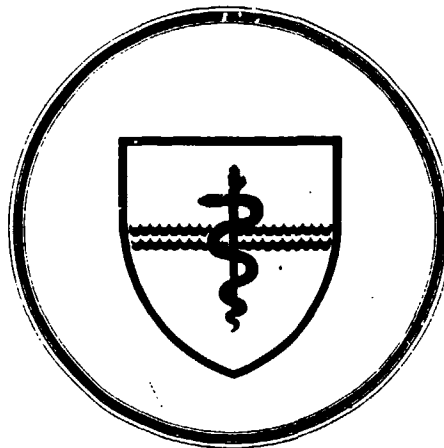


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**NAVAL SUBMARINE MEDICAL
RESEARCH LABORATORY
SUBMARINE BASE, GROTON, CONN.**



A CC/MS ANALYSIS FOR TRIMETHYLOLPROPANE PHOSPHATE ON AIRCRAFT HOSES.

SPECIAL REPORT 88-2

Prepared for:

National Transportation Safety Board
Washington, D. C. 20594

Released by:

Claude A. Harvey, CAPT, MC, USN
Commanding Officer
Naval Submarine Medical Research Laboratory

24 May 1988

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A GC/MS ANALYSIS FOR
TRIMETHYLOLPROPANE PHOSPHATE
ON AIRCRAFT HOSES

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SUMMARY PAGE

PROBLEM

To analyze for the presence of Trimethylolpropane Phosphate, TMP-P, on three pieces of aircraft hoses received from the National Transportation Safety Board in April 1988.

FINDINGS

No TMP-P residue was detectable on the aircraft hoses. If trace amounts of the material were present, they could not be measured because of the masking effects of background material extracted from the hoses. Additional research is needed on the technical aspects of sample preparation for measuring TMP-P adsorbed on surfaces.

APPLICATIONS

Trimethylolpropane Phosphate is a highly toxic byproduct found during heating of certain lubricants. The ability to measure this material in trace amounts in the environment or when deposited on surfaces could aid in the prevention of potentially serious aviation or naval accidents.



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ABSTRACT

Gas chromatographic/mass spectrometric analyses were performed for detection of Trimethylolpropane phosphate (TMP-P) on the pieces of aircraft hose received from the National Transportation Safety Board. This highly toxic compound is formed during heating of certain lubricating materials and is suspected to be involved in causing some vehicular accidents. Methanol was used to extract the hoses, with recovery experiments performed.

Although no TMP-P residue was detected in the extracts from the aircraft hoses, background materials removed from the hoses during the extraction process might have masked the presence of trace amount of the toxic material. Since the analytical technique has much more sensitivity than could be utilized in this work, further research should be performed on better methods for removing TMP-P from surfaces and on the absorption of TMP-P by various materials.

This report describes analyses for the presence of Trimethylolpropane Phosphate, TMP-P, on three pieces of aircraft hose received from The National Transportation Safety Board in April 1988. TMP-P is a highly toxic byproduct formed during the heating of certain lubricants (1,2). The hoses were A) a 26 inch (") length of 1.5" diameter black fiber, wire reinforced, with damage at one end; B) a 4" length of 3" diameter hose of same construction as hose A, also damaged; and C) a 4" length of red rubber hose, fabric reinforced, of 2.8" diameter, apparently undamaged. The damaged hoses appeared to have been subjected to charring.

In an exploratory approach to the extraction of TMP-P from the hoses, samples about 1 inch in length were cut from each end of hose A, from the damaged end of hose B, and from one end of hose C. These pieces of hose were soaked overnight in small beakers containing 50 ml of methanol. The hose sections were then removed and the methanol was allowed to evaporate at room temperature in the stream of air produced by a laboratory hood. The residues from the extractions were redissolved into 2.0 ml of methanol, yielding extracts A-D. Extracts containing undissolved material were centrifuged in an attempt to remove solid residues which seemed to come primarily from the damaged hoses. The reconstituted supernates were also diluted 1:10 with methanol and 2 ul aliquots of both the diluted and undiluted extracts were subjected to gas chromatography/mass spectroscopic (GC/MS) analysis as described previously (3).

