

TECHNICAL NOTE

Ronald Coulombe,¹ Ph.D.

Chemical Markers in Weathered Gasoline

REFERENCE: Coulombe, R., "Chemical Markers in Weathered Gasoline," *Journal of Forensic Sciences*, JFSCA, Vol. 40, No. 5, September 1995, pp. 867-872.

ABSTRACT: GC/MS of different products and fire debris samples were run to detect evidence of the presence of weathered gasoline. Doing so, chemicals characterized as diphenyl disulfides and homologues were detected specifically in gasoline and were not present in creosote as well as other petroleum derivatives. Although in trace amounts, these disulfides are positive evidence of the presence of weathered gasoline and could be considered as markers. Their absence does not, however, disprove the presence of gasoline.

KEYWORDS: forensic science, fire debris analysis, gasoline residue, creosote, chemical markers, diphenyldisulfide

Steam distillation of fire debris is a common recovery technique for volatile compounds [1]. However, sometimes debris does not contain a very volatile fraction but merely heavy fractions just volatile enough to be codistilled with water vapor.

In this project, five samples were examined: a low volatility residue from gasoline, a sample of evaporated diesel fuel, a fire debris sample, a highly evaporated gasoline from a Molotov cocktail and a sample of creosote. The aim was to establish individual and common characteristics. Steam distillation was used to recover the last three samples.

Gasoline processing does not completely eliminate sulfur compounds. Among those present are benzothiophene and its homologues [2]. These products can be detected by GC/MS even though their mass is identical to tetramethylbenzene and homologues. I have found dibenzothiophenes either in gasoline or in different other fire debris samples where detailed analysis could not ascertain the presence of gasoline.

Many families of compounds in weathered gasoline are routinely observed by an ion trap GC/MS. For example, fluorene, biphenyl, indane and their homologues have to be present in a residue if gasoline is present.

This note reports the presence of a third class of low volatility sulfur compounds, the aromatic disulfides. The lowest member detected was diphenyl disulfide at m/z 218. There are three isomers of phenyltolylidysulfide (o, m, p) of m/z 232. There could be a fourth isomer, benzyl phenyldisulfide, but in fact, only three peaks were detected. Theoretically, at m/z 246, there are twelve dimethyl

homologues and seven isomers in the benzyl class (where one or two CH_2 groups are located between the sulfur atoms and the aromatic rings). Many of those compounds are detectable but have not been rigorously identified. There are many theoretical isomers at m/z 260 but only few were detected. No compound at m/z 274 were observed in any of the samples.

In addition to aromatic disulfides, I also looked for the presence of aromatic sulfides.

Experimental

Analyses were performed on five samples. Sample A was gasoline obtained at a local gas station and was left to lose 96% of its original volume by evaporation. Samples B, C and D were recovered by steam distillation. All four samples were run as is. Sample B was a fire debris that capillary GC showed to be highly weathered. Sample C was an unburned cloth that was used as a wick in a Molotov cocktail; this wick was left to evaporate more than a month before recovery. Sample D was a brown substance that had been poured in a well containing fresh water. This substance had features common with evaporated gasoline and was showed to be creosote by GC/MS analysis. Sample E is diesel fuel that was left to evaporate to dryness and then was dissolved in ethyl ether.

Instrumental Analysis

The GC/MS system was a Varian Saturn II equipped with a Varian 3400 Gas Chromatograph (Varian Corp., Palo Alto, CA). Mass acquisition was every two seconds, therefore scan 600 corresponds to a retention time of 20 minutes. The injection port was set at 280°C. The capillary column was a 30 m \times 0.25 mm fused silica DB-5 (5% phenyl methylsilicone) (J&W Scientific, Folsom, CA). The oven was initially held at 50°C for 1 min., then heated to 225°C at 8°C/min. and held. The carrier gas was helium at 5 psi.

Results

Figures 1 to 4 show the distribution pattern of the disulfide homologues in the first four samples, respectively. In the conditions used the m/z 218 peak appeared at scan 650. The m/z 232 peak appeared at scans 682, 686 and 695. The m/z 246 peaks appeared between scans 705 and 755 with the major peaks at scans 718 and 722. The m/z 260 peaks appeared between scans 740 and 800 mainly with the major peaks at scans 742, 752, 762, 775 and 790. All these peaks elute between C_{18} and C_{22} . In the conditions used, the C_{18} and C_{22} peaks of diesel fuel appear at scan 632 and 817, respectively.

Received for publication 1 Aug. 1994; revised manuscript received 13 Feb. 1995; accepted for publication 15 Feb. 1995.

¹Forensic Chemist, Fire and Explosion Division, Direction des expertises judiciaires, Montréal, Québec.

