LBL-35334
UC-600

VOLATILE ORGANIC CHEMICAL EMISSIONS FROM CARPET CUSHIONS: SCREENING MEASUREMENTS

FINAL REPORT

Interagency Agreement CPSC-IAG-92-1134

Prepared for:

Directorate for Health Sciences
U.S. Consumer Product Safety Commission
Washington, D.C. 20207

Submitted by:

Alfred T. Hodgson and Thu A. Phan
Indoor Environment Program
Energy and Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

May 1994

This project was funded with Federal funds from the U.S. Consumer Product Safety Commission and the Office of Atmospheric and Indoor Air Programs of the U.S. Environmental Protection Agency under interagency agreements, CPSC-IAG-92-1134 and CPSC-IAG-92-1120, as well as the Assistant Secretary for Conservation and Renewable Energy, Office of Building Technologies, Building Systems and Materials Division of the U.S. Department of Energy under Contract DE-AC03-76SF00098.

DISCLAIMER

EXECUTIVE SUMMARY

The objective of this study was to screen samples of new carpet cushions for emissions of individual volatile organic compounds (VOCs), total VOCs (TVOC), formaldehyde, and isomers of toluene diisocyanate (TDI). The Consumer Product Safety Commission collected 17 samples that were representative of synthetic-fiber, rubberized-jute, sponge-rubber, bonded-urethane, and prime-polyurethane cushions. For each cushion type, at least one sample was obtained from a dealer; the other samples were collected directly from production facilities. The samples were packaged in heat-sealed Tedlar bags and shipped to the laboratory by air freight. Measurements of the emissions of VOCs, TVOC and formaldehyde from these samples were made over six-hour periods in small-volume (4-L) dynamic chambers. Sensitive gas chromatography-mass spectrometry (GC-MS) techniques were used to identify many of the VOCs emitted by the cushion samples and to obtain quantitative estimates of the emission rates of selected compounds. The two types of polyurethane cushions were separately screened for emissions of TDI in glass 3-L dynamic chambers using a highly sensitive sampling and analytical method that was developed as part of this study.

The quasi steady-state emission rates of TVOC from the 17 cushion samples at six-hours elapsed time ranged from 188 - 7,720 $\mu g\ m^{-2}\ h^{-1}$. The synthetic-fiber, bonded-urethane, and prime-polyurethane cushions generally had the lowest TVOC emission rates; however, one bonded-urethane cushion had the highest measured value. For each type of cushion, the dealer-supplied sample(s) had the lowest TVOC emission rate(s) probably due to the loss of compounds from the bulk materials with time following production. Due to the overlayment of carpet, the TVOC emission rates from cushions installed in residences and other buildings are expected to be lower than those measured in the laboratory.

The chemical classes of VOCs and the identities of the individual compounds emitted by the different types of cushions varied significantly. The synthetic-fiber cushions primarily emitted alkane hydrocarbons ranging in volatility from n-hexane through approximately n-heptadecane (C_{17}). The rubberized-jute cushions emitted a number of C_{10} - C_{17} alkane hydrocarbons, high molecular weight aromatic hydrocarbons including 4-phenylcyclohexene, terpene compounds, aldehydes, and a few other oxidized compounds including acetic acid. The sponge-rubber compounds emitted a large number of aromatic hydrocarbons, a variety of cyclic and unsaturated hydrocarbons, oxidized compounds, and several nitrogen-containing solvents. One of the bonded-urethane cushions emitted many aromatic hydrocarbons which were not predominant in the emissions from the other cushions of this type. These other cushions, however, all emitted a

complex mixture of unsaturated hydrocarbons consisting primarily of C_{11} - C_{15} alkyldienes. The emissions from the bonded-urethane cushions also contained carbonyl compounds, some oxidized compounds, and several nitrogen-containing compounds. All of the bonded-urethane, as well as the prime-polyurethane cushions emitted, appreciable quantities of butylated hydroxytoluene. The emissions from the prime-polyurethane cushions were not as complex. In addition to butylated hydroxytoluene, these emissions were generally dominated by chlorinated compounds, nitrogen-containing compounds, and siloxanes.

The compounds emitted by the five different types of cushions were related to the different manufacturing processes. The sources of the VOCs emitted by the cushions may include machine oils, complex oils purposefully added to the products, solvents, chemical intermediates, contaminants or degradation products, and additives.

Forty-nine individual compounds were quantified. The emissions from the prime-polyurethane cushions were dominated by a few compounds with relatively high emission rates. For these cushions, the compounds with emission rates of approximately 100 $\mu g\ m^{-2}\ h^{-1}$, or more, were styrene, 1,1,1-trichloroethane, 1,3-dichloro-2-propanol, 1,2,3-trichloropropane, butylated hydroxytoluene, N,N-dimethylformamide, 1,4-dimethylpiperazine, and N,N-dimethylacrylamide. The bonded-urethane cushions had distinctly elevated emission rates of butylated hydroxytoluene. One bonded-urethane cushion had a high emission rate of N,N-dimethylacetamide.

The sums of the emission rates of the individual compounds were compared to their respective TVOC emission rates. Complete quantitative analyses of the emissions of VOCs were not practical or possible for most cushion samples. For the thirteen synthetic-fiber, rubberized-jute, sponge-rubber, and bonded-urethane cushions, only about 13 percent of the emissions of TVOC was typically accounted for by the quantitative analysis of individual compounds. A different problem was encountered with the prime-polyurethane cushions for which the sums of the emission rates for the individual compounds typically exceeded the TVOC emission rates. This was due to the relatively low responses of the oxygen- and nitrogen-containing compounds emitted by these cushions relative to the responses of the alkane and aromatic hydrocarbons used to calibrate the TVOC method.

Only one prime-polyurethane cushion was found to emit TDI. The rate was extremely low ($0.07\ \mu g\ m^{-2}\ h^{-1}$), and the occurrence was not confirmed when a duplicate cushion sample was screened. As expected, carpet cushions were not significant sources of formaldehyde emissions.

ACKNOWLEDGMENTS

This project was funded with Federal funds from the U.S. Consumer Product Safety Commission and the Office of Atmospheric and Indoor Air Programs of the U.S. Environmental Protection Agency under interagency agreements, CPSC-IAG-92-1134 and CPSC-IAG-92-1120, as well as the Assistant Secretary for Conservation and Renewable Energy, Office of Building Technologies, Building Systems and Materials Division of the U.S. Department of Energy under Contract DE-AC03-76SF00098.

DISCLAIMER

The content of this publication does not necessarily reflect the views of the U.S. Consumer Product Safety Commission or the U.S. Environmental Protection Agency, nor does mention of trade names, commercial products, or organizations imply endorsement or sanction by these agencies.

INTRODUCTION

Background

The U.S. Consumer Product Safety Commission (CPSC) has received complaints from consumers regarding the occurrence of adverse health effects following the installation of new carpeting (Schachter, 1990). Carpet systems are suspected of emitting chemicals which may be the cause of these complaints, as well as objectionable odors. Carpets themselves have been shown to emit a variety of volatile organic compounds (VOCs). A study performed by Lawrence Berkeley Laboratory (LBL) identified and quantified selected individual VOCs emitted by samples of four new carpets installed in a room-size environmental chamber (Hodgson *et al.*, 1992 and 1993b). Carpet cushions and adhesives are the other components of carpet systems that have the potential to emit VOCs.

Almost no data are available on the identity or the amounts of VOCs emitted by carpet cushions. This lack of data prompted the CPSC and the U.S. Environmental Protection Agency to conduct an investigation of the emissions of VOCs from representative samples of carpet cushions. There are five types of carpet cushions available to consumers. The five types and their approximate market shares are: bonded urethane, 56 percent; prime polyurethane, 33 percent; sponge rubber, six percent; synthetic fiber, three percent; and rubberized jute, two percent. Because of the different manufacturing process, the types of cushions are expected to vary significantly with respect to the identities and amounts of VOCs that are emitted. Samples of 17 different cushions were collected by CPSC field staff in different regions of the U.S. There were four samples each of bonded urethane and prime polyurethane cushions and three samples each of the other three types of cushions. At least one sample of each type was collected from a dealer who was either a wholesaler, retailer or installer. The other samples were collected directly from manufacturers' production facilities.

Objective

The objective of this study was to screen the representative samples of carpet cushions for emissions of individual VOCs, total VOCs (TVOC), formaldehyde, and, for the two types of polyurethane cushions, isomers of toluene diisocyanate (TDI). The measurements of VOCs, TVOC and formaldehyde were made over six-hour periods using small-volume (4-L) dynamic chambers. Sensitive gas chromatography-mass spectrometry (GC-MS) techniques were used to identify many of the VOCs emitted by the cushion samples and to obtain quantitative estimates of

the emission rates of selected compounds. Separate screening measurements were conducted for TDI. The data from the screening measurements were used by the CPSC's Health Sciences Laboratory to help design and conduct week-long measurements of emission rates of selected compounds using 52-L environmental chambers. The data will also used by the CPSC to support a hazard evalution of carpet system materials.

EXPERIMENTAL

Carpet Cushion Samples

The CPSC selected the samples of carpet cushions for the study. Seventeen samples representative of the five types of cushions were collected by CPSC field staff. The samples are listed in Table 1. There were three synthetic-fiber cushions, three rubberized-jute (or jute and hair) cushions, three sponge-rubber cushions, four bonded-urethane cushions, and four prime-urethane cushions. For each cushion type, at least one sample was obtained from a dealer who was either a wholesaler, retailer or installer. The other samples were collected directly from the manufacturers' production facilities.

Immediately following collection, the samples were shipped by overnight air freight to LBL. Each sample received at LBL consisted of nine 30 x 30 cm pieces of cushion packaged in a heat-sealed Tedlar bag. The samples were stored at room conditions in a non-chemistry laboratory prior to screening.

Screening Measurements for VOCs, TVOC, and Formaldehyde

The screening measurements were conducted within 1 - 12 days (median = 4 days) of receipt of a cushion sample (Table 1).

A sample of headspace gas for the analysis of individual VOCs was withdrawn from the Tedlar bag. This was accomplished by attaching a fitting with a syringe needle onto the inlet of a multisorbent sampler (described below). The needle was inserted through the bag into the air space surrounding the cushion, and 200 cm^3 of gas was drawn through the sampler. This sample was used to obtain preliminary data on the composition and concentrations of the VOC emissions. The results of the headspace measurements are not presented in this report.

The cushion samples were then screened for emissions of individual VOCs, TVOC, and formaldehyde using small-volume dynamic chambers (Hodgson and Girman, 1989; Hodgson *et al.*, 1992). These chambers consisted of clean, 1-gal (3.78-L), plated-metal paint cans with lids equipped with two fittings. Dry, clean, nitrogen supplied by a gas cylinder was introduced into a chamber near the bottom through one fitting with a tubing extension. The flow rate of 400 cm^3 min^{-1} was regulated with a needle valve and measured with a mass flowmeter. Gas exited and was sampled at the other fitting. The chamber was maintained at 23° C in an incubator. The parameters for the screening measurements are summarized in Table 2.

A 10 x 10 cm (100 cm^2 or 0.01 m^2) piece was cut from one of the 30 x 30 cm sections of cushion. The piece was weighed and placed into a stainless-steel holder which covered the bottom and cut edges of the cushion. Samples with laminating films or fiber scrims were placed so that the film or scrim was exposed. The chamber was turned on its side, and the holder with the sample was positioned in the chamber midway between the ends with the exposed cushion surface facing upwards. The chamber was then sealed and ventilated. Sealing of the chamber established the initial time for the measurements. Single samples for the analysis of individual VOCs and TVOC were collected at average times of one, three, and six hours after closing the chamber. Samples for formaldehyde were collected from the same chamber over elapsed time intervals of 0-3 and 3-6 hours. The typical sampling rates and sample volumes are given in Table 2.

One screening measurement without a sample present in the chamber was conducted as a blank for each type of cushion. In addition, duplicate measurements were conducted for one of each type of cushion.

Screening Measurements for TDI

The samples of bonded-urethane and prime-polyurethane cushions were screened for emissions of TDI isomers using two methods. The methods utilized different sampling and analytical techniques, but were otherwise similar (Table 2). Both methods employed an all-glass 3-L reaction vessel as the chamber. It was silanized with dichlorodimethylsilane to reduce wall loses of TDI. The chamber was maintained at 23° C in an incubator. A 30 x 23 cm (0.07 m^2) piece of cushion was cut from one of the 30 x 30 cm sections. The piece was inserted into the chamber so that it wrapped around and covered most of the glass wall.

Samples with laminating films or fiber scrims were placed so that the film or scrim was exposed.

For the method using the colorimetric paper-tape sampling media, the chamber was supplied with untreated room air at a flow rate of about 240 cm^3 min^{-1}. The room air, which was free of TDI, provided the humidity which is necessary for the color response to TDI to develop (see below). This air was pulled through the chamber and the flow rate was regulated with an electronic mass-flow controller and pump located downstream of the chamber. All of the air exiting the chamber passed through a filter holder (Part No. 800-300, GMD Systems, Inc., Hendersonville, PA) attached directly to the outlet fitting. The holder contained a TDI test card with the cardboard removed from both sides (Part No. 800-010, GMD Systems, Inc.). This sampling was conducted over a period of about seven hours giving a sample volume of about 100 L.

For the method using the treated-filter sampling media, the chamber was supplied with dry nitrogen from a gas cylinder (Table 2). The inlet flow rate of 300 cm^3 min^{-1} was regulated with an electronic mass-flow controller. All of the air exiting the chamber passed through a glass and stainless-steel filter holder specially constructed to minimize sample losses and contamination (Hodgson *et al.*, 1993a). The filter holder was connected directly to the outlet of the chamber to minimize the exposed surface area. The holder contained a 25-mm diameter borosilicate glass-fiber filter impregnated with the derivatizing reagent for TDI. Samples for TDI were collected over elapsed time intervals of 0 - 3, 3 - 6, and, for some cushions, 21.5 - 25.5 hours. Sample volumes were 54 L.

Recovery efficiencies of TDI from the silanzed chamber ventilated with dry nitrogen were determined by introducing mixed isomers of TDI from a calibrated permeation source to produce known concentrations (Hodgson *et al.*, 1993a). Samples were collected at the chamber outlet using the treated-filter method. After 24 air exchanges (four hours), the concentrations of the 2,4- and 2,6-TDI isomers were 44 and 51 percent of their predicted values. Thus, approximately half of the TDI was lost in the chamber either due to sorption onto the glass surfaces of the apparatus and/or to chemical reactions.

Several screening measurements without samples present in the chamber were conducted as blanks for both TDI methods. Duplicate measurements were conducted for one polyurethane cushion of each type with the paper-tape collection method, and triplicate measurements were conducted for one cushion of each type with the treated-filter method.

Chemical Analyses

VOCs and TVOC

Gas samples for the analysis of selected VOCs and TVOC were collected on multisorbent samplers (Part No. ST032, Envirochem, Inc., Kemblesville, PA) which are packed with glass beads at the inlet followed by Tenax-TA, Ambersorb XE-340 and activated charcoal, in series. The analytical procedures for VOCs collected on multisorbent samplers have previously been described (Hodgson and Girman, 1989). In brief, a sample is thermally desorbed from a sampler with a UNACON 810A (Envirochem, Inc.) inletting system. This instrument passes the sample through dual sequential traps to concentrate the sample. The sample components are introduced into a capillary gas chromatograph (GC) equipped with liquid nitrogen sub-ambient cooling. The GC is connected via a direct capillary interface to an electron impact quadrupole mass spectrometer (MS). The MS was operated to scan a mass range of *m/z* 33-300. The specifications and operating conditions for this analytical system are given in Table 3.

An internal standard consisting of 80 ng of 1-bromo-4-fluorobenzene was added to all samplers, including standards, immediately prior to their analysis. The internal standard was generated by a gravimetrically-calibrated diffusion source and transferred with a gas-tight syringe.

Compounds were identified by comparing the unknown spectra with spectra contained in the EPA/NIH Mass Spectral Data Base (Heller and Milne, 1978). Whenever possible, these identifications were confirmed by analyzing authentic standards of the compounds under identical conditions.

Standards used to confirm compound identifications and for calibrations were usually obtained from Aldrich Chemical Company (Milwaukee, WI). The standard for 4-phenylcyclohexene was produced by Wiley Organics (Columbus, OH).

Compounds for quantitative analysis were selected based on their relative abundance, their potential health effects and the availability of standards. For quantitative analysis, abundant and characteristic mass ions for the compounds of interest were extracted from the total-ion-current (TIC) chromatograms and integrated. The lower limit of quantitation for individual VOCs with the 3-L sample volume was typically 0.7 $\mu g\ m^{-3}$.

For compounds with high to intermediate volatility, a standard gas mixture was prepared by injecting a several microliter aliquot of a liquid mixture of the compounds into a 2-L flask with septum cap which was then heated and maintained at 65° C (Riggin, 1984). A sample was withdrawn from the flask with a gas-tight syringe and injected into a helium gas stream flowing through a conditioned sampler. Multi-point internal-standard calibrations were prepared by analyzing a range of volumes of the gas mixture.

For compounds with relatively low vapor pressures at room temperature, dilute standards were prepared in a low-boiling solvent such as methanol or n-hexane, and a microliter aliquot of the liquid standard was injected directly onto an all-Tenax sampler (Part No. ST023, Envirochem, Inc.). The sampler was purged with about 5 L of helium to remove much of the solvent and analyzed using the normal procedure. Multi-point internal-standard calibrations were prepared by analyzing serial dilutions of the liquid standard.

For the quantitative analysis of TVOC in a sample, the TIC chromatogram was integrated over a retention time interval of 16-54 min using integration parameters (threshold = 16.5, peak width = 0.4 min) that captured almost all of the chromatographic area. The integrated areas minus the area of the internal standard and any significant system contaminants were summed. The mass of the compounds represented by the sum was calculated relative to the known amount of the internal standard. This calculation used an average relative response determined for 13 common alkane and aromatic compounds. This relative response factor was 1.6 (*i.e.*, on average, the common hydrocarbons produced a per-unit mass TIC response that was 1.6 times the per-unit mass response of the internal standard). Because of the variation in the relative TIC response of different classes of compounds, the uncertainty in the method is estimated to be approximately ±40 percent (Wallace *et al.*, 1991).

Formaldehyde

Gas samples for the analysis of formaldehyde were collected on Sep-Pak cartridges impregnated with an acid solution of 2,4-dinitrophenyl hydrazine (DNPH silica cartridges, Part No. 37500, Millipore Corp.). Formaldehyde samples were analyzed using a high-performance liquid chromatograph (HPLC) equipped with a diode-array UV detector. Each cartridge was eluted with 2-ml acetonitrile. The extract was made up to volume in a 2-ml volumetric vial and diluted 1:1 with water. The compounds were separated on a microbore, reverse-phase C_{18} column (Nova-Pak, 2 x 150 mm, Part No. WAT023655, Millipore Corp.) using an isocratic solvent program with a

63:35 v/v mixture of water and acetonitrile as the mobile phase. The formaldehyde hydrazone derivative was detected at a wavelength of 365 nm. A multi-point external calibration was prepared on each day of analysis. The lower limit of quantitation for formaldehyde using a 45-L sample was approximately 4 μg m^{-3}.

TDI

When the colorimetric paper tape is exposed to TDI vapors, the test card changes color from white to pink. The intensity of the pink color stain that develops is directly proportional to the amount of TDI collected. This color change is irreversible. The mass of TDI collected is determined by visually comparing the color stain to a standard reference TDI concentration calculator (Part No. 800-300, GMD Systems, Inc.). The reaction that produces the color change requires humidity. The method has a lower limit of detection of about 100 ng of TDI, or 1 μg m^{-3} for a 100-L sample.

An improved treated-filter method for measuring trace concentrations of TDI in air was developed as part of this study (Hodgson *et al.*, 1993a). The method utilizes the derivatizing agent 1-(2-pyridyl)piperazine (1-2PP) coated onto glass-fiber filters. For analysis, an exposed filter was extracted by immersing it for 15 minutes in 2 mL of mobile phase consisting of a mixture of 35 percent acetonitrile and 65 percent 0.05 M aqueous ammonium acetate. The extract was filtered and analyzed by HPLC with fluorescence detection. Separations were achieved on a base-deactivated microbore column (2 x 150 mm) packed with BDS-Hypersil-C_{18} silica (Part No. 155-46-CPG, Keystone Scientific, Inc., Bellefonte, PA). See Hodgson *et al.* (1993a) for a detailed description of the instrumentation and operating parameters for this analysis.

Urea derivatives of the TDI isomers with 1-2PP were prepared and purified for use as standards. Standard solutions were made by dissolving weighed amounts of the urea derivatives in acetonitrile. The method has a lower limit of detection of about 3 ng of free TDI. Thus, the lower concentration limit for a 54-L sample is about 0.06 μg m^{-3}.

The recovery of TDI from vapor-spiked filters was evaluated during the development of the method (Hodgson *et al.*, 1993a). The estimated recoveries were 76 and 66 percent, respectively, for the 2,4-TDI and 2,6-TDI isomers. No corrections for recovery losses were made in calculating the concentrations or emission rates for this study.

Data Analysis

Source strengths, S ($\mu g\ h^{-1}$), were calculated for the quantified compounds and TVOC at each sampling interval using the following mass-balance equation which assumes steady-state conditions:

$$S = Q\ (C - C_o) \qquad (1)$$

where Q is the inlet gas flow rate ($m^3\ h^{-1}$); C is the chamber concentration ($\mu g\ m^{-3}$) for the sampling interval; and C_o is the chamber blank concentration ($\mu g\ m^{-3}$). These "quasi steady-state" source strengths were divided by the exposed surface area of the cushion sample ($0.01\ m^2$) to yield specific emission rates ($\mu g\ m^{-2}\ h^{-1}$). The steady-state assumption significantly underestimates the source strengths and emission rates if the chamber concentrations are declining rapidly. In general, only the emission rates for the final sampling interval (6 h for VOCs; 3-6 h for formaldehyde) are presented and discussed since these should be the most stable values for the six-hour test periods.

