

The Petroleum-Laced Background

REFERENCE: Lentini JJ, Dolan JA, Cherry C. The petroleum-laced background. *J Forensic Sci* 2000;45(5):968–989.

ABSTRACT: Using passive headspace concentration (ASTM E-1412) and gas chromatographic/mass spectrometric (GC/MS) analysis as described in ASTM E-1618, the authors have studied the volatile components detectable in several kinds of otherwise uncontaminated substrata, including clothing, shoes, household products, building materials, paper products, cardboard, and adhesives. Due to the use of petroleum-derived liquids in the manufacture of these materials, it is frequently possible to detect the liquids, even when the products are several years old. These results point out the need for the use of comparison samples whenever possible.

KEYWORDS: forensic science, criminalistics, fire debris, gas chromatographic analysis, mass spectrometry, petroleum solvents, comparison samples

Adsorption/elution methods for separation and concentration of ignitable liquid residues from fire debris samples, particularly passive headspace concentration as described in ASTM E-1412 (1), are very popular because of their simplicity and because of the non-destructive nature of the separation procedure. More than half of all laboratories participating in recent CTS proficiency tests used some type of passive headspace concentration (2).

Passive headspace concentration is sensitive over a wide range of molecular weights, although fractionation has been shown to occur, depending on the adsorption temperature, somewhere in the neighborhood of C_{20} (3). Incomplete recovery of higher molecular weight compounds causes this fractionation, which can result in data being skewed toward lower molecular weight compounds. In most cases, however, the goal of the analyst is to separate low molecular weight petroleum-based solvents from the substrate, and then determine whether the volatile materials are part of the substrate or part of an ignitable liquid from a separate source. As our ability to detect ever-smaller quantities of petroleum-derived substances improves, our responsibility for providing appropriate interpretations of results increases.

Interference from background materials falls into two basic categories: actual liquid petroleum products that are present in the substrate material, and substrate materials that pyrolyze to form interfering volatile compounds in the range of common ignitable liquids. Previous work has revealed that many items used in homes and buildings are made of synthetic materials that, when exposed to fire conditions, will produce volatile pyrolyzates in the boiling point of range of commonly encountered ignitable liquids

(4–7). Early research focused primarily on the latter category, and studied the pyrolyzates of common building materials such as wood, carpet, and floor tile (6–11). More recent work by Keto (12) discussed the pyrolysis of polyethylene and the similarities between its chromatographic pattern and that of heavy petroleum distillate residues. Phelps, et al. discussed methods for isolating low molecular weight alcohols and acetone from fire debris, but cautioned that these substances were detected in samples of burned debris that had not had these compounds added (13). Each of these studies showed that while pyrolyzates can complicate the identification of ignitable liquids, a careful examination of the data by an experienced analyst could usually differentiate pyrolyzates from ignitable liquids. These works demonstrated the value of control or comparison samples for cases in which the interpretation of the chromatographic or mass spectral data is not straightforward.

Of equal concern to the fire debris analyst are materials that contain petroleum distillates or petroleum-derived solvents. Lentini raised this concern in a paper entitled “Incidental Accelerants,” which discussed the widespread use of kerosene in household products (14). Other research into the presence of petroleum products inherent to the typical fire environment has been scarce. Lentini and Waters discussed the problems associated with the similarity in chromatographic patterns of asphalt pyrolyzates and heavy petroleum distillates (15). A later work described methods for differentiating them from one another (3). Other work on background petroleum products focused on the presence of solvents recovered from shoes, which is a cause for concern as suspects’ shoes are a commonly submitted item in arson investigations (16). Much of the knowledge regarding substrates containing petroleum products of interest has been passed on to fire debris analysts by word-of-mouth. Veteran analysts can provide trainees with this knowledge, and information can be informally exchanged at scientific meetings, but there is little published research that focuses on this subject.

It is the aim of this paper to provide the analyst a reference source that can provide information about petroleum products commonly detected in samples in which there is no foreign ignitable liquid.

Materials and Methods

Sample Preparation

Samples were placed in clean one-quart or one-gallon polyester-lined paint cans, which had been previously baked at 90°C for 16 h. One-third (approximately 7 by 10 mm) of a Pro-Tek strip (Albrayco Laboratories, Inc., Cromwell, CT) was suspended in each can, and the temperature was raised to 80°C for a period of 16 h. The strips were then removed and placed in autosampler vials and extracted with 0.5 mL of diethyl ether, which had been spiked to a

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Received 16 July 1999; and in revised form 5 Nov. 1999, accepted 22 Nov. 1999.

level of 100 ppm with tetrachloroethylene. The ether solutions were then analyzed by GC/MS.

GC/MS Operating Parameters

All samples were run on a Hewlett-Packard (HP) 5890 Series II gas chromatograph connected to an HP Model 5971A mass selective detector. Data analysis was accomplished using HP ChemStation software. The column was a 25 m HP 1, 0.2 mm ID, 0.5 micron film thickness, operated at an initial temperature of 60°C for 6 min, ramped at 20°C per minute to 280°C, and held at 280°C for 4 min. One microliter samples were injected splitless, using an HP Model 7671 Automatic Liquid Sampling System. Ions were scanned from 33 to 300 AMU. In some cases, a selected ion monitoring (SIM) detection mode was used to reduce noise and improve the appearance of extracted ion profiles. The use of the SIM technique for fire debris analysis has been previously described by Lentini (17).

The splitless injection technique was used for all samples to ensure maximum sensitivity. For the more concentrated samples, this resulted in some loss of resolution, particularly for those compounds with shorter retention times.

Results

Household Products

Figure 1 shows the total ion chromatograms of a variety of household products, including furniture and shoe polishes, spray lubricant, and insecticide. The solvents present in these products range from Class 3, medium petroleum distillate (MPD), through Class 5, heavy petroleum distillate (HPD). Although one might find a container at the fire scene indicating a potential source for a solvent detected in a sample, this is not always the case.

Clothing and Fibers

Some fabrics labeled "100% cotton" were observed to produce more than baseline chromatograms. Figure 2 shows the results of tests on several different types of new, unused cloth and fibers. The terry cloth towel in the top chromatogram and the t-shirt both exhibited a homologous series of straight chain aldehydes ranging from C₇ to C₁₀. These aldehydes are easily distinguishable from a series of normal alkanes. The printed t-shirt also revealed the presence of toluene. A pair of boy's pajamas, also labeled "100% cotton," contained a series of alkanes in the kerosene range, and when an extracted ion profile was prepared of ion 105, a C₃-alkylbenzene pattern typical of gasoline was observed (not shown). Other groups of compounds necessary for an identification of gasoline were not observed, so an experienced analyst should not make a misidentification.

A pair of spandex shorts gave a strong pattern typical of kerosene. Kerosene is frequently detected in shop rags and manila rope and has also been observed in some denim fabrics, and in "100% cotton" throw rugs.

Shoes

Total ion chromatograms of several brands of shoes are shown in Fig. 3. With the exception of adhesives, no substrate tested presented more potential problems in interpretation than shoes. Most shoes contain some sort of polymer, and most are held together with some sort of adhesive. Toluene appears to be the most frequently used solvent for adhesives, having been identified in all but

one of the shoes examined. The toluene is apparently trapped in the adhesive elastomer matrix, and is only released upon heating. Despite its high volatility, toluene was detected in significant quantities, even in shoes known to be more than five years old.

Heavy petroleum distillates appear to be present in several "crepe" yellow soles. Other compounds identified in tennis shoes included diethylene glycol and butylated hydroxy toluene (BHT).

A pair of shoes for comparison would seem to be absolutely essential prior to making any decisions about the significance of petroleum products identified on shoes (16).

Paper Products

Newspapers have long been known by fire debris analysts to contain medium to heavy petroleum distillates, yet a search of the literature failed to turn up any published references. Figure 4 shows the alkane ion profile (ion 57) of eight different samples of newsprint. The last sample, a yellow pages telephone directory, was five years old when it was analyzed, demonstrating the persistence of the heavy petroleum distillate. All of these sources of newsprint contain solvents that meet ASTM E-1387 criteria for identification as a heavy petroleum distillate (5).

Magazines were also found to contain substances that produced patterns typical of kerosene as well as isoparaffins and some aromatics. Total ion chromatograms from several magazines are shown in Fig. 5.

Numerous samples of carbonless forms were examined. They were found without exception to contain mixtures of normal alkanes, similar to Exxon's Norpar[®] or a like product. Figure 6 shows the results from six carbonless forms, as well as a sample of Lamplight Farms Ultrapure Lamp Oil, which also consists entirely of normal alkanes.

The printing on the second and subsequent pages of carbonless forms is made visible when two colorless components are brought together to form a highly colored dye. One of the components is impregnated on the top surface of the paper where the printing will appear, and the other component is contained in microspheres full of the dye component and the normal alkane solvent. These microspheres cover the entire back surface of the top form, and range in size from 2 to 20 microns. Figure 7 is a scanning electron micrograph showing the back surface of a carbonless form. These forms contain sufficient amounts of normal paraffins to give a strong signal from a single credit card receipt. Normal paraffins, along with toluene and xylenes, were also identified in paper printed with a laser jet, and in copier toner. Thermal fax paper seems to be one of the few printed paper products that does not contain large quantities of petroleum hydrocarbons. Chromatograms of the office papers are shown in Fig. 8.

Cardboard represents a special class of paper product that is likely to contain petroleum products. A series of homologous aldehydes, similar to that found in some cotton products, is common in cardboard, and may be found in other paper products as well. Compounds detected in the cardboard extracts include limonene, butyl cellosolve[®] (2-butoxyethanol), and cellosolve acetate, as well as the aldehydes. When adhesives are used to seal cardboard boxes, the chromatographic patterns become even more complex, as solvents from both the cardboard and adhesive will be present. Further discussion on the solvents commonly encountered in adhesives is included in the section on adhesives, below. Figure 9 shows five examples of cardboard containing different solvents. A stone container box sealed with adhesive from a hot glue gun contained a significant quantity of isoparaffins.

