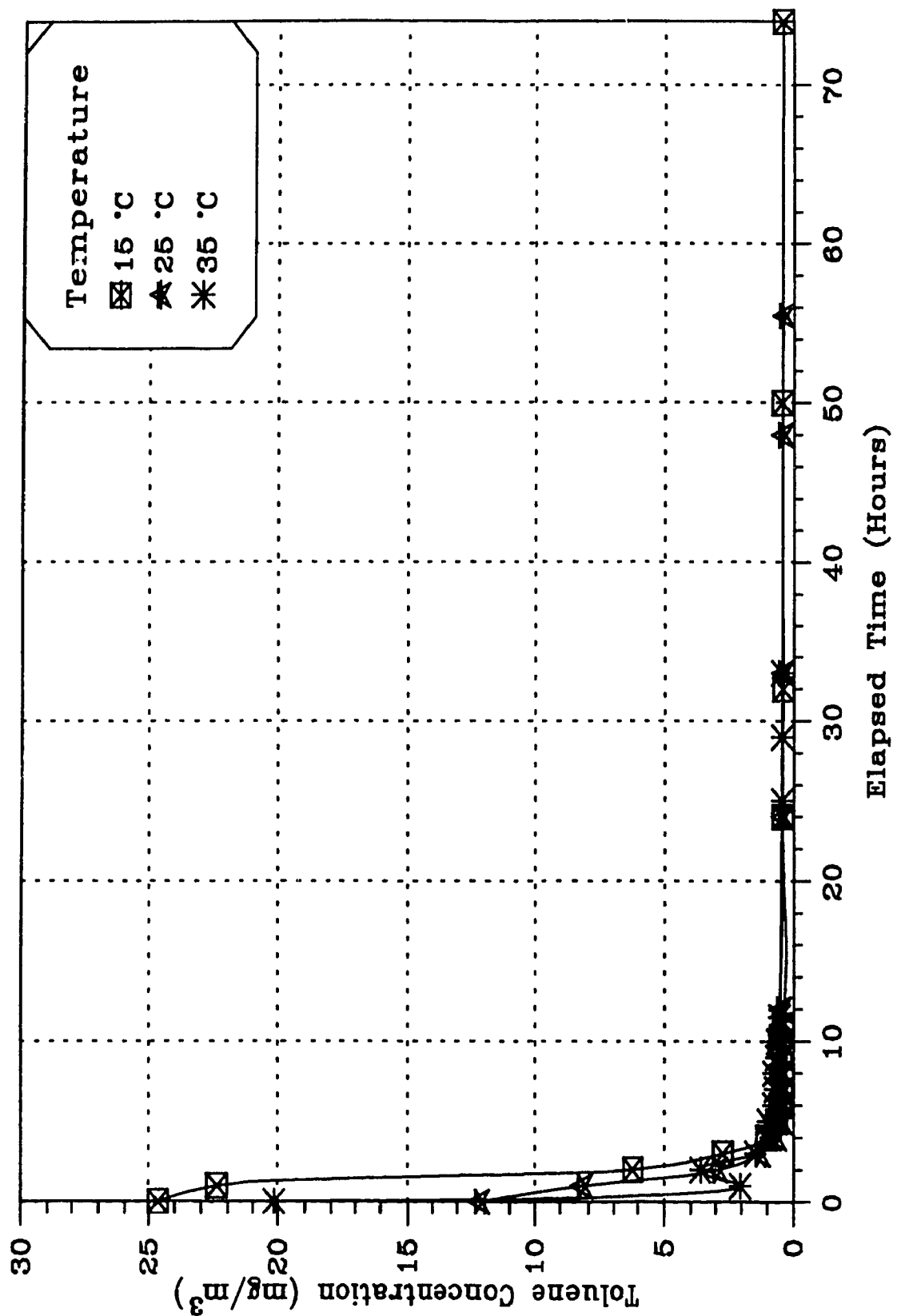


Figure 21: Toluene Concentration versus Time Profiles for Varnish at 1.2 ach and Temperatures 15, 25, and 35 °C

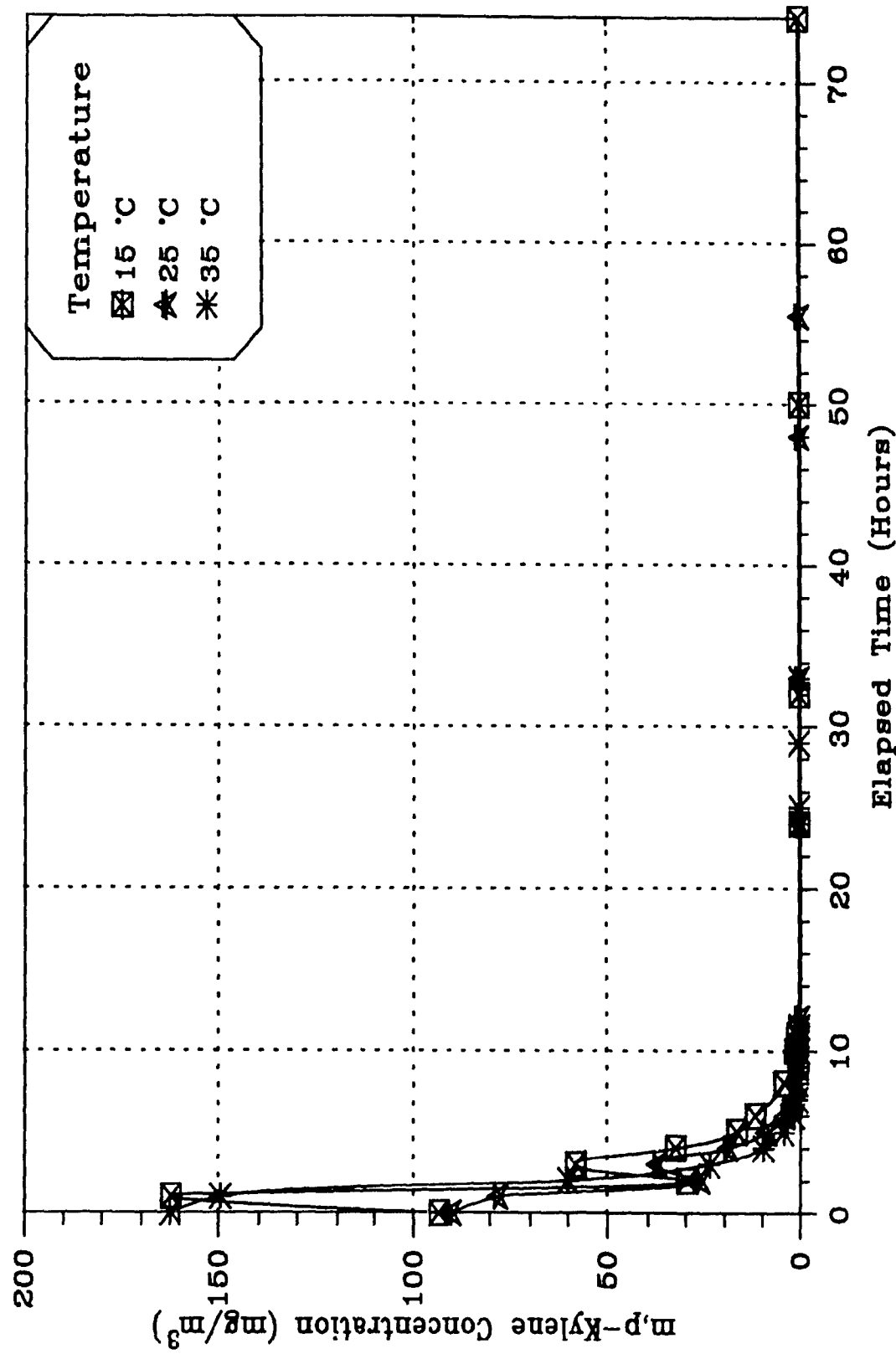


Figure 22: m,p-Xylene Concentration versus Time Profiles for Varnish at 1.2 ach and Temperatures 15, 25, and 35 °C

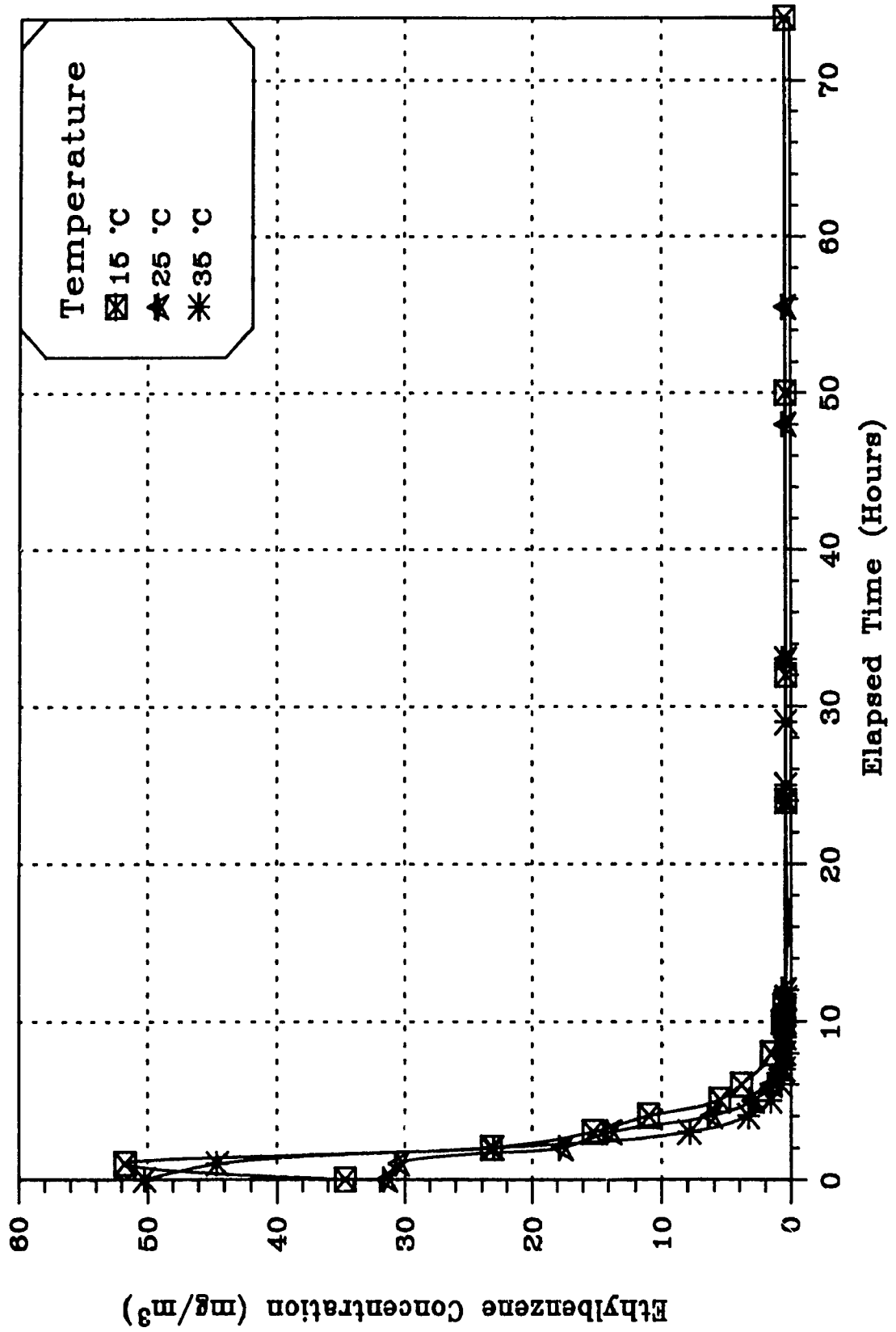


Figure 23: Ethylbenzene Concentration versus Time Profiles for Varnish at 1.2 ach and Temperatures 15, 25, and 35 °C

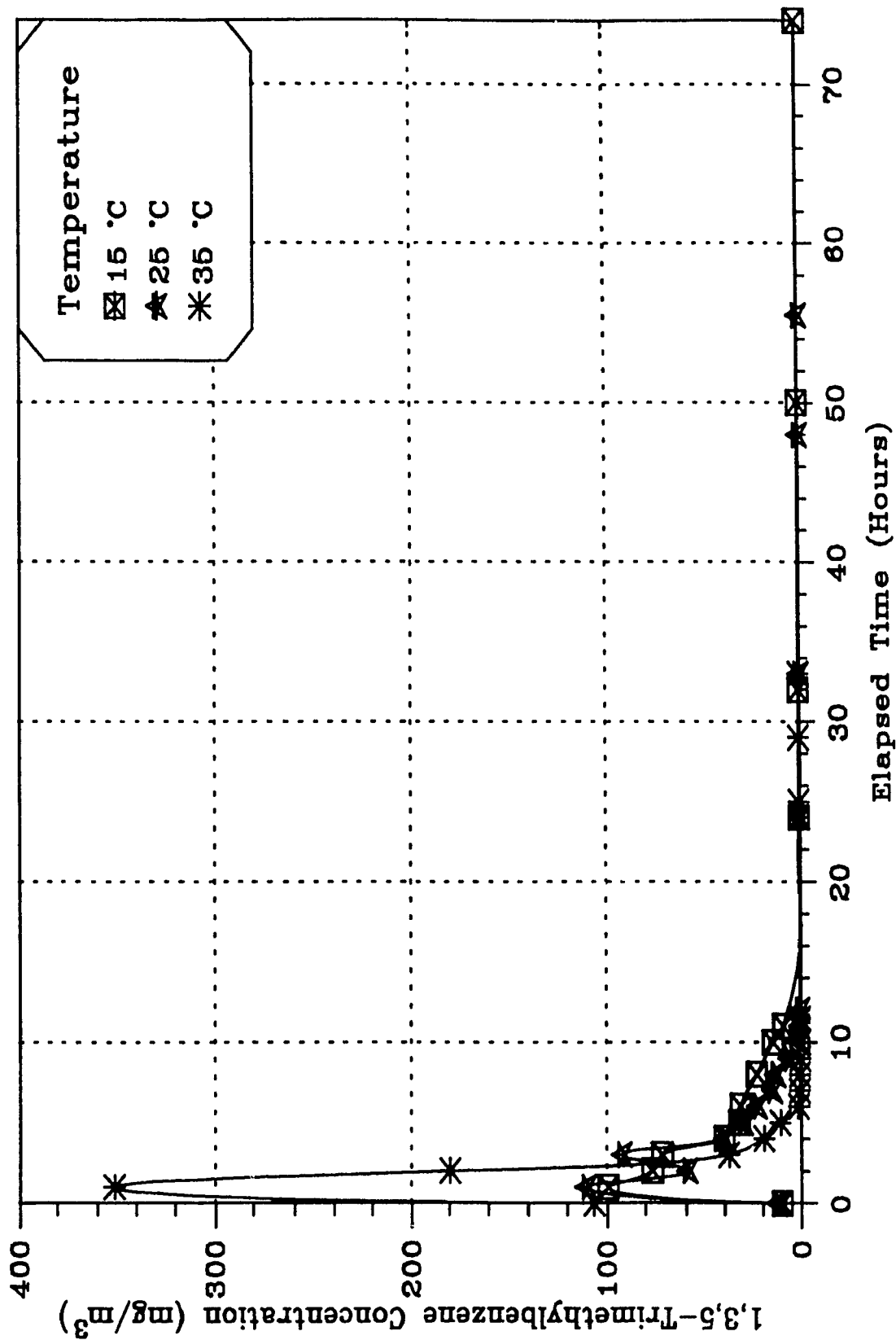


Figure 24: 1,3,5-Trimethylbenzene Concentration versus Time Profiles for Varnish at 1.2 ach and Temperatures 15, 25, and 35°C

the TVOC curve. The curve for 1,3,5-trimethylbenzene is more akin to the TVOC curve. As its concentrations are somewhat higher than the other compounds, it may be a driving/influential factor in establishing the TVOC curve, in spite of the different patterns shown by the other compounds. In fact then, it is truly impossible to generalize the behaviour of individual compounds based on the TVOC curve. If a sample contains a compound known to be an irritant and possibly a threat, the TVOC curve cannot be relied upon to predict its depletion, but rather it must be individually analyzed.

When comparing the maximum concentrations recorded for each compound to the limiting values summarized in Table 3, we see that the measured values are well below these specifications. In spite of this, it may be worth noting that though the concentrations were near depletion at the test end, when the chamber door was opened, a strong smell was still detected. If these levels are well below the limits, it is difficult to imagine the degree of olfactory discomfort one must be exposed to before the limits are reached.

5.2.4 Emission Rate Profiles

The curves representing the calculated emissions rates for both the TVOC and individual compounds are shown in Figures 25 through 29. As one may note, in the case of the varnish the emission factor profiles do follow a single exponential decay, most probably because the peak concentrations occur very near the beginning of the test. The First Order Decay Model can be more accurately applied to this product than to the water-based paint.

As mentioned, expected results follow trends similar to the TVOC and 1,3,5-

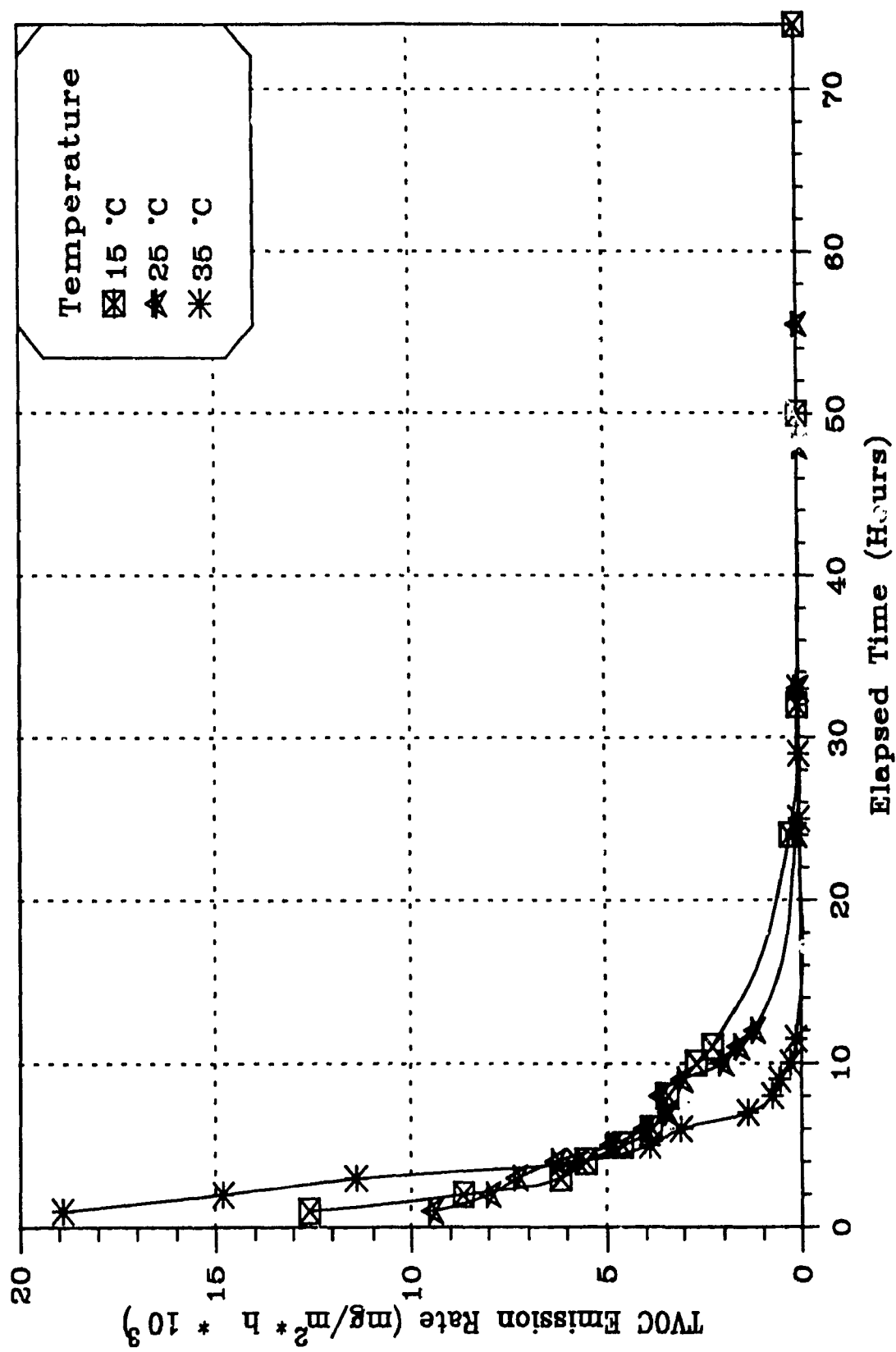


Figure 25: TVOC Emission Rate versus Time Profiles for Varnish at 1.2 ach and Temperatures 15, 25, and 35 °C