Since the presence of high background levels of the ions collected for the selected ion profile analyses made the detection of low levels of TMP-P very difficult, it was necessary to determine whether methodologic errors might be preventing the detection of TMP-P in the extracts. After TMP-P was demonstrated to be stable during the extraction and evaporation steps, several attempts were made to evaluate the minimum levels of TMP-P that might be measured in the presence of the interfering materials in the solutions. Difficulty was encountered during these analyses in adequately eliminating the very fine residues removed from the aircraft hoses which seriously degraded the capillary chromatography process. Considerable equipment downtime resulted. It has not been determined whether these problems might be eliminated with proper application of microfiltration methods.

Because it seemed likely that some of the problems of analyzing the extracts from the hose segments arose from the large amount of extraneous material removed during the overnight soaking process, another extraction procedure was used for an additional segment from each hose. This time a 12" length of hose A was washed, inside and outside, with 100 ml of methanol as a spray from a fine tipped wash bottle. The solvent was collected into a small beaker as it slowly dripped from the hose (extract E). Similarly 1.5-1.8" pieces of hoses B and C were washed with 50 ml of methanol (extracts F and G). After evaporation extract E was reconstituted with 2 ml of methanol and extracts F and G with 1 ml each. In a preliminary analysis, 500 micrograms of TMP-P in methanol was deposited on a 1" piece of hose A and the methanol was allowed to evaporate. Approximately 62% of this TMP-P was recovered when the hose was washed with 8 ml methanol that was then evaporated and reconstituted in 1 ml as had been done with the test extracts.

While somewhat less interfering background material was removed from the hoses by the second extraction procedure, no conclusive evidence of the presence of TMP-P in any of the original or diluted extracts has been obtained. The estimated minimum levels of TMP-P that might be detected in these solutions in the presence of the background interference were 50 ppm TMP-P in a 1:10 dilution of extract E and 20 ppm in a 1:5 dilution of hose extract C. In more concentrated extracts or in extracts A-D, greater levels of TMP-P were required for positive identification.

Figures 1 and 2 show chromatograms of aliquots of representative hose extracts and spectra which partially support our conclusions concerning the presence of TMP-P on the hoses. Figure 1 presents selected ion chromatograms from the analyses of 2 microliter aliquots of hose extracts B and E and spectra from the established retention time of TMP-P. These spectra should be compared with the very characteristic TMP-P spectrum of Figure 2D from the major peak shown in Figure 2C. In all of our experiments, the entire region of the chromatographs where TMP-P should be found were thoroughly examined with spectral background subtracted.

Figures 2A and 2B demonstrate the tendency of TMP-P to be severely masked by background material. The amount of TMP-P added to the solution analyzed in Figure 2B was the same as that of Figure 2C, 25 ppm.

The series of selected ion spectra of Figure 3 are from one of the experiments conducted to determine the minimum detectable amounts of TMP-P in the hose extracts. Figure 3A shows the spectrum from a 1:10 dilution of hose extract E while Figure 3B shows that of a similar solution containing 25 ppm TMP-P (cf. Figs 2A and 2B). In neither case can the presence of TMP-P be detected. The spectrum of Figure 3C (+50 ppm TMP-P) can be judged with reasonable certainty to indicate that TMP-P is contained in the solution, while that of 3D (+75 ppm TMP-P) is nearly identical to the spectrum of Figure 2D.

It should be noted that if a spectrum extends to include the ion at 178 mass\charge units (Figure 3D), that ion was present in detectable amounts. This mass ion, representing the total molecule, is present in very low but measurable levels when pure TMP-P is analyzed. Since only the most characteristic ions of TMP-P were monitored, most of the same ions are evident in all of the spectra presented, but in widely varying ratios.

We have not yet been able to explain the phenomenon of the apparent disappearance of TMP-P into the background of the extracts when added below fairly sharp minimum, or swamping, concentrations. This masking of TMP-P peaks at levels where they would be expected to be very apparent has added to the difficulties encountered in arriving at easy answers concerning the presence or absence of TMP-P on the aircraft hoses.