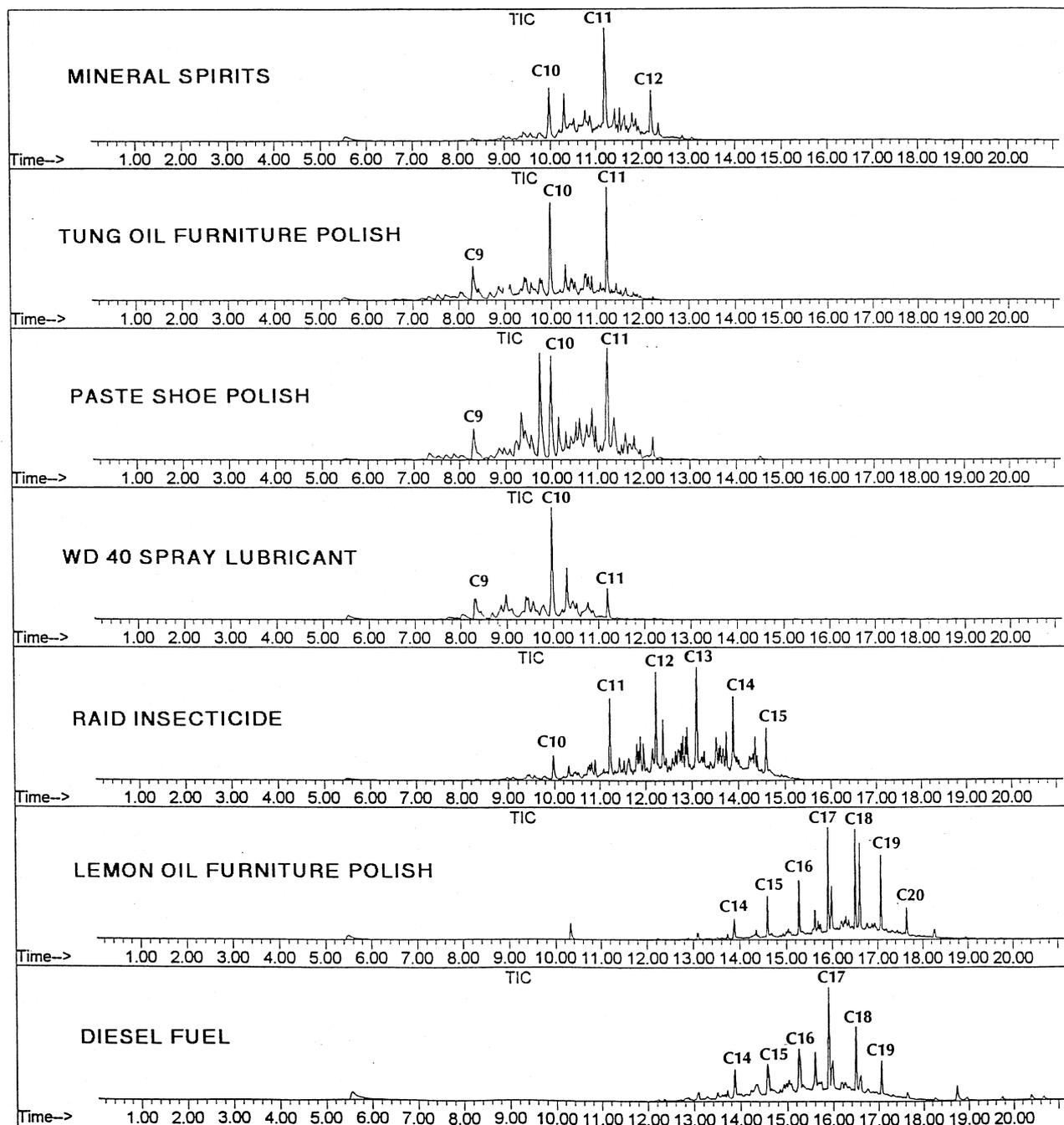


FIG. 1—Total ion chromatograms of common household products compared with mineral spirits and diesel fuel.

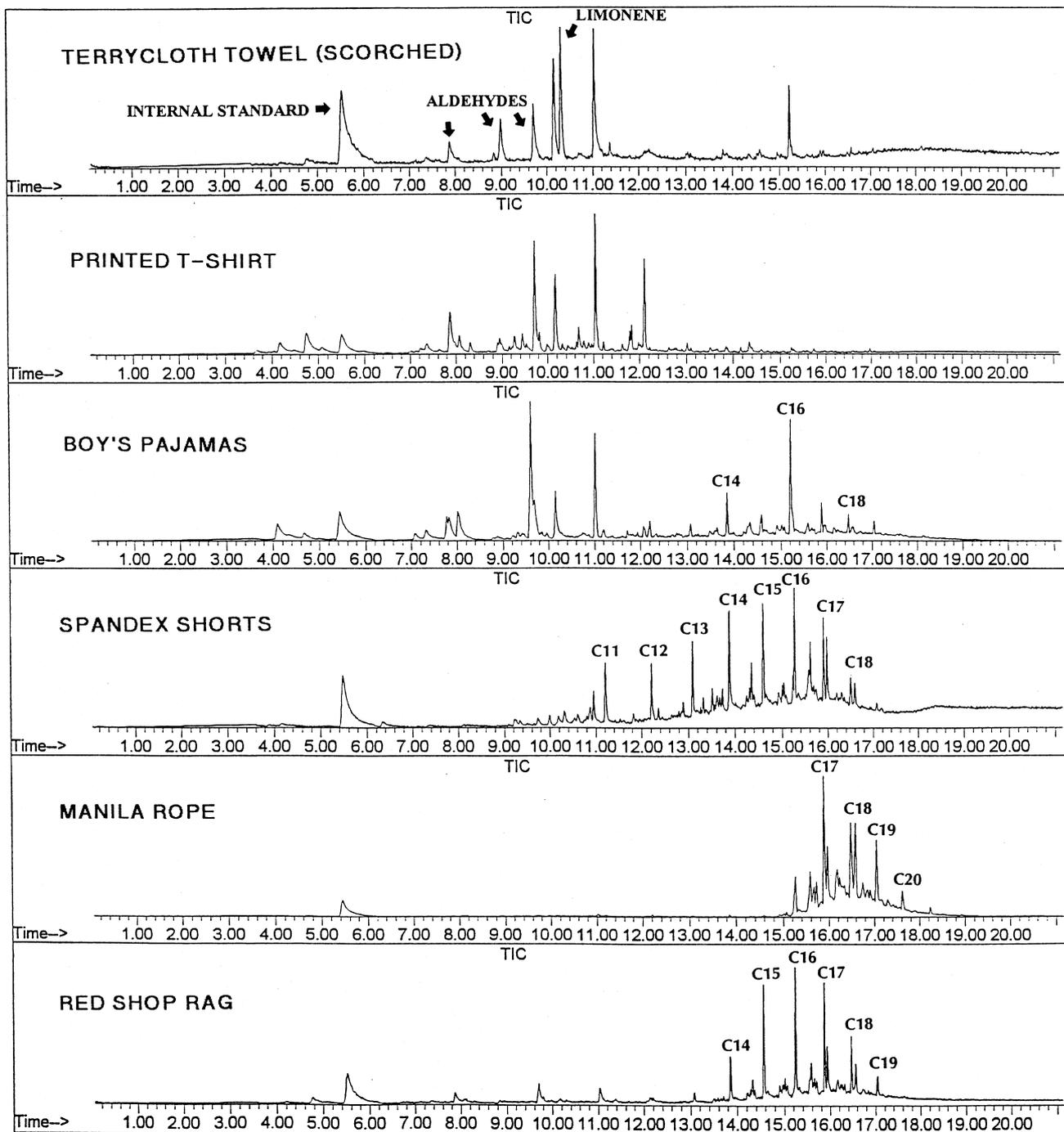


FIG. 2—Total ion chromatograms of clothing and fibers.

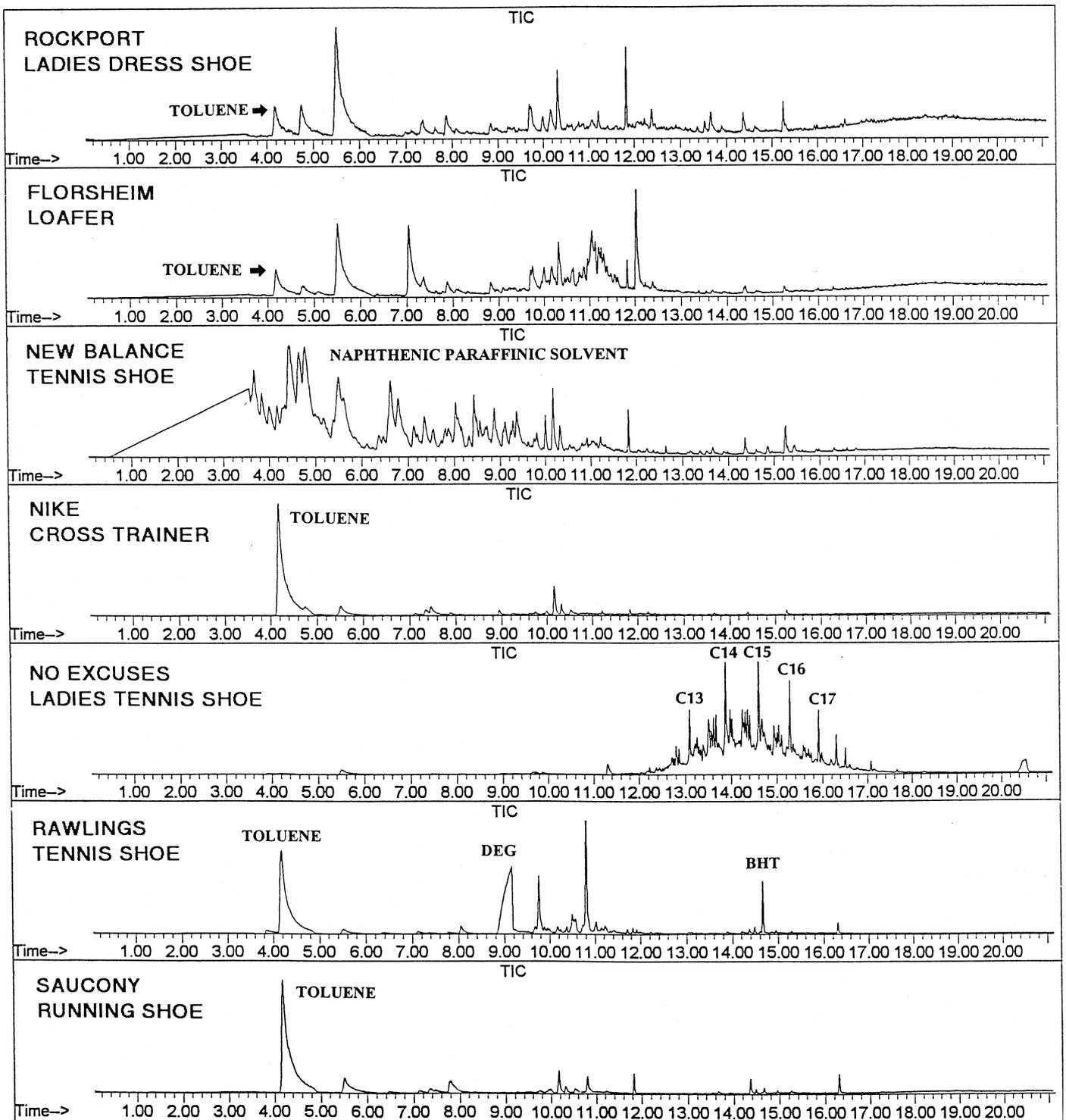


FIG. 3—Total ion chromatograms of seven brands of shoes.

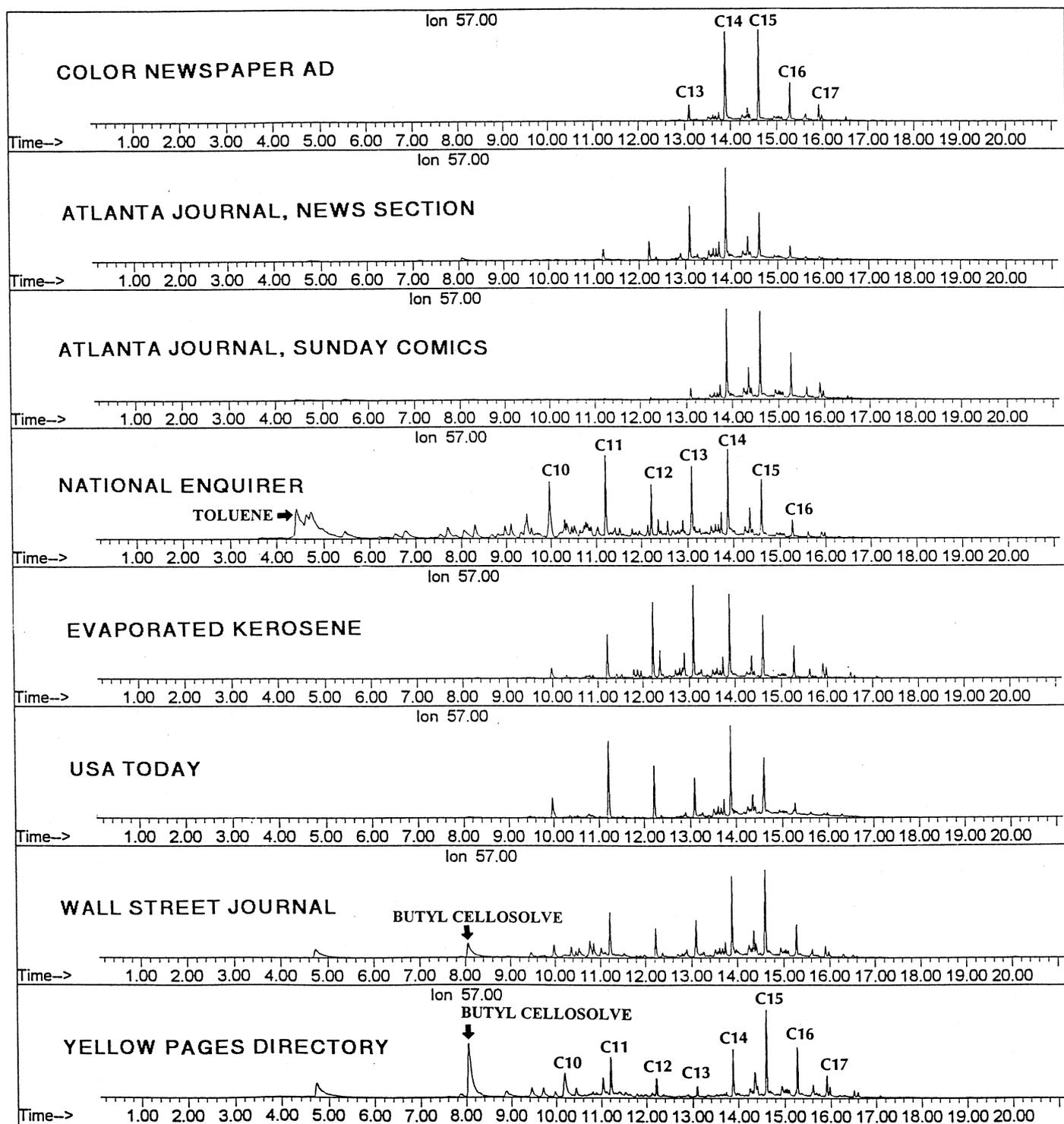


FIG. 4—Alkanes in newsprint. Ion 57 profiles of six newspapers, and a five-year-old yellow pages telephone directory compared with evaporated kerosene.

