

TECHNICAL NOTE

Maureen J. Kocisko,¹ M.F.S

Absorption of Ignitable Liquids into Polyethylene/Polyvinylidene Dichloride Bags

REFERENCE: Kocisko MJ. Absorption of ignitable liquids into polyethylene/polyvinylidene dichloride bags. *J Forensic Sci* 2001; 46(2):356–362.

ABSTRACT: Clear plastic bags are often used for the collection, sampling and storage of ignitable liquid evidence. They are popular because they are easy to store, transport and are inexpensive. Cryovac and Globus brand polyethylene/polyvinylidene dichloride bags were tested for suitability in storing ignitable liquid evidence. Standards of diesel, kerosene and gasoline were placed in the bags and sampled by passive headspace adsorption. The bags were then heated to determine if absorbed components of the standards could be released upon heating. Recovered extracts were analyzed by GC and GCMS. These bags were found to absorb components of diesel, kerosene, and gasoline, and were also found to produce interfering by-products that obstruct the chromatographic results. Evidence containers need to be tested to ensure that low levels of ignitable liquids are not missed.

KEYWORDS: forensic science, criminalistics, arson, ignitable liquids, sampling, evidence bags, polyvinylidene dichloride

Clear plastic bags are used for collecting and storing ignitable liquid evidence. These bags are popular with investigators because they are easy to store and transport, and can accommodate large and awkwardly shaped items of evidence. However, several studies have shown potential problems when using bags for holding ignitable liquid evidence. Demers-Kohl et al. analyzed bags on the basis of size, composition, thickness, tearing strength, puncturing strength, and background contamination (1). Of the six types of bags they tested, not one was suitable in every category. Carlsson et al. found that the ability of different containers to prevent loss of ignitable liquids to the environment and also the manner in which containers are sealed could negatively affect results (2).

The Queensland Police Service and other forensic laboratories within Australia use Cryovac and Globus brand bags to hold evidence that requires ignitable liquid testing. Both manufacturers specify that these bags are made from multi-layer co-extruded polyethylene/polyvinylidene dichloride. In practical use, the bags are not prone to punctures or tearing and come in a wide range of sizes. In addition, these bags offer the benefits of low cost, durability and flexibility. However, polyethylene containers have been

shown to be unsuitable for the storage of hydrocarbons because the ignitable liquids tend to escape (3).

This study focused on characterizing the suitability of polyethylene/polyvinylidene dichloride Cryovac and Globus bags for the storage and collection of evidence containing ignitable liquids. Standards of gasoline, kerosene, and diesel were sampled from each type of bag. Sampling was done at ambient temperature and at 90°C and the results compared by GC and GCMS.

Methods and Materials

Materials

Dichloromethane was analytical grade and obtained from EM Science, Gibbstown, New Jersey. Gasoline and diesel samples were obtained from local Shell and BP gas stations. Kerosene was Diggers brand and obtained from a local supermarket. Activated Charcoal Strips were from Albrayco Laboratories, Inc. and were cut into 3 by 12 mm sections for sampling. Friction lid tins measured 4 L in volume and were supplied by National Can Pty Ltd. Cryovac bags measured 306 by 650 mm with a thickness of 60 µm and were supplied by Cryovac Pty Ltd. Globus bags measured 250 by 600 mm with a thickness of 60 µm and were supplied by the Globus Group of Companies.

Apparatus

Bags were heated in a Clayson OM550 Microprocessor Controller oven. Analyses were conducted using a Perkin Elmer Autosystem XL gas chromatograph with a 25 m by 0.32 mm by 0.5 µm J&W DB-1 column. The gas chromatograph was fitted with a flame ionization detector. For each analysis, the column was held at 40°C for 2.5 min, then increased 10°C/min to 270°C with a final hold of 4 min. The inlet temperature was 240°C. Further analyses were conducted using a Hewlett Packard 6890 series gas chromatograph fitted with a 5973 series mass selective detector. The gas chromatograph had a 30 m by 0.25 mm by 1.0 µm J&W DB-1 column. For each analysis, the column was held at 35°C for 3 min, then increased 5°C/min to 100°C, then increased 10°C/min to 240°C with a final hold of 13 min. The inlet temperature was 240°C. Pyrolysis GCMS was conducted using a Shimadzu GC-17A/QP5000 gas chromatograph mass spectrometer with a 30 m by 0.25 mm by 1.0 µm J&W DB-1 phase column. The Shimadzu was fitted with a CDS pyroprobe with filament probe that pyrolyzed the sample at 770°C. For each run, the column was held at 40°C for 2 min, then increased 8°C/min to 270°C.