While no TMP-P residue was found on the aircraft hoses that were studied, there remains some reasonable doubt concerning the presence of trace amounts of this material. The masking effect of background materials extracted from the hoses, which made the detection of trace levels of TMP-P impossible, suggests that much improvement needs to be made in the handling of samples prior to the

actual analytical steps in this procedure. An analysis of our data indicates that for TMP-P to be detectable on a piece of hose or similar material a few hundred micrograms to a few milligrams of the compound must be present, depending upon the surface on which it is deposited. The greater the surface area that must be extracted, the more likely are the problems of serious background interference. Other factors influencing the minimum detectable quantities are the extent to which the carrier material solubilizes and the amount of charred material that will be transferred into an extract.

It is difficult to estimate the concentration of airborne TMP-P required to deposit milligram quantities on surfaces. The analytical techniques employed here are much more sensitive than the measurable quantities reported would indicate. The weak link in the analysis involves sample handling procedures. These could be much improved with a modest amount of additional research.

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FIGURE 1. (A) Selected Ion Chromatogram from GC/MS Analysis of 2 ul Aliquot of Aircraft Hose Extract B. (B) Chromatogram of Hose Extract E. (C) Spectrum from TMP-P Retention Time of Chromatogram 1A. (D) Spectrum from TMP-P Retention Time of Chromatogram 1B.