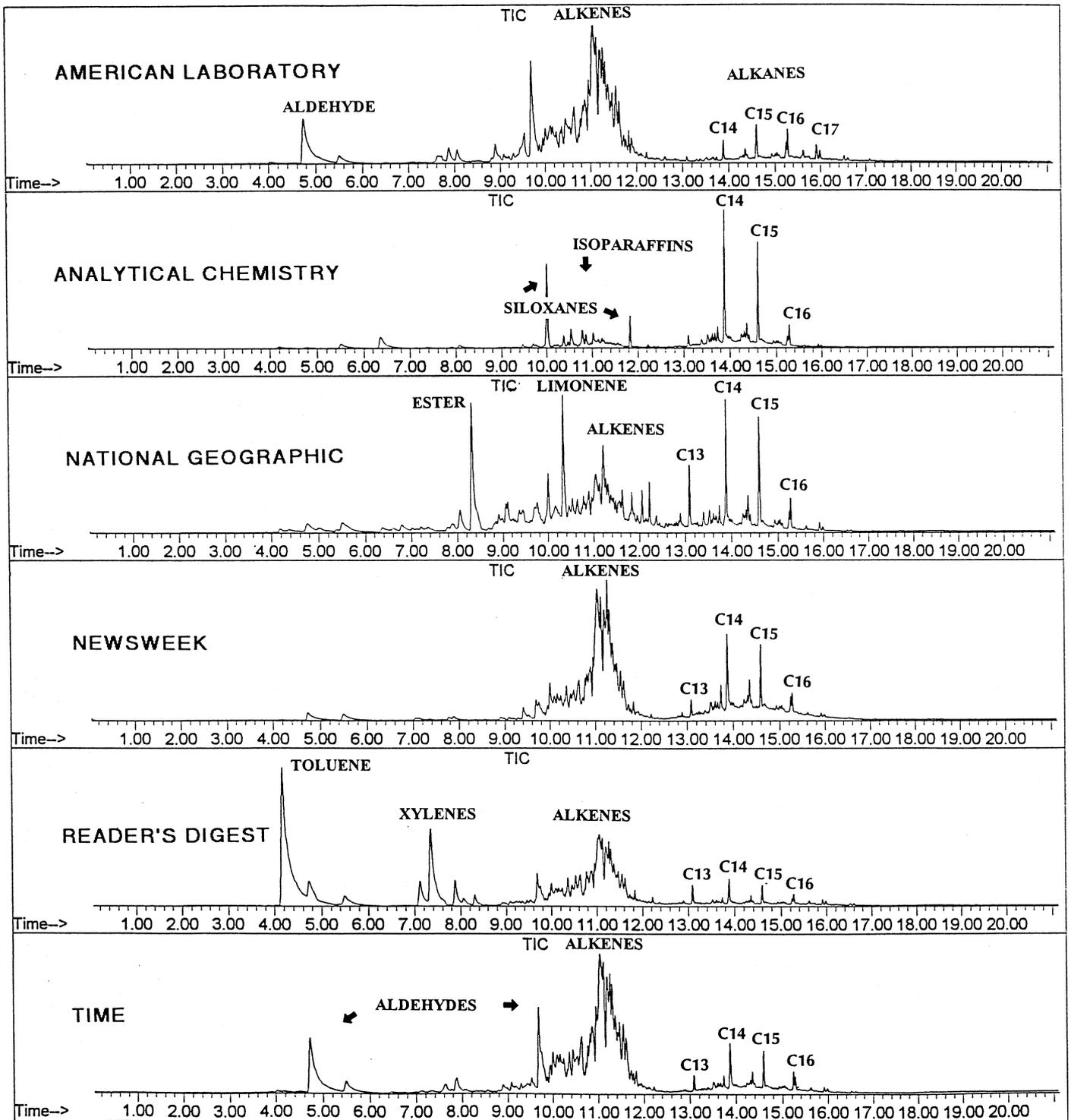


FIG. 5—Total ion chromatograms of six different magazines, showing isoparaffins, normal paraffins, and some light aromatics.

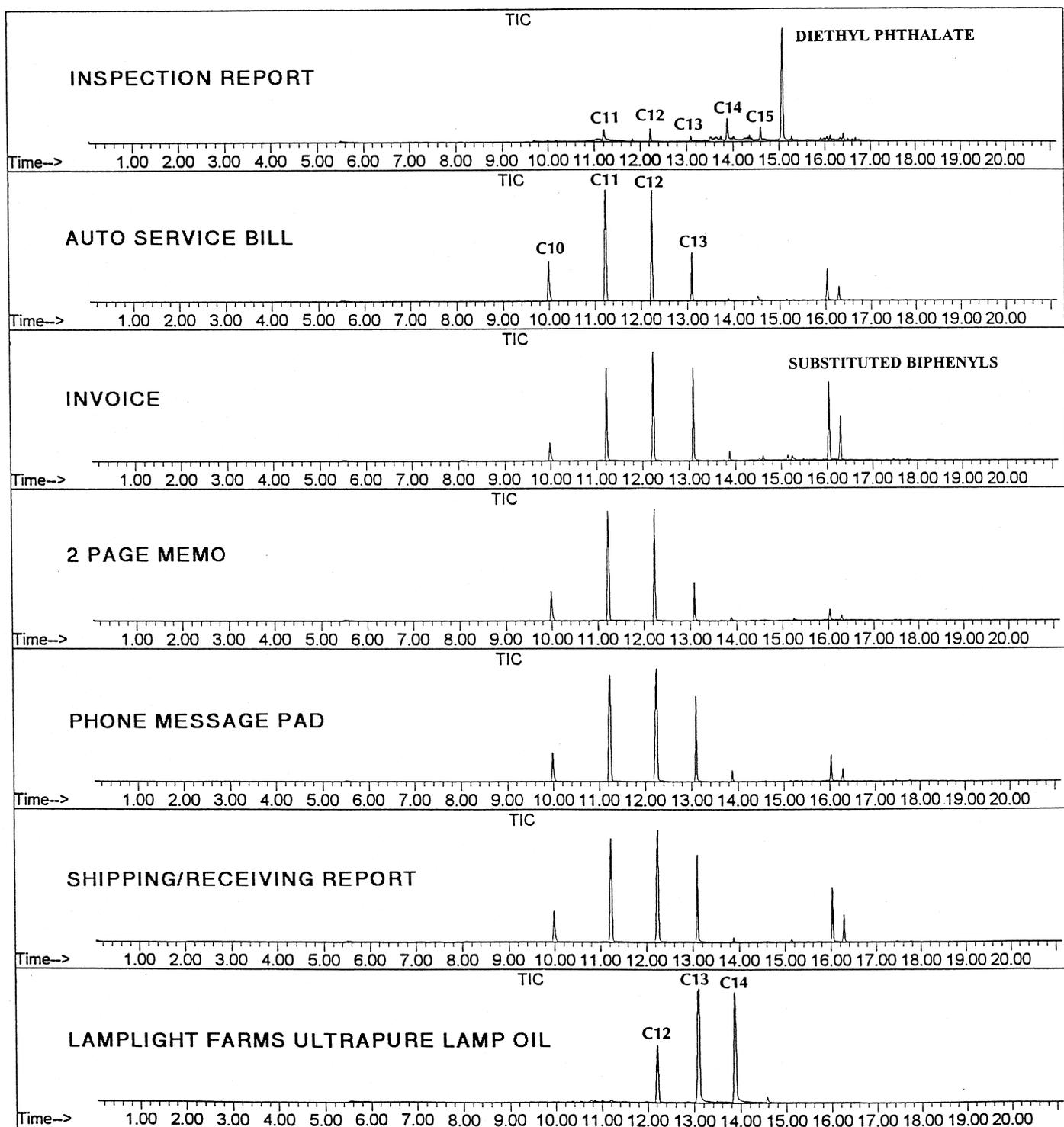


FIG. 6—Normal paraffins from carbonless forms compared with lamp light farms ultrapure lamp oil.

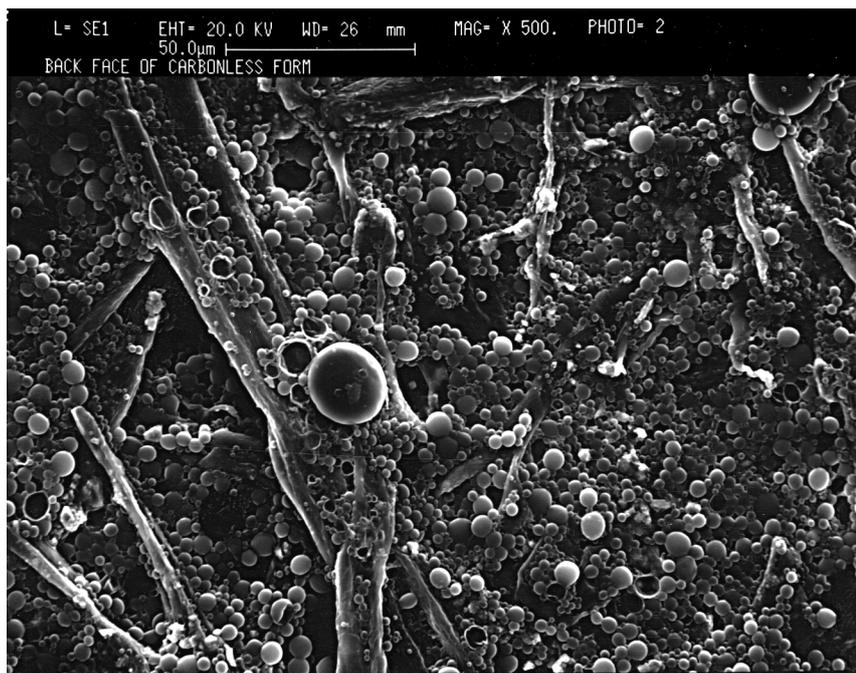


FIG. 7—Scanning electron micrograph of the back surface of a carbonless form, showing microspheres of solvent and dye (500X).