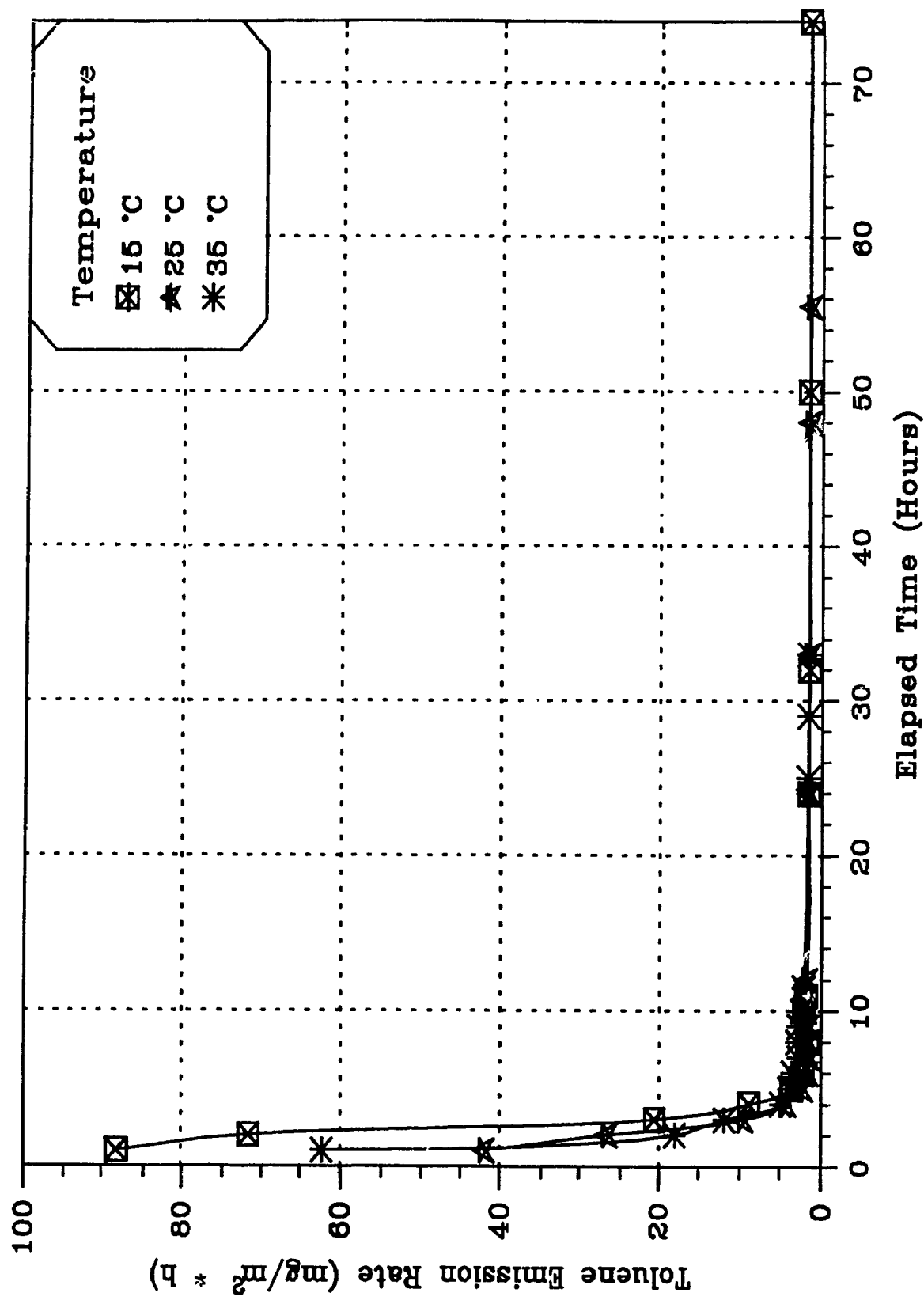


Figure 26: Toluene Emission Rate versus Time Profiles for Varnish at 1.2 ach and Temperatures 15, 25, and 35 °C

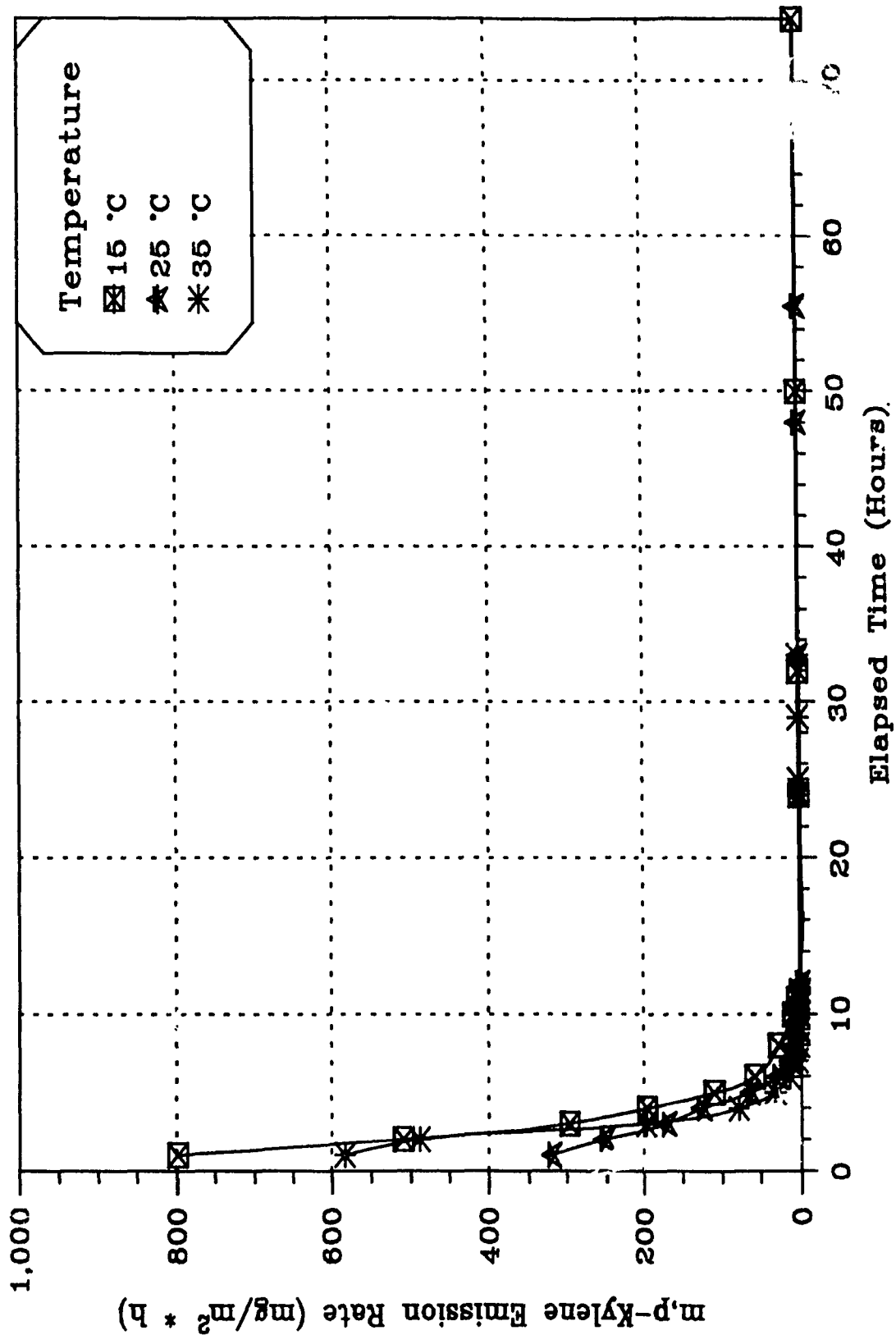


Figure 27: m,p-Xylene Emission Rate versus Time Profile for Varnish at 1.2 ach and Temperatures 15, 25, and 35 °C

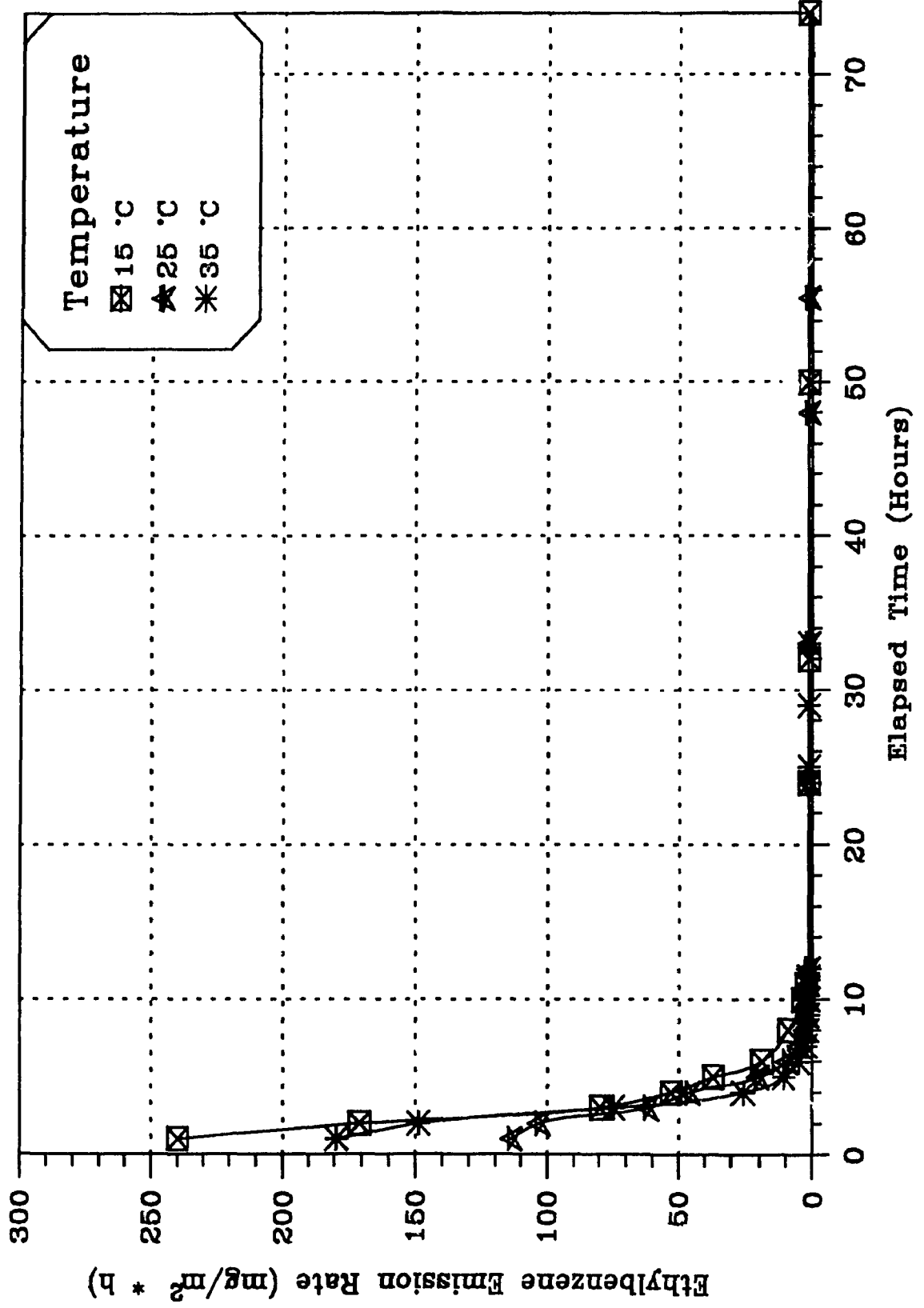


Figure 28: Ethylbenzene Emission Rate versus Time Profiles for Varnish at 1.2 ach and Temperatures 15, 25, and 35 °C

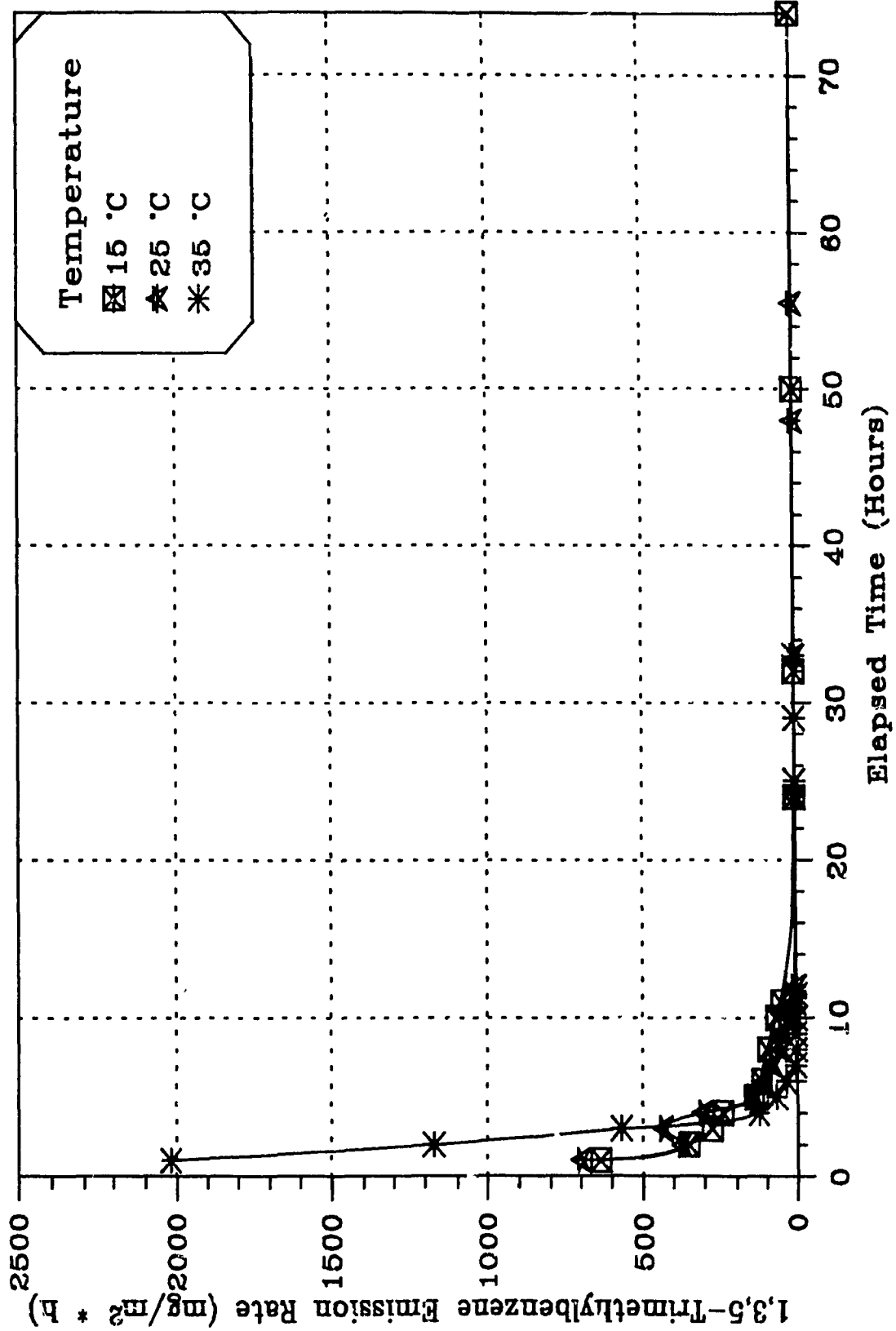


Figure 29: 1,3,5-Trimethylbenzene Emission Rate versus Time Profiles for Varnish at 1.2 ach and Temperatures 15, 25, and 35°C

trimethylbenzene curves, where the emissions increased with temperature, thereby encouraging the faster depletion of the compounds. However, looking at the m,p-xylene and ethylbenzene emission profiles (Figures 27 and 28), the highest emissions were recorded for the 15 °C curve, which also took the longest to reach near depleted values. The toluene emission curve behaves in a combination of these two trends (Figure 26).

CHAPTER VI

HUMIDITY EXPERIMENTS: RESULTS, ANALYSIS & DISCUSSION

6.1 Acrylic Paint Results and Discussion

The results obtained when subjecting samples of acrylic paint to various levels of relative humidity are summarized in Figures 30 through 39.

6.1.1 Temperature and Relative Humidity During Testing

For the duration of each test, the relative humidity was recorded at the inlet and outlet of the chamber. Tests were conducted at three different levels of inlet relative humidity. These were $3 \pm 3\%$ (dry air), $32 \pm 3\%$, and $62 \pm 3\%$. Depending on the inlet humidity conditions, the exit humidity reached very high levels. Peak exit humidities for the three inlet levels were 72.9, 92.0, and 97.7% respectively. These levels dropped to inlet conditions after approximately 36 hours (3% inlet), and 96 hours (32 and 62 % inlet).

The temperature, measured at the outlet, remained fairly constant at $25 \pm 2^\circ\text{C}$ for the duration of all tests.

6.1.2 TVOC Concentration Profile

Figure 30 illustrates the TVOC concentration profile for the paint samples versus time. As shown, the effect of relative humidity on the TVOC profile is erratic. The curves cannot be described as exponential decays. The highest concentrations occur when the

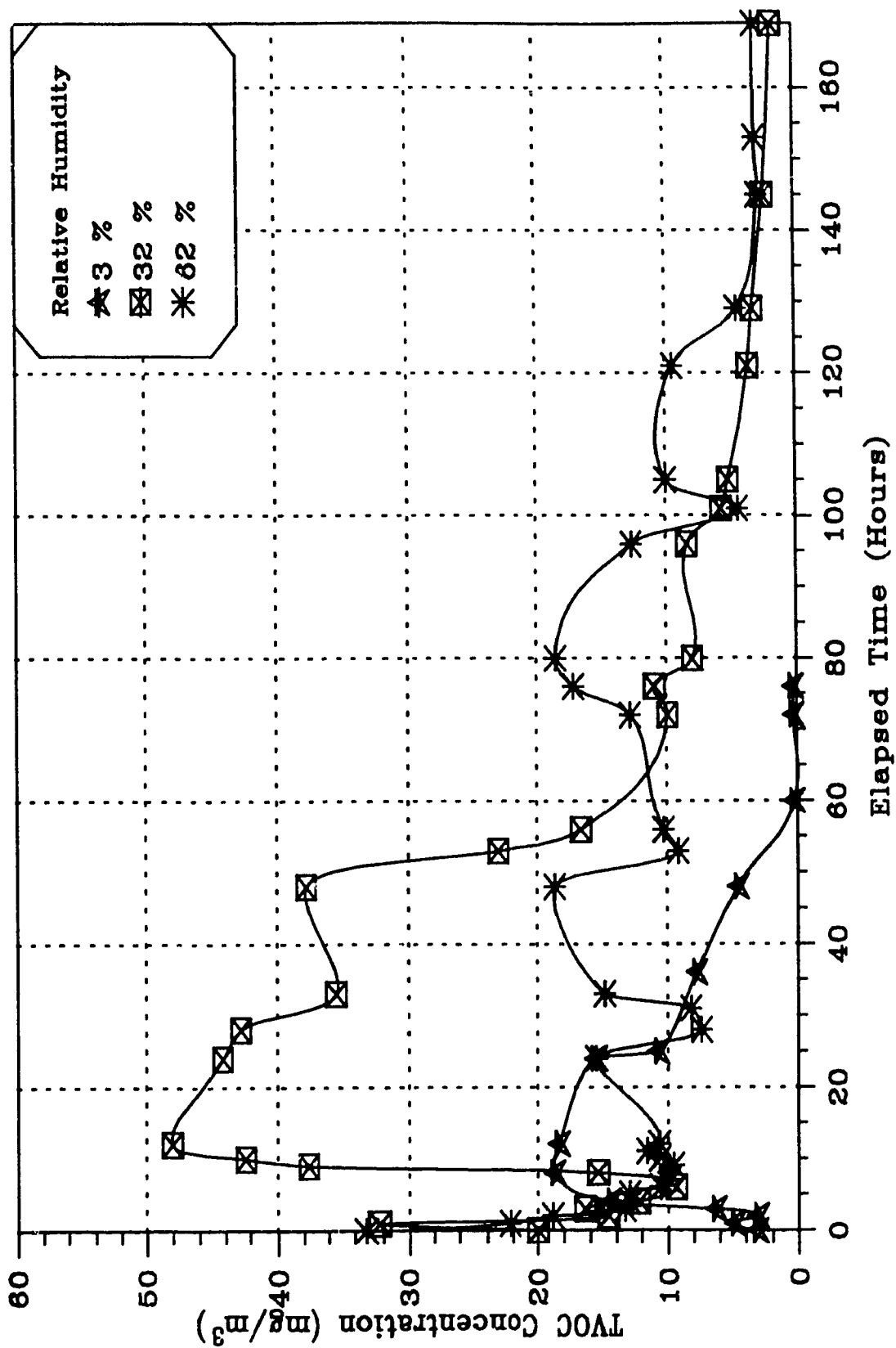


Figure 30: TVOC Concentration versus Time Profiles for Paint at 1.2 ach and Relative Humidity 3, 32, and 62 %

humidity is 32%, but these decay faster than the concentrations recorded for the 62% test. Here, the concentrations fluctuate between 10 and 20 mg/m³ for almost 100 hours before showing signs of decay. Up to 160 hours the curve has reached steady state, but concentrations are not yet depleted. It is curious to see higher concentrations recorded for the 32% test rather than the 62% test. It would seem that the relationship between concentration emissions and relative humidity cannot be generalized as either directly or inversely proportional. At 32%, the humidity may be such that the vapour pressure of the overlying air encourages, rather than inhibits, the release of the VOCs, something which is not as evident at the other two levels tested. The concentrations recorded for the 3% test, not only yields lower concentrations, but reaches near depleted values just under 80 hours.