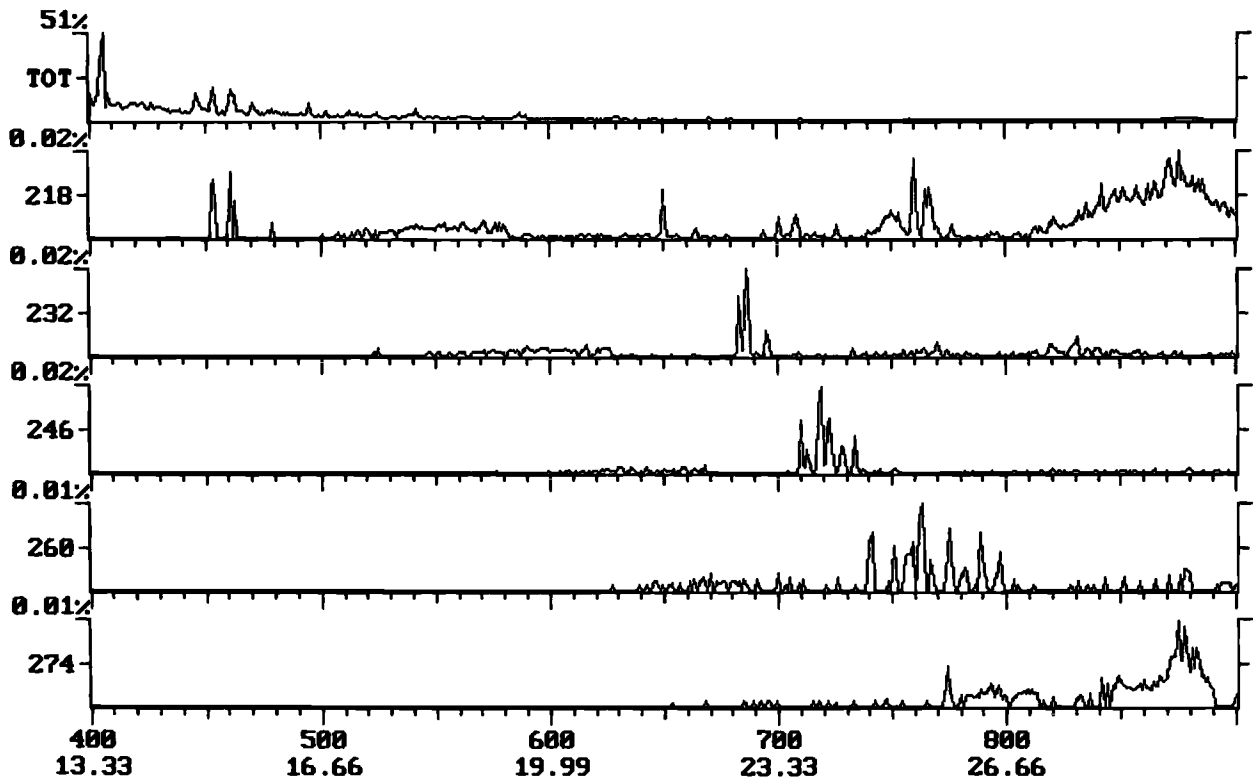


FIG. 1—GC/MS and selected ions of sample A: 96% evaporated gasoline. Diphenyl disulfide is at scan 650.