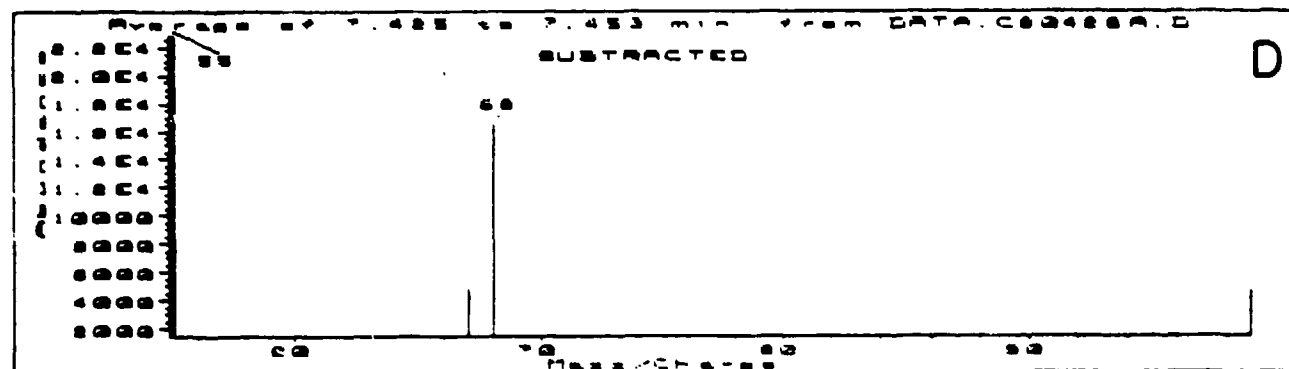
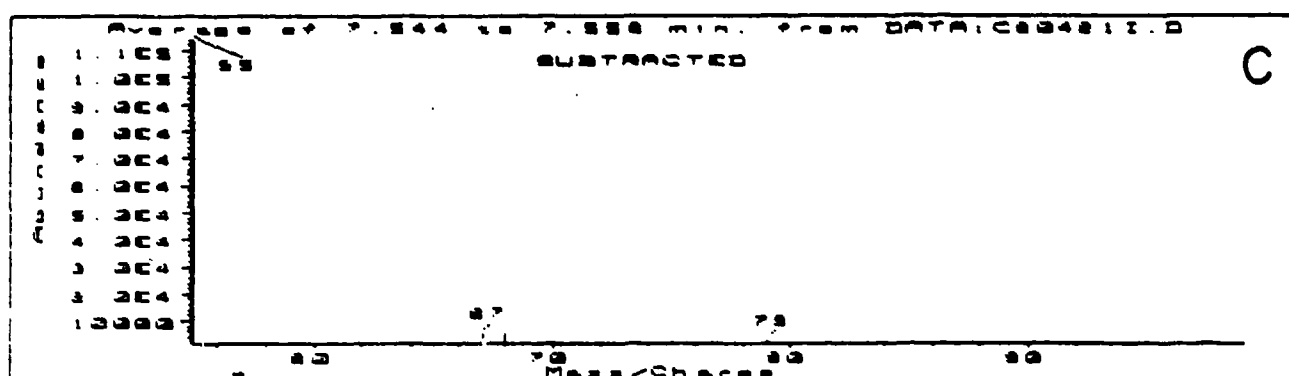
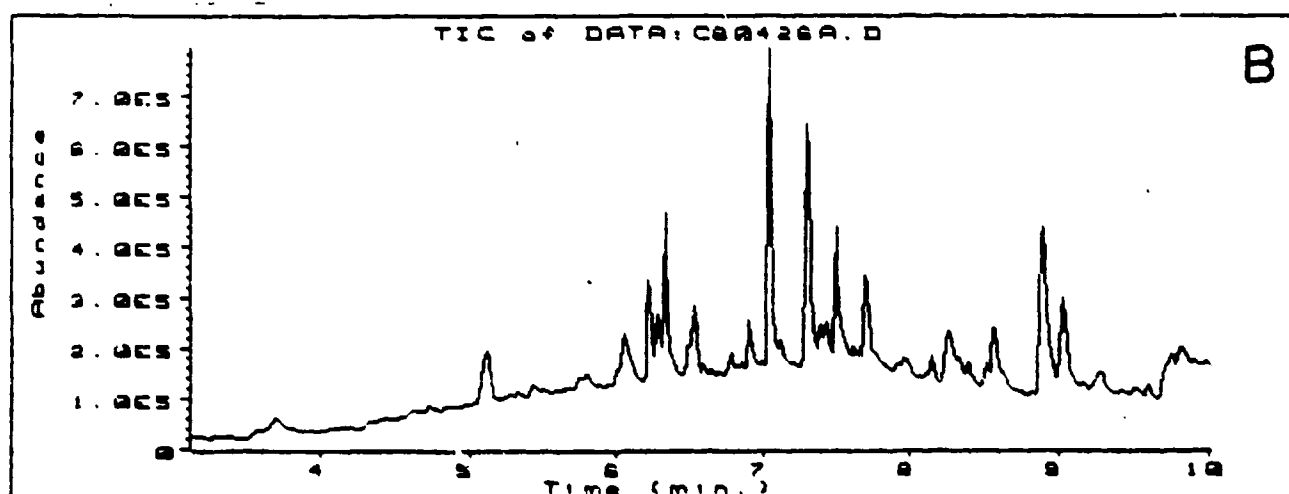
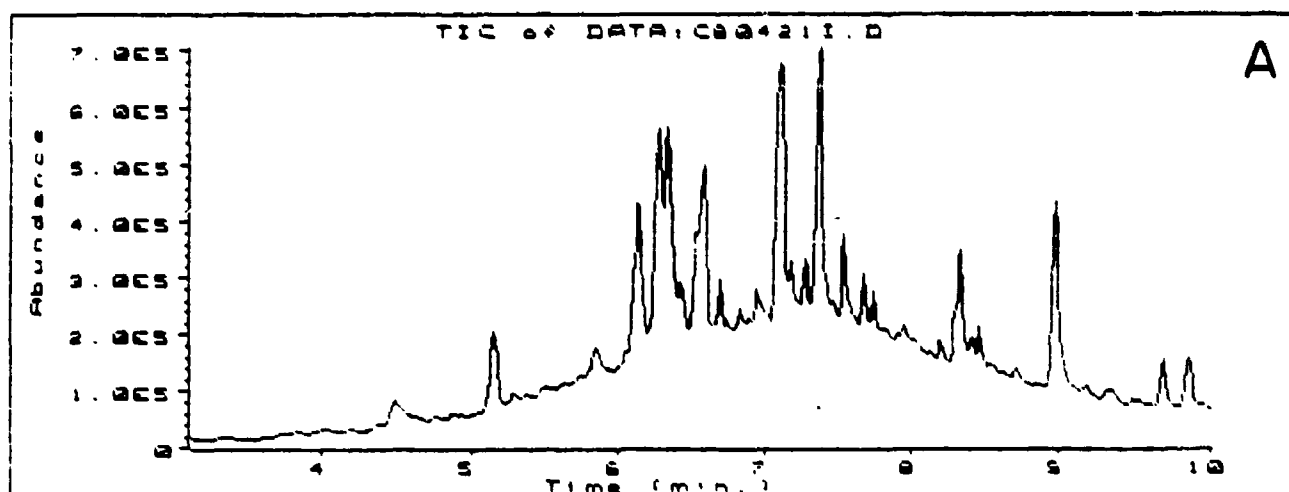


FIGURE 2. (A) Chromatogram of 2 μ l Aliquot of 1:10 Dilution of Aircraft Iose Extract E. (B) Chromatogram of Identical Solution to that of 2A + 25 ppm TMP-P. (C) Chromatogram of 25 ppm TMP-P Reference Solution. (D) Spectrum from Major Peak in 2C.