¹ Scientific Section, Queensland Police Headquarters, Brisbane, QLD 4000 Australia. Current address: 30 East Georgia Street #407, Indianapolis, IN.

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Sample Preparation

Ten μL diesel, 2 μL kerosene or 2 μL gasoline was placed onto a piece of lint free tissue inside Cryovac and Globus bags using a Hamilton syringe. Bags were tied off in a knot half way down, leaving a volume of approximately 4 L. Identical amounts of diesel, kerosene, and gasoline were added to 4 L friction lid tins and sampled under the same conditions. The bags and friction lid tins were sampled by passive headspace for 24 h at ambient temperature us-

ing a 3 by 12 mm charcoal strip. After the charcoal strip and lint free tissue were removed from each bag, the bag was placed in a new friction lid tin with another charcoal strip. This tin was heated to 90°C for 24 h. Charcoal strips were extracted with 0.7 mL dichloromethane for 10 min. The extracted sample underwent GC analysis, with some samples being further analyzed with GCMS.

A control for each bag and the friction lid tin was prepared. This was done by placing a charcoal strip in each bag and tin free of any ignitable liquid. The bags and tin were sample for 24 h at ambient

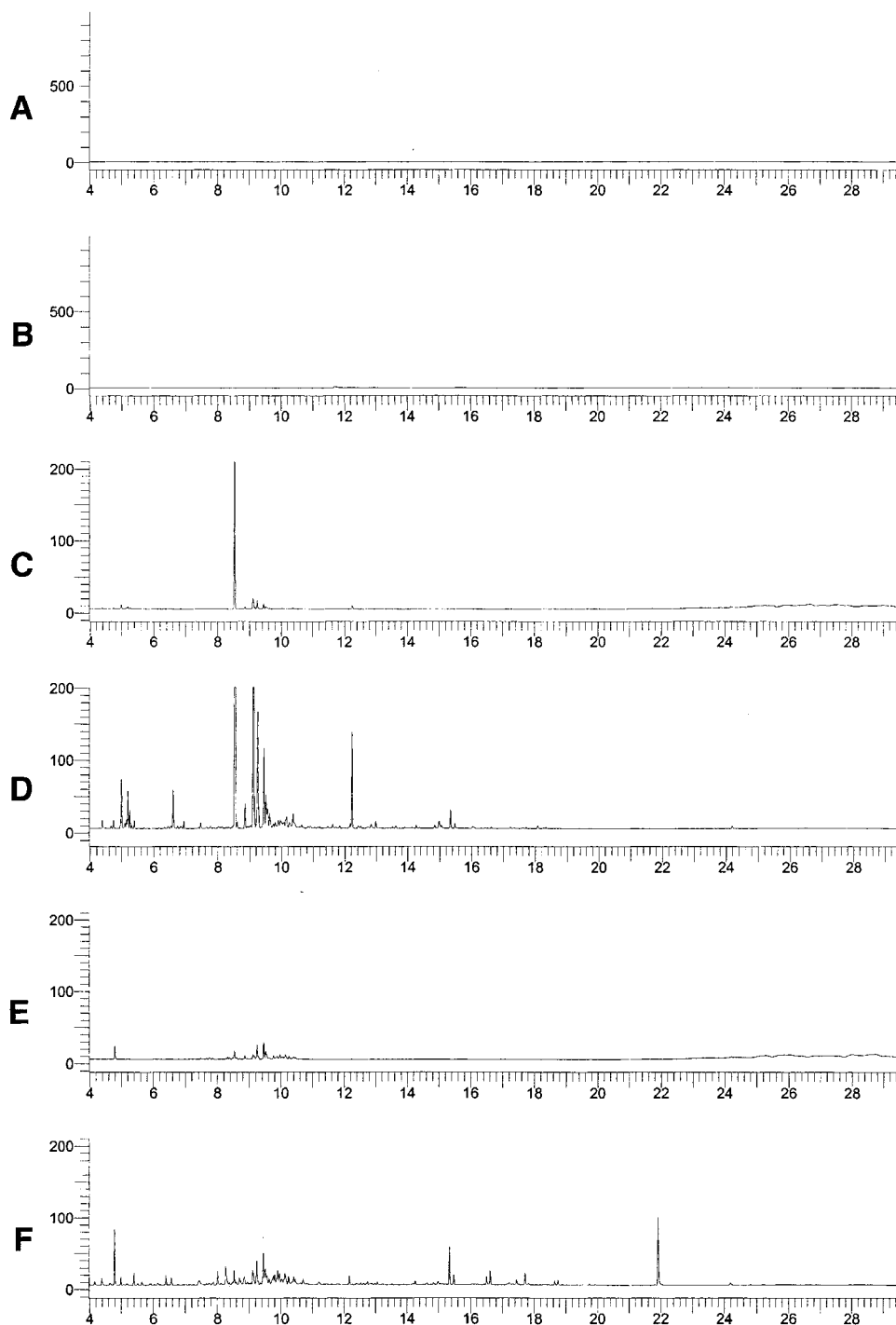


FIG. 1—Chromatograms from controls of empty bags and tins. A: Four L friction lid tin at ambient temperature. B: Four L friction lid tin after heating. C: Cryovac bag at ambient temperature. D: Cryovac bag after heating. E: Globus bag at ambient temperature. F: Globus bag after heating.

temperature, followed by further sampling at 90°C for 24 h. A control of the ambient laboratory air was prepared by placing charcoal strips on the laboratory countertops near the bags and tins for 24 h. A heated control of each ignitable liquid was prepared by placing 10 μ L diesel, 2 μ L kerosene or 2 μ L gasoline onto a piece of lint free tissue in a 4 L friction lid tin with a charcoal strip. These control tins were then heated for 24 h at 90°C.