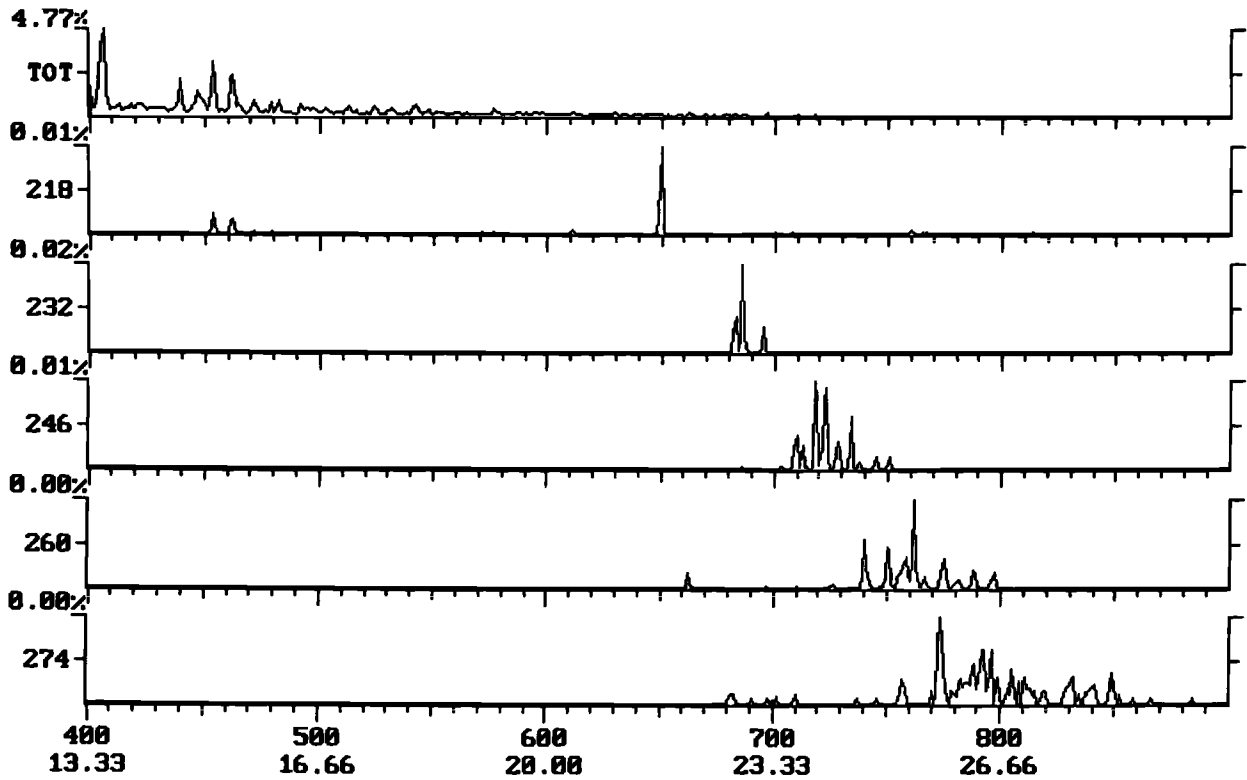


FIG. 2—GC/MS and selected ions of sample B: fire debris residue.

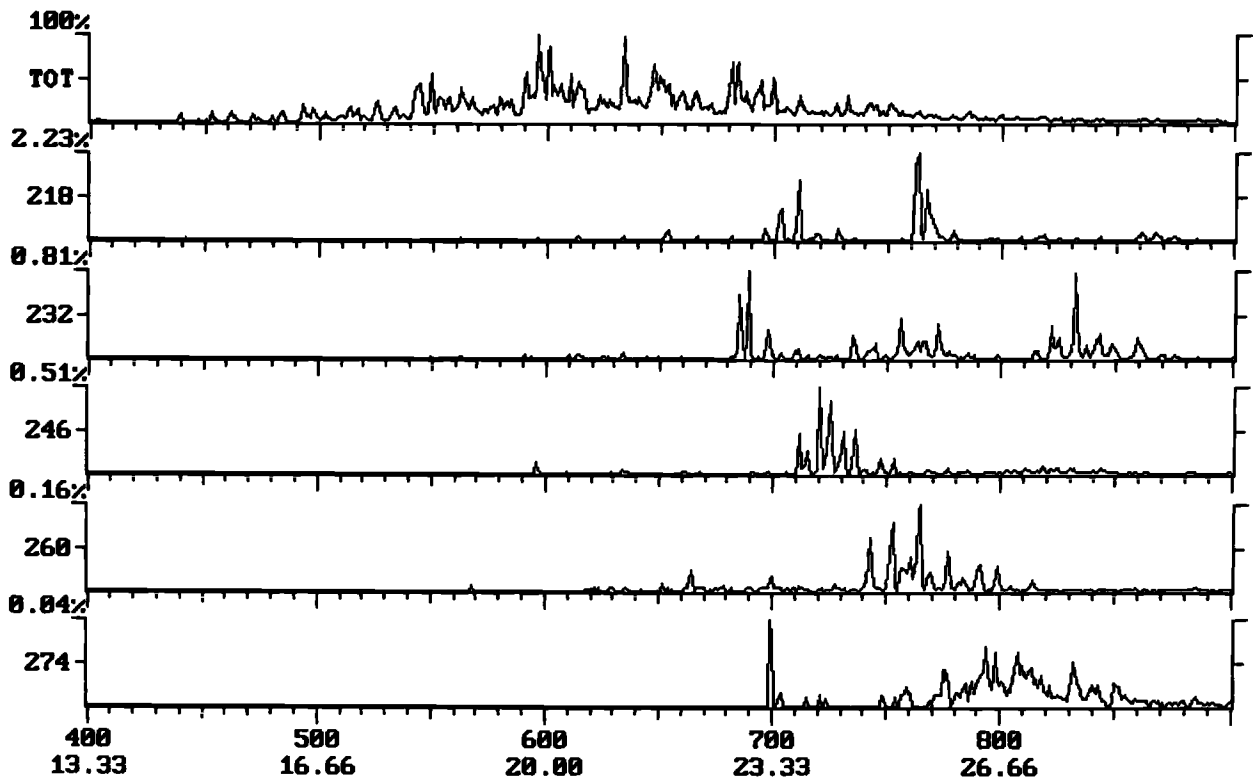


FIG. 3—GC/MS and selected ions of sample C: Molotov cocktail.