6.1.3 Concentration Profiles for Individual Compounds

Figures 31 through 34 show the concentration versus time profiles for the four individual compounds toluene, m,p-xylene, ethylbenzene, and hexanal, respectively. The erratic behaviour of the TVOC curve is also demonstrated for the toluene and m,p-xylene curves (Figures 31 and 32). The effect of the 32 and 62% humidity levels on toluene are quite dramatic. The highest concentrations are noted for the 32% test, however, the 62% values are quite significant up to 160 hours, where it appears to be on the rise again. The 32% values deplete after the 80 hour mark. At 3%, initial peaks are as high as those at 32%, but diminish quite rapidly to near zero values after 24 hours.

For m,p-xylene, the 62% humidity yields the higher concentrations which, though

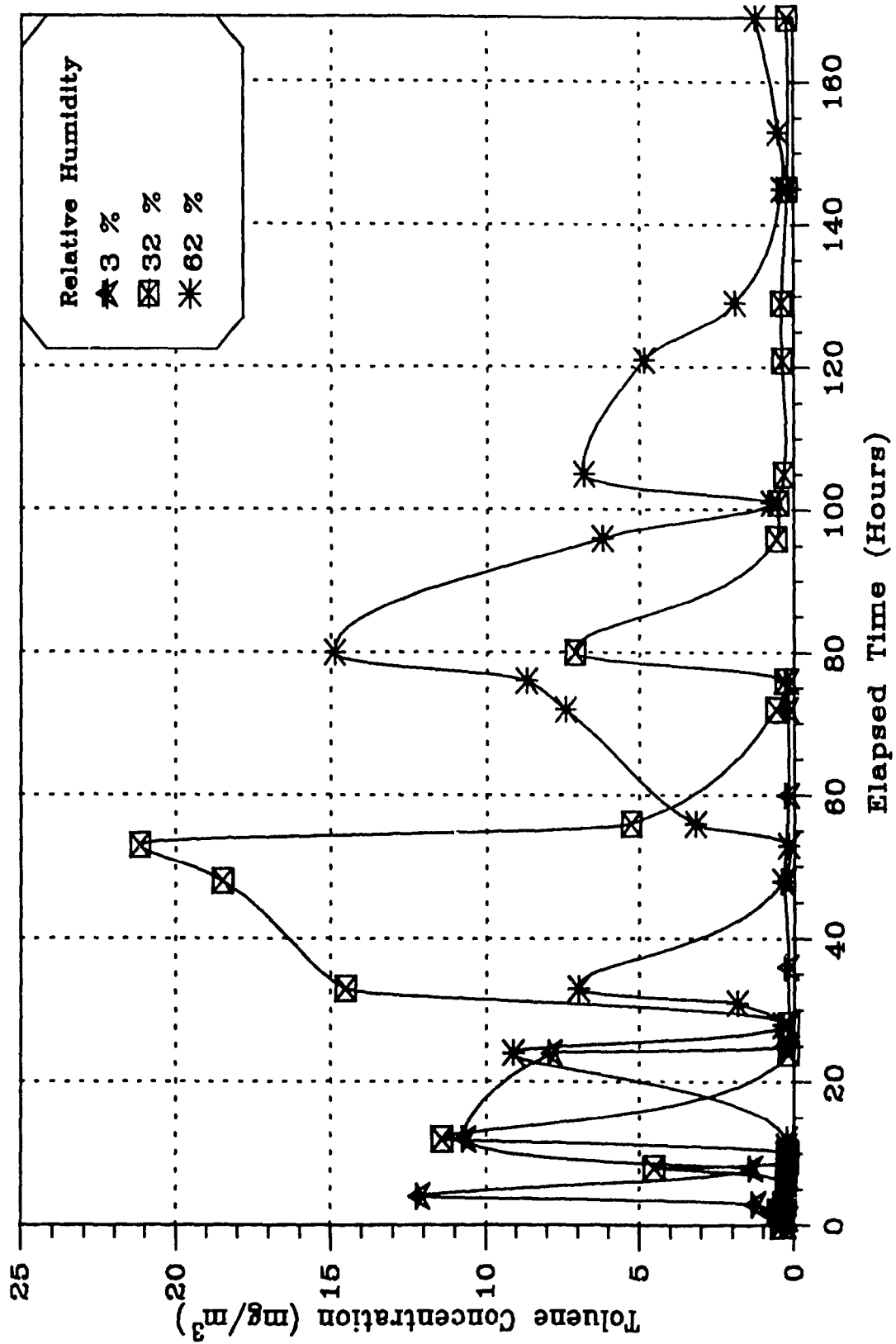


Figure 31: Toluene Concentration versus Time Profiles for Paint at 1.2 ach and Relative Humidity 3, 32, and 62 %

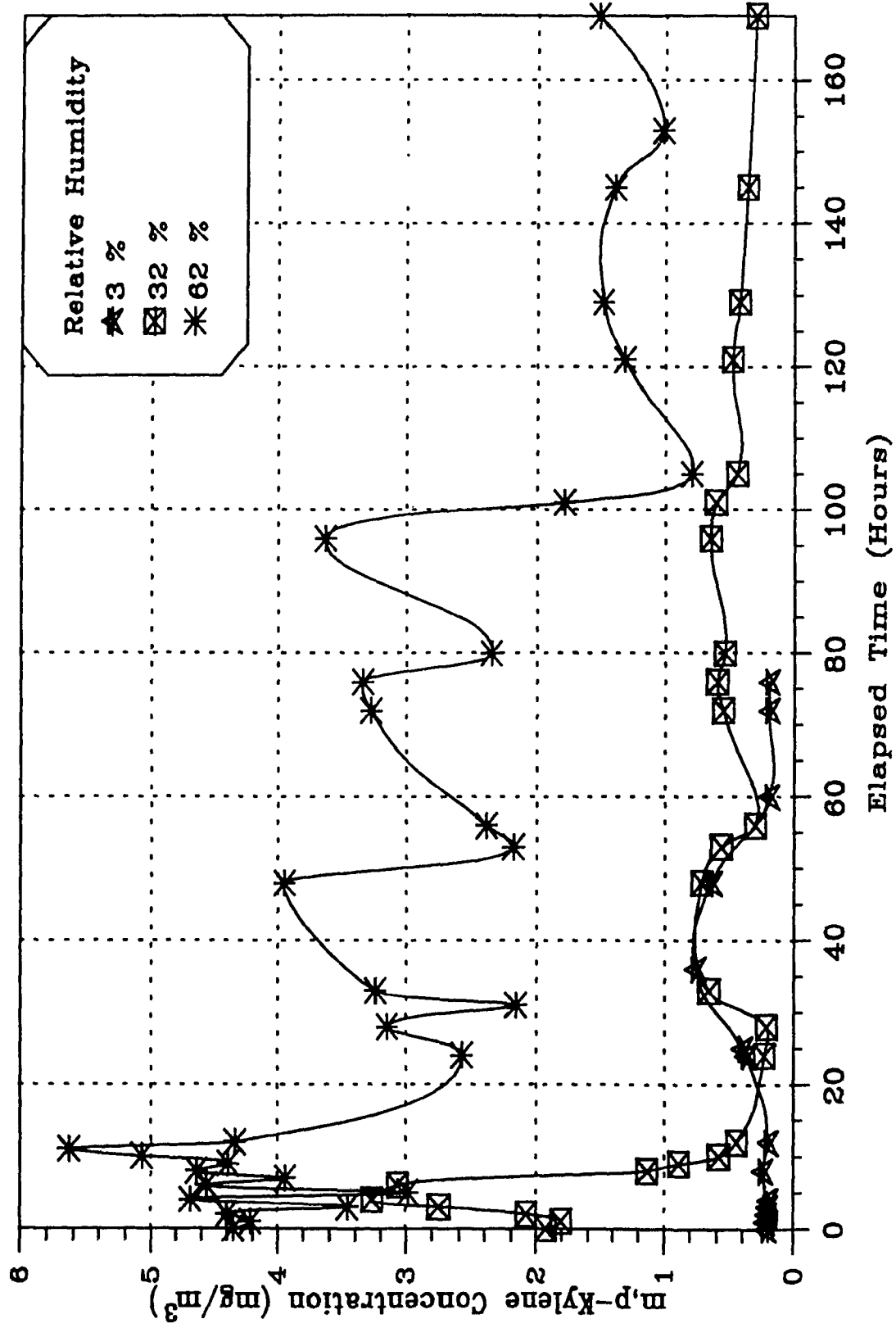


Figure 32: m,p-Xylene Concentration versus Time Profiles for Paint at 1.2 ach and Relative Humidity 3, 32, and 62 %

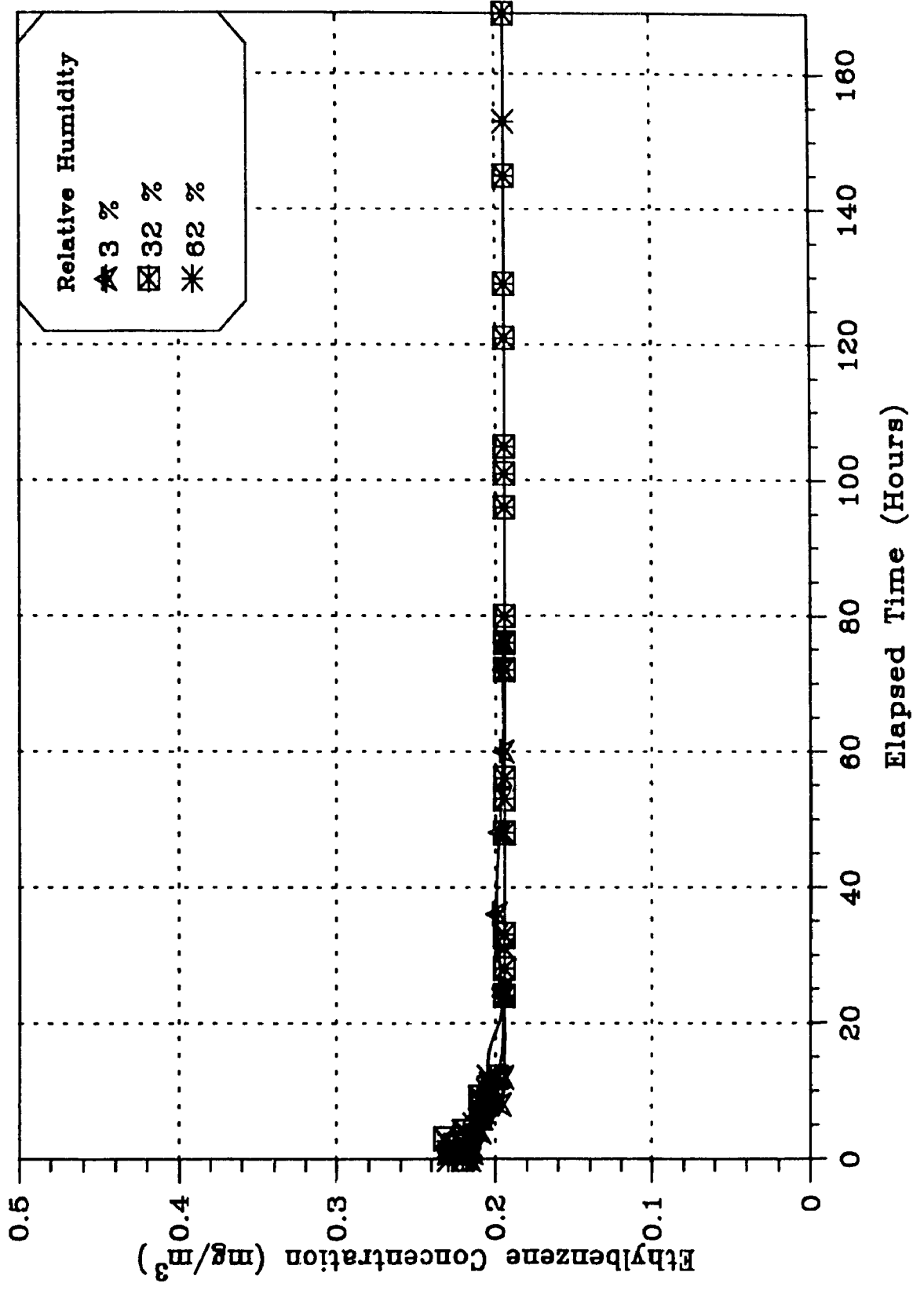


Figure 33: Ethylbenzene Concentration versus Time Profiles for Paint at 1.2 ach and Relative Humidity 3, 32, and 62%

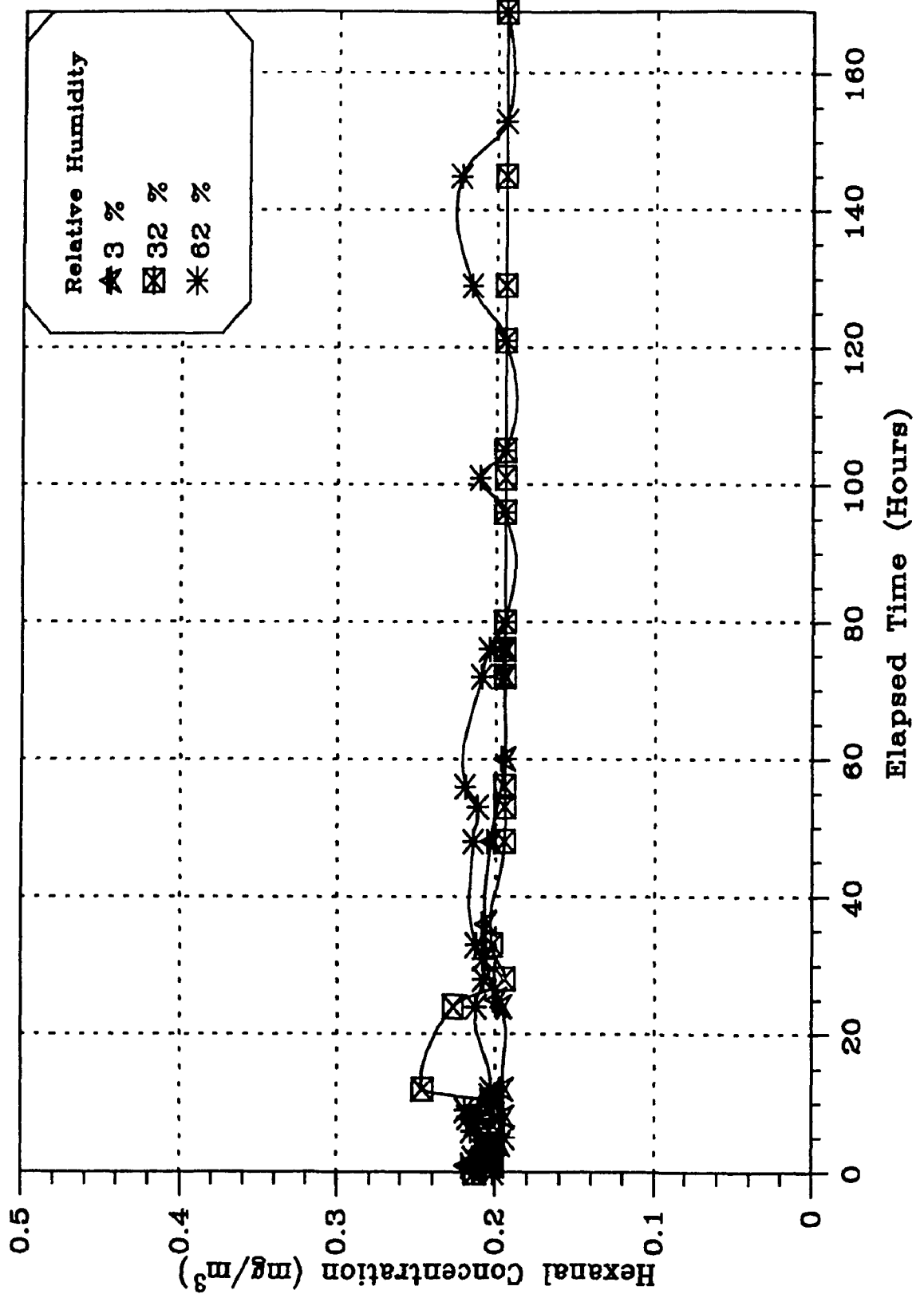


Figure 34: Hexanal Concentration versus Time Profiles for Paint at 1.2 ach and Relative Humidity 3, 32, and 62 %

decreasing, are still significant after 160 hours. At 32%, the concentrations are quite high for the first 12 hours, then start to deplete. However, the depletion is slow with several minor peaks still occurring. At 3%, the highest concentration is only recorded after 40 hours.

Both ethylbenzene and hexanal (Figures 33 and 34) do not show a significant difference between humidity levels tested. For the most part ethylbenzene emissions are quite low, and reach steady state within 24 hours. The hexanal curve shows a minor peak for the 32% test early in the profile, while the 62% test shows several minor peaks.

The impact of the relative humidity on the different compounds considered is quite extraordinary. Toluene and m,p-xylene are greatly effected by the humidity but at different levels. As they also have very abundant concentrations, their reaction to the relative humidity must impact the TVOC concentration profile.

6.1.4 Emission Rate Profiles

Figures 35 through 39 show the emission rate profiles, calculated using Equation (6), for the TVOC and each individual compound discussed above. The emission rate profiles behave in much the same way as the concentration versus time profiles for each compound. For all levels of humidity, the TVOC curves show a slight decrease early on, within 4 hours, after which the fluctuations begin. No trend can be generalized to predict the effect of the emission rate with increasing humidity. This is also true for the individual compounds with the exception of ethylbenzene and hexanal, which may not show a great dependence on the humidity because of their low concentrations.