To test whether ignitable liquids could be extracted from the inner surface of the bag with dichloromethane, two other methods of extraction were employed. Two bags were prepared using the method described above for each ignitable liquid. After 24 h, one of the bags containing each liquid was wiped with a swab dipped in dichloromethane. The swab used to wipe the bag was extracted with 2.0 mL dichloromethane and underwent GC analysis. The other bags had 20 mL of dichloromethane added. The bag was manually shaken for 2 min and then the solvent was poured into a graduated cylinder where it evaporated at ambient temperature to a volume of 2.0 mL; 0.2 μ L of this was injected onto the GC for analysis.

Both the Cryovac and Globus bags were analyzed by pyrolysis GCMS. Cross-sections of unused bags were prepared under an optical light microscope and then placed in CDS quartz tubes, which were loaded into the pyrolysis system for analysis.

Results and Discussion

Chromatograms of the charcoal strips used to sample the bag and tin controls are shown in Fig. 1. Figure 1*a* and 1*b* are chro-

matograms from the friction lid tins before and after heating, respectively. Figure 1*c* is the chromatogram obtained from the Cryovac bag after 24 h of passive headspace sampling. Figure 1*d* is from the same Cryovac bag after 24 h of heating. Figure 1*e* and 1*f* are the chromatograms from the Globus bags, before and after heating. Chromatograms of laboratory ambient air controls did not exhibit any detectable levels of contamination that would have interfered with the results shown above (data not shown). The chromatograms from the friction lid tin controls show that there are no detectable amounts of background hydrocarbon present. The Cryovac and Globus bags themselves each release a series of compounds that are apparent on the chromatograms. Heating increases the amount of material released from the bags. Several of the major peaks were identified as branched alkanes by GCMS analysis (data not shown). Although both manufacturers specified Cryovac and Globus bags were polyethylene/polyvinylidene dichloride, the chromatograms indicate that the bags do not release an identical group of hydrocarbons. Pyrolysis GCMS results of the Cryovac and Globus bags are shown in Figs. 2*a* and 2*b*. The small differences in the respective pyrograms further suggest some chemical differences. Differences in the manufacturing process, different sources of starting material, and/or different chemical additives used may account for variations in the bags. For proprietary reasons, details of the manufacturing processes were not disclosed.