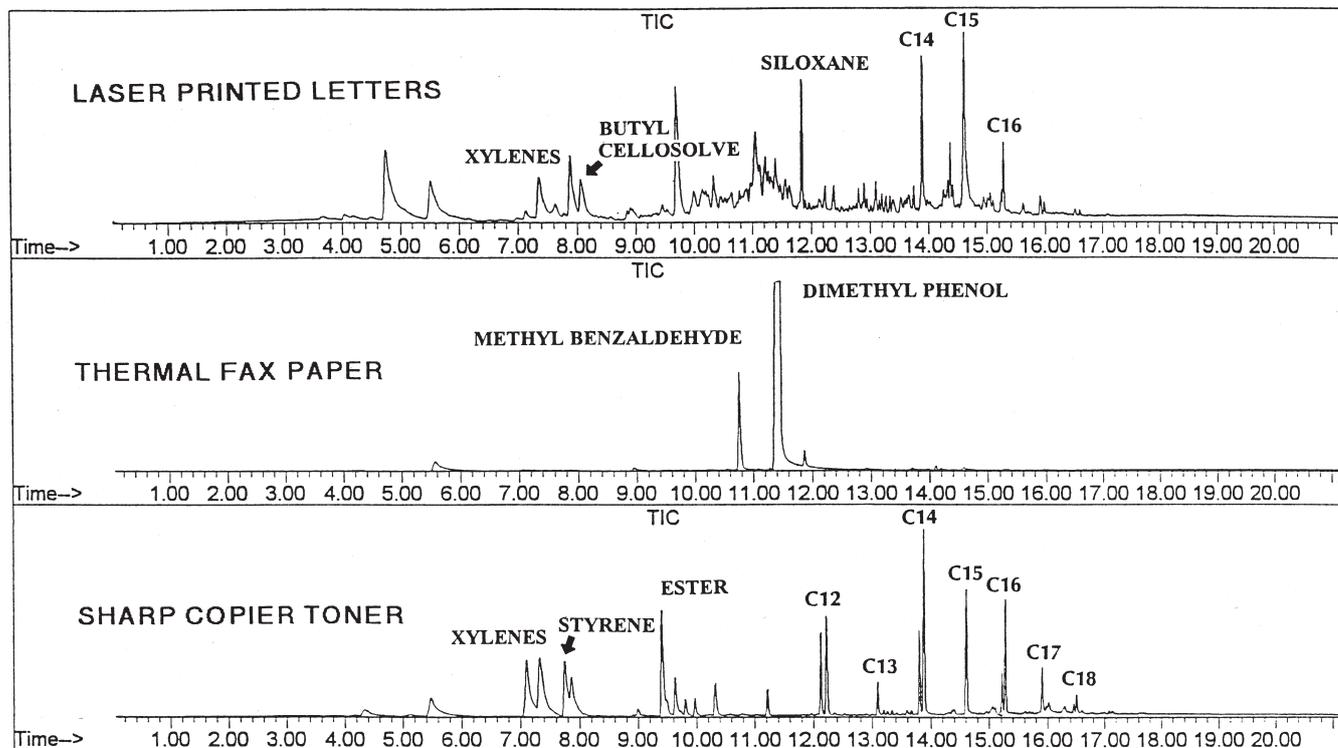


FIG. 8—Total ion chromatograms of common office papers.

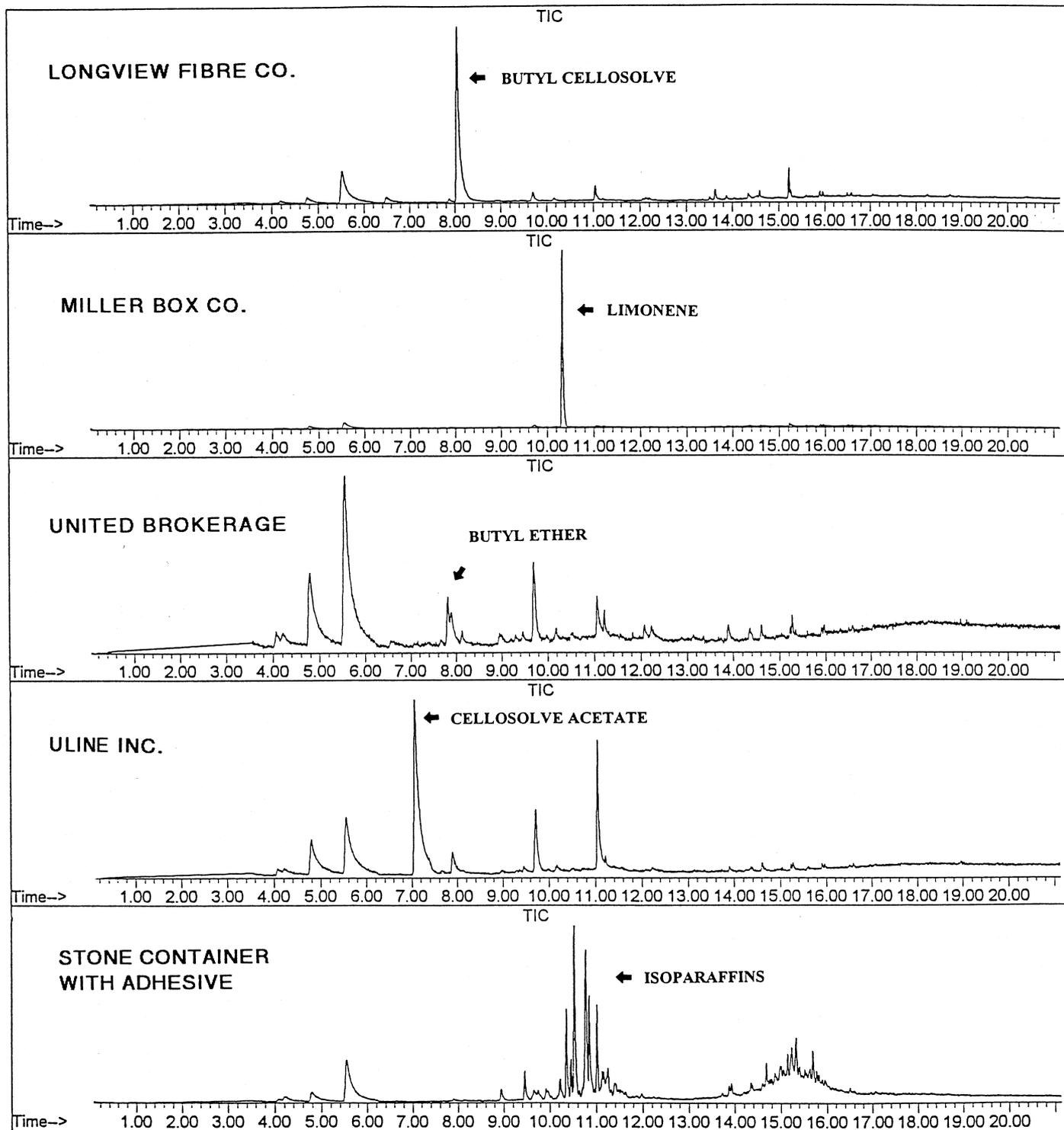


FIG. 9—Total ion chromatograms of five samples of cardboard.

Plastic Bags

Figure 10 shows a good reason to be cautious about samples delivered in, or containing, plastic bags, particularly Zip-lock® bags. Normal alkanes were detected in the 13-gallon white Glad® bag shown in the top chromatogram. Isoparaffins were detected in the 12 by 12 in. evidence bag with a zip-type closure, and kerosene was detected in the one-quart Zip-lock® freezer bag. Under normal use, these bags are not exposed to temperatures high enough to cause off-gassing of the petroleum hydrocarbons.

Building Materials

Building materials represent the most commonly submitted samples of fire debris. Fortunately, most building materials do not contain actual petroleum distillates, although some of the pyrolysis products found in burned carpet may be the same as some of the components of gasoline and common petroleum distillates. It is not unusual to find C₃- and C₄-alkylbenzenes, indenenes, and naphthalenes in samples of burned carpet (4–6). If the analyst is cautious, and observes the relative ratios within the groups of various ions, as well as the inter-group ratios, misidentifications are unlikely.

Other building materials do actually contain petroleum distillates as solvents to increase the flexibility of the material. Asphalt is a special case of a petroleum distillate that is first pyrolyzed in the fire, then fractionated during the sample preparation step to yield a chromatogram remarkably similar to, but distinguishable from, kerosene, or diesel fuel (3). A typical asphalt smoke condensate chromatogram is shown at the top of Fig. 11. The middle chromatogram in Fig. 11 was obtained from a piece of laminated kraft paper used as a moisture barrier between layers of flooring. The

black adhesive between the two layers of brown kraft paper contained an isoparaffinic solvent, indistinguishable from Exxon Isopar® K. It should be noted that some isoparaffinic solvents in this molecular weight range may resemble the evaporated residue of products sold as charcoal lighter fluid, so caution in interpreting data must be used. An appropriate known comparison sample will aid in avoiding misidentifications.

The bottom chromatogram in Fig. 11 shows the volatile components of new Armstrong Caspian® linoleum. Both normal paraffins and isoparaffins are used as solvents in this linoleum.

Floor coatings may present a problem not previously recognized, in that the petroleum distillate solvents that are used in stains and finishes are quite persistent. Even unsealed stain solvents can be easily detected six months after application, as shown in Fig. 12. Such solvents in sealed floors are likely to be even more persistent. As with solvents trapped in plastic bags, shoes and adhesives, there is no reason to believe that the solvents shown in Fig. 12 will not be detectable at some level for years. Further research into this matter is currently underway, and will be reported when the long-term study is completed.

Adhesives

Many of the petroleum products present in everyday items, such as shoes, cardboard, and building materials, are present because those items are held together with adhesives. While it might seem reasonable to believe that the solvents used in adhesives would evaporate quickly, in fact, the solvents seem to remain trapped in the elastomer, and are detectable indefinitely. Figure 13a shows the total ion chromatograms of two 19-year-old samples of structural adhesive that still contain toluene, as well as C₃-alkylbenzenes. In

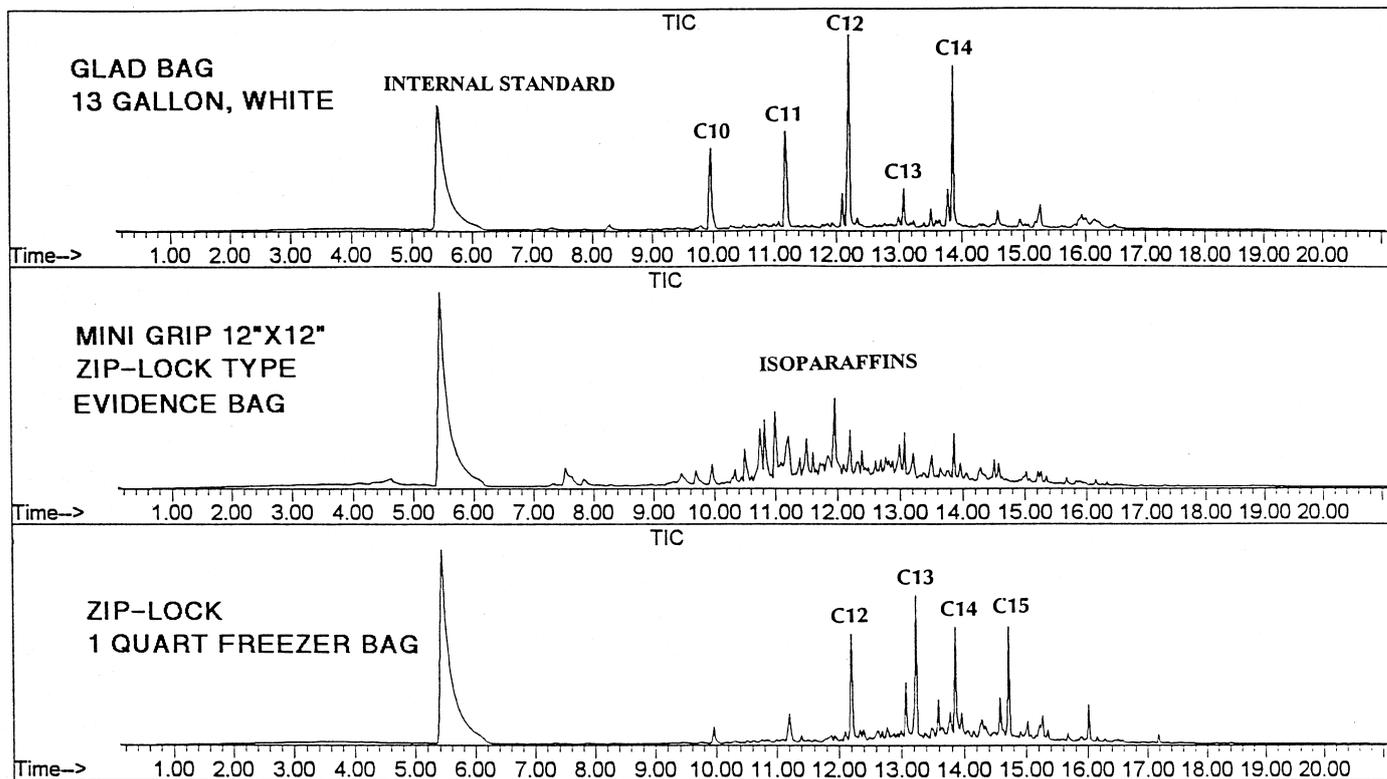


FIG. 10—Total ion chromatograms of three brands of plastic bags.