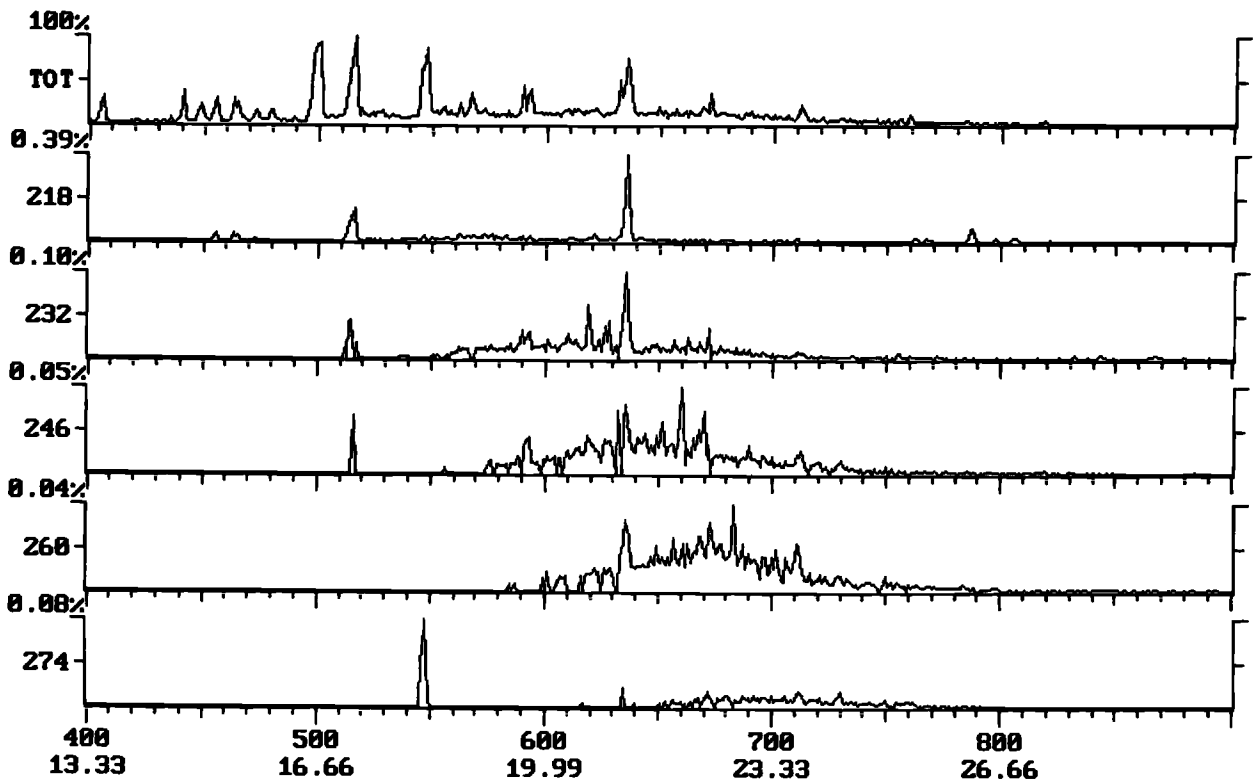


FIG. 4—GC/MS and selected ions of sample D: creosote.