Chromatograms of the charcoal strips used to sample the bags and tins containing 10 μ L of diesel are shown in Fig. 3. Figure 3*a* shows the chromatogram obtained after the addition of diesel to a friction lid tin. Figure 3*b* is the control chromatogram from the ad-

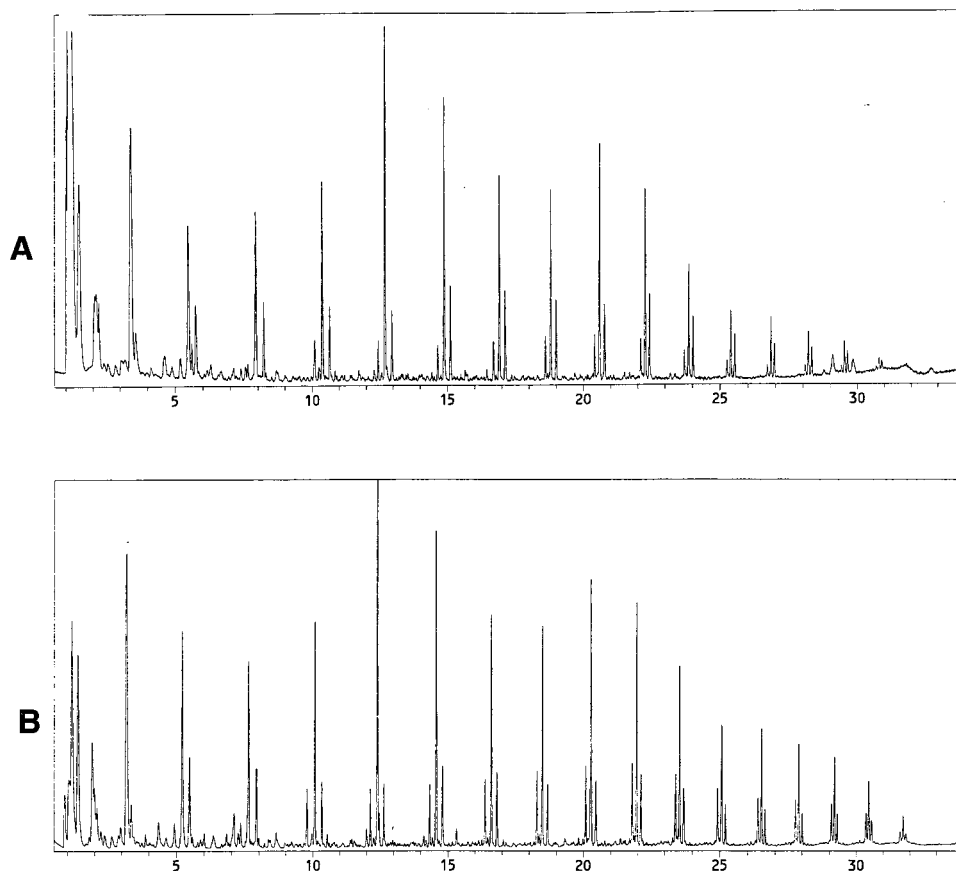


FIG. 2—Pyrograms from cross sections of empty Cryovac bag (A) and Globus bag (B).