The total masses of TVOC that were emitted per square meter of cushion sample over 0-6 h were estimated from the chamber concentration data. The trapezoidal areas resulting from a linear interpolation of the TVOC concentrations at each sampling interval were integrated and summed starting with time zero when there were no emissions. The sums were multiplied by Q and divided by the surface area of the samples to yield specific mass emissions for the six-hour test period ($\mu g\ m^{-2}$). The mass emission values are subject to a number of potential errors and may be under- or overestimated depending upon the temporal profile of emissions. Also, the masses of any compounds sorbed onto the walls of the chamber will not be included.

RESULTS AND DISCUSSION

Emissions of TVOC

The total-ion-current chromatograms of the six-hour samples for each cushion are presented in Figures 1-17. Retention time intervals of 24-54 (or 59) min are shown since very volatile compounds which elute prior to 24 min were generally not present in any of these samples. The internal standard is identified in the chromatograms for reference. These are the chromatograms that were integrated to produce the measures of TVOC.

The specific emission rates of TVOC for the duplicate screening measurements conducted with one of each type of cushion are shown in Figure 18. This figure compares the emission rates at 1, 3, and 6 h for two simultaneously operated chambers. There was good agreement between the paired measurements for all five cushions. The largest discrepancy of ±13 percent of the mean value occurred at six hours with the rubberized-jute cushion. Generally, similar variations were observed for the individual VOCs that were quantified. These duplicate measurements demonstrated that the method has good reproducibility with respect to the chamber operating conditions, sample homogeneity, and the measurement of TVOC and individual compounds. It is also interesting to note that the calculated emission rates of TVOC did not change significantly over the six-hour periods for any of these three cushions.

The emission rate of TVOC for blank chambers averaged 69 $\mu g\ m^{-2}\ h^{-1}$ (n = 10, CV = 44 percent).

The specific emission rates of TVOC from the 17 cushion samples at six-hours elapsed time are compared in Figure 19. The three cushions with the highest emissions rates were: bonded-urethane cushion, BU2; rubberized-jute cushion, RJ1; and sponge-rubber cushion, SR1. The TVOC emission rates for these cushions were 7,720, 3,950, and 2,760 $\mu g\ m^{-2}\ h^{-1}$, respectively. All of these were supplied by manufacturers. The three cushions with the lowest TVOC emission rates were: synthetic-fiber cushion, SF1; prime-polyurethane cushion, PU4; and bonded-urethane cushion, BU4. All were supplied by dealers. Their respective TVOC emission rates were 188, 229, and 480 $\mu g\ m^{-2}\ h^{-1}$. Within each type of cushion, the dealer-supplied sample(s) had the lowest emission rate. This presumably reflects reductions in the amounts of VOCs in the bulk materials with time, due to emissions of these compounds during handling, shipping, and storage.

The estimated specific quantities of TVOC emitted show the same relationship among the 17 cushion samples as the specific emission rates (Figure 20). The manufacturer-supplied bonded-urethane cushion, BU2, emitted 44 mg m^{-2} over the six-hour period. The dealer-supplied prime-polyurethane, PU4, cushion emitted only about 1 mg m^{-2} over the same period.

Qualitative Analysis of VOCs

The individual VOCs emitted by each of the cushion samples in the chamber screening measurements are listed by cushion type in Tables 4-8. These are the compounds that were present in the six-hour samples. An identification was considered to be "confirmed" if its spectrum

and retention time matched those of the standard analyzed under identical conditions. An identification was considered to be "probable" if the unknown compound had a spectrum that closely matched a probable hit in the EPA/NIH Mass Spectral Data Base and a retention time that was realistic with respect to its volatility. Some compounds, such as branched-alkane hydrocarbons which have numerous isomers, were identified only to class level. In many cases, these class identifications were assigned a "probable" confidence level because of the distinctiveness of their spectra. Identifications which were less certain were considered to only be "tentative." Some unknowns were not identified; these are not indicated in the tables.

Table 4 lists the compounds emitted by the synthetic-fiber cushions. There were 46 compounds, eight with confirmed identities. The emissions consisted almost entirely of alkane hydrocarbons ranging in volatility from n-hexane through approximately n-heptadecane (C_{17}). Other detected compounds included methylcyclopentane, limonene, and several other hydrocarbons. There were no chlorinated, oxidized, or nitrogen-containing compounds. The emissions from the three cushions were very similar. However, the manufacturer-supplied cushions emitted more compounds than the dealer-supplied cushion.

Table 5 lists the compounds emitted by the rubberized-jute cushions. There were 70 compounds, 17 with confirmed identities. The emissions from manufacturer-supplied cushion RJ1 consisted predominantly of alkane hydrocarbons ranging in volatility from approximately n-decane through C_{17}. The manufacturer-supplied cushion, RJ2, emitted a number of terpene and sesquiterpene compounds, as well as aldehydes and other oxidized compounds. The dealer-supplied cushion, RJ3, was described as rubberized jute and hair. It primarily emitted aromatic hydrocarbons and higher molecular weight alkane hydrocarbons. All three cushions emitted 4-phenylcyclohexene (4-PCH) and acetic acid. There were also five commonly emitted alkane hydrocarbons.

The compounds detected in the emissions from the sponge-rubber cushions are listed in Table 6. There were 99 compounds, 35 with confirmed identities. Manufacturer-supplied cushion, SR1, had a distinctly different physical appearance than the other two rubber cushions. It emitted 76 of the 99 compounds. These emissions were dominated by a large number of aromatic and other hydrocarbons. The emissions from the other two sponge-rubber cushions were similar to each other. These emissions were primarily aromatic hydrocarbons, oxidized compounds, and nitrogen-containing compounds. Fourteen compounds were emitted by all three cushions. These commonly emitted compounds were n-decane, n-undecane, toluene, xylene

isomers, styrene, naphthalene, 4-PCH, benzaldehyde, 1-hexadecanol acetate, N,N-dimethylformamide, N,N-dimethylacetamide, hexamethylcyclotrisiloxane, and benzothiazole.

Table 7 lists the compounds emitted by the bonded-urethane cushions. There were 64 compounds, 24 with confirmed identities. Dealer-supplied cushion, BU1, emitted 37 of the 64 compounds. The majority of the individual compounds emitted by this cushion were aromatic hydrocarbons ranging in volatility from benzene through C11 alkyl-substituted benzenes. These aromatic hydrocarbons were generally not present in the emissions from the other bonded-urethane cushions. Two oxidized compounds were also unique to BU1. These were 2,2,4-trimethyl-1,3-pentanediol monisobutyrate and 2,2,4-trimethyl-1,3-pentanediol diisobutyrate. The other dealer-supplied sample, BU4, emitted 24 of the 64 compounds. Seven of these were carbonyl compounds, including cyclohexanone, benzaldehyde, 3,5,5-trimethyl-2-cyclohexen-1-one (isophorone) and linear aldehydes. Only two compounds were common to all four bonded-urethane cushions. These were 2,6-di-*tert*-butyl-4-methylphenol (butylated hydroxytoluene or BHT) and an oxidation product of BHT, 2,6-di-*tert*-butyl-2,5-cyclohexadiene-4-ethenyl-2-one. It is probable that this latter compound was an artifact produced by the thermal-desorption analysis of BHT. The emissions from cushions BU2, BU3, and to a lesser extent from BU4, were dominated by a complex mixture of unsaturated hydrocarbons consisting primarily of C_{11} - C_{15} alkyldienes and also containing tricyclodecanes, tricycloundecanes, and hydrogenated indenes and naphthalenes. Because there were so many co-eluting compounds, no attempt was made to further identify compounds within this mixture. The nitrogen-containing compound, 2,3-diethyl-2,3-dimethylbutanedinitrile (probable identification), was emitted by cushions BU1 and BU3.

Only 39 compounds were identified in the emissions from the prime-polyurethane cushions (Table 8). The identities of twenty-one of these were confirmed. Five compounds were common to the emissions of all four cushions. These were BHT and its probable artifact, 2,6-di-*tert*-butyl-2,5-cyclohexadiene-4-ethenyl-2-one, and three siloxane compounds. Dealer-supplied cushion, PU4, emitted the fewest compounds. The prime-polyurethane cushions were distinct from the other cushions in that they emitted more chlorinated and nitrogen-containing compounds. The chlorinated compounds were 1,1,1-trichloroethane, 1-chloro-2,3-epoxypropane (epichlorohydrin), 1,3-dichloro-2-propanol, 1,2,3-trichloropropane, 1,2-dichlorobenzene, and 1,3,5-trichlorobenzene. The nitrogen-containing compounds were N,N-dimethylformamide, 1,4-dimethylpiperazine, N,N-dimethylacetamide, N,N-dimethyl-2-propenamide (N,N-dimethylacrylamide), N,N-dimethylbenzene methanamine, a morpholine compound, and 2,3-diethyl-2,3-dimethyl-butanedinitrile. Unlike the bonded-urethane cushions, none of these cushions emitted significant numbers of unsaturated hydrocarbons.

Sources of VOCs

According to the Carpet Policy Dialogue (Leukroth, 1991), synthetic-fiber cushions are manufactured from waste fibers from the clothing and other textile industries. The fibers are mechanically separated and aligned and then fed into a needle punch loom where the product is punched and needled into itself. In some cases, a resin binder may be used. The emissions from the synthetic-fiber cushion samples were predominantly alkane hydrocarbons. n-Hexane and methylcyclopentane are common solvents. It is possible that many of the hydrocarbons emitted by these cushions derived from lubricants applied to the mechanical manufacturing equipment.

The two principal raw materials for rubberized-jute cushions are jute and latex rubber (Leukroth, 1991). Cattle hair may also be added. Jute is a fibrous plant grown in Bangladesh and Thailand. Jute plants and used burlap bags made from jute are imported for the manufacturing of these cushions. Like synthetic fibers, the jute is mechanically separated, aligned and needle punched. Then, filled styrene-butadiene rubber (SBR) latex is sprayed onto both sides of the product to act as a sealer. The large number of normal and branched alkane hydrocarbons may derive from lubricants. The aromatic hydrocarbons may derive from the SBR latex. For example, the 4-PCH is an unwanted reaction product of styrene and butadiene and is emitted by carpets with SBR latex adhesive on the secondary backing (Black *et al.*, 1991; Hodgson *et al.*, 1992 and 1993b). The terpene and sesquiterpene compounds emitted by cushion RJ2 may be from the jute plant or may have been added as odorants. Limonene is a common odorant. Benzyl acetate is used in perfumery (Sax and Lewis, 1987) and may also have been added as an odorant.

According to the Carpet Policy Dialogue (Leukroth, 1991), natural and/or styrene-butadiene rubber and calcium carbonate or hydrated aluminum oxide filler make up 85 percent of sponge-rubber cushions. The balance is accelerators, blowing agents, plasticizers, anti-oxidants, and other chemicals critical to the vulcanization process. Petroleum or other organic oils are added as plasticizers. The exact ingredients and proportions are proprietary. The complex chemical nature of the product probably accounts for the large number of compounds emitted by the sponge-rubber cushions. The many higher molecular-weight aromatic compounds may predominantly derive from the oils, such as solvent-refined naphthenic distillates. Styrene, 4-vinylcyclohexene, and 4-PCH are emitted by SBR (Black *et al.*, 1991; Hodgson *et al.*, 1992 and 1993b). Benzothiazole may derive from 2-mercaptobenzothiazole and other benzothiazole-based compounds which are used as rubber accelerators (Kirk *et al.*, 1978). N,N-Dimethylformamide and N,N-dimethylacetamide are polar solvents which are probably used in some aspect of the manufacturing process.

The three primary raw materials used in the manufacture of bonded-urethane cushions are scrap polyurethane foam, prepolymer, and laminating film (Leukroth, 1991). The scrap foam, some of which is imported for this use, is leftover material from the fabrication of flexible polyurethane foam for other industries. The prepolymer is the bonding agent for the scraps and is made from a mixture of a catalyst, polyol (polyhydric alcohols), and TDI, or a combination of TDI and methylene bisphenyl isocyanate (MDI). Sometimes, an extender oil, such as a hydrotreated naphthenic distillate, is added. A thin laminating film is bonded to the top side of the cushion at the end of the manufacturing process. It adds strength and makes it easier to slide the carpet over the cushion. The laminating film is polyethylene or a combination of polyethylene and ethylene acrylic acid, or sometimes ethylene vinyl acetate, polymers.

It is likely that an extender oil was the source of the complex mixture of predominantly C_{11} - C_{15} hydrocarbons emitted by three of the bonded-urethane cushions. The BHT was probably present in the scrap foam as an antioxidant. The siloxanes may have been used in the original production of the foam as surfactants (see below). According to a Material Safety Data Sheet (MSDS), styrene may be present in the polyol. Although the type of laminating film used on each cushion is not known, it is possible that some of the qualitative differences in the emissions among the bonded-urethane cushions may have been due to the use of different types of films. The 2,2,4-trimethyl-1,3-pentanediol diisobutyrate emitted by one cushion is used as a plasticizer for polyvinyl chloride materials (Hodgson *et al.*, 1983). The N,N-dimethylacetamide and 1,2-dichlorobenzene are common solvents.

The four raw materials used in the manufacture of prime-polyurethane cushions are polyol, TDI, water, and laminating film (Leukroth, 1991). The polyol, TDI, and water, which make up about 95 percent of the finished product, are reacted together to form the flexible foam. Catalysts, surfactants, and possibly foaming agents are added to the reaction mixture. The polymerization reaction takes place in the presence of a blowing agent, which in the past has been trichlorofluoromethane. The reaction is exothermic, and it takes several days before the reaction is complete and the slabstock or molded foam product is cool. The product is then cut to the proper thickness for use as carpet cushion. At the end of the manufacturing process, the laminating film is fused to the top side of the cushion. This film is the same as is used for bonded-urethane cushions.

As noted above, BHT is probably used as an antioxidant in the manufacture of polyurethane foams. Silicone surfactants are also used in the manufacturing process. These are likely source of the siloxane compounds that were detected in the emissions from all of the

polyurethane cushions. The 1,1,1-trichloroethane emitted by one prime-polyurethane cushion may have been used as a blowing agent. The 1,3-dichloro-2-propanol is an important chemical intermediate because of the reactivity of its functional groups (Kirk *et al.*, 1978). It can react to form 1-chloro-2,3-epoxypropane (epichlorohydrin), and 1,2,3-trichloropropane can be formed as a byproduct of this reaction (*ibid.*). An MSDS indicated that the 1,4-dimethylpiperazine emitted by two cushions was the principle component of an amine catalyst. The other tertiary amine, N,N-dimethylbenzene methanamine, was probably also used as a catalyst. As noted above, N,N-dimethylformamide and N,N-dimethylacetamide are common solvents. The source of N,N-dimethyl-2-propenamide (N,N-diemthylacrylamide) is unknown.

Emissions of Individual VOCs

Volatile organic compounds with confirmed identifications and which, in general, made significant contributions to the emissions from the samples were selected for quantitative analysis in the chamber screening measurements. The 49 quantified compounds are listed in Table 9. Formaldehyde was quantified for all samples, and TDI was quantified by both the paper-tape and treated-filter methods for bonded-urethane and prime-polyurethane samples. There were 8, 15, 22, 20, and 17 compounds respectively quantified for the synthetic-fiber, rubberized-jute, sponge-rubber, bonded-urethane, and prime-polyurethane cushions.

Emission rates at six-hours elapsed time were calculated for each of the quantified VOCs. The results for the synthetic-fiber cushions are presented in Table 10. The emission rates of the individual compounds ranged from 2-47 $\mu g\ m^{-2}\ h^{-1}$ and were generally quite low. No formaldehyde was emitted by these cushions. Since the emissions were dominated by numerous branched alkane hydrocarbons for which there are no readily available standards, the individually-quantified compounds comprised only small fractions of the emissions of TVOC (2-11 percent). The fractions of TVOC that were accounted for by the sums of the individual compounds are depicted in Figure 21.

The emission rates of individual VOCs released by the rubberized-jute cushions are presented in Table 11. The quantified compound with the highest emission rate was limonene at 168 $\mu g\ m^{-2}\ h^{-1}$, which derived from manufacturer-supplied cushion RJ2. The other manufacturer-supplied cushion emitted higher molecular-weight normal alkane hydrocarbons and combined C_2 alkylnaphthalene isomers at relatively high rates. All three cushions emitted 4-PCH. The emission rates of 4-PCH were lower than typical emission rates of this compound from carpets with SBR latex adhesive (Black *et al.*, 1991; Hodgson *et al.*, 1992). Dealer-supplied cushion RJ3

was the only cushion in this study which emitted a quantifiable amount of formaldehyde; although, the rate was relatively low. Again, the individually-quantified compounds comprised only small fractions of the emissions of TVOC (5-16 percent, Figure 21).

Table 12 presents the emission rates of VOCs from the sponge-rubber cushions. The compounds with emission rates in excess of 20 μg m^{-2} h^{-1} were toluene, styrene, methyl-naphthalene isomers, limonene, benzaldehyde, N,N-dimethylformamide, N,N-dimethylacetamide, and benzothiazole. All three cushions emitted measurable amounts of n-decane, n-undecane, toluene, m-,p-xylenes, N,N-dimethylformamide, N,N-dimethylacetamide, and benzothiazole. The two manufacturer-supplied cushions emitted very small amounts of 4-PCH. The individually-quantified compounds comprised between 13 and 29 percent of the emissions of TVOC (Figure 21).

The emission rates of individual VOCs emitted by the bonded-urethane cushions are shown in Table 13. The compounds with emission rates in excess of 20 μg m^{-2} h^{-1} were styrene, 1,2-dichlorobenzene, cyclohexanone, 2,6-di-*tert*-butyl-4-methylphenol (BHT), 2,2,4-trimethyl-1,3-pentanediol diisobutyrate, and N,N-dimethylacetamide. No quantifiable formaldehyde or TDI isomers were emitted by any of these cushions. The different lower limits of quantitation for formaldehyde shown in the table were the result of daily variations in the sensitivity of the analysis. The individually-quantified compounds comprised between 13 and 78 percent of the emissions of TVOC (Figure 21). However, there was considerable uncertainty in the quantitative results for BHT which was emitted by all of these cushions and, with the exception of sample BU2, accounted for substantial portions of their emissions. As noted previously, the compound, 2,6-di-*tert*-butyl-2,5-cyclohexadiene-4-ethenyl-2-one, was probably produced as an artifact by the thermal desorption analysis of BHT. In the samples, the ratio of total-ion-current (TIC) area of this probable artifact to the TIC area of BHT averaged about seven percent. In the standards, the ratio between the TIC areas of the two compounds was typically about 25 percent. This difference would result in an over-estimation of the sample values.

In contrast to the other cushions, the emissions from the prime-polyurethane cushions were dominated by a few compounds with relatively high emission rates (Table 14). Of the 17 compounds quantified for prime-urethane cushions, the compounds with emission rates of approximately 100 μg m^{-2} h^{-1}, or more, were styrene, 1,1,1-trichloroethane, 1,3-dichloro-2-propanol, 1,2,3-trichloropropane, BHT, N,N-dimethylformamide, 1,4-dimethylpiperazine, and N,N-dimethyl-2-propenamide (N,N-dimethylacrylamide). Of these compounds, 1,3-dichloro-2-propanol, N,N-dimethylformamide, 1,4-dimethylpiperazine, and N,N-dimethyl-2-propenamide had

relatively low TIC responses and poor chromatographic peak shapes. In addition, there were analytical problems with BHT as noted above. As a result, the sums of the individual compounds for three of the prime-polyurethane cushions exceeded their respective TVOC values (Table 14 and Figure 21) which are based on an average response factor for hydrocarbons relative to the internal standard.

Cushion PU1 emitted a small amount of toluene-2,4-diisocyanate (2,4-TDI) over the 3 - 6-hour collection period of the screening measurement with the treated-filter sampling media. The 2,6-TDI isomer was not detected. The resulting specific emission rate for 2,4-TDI was 0.07 $\mu g\ m^{-2}\ h^{-1}$. This measurement was repeated using a different piece of the same cushion, and no TDI was detected. Therefore, the finding of an emission of a small amount of 2,4-TDI from Cushion PU3 is uncertain.

Odor Thresholds

Odor influences people's response to, and acceptance of, materials used indoors. Many of the cushion samples in this study had distinctly noticeable odors when the storage bags were opened. Table 15 compares maximum chamber concentrations of individual VOCs at six hours to standardized average odor thresholds as summarized by Devos *et al.* (1990). Two values were obtained from other references (see table). For 19 of the 49 compounds, no odor data were available. The alkane hydrocarbons have odor thresholds that are significantly higher than any of the measured chamber concentrations. Consequently, the synthetic-fiber cushions, which emitted predominantly alkane hydrocarbons, did not produce much odor. In general, higher molecular-weight aromatic hydrocarbons have relatively low odor thresholds. Such compounds were emitted by the rubberized-jute and sponge-rubber cushions and undoubtedly accounted for some of the odors produced by these materials. Rubberized-jute cushions emitted 4-PCH at concentrations slightly above the reported odor threshold of less than 1 ppb (Van Ert *et al.*, 1987). Chlorinated compounds often have relatively high odor thresholds, and, with the exception of 1,2-dichlorobenzene emitted by bonded-urethane sample BU2, odor thresholds for these compounds were several orders of magnitude higher than measured concentrations. Higher molecular-weight aldehydes are quite odorous. The concentrations of nonanal and decanal emitted by rubberized-jute sample RJ2 were slightly below the odor thresholds for these compounds. No odor data were available for 2,6-di-*tert*-butyl-4-methyl phenol; however, it is likely that its odor threshold is relatively high. N,N-Dimethylformamide and N,N-dimethylacetamide, which were emitted at relatively high concentrations by the rubber cushions, have very high odor thresholds and probably did not significantly contribute to the odors produced by the bonded-

urethane and prime-polyurethane cushions. In general, the odors of the cushion samples cannot be entirely accounted for by the odors of the individually-quantified compounds. It is likely that the odors of the individual compounds are approximately additive and that the many compounds which were not quantified contributed to the odors produced by the materials.