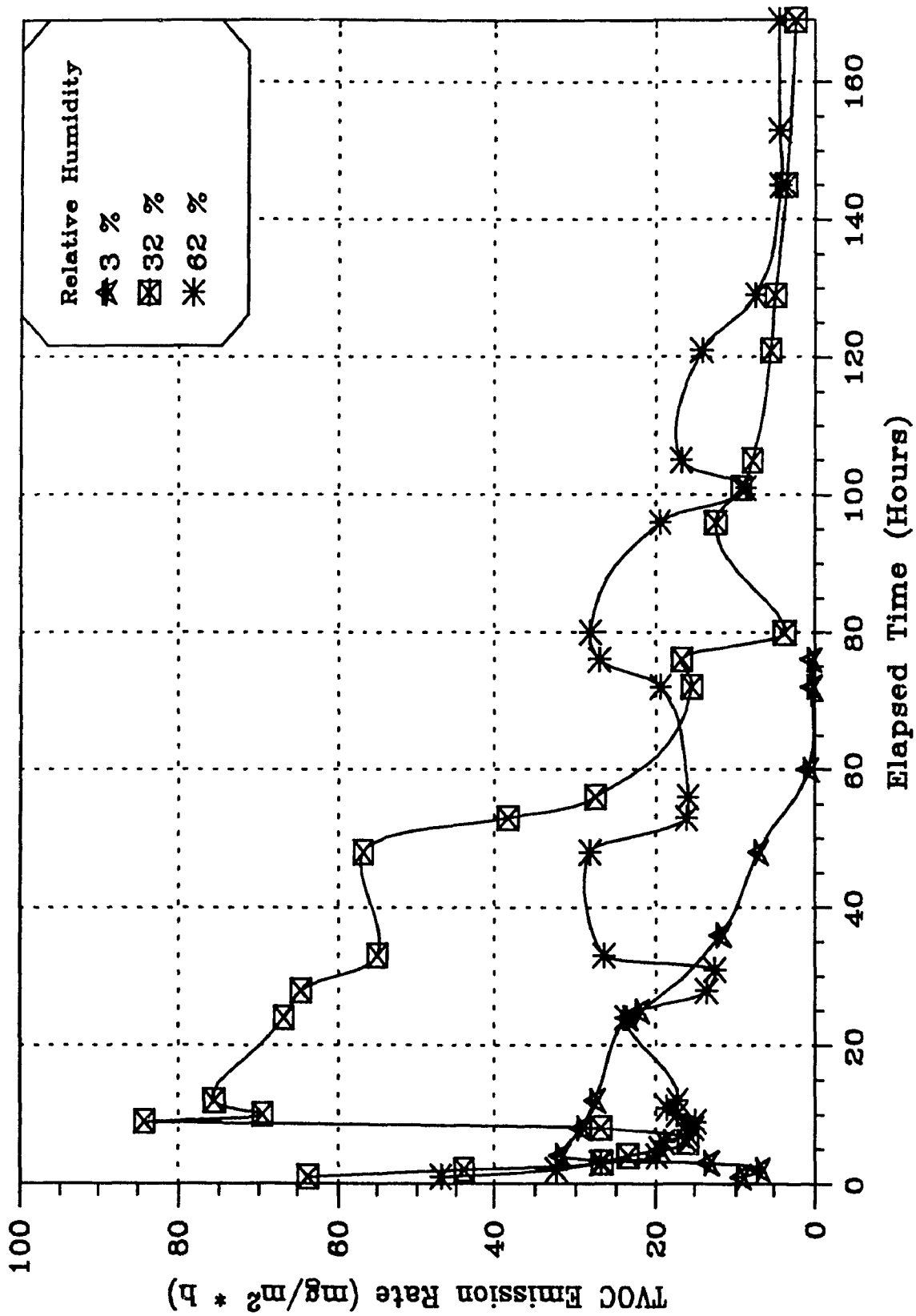


Figure 35: TVOC Emission Rate versus Time Profiles for Paint at 1.2 ach and Relative Humidity 3, 32 and 62 %

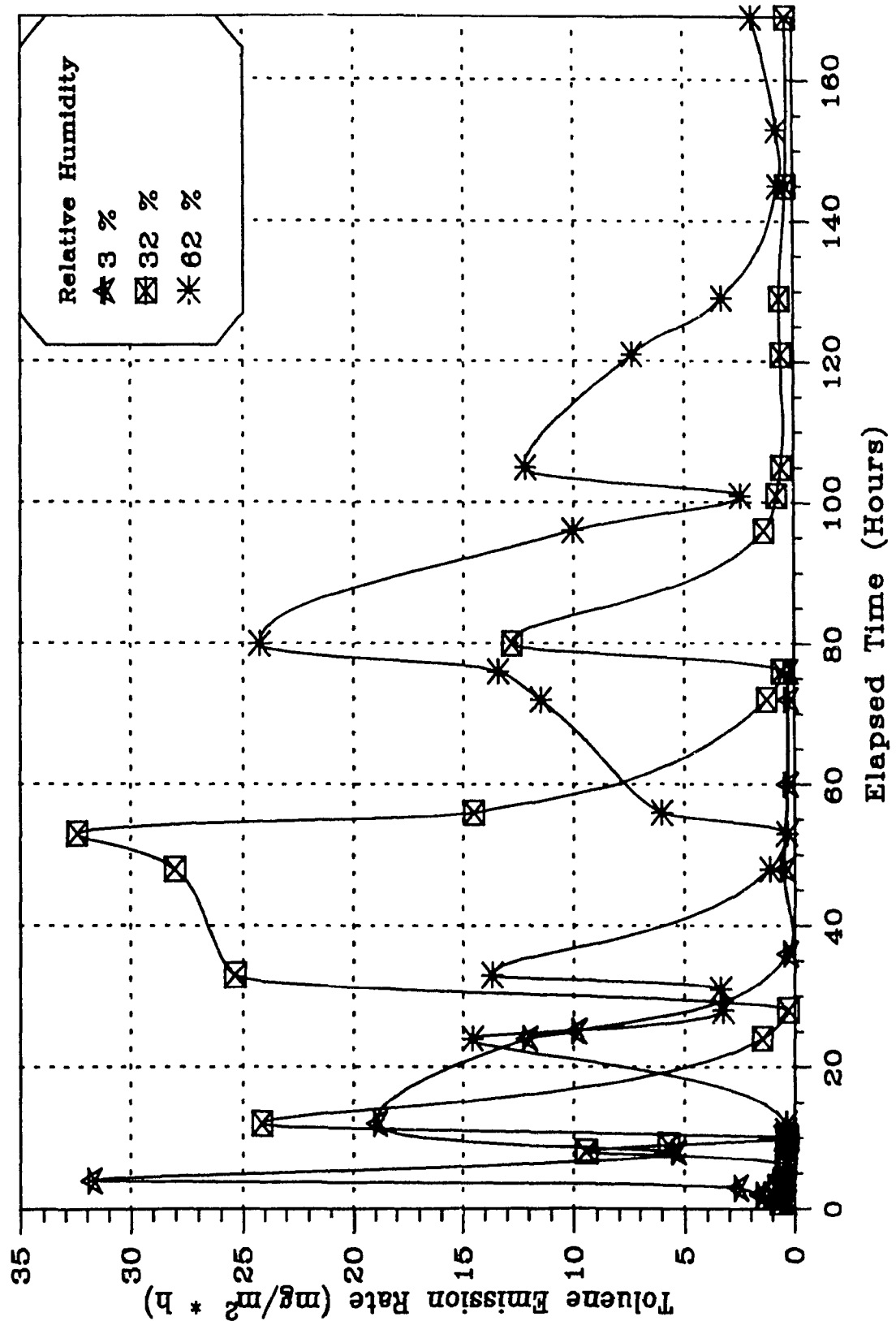


Figure 36: Toluene Emission Rate versus Time Profiles for Paint at 1.2 ach and Relative Humidity 3, 32, and 62 %

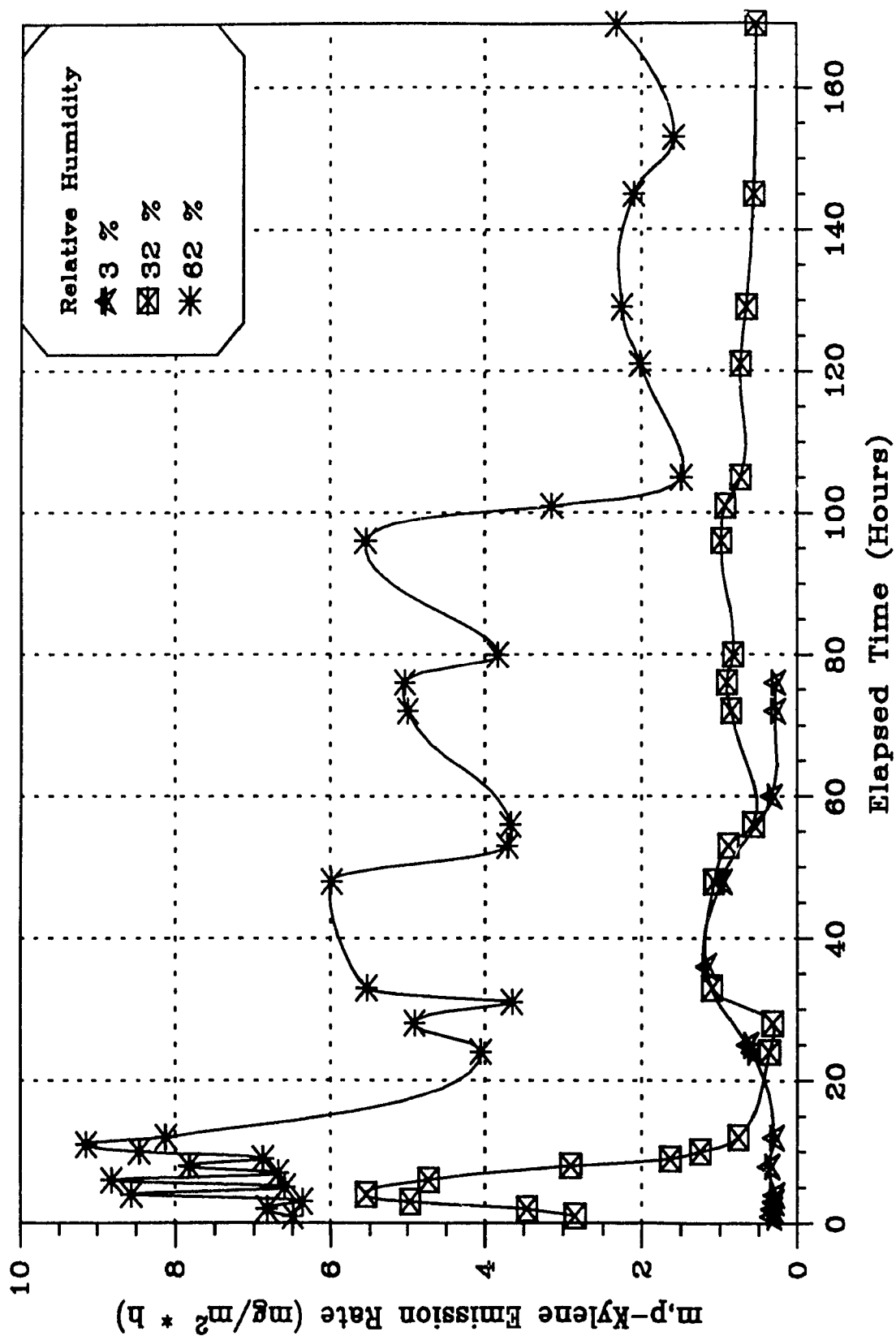


Figure 37: m,p-Xylene Emission Rate versus Time Profiles for Paint at 1.2 ach and Relative Humidity 3, 32 and 62 %

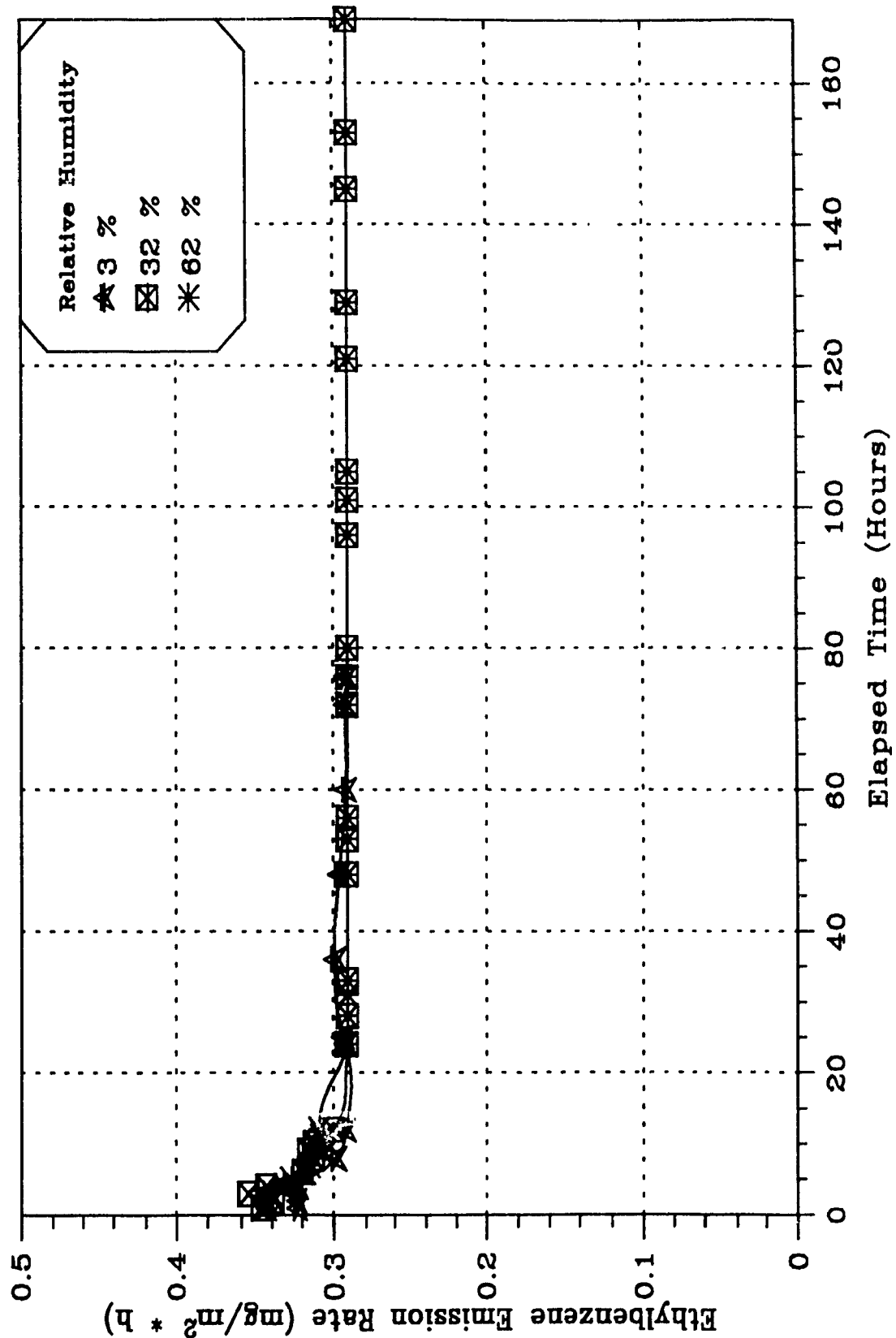


Figure 38: Ethylbenzene Emission Rate versus Time Profiles for Paint at 1.2 ach and Relative Humidity 3, 32, and 62%

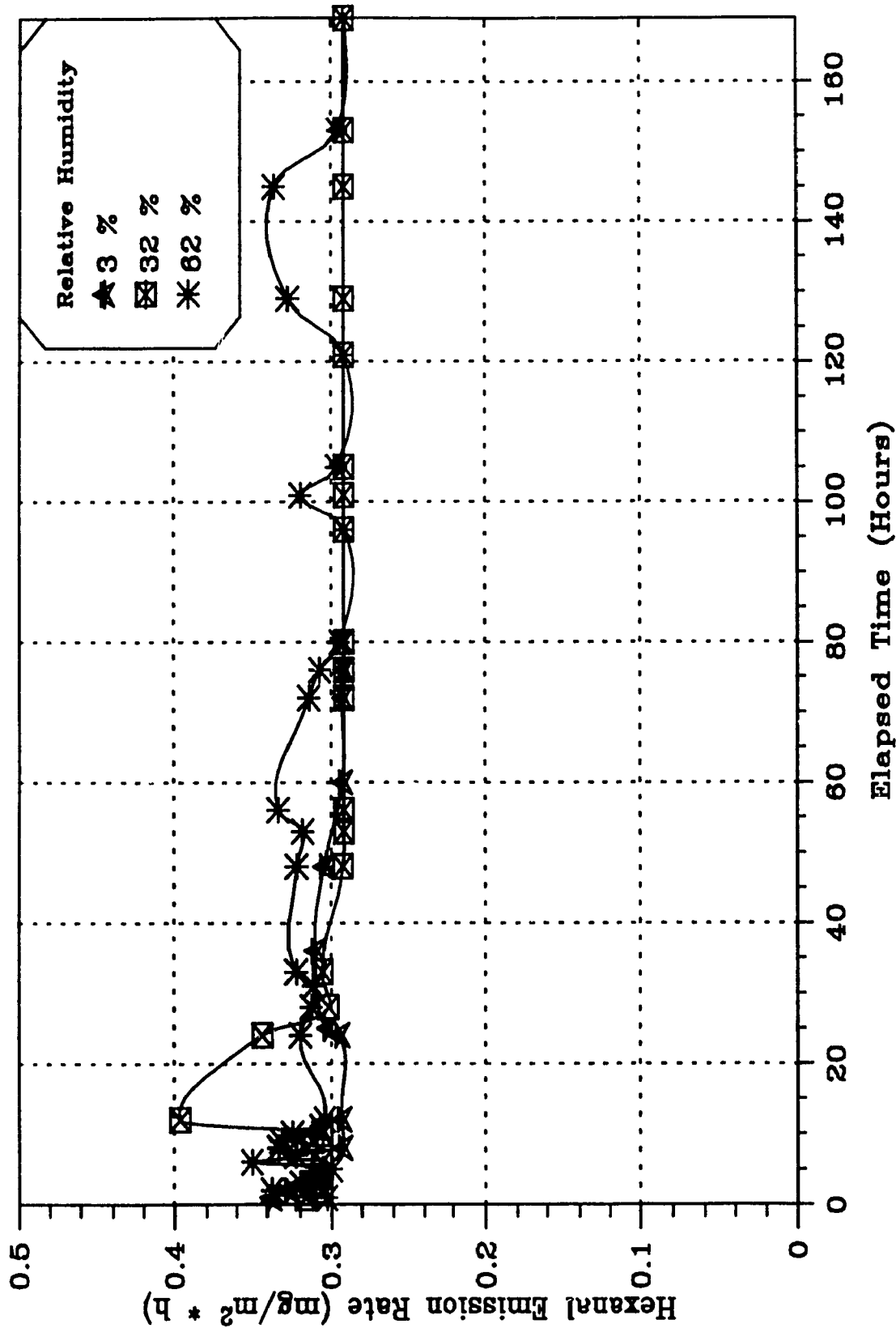


Figure 39: Hexanal Emission Rate versus Time Profiles for Paint at 1.2 ach and Relative Humidity 3, 32, and 62 %

6.2 Varnish Results and Discussion

The results obtained when subjecting samples of varnish to various relative humidities are summarized in Figures 40 through 49.

6.2.1 Temperature and Relative Humidity During Testing

For the varnish tests, the relative humidity levels were set at the same values as for the paint; that is, $3 \pm 3\%$ (dry air), $32 \pm 3\%$, and $62 \pm 3\%$. The outlet humidity levels recorded were not as high as those for paint. Peak exit humidities for the three inlet levels were 12.5, 31.1, and 62.4% respectively. The exit humidity for the 3% test decreased to inlet levels after 12 hours. The outlet humidity for the other tests were very near the inlet conditions for the duration of the test. The sample did not effect the humidity level within the chamber.

The temperature, measured at the outlet, remained fairly constant at $25 \pm 2^\circ\text{C}$ for the duration of all tests.

6.2.2 TVOC Concentration Profile

The TVOC concentration profile for the varnish temperature tests is shown in Figure 40. Contrary to the paint, the concentration profiles for varnish behave exponentially, as expected. Highest concentrations are recorded for the highest humidity level tested. In fact, we can generalize the trend by saying that the higher concentrations occurred with increasing humidity. In spite of this, the three curves merge and deplete at the same time, approximately 24 hours. On a point to point basis, slight fluctuations do

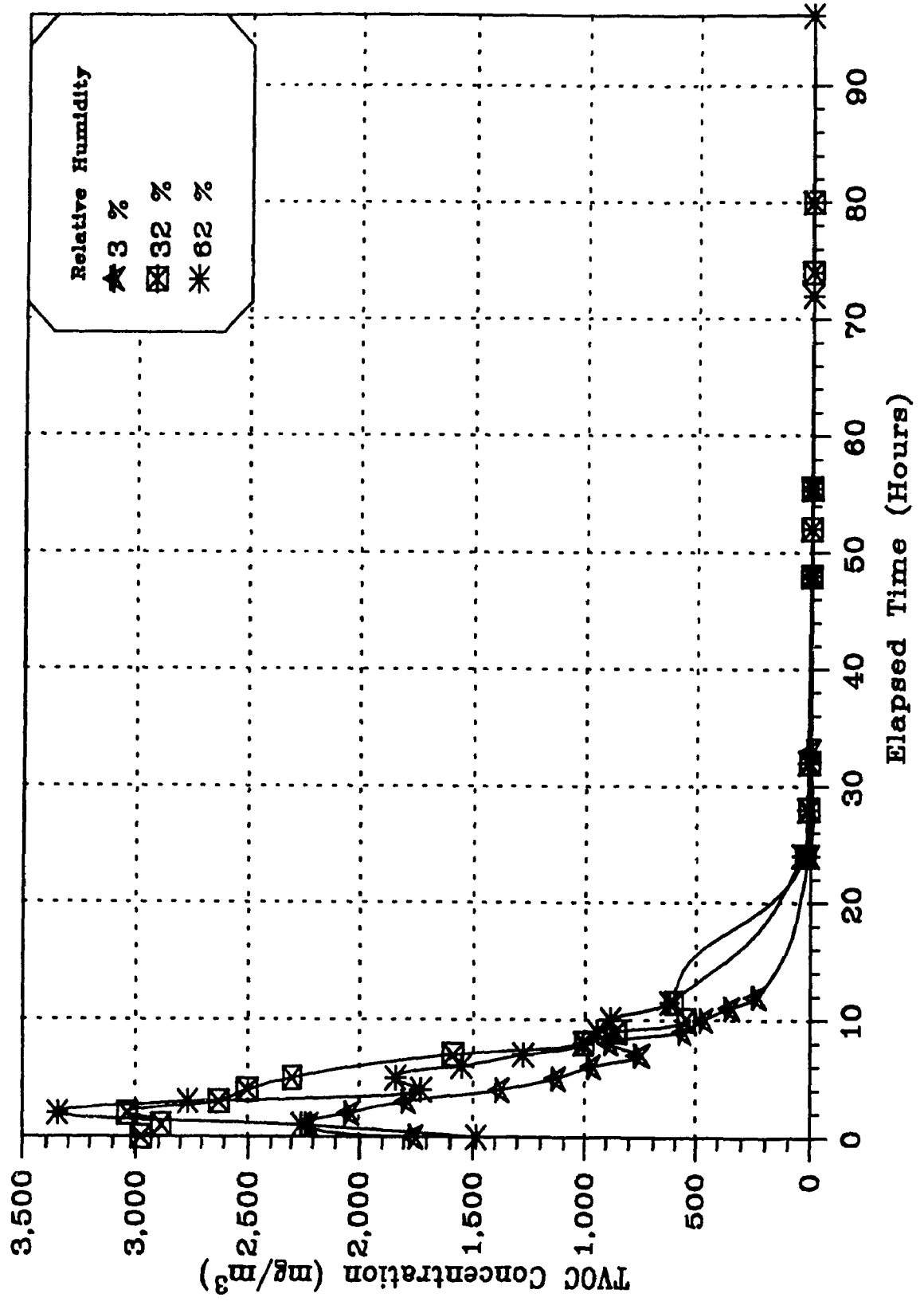


Figure 40: TVOC Concentration versus Time Profiles for Vamish at 1.2 ach and Relative Humidity 3, 32, and 62 %

occur, but no where as significantly as the fluctuations occurring for the paint TVOC. The overall concentrations of varnish are fairly high, however, the peak value is not as high as that measured for the varnish test at 35 °C.