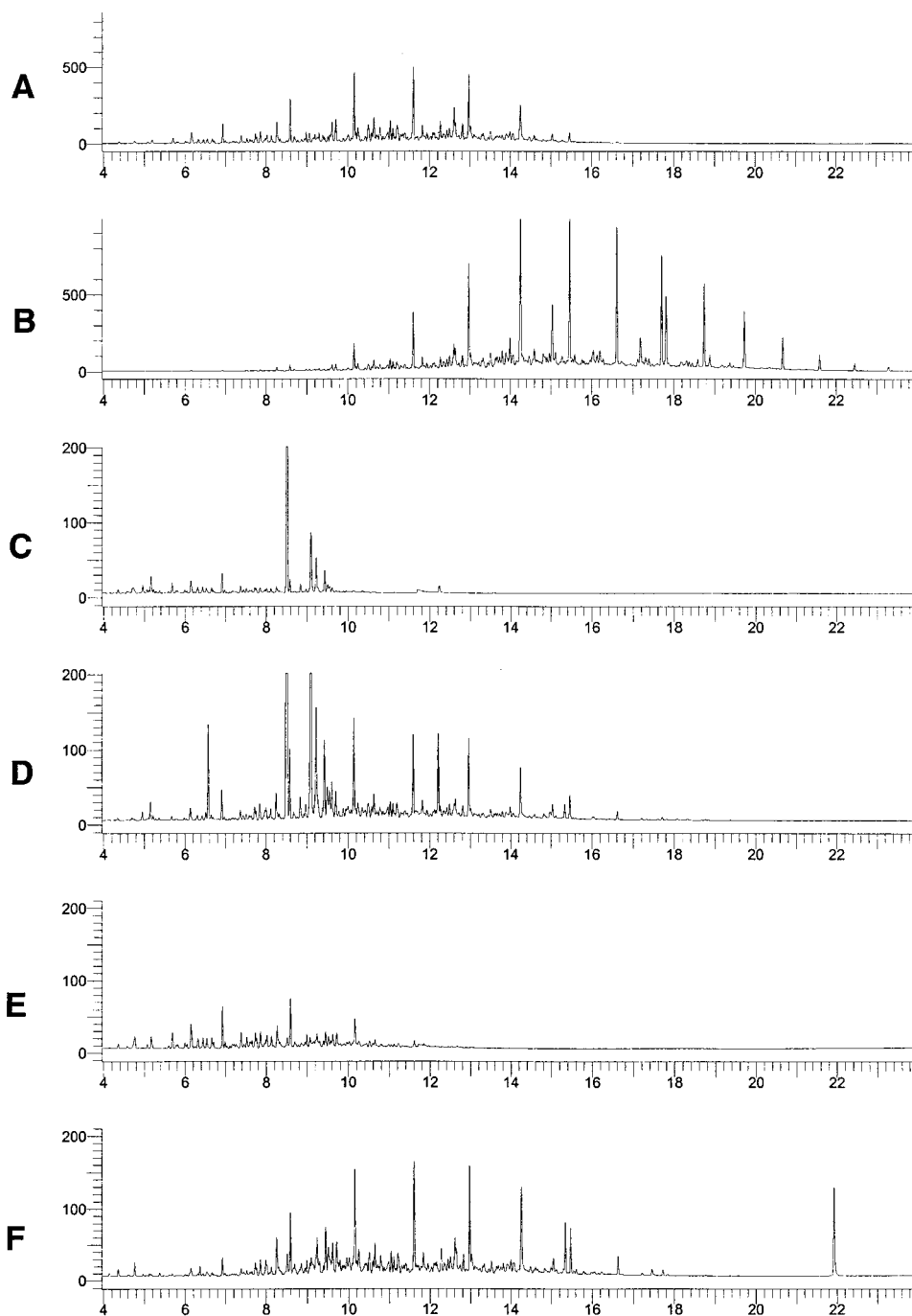


FIG. 3—Chromatograms from the addition of 10 μL of diesel to bags and tin. A: Four L friction lid tin at ambient temperature. B: Four L friction lid tin after heating. C: Cryovac bag at ambient temperature. D: Chromatogram from the bag in Fig. 3C after heating. E: Globus bag at ambient temperature. F: Chromatogram from the bag in Fig. 3E after heating.

dition of diesel to a tin that was then heated for 24 h. Figure 3c shows a chromatogram produced after the addition of diesel to a Cryovac bag before heating, while Fig. 3d is a chromatogram of the same bag used for sampling in Fig. 3c after heating. Figure 3c indicates that the diesel was not detected after 24 h of passive headspace sampling at ambient temperature in a Cryovac bag. While heating releases hydrocarbon peaks from the bags not seen in Fig. 3c, the result in Fig. 3d still lacks several major components of diesel, such as the C_{17} – C_{20} range of n-alkanes that are seen in Fig. 3b. Figures 3e and 3f are chromatograms from the addition of

diesel to a Globus bag before and after heating. In the Globus bag, some of the lower boiling point components are detectable without heating. After heating, more of the lower boiling point components of diesel are present, but as with the Cryovac bag, the result cannot be identified as diesel because major components are missing.