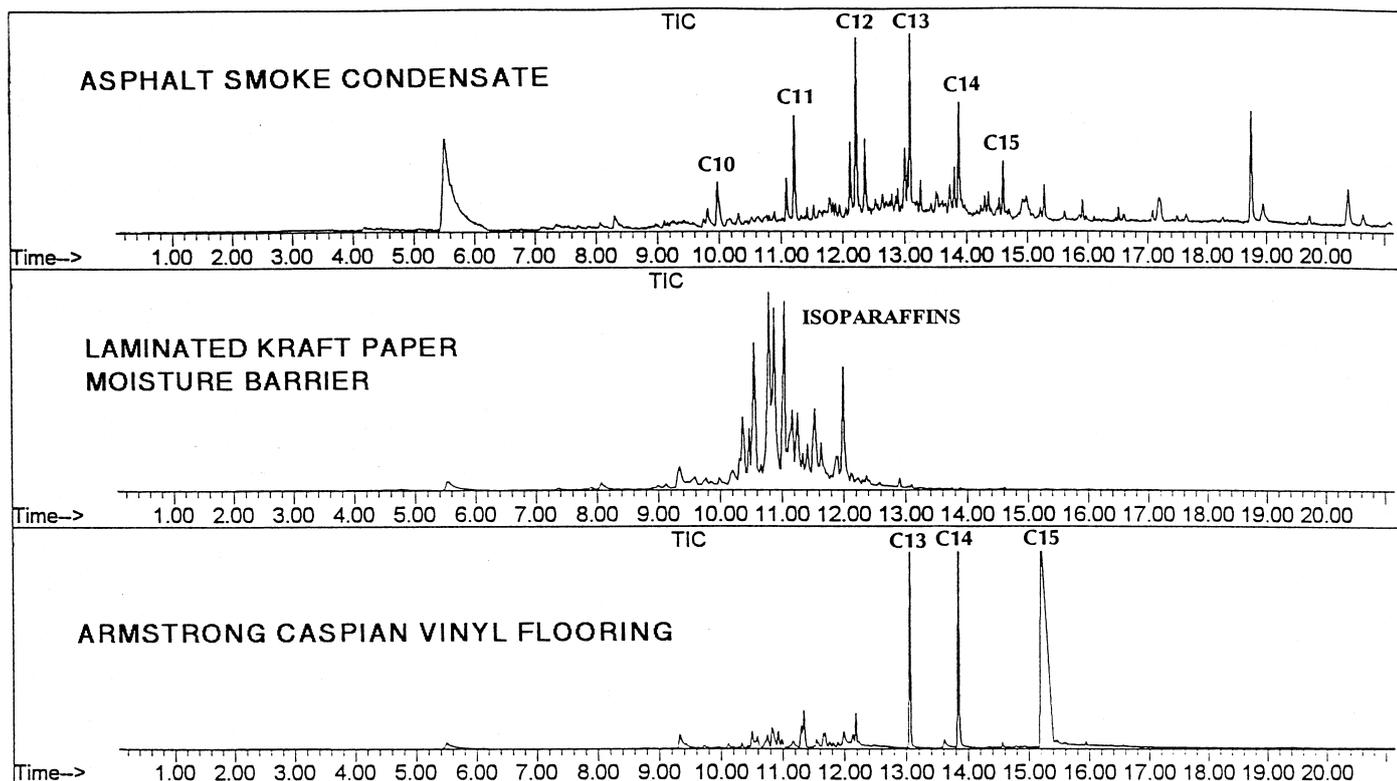


FIG. 11—Total ion chromatograms of building materials containing petroleum products.

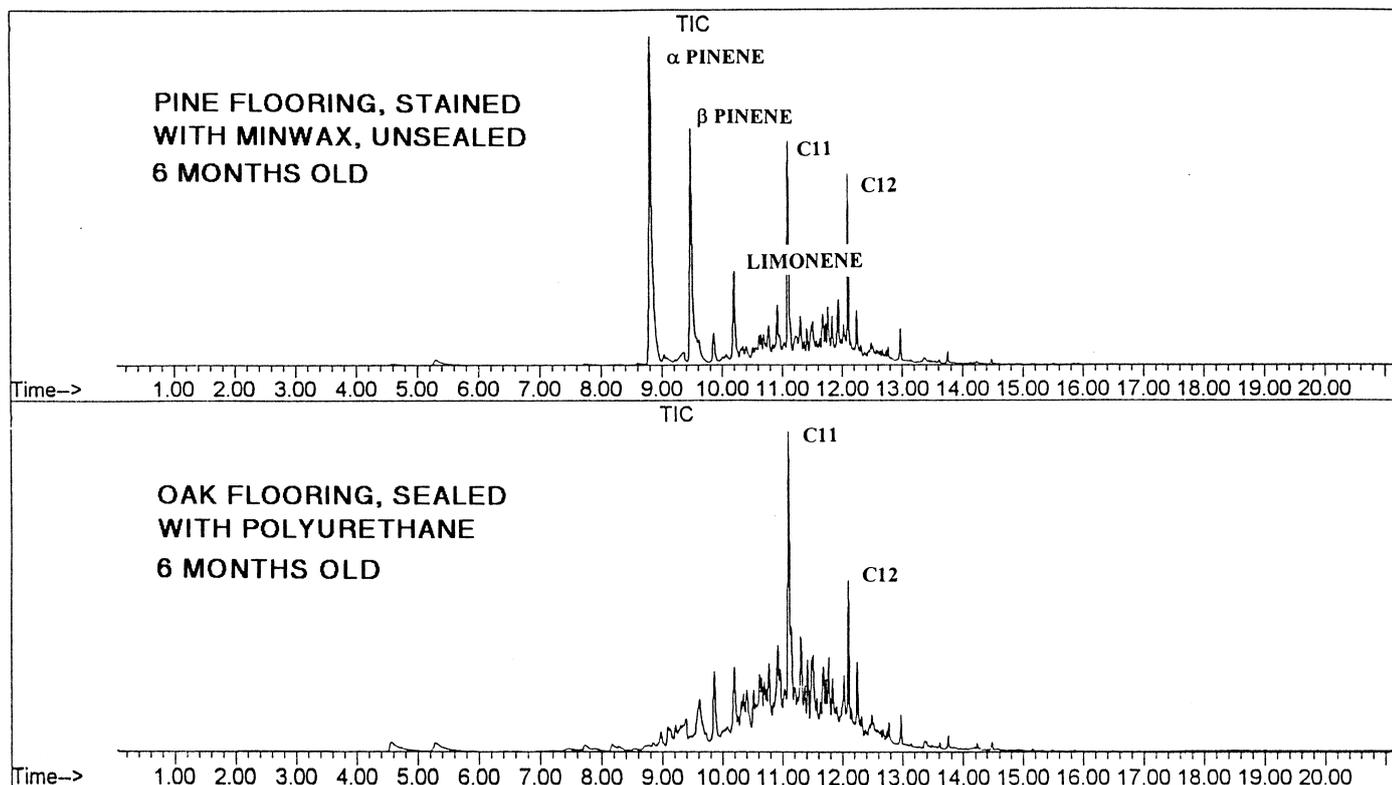


FIG. 12—(Top) Medium petroleum distillate detected on a piece of pine flooring six months after the application of penetrating stain, with no sealer. (Bottom) Medium petroleum distillate detected on a piece of oak flooring six months after the application of polyurethane sealer.

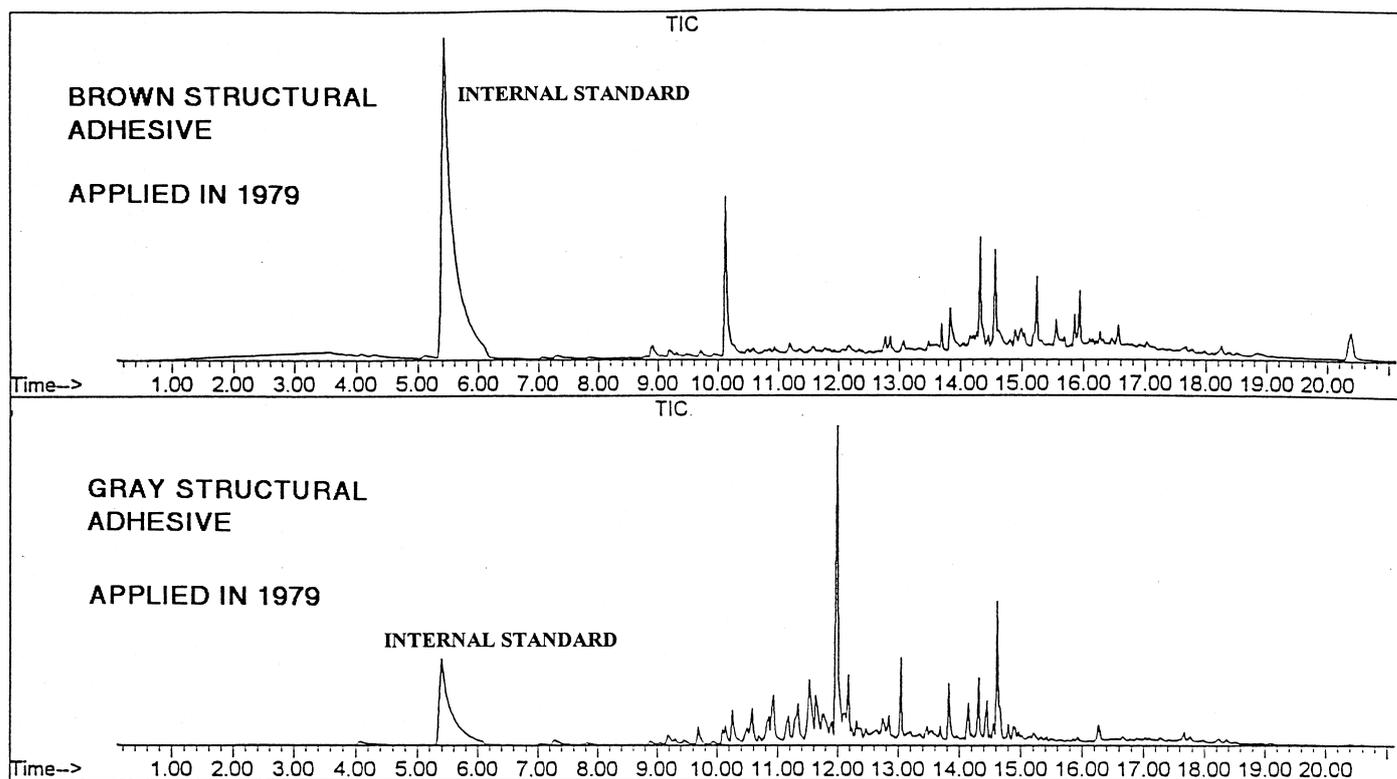


FIG. 13a—Total ion chromatograms of two 19-year-old samples of adhesive.

one of the samples, the C_3 -alkylbenzenes are present in the same distribution as is found in gasoline. Selected ion profiles of extracts of small (5 g) samples of these two adhesives are shown in Figs. 13b and 13c. A gasoline standard, similarly profiled, is shown in Fig. 13d.