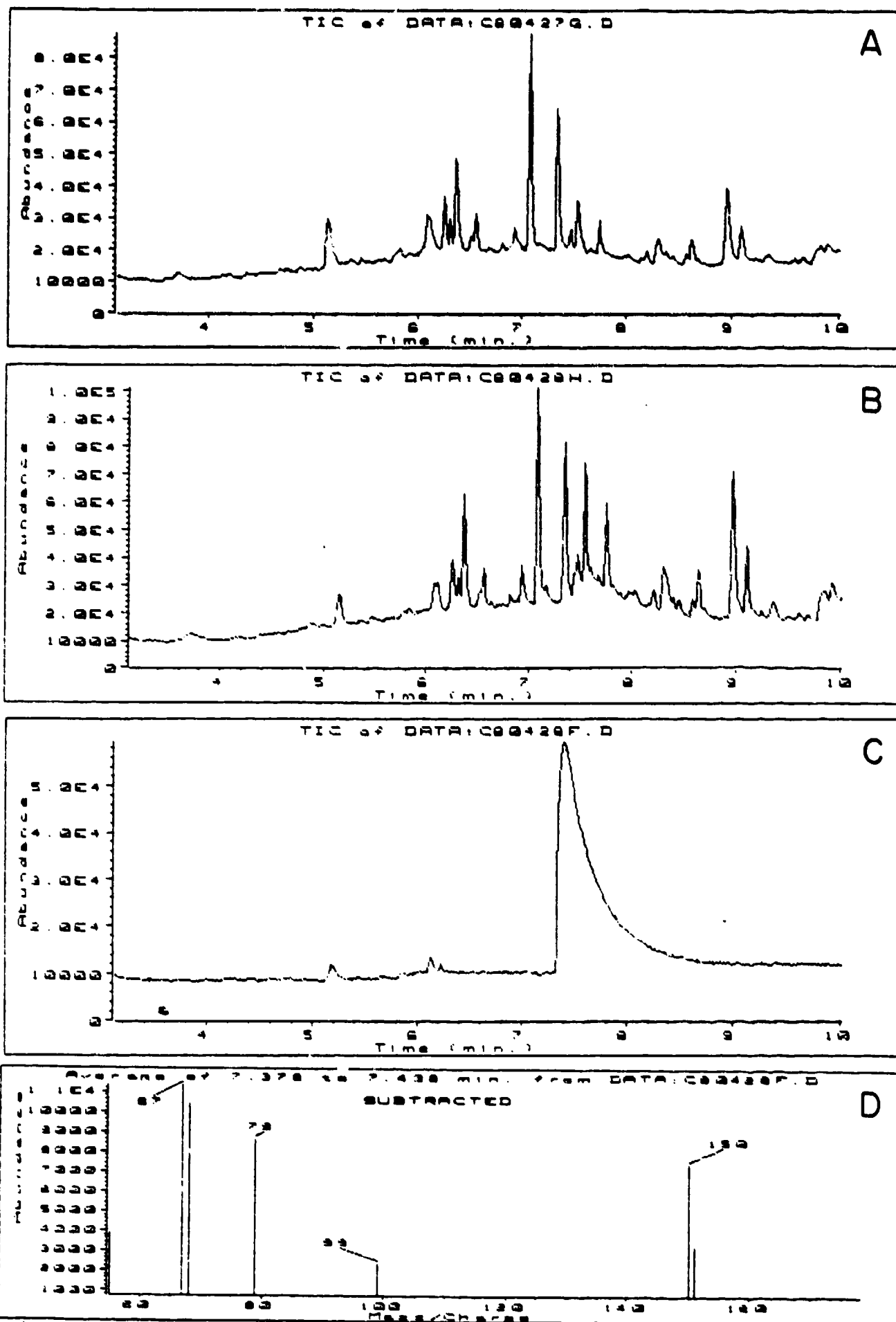
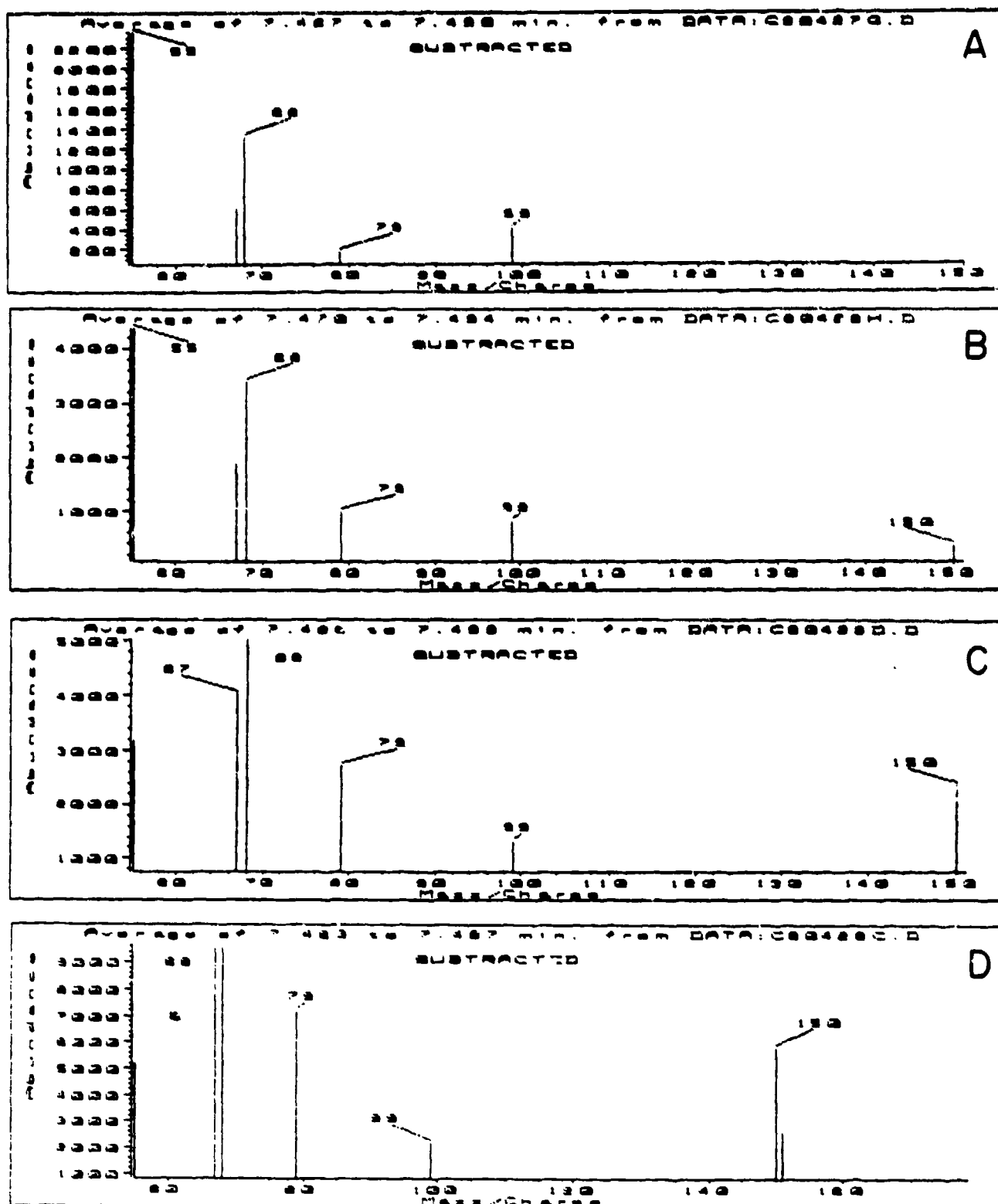


FIGURE 3. All Spectra from Chromatograms of 2 ul Aliquots of 1:10 Dilution of Aircraft Hose Extract E at Retention Time of TMP-P. (A) No TMP-P Added. (B) Extract + 25 ppm TMP-P. (C) Extract + 50 ppm TMP-P. (D) Extract + 75 ppm TMP-P.



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