Comparisons with Previous Data

Almost no data are available on the emissions of VOCs from carpet cushions. A single reference presented data on the emissions of TVOC from three unspecified cushion samples (Black *et al.*, 1991). These measurements were made after 24-hours elapsed time in 50-L chambers operating at one air exchange rate per hour, 25° C, and 50 percent relative humidity. The emission rates are given in Table 16. The range is similar to the range for the 17 cushion samples in this study that were measured after only six-hours elapsed time.

Limitations on Use of Emissions Data

The objective of this screening study was to characterize and compare the emissions of VOCs from five different types of carpet cushions. The measured emission rates of TVOC and individual compounds from the cushions can not be used directly to model emissions for this component of carpet systems in buildings. In carpet installations, the cushions are overlaid with carpets of various construction. A carpet constitutes a diffusion barrier which will presumably lower the emission rates of VOCs emanating from the underlying cushion. In addition, the total length of time over which the compounds from the cushion are emitted to the air may be extended. Additional experiments are needed to determine the impacts of the various carpets on the emissions of VOCs from cushions.

CONCLUSIONS

The emissions from all types of cushions, with the exception of the prime-polyurethane cushions, were relatively complex. As a result, complete quantitative analyses of the emissions of VOCs were not practical. For the thirteen synthetic-fiber, rubberized-jute, sponge-rubber, and bonded-urethane cushions, only about 13 percent of the emissions of TVOC was typically accounted for by the quantitative analysis of individual compounds. This was largely the result of the inability to resolve chromatographically complex mixtures of compounds, to identify specific isomers in a related series of compounds, and to obtain authentic standards of many of the

compounds. A large effort would be required to increase substantially the percentage contributions of the quantified VOCs in these measurements.

Fewer compounds were emitted by the prime-polyurethane cushions. Consequently, it was possible to quantify many of the compounds which dominated their emissions. However, a different methodological problem was encountered. For three of these cushions, the emission rate for sum of the individual compounds exceeded the TVOC emission rate. This was due to a shortcoming of the TVOC method, which to be of general usefulness must be based on an average, or typical, response factor for a broad range of compounds. Since the VOCs emitted from these cushions were primarily oxygen- and nitrogen-containing compounds with generally lower response factors than the alkane and aromatic hydrocarbons used to calibrate the method, the TVOC values were understated.

Despite these limitations, the screening method met the study objectives. The duplicate measurements demonstrated that the screening method has good reproducibility with respect to the chamber operating conditions, sample homogeneity, and the measurement of TVOC and individual compounds. Thus, it was possible to identify significant qualitative and quantitative differences in the emissions of individual VOCs and TVOC both within and among the types of cushions. Measurements conducted over week-long periods in larger environmental chambers at the CPSC will demonstrate if similar emission rates are obtained under different conditions of chamber loading, ventilation rate and relative humidity.

This study found substantial differences in the emission rates of TVOC and individual VOCs among the five different types of cushions. In general, the synthetic-fiber, bonded-urethane, and prime-polyurethane cushions had the lowest TVOC emission rates. However, one bonded-urethane cushion had the highest TVOC emission rate for the study, demonstrating that there can be substantial differences among cushions of a single type. For all five types of cushions, the dealer-supplied sample(s) had the lowest TVOC emission rate. This was undoubtedly due to the loss of compounds with time following production.

One of the motivating factors for this study was the concern that the bonded-urethane and prime-polyurethane cushions might be sources of emissions of TDI isomers which are potent sensory irritants, as well as chemical sensitizers. Only one prime-polyurethane cushion was found to emit any 2,4-TDI. The rate was extremely low (0.07 $\mu g\ m^{-2}\ h^{-1}$), and the occurrence was not confirmed when a duplicate cushion sample was screened. As expected, carpet cushions were not found to be significant sources of formaldehyde emissions. The only cushion which

emitted any formaldehyde was the dealer-supplied rubberized-jute sample, and the rate was relatively low (8 μg m^{-2} h^{-1}). Also, the rubberized-jute and sponge-rubber cushion samples had low emission rates of 4-phenylcyclohexene. In fact, the 4-phenylcyclohexene emission rates from the sponge-rubber cushions were only 2 μg m^{-2} h^{-1}, or less.

The chemical classes of VOCs and the identities of the individual compounds emitted by the five different types of cushions were obviously related to the manufacturing processes. The sources of the VOCs emitted by the cushions may include machine oils, complex oils purposefully added to the products, solvents, chemical intermediates, contaminants or degradation products, and additives. Manufacturing processes would have to be carefully evaluated to specifically identify sources and entry points for the various chemicals. Such evaluations might identify relatively simple opportunities to reduce the content and emissions of VOCs from carpet cushions.

REFERENCES

Amoore, J.E. and Hautala, E. (1983) Odor as an aid to chemical safety: Odor thresholds compared with threshold limit values and volatilities for 214 industrial chemicals in air and water dilution. *J. Applied Toxicology* **3:** 272-290.

Black, M.S., Pearson, W.J. and Work, L.M. (1991) Volatile organic compound emissions from carpet and associated products, Appendix R, Carpet Policy Dialogue Compendium Report. R.W. Leukroth, Jr., Ed., Office of Toxic Substances, U.S. EPA, Washington, D.C., Sept. 27.

Devos, M., Patte, F., Rouault, J., Laffort, P. and Van Gamert, L.J., Eds. (1990) *Standardized Human Olfactory Thresholds.* Oxford University Press, New York, NY.

Heller, S.R. and Milne, G.W.A. (1978) EPA/NIH mass spectral data base, U.S. Nat. Bur. Stand., Nat Stand. Ref. Data Ser., 63, U.S. Govern. Printing Off., Washington D.C.

Hodgson, A.T., Mahanama, R.K.K. and Albert, M.A. (1993a) An impregnated-filter method for measuring trace concentrations of toluene diisocyanates in air. Final Report CPSC-IAG-92-1134. Report LBL-34428, Lawrence Berkeley Laboratory, Berkeley, CA.

Hodgson, A.T., Wooley, J.D. and Daisey, J.M. (1993b) Emissions of volatile organic compounds from new carpets measured in a large-scale environmental chamber. *J. Air Waste Manage. Assoc.* **43:** 316-324.

Hodgson, A.T., Wooley, J.D. and Daisey, J.M. (1992) Volatile Organic Chemical Emissions from Carpets, Final Report CPSC-IAG-90-1256. Report LBL-31916, Lawrence Berkeley Laboratory, Berkeley, CA.

Hodgson, A.T. and Girman, J.R. (1989) Application of a multisorbent sampling technique for investigations of volatile organic compounds in buildings. *Design and Protocol for Monitoring Indoor Air Quality, ASTM STP 1002*, N.L. Nagda and J.P. Harper, Eds., American Society for Testing and Materials, Philadelphia, PA, pp 244-256.

Hodgson, A.T., Girman, J.R., Newton, A.S. and Winkes, A.W. (1983) Emissions of volatile organic compounds from architectural materials with indoor applications. Report LBL-17130, Lawrence Berkeley Laboratory, Berkeley, CA.

Kirk, R.E., Othmer, D.F., Grayson, M. and Ecroth, D., Eds. (1978) *Kirk-Othmer Encyclopedia of Chemical Technology, Third Edition.* John Wiley & Sons, Inc., New York, NY.

Leukroth, R.W., Jr., Ed. (1991) Carpet Policy Dialogue Compendium Report. Office of Toxic Substances, U.S. EPA, Washington, D.C., Sept. 27.

Riggin, R.M. (1984) Compendium of methods for the determination of toxic organic compounds in ambient air, U.S. EPA report EPA-600/4-84-041, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC.

Sax, N.I. and Lewis, R.J., Sr., Eds. (1987) *Hawley's Condensed Chemical Dictionary.* Van Nostrand Reinhold Co. Inc., New York, NY.

Schachter, L. (1990) Carpet related health complaints, Report, U.S. Consumer Product Safety Commission, Washington D.C., July.

Van Ert, M.D., Clayton, J.W., Crabb, C.L. and Walsh, D.W. (1987) Identification and characterization of 4-phenylcyclohexene - an emission product from new carpeting, U.S. EPA-OTS report, January.

Wallace, L., Pellizzari, E. and Wendel, C. (1990) Total organic concentrations in 2,500 personal, indoor, and outdoor air samples collected in the U.S. EPA TEAM studies. *Indoor Air* **4:** 465-477.

Table 1. Identification of carpet cushion samples including receipt and laboratory screening dates.

Cushion Type	I.D.	Source	Receipt Date	Screening Date	Weight/ Area kg m^{-2}
Synthetic fiber	SF2	Manufacturer	03/02/93	03/04/93	1.00
Synthetic fiber	SF3	Manufacturer	03/15/93	03/18/93	0.72
Synthetic fiber	SF1	Dealer	02/16/93	02/17/93	0.56
Rubberized jute	RJ1	Manufacturer	04/26/93	04/30/93	1.48
Rubberized jute	RJ2	Manufacturer	05/10/93	05/13/93	1.37
Rubberized jute & hair	RJ3	Dealer	05/13/93	05/14/93	1.34
Sponge rubber	SR1	Manufacturer	06/21/93	06/29/93	3.70
Sponge rubber	SR2	Manufacturer	06/23/93	06/28/93	3.38
Sponge rubber	SR3	Dealer	07/12/93	07/13/93	3.57
Bonded urethane	BU2	Manufacturer	07/13/93	07/19/93	0.99
Bonded urethane	BU3	Manufacturer	09/13/93	09/16/93	0.73
Bonded urethane	BU1	Dealer	05/28/93	06/09/93	0.81
Bonded urethane	BU4	Dealer	09/16/93	09/21/93	1.05
Prime polyurethane	PU1	Manufacturer	08/09/93	08/13/93	0.54
Prime polyurethane	PU2	Manufacturer	08/09/93	08/17/93	0.48
Prime polyurethane	PU3	Dealer	08/27/93	09/07/93	0.58
Prime polyurethane	PU4	Dealer	08/30/93	09/08/93	0.21

Table 2. Parameters for the screening measurements of carpet cushions.

PARAMETER	VOC Chamber	TDI Chambers	
		Paper Tape	Treated Filter
Material	Plated Steel	Silanized Glass	Silanized Glass
Chamber volume, m^3	3.78×10^{-3}	3.37×10^{-3}	3.37×10^{-3}
Gas	Dry N_2	Room air	Dry N_2
Inlet flow rate, $m^3\ h^{-1}$	2.40×10^{-2}	1.42×10^{-2}	1.80×10^{-2}
Ventilation rate, h^{-1}	6.35	4.21	5.34
Temperature, °C	23.0	23.0	23.0
Sample size, m^2	1.00×10^{-2}	6.97×10^{-2}	6.97×10^{-2}
Sample loading ratio, $m^2\ m^{-3}$	2.65	20.7	20.7
Exposure period, h	6	7	6 - 24
VOC sampling rate, $cm^3\ min^{-1}$	~100	---	---
VOC sample volume, L	~3.0	---	---
Formaldehyde sampling rate, $cm^3\ min^{-1}$	~250	---	---
Formaldehyde sample volume, L	~45	---	---
TDI sampling rate, $cm^3\ min^{-1}$	---	236	300
TDI sample volume, L	---	100	54

Table 3. Specifications and operating conditions for the analytical system used for individual VOCs and TVOC.

COMPONENT	Specifications and Operating Conditions
Column	Restek Rtx-5 30 m x 0.25 mm I.D. x 1.0 µm film
Carrier gas	Helium @ ~1 cm^3 sec^{-1}
Concentrator	UNACON 810A Init. carrier flow time: 1 min Tube chamber heat: 4 min @ 275° C Second. carrier flow time: 5 min Trap 1 heat: 20 sec @ 275° C Trap to trap transfer: 2 min Trap 2 heat: 20 sec @ 275° C
GC Oven	HP 5790A 1°C (17.7 min) 1 - 120° C @ 5° C min^{-1} 120 - 225° C @ 10° C min^{-1} 225° C (1 min)
MSD	HP 5970B On at 16 min SCAN mode: *m/z* 33-300, 1.6 scans sec^{-1}

Table 4. VOCs emitted by manufacturer- and dealer-supplied synthetic-fiber carpet cushions in 4-L chambers at 6-h elapsed time.

COMPOUND	RT (min)	Manufact. SF2	Manufact. SF3	Dealer SF1	Match Quality*
Alkane Hydrocarbons					
n-Hexane	24.7		+		Confirmed
C9 Branched alkane HC	35.1	+	+		Probable
Branched alkane HC	36.5		+		Probable
C9 Branched alkane HC	36.7	+		+	Probable
C10 Branched alkane HC	41.8	+			Probable
Branched alkane HC	42.1	+			Probable
Branched alkane HC	42.2	+			Probable
C12 Branched alkane HC	43.6	+	+		Probable
C12 Branched alkane HC	43.8	+	+	+	Probable
Branched alkane HC	43.9			+	Probable
Branched alkane HC	44.7	+	+		Probable
n-Undecane	44.7	+	+	+	Confirmed
C12 Branched alkane HC	44.9	+	+	+	Probable
C12 Branched alkane HC	45.0	+	+	+	Probable
C12 Branched alkane HC	45.2	+	+		Probable
Branched alkane HC	46.3	+			Probable
n-Dodecane	46.8	+		+	Confirmed
Branched alkane HC	47.0		+		Probable
Branched alkane HC	48.2	+			Probable
Branched alkane HC	48.5	+	+	+	Probable
Branched alkane HC	48.7		+	+	Probable
n-Tridecane	48.7	+	+	+	Confirmed
Branched alkane HC	48.9		+	+	Probable
Branched alkane HC	49.1	+			Probable
Branched alkane HC	49.3	+	+	+	Probable
Branched alkane HC	49.5	+	+	+	Probable
Branched alkane HC	49.6		+	+	Probable
Branched alkane HC	49.7		+		Probable
Branched alkane HC	50.0		+		Probable
Branched alkane HC	50.1		+		Confirmed
n-Tetradecane	50.2	+	+	+	Confirmed
n-Pentadecane	51.8	+	+	+	Probable
Branched alkane HC	52.3	+			Probable
Branched alkane HC	52.5		+	+	Probable
Branched alkane HC	53.0	+			Probable
Branched alkane HC	53.2		+		Probable

Table 4. Continued.

COMPOUND	RT (min)	Manufact. SF2	Manufact. SF3	Dealer SF1	Match Quality*
Aromatic Hydrocarbons					
1,1'-Biphenyl	50.5	+			Probable
Other Hydrocarbons					
Methylcyclopentane	26.2	+	+		Confirmed
C9 Alkene HC	35.9	+	+		
Limonene	43.1		+		Confirmed
C12 Alkene HC	44.2	+	+		Probable
Alkene HC	44.3	+	+	+	Probable
Alkene HC	48.8	+			Probable
Alkene HC	49.0	+	+	+	Probable
Alkene HC	49.1			+	Probable
Miscellaneous Compounds					
Siloxane compound	51.6			+	Probable

*Confirmed = Spectra and retention time of unknown match those of an authentic standard analyzed under the same conditions; Probable = Good match between unknown spectra and spectra in EPA/NIH data base; Tentative = Less certain match between spectra and spectra in EPA/NIH data base.

Table 5. VOCs emitted by manufacturer- and dealer-supplied rubberized-jute carpet cushions in 4-L chambers at 6-h elapsed time.

COMPOUND	RT (min)	Manufact. RJ1	Manufact. RJ2	Dealer RJ3	Match Quality*
Alkane Hydrocarbons					
n-Decane	41.9	+			Confirmed
Branched alkane HC	43.1	+			Probable
Branched alkane HC	43.1	+			Probable
Branched alkane HC	44.1	+			Probable
Branched alkane HC	44.1	+			Probable
Branched alkane HC	44.1	+			Probable
Branched alkane HC	45.1	+			Probable
n-Undecane	46.1	+			Confirmed
Branched alkane HC	46.1	+			Probable
Branched alkane HC	46.1	+			Probable
Branched alkane HC	46.1	+			Probable
n-Dodecane	47.1	+		+	Confirmed
Branched alkane HC	47.1	+			Probable
Branched alkane HC	48.1	+			Probable
Branched alkane HC	48.1	+			Probable
Branched alkane HC	48.1	+			Probable
Branched alkane HC	48.1	+		+	Probable
n-Tridecane	49.1	+		+	Confirmed
Branched alkane HC	49.1	+			Probable
Branched alkane HC	49.1	+			Probable
Branched alkane HC	50.1	+			Probable
Branched alkane HC	50.1	+			Probable
Branched alkane HC	50.1	+		+	Probable
Branched alkane HC	50.1			+	Probable
Branched alkane HC	50.1			+	Probable
n-Tetradecane	50.1	+	+	+	Confirmed
Branched alkane HC	50.1	+			Probable
Branched alkane HC	50.1			+	Probable
Branched alkane HC	51.1	+			Probable
Branched alkane HC	51.1	+			Probable
Branched alkane HC	51.1			+	Probable
n-Pentadecane	52.1	+	+	+	Confirmed
n-Hexadecane	53.1	+	+	+	Confirmed
Branched alkane HC	53.1	+			Probable
Branched alkane HC	54.1	+	+		Probable
Branched alkane HC	54.1			+	Probable
n-Heptadecane	55.1	+	+	+	Probable
Branched alkane HC	55.1	+	+	+	Probable

Table 5. Continued.

COMPOUND	RT (min)	Manufact. RJ1	Manufact. RJ2	Dealer RJ3	Match Quality*
Aromatic Hydrocarbons					
C4 Alkylbenzene isomer	44.1			+	Probable
C4 Alkylbenzene isomer	45.1			+	Probable
1,4-Dimethyl-2-ethenylbenzene	46.1			+	Probable
Naphthalene	47.1			+	Confirmed
2-Methylnaphthalene	49.1	+		+	Confirmed
Dimethyltetrahydronaphthalene	49.1		+		Probable
1-Methylnaphthalene	49.1	+		+	Confirmed
4-Phenylcyclohexene	50.1	+	+	+	Confirmed
Dimethylnaphthalene isomer	51.1	+	+	+	Probable
Dimethylnaphthalene isomer	51.1			+	Probable
Trimethylnaphthalene isomer	53.1			+	Probable
Trimethylnaphthalene isomer	53.1			+	Probable
Other Hydrocarbons					
Terpene HC, mw 136	41.1		+		Probable
Limonene	43.1		+		Confirmed
Terpene HC, mw 136	43.1		+		Probable
Terpene HC, mw 136	44.1		+		Probable
Terpene HC, mw 136	45.1		+		Probable
Alkene HC	50.1	+	+		Probable
Sesquiterpene HC, mw 204	51.1		+		Probable
Sesquiterpene HC, mw 204	51.1		+		Probable
Sesquiterpene HC, mw 204	51.1		+		Probable
Alkene HC	52.1	+	+		Probable
C16 Alkene HC	52.1		+	+	Probable
Carbonyl Compounds					
Benzaldehyde	40.1		+		Confirmed
Nonanal	45.1		+	+	Confirmed
Decanal	47.1		+		Confirmed
Aldehyde compound	50.1		+		Probable
Other Oxidized Compounds					
Acetic acid	27.1	+	+	+	Probable
Benzyl acetate	46.1		+		Confirmed
1,1'-Oxybis-cyclohexane	50.1		+		Probable
Ester of benzoic acid	54.1			+	Probable

Table 5. Continued.

COMPOUND	RT (min)	Manufact. RJ1	Manufact. RJ2	Dealer RJ3	Match Quality*
Miscellaneous Compounds					
Hexamethylcyclotrisiloxane	35.1			+	Confirmed
Octamethylcyclotetrasiloxane	41.1			+	Confirmed

*Confirmed = Spectra and retention time of unknown match those of an authentic standard analyzed under the same conditions; Probable = Good match between unknown spectra and spectra in EPA/NIH data base; Tentative = Less certain match between spectra and spectra in EPA/NIH data base.

Table 6. VOCs emitted by manufacturer- and dealer-supplied sponge-rubber carpet cushions in 4-L chambers at 6-h elapsed time.

COMPOUND	RT (min)	Manufact. SR1	Manufact. SR2	Dealer SR3	Match Quality*
Alkane Hydrocarbons					
n-Decane	41.9	+	+	+	Confirmed
Branched alkane HC	42.6	+			Probable
Branched alkane HC	44.2			+	Probable
n-Undecane	44.7	+	+	+	Confirmed
n-Dodecane	46.9	+		+	Confirmed
n-Tridecane	48.7	+		+	Confirmed
Branched alkane HC	50.0	+			Probable
n-Tetradecane	50.3	+			Confirmed
Aromatic Hydrocarbons					
Benzene	28.0	+			Confirmed
Toluene	32.9	+	+	+	Confirmed
Ethylbenzene	36.9			+	Confirmed
m-,p-Xylene	37.2	+	+	+	Confirmed
Styrene	38.1	+	+	+	Confirmed
o-Xylene	38.2	+	+	+	Confirmed
n-Propylbenzene	40.5	+			Confirmed
2-Ethyltoluene	40.8			+	Confirmed
1,3,5-Trimethylbenzene	41.0	+		+	Confirmed
1,2,3-Trimethylbenzene	41.4	+			Confirmed
1,2,4-Trimethylbenzene	42.0	+		+	Confirmed
C4 Alkylbenzene	42.8	+		+	Probable
C3 Alkylbenzene	43.0	+			Probable
2,3-Dihydro-1H-indene	43.4	+			Probable
C4 Alkylbenzene	43.7	+		+	Probable
C4 Alkylbenzene	43.8			+	Probable
n-Butylbenzene	43.8	+			Confirmed
C4 Alkylbenzene	43.9	+			Probable
C4 Alkylbenzene	44.2	+			Probable
C5 Alkylbenzene	45.1	+			Probable
C5 Alkylbenzene	45.3	+			Probable
C4 Alkylbenzene	45.6	+			Probable
C5 Alkylbenzene	45.9	+			Probable
C5 alkylbenzene	46.0	+			Tentative
C5 Alkylbenzene	46.2	+			Probable
Alkenylbenzene	46.4	+			Probable
C5 Alkylbenzene	46.4	+			Probable

Table 6. Continued.