6.2.3 Concentration Profiles for Individual Compounds

The individual compound concentration profiles for the varnish samples are depicted in Figures 41 to 44. Unlike the TVOC, toluene, m,p-xylene and 1,3,5-trimethylbenzene (Figures 41, 42 and 44) show higher values for the 32% test than for the 62% test. This again shows that trends established for the TVOC do not necessarily stand for individual compounds. The curve for ethylbenzene (Figure 43) shows that the lowest concentrations occurred for the 62% test. The values measured for the 3% and 32% tests are quite similar in order of magnitude.

6.2.4 Emission Rate Profiles

The emission rate profiles for the varnish TVOC and individual compounds are shown in Figures 45 through 49. Again these curves are very similar to their concentration profiles. The ethylbenzene and 1,3,5-trimethylbenzene curves (Figures 48 and 49) show some slight deviations from an exponential decay, especially for the 32% humidity test. In fact, these deviations occur for all three levels of humidity for the 1,3,5-trimethylbenzene curve.

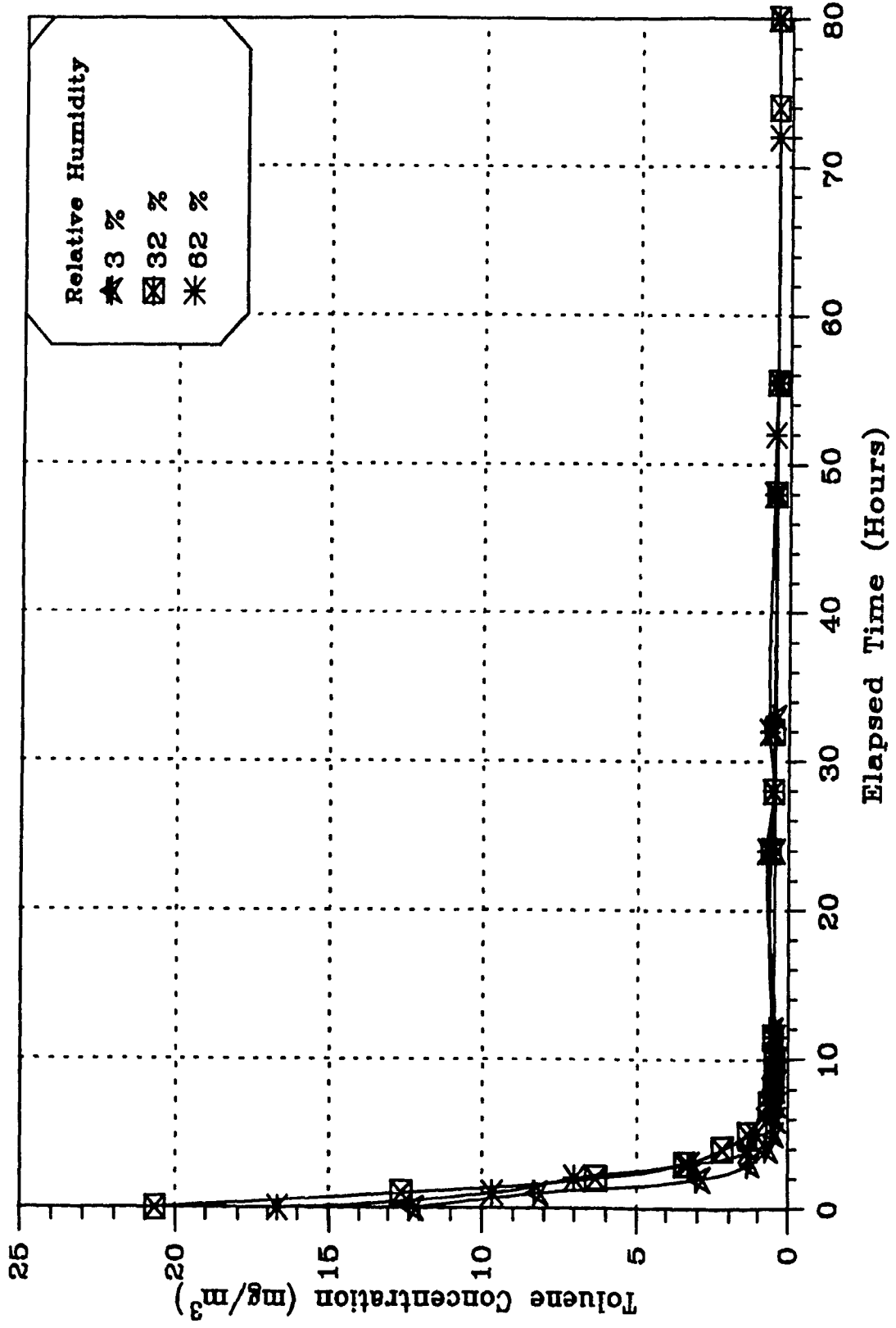


Figure 41: Toluene Concentration versus Time Profiles for Varnish at 1.2 ach and Relative Humidity 3, 32, and 62 %

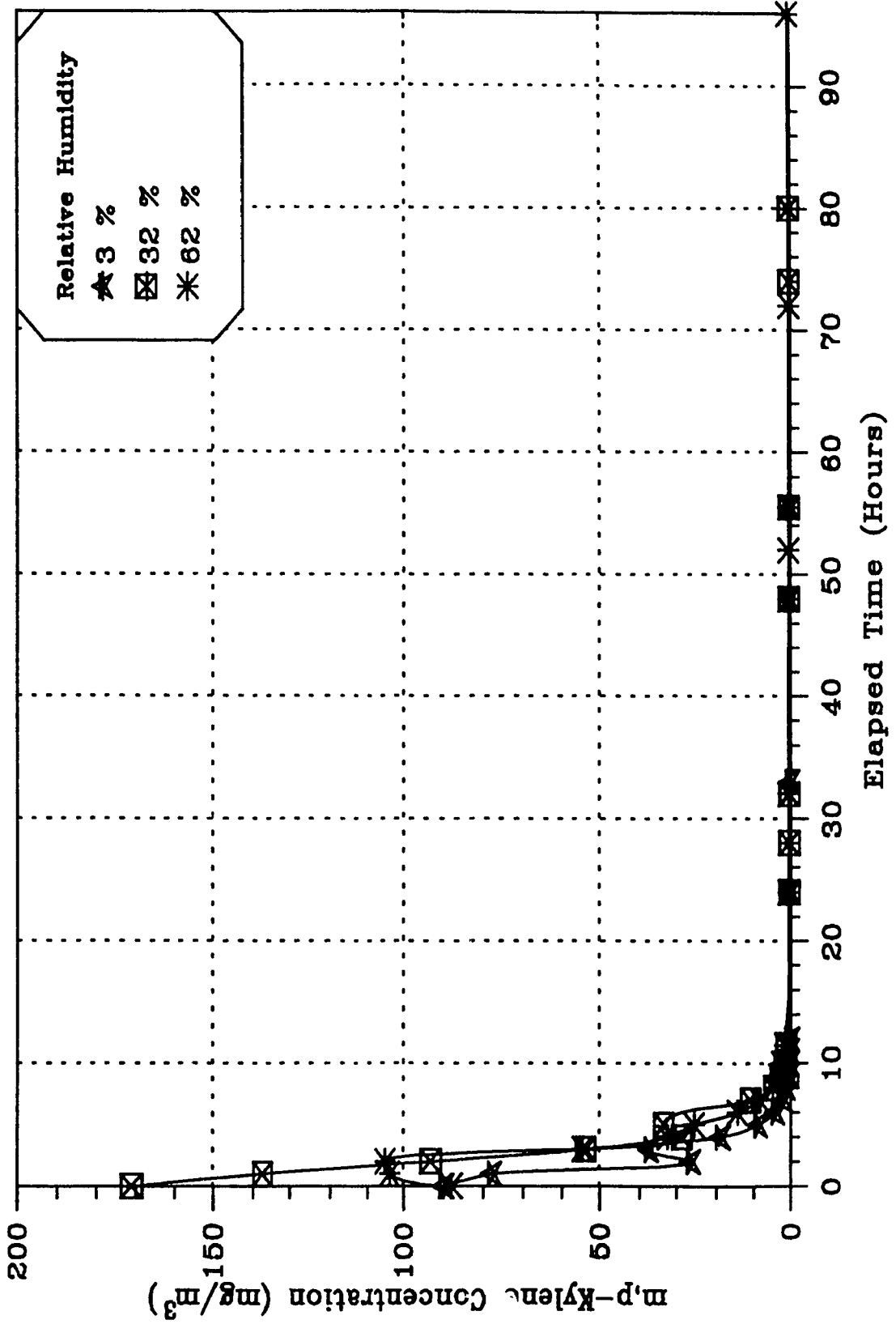


Figure 42: m,p-Xylene Concentration versus Time Profiles for Vamish at 1.2 ach and Relative Humidity 3, 32, and 62 %

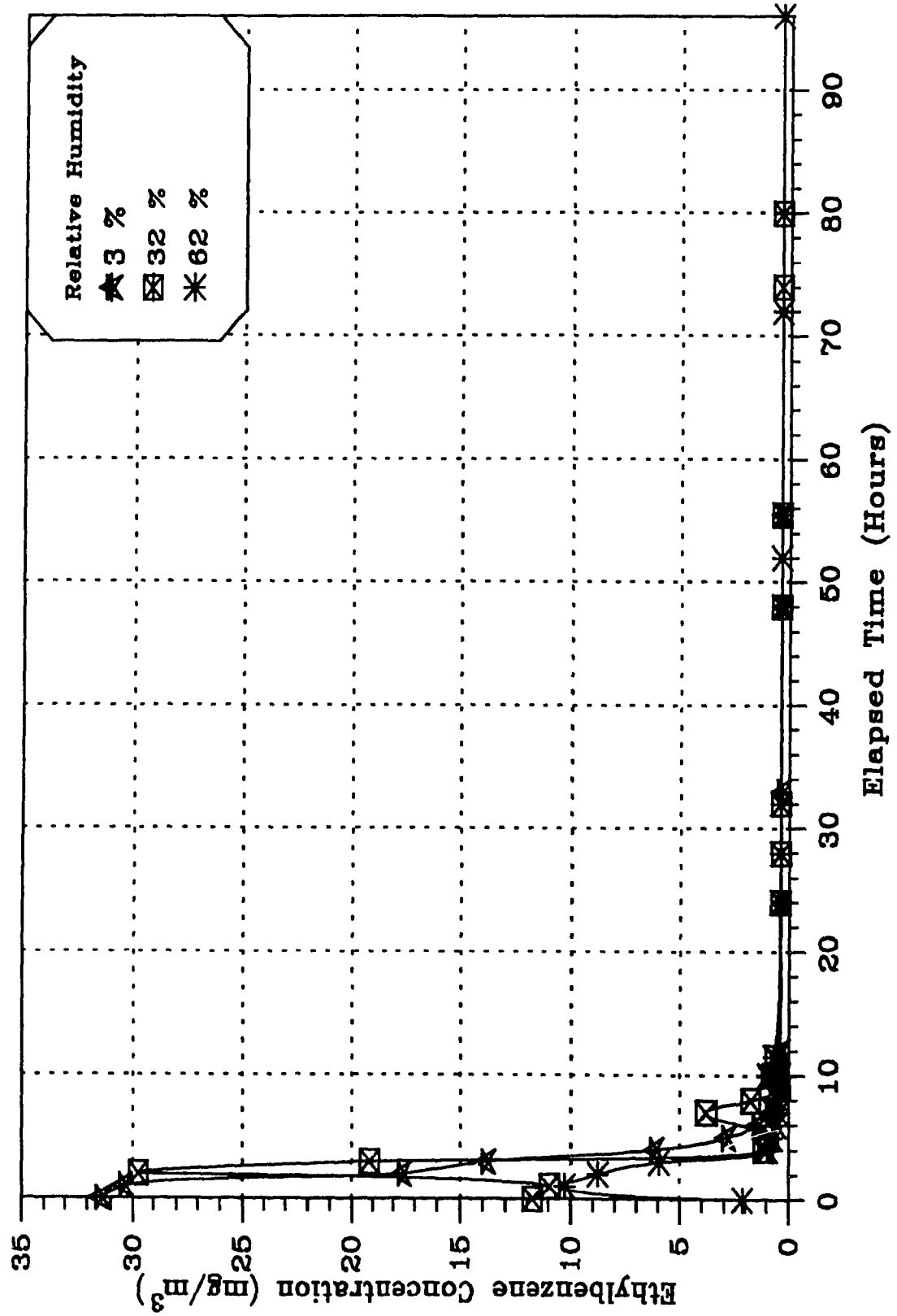


Figure 43: Ethylbenzene Concentration versus Time Profiles for Varnish at 1.2 ach and Relative Humidity 3, 32, and 62%

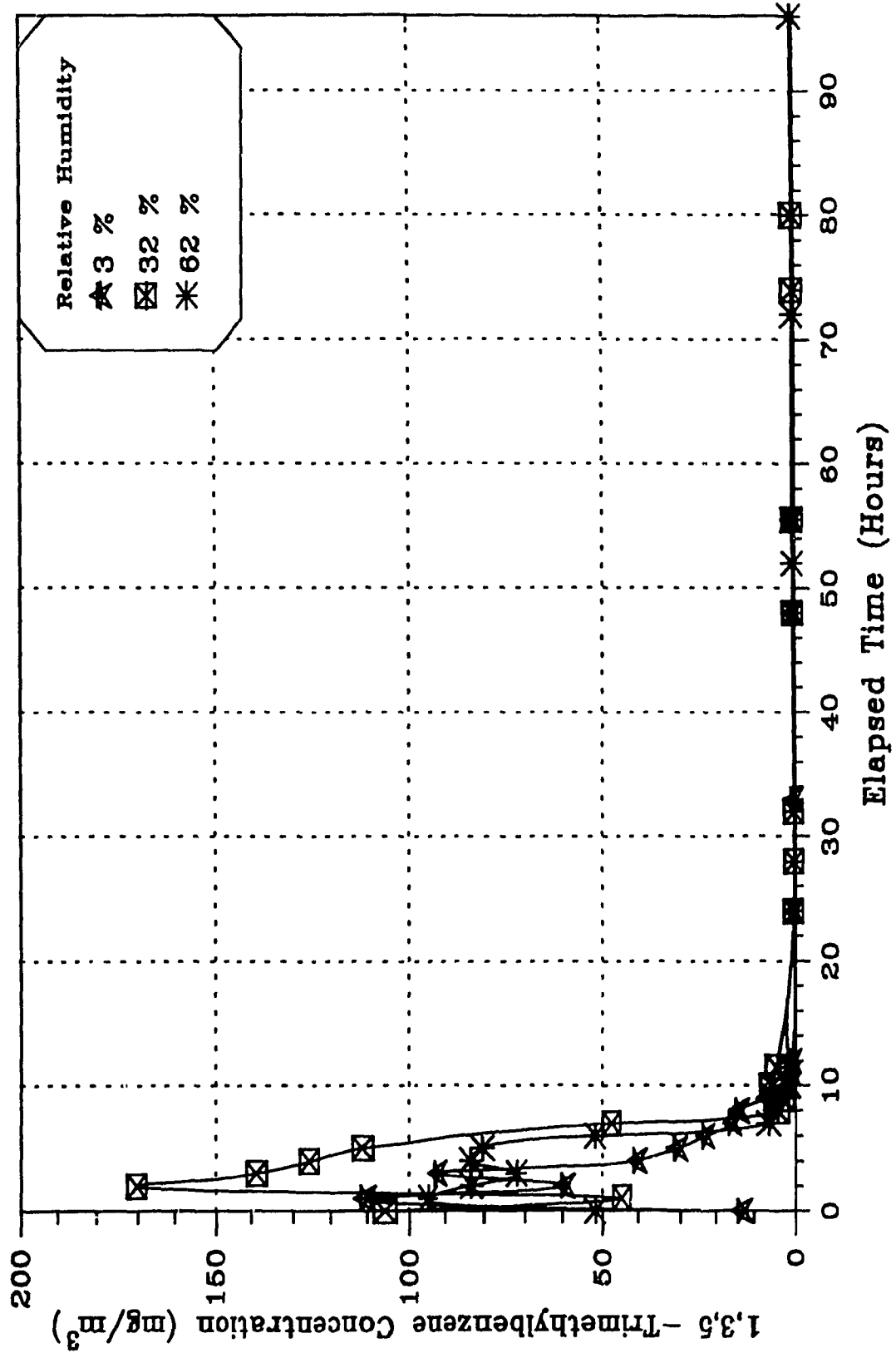


Figure 44: 1,3,5-Trimethylbenzene Concentration versus Time Profiles for Varnish at 1.2 ach and Relative Humidity 3, 32 and 62%

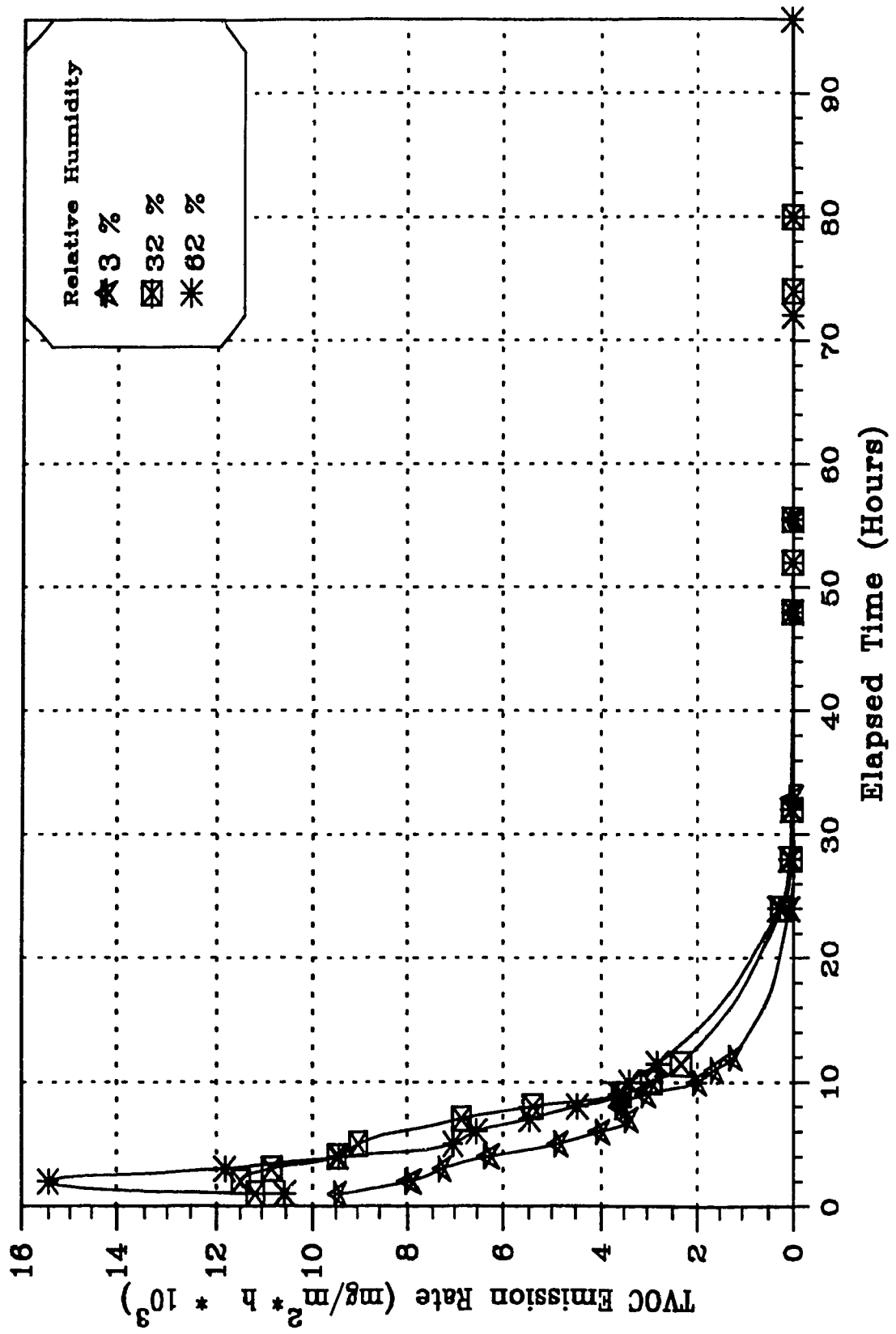


Figure 45: TVOC Emission Rate versus Time Profiles for Varnish at 1.2 ach and Relative Humidity 3, 32 and 62 %