Adhesives may contain and preserve compounds identical to those found in gasoline and in medium petroleum distillates. Figure 14a shows the total ion chromatogram of six different samples of adhesive eight days after application. The same samples, examined 14 months later, yielded virtually identical chromatograms. All contain some amount of toluene. Other petroleum-derived liquids identified in these adhesives include xylenes, MPD's, low molecular weight isoalkanes and cycloalkanes, BHT, and naphthalene.

Two of these structural type adhesives clearly contain an MPD, and when ion 57 is profiled (Fig. 14b), a mixture of alkylcyclohexanes is seen in one adhesive, and a mixture of light isoparaffins is present in another. When ion 105 is profiled (Fig. 14c), three of the adhesives exhibit a C_3 -alkylbenzene pattern indistinguishable from that seen in petroleum products, such as gasoline and MPD's. This is consistent with the presence of an MPD as observed in the total ion chromatogram in three of the adhesives. If only the aromatic profiles of these materials are examined, remarkable similarities are observed between these materials and gasoline (Figs. 15a, 15b, and 13d), however, an experienced analyst would not be likely to identify gasoline in these samples. This comparison points out both the strengths and the weaknesses of extracted ion profiling.

In order to avoid misidentifications, it is necessary to look at additional families of compounds, including the alkanes, cycloalkanes, indenenes, methyl indenenes, and substituted naphthalenes (ions 57, 83, 117, 131, 142, and 156). C_3 -alkylbenzenes are an important diagnostic gasoline component, but over-reliance on this one fam-

ily can lead to error. Even the indenenes are present in some of the structural adhesives, as shown in Figs. 15a and 15b. When all of the ion profiles are examined, however, it is possible to make the distinction between gasoline and adhesive components.

Discussion

This study demonstrates the extent to which petroleum solvents can be detected in common sample matrices to which no foreign ignitable liquids have been added. It is important to remember that in most cases, the petroleum solvents are not a specified part of the product, and the composition may change from time to time without affecting the product's performance. A shoe manufacturer may use toluene one month and xylene the following month. The THF (tetrahydrofuran) solvent used to manufacture cardboard one month may change to butyl ether next month, with no noticeable change in product performance. A newspaper publisher may clean the press with kerosene one day and mineral spirits the next.

Sometimes, samples are submitted to the forensic laboratory with a request to look for a particular compound, such as alcohol or acetone. It is frequently possible to detect these compounds in samples of fire debris, but caution must be exercised in the interpretation of results. Oxygenated species in particular tend to be produced in the combustion of ordinary materials. Both alcohol and acetone have been shown to be products of combustion (13), and their presence is only likely to be significant if the concentration of the compound is significantly higher than the other peaks in the chromatogram.

Likewise, a finding of toluene, xylene, or styrene in a sample may be of little or no significance because such compounds are commonly found as trapped residual solvents, or as pyrolyzates of

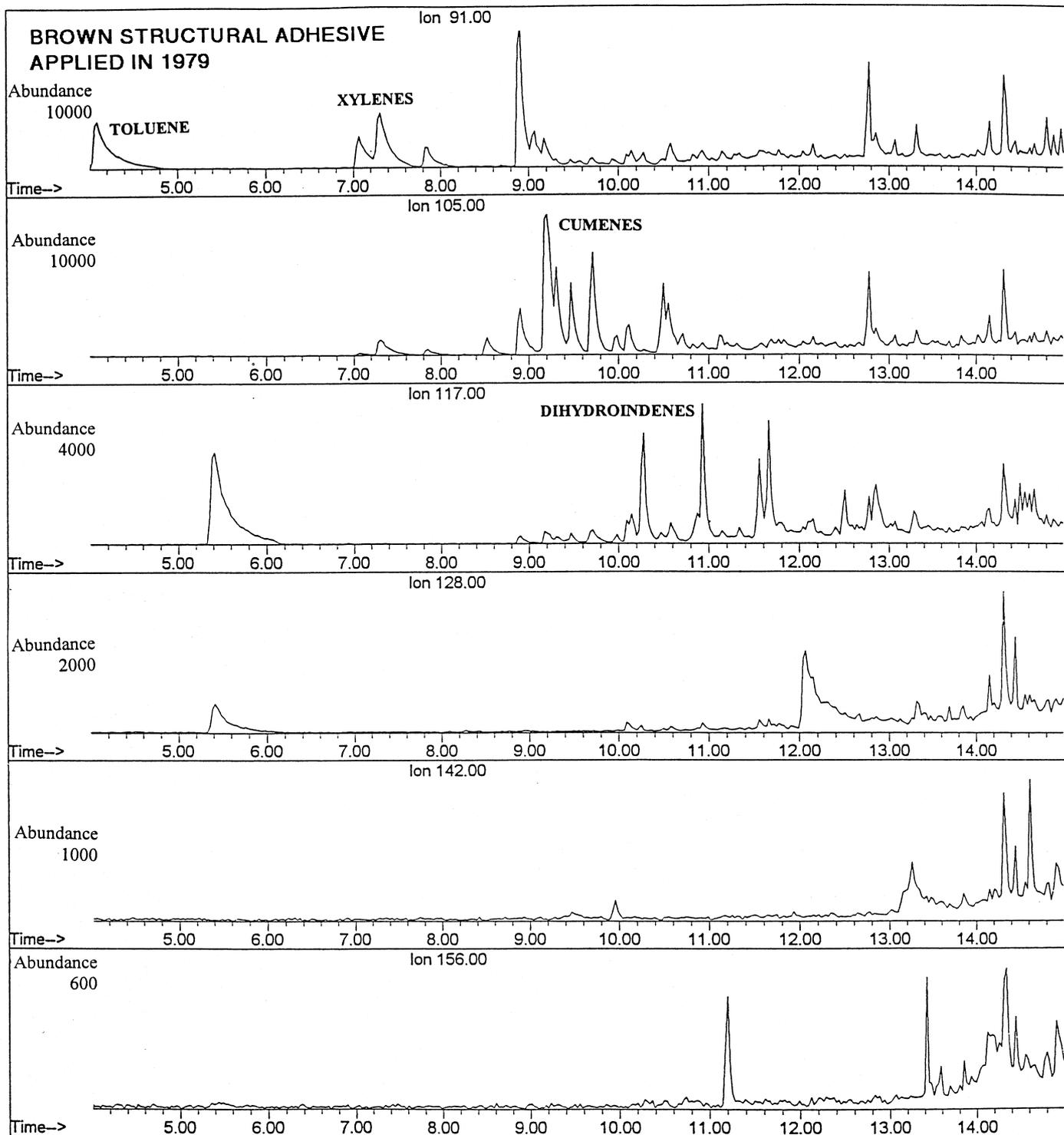


FIG. 13b—Six selected ion profiles of a brown 19-year-old adhesive sample.

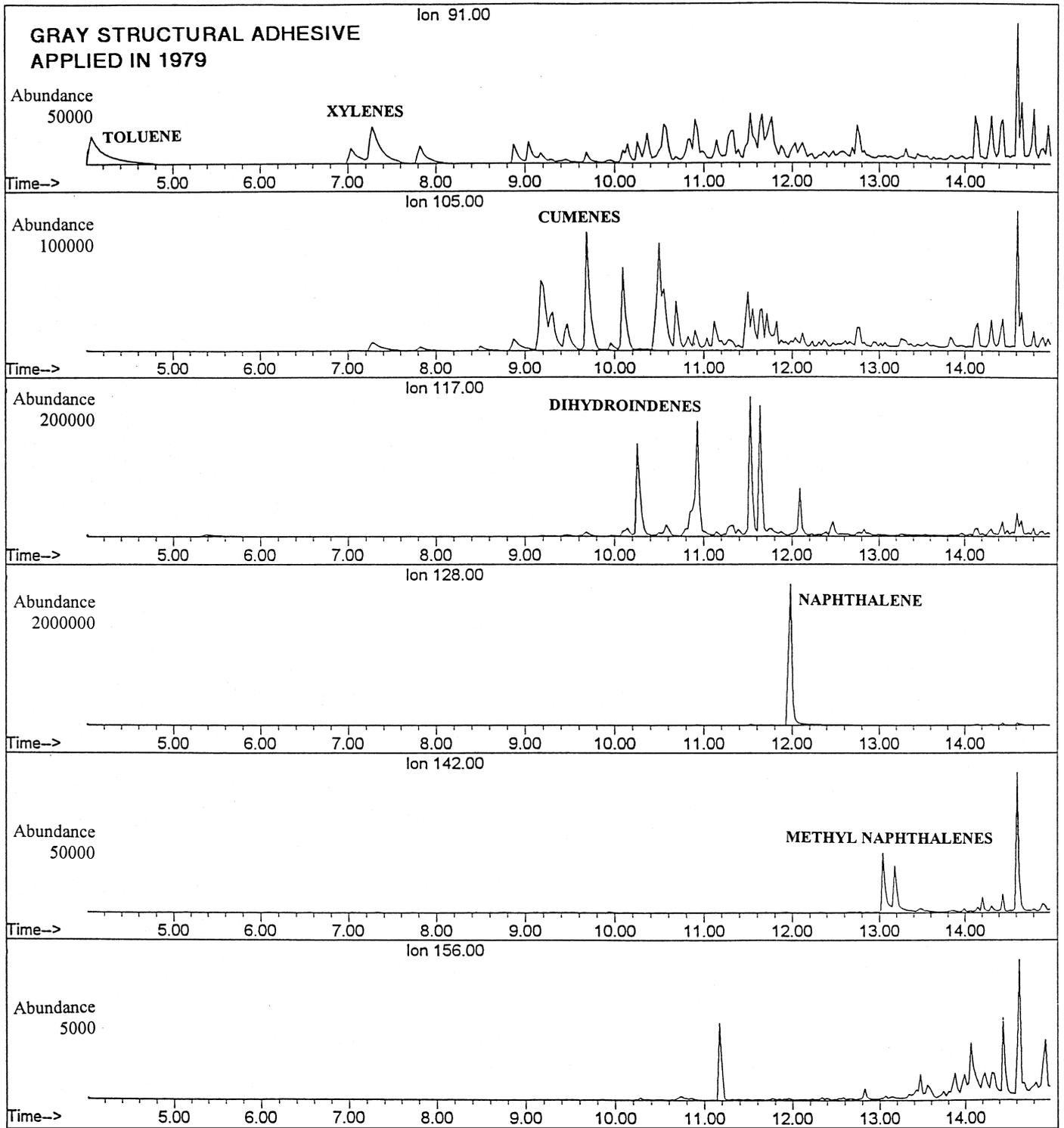


FIG. 13c—Six selected ion profiles of a gray 19-year-old adhesive sample.