COMPOUND	RT (min)	Manufact. SR1	Manufact. SR2	Dealer SR3	Match Quality*
C5 Alkylbenzene	46.5	+			Probable
1,2,3,4-Tetrahydronaphthalene	46.7	+			Probable
C6 Alkylbenzene	46.9	+			Probable
C6 Alkylbenzene	47.0	+			Probable
Naphthalene	47.2	+	+	+	Confirmed
1,2,3,4-Tetrahydromethyl-naphthalene isomer	47.7	+			Probable
1,2-Dimethyl-2,3-dihydro-1H-indene	48.3			+	Probable
C7 Alkylbenzene	48.5	+			Probable
1,2,3,4-Tetrahydromethyl-naphthalene isomer	48.7	+			Probable
1,2,3,4-Tetrahydromethyl-naphthalene isomer	49.2	+			Probable
2-Methylnaphthalene	49.2		+	+	Confirmed
1-Methylnaphthalene	49.5		+	+	Confirmed
2,7-Dimethyl-1,2,3,4-tetrahydronaphthalene	49.6	+			Probable
Cyclohexylbenzene	49.6	+			Probable
2,3-Dihydro-1,1,5-trimethyl-1H-indene	49.7	+			Tentative
4-Phenylcyclohexene	49.8	+	+	+	Confirmed
2-Methyl-1,1'-biphenyl	50.9	+			Probable
Dimethylnaphthalene isomer	51.0			+	Probable
Dimethylnaphthalene isomer	51.2			+	Probable
Other Hydrocarbons					
Methylcylohexane	30.8	+			Confirmed
3-Methyl-1,4-heptadiene	31.8		+		Probable
trans-1,4-Dimethylcyclohexane	33.3	+			Confirmed
Branched alkene HC	34.2	+			Probable
cis-1,4-Dimethylcyclohexane	34.5	+			Confirmed
4-Vinylcyclohexene	35.7	+			Confirmed
C3 Substituted cyclohexane	37.9	+			Probable
C3 Substituted cyclohexane	38.7	+			Probable
Isopropyl cyclohexane	39.2	+			Confirmed
C3 Substituted cyclohexane	39.5	+			Probable
α-Pinene	39.8			+	Confirmed

Table 6. Continued.

COMPOUND	RT (min)	Manufact. SR1	Manufact. SR2	Dealer SR3	Match Quality*
C10 Branched alkene HC	40.6		+		Probable
2,6,6-Trimethylbicylco-(3.1.1)heptane	41.1	+			Probable
C4 Substituted cyclohexane	41.3	+			Probable
Trimethylbicycloheptane isomer	41.6	+			Probable
C4 Substituted cyclohexane	41.8	+			Probable
C11 Branched alkene HC	42.6		+		Probable
Alkene HC	42.8	+			Probable
Limonene	43.1		+	+	Confirmed
C4 Substituted cyclohexane	43.1	+			Probable
C4 Substituted cyclohexene	43.5	+			Probable
Alkene HC	43.6	+			Probable
Decahydronaphthalene	44.0	+			Probable
Branched alkene HC	44.9	+			Probable
Branched alkene HC	45.2	+			Probable
Branched alkene HC	45.4	+			Probable
Branched alkadiene HC	46.1			+	Probable
Branched alkadiene HC	48.7		+		Probable
Branched alkene HC	49.0	+			Probable
Branched alkadiene HC	49.9		+		Probable
Carbonyl Compounds					
Aldehyde compound	40.6	+			Tentative
Benzaldehyde	40.8	+	+	+	Confirmed
Nonanal	44.9			+	Confirmed
Other Oxidized Compounds					
5-Methyl-3-methylene-5-hexen-2-one or 1-(1-cyclohexen-1-yl)-ethanone	37.8		+	+	Tentative
5-Ethenyldihydro-5-methyl-2(3H)-furanone	43.4		+	+	Tentative
1,2-Dimethyl-3-(1-methylene)-cyclopentanol	45.6		+	+	Probable
α,α,4-Trimethyl-3-cyclohexene-1-methanol	47.1		+	+	Probable
1,1'-Oxybisbenzene	50.8		+	+	Probable
1-Hexadecanol acetate	53.0	+	+	+	Tentative

Table 6. Continued.

COMPOUND	RT (min)	Manufact. SR1	Manufact. SR2	Dealer SR3	Match Quality*
Nitrogen-Containing Cmpds.					
Dimethylcyanamide	33.1	+			Probable
N,N-Dimethylformamide	33.8	+	+	+	Confirmed
N,N-Dimethylacetamide	37.3	+	+	+	Confirmed
Miscellaneous Compounds					
Hexamethylcyclotrisiloxane	35.0	+	+	+	Confirmed
Octamethylcyclotetrasiloxane	41.5	+		+	Confirmed
Benzothiazole	48.0	+	+	+	Confirmed

*Confirmed = Spectra and retention time of unknown match those of an authentic standard analyzed under the same conditions; Probable = Good match between unknown spectra and spectra in EPA/NIH data base; Tentative = Less certain match between spectra and spectra in EPA/NIH data base.

Table 7. VOCs emitted by manufacturer- and dealer-supplied bonded-urethane carpet cushions in 4-L chambers at 6-h elapsed time.

COMPOUND	RT (min)	Manuf. BU2	Manuf. BU3	Dealer BU1	Dealer BU4	Match Quality*
Alkane Hydrocarbons						
n-Decane	41.9	+		+		Confirmed
Branched alkane HC	42.7				+	Probable
Branched alkane HC	43.2				+	Probable
Branched alkane HC	43.7		+		+	Probable
Branched alkane HC	43.9		+		+	Probable
Branched alkane HC	44.3		+		+	Probable
n-Undecane	44.8	+	+	+		Confirmed
n-Dodecane	46.9			+		Confirmed
n-Tridecane	48.8			+		Confirmed
n-Tetradecane	50.3			+		Confirmed
Branched alkane HC	50.7				+	Probable
Aromatic Hydrocarbons						
Benzene	28.0			+	+	Confirmed
Toluene	32.9			+	+	Confirmed
Styrene	38.1	+				Confirmed
1,2,4-Trimethylbenzene	41.9			+		Confirmed
C3 Alkylbenzene	43.0		+			Probable
C4 Alkylbenzene	43.7			+		Probable
C4 Alkylbenzene	43.9			+		Probable
C4 Alkylbenzene	44.4			+		Probable
C4 Alkylbenzene	44.5			+		Probable
C4 Alkylbenzene	44.6			+		Probable
1,2,4,5-Tetramethylbenzene	45.4			+		Confirmed
1,2,3,5-Tetramethylbenzene	45.6			+		Confirmed
Ethenylethylbenzene	46.1			+		Probable
C4 alkylbenzene	46.3			+		Probable
Naphthalene	47.2			+		Confirmed
C8 Alkylbenzene	51.2			+		Probable
C8 Alkylbenzene	51.7			+		Probable
C10 Alkylbenzene	52.5			+		Probable
C10 Alkylbenzene	52.6			+		Probable
C10 Alkylbenzene	52.9			+		Probable
C11 Alkylbenzene	53.8			+		Probable
C11 Alkylbenzene	53.9			+		Probable
C11 Alkylbenzene	54.1			+		Probable
C11 Alkylbenzene	55.5			+		Probable
Other Hydrocarbons						
2-Methyl-1-propene trimer	42.3	+				Probable
Branched alkadiene HC	43.1		+			Probable

Table 7. Continued.

COMPOUND	RT (min)	Manuf. BU2	Manuf. BU3	Dealer BU1	Dealer BU4	Match Quality*
Tricyclodecane	45.0	+				Probable
Complex mixture of unsaturated HCs	44-54	+	+		+	Probable
Branched alkene HC	51.7				+	Probable
Branched alkene HC	51.8				+	Probable
Chlorinated Compounds						
Chlorobenzene	36.3		+			Confirmed
1,2-Dichlorobenzene	43.4	+	+			Confirmed
Carbonyl Compounds						
Cyclohexanone	38.3				+	Confirmed
Benzaldehyde	40.9				+	Confirmed
Nonanal	44.9			+		Confirmed
3,5,5-Trimethyl-2-cyclohexen-1-one	45.7				+	Probable
Decanal	47.2			+	+	Confirmed
Undecanal	49.0				+	Tentative
Dodecanal	50.6				+	Tentative
Aldehyde Compound	52.1				+	Probable
Other Oxidized Compounds						
2-Ethylhexanoic acid	45.1		+		+	Probable
2,2,4-Trimethyl-1,3-pentanediol monoisobutyrate	50.2			+		Confirmed
2,6-Di-*tert*-butyl-2,5-cyclo-hexadiene-4-ethenyl-2-one	51.9	+	+	+	+	Probable
2,6-Di-*tert*-butyl-4-methylphenol	52.3	+	+	+	+	Confirmed
2,2,4-Trimethyl-1,3-pentanediol diisobutyrate	53.4			+		Confirmed
Nitrogen-Containing Cmpds.						
N,N-Dimethylacetamide	37.5	+				Confirmed
2,3-Diethyl-2,3-dimethylbutanedinitrile	48.3		+	+		Probable
Miscellaneous Compounds						
Hexamethylcyclotrisiloxane	35.0		+	+	+	Confirmed
Octamethylcyclotetrasiloxane	41.4		+	+	+	Confirmed
Decamethylcyclopentasiloxane	45.8		+	+		Probable
Siloxane compound	49.0		+			Probable
Siloxane compound	50.3	+				Probable
Siloxane compound	51.6				+	Probable
Siloxane compound	52.5	+				Probable

Table 7. Continued.

Notes to table:

*Confirmed = Spectra and retention time of unknown match those of an authentic standard analyzed under the same conditions; Probable = Good match between unknown spectra and spectra in EPA/NIH data base; Tentative = Less certain match between spectra and spectra in EPA/NIH data base.

Table 8. VOCs emitted by manufacturer- and dealer-supplied prime-polyurethane carpet cushions in 4-L chambers at 6-h elapsed time.

COMPOUND	RT (min)	Manuf. PU1	Manuf. PU2	Dealer PU3	Dealer PU4	Match Quality*
Alkane Hydrocarbons						
Branched alkane HC	42.7		+			Probable
Branched alkane HC	43.2		+			Probable
Branched alkane HC	43.9		+			Probable
Branched alkane HC	44.3		+			Probable
n-Dodecane	46.9			+		Confirmed
C13 Branched Alkane HC	46.9			+		Probable
n-Tridecane	48.7			+		Confirmed
n-Tetradecane	50.3			+		Confirmed
n-Pentadecane	52.1			+		Confirmed
Aromatic Hydrocarbons						
Toluene	33.0			+		Confirmed
Ethylbenzene	37.0			+		Confirmed
Stryene	38.1	+		+		Confirmed
1-Propenylbenzene	41.6		+			Probable
Other Hydrocarbons						
Branched alkene HC	46.7		+	+		Probable
Chlorinated Compounds						
1,1,1-Trichloroethane	27.2	+				Confirmed
1-Chloro-2,3-epoxypropane	30.9		+			Confirmed
1,3-Dichloro-2-propanol	38.7		+			Confirmed
1,2,3-Trichloropropane	39.3		+			Confirmed
1,2-Dichlorobenzene	43.4	+				Confirmed
1,3,5-Trichlorobenzene	47.0			+		Confirmed
Oxidized Compounds						
2-Ethylhexanoic acid, methyl ester	43.3		+			Tentative
2,6-Di-*tert*-butyl-2,5-cyclo-hexadiene-4-ethenyl-2-one	51.8	+	+	+	+	Probable
2,6-Di-*tert*-butyl-4-methylphenol	52.3	+	+	+	+	Confirmed
Nitrogen-Containing Cmpds.						
N,N-Dimethylformamide	34.0		+			Confirmed
1,4-Dimethylpiperazine	36.8	+	+			Confirmed
N,N-Dimethylacetamide	37.4		+			Confirmed
N,N-Dimethyl-2-propenamide	40.4		+			Confirmed

Table 8. Continued.

COMPOUND	RT (min)	Manuf. PU1	Manuf. PU2	Dealer PU3	Dealer PU4	Match Quality*
N,N-Dimethylbenzene methanamine	43.5		+			Confirmed
Morpholine compound	44.8		+			Tentative
2,3-Dimethyl-2,3-diethylbutanedinitrile	48.4	+		+		Probable
Miscellaneous Compounds						
Hexamethylcyclotrisiloxane	35.1	+	+	+	+	Confirmed
Octamethylcyclotetrasiloxane	41.5		+	+	+	Confirmed
Siloxane compound	43.6		+			Tentative
Siloxane compound	43.7		+			Tentative
Siloxane compound	45.0		+			Tentative
Decamethylcyclopentasiloxane	45.8	+	+	+	+	Probable
Dodecamethylpentasiloxane	47.4			+		Probable
Siloxane compound	49.0	+	+	+	+	Probable
Siloxane compound	51.5		+			Probable

*Confirmed = Spectra and retention time of unknown match those of an authentic standard analyzed under the same conditions; Probable = Good match between unknown spectra and spectra in EPA/NIH data base; Tentative = Less certain match between spectra and spectra in EPA/NIH data base.

Table 9. VOCs selected for quantitation in emissions screening measurements of synthetic-fiber, rubberized-jute, sponge-rubber, bonded-urethane, and prime-polyurethane carpet cushions.

	Carpet Cushion Type				
COMPOUND	**Synthetic-Fiber**	**Rubber.-Jute**	**Sponge-Rubber**	**Bonded-Urethane**	**Prime-Polyur.**
Alkane Hydrocarbons					
n-Hexane	+				
n-Decane		+	+	+	
n-Undecane	+	+	+	+	
n-Dodecane	+	+	+	+	
n-Tridecane	+	+		+	+
n-Tetradecane	+	+		+	
n-Pentadecane		+			
n-Hexadecane		+			
Aromatic Hydrocarbons					
Toluene			+	+	
Ethylbenzene					+
m-,p-Xylene			+		
o-Xylene			+		
Styrene			+	+	+
1,2,3-Trimethylbenzene			+		
1,2,4-Trimethylbenzene			+	+	
1,3,5-Trimethylbenzene			+		
1,2,4,5-Tetramethylbenzene				+	
1,2,3,5-Tetramethylbenzene				+	
Naphthalene		+	+	+	
2-Methylnaphthalene			+		
1-Methylnaphthalene			+		
C_2 Alkylnaphthalenes		+	+		
4-Phenylcyclohexene		+	+		
Other Hydrocarbons					
Methylcyclopentane	+				
4-Vinylcyclohexene			+		
Limonene	+	+	+		
Chlorinated Compounds					
1,1,1-Trichloroethane					+
1-Chloro-2,3-epoxypropane					+
Chlorobenzene				+	

Table 9. Continued.

COMPOUND	Carpet Cushion Type				
	Synthetic-Fiber	Rubber.-Jute	Sponge-Rubber	Bonded-Urethane	Prime-Polyur.
1,3-Dichloro-2-propanol					+
1,2,3-Trichloropropane					+
1,2-Dichlorobenzene				+	+
1,3,5-Trichlorobenzene					+
Carbonyl Compounds					
Formaldehyde	+	+	+	+	+
Cyclohexanone				+	
Benzaldehyde			+		
Nonanal		+			
Decanal		+			
Other Oxidized Compounds					
Benzyl acetate		+			
2,2,4-Trimethyl-1,3-pentanediol monoisobutyrate				+	
2,6-Di-*tert*-butyl-4-methylphenol				+	+
2,2,4-Trimethyl-1,3-pentanediol diisobutyrate				+	
Nitrogen-Containing Cmpds.					
N,N-Dimethylformamide			+		+
1,4-Dimethylpiperazine					+
N,N-Dimethylacetamide			+	+	+
N,N-Dimethyl-2-propenamide					+
N,N-Dimethylbenzene methanamine					+
Toluene-2,4-diisocyanate				+	+
Miscellaneous Compounds					
Benzothiazole			+		

Table 10. Specific emission rates of target compounds and TVOC emitted by synthetic-fiber carpet cushions in 4-L chambers at 6-h elapsed time.

	Specific Emission Rate (μg m^{-2} h^{-1})		
COMPOUND	**Manufact. SF2**	**Manufact. SF3**	**Dealer SF1**
Alkane Hydrocarbons			
n-Hexane		40.8	
n-Undecane	7.0		1.5
n-Dodecane	4.4		
n-Tridecane	4.1	4.0	3.9
n-Tetradecane	2.6	7.4	5.6
Other Hydrocarbons			
Methylcyclopentane		47.4	
Limonene		11.4	
Carbonyl Compounds			
Formaldehyde	<5.0	<5.0	<5.0
TVOC-TIC	933	1,020	188
Sum VOCs	18.1	111	11.0
Sum VOCs/TVOC	0.02	0.11	0.06

Table 11. Specific emission rates of target compounds and TVOC emitted by rubberized-jute carpet cushions in 4-L chambers at 6-h elapsed time.

COMPOUND	Specific Emission Rate (μg m^{-2} h^{-1}) Manufact. RJ1	Manufact. RJ2	Dealer RJ3
Alkane Hydrocarbons			
n-Decane	1.8		
n-Undecane	4.6		
n-Dodecane	22.7		
n-Tridecane	53.6		6.7
n-Tetradecane	57.1		6.4
n-Pentadecane	56.7		5.0
n-Hexadecane	33.9	3.8	4.4
Aromatic Hydrocarbons			
Naphthalene			13.0
C_2 Alkylnaphthalenes	82.8		
4-Phenylcyclohexene	10.0	25.2	5.5
Other Hydrocarbons			
Limonene		168	
Carbonyl Compounds			
Formaldehyde	<4.0	<4.0	8.0
Nonanal		14.7	
Decanal		6.4	
Other Oxidized Compounds			
Benzyl acetate		19.0	
TVOC-TIC	3,950	1,500	952
Sum VOCs	323	237	49
Sum VOCs/TVOC	0.08	0.16	0.05

Table 12. Specific emission rates of target compounds and TVOC emitted by sponge-rubber carpet cushions in 4-L chambers at 6-h elapsed time.

COMPOUND	Specific Emission Rate (µg m^{-2} h^{-1}) Manufact. SR1	Manufact. SR2	Dealer SR3
Alkane Hydrocarbons			
n-Decane	11.9	12.5	5.8
n-Undecane	13.5	7.8	4.5
n-Dodecane	8.2		
Aromatic Hydrocarbons			
Toluene	6.3	64.5	4.4
m-,p-Xylene	18.5	6.2	7.7
o-Xylene	10.3		
Styrene	41.8	6.2	8.0
1,2,3-Trimethylbenzene	3.9		
1,2,4-Trimethylbenzene	21.2		5.8
1,3,5-Trimethylbenzene	6.0		
Naphthalene		13.5	15.9
2-Methylnaphthalene		24.8	27.9
1-Methylnaphthalene		11.9	22.5
C_2 Alkylnaphthalenes		18.5	16.6
4-Phenylcyclohexene	1.6	2.3	<2.0
Other Hydrocarbons			
4-Vinylcyclohexene	18.1		
Limonene		22.3	6.8
Carbonyl Compounds			
Formaldehyde	<4.0	<4.0	<4.0
Benzaldehyde	24.5	4.7	
Nitrogen-Containing Cmpds.			
N,N-Dimethylformamide	84.3	27.9	21.2
N,N-Dimethylacetamide	62.4	64.9	41.1
Miscellaneous Compounds			
Benzothiazole	37.1	6.2	10.5
TVOC-TIC	2,760	1,670	694
Sum VOCs	370	294	199
Sum VOCs/TVOC	0.13	0.18	0.29

Table 13. Specific emission rates of target compounds and TVOC emitted by bonded-urethane carpet cushions in 4-L chambers at 6-h elapsed time.

COMPOUND	Specific Emission Rate (µg m^{-2} h^{-1}) Manufact. BU2	Manufact. BU3	Dealer BU1	Dealer BU4
Alkane Hydrocarbons				
n-Decane	2.6		4.3	
n-Undecane	7.9	2.9	3.8	
n-Dodecane			5.1	
n-Tridecane			18.4	
n-Tetradecane			13.4	
Aromatic Hydrocarbons				
Toluene			1.3	1.4
Styrene	23.3			
1,2,4-Trimethylbenzene			4.6	
1,2,4,5-Tetramethylbenzene			5.0	
1,2,3,5-Tetramethylbenzene			9.5	
Naphthalene			8.7	
Chlorinated Compounds				
Chlorobenzene		6.6		
1,2-Dichlorobenzene	67.9			
Carbonyl Compounds				
Formaldehyde	<3.0	<5.0	<3.0	<5.0
Cylohexanone				24.2
Other Oxidized Compounds				
2,2,4-Trimethyl-1,3-pentanediol monoisobutyrate			18.8	
2,6-Di-*tert*-butyl-4-methylphenol	273	316	255	351
2,2,4-Trimethyl-1,3-pentanediol diisobutyrate			40.7	
Nitrogen-Containing Cmpds.				
N,N-Dimethylacetamide	650			
Toluene-2,4-diisocyanate	<0.03	<0.03	<0.03	<0.03
TVOC-TIC	7,720	1,030	607	480
Sum VOCs	1,030	326	389	376
Sum VOCs/TVOC	0.13	0.32	0.64	0.78

Table 14. Specific emission rates of target compounds and TVOC emitted by prime-polyuethane carpet cushions in 4-L chambers at 6-h elapsed time.