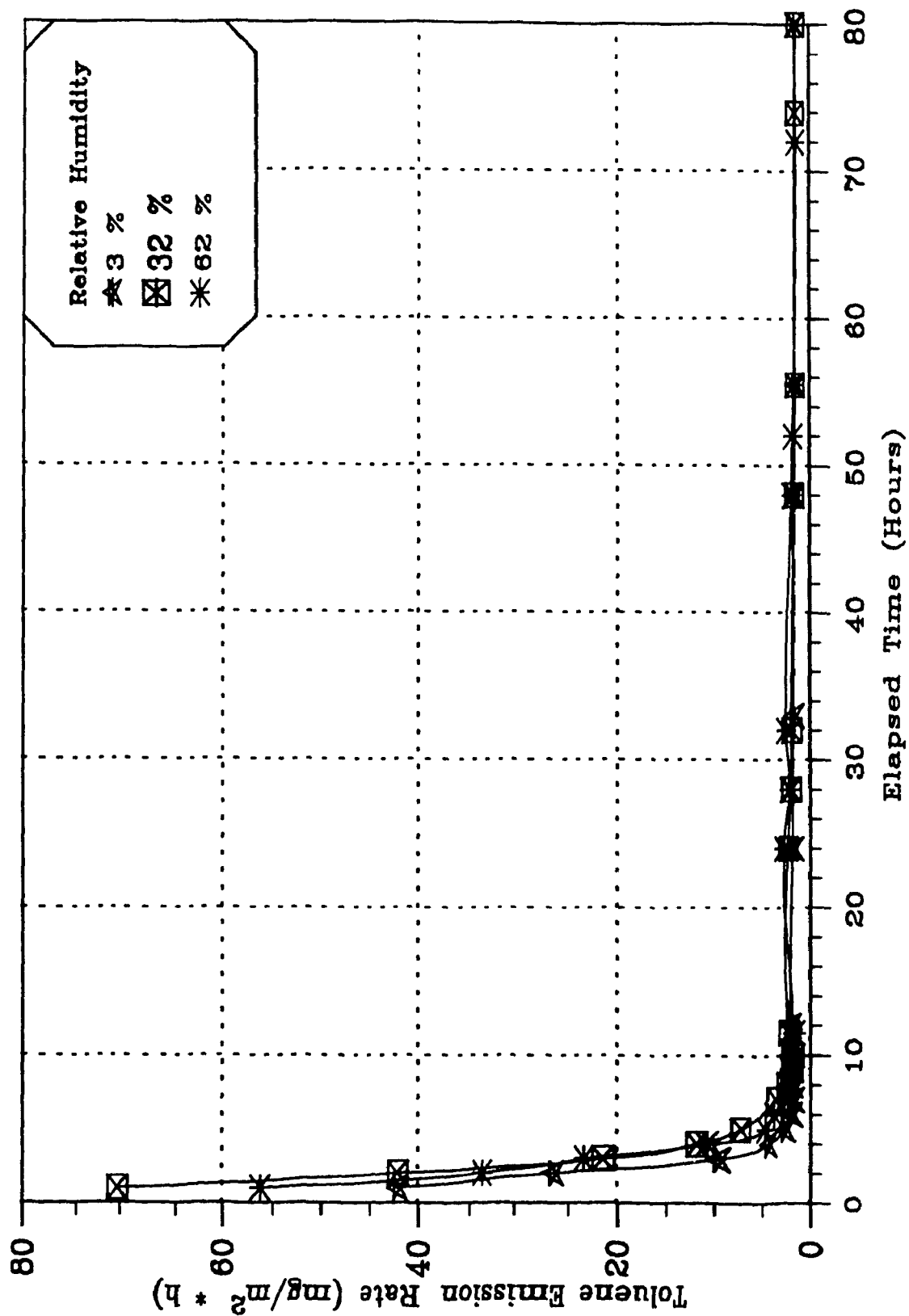


Figure 46: Toluene Emission Rate versus Time Profiles for Varnish at 1.2 ach and Relative Humidity 3, 32, and 62 %

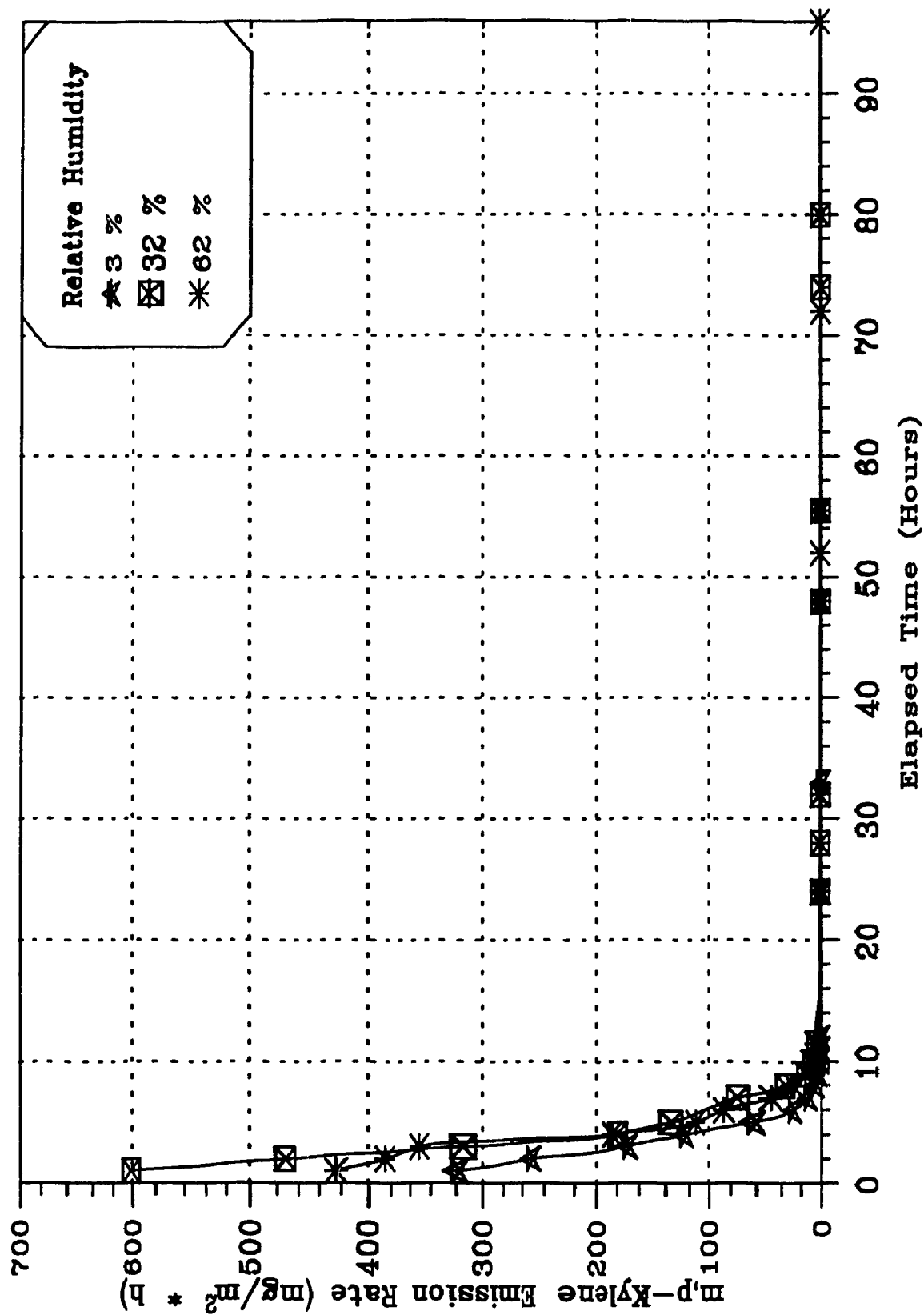


Figure 47: m,p-Xylene Emission Rate versus Time Profiles for Varnish at 1.2 ach and Relative Humidity 3, 32 and 62 %

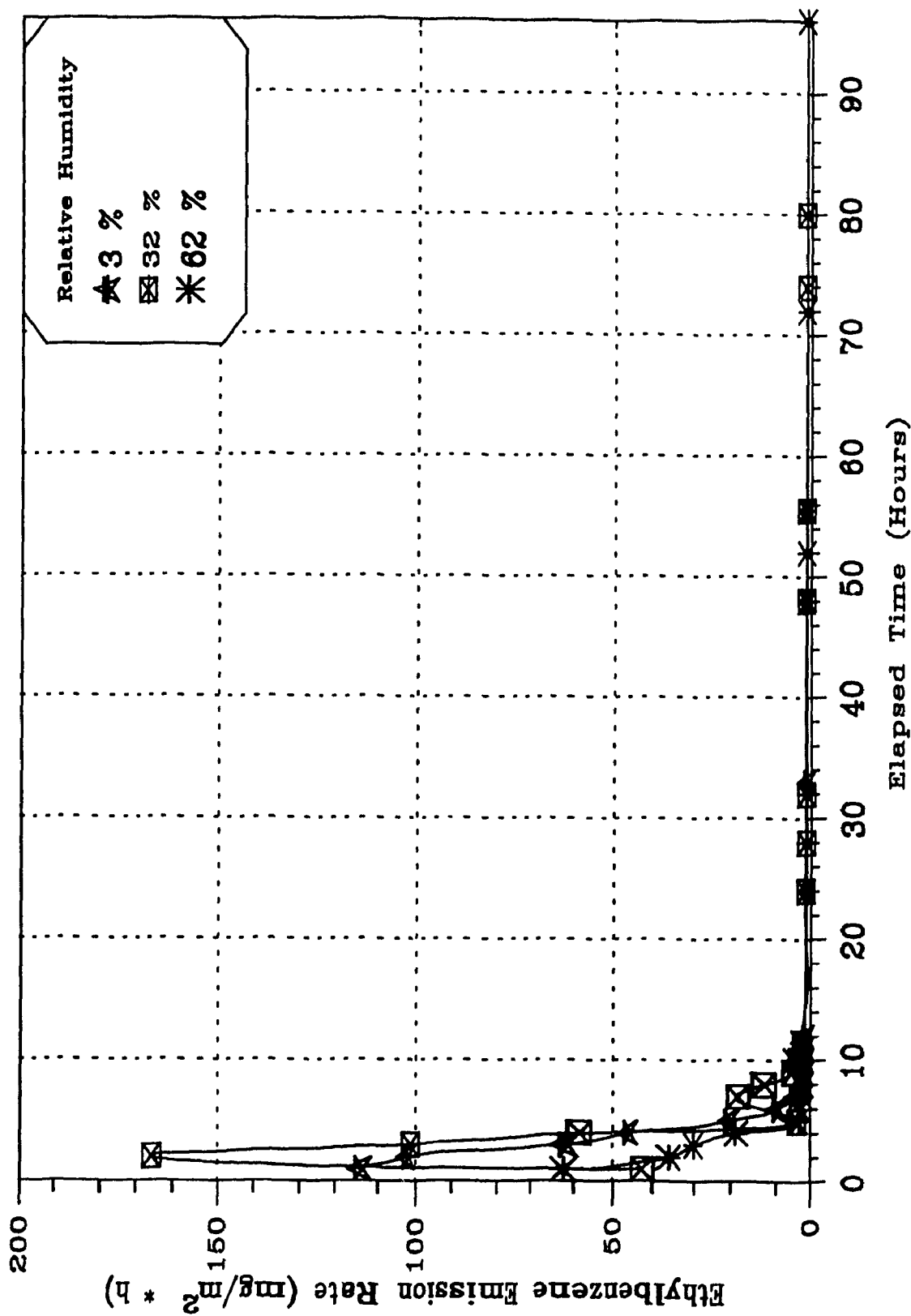


Figure 48: Ethylbenzene Emission Rate versus Time Profiles for Varnish at 1.2 ach and Relative Humidity 3, 32, and 62%

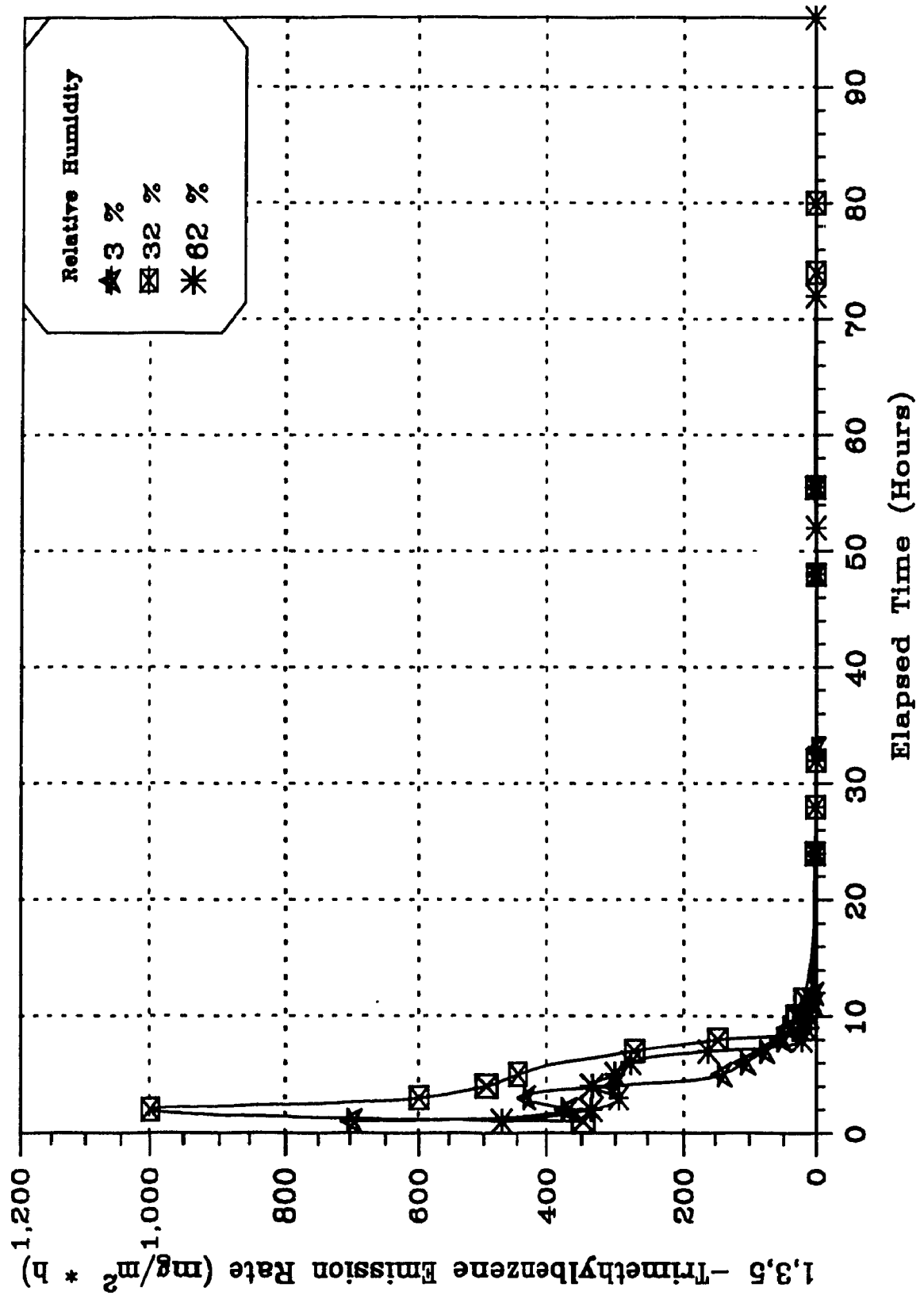


Figure 49: 1,3,5-Trimethylbenzene Emission Rate versus Time Profiles for Varnish at 1.2 ach and Relative Humidity 3, 32 and 62%

CHAPTER VII

APPLICATIONS: THE BAKE-OUT PROCEDURE

7.1 The Bake-Out Procedure

The main procedure of a bake-out involves increasing the indoor temperature to values between 30 to 38 °C for two or more days, while simultaneously increasing the fresh air ventilation throughout the building [91,92,93]. The theory supporting this is that the high temperatures will increase the vapour pressures of the VOCs present in the materials. This will increase the rate of off-gassing of the VOCs. As the VOCs escape into the atmosphere of the building, the fresh air circulation will sweep the VOCs out of the building [92,94]. Several factors must be considered carefully. It is important to obtain high temperatures, therefore the fresh air circulation must not be too significant to prevent the temperature increase; at the same time, it must be effective in removing the VOCs. If the ventilation is inadequate, it may allow time for some materials to reabsorb the VOCs emitted into the atmosphere by other materials in the room. This would create secondary emissions of VOCs and would obscure the results obtained from the bake-outs [23,91]. While it is important to reach high temperatures, it is feared that interior damage may occur if the temperature is too high for too long [23,91]. An example of this is letting the paint dry too quickly, which may lead to premature peeling of the paint. This was in fact witnessed during the temperature tests on the paint samples. At the end of the 15 and 25 °C tests, the paint samples were retrieved from the chamber intact; their surfaces were perfectly smooth. However, at the end of the 35 °C tests, the paint samples

were removed from the chamber with evidence of cracking and flaking all over their surfaces.

7.2 Descriptions of the Bake-Outs During the Two Investigations

Two different bake-out investigations have been conducted [95]. The first study involved the bake-out of both an office and residential building. The second investigation compared the emissions in two similar houses when one underwent bake-out and the other did not.

7.2.1 Investigation 1

The floor plans of the office and residential buildings studied, along with information on their interiors, are shown in Figures 50 and 51, respectively.

The office building, located in Dorval, Quebec, was newly renovated. The air exchange rates and the VOC concentrations were measured before the bake-out. The air exchange rate was measured using the tracer gas technique, in much the same way as was used to test the air mixing in the environmental chamber. VOC concentrations were measured using active charcoal samplers. Table 4 summarizes the air exchange rates measured at different locations in the building. These values represent the air exchange at the instant of measurement and are not representative of long term values.