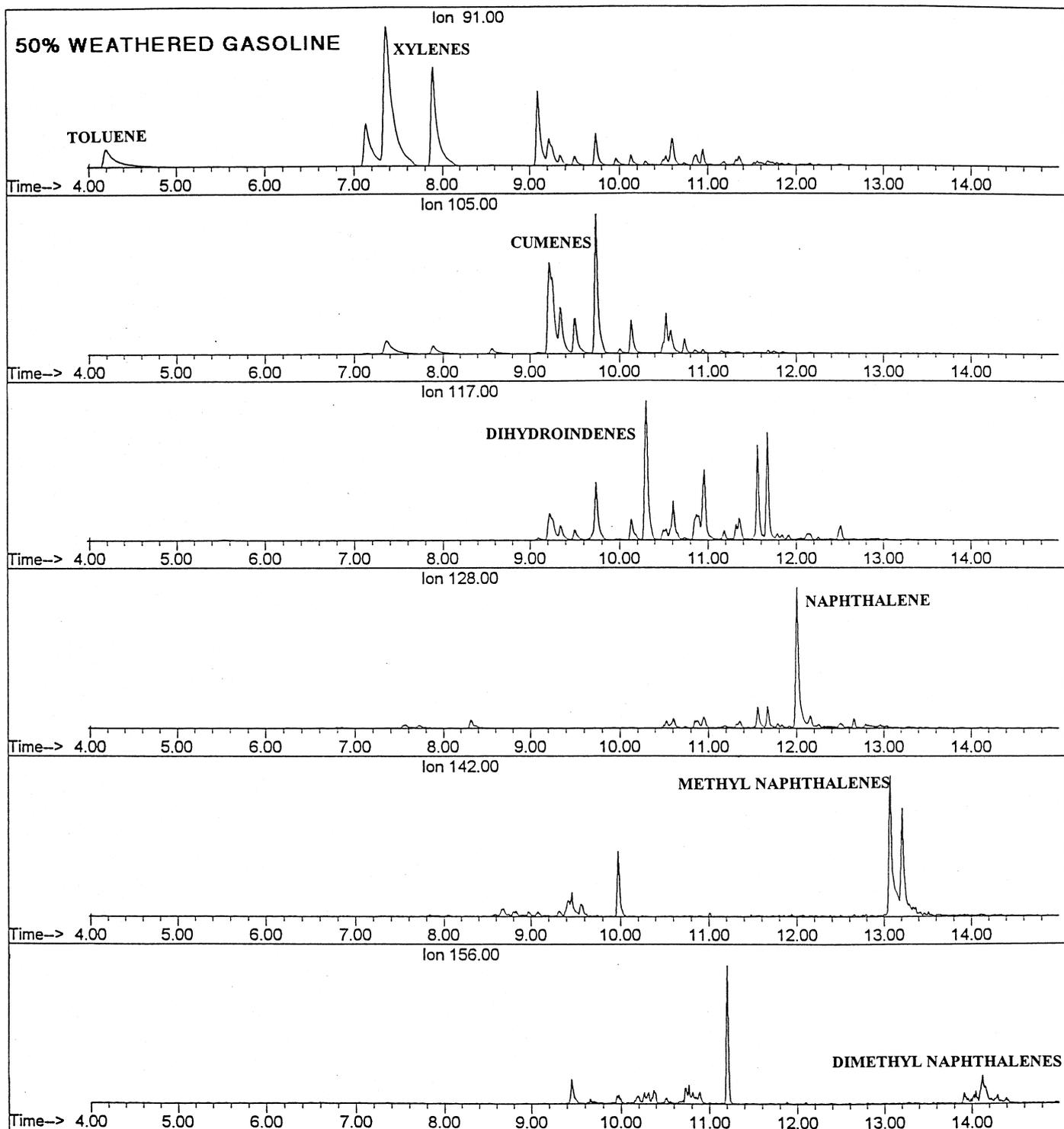


FIG. 13d—Six selected ion profiles of 50% evaporated gasoline.

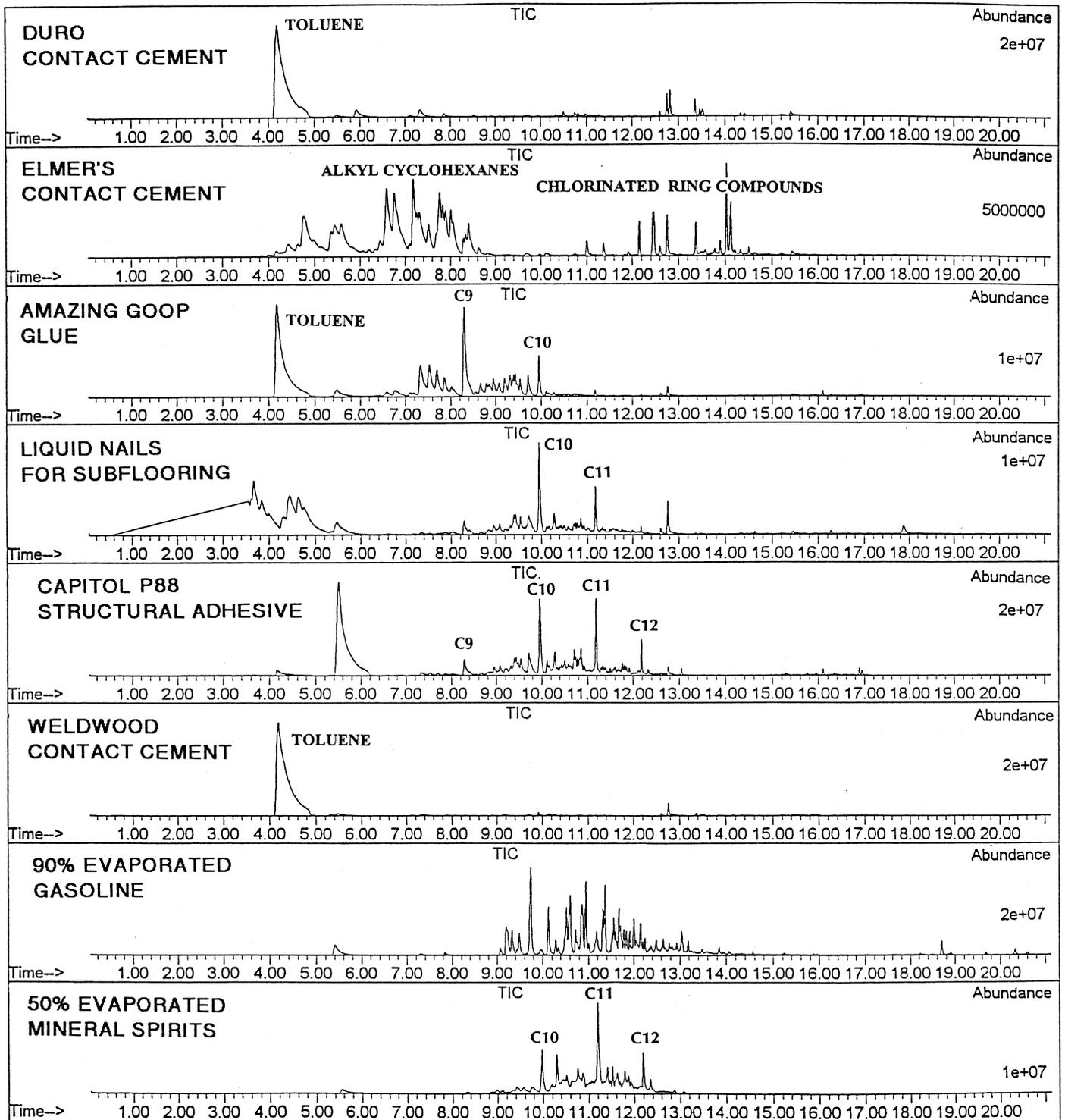


FIG. 14a—Total ion chromatograms of six samples of dried adhesive, compared with gasoline and mineral spirits.

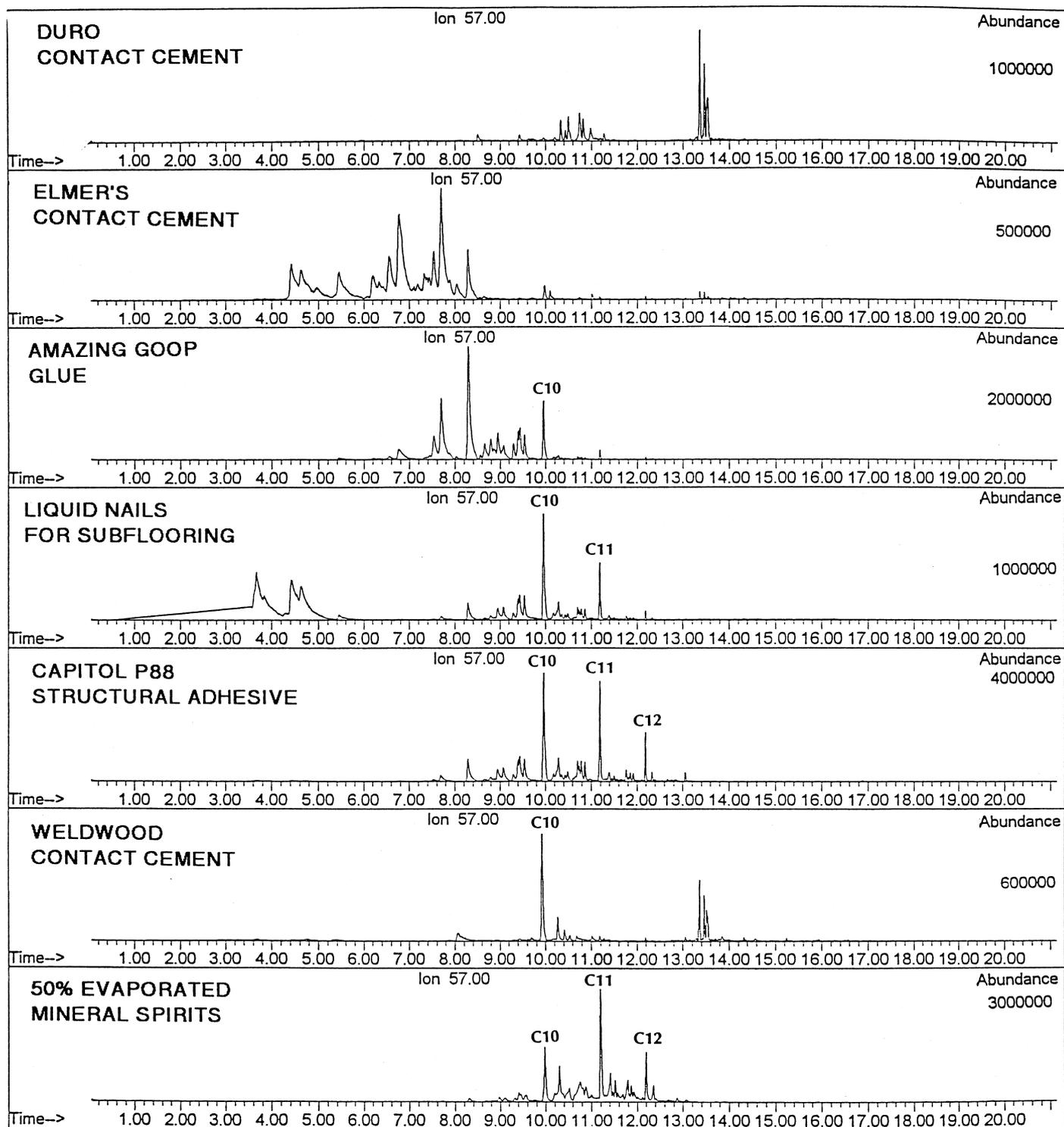


FIG. 14b—Ion 57 mass chromatogram (selected ion profile) of six samples of dried adhesive, compared with mineral spirits.