COMPOUND	Specific Emission Rate (μg m^{-2} h^{-1}) Manufact. PU1	Manufact. PU2	Dealer PU3	Dealer PU4
Alkane Hydrocarbons				
n-Tridecane			12.6	
Aromatic Hydrocarbons				
Ethylbenzene			8.1	
Styrene	91.7		94.3	
Chlorinated Compounds				
1,1,1-Trichloroethane	327			
1-Chloro-2,3-epoxypropane		50.8		
1,3-Dichloro-2-propanol		130		
1,2,3-Trichloropropane		391		
1,2-Dichlorobenzene	22.4			
1,3,5-Trichlorobenzene			17.1	
Carbonyl Compounds				
Formaldehyde	<3.0	<3.0	<3.0	<3.0
Other Oxidized Compounds				
2,6-Di-*tert*-butyl-4-methylphenol	435	488	630	356
Nitrogen-Containing Cmpds.				
N,N-Dimethylformamide		370		
1,4-Dimethylpiperazine	560	10.9		
N,N-Dimethylacetamide		70.9		
N,N-Dimethyl-2-propenamide		475		
N,N-Dimethylbenzene methanamine		19.8		
Toluene-2,4-diisocyanate	0.07	<0.03	<0.03	<0.03
TVOC-TIC	1,060	1,190	880	229
Sum VOCs	1,440	2,010	762	356
Sum VOCs/TVOC	1.36	1.69	0.87	1.55

Table 15. Comparison of maximum concentrations of target compounds in 4-L chambers at 6-h elapsed time with their respective odor thresholds.

COMPOUND	Odor Thresh. (ppb)	Max. Conc. (ppb)	Carpet Cushion Type
Alkane Hydrocarbons			
n-Hexane	21,900	4.8	Synthetic fiber
n-Decane	741	0.9	Sponge rubber
n-Undecane	1,170	0.9	Sponge rubber
n-Dodecane	2,040	1.4	Rubberized jute
n-Tridecane	2,140	3.0	Rubberized jute
n-Tetradecane	ND*	2.9	Rubberized jute
n-Pentadecane	ND	2.7	Rubberized jute
n-Hexadecane	ND	1.5	Rubberized jute
Aromatic Hydrocarbons			
Toluene	1,500	7.1	Sponge rubber
Ethylbenzene	3	0.8	Prime polyurethane
m-,p-Xylene	398	1.8	Sponge rubber
o-Xylene	851	1.0	Sponge rubber
Styrene	145	9.2	Prime polyurethane
1,2,3-Trimethylbenzene	ND	0.3	Sponge rubber
1,2,4-Trimethylbenzene	155	1.8	Sponge rubber
1,3,5-Trimethylbenzene	229	0.5	Sponge rubber
1,2,4,5-Tetramethylbenzene	26	0.4	Bonded urethane
1,2,3,5-Tetramethylbenzene	ND	0.7	Bonded urethane
Naphthalene	15	1.3	Sponge rubber
2-Methylnaphthalene	ND	2.0	Sponge rubber
1-Methylnaphthalene	ND	1.6	Sponge rubber
C_2 Alkylnaphthalenes	ND	5.4	Rubberized jute
4-Phenylcyclohexene	<1**	1.6	Rubberized jute
Other Hydrocarbons			
Methylcyclopentane	ND	5.8	Synthetic fiber
4-Vinylcyclohexene	ND	1.7	Sponge rubber
Limonene	437	12.6	Rubberized jute
Chlorinated Compounds			
1,1,1-Trichloroethane	22,400	25.2	Prime polyurethane
1-Chloro-2,3-epoxypropane	930†	5.6	Prime polyurethane
Chlorobenzene	741	0.6	Bonded urethane

Table 15. Continued.

COMPOUND	Odor Thresh. (ppb)	Max. Conc. (ppb)	Carpet Cushion Type
1,3-Dichloro-2-propanol	ND	10.3	Prime polyurethane
1,2,3-Trichloropropane	ND	27.3	Prime polyurethane
1,2-Dichlorobenzene	72	4.7	Bonded urethane
1,3,5-Trichlorobenzene	324	1.0	Prime polyurethane
Carbonyl Compounds			
Formaldehyde	871	2.7	Rubberized jute
Cyclohexanone	708	2.5	Bonded urethane
Benzaldehyde	42	2.4	Sponge rubber
Nonanal	2	1.1	Rubberized jute
Decanal	1	0.4	Rubberized jute
Other Oxidized Compounds			
Benzyl acetate	145	1.3	Rubberized jute
2,2,4-Trimethyl-1,3-pentanediol monoisobutyrate	ND	0.9	Bonded urethane
2,6-Di-*tert*-butyl-4-methylphenol	ND	29.2	Prime polyurethane
2,2,4-Trimethyl-1,3-pentanediol diisobutyrate	ND	1.5	Bonded urethane
Nitrogen-Containing Cmpds.			
N,N-Dimethylformamide	47,900	51.6	Prime polyurethane
1,4-Dimethylpiperazine	ND	50.0	Prime polyurethane
N,N-Dimethylacetamide	100,000	76.2	Bonded urethane
N,N-Dimethyl-2-propenamide	ND	48.9	Prime polyurethane
N,N-Dimethylbenzene methanamine	ND	1.5	Prime polyurethane
Toluene-2,4-diisocyanate	2,140	0.04	Prime polyurethane
Miscellaneous Compounds			
Benzothiazole	ND	2.8	Rubber

*ND = No data.
**Van Ert *et al.* (1987).
†Amoore and Hautala (1983).
All other odor threshold values from Devos *et al.* (1990).

Table 16. Comparison of specific emission rates of TVOC from carpet cushions measured in this study with TVOC emission rates measured at 24 hours in 50-L chambers by Black *et al.* (1991)[a].

SOURCE/ STATISTICS	ET (h)	Emission Rate ($\mu g\ m^{-2}\ h^{-1}$)
Cushions (this study)	6	
Number		17
Minimum		188
Maximum		7,720
Median		1,020
Cushions (Black *et al.*)	24	
Number		3
Minimum		123
Maximum		3,360
Median		240

[a]Black, M.S., Pearson, W.J. and Work, L.M. (1991) Volatile organic compound emissions from carpet and associated products, Appendix R, Carpet Policy Dialogue Compendium Report. R.W. Leukroth, Jr., Ed., Office of Toxic Substances, U.S. EPA, Washington, D.C. Sept. 27.

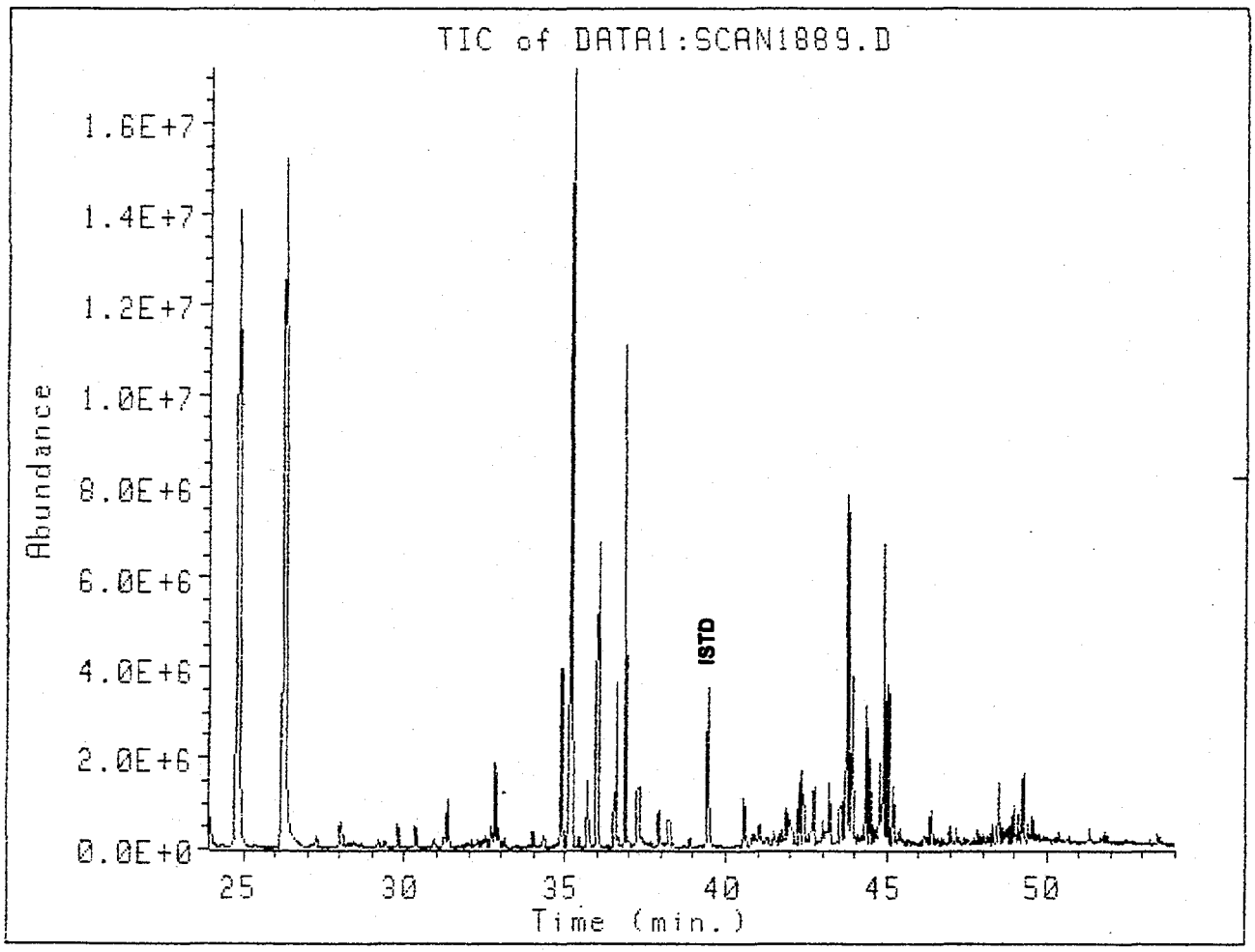

Figure 1. Total-ion-current chromatogram of 6-h chamber sample of VOC emissions from manufacturer-supplied synthetic-fiber carpet cushion, SF2.

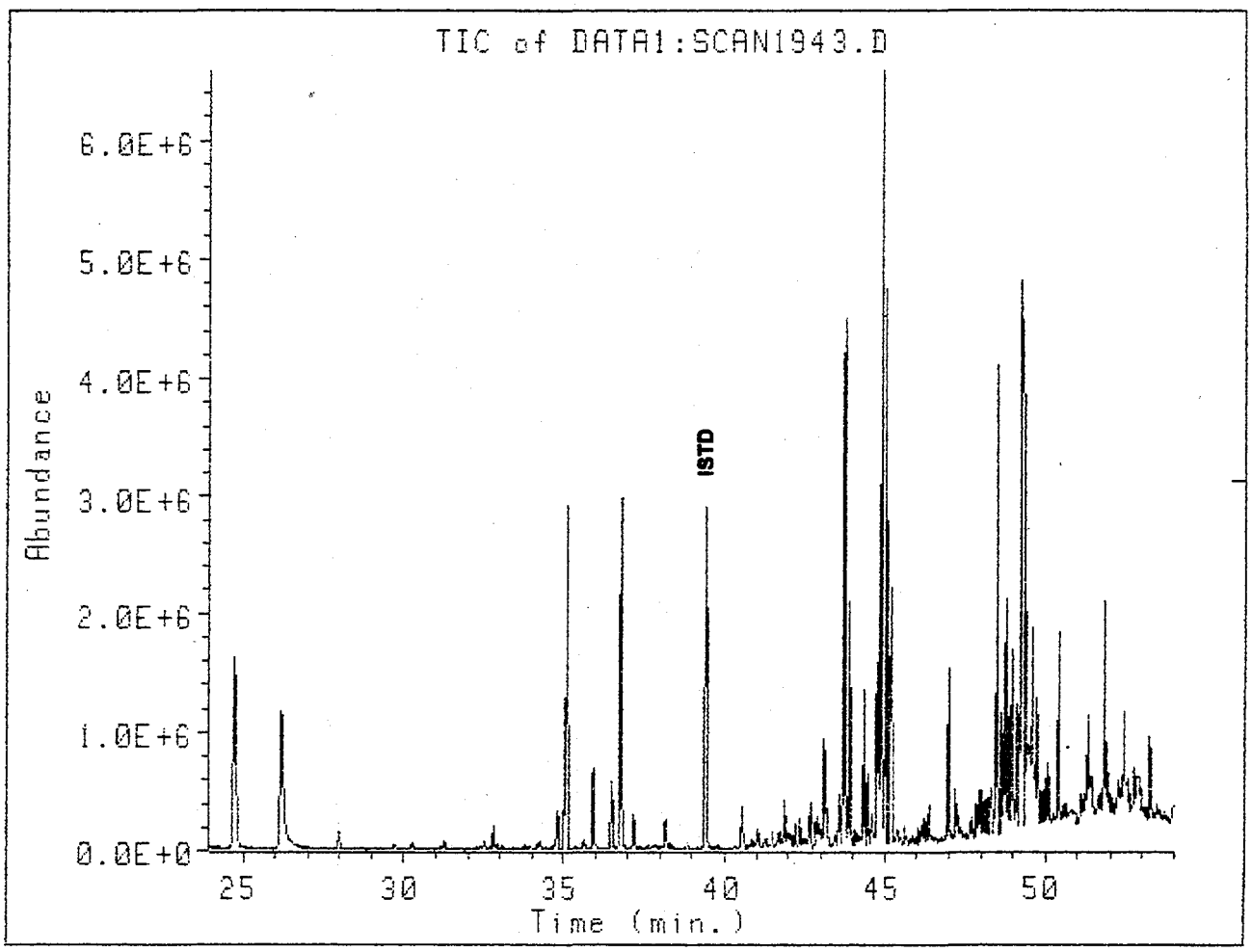

Figure 2. Total-ion-current chromatogram of 6-h chamber sample of VOC emissions from manufacturer-supplied synthetic-fiber carpet cushion, SF3.

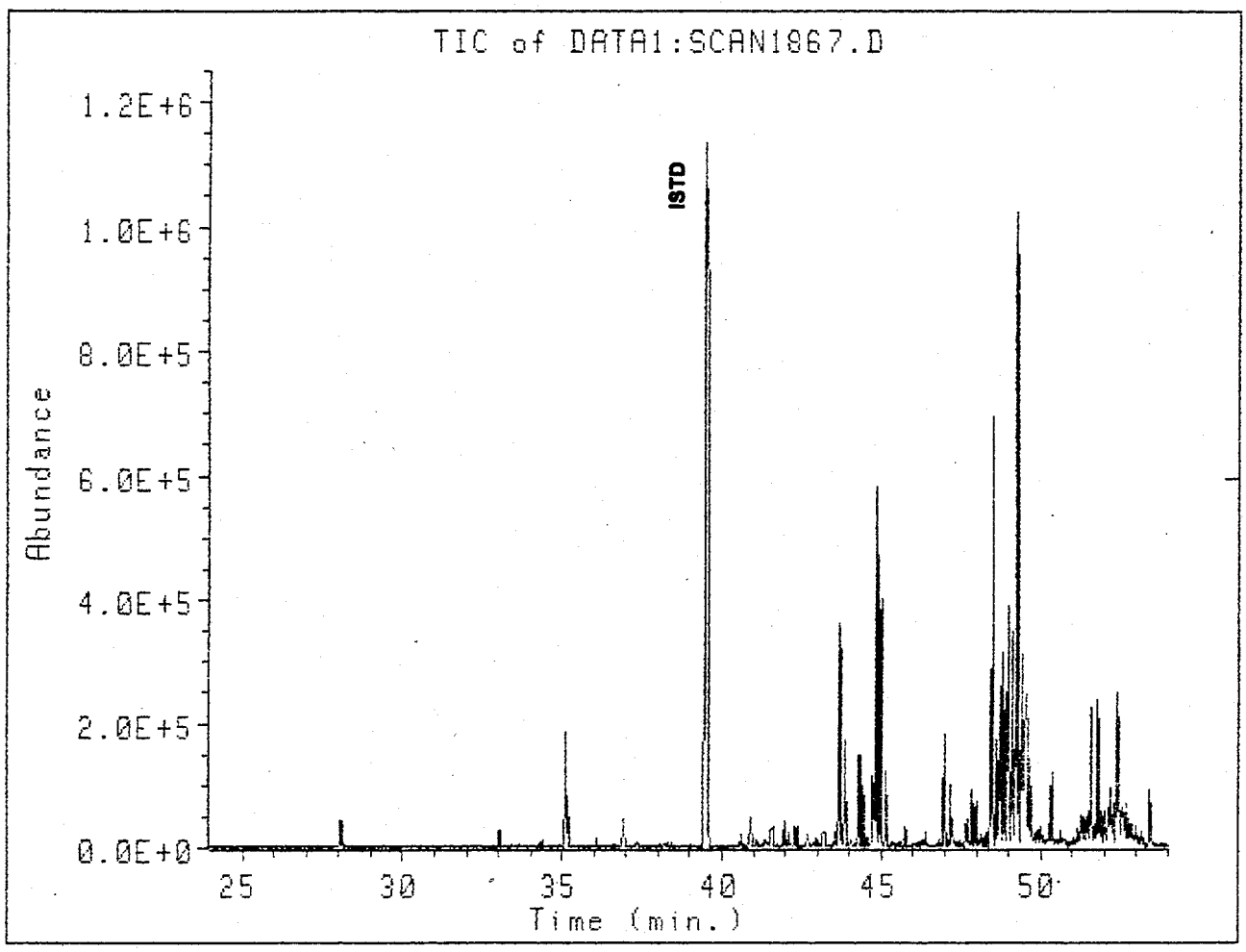

Figure 3. Total-ion-current chromatogram of 6-h chamber sample of VOC emissions from dealer-supplied synthetic-fiber carpet cushion, SF1.

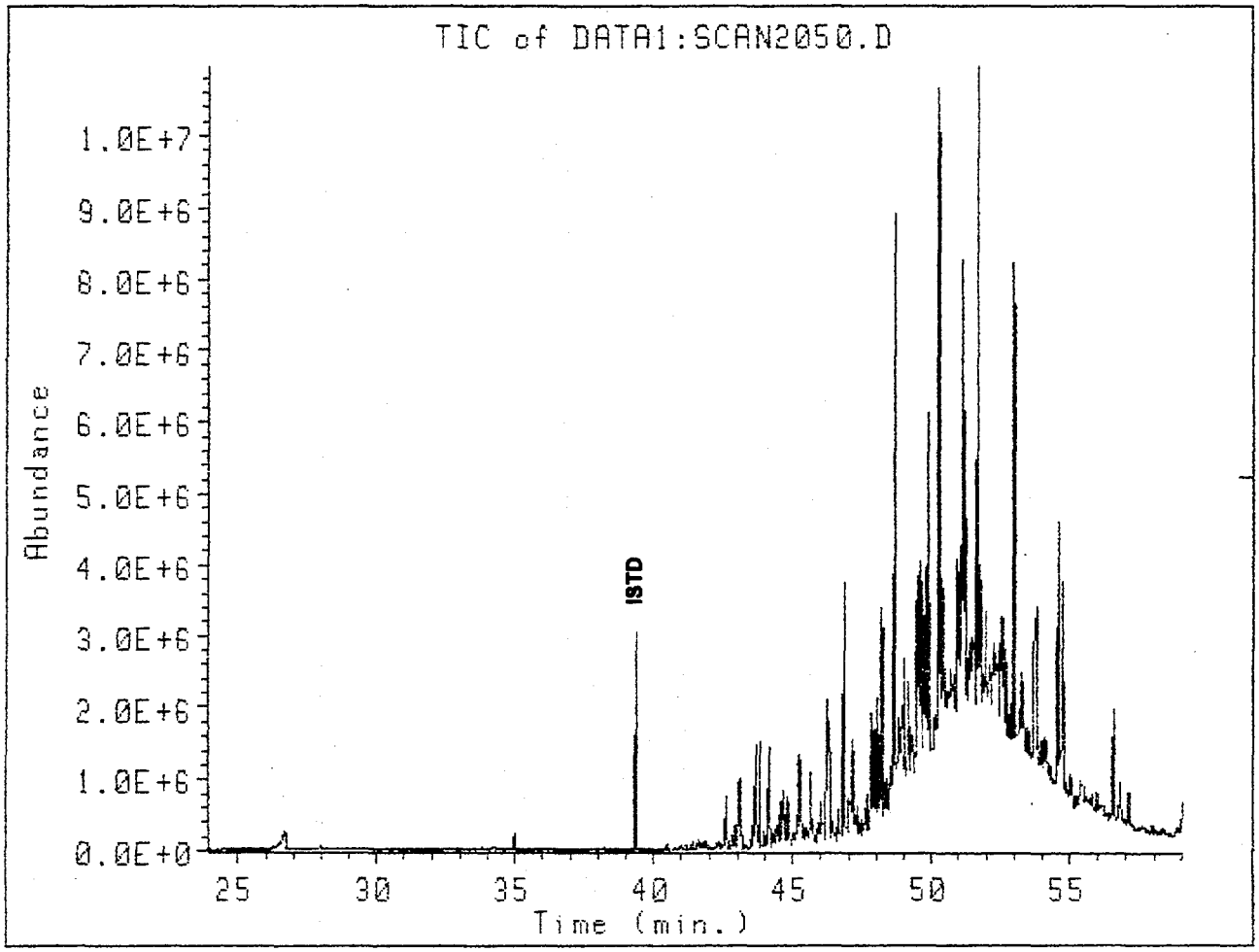

Figure 4. Total-ion-current chromatogram of 6-h chamber sample of VOC emissions from manufacturer-supplied rubberized-jute carpet cushion, RJ1.