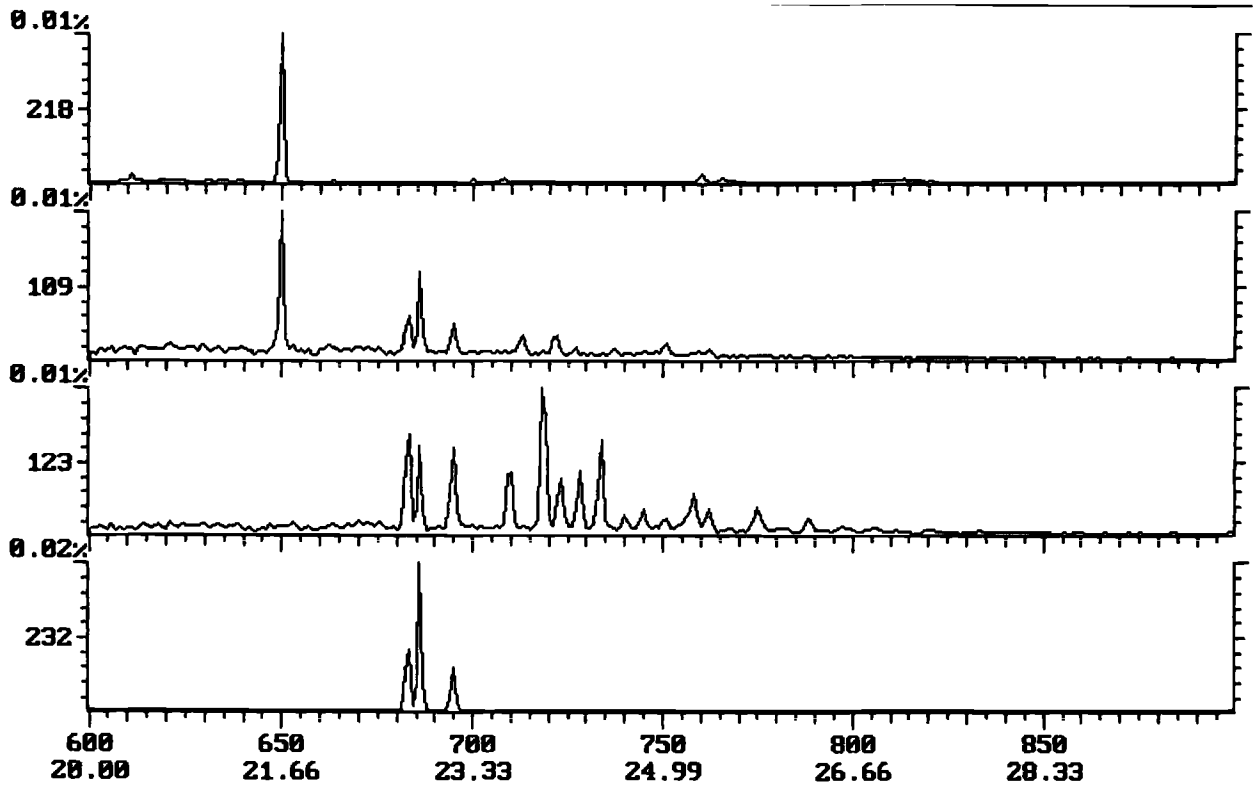


FIG. 5—Sample B: m/z 218 and 232 and their fragmentation.