Chromatograms of the charcoal strips used to sample bags and tins containing 2 μL of kerosene are shown in Fig. 4. Figure 4a is a chromatogram obtained after the addition of kerosene to a friction lid tin sampled at ambient temperature. Figure 4b is a control chromatogram obtained from the addition of kerosene to a friction lid

tin that was then heated for 24 h. Figures 4c and 4d are chromatograms obtained after the addition of kerosene to a Cryovac bag before and after heating, respectively. Figures 4e and 4f are chromatograms from the addition of kerosene to a Globus bag before and after heating. While GC can detect low levels of kerosene in the Cryovac bag before heating, a smaller amount of hydrocarbon is recovered than from the friction lid tin. After heating the Cryovac and Globus bags, recovery of hydrocarbons is increased

so that identification of kerosene is possible in Figs. 4d and 4f. However, the addition of kerosene to Cryovac and Globus bags shows that the bags increase the threshold of detection of kerosene by GC relative to friction lid tins.

Chromatograms of the charcoal strips used to sample the bags and tins containing 2 μL of gasoline are seen in Fig. 5. Figure 5a is the chromatogram obtained after the addition of gasoline to a friction lid tin after 24 h of passive headspace sampling. Figure 5b is a

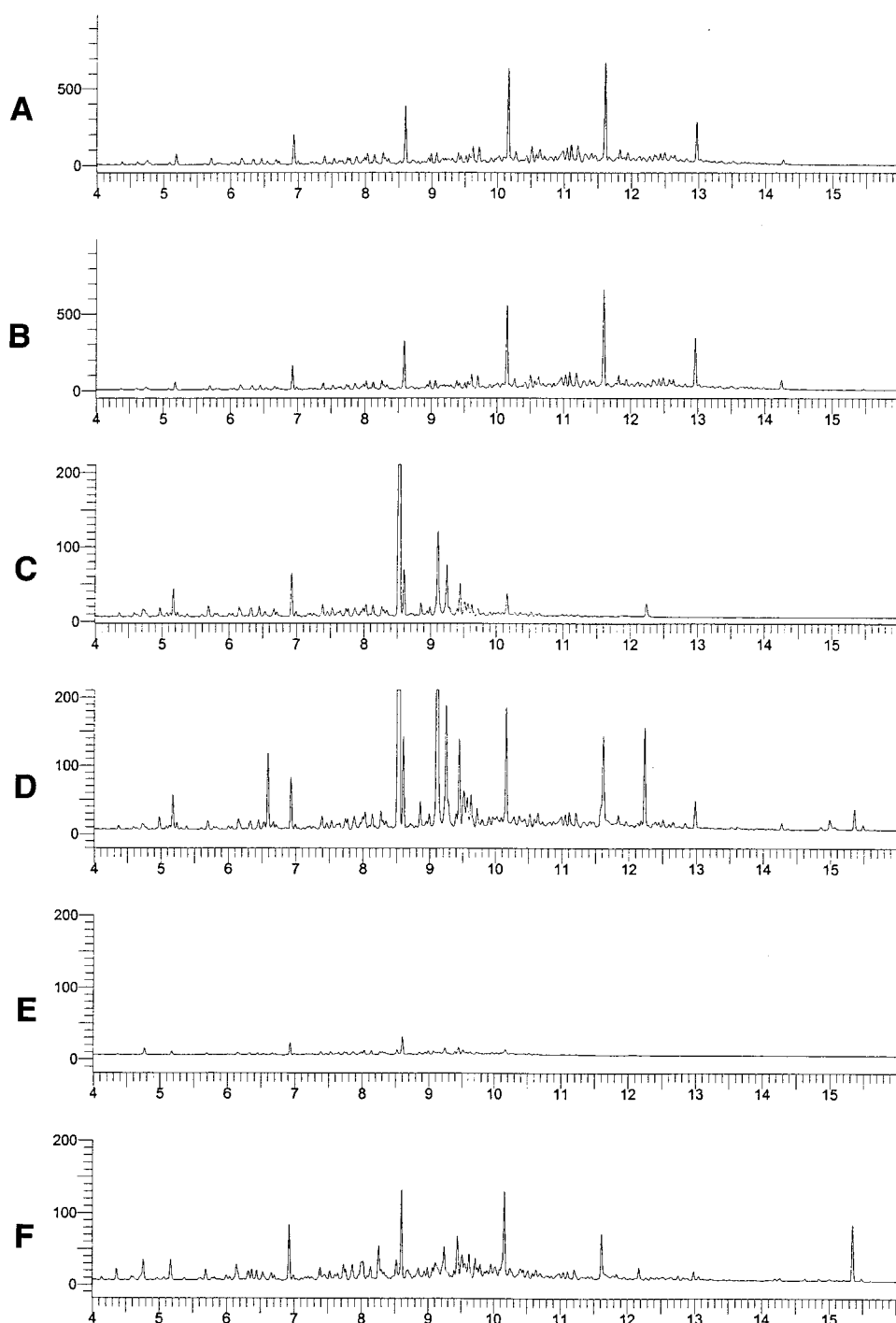


FIG. 4—Chromatograms from the addition of 2 μL of kerosene to the tin and bags. A: Four L friction lid tin at ambient temperature. B: Four L friction lid tin after heating. C: Cryovac bag at ambient temperature. D: Chromatogram from the bag in Fig. 4C after heating. E: Globus bag at ambient temperature. F: Chromatogram from the bag in Fig. 4E after heating.