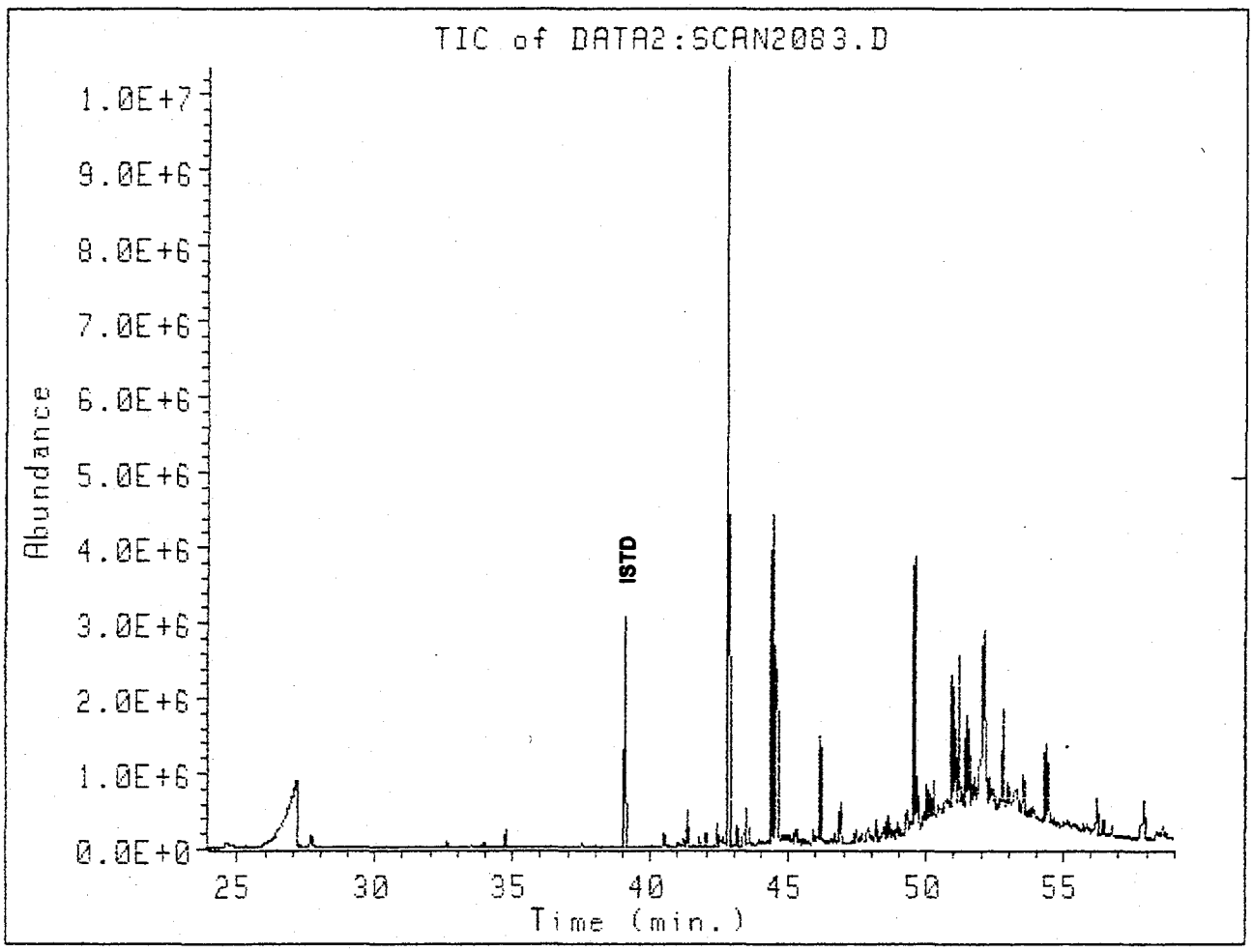

Figure 5. Total-ion-current chromatogram of 6-h chamber sample of VOC emissions from manufacturer-supplied rubberized-jute carpet cushion, RJ2.

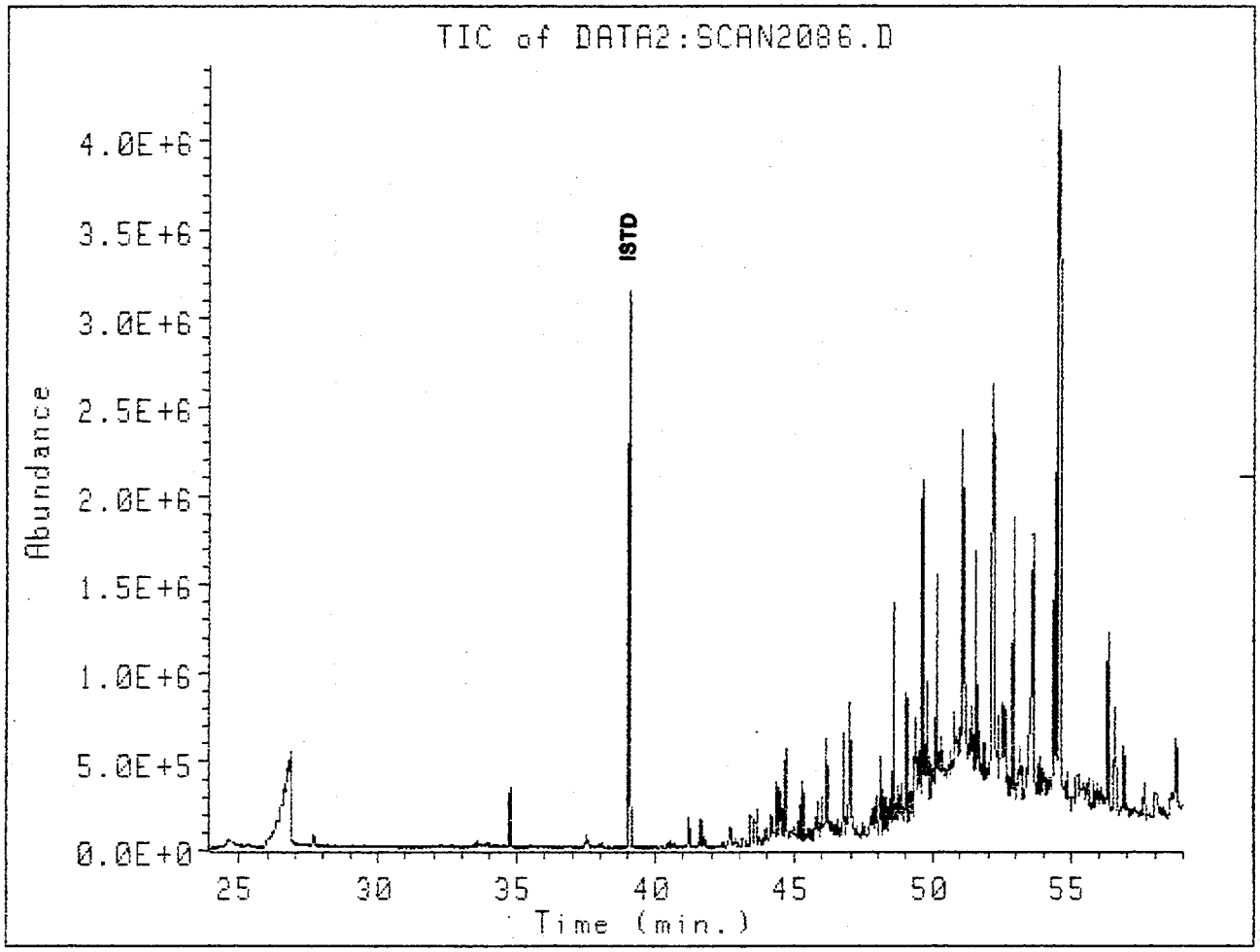

Figure 6. Total-ion-current chromatogram of 6-h chamber sample of VOC emissions from dealer-supplied rubberized-jute and hair carpet cushion, RJ3.

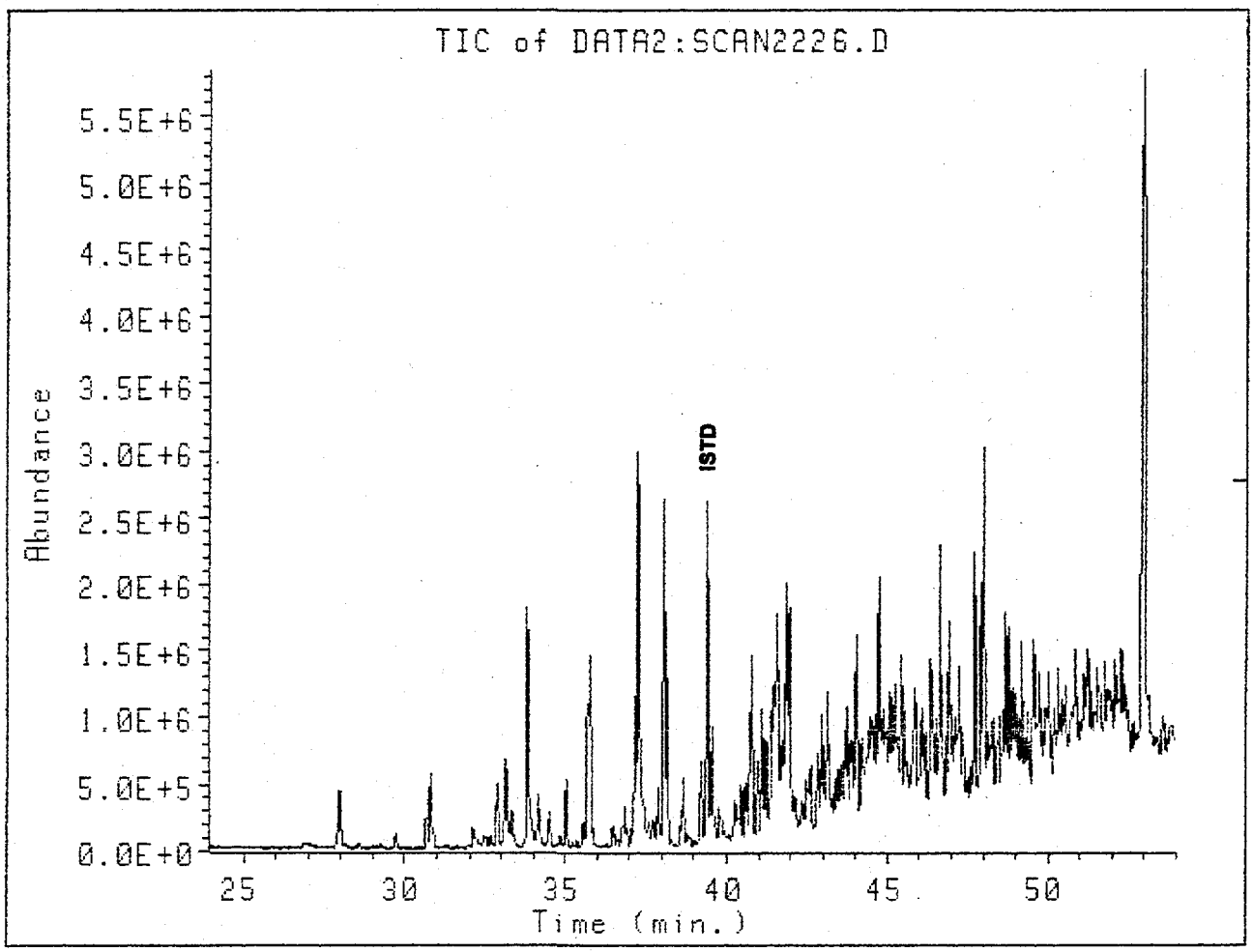

Figure 7. Total-ion-current chromatogram of 6-h chamber sample of VOC emissions from manufacturer-supplied sponge-rubber carpet cushion, SR1.

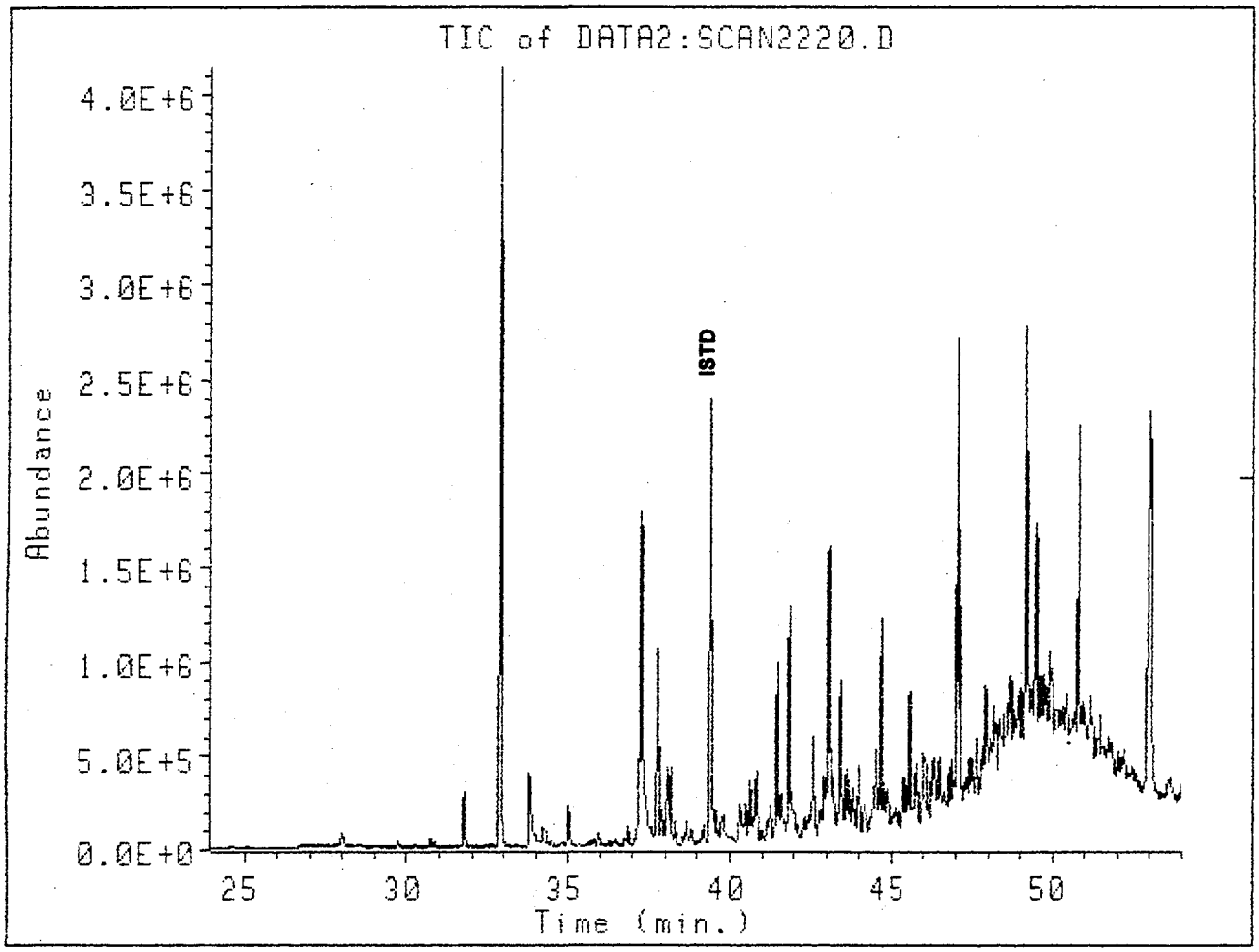

Figure 8. Total-ion-current chromatogram of 6-h chamber sample of VOC emissions from manufacturer-supplied sponge-rubber carpet cushion, SR2.

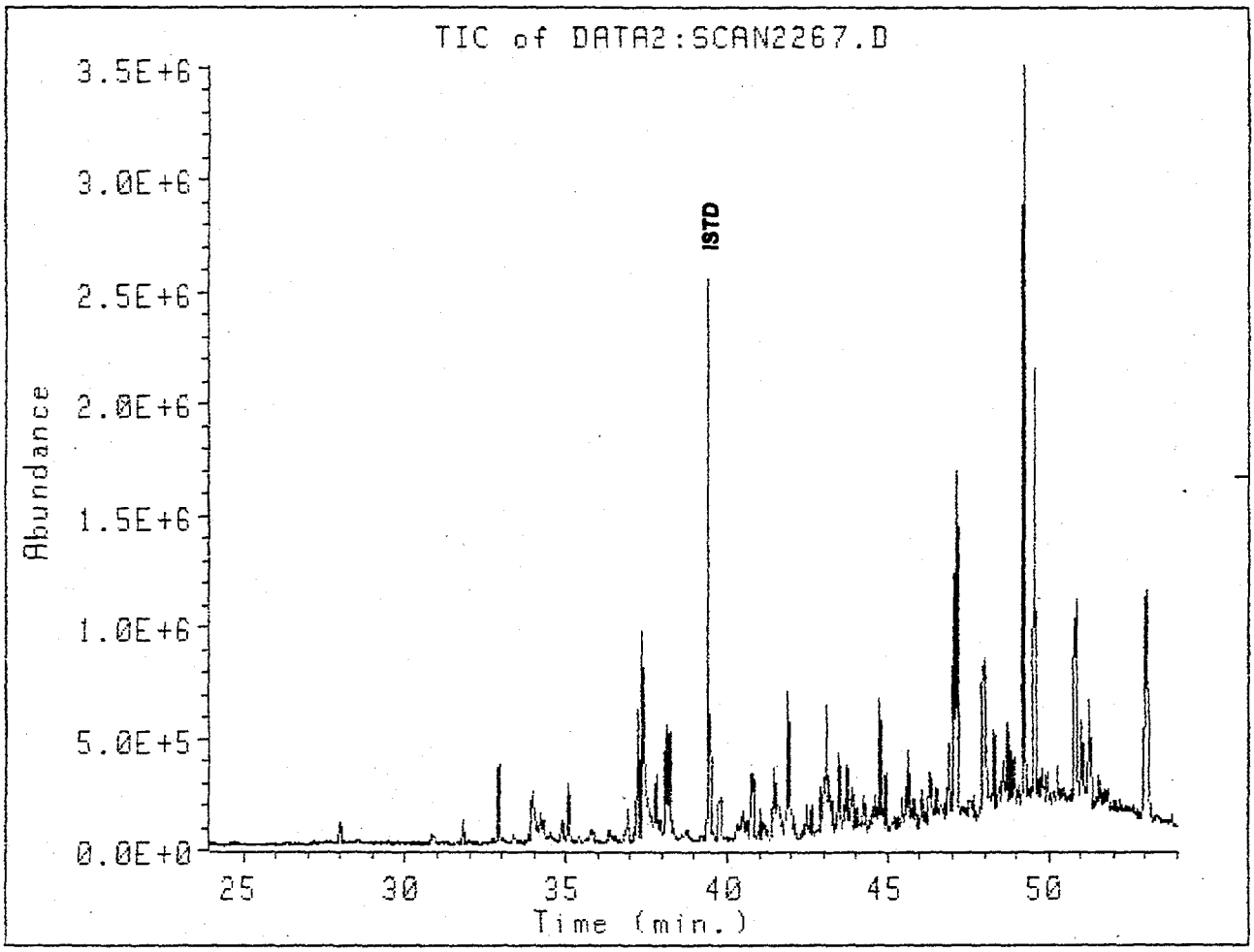

Figure 9. Total-ion-current chromatogram of 6-h chamber sample of VOC emissions from dealer-supplied sponge-rubber carpet cushion, SR3.

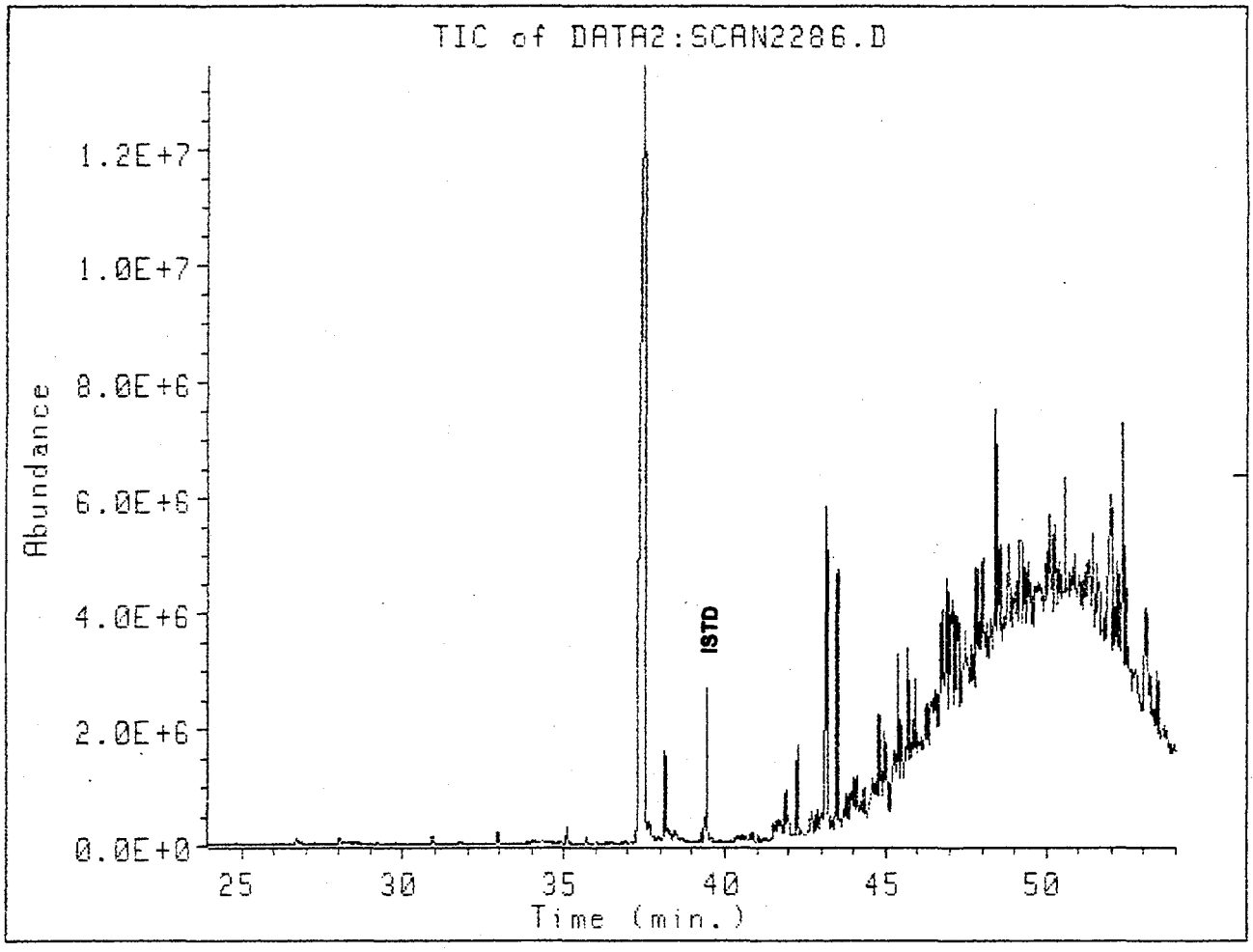

Figure 10. Total-ion-current chromatogram of 6-h chamber sample of VOC emissions from manufacturer-supplied bonded-urethane carpet cushion, BU2.