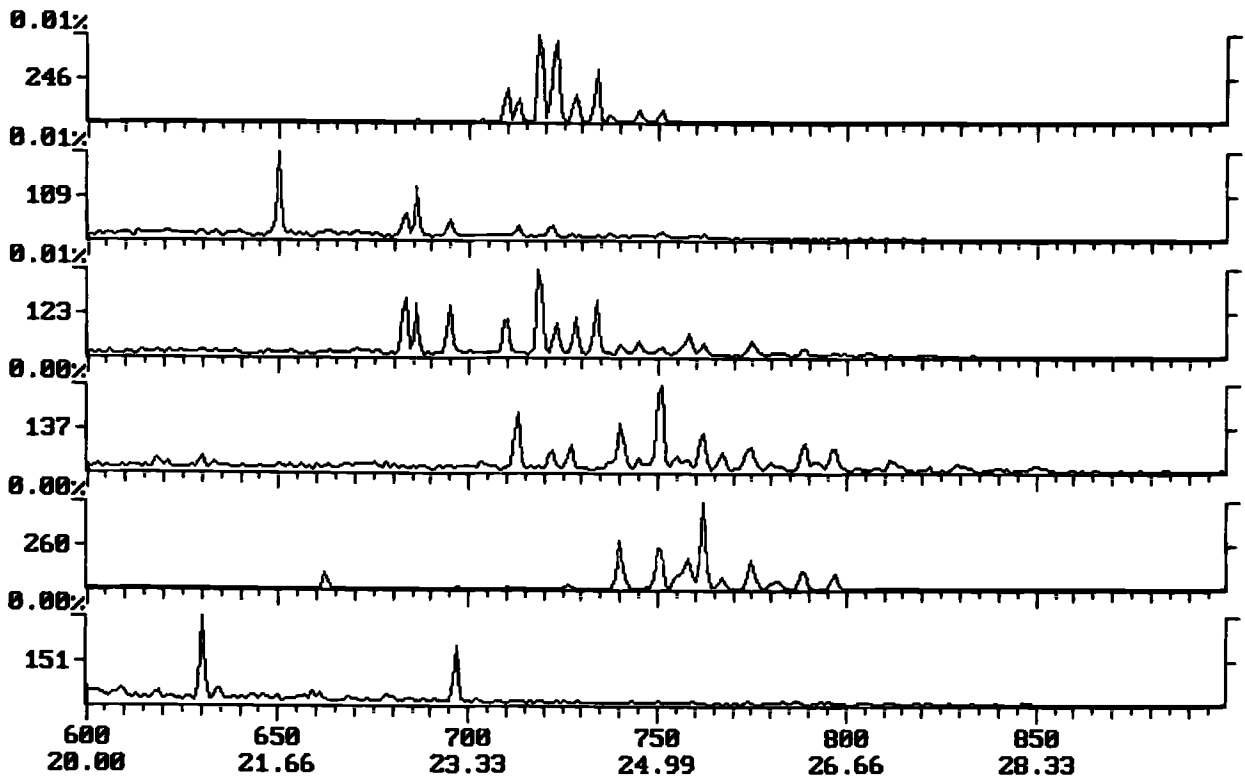


FIG. 6—Sample B: m/z 246 and 260 and their fragmentation.

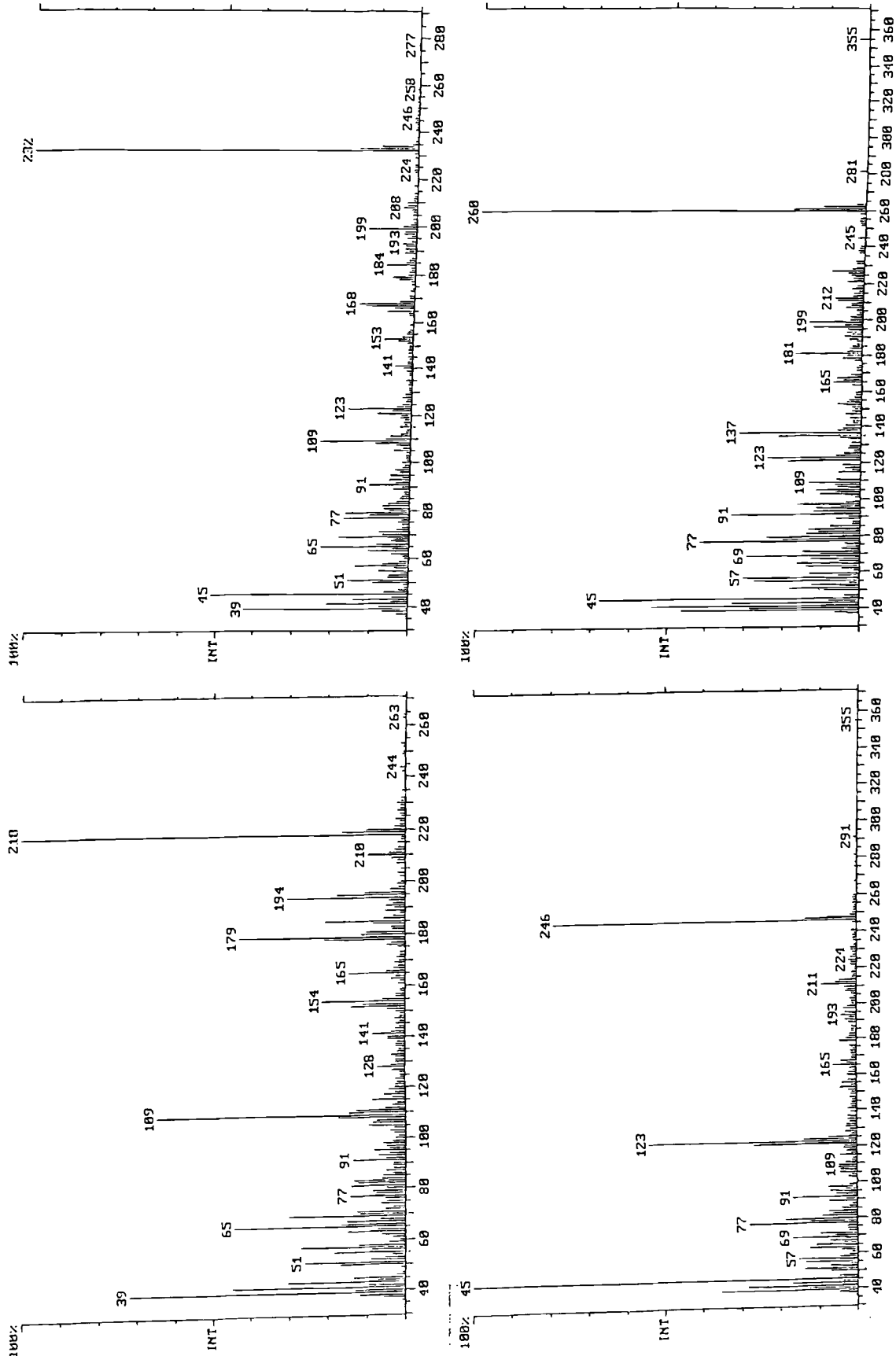


FIG. 7—Sample B: mass spectra of scan 650 (upper left), scan 718 (lower left), and scan 686 (upper right), scan 762 (lower right).