To reach the desired temperature during the bake-out, five heaters were installed throughout the office building. To provide the required ventilation, the exhaust fans in the kitchen and Bathroom #2 were left on. The bake-out began at 5:15 Friday afternoon and

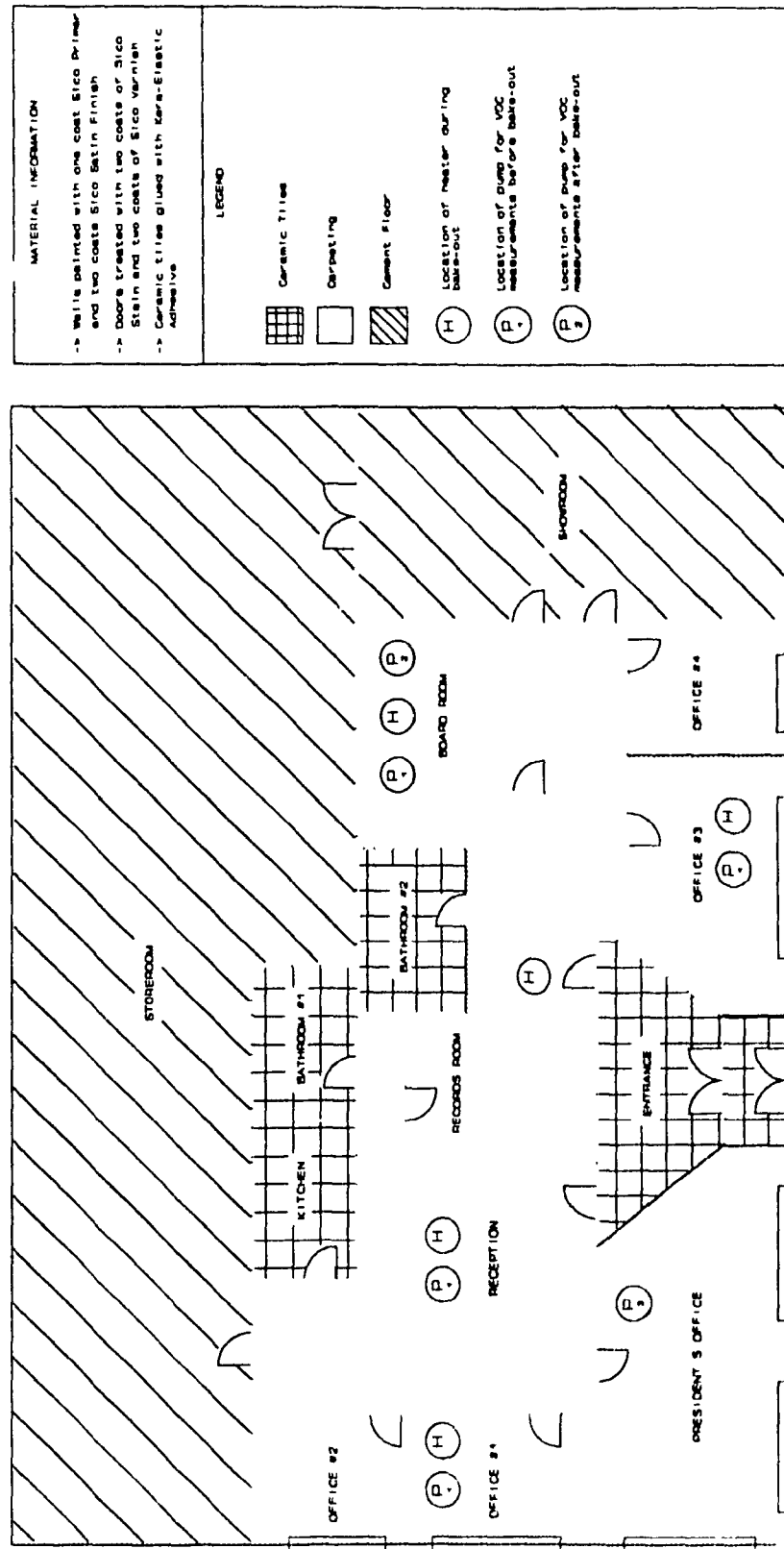
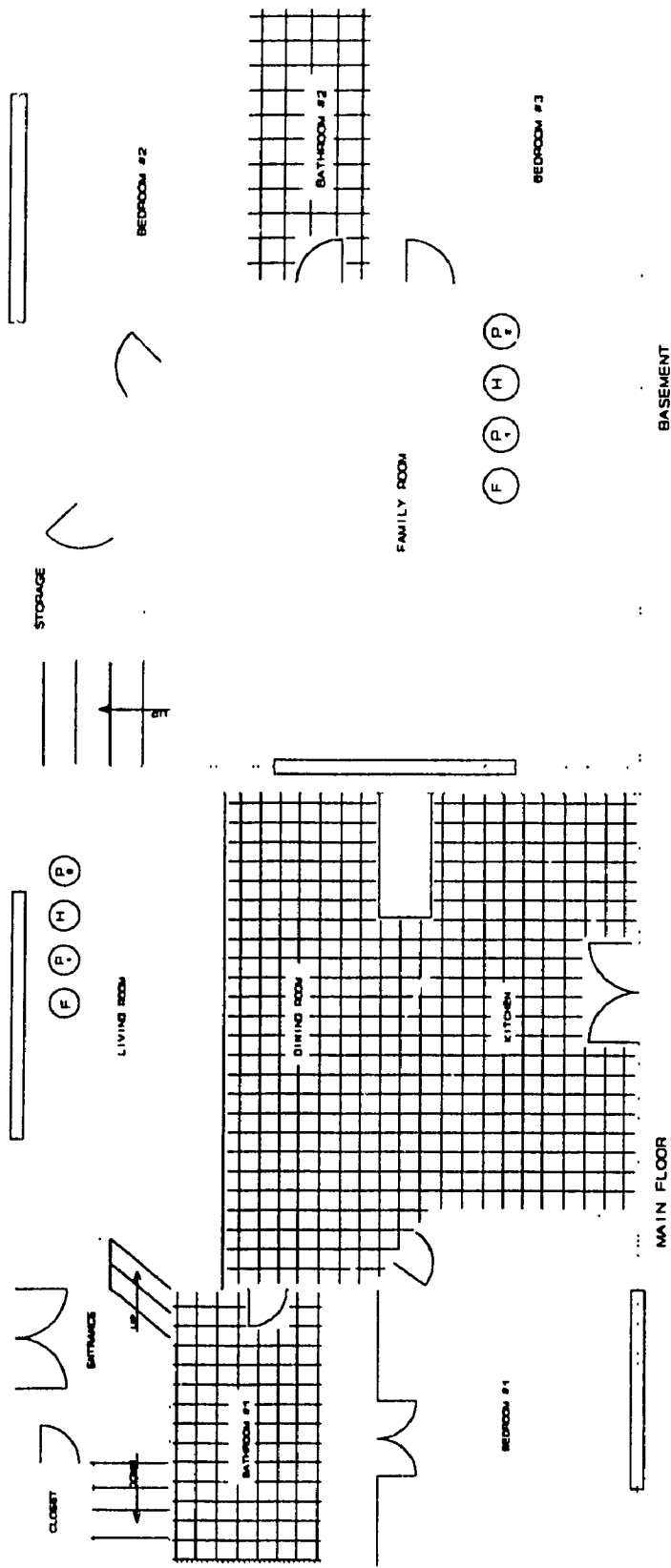


Figure 50: Floor Plan of Office Building and Material Information (Investigation 1)



MATERIAL INFORMATION	LEGEND
-> Particle board cupboards in kitchen.	(F) Location of fan during bake-out
-> Carpeting stapled, not glued, to plywood floor	(P) Location of pump for VOC measurements before bake-out
-> Wooden staircase and railings not varnished	(P) Location of pump for VOC measurements after bake-out
	(H) Location of heater during bake-out
	□ Carpeting
	▣ Linoleum flooring

Figure 51: Floor Plan of Residential Building and Material Information (Investigation 1)

Table 4: Air Exchange Rates Measured in the Office and Residential Buildings

Location	Air Exchange Rate Before Bake-Out (ach)	Air Exchange Rate Immediately Following Bake-Out (ach)	Air Exchange Rate After Bake-Out (ach)
Office Building			
Reception	0.140	-	-
Board Room	0.825	-	-
President's Office	-	-	0.061
Residential Building	0.610	0.264	0.316

ended 9:00 the following Monday morning. Twenty-four days following the completion of the bake-out, the air exchange rates and the VOC concentrations were measured again. Table 5 contains the VOC concentrations measured before and after the bake-out in two locations of the building.

Formaldehyde samples were not measured in the office building because it was decided that its presence would be minimal. This is because products such as melamine cabinets, wall panelling and linoleum flooring are not present in the office building.

The bake-out of the newly constructed residential building, located near Terrebonne, Quebec, followed. The air exchange rates were measured in the living room before, immediately following, and two days after the bake-out. These values are presented in Table 4. VOC concentrations were taken before and after the bake-out, as were formaldehyde samples. The VOC measurements are shown in Table 5.

The formaldehyde concentrations were measured using passive bubbler samples. A solution made up of sodium bisulphite and water was placed into small glass bottles, which were capped tightly. At the measurement location, the cap was removed and a diffusion disk was placed at the open end. A perforated cap was then tightened over the disk. The sample was hung at the measurement location so that the sodium bisulphite solution touched the diffusion disk at all times. The measurement location was chosen such that the sample was free from obstructions; that is, air was circulating freely around the sample. The measuring period was at least twenty-four hours. The solid caps were then replaced on the bottles. The samples were refrigerated and delivered to an independent lab for analysis. The formaldehyde concentrations measured before and after the bake-out were 2.0 and 3.9 micrograms, respectively.

Temperature and relative humidity measurements were taken throughout the bake-out procedure using a seven day recorder. Figures 52 and 53 illustrate the profiles obtained from the recorder, respectively. The thermostats to three baseboard heaters in the house were raised to their maximum. In addition, two portable heaters, one in each the living and family rooms, were installed. This allowed the temperature to rise to the desired levels. Air circulation was achieved by leaving two windows opened ajar by one inch, installing two portable fans, and turning on the oven fan in the kitchen. The windows included those in the living room and Bedroom #2 (Refer to Figure 51). The bake-out began at 4:30 Saturday afternoon and ended the following Monday morning at 8:30.

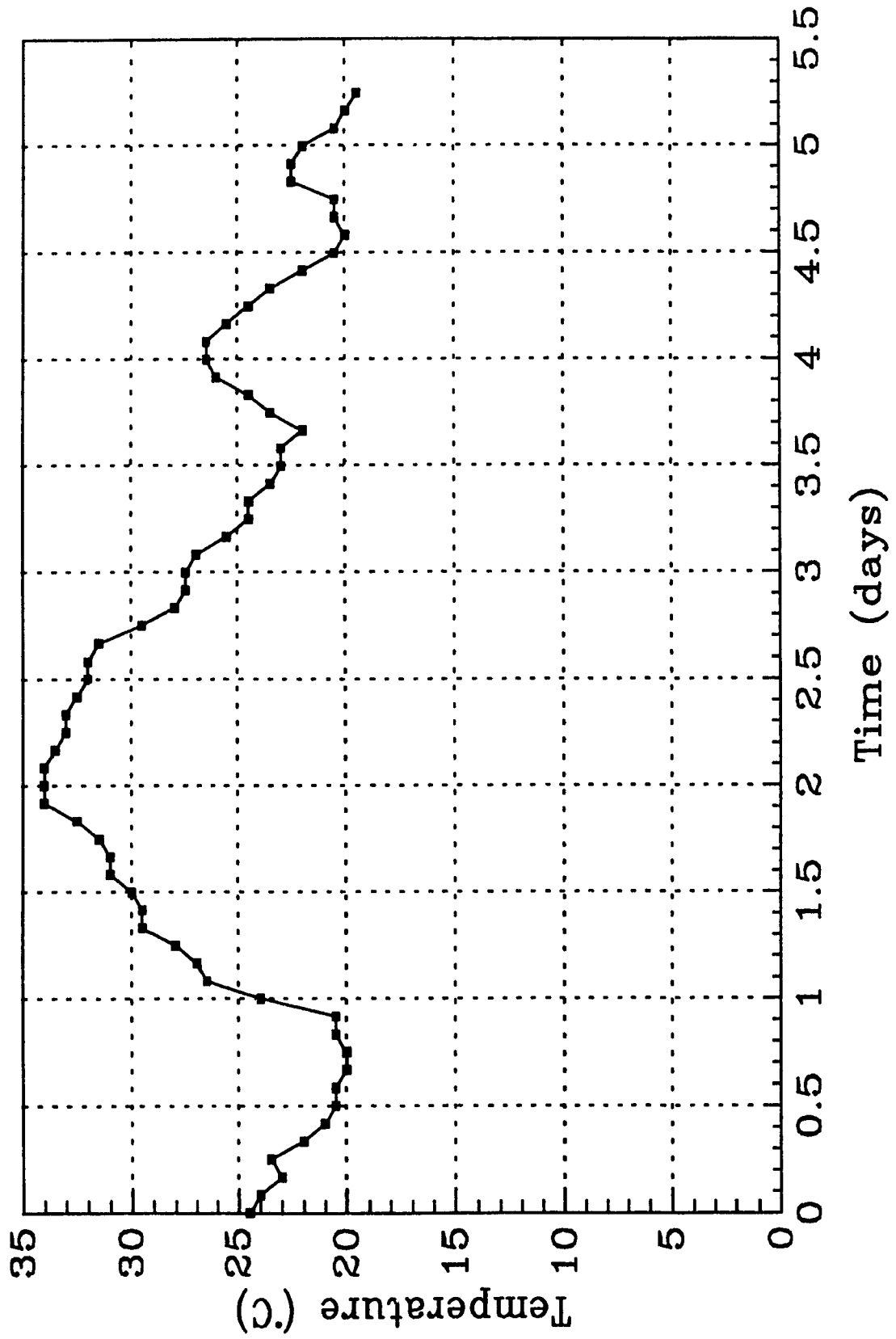


Figure 52: Temperature Profile During the Bake-Out of the Residential Building in Investigation I

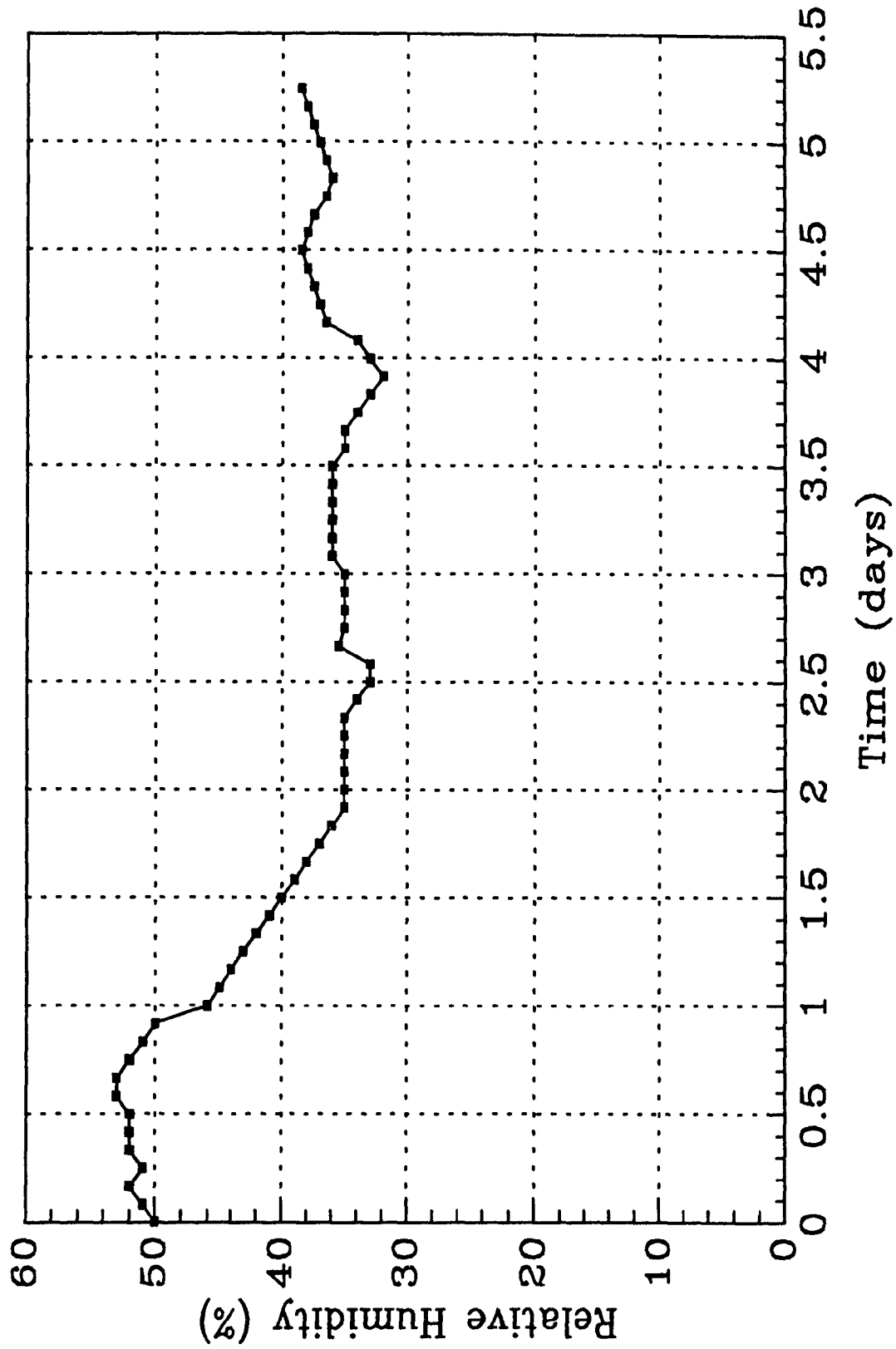


Figure 53: Relative Humidity Profile During the Bake-Out of the Residential Building in Investigation 1

7.2.2 Investigation 2

The objective of this second bake-out investigation was to evaluate the effectiveness of the procedure by comparing the reduction in VOC concentrations when one of two similar buildings underwent a bake-out.

The two houses investigated were newly built, and their construction was completed at approximately the same time. The two houses were located in Laval, Quebec, approximately two blocks from one another.

The first house, called the Future House, was built under the requirements of the Advanced Houses Program. It is a home designed to consume 50% less energy than an R-2000 house. To achieve this end, an innovative wall assembly was used, providing an R-31 value. Further, the house contains a complete home automation system, pollutant metabolizing plants, high quality natural lighting, and other innovative technologies. In addition, to optimize indoor air quality, the house does not include a basement but a third floor mezzanine. Basements are often associated with humidity problems and soil gas infiltration (radon). Its floor plans are depicted in Figure 54.

The second house, called the Ordinary House, was built under the stipulations of the 1990 National Building Code (Canada). Compared to the Future House, the Ordinary House is rather "typical" in that it does not contain the innovative commodities of the Future House. Some construction and interior details include: glued PVC flooring, plush carpeting with foam underlay (not glued), painted gypsum board walls, melamine cupboards, a varnished wooden staircase, exposed concrete in basement, extruded polystyrene insulation, mineral (glass fibre insulation), wood frame construction, and

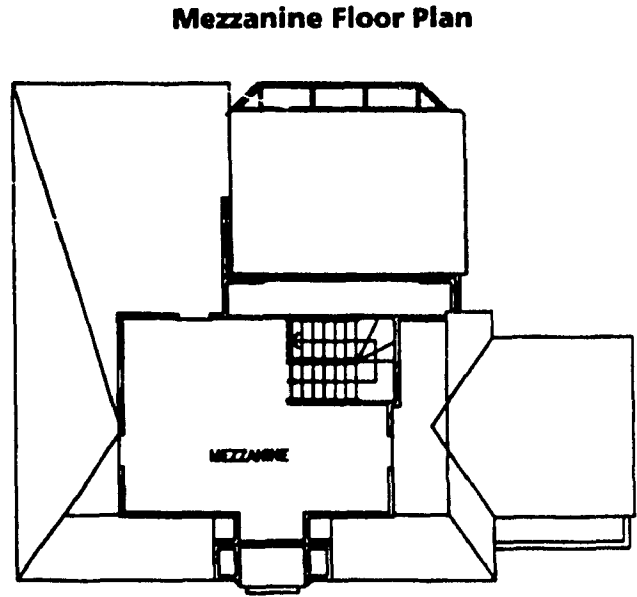
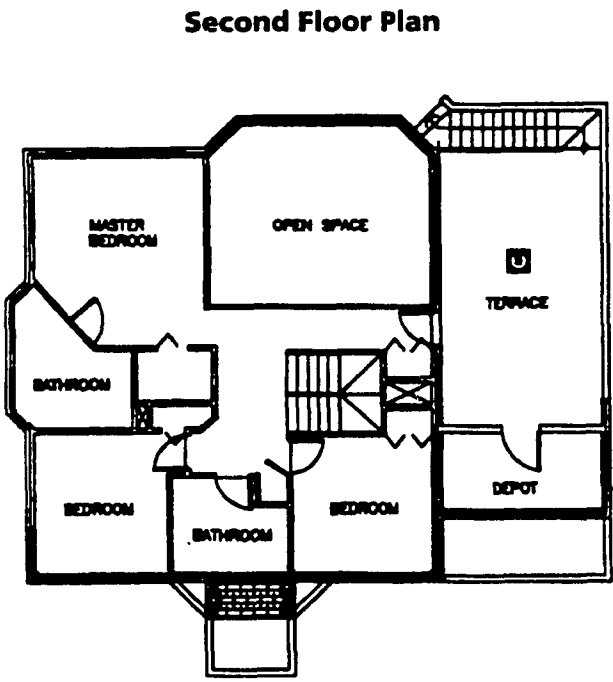
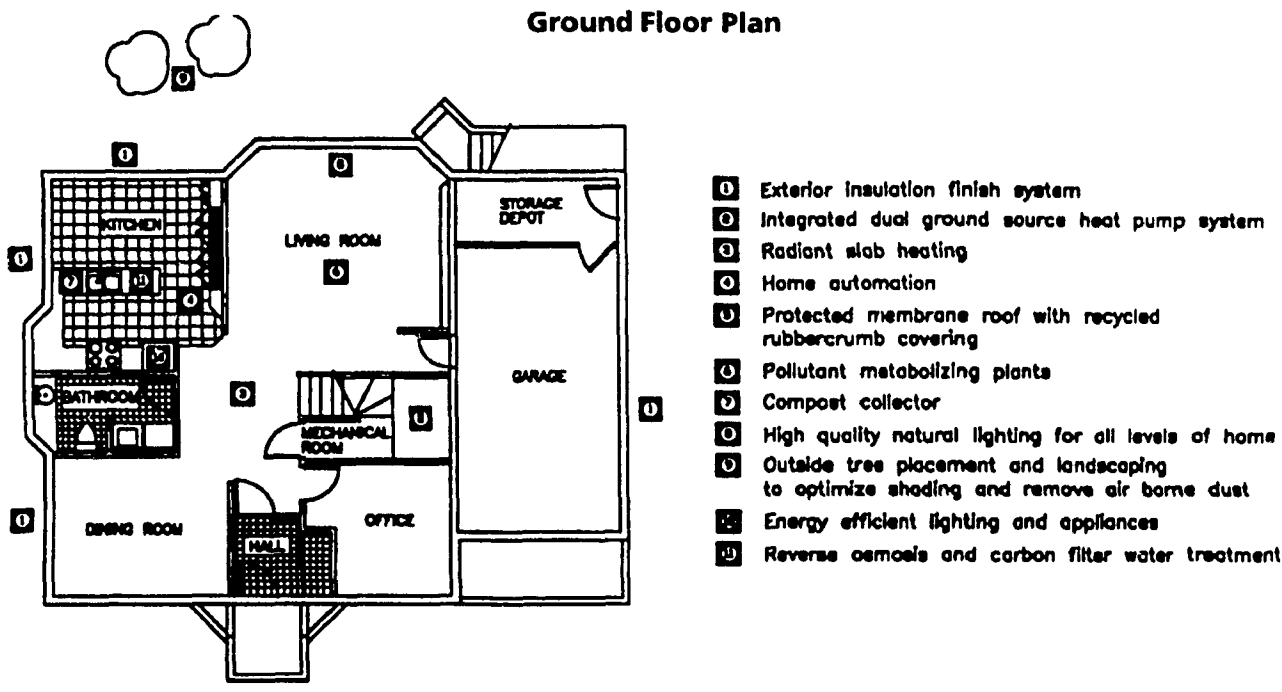


Figure 54: Floor Plan of the Future House

bricks on the exterior.