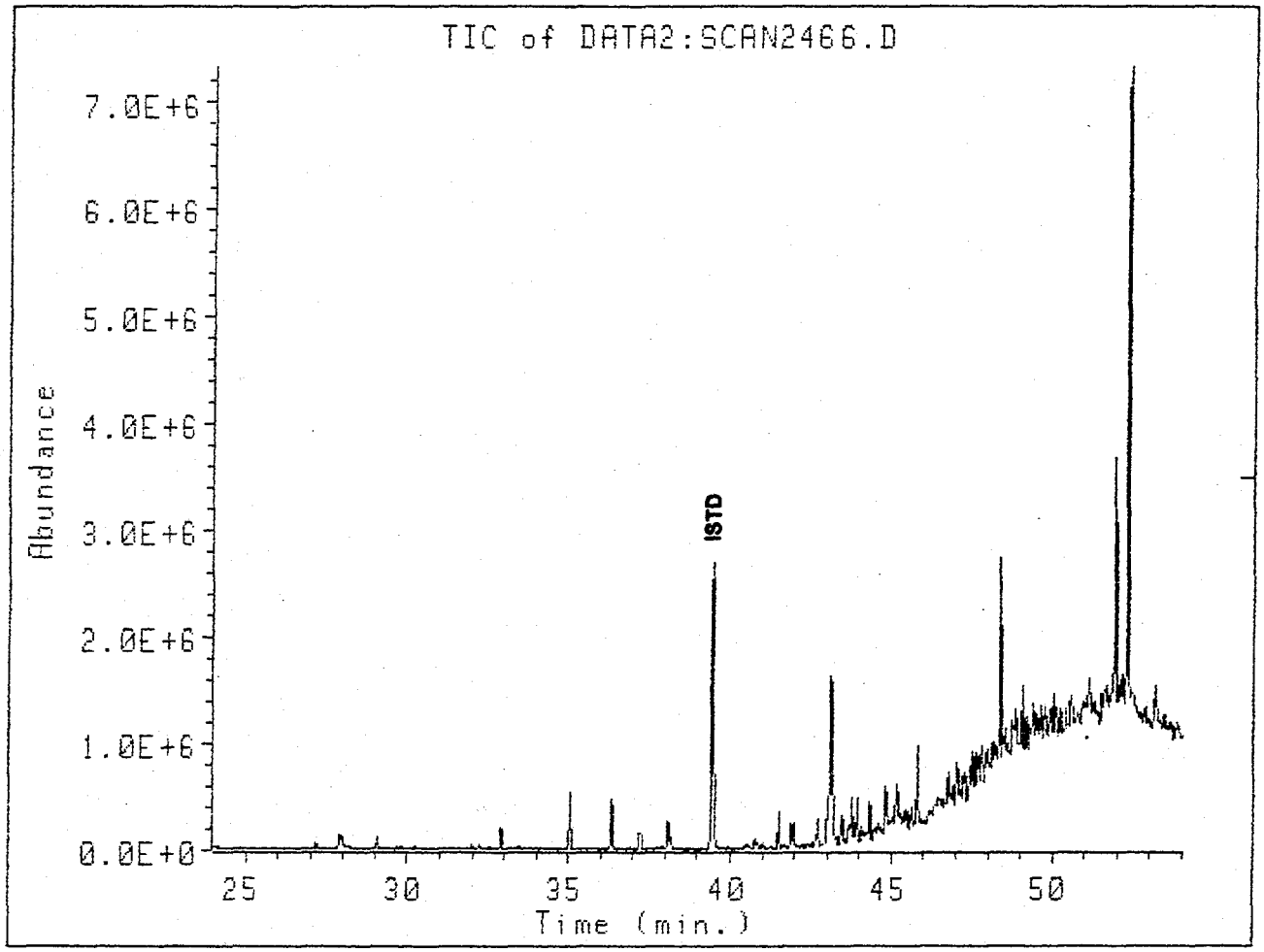

Figure 11. Total-ion-current chromatogram of 6-h chamber sample of VOC emissions from manufacturer-supplied bonded-urethane carpet cushion, BU3.

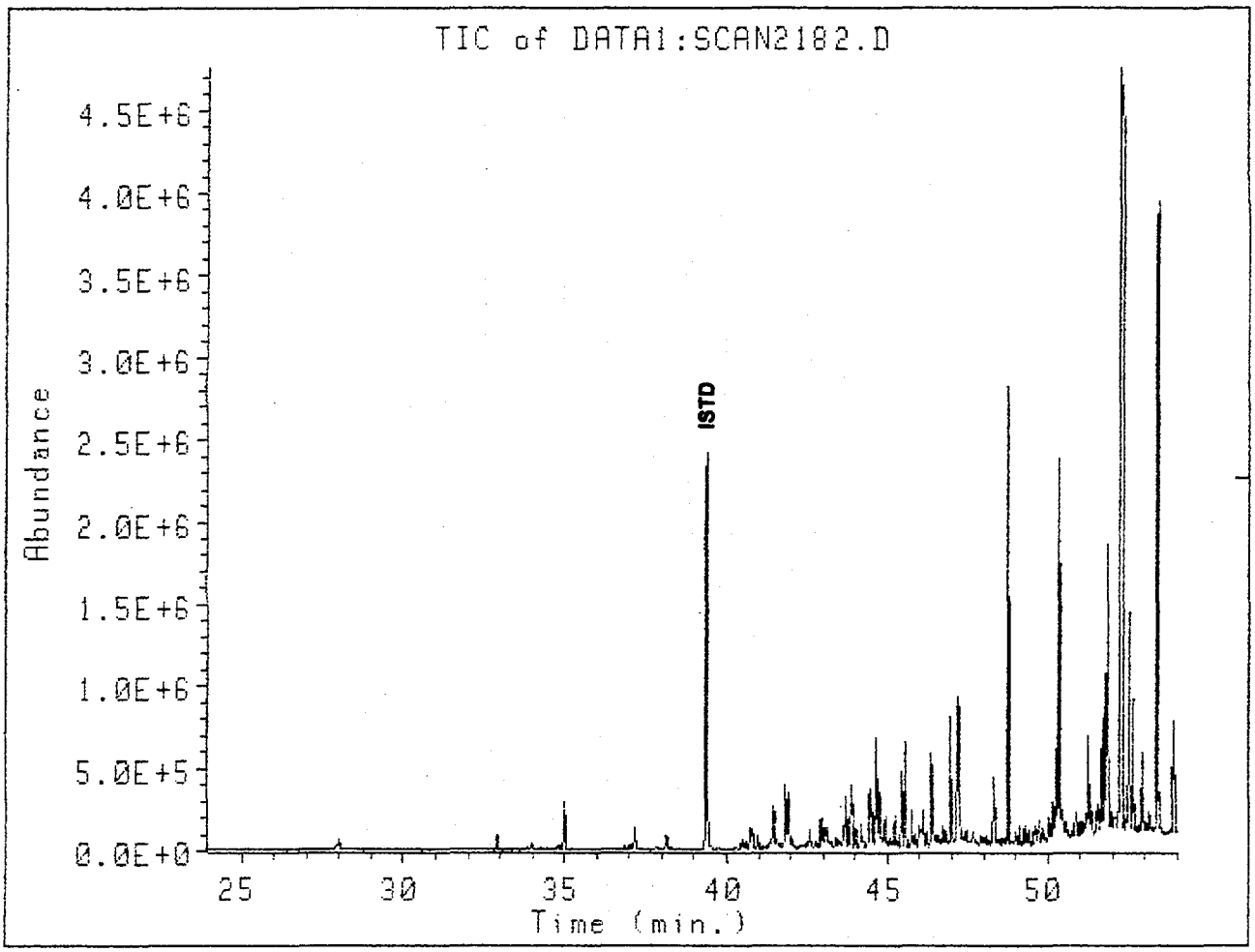

Figure 12. Total-ion-current chromatogram of 6-h chamber sample of VOC emissions from manufacturer-supplied bonded-urethane carpet cushion, BU1.

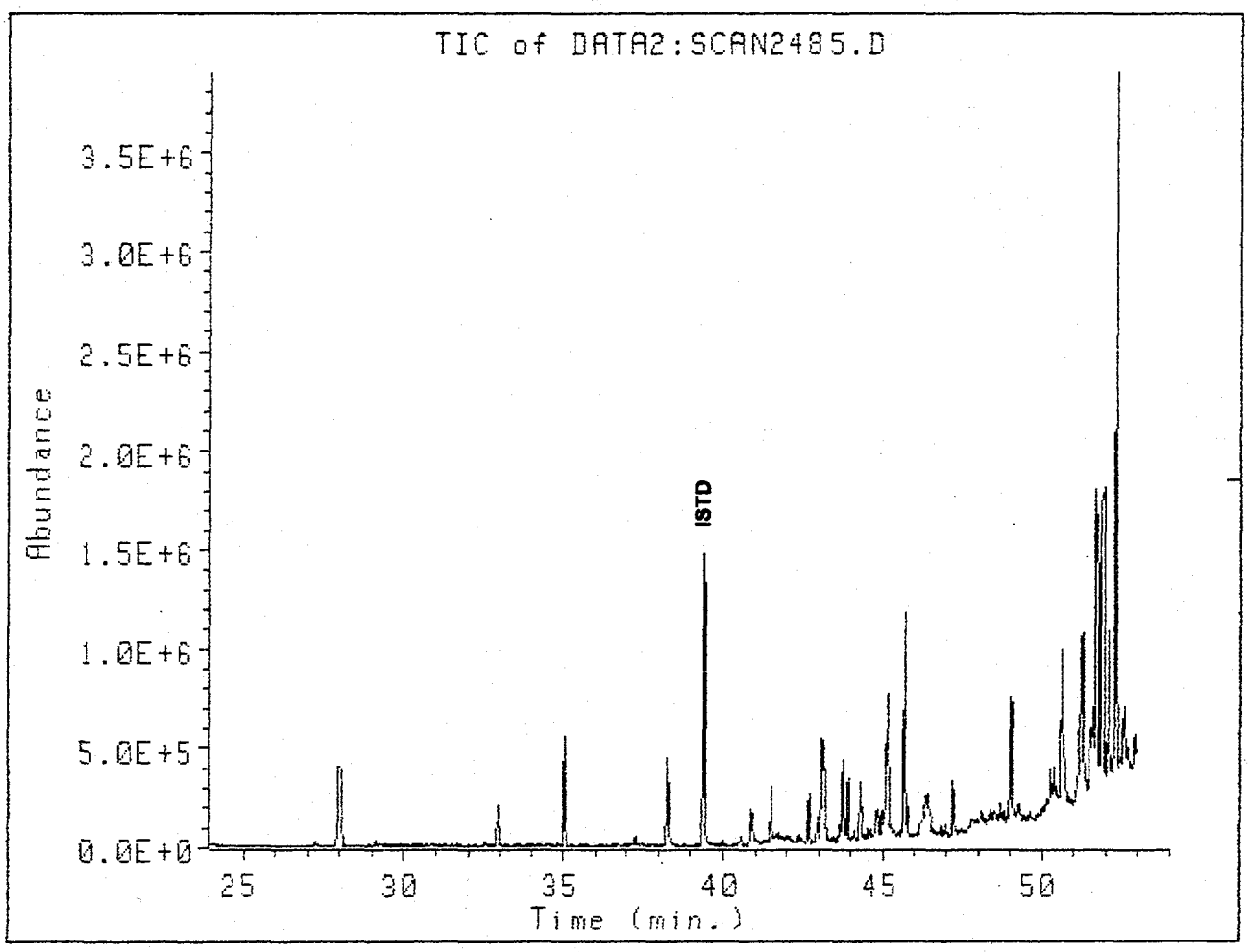

Figure 13. Total-ion-current chromatogram of 6-h chamber sample of VOC emissions from dealer-supplied bonded-urethane carpet cushion, BU4.

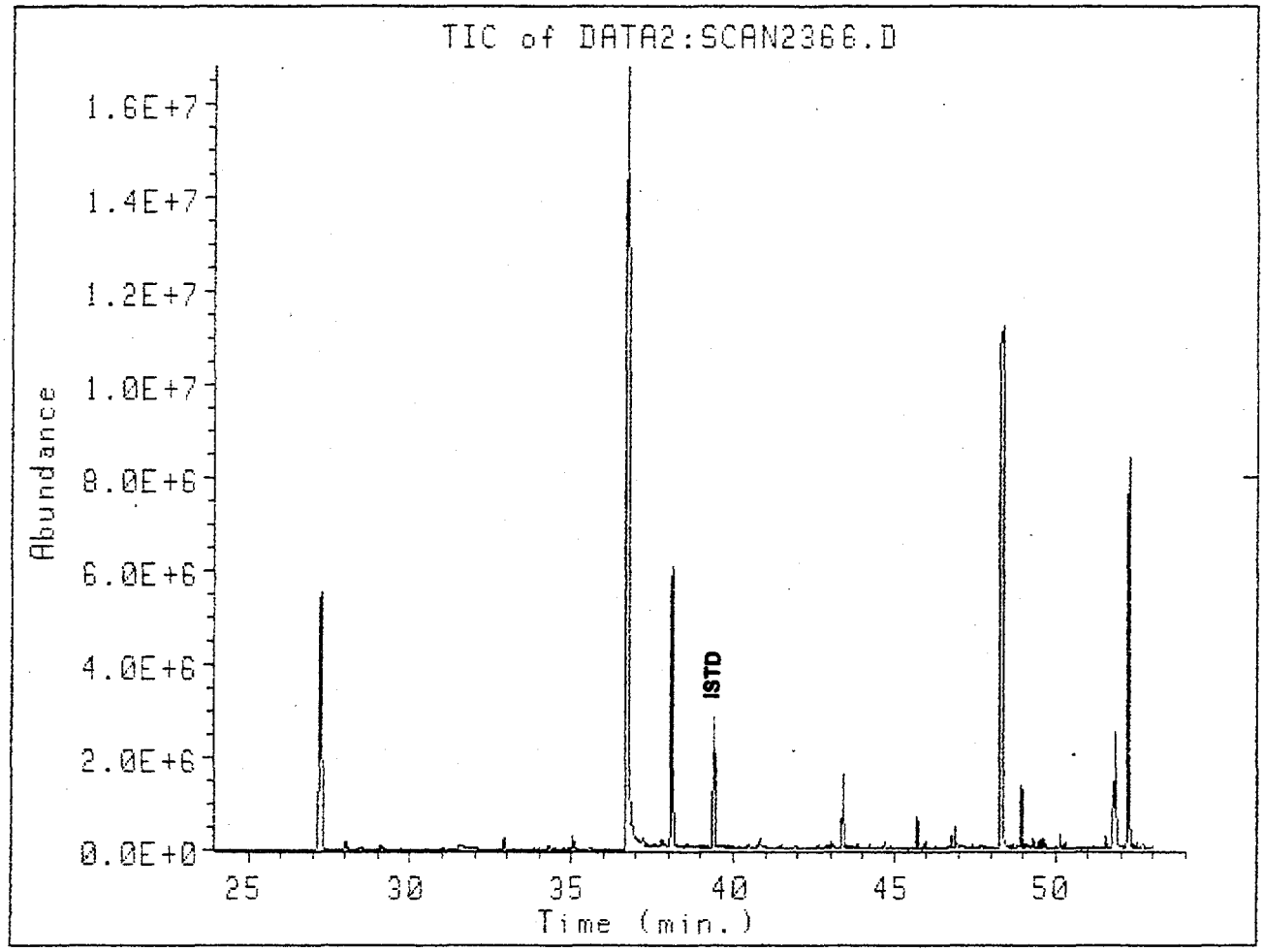

Figure 14. Total-ion-current chromatogram of 6-h chamber sample of VOC emissions from manufacturer-supplied prime-polyurethane carpet cushion, PU1.

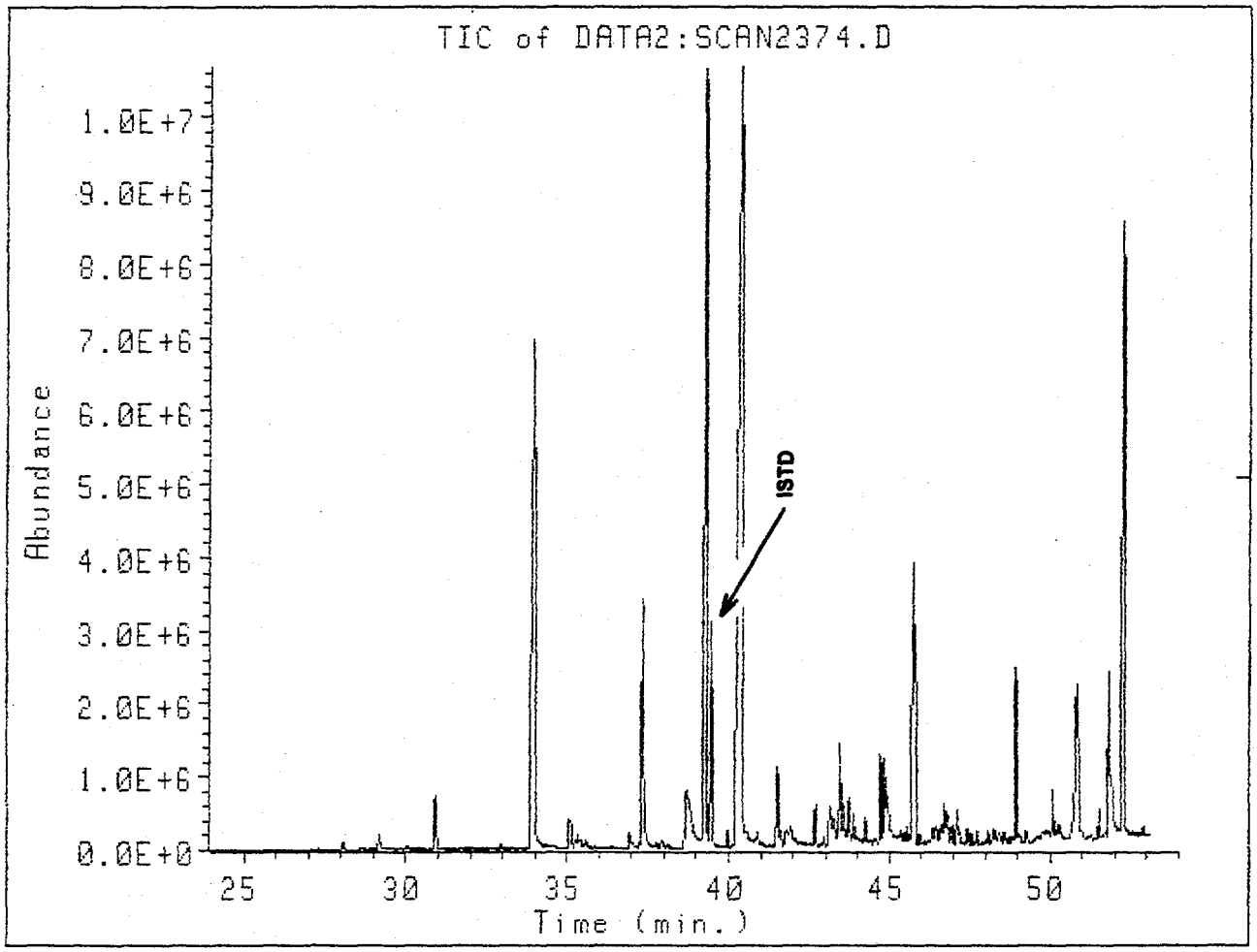

Figure 15. Total-ion-current chromatogram of 6-h chamber sample of VOC emissions from manufacturer-supplied prime-polyurethane carpet cushion, PU2.

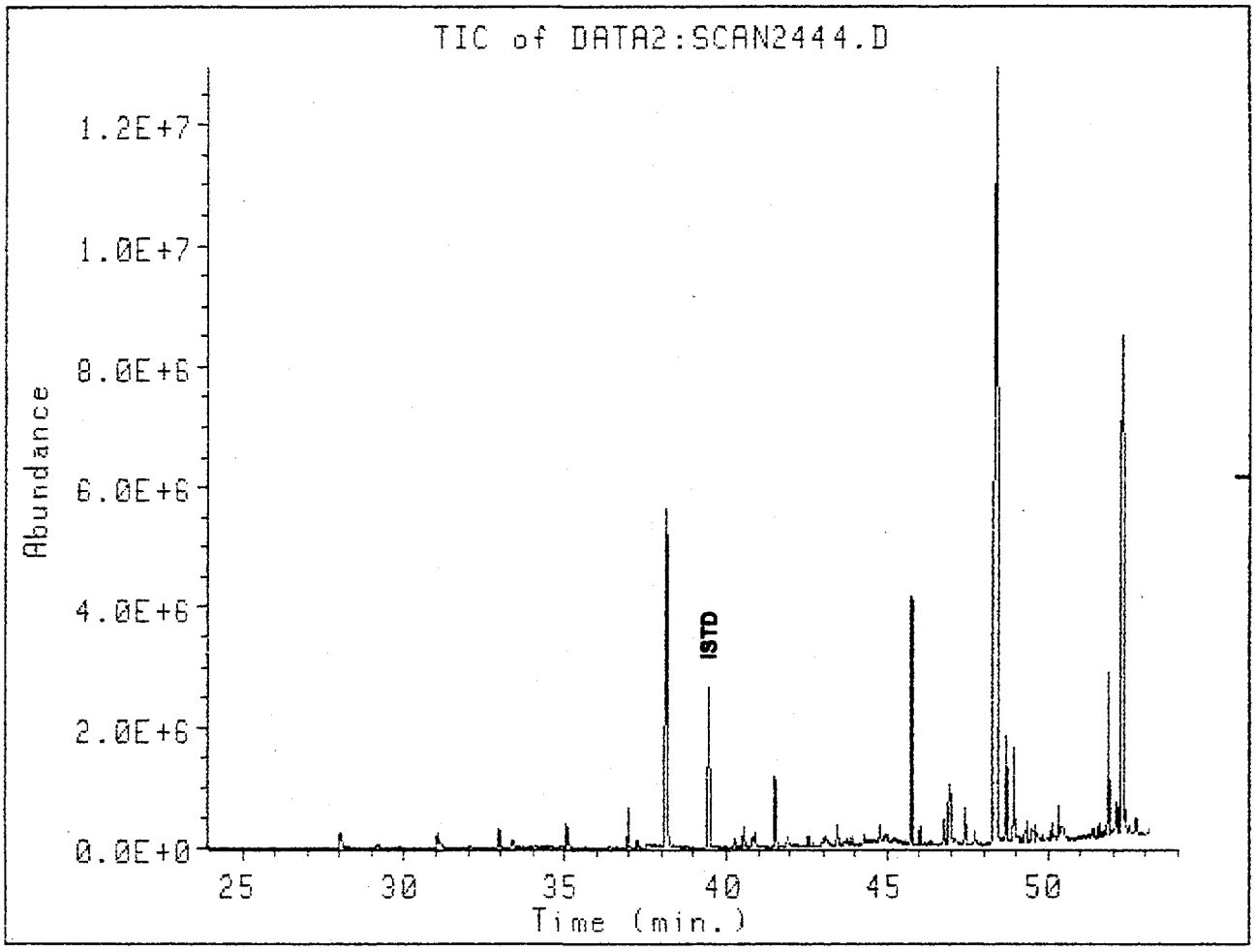

Figure 16. Total-ion-current chromatogram of 6-h chamber sample of VOC emissions from dealer-supplied prime-polyurethane carpet cushion, PU3.