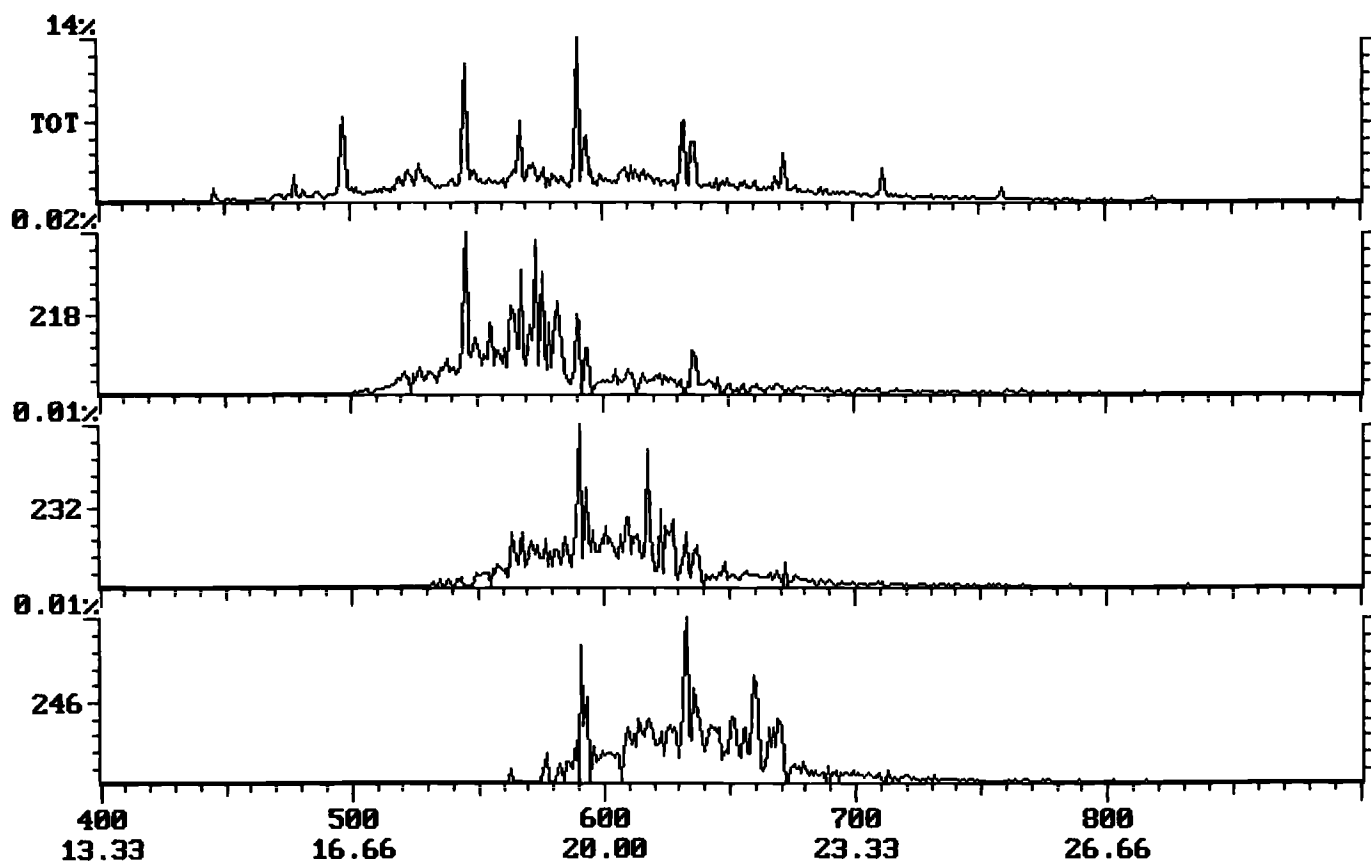


FIG. 8—GC/MS and selected ions of sample E: evaporated diesel fuel.

In order to show that the DPDS appear neatly after steam distillation, sample B was chosen to illustrate their mass fragmentation patterns.

Figure 5 shows the fragmentation pattern of the peaks of m/z 218 and 232. The m/z 218 ion fragments symmetrically giving the thiophenate ion (m/z 109). The m/z 232 ion fragments yielding ions 109 and 123, which corresponds to the methylated homologues.