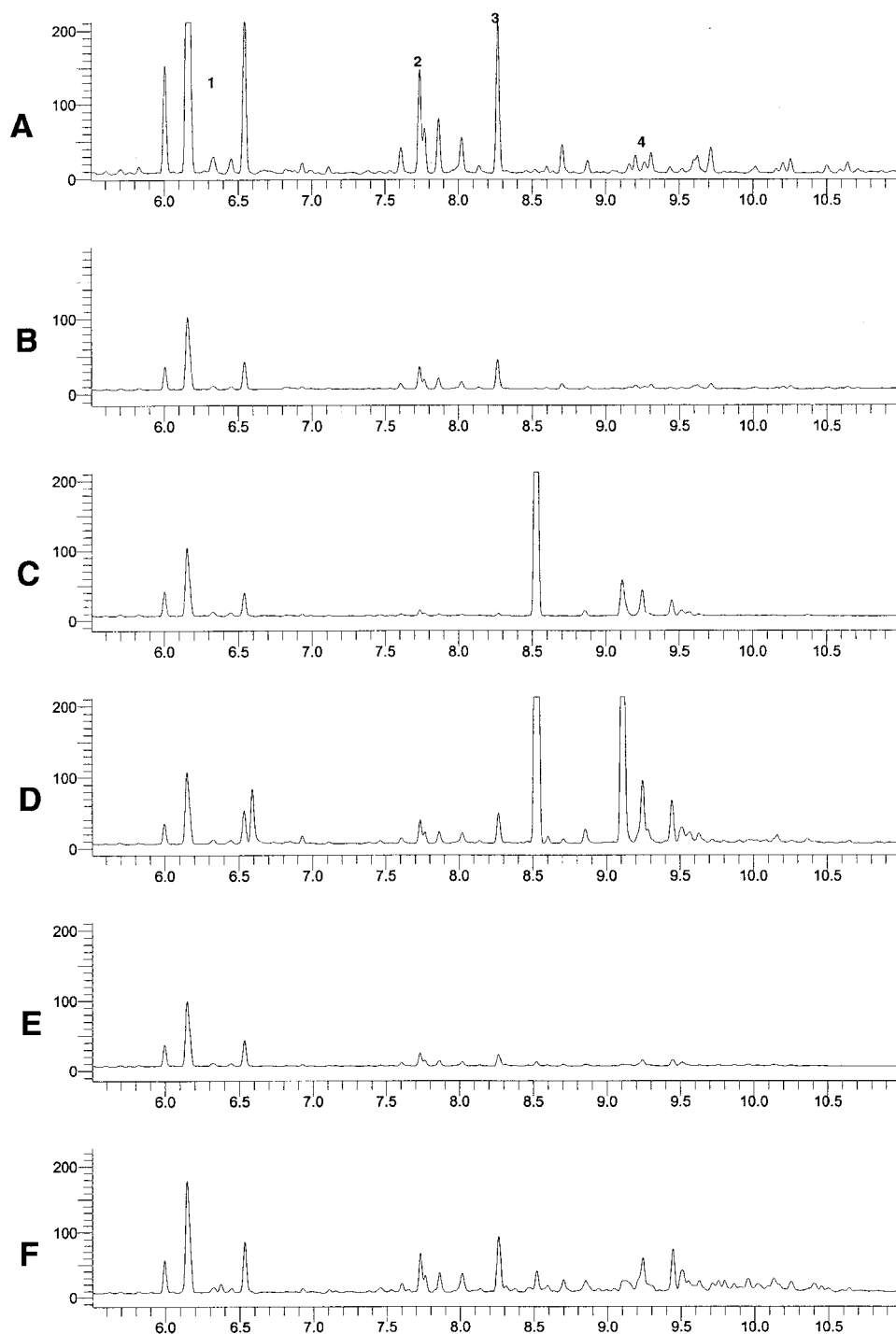


FIG. 5—Chromatograms from the addition of 2 μL of gasoline to the tin and bags. A: Four L friction lid tin. Components of gasoline in A are: (1) ethylbenzene, xylenes (2) m-ethyltoluene (3) 1,2,4-trimethylbenzene (4) C_4 alkylbenzenes B: Four L friction lid tin after heating. C: Cryovac bag at ambient temperature. D: Chromatogram from the bag in Fig. 5C after heating. E: Globus bag at ambient temperature. F: Chromatogram from the bag in Fig. 5E after heating.

control from the addition of gasoline to a friction lid tin that was then heated for 24 h. Figures 5c and 5d are the chromatograms from the addition of gasoline to a Cryovac bag before and after heating. Figures 5e and 5f are chromatograms from the addition of gasoline to a Globus bag before and after heating. Low levels of gasoline are not identifiable in either Cryovac or Globus bags. In the Cryovac

and Globus bags, some of the higher boiling point components such as the C_3 alkylbenzenes are not easily seen. While the ethylbenzene and xylene components of gasoline are present, the branched alkanes from the bags obscure the C_4 alkylbenzenes and naphthalene, making an identification of gasoline unreliable. The lack of C_3 alkylbenzenes, C_4 alkylbenzenes and naphthalene seen

in the chromatograms is due to interfering peaks from the Cryovac and Globus bags and the absorption of gasoline components into the bags. Even though heating increases the intensity of the response for the C₃ alkylbenzenes as seen in the 7.5 to 8.3 min range of Figs. 5*d* and 5*f*, the results still cannot reliably be identified as gasoline due to interference from the bags.

No components of diesel, kerosene, or gasoline were detected from a swab of the interior surface of the bag with dichloromethane. Solvent washing extracted the same background peaks seen in Figs. 1*c* and 1*e*, but no appreciable amount of ignitable liquid was detected (data not shown). It appears that heating is more effective than dichloromethane extraction in releasing absorbed hydrocarbon from the bags.