It was decided to bake-out the Ordinary House and compare the reductions in VOC levels with that of the Future House over the same period of time, approximately three months.

The VOC concentrations measured in two locations of the Future House, at the start and end of the study period are summarized in Table 6.

The measurements of the air exchange rates and the VOC concentrations were made at the Ordinary House simultaneously with those of the Future House. The bake-out of the Ordinary House was performed approximately midway through the study period. The air exchange rates measured in the Ordinary House at the start of the study period, during the bake-out, and at the end of the study period were 0.295, 0.389, and 0.302 ach respectively. Again, these values represent the air exchange measured at that point in time; they are not long term values.

The measured air exchange rates in the atrium of the Future House at the start and end of the study period were 0.0185 and 0.0117 ach, respectively. The ventilation system was not in operation when these measurements were taken. As in Investigation 1, the air exchanges were measured using the tracer gas technique.

The bake-out began on a Wednesday morning and ended the following Saturday morning. In addition to the electrical baseboard heaters in the house, five portable heaters, throughout the house were installed. This allowed the temperature, as shown in Figure 55, to rise to above 32 °C for more than 42 hours of the bake-out (maximum temperature was 35 °C for 6 hours). Figure 56 depicts the relative humidity profile. Air circulation was

Table 6: VOC Concentrations at the Start and End of the Study Period in the Future and Ordinary Houses

VOC	Future House				Ordinary House				
	Living Room	Master Bedroom	Living Room	Bedroom	Living Room	Master Bedroom	Living Room	Bedroom	
	Start of Study Period $\mu\text{g}/\text{m}^3$	End of Study Period $\mu\text{g}/\text{m}^3$	Percent Reduction %	Start of Study Period $\mu\text{g}/\text{m}^3$	End of Study Period $\mu\text{g}/\text{m}^3$	Percent Reduction %	Start of Study Period $\mu\text{g}/\text{m}^3$	End of Study Period $\mu\text{g}/\text{m}^3$	Percent Reduction %
Total Hydrocarbons	N/A	N/A	*	N/A	N/A	*	N/A	N/A	*
Total Aromatics	N/A	N/A	*	N/A	N/A	*	N/A	N/A	*
Benzene	64.81	16.35	74.77	69.44	14.21	79.54	6.18	2.04	66.99
Toluene	3.70	3.67	0.81	3.70	3.01	18.65	2.57	2.45	4.67
Ethylbenzene	74.07	12.69	82.87	76.39	10.93	85.69	3.71	1.45	60.92
m,p-Xylenes	2546.3	129.7	94.91	2546.3	112.0	95.60	86.57	30.64	64.61
Styrene	118.1	13.82	88.29	122.7	6.29	94.87	10.51	1.53	85.44
o-Xylene	62.5	5.36	91.42	64.81	5.19	91.99	24.12	7.35	69.53
Heptane	138.9	12.41	91.06	143.5	10.66	92.57	52.56	15.93	69.69
Octane	254.6	8.74	96.57	277.8	7.11	97.44	43.28	14.5	42.94
Nonane	1041.7	0.56	99.95	1064.8	0.55	99.95	0.62	0.41	33.87
Cumene	12.73	0.85	93.32	13.43	0.79	94.12	3.40	0.41	87.94
Propylbenzene	717.6	15.51	97.84	740.7	0.55	99.93	52.56	4.90	90.68
Methane	0.69	0.85	-23.19	0.69	0.82	-18.84	102.03	0.61	99.40
n-Decane	671.3	6.20	99.08	694.4	18.86	97.28	120.58	10.83	91.02
p-Butylbenzene	0.46	4.51	-880.4	0.46	4.37	-850.0	0.62	4.08	-558.06
Undecane	1412.0	16.92	98.80	1435.2	13.94	99.03	207.2	5.51	97.34
Dodecane	0.69	0.85	-23.19	0.69	0.82	-18.84	213.3	2.86	98.66
p-Cumene	284.7	10.71	96.24	277.78	6.01	97.84	10.19	5.11	87.29

N/A Measurement not available

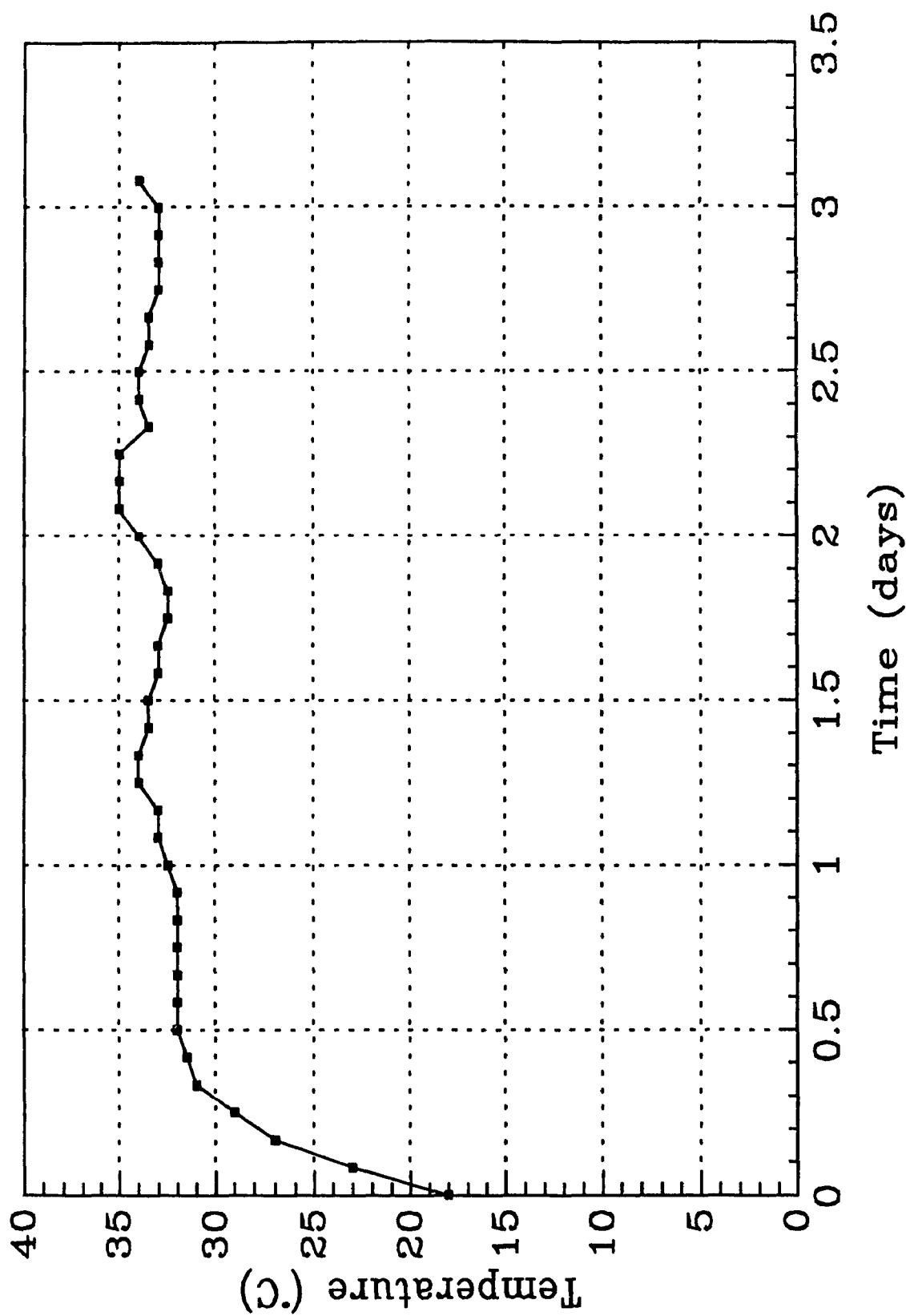


Figure 55: Temperature Profile During the Bake-Out of the Ordinary House in Investigation 2

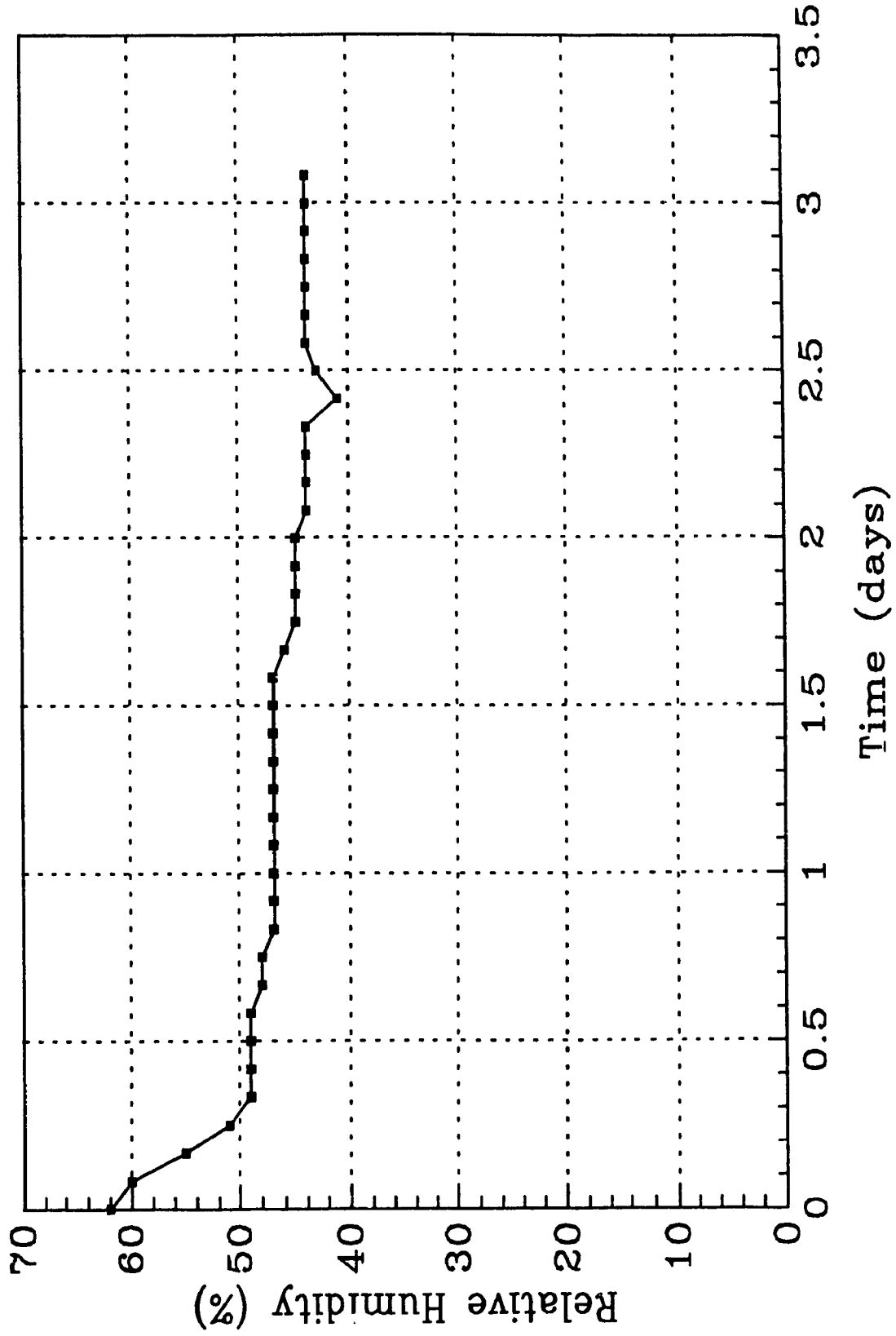


Figure 56: Relative Humidity Profile During the Bake-Out of the Ordinary House in Investigation 2

achieved by leaving windows opened ajar by 1 cm, installing two portable floor fans and turning on the exhaust fans in the kitchen and upper and lower floor bathrooms. Temperature and relative humidity measurements were taken throughout the bake-out procedure using a seven day recorder. Table 6 shows the VOC concentrations before and after the bake-out.

7.3 Results

7.3.1 Investigation 1

The results of this investigation were promising. The concentrations decreased for most of the VOCs in both the office and residential buildings. Overall, the reductions were more pronounced in the office building. However, compared to the residential building, more time (27 days) had elapsed between the end of the bake-out and the time of the post bake-out measurements of the VOC concentrations. Thus, the reductions can be due in part to the regular aging of the products.

The formaldehyde concentration measured in the residential building soon after the bake-out showed an increase of almost 100%. Girman et al [91] observed similar behaviour in their study. The formaldehyde levels increased during the bake-out but, soon after the completion of the bake-out, decreased to their original values. Thus, there was no overall reduction in the concentration of formaldehyde. One explanation for this discrepancy is that high temperatures can increase the hydrolysis of resins containing formaldehyde [91]. The resins will release formaldehyde, increasing its concentration within the material. However, these concentrations will not be close enough to the outer

surface of the material to be swept away. From this experiment, it appears that the building bake-out causes a significant reduction in the emission rates of VOCs. Referring to Table 5, it can be seen that the reductions in VOC concentrations for the residential building range from -332.9% (increase) to as high as 97.12%.

It is believed that the reductions in the living room could have been higher. Unfortunately, the installation of the linoleum flooring in the bathroom and the caulking around the kitchen counter was done on the day between the completion of the bake-out and the post bake-out measurements. This may also explain the increases occurring in the results for ethylbenzene and octane.

7.3.2 Investigation 2

Over the same period of time, the VOC concentrations in both the Future House and the Ordinary House decreased. However, with the exception of a handful of contaminants, the reductions were more pronounced in the Future House, not subjected to the bake-out, than they were in the Ordinary House that was baked-out.

It is important to note that the Future House was built as airtight as possible with a fully automated ventilation system for fresh air. This system will have certainly aided in the flushing out of any unpleasant air constituents. While this illustrates the importance of a well ventilated house, up to the present the majority of new houses built still depend on natural ventilation. In addition, existing naturally ventilated buildings require a means of flushing out high levels of contaminants soon after renovations.

While the bake-out of the Ordinary House did not reduce most VOC levels to as

low as those in the Future House, reductions still occurred.

The results obtained by Hicks et al [93], prove that the success of a bake-out is not guaranteed. In their study, it was observed that the concentrations for the majority of the VOCs increased after the bake-out of a hospital. Also, Offerman et al [97], observed that the bake-out caused only temporary reductions in the contaminant emission rates.

7.4 Comparison to Experimental Temperature Results

The results of the bake-out are very promising, and indicate that this process is an effective procedure in reducing indoor air contaminants in newly built or renovated buildings; the effectiveness can be as high as 97%.

The results of the second experiment, comparing the impact of proper ventilation versus the bake-out procedure in reducing indoor air contaminants in these buildings showed that the proper ventilation of a building could be as effective a technique as the bake-out process.

However, the results of this study cannot be generalized, and a more detailed comparison of these two strategies is required. This is supported by the results obtained in Chapter V for the temperature tests. In an office or house, there are many sources of VOCs. From the tests performed in this research we can see how different each material reacted to temperature increases. The overall TVOC concentrations for varnish support the theory of the bake-out. However, the TVOC of the paint sample shows faster depletion at lower temperatures. If we examine the results on a compound to compound basis, we see further differing reactions. Though an exponential decrease in the emissions

of most compounds occurred, variations were present. Some compounds, such as m,p-xylene for paint, show increases in emissions, though not as significant as its initial peak, later in the test. Other compounds, such as toluene for varnish, appear to deplete faster at room temperature. In which case, increased ventilation would assist this process tremendously.

Further, the results of the emissions tests conducted in the laboratory do not consider the presence of sink effects. As a stainless steel substrate and chamber were used, such effects were considerably minimized and, therefore, negligible compared to the tremendous possibility existing in a house or office. This lends to the possibility that the compounds are not fully depleted to the outdoors, as in the chamber tests, but can be easily reabsorbed by other components in a room.

CHAPTER VIII

CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions: Temperature Results

Knowing how environmental variables effect emissions of a given product can help predict in situ emissions. This is especially of importance during the pre-occupancy period of a newly built or renovated building. The results of this study show that both the temperature and relative humidity have a significant effect on the emissions from paint and varnish. We see that as the temperature increased, the TVOC concentrations and emission rates increased for both the paint and varnish. From Chapter 2, studies such as those conducted by the ASHRAE research subcommittee [60], the EPA [62], and the European Collaborative Action [61], note the same conclusions for other materials. Further, the results are consistent with the trends expected when implementing the Double Exponential Model presented in Chapter 3. However in this study, the individual compounds did not necessarily follow the same trend established for the TVOC. Some compounds show secondary, less significant peaks later in their emission profiles; while other compounds show greater concentrations at the lower temperatures. These profiles contradict expected trends. From the profiles shown in Chapter 5, the individual compounds present in greater concentrations follow the TVOC profile more closely. This indicates that the TVOC profile is influenced by the compounds found in greater abundance in the sample. This demonstrates the possibility that the TVOC value may not be a good indicator for indoor air quality. A product may contain a small quantity of a

compound which is a known irritant. The TVOC profile may indicate that emissions are near zero values after 24 hours. However, this may not be the case for the known irritant. It will, therefore, be necessary to identify the compounds in a given sample and to recognise those compounds which are known irritants. The emission profiles for these compounds should be determined independently of the TVOC values. In this way, immediately following the application or installation of a product, better judgement can be used when determining the time required before occupancy can take place.

Sollinger et al [59] noted that volatile compounds were not strongly influenced by temperature variations. The results here do not support this conclusion.

As mentioned earlier, to date most models developed to predict material emissions are based on TVOC values. The results here show that these models should take into account individual compounds also. Further, some models may not take into account varying environmental conditions. The possibility that some materials are used or installed under different conditions should warrant the development of models which can accommodate changing environmental parameters.

8.2 Conclusions: Relative Humidity Results

The effect of the relative humidity on the emissions from the paint samples was very interesting. The fluctuations were quite significant, and no trend can be established. The concentrations measured for the 32% test approached the values reached during the 35 °C test. While at the same temperature, the 3% and 62% tests, showed lower concentrations. This demonstrates how sensitive the emissions are to the environmental

conditions under which these materials are used.

The results for the varnish TVOC are more consistent with expected trends. The results found here are consistent with the conclusions drawn by the ASHRAE research subcommittee [60]. The effects of relative humidity could not be summarized into a general trend for the emissions from different materials. This is shown by the very different TVOC profiles established for paint and varnish. The two materials behave in very different ways. Tucker [22] noted that highly polar compounds required testing for relative humidity effects. This may be true of the water-based paint. However, the varnish, though following smoother trends, still showed varied effects. Its TVOC increased with increasing humidity, but some of its individual compounds showed higher concentrations for the 32% test.

8.3 Conclusions: Bake-Out Results

The bake-out results show decreased VOC concentrations for most compounds following the procedure. There were several compounds that increased, such as formaldehyde. These results are consistent with the results found by other researchers. However, the results for the second investigation cannot be ignored. It showed that with adequate ventilation, the VOC levels can diminish naturally with the passage of time. In Chapter 5, the concentration profiles for paint at different air exchanges was shown. Though initial concentrations were higher, at the higher exchange rate, depletion occurred faster. However, in a typical house, natural ventilation is usually depended upon. Depending on the air-tightness of the building envelope, the air exchange rates may not

be too high to encourage the flushing of the VOCs from the building. The bake-out may be more useful under such a situation. However, for office and institutional buildings, where mechanical ventilation systems are present, the passage of time can be just as effective as the bake-out procedure with less expense.

8.4 Recommendations

Temperature and Relative Humidity Tests

1. Given the trend set by the TVOC curves, existing models are adequate. The TVOC emission rate and concentration curves with respect to time can be used to validate these models.
2. Other models, taking the temperature and humidity dependence of some compounds into consideration, are required to accurately predict emissions from these compounds.
3. While (2) may not be feasible for all VOCs, possibly more harmful compounds (formaldehyde) can be modelled individually. Also, the most predominant compounds found in materials, which are expected to be implemented under conditions other than typical room settings, should be modelled.
4. For materials as those described in (3), it may be worth establishing the most critical driving force behind the emissions of a particular compound, that is, temperature, relative humidity, surface velocity etc. The emissions from the compound can be modelled under the critical condition.

Bake-Out Procedure

From the results obtained in this study, substantial benefits from the bake-out are not truly realized. The bake-out procedure may not be worth the time, expense and effort due to the following reasons:

- (1) While reductions in VOCs occurred in the bake-out buildings, VOCs were also reduced in the Future House, showing the benefits of adequate ventilation.
- (2) The delicate balance between the amount of heat and ventilation required for a successful bake-out is crucial to prevent sink effects. This may be difficult to ensure.
- (3) The bake-out may not be feasible in the construction of new buildings due to normally tight schedules.

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