Figure 6 shows the fragmentation pattern of the peaks of m/z 246 and 260. The m/z 246 ion yields predominantly ion 123, indicating that the principal isomers are methylated on each aromatic ring. The m/z 137 ion corresponds to dimethylated homologues and is detected at the same scans as m/z 109 ion (scans 722 and 727). The m/z 260 ion yields predominantly ions 123 and 137, without ions 109 and 151 in detectable amounts.

Figure 7 shows the mass spectra of scans 650, 686, 718 and 762. They were taken as examples of one set for each molecular weight. Impurities are clearly visible but the molecular ions are major peaks and the 109, 123 and 137 fragment ions are easily distinguished where applicable.

Figure 8 shows sample E with C_{18} appearing at scan 632. The 218, 232 and 246 m/z ion patterns do not present the features observed for samples A to C. Clearly the disulfides are absent.

After having confirmed the presence of diphenyl disulfide in gasoline, the presence of diphenyl sulfide was looked upon. In sample A and B, for example, the 186 m/z ion pattern, corresponding to the m.w. of diphenyl sulfide, was examined and found to show no peaks. Also, the 200, 214 and 228 m/z in patterns, corresponding to the m.w. of the methylated homologues of diphenyl sulfide were examined and found to show no peaks. There is

no GC/MS evidence of the molecular peak of diphenyl sulfide or any of its methylated homologues.

Discussion

The identification of gasoline in a fire debris residue is achieved by comparison of GC/MS with known residues of gasoline obtained in gas stations. This process implies the examination of different patterns and fragmentations of different species present in the residues.

This is how the uncovering of the presence of this class of disulfide compounds was brought. Residues were examined where all the characteristics of a weathered gasoline were present without the presence of the disulfides. But never has a sample been encountered where the disulfides were present and a gasoline residue was not.

Other usual petroleum products like diesel fuel, heating oil, lamp oil, kerosene and paint thinners were examined and none contain the chemical compounds described in this report, even in weathered samples.

Examination of fire debris residues implies the presence of pyrolysis products. No such disulfides have been detected in fire debris pyrolysates. Analysis of sample A shows that the disulfides are present in the gasoline as such. The analysis of sample D shows they are absent in creosote which has many aromatic compounds common with gasoline.

One has to reason why these disulfides were encountered only in gasoline and not in other petroleum products. One explanation is that the disulfides might not be present in crude oil, although this test has not been performed. But if they were present in

crude petroleum, why would they wind up in gasoline and not in diesel fuel?

Intuitively, the chemical origin of the disulfides might be an oxidative coupling of the corresponding thiols, namely thiophenol and the methylated isomers of thiophenol. It is not known where the thiophenols would originate from, other than the fact that their coupling compounds are found only in gasoline.

One possible explanation for these products not to have been detected previously is that usually sulfur compounds are analyzed in more volatile fractions [3,4] or not by GC/MS [1].

Conclusion

GC/MS analyses of weathered gasoline and fire debris residues containing gasoline has allowed the detection of chemical markers identified as diphenyl disulfide and its homologues.

These disulfides are absent in other petroleum products analyzed.

These disulfides were not detected yet in fire debris pyrolysates received in cases in our laboratory.

References

- [1] Dynes, K. and Thorburn Burns, D., "Identification of Weathered Petrol Residues by High-Resolution Gas Chromatography with Dual Flame Ionisation Detector—Hall Electrolytic Conductivity Detector," *Journal of Chromatography*, Vol. 396, June 19th 1987, pp. 183–189.
- [2] Albro, T. G., Dreifuss, P. A., and Wormsbecher, R. W., "Quantitative Determination of Sulfur Compounds in FCC Gasolines by AED," *Journal of High Resolution Chromatography*, Vol. 16, Jan. 1993, pp. 13–17.
- [3] Quimby, B. D., Giarocco, V., Sullivan, J. J., and McCleary, K. A., "Fast Analysis of Oxygen and Sulfur Compounds in Gasoline by GC-AED," *Journal of High Resolution Chromatography*, Vol. 15, Nov. 1992, pp. 705–709.
- [4] Chawla, B. and DiSanzo, F., "Determination of Sulfur Components by High-Resolution Gas Chromatography with Chemiluminescence Detection," *Journal of Chromatography*, Vol. 589, Jan. 10th 1992, pp. 271–279.

Address requests for reprints or additional information to
 Ronald Coulombe
 Direction des expertises judiciaires
 1701, rue Parthenais
 C.P. 1500, Succ. "C"
 Montréal, Québec, Canada
 H2L 4K6