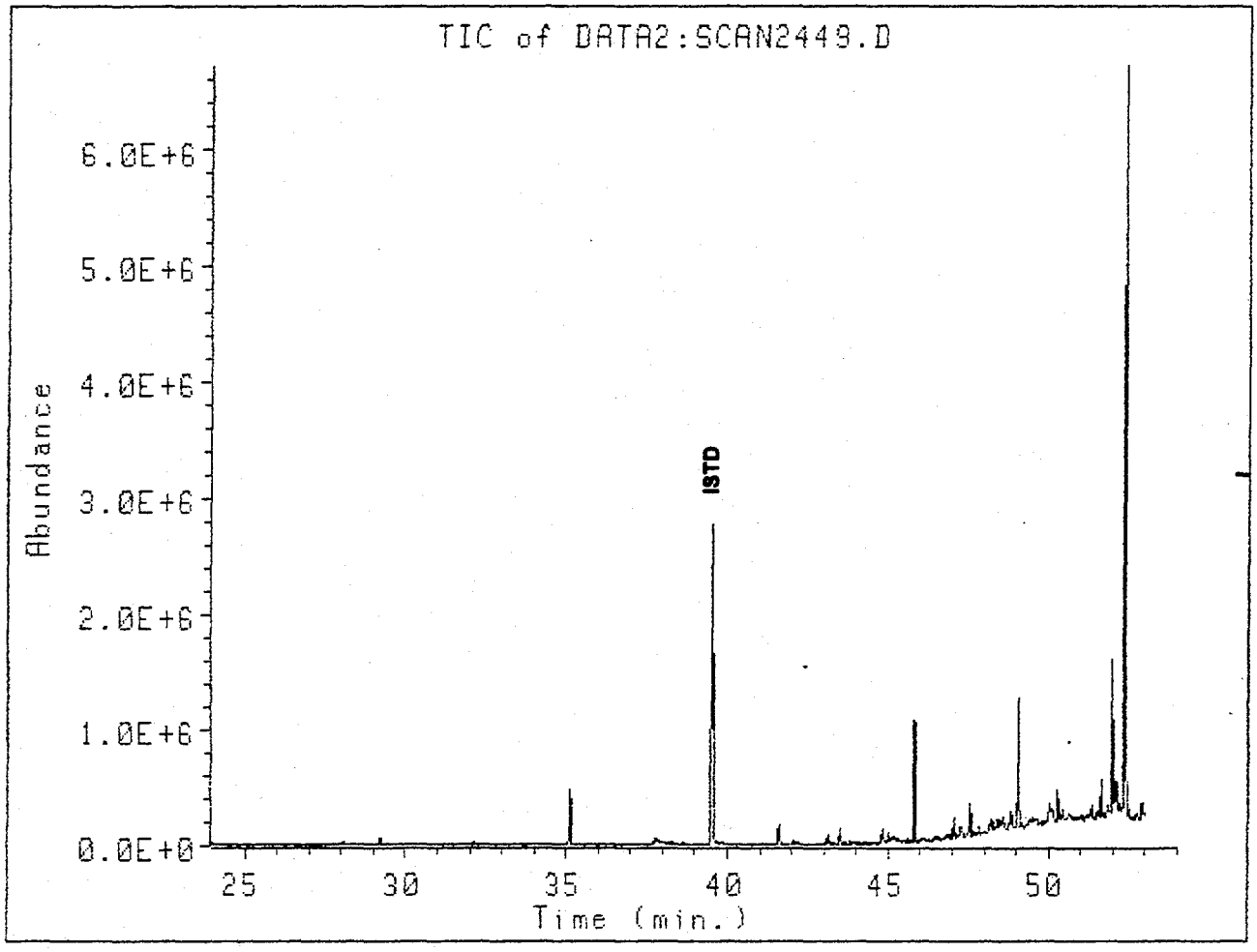

Figure 17. Total-ion-current chromatogram of 6-h chamber sample of VOC emissions from dealer-supplied prime-polyurethane carpet cushion, PU4.

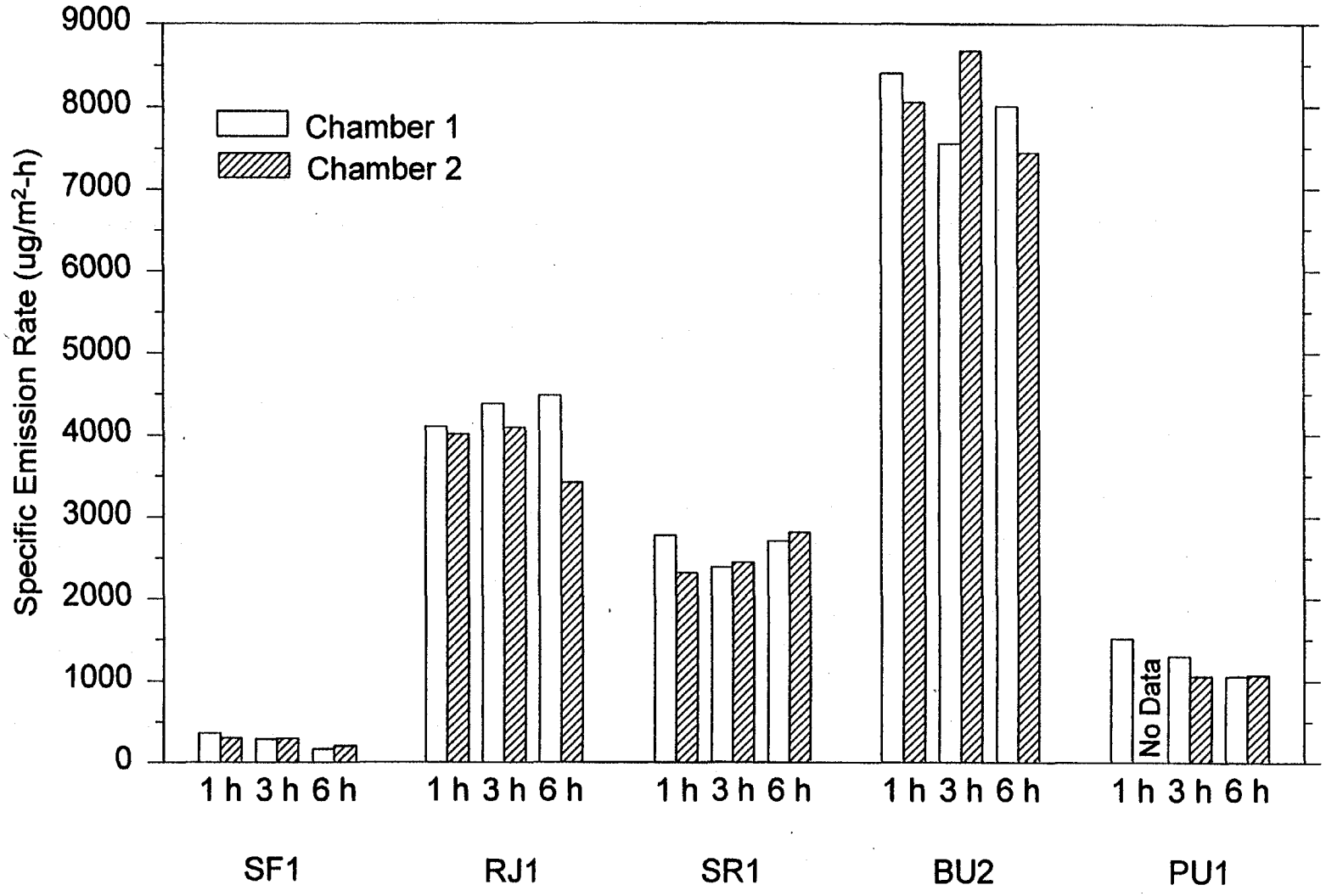

Figure 18. Comparison of duplicate measurements of specific emission rates of TVOC (μg m^{-2} h^{-1}) for synthetic-fiber (SF), rubberized-jute (RJ), sponge-rubber (SR), bonded-urethane (BU), and prime-polyurethane (PU) carpet cushions. Measurements were made in 4-L chambers at elapsed times of 1, 3 and 6 h.

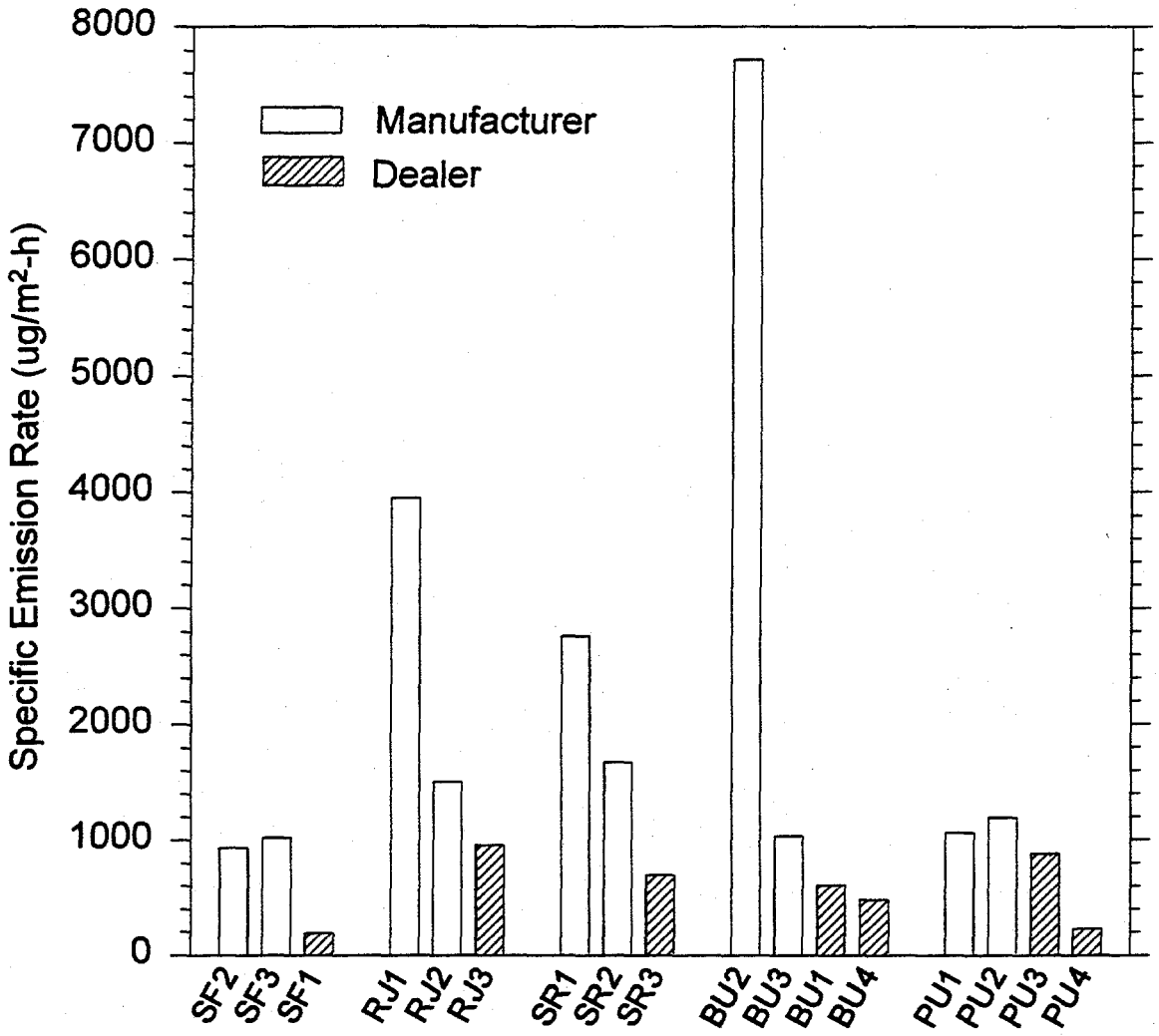

Figure 19. Specific emission rates of TVOC (μg m^{-2} h^{-1}) for synthetic-fiber (SF), rubberized-jute (RJ), sponge-rubber (SR), bonded-urethane (BU), and prime-polyurethane (PU) carpet cushions. Cushion samples were obtained from manufacturers and dealers. Measurements were made in 4-L chambers at 6-h elapsed time.

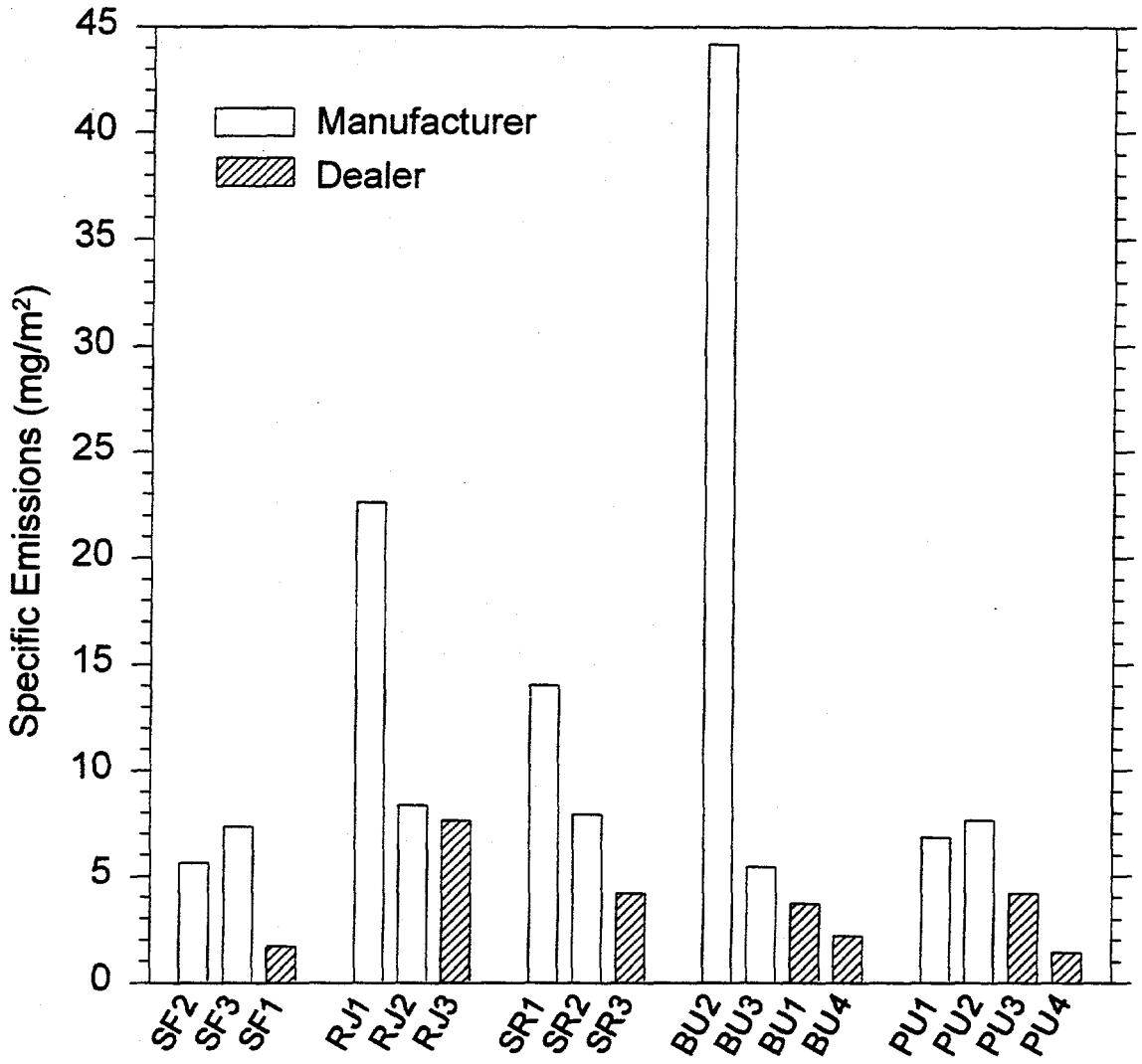

Figure 20. Estimated specific emissions of TVOC (mg m^{-2}) for synthetic-fiber (SF), rubberized-jute (RJ), sponge-rubber (SR), bonded-urethane (BU), and prime-polyurethane (PU) carpet cushions maintained in 4-L chambers for 6 h. Cushion samples were obtained from manufacturers and dealers.

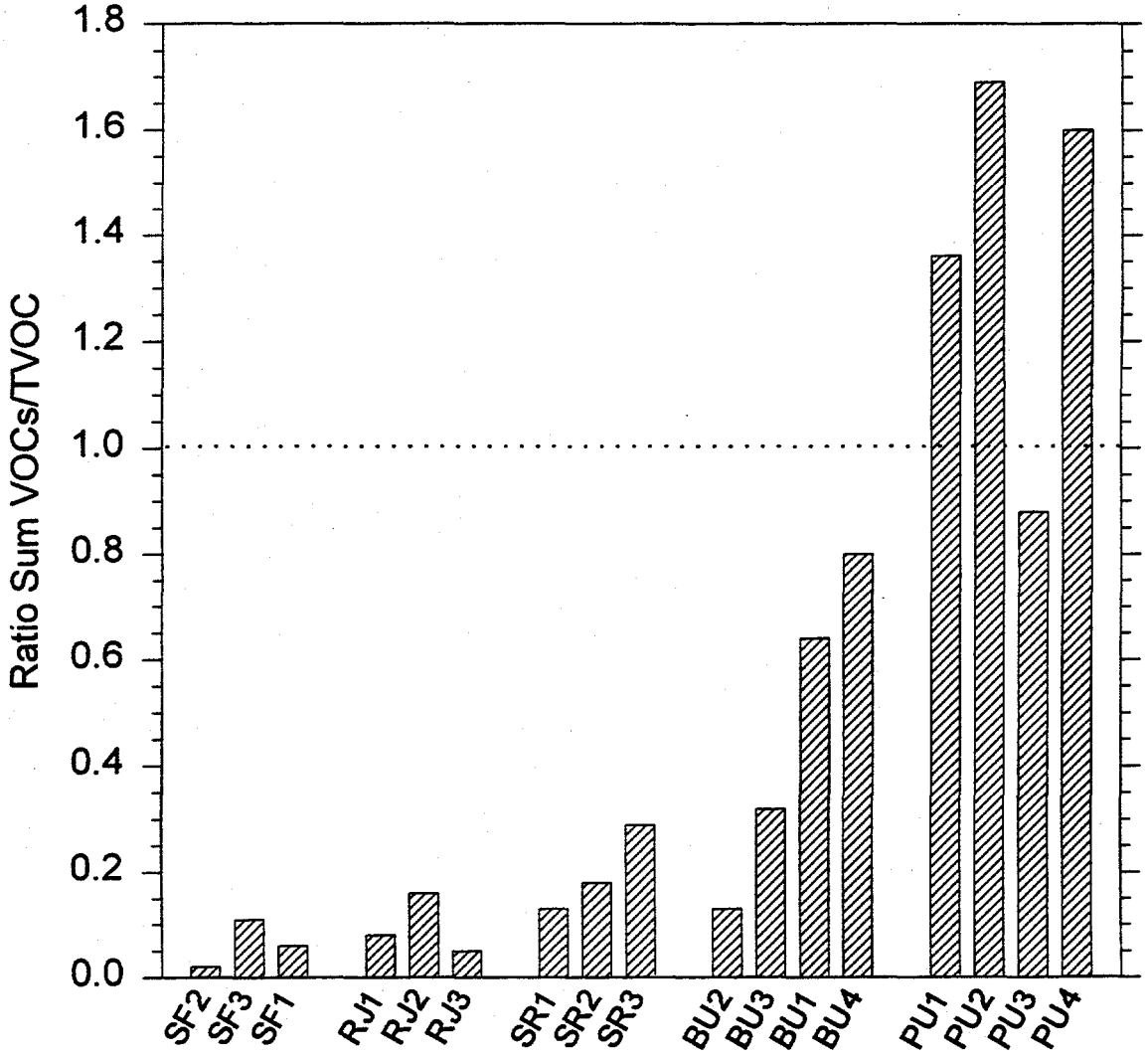

Figure 21. Ratios of the sum of individually-quantified VOCs to TVOC for synthetic-fiber (SF), rubberized-jute (RJ), sponge-rubber (SR), bonded-urethane (BU), and prime-polyurethane (PU) carpet cushions. Measurements were made in 4-L chambers at 6-h elapsed time.