Cryovac and Globus polyethylene/polyvinylidene dichloride bags can mask the presence of a number of materials including low levels of ignitable liquids such as diesel, kerosene, and gasoline. For analysis of diesel, heating the bags produces a result that ambient temperature sampling will miss. However, even the result from the heated bag cannot be identified as diesel due to the absence of components such as the C₁₇–C₂₀ range of n-alkanes. Identification of diesel is complicated by the absence of these higher boiling point components, which are needed to differentiate diesel from kerosene. Analysts unaware of this absorption into the evidence bags could mistakenly identify diesel as a lower boiling point ignitable liquid such as kerosene or medium petroleum distillate. Kerosene can be identified after heating, although the threshold of detection is increased in comparison with the friction lid tin. Gasoline cannot be reliably identified due to interfering branched alkane peaks contributed by the bags, which obscure the higher boiling point components of the C₄ alkylbenzenes and naphthalene. These results indicate that components of ignitable liquids may be absorbed into the bag material, rather than the charcoal sampling strip, at ambient temperatures and that

the bags themselves are producing a result that hinders the identification of ignitable liquids.

The regular testing of containers used to store evidence for flammable and combustible fluid analysis has been suggested (1,2,4). This study shows that polyethylene/polyvinylidene dichloride bags used in Australian laboratories are unreliable containers for ignitable liquid evidence. While clear plastic bags have some advantages over other evidence containers, each type must be tested to determine if they affect the analysis of ignitable liquids as Cryovac and Globus bags do.

Acknowledgments

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Additional information and reprint requests:

Maureen Kocisko
30 East Georgia Street #407
Indianapolis, IN 46204