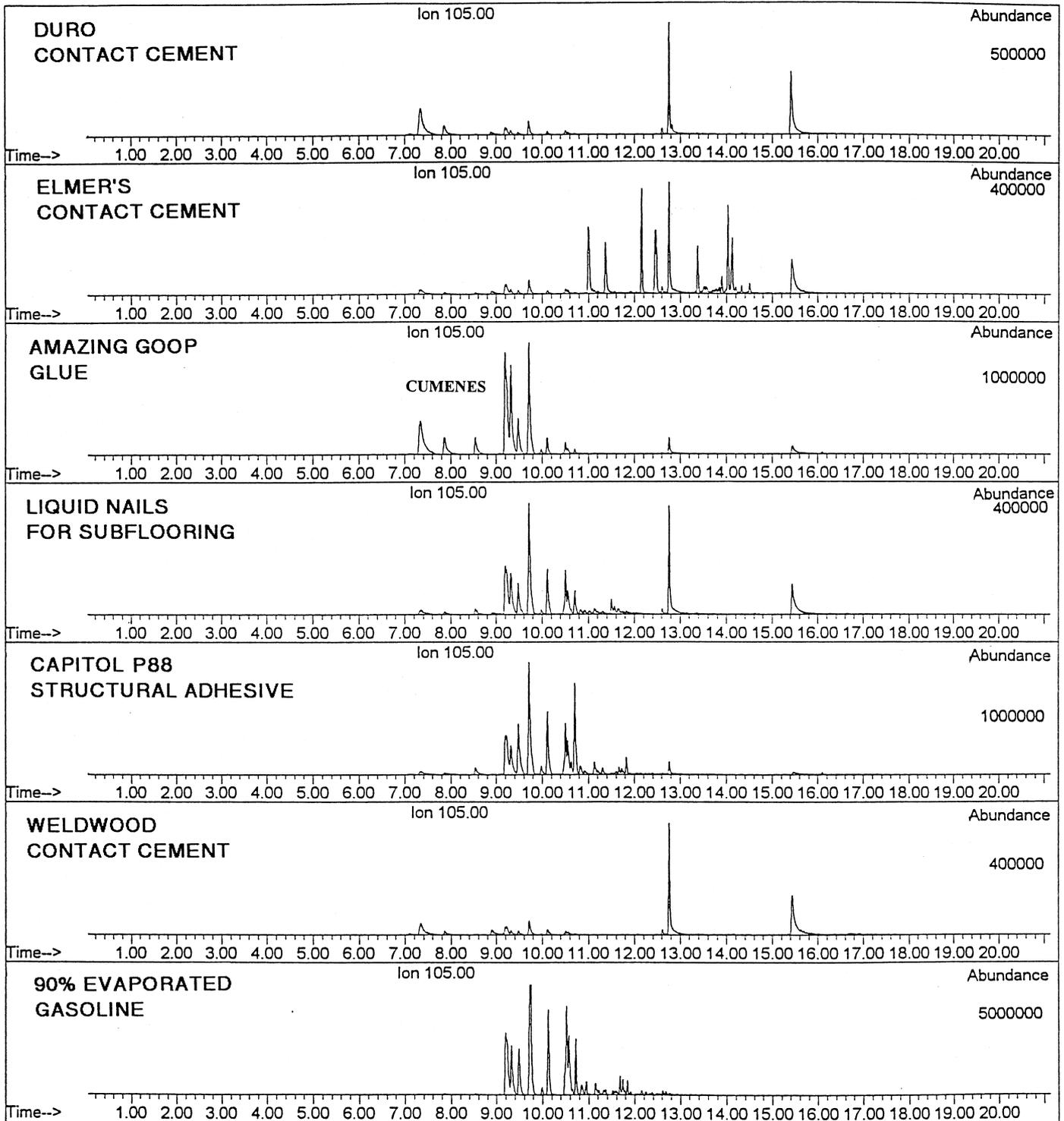


FIG. 14c—Ion 105 mass chromatogram (selected ion profile) of six samples of dried adhesive, compared with gasoline.

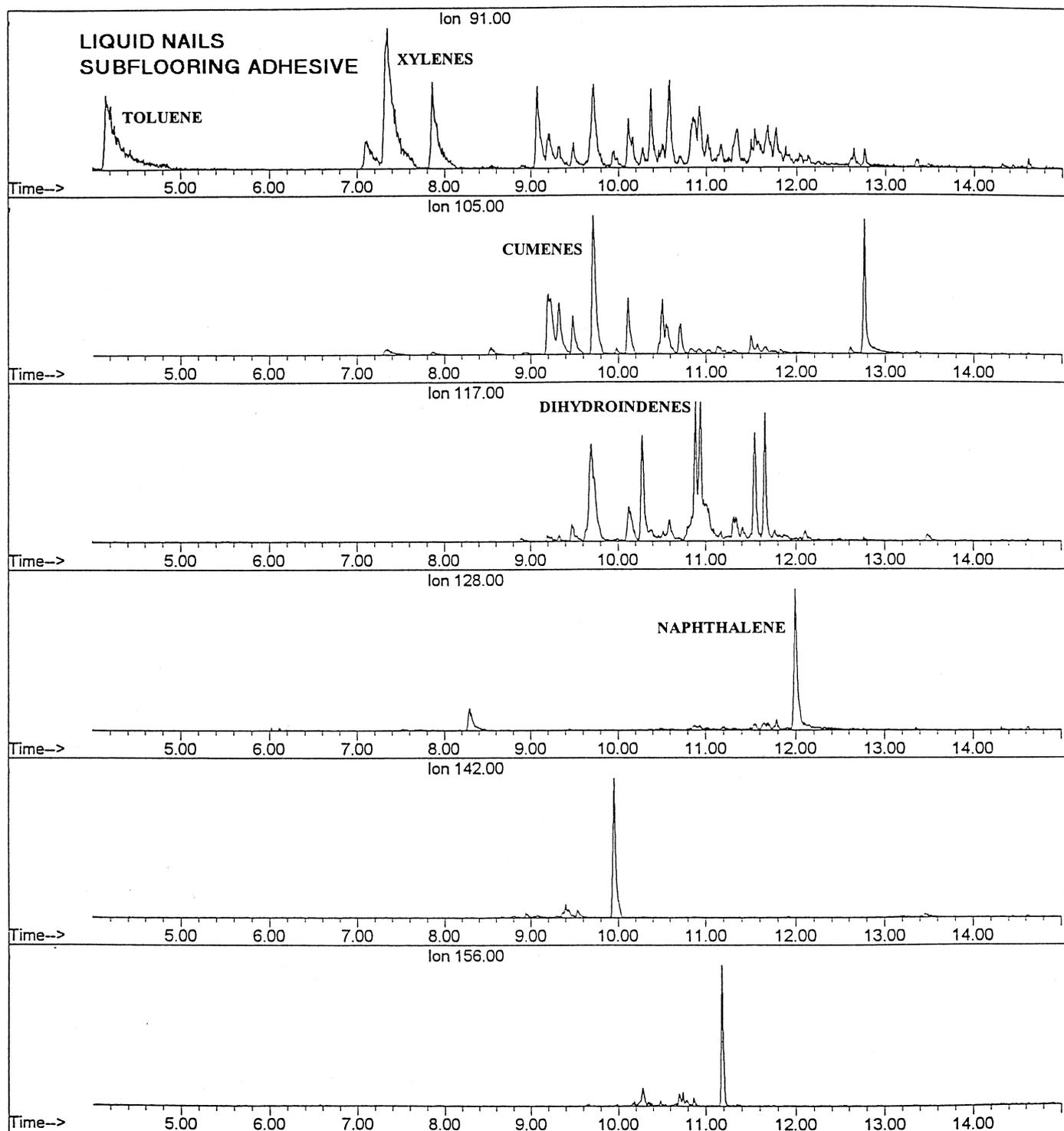


FIG. 15a—Six selected ion profiles of dried Liquid Nails® subflooring adhesive. Compare with Fig. 13d.

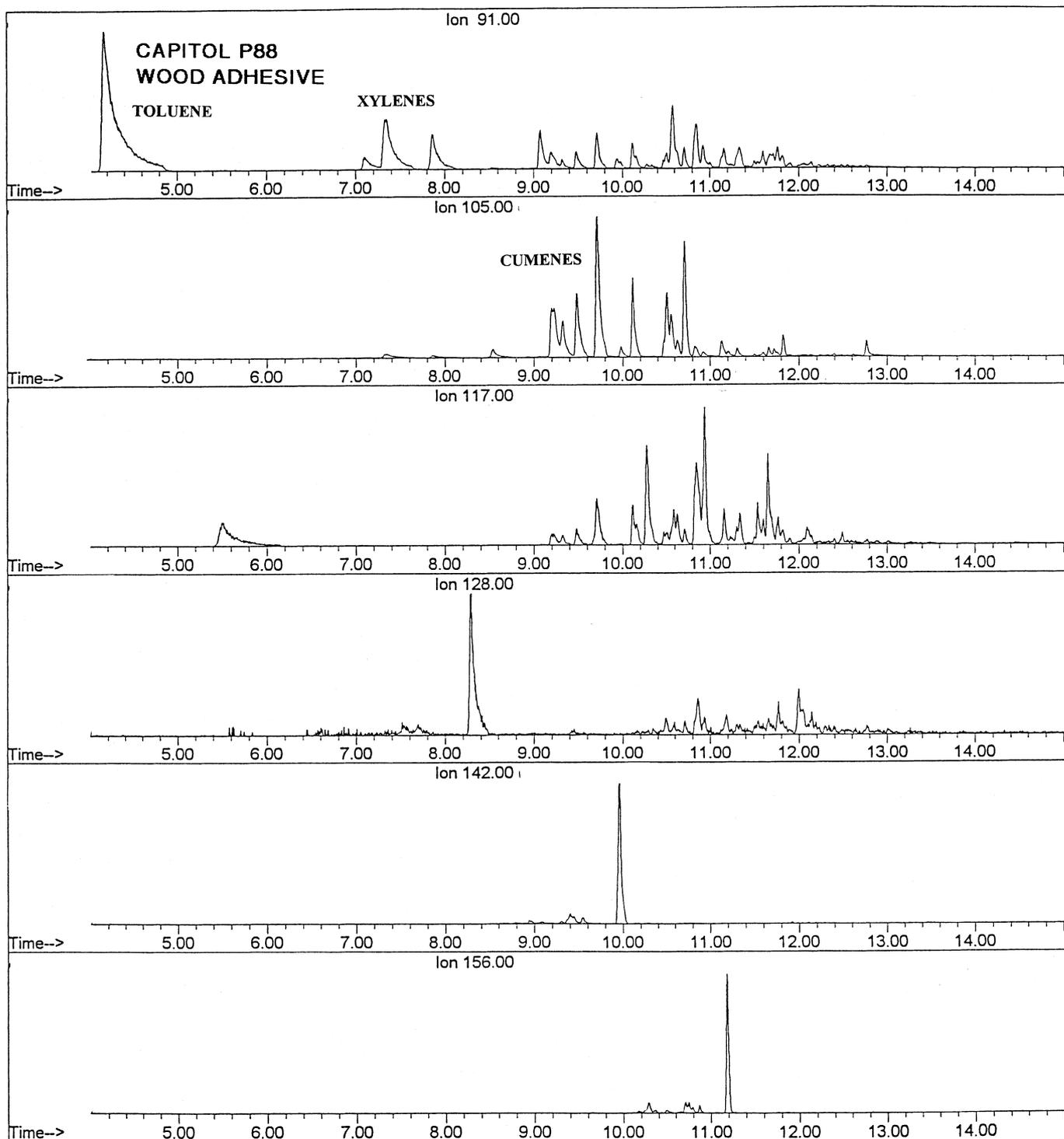


FIG. 15b—Six selected ion profiles of dried Capitol P88® Wood Adhesive. Compare with Fig. 13d.

TABLE 1—Common ignitable liquid residues and sample matrices.

Substance	Potential Source
Toluene, xylenes, C ₃ - and C ₄ -Alkylbenzenes, indenes	Adhesives, polymer decomposition, shoes, clothing
Medium petroleum distillates and heavy petroleum distillates	Adhesives, insecticides, polishes, lubricants, magazines, newsprint, shoes, clothing, asphalt smoke, plasticizers, floor finishes
Isoparaffins	Moisture barriers, adhesives, plasticizers
Normal paraffins	Linoleum, carbonless forms, copier and laser printer toner
Alcohols, acetone	Combustion products

common materials. A large toluene peak accompanied by much smaller concentrations of xylenes and C₃-alkylbenzenes would suggest that the xylenes and C₃-alkylbenzenes did not originate from gasoline.

As the examination of shoes, cardboard, and adhesives has shown, significant background studies must be undertaken in order to attribute any significance to the presence of most single compounds. At the very least, a comparison sample should be obtained.

Groups of compounds, such as the C₃-alkylbenzenes, may be present as part of the sample matrix and often exhibit the same relative concentrations within the group as those found in petroleum distillates. Some materials contain "whole" ignitable liquid residues, such as kerosene, MPD, or isoparaffin mixtures.

The only common ignitable liquid that does not turn up as a component of sample matrices with any regularity is gasoline, but care must be exercised when using ion profiles. Reliance on only one or two families of compounds can lead to misidentifications. Both inter- and intra-group peak ratios must compare favorably in order to make a credible identification.

Table 1 lists common ignitable liquid residues likely to be encountered in a forensic laboratory, and the sample matrices that may be incidental sources for such residues. The interpretation of the finding of these substances, particularly when headspace concentration is the separation method, should be made cautiously, and with the use of comparison samples whenever possible.

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